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The Thermodynamic Functions for $Pu^{3+}(aq)$ and the Entropies for Some Trivalent Actinide Ions[1]

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The heat of solution of pure α-phase plutonium metal has been measured in 6.03 and 2.0 *M* HCl, giving values of -139.4 ± 0.8 and -139.2 ± 0.8 kcal mol^{-1}, respectively. The heat of solution of $PuCl_3 \cdot 6H_2O(c)$ has been measured as -8.260 ± 0.058 kcal mol^{-1}. This value, together with measurements of the solubility of $PuCl_3 \cdot 6H_2O(c)$ and reasonable estimates of the activity and osmotic coefficients, leads to a value of -44.6 gibbs mol^{-1} for the entropy of $Pu^{3+}(aq)$. A consistent set of entropies has been generated for some other actinide(III) ions.

Introduction

The heat of solution of plutonium metal in hydrochloric acid was first reported by Westrum and Robinson in 1949.[3] Since that time plutonium has been shown to exist in at least six allotropic forms, several of which can be obtained as metastable states at room temperature.[4] The crystal phase of the metal used by Westrum and Robinson could not be specified and it is possible that all or part of their material contained more than one crystalline phase. Highly pure samples of plutonium metal, having a well-defined, thermodynamically stable crystal structure are now available and it seemed worthwhile to remeasure this important property of plutonium. While this work was in progress, Cunningham and Fuger[5] reported the results of new measurements on the heat of solution of the pure α-phase metal in 6.0 and 1.5 *M* HCl, and Akhachinskii[6] has recently determined a new value in 6.0 *M* HCl. The results of the present research confirm only the values reported by Fuger and Cunningham.

The aqueous entropy of the plutonium(III) ion is known only as an estimate given by Latimer[7] from a comparison with the entropy of $Gd^{3+}(aq)$. Recent data[8,9] indicate that the entropies of Gd^{3+} and the rare earth ions are much more negative than the values given by Latimer. No direct measurements have been made of the ionic entropy of any tripositive actinide ion. Therefore as a part of this research, measurements have been made which permit an accurate evaluation of the standard partial molal entropy of $Pu^{3+}(aq)$. By comparison with the recent new data[9] on the rare earth entropies a consistent set of entropy values for the actinide(III) ions can be generated.

Experimental Section

The general features of the calorimeter used in this research have been previously described.[10] Briefly, the instrument consists of a tantalum vessel with a 10-cm^3 volume; temperature measurements are made with a sensitive 100-K thermistor bridge amplifier system with automatic recording. Some modifications of the instrument have been made in order to improve sensitivity and performance. The stepping resistors in the variable arm of the bridge were replaced with a "Decastat"[11] resistance helipot which could be varied in 1-ohm increments from 0 to 12 K with an accuracy of ±0.05%. The dc amplifier was replaced with a Leeds and Northrup voltage amplifier (Model 9835-B). A simple voltage divider in the output of this amplifier leads to a modified Brown potentiometric recorder with a 4-mV chart width. At the maximum sensitivity a full-scale deflection on the recorder chart (12 in.) corresponds to approximately 3×10^{-4}°. With a noise level equivalent to about 6×10^{-6}° temperature differences of about 4×10^{-6}° ($\sim 6 \times 10^{-5}$ cal) are detectable.

The calibration heater circuit uses a Sargent Model IV coulometer to supply constant currents of from 5 to 200 mA. Heating times can be adjusted to 0.1 sec with an automatic timer circuit[12] regulated by a 60.000-cps standard tuning fork to ±0.01 sec.

The calorimeter and its submarine jacket assembly were submerged in a 60-gal water thermostat controlled to ±0.0003° for periods of at least 6 hr with a thermistor bridge regulated bath control unit.[13] Cooling water for the thermostat bath was in a separate thermostat controlled at 21.50 ± 0.05° with an Aminco[14] electronic relay operated by a mercury thermoregulator. The submarine jacket was evacuated to 10^{-5} mm with an oil diffusion pump system. The entire apparatus was kept in an air-conditioned room where the average temperature was maintained at 22 ± 2°.

Chemicals.—Two different 0.5-g samples of plutonium metal were used in this research. One sample from the Los Alamos Scientific Laboratory was specified as 99.96% pure metal in the α phase. The analytical data for this material are given below.[15]

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(1) Supported by the U. S. Atomic Energy Commission.

(2) From the Ph.D. Thesis of R. J. Hinchey, Purdue University, 1967.

(3) E. F. Westrum and H. P. Robinson in "The Transuranium Elements," National Nuclear Energy Series IV-14B, G. T. Seaborg, J. J. Katz, and W. M. Manning, Ed., McGraw-Hill Publications, New York, N. Y., 1949, Paper 6.53.

(4) A. E. Kay, "The Metal Plutonium," University of Chicago Press, Chicago, Ill., 1961, Chapter 17.

(5) J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.*, **25**, 1423 (1963).

(6) V. V. Akhachinskii, *Thermodyn. Proc. Symp.*, *1965*, **2**, 561 (1966); *Chem. Abstr.*, **67**, 68232 (1967). The authors are indebted to the referee who noted this reference.

(7) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, Inc., Englewood Cliffs, N. J., 1952.

(8) J. W. Cobble, *Ann. Rev. Phys. Chem.*, **17**, 15 (1966).

(9) R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, **9**, 917 (1970).

(10) G. R. Argue, E. E. Mercer, and J. W. Cobble, *J. Phys. Chem.*, **65**, 2041 (1961).

(11) Manufactured by Electromeasurements Corp., Portland, Ore.

(12) This circuit was designed by Mr. Roy M. Hayes of this laboratory and is described in ref 2.

(13) For details on the construction and operation of this instrument see ref 2.

(14) American Instrument Co., Inc., Silver Springs, Md.

(15) Isotopic analysis of the Los Alamos Sample HOO-1312 is as follows (in atom ratios): Pu^{239}, 1.00; Pu^{240}, $(5.12 \pm 0.08) \times 10^{-2}$; Pu^{241}, $(2.83 \pm 0.08) \times 10^{-3}$; Pu^{242}, $(1.64 \pm 0.16) \times 10^{-4}$. The chemical analysis is as follows (in ppm): Am, 155; O, 20; H, 10; N, 5; C, <10; Fe, <20; Ga, <20; U, 30; F, 2; Th, 21; Zr, <10; W, 55; Ta, <35; Mo, <1. The spectrochemical analysis is as follows (in ppm): Li, <0.2; Be, 1; Ne, 10; Mg, 10; Ca, 10; Al, <5; La, <10; Si, <10; Pb, <2; Cu, <2; Ni, <10; Cr, <5; B, <0.5; Mn, <2; Sn, <1; Bi, <1; Co, <10; Zn, <10.

A second standard sample of reagent grade metal was supplied by the National Bureau of Standards. The metal sample from the Los Alamos Laboratory was used for the heat of solution measurements. The single large piece of metal was brushed free of oxide, wrapped in tantalum foil, and fractured against a steel plate with a hammer. (All manipulations with plutonium were carried out in glove boxes.) Smaller pieces suitable for measurement were chipped from these fragments by striking the top of a scalpel blade held against the metal with a hammer. The α-phase metal cannot be cut with a steel blade. These smaller pieces were burnished with a glass-fiber brush until the surface was bright and shiny and free of oxide when viewed under a microscope. Freshly cleaned samples of the metal in a moderately dry atmosphere retained their bright appearance for several hours. In a very dry, inert atmosphere such samples remained shiny indefinitely. Although no loss of surface brightness was perceptible to the eye, a faint golden tarnish, presumably due to a very thin layer of oxide, was visible under a microscope. Since no increase in weight was detectable during the weighing, the effect of this oxide layer on the measured heat of solution may safely be presumed to be negligible. The samples were sealed in small Pyrex glass sample bulbs with Apiezon wax under an inert atmosphere.

The sample of plutonium from the National Bureau of Standards was used for the preparation of $PuCl_3 \cdot 6H_2O$. The α spectrum of this material taken with a 400-channel analyzer showed that the only other α-active material present was Am^{241}. By comparison with the α spectrum of the Los Alamos metal the amount of americium present could be estimated as approximately 300 ppm. This excess americium also accounts for the slightly higher specific activity of the Bureau of Standards material.

A 40-mg piece of this metal was carefully cleaned and dissolved in 2 ml of oxygen-free, hydrogen-saturated 2 M HCl. The solution was evaporated nearly to dryness by bubbling hydrogen through the liquid heated on an oil bath; the oil bath was then removed and the remainder of the liquid evaporated by bubbling with hydrogen alone. The purple salt was redissolved in oxygen-free conductivity water and evaporated to dryness again to ensure the removal of HCl. The isostructural crystals $NdCl_3 \cdot 6H_2O$ grown in 2–3 N HCl solutions were shown to be free of occluded HCl.[16] The crystals were again dissolved and the solution was evaporated until the appearance of crystals could be seen under a microscope. The saturated solution was removed to the argon-filled glove box for the solubility measurements.

Solid samples of the hexahydrate salt developed a grayish cast upon standing for several days under an inert atmosphere. This was attributed to oxidation induced by the intense α activity of the salt and therefore the salt remaining from the solubility measurements was redissolved in 2 M HCl and reduced with hydrogen using a lightly platinized platinum gauze catalyst according to the procedure described by Connick and McVey.[17] After reduction for about 1 hr at a temperature near 80° the solution was evaporated as before and the salt was weighed and sealed in sample bulbs under an inert atmosphere. The heat of solution measurements were all made within a period of 30 hr after preparation of the salt.

One sample of the salt was taken and analyzed radiometrically in a carefully standardized α proportional counter. This analysis gave 100.9 ± 0.5% of the calculated amount of plutonium corresponding to the formula weight of $PuCl_3 \cdot 6H_2O$. The specific activity of the sample of plutonium from Los Alamos was calculated from the isotopic analysis data in Table I. A standard solution of this material was prepared by dissolving a carefully cleaned and weighed piece of the metal in an accurately known volume of 2 M HCl. Aliquot portions of this solution were deposited on platinum foil planchets evaporated and used to standardize the counter. In the same manner standard samples of the National Bureau of Standards material were prepared and counted and the specific activity of this material was calculated from the known weight of the sample and the calibrated counting geometry of the counter. In all of the counting measurements samples were taken in 5-μl disposable capillary pipets and evaporated on 3-mil platinum foil planchets to give sample thicknesses no greater than 0.05 μg/cm². Although the pipets that were used have a rated accuracy of only 1%, replicate samples of the standard solutions gave a precision of 0.2–0.3% in the counting rates and so it is believed that the accuracy of the counting measurements is best represented by the standard counting error of ±0.5%.

A spectrophotometric analysis of an approximately 0.01 M solution of the salt taken with a Beckman DU spectrophotometer 1 week after preparation indicated that 1–2% of the plutonium had been oxidized to Pu(IV). Presumably most of this oxidation had taken place in the hydrated salt during this time as a result of the effect of the α radiation on the hydrate water molecules. It is possible, moreover, that the absorbing species is not the simple Pu(IV) ion but rather one of the two complex peroxide species[17] which are known to be extremely stable and to have molar extinction coefficients several times greater than that of Pu(IV).[18]

The magnesium metal samples used in testing the calorimeter were cut from a bar of singly distilled metal. Individual pieces were pared to an appropriate size with a razor, washed with dilute HCl and conductivity water, and dried on filter paper. The specimens were examined under a microscope for surface contaminants and fissures in the metal.

THAM [tris(hydroxymethyl)aminomethane], Fisher primary standard, was dried in a desiccator overnight and used without further purification.

J. T. Baker reagent grade hydrochloric acid was diluted to about 6 M and distilled, and the middle fraction of the distillate was retained for preparation of the various acid solutions. Acid solutions were standardized against sodium hydroxide using phenolphthalein indicator.

Weighings.—Microgram samples of plutonium and magnesium were weighed on a quartz fiber torsion balance[19] (sensitivity 0.06 μg). The calibration was verified by a technique described by Kirk[20] using standard weights prepared by evaporation of aliquot portions of standard KCl solutions. Other weighings were made with an automatic Mettler microgram balance (sensitivity 3 μg).

Procedure.—One or more electrical calibrations of the calorimeter were made before and after the chemical reaction. The calibrations and the chemical measurements were made at temperatures a few hundredths of a degree below the equilibrium temperature because of the impossibility of obtaining linear draft lines at temperatures above the equilibrium point.[21] The rate and magnitude of the calibration heating were adjusted to simulate the chemical heating as nearly as possible. Since the heating rates of calibrations and the chemical reaction were very rapid and nearly exponential, the point of 0.6 rise time[22] was used to measure the change in total resistance and heat. The calorie is taken as 4.1840 abs J and errors are reported as standard deviations.

Calibration.—The accuracy and high sensitivity of the instrument were tested by measuring the heat of solution of magnesium in 1.0 M HCl at 25°. The results of these measurements are given in Table I. The average value of seven measurements

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[16] F. H. Spedding and C. F. Miller, *J. Amer. Chem. Soc.*, **74**, 4195 (1952).

[17] R. E. Connick and W. H. McVey, ref 3, Paper 3.4.

[18] J. C. Hindman in "The Actinide Elements," National Nuclear Energy Series IV-14B, G. T. Seaborg and J. L. Katz, Ed., McGraw-Hill Publications, New York, N. Y., 1954, Chapter 9.

[19] Micro-chemical Specialties Co., Berkeley, Calif.

[20] P. L. Kirk, "Quantitative Ultramicroanalysis," John Wiley and Sons, New York, N. Y., 1950, p 84.

[21] This anomalous behavior is attributed to the high rate of radiant energy transfer from the calorimeter to the surroundings. The effect is probably detectable only because of the high temperature sensitivity and low heat capacity of the calorimeter system. For further discussion see ref 2.

[22] H. C. Dickinson, *Bur. Stand.* (*U. S.*), *Bull.*, **11**, 189 (1914).

TABLE I
HEAT OF SOLUTION OF MAGNESIUM IN 1.01 *M* HYDROCHLORIC ACID AT 25°

Sample wt, μg	Heat,[a] cal		ΔH, kcal mol^{-1}
27.004	0.12409		−111.7
45.383	0.20655		−110.7
40.387	0.18599		−112.0
53.829	0.24622		−111.2
33.368	0.15297		−111.5
131.651	0.61170		−111.3
55.970	0.25562		−111.0
6.007	0.02691		−108.9[b]
14.334	0.06663		113.0[b]
		Av	−111.4 ± 0.2

[a] Includes 0.330 kcal mol^{-1} for evaporation of solution by hydrogen. [b] Not included in final average.

gave −111.4 ± 0.2 kcal mol^{-1}, which compares well with the heat of −111.322 ± 0.041 kcal mol^{-1} reported by Shomate and Huffman.[23] Two measurements on the heat of solution of THAM in 0.10 *M* HCl gave an average heat of −7139 ± 54 cal mol^{-1} which is comparable to the values of −7104 ± 4 and 7107 ± 0.9 cal mol^{-1} obtained by others.[24,25] For the plutonium metal samples a small empirical correction was applied for the endothermal effect of breaking a sample bulb. The absorption of heat is probably caused by vaporization of the calorimetric liquid into the dry gas in the bulb. For bulbs sealed in the laboratory atmosphere the observed heat effect was on the average negligible, due, perhaps, to the cancellation of different heat effects.

Results

The Heat of Solution of Plutonium.—Other reports[26,27] on the dissolution of actinide metals in acid have indicated that a black, insoluble hydride or hydrated oxide is formed. Small samples of plutonium metal were dissolved in various concentrations of HCl and the progress of the reaction observed under a microscope. As hydrogen was evolved small, black pieces of material broke away from the main sample. These fragments were observed to dissolve slowly but completely with the evolution of gas. In 6 *M* HCl a 200-μg sample dissolved completely in about 1 min. In 1 *M* HCl an equivalent sample dissolved completely in about 4 min. The rate of dissolution in perchloric acid was generally very much slower.

Within the limits of detection by spectrophotometric analysis (*ca.* 1%) plutonium metal dissolves in oxygen-free HCl to give only the Pu(III) species.[3] However, some preliminary calorimetric measurements indicated that unless oxygen was rigorously excluded from the solution, the measured heats varied between −140 and −146 kcal mol^{-1}. Breaking air-filled sample bulbs in a solution of plutonium(III) chloride gave no thermal effect. Since plutonium hydroxide is known to be extremely susceptible to oxidation,[28] it may be that as the hydrogen ion concentration near the metal is exhausted during the course of the reaction, small amounts of the hydroxide are formed and subsequently oxidized by trace amounts of dissolved oxygen. When the calorimeter solution was purged with hydrogen for about 1 hr and kept under a hydrogen atmosphere, lower and more precise heats were obtained. Under these conditions the chemical reaction is assumed to be

$$\mathrm{Pu(c,\alpha) + 3H^+ = Pu(III) + 1.5H_2} \qquad (1)$$

The results of the heat of solution measurements in 6.0 *M* and 2.0 *M* HCl are shown in Table II.

TABLE II
HEAT OF SOLUTION OF PLUTONIUM METAL

Sample wt, μg	Molarity × 10^4	Heat,[a] cal		ΔH_{298},[b] kcal mol^{-1}
		6.03 *M* HCl		
340.819	1.4260	0.19950		−139.9
92.134	0.3855	0.05389		−139.8
313.815	1.3130	0.18279		−139.2
209.785	0.8778	0.12126		−138.1
338.856	1.4178	0.19901		−140.4
			Av	−139.4 ± 0.8
		2.0 *M* HCl		
227.450	0.9517	0.13362		−140.4
238.811	0.9992	0.13865		−138.8
110.870	0.4639	0.06458		−139.2
208.357	0.8718	0.12057		−138.3
			Av	−139.2 ± 0.8

[a] 0.0005 cal added for heat of bulb breaking. [b] 0.4 kcal mol^{-1} added for vaporization of water by hydrogen.

The Solubility of $PuCl_3$.—The highest stable hydrate of $PuCl_3$ at room temperature is the hexahydrate.[28] By analogy with the rare earths[16] and from the method of preparation of $PuCl_3 \cdot 6H_2O$ it can be assumed that the substance in equilibrium with a saturated solution of $PuCl_3$ is the hexahydrate.

TABLE III
SOLUBILITY OF PLUTONIUM(III) CHLORIDE AT 25°

Sample	Wt of soln, g	Wt of $PuCl_3$, g	Wt of H_2O, g	Molality,[a] mol of $PuCl_3$/1000 g of H_2O
1	0.001275	0.000784	0.000491	4.62
2	0.001149	0.000682	0.000467	4.23
3	0.001112	0.000508	0.000604	2.44[b]
4	0.001326	0.000812	0.000514	4.57

[a] The solid phase was $PuCl_3 \cdot 6H_2O$. [b] The solution was deliberately unsaturated and allowed to reequilibrate before sample 4 was removed.

The solubility measurements were carried out in an inert-atmosphere glove box immediately after preparation of the hydrate salt. One-microliter disposable glass capillary pipets were weighed on a Mettler balance. The pipets were supported on small rings made from aluminum foil and notched to hold the pipet in place. Samples of the solution were removed in the pipets; the pipet and supporting rings were reweighed and the weight of solution was obtained by difference. The amount of $PuCl_3$ in the saturated solution was obtained by counting aliquot portions of a solution prepared by crushing the capillary pipet in an accurately known

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(23) C. H. Shomate and E. H. Huffman, *J. Amer. Chem. Soc.*, **65**, 1625 (1943).
(24) R. I. Irving and I. Wadso, *Acta Chem. Scand.*, **18**, 195 (1964).
(25) S. R. Gunn, *J. Phys. Chem.*, **69**, 2902 (1965).
(26) W. J. James and M. E. Straumanis, *Acta Crystallogr.*, **9**, 376 (1956).
(27) R. C. Young, *J. Inorg. Nucl. Chem.*, **1**, 418 (1959).
(28) B. B. Cunningham in ref 18, Chapter 10, p 397.

volume of 2 *M* HCl. The weight of solvent water was calculated from the difference between the weight of solution and the weight of salt. Table III gives the solubility data in moles of $PuCl_3$/kg of H_2O.

The Heat of Solution of $PuCl_3 \cdot 6H_2O$.—The heat of solution of the salt was measured in oxygen-free conductivity water. The data from these measurements are given in Table IV. The average value of −8.053 ± 0.032 kcal mol^{-1} was extrapolated to infinite dilution to give −8.260 ± 0.058 kcal mol^{-1}. This heat is somewhat less exothermic than the solution heat for the corresponding rare earth chloride $SmCl_3 \cdot 6H_2O$: −9.142 kcal mol^{-1}.[29]

TABLE IV

HEAT OF SOLUTION OF $PuCl_3 \cdot 6H_2O$ AT 25°

Sample wt, mg	Final molarity × 10^4	Heat, cal		ΔH_{298}, kcal mol^{-1}
3.282	7.239	0.05790		−7.998
3.947	8.705	0.07089		−8.143
7.244	15.977	0.12826		−8.023
			Av	−8.056 ± 0.032

Thermodynamic Calculations and Discussion

The Heat of Formation of $PuCl_3$(c).—The heat of formation of $PuCl_3$(c) can be calculated from the thermodynamic cycle

$$Pu(c,\alpha) + X(HCl \cdot YH_2O) = PuCl_3 \cdot [(X-3)HCl \cdot XYH_2O] + 1.5H_2(g) \quad (2)$$

$$1.5H_2(g) + 1.5Cl_2(g) + (X-3)HCl \cdot XYH_2O = X(HCl \cdot YH_2O) \quad (3)$$

$$PuCl_3(c) + (X-3)HCl \cdot XYH_2O = PuCl_3 \cdot [(X-3)HCl \cdot XYH_2O] \quad (4)$$

$$Pu(c,\alpha) + 1.5Cl_2(g) = PuCl_3(c) \quad (5)$$

The heat of reaction 2 in 6.03 *M* HCl was measured in this research as −139.4 ± 0.8 kcal mol^{-1}. At this acid concentration *X* has a value of 60,000 and *Y* a value of 8.1. The change in acid concentration due to the reaction is negligible. The heat of reaction 3 is calculated from auxiliary thermodynamic data[30] as −36.80 kcal mol^{-1}. Westrum and Robinson[3] measured the heat of solution of $PuCl_3$(c) in various concentrations of HCl. Their value for the heat of solution in dilute acid has been confirmed by Cunningham and Fuger[5] and so their values in more concentrated acid are assumed to be correct. In 6.0 *M* HCl they gave −22.15 ± 0.1 kcal mol^{-1} for the heat of reaction 4. The appropriate summation of eq 2–4 gives the heat of formation for reaction 5: $\Delta H_5 = -227.7 \pm 0.8$ kcal mol^{-1}. A similar calculation using −139.2 ± 0.8 kcal mol^{-1} for the heat of reaction 2 in 2.0 *M* HCl gives $\Delta H_5 = -227.3 \pm 0.8$ kcal mol^{-1} and an average value of $\Delta H_f°_{PuCl_3} = -227.5 \pm 0.8$ kcal mol^{-1}. This is in excellent agreement with the value reported by Fuger and Cunningham[5] of −226.8 ± 0.7 kcal mol^{-1} for the standard heat of formation calculated from measured heats of −138.90 ± 0.9 and −138.65 ± 0.7 kcal mol^{-1} in 6.0 and 1.5 *M* HCl, respectively.

Westrum and Robinson[3] gave −31.9 ± 0.2 kcal mol^{-1} for the heat of solution of $PuCl_3$ in infinitely dilute HCl. Using this value we calculate $\Delta H_f°_{Pu^{3+}(aq)} = -138.9 \pm 0.8$ kcal mol^{-1}.

The Heat of Formation of $PuCl_3 \cdot 6H_2O$.—The dissolution of $PuCl_3 \cdot 6H_2O$ gave a heat of −8.056 ± 0.032 kcal mol^{-1} for final solute concentrations of the order of 10^{-3} *M*. Using the infinite dilution value of −8.260 ± 0.058 kcal mol^{-1}, together with the heats of formation and solution of the anhydrous salt, gives the heat of formation of the hexahydrate: $\Delta H_f° = -660.6 \pm 0.8$ kcal mol^{-1}.

The Free Energy of Solution of $PuCl_3 \cdot 6H_2O$.—For the saturated solution the formal description of the equilibrium is given by

$$PuCl_3 \cdot 6H_2O(c) = Pu^{3+}(aq) + 3Cl^-(aq) + 6H_2O \quad (6)$$

Reasonable estimates of the activity coefficient of the solute and the activity of water can be obtained by extrapolation of the osmotic coefficient data of Saegar and Spedding[31] for solutions of the isomorphic[32,33] salt $SmCl_3 \cdot 6H_2O$. The extrapolation gives 9.30 for the mean ionic activity coefficient and 3.13 for the activity of water in the saturated solution. Using these values and the measured solubility, the free energy of solution of $PuCl_3 \cdot 6H_2O$ is calculated to be $\Delta F_6° = -7207$ cal mol^{-1}. The free energy value was based upon $SmCl_3 \cdot 6H_2O$ for two reasons: (1) Sm^{3+} is the rare earth homolog of Pu^{3+}; (2) actinide(III) ions have been demonstrated to show a slightly more pronounced tendency toward complex ion formation with chloride than the corresponding rare earth ions.[34] Qualitatively, a somewhat greater degree of complex ion formation would be expected to decrease the activity coefficient of the solute[35] leading to a more positive free energy of solution. Consequently, −7207 cal mol^{-1} probably represents the lower limit of the free energy.

The Entropy of Pu^{3+}(aq).—From the enthalpy and free energy values determined for reaction 6 the entropy change in the solution process is calculated to be $\Delta S° = -3.53$ gibbs mol^{-1}. Accurate estimates of the entropy of $PuCl_3 \cdot 6H_2O$(c) can be made from the entropy of $SmCl_3 \cdot 6H_2O$[9] based on the low-temperature heat capacity data of Pfeffer and his associates.[36] The entropies of the rare earth salts are

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[29] F. H. Spedding and J. P. Flynn, *J. Amer. Chem. Soc.*, **76**, 1474, 1477 (1954).

[30] Auxiliary thermodynamic data for which no references are given are taken from the most recent edition of "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., Oct 1965, Part 1.

[31] V. W. Saegar and F. H. Spedding, U. S. Atomic Energy Commission Report IS-338, Ames Laboratory, Ames, Iowa, 1960.

[32] E. Staritzky and A. L. Truitt in ref 18, Chapter 19, p 801.

[33] V. I. Iveronova, V. P. Tarašova, and M. M. Umanskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **15**, 164 (1951); *Chem. Abstr.*, **45**, 8841*g* (1951); **46**, 4313*c* (1952).

[34] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, *J. Amer. Chem. Soc.*, **76**, 1461 (1954).

[35] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions" 2nd revised, Butterworth and Co., London, 1965, Chapter 9.

[36] (a) W. Pfeffer, *Z. Phys.*, **164**, 295 (1961); (b) K. H. Hellwege, F. Kuch, K. Nieman, and W. Pfeffer, *ibid.*, **162**, 359 (1961); (c) W. Pfeffer, *ibid.*, **162**, 413 (1961); (d) W. Pfeffer, *ibid.*, **168**, 305 (1963).

divisible into magnetic and crystal lattice contributions, and it will be assumed that the corresponding isostructural actinide salts can be treated similarly. The lattice entropy of $SmCl_3 \cdot 6H_2O$ has the value of 94.6 gibbs mol^{-1}. Adding 1.39 gibbs mol^{-1} for the greater mass of Pu[37] and 3.56 gibbs mol^{-1} for the magnetic entropy of $Pu^{3+}(^6H_{5/2})$ gives 99.6 gibbs mol^{-1} for the total entropy of $PuCl_3 \cdot 6H_2O$. The entropy of Pu^{3+}(aq) can then be calculated as -44.6 gibbs mol^{-1}. This value can be compared with the previous value of -39 gibbs mol^{-1} given by Latimer[7] which was based upon the older entropy of Gd^{3+} of -43 gibbs mol^{-1}.

The Free Energy of Formation of Pu^{3+}(aq).—The free energy of formation of Pu^{3+}(aq) can now be calculated more accurately than was possible previously. The entropy of Pu(c) is estimated[38] to be 12.3 gibbs mol^{-1} so that the entropy of formation of Pu^{3+}(aq) becomes -10.1 gibbs mol^{-1}. From the present value of $\Delta H_f°$ of Pu^{3+}(aq) of -138.9 ± 0.8 kcal mol^{-1}, the free energy of formation is calculated to be -135.8 ± 1.2 kcal mol^{-1}. The oxidation–reduction potential for Pu^{3+}(aq) (see eq 7) then be-

$$Pu(c) = Pu^{3+} + 3e^- \qquad (7)$$

comes $E° = 1.96 \pm 0.02$ V.

Entropies of the Trivalent Actinide Ions.—The entropies of the other trivalent actinide ions can be estimated from Pu^{3+}(aq) by the same procedure used for the lanthanide ions.[9] It will be assumed that the aqueous ions have an internal electronic entropy due to the degeneracy of the ground state equal to $R \ln (2J + 1)$. The entropy due to the radius and charge effect[39] will be assumed to have the same functional dependence as observed for the lanthanides[9] but displaced 6.2 gibbs mol^{-1} as indicated by the present Pu^{3+}(aq) data. The "adjusted" (total minus electronic entropy), electronic, and total ionic entropies are summarized for some actinide ions in Table V. For this purpose the ionic crystal radii of Zachariasen[40] have been used. The arguments for the assignment of the electronic ground states have been given previously by Katz and Seaborg.[41] It should be noted, however, that the magnetic susceptibilities of the aqueous trivalent actinide ions parallel but are somewhat lower than the susceptibilities of the corresponding lanthanides. This decrease can be attributed to a Stark splitting of the ionic term states and possibly a partial failure of the Russell–Saunders coupling approximation. However the estimations of S_e given in Table V appear to be the best that can be made at present.

TABLE V
ESTIMATED IONIC ENTROPIES (GIBBS MOL^{-1})
BASED ON Pu^{3+}(aq) AT 25°

M^{3+}(aq)	r_c,[a] Å	$(1/r_c)^2$	$\bar{S}_{adj}°$	Assumed ionic state	S_e[b]	$\bar{S}°$
Ac	1.11	0.812	−43.3	$^1S_0$	0.0	−43.3
Th	(1.08)	0.857	−44.5	$^2F_{5/2}$	3.6	−40.9
Pa	(1.05)	0.906	−45.7	$^3H_4$	4.4	−41.3
U	1.03	0.943	−46.7	$^4I_{9/2}$	4.6	−42.1
Np	1.01	0.980	−47.7	$^5I_4$	4.4	−43.3
Pu	1.00	1.00	−48.2	$^6H_{5/2}$	3.6	−44.6
Am	0.99	1.02	−48.7	$^7F_0$	0.0	−48.7
Cm			(−49)	$^8S_{7/2}$	4.1	(−45)

[a] Ionic radii are from ref 40. [b] $S_e = R \ln (2J + 1)$.

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[37] G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Publications, New York, N. Y., 1961, p, 517.

[38] "Tables of Thermodynamic Data," Technical Reports Series, No. 38, International Atomic Energy Agency, Vienna, Austria, 1964, p 8.

[39] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

[40] W. H. Zachariasen in ref 18, Chapter 18.

[41] J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Eements," John Wiley and Sons, New York, N. Y., 1957.