On the Formal Potential of the Cerium(IV)–Cerium(III) Couple at −5 °C in 6.5 mol kg^{-1} $HClO_4$

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In order to establish the formal potential E^f of the Ce^{IV}–Ce^{III} couple, the e.m.f. of the cell (i) has been studied at −5 °C as a function of the concentrations of both Ce^{III} and Ce^{IV}. The

$$\text{Glass electrode}\ \left\|\ \begin{array}{l} B_4\ \mathrm{Ce^{IV}} \\ B_3\ \mathrm{Ce^{III}} \\ 6.5 - 4B_4 - 3B_3 \approx 6.5\ \mathrm{mol\ kg^{-1}\ H^+} \\ 6.5\ \mathrm{mol\ kg^{-1}\ ClO_4^-} \end{array}\ \right\|\ \mathrm{Pt} \qquad \text{(i)}$$

comprehensive set of redox potential data, at concentrations of Ce^{III} and Ce^{IV} ranging from 0.01 to 0.1 and from 0.001 to 0.125 mol kg^{-1} respectively, have been explained according to the equilibrium: $2\mathrm{Ce^{IV}} \rightleftharpoons [\mathrm{Ce^{IV}}]_2$. From these data, both the equilibrium constant, K_D = 15 ± 2 kg mol^{-1}, and the limiting value, as the cerium(IV) concentration approaches zero, of the formal redox potential, E^f (I = 6.5 mol kg^{-1}, −5 °C) = 1 755 ± 2 mV, against the molal hydrogen electrode at −5 °C, have been calculated. Additional experimental data, gathered in order to find the correct chemical formulae of both the monomeric and the dimeric species, are also discussed.

The first systematic attempts to determine the formal potential of the Ce^{IV}–Ce^{III} couple were carried out at 25 °C by Kunz[1] in H_2SO_4, Noyes and Garner[2] in HNO_3, and Smith and Getz[3] in solution 1—8 N of different strong acids. Although this last work is often taken as a reference by most analytical textbooks[4,5] and reviews,[6] it can be subject to some criticism. First, the activity coefficients of the reacting species were not kept constant, the acid concentration varying over broad ranges, so that no useful correlation can be drawn between these data. Nor should the observed e.m.f. variations be attributed, as the authors do, only to complex formation. Indeed, on raising the concentration of $HClO_4$ they found that the e.m.f. increases, while it should decrease if Ce^{IV} forms complexes. A second objection is that the concentrations of both the oxidized and the reduced cerium ions were not varied at all. So it is impossible to establish the presence of polynuclear species, if any.

Some years later Sherrill *et al.*[7] carried out some e.m.f. measurements at 25 °C in solutions ranging from 2.4 to 0.2 mol dm^{-3} $HClO_4$ (sometimes in the presence of $NaClO_4$); from the experimental data, they could exclude any complexation by perchlorate ions and concluded that the prevailing oxidized species were the hydrolyzed $[Ce(OH)]^{3+}$ and $[Ce(OH)_2]^{2+}$ ions, rather than the Ce^{4+} aqua ion. However, they failed correctly to explain the strong dependence of their data on cerium(IV) concentration.

Several authors subsequently investigated the problem of cerium(IV) hydrolysis in different media, both by e.m.f.[8–10] and spectrophotometric[11–13] measurements. The matter has been reviewed by Baes and Mesmer.[14] All of these authors agree that Ce^{IV} is extensively hydrolyzed even in concentrated acid solutions, and that some of the hydrolysis products are polynuclear.[8,10–12,15,16] However, there is some disagreement about the nature of the hydrolysis products and the related equilibrium constants.

All of these discrepancies may be caused by the experimental difficulties in obtaining accurate and reproducible data for cerium(IV) solutions, due to their high oxidizing power. This instability toward reduction by water molecules may be decreased by strong complexing anions such as sulphate,[3,17,18] but it is enhanced by the presence of impurities of different types, introduced into the solution during its preparation or storage: for example, solid microparticles which may act as a catalyst toward reduction of Ce^{IV}, or a stoicheiometric excess of oxidizing agents.

The present work has been undertaken in order to circumvent these experimental difficulties and to clarify the nature of the cerium(IV) species present in a highly acidic but weak complexing medium. This has been done by extending to the cerium-(IV), -(III) system the experimental approach already developed in the study of silver-(II), -(I)[19] and cobalt-(III), -(II).[20]

Results and Discussion

Method of Investigation.—Because the stabilization of the cerium(IV) test solution represents the main problem, the measurements were carried out at high acidity and low temperature. The choice of 6.5 mol kg^{-1} (5 mol dm^{-3} at 25 °C) $HClO_4$ as ionic medium and of the temperature of −5 °C has already been successful[19,20] in stabilizing strong oxidant solutions, enough to obtain accurate and reproducible e.m.f. data.

The junction-free cell (I) was studied at −5 °C, concurrently

$$-\ \text{Glass electrode/Solution S/Pt}\ + \qquad \text{(I)}$$

with cell (II) which contains a liquid junction, in order to test

$$-\ \text{Reference electrode/Solution S/Pt}\ + \qquad \text{(II)}$$

the glass electrode behaviour; S represents a test solution of the general composition B_4 Ce^{IV}, B_3 Ce^{III}, $6.5 - 4B_4 - 3B_3 \approx 6.5$ mol kg^{-1} H^+, and 6.5 mol kg^{-1} ClO_4^-, and the reference half-cell is cell (III).

$$6.40\ \mathrm{mol\ kg^{-1}\ HClO_4,\ 0.1\ mol\ kg^{-1}\ AgClO_4/Ag} \qquad \text{(III)}$$

Table 1. Summary of data from 16 different runs. For each parameter are reported the limits between which it was varied; m_{ox}, m_3, and m_H represent the molalities of the oxidized species, Ce^{III}, and H^+ respectively; subscripts G and R refer to data from cells (I) and (II) respectively

Run	m_{ox}	m_3	m_H	E'_G/mV	E'_R/mV
1	0.104 —0.0289	0.0664—0.0191	6.06—6.30	1 734.1—1 744.0	1 735.4—1 744.3
2	0.0891—0.0320	0.0815—0.0306	6.06—6.27	1 735.3—1 743.4	1 736.1—1 743.2
3	0.0750—0.0023	0.0533—0.0523	6.07—6.28	1 735.1—1 750.9	1 735.5—1 750.5
4	0.0542—0.0314	0.0314—0.0304	6.25—6.38	1 742.6—1 757.0	1 742.7—1 756.1
5	0.125 —0.0079	0.0703—0.0683	5.90—6.21	1 734.6—1 752.0	1 735.9—1 752.2
6	0.0012—0.0776	0.0489—0.0516	6.25—6.07	1 751.2—1 735.9	1 750.8—1 736.0
7	0.0048—0.0868	0.0409—0.0430	6.24—6.07	1 750.0—1 734.6	1 748.3—1 735.2
8	0.0036—0.0846	0.0285—0.0298	6.38—6.20	1 751.5—1 735.3	1 750.7—1 735.4
9	0.0024—0.0958	0.0697—0.0735	6.25—5.97	1 755.0—1 737.0	1 754.7—1 736.7
10	0.0009—0.0476	0.0357—0.0359	5.00—5.01	1 745.8—1 733.3	1 744.0—1 732.3
11	0.0595—0.0082	0.0418—0.0422	4.52—4.49	1 731.9—1 742.9	1 729.6—1 740.2
12	0.0441—0.0099	0.0413—0.0119	3.83—3.80	1 726.5—1 734.5	1 726.8—1 734.7
13	0.0150—0.0045	0.0791—0.0770	3.02—3.02	1 728.1—1 732.9	1 727.7—1 731.9
14	0.0037—0.0368	0.0499—0.0530	3.00—2.99	1 728.7—1 719.0	1 728.4—1 718.0
15	0.0066—0.0013	0.0124—0.0105	6.28—4.67	1 749.0—1 693.4	1 745.3—1 742.6
16	0.0238—0.0059	0.0085—0.0090	6.23—3.86	1 744.7—1 739.3	1 739.1—1 741.3

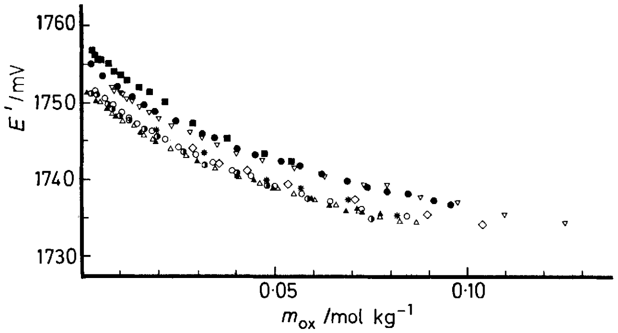

Figure 1. Plots of E', as derived from data from cell (I) by means of equation (1), against the total concentration of the oxidized species, m_{ox}, for nine different runs in nearly 6.5 mol kg^{-1} $HClO_4$. Additional information about each run is collected in Table 1. Runs: 1 (◇), 2 (*), 3(◑), 4 (■), 5 (▽), 6 (▲), 7 (△), 8 (○), and 9 (●)

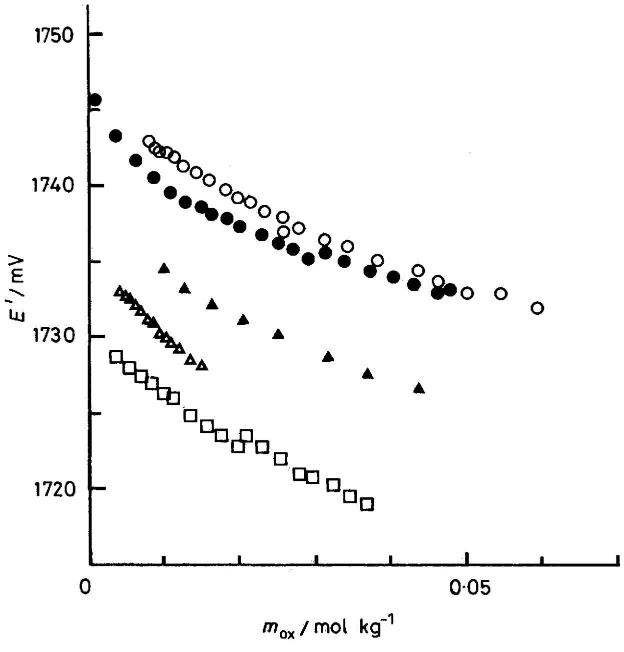

Figure 2. Plots as in Figure 1 for runs 10—14 carried out at different m_H values in 6.5 mol kg^{-1} ClO_4^-. Additional information about each run is collected in Table 1. Runs: 10 (●), 11 (○), 12 (▲), 13 (△), and 14 (□)

Here and in the following, Ce^{IV} will generally indicate all the species containing cerium in the oxidation state IV, whatever their chemical formulae.

E.m.f. measurements on cells (I) and (II) were carried out at −5 °C varying the concentrations of the reacting species in S by stepwise additions of a solution T, 6.5 mol kg^{-1} in ClO_4^-, but having a different cationic composition in each of the following cases: (*a*) in runs 1 and 2, cerium free, but $B = (B_4 + B_3)$ mol kg^{-1} in La^{III} and $(6.5 - 3B)$ mol kg^{-1} in H^+; (*b*) in runs 3—5, Ce^{IV} free, having the same cerium(III) concentration as solution S; (*c*) in runs 6—9, much higher cerium(IV) concentration, but the same concentrations of Ce^{III} and H^+ as those of solution S; (*d*) in runs 10—14, the same composition as in cases (*a*), (*b*), or (*c*), but some of the H^+ ions were replaced by Na^+.

So, during all of the 14 runs, the concentrations of H^+ and ClO_4^- were held constant. Procedure (*a*) allowed a cerium(IV) dilution at nearly constant Ce^{IV}/Ce^{III} ratio, while, at nearly constant cerium(III) concentration, Ce^{IV} was diluted by following procedure (*b*) and concentrated by following (*c*). The three kinds of experiments were repeated, following procedure (*d*).

In Table 1, run by run, are reported the initial and final compositions of the test solution, as a consequence of the addition of solution *T*; the last two columns report the corresponding values of E' calculated by means of equations (1) and (2). The concentration of Ce^{IV} varied from 0.001 to 0.125 mol kg^{-1}, that of Ce^{III} from 0.01 to 0.08 mol kg^{-1}, that of H^+ from 6.5 to 3.0 mol kg^{-1}, and the ratio Ce^{IV}/Ce^{III} ranged from 0.025 to 2.84:1.

The e.m.f. values of cells (I) and (II), E_I and E_{II}, can be combined with data from the analytical composition of S to give equation (1) or (2) where E^0_G is the concentration-independent

$$E' = E_I - 53.2 \log m_{ox}/m_3 m_H + E^0_G \quad (1)$$

$$E' = E_{II} - 53.2 \log m_{ox}/m_3 + E_{RE} \quad (2)$$

term in the equation for the half-cell potential of the glass electrode, E_{RE} is the potential of the reference half-cell (III), m_{ox} is total molality of the oxidized species, while m_3 and m_H are the molalities of the Ce^{III} and H^+ in S. Experimental details for measuring both E^0_G and E_{RE} against the molal hydrogen electrode and to test their reproducibility have already been reported;[19,20] as found for other systems, the results from cells (I) and (II) were always in good agreement.

According to the choice of the background electrolyte as the reference state, since the sum $(m_{ox} + m_3)$ never exceeded 5% of the total perchlorate concentration, the activity factors of the reacting species could be set equal to 1 in equations (1) and (2);[19,20] for the same reason, the variations in the liquid junction potential in cell (II) could be neglected in equation (2).[19,20]

Values of E' from cell (I) are plotted against m_{ox} for runs 1—9 in Figure 1, and for runs 10—14 in Figure 2. The 14 runs show some common features. (*i*) Dilution at constant Ce^{IV}/Ce^{III} ratio leads to an e.m.f. increase of about 10 mV for a four-fold dilution; E' values, from equations (1) and (2), show the same increase. (*ii*) Similarly, following procedure (*b*), E' increases, while it decreases following procedure (*c*). (*iii*) As shown in Figure 1, data obtained by different methods at the same m_H are in good agreement; the experimental points have a common limiting value E^f as m_{ox} approaches zero. (*iv*) The same effects occur at each acidity, with E^f being lower the lower is the concentration of H^+ investigated.

Treatment of Data.—The analytical procedure used to determine the composition of solution S allows one to know only the total molality of the oxidized species, denoted as m_{ox}. Concerning the actual nature of the oxidized species, four hypotheses may be considered: (*a*) no oxidized species other than the solvated ion is present so that $m_{ox} = m_4$, the concentration of free Ce^{4+} aqua ion; (*b*) hydrolyzed species are formed so that m_{ox} differs from m_4 by a term which depends on m_H; (*c*) polynuclear species are formed so that m_{ox} differs from m_4 by a term which depends on m_{ox} itself; (*d*) mixed polynuclear products are formed[8] so that m_{ox} differs from m_4 by a term which depends also on m_3.

Figures 1 and 2 show a clear dependence of E' both on m_{ox} and m_H, so confirming the validity of hypotheses (*b*) and (*c*); for the same reasons, hypothesis (*a*) is not true and the solvated Ce^{4+} ion is never the only oxidized species in the test solutions. Finally, E' does not seem to show any dependence on m_3, thus mixed polynuclear products are not formed.

The experimental evidence of the occurrence of cerium(IV) polynuclear hydrolyzed species in S requires an investigation of the hydrolysis equilibria, together with the redox one. Unfortunately, the medium used has so high an acidity that the classical approach[21] to the study of metal-ion hydrolysis cannot be applied. So the problem has been faced in two steps. First, from the dependence of E' on m_{ox} at constant m_H, the number of metal ions in the polynuclear species were obtained, together with a constant value of the formal redox potential E^f for the couple Ce^{IV}–Ce^{III}, for each m_H value. Secondly, from the dependence of E^f on m_H the number of hydroxyls bound to each Ce^{IV}, and the related hydrolysis constants, have been evaluated.

Polynuclear Species.—For simplicity, the following computational approach has been applied only to data from cell (I), but the same results would be obtained from data from cell (II). The simplest way to explain the trend of E' shown in Figure 1 is to make the hypothesis, as have other authors,[8,10—12,15,16] that, in concentrated perchloric acid solutions, only monomers and dimers of Ce^{IV} are present, according to equilibria (3) and (4) in which both x and y can have one or more values.

$$Ce^{4+}(aq) + xH_2O \rightleftharpoons [Ce(OH)_x]^{(4-x)+} + xH^+ \quad (3)$$

$$2Ce^{4+}(aq) + yH_2O \rightleftharpoons [Ce_2(OH)_y]^{(8-y)+} + yH^+ \quad (4)$$

The overall stoicheiometric constants can be expressed as in equations (5) and (6) where $m_{1,x}$ and $m_{2,y}$ are the molalities of the monomeric and dimeric hydrolysis products respectively.

$$\beta_{1,x} = m_{1,x}m_H{}^x/m_4 \quad (5)$$

$$\beta_{2,y} = m_{2,y}m_H{}^y/m_4{}^2 \quad (6)$$

At constant m_H, $Q_{1,x}$ and $Q_{2,y}$ are constant too [equations (7) and (8)]. The mass balance (9) of the oxidized species can

$$Q_{1,x} = \beta_{1,x}/m_H{}^x = m_{1,x}/m_4 \quad (7)$$

$$Q_{2,y} = \beta_{2,y}/m_H{}^y = m_{2,y}/m_4{}^2 \quad (8)$$

$$m_{ox} = m_4(1 + \Sigma Q_{1,x}) + 2m_4{}^2\Sigma Q_{2,y} \quad (9)$$

be rearranged to give equation (10) where three new terms

$$m_{ox} = m_M + 2Km_M{}^2 \quad (10)$$

(11a)—(11c), constant at constant m_H, have been used and m_M

$$M = 1 + \Sigma Q_{1,x} \quad (11a)$$

$$D = \Sigma Q_{2,y} \quad (11b)$$

$$K = D/M^2 \quad (11c)$$

stands for the summation (12) over the monomeric cerium(IV)

$$m_M = m_4M \quad (12)$$

species; it differs from m_4 by a term M which is a function of m_H only.

If the starting hypothesis expressed by equilibria (3) and (4) is correct, the term E^f in equation (13) is a constant at constant m_H

$$E^f = E_I + E^0{}_G + 53.2 \log(m_3m_H/m_M) \quad (13)$$

and can be defined as the formal redox potential of the couple Ce^{IV}–Ce^{III} at −5 °C and at the acidic concentration under investigation, if no polymers are formed.

The term m_M can be calculated by solving equation (10). For different values of K, from equations (1), (13), and (14), equation

$$m_M = [(1 + 8Km_{ox})^{\frac{1}{2}} - 1]/4K \quad (14)$$

$$Y = E' - E^f = 53.2 \log[(1 + 8Km_{ox})^{\frac{1}{2}} - 1]/4Km_{ox} \quad (15)$$

(15) gives a set of normalized curves Y against m_{ox} and can be drawn and superimposed on the experimental curves of E' against m_{ox}, as shown in Figure 3, where only data for run 5 are reported, to avoid confusion. The limiting value of these curves for m_{ox} tending to 0 is $Y = 0$ for each value of K. The curve Y_K which best fits the experimental points gives the best value of K and $E' = E^f$ for $Y = 0$. A value of E^f for each experimental point can be calculated by inserting the best value of K into equation (15). For each run, these E^f values are in good agreement with the one obtained graphically.

Otherwise, a different graphical method can be used: from equations (1) and (14), one obtains (16) and (17) which, inserted

$$m_{ox} = m_3m_H\,10^{(E_I - E' + E^0{}_G)/53.2} \quad (16)$$

$$m_M = m_3m_H\,10^{(E_I - E^f + E^0{}_G)/53.2} \quad (17)$$

in equation (10), after rearranging, gives (18).

$$10^{-E'/53.2} = 10^{-E^f/53.2} + 2K\,10^{-2E^f/53.2}m_{ox}\,10^{E'/53.2} \quad (18)$$

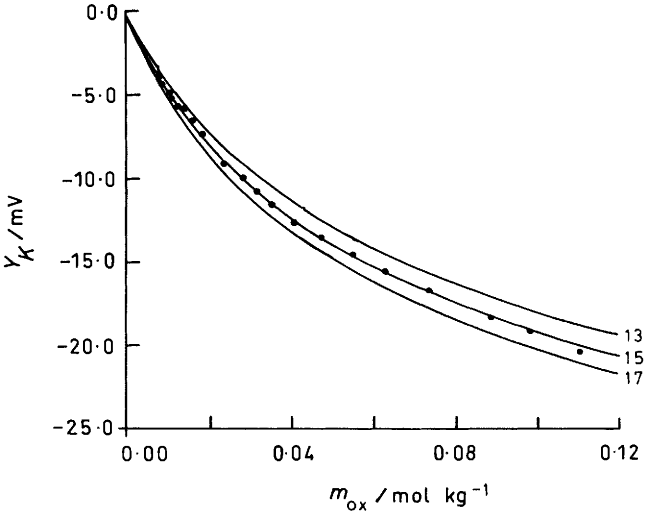

Figure 3. Normalized curves of Y_K against m_{ox}, calculated by means of equation (15), superimposed on data from run 5. The best fit is the curve for which $K = 15$ kg mol^{-1}, while $Y_{15} = 0$ for $E^f = 1\,756$ mV

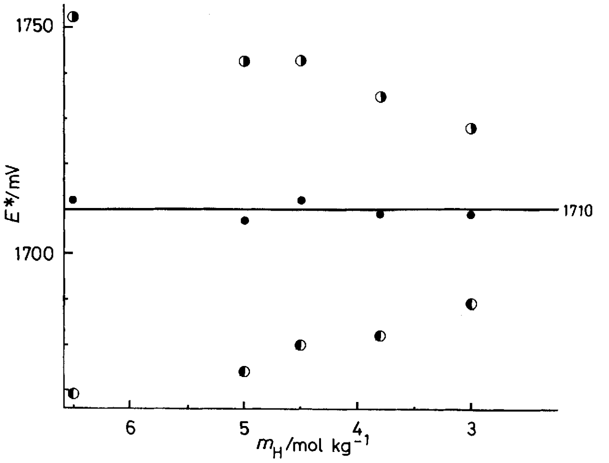

Figure 4. Plot of E^*, calculated by means of equation (21), against m_H, at various values of x: 0 (◑), 1 (●), or 2 (◐). The solid line gives the best fit for $x = 1$

From a least-squares treatment of the data from each run, the pairs K,E^f were obtained. The experimental data were always well fitted by a straight line, with correlation coefficients always greater than 0.99. Good agreement was found between both the K and E^f values obtained for each run and from the two different methods. For the two parameters, in 6.5 mol kg^{-1} $HClO_4$, the mean of the means yields $K = 15 \pm 2$ kg mol^{-1} and $E^f = 1\,755 \pm 2$ mV against the molal hydrogen electrode at -5 °C.

The above procedures were applied also to runs 10—14, at different constant values of m_H; Table 2 summarizes data at all of the acidity levels.

Table 2. Values of K and E^f at -5 °C and various acidity levels; E^f is reported against the molal hydrogen electrode

m_H	K/kg mol^{-1}	E^f/mv
6.5	15 ± 2	1 755 ± 2
5.0	13 ± 2	1 743 ± 1
4.5	15 ± 1	1 743 ± 2
3.8	15 ± 1	1 735 ± 1
3.0	17 ± 2	1 728 ± 3

Mononuclear Species.—Data in Table 2, confirming the already noted decrease in E^f with m_H, give important additional information: K remains constant, within the experimental errors, although from equations (7), (8), and (11a)—(11c) it should be a function of m_H. The simplest way to explain this is to assume that the following three hypotheses are valid simultaneously. (*i*) One species alone largely predominates between the monomeric ones (including the unhydrolyzed solvated ion); (*ii*) One species alone largely predominates between the dimeric ones; (*iii*) The number y of OH^- groups bound to the dimeric species is exactly twice the number x of OH^- groups bound to the monomeric one. If this happens, equations (11a)—(11c) become (19a)—(19c), justifying the constancy of K at various m_H values.

$$M = Q_{1,x} = \beta_{1,x}/m_H{}^x \tag{19a}$$

$$D = Q_{2,y} = \beta_{2,y}/m_H{}^y \tag{19b}$$

$$K = D/M^2 = \beta_{2,y}/m_H{}^y \cdot m_H{}^{2x}/\beta_{1,x}{}^2 = \beta_{2,y}/\beta_{1,x}{}^2 \tag{19c}$$

More information can be gained from the variation of E^f with m_H. If the e.m.f. of cell (I) is written as in equation (20) in accordance with the above hypothesis, from equations (12), (13), and (19a), equation (21) is obtained where the left-hand side has a constant value, while the right is experimentally known (see Table 2).

$$E_I = E^{0\prime} + 53.2\log(m_4/m_3m_H) - E^0{}_G \tag{20}$$

$$E^{0\prime} - 53.2\log\beta_{1,x} = E^f - x\,53.2\log m_H \tag{21}$$

In Figure 4 the sum $E^* = E^f - x\,53.2\log m_H$ is plotted against m_H for various x values; it is evident that E^* is constant only for $x = 1$. As a further check, in runs 15 and 16, to a solution S a cerium(III) solution in $HClO_4$ containing some $La(ClO_4)_3$ was added in order to lower both the concentrations of Ce^{IV} and H^+ at constant concentrations of Ce^{III} and ClO_4^-.

Lanthanum(III) perchlorate was chosen because its activity coefficient is reported to show a variation with concentration very similar to that shown by $LiClO_4$.[22] The activity coefficient of $LiClO_4$ varies with concentration very similarly to that of $HClO_4$.[23] So, owing to the very low solubility of $LiClO_4$, $La(ClO_4)_3$ is preferred, in order to minimize any undesired effect due to activity coefficient variations. Some experiments were carried out in order to test the effects of the substitution of H^+ with Na^+ or La^{III} on the e.m.f. of cells like the ones used in the present work. Over the whole range of perchloric acid concentration studied, it was found that these effects were of a few millivolts only, indeed much lower than the e.m.f. variations discussed here as due to hydrolysis equilibria. These small corrections were introduced in the data of Table 2 and Figures 4 and 5.

For runs 15 and 16, values of E^* were computed by combining equations (13) and (21) for data from cell (I), and equations (2) and (21) for data from cell (II). These E^* values are independent of m_H, and in good agreement with those of Figure 4. The average value of E^* was $1\,710 \pm 2$ mV, from 6.5 to 3.0 mol kg^{-1} H^+, against the molal hydrogen electrode at -5 °C.

$$E^* = E_I + E^0{}_G + 53.2\log m_3/m_H \tag{22}$$

This term contains both $E^{0\prime}$ and $\beta_{1,1}$; a separate determination of $E^{0\prime}$ is made difficult, if not impossible, by the need to prepare a solution in which the solvated Ce^{4+} ion is the

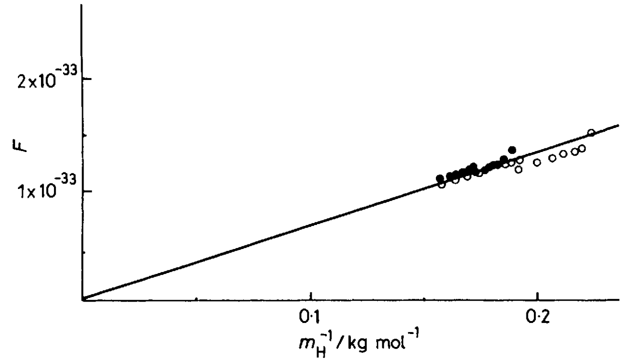

Figure 5. Graphical determination of $E^{0\prime}$ and $\beta_{1,1}$. Data for runs 15 (●) and 16 (○) are reported in the form $F = 10^{-E^f/53.2}$ against $1/m_H$

prevailing species. This requires m_H values higher than the ones used here, thus improving the oxidizing power of cerium(IV) solutions and lowering, even at -5 °C, their stability. Moreover, any rise in m_H above 6.5 mol kg^{-1} would vary the anionic composition of the solution, compared with that of the chosen reference state.

Data from runs 15 and 16 allow a rough evaluation of both $E^{0\prime}$ and $\beta_{1,1}$. Rewriting equation (11a) as (23), from equations (20) and (13) one obtains (24) and finally (25).

$$M = 1 + \beta_{1,1}/m_H \qquad (23)$$

$$E^{0\prime} = E^f + 53.2 \log (1 + \beta_{1,1}/m_H) \qquad (24)$$

$$10^{-E^f/53.2} = 10^{-E^{0\prime}/53.2} + 10^{-E^{0\prime}/53.2}\,\beta_{1,1}/m_H \qquad (25)$$

A plot of $10^{-E^f/53.2}$ against $1/m_H$ is shown in Figure 5. The graphical treatment, applied to data from runs 15 and 16, gives $E^{0\prime} = 1.84 \pm 0.02$ V and $\log \beta_{1,1} = 2.50 \pm 0.06$.

Conclusions

The results of this work show that, under the present experimental conditions, two main hydrolysis equilibria (26) and (27)

$$\mathrm{Ce^{4+}(aq) + H_2O \rightleftharpoons [Ce(OH)]^{3+} + H^+} \qquad (26)$$

$$\mathrm{2Ce^{4+}(aq) + 2H_2O \rightleftharpoons [Ce_2(OH)_2]^{6+} + 2H^+} \qquad (27)$$

take place in oxidized cerium solutions, in the presence of weak complexing anions. The related β values are large enough to limit the range of predominance of the mononuclear species to very dilute solutions (less than 0.002 mol kg^{-1}). Moreover, even in such acidic solutions, the solvated Ce^{4+} ion is only a minor species. This result is not surprising: Sherrill *et al.*[7] first assumed that in 2.4 mol dm^{-3} $HClO_4$ at 25 °C the prevailing cerium(IV) species was $[Ce(OH)]^{3+}$; this was later confirmed by Baker *et al.*,[9] while Kraus *et al.*[24] concluded, from a spectrophotometric study, that Ce^{IV} is still extensively hydrolyzed also in 10 mol dm^{-3} $HClO_4$.

As a further check, recently Lindgren,[25] from 1 mol dm^{-3} H_2SO_4 solutions, precipitated a solid of formula $Ce_2(OH)_2(H_2O)_4(SO_4)_3$, containing discrete $[Ce_2(OH)_2(H_2O)_4]^{6+}$ units, where two Ce^{IV} are connected by two OH^- bridges; these units are linked to each other by $SO_4{}^{2-}$ ions in a three-dimensional network.

Finally we repeated some of the experiments at 25 °C. Despite the experimental difficulties in preparing and maintaining such 'hot' solutions, in which the instability of the oxidized species is greatly enhanced, the data were fitted by the same simple model of dimers.

Experimental

All the solutions were prepared in twice distilled water; their concentrations were determined as mol kg^{-1} of solution, and then converted into mol kg^{-1} solvent.

Materials and Analysis.—Perchloric acid of high purity was prepared and analyzed as described.[19]

Cerium(III) perchlorate solutions were prepared starting from $CeCl_3 \cdot 7H_2O$. The commercial product, crystallized from water, was precipitated as cerium(III) oxalate;[26a] it was then converted at 900 °C into a red-orange powder of CeO_2, which, on cooling, became pale yellow. Although almost insoluble in acids,[27] it was however dissolved in concentrated $HClO_4$, using HBr as a reducing agent,[15] according to equation (28). The Br_2 formed

$$\mathrm{CeO_2 + Br^- + 4H^+ \longrightarrow \tfrac{1}{2}Br_2 + Ce^{3+} + 2H_2O} \qquad (28)$$

and the excess of HBr were driven off, by boiling under N_2, leaving a colourless solution, from which, on cooling, colourless needle-like crystals of $Ce(ClO_4)_3$ separated; these were filtered off and dissolved in *ca.* 6.5 mol kg^{-1} $HClO_4$. From this stock solution, diluted ones of the required concentrations of Ce^{III}, H^+ and Na^+ or La^{III} were prepared. Their cerium(III) concentrations were determined according to Willard and Young,[28] while the acid content was titrated with standard NaOH, using methyl red as indicator; if present, the concentrations of Na^+ or La^{III} were calculated by dilution of the stocks; the perchlorate content, always about 6.5 mol kg^{-1}, was obtained as a sum of the cation concentrations.

Cerium(IV) perchlorate solutions were prepared by electrolytic oxidation at -5 °C, at a platinum anode, of cerium(III) solutions; a sintered glass disk separated the platinum cathode from the bulk solution. The electrolysis was generally performed overnight with a current density between 5 and 15 mA cm^{-2}, giving a yield of about 70%. The cerium(IV) concentration of these solutions was determined by withdrawing a sample with a precooled pipette and pouring it into an excess of a cold iron(II) solution. Reduction of Ce^{IV} soon took place, as denoted by the change in colour from yellow to colourless. The excess of iron(II) was determined with a standard cerium(IV) solution, using ferroin as indicator, in 9 mol dm^{-3} H_2SO_4. These determinations were performed on two or three different samples always at the beginning and at the end of each run, and often in the middle of it, in order to take into account the decomposition of Ce^{IV} which occurs during the run, which generally lasted 3—4 h. This decomposition never exceeded 10% of the initial value and was lower, the lower the hydrogen-ion concentration of the solution. The concentration of Ce^{III} in the oxidized solutions was obtained as the difference from the total cerium content.

A sodium perchlorate stock solution was prepared from $HClO_4$ and a slight excess of crystallized $NaHCO_3$; the resulting solution was stored for about a week (to allow heavy metal hydroxides to settle), filtered, neutralized with $HClO_4$, and the CO_2 driven off. After concentration under N_2 bubbling, to prevent local heating, the solid $NaClO_4$ separated; it was filtered off, dried, and dissolved in water. Its concentration was determined by drying at 110 °C a weighed sample, then weighing the white residue.

Lanthanum perchlorate stock solution was prepared from La_2O_3 and $HClO_4$; La^{III} was titrated with standard ethylenediaminetetra-acetate at pH 5 using xylenol orange as indicator.[26b]

Equipment.—The equipment and electrodes for e.m.f. measurements have already been described.[19]

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