[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Thermodynamic Functions and Formal Potentials of the Plutonium(V)–(VI) Couple[1]

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The formal potential of the PuO_2^+–PuO_2^{+2} couple has been determined by potentiometric titrations of plutonyl ion with I^- and with Pu^{+3} as reducing agents. A value of −0.9164 ± 0.0002 volt was obtained for this couple in molar perchloric acid at 25.00°. The equilibrium quotient, $(Pu^{+3})(PuO_2^{+2})/(Pu^{+4})(PuO_2^+)$, was calculated to be 12.8 ± 0.4 in molar perchloric acid at 25.00° from the difference between the formal potentials of the Pu^{+3}–Pu^{+4} and the PuO_2^+–PuO_2^{+2} couples. The formal potential of the PuO_2^+–PuO_2^{+2} couple has been measured as a function of temperature between 6 and 25° in molar perchloric acid from which the thermodynamic quantities for the reaction, $PuO_2^+ + H^+ \rightleftarrows PuO_2^{+2} + {}^1/_2H_2$, have been found to be: $\Delta F = 21.13$ kcal./mole, $\Delta H = 22.9$ kcal./mole and $\Delta S = 5.9$ e.u. Thus the entropy difference, $\bar{S}_{PuO_2^{+2}} - \bar{S}_{PuO_2^+}$, was calculated to be −9.7 e.u. and the entropy of the PuO_2^+ ion is −19.2 e.u. since from studies of the temperature dependence of the disproportionation of Pu^{+4} and of the temperature dependence of the Pu^{+3}–Pu^{+4} couple the entropy of the PuO_2^{+2} ion has been calculated to be −28.9 e.u. A formal potential diagram of the plutonium couples in molar perchloric acid at 25° has been obtained.

Introduction

No direct measurements of the PuO_2^+–PuO_2^{+2} couple in molar perchloric or in molar hydrochloric acid appear to have been made previously; however, Connick[2] estimated a value of −0.925 v. for this couple in molar perchloric acid from the Pu^{+3}–Pu^{+4} formal potential and from the spectrophotometric data of Kasha[3] relating to the equilibrium, $Pu^{+4} + PuO_2^+ \rightleftarrows Pu^{+3} + PuO_2^{+2}$. The PuO_2^+ ion is unstable with respect to disproportionation in solutions of high acidity; the region of optimum stability appears to be at a *p*H of about 3.5.[4] Kraus and Moore[5] obtained a value of −0.935 ± 0.015 volt for the PuO_2^+–PuO_2^{+2} couple in perchloric acid at a *p*H of about 3 at 25°. Although this couple is virtually hydrogen ion independent between a *p*H of zero and three, the effect of ionic strength is probably not zero.

In the present work, plutonyl solutions of known concentrations were prepared by the ozonization of Pu^{+3} in perchloric acid. The reduction of PuO_2^{+2} to PuO_2^+ was accomplished with I^- and also with Pu^{+3}. The potentiometric titrations of the plutonyl ion were performed with sufficient rapidity to avoid the complications which would arise from the disproportionation of PuO_2^+.

Experimental

The experimental apparatus has been described in a previous communication.[6] Weight burets were used to add the reducing agents to the plutonyl solutions. The temperature of the plutonium solutions was maintained within ±0.01° during the course of an experiment, and was obtained from measurements of the resistance of a type 20D Western Electric thermistor which was calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The hydrogen for the hydrogen electrode was electrolytic grade purified by passing it through a uranium furnace heated to 600°. An atmosphere of helium was maintained over the plutonium solutions. The helium was passed over heated copper and both gases were saturated with water vapor at the cell temperature to minimize concentration changes because of evaporation. The plutonyl solutions were prepared by the ozonization of Pu^{+3} solutions of known concentrations. The latter were prepared by dissolving a known weight of oxide-free metal in a weighed quantity of standardized 71% Mallinckrodt reagent grade perchloric acid. Water redistilled from alkaline permanganate was used in the preparation of all solutions. Dissolved ozone was removed from the plutonyl solutions by bubbling helium through the solutions for about 15 minutes; the solutions were then used immediately to avoid changes in the plutonyl ion concentration as a result of the alpha reduction process.

Results and Discussion

The earlier[5] direct measurements of the PuO_2^+–PuO_2^{+2} couple in solutions of low acidity included rather large uncertainties because of the unknown liquid junction potentials. In the present work the liquid junction potential has been made essentially zero. The formal potential of the PuO_2^+–PuO_2^{+2} couple was obtained from measurements of the potential of the cell, Pt; PuO_2^+, PuO_2^{+2}, $HClO_4(c_1)$; $HClO_4(c_1)$; H_2, Pt. The total plutonium concentration was usually about 0.001 *M*.

Reduction with Sodium Iodide.—In the titration of PuO_2^+ with sodium iodide, the concentration of PuO_2^+ and the $[PuO_2^{+2}]/[PuO_2^+]$ ratio were determined from the stoichiometry of the reaction, $PuO_2^{+2} + I^- \rightarrow PuO_2^+ + 1/2I_2$. The results of a titration of plutonyl ion with sodium iodide in molar perchloric acid are given in Table I.

TABLE I

THE DETERMINATION OF THE PuO_2^+–PuO_2^{+2} FORMAL POTENTIAL BY REDUCTION OF PLUTONYL ION WITH SODIUM IODIDE IN 1 *M* $HClO_4$ AT 25°

Wt. of NaI, mg.	PuO_2^+, %	$[PuO_2^{+2}]/[PuO_2^+]$	0.05915 log $[PuO_2^{+2}]/[PuO_2^+]$	E_{cell}	$E^{0\prime}$
0.000	0.000	...	...	...	...
1.932	3.296	29.34	0.08680	−0.99951	−0.91659
3.049	5.206	18.21	.07455	.98708	.91641
4.123	7.037	13.21	.06630	.97889	.91647
5.177	8.834	10.32	.05995	.97260	.91653
6.124	10.608	8.43	.05476	.96721	.91633
7.235	12.350	7.10	.05034	.96300	.91654
8.264	14.104	6.09	.04641	.95904	.91651

Total moles of Pu = 3.908×10^{-4} Mean −0.9165 ± 0.0001

In agreement with the observations of Kraus and Moore,[5] after each addition of sodium iodide some time was required before a stable potential reading was obtained. Essentially constant cell potential values were found within two minutes after each

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[1] This work was done under the auspices of the Atomic Energy Commission. Presented before the Division of Physical and Inorganic Chemistry at the 129th meeting of The American Chemical Society, Dallas, Texas, April 12, 1956.

[2] R. E. Connick, "The Actinide Elements," Natl. Nuclear Energy Ser., IV, **14A**, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, p. 234.

[3] M. Kasha, "The Transuranium Elements," Natl. Nuclear Energy Ser., IV, 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 310.

[4] L. H. Gevantman and K. A. Kraus, ref. 3, p. 500.

[5] K. A. Kraus and G. E. Moore, ref. 3, p. 550.

[6] S. W. Rabideau, THIS JOURNAL, **75**, 798 (1953).

addition of sodium iodide. From the consistency of the $E^{0\prime}$ values in Table I it appears that the slowness in obtaining a stable potential was not because of the disproportionation of PuO_2^+. Either the reduction reaction is slow, or some time is required for equilibrium to be established at the platinum electrode. A value of -0.0039 volt has been applied to the $E^{0\prime}$ values of Table I for the barometric pressure correction of the hydrogen electrode.

Reduction with Pu^{+3}.—In the titrations of plutonyl ion in which Pu^{+3} was used as the reductant, the stoichiometry of the rapid equilibrium reaction, $PuO_2^{+2} + Pu^{+3} \rightleftarrows Pu^{+4} + PuO_2^+$, was used to obtain the concentrations of PuO_2^+ and PuO_2^{+2}. Although both Pu^{+4} and PuO_2^+ are unstable with respect to disproportionation reactions, the concentrations of these ions were low and the extent of the concentration changes as a result of disproportionation reactions was negligibly small. Since the Pu^{+4} and PuO_2^+ concentrations are equal, the final $[PuO_2^{+2}]/[PuO_2^+]$ ratio can be obtained from the cell e.m.f., the Pu^{+3}–Pu^{+4} formal potential,[7,8] and the initial Pu^{+3} and PuO_2^{+2} concentrations. If $x = [Pu^{+4}] = [PuO_2^+]$, and a and b are the initial concentrations of PuO_2^{+2} and Pu^{+3}, respectively, then the final $[Pu^{+4}]/[Pu^{+3}]$ ratio equals $x/(b - x)$, and the final $[PuO_2^{+2}]/[PuO_2^+]$ ratio equals $(a - x)/x$. The value of x is determined from the relation $\ln x = (E_{\text{cell}} - E^{0\prime}_{3,4})F/RT$, where E_{cell} is the cell e.m.f. and the other symbols have their usual significance. The results of a titration of plutonyl ion with Pu^{+3} are given in Table II.

TABLE II

THE DETERMINATION OF THE PuO_2^+–PuO_2^{+2} FORMAL POTENTIAL IN 1 *M* $HClO_4$ AT 25° BY REDUCTION OF PLUTONYL ION WITH Pu^{+3}

Total initial $PuO_2^{+2} = 4.502 \times 10^{-4}$ mole; pressure correction of H_2 electrode = -0.0039 volt

Wt. of Pu^{+3}, mg.	$[Pu^{+4}]/[Pu^{+3}]$	$[PuO_2^{+2}]/[PuO_2^+]$	0.05915 log $[PuO_2^{+2}]/[PuO_2^+]$	E_{cell}	$E^{\circ\prime}$, v.
0.000	...	...	...	...	...
1.795	5.465	69.92	0.10911	−1.02140	−0.91642
2.370	4.282	55.00	.10294	1.01513	.91632
2.917	3.598	46.14	.09843	1.01066	.91636
3.473	3.108	39.95	.09473	1.00690	.91630
3.953	2.799	35.95	.09202	1.00421	.91632
4.580	2.492	31.92	.08896	1.00123	.91640
				Mean	−0.9164 ± 0.0001

Good agreement was obtained for the value of the PuO_2^+–PuO_2^{+2} couple in molar perchloric acid at 25° irrespective of whether I^- or Pu^{+3} was used as the reductant.

Temperature Dependence of PuO_2^+–PuO_2^{+2} Formal Potential.—The PuO_2^+–PuO_2^{+2} couple was measured as a function of temperature in molar perchloric acid between 6 and 25°. The reductant used was Pu^{+3}. Attempts were made to perform the titrations at 35°, but at this temperature the disproportionation of PuO_2^+ was not negligibly small as evidenced by a definite trend in the $E^{0\prime}_{5,6}$ results. Although no slowness was detected in the reaction between Pu^{+3} and PuO_2^{+2} from 15 to 25°, approximately one-half minute was required for the cell potential to become constant after the addition of Pu^{+3} at 6°. The equilibrium quotient for the reaction $Pu^{+4} + PuO_2^+ \rightleftarrows PuO_2^{+2} + Pu^{+3}$ is given by the expression $K = [PuO_2^{+2}]\,[Pu^{+3}]/[PuO_2^+]\,[Pu^{+4}]$. The value of K at a given temperature can be obtained from the relation $\ln K = (E^{0\prime}_{3,4} - E^{0\prime}_{5,6})\,F/RT$. This equilibrium quotient is of value in the determination of the composition of plutonium solutions.[9] This equilibrium quotient has also been determined by a spectrophotometric method. Measurements were made at 25° in molar perchloric acid with the Cary Model 14 spectrophotometer at 830.4 mμ, the PuO_2^{+2} peak. The molar extinction coefficient of the plutonyl ion at this wave length was found to be 560. Known concentrations of Pu^{+3} and PuO_2^{+2} were mixed and the observed optical densities were extrapolated to the time of mixing. This was necessary because of the slight disproportionation of Pu^{+4}. With trial values of K, a comparison between the calculated and observed optical densities could be made. By this method of successive approximations a value of 13.8 ± 1 was obtained for the value of K. Within the limits of experimental error this result is in agreement with the value derived from the formal potentials. The direct quantitative determination of small amounts of PuO_2^+ by spectrophotometric methods is difficult since the molar extinction coefficient of the most prominent peak of this ion is only about 17.[4] In Table III values of this equilibrium quotient are given together with the PuO_2^+–PuO_2^{+2} formal potentials as functions of temperature.

TABLE III

TEMPERATURE DEPENDENCE OF THE PuO_2^+–PuO_2^{+2} FORMAL POTENTIAL 1 *N* MOLAR PERCHLORIC ACID

Temp., °C.	K	$E^{0\prime}$, v.	$E^{0\prime}/T \times 10^3$, v. deg.$^{-1}$	$1/T \times 10^3$, deg.$^{-1}$
6.62	4.5	−0.9189	3.2843	3.5742
15.95	7.3	.9184	3.1767	3.4589
25.00	12.8	.9164	3.0735	3.3539

From a plot of $E^{0\prime}/T \times 10^3$ *versus* $1/T \times 10^3$ the heat of the reaction $PuO_2^+ + H^+ \rightleftarrows PuO_2^{+2} + {}^1/_2\,H_2$ in molar perchloric acid at 25° is found to be 22.9 kcal./mole. Thus, at 25°, $\Delta F = 21.13$ kcal./mole and $\Delta S = 5.9$ e.u. Since from studies of the temperature dependence of the disproportionation of Pu^{+4} and of the Pu^{+3}–Pu^{+4} couple[8] the entropy of PuO_2^{+2} has been found to be -28.9 e.u., the entropy of the PuO^+ ion is calculated to be -19.2 e.u. Brewer, *et al.*,[10] estimated the entropy difference between PuO_2^+ and PuO_2^{+2} to be 32 e.u. from entropy differences of simple +1 and +2 ions. Cohen and Hindman[11] have suggested that this difference is too large, and that these oxygenated ions should not be treated as simple singly and doubly charged ions. In agreement with their ob-

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(7) S. W. Rabideau and J. F. Lemons, THIS JOURNAL, **73**, 2895 (1951).

(8) S. W. Rabideau and H. D. Cowan, *ibid.*, **77**, 6145 (1955).

(9) Kasha, see ref. 3, p. 311, obtained a value of 10.7 for this equilibrium quotient from spectrophotometric studies in 0.1 *M* perchloric acid at unit ionic strength and at a temperature of 25°. However, in his study both the $[Pu^{+4}]$ and the $[PuO_2^+]$ were small as compared to the $[PuO_2^{+2}]$.

(10) L. Brewer, L. Bromley, P. W. Gilles and N. Lofgren, "The Transuranium Elements," Natl. Nuclear Energy Ser., IV, 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 861.

(11) D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4682 (1952).

servation, the entropy difference between the PuO_2^{+} and PuO_2^{+2} ions in molar perchloric acid at 25° has been found to be 9.5 e.u. in the present work. An interesting comparison of entropy changes for similar reactions of neptunium and plutonium in 1 *M* perchloric acid at 25° can be made. For the reactions $X^{+3} + H^{+} \rightleftarrows X^{+4} + \frac{1}{2}H_2$ and $XO^{+2} + H^{+} \rightleftarrows XO_2^{+2} + \frac{1}{2}H_2$, Cohen and Hindman[11] found −31.2 and 6.4 e.u. for neptunium ions, whereas for plutonium ions the values of the entropy differences have been found to be −30.2 and 6.0 e.u., respectively. However, for the reaction $X^{+4} + 2H_2O \rightleftarrows XO_2^{+} + 3H^{+} + \frac{1}{2}H_2$, the value of 62.3 e.u. has been reported[11] for neptunium and a value of 50.1 e.u. has been computed from the plutonium (III)-(IV) and (V)-(VI) couples together with the Pu(IV) disproportionation results.[1] It appears that the difference between these two ΔS values reflects a measure of the difference in the structure of the neptunium and the plutonium ions.

Complexing of PuO_2^{+2} by Chloride Ion.—From alterations in the absorption spectrum of plutonyl ion as the solvent is changed from perchloric to hydrochloric acid it has been concluded that a chloride complex is formed.[12] It has been observed that a color change visible to the unaided eye occurs upon the addition of hydrochloric acid to a perchloric acid solution of plutonyl ion. A solution of plutonyl ion was prepared by the ozonization of a perchloric acid solution of Pu^{+3}. At the completion of the oxidation period, the dissolved ozone was removed by bubbling helium through the solution, then a weighed quantity of standardized hydrochloric acid was added to make the final concentration 0.50 *M* hydrochloric–0.50 *M* perchloric acid. The plutonyl ion was titrated with P^{+3} in acid of the same composition. The Pu^{+3}–Pu^{+4} formal potential in 0.50 *M* hydrochloric–0.50 *M* perchloric acid, −0.9750 volt, was used in the computation of the ratio, $\Sigma(Pu^{IV})/(Pu^{+3})$, thus the assumption that the $\Sigma(Pu^{IV}) = (PuO_2^{+})$ is not invalidated by the chloride complexing of Pu^{+4}. A value of −0.9124 ± 0.0001 volt was obtained for the PuO_2^{+}–PuO_2^{+2} formal potential in this solvent at 25°. The more positive value of this couple in 0.50 *M* hydrochloric–0.50 *M* perchloric acid appears to indicate the formation of a plutonyl chloride complex. Since formal potential measurements yield only *differences* in the stabilities of the complex ions, it is necessary to use some other means to obtain the degrees of complexing of one of the ions directly.

Potentials of Plutonium Couples.—In Table IV are given the formal potentials of the plutonium couples in molar perchloric acid at 25.00°. The Pu^{+3}–Pu^{+4} and the PuO_2^{+}–PuO_2^{+2} potentials have been measured directly. The remainder of the potentials have been calculated from these values and the Pu^{+4} disproportionation equilibrium quotient.

TABLE IV

FORMAL POTENTIALS OF PLUTONIUM COUPLES AT 25°

(1) 1 *M* $HClO_4$

$$\begin{tikzcd} Pu^{+3} \arrow[r, dash, "-0.9819"] \arrow[rrr, dash, bend right, "-1.0228"'] & Pu^{+4} \arrow[r, dash, "-1.1721"] \arrow[rr, dash, bend right, "-1.0433"'] & PuO_2^{+} \arrow[r, dash, "-0.9133"] & PuO_2^{+2} \end{tikzcd}$$

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[12] R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, "The Transuranium Elements," Natl. Nuclear Energy Ser., IV, 14-B McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 559.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Thermodynamic Functions of Alkylnaphthalenes from 298 to 1500°K.[1]

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The values of the heat content function, free energy function, heat capacity and entropy of the dimethylnaphthalenes (except 1,8-dimethylnaphthalene), of the 1-*n*-alkylnaphthalenes and 2-*n*-alkylnaphthalenes and of three methylethylnaphthalenes have been calculated by the method of increments. The functions are tabulated from 298 to 1500°K. The barriers to internal rotation of the methyl group in 1- and 2-methylnaphthalenes have been determined to be approximately 3.8 and 2.3 kcal./mole, respectively. The entropy uncertainty of approximately 0.5 cal./deg. mole yields ranges 2.5–5.6 and 0.9–3.5 kcal./mole for the potential barriers.

Values of the thermodynamic functions of naphthalene in the ideal gas state have recently been calculated on the basis of a complete vibrational assignment for this molecule.[2] These functions, together with the previously published functions of paraffins[3,5] and alkylbenzenes,[4,5] furnish the basis for a calculation of the thermodynamic properties of various alkylnaphthalenes.

We have used the method of increments[6] to calculate values of the heat content function, free energy function, heat capacity and entropy of all dimethylnaphthalenes (except 1,8-dimethylnaphthalene), all 1-*n*-alkylnaphthalenes and 2-*n*-alkylnaphthalenes and 2-methyl-3-ethyl-, 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. In certain cases the potential barriers to internal rotation are ex-

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[1] This research was a part of the program of Research Project 50 of the American Petroleum Institute.

[2] A. L. McClellan and G. C. Pimentel, *J. Chem. Phys.*, **23**, 245 (1955).

[3] K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

[4] Taylor, Wagman, Williams, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

[5] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[6] For a discussion of this method see, for example, reference 5.