

ON THE ELUCIDATION OF MECHANISMS OF ELECTRODE REACTIONS BY COMBINATION OF A.C.- AND FARADAIC RECTIFICATION POLAROGRAPHY

APPLICATION TO THE $Zn^{2+}/Zn(Hg)$ AND $Cd^{2+}/Cd(Hg)$ REDUCTION*

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INTRODUCTION

In a recent paper¹ by Reinmuth the importance of second-order methods in the study of the kinetics of more complex electrode reactions was emphasized. Definite information about the reaction order can be obtained by comparing results from first- and second-order methods. In the present paper we will make an effort to bring these theories closer to practice, using faradaic rectification polarography as the second-order method.

At first the $Zn^{2+}/Zn(Hg)$ electrode reaction will be studied. This reaction is reported²⁻⁶ to be first order with respect to the concentrations of the ox- and red-component, but does not obey the simple absolute rate theory. The equations for faradaic rectification polarography, derived and tested in our previous papers^{7,8}, are in principle applicable to such systems.

Secondly the $Cd^{2+}/Cd(Hg)$ electrode reaction in 1 M KCl will be examined. For this reaction different methods seem to yield different values for the kinetic parameters⁹. Some authors^{10,11} propose as a mechanism. The electrochemical formation of the Cd^+ or Cd_2^{2+} intermediate, followed by rapid disproportionation. For systems like these the rate equations are not necessarily linear with the concentrations and the equations derived earlier for faradaic rectification polarography need some modification.

THEORY

In the case that the current density, i , can be written as some analytical function of the electrode potential (E) and the concentrations of the ox- and red-component at the electrode surface, c_O and c_R , Reinmuth has given the second-order expansion of i as a function of the perturbations from the equilibrium condition and the 3 first order and 6 second order partial derivatives. By introduction of Nernst's law the number of independent first-order derivatives reduces to one and the

* Dedicated to Dr. J. E. B. Randles on the occasion of his retirement from the Chemistry Department, University of Birmingham.

number of second-order derivatives to three. From these four potential-dependent parameters it will, in general, still be difficult to make a conclusion about the reaction mechanism and in our opinion the analytical procedure then will be to compare the experimental results with the predictions obtained from different models. The 9 partial derivatives are then prescribed by the rate equation pertaining to the mechanism under consideration and if this rate equation obeys Nernst's law the partial derivatives will automatically show the required interdependence.

For the faradaic rectification polarography we will start from a second-order expansion expressed in perturbations from the mean situation:

$$\Delta i = b\Delta c_R - a\Delta c_O + (RT/nF\theta)\Delta\varphi + OF\Delta c_O\Delta\varphi + RF\Delta c_R\Delta\varphi + FF(\Delta\varphi)^2 + OO(\Delta c_O)^2 + RR(\Delta c_R)^2 + OR\Delta c_O\Delta c_R \quad (1)$$

where Δc_O , Δc_R and $\Delta\varphi$ are the deviations from the mean surface concentrations \bar{c}_O and \bar{c}_R and from the mean quantity $\bar{\varphi}$ ($= (nF/RT)[\bar{E} - E^0]$) respectively. The expressions for the three first-order derivatives (a , b , $RT/nF\theta$) and the six second-order derivatives (OF , RF , FF , OO , RR , OR) may be obtained by algebraical derivation from the rate equation under test, say $i = f(\varphi, c_O, c_R)$, or in a less elegant but more straightforward way via elaboration of

$$\Delta i = f(\bar{\varphi} + \Delta\varphi, \bar{c}_O + \Delta c_O, \bar{c}_R + \Delta c_R) - f(\bar{\varphi}, \bar{c}_O, \bar{c}_R) \quad (2)$$

as is done in ref. 7. When sinusoidal deviations from the mean current are used ($\Delta i = i_m \sin \omega t$) the Warburg relations read

$$\Delta c_i = \pm (i_m/nF)(2\omega D_i)^{-\frac{1}{2}}(\sin \omega t - \cos \omega t) \quad (3)$$

where the plus and minus signs refer to the ox- and red-component respectively. Following the same route as in ref. 7, *i.e.* integrating eqn. 1 over the time after substitution of the first-order approximation for $\Delta\varphi$ in the second-order terms, we obtain for the faradaic rectification voltage:

$$\Delta E_F = -\frac{nF}{RT} \frac{i_m^2 \theta^2}{2} \left\{ \frac{p+2}{nFp(2\omega)^{\frac{1}{2}}} \left(\frac{OF}{D_O^{\frac{1}{2}}} - \frac{RF}{D_R^{\frac{1}{2}}} \right) + FF \frac{nF\theta}{RT} \left(\frac{p^2+2p+2}{p^2} \right) + \frac{RT}{n^3 F^3 \theta \omega} (OOD_O^{-1} + RRD_R^{-1} - ORD_O^{-\frac{1}{2}} D_R^{-\frac{1}{2}}) \right\} \quad (4)$$

with

$$p = nF [b(2\omega D_R)^{-\frac{1}{2}} + a(2\omega D_O)^{-\frac{1}{2}}]^{-1} \quad (5)$$

The first-order parameters θ and p represent, respectively, the charge-transfer resistance and the irreversibility quotient. One has $p = \cotg \Phi - 1$, where Φ is the phase angle of the faradaic impedance.

Equation 4 expresses the faradaic rectification voltage in a general way. In the following, several mechanisms will be considered, being in principle applicable to transfer reactions involving two electrons. The predicted rate equations and some combinations of partial derivatives determining the faradaic rectification voltage under d.c.-reversible conditions are collected in Table 1.

(i) *First order single-step mechanism*

If the transition state of the reaction involves the total charge to be

transferred, the electrons are said to be transferred simultaneously. Then the rate equation reads

$$i = nF [\bar{k}c_R - \bar{k}c_O] \quad (6a)$$

Since the Nernst equation should hold if $i=0$, this can be accounted for by the notation.

$$i = nF K(\varphi)[c_R - c_O \exp(-\varphi)] \quad (6b)$$

where $K(\varphi)$ is the rate constant of the oxidation reaction.

Evaluation of the partial derivatives gives for the rectification voltage:

$$\begin{aligned} \Delta E_F = & - \frac{(nF\theta i_m)^2 K(\bar{\varphi})}{2RT} \frac{p+2}{nFp(2\omega)^{\frac{1}{2}}} \left[\frac{(1-A)\exp(-\bar{\varphi})}{D_O^{\frac{1}{2}}} - \frac{A}{D_R^{\frac{1}{2}}} \right] \\ & + \frac{\theta nF}{2RT} \frac{p^2 + 2p + 2}{p^2} [(A^2 + A')\bar{c}_R - (1 - 2A + A^2 + A')\bar{c}_O \exp(-\bar{\varphi})] \end{aligned} \quad (7)$$

with

$$\begin{aligned} A &= \frac{d \ln K(\varphi)}{d\varphi} \quad \text{and} \quad A' = \frac{dA}{d\varphi} \\ p &= (2\omega)^{\frac{1}{2}} K(\varphi)^{-1} [D_R^{-\frac{1}{2}} + D_O^{-\frac{1}{2}} \exp(-\bar{\varphi})]^{-1} \end{aligned} \quad (8a)$$

For the charge-transfer resistance we find

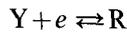
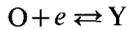
$$\theta = \frac{RT}{n^2 F^2 K(\varphi)} [A\bar{c}_R + (1-A)\bar{c}_O \exp(-\varphi)]^{-1} \quad (8b)$$

Within the framework of the absolute rate theory we have $K(\varphi) = k_{sh} \exp(\alpha\varphi)$, k_{sh} being the standard heterogeneous rate constant and $\alpha=A$ the charge-transfer coefficient. Equations (7) and (8) are then similar to equations^{7,12} previously presented.

In d.c.-reversible systems, where $\bar{c}_O/\bar{c}_R = \exp(\bar{\varphi})$, the terms with $A^2 + A'$ cancel out.

(ii) First order two-step mechanism with reversed standard potentials

Opposite to the case described above, the reaction may proceed via two transition states, each involving one electron, corresponding to the scheme.



For both steps the "classical" rate equations can be written as

$$i_1 = F[\bar{k}_1 c_Y - \bar{k}_1 c_O] = F k_{sh1} [c_Y \exp(\alpha_1 \varphi_1) - c_O \exp(-\beta_1 \varphi_1)] \quad (9a)$$

$$i_2 = F[\bar{k}_2 c_R - \bar{k}_2 c_Y] = F k_{sh2} [c_R \exp(\alpha_2 \varphi_2) - c_Y \exp(-\beta_2 \varphi_2)] \quad (9b)$$

where φ_1 and φ_2 are related to the standard potentials E_1^0 and E_2^0 of the separate steps: $\varphi_i = (E - E_i^0) F/RT$. The symbols k_{shi} and $\alpha_i = 1 - \beta_i$ denote apparent kinetic parameters, including the Frumkin and other double-layer effects.

In the simplest model it is assumed that Y does not react with the solvent, neither is it adsorbed in significant amounts at the electrode interface. If, moreover, the standard potential of the second step is much larger than that of the first step

($E_2^0 \gg E_1^0$), c_y will be negligibly small with respect to either c_o or c_r in the region of the polarographic wave. In that case the diffusional flux of Y is negligible and consequently $i_1 = i_2 = \frac{1}{2} i$, where i is the total faradaic current^{13,14}. Eliminating the unknown concentration c_y from (9a) and (9b) and expressing the unknown standard potentials E_1^0 and E_2^0 in the E^0 of the overall reaction and $\Delta E^0 = E_2^0 - E_1^0$ with the aid of the thermodynamic relation $2E^0 = E_1^0 + E_2^0$, we find

$$i = \frac{2Fk'_{sh_1}k'_{sh_2}}{k'_{sh_1} \exp(\frac{1}{2}\alpha_1\varphi) + k'_{sh_2} \exp(-\frac{1}{2}\beta_2\varphi)} \left[c_r \exp\left(\frac{\alpha_1 + \alpha_2}{2}\varphi\right) - c_o \exp\left(-\frac{\beta_1 + \beta_2}{2}\varphi\right) \right] \quad (10)$$

where

$$k'_{sh_1} = k_{sh_1} \exp(-\frac{1}{2}\beta_1 \Delta E^0 F/RT) \quad (11a)$$

$$k'_{sh_2} = k_{sh_2} \exp(-\frac{1}{2}\alpha_2 \Delta E^0 F/RT) \quad (11b)$$

Since $\Delta E^0 = 2(E^0 - E_1^0) = -2(E^0 - E_2^0)$, it follows from eqns. (9a), (9b) and (11a), (11b) that $k'_{sh_1} = \bar{k}_1(E^0)$ and $k'_{sh_2} = \bar{k}_2(E^0)$. So k'_{sh_1} is the rate constant of the reduction reaction of the first step at $E = E^0$ and k'_{sh_2} is the rate constant of the oxidation reaction of the second step at $E = E^0$.

Equation (10) may be written in the form of eqn. (6), so with the proper expressions for $K(\varphi)$, A and A' , it is possible to calculate the faradaic rectification signal and the charge-transfer resistance for different sets of parameters with eqns. (7) and (8).

Since, in this way of treatment, $K(\varphi)$ contains two rate constants, two extreme cases may be considered:

$$(a) k'_{sh_1} \exp(\frac{1}{2}\alpha_1\varphi) \ll k'_{sh_2} \exp(-\frac{1}{2}\beta_2\varphi),$$

leading to

$$K(\varphi) = k'_{sh_1} \exp[\frac{1}{2}(\alpha_1 + 1)\varphi]$$

so

$$A = \frac{1}{2}(\alpha_1 + 1) \text{ and } A' = 0$$

This case, in which evidently the first step is rate-determining, is favoured at more negative potentials.

(b) On the other hand the second step may be rate-determining if the potential is sufficiently positive:

$$k'_{sh_1} \exp(\frac{1}{2}\alpha_1\varphi) \gg k'_{sh_2} \exp(-\frac{1}{2}\beta_2\varphi)$$

leading to

$$K(\varphi) = k'_{sh_2} \exp(\frac{1}{2}\alpha_2\varphi)$$

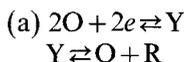
with

$$A = \frac{1}{2}\alpha_2 \text{ and } A' = 0$$

If one of these cases predominates in the entire region of the polarographic wave, the kinetic parameters evaluated do not allow us to distinguish between a two-step mechanism with *e.g.* $\alpha_1 \approx \alpha_2 \approx 0.5$ or a single-step mechanism with *e.g.* $\alpha \approx 0.75$ or 0.25. Only if the intermediate situation prevails, evidence for the two-step mechanism follows from the potential dependence of $K(\varphi)$, since the apparent anodic-transfer coefficient will change from about 0.75 to 0.25 going from negative to positive potentials.

(iii) Mechanisms involving an electrochemical step followed or preceded by a second order heterogeneous chemical step

The common feature of these mechanisms is that the intermediate Y is involved in a disproportionation reaction to form O and R. Again it is assumed that Y does not react with the solvent, is not significantly adsorbed, and that its diffusional flux is negligible. Consequently the net rates r_e and r_c of the electrochemical step and the chemical step are equal. These net rates can be written in the usual mathematical forms using the rate constants \bar{k}_e for the oxidation, \bar{k}_e^{-1} for the reduction, \bar{k}_c for the disproportionation and \bar{k}_c^{-1} for the recombination reaction. Four types of mechanisms will be distinguished.



the intermediate being a "double ion". A similar treatment to that in the foregoing section (equating r_e and r_c , eliminating c_y , with introduction of the proper Nernst equations) leads to the rate equation

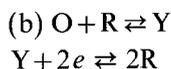
$$i = 2FK(\varphi)c_O[c_R - c_O \exp(-\varphi)] \quad (12)$$

with

$$K(\varphi) = \frac{\bar{k}_e \bar{k}_c}{\bar{k}_e + \bar{k}_c} \frac{1}{K_c}$$

where K_c is the equilibrium constant of the chemical reaction. Apart from double-layer effects, the chemical rate constant \bar{k}_c can be expected to be potential-independent, whereas the electrochemical rate constant \bar{k}_e may be written as $\bar{k}_e = k_{sh} \exp(\alpha_1 \varphi_1) = k_{sh} \exp[\alpha_1(E^0 - E_1^0)F/RT] \exp(\alpha_1 \varphi) = k_{sh} K_c^{z_1} \exp(\alpha_1 \varphi)$.

If the electrochemical step is rate-determining ($\bar{k}_c \ll \bar{k}_e$), we have $k(\varphi) = \bar{k}_c/K_c$, potential-independent. If the chemical step is rate-determining, we have $k(\varphi) = \bar{k}_e/K_c = \bar{k}_e$, potential independent.



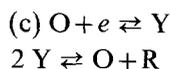
Being the counterpart of (a), this mechanism leads to the rate equation:

$$i = 2FK(\varphi)c_R[c_R - c_O \exp(-\varphi)] \quad (13)$$

with

$$K(\varphi) = \frac{\bar{k}_e \bar{k}_c}{\bar{k}_e + \bar{k}_c} \frac{\exp(\varphi)}{K_1}$$

If the chemical step is rate-determining, $K(\varphi)$ becomes proportional to $\exp(\varphi)$.



The general rate equation for this mechanism is fairly complicated. If, however, the chemical step is rate-determining, the rate equation is similar to eqn. (12a) with $K(\varphi) = k_c$.

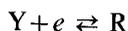
If, on the other hand, the electrochemical step is rate-determining the rate equation becomes

$$i = 2FK(\varphi)c_O^{\frac{1}{2}}[c_R^{\frac{1}{2}} - c_O^{\frac{1}{2}} \exp(-\frac{1}{2}\varphi)] \quad (14)$$

with

$$K(\varphi) = \bar{k}_c / K_c^{\frac{1}{2}}$$

So, in terms of the absolute rate theory, $K(\varphi)$ is potential-dependent, viz. $K(\varphi) = 2\alpha_1 \varphi$.



For the case where the chemical step is rate-determining eqn. (12b) applies with $K(\varphi) = \bar{k}_c \exp(\varphi)$. If the electrochemical step is rate-determining we have

$$i = 2 FK(\varphi) c_R^{\frac{1}{2}} [c_R^{\frac{1}{2}} - c_O^{\frac{1}{2}} \exp(-\frac{1}{2}\varphi)] \quad (15)$$

with

$$K(\varphi) = \bar{k}_e = k_{sh} \exp(\alpha_2 \varphi_2) = k_{sh} K_c^{-\frac{1}{2}\alpha_2} \exp(\frac{1}{2}\alpha_2 \varphi).$$

The different partial derivatives for eqn. (1), derived from eqns. (12)–(15) in the case of d.c.-reversibility ($\bar{c}_O/\bar{c}_R = \exp \bar{\varphi}$) are given in Table 1. For completeness this table also contains the derivatives pertaining to eqn. (6) in the d.c.-reversible case.

TABLE 1

PARTIAL DERIVATIVES AS DEFINED BY EQN. (1) FOR SOME D.C.-REVERSIBLE SYSTEMS

Rate equation	Linear (eqn. 6)	Eqn. (12a)	Eqn. (12b)	Eqn. (13a)	Eqn. (13b)
b	nFK	$nFK\bar{c}_O$	$nFK\bar{c}_R$	$\frac{1}{2}nFK \exp(\frac{1}{2}\bar{\varphi})$	$\frac{1}{2}nFK$
a	$b \exp(-\bar{\varphi})$	$b \exp(-\bar{\varphi})$	$b \exp(-\bar{\varphi})$	$b \exp(-\bar{\varphi})$	$b \exp(-\bar{\varphi})$
$RT/nF\theta$	$nFK\bar{c}_R$	$nFK\bar{c}_O\bar{c}_R$	$nFK\bar{c}_R^2$	$\frac{1}{2}nFK\bar{c}_R \exp(\frac{1}{2}\bar{\varphi})$	$\frac{1}{2}nFK\bar{c}_R$
OF	$a(1-A)$	$a(2-A)$	$a(1-A)$	$a(1-A)$	$a(\frac{1}{2}-A)$
RF	bA	bA	$b(1+A)$	bA	$b(\frac{1}{2}+A)$
$FF \cdot nF\theta/RT$	$A-\frac{1}{2}$	$A-\frac{1}{2}$	$A-\frac{1}{2}$	$A-\frac{1}{4}$	$A-\frac{1}{4}$
$OO \cdot RT/nF\theta$	0	$-a^2$	0	$-\frac{1}{4}a^2$	$\frac{1}{4}a^2$
$OR \cdot RT/nF\theta$	0	ab	$-ab$	$\frac{1}{2}ab$	$-\frac{1}{2}ab$
$RR \cdot RT/nF\theta$	0	0	b^2	$-\frac{1}{4}b^2$	$\frac{1}{4}b^2$

EXPERIMENTAL

All measurements were performed in freshly prepared solutions of p.a. grade chemicals. The Cd^{2+} solutions were acidified to $\text{pH} \approx 3$. Rectification signals were measured at a dropping mercury electrode, with the set-up described earlier⁸. The d.c. polarograms were recorded manually at the same DME. Impedance measurements were carried out with the aid of an a.c.-bridge¹⁵.

ANALYSIS PROCEDURES

Rectification signals ΔE_m are related to the faradaic rectification voltage ΔE_F by

$$\Delta E_m = \Delta E_F(1-\tau) + \tau \Delta E_c \quad (16)$$

where τ is a first-order parameter representing the charging of the double-layer capacity by the rectification current¹⁶. The rectification of the double layer ΔE_c is calculated from the double-layer capacity-potential curve^{16,8}.

The impedance data were analysed in the usual way¹⁷. Values of θ and p were determined as a function of potential.

In order to fit the data obtained to a certain model, theoretical values of ΔE_m , θ and p must be calculated for different sets of parameters, inherent to the model. For that purpose also the values of the mean surface concentrations at each potential are needed. As it is assumed that the intermediate does not undergo mass transport or react with the solvent, the concentrations \bar{c}_O and \bar{c}_R will be related to each other and the d.c.-current by the usual flux equations

$$\bar{i} = nF(D_O/\delta_O)(\bar{c}_O - c_O^*) \approx -nF(D_R/\delta_R)(\bar{c}_R - c_R^*) \quad (17)$$

where δ represents the thickness of the diffusion layer. Thus the mean surface concentrations can be calculated from the d.c.-polarogram. In many cases, however, expressing the mean surface concentrations as a function of potential is more convenient. Combination of eqn. (17) with first order rate equations (eqns. (6) and (10)) gives fairly simple expressions for \bar{c}_O and \bar{c}_R . Combination with second order rate equations (eqns. (12) and (13)) is more complex and requires the solution of a quadratic equation. For d.c.-reversible systems (the Cd²⁺-reduction in KCl) eqn. 17 together with the relationship $\bar{c}_O/\bar{c}_R = \exp(\bar{\varphi})$ provides explicit solutions for the mean surface concentrations.

RESULTS AND DISCUSSION

(i) The Zn²⁺/Zn(Hg) electrode reaction

The Zn²⁺/Zn(Hg) reaction has been studied by several authors. Blackledge and Hush⁶, and later Sluyters-Rehbach *et al.*³ found an acceleration of the reaction if strongly adsorbed ions, such as I⁻, Br⁻, CNS⁻ are present. In the study of this effect some trouble was caused by the fact that in non-adsorbed supporting electrolytes (NaClO₄, KCl) the transfer coefficient was also found to be potential-dependent, which was understood to point to a multistep mechanism as described by Vetter¹³ and Hurd¹⁴. Later on this was confirmed by measurements of Salié² and Hurlen and Eriksrud⁴, although the reported values of the kinetic parameters of both steps do not agree satisfactorily. In order to confirm our basic knowledge of the Zn²⁺/Zn(Hg) electrode reaction, we chose MgSO₄ as a non-adsorbed supporting electrolyte, allowing high concentrations of ZnSO₄ without large changes in the double-layer structure.

Rectification polarograms were recorded in a large potential region at 100, 200 and 400 kHz. When reduced to the same a.c.-voltage across the electrode, the three polarograms are almost identical, indicating that at those frequencies the Warburg impedance is small in comparison with the charge-transfer resistance, and that the relationship $i_1 = i_2$ is still valid, excluding adsorption of the intermediate at the electrode surface². The data were analysed following the general eqns. (7) and (8).

From impedance measurements, partially carried out in pure ZnSO₄ solutions, at each potential the charge-transfer resistance (θ), the Warburg impedance (σ) and the double-layer capacity are calculated. The double-layer capacity in 0.5 M ZnSO₄ is found to be not significantly different from that in 0.5 M MgSO₄. A straight line with slope $(2F/RT)$ is obtained plotting $\ln \sigma$ vs. potential in the anodic region. Extrapolation to $\ln \sigma = (D_O/D_R)^{1/2}$ gives¹⁸ $E^0 = -1018$ mV vs. SCE. (We used¹⁹ $D_R = 2D_O = 16 \times 10^{-6}$.)

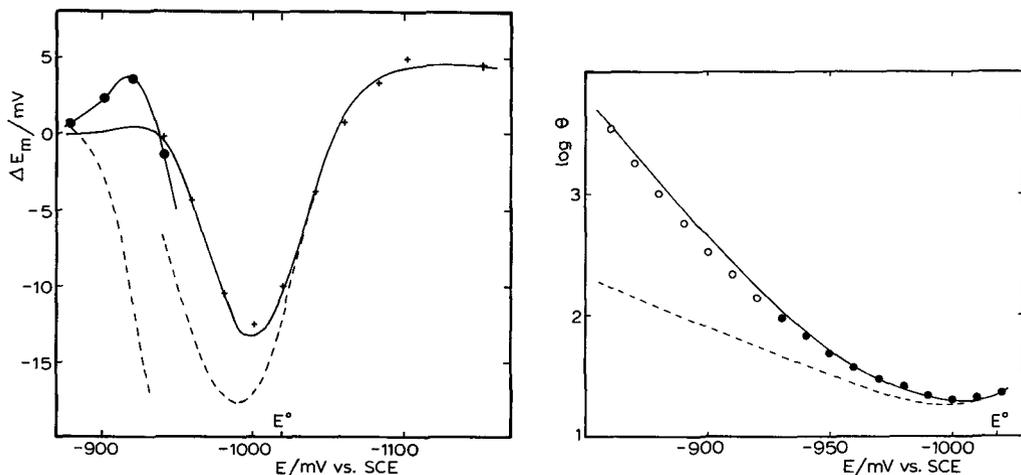


Fig. 1. Rectification polarogram of the $Zn^{2+}/Zn(Hg)$ electrode in $0.5 M MgSO_4 + ZnSO_4$. Frequency: 200 kHz, a.c.-electrolysis time 1.6 ms, drop time 4 s, drop area $1.2 mm^2$. Measured signals: (●) $c_{Zn^{2+}} = 20 mmol l^{-1}$, (+) $c_{Zn^{2+}} = 2 mmol l^{-1}$. Theoretical polarograms: (—) curve based on $\alpha_1 = 0.52$, $\alpha_2 = 0.53$, $k_{sh1} = 1.46 \times 10^{-3}$, $k_{sh2} = 32 \times 10^{-3}$, (---) curve based on the apparent parameters in the cathodic region: $\alpha = 0.76$, $k_{sh} = 1.46 \times 10^{-3}$.

Fig. 2. The charge-transfer resistance in the anodic potential region. Measured points: (●) $c_{Zn^{2+}} = 5 mmol l^{-1}$, (○) $c_{Zn^{2+}} = 0.5 mol l^{-1}$ (Log 100θ is plotted). Symbols for curves as in Fig. 1.

The parameters describing the rectification polarograms at best are very close to those describing the impedance measurements. In Figs. 1 and 2 the charge-transfer resistance and a rectification polarogram at 200 kHz, calculated with

$$\alpha_1 = 0.52 \quad k_{sh1} = 1.46 \times 10^{-3} \text{ cm s}^{-1}$$

and

$$\alpha_2 = 0.53 \quad k_{sh2} = 32 \times 10^{-3} \text{ cm s}^{-1}$$

are compared with the corresponding measured curves. The value for E^0 , computed from these parameters and the half-wave potential of the d.c.-polarogram, is found equal to that determined from the $\ln \sigma$ vs. E plot.

In order to apply the Frumkin correction ϕ_2 -potentials in $0.5 M MgSO_4$ were calculated by integration of the C_d -curve, starting at the potential of zero charge²⁰. This potential was measured as the open-circuit potential of a streaming mercury electrode²¹. ($E_{zc} = -428 \text{ mV vs. SCE}$). The ϕ_2 -potentials in the potential region from -800 to -1400 mV vs. SCE are given by $\phi_2 = -31.53 + 26.56x + 12.12x^2 + 15.71x^3 \text{ mV}$ with $x = (E \text{ vs. SCE} + 1100) \times 10^{-3}$.

The value of ϕ_2 at -1018 mV vs. SCE was used to calculate the "true" kinetic parameters:

$$(k'_{sh1})^{\dagger} = k'_{sh1} \exp[(\alpha'_1 + 1)\phi_2 F/RT] \text{ with } \alpha'_1 = \left(\alpha_1 + \frac{\partial \phi_2}{\partial E}\right) \left(1 - \frac{\partial \phi_2}{\partial E}\right)^{-1}$$

and

$$(k'_{sh2})^{\dagger} = k'_{sh2} \exp[\alpha'_2 \phi_2 F/RT] \text{ with } \alpha'_2 = \alpha_2 \left(1 - \frac{\partial \phi_2}{\partial E}\right)^{-1}$$

The values obtained are

$$\alpha_1' = 0.57, (k_{sh1}') = 2.4 \times 10^{-4} \text{ cm s}^{-1}$$

$$\alpha_2' = 0.55, (k_{sh2}') = 17 \times 10^{-3} \text{ cm s}^{-1}$$

These results are very close to those found² in NaClO₄, despite the fact that in the sulphate system ZnSO₄ is poorly dissociated²⁸, which means that the rate constants pertain to a standard potential which is 30 mV more negative than in NaClO₄.

Both the agreement between first- and second-order techniques and the fact that a change of a factor of 100 in the concentration causes no discontinuity in the θ vs. E curve confirm the linearity of the reaction rate with respect to the concentrations. The charge-transfer coefficient of the first as well as that of the second step are nearly 0.5, which is felt to be an argument in favour of the multistep mechanism.

(ii) *The Cd²⁺/Cd(Hg) reaction in 1 M KCl*

Complex impedance measurements on the Cd²⁺/Cd(Hg) reaction in KCl are presented by several authors^{2, 22-24}, but, in general, the high reaction rate lies just beyond the possibilities of this method. The most reliable results seem to be those of Salié², reporting $k_{sh} = 3.5 \text{ cm s}^{-1}$ and $\alpha = 0.25$. These results appear to be confirmed by single-pulse²⁵ and faradaic rectification^{26, 27} measurements. With both methods, however, there are some complications: In the pulse method the slope of the overpotential vs. $t^{\frac{1}{2}}$ -plot deviates from the theoretical slope, and rectification measurements show α to change from 0.2 to 0.3 in a potential region of 40 mV, while from analysis of the zero points of the rectification polarograms $\alpha \approx 0.1$ is calculated. Recently van Leeuwen⁹ performed g.r.c.-pulse measurements and, although these measurements could be interpreted very well with $\alpha = 0.64$ and $k_{sh} = 1 \text{ cm s}^{-1}$, the difference between these results and those from other methods indicates some complexity of the electrode reaction.

In order to get some more definite information about the reaction, rectification polarograms at five frequencies in a wider potential range were recorded. The theoretical polarograms are computed with $E^0 = -644 \text{ mV vs. SCE}$ and $D_R = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, values that are calculated from equilibrium potential and impedance measurements at amalgam electrodes ($c_R = 10$ and $c_R = 1 \text{ mmol l}^{-1}$). Furthermore $D_O = 9 \times 10^{-6}$ is used^{2, 25}.

At first the Cd²⁺/Cd(Hg) reaction was interpreted in terms of a multistep mechanism analogous to the Zn²⁺/Zn(Hg) reaction. However, no set of parameters could be found leading to satisfactory concurrence with the measurements. Next, for each potential $K(\varphi)$ and A were solved from the frequency-dependence of the rectification signal, still assuming a first-order reaction rate. At all potentials the frequency-dependence of ΔE_m could be described by these two parameters. The $\ln K(\varphi)$ values obtained are represented in Fig. 3, together with their slopes (A values). The k_{sh} and α values in the anodic potential region approach those calculated from impedance measurements². On the other hand, the k_{sh} and α values that we find at far cathodic potentials seem to be in better agreement with the values obtained with the g.r.c.-pulse method⁹.

Furthermore, unless a very complicated curve with a large number of inflection points is assumed, it is not possible to draw a $K(\varphi)$ -curve which is at each

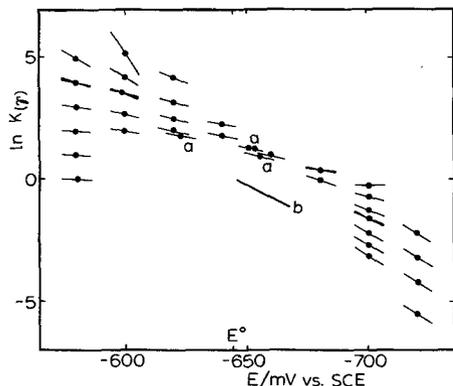


Fig. 3. Values and slopes of $\ln K(\varphi)$ as computed from faradaic rectification signals at different frequencies on the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ electrode in $1\text{ M KCl} \cdot c_{\text{Cd}^{2+}} = 3\text{ mmol l}^{-1}$, a.c.-electrolysis time 1.6 ms, drop time 3.3 s, drop area 2 mm^2 . At some potentials concordance with the measurements is obtained for a wide range of $\ln K(\varphi)$ values in combination with different A -values (slopes). (a) From other faradaic rectification measurements²⁷, (b) from g.r.c.-pulse measurements⁹.

point in agreement with $d \ln K(\varphi)/d\varphi$. Therefore, one, or more, of the following conclusions may be drawn.

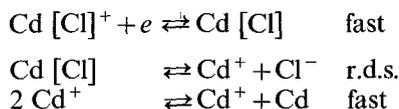
(1) The frequency-dependence of ΔE_m is altered by adsorption of one of the electroactive species at the electrode surface.

(2) The frequency-dependence of ΔE_m is more complex because two or more reactions occur simultaneously.

(3) The reaction rate is not linear with respect to the concentrations of the ox and red-component, in which case eqn. 3 should be used. For this case, the four rate equations, as described in Table 1, were tested on the measurements. They tend to describe the measurements better if c_0 is represented to a certain amount in K .

Equation 12 was proposed to apply by Biegler *et al.*¹¹. With this model we achieved a good fit only in the anodic potential region (-580 to -640 mV vs. SCE), with $\alpha \approx 0.2$ and $K(\varphi) = 1.5 \times 10^6 \exp(0.2\varphi)\text{ cm}^4\text{ s}^{-1}\text{ mol}^{-1}$. The large value of the rate constant has been discussed by the authors of ref. 11.

A better fit was obtained with rate eqn. (14) with a constant $K(\varphi)$ ($= 7.5\text{ cm s}^{-1}$, *cf.* Fig. 4). The fact that the rate constant is potential-independent could indicate that the actual rate-determining step is chemical instead of electrochemical. Therefore the mechanism underlying this rate equation could be



This reaction scheme also accounts for the fact that the transfer reaction is evidently accelerated by the presence of chloride ions.

As for this system

$$RT/nF\theta = \frac{1}{2}nFK \exp\left(\frac{1}{2}\varphi\right)\bar{c}_R \quad (18)$$

where $K = 7.5\text{ cm s}^{-1}$, application of any analysis procedure for linear reactions and first-order methods should give $\alpha^a = 0.5$ and $k_{\text{sh}}^a \approx 4$ (see Table 1). Faradaic

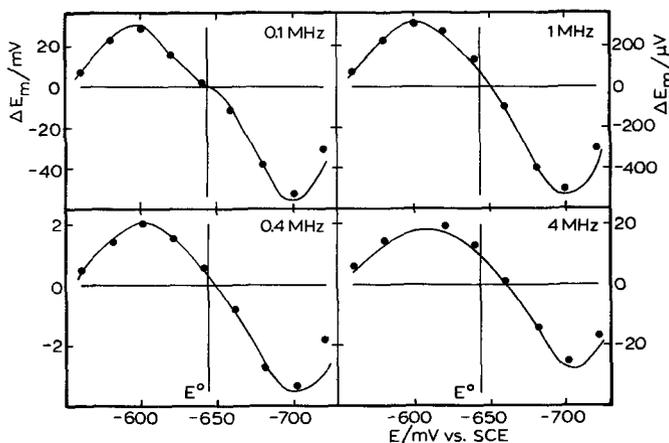


Fig. 4. Measured faradaic rectification signals compared with polarograms calculated on the basis of eqn. (13a) with $K=7.5 \text{ cm s}^{-1}$. (The 2 MHz curve resembles the other curves and is omitted for convenience.)

rectification signals at high frequencies and nearby E^0 are mainly determined by the term $FF\theta nF/RT$ (equal to $A-0.25$ in this case and $A-0.5$ for linear systems). So with $A=0$, α^a based on linear analysis of faradaic rectification measurements should tend to 0.25, a value which is indeed reported^{26, 27}.

Though in the foregoing some possibilities for the reaction mechanism are given, and others are excluded, solid positive conclusions cannot be drawn on the basis of the recorded faradaic rectification polarograms and must await further experimentation.

The measured rectification polarograms clearly indicate that the Cd²⁺/Cd(Hg) electrode reaction in 1 M KCl is not a simple system that can be described according to the absolute rate theory with a standard heterogeneous rate constant and a charge-transfer coefficient, and that analysis procedures based on this assumption should be avoided, even though they might give consistent results.

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SUMMARY

The theory of faradaic rectification polarography is extended to systems of higher order stoichiometry. The couples Zn²⁺/Zn(Hg) in 0.5 M MgSO₄ and Cd²⁺/Cd(Hg) in 1 M KCl are studied with the aid of this technique in a wide potential range. The Zn²⁺/Zn reaction is interpreted as a multistep mechanism. The Cd²⁺/Cd reaction did not appear to be a simple linear reaction. Some higher order mechanisms are tested using the measurements.

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