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Faradaic Impedance of Fast Electrode Processes as Measured by an Impedance Bridge Using an Inductor

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An impedance bridge using an inductor in parallel with the cell is proposed for accurate measurement of kinetic parameters of fast electrode processes. The theory and method of analysis are given in detail. Its applicability was proved up to at least 50 kc, and possibly at higher frequencies. The kinetic parameters obtained by this method for the electrode reaction Cd^{2+}+2e=Cd(Hg) in M Na$_2$SO$_4$ at the D. M. E. were α=0.17, and k°=0.064 cm/sec (25°C).

A conventional impedance bridge1) for measurement of faradaic impedance is composed of resistors and capacitors, and the faradaic impedance is replaced by a series or parallel R-C network. This type of a.c. bridge has shown its usefulness in evaluating kinetic parameters of electrode processes, although it can not be applied to measurement at frequencies higher than several ten thousands cps due to its low response. The reason can easily be understood from the fact that the faradaic impedance is in parallel with the differential capacity, and that the impedance of the latter is very small at higher frequencies.

However, high frequency is necessary in order to evaluate the kinetic parameters of fast electrode processes.[*1]

For capacity measurement, Melik-Gaikazyan2) recommended the use of a very small inductance in series with the cell, and Lorenz suggested the use of a T-bridge.3) In this paper it is tentatively proposed to use an inductor[*2] in parallel with the cell in an a.c. bridge in order to improve its applicability at higher frequencies. The inductor used was in parallel with the cell so as to be in resonance with the capacitive component of the electrode-solution double layer so that the impedance of the imaginary component will be infinite. (The series resonant circuit was also investigated, with the details omitted here because of its complexity for practical use.) It was found that this improved a.c. bridge can be used up to at least 50 kc. The method of analysis is described in detail with an application to the fast electrode process, Cd^{2+}+2e=Cd(Hg), at the dropping mercury electrode.

Experimental

Reagents and Solution. All the reagents were of analytical grade. The solution contained 0.5 mM Cd^{2+} (weighed as CdSO$_4\cdot$H$_2$O) in M Na$_2$SO$_4$ as the supporting electrolyte. Purified nitrogen was used for deaeration, and measurement was carried out in a nitrogen atmosphere. Temperature was kept constant at 25±0.1°C.

Electrode and Cell. The working electrode was a dropping mercury electrode (DME), and it was made of capillary tubing used in a usual Hg-thermometer. In the top of the capillary (17 cm in length) a Pt wire (0.012 cmϕ, 5 cm in length) was inserted, and the upper part of the capillary was constricted in order to give an appropriate flow rate of mercury. The lifetime of the D. M. E. was about 6 sec in the open circuit. A hammer was used to give drops at 4.0 sec intervals. The resistance of the DME was as small as 4.5 Ω. The auxiliary electrode was a smooth Pt cylinder, and a saturated-Hg$_2$SO$_4$ electrode (SSE) was used as the reference.

Generation of Reductant *in situ*. A potentiometer circuit (P in Fig. 1A) was used to give an optional

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1) D. C. Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946); **71**, 2975 (1949); *J. Phys. Chem.*, **61**, 701 (1957); J. E. B. Randles, *Trans. Faraday Soc.*, **50**, 1246 (1954); J. Shön, W. Mehl and H. Gerischer, *Z. Electrochem.*, **59**, 144 (1955).

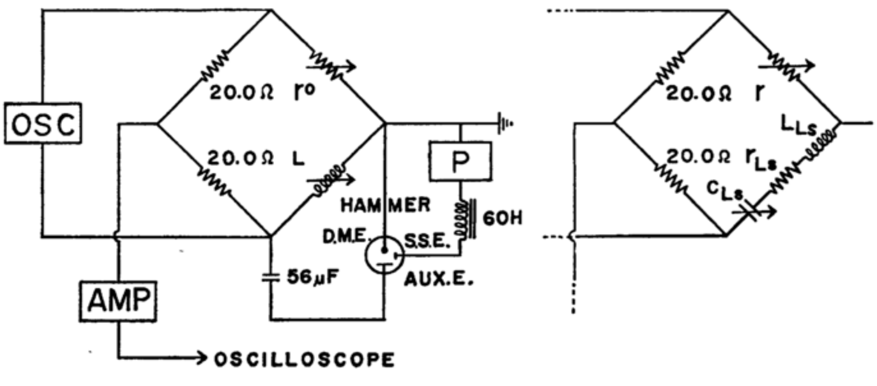
[*1] When diffusion is the sole mode of mass transfer, the average flux of the reducing species diffusing toward a plane electrode is given by $2C^*(D/\pi t)^{1/2}$, where C^* is the bulk concentration of the reducing species, D the diffusion coefficient, and t the time elapsed since the beginning of the electrolysis. In a process with mixed control by both mass- and charge-transfer, this conclusion is qualitatively valid, and diffusion is no longer rate-determining for a measurement with very short electrolysis time, or at a sufficiently high frequency, the concentration gradient in the diffusion layer being steep enough. Thus the evaluation of kinetic parameters of fast charge transfer processes inherently necessitates measurement in a very short time interval, or the application of high frequency.

2) V. I. Melik-Gaikazyan, *Zhur. Fiz. Khim.*, **26**, 560 (1952); V. I. Melik Gaikazyan and P. Dolin, *Doklady Akad. Nauk S. S. S. R.*, **66**, 409 (1949).

3) W. Lorenz, *Z. physik. Chem. Neue Folge*, **26**, 424 (1960).

[*2] The authors are indebted to Professor T. Kambara of Hokkaido University for his suggestion to use an inductor in series with the cell in order to improve the sensitivity of an a. c. polarograph.4)

4) T. Kambara and K. Hasebe, *Rev. Polarography (Japan)*, **13**, 132 (1966).



A B

Fig. 1. A: Bridge circuit for the faradaic impedance measurements. OSC, audio-generator; P, potentiometer; AMP, selective amplifier.

B: Bridge circuit for the measurement of the real (r_{Ls}) and imaginary (L_{Ls}) components of the inductor L in resonance with the cell.

electrode potential. Thus the reductant was generated *in situ,* and the concentrations of the oxidant (C_O) and reductant (C_R) at the pre-electrode layer can be calculated from polarographic theory, *i. e.,*

$$C_O = C_O^*\left(1-\frac{i}{i_d}\right) \tag{1}$$

$$C_R = C_O^*\left(\frac{D_O}{D_R}\right)^{1/2}\cdot\frac{i}{i_d} \tag{2}$$

where C_O^* is the bulk concentration of the reducing species, i the current flowing at a given potential, i_d the diffusion-controlled current, and the D's are the diffusion coefficients. The current was recorded by a Shimadzu Model RP-3 polarograph.

A. C. Bridge. The a. c. voltage applied to the cell was about 5 mV peak to peak and was supplied from an audio-generator, Trio Model AG-10 (OSC in Fig. 1A). The frequency was calibrated by a crystal oscillator (15 kc). The out-put of the bridge was fed to a selective amplifier (AMP in Fig. 1A), Yokogawa-Hewlett-Packard, Model AL-11, and was detected by a synchro-oscilloscope, Iwasaki Model SS-5302 with a plug-in amplifier, Model SP-30H-A.

The bridge circuit is shown in Fig. 1, where a variable inductor (L in Fig. 1, 400 μH—1 mH) was connected in parallel with the cell. A large capacitor (56 μF) was used in series with the cell in order to shut off the potentiometer circuit. The two resistors in the two arms of the bridge were 20.0 Ω and inductanceless. A variable resistor (r° in Fig. 1) used for balancing the bridge was composed of a decade box (0.1 Ω—1.1 kΩ in 4 stages) and a manganin wire (0.01 Ω—0.1 Ω) with a sliding contact.

The bridge balance was detected at the maximum size of the mercury drop. The surface area of the DME was calculated by means of the following equation:

$$S(\mathrm{cm}^2,\ 25^\circ\mathrm{C}) = 0.00852\ (mt)^{2/3}, \tag{3}$$

where m is the rate of flow of mercury in mg/sec, and t the life-time of the DME (=4.0 sec using the hammer).

Theoretical

Equivalent Circuit of the Cell. The equivalent circuit of the cell components is illustrated in Fig. 2A, where r_{cap} is the capillary resistance, r_e the solution resistance, r_s, and C_s the series resistive, and capacitive components of the faradaic impedance, respectively, and C_l the differential capacity of the double layer. The total impedance

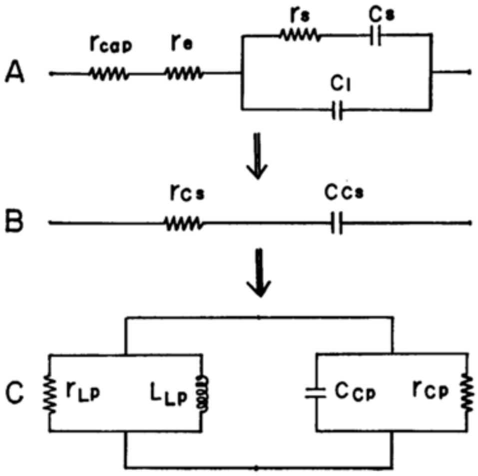


Fig. 2. Conversion scheme of the equivalent circuit of the cell.

A: Equivalent circuit of the overall cell circuit: r_{cap}, capillary resistance; r_e, solution resistance; r_s and C_s; series resistive and capacitive components of the faradaic impedance, respectively; C_l, differential capacity of the double layer.

B: Equivalent simple series circuit.

C: Equivalent simple parallel circuit of the cell and inductor in a resonant condition: The suffix, C or L represents the cell or inductor, respectively.

(Z) of this cell circuit is represented by:

$$Z = Z_{\text{real}} + \frac{1}{j} Z_{\text{imaginary}} \tag{4}$$

with

$$Z_{\text{real}} = r_{\text{cap}} + r_e + \left(\frac{1}{\omega C_l}\right)^2 \frac{r_s}{r_s^2 + \left(\frac{1}{\omega C_s} + \frac{1}{\omega C_l}\right)^2} \tag{5}$$

and

$$Z_{\text{imaginary}} = \frac{1}{\omega C_l} - \left(\frac{1}{\omega C_l}\right)^2 \frac{\frac{1}{\omega C_s} + \frac{1}{\omega C_l}}{r_s^2 + \left(\frac{1}{\omega C_s} + \frac{1}{\omega C_l}\right)^2} \tag{6}$$

In Eqs. (5) and (6), r_{cap} and r_e can be determined separately, and C_l at a given potential can also be determined by using the base line shown in the plot of C_{Cs} *versus* E (Fig. 5).

Conversion to an Equivalent Simple Series Circuit of the Cell. In order to evaluate r_s and C_s in Eqs. (5) and (6), a conversion of the equivalent circuit in Fig. 2A to an equivalent simple series circuit as shown in Fig. 2B was made. Then the total impedance (Z) in Eq. (4) becomes:

$$Z = r_{\text{Cs}} + \frac{1}{j\omega C_{\text{Cs}}} \tag{7}$$

with $$Z_{\text{real}} = r_{\text{Cs}} \tag{8}$$

and $$Z_{\text{imaginary}} = \frac{1}{\omega C_{\text{Cs}}} \tag{9}$$

Equations (5), (6), (8) and (9) lead to the following expressions for r_s and $1/\omega C_s$;

$$r_s = \left(\frac{1}{\omega C_l}\right)^2 \frac{r_{\text{Cs}} - r_{\text{cap}} - r_e}{(r_{\text{Cs}} - r_{\text{cap}} - r_e)^2 + \left(\frac{1}{\omega C_l} - \frac{1}{\omega C_{\text{Cs}}}\right)^2} \tag{10}$$

$$\frac{1}{\omega C_s} = \left(\frac{1}{\omega C_l}\right)^2 \frac{\frac{1}{\omega C_l} - \frac{1}{\omega C_{\text{Cs}}}}{(r_{\text{Cs}} - r_{\text{cap}} - r_e)^2 + \left(\frac{1}{\omega C_l} - \frac{1}{\omega C_{\text{Cs}}}\right)^2} - \frac{1}{\omega C_l} \tag{11}$$

Inductor in Resonance with Cell. In the circuit shown in Fig. 1A the inductor is in parallel with the cell, and at the null point of the bridge the cell and inductor are in a resonant condition. The condition is taken into account by the conversion of the equivalent circuit given in Fig. 2B into the equivalent parallel circuit given in Fig. 2C. In Fig. 2C the inductor is also represented by an equivalent parallel circuit.

The resonant condition, in general, is given by

$$\omega L = \frac{1}{\omega C} \tag{12}$$

Accordingly, one is lead to the following relationship,

$$\omega L_{\text{Lp}} = \frac{1}{\omega C_{\text{Cp}}} \tag{13}$$

and

$$\frac{1}{r^\circ} = \frac{1}{r_{\text{Lp}}} + \frac{1}{r_{\text{Cp}}} \tag{14}$$

These parallel components are equivalent to the series components given in Fig. 2B, so that

$$r_{\text{Cs}} = \frac{\frac{1}{r_{\text{Cp}}}}{\left(\frac{1}{r_{\text{Cp}}}\right)^2 + (\omega C_{\text{Cp}})^2} \tag{15}$$

$$\frac{1}{\omega C_{\text{Cs}}} = \frac{\omega C_{\text{Cp}}}{\left(\frac{1}{r_{\text{Cp}}}\right)^2 + (\omega C_{\text{Cp}})^2} \tag{16}$$

Evaluation of Inductive and Resistive Components of the Inductor in Resonance with the Cell. The series inductive (L_{Ls}) and resistive (r_{Ls}) components of the inductor in resonance with the cell were measured by the impedance bridge shown in Fig. 1B. Under a series resonant condition, that is, at bridge balance, the following equation holds,

$$\omega L_{\text{Ls}} = \frac{1}{\omega C_{\text{Ls}}} \tag{17}$$

Conversion of Eq. (17) into a parallel equivalent circuit leads to the following expression;

$$\frac{1}{r_{\text{Lp}}} = \frac{r_{\text{Ls}}}{r_{\text{Ls}}^2 + \left(\frac{1}{\omega C_{\text{Ls}}}\right)^2} \tag{18}$$

Combining Eqs. (14), and (18), one obtains

$$\frac{1}{r_{\text{Cp}}} = \frac{1}{r^\circ} - \frac{1}{r_{\text{Lp}}} \tag{19}$$

and $$\omega C_{\text{Cp}} = \frac{\frac{1}{\omega C_{\text{Ls}}}}{r_{\text{Ls}}^2 + \left(\frac{1}{\omega C_{\text{Ls}}}\right)^2} \tag{20}$$

Method of Analysis of Experimental Data. The values of r°, r_{Ls}, and C_{Ls} can be directly determined by experiment. By using these data, C_{Cp} is calculated by Eq. (20), and $1/r_{\text{Cp}}$ is calculated by Eqs. (18) and (19). Then r_{Cs} and $1/\omega C_{\text{Cs}}$ are evaluated from Eqs. (15) and (16). Finally, r_s and $1/\omega C_s$ can be evaluated from Eqs. (10) and (11), using the values for r_{cap}, r_e, and C_l.

Results and Discussion

Variation of Bridge Component Values with Frequency. The bridge was composed of inductanceless resistors, and moreover, precaution was paid to the arrangement of the circuit in order to avoid any possible stray capacity. But the rather high resistance of the inductor may introduce bad effect. Figure 3 shows the direct reading of a standard resistor (20.0 Ω), and a capacitor (1.0000 μF) network which replaces the cell circuit in Fig. 1A. The variation in component values with frequency was fairly large. The ratio of the direct reading to the standard value at each frequency was used for calibration.

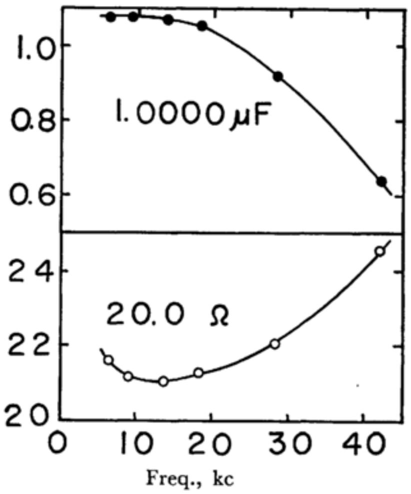


Fig. 3. Frequency dependence of direct reading values of the series $R(20.0\,\Omega)-C(1.0000\,\mu F)$ network.

Application to the Electrode Process $Cd^{2+}+2e=Cd(Hg)$ at the DME. The ability of this improved impedance bridge was tested by a fairly rapid electrode process, $Cd^{2+}+2e=Cd(Hg)$ in M Na_2SO_4 at the DME. The electrode process was assumed to involve no kinetic complication. Cd(II) ions (5×10^{-7} mol/cm^3) developed a well-defined polarographic wave in M Na_2SO_4. The half-wave potential was -1.020_5 V *vs.* SSE. The reductant (Cd(Hg)) was generated *in situ* by the application of a d.c. potential to the working electrode. The concentrations of the oxidant and reductant at the pre-electrode layer were calculated by Eqs. (1) and (2), using the polarographic data. The values, $D_O=0.72\times10^{-5}$ cm^2/sec and

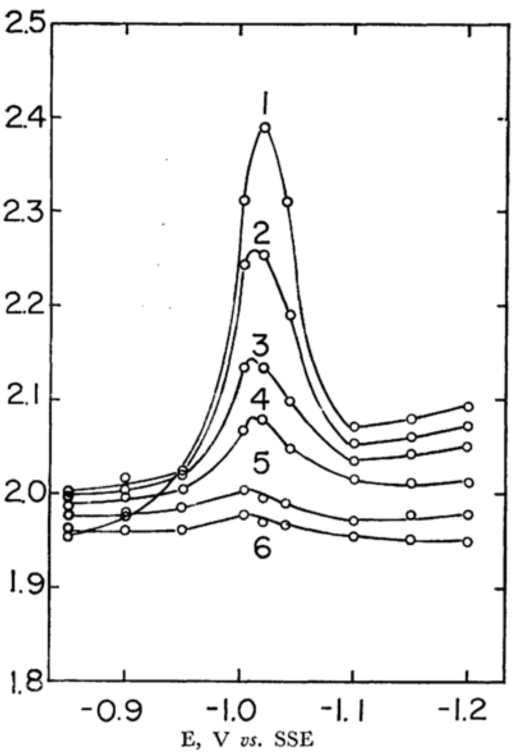


Fig. 4. Variation of the equivalent simple series resistive component (r_{Cs}) with potential at frequencies, 6.42 kc (Curve 1), 9.12 kc (Curve 2), 13.92 kc (Curve 3), 18.45 kc (Curve 4), 28.25 kc (Curve 5), and 41.99 kc (Curve 6).

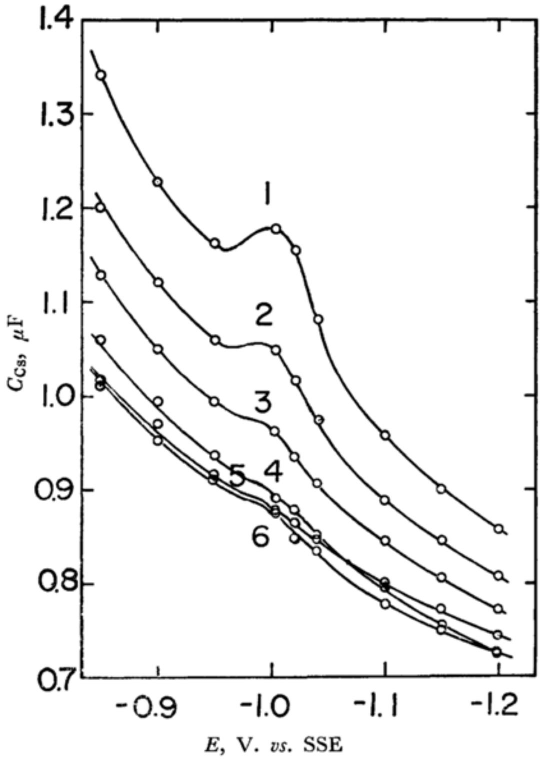


Fig. 5. Variation of the equivalent simple series capacitive component (C_{Cs}) with potential at frequencies, 6.42 kc (Curve 1), 9.12 kc (Curve 2), 13.92 kc (Curve 3), 18.45 kc (Curve 4), 28.25 kc (Curve 5), and 41.99 kc (Curve 6).

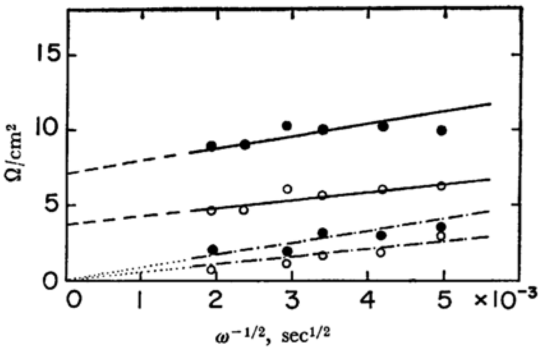


Fig. 6. Plot of the series components, r_s and $1/\omega C_s$, of the faradaic impedance *versus* $\omega^{-1/2}$ for the electrode reaction, $Cd^{2+}+2e=Cd(Hg)$ in M Na_2SO_4 at 25°C: —●— r_s at $E_{3/4}$, --●-- $1/\omega C_s$ at $E_{3/4}$, —○— r_s at $E_{1/4}$, --○-- $1/\omega C_s$ at $E_{1/4}$.

$D_R = 1.63\times10^{-5}$ cm²/sec5) were used for calculation.

Figures 4 and 5 show the variation of r_{Cs} and C_{Cs}, evaluated at frequencies of 6.42, 9.12, 13.92, 18.45, 28.25 and 41.99 kc with potential. Irregularities in the base line of the curves in Figs. 4 and 5 are attributed to the variation in the surface area of the DME in each measurement.

The values obtained for the series components, r_s and $1/\omega C_s$, of the faradaic impedance were plotted against $\omega^{-1/2}$ in Fig. 6.

According to theory on faradaic impedance6)

$$r_s = \frac{\boldsymbol{R}T}{n\boldsymbol{F}}\left\{\frac{1}{I^\circ}+\frac{1}{2^{1/2}n\boldsymbol{F}\omega^{1/2}}\left(\frac{1}{C_OD_O{}^{1/2}}+\frac{1}{C_RD_R{}^{1/2}}\right)\right\} \tag{21}$$

$$\frac{1}{\omega C_s} = \frac{\boldsymbol{R}T}{n\boldsymbol{F}}\left\{\frac{1}{2^{1/2}n\boldsymbol{F}\omega^{1/2}}\left(\frac{1}{C_OD_O{}^{1/2}}+\frac{1}{C_RD_R{}^{1/2}}\right)\right\}, \tag{22}$$

where I° is the exchange current density, and ω the radial frequency. In accordance with this theory, the plots of r_s and $1/\omega C_s$ *versus* $\omega^{-1/2}$ gave straight lines as shown in Fig. 6. The value of I° was obtained from the intercept of the plot as:

$$I^\circ = \frac{\dfrac{\boldsymbol{R}T}{n\boldsymbol{F}}}{(r_s)_{\omega^{-1/2}\to0}} \tag{23}$$

and the numerical values of r_s extrapolated to infinite frequency were 3.5, 4.8 and 7.5 Ω at $E_{1/4}$, $E_{1/2}$ and $E_{3/4}$ respectively.

The transfer coefficient (α) was evaluated through use of the equation of Laitinen, Tischer, and Roe,7) *i. e.*,

$$\frac{\partial \ln\left(\dfrac{I^\circ}{C_O}\right)}{\partial \ln\left(\dfrac{C_R}{C_O}\right)} = \alpha \tag{24}$$

Figure 7 shows the plot of $\log(I^\circ/C_O)$ *versus* $\log(C_R/C_O)$. From the slope of the plot the value of α was found to be as great as 0.17.

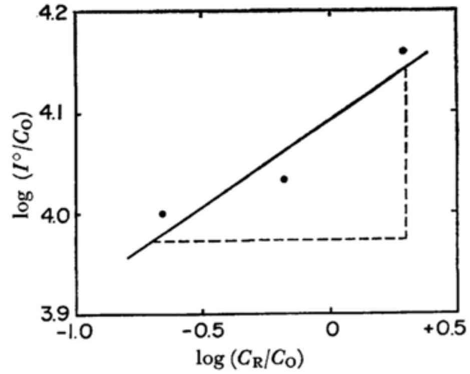


Fig. 7. Plot of $\log(I^\circ/C_O)$ *versus* $\log(C_R/C_O)$. The inclination $=\alpha=0.17$

The heterogeneous rate constant (k°) of the electrode reaction was computed by the following equation,

$$I^\circ = n\boldsymbol{F}k^\circ C_O{}^{1-\alpha}C_R{}^\alpha \tag{25}$$

The kinetic parameters evaluated by this method are illustrated in Table 1, and related values previously reported are given in Table 2.

TABLE 1. KINETIC PARAMETERS OF THE ELECTRODE REACTION, $Cd^{2+}+2e=Cd(Hg)$, IN M Na_2SO_4 AT THE D.M.E. (25°C)

Electrode potential, V *vs.* SSE	$(r_s)_{\omega^{-1/2}\to0}$ Ω/cm²	I° A/cm²	α	k° cm/sec
$E_{1/4}=-1.001_5$	3.5	0.0037		0.066
$E_{1/2}=-1.020_5$	4.8	0.0027	0.17	0.060
$E_{3/4}=-1.040_5$	7.0	0.0018		0.066
mean				0.064

In Table 2 the values of k° are comparatively low in most cases of the hanging mercury drop electrode. Moreover, the values show a trend to decrease with the lapse of time after the electrode is put into the solution. The authors ascribed this trend to the contamination of the electrode surface by the adsorption of surface active materials.

In the case of the DME, the electrode surface

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5) M. von Stackelberg and V. Toome, *Z. Elektrochem.*, **58**, 226 (1954); H. Strehlow, Dissertation, Bonn (1949).

6) D. C. Grahame, *J. Electrochem. Soc.*, **99**, 370 (1952).

7) H. A. Laitinen, R. P. Tischer and D. K. Roe, *J. Electrochem. Soc.*, **107**, 546 (1960).

TABLE 2. VALUES REPORTED FOR THE HETEROGENEOUS RATE CONSTANT FOR $Cd^{2+} + 2e = Cd(Hg)$ IN SULFATE SOLUTION

Supporting electrolyte	Temp. °C	k° cm/sec		Ref.
0.5 M Na_2SO_4	—	0.042	Hanging drop	(8)
0.5 M Na_2SO_4	20	0.026	Hanging drop, Voltage step	(9)
—	0	0.0038	Hanging drop after 2 hr	(10)
—	0	0.037	Hanging drop after 20 min	(10)
—	0	~0.2	DME	(10)
0.5 M Na_2SO_4	25	0.25	DME*,**	(11)
0.5 M K_2SO_4	22	~0.08	Radiofreq. polarograph	(12)
1 M Na_2SO_4	25	0.045	Hanging drop, Current step	(13)
1 M Na_2SO_4	25	~0.3	DME**	(11)
1 M Na_2SO_4	25	~0.1	DME**	(11)
1 M Na_2SO_4	—	0.0137 0.0116 0.067 0.051	Hanging drop, Potential-step-integral method	(14)

Unless otherwise noted, the measurement was carried out by the a. c. method.
* Calculated from data of frequencies up to 1 kc. ** An incorrect equation was used for the calculation, which was later admitted to be incorrect by Breyer and Bauer.[15]

is renewed every 2 or 3 sec, so that the contamination is much smaller than in the case of the hanging mercury drop. Thus, the values of k° obtained by the DME were much higher, as shown in Tables 1 and 2. Some data obtained by the faradaic impedance method with the DME, in Table 2, however, were computed from measurements at frequencies up to 1 kc, and the authors pointed out the discrepancy between the experimental data and the theory at frequencies higher than 1 kc.[11,16] This discrepancy seems to be attributed to the lack of correction for the bridge components in the high frequency range (*cf*. Fig. 3).

When diffusion is the sole mode of mass-transfer, the average flux of the reducing species toward a plane electrode is given by $2C_O^*(D/\pi t)^{-1/2}$, t being the electrolysis time. In a process with mixed control by both mass- and charge-transfer, this conclusion is qualitatively valid, and diffusion is no longer rate-determining for measurements in sufficiently short time intervals or at a sufficiently high frequency of electrolysis. Accordingly, the reason is well understood why our datum ($k^\circ = 0.064$ cm/sec) shows fairly good agreement with Barker's datum[12] ($k^\circ = \simeq 0.08$ cm/sec), which has been obtained by the faradaic rectification method at very high frequencies (500 kc). It is worth consideration that in the faradaic rectification method the accuracy of determining the kinetic parameters is low due to the uncertainty in evaluating the radio-frequency voltage applied to the electrode-solution interface,[17] while the faradaic impedance method is sufficiently accurate so as to give at least three significant figures in the measurement of the bridge components. Our datum also shows good agreement with some data obtained by Christie *et al.*,[14] who used a modified potential-step method. In view of this agreement, the general feature of our method appears well substantiated.

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