

## Electrode Impedance Measurements on the Cerium(IV)-Cerium(III) Couple in Perchloric Acid Solutions

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A small platinum electrode, immersed in a solution of cerium(III) and cerium(IV) perchlorates in 3 M perchloric acid, is polarized by a sinusoidal alternating voltage of small amplitude, and the impedance of the metal-solution interface is determined. Owing to the high redox potential of the cerium couple the total impedance includes two parallel faradaic impedances, one of them due to the oxygen-water couple. From the measurements the rate of the electron transfer step of the cerium couple is calculated, and the result is shown to be in accord with a previous isotopic exchange investigation.

The rate of the charge transfer of the oxygen evolution on platinum is also obtained from the impedance measurements combined with separate determinations of the over-all rate of reaction. It is found that the rate-determining step is not the charge transfer but a subsequent reaction.

Furthermore, it is demonstrated that the steady-state potential of the platinum electrode is very nearly equal to the redox potential of the cerium couple.

The heterogeneous exchange reaction between cerium(III) and cerium(IV) at platinum surfaces was investigated in a previous work (Fronæus and Östman<sup>1</sup>) by means of a radioactive cerium isotope. At 0°C and in approximately 3 M perchloric acid as an ionic medium the following relationship was obtained for the rate  $r$  of the over-all exchange reaction

$$\frac{1}{r} = \frac{1.25 \times 10^{10}}{c^{1.5}q^{0.5}} + \frac{2.0 \times 10^9}{c} \quad (1)$$

when  $r$  is expressed in mole · cm<sup>-2</sup> · sec<sup>-1</sup> and the concentrations  $c$  and  $q$  of cerium(IV) and cerium(III) are expressed in mM. The relationship was established for small values (< 10 mM) of  $c$  and  $q$ .

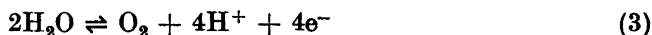
By comparing this expression with the one theoretically derived<sup>1</sup>, it is found that the first term on the right-hand side of (1) is equal to the reciprocal of the rate  $r_0$  of the electron transfer, and the second term is equal to the reci-

procal of the rate  $r_d$  of the diffusion of cerium(IV) to and from the electrode. Thus it was concluded that these two steps are the rate-determining ones. Furthermore, the exponent 1.5 of  $c$  in the expression for  $r_0$  indicates <sup>1</sup> that the oxidizing species predominating in the electron transfer step is a dinuclear hydrolysis product of cerium(IV).

The purpose of the present investigation was to check these results and, for this reason, electrode impedance measurements were chosen, since by this method <sup>2</sup> it is generally possible to determine the rate of the electron transfer, even if this step is rather rapid in comparison with the diffusion processes. However, the present case is complicated by the fact that water is slowly oxidized at the electrode owing to the high redox potential of the cerium(IV)—cerium(III) couple, and the oxygen-water couple will interfere with the measurements. This complication is common to the electrical methods available.

#### THEORETICAL

At the platinum electrode we have simultaneously the following two overall electrode reactions



The electron transfer steps of these reactions are denoted



where  $n = 1$  refers to the cerium couple and  $n = 2$  to the oxygen-water couple.

For the current densities  $\vec{i}_n$  and  $\overleftarrow{i}_n$  of the forward and reverse reactions of (4) we have the expressions <sup>1</sup>

$$\vec{i}_n = k_n' [\text{A}_n] \exp \left\{ \frac{\alpha_n eF}{RT} \right\} \quad (5)$$

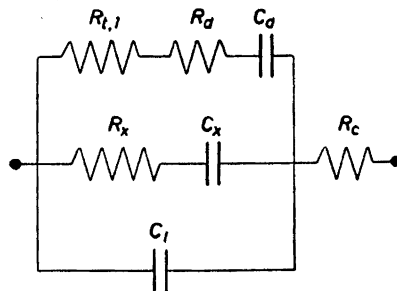
$$\overleftarrow{i}_n = k_n'' [\text{B}_n] \exp \left\{ - \frac{(1-\alpha_n)eF}{RT} \right\} \quad (6)$$

Here  $k_n'$ ,  $k_n''$ , and  $\alpha_n$  should be constants, the transfer coefficients  $\alpha_n$  fulfilling the condition  $0 < \alpha_n < 1$ . If the electrode potential  $e$  is adjusted at the redox potential  $e_n$  of the couple  $\text{B}_n$ — $\text{A}_n$  we get  $\vec{i}_n = \overleftarrow{i}_n = i_{0,n}$ , where  $i_{0,n}$  is the exchange current density of the couple. Then the concentrations of  $\text{A}_n$  and  $\text{B}_n$  close to the electrode become equal to the equilibrium values  $[\text{A}_n]_0$  and  $[\text{B}_n]_0$ , and thus for an arbitrary value of  $e$  we get

$$\vec{i}_n = i_{0,n} \frac{[\text{A}_n]}{[\text{A}_n]_0} \exp \left\{ \frac{\alpha_n(e-e_n)F}{RT} \right\} \quad (7)$$

$$\overleftarrow{i}_n = i_{0,n} \frac{[\text{B}_n]}{[\text{B}_n]_0} \exp \left\{ - \frac{(1-\alpha_n)(e-e_n)F}{RT} \right\} \quad (8)$$

Fig. 1. Equivalent circuit of the electrochemical cell.  $R_{t,1}$ ,  $R_d$ , and  $C_d$  = transfer resistance, diffusion resistance, and diffusion capacity of the cerium couple;  $R_x$  and  $C_x$  = equivalent series resistance and capacity of the oxygen-water couple;  $C_l$  = double layer capacity;  $R_c$  = cell resistance.



Furthermore, for the contribution  $i_n$  of the couple  $B_n$ — $A_n$  to the total anodic current density we have the relationship

$$i_n = \overset{\rightarrow}{i_n} - \overset{\leftarrow}{i_n} \quad (9)$$

If the measurement cell consists of two platinum electrodes immersed in the solution and a sinusoidal alternating voltage is applied to the cell, the equivalent circuit can be represented as in Fig. 1. There are two so-called faradaic impedances, corresponding to the electrode reactions (2) and (3), and further the ordinary double layer capacity  $C_l$ . These parallel impedances are in series with the resistance  $R_c$  of the cell solution.

For small amplitudes ( $< 10$  mV) of the applied alternating voltage the faradaic impedance connected with the cerium couple can be divided into the resistance  $R_{t,1}$ , due to the electron transfer step, and a diffusion impedance, composed of the resistance  $R_d$  and the capacity  $C_d$ . Under the condition stated  $R_{t,1}$  is evidently equal to  $(\partial e / \partial i_1)_{[A_1], [B_1]}$  for  $e = e_0$ , where  $e_0$  is the steady-state potential of the electrode. Now, from an investigation by Sherill, King and Spooner<sup>3</sup> it is found that at a constant concentration (0.5 M) of perchloric acid and at cerium(IV) concentrations  $< 10$  mM the dependence of  $e_0$  upon  $c$  and  $q$  is approximately in accordance with Nernst's formula. Thus it is very probable that  $e_0$  is very nearly equal to the redox potential  $e_1$  of the cerium couple. Then, remembering that  $[A_1] = [A_1]_0$  and  $[B_1] = [B_1]_0$  for  $e = e_1$ , we obtain from eqns. (7)—(9)

$$R_{t,1} = \frac{RT}{F} \cdot \frac{1}{i_{0,1}} \quad (10)$$

For diffusion impedances it has been shown before, *e.g.*, by Randles<sup>2</sup>, Ershler<sup>4</sup>, and Gerischer<sup>5</sup>, that  $\omega C_d R_d = 1$  and, furthermore, that  $R_d$  is proportional to  $\omega^{-\frac{1}{2}}$ , where  $\omega = 2\pi\nu$  and  $\nu$  is the frequency of the alternating current. Thus, if other experimental conditions are fixed we can put

$$R_d = \frac{K}{\sqrt{\omega}}; \quad C_d = \frac{1}{K\sqrt{\omega}} \quad (11)$$

where  $K$  is a constant.

The expressions for  $R_x$  and  $C_x$ . On the basis of investigations of the oxygen evolution at electrodes (cf. Hickling <sup>6</sup> and Bockris <sup>7</sup>) we may presume for the oxygen-water couple that  $A_2$  is equal to  $\text{OH}^-$  or in acid solutions  $\text{H}_2\text{O}$ , and that  $B_2$  is the radical  $\text{OH}$  adsorbed on the platinum surface. In this case there is no diffusion impedance, but if the reaction between the adsorbed radicals is a slow process another impedance will result, and we will establish the dependence of the resistance  $R_x$  and the capacity  $C_x$  (see Fig. 1) upon  $\omega$ .

For the variation in the electrode potential  $e$  with time  $t$  the differential equation

$$\frac{de}{dt} = R_x \frac{di}{dt} + \frac{i}{C_x} \quad (12)$$

is valid if  $i$  is the alternating current through this impedance. We can put  $i = I \sin \omega t$ , where  $I$  is the amplitude. Hence, we get

$$\frac{de}{dt} = \omega I R_x \cos \omega t + \frac{I}{C_x} \sin \omega t \quad (13)$$

Combining eqns. (7)–(9) we obtain  $i_2$  expressed as a function of  $e$  and  $[\text{B}_2]$ , since  $[\text{A}_2] = [\text{A}_2]_0$  according to the presumption above. A differentiation of this function gives

$$\frac{de}{dt} = R_{i,2} \frac{di_2}{dt} + R_{i,2} \frac{i_2}{[\text{B}_2]} \frac{d[\text{B}_2]}{dt} \quad (14)$$

where  $R_{i,2}$  is the electron transfer resistance of the oxygen-water couple at the electrode potential  $e_0$  and is given by the expression

$$\frac{1}{R_{i,2}} = \frac{F}{RT} \left\{ i_2^{\rightarrow} \alpha_2 + i_2^{\leftarrow} (1 - \alpha_2) \right\} \quad (15)$$

For  $i_2$  we have  $i_2 = (i_2)_{e=e_0} + I \sin \omega t$  and hence  $di_2/dt = \omega I \cos \omega t$ . ■

Now we represent by  $f([\text{B}_2])$  the rate of the reaction between the radicals adsorbed on the electrode surface. Then, if  $[\text{B}_2]$  is expressed in moles per unit area,  $i_2 F^{-1}$  will be the net rate at which the radicals are supplied by the electron transfer step. Hence, we obtain the differential equation

$$\frac{d[\text{B}_2]}{dt} + f([\text{B}_2]) = \frac{(i_2)_{e=e_0}}{F} + \frac{I}{F} \sin \omega t \quad (16)$$

where the first term in the right member is a constant.

For very small amplitudes the solution of eqn. (16) is of the form

$$[\text{B}_2] = a + \frac{I(b \sin \omega t - \omega \cos \omega t)}{(b^2 + \omega^2)F} + \varphi(t) \quad (17)$$

where the constants  $a$  and  $b$  fulfil the conditions

$$f(a) = \frac{(i_2)_{e=e_0}}{F}; \quad b = \left( \frac{df}{d[\text{B}_2]} \right)_{[\text{B}_2]=a} \quad (18)$$

In (17) the non-sinusoidal term  $\varphi(t)$  is negligible for  $t$ -values which are not very small. Then, differentiating this equation with respect to  $t$  and combining the expression obtained with (14) we get

$$\frac{de}{dt} = \omega I R_{i,2} \left\{ \cos \omega t + \frac{\overleftarrow{i}_2 (b \cos \omega t + \omega \sin \omega t)}{[B_2](b^2 + \omega^2)F} \right\} \quad (19)$$

An equating of the coefficients of  $\cos \omega t$  and  $\sin \omega t$  in (13) and (19) gives the final expressions for  $R_x$  and  $C_x$

$$R_x = R_{i,2} \left\{ 1 + \frac{\overleftarrow{i}_2 b}{[B_2](b^2 + \omega^2)F} \right\} \quad (20)$$

$$\frac{1}{C_x} = \frac{\overleftarrow{i}_2 R_{i,2} \omega^2}{[B_2](b^2 + \omega^2)F} \quad (21)$$

From (21) it is seen that the capacity  $C_x$  increases with the concentration of the adsorbed radicals, and if the reaction rate  $f([B_2])$  is very low, which means a small value of  $b$ , the capacity is but slightly dependent on the frequency. It is also evident from (15) and (21) that if  $\overrightarrow{i}_2 \gg \overleftarrow{i}_2$  for  $e = e_0$ , then the oxygen-water couple will give rise to the transfer resistance  $R_{i,2}$  only.

The determination of the exchange current density  $i_{0,1}$ . The three parallel impedances in Fig. 1 can be replaced by an equivalent circuit, consisting of a resistance  $R_p$  and a capacity  $C_p$  connected in parallel. Then, by means of well-known transformation formulas for impedances we get

$$\frac{1}{R_p} = \frac{\omega^2 C_d^2 (R_{i,1} + R_d)}{1 + \omega^2 C_d^2 (R_{i,1} + R_d)^2} + \frac{\omega^2 C_x^2 R_x}{1 + \omega^2 C_x^2 R_x^2} \quad (22)$$

$$C_p = C_l + \frac{C_d}{1 + \omega^2 C_d^2 (R_{i,1} + R_d)^2} + \frac{C_x}{1 + \omega^2 C_x^2 R_x^2} \quad (23)$$

If the expressions for  $R_d$ ,  $C_d$ ,  $R_x$ , and  $C_x$  in eqns. (11), (20), and (21) are taken into consideration the following relationships are approximately valid at high frequencies

$$\frac{1}{R_p} = \frac{1}{R_{i,1}} + \frac{1}{R_{i,2}} \left\{ 1 + \frac{|K'|}{V\omega} \right\} \quad (24)$$

$$C_p = C_l + \frac{K'}{\omega V \omega} \quad (25)$$

where the coefficient  $K'$  is  $>0$  and independent of the frequency.

Accordingly,  $R_p^{-1}$  and  $C_p$  experimentally determined should be plotted against  $\nu^{-\frac{1}{2}}$  and  $\nu^{-\frac{3}{2}}$ , respectively, and extrapolated to  $\nu = \infty$  giving  $R_{i,1}^{-1} + R_{i,2}^{-1}$  and  $C_l$ . Then, denoting the intercept on the  $R_p^{-1}$ -axis by  $R_i^{-1}$  and observing that  $i_{0,1} = r_0 F$ , where the rate of the electron transfer of the cerium couple is expressed in moles per unit area and unit time, we obtain from (10) and (15)

$$\frac{RT}{F^2 R_i} = r_0 + \frac{\overrightarrow{i}_2 \alpha_2}{F} + \frac{\overleftarrow{i}_2 (1 - \alpha_2)}{F} \quad (26)$$

If we choose  $c = q$  and keep  $[H^+]$  at a fixed value the overvoltage  $e_0 - e_2$  ( $\approx e_1 - e_2$ ) of the oxygen-water couple will be constant and consequently also the current densities  $\vec{i}_2$  and  $\overleftarrow{i}_2$ . On the other hand, for  $c = q$  it is found from (1) that  $r_0$  is proportional to  $c^2$ , if the results obtained in the isotopic exchange investigation are reliable. Then, by determining  $R_i$  for various values of  $c$  we can arrive at the corresponding rates  $r_0$ .

*A test on the existence of an impedance due to the oxygen-water couple.* The two faradaic impedances in Fig. 1 can be replaced by a single impedance, consisting of a resistance  $R_s$  and a capacity  $C_s$  in series. The expressions for  $R_s$  and  $C_s$  are rather complicated, but at high frequencies we get the following approximate formulas

$$R_s = \beta(R_{i,1} + \frac{K}{\sqrt{\omega}}) \quad (27)$$

$$\frac{1}{\omega C_s} = \frac{\beta^2 K}{\sqrt{\omega}} + \frac{(1-\beta)^2}{\omega C_x} \quad (28)$$

where  $\beta = R_x(R_{i,1} + R_x + R_d)^{-1}$ . Thus, if  $R_x = \infty$  we have  $\beta = 1$ , whereas  $\beta < 1$  for finite values of  $R_x$ . In the first-mentioned case two parallel straight lines should be obtained, when  $R_s$  and  $(\omega C_s)^{-1}$  are plotted against  $\nu^{-\frac{1}{2}}$ . On the other hand, if  $\beta < 1$  the quantity  $(\omega C_s)^{-1}$  may increase more rapidly than  $R_s$  for increasing values of  $\nu^{-\frac{1}{2}}$ , since according to (21)  $C_x$  should be fairly independent of the frequency.

It can be mentioned that ordinarily<sup>8-10</sup> an extrapolation of  $R_s$  is used for the determination of  $R_i$ . However, in those cases where  $C_p - C_i \ll C_p$  but  $\omega R_p(C_p - C_i)$  is not  $\ll 1$  the resistance  $R_s$  cannot be calculated with sufficient accuracy for such a determination.

## MEASUREMENTS AND CALCULATIONS

*Experimental details.* The cell used in the impedance measurements was similar to that of Vetter<sup>8</sup>. The small, polarizable electrode was a platinum wire with a diameter of 0.32 mm and a length of 30 mm. It was placed as the axis of a cylindrical platinum electrode with a diameter of 10 mm and a length of 30 mm. The solution contained cerium(III) and cerium(IV) perchlorates in equal concentrations, and as supporting electrolyte 3.00 M perchloric acid was used<sup>1</sup>.

The impedance of the cell was measured with an a.c. Wheatstone bridge circuit, properly shielded. Two of the arms consisted of two equal standard resistors, and in the fourth arm, adjacent to the cell, there were a decade resistor and a decade condenser, connected in parallel for technical reasons. The bridge was fed with an oscillator whose output was adjusted so that the amplitude of the voltage applied to the cell was about 7 mV. A cathode-ray oscillograph combined with a preamplifier served as a balance indicator of high sensitivity.

*Calculations.* From the readings on the decade resistor and the condenser, when the bridge was balanced, the corresponding values for an equivalent series arrangement of the resistance and the capacity were computed. Since the apparatus did not permit measurements at very high frequencies the electrolyte resistance  $R_e$  could not be determined directly but was calculated from

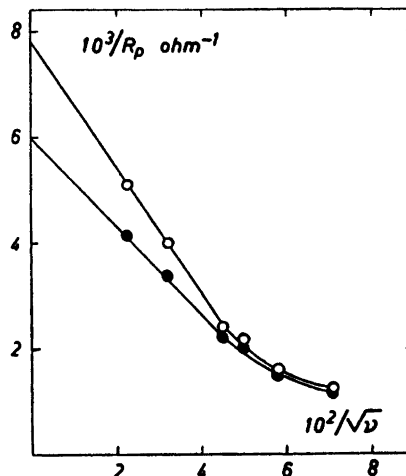


Fig. 2. The conductance  $R_p^{-1}$  as a function of  $\nu^{-\frac{1}{2}}$  ( $\nu$  = frequency) at the cerium concentrations  $c = q = 3.00$  mM (●) and  $c = q = 6.00$  mM (○).

the specific conductivity of 3 M perchloric acid and the electrode dimensions ( $R_e = 0.30$  ohm at  $20^\circ\text{C}$ ). After subtraction of  $R_e$  from the series resistance a re-calculation of the equivalent parallel arrangement was performed, giving the values of  $R_p$  and  $C_p$ .

For the cerium concentrations  $c = q = 3.00$  mM and  $6.00$  mM, which are within the ranges used in the isotopic exchange investigation<sup>1</sup>, the measurements were at first carried out at  $20^\circ\text{C}$ . In Fig. 2  $R_p^{-1}$  has been plotted against  $\nu^{-\frac{1}{2}}$ . Owing to the rather great values of both  $C_p$  and  $R_p$  the resistance could not be determined with sufficient accuracy at high frequencies, and accordingly  $R_p$  has been given only for  $\nu \leq 2000$  cycles  $\cdot$  sec<sup>-1</sup>. As predicted by the theory the curves are approximately straight-lined at the lower values of  $\nu^{-\frac{1}{2}}$  and can be used for extrapolations to  $\nu = \infty$ . In Fig. 3 the capacity  $C_p$  has been plotted against  $\nu^{-\frac{3}{2}}$ . Since the variation in  $C_p$  is small we should get fairly accurate determinations of the double layer capacity  $C_l$  by the extrapolations to  $\nu = \infty$ .

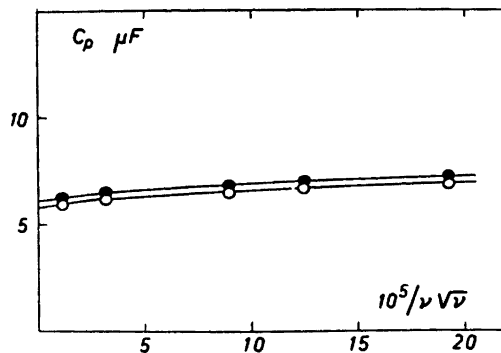


Fig. 3. The capacity  $C_p$  as a function of  $\nu^{-\frac{3}{2}}$  at the cerium concentrations  $c = q = 3.00$  mM (●) and  $c = q = 6.00$  mM (○).

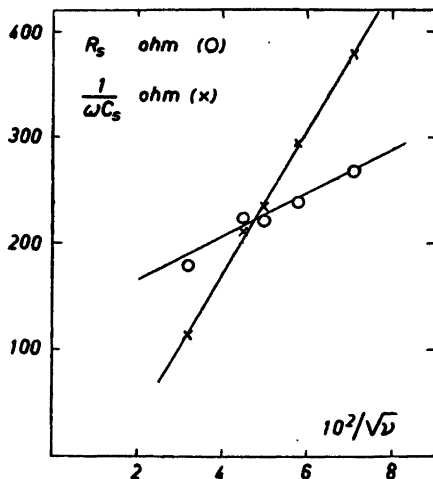


Fig. 4. The quantities  $R_s$  (O) and  $1/\omega C_s$  (x) as functions of  $\nu^{1/2}$  at the cerium concentrations  $c = q = 6.00$  mM.

From  $R_p$  and the difference  $C_p - C_i$  the equivalent circuit consisting of the resistance  $R_s$  and the capacity  $C_s$  in series was calculated. In Fig. 4  $R_s$  and  $(\omega C_s)^{-1}$  have been plotted against  $\nu^{1/2}$ . It is seen that  $(\omega C_s)^{-1}$  increases more rapidly than  $R_s$  with  $\nu^{1/2}$ , and according to the theory above this means that the faradaic impedance due to the oxygen-water couple influences the measurements.

The values of  $R_i^{-1}$  and  $C_i$  arrived at refer to the two electrodes of the cell. Thus we have to divide by the factor  $s_1 s_2 (s_1 + s_2)^{-1} = 0.30$  cm<sup>2</sup>, where  $s_1$  and  $s_2$  are the surface areas of the electrodes, in order to obtain the corresponding quantities per unit area of the interface. Since in the present case  $s_1 = 0.03 s_2$  the impedance of the great electrode is only a correction term. For  $C_i$  a value of about  $20 \mu\text{F} \cdot \text{cm}^{-2}$  is obtained at the cerium concentrations used.

In Table 1 the values of  $RTF^{-2}R_i^{-1}$  are given. The corresponding rates  $r_0$  in the next column have been calculated from eqn. (26) as described in the theoretical section. Some impedance measurements were also performed at 0°C, since the isotopic exchange measurements were carried out at this temperature. However, at 0°C it was possible to determine  $R_p$  with sufficient accuracy only at low frequencies. Then it was found that the  $R_p$ -values were about half as

Table 1. The rate of the electron transfer step of the cerium(IV)-cerium(III) couple on platinum in the presence of 3 M perchloric acid. The quantities in the columns 2-7 are expressed in mole  $\cdot$  cm<sup>-2</sup>  $\cdot$  sec<sup>-1</sup>.

$c = q$ mM	$\frac{RT}{F^2 R_i} \times 10^9$		$r_0 \times 10^9$		$r_0 \times 10^9$	$r_d \times 10^9$
	20°C	0°C	20°C	0°C	Tracer method; 0°C	
3.00	5.2	2.5	0.5	0.25	0.72	1.5
6.00	6.8	3.5	2.0	1.0	2.9	3.0



great as the corresponding values obtained at 20°C. Accordingly we may conclude that the same thing is valid for the rate  $r_0$ , as is indicated in Table 1.

From the measurements at 20°C the calculations give  $\vec{i}_2\alpha_2 + \overleftarrow{i}_2(1 - \alpha_2) = 0.45 \text{ mA} \cdot \text{cm}^{-2}$ . Now according to Hickling and Hill<sup>11</sup> the transfer coefficient  $\alpha_2$  is about 0.5 for platinum in acid solution, and using this value we get  $\vec{i}_2 + \overleftarrow{i}_2 = 0.90 \text{ mA} \cdot \text{cm}^{-2}$ . The current density  $i_2 = \vec{i}_2 - \overleftarrow{i}_2$  of the oxygen evolution at the steady-state potential  $e_0$  is equal to the current density of the simultaneous heterogeneous reduction of cerium(IV) and can be measured separately. To this end 15 ml of a solution with  $c = q = 20.0 \text{ mM}$  and the perchloric acid concentration 3 M was shaken at 20°C for 45 hours with a platinum foil, the surface area of which was 8 cm<sup>2</sup>. Then it was found that as a mean value  $5.3 \times 10^{-2}$  mmoles of cerium(IV) had been reduced. During the same time about  $10^{-3}$  mmoles had been reduced in the homogeneous reaction. Hence we get  $i_2 = 4 \times 10^{-3} \text{ mA} \cdot \text{cm}^{-2}$  at the potential<sup>3</sup>  $e_0 = 1.67 \text{ V}$ . For the oxygen-water couple we compute  $e_2 = 1.25 \text{ V}$  at  $[\text{H}^+] = 3 \text{ M}$ , giving us the overvoltage  $e_0 - e_2 = 0.43 \text{ V}$ . The current density obtained is consistent with the measurements by Hickling and Hill<sup>11</sup>. Combining the values of  $\vec{i}_2 + \overleftarrow{i}_2$  and  $\vec{i}_2 - \overleftarrow{i}_2$  we obtain  $\vec{i}_2 = 0.45 \text{ mA} \cdot \text{cm}^{-2}$ . Thus the resultant rate of the oxygen evolution at platinum is much less than the rate of discharge of OH<sup>-</sup> or H<sub>2</sub>O.

Furthermore, since  $i_1 + i_2 = 0$  at the steady-state potential  $e_0$ , we get from eqns. (7)–(9) the approximate relationship

$$e_1 - e_0 = \frac{RT}{F^2} \frac{i_2}{r_0^{\ddagger}} \quad (29)$$

if the value of  $e_1 - e_0$  is so small that we can put  $[A_1] \approx [A_1]_0$  and  $[B_1] \approx [B_1]_0$  and apply the approximation  $\exp(y) \approx 1 + y$  to the exponential functions containing  $e_1 - e_0$ . Combining the  $i_2$ -value with the rate  $r_0$  at 20°C we find  $e_1 - e_0 = 2 \text{ mV}$  for  $c = q = 3.00 \text{ mM}$ , which confirms the validity of the approximation. Consequently, the steady-state mixed potential is very nearly equal to the redox potential of the cerium(IV)-cerium(III) couple.

## DISCUSSION

In the last two columns of Table 1 the rate  $r_0$  and the rate  $r_d$  of the diffusion of cerium(IV) have been calculated from the two terms in the right member of eqn. (1). It is seen that the impedance measurements and the radioactive tracer method give the same order of magnitude for  $r_0$ . The agreement is satisfactory if we take into consideration that possibly the surface states of the electrodes used in the two investigations were not the same, though the platinum wires were treated in the same way<sup>1</sup> prior to use. Thus a very good support is obtained for the result arrived at in the previous investigation<sup>1</sup> that  $r_0 \leq r_d$  for the concentrations used, so that  $r_0$  has a considerable influence upon the over-all rate of the heterogeneous exchange reaction.

From a comparison between the values of  $i_2 F^{-1} = 4 \times 10^{-11}$  mole  $\cdot$  cm $^{-2}$   $\cdot$  sec $^{-1}$  and  $r_d$  it is found that the rate of reduction of cerium(IV) at the steady-state potential is only 1 to 2 % of the rate of diffusion of cerium(IV) to and from the electrode. Consequently we have also confirmed the assumption in the previous investigation that the cerium concentrations at the interface are not affected appreciably by this reduction.

On the other hand, at the low cerium(IV) concentrations used, necessitated by the intricate hydrolysis of the cerium(IV) ion in perchloric acid solutions, the term  $r_0$  in the right member of (26) is rather small in comparison with the constant term. Thus, even if several concentrations within the narrow range given are used it is impossible to carry out impedance measurements with such an accuracy that we can get an independent check on the relation  $r_0 = \text{constant} \cdot c^2$  (for  $c = q$ ), presupposed in the calculations above. It is evident that in the present case the radioactive tracer method is superior to the impedance measurements.

Interesting information about the heterogeneous oxygen evolution has been obtained in this investigation. From the calculations we arrive at the conclusion that under the conditions given the oxygen evolution is controlled not by the discharge step but by the subsequent reaction between the radicals OH, adsorbed on the platinum. This result is in agreement with recent investigations. Thus according to Bockris<sup>7</sup> the rate-determining step of the oxygen evolution is the following one:  $2 \text{OH} \rightarrow \text{H}_2\text{O}_2$ , where OH and  $\text{H}_2\text{O}_2$  are adsorbed on the platinum electrode.

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