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Oxidation Potential of the Pu(III)-Pu(IV) Couple in Percloric Acid So lution. Heat Content and Entropy Change

Author

Connick, Robert E.

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Oxidation Potential of the Pu(III) - Pu(IV) Couple in Perchloric Acid Solution. Heat Content and Entropy Change.

by

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R. E. Connick and W. H. McVey

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Abstract

It was expected that the Pu^{+3} - Pu^{+4} potentials in perchloric and in hydrochloric acid would differ principally because of chloride complexing of Pu^{+4} in the hydrochloric acid system. The values of the potentials previously reported in the project literature are inconsistent with this idea. Since it was believed that the measurements in the perchloric acid system were in error, the EMF of the cell:

$$Pt:\ H_2:\ 1\ M\ HClO_4;\ 1\ M\ HClO_4,\ Pu(ClO)_4)_3,\ Pu(ClO_4)_4:\ Au$$

was determined at 25°C. The value of -0.982 volts, which was obtained for the reaction $Pu^{+3} + H^+ = Pu^{+4} + 1/2\ H_2$ in 1 M perchloric acid, differs significantly from the previously reported value and is consistent with the idea that Pu^{+4} is partially complexed by chloride ion in 1 M HCl.

From the data on the disproportionation of Pu^{+4} in 1 M perchloric acid and the Pu^{+3} - Pu^{+4} potential, a formal potential scheme involving the +3, +4 and +6 oxidation states of plutonium was derived:

$$\begin{tikzcd}
Pu^{+3} \arrow[r, dash, "-0.982"] \arrow[rr, dash, bend right, "-1.0095"'] & Pu^{+4} \arrow[r, dash, "-1.023"] & PuO_2^{++}
\end{tikzcd}$$

The EMF of the above cell was also measured at different temperatures and the change in heat content for the reaction $Pu^{+3} + H^+ = Pu^{+4} + 1/2\ H_2$ was calculated to be +13.52 kcal/mole. This value is to be compared with 11.3 kcal/mole obtained by Evans from calorimetric measurements.

Using the values of ΔH and ΔF obtained for the reaction $Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$, ΔS was calculated to be -31 e.u. at 25°. From an estimated entropy value for Pu^{+3}, the entropy of Pu^{+4} was found to be -77 e.u.

It was possible to calculate a value of -18 e.u. for PuO_2^{++} from the data on the heat of oxidation of Pu^{+3} to PuO_2^{++}. The entropies of the three oxidation states of plutonium compare very closely with those of uranium.

[redacted]

Introduction

The oxidation potential for the couple $Pu^{+3} = Pu^{+4} + e^-$ has been reported by Hindman et al[1,2] to be -0.945 volts in 1 M* perchloric acid and -0.966 volts in 1 M hydrochloric acid at 25°C. These potentials can differ appreciably** only because of a change in the activity coefficients of Pu(III) and Pu(IV) in going from perchloric acid to hydrochloric acid. Significant changes in these activity coefficients might occur through complex ion formation. There is no evidence that perchlorate ion complexes any +3 or +4 ions in aqueous solution and some evidence that it

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[1] J. C. Hindman, CN-2289, p 1, November 1, 1944.

[2] J. J. Howland, Jr., K. A. Kraus and J. C. Hindman, CN-1371, p 8, March 1, 1944

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*The symbol M is used throughout this paper to indicate concentrations expressed moles per liter of solution at 25°C.

**The potentials are affected to a small extent by the activity coefficients of HCl and $HClO_4$ and by boundary potentials. The potential for the plutonium couple in 1 M $HClO_4$ was determined relative to a saturated calomel reference cell. The potential of the calomel half-cell, -0.246 volts, was subtracted from the measured voltage of the cell to give -0.945 volts for the Pu(III) - Pu(IV) potential, assuming zero boundary potential. The value for 1 M HCl was obtained from the cell

$$Ag: AgCl: 1\ M\ HCl,\ 1\ M\ HCl,\ PuCl_3,\ PuCl_4:\ Pt$$

The boundary potential should have been negligible as the plutonium was present at a low concentration. A value for the potential of the Ag-AgCl electrode was calculated from the standard potential for this couple, corrected for the activity coefficient of chloride ion. This activy coefficient was arbitrarily assumed to be equal to the mean activity coefficient of 1 M HCl. The Ag-AgCl potential was then subtracted from the observed voltage of the cell to give -0.966 volts for the Pu(III) - Pu(IV) potential. Although this method of treatment of the data is not thermodynamically rigorous, the errors thus introduced could not possibly account for the reported difference in the potential in 1 M $HClO_4$ and 1 M HCl.

does not form complexes with Pu^{+3} and Pu^{+4}.[3] On the other hand it is well known that chloride ion complexes Pu^{+4} although there is no evidence of its complexing Pu^{+3} in 1 M hydrochloric acid.[3] If it is assumed that the change in the potential in going from perchloric acid solution to hydrochloric acid solution, to a first approximation, is caused by chloride complexing of Pu(IV), the potential for the reaction in perchloric acid should be more negative than that for the hydrochloric acid solution. Just the opposite change has been reported in the above cited work.

It seemed desirable to redetermine the potential of the reaction in perchloric acid solution to verify or disprove the above reasoning. It was believed that the error, if it existed, was in the perchloric acid data rather than the hydrochloric acid data as the latter work was very carefully carried out.

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[3] J. C. Hindman, P. P. R., Volume 14A, Chapter IV.

[redacted]

Further evidence that the perchloric acid measurement was in error came from a value of -1.067 volts given by Hindman[1] for the Pu(IV) - Pu(VI) couple in 1 M perchloric acid. Combining this value with the Pu(III) - Pu(IV) potential one obtains -0.122 volts for the reaction

$$3\ \mathrm{Pu(IV)} = \mathrm{Pu(VI)} + 2\ \mathrm{Pu(III)} \qquad (1)$$

in 1 M perchloric acid at 25°C. From this datum one calculates a value of the equilibrium quotient expressed in terms of gross concentrations

$$K = \frac{(\mathrm{Pu(VI)})\ (\mathrm{Pu(III)})^{2^{*}}}{(\mathrm{Pu(IV)})^{3}} = 8 \times 10^{-5}$$

However, this value is in disagreement with the directly measured value of this equilibrium quotient in 1 M perchloric acid at 25°C, which Kasha[4] found to be K = 0.041.

Therefore, either one or both of the perchloric acid solution potentials must be in error. If it is true that the Pu(III) - Pu(IV) potential in 1 M $HClO_4$ is more negative than reported, corresponding to the most reasonable assumptions as to complexing, the correction would be in the right direction to bring the equilibrium constant calculated from potential measurements into better agreement with the directly measured value. Thus, if it is assumed that Hindman's value for the Pu(IV) - Pu(VI) potential is correct, one calculates for the Pu(III) - Pu(IV) potential, using Kasha's data for the disproportionation, a value of -1.026 volts.

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[4] M. Kasha, CN-3737, December 19, 1946.

*Parenthesis will be used to represent concentrations of the enclosed species in moles per liter of solution at 25°C.

It does not seem likely, however, that the chloride complexing of Pu(IV) is sufficiently strong to change this value to -0.966 volts in 1 M hydrochloric acid. It was therefore believed that both potential values for 1 M perchloric acid might be in error.

A value for the heat of oxidation of Pu^{+3} to Pu^{+4} has been determined by Evans[5] by direct calorimetric measurement. Since the measurement of the temperature coefficient of a cell provides a convenient method of evaluating this quantity as well as the entropy change, it seemed worthwhile to extend the cell measurements to other temperatures in order to measure ΔH and ΔS and check the direct calorimetric measurement.

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[5] M. W. Evans, CN-3138, August 31, 1945 and erratum to CN-3138 by L. Brewer, L. A. Bromley, B. J. Fontana, P. W. Gilles and N. Lofgren, October 29, 1945.

Experimental Measurements

The potential of the Pu(III) - Pu(IV) couple in 1 M $HClO_4$ was determined by measuring the potential of the cell

$$Pt:\ H_2:\ 1\ M\ HClO_4;\ 1\ M\ HClO_4,\ Pu(ClO_4)_3,\ Pu(ClO_4)_4:\ Au$$

This cell had essentially no liquid junction as the concentration of plutonium was always small. The experimental details of the measurements are given below.

In addition to the above cell, measurements were carried out on the potential of the reaction

$$Fe^{++} + H^{+} = Fe^{+++} + 1/2\ H_2 \qquad (2)$$

in order to test the apparatus and check the accuracy of the method.

Preparation of Solutions - The plutonium used in these experiments was from a stock solution of purified plutonium in nitric acid. It was hoped that a plutonium(IV) perchlorate solution could be prepared simply by dissolving plutonium(IV) hydroxide in perchloric acid. However, it was found impossible to obtain complete solution of the hydroxide which persisted partly in a colloidal state. To circumvent this difficulty the plutonium was oxidized to the +6 state by bromate at 100°C and precipitated as barium plutonate by the addition of barium hydroxide. The precipitate was washed with a barium hydroxide solution and then dissolved in 1 M perchloric acid. The precipitation procedure was repeated twice. For the purpose of calculating the acidity of the final solution it was necessary to correct for the amount of acid used in dissolving the precipitate. As the composition of the precipitate was unknown, it was arbitrarily assumed to be half $BaPuO_4$ and half $BaPu_2O_7$. A correction was also made for the amount of barium hydroxide held up in the precipitate. The amount of acid used to dissolve the the precipitate and to react with the held-up $Ba(OH)_2$ was only 4% of the total acid added, so the above assumption should not introduce an appreciable error. Additional perchloric acid was then added to make the solution 1.00 M. Sufficient hydrogen peroxide was added to reduce about one-third of the plutonium to the +4 oxidation state and two-thirds to the +3 state. The Pu(III) concentration was made higher than the Pu(IV) concentration to minimize the amount of Pu(VI) which would be formed by disproportionation of Pu(IV). The total plutonium concentration used in the experiment was 4.68×10^{-3} M.

The solution for the iron measurements was prepared by dissolving G. Frederick Smith ferrous perchlorate in 0.1 M $HClO_4$ to give an approximately 0.1 M solution of Fe^{++}. Hydrogen peroxide was added to make the ferric to ferrous ratio about 2.5 and the solution was diluted with perchloric acid to a concentration of 0.50 M $HClO_4$. The total iron concentration used in the experiment was 9.203×10^{-3} M.

The perchloric acid solutions were prepared by diluting G. Frederick Smith double vacuum distilled 12 M perchloric acid with conductivity water. The concentration was standardized using the mercuric oxide-potassium iodide method.

<u>The Cell</u> - The cell arrangement was essentially that used by Sherrill and Haas[6], except that theconventional type of hydrogen electrode was used. The cell was constructed with two hydrogen electrodes in the H_2-H^+ half cell and two gold electrodes in the Pu^{+3} - Pu^{+4} or Fe^{+2} - Fe^{+3} half cell compartment. The two half

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[6] M. S. Sherrill and A. J. Haas, Jr., J. Am. Chem. Soc. <u>58</u>, 952 (1936).

cells were separated by a ground glass joint, contact being made through the thin film of liquid in the joint. The resistance of the cell was about 4000 ohms.

Arrangements were made for pre-saturating the hydrogen gas with water vapor from a perchloric acid solution of the same compostion as that in the cell before the hydrogen entered the cell. Very pure hydrogen, prepared by electrolysis of water and passed over a hot nickel catalyst, was used.

The platinum electrodes in the hydrogen compartment of the cell were platinized in the usual manner in a chloroplatinic acid solution at a low current density. High purity platinum was used for the electrodes and in preparing the chloroplatinic acid solution. When the system had been thoroughly swept out with hydrogen gas the two electrodes usually agreed to within 0.02 millivolt. Complete sweeping of the cell took considerable time and, when incomplete, the potential measured by the electrode would rise and fall as each hydrogen bubble formed and broke away from the electrode. This effect was probably caused by oxygen which had not been removed from the solution.

The cell was constructed with ground glass joints and traps so as to make a completely sealed system. There was a tube leading into the solution in the iron or plutonium part of the cell through which helium could be bubbled. This was for the purpose of removing oxygen from this part of the cell and for the purpose of affording some stirring of the solution.

Considerable difficulty was experienced at first in obtaining the same potential reading from both gold electrodes. The potential varied erratically when the solution was stirred by bubbling helium through it. Shiny platinum electrodes) were tried with no better success. Cleaning the electrodes in aqua regia helped in neither case. From the behavior of the electrodes it was concluded that these effects were caused by impurities in the metals. Therefore some very pure gold was obtained and it was found that the irreproducible behavior was eliminated. Using high purity, shiny gold which had been cleaned only with carbon tetrachloride vapor, the two gold electrodes usually read to within 0.02 millivolts of each other. In addition, the same reading was obtained with a very pure platinum electrode cleaned in the same manner.

The cell was immersed in an oil thermostat. At a given temperature the temperature was maintained constant to ± 0.02°. The temperatures were read from accurate mercury thermometers to which were applied stem corrections and National Bureau of Standards corrections supplied with the thermometers. During most of the experiments, measurements of the potential of the cell were taken at five degree intervals from 10°C to 35°C. The potential measurements were continued at a particular temperature until the potential reading had remained constant for a period of 30 minutes or more.

The electrical circuit was relatively simple, consisting of the cell, a standard cell, a galvanometer and potentiometer. There was a switching arrangement for taking readings from any desired pair of the four electrodes. All connections were shielded. The standard cell was a Weston Standard Cell with a potential of 1.01935 absolute volts. The galvanometer was a Rubicon with a sensitivity of 0.0012 a/mm, an external critical dampening resistance of 11,000 ohms, an internal resistance of 455 ohms and a period of 4.7 seconds. The potentiometer used was a Rubicon High Precision Type B, which could be read to 0.02 millivolts. The instruments were connected in the normal manner.

Analyses - The analyses of both the iron and plutonium[7] solutions were carried out using an oxidation-reduction titration with ceric sulfate as the oxidizing agent and orthophenanthroline ferrous complex as the indicator. The +2 iron and the +3 plutonium were determined by direct titration of the solutions in 1 M sulfuric acid. Plutonium is oxidized only to the +4 state by ceric ion under these conditions. The total iron and plutonium[7] were determined by titrations of the solutions after they had been run through a Jones reductor, the iron being all reduced to the +2 state and the plutonium being all reduced to the +3 state. The +3 iron and +4 plutonium concentrations were then determined by difference. There was no Jones reductor blank detectable above the normal indicator blank. The indicator blank correction was about 3% of the volume of ceric solution required for titration of the totals and was reproducible to within ± 2% of its own value. The iron titrations agreed to within ± 0.2% of the mean. The plutonium titration data are presented later. Actually it is not necessary to know the concentrations of Fe(II) and Fe(III) or Pu(III) and Pu(IV) for the determination of ΔH, as long as the ratio of the concentration of Fe(II) to Fe(III) and the ratio of Pu(III) to Pu(IV) remain constant for a series of experiments at different temperatures. Furthermore, only the ratio of the concentrations of Pu(III) and Pu(IV) and the ratio of the concentrations of Fe(II) and Fe(III) are needed for the calculation of potentials.

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[7] C. W. Koch, CN-3495, April 24, 1946.

Experimental Results and Calculations

The data from two, duplicate experiments on the iron-hydrogen cell, are presanted in Table 1. The EMF values listed in the second and seventh columns are the directly measured EMF's for the cell corrected to one atmosphere pressure of hydrogen. Correction was made for the barometric pressure, water vapor pressure, hydrostatic pressure in the bubblers placed outside thecell and hydrostatic pressure in the hydrogen electrode compartment itself.

The value of ΔH for the reaction may be obtained from the equation

$$\left(\frac{\partial\left(\frac{E}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = -\frac{\Delta H}{n\ F}$$

where E is the electromotive force for the cell reaction, T the absolute temperature, P the pressure, n the electron change of the reaction and F Faraday's constant. The values of $\frac{E}{T}$ of Table 1 have been plotted against $\frac{1}{T}$ in Figure 1. In each case a straight line has been drawn tangent to the curve of the points at 25°C. Actually there is no appreciable curvature in the data of the first experiment and only a slight curvature in the case of the second experiment, indicating a nearly constant value of ΔH over the temperature range investigated. The values of ΔH for the cell reaction at 25°C, read from the slopes of the curves, are 10,000 calories per mole of iron for experiment 1 and 9,890 calories per mole for experiment 2.

Table 1

EMF of the Cell; Pt: H_2: 0.5 M $HClO_4$; 0.5 M $HClO_4$, $Fe(ClO_4)_2$, $Fe(ClO_4)_3$: Au, at Various Temperatures.

2.658×10^{-3} M $Fe(ClO_4)_2$, 6.545×10^{-3} M $Fe(ClO_4)_3$, 0.5036 M $HClO_4$

Experiment 1				Experiment 2			
Temp°C	EMF[a]	$\frac{EMF}{T} \times 10^3$	$\frac{1}{T} \times 10^3$	Temp°C	EMF[a]	$\frac{EMF}{T} \times 10^3$	$\frac{1}{T} \times 10^3$
25.18	0.78026	2.6153	3.3520	24.96	0.78014	2.6169	3.3540
10.96	0.76404	2.6891	3.5198	19.96	0.77410	2.6409	3.4112
17.95	0.77218	2.6525	3.4352	14.96	0.76803	2.6657	3.4709
34.97	0.79193	2.5701	3.2455	9.96	0.76204	2.6916	3.5323
				24.96	0.78009	2.6167	3.3540
				29.96	0.78590	2.5927	3.2994
				34.97	0.79176	2.5696	3.2459
				24.96	0.77998	2.6163	3.3540

$Fe^{+2} + H^+ = Fe^{+3} + 1/2\ H_2$
(25.0°C, 1 atmos. H_2, equal (and small) concns. Fe^{++} and Fe^{+++}, corrected to unit concentration of H^+)

	Exp. 1	Exp. 2
ΔH =	10.00 kcal mole	9.89 kcal/mole
E_f =	-0.7395 volts	-0.7393 volts

[a] EMF corrected to 1 atm. H_2 pressure

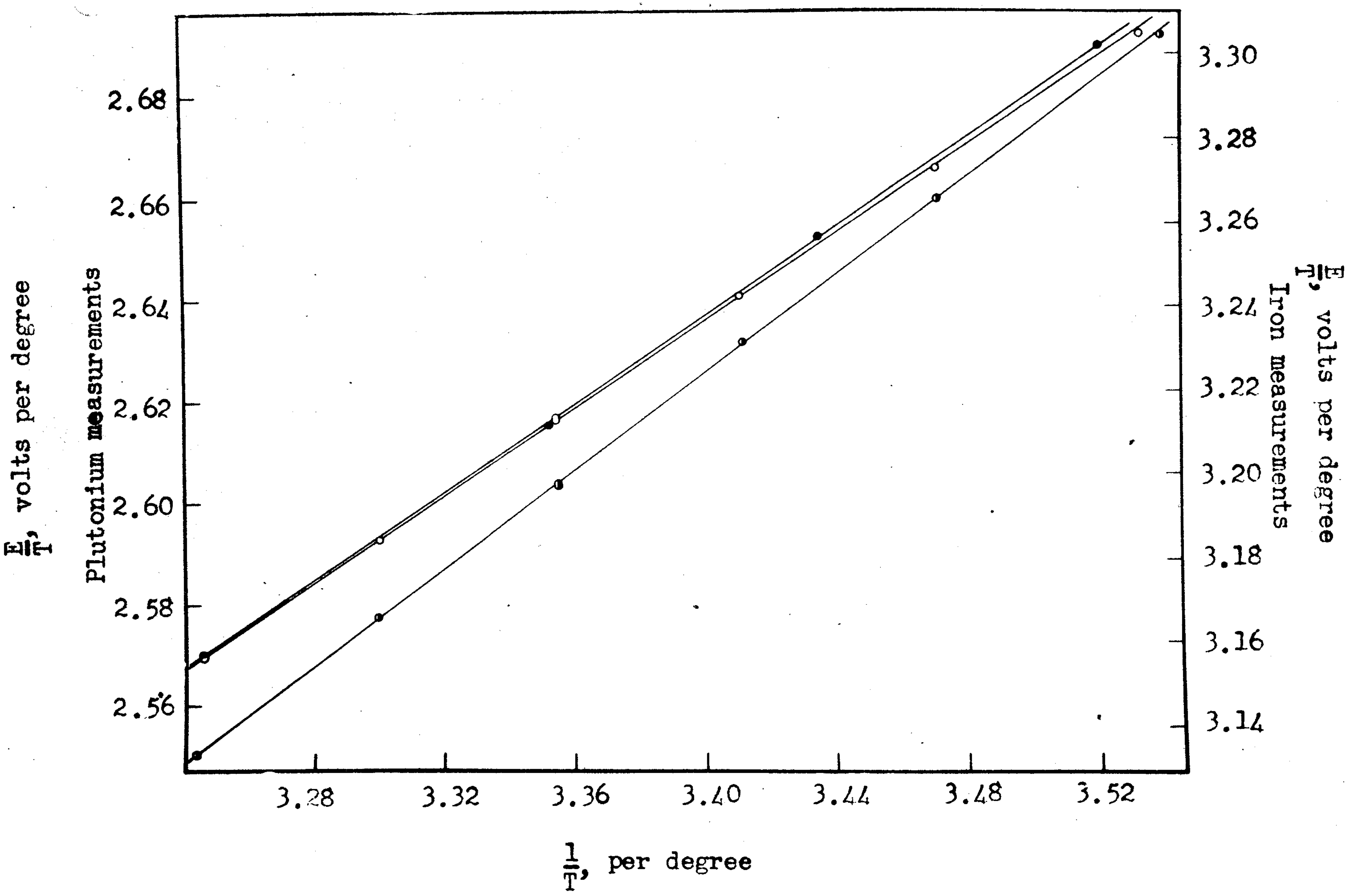

Figure 1.

Plots of $\frac{E}{T}$ versus $\frac{1}{T}$ for Iron and Plutonium Cells.

●, ○ Iron Values, ◑ Plutonium Values.

Two series of cell measurements were made on the Pu(III)-Pu(IV) couple, one in which the temperature was varied and the other in which the temperature was maintained at 25.00°C. The data for the first series are given in Table 2. The first column gives the time at which the EMF reading was recorded. The third column lists the experimentally measured EMF values of the cell corrected to one atmosphere hydrogen pressure as described for the iron cell. In the case of plutonium several additional corrections must be made.

An appreciable correction is introduced by the gradual decrease in average oxidation number of the plutonium. The plutonium in the +4 state is slowly reduced by species formed in the passage of its own alpha particles through the solution. The rate of this reduction in 1 M $HClO_4$ at 25°C corresponds to a decrease in average oxidation number of 0.0128 per day according to measurements of Kasha[4]. This figure was checked in the present work by comparison of EMF values for the two series of plutonium experiments which were carried out three days apart and in which the same plutonium stock solution was used. The amount of reduction caused by alpha particles as deduced from the change in the Pu(III)-Pu(IV) potential agreed almost exactly with that calculated from Kasha's value.

In the fourth column of Table 2 are the EMF values corrected to one atmosphere hydrogen pressure and corrected for the reduction caused by alpha particles. The alpha particle correction has been made relative to the first EMF reading. It was assumed that the rate of reduction by alpha particles is temperature independent.

Consideration must be given to the correction for the dispro-

Table 2

EMF of the Cell; Pt: H_2: 1 M $HClO_4$; 1 M $HClO_4$, $Pu(ClO_4)_3$, $Pu(ClO_4)_4$: Au
at various Temperatures.

3.50×10^{-3} M $Pu(ClO_4)_3$, 1.18×10^{-3} M $Pu(ClO_4)_4$, 0.998 M $HClO_4$

Time hrs.	Temp., °C	EMF of cell corrected to one atmos. H_2	EMF at one atmos. H_2, corrected for α-particle reduction	$\frac{EMF^a}{T} \times 10^3$	$\frac{10^3}{T}$
0	9.41	0.93375	0.93375	3.3045	3.5389
1	14.92	0.94076	0.94092	3.2662	3.4713
2	19.92	0.94698	0.94721	3.2319	3.4120
3	24.94	0.96307	0.95339	3.1982	3.3546
4	29.96	0.95925	0.95964	3.1659	3.2990
5	35.01	0.96518	0.96564	3.1335	3.2450
6	24.94	0.95261	0.95315	3.1974	3.3546

$Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$

(25.0°C, 1.00 M $HClO_4$, 1 atmos. H_2, equal (and small) concns. Pu^{+3} and Pu^{+4})

$\Delta H = 13.52$ kcal per mole

$E_f = -\ 0.9818$ volts

[a] This is the EMF of the preceding column which is corrected to one atmosphere H_2 and corrected for reduction caused by alpha particles.

portionation of Pu(IV) to Pu(III) and Pu(VI) according to the equation.

$$3\ \mathrm{Pu(IV)} \xrightleftharpoons{K} 2\ \mathrm{Pu(III)} + \mathrm{Pu(VI)} \qquad (1)$$

The concentration of Pu(IV) was kept small relative to the concentration of Pu(III) in order to minimize the extent of this reaction. From the value of K for the above reaction in 1 M $HClO_4$ at 25°C[4] and using the heat data obtained in the present work and the heat of oxidation of Pu(III) to Pu(VI) measured by Evans[5], one can calculate approximately the extent of disproportionation at equilibrium for each of the temperatures of Table 2. These values are given in Table 3 in terms of the ratio of the concentration of Pu(VI) to Pu(IV) at equilibrium. In the last column is tabulated the calculated difference between the potential for no disproportionation and the potential for equilibrium disproportionation. It is seen that this correction would be quite large if the disproportionation equilibrium is truly attained. Fortunately there is good evidence that this is not the case. From the data of Kasha on the disproportionation of Pu(IV) in 1 M $HClO_4$ at 25°C, a rate constant of 1.3×10^{-2} liters moles^{-1} min^{-1} may be estimated, assuming that the reaction is second order with respect to the plutonium(IV) concentration. One calculates that with the plutonium concentration used in the experiment of Table 2 only 0.07% of the Pu(IV) would disproportionate per hour at 25°C. Thus at 25°C and and lower temperatures the changes in concentration during the time of the experiment should be negligible. At 30° and 35° the rate probably increases. It is not possible to predict the increase; however, the correction introduced can be estimated in another way. The original Pu(III) - Pu(IV) solution should have

Table 3

Relative Concentrations of Pu(VI) and Pu(IV) and the EMF Correction at Disproportionation Equilibrium for the Experimental Conditions of Table 2.

Temp., °C	$\frac{(Pu(VI))}{(Pu(IV))}$	ΔEMF
35	0.029	0.0027 volts
30	0.012	0.0011
25	0.0044	0.00042
20	0.0015	0.00016
15	0.00052	0.00005
9.5	0.00015	0.00002

been at equilibrium with respect to the disproportionation equilibrium at 25°C as it had stood for some time in a 25.0°C thermostat. The first readings were taken at low temperatures where reproportionation tends to occur but the rate should be negligible. Therefore at the first 25° point the solution still should have been at equilibrium with respect to disproportionation at 25°C. On heating to 30° and 35° some disproportionation may have occurred. The cell was then rapidly cooled to 25° so that there was no chance for appreciable reproportionation to take place. Therefore, any appreciable disproportionation at the higher temperatures should have been made evident by a difference in the two 25° readings, i.e., the last 25° point should give a lower EMF value. It is seen from Table 2 that the two values are actually quite close to each other and the small difference of 0.2 millivolts is in the direction to be expected for the above correction.* It is possible, therefore, that the EMF measured at 35°C should be increased ca. 0.2 millivolts to correspond to the measurements at lower temperatures. Presumably the 30° point would be raised something less than 0.1 millivolts. In any case these corrections are small and should not affect the calculation of ΔH seriously.

The extent of disproportionation at equilibrium at 25°, which from the above reasoning was presumed to be constant throughout the experiment, does not affect the calculation of ΔH, since this

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*It is conceivable that the observed difference between the two 25° readings is due to an increased rate of alpha particle reduction of plutonium at the higher temperatures. There is some slight evidence[8] of such a temperature effect on this rate under other conditions.

correction raises or lowers all points of the $\frac{E}{T}$ versus $\frac{1}{T}$ curve the same amount and only the slope is used in the calculation. The correction was made in the calculation of the formal potential, E_f*, given in Table 2; the correction amounts to only 0.42 millivolts.

The purpose of the second experiment with plutonium was to obtain a precise value for the EMF of the Pu(III) - Pu(IV) couple versus the H_2 - H^+ couple in 1 M $HClO_4$ at 25°C. The EMF of the cell was measured for a considerable period of time at constant temperature. The data are recorded in Table 4. The second column gives the measured EMF of the cell corrected to one atmosphere pressure of hydrogen as described for the previous experiments. The third column lists the EMF after correction for reduction of plutonium caused by alpha particles, the correction having been made arbitrarily to a time of 252 minutes after the first EMF reading. From the data it is seen that the potential was very steady during a period of over three hours.

The titration data for the analysis of Pu(III) and Pu(IV) for both plutonium experiments are given in Table 5. It was assumed in the titration of Pu(III), that any Pu(VI) present in the sample would rapidly combine with Pu(III) to form Pu(IV), when sulfuric acid was added before the titration. Using these data the formal potentials in Tables 2 and 4 were calculated

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*The formal potential of a reaction under a given set of conditions is the directly measured cell potential corrected to unit concentration of the substances entering into the reaction. The formal potential for an oxidation-reduction couple is the formal potential of the reaction of the couple with the H_2 - H^+ couple.

Table 4

EMF of the Cell: Pt: H_2: 1 M $HClO_4$; 1 M $HClO_4$, $Pu(ClO_4)_3$, $Pu(ClO_4)_4$: Au at 25°C

3.71×10^{-3}M $Pu(ClO_4)$, 0.96×10^{-3}M $Pu(ClO_4)_3$,

0.998 M $HClO_4$

Time (min)	EMF of cell corrected to one atmos. H_2	EMF of cell at one atmos. H_2, corrected for α-particle reduction
0	0.94766 volts	0.94736 volts
42	0.94770	0.94745
65	0.94763	0.94741
86	0.94761	0.94741
107	0.94760	0.94742
136	0.94758	0.94744
162	0.94754	0.94743
192	0.94746	0.94739
	Ave.	0.94741 volts

$Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$ $\quad E_f = -0.9824$ volts

(25.0°C, 1.00 M $HClO_4$, 1 atmos.
H_2, equal (and small) concns.
Pu^{+3} and Pu^{+4})

Table 5

Plutonium Analyses

(Titrated with 7.791 x 10^{-3}M $Ce(SO_4)_2$ Solution)

Experiment of Table 2

	Sample	titer	blank	concn., un-corrected	concn. corrected for α-particle reduction
Analysis Pu(III)	4.981 ml	2.390 ml	0.135 ml	3.527 x 10^{-3} M	3.535 x 10^{-3} M
	4.981	2.380	0.135	3.512	3.517
	4.981	2.320	0.110	3.457	3.440
				Ave.	3.497 x 10^{-3} M
Analysis total Pu	4.981	3.098	0.110	4.674	4.674 x 10^{-3} M

Experiment of Table 4

	Sample	titer	blank	concn., un-corrected	concn. corrected for α-particle reduction
Analysis Pu(III)	4.981 ml	2.483 ml	0.110 ml	3.712 x 10^{-3} M	3.713 x 10^{-3} M
	4.981	2.498	0.110	3.735	3.736
	4.876	2.307	0.110	3.686	3.684
				Ave.	3.711 x 10^{-3} M
Analysis total Pu	4.981	3.091	0.110	4.663	4.663
	4.981	3.098	0.110	4.674	4.674
				Ave.	4.669 x 10^{-3} M

for the cell reaction

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

at 25.0°C, one atmosphere pressure of hydrogen, 1.00 M $HClO_4$ and equal (and small) concentrations of Pu(III) and Pu(IV). Correction was made for the small amount of disproportionation in each case.

The analysis for Pu(III) was somewhat erratic as shown by the data of Table 5. The variation in the titer was well outside the precision of the analysis, as demonstrated by the iron analyses and the analysis for total plutonium. The cause of this effect is unknown.

Discussion of Fe(II) - Fe(III) Cell Results

From the slope of the E/T curves of Figure 1, values of ΔH of 10.00 and 9.89 kcal. per mole (of iron) for the reaction:

$$Fe^{++} + H^{+} = Fe^{+++} + 1/2\ H_2 \qquad (2)$$

at 25.0°C and in 0.50 M $HClO_4$ are calculated for experiments 1 and 2 respectively. These results agree fairly well, yet appear to differ by about the maximum that would be expected from the precision of the experimental procedure. The EMF readings of the four combinations of electrodes gave readings consistently within 0.1 millivolts of each other. To bring one of the ΔH values into agreement with the other would require an error of 0.2 millivolts in opposite directions at the highest and lowest temperature points of one of the experiments. An error in the temperature reading of 0.1° at one of the extreme temperatures changes the value of ΔH only 30 calories.

Fontana[9,10] has determined the heat of the reaction

$$Fe^{+2} + 1/2\ H_2O_2 + H^{+} = Fe^{+3} + H_2O \qquad (4)$$

in 0.49 M $HClO_4$ at 25°C by direct calorimetric measurement. By combining this value with the heat of decomposition of hydrogen peroxide and the heat of reaction of hydrogen and oxygen to form water, he calculated a value of ΔH for 0.5 M $HClO_4$ at 25°C for the reaction

$$Fe^{++} + H^{+} = Fe^{+++} + 1/2\ H_2 \qquad (2)$$

$$\Delta H = 9.58 \pm 0.12 \text{ kcal/mole}$$

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[9] B. J. Fontana, CC-3482, March 29, 1946.

[10] B. J. Fontana, MB-267, October 18, 1946.

Fontana's measurement of the H_2O_2 - Fe^{++} heat of reaction was made in 0.49 M $HClO_4$ and with an initial Fe^{++} concentration of 0.025 M. Therefore his experiments were carried out under conditions which are similar to those used in the present work and the ΔH values should be comparable. The average value of 9.95 kcal per mole from this work appears to differ from Fontana's result of 9.58 kcal per mole by considerably more than the estimated uncertainty in the two values. It does not seem likely that the slight difference in experimental conditions could account for the discrepancy.

From the two iron experiments of Table 1 an average value of -0.7570 volts is calculated for the reaction

$$Fe^{++} + H^+ = Fe^{+++} + 1/2\ H_2 \qquad (2)$$

at one atmosphere pressure of hydrogen, in 0.504 M $HClO_4$, at 25°C and with equal (and small) concentrations of Fe^{++} and Fe^{+++}. Correcting this value to unit concentration of H^+ one obtains -0.7394 volts for the "formal potential" of the ferrous-ferric electrode under the above conditions. The best data in the literature with which this value may be compared are those of Schumb, Sherrill and Sweetser[11]. These authors measured the equilibrium for the reaction

$$Fe^{++} + Ag^+ = Fe^{+++} + Ag \qquad (5)$$

in perchloric acid at 25°C. Assuming that the activity coefficient of Ag^+ was equal to the activity coefficient of H^+. they calculated values for the formal potential of the reaction of equation (2) at various perchloric acid concentrations. Interpolating their

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[11] W. C. Schumb, M. S. Sherrill and S. B. Sweetser, J. Am. Chem. Soc., 59, 2360 (1937).

data one obtains a value of -0.742 volts which is to be compared with the value of -0.7394 volts calculated from the present work. The two values agree within the accuracy of the determinations since the assumption as to the equality of the activity coefficients of Ag^+ and H^+ could easily introduce an error of several millivolts.

Discussion of the Plutonium Cell Measurements

From the slope of the line of the plot of $\frac{E}{T}$ versus $\frac{1}{T}$ for plutonium in Figure 1, one calculates for the reaction

$$Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$$

$$\Delta H_{298} = 13.52 \text{ kcal/mole Pu} \qquad (3)$$

in 1.00 M $HClO_4$ at 25°C. The precision of the measurements should be equivalent to that already discussed for the iron cell measurements, although the absolute accuracy may be less as would be indicated by the two ΔH values obtained with the iron cell.

From the measurement of the heat of the reaction

$$3\ Pu^{+3} + HCrO_4^{-} + 7\ H^{+} = 3\ Pu^{+4} + Cr^{+3} + 4\ H_2O \qquad (6)$$

in 0.50 M $HClO_4$, determined by Evans[5] by direct calorimetric measurement, and using Fontana's[9,10] values for the heat of the reactions*

$$3\ Fe^{++} + HCrO_4^{-} + 7\ H^{+} = 3\ Fe^{+++} + Cr^{+++} + 4\ H_2O \qquad (7)$$

$$Fe^{++} + H^{+} = Fe^{+++} + 1/2\ H_2 \qquad (2)$$

in 0.5 M $HClO_4$, one calculates for the reaction*

$$Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$$

$$\Delta H_{298} = 11.3 \text{ kcal per mole Pu} \qquad (3)$$

in 0.5 M $HClO_4$ at 25°C. If, instead of Fontana's value for the

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*Actually, under the conditions of the experiment there was considerable $Cr_2O_7^{=}$ present as well as $HCrO_4^{-}$. However, Fontana carried out the measurement of the heat of oxidation of Fe^{++} by $HCrO_4^{-}$ under the same concentration conditions that Evans used for measurement of the heat of oxidation of Pu^{+3} by $HCrO_4^{-}$. The $HCrO_4^{-}$-Fe^{++} heat work by Fontana is as yet unpublished.

heat of the reaction

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

the value for the heat of this reaction obtained in the present work from the iron cell measurements is used, one obtains for reaction (3)

$$\Delta H_{298} = 11.7 \text{ kcal per mole Pu.}$$

The agreement between these values of ΔH and the value of 13.52 kcal per mole obtained in this work from the plutonium cell measurements is only fair. The calorimetric measurements were made in 0.5 M $HClO_4$ while the cell results are for 1.00 M $HClO_4$. However, a rough estimate of the activity coefficient correction in going from 0.50 M $HClO_4$ to 1.00 M $HClO_4$ indicates that the difference in the heats from this source would probably amount to only about 200 calories or less, so it seems unlikely that this is the main source of the difference. The chief uncertainty in the calorimetrically measured value is in Evan's measurement of the heat of oxidation of Pu^{+3} by $HCrO_4^-$. It is not possinle to judge accurately the error, but it appears it could be over one kilocalorie. Therefore the calorimetric value may lie within experimental error of the value of ΔH from cell measurements, which should be correct to within 0.5 kcal.

The values of E_f for the reaction

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

given in Table 2 and Table 4 are -0.9818 volts and -0.9824 volts respectively. These values are for the reaction at one atmosphere pressure of hydrogen, 1.00 M $HClO_4$ and equal (and small) concentrations of Pu(III) and Pu(IV). These values were obtained using an average value for the Pu(III) analysis in each experiment in correcting the ratio of the Pu(III) and the Pu(IV) concentrations to unity. If instead, the highest and lowest values obtained for the Pu(III) concentration (the Pu(IV) concentration still being obtained by difference) were used, E_f values would be obtained differing in the experiment of Table 2 by 0.0028 volts and by 0.0017 volts in the experiment of Table 4.

For the following reaction we then have

$$Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2 \qquad (3)$$
$$E_f = -0.982 \pm 0.001 \text{ volt}$$

the limit of accuracy being set by the accuracy of the Pu(III) analysis.

Using this value for the EMF of the cell and the value of ΔH for the reaction obtained from the plutonium cell measurements, one may calculate ΔF and ΔS for reaction (3). The values for these quantities are listed in Table 6. The value of ΔH obtained by Evans[5] by calorimetric measurement in 0.5 M $HClO_4$ and the value of ΔS calculated from this ΔH and the ΔF from the present work are also given for comparison.

Table 6

Summary of Values for ΔF, ΔH and ΔS at 25°C in 1 M $HClO_4$ at One Atmosphere Pressure of Hydrogen

Reaction: $Pu^{+3} + H^{+} = Pu^{+4} + 1/2\ H_2$

	This work	Evans
ΔF	22.65 kcal per mole Pu	
ΔH	13.5 kcal per mole Pu	11.7 kcal per mole Pu
ΔS	-31 e.u.	-37 e.u.

The EMF data of this work may be combined with the Pu(IV) disproportionation data of Kasha[4] for 1 M $HClO_4$ at 25°C and the heat data of Evans[5] for the oxidation of Pu^{+3} to PuO_2^{++} in 0.5 M $HClO_4$ at 25°C, to obtain thermodynamic quantities for the reaction

$$Pu^{+3} + 2\,H_2O = PuO_2^{++} + 3/2\,H_2 + H^+ \tag{8}$$

The data are given Table 7. No attempt was made to correct Evan's heat data from 0.5 M $HClO_4$ to 1.0 M $HClO_4$.

Table 7

Summary of Values for ΔF, ΔH and ΔS at 25°C in 1 M $HClO_4$ at One Atmosphere Pressure of Hydrogen

Reaction: $Pu^{+3} + 2\,H_2O = PuO_2^{++} + 3/2\,H_2 + H^+$

ΔF	69.84 kcal per mole Pu	Kasha and this work
ΔH	77.8 kcal per mole Pu	Evans
ΔS	+26.6 e.u.	

It is of interest to calculate the entropies of the individual plutonium ions. In order to do this it is necessary to make several assumptions; hence the values are only approximate. For the purpose of these calculations, the entropy of hydrogen ion in 1 M $HClO_4$ was arbitrarily assumed to be zero, and the entropy used for water was that of pure water. Further, using this type of data, it is necessary to know a value of the entropy of one of the oxidation states in order to calculate the other two. A value of the entropy of Pu^{+3} has been estimated by Brewer et al[12] from that of Gd^{+3}, by making corrections for mass and ionic radius effects on the entropy. A correction was made for the magnetic entropy of Gd^{+3} but none for Pu^{+3}, and no correction was made for the fact that the Gd^{+3} entropy was for infinite dilution. The value obtained by Brewer et al is

$S_{Pu^{+3}} = -30.9$ e.u.

Using the value for ΔS of the reaction given in Table 6 one calculates from the following equation

$$S_{Pu^{+4}} + 1/2\ S_{H_2} - S_{Pu^{+3}} - S_{H^+} = -30.6 \text{ e.u.}$$

a value for the entropy of Pu^{+4}:

$$S_{Pu^{+4}} = -77.1 \text{ e.u.}$$

The same type of calculation may be made to obtain the entropy of PuO_2^{++}. The same assumptions are involved here as are involved in calculating the entropy of Pu^{+4} with the further difficulty that the Pu^{+3} - PuO_2^{++} heat data are based on measurements in 0.5 M $HClO_4$. One calculates from the data of Table 7

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[12] L. Brewer, L. Bromley, P. W. Gilles and N. Lofgren, BC-88, October 10, 1947.

$$S_{PuO_2^{++}} = \Delta S + 2\ S_{H_2O} + S_{Pu^{+3}} - S_{H^+} - 3/2\ S_{H_2}$$

$$S_{PuO_2^{++}} = -17.6 \text{ e.u.}$$

The values of the entropies of Pu^{+3}, Pu^{+4} and PuO_2^{++} are summarized in Table 8 and compared with those of U^{+3}, U^{+4} and UO_2^{++} obtained by averaging values given by Brewer et al.[13] and Fontana[14] for U^{+3} and U^{+4}, and the value given by Coulter, Pitzer and Latimer[15] for the entropy of UO_2^{++}. The uranyl value is for infinite dilution while the U^{+3} and U^{+4} values were calculated using assumptions similar to those employed in the calculation of the plutonium entropies. The striking parallelism in the entropy values for uranium and plutonium is much closer than would necessarily be expected because of the many approximations made and the unpredictable behavior of the magnetic entropy of these ions.

Using the value of the Pu^{+3} - Pu^{+4} formal oxidation potential obtained in the present work in 1.00 M $HClO_4$ at 25°C and Kasha's[4] value for the disproportionation equilibrium quotient in 1.00 M $HClO_4$ at 25°C

$$3\ Pu^{+4} + 2\ H_2O = 2\ Pu^{+3} + PuO_2^{++} + 4\ H^+$$

$$K = 0.041$$

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[13] L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, BC-82, April 1, 1947.

[14] B. J. Fontana, BC-66, April 1, 1947.

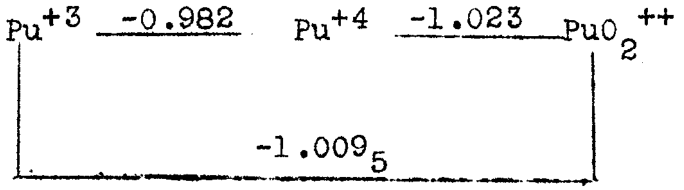
[15] L. V. Coulter, K. S. Pitzer, and W. M. Latimer, J. Am. Chem. Soc., 62 2845 (1940).

Table 8

Entropies of Pu^{+3}, Pu^{+4} and PuO_2^{++} and those of U^{+3}, U^{+4} and UO_2^{++} at 25°C/

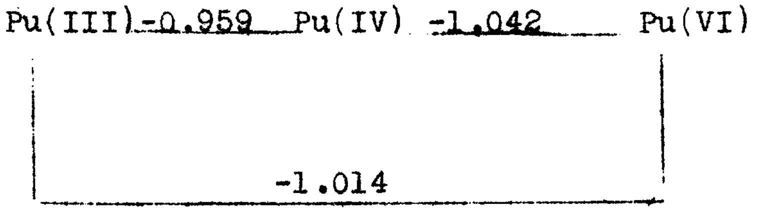
	Oxidation State		
	+3	+4	+6
Pu	-31 e.u.	-77 e.u.	-18 e.u.
U	-31 e.u.	-78 e.u.	-17 e.u.

it is then possible to set up a formal potential scheme for plutonium in 1.00 M $HClO_4$ at 25°C:



It is to be emphasized that these potentials apply to the reaction of the plutonium couple with the hydrogen couple at 25°C in 1 M $HClO_4$ and with the substances involved in the reaction all corrected to unit concentration.

The analogous potential scheme for plutonium in 1.00 M HCl at 25°C may be calculated. From Hindman's[1] measurement of the Pu(III) - Pu(IV) couple versus the Ag - AgCl couple one can calculate the Pu(III) - Pu(IV) formal potential in 1 M HCl, i.e., the potential of the Pu(III) - Pu(IV) couple versus the H_2 - H^+ couple. Using the value of the disproportionation constant of Pu(IV) for 1 M HCl and 25°C, determined by Kasha and Sheline[8], the formal potentials of the Pu(IV) - Pu(VI) and Pu(III) - Pu(VI) couples can be calculated and are shown in the following potential diagram:



It is seen that the Pu^{+3} - Pu^{+4} potential in 1.00 M HCl is more positive than in 1.00 M $HClO_4$. This is to be expected, as mentioned earlier, if Pu^{+4} is complexed by chloride ion. If one assumes (in agreement with the best available information[3]) that Pu^{+3} is not complexed by ClO_4^-, and that $\frac{\gamma_{Pu^{+3}}\,\gamma_{H^+}}{\gamma_{Pu^{+4}}}$ is the same in 1 M perchloric acid as in 1 M hydrochloric acid, one calculates from these data that 59% of the Pu^{+4} is complexed in 1.00 M HCl. This is in good agreement with a value of 66% obtained by Reas[16] from measurements of the activity of $PuCl_4$ in 1.00 M HCl and the activity of $Pu(ClO_4)_4$ in 1.00 M $HClO_4$. In the calculation based on Reas' data it was assumed that $\frac{\gamma_{Pu^{+4}}}{\gamma_{H^+}^4}$ had the same value in 1 M hydrochloric acid as in 1 M perchloric acid.

The above conclusion as to chloride complexing of Pu(IV) in hydrochloric acid is also in qualitative agreement with determinations of chloride complexing by two other methods. The first[17] made use of the exchange equilibrium of Pu(IV) between perchloric and hydrochloric acid solutions and an ion exchange resin. The data indicated approximately 30% complexing by chloride ion in 1 M HCl. In the second method[18] the complexing of Pu(IV) by nitrate ion was compared in hydrochloric acid and perchloric acid solutions. From the interference of chloride ion on the complexing of Pu^{+4} by nitrate ion, it was estimated that about 30% of the Pu(IV) would be complexed by chloride ion in a solution containing 1 M HCl and 1 M $HClO_4$.

By means of a comparison of either the Pu(III) - Pu(VI) or the Pu(IV) - Pu(VI) couples in perchloric acid and in hydrochloric acid it should be possible to draw some conclusions concerning the complexing of PuO_2^{++} by chloride ion. For the purpose of this

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[16] W. H. Reas, unpublished work

[17] L. Myers, E. Conn and B. Ketelle, CN-2819, p 14, May 15, 1945.

[18] J. C. Hindman, PPR, Volume 14B, No. 4.5.

discussion the Pu(III) - Pu(VI) couple will be considered. Since the potential in hydrochloric acid is more negative than in perchloric acid, it would be conclued that Pu^{+3} is more complexed by chloride ion than is PuO_2^{++}. This is not believed to be the case, as there is no other evidence of chloride complexing of Pu^{+3} in 1 M HCl but definite evidence of chloride complexing of PuO_2^{++}[19,3] from studies of the Pu(VI) absorption spectrum.

The value of the Pu(III) - Pu(VI) potential in 1 M HCl depends on the value of the Pu(IV) disproportionation quotient in 1 M HCl as well as the value of the Pu(III) - Pu(IV) potential in 1 M HCl. Since the disproportionation is small in this system, the amount of Pu(VI) formed is very small, i.e., of the order of 2%. The analysis for this amount of Pu(VI) formed in the disproportionation would have to be in error by a factor of ca. 1.7 in order to make the Pu(III) - Pu(VI) potential in 1 M $HClO_4$ more negative than in 1 M HCl. Because of the small amount of Pu(VI) present, an error of this magnitude is not entirely impossible.

Alternatively, the discrepancy may arise from specific activity effects. The ionic strength in each solution was unity, yet the activity coefficients of ions such as Pu^{+4} may not be the same in 1 M $HClO_4$ as in 1 M HCl even if there were no complexing. However it is not believed that a difference as large as is observed could arise from this effect.

Finally, if the directly measured Pu(III) - Pu(IV) potential in either HCl or $HClO_4$ were in error by 4.5 millivolts, the Pu(III)-Pu(VI) potential in both systems could be equal. This would correspond to an error in the ratio of concentration of

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[19] M. Kasha and G. E. Sheline, CN-2680, January, 1945.

Pu(III) to Pu(IV) in the EMF determination of 20%, if the entire error were assumed to be in this ratio. An error of 5 millivolts seems a little too large, so this is probably the least likely explanation for the observed results.

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