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Contribution from the Radiation Laboratory
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THE HEAT OF SOLUTION OF NEPTUNIUM
METAL AND THE HEATS OF FORMATION OF THE
NEPTUNIUM CHLORIDES. A MICROCALORIMETER
FOR HEAT OF SOLUTION MEASUREMENTS.

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Introduction. The increasing interest in, and availability of, the synthetically produced transuranium elements creates a need for precise thermodynamical and thermochemical data on these elements and their compounds for the understanding and correlation of the chemical behaviour 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 these synthetic elements available and the health hazard of working with large quantities of highly radioactive alpha emitters. Furthermore, the generation of energy within the sample by radioactive disintegration, coupled with low thermal conductivities, makes improbable the achievement of a uniform temperature throughout a massive sample. The quantity of material available and the correspondingly small enthalpy change produced, together with consideration of the duration of the reaction and the time available for the research, dictated the construction of a microcalorimeter of small heat capacity and considerable temperature sensitivity. As a matter of expediency, the thermostat, chassis, and circuits of a calorimeter already described⁽¹⁾ were modified and only those changes and special problems connected with the conversion will be described.

(1) Edgar F. Westrum, Jr. and H. P. Robinson. National Nuclear Energy Series, Volume 14B, Part 2, The Transuranium Elements, pg. 889 McGraw Hill (New York) (1949).

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The calorimeter was designed to measure precisely and accurately the heat evolved in solution processes taking place relatively rapidly - for example within a matter of one to fifteen minutes-on milligram quantities of metals. A more elaborate calorimeter needed to measure a heat liberation or adsorption occurring over a period of the order of an hour, as for example in the solution of a difficultly soluble oxide, has been constructed and will be described in another paper.

Thermostat. The bath used by Westrum and Robinson⁽¹⁾ was modified in that the toluene-mercury control unit was replaced by one giving more accurate temperature control and requiring less maintenance. This thermoregulator (to be described in a subsequent paper) consists of an electrical bridge including a resistance thermometer and three other arms of manganin resistors immersed in an oil bath. The resistance thermometer incorporated about 0.65 kilometers of #40 B. and S. gauge enamelled copper wire wound bifilarly on a hollow stainless steel cylinder about 10 cm. in diameter and 35 cm. long with an insulation of 1 mil thick polystyrene sheet. A protective stainless steel sheath was welded over the winding and the cylinder was so placed that a good fraction of the turbulent flow of the bath passed through it. The bridge unbalance signal due to a thermoresistance change of the copper wire is fed into a breaker-type amplifier of gain approximately 10^5 and enhanced sufficiently to activate a thyatron circuit in which the thermostat heater is located. The proportional control yields maximum fluctuations smaller than a thousandth of a degree at the calorimeter position over periods longer than the duration of the runs.

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Calorimeter. The general features of the calorimeter may be seen by reference to Figure 1.⁽²⁾ It is contained within a stainless steel

(2) Cf. Figure 3. AECD - 1903 (1948)

submarine (E) which is supported on a small cross sectional shaft of the same material. The two external leads to the unit (A) are of #12 gauge copper wire making contact through massive copper binding posts within a massive stainless steel hood. The fine copper leads (C) to the calorimeter are imbedded in paraffin (G) down through the support shaft. The calorimeter itself is supported by a machined, thin-walled, lucite tube terminating in a screw thread at the lower end and broadening out at the top end to provide a mounting for the minute copper jacks and lugs used to connect the thermometer and heater. The submarine provides a dead air gap of a centimeter, the optimum width for the present specification from the considerations of White⁽³⁾.

(3) W.P. White, The Modern Calorimeter, New York (1928).

The reaction chamber is machined from tantalum rod and contains about 8 cc. of solution during operation. It is 2.5 cm. in diameter and has 0.2 mm. thick walls. A screw closure near the top provides a vapor tight seal against a lapped seat and 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. gauge annealed, enamelled copper wire

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which serves in the double capacity of a resistance thermometer and a heater coil with a very small lag. Two 3 cm. lengths of this wire extend across the air gap and are soldered into relatively massive "micro" lugs which make good contact over a considerable area with corresponding jacks (D) mounted in the lucite support base (J) with a copper set screw. Manganin leads were used between (D) and (B). The solution is stirred by means of a tetradentive platinum propellor driven by a slender quartz shaft (H) about a millimeter in diameter. The top end of the quartz shaft is clamped in a plastic collet in the stirring head mechanism (F) which is driven by a 75 r.p.m. synchronous motor connected thru a flexible shaft.

The samples to be dissolved were contained in fragile glass sample bulbs similar to those already described⁽⁴⁾ except that the

(4) Edgar F. Westrum, Jr. AECD- 1903 Figure 2a.

present bulbs were especially thin walled with flat bottoms to facilitate breaking and had a capacity of only about fifty microliters. These bulbs were sealed onto the stirring shaft just below the propellor and were shattered by means of a two millimeter depression of the stirring shaft without interference with the rotational motion. A protrusion was machined into the calorimeter bottom to act as an anvil upon which to break the bulb.

Control and Measurement Circuits. No change was made in the resistance thermometric circuit except for the introduction of a double pole switch to make possible an interconnection with the energy circuit. The measurement branch energy circuit was modified by the introduction of the

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of a potential divider parallel to the thermometer-heater and the use of an auxiliary Rubicon potentiometer to permit a determination of the resistance of the thermometer while in use as a heater. A timer circuit consisted of a standard 1000 cycle oscillator whose signals go through dividing and scaling circuits to provide pulses at four second intervals. These impulses were used to activate a latching relay so that precisely determined time intervals were obtained.

Semi-automatic operation. An ingenious, self-balancing galvanometer circuit engineered by H.P. Robinson made the operation of the calorimeter semi-automatic by providing a "temperature" versus time trace covering the entire experimental period of the run, thus eliminating the necessity of balancing the thermometer circuit periodically and interpolating the dial setting with a high sensitivity galvanometer. The device consisted of a high sensitivity, self-balancing galvanometer which, by the development of a counter potential (exactly equal to that developed across the bridge involving the resistance thermometer) maintained itself in a null position defined by a photocell and by plotting the counter potential on a Leeds and Northrup Speedomax recorder yielded a function nearly linear with respect to temperature as a function of time during the drift, heat input, and reaction intervals. The instrument performed very well and a number of calibration runs were made with its assistance, but the slight factor of sensitivity lost by its use made it undesirable to employ it during the neptunium runs.

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Operation and Performance. The relative temperature sensitivity of the calorimeter is about 2×10^{-5} degrees and since the total heat capacity is about ten calories, the thermal precision is of the order of 2×10^{-4} calories. Consequently, to obtain results accurate to about one percent, a thermal process liberating about 0.2 of a calorie is required. This corresponds to a temperature rise of 0.02°C or to about 240 micrograms of a transuranium element with a heat of solution of the order of 200 kilocalories per mole. The thermal leakage modulus of the calorimeter was observed to be 2×10^{-2} minute⁻¹. The observed drift of the combined heats of stirring and energy required for the operation of the resistance thermometer was about 2×10^{-4} degrees 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°C , (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) careful observation of the foredrift, breaking the sample container, and observation of the afterdrift until a linear 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 as a 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

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energy in the coil and its 99% registration on the galvanometric system on 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 (a), calculation of the energy equivalent of the weighed parts, and (b) the determination of the heat capacity by electrical energy inputs at rates from one fourth to four times that employed in the reactions under studies. 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 involves the calibration of the resistance thermometer on a centigrade scale, which was achieved by immersing the calorimeter covered by a thin rubber sac directly (submarine 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.

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 HCl. The results of these runs are indicated in Table I. They compare very favorably with literature values.

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Table I.

Observed Heat of Solution of KCl in Water

<u>Run Number</u>	<u>Sample Weight</u>	<u>Heat evolved cal.</u>	<u>Kcal/mol.</u>
17	11.178	0.624	4.16*
18	14.250	0.793	4.15*
19	15.602	0.875	4.18*

Observed Heat of Solution of KNO_3 in Water

4	12.747	1.052	8.34
5	8.168	0.6757	8.36
14	8.133	0.6716	8.35*
15	7.522	0.62045	8.35*

Observed Heat of Reaction of Fe in 1.0 molar HCl

45	1.109	5.056	111.2
46	0.2918	1.3318	111.3
47	0.1301	0.5937	111.3

*values marked with an asterisk were obtained by use of the semi-automatic circuit.

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Neptunium Metal. The neptunium metal was prepared on the milligram scale by a process already described⁽⁵⁾ and the spectrochemical

(5) Edgar F. Westrum, Jr. and LeRoy Eyring, ANL-EFW-35.

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 Np 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.

The neptunium was observed to be in the Np(IV) oxidation state at the end of the runs. Trial dissolution experiments were made on comparable quantities of metal and hydrogen saturated acid directly 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 was involved.

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Table II.

Heat of Reaction of Neptunium Metal in
 8.81 gms of 1.500 N HCl and 0.00500 N Na_2SiF_6 at 25.0°C .

Sample weight (mg, vacuo)	Heat evolved (calories)	Observed ΔH (Reaction) kcal/mole
0.456	0.318	-165.7
0.722	0.515	-165.7
1.456	1.0175	-165.9
1.408	0.9608	-165.6
1.906	1.3285	-165.7
		<hr/>
		-165.7 $\pm$ 0.2

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Discussion.

The highly positive value of the Np-Np(III) couple insures the ready dissolution of neptunium in dilute hydrochloric acid, but the negative value of the III-IV couple (-0.14 volts 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.

on the assumption that the solution is initially saturated with H_2 and that in spite of the precautions taken an appreciable concentration of oxygen is present to provide the oxidation. Correction 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,⁽⁶⁾ one obtains $\Delta H = -132.5$ kcal for the formation of

(6) unless other sources are indicated, auxiliary thermodynamic data are obtained from "Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Washington, D.C. (1947)

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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 heats of dilution and ionic radius noted by Westrum and Robinson⁽⁷⁾

(7) E. F. Westrum, Jr. and H. P. Robinson. NNES. The Transuranium Elements: Research Papers: Paper 6.50 McGraw Hill, New York (1949)

a value of $-134.4 \text{ kcal mole}^{-1}$ is obtained for the apparent molal heat of formation of Np(IV) in 1 molal HCl. Using the best value $-5.9 \pm 2 \text{ kcal.}$ for ΔH of the $\text{Np(III)} \rightarrow \text{Np(IV)}$ potential recommended by Brewer⁽⁸⁾ gives a ΔH of $-128.5 \pm$ kilocalories as the apparent

(8) Leo Brewer, L. Bromley, P. Gilles and Norman Lofgren, MDDC - 1417 (1948)

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 ⁽⁷⁾, UCl_4 ⁽⁸⁾, UCl_3 ⁽⁸⁾, and PuCl_3 ^(9,10) as a rough function of ionic radius and hydrogen

(9) E. F. Westrum, Jr. and H. P. Robinson, NNES Vol. 14B The Transuranium Elements: Research Papers Part 2. Paper 6.53. McGraw N.Y. (1949).

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

ion concentration. On this basis values of 217 ± 2 and

$238 \pm 1 \text{ Kcal.}$ are obtained as the molal heat of formation

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of crystalline NpCl_3 and NpCl_4 , respectively.

The differences of the order of two kilocalories, between our values and those calculated by Brewer⁽⁸⁾ arise in part from his interpretation of reaction(2) as one involving dissolved rather than gaseous hydrogen. Inasmuch as the solution was initially saturated with hydrogen at a slightly lower temperature and that comparable dissolution experiments on this and other transuranium in metals on this scale under similar conditions clearly indicates that most of the hydrogen does escape--and that it is virtually saturated with water vapor.

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