

ON THE IMPEDANCE OF GALVANIC CELLS—XVI THE IMPEDANCE OF THE DROPPING MERCURY ELECTRODE IN AQUEOUS 1 M KCl WITH K^+ DISCHARGE*

M. SLUYTERS-REHBACH and J. H. SLUYTERS
Laboratory of Analytical Chemistry, State University, Utrecht, Netherlands

Abstract—The discharge of K^+ ions at the dropping mercury electrode (dme) in 1 M KCl solution at 25°C has been studied by means of analysis of the electrode impedance at different frequencies, using the complex plane method. It is shown that the electrode reaction is almost entirely diffusion-controlled, but a slight influence of activation polarization on the faradaic impedance can be detected at potentials between -1.95 and -2.0 V(sce). The heterogeneous rate constant k_{sh} is estimated as *ca* 0.7 cm/s. Values of the double layer differential capacitance in the potential region where the electrode reaction occurs are calculated. Special attention is given to the inaccuracy of the results inherent in the method.

Résumé—La décharge des ions K^+ à l'électrode à gouttes de mercure dans une solution de KCl unimolaire à 25°C a été étudiée en appliquant la méthode d'analyse de l'impédance de l'électrode dans la plan complexe. On montre que la réaction est contrôlée presque totalement par la diffusion des ions K^+ . Tout de même une mince influence de la polarisation d'activation sur l'impédance faradique a été observée entre $-1,95$ et $-2,0$ V vs l'électrode de calomel saturée. La valeur de la constante de réaction hétérogène k_{sh} vaut environ 0,7 cm/s. Les valeurs de la capacité différentielle de la couche double aux potentiels, où la réduction de K^+ a lieu, sont calculées et rapportées. On fait attention spécial à la précision des résultats, qui est liée à la méthode de calcul appliquée.

Zusammenfassung—Die Entladungsreaktion von Kaliumionen an der tropfenden Quecksilberelektrode in einer molaren KCl-Lösung bei 25°C wurde untersucht mittels der Analyse der Zellimpedanz bei verschiedenen Frequenzen nach der Methode der komplexen Ebene. Es wird gezeigt, dass bei Potentialen von $-1,95$ bis $-2,0$ V bezogen auf die gesättigte Kalomelektrode die Aktivierungspolarisation einen kaum merkbaren Anteil hat an der Faraday-Impedanz. Die heterogene Reaktionsgeschwindigkeitskonstante k_{sh} wurde berechnet zu *ca* 0,7 cm/s. Die differentielle Doppelschichtkapazität wurde bestimmt bei Potentialen, bei denen der Elektrodenprozess stattfindet. Es wird ins besonders die Genauigkeit der bestimmten Kapazitätswerte, die mit der Berechnungsmethode, zusammenhäng diskutiert.

INTRODUCTION

THE complex plane analysis of cell impedances has been proved to be useful for the study of electrode reactions, especially in those cases where the double layer capacitance cannot be measured in the absence of the electroactive species.¹ In this series we have reported the investigation of such cases, namely the electrode reactions $Tl^+/Tl(Hg)$ in 1 M KNO_3 ,² Hg_2^{++}/Hg in 1 M and 0.1 M $HClO_4$,³ and $H^+/H_2(Hg)$ in 1 M $HClO_4$,⁴ for which both the kinetic parameters and the double layer capacitance in the presence of the electroactive species could be evaluated. These electrode reactions appeared to be either totally diffusion-controlled (Tl^+ and Hg_2^{2+}) or totally charge-transfer controlled (H^+), which facilitated the analysis of the impedance measurements.

In this paper we present the analysis of the impedance of a dropping mercury electrode (dme) in 1 M KCl at potentials where the K^+ ion is discharged. This electrode reaction is almost completely diffusion-controlled, but it will be shown that a slight influence of activation polarization can be detected if the analysis is performed carefully. Since this result has a considerable effect on the calculated values of the

* Manuscript received 5 February 1965.

double layer capacitance in the potential region of the electrode reaction, special attention will be given to the reliability of these values. In this connexion we first give a short survey of the theoretical background of the analysis procedure.

THEORY

In part VI¹ it is shown that at fixed frequency and electrode potential the real component Z' and the imaginary component Z'' of the cell impedance are related by

$$\left[Z' - R_{\Omega} + \frac{1}{2\omega C(p+1)} \right]^2 + \left[Z'' - \frac{1}{2\omega C} \right]^2 = \frac{(p+1)^2 + 1}{4\omega^2 C^2 (p+1)^2} \quad (1)$$

in which R_{Ω} is the ohmic resistance, ω the angular frequency and C the double layer capacitance, whereas the "irreversibility quotient" p is given by the transfer resistance θ and the Warburg coefficient σ ,

$$p = \frac{\theta}{\sigma\omega^{-1/2}} = p'\sqrt{\omega}. \quad (2)$$

Usually R_{Ω} can be obtained more or less easily, *eg* from the cell impedance at high frequencies or at potentials where the faradaic impedance is infinite. Hence from (1) it follows that the double layer capacitance C can be calculated from $Z' - R_{\Omega}$ and Z'' with the expression

$$\omega C = \frac{Z'' - \frac{1}{p+1}(Z' - R_{\Omega})}{(Z' - R_{\Omega})^2 + (Z'')^2} \quad (3)$$

if p is known.

From another relation between $Z' - R_{\Omega}$ and Z'' , it can be deduced¹ that a quantity q can be calculated,

$$q = \frac{(Z' - R_{\Omega})^2 + (Z'')^2}{Z' - R_{\Omega}}. \quad (4)$$

This quantity is related to θ and σ by

$$q = \theta + \sigma\omega^{-1/2} + \frac{\sigma^2\omega^{-1}}{\theta + \sigma\omega^{-1/2}} \quad (5)$$

or to σ and p or p' by

$$q = \sigma\omega^{-1/2} \left[p + 1 + \frac{1}{p+1} \right] + \sigma\omega^{-1/2} \left[p'\sqrt{\omega} + 1 + \frac{1}{p'\sqrt{\omega} + 1} \right]. \quad (6)$$

Since both σ and p depend on the electrode potential, q is also a function of electrode potential. If the potential is fixed the values of σ and p' —and consequently of p at each frequency—can be obtained if q is determined for at least two different frequencies. From σ and p' the value of θ can be calculated, which yields the kinetic parameters k_{sh} (rate constant) and α (transfer coefficient). The value of p can be inserted into (3), yielding the double layer capacitance.

This evaluation of p' , however, is possible only if p' exceeds a certain value, so that the factor $[p + 1 + (1/p + 1)]$ exhibits a significant frequency dispersion over the frequency range in which q can be determined with sufficient accuracy. Experience

has shown that this range is about 400–10000 c/s.⁵ In Fig. 1 it can be seen that the detection limit of p' is ca 1.5×10^{-3} (dispersion 5%). It seems to us that the best way to determine such low values of p' is to plot $q\sqrt{\omega}$ against $\sqrt{\omega}$ and to fit this plot into calculated curves for different values of p' . The accuracy of the result will depend on the accuracy with which q is determined.

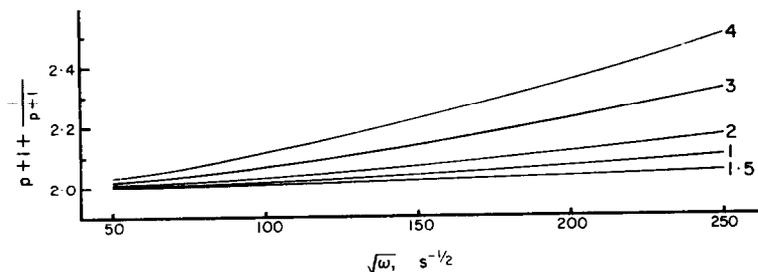


FIG. 1. The factor $p + 1 + (1/p + 1)$ as a function of frequency. Numbers denote values of p' in $10^{-3} \text{ s}^{1/2}$.

The influence of an error Δp in p on the calculated value of the double layer capacitance can be estimated in the following way. If C_a is the apparent value, calculated with p , and C_r the real value, to be calculated with $p + \Delta p$, it can be derived from (3) and (4) that

$$C_r - C_a = \frac{1}{\omega q} \frac{\Delta p}{(p + 1)(p + \Delta p + 1)} = \frac{1}{q\omega^{1/2}} \frac{\Delta p'}{(p + 1)(p + \Delta p + 1)},$$

and with (6),

$$C_r - C_a = \frac{\Delta p'}{\sigma} \frac{1}{(p + 1)\{(p + \Delta p + 1)^2 + 1\}}. \quad (7)$$

Evidently the error in C is large for large concentrations of the electroactive species (σ is inversely proportional to concentration). It is smaller at higher frequencies where p increases.

On the other hand it should be noticed that at high frequencies $Z' - R_\Omega$ is small, so that the error inherent in the determination of the ohmic resistance introduces a considerable inaccuracy in the calculated value of the double layer capacitance.

Recently de Levie⁶ proposed a graphical determination of the double layer capacitance in the presence of an electrode reaction by means of a plot in the "admittance-divided-by- ω plane". The abscissa A'/ω and the ordinate A''/ω of this plane are given by

$$\frac{A'}{\omega} = \frac{1}{\omega} \frac{Z' - R_\Omega}{(Z' - R_\Omega)^2 + (Z'')^2} = \frac{1}{\omega q}, \quad (8a)$$

$$\frac{A''}{\omega} = \frac{1}{\omega} \frac{Z''}{(Z' - R_\Omega)^2 + (Z'')^2} = C + \frac{A'/\omega}{p + 1} = C + \frac{1}{\omega q(p + 1)}. \quad (8b)$$

The double layer capacitance is found as the intercept of the plot on the A''/ω -axis. So the method is in fact an extrapolation to infinite frequency, which implies the disadvantage that the result strongly depends on the measurements at high frequencies, where the error, due to the inaccuracy of R_Ω , is large.

Moreover, it can be calculated that in the frequency range 400–10000 c/s the plot is apparently a straight line with slope 45° if $p' < 2 \times 10^{-3}$ (deviation less than 5%). This means that cases with $0 < p' < 2 \times 10^{-3}$ cannot be distinguished from the case where $p' = 0$ (pure diffusion control) and that in those cases the double layer capacitance will be determined erroneously by extrapolation of the straight line. In reality the slope should deviate from 45° , since at infinite frequency it is 0° . The resulting error in C can be estimated if one writes for the apparent value ($p = 0$)

$$C_a = \frac{A''}{\omega} - \frac{A'}{\omega},$$

and for the real value

$$C_r = \frac{A''}{\omega} - \frac{A'/\omega}{\Delta p + 1},$$

leading to

$$C_r - C_a = \frac{A'}{\omega} \frac{\Delta p}{\Delta p + 1} = \frac{1}{\omega q} \frac{\Delta p}{\Delta p + 1} = \frac{\Delta p'}{\sigma} \frac{1}{(\Delta p + 1)^2 + 1}, \quad (9)$$

which is similar to (7), with $p = 0$. Note that ω and Δp refer to the higher limit of the frequency range.

In the following we shall apply the two methods, described in this section, to the discharge of K^+ ions in a 1 M KCl solution at a dropping mercury electrode, at 25°C .

EXPERIMENTS, RESULTS AND DISCUSSION

The impedance measurements were performed as described earlier.⁵ Though it implies some disadvantage (the ohmic resistance is rather large), a dropping mercury electrode was preferred to a hanging mercury drop electrode for fear that hydrogen discharge would occur at the platinum wire of the latter.

In Fig. 2 complex impedance plane plots (for varying frequency) at different potentials are represented. It is evident that the redox reaction proceeds markedly at potentials < -1.8 V (sce).¹ The measurements were extended only to -2.0 V since at lower potentials Z'' and $Z' - R_\Omega$ cannot be measured with sufficient accuracy. The shape of the curves suggests that the reaction proceeds rather reversibly (*cf* part I of this series⁷). For more exact conclusions, however, a careful analysis is needed.

The ohmic resistance

At potentials > -1.9 V the ohmic resistance can be obtained by extrapolation of the impedance plots in Fig. 2 to infinite frequency. At more negative potentials, however, this extrapolation would not lead to an unambiguous result.

Unfortunately, beyond -1.8 V the applied potential has a great influence on the flow rate of the mercury (it increases with decreasing potential) so that the height of the mercury reservoir had to be adjusted in order to obtain a regular drop fall by means of the tapping device. Consequently the drop area, pertaining to the measured impedance values, was potential dependent, so that R_Ω at a given potential could not be identified directly with the ohmic resistance at potentials > -1.8 V where no redox reaction occurs. Therefore we developed the following procedure:

At -1.75 V R_Ω was measured using a frequency of 10 Kc/s (accuracy 0.2Ω) for various heights of the mercury reservoir. For each level the radius r of the mercury drops was determined from drop weights (accuracy 0.2%) assuming that the drops

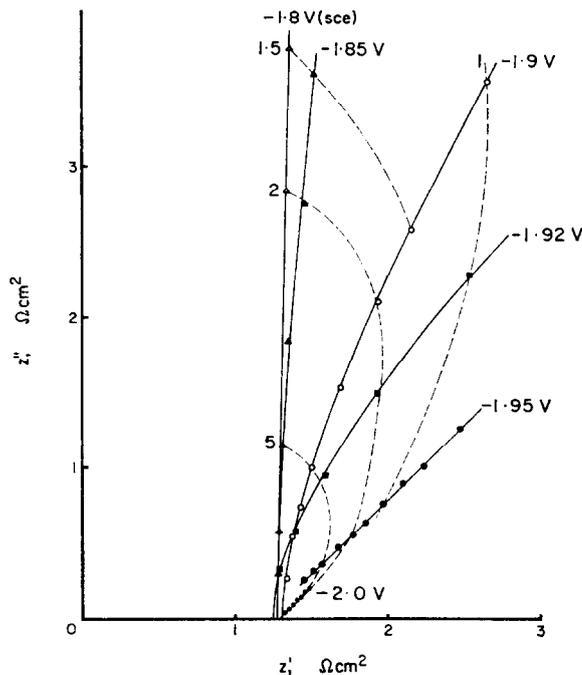


FIG. 2. Complex plane plot for varying frequency at different potentials (drawn lines). Numbers denote potentials in V(sce). The dashed lines connect points of equal frequency, denoted in Kc/s.

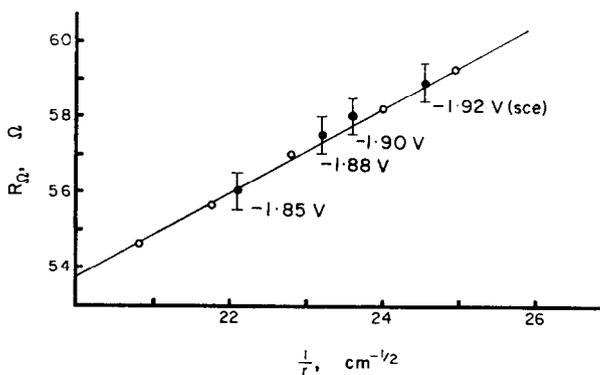


FIG. 3. The ohmic resistance as a function of the reciprocal radius of the mercury drops. ○, at potentials where no redox reaction occurs (-1.75 V(sce)); ● at potentials where K⁺ ions are discharged (obtained by extrapolation to infinite frequency).

were spherical. A plot of R_{Ω} against $1/r$ yields—as theory predicts⁸—a straight line (Fig. 3). The slope of the line, $1.1 \Omega \text{ cm}$, agrees very well with the empirical coefficient $3\rho/8\pi$, observed by Kolthoff *et al*⁹ ($\rho =$ specific resistance; for 1 M KCl at 25°C, $\rho = 8.95 \Omega \text{ cm}^{10}$). The values of R_{Ω} , determined by extrapolation (accuracy 0.5Ω) at -1.8 , -1.85 , -1.90 and -1.92 fit well into the line. So it is reasonable to assume that at more negative potentials R_{Ω} can be determined from the radius r of the mercury drops by means of this “calibration line”. In this way the ohmic resistance could be obtained with an accuracy better than $0.005 \Omega \text{ cm}^2$.

Evaluation of p' , σ and C

Since p' is largest near to the standard potential of the redox couple,¹ its value should be determined preferably at some potentials as low as possible. From the potential dependency of p' the values at higher potentials can be deduced. If $E \gg E_0$ one has¹

$$p' = \frac{\sqrt{(D_{\text{Red}})}}{k_{\text{sh}}} e^{-\alpha n F (E - E_0) / RT}. \quad (10)$$

So a plot of $\log p'$ against E yields the values of p' at any potential $E \gg E_0$ and in addition the transfer coefficient α .

Therefore we determined values of q (equation 4) for different frequencies at -1.95 , -1.97 , -1.98 , -1.99 and -2.0 V (sce). As an example, the data for -1.98 V are collected in Table 1.

TABLE 1. -1.98 V, $R_\Omega = 1.28 \pm 0.005 \Omega \text{ cm}^2$

Frequency c/s	$Z' - R_\Omega$ $\Omega \text{ cm}^2$	Z'' $\Omega \text{ cm}^2$	q $\Omega \text{ cm}^2$	$q\sqrt{\omega}$	C $\mu\text{F}/\text{cm}^2$	ΔC from $\Delta p'$	A'/ω $\mu\text{F}/\text{cm}^2$	A''/ω $\mu\text{F}/\text{cm}^2$
420	0.403	0.374	0.75	38.5	18	15	505	470
620	0.348	0.328	0.66	41.0	25	13	390	367
820	0.304	0.283	0.57	40.6	24	12	342	318
1000	0.271	0.260	0.52	41.2	34	12	306	294
1500	0.222	0.208	0.42	40.5	30	11	254	238
2000	0.194	0.185	0.37	41.5	34	10	215	205
3000	0.156	0.150	0.30	41.2	35	10	177	170
5000	0.121	0.121	0.242	42.9	38	8	132	132
7000	0.099	0.104	0.208	43.5	41	7	109	115
10000	0.077	0.087	0.176	44	45	6	91	103
error:	0.01 $\Omega \text{ cm}^2$	2 %	2 %	2 %	12 $\mu\text{F}/\text{cm}^2$		2 %	12 $\mu\text{F}/\text{cm}^2$

It should be noted that at each frequency the measured values of $Z' - R_\Omega$ and Z'' are approximately equal at this and the other potentials mentioned. From (4) it can be deduced that in this case $q \approx 2Z''$ and moreover that the comparatively large error in $Z' - R_\Omega$ has little or no influence on the error in q .

Evidently $q\sqrt{\omega}$ increases slightly, but significantly, with frequency. From a plot of $q\sqrt{\omega}$ against $\sqrt{\omega}$ (Fig. 4) it can be deduced that $0.0015 < p' < 0.003$ or $p' = (2.25 \pm 0.75) \times 10^{-3}$. With this result the tabulated capacitance values have been calculated according to (3). In addition the error $\Delta C = C_r - C_\infty$, according to (7) with $\sigma = 20.2$ and $\Delta p' = 0.75 \times 10^{-3}$, are listed. The error in the capacitance, introduced by $Z' - R_\Omega$, amounts to $12 \mu\text{F}/\text{cm}^2$ at all frequencies.

In the same way the most probable values of σ and p' at the various potentials have been determined (Fig. 4). The results are reported in Table 2, together with the resulting values of θ (equation 2) and the mean values of C (equation 3).

Plotting of $\log p'$ against potential (Fig. 5) yields as the most probable value $\alpha = 0.15 \pm 0.15$. It should be noticed that this low value, an incidental property of the electrode reaction, makes the analysis rather difficult: if α had been larger a steeper potential dependence of p' and consequently more reliable values would have been found.

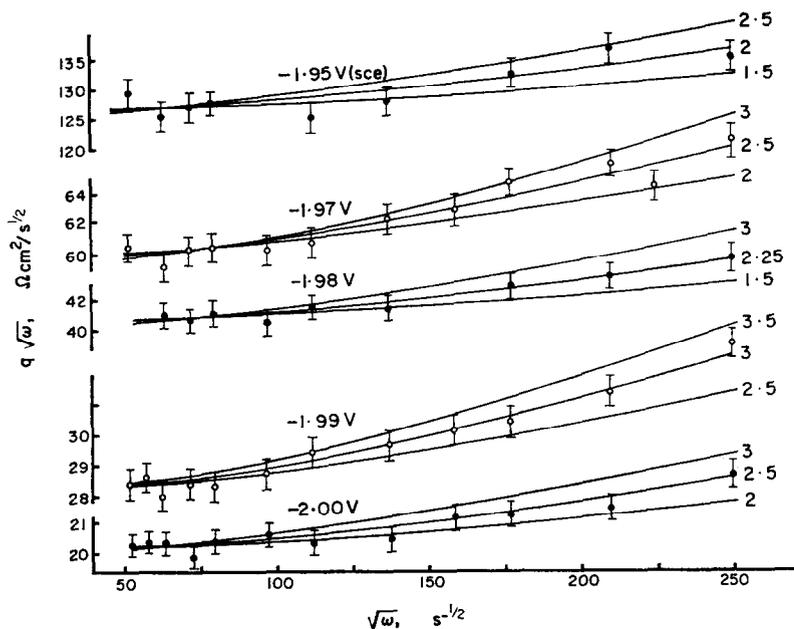


FIG. 4. Frequency-dependence of $q\sqrt{\omega}$ at various potentials (denoted in V (sce)). The lines represent calculated curves for different values of p' (denoted in $10^{-2} \text{ s}^{1/2}$) and the most probable values of σ .

TABLE 2.

Potential V (sce)	$p' \cdot 10^2$ $\text{sec}^{1/2}$	σ $\Omega \text{ cm}^2 \text{ sec}^{-1/2}$	θ $\Omega \text{ cm}^2$	C $\mu\text{F}/\text{cm}^2$	ΔC due to $\Delta p'$	ΔC due to $(Z' - R\Omega)$
-1.95	2 ± 0.5	63 ± 2	0.13 ± 0.03	24.5	± 2.5	± 1.5
-1.97	2.5 ± 0.75	29.7 ± 0.3	0.075 ± 0.02	33	± 6	± 4
-1.98	2.25 ± 0.75	20.2 ± 0.2	0.045 ± 0.015	34	± 9	± 12
-1.99	3.0 ± 0.5	14.0 ± 0.2	0.042 ± 0.007	53	± 10	± 20
-2.00	2.5 ± 0.5	10.0 ± 0.2	0.025 ± 0.005	90	± 15	± 50

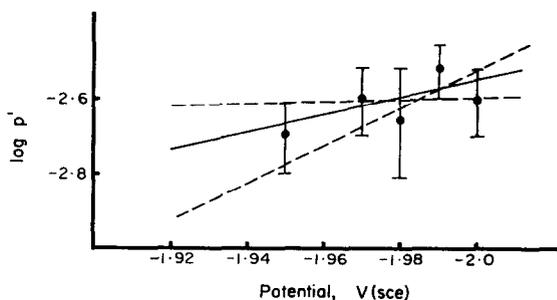


FIG. 5. Plot of $\log p'$ against electrode potential. The full line indicates the most probable slope. The dashed lines indicate the limits of the slope.

Our result for α does not agree with that of Imai and Delahay obtained by the method of faradaic rectification.¹¹ It seems to us, however, that the latter may be incorrect, since it is obtained by erroneously applying the approximation $p + 1 \gg 1$ (see also our comment on the application of faradaic rectification to the $\text{Hg}_2^{2+}/\text{Hg}$ electrode¹²). Moreover—if the negative sign is not omitted—the rectification shift, as measured by Imai and Delahay, decreases with increasing frequency, whereas theory predicts an increase.

From the values of θ in Table 2, together with that of α , the heterogeneous reaction rate constant k_{sh} could be calculated,¹ if the standard potential E_0 of the redox couple $\text{K}^+/\text{K}(\text{Hg})$ in 1 M KCl at 25°C were known. Unfortunately we do not have reliable

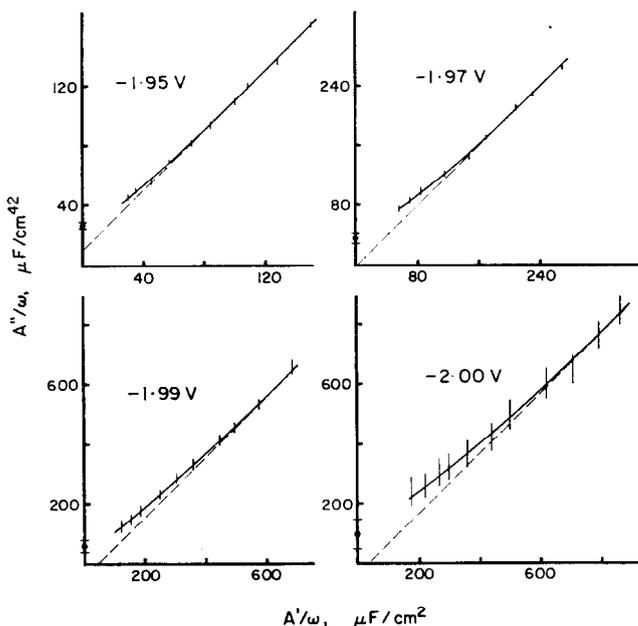


FIG. 6. Plot of A''/ω against A'/ω . The vertical lines indicate the limits of the ordinate of the points, as determined by the accuracy of the measured values of $Z' - R_{\Omega}$. The points on the A'/ω -axes indicate the values of the double layer capacitance, reported in Table 2. The dashed lines are drawn with a slope of 45°.

data on E_0 . According to Heyrovsky,¹³ the half-wave potential $E_{1/2}$ of the electrode reaction in 1 M solutions is *ca* -2.13 V (sce). Taking the diffusion coefficients of the K^+ ions and the K atoms in the amalgam as approximately equal, it can be calculated with $E_{1/2} = -2.13$ that k_{sh} is of the order of 0.7 cm/s, which is somewhat larger than the value reported by Randles¹⁴ for the $\text{K}^+/\text{K}(\text{Hg})$ reaction in 1 M tetramethylammonium hydroxide. With $E_{1/2} = -2.13$, from σ in Table 2 the diffusion coefficient D_{K^+} of the K^+ ions can be calculated to be 0.9×10^{-5} cm²/s, which is a reasonable value.

In Fig. 6 the method of de Levie⁶ is applied by plotting A''/ω against A'/ω for the various potentials (see also Table 1). It is seen that at -1.95 V the curve can hardly be distinguished from a 45° line. At lower potentials curved plots are obtained, but at the highest frequency (10 Kc/s) the slope of the plots amounts still *ca* 40°, so that the extrapolation to infinite frequency ($A'/\omega = 0$, slope = 0°) is not feasible without a serious uncertainty. A better result can be obtained only by trial and error, *eg* by

fitting the measured points into a calculated curve (pre-calculated with the help of estimated values of C , θ and σ), but this procedure would be as laborious as our calculation method and the accuracy, which again depends on the error in p' and $Z' - R_\Omega$, about the same.

From Fig. 5, the values of p' at potentials > -1.95 V (sce) can be estimated. These values have been used for the calculation of C and σ as a function of potential from impedance measurements performed with a frequency of 1000 c/s. The results are tabulated in Table 3. The values of $Z' - R_\Omega$ and Z'' are obtained as described above.

TABLE 3. 1000 c/s

Poten- tial -V (sce)	$Z' - R_\Omega$ $\Omega \text{ cm}^2$	Z'' $\Omega \text{ cm}^2$	q $\Omega \text{ cm}^2$	p' $10^{-2} \text{ s}^{1/2}$	σ $\Omega \text{ cm}^2/\text{s}^{1/2}$	C $\mu\text{F}/\text{cm}^2$	ΔC ($\Delta p' = 5 \cdot 10^{-4}$)	$\frac{\Delta C}{\Delta(Z' - R_\Omega)}$ $= 0 \cdot 01$
1.0						16.5		
1.1						16.3		
1.2						16.6		
1.3						17.0		
1.4						17.8		
1.5						18.65		
1.6						19.85		
1.7						21.5		
1.8	0.10	6.73	454	1	18000	23.3	0.01	0.035
1.825	0.23	6.42	180	1.1	7130	23.9	0.03	0.04
1.85	0.465	5.92	75.7	1.2	3000	24.8	0.065	0.045
1.86	0.61	5.64	52.8	1.25	2080	25.2	0.1	0.05
1.87	0.90	5.27	31.8	1.3	1250	24.7	0.15	0.055
1.88	1.01	4.82	24.1	1.4	950	25.6	0.2	0.065
1.89	1.23	4.33	16.5	1.5	650	25.2	0.3	0.08
1.90	1.41	3.69	11.05	1.6	435	24.9	0.4	0.1
1.91	1.39	2.87	7.45	1.7	293	25.6	0.6	0.15
1.92	1.30	2.24	5.20	1.8	205	26.2	0.9	0.25
1.93	1.13	1.60	3.39	1.9	133	25.7	1.3	0.4
1.94	0.95	1.18	2.42	2.0	95.0	25.7	2	0.7
1.95	0.71	0.81	1.65	2.15	64.5	27.4	2.6	1.3
1.96	0.55	0.57	1.14	2.3	44.5	26.6	4	2.5
1.97	0.38	0.38	0.76	2.4	29.6	33	6	5.5
1.98	0.27	0.26	0.52	2.6	20.3	40	9	11
1.99	0.19	0.18	0.36	2.7	14.0	58	12	23
2.00	0.13	0.13	0.26	2.8	10.1	90	16	47

It is easily verified that a plot of $\log \sigma$ against potential yields a straight line with slope -16.6 , in accordance with the theory¹ of the potential dependence of the faradaic impedance if mass transfer to the electrode surface is governed by semi-infinite linear diffusion. This means that no influence of migration is detected, though no other cations than K⁺ are present.

The capacitance values at potentials > -1.80 V, where no redox reaction occurs, have been measured directly. They are in good agreement with the corresponding values published by Grahame and Parsons.¹⁵ The slight increase with decreasing potential is continued in the region of the K⁺ discharge down to -1.96 V (sce). Beyond this potential a rather steep increase is observed, but the uncertainty in C does not allow a definite decision as to its significance.

REFERENCES

1. M. SLUYTERS-REHBACH and J. H. SLUYTERS, *Recl. Trav. Chim.* **82**, 525 (1963).
2. M. SLUYTERS-REHBACH, B. TIMMER and J. H. SLUYTERS, *Recl. Trav. Chim.* **82**, 553 (1963).
3. M. SLUYTERS-REHBACH and J. H. SLUYTERS, *Recl. Trav. Chim.* **83**, 217, 967 (1964).
4. M. SLUYTERS-REHBACH and J. H. SLUYTERS, *Recl. Trav. Chim.* **83**, 581 (1964).
5. M. SLUYTERS-REHBACH and J. H. SLUYTERS, *Recl. Trav. Chim.* **82**, 535 (1964).
6. R. DE LEVIE, *Electrochim. Acta* **10**, 395 (1965).
7. J. H. SLUYTERS, *Recl. Trav. Chim.* **79**, 1092 (1960).
8. D. ILKOVIC, *Coll. Czech. Chem. Comm.* **8**, 13 (1936).
9. I. M. KOLTHOFF, J. C. MARSHALL and S. L. GUPTA, *J. Electroanal. Chem.* **3**, 209 (1962).
10. C. D. HODGMAN, *Handbook of Chemistry and Physics*, p. 2149. Chemical Rubber Publishing, Cleveland (1951).
11. H. IMAI and P. DELAHAY, *J. Phys. Chem.* **66**, 1683 (1962).
12. M. SLUYTERS-REHBACH and J. H. SLUYTERS, *Recl. Trav. Chim.* **83**, 983 (1964).
13. J. HEYROVSKY, *Polarographisches Praktikum*, p. 97. Springer, Berlin (1960).
14. J. E. B. RANGLES and K. W. SOMERTON, *Trans. Faraday Soc.* **48**, 951 (1952).
15. D. C. GRAHAME and R. PARSONS, *J. Am. Chem. Soc.* **83**, 1291 (1961).