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Lawrence Radiation Laboratory
Berkeley, California

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OXIDATION POTENTIAL OF THE Ce(III) - Ce(IV) COUPLE
AS A FUNCTION OF TEMPERATURE IN PERCHLORIC ACID
SOLUTIONS— THERMODYNAMIC PROPERTIES

Harry Lee Conley

(M. S. Thesis)

August 22, 1960

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Contents

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Harry Lee Conley

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ABSTRACT

The temperature coefficient of the cerous-ceric oxidation potential has been measured in molal perchloric acid. E_f, dE_f/dT, ΔH, ΔF, ΔS, and ΔC_p have been determined for the reactions,

$$Ce(OH)^{+3} + 1/2\ H_2 = Ce^{+3} + H_2O), \qquad (1)$$

$$Ce^{+4} + 1/2\ H_2 = Ce^{+3} + H^+ , \qquad (2)$$

at $25°C$ and a total cerium concentration of zero. E_f for reaction (1) is in good agreement with the value found by Sherrill, King, and Spooner.[5] ΔH, ΔF, and ΔS values for reaction (1) at ceric perchlorate concentrations of 0.005 and 0.025 molal have also been determined and found to be in good agreement with the calorimetric values of Evans[10] and Fontana.[11] Evans and Fontana worked with ceric perchlorate concentrations of 0.005 and 0.025 molal, respectively, in half molal perchloric acid.

From the temperature coefficient of the equilibrium constant K_D, ΔH, ΔF, and ΔS have been determined for the reaction,
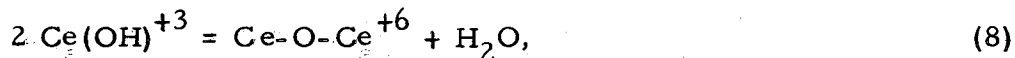
$$2\ Ce(OH)^{+3} = Ce\text{-}O\text{-}Ce^{+6} + H_2O, \qquad (8)$$

at $25°C$. These results have been compared with those of Hardwick and Robertson.[9]

Entropies have been calculated for the ions Ce^{+3}, Ce^{+4}, $Ce(OH)^{+3}$, $Ce(OH)_2^{+2}$ and $Ce-O-Ce^{+6}$. By the use of entropy considerations, the ceric ion has been shown to be hydrolyzed in molal perchloric acid.

On the assumption that

$$[Ce(IV)] = [Ce^{+4}] + [Ce(OH)^{+3}] + 2[Ce-O-Ce^{+6}], \qquad (13)$$

(the brackets indicate molalities) and with Hardwick and Robertson's[9] values for K_D and K_1 at $25°C$— where K_1 is the equilibrium constant for the first hydrolysis of ceric ion—values of $[Ce^{+4}]$ were calculated from the experimentally determined values of $[Ce(IV)]$. $[Ce(IV)]$ is the total concentration of cerium in the plus four oxidation state. It was found that these values of $[Ce^{+4}]$ could be combined with the corresponding cell potentials to calculate constant values of the formal potential of reaction (2) over a wide range of $[Ce(IV)]$ values.

It was found that during any given run the cell potential varied with time in the same manner as that found by Saltonstall[2] and Sherrill, King, and Spooner.[5]

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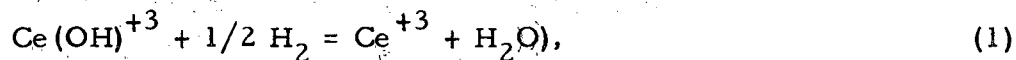
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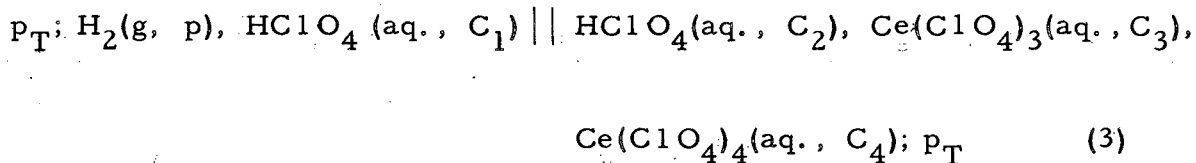Berkeley, California

August 22, 1960

INTRODUCTION

The cerous-ceric potential has been studied in a number of acids by several different investigators. A brief summary[1] of these studies is available. There has been only one report[2] of a temperature coefficient study of this potential. The latter study was made in half formal sulfuric acid.

Perchloric acid was chosen as the medium for this study in order to minimize the complexing of the cerium ions. The problems of hydrolysis and polymerization still exist and the attempted solution of these problems will be discussed in the section on treatment of results.

The cell studied may be written as follows:

$$P_T; H_2(g, p), HClO_4 (aq., C_1) \mid\mid HClO_4(aq., C_2), Ce(ClO_4)_3(aq., C_3),$$

$$Ce(ClO_4)_4(aq., C_4); P_T \qquad (3)$$

The electrode in the hydrogen half-cell was platinized platinum and that in the cerium half-cell bright platinum. The concentrations are in terms of molality. The vertical bars represent a liquid junction which will be discussed along with the cell potential and cell reaction in the section on treatment of results. Potential measurements were made at the following total cerium concentrations ($[Ce_{tot.}] = C_T = C_3 + C_4$), 0.1, 0.01, 0.001 and 0.0002 molal, and at the following temperatures,

8.01, 16.41, 25.00, 35.31, and 45.27^{O}C. At the concentration of 0.0002 molal the potentials were very unsteady and insensitive. The null point was difficult to obtain and the potentiometer reading could be changed by several millivolts without a deflection of the galvanometer. Therefore the results at this concentration were not used in the final analysis of the data. The situation was better at lower temperatures but still unsatisfactory.
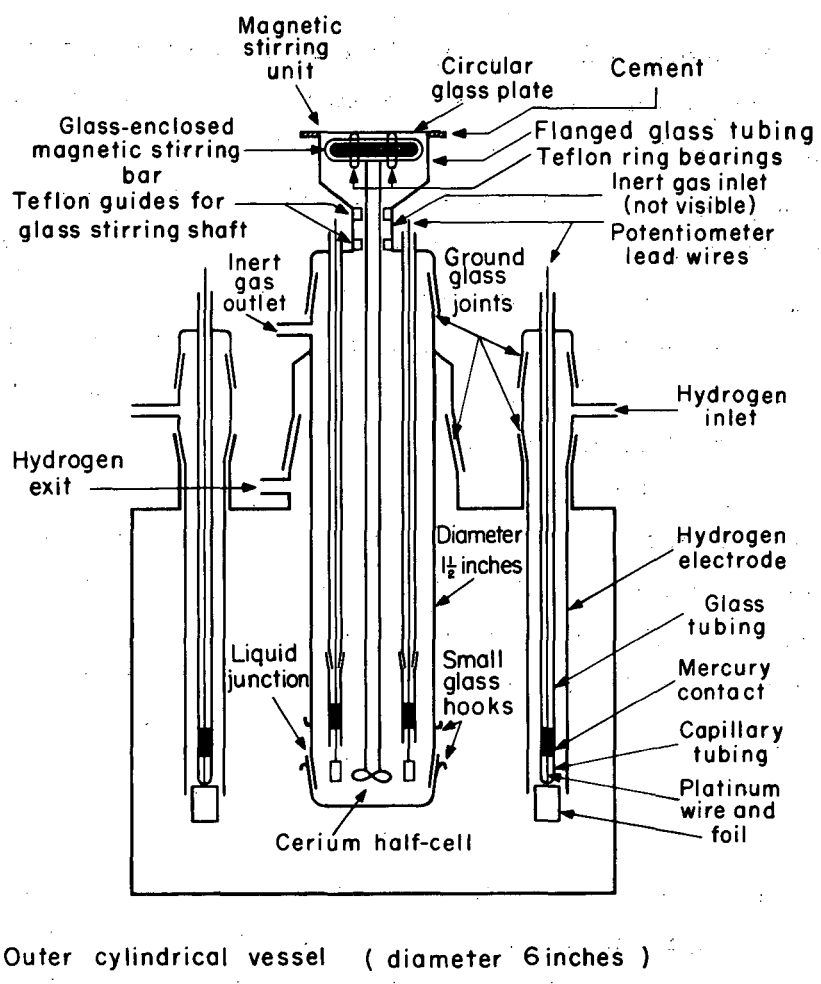
PART I. EXPERIMENTAL

A. Electrical Circuit

A Leeds and Northrup Type K-2 potentiometer and high-sensitivity galvonometer were used in measuring the cell potentials. In addition to the standard cell for calibrating the potentiometer, it was necessary to use another standard cell in series with, and is opposition to the experimental cell because the latter cell potential otherwise was too high to be read on the potentiometer. The potential of this opposing standard cell was added to the measured potential to obtain the potential of the experimental cell. The potentials of the standard cells were measured at $25.0^{\circ}C$ with a precision of ± 0.01 mv by the Laboratory meter shop. The accuracy of the Leeds and Northrup potentiometer was determined by comparison with the standard potentiometer. Over its range the Leeds and Northrup potentiometer was never in error by greater than 0.01 mv and the error was generally 0.002 to 0.006 mv. The standard cells were kept at $25.0 \pm 0.1^{\circ}C$ and all leads were shielded. The experimental potentials were read to ± 0.01 mv.

B. Cell

A sketch of the cell is given in Fig. 1. Pyrex glass was used in constructing the cell. Tank hydrogen was passed over platinized asbestos at $500^{\circ}C$, through a 5-molar sodium hydroxide solution, a bubbler containing acid of the same concentration as that in the cell, a long copper U-tube, and finally into the hydrogen electrode. Care was taken to prevent spray from the sodium hydroxide solution from reaching the acid bubbler. From the large cylindrical vessel the hydrogen passed into another acid bubbler thus assuring a closed system. The rate-of-flow of hydrogen into each electrode was regulated by means of stopcocks greased only at the top and bottom in order to prevent contact between the gas and the grease. The cell, bubblers, and U-tubes were placed in a water bath at a temperature controlled to $\pm 0.01^{\circ}C$.

Fig. 1. Experimental cell.

The temperature was read with a mercury-in-glass thermometer calibrated against a platinum resistance thermometer that had been calibrated against a National Bureau of Standards resistance thermometer.

Platinum wire of 10-mil diameter and foil of 2- mil thickness were used to make the hydrogen and the cerium electrodes. The hydrogen electrodes were about 7×20 mm and the cerium electrodes about 6×10 mm. A short length of capillary tubing was sealed to a piece of regular tubing of the same outside diameter. The 10-mil wire would just slip through the bore of the capillary tubing. The wire was sealed to the capillary tubing by heating the latter to a molten state in a gas-oxygen flame. The foil was spot-welded to the wire. A mercury contact was used between the platinum wire and the copper lead wire from the potentiometer.

The hydrogen electrodes were platinized according to the method of Popoff, Kunz, and Snow.[3] The agreement between any two of these electrodes was 0.01 mv, or better.

Some difficulty was encountered in preparing satisfactory cerium half-cell electrodes. Electrodes cleaned in nitric acid, sodium hydroxide, or both, and then rinsed in distilled water gave potential differences of about 0.1 to 0.3 mv which become larger with time. In order to check the cerium half-cell electrodes, two electrodes were placed in a cerous-ceric perchlorate solution and the small potential difference between the electrodes was read on the potentiometer. The technique given by Clark[4] for welding the wire to the foil was tried next and the electrode was then heated to a white heat and not otherwise cleaned. Electrodes prepared in this manner gave potential differences generally smaller than 0.1 mv. The electrodes were stored in cerium solutions. After the electrodes were stored in a solution of a given cerium concentration they came to equilibrium with a solution of different concentration in 20 to 30 minutes.

During a run the average deviation between the potentials of the
four possible pairs of the two cerium half-cell electrodes and the two
hydrogen electrodes was generally 0.1 mv or less. The average devi-
ation was generally less at higher concentrations of total cerium.

The electrical contact between the cerium half-cell and the
hydrogen half-cell was the thin film of solution in the ground glass
joint. The contact surfaces in the joint were made very smooth by
placing fine carborundum powder and water between them and twisting
the joint. The volume of solution placed in the cerium half-cell was
about 30 ml and this required about 1800 ml of acid in the outer vessel
to bring the two solutions to the same level. The ground-glass cap
was held in place by wetting the joint with some of the acid solution
in the hydrogen half-cell and then pushing it tightly over the inner tube.
By means of the small glass hooks and platinum wire the cap could be
further secured to the inner tube. A ceric perchlorate tracer solution
was placed in the half-cell and an acid solution in the outer vessel in
order to test for diffusion. No activity could be detected in aliquots
of the acid in the outer vessel taken at one-hour intervals for a total
time of eight hours. After ten hours the activity measured in the outer
vessel corresponded to a diffusion of about 0.01% of the activity in the
inner vessel. The resistance of the cell was about 20,000 ohms.

The cerium solution was stirred by placing an inverted Precision
Scientific Company "Mag-Mix" almost against the glass plate of the
cell stirring unit. Teflon rings around the glass-enclosed magnetic
stirring bar and teflon guides around the shaft allowed the unit to
operate smoothly even at nearly the maximum output of the "Mag-Mix".
The hydrogen half-cell was stirred by a similar unit (not shown in Fig. 1)
which entered the outer vessel at the top edge at an angle of about 45 deg.
The stirring shaft of this unit extended below the cerium half-cell. The
stirring units were especially designed for use in a closed system.

Provision was made for passing argon gas either through or over the cerium solution. The argon was made oxygen-free by passing it through uranium filings at $500^{\circ}C$. It was then passed through a system similar to the one for hydrogen except that no sodium hydroxide scrubber was used.

C. Solutions and Analysis

The three major reagents used in preparing the cell solutions were G. F. Smith Chemical Company's 0.5 molar ceric perchlorate in 6 molar perchloric acid, 70% perchloric acid from the same company, and the Laboratory's distilled water redistilled from alkaline permanganate. Spectrographic analysis revealed the following impurities in the three reagents:

1. Ceric perchlorate, 1×10^{-3} ml sample, calcium (0.1 μg), iron (0.01 μg), and magnesium (0.03 μg);
2. Perchloric acid, 50×10^{-3} ml sample, calcium (0.05 μg), and aluminum (0.03 μg);
3. Redistilled water, 100×10^{-3} ml sample, calcium (0.03 μg) and iron (0.01 μg).

The ceric perchlorate sample contained about 50 μg of cerium. The ceric perchlorate and perchloric acid were analyzed quantitatively for ceric ion concentration and hydrogen ion concentration by titration methods to be described and then weighed amounts of each were combined with a weighed amount of redistilled water to give a final concentration of 1.0 molal acid and about 0.1 molal ceric perchlorate. To this solution enough 30% hydrogen peroxide (preservative free) was then added to give roughly equal concentrations of cerous and ceric perchlorate. The solution was then successively diluted with weighed amounts of 1.0 molal perchloric acid, prepared for the hydrogen half-cell, to give solutions having total cerium concentrations of 0.01, 0.001, and 0.0002 molal.

Weight burets were used in all titrations and the analytical methods used were essentially the same as those of Sherrill, King, and Spooner.[5] Two 5-ml aliquots of the cell solution were used for each of the ceric perchlorate and the total cerium determinations. Two 5-ml aliquots were used for each of the cerium solution and hydrogen half-cell acid determinations. The ceric perchlorate concentration was determined by diluting with one molar sulfuric acid and titrating with a standard ferrous solution. Total cerium was determined as ceric perchlorate after all the cerium was oxidized to the ceric state by the ammonium persulfate-silver nitrate method.[6] The ferrous solutions were made with ferrous ammonium sulfate and were 0.5 M in sulfuric acid. The ferrous solutions were kept under argon and were standardized before each use against standard ceric sulfate solutions which were standardized against National Bureau of Standards arsenious oxide by use of osmium tetroxide catalyst. When the cell solution was 0.002 molal in total cerium, a 10-ml sample was used for each of the ceric perchlorate and the total cerium determinations. The cerous perchlorate concentration was calculated as the difference between the total cerium and ceric perchlorate concentrations. A measured volume of ferroin was used as the indicator for the oxidation-reduction titrations. A correction was made for the ferrous sulfate in the indicator. In order to determine the acid concentration of cerium half-cell solutions, it was necessary to remove ceric ion. This was done by the reduction of all cerium to the cerous state with a drop or two of 3% hydrogen peroxide followed by addition of sodium oxalate and then by washing the cerous oxalate precipitate with ten 10 to 15 ml portions of distilled water. The filtrate was then titrated with carbonate-free sodium hydroxide solution standardized against potassium acid phthalate. The acid concentration thus determined was corrected for the acid formed by the oxidation of hydrogen peroxide by ceric perchlorate. The indicator used for the acid-base titrations was phenolphthalein.

D. Procedure

The purpose of this section is to describe a typical run. The bath for the cell and the bath for the standard cells were brought to equilibrium at the desired temperature. The outer vessel, with the hydrogen electrodes in place, and the acid bubblers were filled with the appropriate volumes of perchloric acid solution and the cerium half-cell placed in position without any cerium solution or electrodes. The cerium solution was placed in a small volumetric flask which was placed in the bath along with the outer vessel and bubblers. The stirring unit in the outer vessel was started at this point in order to hasten attainment of thermal equilibrium. After about one hour, the cerium solution was added to the cerium half-cell and the bright platinum electrodes placed in the half-cell. The potentiometer leads were then placed in the mercury contacts, the stirring unit in the cerium half-cell started, and hydrogen gas admitted to the hydrogen electrodes. It was found that it made no difference whether or not argon gas was passed into the cerium half-cell, therefore it was usually not used in the experiment. The four possible potentials were usually read at half-hour intervals for 3 to 4 hours. In general, the potential rose to a maximum value in about an hour and then gradually decreased at the rate of about 0.02 to 0.4 mv/hr depending on the temperature and concentration. The maximum value of the initial rise also varied with temperature but was roughly 1 mv above the potential at the end of the first half hour. This same general change of the potential with time was also obtained by Sherrill, King, and Spooner,[5] who studied the potential at 25°C in perchloric acid. Saltonstall,[2] who studied the potential in 0.5 formal sulfuric acid, also observed the same effect with the rate of decrease being somewhat smaller. Sherrill, King, and Spooner[5] attribue the initial rise to the attainment of equilibrium in the cell and Saltonstall attributes it to the attainment of equilibrium by the hydrogen electrodes. In one of the runs carried out in the research reported here, the potential was not read until one hour after the hydrogen

was admitted to the cell and it was found that thereafter the potential decreased. Sherrill, King, and Spooner[5] have attributed the decrease in potential to the spontaneous reduction of ceric perchlorate by the reaction,

$$4Ce(ClO_4)_4 + 2 H_2O = 4 Ce(ClO_4)_3 + 4 HClO_4 + O_2, \qquad (4)$$
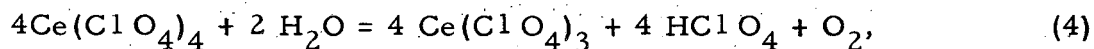
which may be catalyzed by the platinum electrodes. Saltonstall, who measured the ceric sulfate concentration before and after each experiment, found that a decrease occurred and stated that the decrease in potential was due to this decrease in concentration. A similar result was obtained in this work. At a ceric perchlorate concentration of 0.0064 molal at $16^{\circ}C$ there was a 0.75% decrease in the ceric perchlorate molality in the cell solution during the time of the run which was four hours. During this run the same cerium solution in a small volumetric flask in the bath at $16^{\circ}C$ showed a decrease of only 0.20%. This supports the idea that platinum catalyzes the reduction of ceric perchlorate. Using the initial and final concentrations of ceric and cerous ions, it was calculated that a decrease of about 0.6 ml should have occurred during the run. One hour after the run had started the potential reached a maximum and then decreased a total of about 0.1 mv until the end of the run. It is apparent that most of the ceric ion reduction occurred during the first hour of the run. It is also evident that during the first part of the run the factor (or factors) that tends to increase the potential predominates over this ceric ion reduction which tends to reduce the potential.

The time required for a run was three to four hours after the hydrogen was admitted. At the end of each run the temperature and barometric pressure were recorded and the ceric perchlorate concentration determined as soon as possible and then the various other concentrations were determined.

PART II. TREATMENT AND DISCUSSION OF RESULTS

The formal potential, E_f, of the cell (3) may be written as

$$E_f = E_c + \frac{RT}{n\mathcal{F}} \ln \frac{C_3}{C_4} \frac{C_1}{P_{H_2}^{1/2}} + E_j \qquad (5)$$

where E_c is the cell potential, R is the gas constant, T the temperature in degrees Kelvin, n the number of electrons involved in the cell reaction, $\mathcal{F}$ the Faraday constant, and E_j the junction potential. C_3 and C_4 are the molalities of the cerous and ceric perchlorate, respectively, in the cerium half-cell. C_1 is the molality of the perchloric acid in the hydrogen half-cell; P_{H_2} is the hydrogen gas pressure in the hydrogen half-cell. It was determined from the barometric pressure (corrected to $0^\circ C$ and standard gravity) corrected for the vapor pressure of water and the hydrostatic pressure in the cell and the bubblers.

E_j may be written as $E_j = E_J + E'_J$. E_J results from difference $C_2 - C_1$ which was kept small allowing E_J to be neglected. E'_J is due to the presence of cerium in one half of the cell. By extrapolation of E_f to a total cerium concentration of zero, each side of the cell becomes the same and E'_J and E_j are both zero. Actually E_f was plotted against C_4 rather than the total cerium concentration for reasons to be given later but, since $[Ce_{tot.}] \longrightarrow 0$ as $C_4 \longrightarrow 0$, and, since $C_4 = 0$ corresponds to $[Ce_{tot.}] = 0$, E'_J can also be eliminated by this type plot.

It should be pointed out that C_4 is the concentration of cerium in the plus four oxidation state regardless of what actual species are present. More specifically, C_4 is the concentration of ceric perchlorate as determined analytically. It is difficult to say what species make up a ceric perchlorate solution and a considerable amount of work has been done on this problem. A list of papers concerning this work and a brief summary of data derived from this work are available.[7a] It is generally
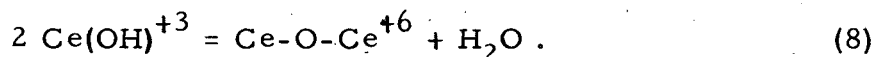
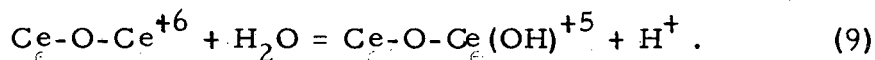assumed that the ceric ion is both hydrolyzed and polymerized. The first hydrolysis may be written as,

$$Ce^{+4} + H_2O = Ce(OH)^{+3} + H^+ , \qquad (6)$$
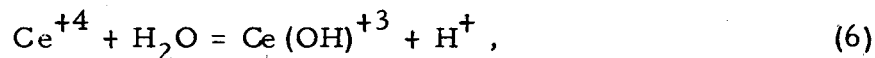
and the second hydrolysis as,

$$Ce(OH)^{+3} + H_2O = Ce(OH)_2^{+2} + H^+ . \qquad (7)$$
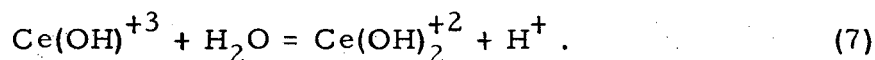
The formation of the dimer is postulated[8] to occur as

$$2 Ce(OH)^{+3} = Ce-O-Ce^{+6} + H_2O . \qquad (8)$$

The dimer may also undergo hydrolysis,

$$Ce-O-Ce^{+6} + H_2O = Ce-O-Ce(OH)^{+5} + H^+ . \qquad (9)$$

The various equilibrium constants for the above reactions may be written as follows (using molalities instead of activities):

$$K_1 = \frac{[Ce(OH)^{+3}][H^+]}{[Ce^{+4}]} , \qquad (6')$$

$$K_2 = \frac{[Ce(OH)_2^{+2}][H^+]}{[Ce(OH)^{+3}]} , \qquad (7')$$

$$K_D = \frac{[Ce-O-Ce^{+6}]}{[Ce(OH)^{+3}]^2} , \qquad (8')$$

$$K_{D1} = \frac{[Ce-O-Ce(OH)^{+5}][H^+]}{[Ce-O-Ce^{+6}]} . \qquad (9')$$

From Equation (8'), we obtain

$$[Ce-O-Ce^{+6}] = K_D [Ce(OH)^{+3}]^2 , \qquad (10)$$

and from Equation (6'), we have

$$[Ce(OH)^{+3}] = \frac{K_1[Ce^{+4}]}{[H^+]} \quad .$$ (11)

By assuming $[H^+] = 1$ and by substituting Eq. (11) into Eq. (10) we have

$$[Ce-O-Ce^{+6}] = K_D K_1^2 [Ce^{+4}]^2 \quad .$$ (12)

Now it is assumed that

$$[Ce(IV)] = [Ce^{+4}] + [Ce(OH)^{+3}] + 2[Ce-O-Ce^{+6}] \quad ,$$ (13)

where $[Ce(IV)] = C_4$, then by use of Equations (10) and (12) it can be shown that,

$$[Ce(IV)] = \left(\frac{[Ce-O-Ce^{+6}]}{K_D K_1^2}\right)^{1/2} + \left(\frac{[Ce-O-Ce^{+6}]}{K_D}\right)^{1/2} + 2[Ce-O-Ce^{+6}]$$

$$= 2[Ce-O-Ce^{+6}] + [Ce-O-Ce^{+6}]^{1/2} \left[\left(\frac{1}{K_D K_1^2}\right)^{1/2} + \left(\frac{1}{K_D}\right)^{1/2}\right] \quad ,$$

(14)

Using k for the bracketed expression containing only equilibrium constants in Eq. (14), the following expression for $[Ce-O-Ce^{+6}]$ can be obtained:

$$[Ce-O-Ce^{+6}] = \left(-\frac{k + \sqrt{k^2 + 8[Ce(IV)]}}{4}\right)^2 \quad .$$ (15)

Thus, for small values of $[Ce(IV)]$, $[Ce-O-Ce^{+6}] = 0$. Using the values of K_1 and K_D at $25^\circ C$ from the work of Hardwick and Robertson,[9] k^2

can be calculated to be 0.086. Using a value of 10^{-3} for $[Ce(IV)]$ it can be calculated that the ratio $[Ce-O-Ce^{+6}]\,/\,[Ce(IV)]$ is about 0.01. If $[Ce(IV)]$ is 10^{-4} this same ratio is about 0.0001. Thus it is seen that as the total concentration of ceric ion approaches small values the concentration of the dimer becomes negligible. Furthermore, since the concentration of larger polymers would be expected to be small compared with the concentration of the dimer, it can be assumed that the polymer concentration in general becomes negligible as the concentration of ceric ion becomes small.

In order to make an approximate correction for the effect of polymerization on the potential, it can be assumed that the major polymeric species present is a dimer and an expression for the formal potential, E_f' , which includes the effect of dimerization, can be written as follows:

$$E'_f = E_c + \left(\frac{RT}{n\mathcal{F}}\right) \ell n \; \frac{C_3}{qC_4} \; \frac{C_1}{p_{H_2}^{1/2}} + E_j \; . \tag{16}$$

This expression for the formal potential is the same as the previous one, given in Equation (5), except that a factor q has been added. This factor is the fraction of total $Ce(IV)$ concentration which is monomeric and thus qC_4 is the concentration of undimerized, or monomeric $Ce(IV)$. Therefore, E'_f is the formal potential corresponding to monomeric ceric ion reduced to cerous ion. Equation (16) may be rewritten as

$$E_{f'} = \left[E_c + \left(\frac{RT}{n\mathcal{F}}\right) \ell n \; \frac{C_3}{C_4} \; \frac{C_1}{p_{H_2}^{1/2}} + E_j \right] + \left(\frac{RT}{n\mathcal{F}}\right) \ell n \; \frac{1}{q}$$

$$= E_f + \left(\frac{RT}{n\mathcal{F}}\right) \ell n \; \frac{1}{q} \; . \tag{17}$$

E_f is given by Equation (5); q may be evaluated as follows:

$$q = \frac{M}{\Sigma} \; , \tag{18}$$

where M stands for the concentration of monomeric $Ce(IV)$ and Σ stands for the concentration of total $Ce(IV)$. The equilibrium between monomeric $Ce(IV)$, M, and dimeric $Ce(IV)$, D, may be expressed as

$$M + M = D , \tag{19}$$

and the equilibrium quotient, K_D, becomes

$$K_D = \frac{D}{M^2} , \tag{20}$$

where M and D stand for the concentrations of the monomeric and dimeric species, respectively. This K_D is equivalent to the one given by Equation (8') if $M = [Ce(OH)^{+3}]$. If it is assumed that the ceric ion exists mainly as $Ce(OH)^{+3}$ in one molal acid, then $M = [Ce(OH)^{+3}]$. Later, this assumption will be shown to be valid. It is evident that,

$$\Sigma = M + 2 D. \tag{21}$$

Equations (18), (20), and (21) may be combined to give

$$q = \frac{M}{\Sigma} = \frac{M}{M + 2 D} = \frac{M}{M + 2 K_D M^2} = \frac{1}{1 + 2 K_D M} , \tag{22}$$

and,

$$\frac{1}{q} = 1 + 2 K_D M . \tag{23}$$

The experimental results cannot be used to calculate q by Equation (22), since what is known experimentally is Σ and not M. Thus M must be evaluated in terms of Σ and this may be done in the following manner. From Equations (20) and (21) it is seen that

$$\Sigma = M + 2 K_D M^2 , \tag{24}$$

and therefore

$$M = \frac{-1 + \sqrt{1 + 8 K_D \Sigma}}{4 K_D} . \tag{25}$$

By the substitution of this expression for M into the right-hand side of the following equation we have,

$$M = \frac{\Sigma}{1 + 2 K_D M} \quad , \text{ (from Equation (22))},$$

and we obtain

$$M = \frac{\Sigma}{1 + \dfrac{(-1 + \sqrt{1 + 8 K_D \Sigma})}{2}} = \frac{2 \Sigma}{1 + \sqrt{1 + 8 K_D \Sigma}} \quad , \quad (26)$$

Further substitution of this expression for M into Equation (23) yields

$$\frac{1}{q} = 1 + \frac{4 K_D \Sigma}{1 + \sqrt{1 + 8 K_D \Sigma}} \quad . \tag{27}$$

$1/q$ in Equation (17) is replaced by this expression, we have,

$$E_f{}_1 = E_f + \left(\frac{RT}{n \mathcal{F}}\right) \ln \left[1 + \frac{4 K_D \Sigma}{1 + \sqrt{1 + 8 K_D \Sigma}} \right] . \tag{28}$$

If $8 K_D \Sigma \ll 1$, then

$$E_f' = E_f + \left(\frac{RT}{n \mathcal{F}}\right) \ln (1 + 2 K_D \Sigma) , \tag{29}$$

and, since $8 K_D \Sigma \ll 1$, then $2 K_D \Sigma \ll 1$ and,

$$E_f' = E_f + \left(\frac{RT}{\mathcal{F}}\right) 2 K_D \Sigma ,$$

or

$$E_f = E_{f_1} - \left(\frac{RT}{n \mathcal{F}}\right) 2 K_D \Sigma . \tag{30}$$

Thus a plot of E_f against Σ (or C_4) should become a straight line with a slope of $- RT \, 2K_D / n \mathcal{F}$ at low values of Σ. At $\Sigma = 0$, $E_f = E_f'$.

By use of the experimental results at each temperature, values of E_f were calculated by means of Equation (5). A plot of E_f against Σ was extrapolated to $\Sigma = 0$ to obtain E_f'. This plot is shown in Fig. 2. A summary of the pertinent data is given in Table I. Data for constructing Fig. 2 (a, b, c) is given in Table II.

The above procedure does not take into account hydrolysis of ceric ion. In order to make some correction for the effect of hydrolysis on the potential, it is assumed that at very low concentrations,

$$C_4 = [Ce^{+4}] + [Ce(OH)^{+3}] . \tag{31}$$

This assumption neglects any second hydrolysis of ceric ion. There is some evidence for this second hydrolysis,[7a] however, the concentration of dihydrolyzed ceric ion, $Ce(OH)_2^{+2}$, should be small compared with the concentration of monohydrolyzed ceric ion, $Ce(OH)^{+3}$. Furthermore, only the first hydrolysis has been studied as a function of temperature. The formal potential, E_f', which involves free ceric ion, Ce^{+4}, may be written,
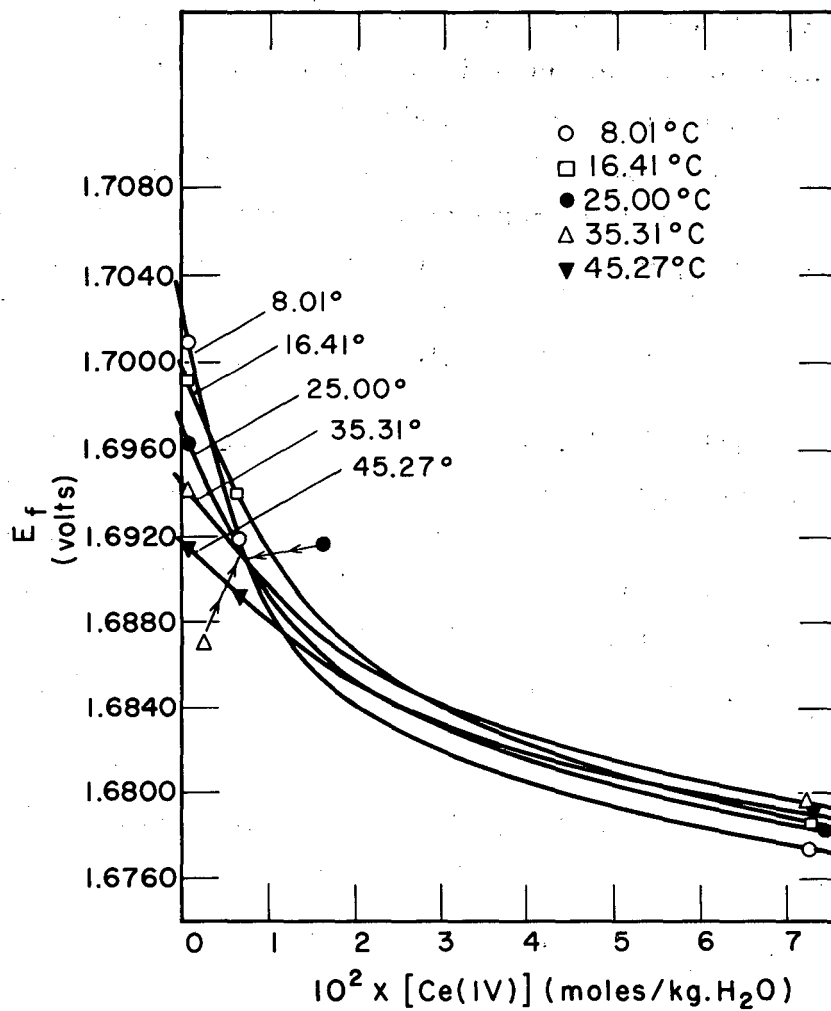
$$E_f' = E_c + \left(\frac{RT}{n\mathcal{F}}\right) \ln \frac{C_3}{[Ce^{+4}]} \frac{C_1}{p_{H_2}^{1/2}} . \tag{32}$$

From Equations (6') and (31) it can be shown that,

$$[Ce^{+4}] = \frac{C_4}{1 + (K_1/C_2)} , \tag{33}$$

where C_2 is the perchloric acid concentration in the cerium half-cell. Substituting Equation (33) in Equation (32), we have

$$E_f' = E_c + \left(\frac{RT}{n\mathcal{F}}\right) \ln \frac{C_3}{C_4} \frac{C_1}{p_{H_2}^{1/2}} + \left(\frac{RT}{n\mathcal{F}}\right) \ln \left(1 + \frac{K_1}{C_2}\right)$$

$$= E_f + \left(\frac{RT}{n\mathcal{F}}\right) \ln \left(1 + \frac{K_1}{C_2}\right) . \tag{34}$$

Fig. 2.   Graph of E_f as a function of [Ce(IV)] .

Table I. Data for calculating $E_f = E_c + (\frac{RT}{n\mathcal{F}}) \ln \frac{C_3}{C_4} \frac{C_1}{p_{H_2}^{1/2}}$

Temp. (°K)	$p_{H_2}^{1/2}$	C_1	C_3	C_4	E_c	E_f	$E_{f'}$ (E_f at C_4=0)
281.17	0.9881	1.0126	0.1430×10^{-3}	0.1320×10^{-3}	1.70	1.70	1.7019
	0.9881	1.0126	0.4871×10^{-3}	0.6811×10^{-3}	1.7081	1.7006	
	0.9878	1.0126	0.3684×10^{-2}	0.6650×10^{-2}	1.7053	1.6916	
	0.9873	1.0126	0.3263×10^{-1}	0.7181×10^{-1}	1.6959	1.6774	
289.57	0.9861	1.0106	0.0828×10^{-3}	0.1178×10^{-3}	1.69	1.69	1.6995
	0.9862	1.0106	0.4923×10^{-3}	0.5992×10^{-3}	1.7032	1.6989	
	0.9862	1.0106	0.4251×10^{-2}	0.6368×10^{-2}	1.7031	1.6937	
	0.9861	1.0106	0.3246×10^{-1}	0.7203×10^{-1}	1.6979	1.6786	
298.16	0.9746	0.9964	0.0930×10^{-3}	0.1132×10^{-3}	1.65	1.68	1.6966
	0.9752	0.9964	0.4336×10^{-3}	0.7606×10^{-3}	1.7099	1.6960	
	0.9760	0.9964	0.3271×10^{-2}	0.7228×10^{-2}	1.7106	1.6907	
	0.9770	0.9964	0.3077×10^{-1}	0.7360×10^{-1}	1.7001	1.6782	
308.47	0.9670	1.0065	0.2471×10^{-3}	0.0670×10^{-3}	1.67	1.70	1.6941
	0.9671	1.0079	0.6326×10^{-3}	0.5576×10^{-3}	1.6892	1.6938	
	0.9669	1.0079	0.3534×10^{-2}	0.7034×10^{-2}	1.7080	1.6908	
	0.9637	1.0110	0.3183×10^{-1}	0.7142×10^{-1}	1.6997	1.6795	
318.43	0.9388	1.0130	0.3728×10^{-3}	0.0677×10^{-3}	1.63	1.68	1.6914
	0.9392	1.0130	0.6447×10^{-3}	0.5180×10^{-3}	1.6816	1.6912	
	0.9387	1.0130	0.3945×10^{-2}	0.6642×10^{-2}	1.7012	1.6890	
	0.9425	1.0110	0.3312×10^{-1}	0.7244×10^{-1}	1.6985	1.6789	

(a) p_{H_2} is the pressure of hydrogen gas in atmos. ; (b) C_1 is the molality of perchloric acid in hydrogen half-cell; (c) C_3 is the molality of cerous perchlorate; (d) C_4 is the molality of ceric perchlorate; (e) E_c is the cell potential in volts; (f) E_f is the formal potential in volts.

Table II.   Data for constructing Fig. 2, (a, b, c)

| Temp. (^{O}K)	K_1	K_D
278.16	0.87	110
288.16	2.1	41.5
298.16	5.2	16.5
308.16	15.0	3.1

(a) The values are taken from Ref. 9.

(b) K_1 is the equilibrium constant for first hydrolysis of ceric ion.

(c) K_D is the equilibrium constant for dimerization.

Since C_2 was kept very nearly constant throughout the experiment, E'_f amounts to E_f plus a constant term at each temperature. In order to include the correction for dimerization it is necessary to use E'_f for E_f. Thus a new E'_f, E''_f, can be defined as follows:
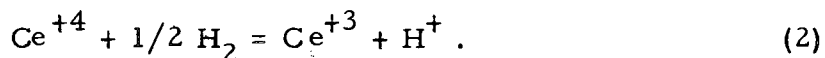
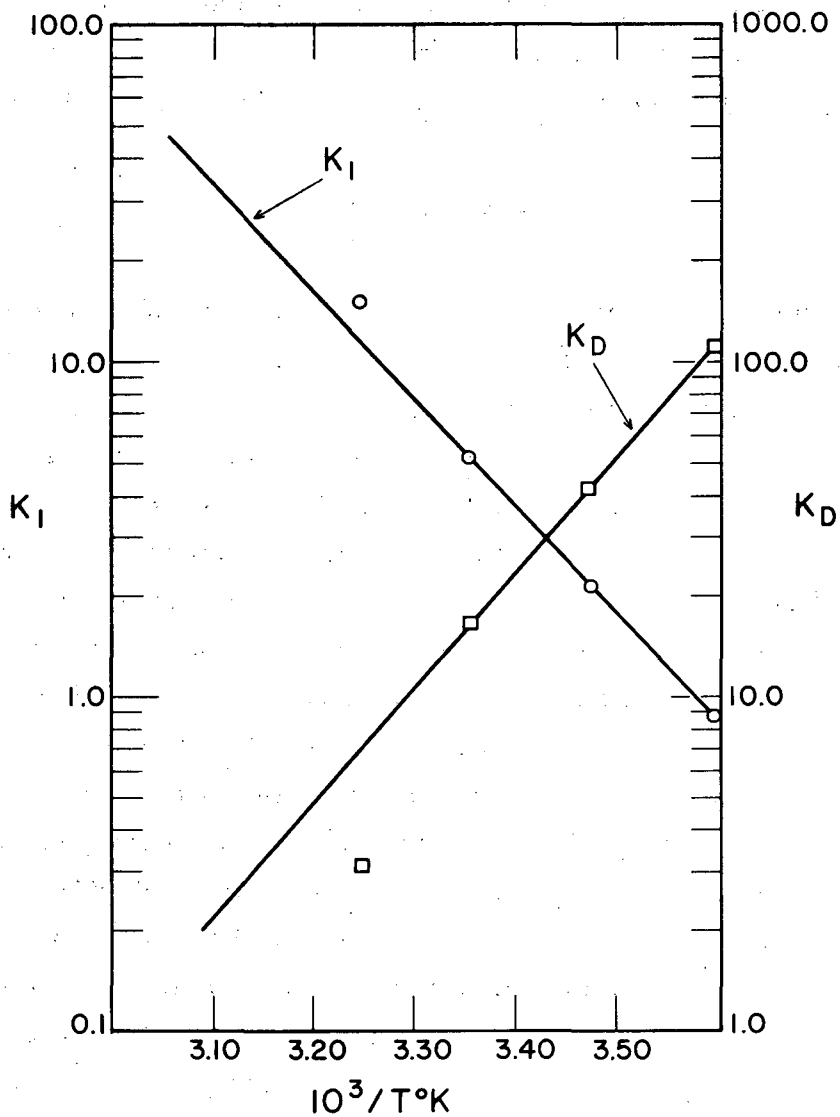$$E''_f = E'_f + (\frac{RT}{n\mathcal{F}}) \ln \left(1 + \frac{K_1}{C_2}\right) . \tag{35}$$

The values of E'_f were determined as described above and the values of C_2 were determined experimentally. The values of C_2 used in the calculations were the averages of the three experimental values at each temperature. The values of K_1 at each temperature were obtained from a plot of log K_1 against $1/T^{\circ}K$. This plot is shown in Fig. 3. The data for constructing this plot were taken from the work of Hardwick and Robertson. [9] Since these workers did not extend their experiments to temperatures above $35^{\circ}C$ and, since the data in the above plot at this temperature do not lie near the straight lines determined by the data at lower temperatures, no evaluation of K_1 and K_D (and thus E''_f) were made at the experimental temperature of $45.27^{\circ}C$. K_D is not used in evaluating E''_f but is used later. At a temperature of $35^{\circ}C$ it was decided to use the values of K_1 and K_D as read from the extrapolation of the straight lines determined by the lower temperature data in the plot (Fig. 3), rather than use the experimental values of Hardwick and Robertson for K_1 and K_D at this temperature. Data used for the calculation of values of E''_f from Equation (35) are given in Table III.

If it is assumed that the principal monomeric species of Ce(IV) is $Ce(OH)^{+3}$, then E'_f corresponds to the reaction,

$$Ce(OH)^{+3} + 1/2\ H_2 = Ce^{+3} + H_2O . \tag{1}$$
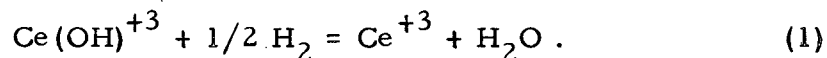
From the above discussion it is evident that E''_f corresponds to the reaction,

$$Ce^{+4} + 1/2\ H_2 = Ce^{+3} + H^+ . \tag{2}$$

Fig. 3. Log K_1 and log K_D as functions of $1/T$. Data from Ref. 9.

MU-22009

Table III. Data for calculating $E''_f = E'_f + (\frac{RT}{n\mathcal{F}}) \ln \left(1 + \frac{K_1}{C_2}\right)$ [a,b,c,d]

Temp. (°K)	K_1	C_2	E'_f	E''_f
281.17	1.1	1.01	1.7019	1.7199
289.57	2.5	1.02	1.6995	1.7308
298.16	5.2	1.02	1.6966	1.7431
308.47	11.8	1.02	1.6941	1.7615

a. The E'_f values are from Table I; K_1 values are interpolated from Fig. 2; C_2 values are experimental.

b. C_2 is the molality of perchloric acid in cerium half-cell.

c. E'_f see Table I.

d. E''_f is the formal potential for the reaction, $Ce^{+4} + 1/2\ H_2 = Ce^{+3} + H^+$

Furthermore, both of these formal potentials correspond to their respective reactions at a total cerium concentration of zero in one molal perchloric acid.

E'_f and E''_f are plotted as functions of temperature in Fig. 4. It is seen that dE/dT is negative and constant for E'_f but is positive and increases with increasing temperature in the case of E''_f. For E'_f, dE/dT is -0.28 mv per degree. At $25°C$ dE/dT is + 1.54 mv per degree for E''_f. The value of dE/dT for E'_f is in remarkable agreement with the value of -0.27 mv per degree for E'_f found by Saltonstall,[2] particularly when one considers that the latter's work was done in sulfuric acid where sulfate ion complexing has been shown to occur for both cerous and ceric ions.[12b] The potentials of Saltonstall also correspond to a total cerium concentration of zero.

From the equation

$$\left(\frac{\partial E/T}{\partial 1/T}\right)_p = -\frac{\Delta H}{n\mathscr{F}}, \tag{36}$$

where n, T, and $\mathscr{F}$ are the same as in Equation (5), the heats of reaction, $\Delta H'$ and $\Delta H''$, of reactions (1) and (2), respectively, can be determined. $(\partial E/T/\partial 1/T)_p$ is the slope of the curve resulting from a plot of E/T against $1/T$. Such a plot is shown for E'_f and E''_f in Fig. 5. From Fig. 5, it is seen that $\Delta H'$ is constant with temperature whereas $\Delta H''$ becomes more negative as the temperature increases. Since,

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p, \tag{37}$$

it is evident that $\Delta C'_p$ is zero. $\Delta C''_p$ was found to be +0.2 kcal/deg/mole at $25°C$ from a plot of $\Delta H''$ against temperature shown in Fig. 6. $\Delta C'_p$ and $\Delta C''_p$ are the changes in heat capacity for cell reactions (1)
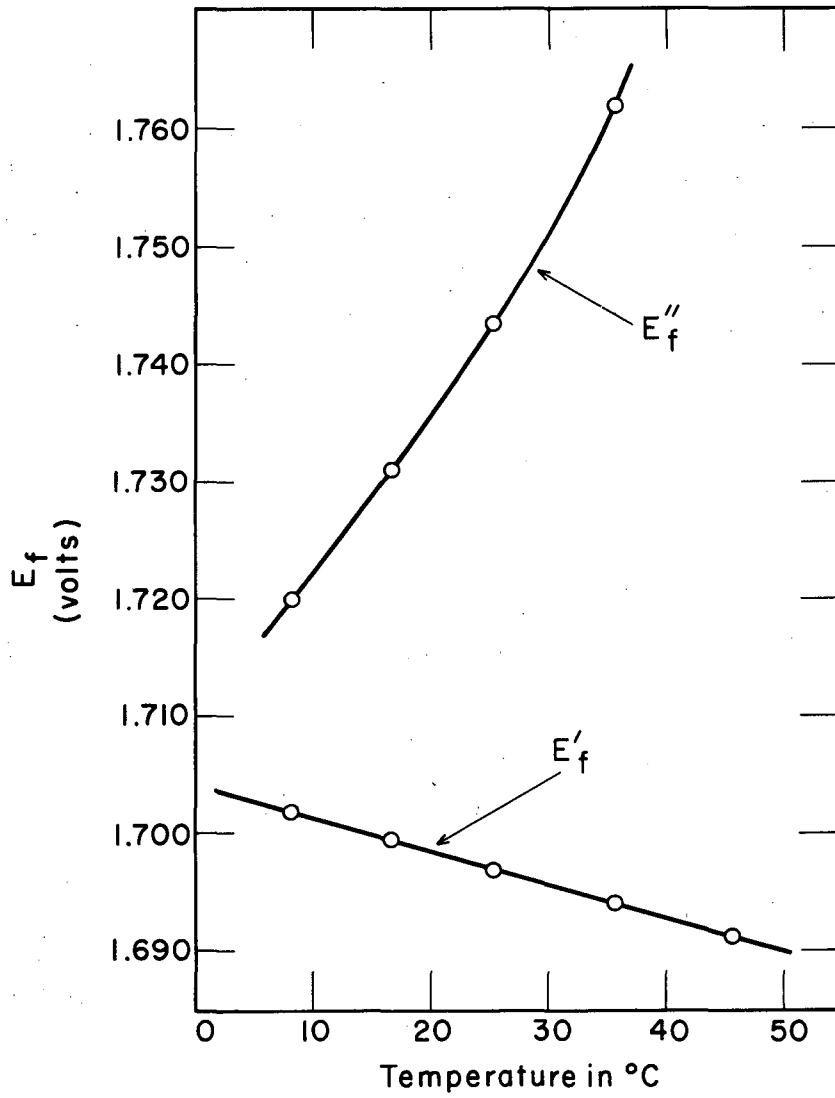
Fig. 4. E'_p and E''_p as a function of temperature.

and (2), respectively. At $25.00 \pm 0.01^{\circ}C$, $\Delta H'$ and $\Delta H''$ were found to be -41.04 ± 0.40 and -28.9 ± 0.8 kcal/mole, respectively. The precisions of the ΔH values were estimated by considering an error of $0.01^{\circ}C$ in T and 0.2 mv in E and applying these errors so as to change the slopes of the curves by a maximum value. The precision for $\Delta H''$ is somewhat less than that for $\Delta H'$ because of the added error in drawing the tangent to the curve of E''_f/T against $1/T$. Using E'_f and E''_f, at $25.00 \pm 0.01^{\circ}C$, $\Delta F'$ and $\Delta F''$ were calculated to be -3912 ± 0.01 and -40.20 ± 0.01 kcal/mole, respectively, by use of the equation

$$\Delta F = -n E\mathcal{F} . \tag{38}$$

By use of the equation

$$\Delta F = \Delta H - T\Delta S, \tag{39}$$

at $25.00 \pm 0.01^{\circ}C$, $\Delta S'$ and $\Delta S''$ are -6.4 ± 0.4 and $+37.8 \pm 0.8$ entropy units, respectively.

Evans[10] and Fontana[11] have measured $\Delta H'$ calorimetrically. Their work was done in 0.5 molar perchloric acid, Evans using 0.005 molal and Fontana 0.025 molal ceric perchlorate. $\Delta H'$ was found to be -39.5 and -37.88 kcal/mole by Evans and Fontana, respectively. It is difficult to correct the calorimetric data to the experimental conditions of the potentiometric data, namely, one molal acid and zero total cerium concentration. However, the potentiometric data may be roughly corrected to the conditions of the calorimetric data. This can be done by neglecting the effect of the difference in acid concentration and selecting values of E_f from Fig. 2 to correspond to ceric perchlorate molalities of 0.005 and 0.025. $\Delta H'$ is then calculated to be -39.7 and -38.0 kcal/mole at 0.005 and 0.025 molal ceric perchlorate, respectively. These values are in remarkably good agreement with those of Evans[10] and Fontana.[11] $\Delta F'$ and $\Delta S'$ values calculated at these same ceric perchlorate
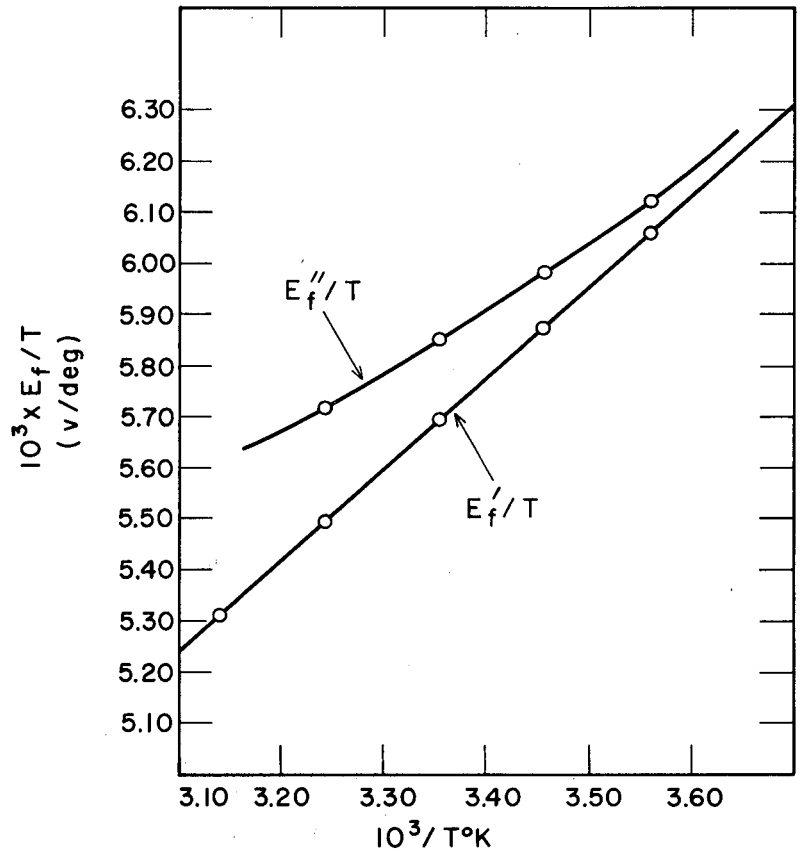
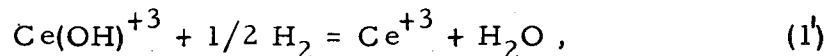Fig. 5. Graph of E'_f/T and E''_f/T versus $1/T$.
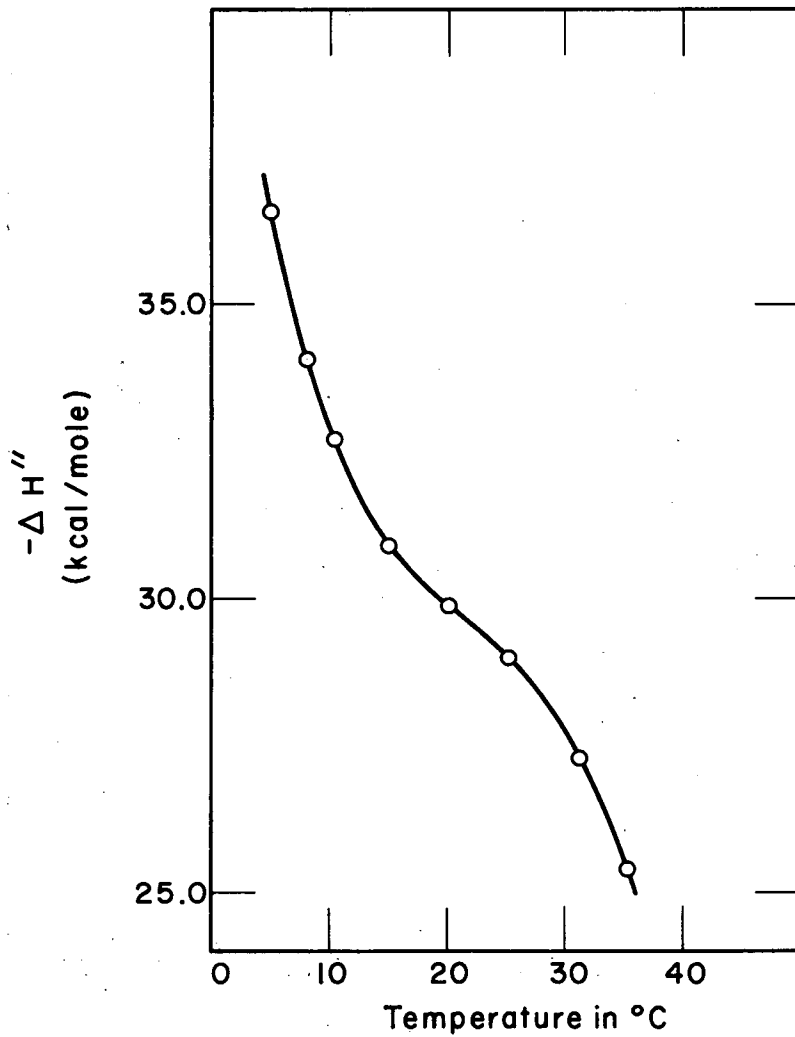
Fig. 6. $\Delta H''$ as a function of temperature.

MU−22012

concentrations were also found to be in good agreement with the same values as found by Evans and Fontana. A summary of the thermodynamic data given above and from Saltonstall's[2] work is given in Table IV.
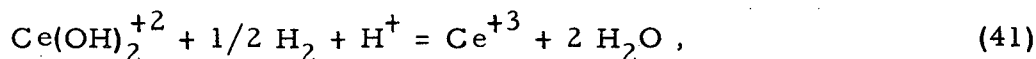
If the reaction corresponding to E'_f is assumed to be

$$Ce(OH)^{+3} + 1/2 \ H_2 = Ce^{+3} + H_2O , \tag{1'}$$

then it can be calculated that,

$$S_{Ce(OH)^{+3}} - S_{Ce^{+3}} = + 7.5 \text{ e.u.} ; \tag{40}$$

or if the reaction is assumed to be

$$Ce(OH)_2^{+2} + 1/2 \ H_2 + H^+ = Ce^{+3} + 2 \ H_2O , \tag{41}$$

it can be calculated that

$$S_{Ce(OH)_2^{+2}} - S_{Ce^{+3}} = + 24.2 \text{ e.u.} \tag{42}$$

Finally, if the reaction is

$$Ce^{+4} + 1/2 \ H_2 = Ce^{+3} + H^+ \tag{2'}$$
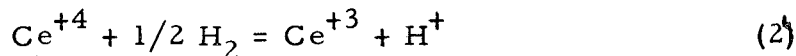
then,

$$S_{Ce^{+4}} - S_{Ce^{+3}} = - 9.2 \text{ e.u.} \tag{43}$$

If the reaction corresponding to E''_f is assumed to be that given by Equation (2) it can be calculated that,

$$S_{Ce^{+4}} - S_{Ce^{+3}} = - 53.4 \text{ e.u.} \tag{44}$$

Equation (44) is evidently more accurate than Equation (43) as $S_M^{+4} - S_M^{+3}$ is about -50 entropy units.[12,13] This result supports the assumption made above that E''_f, and not E'_f, corresponds to reaction (2). This result also supports the conclusion that the ceric ion is

Table IV. Thermodynamic data (at 25°C)

Reference	$\Delta H'$ (kcal/mole)	$\Delta F'$ (kcal/mole)	$\Delta S'$ (entropy units)	$\Delta H''$ (kcal/mole)	$\Delta F''$ (kcal/mole)	$\Delta S''$ (entropy units)	Conditions			
							$HClO_4$ (conc.) molal	$C_e(ClO_4)_4$ (conc.) molal	H_2SO_4 (conc.) formal	$C_e(SO_4)_2$ (conc.) formal
Evans[10]	-39.5^a	-38.5^a	-3.4^a				0.5	0.005		
Fontana[11]	-37.9^a	-38.7^a	2.7^a				0.5	0.025		
This work	-39.7^a	-38.9^a	-2.7^a				1.0	0.005		
This work	-38.0^a	-38.8^a	2.7^a				1.0	0.025		
This work	-41.0^a	-39.1^a	-6.4^a				1.0	0.000		
Saltonstall[2]	-35.6^a	-33.7^a	-6.1^a						0.5	0
This work				-28.9^b	-40.2^b	37.8^b	1.0	0		

a. These values refer to the reaction $C_e(OH)^{+3} + 1/2H_2 = C_e^{+3} + H^+$

b. These values refer to the reaction $C_e^{+4} + 1/2H_2 = C_e^{+3} + H^+$

hydrolyzed in one molal perchloric acid. As the monohydrolyzed ceric ion with a charge of plus three would be expected to have an entropy value near the entropy value of the cerious ion, Equation (40) further supports this conclusion. This has also been pointed out by Evans[10] and Fontana.[11] It should be mentioned that Equation (42) is also reason- able since the dihydrolyzed ceric ion with a charge of plus two would be expected to have an entropy value more positive than that of the cerious ion. It is unlikely that E'_f is the formal potential of both reactions (1') and (41), therefore it is unlikely that both equations are correct. Furthermore, with available data[7c, 12, 13] we can can calculate,

$$S_{U(OH)}^{+3} - S_{U}^{+3} = + 4 \text{ e. u. ,} \tag{45}$$

and

$$S_{Pu(OH)}^{+3} - S_{Pu}^{+3} = - 12 \text{ e. u.} \tag{46}$$

It is seen that this same entropy difference for cerium, +7.5 entropy units, given by Equation (40), is in fairly good agreement with the uranium value but not with the plutonium value. Part of the difficulty outlined above is a result of the limiting assumptions made concerning the various species of ceric ion present. Therefore the above results cannot present any precise information concerning these species but the results do indicate that the ceric ion is hydrolyzed.

In the above calculations and the ones to follow, the entropy of H^+ has been assumed to be zero and the entropies of H_2(gas) and H_2O (liquid) were taken from Latimer.[14a]

Entropies in Table V have been calculated using data from Refs. 7, 12, 13, 14 by estimating the entropy of the cerous ion from that of the gadolinium ion and with corrections for mass, radius and magnetic en- tropy using Latimer's method[14b] for Gd^{+3}, used in estimating the entropy of Ce^{+3} as given by Powell and Latimer.[15] Entropies of various ions other than cerium are given for comparison. The entropy of the cerous ion

Table V. Ionic entropies

Ion	La	Ce	Pr	U	Np	Pu
M^{+3}	-39^a	-38^a	-41^a	-31^a	-37^a	-39^a
M^{+4}		-91		-78	-84	-87
$M(OH)^{+3}$		-30		-27		-51
$M(OH)^{+2}$		-14				
$M-O-M^{+6}$		-99				

(a). Values are in entropy units.

seems to be a little too positive. The entropy of the ceric ion appears to be too negative when compared to the entropies of the ions U^{+3}, Np^{+4}, and Pu^{+4}. That the ceric ion entropy is too negative is also indicated by the fact that it lies somewhat below Latimer's plot[14b] of corrected entropy versus Z/r_e^2 where Z is the numerical value of the charge and r_e is the crystal radius plus 2. The value estimated by Latimer's plot is -78 entropy units. The entropy of the ion, $Pu(OH)^{+3}$, is too negative compared with the entropies of the corresponding cerium and uranium ions.

The value of E'_f at 25°C, 1.697 volts, is in good agreement with 1.700 volts as determined by Sherrill, King, and Spooner.[5] Using the experimental data at 25°C and calculating $[Ce^{+4}]$ from the values of K_1 and K_D (given by Hardwick and Robertson),[9] the following values for E''_f were calculated: 1.743 at $C_4 = 0.76 \times 10^{-3}$, 1.742 at $C_4 = 0.72 \times 10^{-2}$, and 1.742 volts at $C_4 = 0.74 \times 10^{-1}$ molal. It is evident that a constant value of E''_f can be calculated by using the equilibrium data of Hardwick and Robertson. It is also evident that these values of E''_f are in good agreement with the value of 1.7431 as given in Table II-b for E''_f at 25°C and zero total cerium concentration.

As described above, a plot of E_f against Σ (or C_4) should approach a straight line with a slope of $-RT \, 2K_D/n\mathscr{F}$ at small values of $/$. K_D is the equilibrium constant for the formation of the dimer from the monomer. Values of K_D were determined from the slopes of the straight lines at very low C_4 values in Fig. 1. These values of K_D are given in Table VI along with the values of K_D of Hardwick and Robertson.[9] Values of $\log K_D$ are plotted against $1/T°K$ in Fig. 7. The method of averages[16] was used to construct the straight line in Fig. 7. From the equation

$$\ln K_D = \frac{\Delta H_D}{RT} + C , \tag{47}$$

where ΔH_D is the heat of dimerization, C is a constant, and the slope of the straight line in Fig. 7, ΔH_D was determined to be -8.2 kcal/mole.

Table VI. Thermodynamic data for dimerization

Temp. (°C)	Hardwick and Robertson	This work	Hardwick and Robertson	This work	Hardwick and Robertson	This work	Hardwick and Robertson	This work
8.01	82.0	37						
16.41	36.0	20						
25.00	16.5	17	-16	-8.2	-1.7	-1.7	-48.3	-22
35.00	6.7	9.2						
45.00		6.7						

(a). ΔH_D and ΔF_D are the heat and free-energy changes (kcal/mole) for dimerization.

(b). ΔS_D is the entropy change (entropy units) for dimerization.
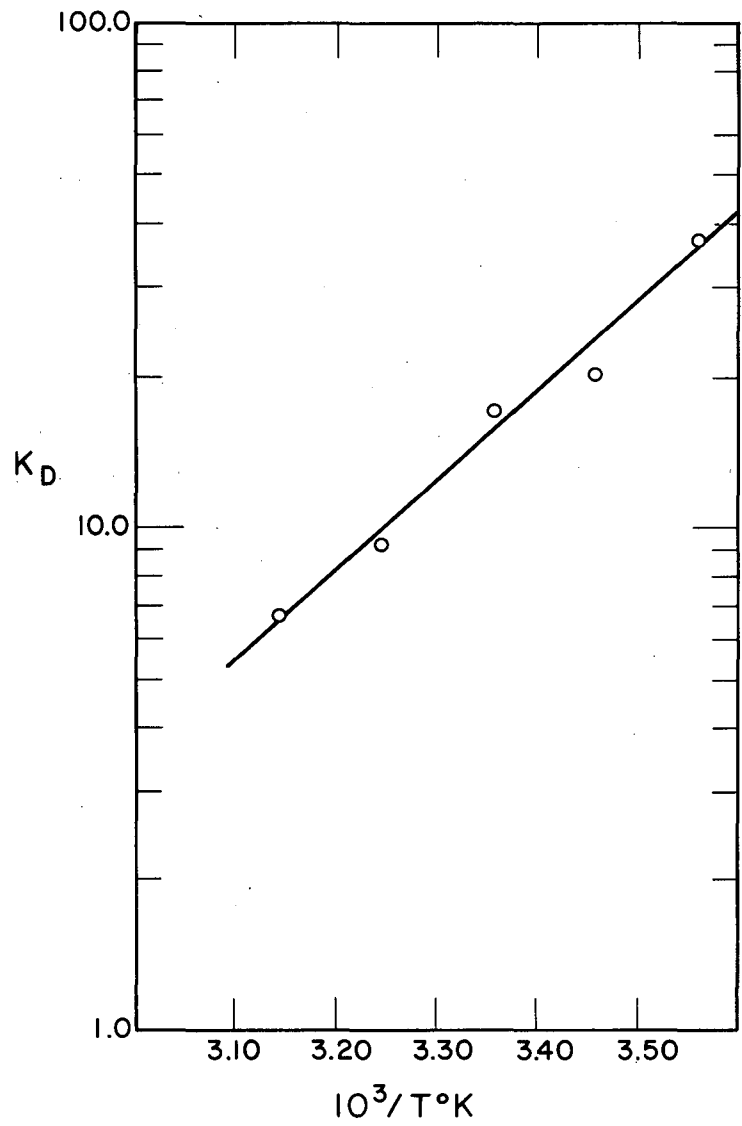
Fig. 7. Log K_D as a function of $1/T$.

MU – 22013

From the equation,

$$\Delta F_D = - RT \ln K_D ,\qquad\qquad (48)$$

ΔF_D was determined to be -1.7 kilocalories per mole at 25°C and from Equation (39) ΔS_D was calculated to be -22 entropy units, also at 25°C. If the monomer and the dimer are assumed to be $Ce(OH)^{+3}$ and $Ce-O-Ce^{+6}$, respectively, it can be calculated that the entropy of the ion $Ce-O-Ce^{+6}$ is -99 entropy units, using the entropy value of $Ce(OH)^{+3}$ as given in Table V. Hardwick and Robertson[9] found $\Delta H_D = -16$ kilocalories, $\Delta F_D = -1.7$ kilocalories and $\Delta S_D = -48.3$ entropy units, all at 25°C. The value of ΔF_D found in this work is seen to be identical with the value found by the latter workers. However, the ΔH_D and ΔS_D values are not in good agreement.
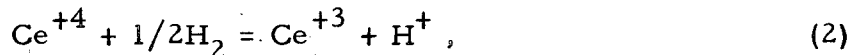
SUMMARY

For the reaction,
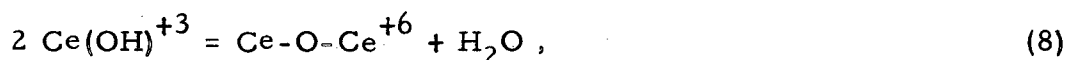
$$Ce(OH)^{+3} + 1/2H_2 = Ce^{+3} + H_2O, \qquad (1)$$
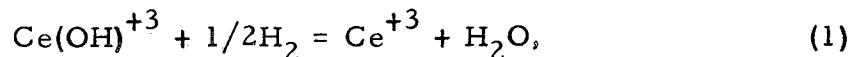
at $25.00 \pm 0.01^{\circ}C$ and at a total cerium concentration of zero, the
following thermodynamic values have been determined: $E_f = 1.6966 \pm 0.0002$
volts, $dE/dT = -0.28$ mv per degree, $\Delta H = -41.04 \pm 0.40$ kilocalories
per mole, $\Delta F = -39.12 \pm 0.01$ kilocalories per mole, $\Delta S = -6.4 \pm 0.4$
entropy units, and $\Delta C_p = 0$. The value of E_f is in good agreement
with the value of 1.7000 v found by Sherrill, King, and Spooner.[5]
dE/dT and ΔH were constant over the temperature range studied.
The value of dE/dT is in good agreement with -0.27 mv per degree
as found by Saltonstall[2] who worked in half formal sulfuric acid. At
a ceric perchlorate concentration of 0.005 molal it was found that
$\Delta H = -39.7$, $\Delta F = -38.9$ and $\Delta S = -2.7$. These values are in good
agreement with those found by Evans[10] at 0.005 molal ceric perchlorate.
Evans' values are: $\Delta H = -39.5$, $\Delta F = -38.5$ and $\Delta S = -3.4$. At a
ceric perchlorate concentration of 0.025 molal it was found that
$\Delta H = -38.0$, $\Delta F = -38.3$, and $\Delta S = +2.7$. These values are in good
agreement with those for $\Delta H = -37.9$, $\Delta F = -38.7$, and $\Delta S = +2.7$
as found by Fontana[11] at 0.025 molal ceric perchlorate. Saltonstall[2]
found $\Delta H = -35.6$, $\Delta F = -33.7$, and $\Delta S = -6.1$ at a total cerium
concentration of zero.

For the reaction,

$$Ce^{+4} + 1/2H_2 = Ce^{+3} + H^+, \qquad (2)$$

the following thermodynamic values have been determined at $25.00 \pm 0.01^{\circ}C$
and a total cerium concentration of zero, $E_f = 1.7431 \pm 0.0002$ volts,
$dE/dT = +1.54$ mv per degree, $\Delta H = -28.9 \pm 0.8$ kcal per mole,
$\Delta F = -40.20 \pm 0.01$ kcal per mole, $\Delta S = +37.8 \pm 0.8$ entropy units, and
$\Delta C_p = +0.2$ kcal per mole per degree. dE/dT increased with increasing
temperature. ΔH becomes more negative as the temperature increases.

For the reaction,

$$2\ Ce(OH)^{+3} = Ce\text{-}O\text{-}Ce^{+6} + H_2O\ , \tag{8}$$

at $25.00 \pm 0.01°C$ and a total cerium concentration of zero, the following thermodynamic values have been determined: $K_D = [Ce\text{-}O\text{-}Ce^{+6}]$/ $[Ce(OH)^{+3}] = 17$, $\Delta H = -8.2$ kcal per mole, $\Delta F = -1.7$ kcal per mole, and $\Delta S = -22$ entropy units. Hardwick and Robertson[9] found $K_D = 16.5$, $\Delta H = -16$, $\Delta F = -1.7$, and $\Delta S = -48.3$ at this temperature.

The entropy of Ce^{+3} has been estimated to be -38 entropy units, by use of Latimer's method[14b] to estimate ionic entropies. Utilizing this value and the values given above for ΔS at zero total cerium concentration, the following ionic entropies (in entropy units) were calculated: $S_{Ce^{+4}} = -91$, $S_{Ce(OH)^{+3}} = -30$, $S_{Ce(OH)_2^{+2}} = -14$, and $S_{Ce\text{-}O\text{-}Ce^{+6}} = -99$. The ionic entropy $S_{Ce^{+4}}$ estimated by Latimer's plot[14b] of corrected entropy versus Z/r_e^2, where Z is the numerical value of the ionic charge and r_e is the crystal radius plus 2, is -78 entropy units. The entropy difference $S_{Ce(OH)^{+3}} - S_{Ce^{+3}} = +8$ supports the conclusion that the ceric ion is hydrolyzed in one molal perchloric acid.

Using the values of Hardwick and Robertson[9] for K_D and K_1 at $25°C$ (K_1 is the equilibrium constant for the first hydrolysis of the ceric ion), it is possible to calculate the concentration of free ceric ion, Ce^{+4}. The values of $[Ce^{+4}]$ thus calculated and the corresponding experimental potentials at $25°C$, made it possible to calculate constant values for the formal potential of reaction (2) given above. The results are: $E_f = -1.743$ at $[Ce(IV)] = 0.76 \times 10^{-3}$, $E_f = 1.742$ at $[Ce(IV)] = 0.72 \times 10^{-2}$ and, $E_f = 1.742$ volts at $[Ce(IV)] = 0.74 \times 10^{-1}$ molal. These calculated values of E_f were found to be in good agreement with the experimentally determined value of 1.7431 at a total cerium concentration of zero.

During any given experimental reported in this work the variation of the cell potential with time was the same as that found by Saltonstall[2] and Sherrill, King, and Spooner.[5] This variation is an initial, relatively fast rise followed by a gradual decrease. It was also found that if ample time was allowed for the hydrogen electrodes to come to equilibrium, the potential gradually decreased thereafter. In one of the runs in this work the decrease in ceric ion concentration in the cell was compared with the same decrease in an identical cerium solution in a volumetric flask at the same temperature of the cell. The decrease in the cell was 0.75% of the original value and that in the flask was only 0.20%. This indicates that platinum catalyzes the reduction of ceric ion. This decrease in ceric ion concentration tends to decrease the potential. Therefore, the initial rise in potential is due to the attainment of equilibrium by the hydrogen electrodes and the following gradual decrease is caused by the slow reduction of ceric ion. These are the same conclusions drawn by Saltonstall[2] and Sherrill, King, and Spooner.[5]

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