THE TEMPERATURE COEFFICIENT OF THE CERIC - CEROUS ELECTRODE

by

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INTRODUCTION

Compounds of ceric cerium have been proven to have rather unusual oxidizing properties. In acid solutions, such reactions proceed quickly to completion and usually in the absence of any secondary changes. Because of these two properties it should be possible to evaluate rather accurately the change in free energy accompanying a reaction wherein the cerium ion undergoes a valence change.

The potential of the ceric-cerous electrode has been measured by Bauer and Glaessner (Bauer and Glaessner, Z.Elektrochem., 9, 534, (1903), and by Kunz (Kunz, J. Am. Chem. Soc., 53, 98, (1931). The measurements of Bauer and Glaessner were made at room temperature. A normal calomel electrode was used for reference, and saturated potassium chloride solution as an intermediate electrolyte. The acidity of the solutions was not carefully controlled. These factors seriously limited the accuracy of the measurements. The measurements of Kunz were made at only one temperature, 25°C. ±0.01°, against a hydrogen electrode in sulfuric acid solution of the same concentration as that in the cerium half-cells. Two concentrations of acid were used;- 0.5 formal and 1.0 formal. A flowing junction was employed to maintain a constant liquid-liquid potential.

Because of the solubilities of ceric and cerous ammonium sulfates, and because of the stability of solutions of these salts, it was decided to determine the potential of the ceric-cerous electrode using these double salts of cerium, and to

extend the temperature range of the measurements, since the temperature coefficient of the electrode has not been previously determined.

The purposes of this investigation were, then, to measure the potential of the ceric-cerous electrode in sulfuric acid solution, utilizing double salts of cerium, - ceric and cerous ammonium sulfates; to determine the effect of the ammonium sulfate upon the potential of the electrode; to determine the temperature coefficient of the electrode, and from these data to calculate the decrease in free energy and decrease in heat content for the reaction $Ce'''' + e \longrightarrow Ce'''$.

The cell measured was;-

$$Pt+H_2, H_2SO_4(0.5f), H_2SO_4(0.5f) + \begin{matrix} 2(NH_4)_2SO_4.Ce(SO_4)_2(c'') \\ (NH_4)_2SO_4.Ce_2(SO_4)_3(c') \end{matrix} , Pt$$

There are three sources of potential in this cell;- the potential of the hydrogen electrode, the potential of the liquid junction, and the potential of the ceric-cerous electrode. By making the concentration of sulfuric acid in both half-cells equal, and by keeping the concentration of the cerium salts very small in comparison with that of the sulfuric acid, the potential of the liquid junction was made negligably small.

APPARATUS AND MATERIALS

The cell was a modification of one used in this laboratory by Larson (Larson, Thesis, M. S. C. (1931) in measuring activities of solutions of hydrobromic acid. Each half-cell, constructed from pyrex tubing, (Fig. 1, a, b.) was closed by a ground glass stopper (h) bearing a platinum elec-

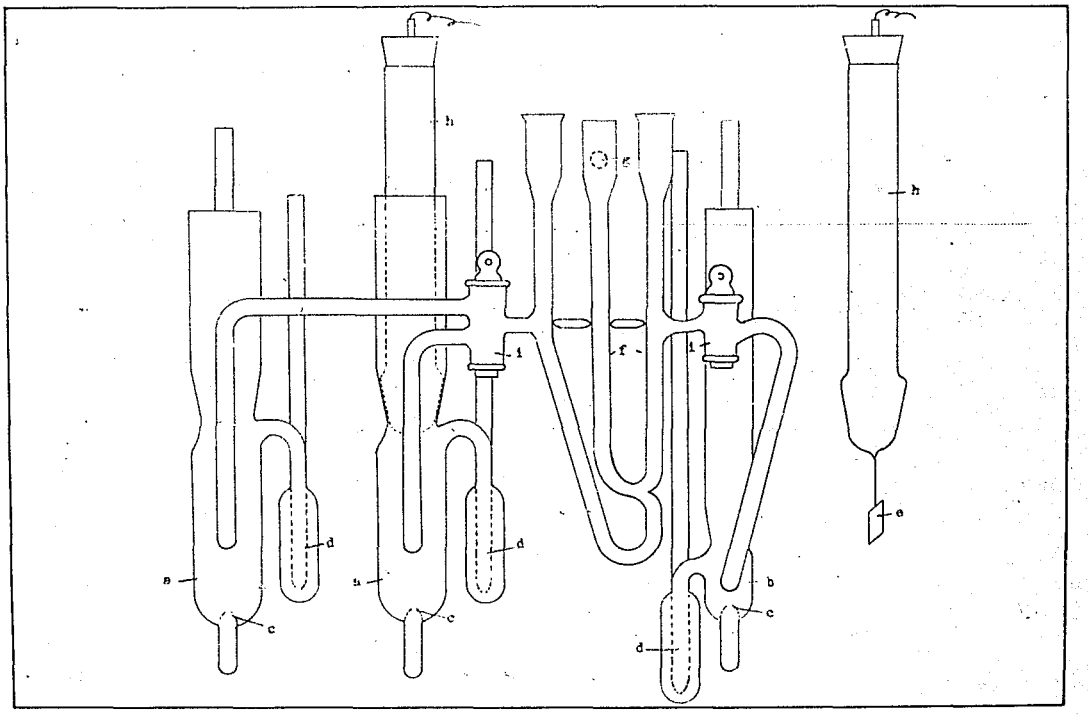

Fig. 1.

trode (e). A jet (c) entered at the bottom of each half-cell to permit saturation of the liquid with gas. Two cerium half-cells were connected to one hydrogen half-cell through a flowing junction (f) (Lamb and Larson, J. Am.Chem. Soc., 42, 229, (1920). Stopcocks (i) were greased lightly on the top and bottom edges only, in order that a good electrical contact might be maintained throughout the cell without stopcock leakage. The gases escaped from the half-cells through the traps (d).

Ceric and cerous ammonium sulfates corresponding to the formulas

$$2(NH_4)_2SO_4.Ce(SO_4)_2.2H_2O$$
$$(NH_4)_2SO_4.Ce_2(SO_4)_3.8H_2O$$

were prepared especially for this work (Prepared by Oscar T. Coffelt, Jackson, Mich.). A good grade of conductivity water was used in making solutions. This was heated and evacuated immediately before use in order to remove any oxygen or other gases which might interfere with the potential, or cause oxidation or reduction in the cerium half-cells.

Temperature was controlled by two thermostatic water baths, one being held constant at $25^{\circ}C. \pm 0.01^{\circ}$, the other being operated alternately at 15° and $35^{\circ}C$.

Hydrogen for the hydrogen electrode was generated by electrolysis of a 7% solution of sodium hydroxide between nickel gauze electrodes. The gas was passed over a heated platinum spiral to remove oxygen, and through a saturator before entering the hydrogen half-cell.

Tank nitrogen was purified by bubbling through an alkaline pyrogallol solution, washing with water, and passing over a heated copper gauze in a combustion furnace. The gas was passed through a saturator before entering the cerium half-cell.

Hydrogen electrodes were prepared according to the directions of Popoff, Kunz and Snow (Popoff, Kunz, and Snow, J.Phys. Chem., 1059, (1928), with the exception that they were not gold plated.

Potential was measured to 0.00001 volts by means of a Queen Standard potentiometer model E-3040, in conjunction with a Leeds and Northrup Type R galvanometer, No. 2500F. The galvanometer, potentiometer, working battery, thermostatic baths, and cells, were shielded and put on an equipotential base, according to the system of W. P. White (W. P. White, J. Am. Chem. Soc., 36, 2011, (1914). The standard of e.m.f. was an Eppley standard cell which was measured and certified by the U. S. Bureau of Standards. This cell was immersed in the 25° bath in a waterproof box.

ANALYTICAL METHODS

Analysis of Cerium Solutions; - The primary standard used in all cerium analysis was Bureau of Standards sodium oxalate, dried in the oven for one hour at 120°C. A standard solution of ceric sulfate, about 0.01 N (weight normality) was standardized against sodium oxalate, using the method of Walden, Hammett, and Chapman (Walden, Hammett, and Chapman, J. Am.

Chem. Soc., 55, 2649, (1933). Weight burettes were used in all analyses. A quantity of ferrous ammonium sulfate solution about 0.01 N. was prepared and stored under hydrogen to prevent oxidation by the air. In spite of this precaution, some oxidation occurred, and the ferrous ammonium sulfate solution was checked daily against the standard ceric sulfate solution.

Some ortho-phenanthroline-ferrous complex indicator was prepared, following the directions of Walden, Hammett, and Chapman (ref. above) and this indicator was used in all cerium analysis.

Two 14 ml. portions were withdrawn from each cerium half-cell for analysis, and weighed in 125 ml. flasks. To each was added 0.6 ml. of concentrated sulfuric acid. One portion from each half-cell was then titrated directly with ferrous ammonium sulfate solution to determine the ceric content (see note I). The other portions were oxidized with ammonium persulfate using silver nitrate as a catalyst (Willard and Young, J. Am. Chem. Soc., 50, 1322 and 1379, (1928), to determine the total cerium content. The cerous content was found by difference.

Note I. All cerium concentrations unless specifically stated otherwise, are expressed in millimoles of cerium per thousand grams of solution.

Analysis of Sulfuric Acid Solutions; - This analysis was accomplished by a direct titration with sodium carbonate, using methyl orange indicator. The titration was carried out nearly to the end point, the solution boiled to expel carbon dioxide, cooled, and the titration completed. The sodium carbonate used in this analysis had been especially prepared from sodium bicarbonate by heating to 300°C.

PREPARATION OF SOLUTIONS

Sulfuric Acid Solutions; - C. P. sulfuric acid was diluted to make a large quantity of approximately 50% acid. This was stored in a large glass stoppered bottle. A portion of this acid was weighed carefully and dissolved in a weighed quantity of evacuated distilled water to make about a liter of approximately 0.5 formal acid. This was carefully analyzed by the method given above. From this determination was calculated the exact weight of the 50% acid to be added to a thousand grams of water to make a solution exactly 0.5 formal. Subsequent analyses of the 0.5 formal acid made up by this method proved that the concentration of the acid did not vary more than one part in a thousand. About 4000g. of 0.5 formal acid was made up at a time.

Ceric - cerous Ammonium Sulfate Solutions; - Small weighed portions of the crystalline ceric and cerous ammonium sulfates were analyzed to determine the ceric and total cerium contents, and the quantities necessary to make solutions of the desired concentrations of ceric and cerous salts were

dissolved directly in the 0.5 formal sulfuric acid. The solutions thus formed were allowed to stand over night in order to allow any possible insoluble particles to settle. The solutions were decanted under nitrogen pressure, and placed in the cerium half-cells. About 2000g. of solution was made up at a time.

EXPERIMENTAL METHODS AND CALCULATIONS

Two units, each composed of two cerium half-cells and one hydrogen electrode were filled at a time.

Filling the Cerium Half-cells; - The half-cell was flushed out for a time with a slow stream of nitrogen. The half-cell, the nitrogen inlet tube and jet, and the corresponding half of the flowing junction were rinsed several times with the solution with which they were to be filled, the rinsing portions being withdrawn by suction. The half-cell and trap were filled to the proper level, and the ground glass stopper, bearing a bright platinum foil electrode was rinsed and put in place. The tube leading from the trap was closed with a rubber plug, and the pressure of the nitrogen forced the liquid up into the flowing junction, at which point the three-way stopcock was closed. The plug was immediately removed from the trap outlet and substituted for the nitrogen tube, thus sealing the half-cell until the others were filled.

Filling The Hydrogen Half-cells; - The hydrogen electrode vessels were filled with 0.5 formal sulfuric acid in the same manner as the cerium half-cells, hydrogen being substituted

for nitrogen.

The saturators were filled with the same solutions, respectively, connected to the gas inlet tubes of the half-cells, and the whose assembly placed in the 15° thermostat. The gas flow was regulated by means of small pinch clamps, the hydrogen so that it passed through the solution at the rate of about one bubble per second, and the nitrogen at the rate of about one bubble every two or three seconds, since its only functions were to exclude air, and to gently agitate the solution in the cerium half-cells. The separatory funnels which supplied the liquids to the flowing junctions were filled and put in place. The waste tubes were connected to the flowing junction outlets, (Fig. 1, g) which completed the preliminary procedure for the measurement of the e.m.f. of the cells.

Each of the solutions was analyzed for the ceric and the cerous content.

Measurements; - With the small hydrogen electrode vessels, consistent measurements could be made an hour after placing the cells in the thermostat. With the larger vessels, several hours elapsed before equilibrium was reached, and in this case it was found to be advisable to slightly increase the rate of flow of hydrogen. The cells were measured at intervals over a twenty-four hour period, in order to definitely establish equilibrium in the half-cells. By means of a bridge, the two hydrogen electrodes could be measured against each other, and this was done occasionally, to make sure that both were in a state of equilibrium.

At the end of approximately twenty-four hours, two portions were withdrawn from one of the cerium half-cells, and analyzed according to the procedure outlined above. The cells were then moved into the 25° thermostat, and measured as before. The flowing junctions were operated only a short period of time before readings were taken. Due to the long period of time over which the cells were measured, a prohibitive quantity of solution would have been necessary, had the junctions been operated continuously. While in operation, solution flowed through the junctions at a rate of about one drop of each liquid per second.

While the cells were being measured at 25°, the temperature of the 15° thermostat was raised by means of auxiliary heaters to 35°, and a thermoregulator and Beckmann thermometer which had been set at 35° were substituted for those set at 15°. The bulbs of the latter were immersed in cold running water until needed in order to keep them set at the proper temperature.

When the cells had been measured over the twenty-four hour period at 25°, portions were withdrawn from another cerium half-cell and analyzed as before. The cells were then placed in the 35° thermostat where the measurements were repeated. Inasmuch as measurements were more difficult at this higher temperature, and the change in ratio within the cerium half-cells was accelerated, it was thought best to reserve two half-cells for analysis at this temperature.

Each time cells were measured, the date, time, reading of the Beckmann thermometer, barometer, and temperature of the barometer were recorded.

Calculation of the Temperature and Pressure Corrections for the Hydrogen Electrode: - For clarity, let us add to the hydrogen electrode of the oxidation-reduction cell, a pressure cell consisting of two hydrogen electrodes, both in 0.5 formal sulfuric acid, one being under a pressure of one atmosphere, and the other, connected to the hydrogen electrode of the oxidation-reduction cell, under the same pressure as the latter, for example, 740 mm. of mercury; the two cells may then be written as follows:

Pt $H_2(1)$, H (0.5f X a), $H_2(740/760)$ Pt Pt $H_2(740/760)$. ..Pt

Assuming that two faradays of positive electricity are passed through the pressure cell to the right, the change in state is:

$$\tfrac{1}{2}H_2(1) - e \longrightarrow H^+(0.5f \text{ X } a)$$

$$H^+(0.5f \text{ X } a) + e \longrightarrow \tfrac{1}{2}H_2(740/760)$$

$$\tfrac{1}{2}H_2(1) \longrightarrow \tfrac{1}{2}H_2(740/760)$$

Substituting in the Nernst equation:

$$E = E_o - \frac{RT}{NF} \ln \frac{(740/760)^{\frac{1}{2}}}{1^{\frac{1}{2}}}$$

or, at 25°C.:

$$E = E_o - \frac{.0591}{2} \log (740/760)$$

$$E = 0.00034 \text{ volts.}$$

This is the temperature and pressure correction for the

hydrogen electrode, to be added to the measured E of the oxidation-reduction cell. Three series of these corrections were calculated, one for each of the three temperatures used in the measurements, at pressures ranging between 690 mm. and 760 mm. of mercury, and these were incorporated in a graph (Fig. 2) from which the corrections could be quickly determined as soon as the partial pressures of the hydrogen in the half-cells were known.

These partial pressures of hydrogen were calculated as suggested by Ellis (Ellis, J. Am. Chem. Soc., 38, 737, (1916). The vapor pressures of 0.5 formal sulfuric acid at the three temperatures were interpolated from data given in the International Critical Tables (I. C. T. Vol. III, p.303).

The vapor pressure of the sulfuric acid was subtracted from the barometric pressure corrected to 0°C. To this was added the mercury equivalent of the column of liquid in the half-cell, measured from the middle of the platinum foil to the surface of the liquid, and the mercury equivalent of the column of sulfuric acid in the trap. Mercury equivalents of sulfuric acid were calculated from density data in the International Critical Tables (I. C. T. Vol.III, p. 156).

Calculation of the Ceric-cerous Electrode Corrections: - The reaction which would occur in the cerium half-cell if one faraday of positive electricity was passed to the right is:

$$Ce''''(c'' \times a'') + e \longrightarrow Ce'''(c' \times a')$$

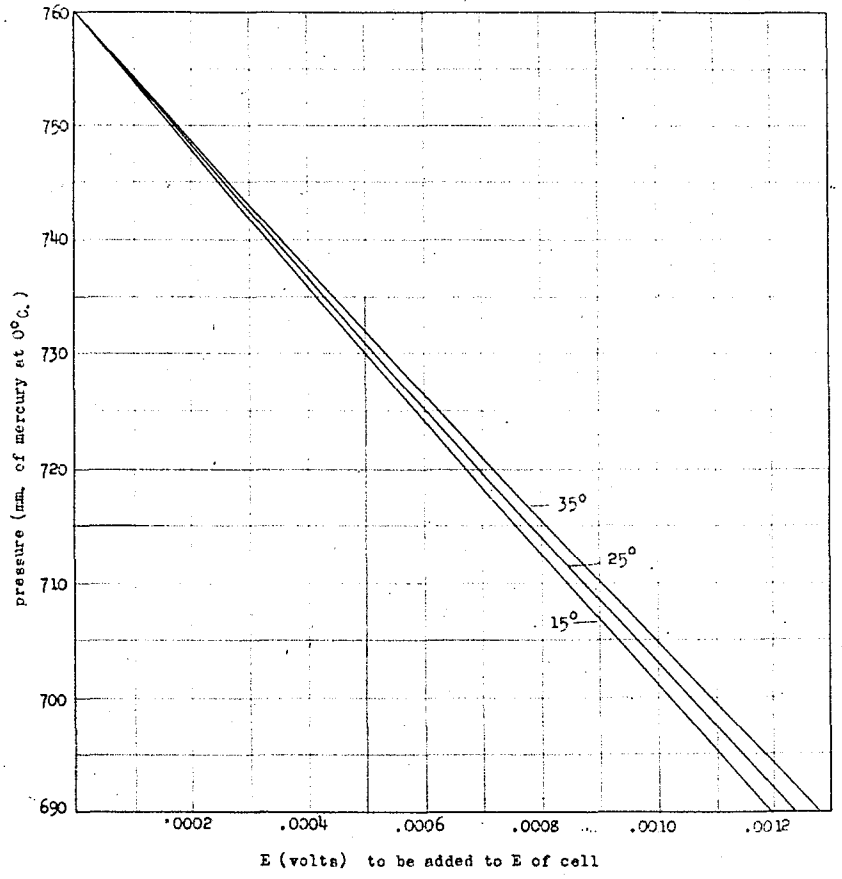

Fig. 2. Pressure and temperature corrections for hydrogen electrode.

Substituting in the Nernst equation:

$$E = E_o - \frac{RT}{NF} \ln \frac{Ce'''(c')}{Ce''''(c'')} \qquad \text{(Note 2)}$$

$$E = E_o - .0591 \log \frac{Ce'''(c')}{Ce''''(c'')} \qquad \text{at } 25^oC.$$

Calculation of $-\Delta F$ and $-\Delta H$: By extrapolating to zero, the e.m.f. values at zero concentration of cerium were found. These three potentials were found to conform to the equation type: $y = a + bx + cx^2$. When $y = 1$ (15^o), 0 (25^o), and -1 (35^o), and x the potentials in increasing order, the constants were ; $a = 1.4626$, $b = 0.00265$, and $c = 0.00035$. From this equation and these constants, intermediate values of x were found, and were plotted with the experimental values (Fig. 3). An empirical equation was fitted to these data:

$$E = 1.86048 - 0.002405T + 0.00000359T^2$$

From this equation values of the temperature coefficient, $\frac{dE}{dT}$ were calculated at 15^o, 25^o, and 35^oC.:

$$\frac{dE}{dT} = -.002405 + 2(.00000359T)$$

From the Gibbs - Helmholtz equation:

$$-\Delta H = NF(E - T\frac{dE}{dT})$$

Note 2. Since the activities of the cerous and ceric ions are not known, it must be assumed that these activities are proportional to the concentrations in the two states of valency. Ce'''(c') and Ce''''(c'') will, therefore, be interpreted as the total concentrations of cerium in the trivalent and quadrivalent forms, respectively, expressed in millimoles of cerium per thousand grams of solution.

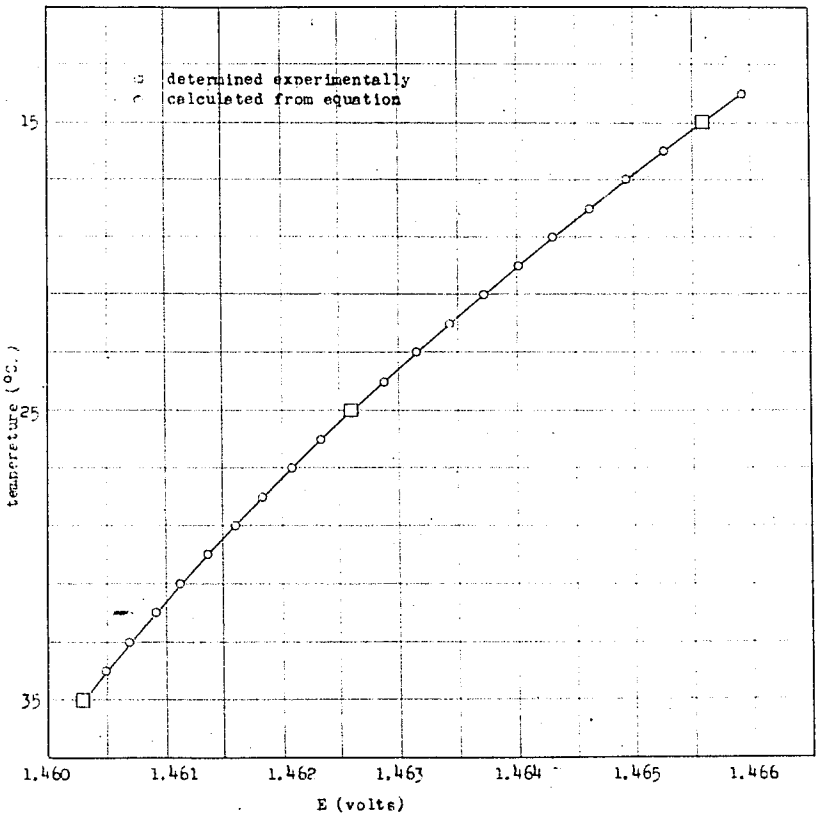

Fig. 3. Temperature - potential curve at zero concentration of cerium.

values of $-\Delta H$ at the three temperatures and zero concentration of cerium in 0.5 formal sulfuric acid were calculated for the reaction $Ce'''' + e \rightarrow Ce'''$. From the free energy equation :

$$-\Delta F = ENF$$

values of $-\Delta F$ were calculated for the same reaction.

EXPERIMENTAL DATA AND DISCUSSION

From the data of the individual cells it may be noticed that in certain cases the potential of the ceric-cerous electrode drifted downward over a period of time. It was determined by analysis that this decrease in potential was the result of a change taking place in the cerium half-cell, which is expressed by the reaction $Ce'''' + e \rightarrow Ce'''$. This change altered the ceric-cerous ratio, and thus caused a lowering of the potential. The magnitude of this potential drift was rarely greater than 0.01 millivolt per hour, and was usually much less. In a few cases the potential of a cell increased during the first few hours; this, however, was due to the fact that the hydrogen electrode had not yet come to equilibrium.

The final potential of each cell was calculated from the value recorded immediately before analysis, and the results of the analysis. The consistency of the results and the fact that the final values could be accurately reproduced after varying periods of time, and with ratios which varied slightly, justified this treatment of results. The

Cell No. 1 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
22	15	740.1	0.00051	1.46041	1.46092	
23		739.7	0.00052	1.46038	1.46090	
25		739.1	0.00052	1.46035	1.46087	
26.5		739.1	0.00052	1.46035	1.46087	
39	25	735.7	0.00080	1.45712	1.45792	
40		735.6	0.00080	1.45710	1.45790	
41		735.0	0.00081	1.45708	1.45789	
68	35	728.8	0.00128	1.45401	1.45529	
71		732.0	0.00123	1.45405	1.45528	
72		733.1	0.00122	1.45405	1.45527	1.4558

Analysis of cerium solution

	before filling cell	after measuring cell
Ce^{+++}	9.862	10.055
Ce^{++++}	9.981	9.855
$Ce^{+++} + Ce^{++++}$	19.843	19.910
Ce^{+++} / Ce^{++++}	1.012	1.020
log		0.00860
correction		0.00052

Cell No. 2. Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
22	15	740.1	0.00051	1.46027	1.46078	
23		739.7	0.00052	1.46026	1.46078	
26.5		739.1	0.00052	1.46040	1.46092	1.4612

Analysis of cerium solution

	before filling cell	after measuring cell
Ce^{+++}	9.862	9.985
Ce^{++++}	9.981	9.853
$Ce^{+++} + Ce^{++++}$	19.843	19.838
Ce^{+++} / Ce^{++++}	1.012	1.013
log		0.00561
correction		0.00032

Cell No. 3 — Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
22	15	740.1	0.00051	1.46027	1.46078	
23		739.7	0.00052	1.46026	1.46078	
26.5		739.1	0.00052	1.46040	1.46092	
39	25	735.7	0.00080	1.45702	1.45782	
40		735.6	0.00080	1.45700	1.45780	
41		735.0	0.00081	1.45698	1.45789	1.4582

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	9.862	9.988
Ce''''	9.981	9.858
Ce''' + Ce''''	19.843	19.846
Ce'''/ Ce''''	1.012	1.013
log correction		0.00561 0.00032

Cell No. 4 — Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	E_{obs}	E corr, to 760 mm.	E_o
1.5	15	739.0	0.00053	1.46073	1.46126	
18.5		733.8	0.00062	1.46076	1.46138	
19.5		734.1	0.00060	1.46076	1.46136	1.4617

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	7.962	7.980
Ce''''	7.879	7.881
Ce''' + Ce''''	15.841	15.861
Ce'''/ Ce''''	1.011	1.013
log correction		0.00561 0.00032

Cell No. 5 Ce electrode No. II

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
14	35	738.0	0.00110	1.45407	1.45517	
14.5		737.6	0.00110	1.45414	1.45524	
15		737.8	0.00110	1.45414	1.45524	
16		737.3	0.00111	1.45414	1.45525	
22.5	15	735.2	0.00056	1.45997	1.46053	
23		735.2	0.00056	1.46005	1.46061	
25.5		735.9	0.00055	1.46038	1.46093	
29		737.9	0.00051	1.46061	1.46102	
39	25	739.8	0.00070	1.45783	1.45853	
40		74010	0.00070	1.45776	1.45846	
41		740.1	0.00070	1.45776	1.45846	
42		740.4	0.00069	1.45780	1.45849	
43.5		740.4	0.00069	1.45781	1.45850	1.4589

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	8.067	8.085
Ce''''	7.969	7.960
$Ce''' + Ce''''$	16.036	16.045
Ce'''/ Ce''''	1.012	1.016
log		0.00689
correction		0.00040

Cell No. 6 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
4	35	734.4	0.00120	1.45514	1.45634	
6		734.1	0.00121	1.45505	1.45626	
22.5		736.4	0.00118	1.45507	1.45625	
23		736.3	0.00118	1.45509	1.45627	
23.5		736.3	0.00118	1.45508	1.45626	
28.5	25	735.1	0.00083	1.45784	1.45867	
30		734.5	0.00084	1.45784	1.45868	
46.5		733.0	0.00086	1.45776	1.45862	
47		732.9	0.00086	1.45777	1.45863	
47.5		732.8	0.00085	1.45777	1.45862	1.4588

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	8.057	8.010
Ce''''	7.965	7.968
$Ce''' + Ce''''$	16.022	15.978
Ce'''/ Ce''''	1.0115	1.005
log		0.00217
correction		0.00013

Cell No. 7 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n, (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
4	35	734.4	0.00120	1.45515	1.45635	
6		734.1	0.00121	1.45508	1.45629	
22.5		736.4	0.00118	1.45511	1.45629	
23		736.3	0.00118	1.45514	1.45632	
23.5		736.3	0.00118	1.45511	1.45629	1.4565

Analysis of Cerium solution

	before filling cell	after measuring cell
Ce'''	8.057	8.030
Ce''''	7.965	7.972
Ce''' + Ce''''	16.022	16.002
Ce'''/ Ce''''	1.0115	1.007
log		0.00303
correction		0.00018

Cell No. 8 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
18.5	25	745.4	0.00060	1.45843	1.45903	
19		744.6	0.00062	1.45842	1.45904	
21		744.1	0.00062	1.45842	1.45904	
23	15	742.6	0.00045	1.46141	1.46186	
42.5		734.1	0.00060	1.46104	1.46164	
66		741.8	0.00046	1.46105	1.46151	
67		741.5	0.00047	1.46106	1.46153	
68		740.5	0.00048	1.46100	1.46148	
69.5	35	740.1	0.00106	1.45555	1.45661	
70.5		739.8	0.00107	1.45532	1.45637	
71.5		739.4	0.00107	1.45511	1.45618	
88		742.1	0.00102	1.45480	1.45582	
89		742.1	0.00102	1.45479	1.45581	1.4572

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	6.037	6.228
Ce''''	5.985	5.914
Ce''' + Ce''''	12.022	12.141
Ce'''/ Ce''''	1.009	1.053
log		0.02243
correction		0.00137

Cell No. 9 Ce electrode No. II

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
18.5	25	745.4	0.00060	1.45855	1.45915	
19		744.6	0.00062	1.45853	1.45915	
21		744.1	0.00062	1.45856	1.45918	
23	15	742.6	0.00045	1.46155	1.46200	
42.5		734.1	0.00060	1.46125	1.46185	
66		741.8	0.00046	1.46139	1.46185	
67		741.5	0.00047	1.46140	1.46187	
68		740.5	0.00048	1.46137	1.46185	
69.5	35	740.1	0.00106	1.45588	1.45694	
70.5		739.8	0.00107	1.45581	1.45688	
88		742.1	0.00102	1.45544	1.45646	
89		742.1	0.00102	1.45549	1.45651	1.4572

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	6.037	6.121
Ce''''	5.985	5.961
$Ce''' + Ce''''$	12.022	12.082
Ce'''/ Ce''''	1.009	1.027
log		0.01157
correction		o.00070

Cell No. 10 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
18.5	25	745.4	0.00060	1.45853	1.45913	
19		744.6	0.00062	1.45851	1.45913	
21		744.1	0.00062	1.45854	1.45916	
23	15	742.6	0.00045	1.46160	1.46205	
24		742.1	0.00046	1.46158	1.46204	
42.5		734.1	0.00060	1.46123	1.46183	
67		741.5	0.00047	1.46100	1.46147	
68		740.5	0.00048	1.46134	1.46182	
69.5	35	740.1	0.00106	1.45419	1.45525	
89		742.1	0.00102	1.45551	1.45653	
93		741.7	0.00103	1.45544	1.45647	1.4572

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	6.037	6.118
Ce''''	5.985	5.959
$Ce''' + Ce''''$	12.022	12.077
Ce'''/ Ce''''	1.009	1.027
log		0.01157
correction		0.00070

Cell No. 12 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm	E_o
18.5	25	745.4	0.00060	1.45841	1.45901	
19		744.6	0.00062	1.45841	1.45903	
21		744.1	0.00062	1.45846	1.45908	
23	15	742.6	0.00045	1.46150	1.46195	
24		742.1	0.00046	1.46154	1.46200	
42.5		734.1	0.00060	1.46117	1.46177	
68		740.5	0.00048	1.46130	1.46178	
69.5	35	740.1	0.00106	1.45402	1.45508	
89		742.1	0.00102	1.45544	1.45646	
93		741.7	0.00103	1.45548	1.45651	1.4572

Analysos of cerium solution

	before filling cell	after measuring cell
Ce'''	6.037	6.107
Ce''''	5.985	5.942
Ce''' + Ce''''	12.022	12.049
Ce'''/ Ce''''	1.009	1.028
log		0.01199
correction		0.00073

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Cell No. 13 Ceelectrode No. I

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
4	35	734.4	0.00120	1.45583	1.45703	
6		734.1	0.00121	1.45568	1.45689	
22.5		736.4	0.00118	1.45560	1.45678	
23		736.3	0.00118	1.45565	1.45683	
23.5		736.3	0.00118	1.45567	1.45685	
28.5	25	735.1	0.00083	1.45842	1.45925	
30		734.5	0.00084	1.45840	1.45924	
46.5		733.0	0.00086	1.45832	1.45918	
47		732.9	0.00086	1.45832	1.45918	
47.5		732.8	0.00085	1.45832	1.45917	1.4595

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	6.005	6.008
Ce''''	5.929	5.936
Ce''' + Ce''''	11.934	11.944
Ce'''/ Ce''''	1.013	1.012
log		0.00518
correction		0.00031

Cell No. 14 Ce electrode No. II

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
4	35	734.4	0.00120	1.45584	1.45704	
6		734.1	0.00121	1.45570	1.45691	
22.5		736.4	0.00118	1.45568	1.45686	
23		736.3	0.00118	1.45569	1.45687	
23.5		736.3	0.00118	1.45570	1.45688	1.4573

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	6.005	6.022
Ce''''	5.929	5.931
Ce''' + Ce''''	11.934	11.953
Ce'''/ Ce''''	1.013	1.015
log		0.00647
correction		0.00040

Cell No. 15 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
8	35	742.3	0.00102	1.45680	1.45782	
12.5		742.9	0.00101	1.45680	1.45781	
21.5	25	744.9	0.00061	1.45931	1.45992	
23		744.7	0.00062	1.45929	1.45991	
23.5		744.7	0.00062	1.45927	1.45989	
41	15	745.2	0.00040	1.46214	1.46254	
50		744.9	0.00041	1.46196	1.46237	
51.5		744.3	0.00042	1.46192	1.46234	
73.5		740.5	0.00048	1.46177	1.46225	1.4631

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	4.028	4.096
Ce''''	3.995	3.963
Ce''' + Ce''''	8.023	8.059
Ce'''/ Ce''''	1.008	1.034
log		0.01452
correction		0.00083

Cell No. 16 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
8	35	742.3	0.00102	1.45685	1.45787	
12.5		742.9	0.00101	1.45686	1.45785	
21.5	25	744.9	0.00061	1.45948	1.46009	
23		744.7	0.00062	1.45948	1.46010	
23.5		744.7	0.00062	1.45945	1.46007	
41	15	745.2	0.00040	1.46241	1.46281	
50		744.9	0.00041	1.46229	1.46269	
51.5		744.2	0.00042	1.46225	1.46267	
73.5		740.5	0.00048	1.46212	1.46260	1.4631

Analysis of cerium solution

	before filling cell	after measuring cell
Ce^{+++}	4.028	4.063
Ce^{++++}	3.995	3.984
$Ce^{+++} + Ce^{++++}$	8.023	8.047
Ce^{+++} / Ce^{++++}	1.008	1.020
log		0.00860
correction		0.00049

Cell No. 17 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
1.5	35	738.9	0.00110	1.45676	1.45786	
2		738.5	0.00111	1.45676	1.45787	
2.5		738.0	0.00112	1.45673	1.45785	
4.5		737.5	0.00113	1.45669	1.45782	
10		735.6	0.00117	1.45662	1.45779	
10.5		735.4	0.00117	1.45660	1.45777	
18	25	734.0	0.00083	1.45906	1.45989	
19		734.0	0.00083	1.45905	1.45988	
20		734.4	0.00082	1.45905	1.45987	
22	15	734.6	0.00061	1.46213	1.46274	
23.5		734.6	0.00061	1.46212	1.46273	1.4632

Analysis of cerium solution

	before filling cell	after measuring cell
Ce^{+++}	4.026	4.055
Ce^{++++}	4.004	3.989
$Ce^{+++} + Ce^{++++}$	8.030	8.044
Ce^{+++} / Ce^{++++}	1.005	1.017
log		0.00732
correction		0.00045

Cell No. 18 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr, to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
16.5	15	742.5	0.00047	1.46220	1.46267	
17.5		742.3	0.00047	1.46226	1.46273	
18.5		742.3	0.00047	1.46226	1.46273	1.4632

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	4.015	4.021
Ce''''	3.938	3.942
Ce''' + Ce''''	7.953	7.963
Ce''' / Ce''''	1.020	1.020
log		0.00860
correction		0.00049

Cell No. 19 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
16.5	15	742.5	0.00047	1.46194	1.46241	
17.5		742.3	0.00047	1.46190	1.46237	
18.5		742.3	0.00047	1.46194	1.46241	
24	25	741.8	0.00069	1.45913	1.45982	
34		738.9	0.00074	1.45913	1.45987	
36		738.2	0.00075	1.45909	1.45984	
38		737.7	0.00076	1.45910	1.45986	
39.5		736.5	0.00079	1.45907	1.45986	
41		736.1	0.00079	1.45905	1.45984	1.4604

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	4.015	4.018
Ce''' + Ce''''	7.953	7.954
Ce''''	3.938	3.936
Ce''' / Ce''''	1.020	1.021
log		0.00903
correction		0.00053

Cell No. 20 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
16.5	15	742.5	0.00047	1.46193	1.46240	
17.5		742.3	0.00047	1.46188	1.46235	
18.5		742.3	0.00047	1.46192	1.46239	
24.0	25	741.8	0.00069	1.45912	1.45981	
34		738.9	0.00074	1.45912	1.45986	
36		738.2	0.00075	1.45907	1.45982	
38		737.7	0.00076	1.45910	1.45986	
39.5		736.5	0.00079	1.45907	1.45986	
41		736.1	0.00079	1.45904	1.45983	
47	35	733.5	0.00121	1.45637	1.45758	
58		730.2	0.00127	1.45621	1.45748	
60		731.5	0.00125	1.45621	1.45746	
62		731.7	0.00124	1.45623	1.45747	
64		732.3	0.00122	1.45625	1.45747	
65		732.6	0.00123	1.45626	1.45749	1.4582

Analysis of cerium solution

	before filling cell	after measuring cell
Ce^{+++}	4.015	4.033
Ce^{++++}	3.938	3.929
$Ce^{+++} + Ce^{++++}$	7.953	7.962
Ce^{+++} / Ce^{++++}	1.020	1.026
log		0.01115
correction		0.00068

Cell No. 21 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
3	15	734.6	0.00061	1.45004	1.45965	
16		737.6	0.00055	1.45012	1.45067	
17		738.6	0.00054	1.45017	1.45071	
18.5		738.8	0.00053	1.45018	1.45071	
20		739.0	0.00053	1.45020	1.45073	
22		740.6	0.00050	1.45020	1.45070	
40	25	746.1	0.00061	1.44689	1.44750	
41		745.3	0.00063	1.44686	1.44749	
45		742.6	0.00068	1.44680	1.44748	
46.5		741.7	0.00069	1.44680	1.44749	
51	35	740.7	0.00090	1.44373	1.44463	
63		741.2	0.00089	1.44372	1.44461	
64.5		741.3	0.00089	1.44371	1.44460	1.4587

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	3.346	3.342
Ce''''	1.965	1.966
$Ce''' + Ce''''$	5.311	5.308
Ce'''/ Ce''''	1.703	1.700
log		0.23045
correction		0.01408

Cell No. 22 Ce electrode No. II

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
3	15	734.6	0.00061	1.45005	1.45066	
16		737.6	0.00055	1.45013	1.45068	
17		738.6	0.00054	1.45016	1.45070	
18.5		738.8	0.00053	1.45018	1.45071	
20		789.0	0.00053	1.45020	1.45073	
22		740.6	0.00050	1.45019	1.45069	1.4639

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	3.346	3.334
Ce''''	1.965	1.962
$Ce''' + Ce''''$	5.311	5.296
Ce'''/ Ce''''	1.703	1.699
log		0.23019
correction		0.01316

Cell No. 23 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
3	15	734.6	0.00061	1.44999	1.45060	
16		737.6	0.00055	1.45001	1.45056	
17		738.6	0.00054	1.45006	1.45060	
18.5		739.0	0.00053	1.45012	1.45065	
22		740.6	0.00050	1.45011	1.45064	
40	25	746.1	0.00061	1.44682	1.44743	
41		745.3	0.00063	1.44680	1.44743	
45		742.6	0.00068	1.44673	1.44741	
46.5		741.7	0.00069	1.44674	1.44743	
51	35	740.7	0.00090	1.44366	1.44456	
63		741.2	0.00089	1.44364	1.44453	
64.5		741.3	0.00089	1.44363	1.44452	1.4586

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	3.346	3.337
Ce''''	1.965	1.962
$Ce''' + Ce''''$	5.311	5.229
Ce'''/ Ce''''	1.703	1.701
log		0.23070
correction		0.01410

Cell No. 24 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr.to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr.to 760 mm.	E_o
3	15	734.6	0.00061	1.44998	1.45059	
16		737.6	0.00055	1.45003	1.45058	
17		738.2	0.00054	1.45007	1.45061	
18.5		738.8	0.00053	1.45011	1.45064	
20		839.0	0.00053	1.45013	1.45066	
22.		740.6	0.00050	1.45012	1.45062	
40	25	746.1	0.00061	1.44684	1.44745	
41		745.3	0.00063	1.44681	1.44744	
42		742.6	0.00068	1.44674	1.44742	
46.5		741.7	0.00069	1.44675	1.44744	1.4610

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	3.346	3.346
Ce''''	1.965	1.977
$Ce''' + Ce''''$	5.311	5.323
Ce'''/ Ce''''	1.703	1.692
log		0.22840
correction		0.01351

Cell No. 25 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
8	35	742.3	0.00102	1.45666	1.45786	
12.5		742.9	0.00101	1.45720	1.45821	
21.5	25	744.9	0.00061	1.45987	1.46048	
23		744.7	0.00062	1.45988	1.46050	
23.5		744.7	0.00062	1.45987	1.46049	
41	15	745.2	0.00040	1.46266	1.46306	
50		744.9	0.00041	1.46256	1.46297	
51.5		744.2	0.00042	1.46253	1.46295	
73.5		740.5	0.00048	1.46233	1.46281	1.4641

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	2.038	2.071
Ce''''	1.991	1.971
$Ce''' + Ce''''$	4.029	4.042
Ce'''/ Ce''''	1.024	1.051
log		0.02160
correction		0.00128

Cell No. 26 Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
20	15	742.0	0.00048	1.46305	1.46353	
21		742.1	0.00048	1.46307	1.46355	
22		742.1	0.00048	1.46307	1.46355	
53	25	737.9	0.00076	1.45945	1.46019	
54		737.8	0.00076	1.45958	1.46034	
55		738.2	0.00077	1.45956	1.46033	
55.5		738.1	0.00078	1.45955	1.46033	
74.5	35	737.7	0.00113	1.45696	1.45809	
75.5		737.7	0.00113	1.45695	1.45808	
76.5		738.3	0.00112	1.45697	1.45809	1.4596

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	1.0331	1.0343
Ce''''	0.9794	0.9776
$Ce''' + Ce''''$	2.0125	2.0119
Ce'''/ Ce''''	1.055	1.058
log		0.02449
correction		0.00150

Cell No. 27 Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
20	15	742.0	0.00048	1.46297	1.46345	
21.		742.1	0.00048	1.46301	1.46349	
22		742.1	0.00048	1.46301	1.46349	
53	25	737.9	0.00076	1.45957	1.46031	
54		737.8	0.00076	1.45969	1.46045	
55		738.2	0.00077	1.45968	1.46045	
55.5		738.1	0.00078	1.45968	1.46046	1.4619

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	1.0331	1.0313
Ce''''	0.9794	0.9754
$Ce''' + Ce''''$	2.0125	2.0067
Ce'''/ Ce''''	1.055	1.057
log correction		0.02407
		0.00142

Cell No. 28 Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
20	15	742.0	0.00048	1.46295	1.46343	
21		742.1	0.00048	1.46300	1.46348	
22		742.1	0.00048	1.46300	1.46348	1.4649

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	1.0331	1.0412
Ce''''	0.9794	0.9872
$Ce''' + Ce''''$	2.0125	2.0248
Ce'''/ Ce''''	1.055	1.055
log correction		0.02325
		0.00133

Cell No. 1A Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
13	15	749.7	0.00035	1.46264	1.46299	
14		749.4	0.00035	1.46262	1.46297	
15		749.0	0.00036	1.46277	1.46313	
18		747.2	0.00039	1.46279	1.46318	
20.5		746.7	0.00040	1.46285	1.46325	
21.5		746.6	0.00040	1.46281	1.46321	1.4645

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	5.901	5.878
Ce''''	5.581	5.581
Ce''' + Ce''''	11.482	11.459
Ce''' / Ce''''	1.057	1.053
log		0.02243
correction		0.00128

Cell No. 2A Ce electrode No. II

Time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
13	15	749.7	0.00035	1.46267	1.46302	
15		749.0	0.00036	1.46278	1.46314	
18		747.2	0.00039	1.46279	1.46318	
20.5		746.7	0.00040	1.46285	1.46325	
21.5		746.6	0.00040	1.46283	1.46323	
34.5	25	741.6	0.00070	1.45977	1.46047	
36.5		740.5	0.00071	1.45974	1.46045	
38		740.2	0.00072	1.45974	1.46046	
40		738.8	0.00074	1.45970	1.46044	
42		738.2	0.00076	1.45969	1.46045	
64	35	741.4	0.00106	1.45711	1.45817	
65		741.3	0.00106	1.45705	1.45811	
66		741.2	0.00106	1.45708	1.45814	1.4596

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	5.901	5.899
Ce''''	5.581	5.571
Ce''' + Ce''''	11.482	11.470
Ce''' / Ce''''	1.057	1.058
log		0.02449
correction		0.00150

Cell No. 3A Ce electrode No. III

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
13	15	749.7	0.00035	1.46188	1.46223	
20.5		746.7	0.00040	1.46275	1.46315	
21.5		746.6	0.00040	1.46276	1.46316	
34.5	25	741.6	0.00070	1.45966	1.46036	
36.5		740.5	0.00071	1.45965	1.46036	
38		740.2	0.00072	1.45966	1.46038	
39		739.2	0.00074	1.45962	1.46036	
40		738.8	0.00074	1.45960	1.46034	
42		738.2	0.00076	1.45959	1.46035	1.4617

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	5.901	5.878
Ce''''	5.581	5.573
Ce''' + Ce''''	11.482	11.451
Ce'''/ Ce''''	1.057	1.055
log		0.02325
corredtion		0.00137

Cell No. 4A Ce electrode No. IV

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
13	15	749.7	0.00035	1.46189	1.46224	
20.5		746.7	0.00040	1.46276	1.46316	
21.5		746.6	0.00040	1.46276	1.46316	
36.5	25	740.5	0.00071	1.45967	1.46038	
38		740.2	0.00072	1.45966	1.46038	
39		739.2	0.00074	1.45965	1.46039	
40		738.8	0.00074	1.45962	1.46036	
42		738.2	0.00076	1.45961	1.46037	
64	35	741.4	0.00106	1.45684	1.45790	
65		741.3	0.00106	1.45686	1.45792	
66		741.2	0.00106	1.45687	1.45793	1.4596

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	5.901	5.891
Ce''''	5.581	5.567
Ce''' + Ce''''	11.482	11.458
Ce'''/ Ce''''	1.057	1.058
log		0.02449
correction		0.00150

Cell No. 5A Ce electrode No. I

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm	E_o
12	15	741.2	0.00052	1.46227	1.46279	
12.5		741.1	0.00052	1.46224	1.46276	
13		741.0	0.00053	1.46222	1.46275	
13.5		741.0	0.00053	1.46225	1.46278	
14		740.8	0.00053	1.46226	1.46279	1.4647

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	0.995	1.005
Ce''''	0.927	0.929
Ce''' + Ce''''	1.922	1.934
Ce'''/ Ce''''	1.073	1.082
log		0.03423
correction		0.00195

Cell No. 6A Ce electrode No. II

time (hrs)	temp. (°C.)	bar. p. corr. to 0°C.	press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	E_o
12	15	741.2	0.00052	1.46216	1.46268	
12.5		741.1	0.00052	1.46212	1.46264	
13		741.0	0.00053	1.46212	1.46265	
13.5		741.0	0.00053	1.46214	1.46267	
14		740.8	0.00053	1.46215	1.46268	
19.5	25	737.9	0.00079	1.45918	1.45997	
23		739.4	0.00080	1.45913	1.45993	
40.5		743.1	0.00070	1.45892	1.45962	
41		743.0	0.00070	1.45894	1.45964	
41.5		742.5	0.00071	1.45892	1.45963	
42		742.3	0.00071	1.45891	1.45962	
42.5		742.2	0.00072	1.45890	1.45962	
64.5	35	741.1	0.00106	1.45612	1.45718	
65		741.0	0.00106	1.45610	1.45716	
66		740.4	0.00108	1.45604	1.45712	
66.5		740.3	0.00108	1.45604	1.45712	1.4598

Analysis of cerium solution

	before filling cell	after measuring cell
Ce'''	0.995	1.012
Ce''''	0.927	0.916
Ce''' + Ce''''	1.922	1.928
Ce'''/ Ce''''	1.073	1.105
log		0.04336
correction		0.00264

time (hrs)	Cell No. 7A temp. (°C.)	bar. p. corr. to 0°C.	Ce electrode No. IV press. corr'n. (E)	$E_{obs.}$	E corr. to 760 mm.	Eo
12	15	741.2	0.00052	1.46217	1.46269	
12.5		741.1	0.00052	1.46216	1.46268	
13		741.0	0.00053	1.46216	1.46269	
13.5		741.0	0.00053	1.46218	1.46271	
14		740.8	0.00053	1.46219	1.46272	
19.5	25	737.9	0.00079	1.45926	1.46005	
23		739.4	0.00080	1.45923	1.46003	
40.5		743.1	0.00070	1.45915	1.45985	
41		743.0	0.00070	1.45915	1.45985	
41.5		742.5	0.00071	1.45913	1.45984	
42		742.3	0.00071	1.45911	1.45982	
42.5		742.1	0.00072	1.45911	1.45983	1.4619

Analysis of cerium solution

	before filling cell	after measuring cell
$Ce^{'''}$	0.995	1.002
$Ce^{''''}$	0.927	0.923
$Ce^{'''} + Ce^{''''}$	1.922	1.925
$Ce^{'''} / Ce^{''''}$	1.073	1.086
log		0.03583
correction		0.00212

data for the individual cells are recorded on pages 17-34.

The final values for the cells containing cerous and ceric ammonium sulfates are recorded in Tables I, II, and III. These data are expressed graphically in Fig. 4. From this graph it is evident that the potential is dependent upon the total concentration of ceric and cerous ammonium sulfates. Kunz (Kunz, J. Am. Chem. Soc., 53, 98, (1931)) showed that the potential of this electrode in sulfuric acid of a fixed concentration was practically independent of the total concentration of cerium sulfates. He also showed that in a higher concentration of sulfuric acid, the potential of the electrode was lower. A graph of Kunz' data is shown in Fig. 5. The independence of the potential on the total concentration of cerium sulfates was further corroborated by the preparation of cells at two widely separated concentrations of total cerium with the ratio equal to approximately one, using ceric and cerous sulfates in the absence of ammonium sulfate, in 0.5 formal sulfuric acid. These salts were prepared by igniting some ceric ammonium sulfate strongly for several hours to convert to the oxide, heating with concentrated sulfuric acid to convert to the sulfate, and dissolving in water. Part of the solution was reduced with hydrogen peroxide, and both portions evaporated slowly to obtain crystals of ceric and cerous sulfates. Table IV shows the data from these cells, and they are expressed graphically in Fig. 6.

After measurement and analysis of these cells was com-

Table I. (15°C.)

Cell No.	Total Ce	Ce'''/Ce''''	$E_{corr.}$ to 760 mm.	E_o
2	19.838	1.013	1.4609	1.4612
4	15.861	1.013	1.4614	1.4617
11	11.999	1.025	1.4618	1.4624
15	8.059	1.034	1.4623	1.4631
16	8.047	1.020	1.4626	1.4631
17	8.044	1.017	1.4627	1.4632
18	7.963	1.020	1.4627	1.4632
22	5.296	1.699	1.4507	1.4639
25	4.042	1.051	1.4628	1.4641
28	2.025	1.055	1.4635	1.4649

Table II (25°C.)

Cell No.	Total Ce	Ce'''/Ce''''	$E_{corr.}$ to 760 mm.	E_o
3	19.846	1.013	1.4579	1.4582
5	16.045	1.016	1.4585	1.4589
6	15.978	1.005	1.4586	1.4588
13	11.944	1.012	1.4592	1.4595
19	7.954	1.021	1.4598	1.4604
24	5.323	1.692	1.4474	1.4610
27	2.007	1.057	1.4605	1.4619

Table III (35°C.)

Cell No.	Total Ce	Ce'''/Ce''''	$E_{corr.}$ to 760 mm.	E_o
1	19.855	1.020	1.4553	1.4558
7	16.002	1.007	1.4563	1.4565
8	12.142	1.053	1.4558	1.4572
9	12.081	1.027	1.4565	1.4572
10	12.077	1.027	1.4565	1.4572
12	12.049	1.028	1.4565	1.4572
14	11.953	1.015	1.4569	1.4573
20	7.962	1.026	1.4575	1.4582
21	5.308	1.700	1.4446	1.4587
23	5.299	1.701	1.4445	1.4586
26	2.012	1.058	1.4581	1.4596

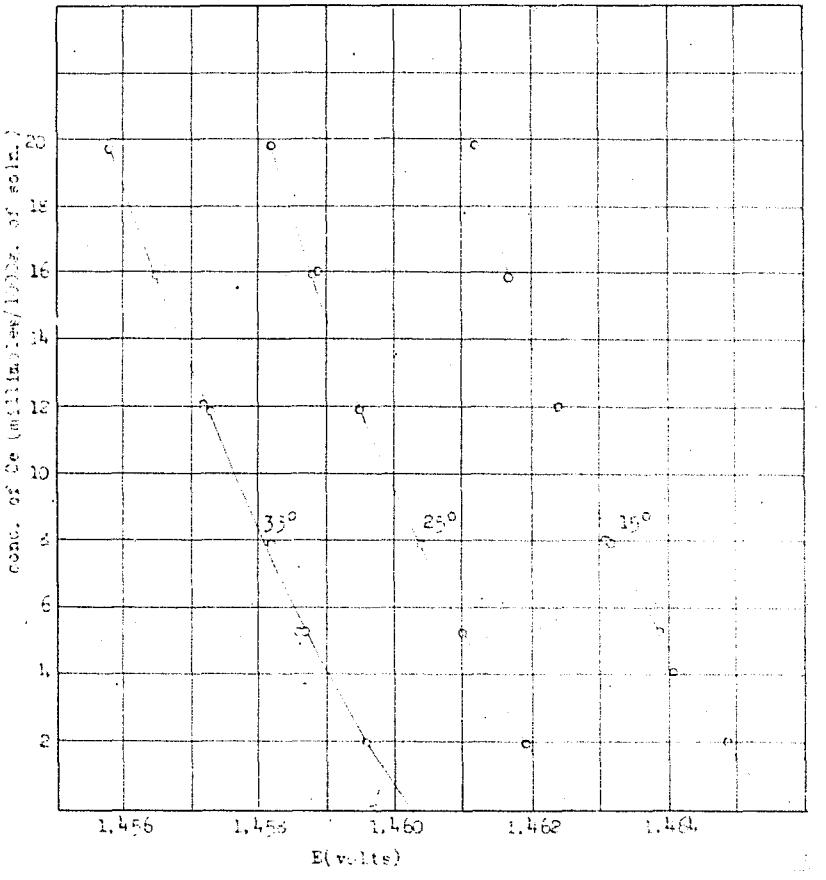

Fig. 4. Concentration - potential curves of ceric - cerous ammonium sulfate cells at 15°, 25°, and 35°C. in 0.5 formal sulfuric acid.

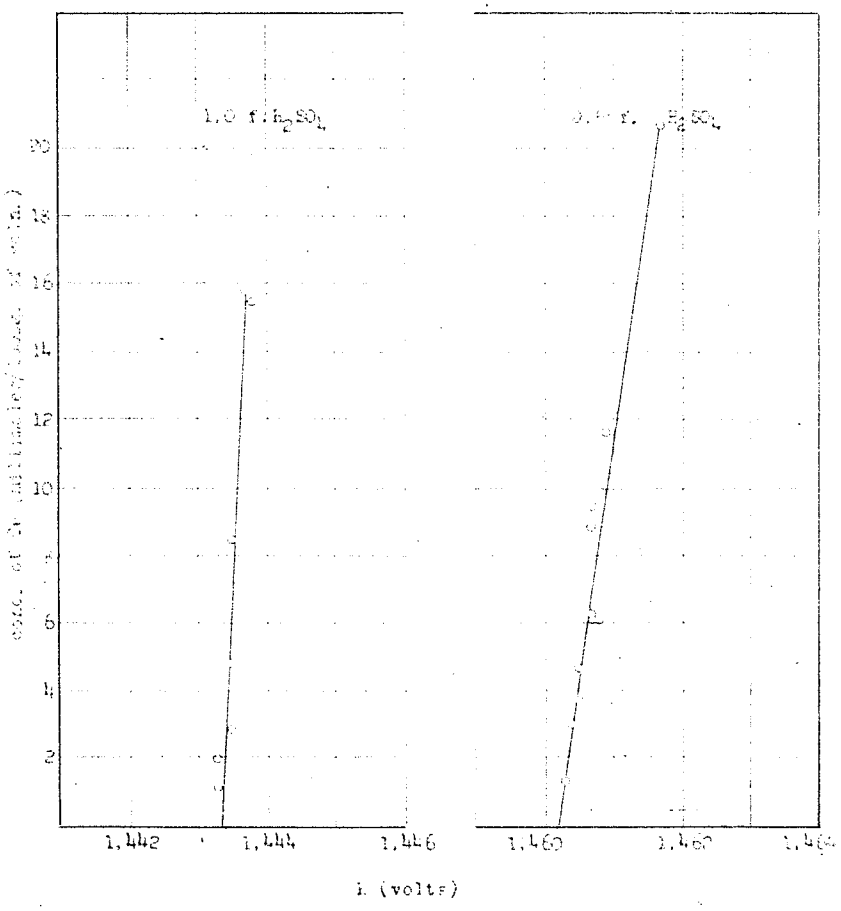

Fig. 5. Concentration - potential curves of ceric - cerous sulfate cells (Kunz) at 25°C. in 1.0 and 0.5 formal sulfuric acid.

Table IV

Cell No.	temp.	Total Ce	Ce'''/Ce''''	$E_{corr.}$ to 760 mm	E_o
1A	15	11.459	1.053	1.4632	1.4645
5A		1.934	1.082	1.4628	1.4647
3A	25	11.451	1.055	1.4604	1.4617
7A		1.925	1.086	1.4598	1.4619
2A	35	11.470	1.058	1.4581	1.4596
4A		11.458	1.058	1.4581	1.4596
6A		1.928	1.105	1.4571	1.4598

Table V

time (hrs)	Total Ce concentration 11.482 additions to electrode II	Ce'''/Ce'''' 1.05 electrode I	electrode II	drop in E
8	none	1.45706	1.45696	
26	0.075g. $(NH_4)_2SO_4$	1.45681	1.45493	0.00178
55	0.075g. $(NH_4)_2SO_4$	1.45643	1.45273	0.00182
72	12 drops conc. H_2SO_4	1.45629	1.45088	0.00171

Table VI

$-\Delta H$ and $-\Delta F$ for the reaction $Ce'''' + e \rightarrow Ce'''$ in 0.5f sulfuric acid at different temperatures.

temp. (°C.)	E (volts)	$\frac{dE}{dT}$	$-\Delta H$ (cal.)	$-\Delta F$ (cal.)
15	1.4656	0.000337	36,033	33,795
25	1.4626	0.000265	35,547	33.726
35	1.4603	0.000194	35,050	33,673

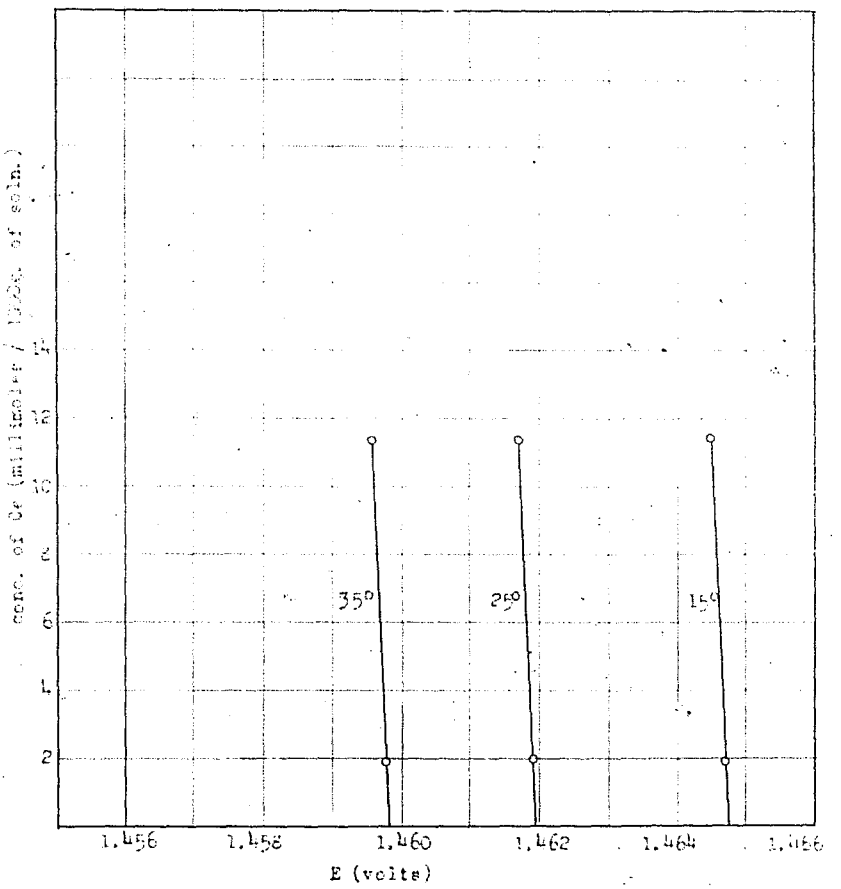

Fig. 6. Concentration - potential curves of ceric - cerous sulfate cells at 15°, 25°, and 35°, in 0.5 formal sulfuric acid.

pleted, two of the cerium half-cells were refilled with the solution in which the total concentration of cerium was 11.482 millimoles per thousand grams of solution. When they had come to equilibrium, a quantity of solid ammonium sulfate (0.075g) calculated to be equal to the quantity which would have been present had the solution originally been prepared from ceric and cerous ammonium sulfates, was added to the solution in one of the cerium half-cells. When the solid was completely dissolved and distributed throughout the solution in the half-cell (when the potential had ceased to vary), another equal addition was made. When equilibrium was again established, twelve drops of concentrated sulfuric acid was added to the half-cell. Equilibrium values of potential corrected to 760 mm. pressure are recorded in Table V. From these data it may be seen that the addition of sulfate ion to the solution lowers the potential of the ceric-cerous electrode, whether it be added as ammonium sulfate or sulfuric acid. The explanation of this behavior may be as follows: Since the potential of the ceric-cerous electrode in sulfuric acid of a fixed concentration is dependent upon the ratio

$$\frac{Ce'''(c' \times a')}{Ce''''(c'' \times a'')}$$

(a' and a" being the activities of the ceric and cerous ions, respectively), it is probable that the sulfate ion exercises its influence on the potential by effecting a change in the activities of one or both of these two ions. The effect, as stated previously, is a decrease in potential, which is caused

by an increase in the above ratio. This ratio increase may be brought about by either or both of two changes: first, by increasing the activity of the cerous ion; and second, by decreasing the activity of the ceric ion. This latter seems to be the more probable, since the tendency of the ceric ion to hydrolyze and form complexes is much more pronounced than that of the cerous ion.

The change in potential with respect to total concentration of cerium in the work of Kunz and in that part of this work comparable to his, is slight in both cases, but in opposite direction. According to Kunz, the potential in 0.5 formal acid decreased 0.8 millivolts as the concentration of cerium decreased from 11 to 0 millimoles of cerium per thousand grams of solution. In the present work, over the same concentration range, the potential increased 0.3 millivolts. This difference in direction of change with concentration is smaller, however, than the difference between the final values at 25° C. when extrapolated to zero concentration of cerium, Kunz' value being 1.4602 volts, and that of this experiment, 1.4620 volts.

At zero concentration of ceric and cerous ammonium sulfates, the effect of the ammonium sulfate as well as that of the junction potential should become zero, so the extrapolation of the curves in Fig. 4 gives the normal oxidation-reduction potential of the ceric-cerous electrode in 0.5 formal sulfuric acid at 15°, 25°, and 35° C., measured against a

hydrogen electrode at 25°C. and 760 mm. of mercury in 0.5 formal sulfuric acid.

It should be noted that while the values for the potential at zero concentration of cerium obtained from measurements of the cerium ammonium sulfate cells, and those from the cerium sulfate cells differ by approximately 0.5 mv., the temperature coefficients for the two groups of cells are identical, within the limits of experimental error.

The values of free energy decrease and decrease in heat content ($-\Delta F$ and $-\Delta H$) recorded in Table VI are large, as would be expected from a system with such a high potential. The fact that the free energy decrease for the reaction $Ce''''+e \rightarrow Ce'''$ is positive, denotes that the reaction will proceed spontaneously in the direction of the equation. The fact that the decrease in heat content is greater than the free energy decrease, denotes that the system gives off heat as the reaction proceeds. Values for this reaction as determined calorimetrically are not available at the present time.

SUMMARY

1. The oxidation reduction-potential of the ceric-cerous electrode in 0.5 formal sulfuric acid has been determined at three temperatures. Referred to a hydrogen electrode in 0.5 formal sulfuric acid at 760 mm. pressure and 25° C., the values are: at 15° -1.4656; at 25° -1.4626; at 35° -1.4603 volts.

2. The effect of ammonium sulfate or sulfuric acid on the potential of the ceric-cerous electrode is to decrease the potential of the electrode.

3. The temperature coefficient of the electrode has been determined at three temperatures. The values are at 15° - 0.00033; at 25° - 0.00027; at 35° - 0.00020 volts per degree.

4. The decrease in heat content (- ΔH) for the reaction $Ce''''+e \longrightarrow Ce'''$ has been determined at three temperatures. The values are: at 15° - 36,033 cal.; at 25° - 35,547 cal.; at 35° - 35,050 cal.

5. The free energy decrease (- ΔF) for the above reaction has been determined at three temperatures. The values are: at 15° - 33,795 cal.; at 25° - 33, 726 cal.; at 35° - 33,673 cal.