THE HEAT OF FORMATION OF THORIUM SESQUISULFIDE
LeRoy Eyring and Edgar F. Westrum, Jr.
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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 Th$_2$S$_3$ from rhombic sulfur and crystalline thorium is calculated as 258.6 kcal.

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$_2$S$_3$) 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. Frequent

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

Tests indicated that 96.95 ± 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 ± 0.2% of an insoluble residue of ThO₃ or ThO₂. An accurately weighed 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 H₂S 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 H₂S distilled over into a flask containing an excess of aqueous silver nitrate. The Ag₂S 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$_2$S$_3$ in acid solution are tabulated in Table 1. 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$_2$SiF$_6$. 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 HCl solvent. The experiments were performed at 25.00°C. The molecular weights of Th$_2$S$_3$ and ThO$_2$ are taken as 560.42 and 264.12, respectively.

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Table I.

The Heat of Solution of Th$_2$S$_3$ in 212.29 grams of 6.000 Molar HCl
at 25°C.

<table>
<thead>
<tr>
<th>Run Designation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D*</th>
<th>E*</th>
<th>F*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimoles of Th$_2$S$_3$ weighed</td>
<td>0.69106</td>
<td>0.60134</td>
<td>0.52416</td>
<td>0.70624</td>
<td>0.61456</td>
<td>0.29531</td>
</tr>
<tr>
<td>Millimoles of Th$_2$S$_3$ dissolved</td>
<td>0.4762</td>
<td>0.5320</td>
<td>0.5086</td>
<td>0.6850</td>
<td>0.5972</td>
<td>0.2864</td>
</tr>
<tr>
<td>Millimoles of H$_2$S dissolved</td>
<td>1.343</td>
<td>1.641</td>
<td>1.421</td>
<td>1.932</td>
<td>1.684</td>
<td>0.807</td>
</tr>
<tr>
<td>Observed heat liberated (cal)</td>
<td>62.75</td>
<td>76.86</td>
<td>67.06</td>
<td>90.46</td>
<td>78.71</td>
<td>37.74</td>
</tr>
<tr>
<td>Corrected heat evolved** (cal)</td>
<td>63.26</td>
<td>77.48</td>
<td>67.60</td>
<td>91.18</td>
<td>79.34</td>
<td>38.04</td>
</tr>
<tr>
<td>Molal heat of solution of Th$_2$S$_3$***(kcal.)</td>
<td>132.8</td>
<td>133.1</td>
<td>132.9</td>
<td>133.1</td>
<td>132.9</td>
<td>132.8</td>
</tr>
</tbody>
</table>

*Runs D, E, and F contain 0.005 molar concentration of Na$_2$SiF$_6$.

**Includes correction for H$_2$O vaporized by escape of H$_2$S and H$_2$ and for the reaction H$_2$S(sq) —— H$_2$S(g).

***Reaction (2) text.

The Heat of Formation of Th$_2$S$_3$

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

(1) \( \text{Th}(c) + [\text{aHCl}, \text{bH}_2\text{O}] = [\text{ThCl}_4, (a-4)\text{HCl}, \text{bH}_2\text{O}] + 2\text{H}_2(g) \)

(2) \( \text{Th}_2\text{S}_3(c) + [\text{aHCl}, \text{bH}_2\text{O}] = [2\text{ThCl}_4, (a-8)\text{HCl}, \text{bH}_2\text{O}, 3\text{H}_2\text{S}] \text{(aq)} + \text{H}_2(g) \)

(3) \( 3\text{H}_2(g) + 3\text{S}(\text{R}) + [2\text{ThCl}_4, (a-8)\text{HCl}, \text{bH}_2\text{O}] = [2\text{ThCl}_4, (a-8)\text{HCl}, \text{bH}_2\text{O}, 3\text{H}_2\text{S}] \)

(4) \( 2[\text{ThCl}_4, (a-4)\text{HCl}, \text{bH}_2\text{O}] = [\text{aHCl}, \text{bH}_2\text{O}] + [2\text{ThCl}_4, (a-8)\text{HCl}, \text{bH}_2\text{O}] \)

(5) \( 2\text{Th}(c) + 3\text{S}(\text{R}) = \text{Th}_2\text{S}_3(c) \)

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 \( \text{H}_2\text{S} \) in the hypothetical standard state of unit molality in aqueous solution\(^8\) is given as -9.4 kcal mole\(^{-1}\). The enthalpy change for the reaction \( \text{H}_2\text{S} \text{(aq)} = \text{H}_2\text{S} \text{(g)} \) is given as 4.6 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:

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

from thorium and rhombic sulfur. If gaseous sulfur is used as the reference state, the heat of formation of the thorium sesquisulfide is $305.4 \text{ kcal. mole}^{-1}$.

Comparison of this value with the corresponding heat of formation of Ce$_2$S$_3$ leads to limiting values for the heat of formation of thorium (III) halides. The argument has already been presented$^9$ and need not be repeated here. An attempt by Warf to prepare the trivalent thorium fluoride was not successful$^{10}$ although Hayek and Rheiner$^{11,12}$ and Anderson and D'Eya$^{13}$ claim to have prepared thorium (III) iodide.

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


$^{11}$E. Hayek and Th. Rheiner, Experimentia 9 114 (1949).

$^{12}$E. Hayek and Th. Rheiner, Monatsheften fur Chemie 82 575 (1951).