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The Mechanism of the Exchange Reaction between Cerium(III) and Cerium(IV) at Platinum Surfaces

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The heterogeneous electron exchange reaction between cerium(III) and cerium(IV) at platinum surfaces under equilibrium electrode potential is investigated in a perchlorate ionic medium by means of a radioactive tracer. A general relationship for the combination of rates of consecutive steps in exchange reactions is given. From the kinetic law obtained in the present case it is established that at 0° C and in approximately 3 M perchloric acid the resultant rate of the reaction is controlled both by the electron transfer step and by the diffusion of cerium(IV) up to the interface.

The measurements indicate that the uptake of electrons from platinum by cerium(IV) takes place *via* a dimer of cerium(IV). Thus this species together with the corresponding mixed cerium(III)—cerium(IV) product, operating in the reverse process, are directly potential adjusting, although the concentrations of both species are very low in comparison with the total concentrations of cerium.

The mechanism proposed is discussed in connection with other facts about some homogeneous redox reactions in which cerium is involved.

Few kinetic investigations on the mechanisms of electrode reactions of inorganic redox systems have been reported in the literature, and electrical methods alone have been used in these studies. In some cases, *e. g.* the redox systems Fe^{3+} / Fe^{2+}, Mn^{3+} / Mn^{2+}, and Ce(IV) / Ce(III), it has been found [1–4] that the electron transfer step and the over-all electrode reaction are the same, while for other systems [5], *e. g.* Mn^{4+}/Mn^{3+}, they may be different, even though the over-all electrode reaction is very simple.

In the investigation of the cerium(IV) / cerium(III) system Vetter [4] used sulphuric acid as an additional electrolyte. However, it is known that both the cerium(III) ion (Fronæus [6]) and especially the cerium(IV) ion (Hardwick and Robertson [7]) can form three mononuclear sulphate complexes and that the hydrolysis of cerium(IV) is suppressed by this complex formation. For this reason it is probable that the electron transfer step found [4] in sulphuric acid refers to sulphate complexes.

On the other hand it has been shown by Hardwick and Robertson [8] that hydrolysis of the cerium(IV) ion occurs in perchloric acid solutions, partly with the formation of a dinuclear species. Furthermore, Gryder and Dodson [9] found that the rate of the homogeneous exchange reaction between cerium(III) and cerium(IV) is a linear function of the reciprocal of the perchloric acid concentration.

It was therefore to be expected that the electron transfer step of the heterogeneous exchange reaction in perchloric acid at platinum surfaces would be less simple than in sulphuric acid solutions. Thus the present investigation was started with the aim of elucidating the mechanism of this exchange reaction by the use of a radioactive cerium isotope.

In those cases where the electron transfer step is not very rapid in comparison with the rate of diffusion of the exchanging species up to the interface, the radioactive tracer method can give the rate of the first-mentioned step at equilibrium potential. The method has the advantage over electrical methods of being uninfluenced by small amounts of other redox systems present as impurities or formed from the solvent, and which are in redox equilibrium with the main system. The tracer method has been successfully employed by us in a previous investigation [10] of an electrode reaction of a different type.

THEORETICAL

The following notation is used for total concentrations.

c_a, q_a = concentrations of radioactive cerium(IV) and cerium(III).

c_i, q_i = concentrations of inactive cerium(IV) and cerium(III).

$c = c_a + c_i$

$q = q_a + q_i$

The kinetic law for the electron transfer step

According to Hardwick and Robertson [8] cerium(IV) is present as a mixture of Ce^{4+}, $CeOH^{3+}$, and a dimer, denoted Ce_2O^{6+}, in perchlorate solutions containing perchloric acid. Thus, to make a general treatment of the over-all electrode reaction

$$Ce(IV) + e^- \text{ (electrode)} \rightleftharpoons Ce(III) \tag{1}$$

we must presuppose that we have a set of simultaneous one-electron transfer steps of the type

$$\overset{IV}{Ce_j}(OH)_n^x + e^- \text{ (electrode)} \rightleftharpoons \overset{III\ IV}{CeCe_{j-1}}(OH)_n^{x-1} \tag{2}$$

combined with the hydrolytic equilibria

$$\overset{IV}{Ce_j}(OH)_n^x + nH^+ \rightleftharpoons jCe^{4+} + nH_2O \tag{3}$$

$$\overset{III\ IV}{CeCe_{j-1}}(OH)_n^{x-1} + nH^+ \rightleftharpoons Ce^{3+} + (j-1)Ce^{4+} + nH_2O \tag{4}$$

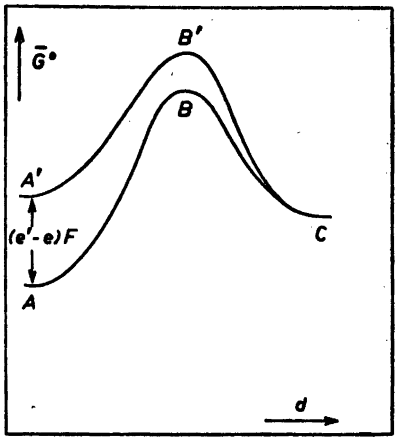

Fig. 1. The standard electrochemical free energy $\bar{G}^\circ$ during the electron transfer as a function of the distance d of the electron from the electrode surface.

Here $n \geqq 0$ for $j = 1$ and $n \geqq 2$ for $j = 2$. Within a limited range of values of q and c and at a fixed value of the perchloric acid concentration we can assume that the rates $\vec{r}$ and $\overleftarrow{r}$ of one of the reactions of type (2) predominate, and then these rates are practically equal to the total rates of the electron transfer in both directions. It should be emphasised that the concentrations of the species responsible for the electron transfer may be very small in comparison with q and c (*cf.* Fronæus and Östman [10]).

In Fig. 1 the standard electrochemical free energy during the electron transfer, $\bar{G}^0$, is represented as a function of the distance d of the electron from the electrode surface. The value of $\bar{G}^0$ at A refers to the left-hand side of (2) at a fixed value e' of the electrode potential while the value at C is that of the right-hand side of (2) just outside the rigid part of the electrode double layer. The steepness of the curve AB depends upon the so-called image force between the electrode and the electron(*cf.* Pitzer [11]).

When the electrode potential is decreased from e' to e the new energy barrier A'B'C is obtained, the increase in $\bar{G}^0$ at A being $(e'—e)F$ and for the activated state $\alpha(e'—e)F$, where $0<\alpha<1$. Thus it is evident that the electrochemical free energy of activation of the forward reaction of (2) decreases by the quantity $(1—\alpha)\ (e'—e)F$ and that of the reverse reaction increases by the quantity $\alpha(e'—e)F$. Then if e is the equilibrium electrode potential we have $\vec{r} = \overleftarrow{r} = r_0$ and for r_0 the following expressions are obtained

$$r_0 = k_1\ [\overset{IV}{Ce}_j(OH)_n^s]\ \exp\left\{\frac{(1—\alpha)\ (e'—e)\ F}{RT}\right\} \tag{5}$$

$$r_0 = k_2\ [\overset{III\ IV}{CeCe}_{j-1}(OH)_n^{s-1}]\ \exp\left\{-\frac{\alpha(e'—e)\ F}{RT}\right\} \tag{6}$$

where k_1 and k_2 denote the specific rates of the forward and reverse reactions at the electrode potential e'. For a survey of deductions of equations of the types (5) and (6) in the literature the reader is referred to a paper by Vetter [12].

Variations in the ζ-potential are suppressed in the presence of perchloric acid at a high and constant concentration as an additional electrolyte [13], and then the concentrations of the electron transferring species in the diffuse double layer are proportional to the corresponding concentrations in the bulk of the solution. Then if the latter concentrations are introduced in (5) and (6) the coefficients k_1 and k_2 should still be constants, provided, of course, that the state of the electrode surface is reproducible.

Furthermore, if, as usual, we presuppose that the inner potential in the solution phase varies linearly with d through the rigid part of the double layer, the transfer coefficient α should be a constant and, in the case of a symmetrical energy barrier, have the value 0.5.

Eliminating $e' - e$ from (5) and (6) we get

$$r_0 = \text{constant} \cdot [\overset{\text{IV}}{\text{Ce}}_j(\text{OH})_n^x]^{\alpha} \; [\overset{\text{III IV}}{\text{CeCe}}_{j-1}(\text{OH})_n^{x-1}]^{1-\alpha} \tag{7}$$

Then we apply the law of mass action to the equilibria (3) and (4), and the expressions obtained are combined with (7) giving

$$r_0 = \text{constant} \cdot [\text{Ce}^{4+}]^{j-1+\alpha} \; [\text{Ce}^{3+}]^{1-\alpha} \tag{8}$$

since $[\text{H}^+]$ is kept constant.

From the known effect of temperature on the equilibrium constants of the hydrolytic reactions [8] of Ce^{4+} it can be calculated that the concentration of the dimer is $\leqq 2.5$ % of c at 0° C, in 2.82 M perchloric acid as ionic medium, and at c-values $\leqq 8.5$ mM (the conditions for the measurements in the present investigation). The concentration of $\overset{\text{III IV}}{\text{CeCe}}(\text{OH})_n^{x-1}$ is also certainly very small, since an extinctiometric investigation by King and Pandow [14] indicates that the system cerium(III)/cerium(IV) in perchloric acid solutions does not exhibit "interaction absorption".

Thus the mononuclear species predominate, and we have $[\text{Ce}^{4+}] \approx 0.86\, c$ throughout the measurements at our acid concentrations. Furthermore, since no hydrolysis of Ce^{3+} occurs in perchloric acid solutions [6] $[\text{Ce}^{3+}] = q$, and introducing these expressions into (8) we finally obtain

$$r_0 = k_0 \; c^{j-1+\alpha} q^{1-\alpha} \tag{9}$$

where k_0 is a constant.

The resultant rate of the heterogeneous reaction

The rate r of the heterogeneous reaction is composed of the rates of at least three consecutive steps; the rate r_1 of the diffusion of cerium(III) to and from the electrode surface, the rate r_0 of the electron transfer in both directions, and the rate r_2 of the diffusion of cerium(IV) to and from the electrode, expressed in moles per unit surface area and unit time.

Of r_1 moles of cerium(III) diffusing to the electrode surface only r' moles take part in the electron transfer reaction. Now, since the fraction $r_0/(r_0+r_1)$

of all cerium(III) appearing and disappearing at the electrode is due to the electron transfer reaction we have the relation $r'/r_1 = r_0/(r_0 + r_1)$ or

$$\frac{1}{r'} = \frac{1}{r_0} + \frac{1}{r_1} \tag{10}$$

Evidently r' is the rate of transfer of cerium(III) from the solution outside the diffusion layer to cerium(IV) at the electrode surface. As the deduction is independent of the mechanisms of the two steps, the resultant rate r can be obtained by combination of r' and r_2 in the same way, and we get

$$\frac{1}{r} = \frac{1}{r_0} + \frac{1}{r_1} + \frac{1}{r_2} \tag{11}$$

If the reversible reactions (3) and (4) are not extremely rapid these steps must also be taken into consideration, and the reciprocals of their rates added to the sum on the right side of (11). Thus the reciprocals can be treated as kinetic resistances.

Obviously this fundamental law for the combination of rates of consecutive steps is *generally* applicable to exchange reactions, where all concentrations are independent of time and consequently for every step the rates are equal in both directions. For heterogeneous reactions (not exchange reactions) composed of a diffusion step and a reaction at an interface it has been shown previously [15,16] that a law of the type (10) is valid in the simplest case with a first order surface reaction.

For the diffusion rates r_1 and r_2 we have the following expressions

$$r_1 = \frac{D_1\, q}{\delta} \tag{12}$$

$$r_2 = \frac{D_2\, c}{\delta} \tag{13}$$

where δ is the thickness of the diffusion layer and D_1 the diffusion coefficient of the cerium(III) ion. D_2 is an average diffusion coefficient [17] of cerium(IV) valid at the fixed concentration ratios of the mononuclear cerium(IV) species.

EXPERIMENTAL

Chemicals. Radioactive cerium(III) perchlorate (containing some ^{141}Ce from Harwell, England) and inactive cerium(III) and cerium(IV) perchlorate solutions were prepared and analysed in the way described in previous papers [6,18]. All the stock solutions used were 2.82 M with respect to perchloric acid. The concentration of cerium(IV) was redetermined every day since the solution of cerium(IV) perchlorate was not stable but slowly oxidized water.

A 4.5 M solution of nitric acid was freed from oxides of nitrogen by bubbling air through for some hours at 60—80° C, and it was checked that the solution had no reducing effect on cerium(IV).

Diethyl ether was distilled once and stored in contact with sodium.

Exchange measurements. Cerium(III) perchlorate, cerium(IV) perchlorate and perchloric acid were mixed and tempered in a thermostat at 0° C. 15 ml of the mixture were introduced into a reaction vessel, which could be shaken in the thermostat, and 1.00 ml of the radioactive cerium(III) perchlorate solution was added quickly. After a certain

time, varying from 2 to 30 minutes, 10 ml of the solution were withdrawn and added to a mixture of 25 ml 4.5 M nitric acid and 50 ml ether. In the presence of the nitric acid cerium(IV) is rapidly extracted into the ether and this is a satisfactory and convenient method for the separation of the exchanging species, given by Gryder and Dodson [9]. After extraction the ether phase was washed once with 25 ml of the nitric acid, and the cerium(IV) was reduced with 10 ml aqueous hydrogen peroxide, causing a re-extraction of all the cerium into the aqueous phase. The gamma radioactivity of a fixed volume of the last-mentioned phase was determined with a scintillation detector (Tracerlab P-20) under reproducible geometry.

For every set of values of c and q two series of measurements were performed, one in the absence of platinum, giving the rate of the homogeneous exchange, and another with a platinum wire of 40 cm^2 surface area in the reaction vessel. In the last-mentioned case the solution was shaken so that the diffusion layer at the electrode had a fixed thickness throughout the measurements. Furthermore, the platinum wire was heated in an alcohol flame just before use, since it was very important to have the surface of the electrode in a reproducible state.

The radioactivity of cerium(IV) when approximate equilibrium with respect to isotopic mixing had been attained was determined on separate solutions, where the homogeneous exchange had proceeded for at least ten half reaction times, by the procedure described above.

It should be mentioned here that the reaction between cerium(IV) and water is so slow at 0° C, even in the presence of platinum, that it could have no influence on the exchange measurements during the reaction times used.

THE EXPERIMENTAL OVER-ALL RATE OF EXCHANGE

The differential equation for the total radioactive exchange

$$\overset{*}{\mathrm{Ce}}(\mathrm{III}) + \mathrm{Ce}(\mathrm{IV}) \rightleftharpoons \overset{*}{\mathrm{Ce}}(\mathrm{IV}) + \mathrm{Ce}(\mathrm{III}) \tag{14}$$

has the following general form [10]

$$\frac{\mathrm{d}c_a}{\mathrm{d}t} = \left(\frac{sr}{v} + R\right)\frac{c_i q_a - c_a q_i}{c\,q} \tag{15}$$

where s (= 40 cm^2) is the surface area of the platinum, v (= 16 ml) the volume of the reaction mixture, and R the rate of the homogeneous exchange reaction. If the measured radioactivity of cerium(IV) is denoted x at time t and x_∞ when the isotopic mixing has attained equilibrium the fraction exchanged will be equal to x/x_∞. If we further note that c_i and q_i are practically equal to the total concentrations c and q, integration of (15) gives

$$\ln\left(1-\frac{x}{x_\infty}\right) = -\left(\frac{sr}{v} + R\right)\cdot\frac{c+q}{qc}\cdot t \tag{16}$$

When $\ln(1-x/x_\infty)$ is plotted against t a straight line should be obtained, from the slope of which the value of R (in the absence of platinum) or $sr/v+R$ can be calculated. Since the separation with ether was performed in exactly the same way for all the solutions in a series of measurements, corresponding

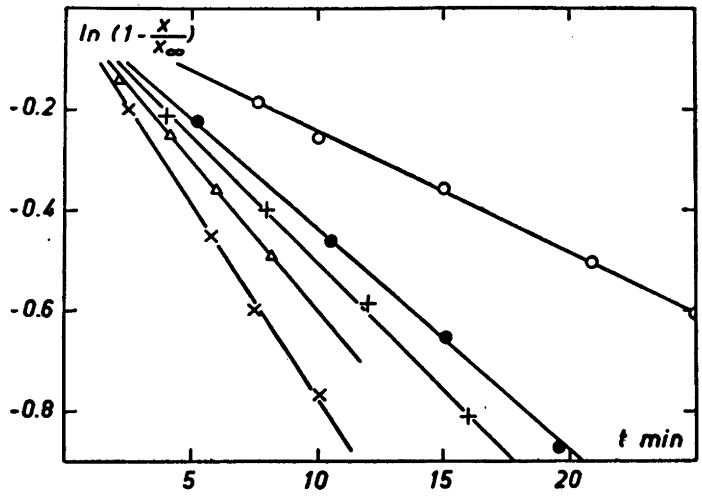

Fig. 2. $\ln(1-x/x_\infty)$ as a function of t in the homogeneous exchange for various values of c and q. —— *c = 2.18 mM, q = 2.18 mM (○); c = 2.18 mM, q = 5.43 mM ●; c = 2.18 mM, q = 10.34 mM (×); c = 4.25 mM, q = 6.14 mM (+); c = 8.21 mM, q = 4.85 mM (△).*

to fixed values of c and q, the fraction x/x_∞ should be independent of any slight incompleteness in the separation of cerium(IV).

The graphs in Fig. 2 represent the measurements of R for different values of c and q. An extrapolation of the straight lines obtained shows that $x = 0$ for $t = 0$, proving that the separation procedure does not induce any exchange. In passing it can be mentioned that R/q is a linear function of c, as found also by Gryder and Dodson [9]. The measurements with platinum in the reaction solution are represented in Figs. 3 and 4. Straight lines are also obtained in this case if very small values of t are not used in the runs corresponding to the lowest values of the rate r of the heterogeneous exchange.

It was necessary to keep $c \cdot q < 4 \times 10^{-5}$ M² in order to make the exchange rate conveniently measureable. On the other hand, the specific activity of the radioactive cerium(III) preparation available set the lower limit to the ranges of values of c and q.

Introducing the expressions (9), (12), and (13) for r_0, r_1, and r_2 into (11) we get the following relationship

$$\frac{q}{r} = \frac{q^a}{k_0\, c^{j-1+a}} + \frac{\delta}{D_1} + \frac{\delta\, q}{D_2\, c} \qquad (17)$$

From (17) it is evident that for $j = 1$ the quantity q/r should be a function of q/c only and increase monotonicly for increasing values of q/c. However, an inspection of Table 1, where the results from the exchange measurements are given, shows that this is not the case under the experimental conditions used. There remains the alternative $j = 2$, and the possibility of determining

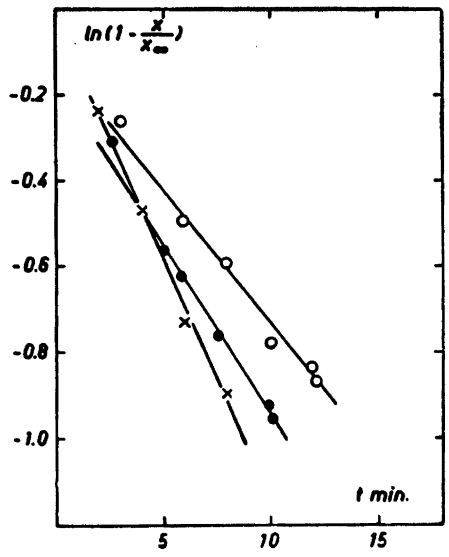

Fig. 3. $\ln(1-x/x_\infty)$ as a function of t in the mixed heterogeneous and homogeneous exchange for c = 2.18 mM and various values of q. —— q = 2.18 mM (○); q = 5.43 mM (●); q = 10.34 mM (×).

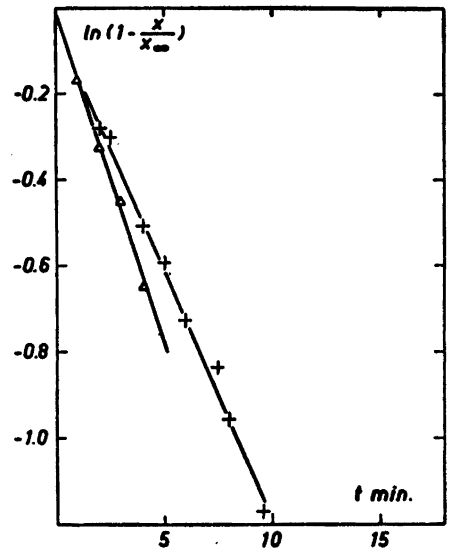

Fig. 4. The same function as in Fig. 3 for various values of c and q. —— c = 4.25 mM, q = 6.14 mM (+); c = 8.21 mM, q = 4.85 mM (△).

values of the parameters k_0, α, δ/D_1, and δ/D_2 by this approach will be investigated.

At the highest value of c and the lowest value of q/c the ratio q/r becomes so small that we can conclude that the constant term δ/D_1 is negligible. In a perchloric acid medium, where no complexing anions are present, the cerium (IV) ion is more strongly hydrated than the cerium(III) ion. Thus the difference between D_1 and D_2 should be greater than *e. g.* in a sulphuric acid medium [4], where complex formation certainly reduces the hydration of especially the cerium(IV) ion.

Table 1. The rates R and r of the homogeneous and heterogeneous exchange reactions for different values of the total cerium (III) and cerium (IV) concentrations.

c mM	q mM	$\frac{q}{c}$	R mM. min^{-1}	$\frac{sr}{v}+R$ mM · min^{-1}	$r \times 10^8$ mole · cm^{-2}.min^{-1}	$\frac{q}{r}$ cm^{-1} · min	$\frac{q}{r_{calc}}$ cm^{-1}.min
2.18	2.18	1.00	0.026	0.067	1.65	130	130
2.18	5.43	2.49	0.068	0.125	2.30	235	235
2.18	10.34	4.75	0.137	0.205	2.70	380	370
4.25	6.14	1.45	0.129	0.285	6.25	98	107
8.21	4.85	0.59	0.185	0.470	11.4	42.5	39.5

The following procedure was applied to determine the other parameters. For different values of α between 0 and 1, the quantities k_0 and δ/D_2 were calculated from corresponding values of q/r, c, and q in the first two lines of Table 1. With every set of parameters, q/r was calculated for the other c- and q-values, and it was found that the best fit with all the measurements was obtained for $\alpha = 0.50 \pm 0.05$. Then the relationship

$$\frac{1}{r} = \frac{211}{c^{1.5}\, q^{0.5}} + \frac{33}{c} \tag{18}$$

is obtained when c and q are expressed in mM and r in mM · cm · min^{-1}. In the last column of Table 1 the values of q/r have been calculated from this formula, and it is seen that they are in good agreement with the measured values. It is easily checked that no fit with all measurements can be obtained for $j > 2$. At the lowest cerium(IV) concentrations used $r_0 < r_2$, and for the highest c-values r_0 and r_2 are practically equal. Thus r_0 has a considerable influence on the resultant rate r.

We further obtain $D_2/\delta = (0.50 \pm 0.10) \times 10^{-3}$ cm · sec^{-1} from the measurements. A value of the average diffusion coefficient D_2 in the acid medium used is not known, but we can presuppose it to be of the order of magnitude 10^{-6} cm^2 · sec^{-1} (*cf.* Vetter [4]), giving us $\delta \approx 10^{-3}$ cm. This is a very plausible δ-value [19] at low relative velocities between the platinum and the solution, and there is nothing in the measurements that indicates an influence of the rates of the reactions (3) and (4) upon the total rate of the heterogeneous exchange.

DISCUSSION

We arrive at the following conclusions from the results of the present investigation.

(a) Within the concentration ranges of cerium(III) and cerium(IV) used and in approximately 3 M perchloric acid as an ionic medium the rate of the heterogeneous exchange reaction is controlled both by the electron transfer step and by the diffusion of cerium(IV), whereas the diffusion of cerium(III) seems to be too rapid to influence markedly the rate of exchange. Thus the tracer method is very suitable for the investigation of the mechanism of the electrode reaction.

(b) The hydrated cerium(IV) ion and its mononuclear hydrolysis products do not take up electrons appreciably from the platinum. This process takes place solely by way of a *dinuclear hydrolysis product*, although its concentration is only between 0,5 and 2.5 % of the total cerium (IV) concentration. As mentioned above the concentration of the corresponding mixed cerium(III)—cerium(IV) hydrolysis product, formed as an intermediate in the taking up of one electron and operating in the reverse process, must also be very low. The two dinuclear hydrolysis products mentioned are evidently the cerium species *directly* involved in the adjustment of the equilibrium electrode potential.

The results of some investigations of homogeneous reactions make conclusion (b) above very plausible. Thus Heidt and Smith [20] have investigated

the photochemical oxidation of water by cerium(IV) perchlorate in perchloric acid solutions and Kolp and Thomas [21] have studied the corresponding thermal reaction, and in both cases the measurements indicate that the oxidation is caused by a reactive dimer of cerium(IV).

It should also be mentioned that in a previous work by the present authors [18], dealing with the reaction between cerium(III) and persulphate, it was found that the rate of electron transfer is increased considerably by the coordination of sulphate ions to the cerium(III) ion. From the results of the present investigation it is evident that the coordination of a mononuclear hydrolysis product of cerium(IV) to the cerium(III) ion with the liberation of hydrogen ions has a similar effect in the electrode reaction studied. Also here the effect may be caused by a decrease in the energies of hydration (*cf.* Ref.[18]) or by a promotion of the 4*f* electron to a higher energy level. In this way we obtain a plausible explanation of the difference between the mechanisms of the electrode reactions in sulphuric acid [4] and in perchloric acid.

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