

## FARADAIC RECTIFICATION: AN AMENDED TREATMENT—II. EXPERIMENTAL VERIFICATION\*

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**Abstract**—The conclusions arrived at in Part I<sup>1</sup> of this series have been verified experimentally with Cd<sup>2+</sup>/Cd(Hg) in M NaClO<sub>4</sub>, Fe<sup>2+</sup>/Fe<sup>3+</sup> in M oxalate and Cd<sup>2+</sup>/Cd(Hg) in M KCl. The numerical method leads to values of the rate constant  $k_{sh}$  that agree with those obtained by graphical extrapolation only if the reaction is rather irreversible. In the case of fast reactions the classical extrapolation method is shown to lead to serious errors.

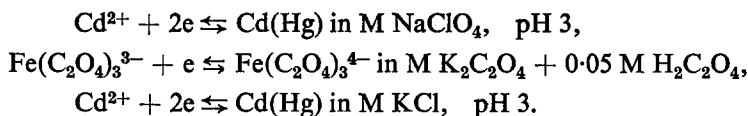
**Résumé**—Par la voie expérimentale on a vérifié les conclusions décrites dans la partie I<sup>1</sup> pour les systèmes Cd<sup>2+</sup>/Cd(Hg) en M NaClO<sub>4</sub>, Fe<sup>2+</sup>/Fe<sup>3+</sup> en M oxalate et Cd<sup>2+</sup>/Cd(Hg) en M KCl. On a trouvé que la méthode numérique donne des valeurs de la constante de vitesse  $k_{sh}$  s'accordant avec celles obtenues par extrapolation graphique uniquement au cas où la réaction est relativement irréversible. Dans le cas d'une réaction rapide, on a démontré que la méthode d'extrapolation classique mène à de graves erreurs.

**Zusammenfassung**—Mittels die Cd<sup>2+</sup>/Cd(Hg) in M NaClO<sub>4</sub>, die Fe<sup>2+</sup>/Fe<sup>3+</sup> in M Oxalat und die Cd<sup>2+</sup>/Cd(Hg) in M KCl Elektroden werden die Folgerungen aus Teil 1 experimental geprüft. Es wird gezeigt das die numerische Methode nur Werte für die Reaktionskonstante liefert, welche übereinstimmen mit denen erhalten mit der graphische Extrapolation, falls die Reaktion ziemlich irreversibel ist. Sonst, wenn die Reaktion schnell ist, wird das klassische Extrapolationsverfahren zu ernsthafte Fehler führen.

### INTRODUCTION

IN A RECENT paper<sup>1</sup> the applicability of the faradaic rectification method was discussed for the determination of the standard rate constant  $k_{sh}$  and the charge transfer coefficient  $\alpha$  of an electrode reaction. Two new approaches were proposed, namely the "numerical method" and the "zero-point method". It was argued that these two methods are to be preferred to the original "graphical method", proposed by Delahay *et al.*<sup>2,3</sup> and in any case should be used to check the results of the graphical method.

In this paper these statements are verified on the basis of experiments. Three electrode reactions with increasing degrees of reversibility have been examined,



The kinetic parameters obtained with the several procedures are compared, and, as far as possible, with results from other relaxation methods reported in the literature.

### EXPERIMENTAL

#### *Apparatus and measuring procedure*

The electrical circuit, in principle similar to that used by Senda, Imai and Delahay,<sup>4</sup> is schematically shown in Fig. 1.

A sine-wave generator SWG is modulated by a pulse generator PG synchronized on the line frequency to avoid 50 Hz hum. The modulation time was chosen as short

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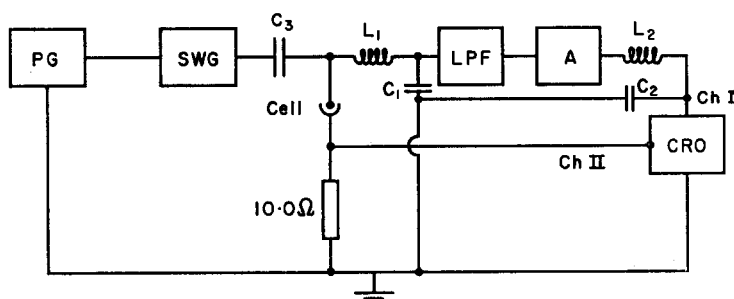


FIG. 1. SWG, Signal generator model 606A: Hewlett-Packard  
 A, Low noise amplifier model 465A. Hewlett-Packard  
 CRO, Oscilloscope type 547 Tektronix, provided with a type 1A1 dual trace plug-in unit.  
 PG, Pulse generator system 1000: Exact Electronics  
 LPF, active low pass filter type 3202: Krohn-Hite company.

as possible in order to avoid excessive heating of the solution. However, the modulation time should be long enough for the rectification signal to reach a virtually constant value, indicating that charging of the double layer corresponding to the proper value of  $\Delta E_{\infty}$  is established. It was assumed that spurious heating did not occur, if in a small extension of the modulation time the rectification signal exhibited no further change. The resulting sine-wave train, generally with a duration of 0.1–0.5 ms, is led through a leak-free capacitor ( $C_3$ , 0.066  $\mu\text{F}$ ) and the galvanic cell. The capacitor avoids dc flow through the sine-wave generator.

In series with the cell, an inductance-free resistance (10.0  $\Omega$ ) is used for measuring the ac through the cell by means of a cathode ray oscilloscope (CRO).

The lower frequent part of the cell response is isolated by means of a low pass filter LPF and the resulting dc pulse is amplified by means of a low-noise wide band amplifier A with a maximum amplification of 40 dB. The passive low-pass filter  $L_1$ – $C_1$  is needed in order to avoid overload on the active low-pass filter LPF. The filter  $L_2$ – $C_2$  eliminates the noise picked up by the amplifier A. Finally the amplitude  $\Delta E_{\infty}$  of the dc pulse is measured on the second channel of the CRO.

Since for theoretical reasons  $\Delta E_{\infty}$  should not exceed 0.2 mV,<sup>5</sup> if possible, the ac was adjusted so that a rectification signal with an amplitude of exactly 0.2 mV was obtained.

#### *Cell and electrode construction*

A small polarographic cell with a capacity of about 25 ml was used. The cell was placed in a well earthed copper box, in order to avoid transmitting, and to reduce the pick-up of disturbing signals as much as possible. The cell was thermostated at  $25 \pm 0.1^\circ\text{C}$ .

Instead of a dme, a micrometer all-glass syringe provided with a capillary was used. The micrometer syringe outfit was fitted with a small electric motor and a magnetic hammer, constructed in such a way that every 10 s a fresh amalgam or mercury drop was pushed out of the capillary. In this way the advantages of the dme and the hanging mercury-drop electrode were combined. Measurements with dilute amalgams were performed with the dme, in order to avoid oxidation of the amalgam.

## RESULTS

From the measured faradaic rectification signal  $\Delta E_\infty$  and the applied ac amplitude  $i_A$  the quantity  $F_r = \Delta E_\infty \omega^2 C_d^2 / i_A^2$  was calculated as a function of frequency, using double-layer capacitance data pertaining to the base electrolyte solution at the same potential as the equilibrium potential of the redox system. The following values for  $C_d$  were used:  $28 \mu\text{F}/\text{cm}^2$  for  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in 1 M  $\text{NaClO}_4$ ,<sup>6</sup>  $26\text{--}29 \mu\text{F}/\text{cm}^2$  for  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in 1 M  $\text{KCl}$ ,<sup>6,8</sup> and  $43 \mu\text{F}/\text{cm}^2$  for the ferric–ferrous oxalate couple. (The latter was measured separately using an ac bridge). The results are plotted in Figs. 2–4.

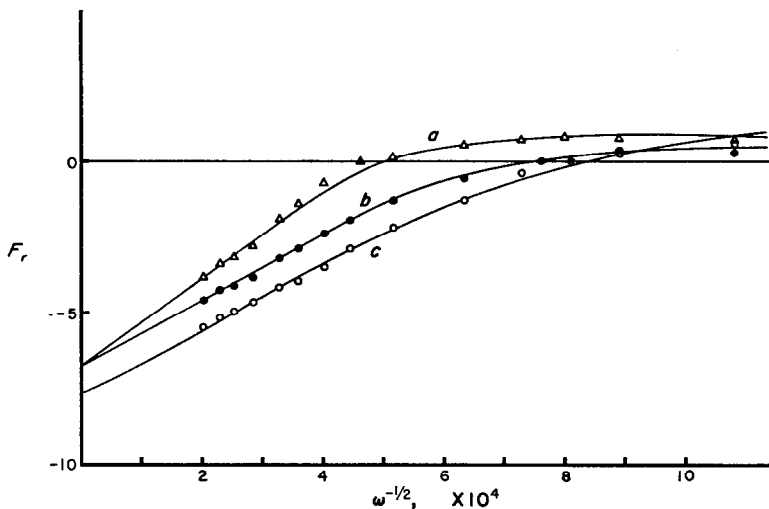


FIG. 2. Plot of  $F_r$  against  $\omega^{-1/2}$  for  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in 1 M  $\text{NaClO}_4$ , pH 3. *a*, 30 mM  $\text{Cd}^{2+}/2$  mM  $\text{Cd}(\text{Hg})$ ; *b*: 20 mM  $\text{Cd}^{2+}/2$  mM  $\text{Cd}(\text{Hg})$ ; *c*: 7.5 mM  $\text{Cd}^{2+}/1$  mM  $\text{Cd}(\text{Hg})$ .

(a)  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in 1 M  $\text{NaClO}_4$ , pH 3

This system is—in the scope of the faradaic rectification method—fairly irreversible and consequently suitable for testing the experimental set-up and the analysis procedures described previously.<sup>1</sup> The kinetic parameters of the electrode reaction have been determined by Kooijman and Sluyters<sup>6,7</sup> using the galvanostatic single-pulse method, as  $k_{\text{sh}} = 0.46 \pm 0.03$  cm/s,  $\alpha = 0.20 \pm 0.03$ ,  $D_0 = 8 \times 10^{-6}$  cm<sup>2</sup>/s and  $D_R = 9 \times 10^{-6}$  cm<sup>2</sup>/s.

The extrapolation procedure introduced by Delahay *et al*<sup>2</sup> is based on the approximate expression for  $F_r$ ,

$$F_r = \frac{\Delta E_\infty \omega^2 C_d^2}{i_A^2} = \frac{nF}{RT} \left\{ \frac{2\alpha - 1}{4} - \frac{1}{2} \left[ \alpha - \frac{r}{r+1} \right] \frac{\omega^{-1/2}}{p'} \right\} \quad (1)$$

where

$$r = \frac{C_0^\circ \sqrt{D_0}}{C_R^\circ \sqrt{D_R}} \quad (2)$$

and

$$p' = \frac{p}{\sqrt{\omega}} = \frac{\sqrt{2} D_0^{(1-\alpha)/2} D_R^{\alpha/2}}{k_{\text{sh}}} \cdot \frac{r^\alpha}{r+1} \quad (3)$$

$C_0^\circ$  and  $C_R^\circ$  are the equilibrium concentrations, the other symbols having their

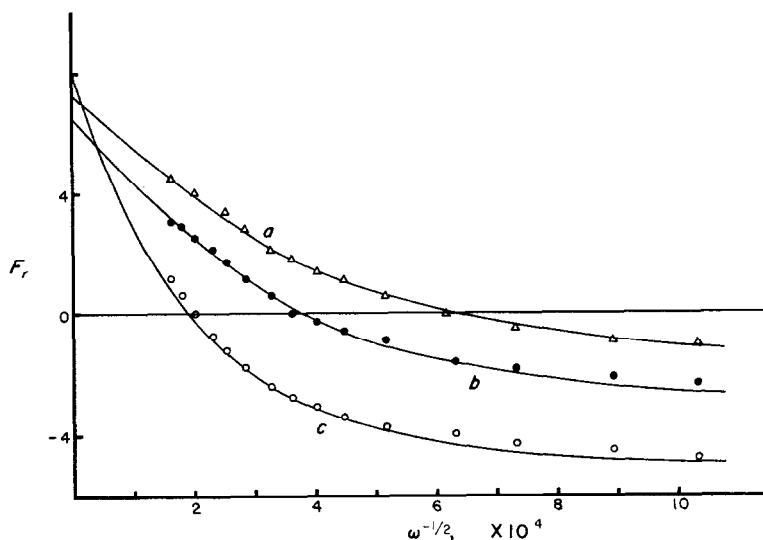


FIG. 3. Plot of  $F_r$  against  $\omega^{-1/2}$  for  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{Fe}(\text{C}_2\text{O}_4)_4^{4-}$  in M  $\text{K}_2\text{C}_2\text{O}_4 + 0.05 \text{ M H}_2\text{C}_2\text{O}_4$ .  
*a*, 3 mM  $\text{Fe}^{3+}/10 \text{ mM Fe}^{2+}$ ; *b*, 2 mM  $\text{Fe}^{3+}/10 \text{ mM Fe}^{2+}$ ; *c*, 1 mM  $\text{Fe}^{3+}/10 \text{ mM Fe}^{2+}$ .

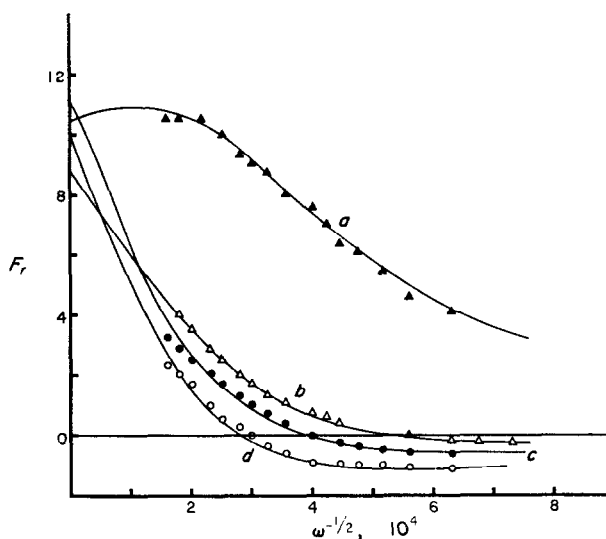


FIG. 4. Plot of  $F_r$  against  $\omega^{-1/2}$  for  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in M KCl, pH 3.  
*a*, 10 mM  $\text{Cd}^{2+}/2 \text{ mM Cd}(\text{Hg})$ ; *b*, 3 mM  $\text{Cd}^{2+}/5 \text{ mM Cd}(\text{Hg})$ ;  
*c*, 2.5 mM  $\text{Cd}^{2+}/5 \text{ mM Cd}(\text{Hg})$ ; *d*, 2 mM  $\text{Cd}^{2+}/5 \text{ mM Cd}(\text{Hg})$ .

usual meaning. The Ox/Red ratio  $r$  may be considered as a known parameter, calculated with the diffusion coefficients mentioned.

In Fig. 2 the points between  $\omega^{-1/2} = 4 \times 10^{-4}$  and  $2 \times 10^{-4}$  lie on virtually straight lines, which on application of (1) give the  $\alpha$  and  $k_{sh}$  values reported in Table 1.

With these results it can be calculated that in the quoted frequency range the system is sufficiently irreversible ( $p > 4$  even in the unfavourable case, where  $r \approx 15$ )

TABLE 1

Electrode reaction	Curve	$r$	$\alpha$	Extrapolation method		Numerical method	
				$k_{sh}$	Average value	$k_{sh}$	Average value
Cd <sup>2+</sup> /Cd(Hg) in M NaClO <sub>4</sub>	<i>a</i>	14.2	0.34	0.47 cm/s	$\alpha = 0.32 \pm 0.03$	0.46 cm/s	$\alpha = 0.32 \pm 0.02$
	<i>b</i>	9.4	0.32	0.46 cm/s	$k_{sh} = 0.46 \pm 0.04$	0.42 cm/s	$k_{sh} = 0.44 \pm 0.03$
	<i>c</i>	7.1	0.31	0.44 cm/s		0.44 cm/s	
Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>2-</sup> /Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>4-</sup> in M K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.05 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	<i>a</i>	0.3	0.83	0.87 cm/s	$\alpha = 0.78 \pm 0.04$	1.16 cm/s	$\alpha = 0.86 \pm 0.04$
	<i>b</i>	0.2	0.79	0.87 cm/s	$k_{sh} = 0.86 \pm 0.03$	1.13 cm/s	$k_{sh} = 1.16 \pm 0.04$
	<i>c</i>	0.1	0.72	0.84 cm/s		1.20 cm/s	
Cd <sup>2+</sup> /Cd(Hg) in M KCl	<i>a</i>	5.0	0.83	—		4.2 cm/s	
	<i>b</i>	0.6	0.67	2.7 cm/s	$\alpha = 0.65 \pm 0.03$	3.6 cm/s	$\alpha = 0.75 \pm 0.03$
	<i>c</i>	0.5	0.65	2.4 cm/s	$k_{sh} = 2.5 \pm 0.3$	4.6 cm/s	$k_{sh} = 4.1 \pm 0.5$
	<i>d</i>	0.4	0.63	2.3 cm/s		4.2 cm/s	

to permit the simplification of the general equation<sup>1</sup> with  $(p+2)/(p^2+2p+2) \approx 1/p$ .<sup>1</sup> Moreover, the terms in  $\sigma$  in the denominator of the general equation [see (4)] appear to be negligible with respect to  $p^2+2p+2$ , which justifies the other simplification, *ie*  $V_A \approx \omega C_d/i_A$ , so that it may be concluded that in this case the extrapolation method leads to fairly reliable results.

This is confirmed by the results of the numerical method, which have been obtained by fitting the measured  $F_r$  values in the whole frequency range to theoretical curves calculated with the general equation<sup>1</sup>

$$F_r = \frac{\Delta E_\infty \omega^2 C_d^2}{i_A^2} = \frac{nF}{4RT} \left\{ \frac{(2\alpha - 1)(p^2 + p) + \frac{r-1}{r+1}(p+2)}{(p+1)^2 + (\sigma^{-1} C_d^{-1} \omega^{-1/2} + 1)^2} \right\}, \quad (4)$$

where

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left( \frac{1}{C_O^\circ \sqrt{D_O}} + \frac{1}{C_R^\circ \sqrt{D_R}} \right). \quad (5)$$

The values of  $\alpha$  and  $k_{sh}$  giving the best fitting theoretical curves, *viz* the lines in Fig. 2, are also given in Table 1.

The rate constant  $k_{sh} = 0.44 \pm 0.03$  cm/s is in excellent agreement with the results of the galvanostatic pulse method,<sup>7</sup> but the agreement of the  $\alpha$  values is less satisfactory. The question arises, to what extent this can be caused by an erroneous choice of the double-layer capacitance  $C_d$ , necessary to calculate  $F_r$  from the experimental data. The possibility should not be overlooked that  $C_d$  is influenced by the large concentrations of cadmium in the solution. However,  $\alpha$  is much less sensitive for  $C_d$  than  $k_{sh}$  (an increase of 25 per cent in  $C_d$  would reduce  $\alpha$  to 0.25, but increase  $k_{sh}$  to 0.6 cm/s), so that this seems not very probable.

Uncertainty due to the double-layer capacitance would not interfere in the third analysis method, the zero-point method. If, for a given Ox/Red ratio  $r$ ,  $\Delta E_\infty$  is zero at frequency  $\omega_0$ , one has from (4) and (3),

$$\frac{2\omega_0 D r^{2\alpha} + (2\omega_0 D r^{2\alpha})^{1/2} k_{sh}(r+1)}{(2\omega_0 D r^{2\alpha})^{1/2} k_{sh} + 2k_{sh}^2(r+1)} = \frac{(r-1)}{(1-2\alpha)}, \quad (6)$$

where

$$D = D_0^{(1-\alpha)} D_R^\alpha.$$

In principle the two unknowns  $k_{sh}$  and  $\alpha$  can be solved from (6) by applying it to two "zero frequency points" obtained for two different values for  $r$ .

Because of the complexity of (6), this is most efficiently done by rewriting it

$$k_{sh} = \frac{(2\omega_0 D r^{2\alpha})^{1/2} \{1 - \alpha(r+1) \pm [\alpha^2(r+1)^2 - 2\alpha(2r^2 + r - 1) + (2r^2 - 1)]^{1/2}\}}{2(r^2 - 1)} \quad (7)$$

and calculating  $k_{sh}$  as a function of  $\alpha$  for the different zero points, after insertion of the experimental  $\omega_0$  and  $r$  values. On comparing the obtained pairs of  $k_{sh}$  and  $\alpha$ , the proper solution will be found as that pair which all experiments have in common, of course within the experimental accuracy. The latter is mainly determined by the accuracy in  $\omega_0$  (*ca* 10 per cent), which imposes an error of 5 per cent in  $k_{sh}$ . Unfortunately, a "false" solution also exists, namely " $\alpha$ " = 0.5, " $k_{sh}$ " = 0. The spacing

between " $k_{sh}$ " values at the "wrong" values of " $\alpha$ " in between is sometimes insufficient to exceed the experimental error, especially if  $\alpha$  is close to 0.5.

From Table 2 it can be seen that this involves a rather poor accuracy in estimating the proper result for the  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  system in  $\text{M NaClO}_4$ :  $0.3 < k_{sh} < 0.5$  and  $0.2 < \alpha < 0.4$ .

TABLE 2.  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  ELECTRODE REACTION IN  $\text{M NaClO}_4$ ;  $k_{sh}$  IN  $\text{cm/s}$  FOR VARIOUS CHOSEN VALUES OF  $\alpha$

$r$	$\omega_0$	$\alpha = 0$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.45$
14.2	$4.35 \times 10^6 \text{ rad/s}$	0.44	0.48	0.49	0.45	0.32	0.20
9.4	$1.73 \times 10^6 \text{ rad/s}$	0.43	0.45	0.44	0.39	0.27	0.16
7.1	$1.52 \times 10^6 \text{ rad/s}$	0.56	0.56	0.54	0.45	0.31	0.18

(b)  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{Fe}(\text{C}_2\text{O}_4)_3^{4-}$  in  $\text{M K}_2\text{C}_2\text{O}_4 + 0.05 \text{ M H}_2\text{C}_2\text{O}_4$

Unpublished studies of this system performed in our laboratory with the galvanostatic single-pulse method<sup>6</sup> and the impedance method<sup>9</sup> gave  $1 < k_{sh} < 3 \text{ cm/s}$ , which is about the limit of the scope of these methods. Consequently, they cannot give a reliable value of the transfer coefficient. The diffusion coefficients are found to be equal,  $D_O = D_R = 4 \times 10^{-6} \text{ cm}^2/\text{s}$ .

In Fig. 3 it can be seen that the extrapolation method is less useful than in the preceding case. This manifests itself clearly in the results represented in Table 1. The extrapolation method yields values for  $\alpha$  and  $k_{sh}$  systematically smaller than those obtained by the numerical method. Still, the consistency of  $\alpha$  and  $k_{sh}$  for different Ox/Red ratios is approximately equal for both methods, so that an error of easily 30 per cent in  $k_{sh}$  is made if the extrapolation method is applied.

The zero-point method can be used for this system, partially because of the extreme  $\alpha$ -value. The results, Table 3,  $1.10 < k_{sh} < 1.20 \text{ cm/s}$  and  $0.80 < \alpha < 0.88$ , are in very good agreement with those of the numerical procedure, and justify therefore the choice of  $43 \mu\text{F}/\text{cm}^2$  for  $C_a$  in the latter.

(c)  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  in  $\text{M KCl}$ , pH 3

No reliable data on the kinetic parameters of this electrode reaction have been published, since this reaction is too reversible for a successful application of other relaxation methods: Kooijman and Sluyters<sup>6</sup> reported  $k_{sh} > 5 \text{ cm/s}$ . Earlier ac bridge measurements<sup>8</sup> led us to the conclusion that  $k_{sh} > 12 \text{ cm/s}$ . The diffusion coefficients evaluated from these experiments are approximately  $D_O = D_R = 9 \times 10^{-6} \text{ cm}^2/\text{s}$ . Values for  $C_a$  are for curve *a*,  $29 \mu\text{F}/\text{cm}^2$ , and for *b*, *c* and *d*,  $26 \mu\text{F}/\text{cm}^2$ .

In Fig. 4 it can be seen that with the faradaic rectification method a distinct deviation from reversible behaviour can be observed. So, from a careful analysis an estimation of the kinetic parameters must be possible. Table 1 shows that the extrapolation method leads, for the curves *b*, *c* and *d* (Fig. 4), to mutually fitting values for  $\alpha$  and  $k_{sh}$ . Curve *a*, on the other hand, leads to a deviating value for  $\alpha$ , while no information about  $k_{sh}$  is obtained because in (1) the term  $(\alpha - r/(r + 1)) \approx 0$ . If the results of the extrapolation method are used to calculate  $F_r$  vs  $\omega^{-1/2}$  curves with the rigorous (4), a large discrepancy is found from the experimental points, so that it may be concluded that the  $\alpha$  and  $k_{sh}$  values obtained by extrapolation must be erroneous.

TABLE 3.  $k_{\text{an}}$  IN  $\text{cm}^2/\text{s}$  FOR VARIOUS CHOSEN VALUES OF  $\alpha$  FOR THE FERRIC FERROUS OXALATE COUPLE, CALCULATED WITH (6)

$r$	$\omega_0$	$\alpha = 0.70$	$\alpha = 0.75$	$\alpha = 0.80$	$\alpha = 0.82$	$\alpha = 0.84$	$\alpha = 0.86$	$\alpha = 0.88$	$\alpha = 0.90$	$\alpha = 0.95$
0.3	$2.7 \times 10^6 \text{ rad/s}$	0.85	0.96	1.06	1.09	1.13	1.15	1.18	1.21	1.25
0.2	$7.23 \times 10^6 \text{ rad/s}$	0.94	1.05	1.13	1.16	1.18	1.20	1.21	1.23	1.26
0.1	$25 \times 10^6 \text{ rad/s}$	0.99	1.06	1.11	1.11	1.12	1.12	1.12	1.12	1.11

TABLE 4.  $k_{\text{an}}$  IN  $\text{cm}^2/\text{s}$  FOR VARIOUS CHOSEN VALUES OF  $\alpha$  FOR THE  $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$  COUPLE IN M KCl, CALCULATED WITH (6)

$r$	$\omega_0$	$\alpha = 0.55$	$\alpha = 0.60$	$\alpha = 0.65$	$\alpha = 0.70$	$\alpha = 0.75$	$\alpha = 0.80$	$\alpha = 0.85$	$\alpha = 0.90$	$\alpha = 0.95$	$\alpha = 1.0$
0.6	$3.45 \times 10^6 \text{ rad/s}$	1.2	2.1	2.9	3.7	4.3	4.9	5.5	6.0	6.4	6.8
0.5	$6.28 \times 10^6 \text{ rad/s}$	1.2	2.1	2.9	3.6	4.2	4.8	5.3	5.7	6.1	6.4
0.4	$12.2 \times 10^6 \text{ rad/s}$	1.3	2.2	3.0	3.7	4.3	4.8	5.2	5.6	5.9	6.2



Since the curves *b*, *c* and *d* have a zero point, it might be possible to obtain more reliable results with the zero-point method.

From Table 4, however, the only conclusion that can be drawn is that  $0.5 < \alpha < 1$  and  $k_{sh} < 7$ . This may be due to the fact that rather close values for *r* are chosen. Extension of the Ox/Red ratio range is not very useful: for larger *r* the zero point is shifted to lower frequency where the electrode reaction behaves more reversibly; for smaller *r* the experimentally accessible frequency range is exceeded.

Consequently, only the numerical method is useful. The results reported in Table 1, are fairly consistent. However, it will be clear that the absolute reliability should be considered carefully. The diagrams in Figs. 5a, 5b and 5c may give an idea in this direction. In Fig. 5a, three curves are calculated for one  $k_{sh}$  value and for three different  $\alpha$  values. The value of  $\alpha$  for which the experimental curve fitted in the best way, was used for calculating the three curves of Fig. 5b, where only the value of

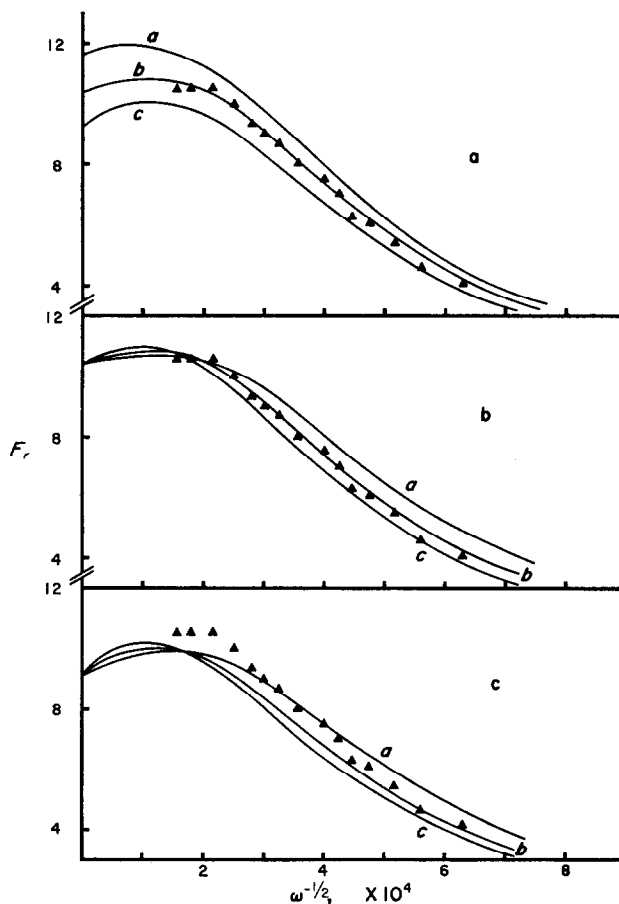


FIG. 5. Plot of  $F_r$  against  $\omega^{-1/2}$  for 10 mM  $\text{Cd}^{2+}/2$  mM  $\text{Cd}(\text{Hg})$  in M KCl, pH 3 (curve *a*, Fig. 4).

Calculated curves:

a: *a*,  $\alpha = 0.79$ , *b*,  $\alpha = 0.76$ ; *c*,  $\alpha = 0.73$ .  $k_{sh} = 4$  for all three curves.

b: *a*,  $k_{sh} = 3$  cm/s; *b*,  $k_{sh} = 4$  cm/s; *c*,  $k_{sh} = 5$  cm/s.  $\alpha = 0.76$  for all three curves.

c: *a*,  $k_{sh} = 3$  cm/s; *b*,  $k_{sh} = 4$  cm/s; *c*,  $k_{sh} = 5$  cm/s.  $\alpha = 0.73$  for all three curves.

$k_{sh}$  was varied. Finally, in Fig. 5c three curves were calculated for the same  $k_{sh}$  values used in Fig. 5b, but for a deviating value for  $\alpha$ . In this way the accuracy of the numerical method, *ie* the effect of a change in  $\alpha$  and  $k_{sh}$  on the procedure, can easily be shown.

#### DISCUSSION

The present investigation clearly demonstrates that the kinetic parameters obtained by extrapolation of faradaic rectification data to infinite frequency (the extrapolation method) can be seriously in error, though the results from experiments with different Ox/Red ratio are virtually consistent. As a rule, the results must be distrusted, if  $k_{sh}$  is found to exceed 0.5 cm/s. This limit is, of course, dependent on the limit of the accessible frequency range, which in our case is 16 MHz. In our opinion, it is doubtful whether experimental difficulties inherent to extension to higher frequencies can be excluded sufficiently.

Despite the advantages of eliminating the necessity to measure the double-layer capacitance and the ac amplitude, the zero-point method is disappointing as an independent method. Evidently widely spaced values for  $r$  should be chosen to prevent two equations of the form of (6) from becoming practically identical. However, extreme Ox/Red ratios are too sensitive for oxidation or reduction of the less stable component. This could be improved by incorporating a dc polarizing circuit in the electrical set-up, so that the less stable component could be generated *in situ*. Nevertheless, the zero-point method is useful in combination with either the extrapolation method or preferably the numerical method. Especially if  $\alpha$  is known, a sharp determination of  $k_{sh}$  is possible, as can be seen from Tables 2-4.

The most secure way to obtain information from faradaic rectification experiments is the numerical method, the procedure of which is extensively described in the present and in the preceding paper.<sup>1</sup> It may be noted that this procedure requires knowledge of the same data ( $i_A$ ,  $C_d$ ,  $D_O$ ,  $D_R$ ) as are needed for the extrapolation method. If possible the analyses should be done with different Ox/Red ratios and preferably at least one of the experimental  $F$ , *vs*  $\omega^{-1/2}$  curves should comprise a zero point, so that the chosen value of  $C_d$  can be checked. In this way the potentialities of the faradaic rectification method really exceed those of the other known relaxation methods: even for a very rapid electrode reaction such as the cadmium system in KCl, both the rate constant and the transfer coefficient can be determined with high precision (0.03 in  $\alpha$  and 10 per cent in  $k_{sh}$ ). The method is therefore particularly useful for a careful examination of the kinetic parameters of rapid electrode reactions under various circumstances. For example, our present results reveal a strong influence of the nature of the supporting electrolyte not only on the rate constant of the Cd<sup>2+</sup>/Cd(Hg) electrode reaction, which has been observed before,<sup>6</sup> but also on the transfer coefficient, which to our knowledge has not been reported earlier.

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