

occurrence of barium and strontium ions in the crystal lattice.

It is of interest to note that the entropy of barium metatitanate at 298.16°K. is slightly lower than that of the strontium compound, despite its greater molecular weight.

The entropies of formation from the constituent

oxides, calculated from the data in Table II and Kelley's¹⁰ values for the oxides, are -3.0, 1.0 and 0.3 cal./deg. mole, respectively. These values are of the magnitude found by Shomate¹ for titanates of iron, calcium and magnesium.

(10) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

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

The Heat of Solution of Neptunium Metal and the Heats of Formation of Some Neptunium Chlorides. A Microcalorimeter for Heat of Solution Measurements¹

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The heat of reaction of milligram amounts of neptunium metal with 1.5 *M* HCl containing 0.005 *M* Na₂SiF₆ was found to be -165.7 ± 0.2 kcal. per mole at 25°. This value combined with other data yields -132.9 ± 1 and -127.4 ± 1 kcal. per mole for the apparent molal heats of formation of Np(IV) and Np(III) in 1.0 molal HCl. By comparing the heats of solution of other isomorphous actinide chlorides, those of NpCl₃ and NpCl₄ are estimated and heats of formation of 216 ± 1 kcal. per mole for NpCl₃ and 238 ± 1 kcal. per mole for NpCl₄ are obtained. A convenient precise calorimeter suitable for the determination of heats of relatively rapid reactions for milligram quantities of materials is described and its performance indicated.

The increasing interest in, and availability of, the synthetically produced transuranium elements occasions a need for precise thermodynamical and thermochemical data on these elements and their compounds for the understanding and correlation of the chemical behavior of these substances. The procurement of thermochemical data on the transuranium elements has involved, and perhaps will continue to involve, quantities of material on the order of a milligram because of the exceedingly small quantities of many of these synthetic elements available and the health hazard of working with large quantities of highly radioactive α -emitters. Furthermore, the generation of energy within the sample by radioactive disintegration and the low thermal conductivities of the metals and compounds make the achievement of a uniform temperature throughout a massive sample difficult. The small quantities of transuranium elements available, the correspondingly small enthalpy change produced, and an anticipated reaction time less than 10 minutes made desirable the construction of a well stirred microcalorimeter of small heat capacity and considerable temperature sensitivity. The thermostat, and circuits of a calorimeter already described³ were modified; only the most important changes will be indicated here.

Thermostat.—The toluene-mercury thermoregulator was replaced by one in which the temperature-sensing mechanism was the resistance of about 0.7 kilometer of No. 40 copper wire. This resistance thermometer served as one arm of a bridge, the unbalance of which is fed into a breaker-type

amplifier of gain approximately 10⁵ and enhanced sufficiently to activate a thyatron circuit including the thermostat heater. This proportional controller yielded maximum fluctuations much smaller than a thousandth of a degree at the calorimeter position over periods longer than the duration of the runs.

Calorimeter.—The general features of the calorimeter⁴ may be seen by reference to Fig. 1. It is contained within a stainless steel submarine (D) which is supported on a small cross sectional shaft (E) of the same material. The two external leads to the unit are of No. 12 B. and S. gage copper wire and make contact through massive copper binding posts to fine manganin leads (A) imbedded in paraffin. The calorimeter itself is supported by a machined, thin-walled lucite tube (F) terminating in a screw thread at the lower end. The submarine provides a dead air gap of a centimeter width in accord with the considerations of White.⁵ The reaction chamber (G) 2.5 cm. in diameter with 0.2-mm. thick walls is machined from tantalum rod and contains about 8 cc. of solution during operation. A screen closure near the top provides a vapor tight seal against a lapped seat; the threaded connection to the lucite shaft is also vapor tight. The portion of the cylindrical shell in contact with the solution is bifilarly wound with about 16 meters of No. 40 B. and S. gage, annealed, enamelled copper wire which serves both as a resistance thermometer and as a heater coil with very small lags. Two 3-cm. lengths of this wire extend across the air gap and are soldered into lugs and held by a copper set screw in good contact over a considerable area of the corresponding jacks (B) mounted in lucite. The solution is stirred by means of a tetravalent, platinum propeller driven by a slender quartz shaft (C) about a millimeter in diameter. The top end of the quartz shaft is clamped in a plastic collet driven through a flexible shaft by a 75 r.p.m. synchronous motor.

The samples to be dissolved were contained in fragile glass sample bulbs similar to those already described except that the present bulbs were especially thin walled with flat bottoms to facilitate breaking and had a capacity of fifty microliters. These bulbs were sealed onto the stirring shaft just below the propeller and were shattered against a projection by means of a two millimeter depression of the stirring shaft without interference with the rotational motion.

Operation and Performance.—The relative temperature sensitivity of the calorimeter is about 2×10^{-5} degree and the total heat capacity is about nine calories per degree. Consequently, to obtain results accurate to a few tenths of a per cent., a thermal process liberating about 0.2 calorie is

(1) This research was performed under the auspices of the U. S. Atomic Energy Commission mainly in 1946-1947 and was reported in part by Edgar F. Westrum, Jr., in U. S. Atomic Energy Commission Declassified Document AECD-1903 (April, 1948). Presented at the 118th National Meeting, American Chemical Society, Chicago, Ill., September 6, 1950.

(2) (a) Department of Chemistry, University of Michigan, Ann Arbor, Michigan. (b) Department of Chemistry and Chemical Engineering, The State University of Iowa, Iowa City, Iowa.

(3) Edgar F. Westrum, Jr., and H. P. Robinson, National Nuclear Energy Series, Volume 14B, "The Transuranium Elements," Part 2, Research Paper 6.51, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) Edgar F. Westrum, Jr., Atomic Energy Commission Declassified Report, AECD-1903. (1948).

(5) W. P. White, "The Modern Calorimeter," Reinhold Publishing Corp., New York, N. Y., 1928.

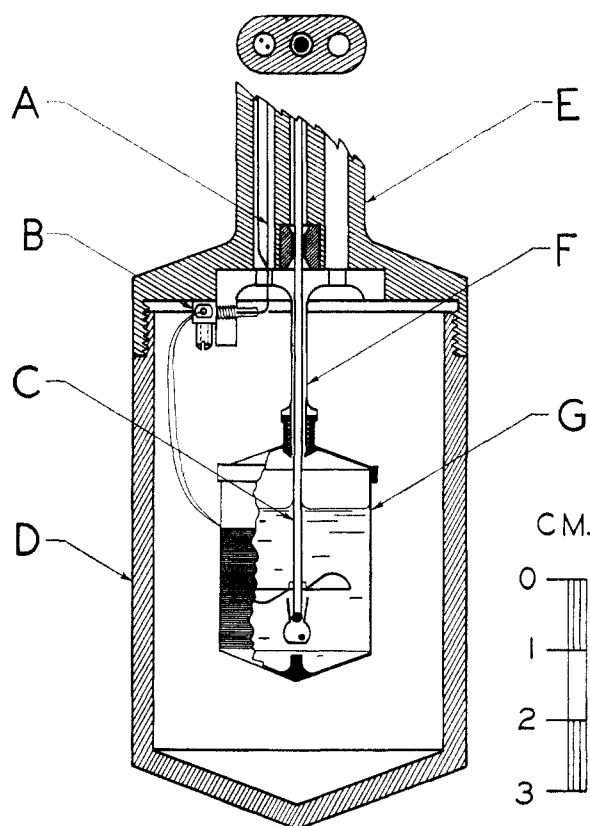


Fig. 1.—Schematic cross-sectional diagrams of micro-calorimeter.

required. This corresponds to a temperature rise of 0.02° or to about 240 micrograms of a transuranium element with a heat of solution of the order of 200 kcal. per mole. The thermal leakage modulus of the calorimeter was observed to be 2×10^{-2} minute $^{-1}$. The observed drift due to the combined heat of stirring and energy required for the operation of the resistance thermometer was about 2×10^{-4} degree per minute.

A normal pattern of determination in the calorimeter involves: (a) loading and assembly of the calorimeter at a temperature a few tenths of a degree below 25° , (b) electrical calibrations of the calorimeter at a rate and with an amount of energy comparable to that obtained during the solution of the sample, (c) observation of the foredrift, breaking the sample container, and observation of the afterdrift until a drift consistent with the temperature of the calorimeter is obtained and (d) more electrical energy inputs. Breaking the bulb was a process which blank runs indicated involved no detectible net energy change—probably the result of the approximate cancellation of several effects.

Calibration.—Inasmuch as the heater was wound on the outside of the calorimeter it was necessary to establish that the lag was small and that superheating of the coil did not occur. Auxiliary experiments established a lag of less than ten seconds between the production of energy in the coil and its 99% registration on the galvanometric system of the resistance thermometer. The absence of superheating of the coil sufficient to make the correction for heat exchange invalid was demonstrated by determination of the resistance of the heater during a sequence of alternate drifts and energy inputs.

Calibration of the calorimeter included calculation of the energy equivalent of the weighed parts, and the determination of the heat capacity by electrical energy inputs at rates from one-fourth to four times that employed in the reactions studied. These determinations had a precision better than $\pm 0.2\%$ and were in agreement with the calculated heat capacity within the same limit. The above comparison involved the calibration of the resistance thermometer on a centigrade scale, which was achieved by immersing the calorimeter covered by a thin rubber sac directly (sub-

marine not in place) into the thermostat and comparison of the decade box settings with the temperature of a calibrated differential thermometer over a two degree range. A defined thermochemical calorie equal to 4.1840 absolute joules was employed.

Three chemical calibrations were likewise made to establish the precision and accuracy of the instrument for heat of reaction use. These were the heat of solution of KCl and KNO_3 in water and the heat of solution of magnesium metal crystals in 1.0 M HCl. The results of these runs are indicated in Table I. They compare very favorably with literature values.⁶

TABLE I

OBSERVED MOLAL HEAT OF SOLUTION OF KCl IN WATER⁷

Sample weight, mg.	Heat evolved, calories	ΔH , kcal.
11.178	0.624	4.16
14.250	.793	4.15
15.602	.875	4.18

Observed Molal Heat of Solution of KNO_3 in Water

12.747	1.052	8.34
8.168	0.6757	8.36
8.133	.6716	8.35
7.522	.62045	8.35

Observed Molal Heat of Reaction of Mg in 1.0 molar HCl

1.109	5.056	-111.2
0.2918	1.3318	-111.3
0.1301	0.5937	-111.3

Neptunium Metal.—The neptunium metal was prepared on the milligram scale by a process already described⁸ and the spectrochemical analysis reported there is also typical of these samples and the calorimeter solution after dissolution of the metal. Five separate determinations were made on the heat of reaction of neptunium metal with the 1.500 molar HCl in the presence of 0.00500 molar Na_2SiF_6 . It was noted that attempts made to dissolve the metal in the absence of fluosilicate yielded a black residue containing an appreciable fraction of the neptunium. Although the nature of the residue was not ascertained it is believed that this is analogous to the black residue obtained on the dissolution of pure thorium metal in hydrochloric acid in the absence of a small concentration of fluosilicate. The neptunium metal samples were weighed on an Ainsworth microbalance, placed in thin bottomed glass bulbs, and sealed to the end of the stirring shaft. The hydrochloric acid saturated with hydrogen was weighed into the tantalum shell and the calorimeter assembled. Electrical calibrations were made before and after each run. The data are presented in Table II.

TABLE II

MOLAL HEAT OF REACTION OF NEPTUNIUM METAL IN 8.81 G. OF 1.500 MOLAR HCl AND 0.00500 MOLAR Na_2SiF_6 AT 25°

Sample weight, mg. <i>in vacuo</i>	Heat evolved, calories	Corrected, ^a ΔH (Reaction)-kcal.
0.456	0.318	-165.7
0.782	0.545	-165.7
1.458	1.0175	-165.9
1.408	0.9808	-165.6
1.906	1.3285	-165.7
		-165.7 \pm 0.2

^a Includes a correction of 0.4 kcal. per mole for vaporization of the solvent.

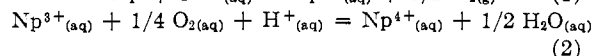
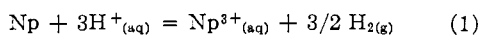
(6) (a) For KCl: 4.17 kcal. per mole from "Selected Values of Chemical Thermodynamic Properties." (b) For KNO_3 : 8.37 kcal. per mole from "Selected Values of Chemical Thermodynamic Properties." (c) For Mg: 111.32 ± 0.04 kcal. per mole reported by C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

(7) Reported in Atomic Energy Commission Document MB-1P-186 (April, 1947).

(8) Edgar F. Westrum, Jr., and LeRoy Eyring, THIS JOURNAL, **73**, 3396 (1951).

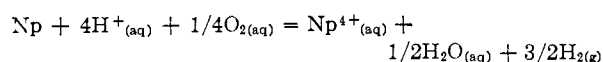
Discussion

The highly positive value of the Np-Np(III) couple ensures the ready dissolution of neptunium in dilute hydrochloric acid, but the negative value of the (III)-(IV) couple (-0.14 volt in 1 molal HCl) is such that dissolved oxygen will oxidize it rapidly to the (IV) state, but not further. The observed heat of solution corresponds therefore to the sum of two reactions in 1.55 molal hydrochloric acid at 298°K .

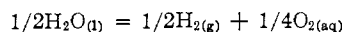


Auxiliary experiments on comparable quantities of neptunium made both in the presence and in the absence of dissolved oxygen in the hydrogen saturated solvent indicated clearly that $3/2$ of a mole of hydrogen was evolved in the oxidation of the metal to the (III) state and that oxidation to the (IV) state took place only in the presence of dissolved oxygen and then without further hydrogen evolution. The determination of hydrogen evolved was facilitated by an apparatus designed by us, previously described,⁹ and calibrated with dissolution of pure zinc metal. The oxidation state of the neptunium was determined spectrophotometrically. Dissolution experiments were also made on comparable quantities of metal and hydrogen saturated acid in the Beckman spectrophotometer with the instrument preset to a prominent Np(IV) peak. The immediate appearance of the peak indicated that a very rapid reaction to the (IV) state is involved. The calorimetric solution was observed to contain only neptunium in the (IV) oxidation state at the end of the run. We have eliminated the possibility that reduction of hydrogen ion is responsible for the oxidation of Np(III) to Np(IV) in the presence of dissolving Np metal.

The over-all calorimetric reaction is, therefore



Corrections for heat of dilution of the acid and the salt at constant ionic strength are negligible and the effect of fluosilicate ion is neglected. Consequently, taking the molal heat of the reaction



as 33.2 kcal.¹⁰ one obtains $\Delta H = -132.5$ kcal. for

(9) B. B. Cunningham, *Nucleonics*, **5**, No. 5, 62-85, Nov. (1949).

(10) Unless other sources are indicated, auxiliary thermodynamic

the formation of Np(IV) in 1.55 molal HCl. From the effect of the HCl concentration on the heat of solution of ThCl_4 as a function of acid concentration only and from the rough correlation of heat of dilution and ionic radius noted by Westrum and Robinson¹¹ a value of -132.9 ± 1 kcal. mole⁻¹ is obtained for the apparent molal heat of formation of Np(IV) in 1 molal HCl. Using the best value, -5.5 ± 0.2 kcal., for the heat of oxidation of Np(III) \rightarrow Np(IV) determined from the temperature coefficient of the cell potential¹² yields -127.4 ± 1 as the apparent molal heat of formation of Np(III) in 1 molal hydrochloric acid.

To obtain estimates for the heats of formation of the solid neptunium chlorides we estimate the heats of solution of solid compounds in 1.0 molal HCl by extrapolation of the experimental data on the heats of solution of ThCl_4 ,¹¹ UCl_4 ,¹³ UCl_3 ¹³ and PuCl_3 ^{14,15} as a rough function of ionic radius and hydrogen ion concentration. On this basis values of 216 ± 1 and 238 ± 1 kcal. are obtained as the molal heat of formation of crystalline NpCl_3 and NpCl_4 , respectively.

The differences of about a kilocalorie between our values and those calculated by Brewer¹⁸ arise in part from his interpretation of reaction (2) as one involving dissolved rather than gaseous hydrogen. The solution was initially saturated with hydrogen at a slightly lower temperature and our comparable dissolution experiments on this and other transuranium metals on this scale under similar conditions clearly indicate that all ($\pm 2\%$) of the hydrogen does escape and that it is virtually saturated with water vapor.

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data are obtained from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1947.

(11) E. F. Westrum, Jr., and H. P. Robinson, NNES "The Transuranium Elements," Research Papers, Paper 6.50, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(12) J. C. Hindman, private communication, 1951.

(13) L. Brewer, L. Bromley, P. Gilles and N. Lofgren, Manhattan Project Report, MDDC, 1417 (1948).

(14) E. F. Westrum, Jr., and H. P. Robinson, NNES Vol. 14B, "The Transuranium Elements," Research Papers, Part 2, Paper 6.53, McGraw-Hill Book Co., New York, N. Y., 1949.

(15) H. P. Robinson and E. F. Westrum, Jr., *ibid.*, Paper 6.54.