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

The Heat of Formation of Thorium Tetrachloride[1a]

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Current interest in the elements of the actinide series implies a scientific and technical requirement of accurate thermodynamic data on the compounds of members of this series. Some measurements by Westrum and Robinson[2] on the heat of solution of thorium tetrachloride in several concentrations of hydrochloric acid indicated that as a result of neglecting the concentration of the acid used to dissolve the thorium metal in the evaluation and combination of the experimental data, the heat of formation of thorium tetrachloride reported by Chauvenet[3] is about nine kilocalories too large. Even after the application of this correction, the reported heat of formation appeared surprisingly large. Furthermore it is unlikely, on the basis of recent information,[4] that pure thorium metal would have been obtained by the process described by Chauvenet.

The present measurements were made on two different very pure samples of thorium metal prepared by the Ames Laboratory of the Atomic Energy Commission at Iowa State College and some microscopic crystals of anhydrous thorium tetrachloride obtained indirectly from Lindsay Light and Chemical Co.

Thorium metal does not appear to dissolve completely in 6 *M* HCl at room temperature even on long standing. The bulk of the metal (*ca.* 75%) dissolves quite readily in a short time giving rise to a voluminous black residue the exact composition of which has not been determined. This residue can be dissolved by more stringent treatment such as the addition of fluosilicate, etc., leaving only a relatively small white precipitate. The addition of a very small concentration of sodium fluosilicate (Na_2SiF_6) to the acid effects solution of more than 98% of the sample leaving only the white crystalline residue of thorium dioxide known to be present in the original sample.

Purity of the Materials

Samples of pure thorium metal prepared by the reduction of thorium tetrafluoride with zinc and subsequent removal of the zinc by vacuum distillation were made available to us. A section cut from the middle portion of the ingot identified as H-3-15 was the source of our samples and the analytical samples from which were obtained the following information relative to the purity of the metal by the Analytical Section of the Metallurgical Laboratory. Duplicate assays yielded the following information: Th (99.5, 99.7%); C (600, 560 p. p. m.); N (773, 795 p. p. m.), and H (133, 135 p. p. m.). Spectrochemical analyses set limits on the maximum amounts of metallic impurities as less than one part per million of B, Bi, Cd, K and Li; less than ten p. p. m. of Ag, As, Ca, Na, Sb and Sn; less than 20 p. p. m. of Co, Cr, Ni and P; less than 100 p. p. m. of Al and Mo; less than 200 p. p. m. of Ti. Elements detected were 10 p. p. m. of Be, 20 p. p. m. of Cu, 40 p. p. m. of Pb, 70 p. p. m. of Mn, 200 p. p. m. of Si, 800 p. p. m. of Mg and 2000 p. p. m. of Zn. Survey experiments upon another sample of metal identified as AEC-21 with a similar typical analysis showed entirely similar behavior. Separate measurements of the hydrogen evolved upon dissolution of metal in hydrochloric acid solutions containing fluosilicate confirmed the purity of the metal and the completeness of dissolution under the calorimetric conditions. The metal increases in weight 13.86% on combustion in air corresponding to 100.3% of free metal if the light impurities are neglected in the calculation.

Crystals about 2 mm. in length of anhydrous thorium tetrachloride prepared by Lindsay Light and Chemical Company carried an analysis of 62.8% Th and 37.8% Cl (theoretical: 62.07% Th and 37.93% Cl).

Sodium fluosilicate of C. P. grade was used. The aqueous hydrochloric acid was standardized against mercuric oxide.

Experimental Method and Data

The heat of solution measurements were made in a calorimeter previously described.[5] Calibrations of the electrical resistances and the heat capacity of the system were confirmed after shipment of the instrument.

The heat of solution of thorium tetrachloride data are presented in Table I. The data for 6.0 *M* HCl are in excellent agreement with the value 44.21 ± 0.1 kcal./mole obtained by Westrum and Robinson[1] on finely divided, crystalline vacuum sublimed anhydrous thorium tetrachloride. The difference in the observed heat of solution in the presence of the Na_2SiF_6 is definitely beyond experimental error. It was noted that the time required for

TABLE I

THE HEAT OF SOLUTION OF THORIUM TETRACHLORIDE IN 6.004 *M* HYDROCHLORIC ACID AT 25°

Mol. wt. $ThCl_4$, 373.95; weight of acid, 212.25 g. (*in vacuo*)

Run	Mmoles $ThCl_4$ (*in vacuo* wt. of samples)	Mmoles $ThCl_4$ (by oxalate pptn.)	Obs. heat evolved, cal.	Heat of soln., kcal./mole
A	0.4423	0.4424	19.59	−44.29
B	.8247	.8254	36.49	−44.25
C	1.0450	1.0445	46.29	−44.30
			Average	−44.28 ± 0.06
With 0.00500 *M* Sodium Fluosilicate Added				
D	1.0627	1.0638	47.38	−44.58
E	0.5633	0.5630	25.11	−44.58
			Average	−44.58 ± 0.08

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[1] (a) This work was performed under Manhattan District Contract W-31-109-Eng-38 in 1946 at the Radiation Labratory of the University of California at Berkeley; (b) Department of Chemistry, The State University of Iowa, Iowa City, Iowa; (c) Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[2] E. F. Westrum, Jr., and H. P. Robinson, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.50 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

[3] E. Chauvenet, *Ann. chim. phys.*, Series 8, Volume 23, 425 (1911).

[4] R. W. Nortorf, A. S. Wilson, R. E. Rundle, A. S. Newton and J. E. Powell, reported in Manhattan Project Document CC-2722 March 8, 1945.

[5] Westrum and Robinson, *op. cit.*, Paper No. 6.51.

practical completion of the thermal effect was 2, 3 and 4 minutes in runs A, B and C, respectively; approximately a minute was required in the presence of Na_2SiF_6.

The amount of thorium dissolved was determined by precipitation of thorium oxalate and gravimetric determination of the dioxide. The interference of the small concentration of fluosilicate was noted, but by carrying out the analyses in a reproducible manner an empirically determined correction was applicable.

Table II

The Heat of Solution of Thorium Metal in 6.004 *M* Hydrochloric Acid with 0.00500 *M* Sodium Fluosilicate Added at 25°

At. wt. of Th, 232.12; wt. of acid, 212.25 g. (*in vacuo*)

Run	J	K
Mmoles. of Th (vac. wt. samples)	0.4515	0.4446
Mmoles. dissolved (by oxalate pptn.)	0.4449	0.4379
Per cent. in solution	98.5	98.5
Obs. heat evolved, cal.	80.70	79.39
Obs. heat of soln., kcal./mole	181.6	181.4
Cor. heat of soln.,[a] kcal./mole	181.8	181.6

[a] Correction applied for evaporation of solution by hydrogen evolution, dissolution of light metals and reaction of thorium compounds present as impurities.

The Heat of Formation

The following cycle is used to evaluate the heat of formation

$$\mathrm{Th}(c) + [a\mathrm{HCl},\ b\mathrm{H_2O}] = [\mathrm{ThCl_4},\ (a-4)\mathrm{HCl},\ b\mathrm{H_2O}] + 2\mathrm{H_2}(g) \quad (1)$$

$$\mathrm{ThCl_4}(c) + [a\mathrm{HCl},\ b\mathrm{H_2O}] = [\mathrm{ThCl_4},\ a\mathrm{HCl},\ b\mathrm{H_2O}] \quad (2)$$

$$2\mathrm{H_2}(g) + 2\mathrm{Cl_2}(g) + [\mathrm{ThCl_4}(a-4)\mathrm{HCl},\ b\mathrm{H_2O}] = [\mathrm{ThCl_4},\ a\mathrm{HCl},\ b\mathrm{H_2O}] \quad (3)$$

$$\mathrm{Th}(c) + 2\mathrm{Cl_2}(g) = \mathrm{ThCl_4}(c) \quad (4)$$

Typical values are: $a = 2400$, $b/a = 8.105$

Reactions (1) and (2) correspond to the experimental measurements of the heat of solution of thorium metal and thorium tetrachloride, respectively. Reaction (3) is evaluated as the apparent heat of formation of hydrochloric acid in the 6.684 *m* aqueous solution from the heat of formation of the infinitely dilute aqueous solution of hydrogen chloride,[6,7] and the relative molal heat content of the 6 *M* acid. The heat of this reaction is assumed to be uninfluenced by the small concentration of the thorium salt since the ionic strengths of the solutions will be nearly unchanged by its removal.

The heat of formation of $ThCl_4$ at 25° is, therefore

$$\Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3$$
$$= -181.7 + 44.6 - 4(36.84) = 284.5 \text{ kcal./mole}$$

A linear extrapolation of the heat of solution of thorium tetrachloride from one molar[2] concentration of hydrogen chloride to infinite dilution yields a value of −60.0 for the heat of solution in the infinitely dilute acid. The heat of formation of the thorium ion $\mathrm{Th} + 4\mathrm{H^+(aq)} = \mathrm{Th^{+4}(aq)} + 2\mathrm{H_2(g)}$ is calculated to be −184.4 kcal./mole by combining the above value with the heat of formation of the infinitely dilute aqueous solution of hydrogen chloride[7] and the heat of formation of $ThCl_4$.

Credit for the performance of this work is gratefully shared with those who supplied the materials and the analyses of them. This applies especially to the Manhattan Project at Ames for the thorium metal, the Analytical Section of the Metallurgical Laboratory for chemical and spectrographic analysis of the thorium metal and the thorium tetrachloride, and to Winifred Heppler for technical assistance.

Summary

The heats of solution of thorium metal and of thorium tetrachloride in six molar hydrochloric acid have been measured. The addition of a very small concentration of sodium fluosilicate was required to obtain quantitative solution of the metal. The heat of formation of $ThCl_4(c)$ is calculated to be −284.5 kcal./mole at 25° and is markedly lower than the value reported in the literature.

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(6) F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679 (1932).

(7) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Washington (1947).