face and interfacial tension methods in studying the nature of reactions in solution.

Kolthoff and Lingane[18] point out that the rate of flow of a given amount of mercury from a set capillary under a constant pressure head on the dropping mercury and at constant temperature is practically independent of the medium in which the drop forms. The drop time, however, is directly proportional to the interfacial tension at the mercury–medium interface. In the present results both quaternary salts and the dyes employed influence the mercury–medium interfacial tension. This is the basis for calling the drop time results here "effective" interfacial tension measurements.

Pronounced changes in the "effective" mercury–medium interfacial tension have been observed in polarographic work when surface-active substances are present. Damping and shifting of polarographic waves seem to accompany these changes. This phenomenon has been made[19,20] the basis for quantitative determinations of surface-active substances by polarographic adsorption analyses. Recent results[21] explain the nature of the adsorption phenomenon.

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[18] Kolthoff and Lingane, *Chem. Revs.*, **24**, 1 (1939).

[19] Schwartz, Shroder and Stackelberg, *Z. Elektrochem.*, **48**, 6 (1942).

[20] Stackelberg and Schutz, *Kolloid-Z.*, **105**, 20 (1943).

[21] Colichman, THIS JOURNAL, **72**, 4036 (1950).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AND RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

Oxidation Potentials of the Pu(III)–Pu(IV) and Fe(II)–Fe(III) Couples in Perchloric Acid Solution—Heat Content and Entropy Changes[1]

BY ROBERT E. CONNICK AND WILLIAM H. MCVEY

The formal potential of the cell: Pt:H_2:1 *M* $HClO_4$; 1 *M* $HClO_4$, $Pu(ClO_4)_3$, $Pu(ClO_4)_4$: Au was found to be −0.982 volt at 25°. This value differs significantly from that previously reported and is consistent with the idea that Pu^{+4} is partially complexed by chloride ion in 1 *M* HCl. A formal potential scheme involving the +3, +4 and +6 oxidation states of plutonium in 1 *M* perchloric acid was derived. The e.m.f. was measured as a function of temperature and the change in heat content for the reaction $Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2$ was found to be +13.52 kcal./mole, compared with 11.3 kcal./mole obtained by Evans from calorimetric measurements. Approximate entropies for the ions Pu^{+4} and PuO_2^{++} were found to be −77 and −18 e.u., respectively. These are very nearly equal to those for the corresponding ions of uranium. The heat and free energy of the reaction $Fe^{++} + H^+ = Fe^{+++} + {}^1/_2H_2$ were measured and compared with previously determined values.

Introduction

The oxidation potential of the couple $Pu^{+3} = Pu^{+4} + e^-$ has been reported by Hindman, *et al.*,[2,3,4] to be −0.945 volt in 1 *M*[5] perchloric acid and −0.966 volt in 1 *M* hydrochloric acid at 25°. These potentials can differ appreciably[6] 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 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 does not form complexes with Pu^{+3} and Pu^{+4}.[7] 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.[7] If it is assumed that the potentials in perchloric acid and hydrochloric acid solution differ primarily because of chloride complexing of Pu(IV), the potential for perchloric acid should be more negative. Just the opposite has been reported in the above cited work.

It was believed that the error, if it existed, lay in the perchloric acid data as the hydrochloric acid measurements were very carefully performed.

Further evidence that the perchloric acid measurement might be in error came from combining the value of −1.067 volts given by Hindman[2] for the Pu(IV)–Pu(VI) couple in 1 *M* perchloric acid with the Pu(III)–Pu(IV) potential to give −0.122 volt for the reaction

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

in 1 *M* perchloric acid at 25°. From this datum one calculates a value of 8×10^{-5} for the equilibrium quotient expressed in terms of gross concentrations

$$K = (Pu(VI))(Pu(III))^2/(Pu(IV))^3$$

where parentheses are used to indicate concentrations in moles per liter of solution at 25°. This value, however, is in disagreement with the directly measured value which Kasha[8] found to be K = 0.041.

In repeating the e.m.f. measurements in perchloric acid it seemed desirable to extend the determinations to other temperatures in order to obtain the heat and entropy of the reaction. Evans[9] had previously measured the heat of oxidation of Pu^{+3} to Pu^{+4} calorimetrically.

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[1] Research performed under the auspices of the United States Atomic Energy Commission.

[2] J. C. Hindman, Manhattan District Project Report CN-2289, p. 1, November 1, 1944.

[3] J. J. Howland, Jr., K. A. Kraus and J. C. Hindman, Manhattan District Project Report CN-1371, p. 8, March 1, 1944.

[4] J. J. Howland, Jr., J. C. Hindman and K. A. Kraus, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, p. 133.

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

[6] The liquid junction potentials present in the cell measurements could not possibly account for the reported difference in the potential in 1 *M* $HClO_4$ and 1 *M* HCl.

[7] J. C. Hindman, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, p. 370.

[8] M. Kasha, *ibid.*, p. 295.

[9] M. W. Evans, *ibid.*, p. 282.

Experimental

The potential of the Pu(III)–Pu(IV) couple in 1 *M* $HClO_4$ was determined by measuring the e.m.f. of the cell

$$\text{Pt}:\text{H}_2:1\ M\ \text{HClO}_4:1\ M\ \text{HClO}_4,\ \text{Pu(ClO}_4)_3,\ \text{Pu(ClO}_4)_4:\text{Au}$$

This cell had essentially no liquid junction as the concentration of plutonium was always small. Measurements were made of the potential of the reaction

$$\text{Fe}^{++} + \text{H}^{+} = \text{Fe}^{+++} + {}^1/_2\text{H}_2 \qquad (2)$$

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

Preparation of Solutions.—Plutonium(IV) hydroxide is extremely difficult to dissolve in perchloric acid without the formation of colloidal material. To circumvent this difficulty the plutonium was oxidized to the +6 state by bromate at 100° and precipitated as barium plutonate by the addition of barium hydroxide. The precipitate was washed with a barium hydroxide solution and dissolved in 1 *M* perchloric acid. The precipitation procedure was twice repeated. The solid was dissolved to give a solution 1.00 *M* in perchloric acid. 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) (see equation 1). The total plutonium concentration used in the experiment was 4.67×10^{-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 was 9.20×10^{-3} *M*.

Perchloric acid solutions were prepared by diluting G. Frederick Smith double vacuum distilled 12 *M* perchloric acid with conductivity water. They were standardized by the mercuric oxide–potassium iodide method.[10]

The Cell.—The cell arrangement was essentially that described by Sherrill and Haas,[11] except that the conventional 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 plutonium (or iron) compartment. The two half 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 presaturating the hydrogen gas with water vapor from a perchloric acid solution of the same composition 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 were platinized in the usual manner in a chloroplatinic acid solution at a low current density. When the system had been thoroughly swept out with hydrogen gas the two electrodes usually agreed to within 0.02 millivolt.

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, for the purpose of removing oxygen from this part of the cell and affording some stirring of the solution.

Electrodes of very pure, shiny gold gave potential readings within 0.02 millivolt of each other; very pure, platinum electrodes behaved similarly. With less pure gold and platinum, erratic results were obtained. The electrodes were cleaned with carbon tetrachloride vapor.

The cell was immersed in an oil thermostat; 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 them. During most of the experiments, measurements of the potential of the cell were taken at 5° intervals from 10 to 35°. The potential measurements were continued at a particular temperature until the potential reading had remained constant for a period of 30 minutes or more.

A standard electrical circuit was used. The readings were made with a Rubicon High Precision Type B potentiometer, which could be read to 0.02 millivolt.

Analyses.—The analysis of both the iron and plutonium[12] solutions were made 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[12] 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 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 correction, which 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 these ratios are needed for the calculation of potentials.

Results

The data from two duplicate experiments on the iron–hydrogen cell, are presented in Table I. The e.m.f. values listed in the second and third columns are the directly measured e.m.f.'s for the cell corrected to one atmosphere pressure of hydrogen. Correction was made for the barometric pressure, water vapor pressure and hydrostatic pressure in the bubblers and inside the cell.

TABLE I

E.M.F. 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 $2.658 \times 10^{-3}M$ $Fe(ClO_4)_2$, $6.545 \times 10^{-3}M$ $Fe(ClO_4)_3$, 0.5036 *M* $HClO_4$

	Temp., °C.	E.m.f.[a]	E.m.f./*T* × 10³	1/*T* × 10³
Expt. 1	25.18	0.78026	2.6153	3.3520
	10.96	.76404	2.6891	3.5198
	17.95	.77218	2.6525	3.4352
	34.97	.79193	2.5701	3.2455
Expt. 2	24.96	.78014	2.6169	3.3540
	19.96	.77410	2.6409	3.4112
	14.96	.76803	2.6657	3.4709
	9.96	.76204	2.6916	3.5323
	24.96	.78009	2.6167	3.3540
	29.96	.78590	2.5927	3.2994
	34.97	.79176	2.5696	3.2459
	24.96	.77998	2.6163	3.3540

$Fe^{+2} + H^{+} = Fe^{+3} + {}^1/_2H_2$; 25.0°, 1 atm. H_2, equal (and small) concn. Fe^{++} and Fe^{+++}, corrected to unit concentration of H^+.

	Expt. 1	Expt. 2
$\Delta H =$	10.00 kcal./mole	9.89 kcal./mole
$Ef =$	−0.7395 volt	−0.7393 volt

[a] E.m.f. corrected to 1 atm. H_2 pressure.

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

$$\left(\frac{\partial \text{E}/\text{T}}{\partial 1/\text{T}}\right)_{\text{P}} = -\frac{\Delta H}{nF}$$

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(10) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience Publishers, Inc., New York, N.Y., 1947.

(11) M. S. Sherrill and A. J. Haas, Jr., THIS JOURNAL, 58, 952 (1936).

(12) C. W. Koch, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, Vol. 14B p. 1337

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 E/T of Table I have been plotted against $1/T$ in Fig. 1. In each case a straight line has been drawn tangent to the curve of the points at 25°. 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°, 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.

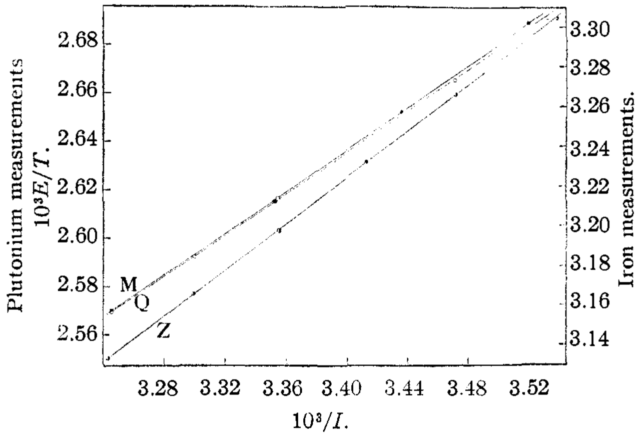

Fig. 1.—Plots of E/T *versus* $1/T$ for iron and plutonium cells: ●, and ○, iron data, curves M and Q; ◑, plutonium data, curve Z.

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°. The data for the first series are given in Table II. The first column gives the time at which the e.m.f. reading was recorded. The third column lists the experimentally measured e.m.f. 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.

TABLE II

E.M.F. 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, hr.	Temp., °C.	E.m.f. of cell corrected to one atm. H_2	E.m.f. at one atm. H_2, corrected for α-particle reduction	From preceding col.: e.m.f./T × 10^3	$10^3/T$
0	9.41	0.93375	0.93375	3.3045	3.5389
1	14.92	.94076	.94092	3.2662	3.4713
2	19.92	.94698	.94721	3.2319	3.4120
3	24.94	.95307	.95339	3.1982	3.3546
4	29.96	.95925	.95964	3.1659	3.2990
5	35.01	.96518	.96564	3.1335	3.2450
6	24.94	.95261	.95315	3.1974	3.3546

$Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2$; 25.0°, 1.00 M $HClO_4$, 1 atm. H_2, equal (and small) concn. Pu^{+3} and Pu^{+4}; ΔH = 13.52 kcal. per mole; E_f = **−0.9818** volt.

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° corresponds to a decrease in average oxidation number of 0.0128 per day according to measurements of Kasha.[8] This figure was checked in the present work by comparison of e.m.f. values for the two 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 II are the e.m.f. values corrected to one atmosphere hydrogen pressure and corrected for the reduction caused by alpha particles relative to the first e.m.f. reading. It was assumed that the rate of reduction by alpha particles is temperature independent.

Consideration must be given to the correction for the disproportionation of Pu(IV) to Pu(III) and Pu(VI) according to eq. (1). The plutonium solution had stood sufficiently long at 25° before the start of each experiment to allow this equilibrium to be established. The concentration of Pu(IV) was kept small relative to that of Pu(III) in order to minimize the extent of this reaction. From the value of K for eq. (1) in 1 M $HClO_4$ at 25°[8] and using the heat data obtained in the present work and the heat of oxidation of Pu(III) to Pu(VI) measured by Evans,[9] one can calculate approximately the extent of disproportionation at equilibrium for each of the temperatures of Table II. The correction to the e.m.f. amounts to 0.0027, 0.00042 and 0.00002 volt at 35, 25 and 9.5°, respectively, if equilibrium is attained at each temperature. Actually this appears not to be the case. From the data of Kasha[8] one estimates that only 0.07% of the Pu(IV) would disproportionate per hour at 25°. Thus at 25° 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 by the difference in the e.m.f. at 25° before and after heating to 35°. The cell was rapidly cooled from 35 to 25° so that there was no chance for appreciable reproportionation to take place. It is seen from Table II that the two values are actually quite close to each other and the small difference of 0.2 millivolt is in the direction to be expected for the above correction.[13] It is possible, therefore, that the e.m.f. measured at 35° should be increased *ca.* 0.2 millivolt to correspond to the measurements at lower temperatures. Presumably the 30° point would be raised something less than 0.1 millivolt. In any case these corrections are small and should not affect the calculation of ΔH seriously.

[13] 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 of such a temperature effect on this rate under other conditions (M. Kasha and G. E. Sheline, *ibid.*, p. 220).

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 correction raises or lowers all points of the E/T *versus* $1/T$ curve the same amount and only the slope is used in the calculation. The correction was made in calculating the formal potential, E_f,[14] given in Table II.

The purpose of the second experiment with plutonium was to obtain a precise value for the e.m.f. of the Pu(III)–Pu(IV) couple *versus* the H_2–H^+ couple in 1 M $HClO_4$ at 25°. The e.m.f. was measured for a considerable period of time at constant temperature (see Table III). The alpha particle correction was made arbitrarily to a time of 252 minutes after the first e.m.f. reading. From the data it is seen that the potential was very steady during a period of over 3 hours.

TABLE III

E.M.F. 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°

$3.71 \times 10^{-3} M$ $Pu(ClO_4)_3$, $0.96 \times 10^{-3} M$ $Pu(ClO_4)_4$, 0.998 M $HClO_4$

Time (min.)	E.m.f. of cell corrected to one atm. H_2, volt	E.m.f. of cell at one atm. H_2, corrected for α-particle reduction, volt
0	0.94766	0.94736
42	.94770	.94745
65	.94763	.94741
86	.94761	.94741
107	.94760	.94742
136	.94758	.94744
162	.94754	.94743
192	.94746	.94739
		Av. 0.94741

$Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2$; 25.0°, 1.00 M $HClO_4$, 1 atm. H_2, equal (and small) concn. Pu^{+3} and Pu^{+4}; $E_f = -0.9824$ volt.

The titration data for the analysis of Pu(III) and Pu(IV) for both plutonium experiments are given in Table IV. 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 Table II and III were calculated for the cell reaction

$$Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2 \qquad (3)$$

at 25.0°, 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 IV. 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.

TABLE IV

PLUTONIUM ANALYSES

TITRATION WITH 7.791×10^{-3} M $Ce(SO_4)_2$ SOLUTION

Experiment	Total Pu × $10^{-3}M$	Pu(III)[a] × $10^{-3}M$
Table II	4.674	3.535
		3.517
		3.440
		Av. 3.497
Table III	4.663	3.713
	4.674	3.736
		3.684
		Av. 3.711

[a] Corrected for α-particle reduction.

Discussion of Fe(II)–Fe(III) Cell Results.—From the slope of the E/T curves of Fig. 1, values of ΔH of 10.00 and 9.89 kcal. per mole (of iron) for reaction (2) at 25.0° 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 four combinations of electrodes gave readings consistently within 0.1 millivolt of each other. To bring one of the ΔH values into agreement with the other would require an error of 0.2 millivolt 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[15] has determined the heat of the reaction

$$Fe^{+2} + {}^1/_2H_2O_2 + H^+ = Fe^{+3} + H_2O \qquad (4)$$

in 0.49 M $HClO_4$ at 25° 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 $\Delta H = 9.53 \pm 0.12$ kcal./mole iron for reaction (2) at 25° and for 0.5 M $HClO_4$. Fontana's measurement of the H_2O_2–Fe^{++} heat of reaction was made with an initial Fe^{++} concentration of 0.025 M. These conditions 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 9.53 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 I an average value of -0.7570 volt is calculated for reaction (2) at one atmosphere pressure of hydrogen, in 0.504 M $HClO_4$, at 25° and with equal (and small) concentrations of Fe^{++} and Fe^{+++}. Correcting to unit concentration of H^+ one obtains -0.7394 volt 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[16] who measured the equilibrium

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

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[14] 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.

[15] B. J. Fontana, "The Chemistry and Metallurgy of Miscellaneous Materials," National Nuclear Energy Series, Division IV, Plutonium Project Record, Vol. 19B, McGraw-Hill Book Co., Inc., 1950, p. 321.

[16] W. C. Schumb, M. S. Sherrill and S. B. Sweetser, THIS JOURNAL, **59**, 2360 (1937).

in perchloric acid at 25°. Assuming that the activity coefficient of Ag^+ was equal to the activity coefficient of H^+, they calculated values for the formal potential of eq. (2) at various perchloric acid concentrations. Interpolating their data one obtains −0.742 volt which is to be compared with the −0.7394 volt 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 plot of E/T *versus* $1/T$ for plutonium in Fig. 1, one calculates for reaction (3)

$$\Delta H_{298} = 13.52 \text{ kcal./mole Pu}$$

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

From the measurement of the heat of the reaction

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

in 0.50 M $HClO_4$, determined by Evans[9] by direct calorimetric measurement, and using Fontana's[15,17] values for the heats of reaction (2) and the reaction

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

in 0.5 M $HClO_4$, one calculates for reaction (3)

$$\Delta H_{298} = 11.3 \text{ kcal. per mole Pu}$$

in 0.5 M $HClO_4$ at 25°. If, instead of Fontana's value for the heat of reaction (2) the value obtained in the present work from the iron cell measurements is used, one obtains for reaction (3) $\Delta H_{298} = 11.7$ 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 correction 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 discrepancy. The chief uncertainty in the calorimetrically measured value is in the heat of oxidation of Pu^{+3} by $HCrO_4^-$. It is not possible 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 reaction (3) given in Table II and Table III are −0.9818 and −0.9824 volt, respectively. They are for one atmospheric pressure of hydrogen, 1.00 M $HClO_4$ and equal (and small) concentrations of Pu(III) and Pu(IV). The average value for the Pu(III) analysis in each experiment was used 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 II by 0.0028 volt and by 0.0017 volt in the experiment of Table III.

For reaction (3) we then have

$$E_f = -0.982 \pm 0.001 \text{ volt}$$

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

Using this value for the e.m.f. of the cell and ΔH for the reaction obtained from the plutonium cell measurements, one calculates the values of ΔF and ΔS for reaction (3) shown in Table V. The value of ΔH obtained by Evans[9] by calorimetric measurement in 0.5 M $HClO_4$ and of ΔS calculated from this ΔH and the ΔF from the present work are also given for comparison.

TABLE V

SUMMARY OF VALUES FOR ΔF, ΔH AND ΔS AT 25° IN 1 M $HClO_4$ AT ONE ATMOSPHERE PRESSURE OF HYDROGEN FOR THE REACTION $Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2$

	This work	Evans
ΔF, kcal. per mole Pu	22.65	
ΔH, kcal. per mole Pu	13.5	11.7
ΔS, e.u.	−30.6	−37

The e.m.f. data of this work may be combined with the Pu(IV) disproportionation data of Kasha[8] for 1 M $HClO_4$ at 25° and the heat data of Evans[9] for the oxidation of Pu^{+3} to PuO_2^{++} in 0.5 M $HClO_4$ at 25°, to obtain thermodynamic quantities for the reaction

$$Pu^{+3} + 2H_2O = PuO_2^{++} + {}^3/_2H_2 + H^+ \quad (8)$$

The values of ΔF, ΔH and ΔS for 25°, 1 M perchloric acid and one atmosphere of hydrogen are 69.84 kcal. per mole Pu, 77.8 kcal. and +26.6 e.u., respectively. No attempt was made to correct Evans' heat data from 0.5 to 1.0 M $HClO_4$.

Entropies of Plutonium Ions.—It is of interest to calculate the entropies of the individual plutonium ions. 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. It is necessary to know a value of the entropy of one of the ions in order to calculate the other two. The entropy of Pu^{+3} has been estimated by Brewer, *et al.*,[18] 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. With these approximations $S_{Pu^{+3}} = -30.9$ e.u. Combining this value with ΔS in the second column of Table V and the entropy of hydrogen gas gives $S_{Pu^{+4}} = -77$ e.u. Similarly, using the data of reaction (8), the entropy of PuO_2^{++} is found to be −18 e.u.

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[17] 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.

[18] L. Brewer, L. Bromley, P. W. Gilles and N. Lofgren, U. S. Atomic Energy Commission Declassified Report AECD 2661.

In Table VI the entropies of Pu^{+3}, Pu^{+4} and PuO_2^{++} are compared with those of the corresponding uranium ions. The data for U^{+3} and U^{+4} were obtained by averaging the values given by Brewer, *et al.*,[19] and Fontana[20]; the value for UO_2^{++} is from the work of Coulter, Pitzer and Latimer.[21] 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.

TABLE VI

ENTROPIES OF Pu^{+3}, Pu^{+4}, PuO_2^{++}, U^{+3}, U^{+4} AND UO_2^{++} AT 25°

Oxidation state	Entropy, e.u. +3	+4	+6
Pu	−31	−77	−18
U	−31	−78	−17

Formal Potential Scheme.—By combining the formal oxidation potential of the Pu^{+3}–Pu^{+4} couple with Kasha's value of the equilibrium constant of eq. (1), one obtains the potential scheme

$$Pu^{+3} \xrightarrow{-0.982} Pu^{+4} \xrightarrow{-1.023} PuO_2^{++} \qquad \underbrace{Pu^{+3} \quad\quad PuO_2^{++}}_{-1.009_5}$$

It is to be emphasized that these potentials apply to the reaction of the plutonium couple with the hydrogen couple at 25° 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° may be calculated. From Hindman's[3] 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 at 25°, determined by Kasha and Sheline,[22] the formal potentials of the Pu(IV)–Pu(VI) and Pu(III)–Pu(VI) couples can be obtained and are shown in the potential diagram

$$Pu(III) \xrightarrow{-0.959} Pu(IV) \xrightarrow{-1.042} Pu(VI) \qquad \underbrace{Pu(III) \quad\quad Pu(VI)}_{-1.014}$$

Chloride Complexing.—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 if Pu^{+4} is complexed by chloride ion. If one assumes (in agreement with the best available information[7]) that Pu^{+3} is not complexed by ClO_4^- or Cl^-, Pu^{+4} is not complexed by ClO_4^- and $(\gamma_{Pu^{+4}}\gamma_{H^+})/(\gamma_{Pu^{+3}})$ 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[23] 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 $\gamma_{Pu^{+4}}/\gamma_{H^+}$ 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[24] 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[25] 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 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 concluded 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^{++}[26,7] 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 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)

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[19] L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, U. S. Atomic Energy Commission Declassified Report MDDC-1543, September 20, 1945.

[20] B. J. Fontana, University of California Radiation Laboratory Report, BC-66, April 1, 1947 (declassified).

[21] L. V. Coulter, K. S. Pitzer and W. M. Latimer, THIS JOURNAL, **62**, 2845 (1940).

[22] M. Kasha and G. E. Sheline, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, p. 180.

[23] W. H. Reas, unpublished work, this Laboratory.

[24] L. Myers, E. Conn and B. Ketelle, Manhattan Project Report CN-2819, p. 14, May 15, 1945.

[25] J. C. Hindman, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 388.

[26] R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, *ibid.*, p. 559.

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 Pu(III) to Pu(IV) in the e.m.f. determination of 20%, if the entire error were assumed to be in this ratio. An error of 4.5 millivolts seems too large, so this is probably the least likely explanation for the observed results.

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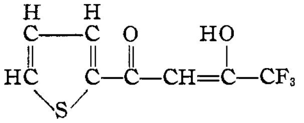
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Activity Coefficient of Thenoyltrifluoroacetone in Benzene Solution[1]

BY EDWARD L. KING[2] AND WILLIAM H. REAS[3]

The activity coefficient of thenoyltrifluoroacetone in benzene solution has been determined by a study of the distribution of thenoyltrifluoroacetone between benzene and aqueous solutions. This activity coefficient may be calculated by using the empirical equation, $y_B = 1 - 0.24(TTA)_B^{0.48}$, which represents the experimental data quite well. The activity coefficients are required data in the interpretation of metal ion extraction studies in which this substance is used as the chelating agent.

The distribution of metal ions between an aqueous solution and an organic solvent containing a derivative of acetylacetone is useful for the separation of metals from one another as in the work on zirconium and hafnium by Huffman and Beaufait[4] and Larsen and Schultz.[5] Fundamental data on complex ion and hydrolysis equilibria involving metal ions as in the work on zirconium by Connick and McVey[6] may also be obtained from distribution studies. If, in such studies, the concentration of the chelating agent is varied, its activity coefficient may vary in one or both phases. If this is the case, the variation in the activity coefficient must be known before the metal ion distribution coefficient data can be interpreted in anything more than qualitative terms. The derivative of acetylacetone which has been studied in the present work is thenoyltrifluoracetone; this was first prepared by Reid and Calvin.[7] This compound, hereafter referred to as TTA, is a weak acid having the following structure in the enol form



The purpose of the present work was to determine the activity coefficient of TTA in its benzene solutions.

The equilibrium which is established when TTA is distributed between an aqueous solution and a benzene solution may be represented by the equation

$$\text{TTA (in water)} = \text{TTA (in benzene)}$$

for which the equilibrium constant is

$$K = (TTA)_B y_B/(TTA)_W y_W$$

where $(TTA)_B$ and $(TTA)_w$ are the concentrations of TTA in moles per liter of solution in the benzene and water phases, respectively. The y_B and y_W are the activity coefficients of TTA in benzene and water. Defining the distribution coefficient, D, as $D = (TTA)_B/(TTA)_W$ it is seen that $K = Dy_B/y_W$. Since the distribution coefficient is approximately 40, it would be expected that variations in the activity coefficient of TTA in the benzene phase would become appreciable under concentration conditions for which the activity coefficient of the TTA in the aqueous phase in equilibrium is unity. This assumption that y_W is unity in the aqueous phase is supported on the findings of Saylor, Stuckey and Gross[8] who have measured the Henry's law constants for benzene, ethylene dichloride and diethyl ketone in aqueous solution by direct vapor pressure measurements. It was found that the first two substances obeyed Henry's law over the concentration ranges studied, that is, up to concentrations of 0.024 and 0.091 mole/1000 g. water, respectively. The Henry's law constant for diethyl ketone started to deviate at concentrations above 0.4 mole/1000 g. water. It seems reasonable, therefore, to assume that Henry's law is obeyed by TTA in water solution up to a concentration of 0.03 mole/liter, the highest concentration studied here. If the activity coefficient for the TTA in the benzene phase is chosen as unity in the infinitely dilute solution, the activity coefficient at a concentration c is given by the equation $(y_B)_c = D_0/D_c$ where D_0 and D_c are the distribution coefficients at infinite dilution and the concentration c in the benzene phase, respectively.

Experimental Work.—The distribution coefficient of TTA between benzene and a 0.115 M HCl solution has been determined at various concentrations of TTA. Experiments were carried out by shaking in sealed containers known volumes of a benzene solution of TTA and an aqueous solution in a thermostat at 25.0°. As is described elsewhere,[9] the behavior in short time distribution experiments is unusual. In the experiments described here aliquots were removed at various times until equilibrium was established. This generally requires less than 4 days.

The TTA used in this experimental work was prepared and purified (by vacuum distillation) by Dr. J. C. Reid. Reagent grade thiophene free benzene was used. The standard solutions of TTA were prepared by dissolving weighed quantities of dry TTA in benzene or dilute aqueous acid.

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[1] This research was carried out in the Radiation Laboratory and the Chemistry Department of the University of California under the auspices of the Manhattan District, Corps of Engineers during 1945 and 1946.

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[3] General Electric Company, Hanford Works, Richland, Washington.

[4] E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[5] E. M. Larsen and B. Schultz, *ibid.*, **72**, 3610 (1950).

[6] R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

[7] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

[8] Saylor, Stuckey and Gross, *ibid.*, **60**, 373 (1938).

[9] E. L. King and W. H. Reas, *ibid.*, **73**, 1806 (1951).