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THE HEAT OF FORMATION OF THORIUM SESQUISULFIDE

LeRoy Eyring and Edgar F. Westrum, Jr.

April 7, 1953

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THE HEAT OF FORMATION OF THORIUM SESQUISULFIDE¹

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April 7, 1953

¹This work was performed under Manhattan District Contract W-31-109 - Eng 38 in 1946 at the Radiation Laboratory, Berkeley.

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Iowa City, Iowa.

³Department of Chemistry, University of Michigan, Ann
Arbor, Michigan.

ABSTRACT

The heat of solution of thorium sesquisulfide was determined in 6.000 molar HCl at 25° C. to ascertain the stability of the thorium (III) halides. The molal heat of formation of Th₂S₃ from rhombic sulfur and crystalline thorium is calculated as 258.6 kcal.

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THE HEAT OF FORMATION OF THORIUM SESQUISULFIDE¹

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The stability of the thorium (III) oxidation state is a matter of considerable interest in understanding the nature of the actinide elements. As a prelude to attempts to prepare a trihalide of thorium, we determined the heat of solution of thorium sesquisulfide (Th_2S_3) in aqueous hydrochloric acid and calculated its heat of formation. These quantities are of interest in considering the applicability of thorium sesquisulfide as a refractory material and in deducing the probable stabilities of thorium (III) halides.

Experimental

These measurements were made with a calorimeter, the calibration and operation of which are described elsewhere.⁴

⁴E. F. Westrum, Jr., and H. P. Robinson, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Trans-uranium Elements: Research Papers," McGraw-Hill Book Co., Inc., New York, 1949, Paper Nos. 6.50 and 6.51.

Frequent electrical calibrations were in complete accord with previous determinations of the heat capacity of the calorimeter.

A two gram sample of thorium sesquisulfide prepared by Dr. Leo Brewer and his co-workers⁵ was made available to us.

⁵E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, J. Am. Chem. Soc., 72, 4019 (1950).

Tests indicated that $96.95 \pm 0.2\%$ of the thorium sesquisulfide sample dissolved in aqueous HCl, liberated H₂ and H₂S, gave a solution with a S/Th ratio of 1.500 ± 0.005 , and left $3.05 \pm 0.2\%$ of an insoluble residue of ThOS or ThO₂.⁶ An accurately weighed

⁶L. Brewer, Manhattan Project Documents, MB-LB-123 and MB-LB-126 (1945).

quantity of thorium sesquisulfide was sealed into thin bottomed sample bulbs under an atmosphere of anhydrous nitrogen. In the calorimeter, each sample was reacted with 6.000 molar HCl which had been standardized against mercuric oxide and saturated with H₂. The

amount of thorium dissolved was determined by gravimetric analysis of the calorimeter solution after each run.

The quantity of H_2S which remained dissolved in the calorimeter was established in order that appropriate corrections could be made for it. The solution from the calorimeter was filtered rapidly and transferred to a sealed flask fitted with a delivery tube. Upon boiling the solution, the H_2S distilled over into a flask containing an excess of aqueous silver nitrate. The Ag_2S residue was filtered, washed with hot water, dissolved in concentrated nitric acid, and titrated with 0.1 M KSCN.

To determine thorium, the calorimeter solution was neutralized with 15 M ammonium hydroxide, heated to boiling, and the thorium precipitated as thorium oxalate upon very slow addition of an excess of aqueous oxalic acid solution. The precipitate was allowed to stand several hours and was then filtered, washed, and ignited to constant weight as ThO_2 . A small, empirically determined correction was required to correct for the complexing action of the fluosilicate present in certain determinations. The six determinations of the heat of reaction of Th_2S_3 in acid solution are tabulated in Table I. Runs A, B and C were made with 6.000 molar HCl and in each the reaction lasted 10 to 12 minutes. Determinations D, E and F were made in precisely the same way except that the hydrochloric acid was 0.005 molar with respect to Na_2SiF_6 . In these runs the reaction time was 6 to 8 minutes. The fluosilicate was added in order that the data could be compared without correction with heat of solution data of the metal dissolved in the fluosilicate

Table I.

The Heat of Solution of Th_2S_3 in 212.29 grams
of 6.000 molar HCl at 25° C.

Run Designation	A	B	C	D ^a	E ^a	F ^a
Millimoles of Th_2S_3 weighed	0.49106	0.60134	0.52416	0.70624	0.61456	0.29531
Millimoles of Th_2S_3 dissolved	0.4762	0.5820	0.5086	0.6850	0.5972	0.2864
Millimoles of H_2S dissolved	1.343	1.641	1.421	1.932	1.684	0.807
Observed heat liberated (cal.)	62.75	76.86	67.06	90.46	78.71	37.74
Corrected heat evolved ^b (cal.)	63.26	77.48	67.60	91.18	79.34	38.04
Molal heat of solution of Th_2S_3 ^c (kcal.)	132.8	133.1	132.9	133.1	132.9	132.8

^aRuns D, E and F contain 0.005 molar concentration of Na_2SiF_6 .

^bIncludes correction for H_2O vaporized by escape of H_2S and H_2 and for the reaction $\text{H}_2\text{S}(\text{aq}) \longrightarrow \text{H}_2\text{S}(\text{g})$.

^cReaction (2) text.

HCl solvent.⁷ The experiments were performed at 25.00° C. The

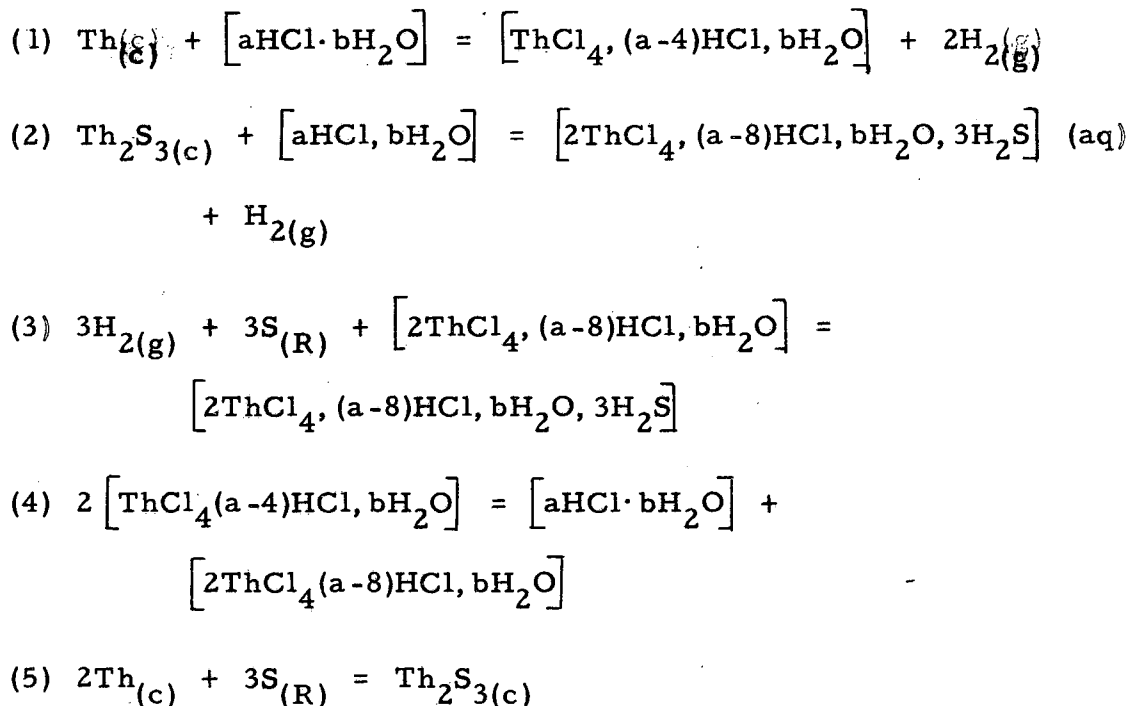
⁷L. Eyring and E. F. Westrum, Jr., J. Am. Chem. Soc.,
72, 5555 (1950).

molecular weights of Th₂S₃ and ThO₂ are taken as 560.42 and 264.12, respectively.

The Heat of Formation of Th₂S₃

The series of reactions represented in Table II are the basis for the calculation of the heat of formation. The small concentration of fluosilicate in the 6.0 molar HCl is understood to be present.

Table II



Reaction (1) is evaluated from the heat of solution of thorium metal.

Reaction (2) represents the heat of solution of thorium sesquisulfide

from this work. The apparent heat of formation of hydrogen sulfide in 6.0 molar aqueous HCl is not available; however, the heat of formation of H_2S in the hypothetical standard state of unit molarity in aqueous solution⁸ is given as $-9.4 \text{ kcal. mole}^{-1}$. The enthalpy

⁸Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Circular 500, Washington, D. C. (1952).

change for the reaction $H_2S_{(aq)} = H_2S_{(g)}$ is given as $4.6 \text{ kcal. mole}^{-1}$. Furthermore, the hydrogen and the hydrogen sulfide leaving the solution will be saturated with water and a correction must be applied for the water vaporized. Because the solution had been saturated with hydrogen at the beginning of the experiments, it was assumed that this condition prevailed at the end. The thermal effect of equation (4) is negligible under the experimental conditions.

The heat of formation, Reaction (5), at 25° C is therefore:

$$\Delta H_5 = 2\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 = -258.6 \text{ kcal. mole}^{-1}$$

from thorium and rhombic sulfur. If gaseous sulfur is used as the reference state, the heat of formation of the thorium sesquisulfide is $-303.4 \text{ kcal. mole}^{-1}$.

Comparison of this value with the corresponding heat of formation of Ce_2S_3 leads to limiting values for the heat of formation of thorium (III) halides. The argument has already been presented⁹

⁹L. Brewer, U.S. Atomic Energy Commission Declassified Document. AECD-1911 (1948).

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and need not be repeated here. An attempt by Warf to prepare the trivalent thorium fluoride was not successful¹⁰ although

¹⁰J. C. Warf, U.S. Atomic Energy Commission Declassified Document. AECD-2654 (1947).

Hayek and Rehner^{11, 12} and Anderson and D'Eye¹³ claim to have

¹¹E. Hayek and Th. Rehner, Experientia S 114 (1949).

¹²E. Hayek and Th. Rehner, Monatsheften fur Chemie, 82, 575 (1951).

¹³J. S. Anderson and R. W. M. D'Eye, J. Chem. Soc., Supplement 2 - 244 (1949).

prepared thorium (III) iodide.

The technical assistance of Winifred Heppler and the motivating influence of Dr. Leo Brewer are gratefully acknowledged.

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