tion fits very much better than the square law ($\lambda^2 = a + bn$). In the ionic series the agreement between calculated and observed values is only slightly better than that obtained from the linear equation ($\lambda = a + bn$). It is unfortunate that we did not succeed in measuring the spectra of still higher members of the series. With $n = 8$, the difference between the two equations would be demonstrable.

The spectra of all vinylogous series show $\bar{\nu}$ decreasing by decreasing amounts with increase in n, but the way in which they decrease is not always that shown in the above equation. It is true that in the series $C_6H_5(CH{=}CH)_nC_6H_5$ up to $n = 7$ values of T, R and γ can be chosen so that the spectrum fits the equation, except when $n = 0$. With the same exception the spectra also fits the equation $\lambda^2 = a + bn$. But the spectra of series of the type $R_2\overset{+}{N}{=}CH(CH{=}CH)_n\text{-}NR_2$ do not fit the equation, no matter what choice is made for T, R and γ. However, the spectra of these vinylogous series obey the more general equation $\bar{\nu} = T - \sum_n f(n)$, where $f(n)$ is the effect of interpolating the nth vinyl group and decreases with n but does not become negative. It is probable that the expression $\sum_n f(n)$ with the above restrictions of $f(n)$ always gives the effect of the conjugate system $(CH{=}CH)_n$ on the energy of a reaction of a functional group with which it is in resonance, but that the agreement obtained by using $f(n) = R\gamma^n$ in these experiments is largely fortuitous.

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[Contribution from the Department of Chemistry and the Radiation Laboratory, University of California, Berkeley]

The Heat of Formation of Thorium Sesquisulfide[1]

By LeRoy Eyring[2a] and Edgar F. Westrum, Jr.[2b]

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The heat of solution of thorium sesquisulfide was determined in 6.000 molar HCl at 25° to ascertain the stability of the thorium(III) halides. The molal heat of formation of Th_2S_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_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.[3] 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-workers[4] was made available to us. Tests indicated that 96.95 ± 0.2% of the thorium sesquisulfide sample dissolved in aqueous HCl, liberated H_2 and H_2S, gave a solution with a S/Th ratio of 1.500 ± 0.005, and left 3.05 ± 0.2% of an insoluble residue of ThOS or ThO_2.[5] Accurately weighed quantities of thorium sesquisulfide were sealed into thin bottomed sample bulbs under an atmosphere of anhydrous nitrogen. In the calorimeter, each sample reacted with 6.000 M HCl which had been standardized against mercuric oxide and saturated with H_2. 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 M 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 M 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 HCl solvent.[6] The experiments were performed at 25.00°. The molecular weights of Th_2S_3 and ThO_2 are taken as 560.42 and 264.12, respectively.

The Heat of Formation of Th_2S_3

The series of reactions represented in Table II are the basis for the calculation of the heat of formation. The small concentration of fluorosilicate in the 6.0 M HCl is understood to be present. The heat of reaction (1) is evaluated from the heat of

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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.

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

(3) E. F. Westrum, Jr., and H. P. Robinson, "National Nuclear Energy Series, Vol. 14B, The Transuranium Elements, Part I, Research Papers 6.50 and 6.51," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, This Journal, **72**, 4019 (1950).

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

(6) L. Eyring and E. F. Westrum, Jr., This Journal, **72**, 5555 (1950).

TABLE I

THE HEAT OF SOLUTION OF Th_2S_3 IN 212.29 G. OF 6.000 *M* HCl AT 25°

Run designation	A	B	C	D[a]	E[a]	F[a]
Th_2S_3 weighed, mmoles	0.49106	0.60134	0.52416	0.70624	0.61456	0.29531
Th_2S_3 dissolved, mmoles	0.4762	0.5820	0.5086	0.6850	0.5972	0.2864
H_2S dissolved, mmoles	1.343	1.641	1.421	1.932	1.684	0.807
Obsd. heat liberated, cal.	62.75	76.86	67.06	90.46	78.71	37.74
Cor. heat evolved,[b] cal.	63.26	77.48	67.60	91.18	79.34	38.04
Molal heat of sol. of Th_2S_3,[c] kcal.	132.8	133.1	132.9	133.1	132.9	132.8
Av. molal heat of soln. of Th_2S_3,[c] kcal.			132.9 ± 0.1			

[a] Runs D, E and F contain 0.005 *M* concentration of Na_2SiF_6. [b] Includes correction for H_2O vaporized by escape of H_2S and H_2 and for the reaction $H_2S(aq) \rightarrow H_2S(g)$. [c] Reaction (2) Table II.

solution of thorium metal[6]; that of reaction (2) is represented by the heat of solution of thorium sesquisulfide from Table I. The apparent heat of formation of hydrogen sulfide in 6.0 *M* aqueous HCl is not available; however, the heat of formation of H_2S in the hypothetical standard state of unit molality in aqueous solution[7] is given as −9.4 kcal. mole^{-1}. The enthalpy change for the reaction $H_2S(aq) = H_2S(g)$ 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.

TABLE II

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

$$\mathrm{Th_2S_3(c)} + [a\mathrm{HCl},\ b\mathrm{H_2O}] = [2\mathrm{ThCl_4},\ (a-8)\mathrm{HCl},\ b\mathrm{H_2O},\ 3\mathrm{H_2S}](aq) + \mathrm{H_2(g)} \quad (2)$$

$$3\mathrm{H_2(g)} + 3\mathrm{S(R)} + [2\mathrm{ThCl_4},\ (a-8)\mathrm{HCl},\ b\mathrm{H_2O}] = [2\mathrm{ThCl_4},\ (a-8)\mathrm{HCl},\ b\mathrm{H_2O},\ 3\mathrm{H_2S}] \quad (3)$$

$$2[\mathrm{ThCl_4},\ (a-4)\mathrm{HCl},\ b\mathrm{H_2O}] = [a\mathrm{HCl},\ b\mathrm{H_2O}] + [2\mathrm{ThCl_4},\ (a-8)\mathrm{HCl},\ b\mathrm{H_2O}] \quad (4)$$

$$2\mathrm{Th(c)} + 3\mathrm{S(R)} = \mathrm{Th_2S_3(c)} \quad (5)$$

The heat of formation, reaction (5), at 25° is therefore

$$\begin{aligned}\Delta H_5 &= 2\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4\\ &= 2(-181.7) - (-132.8) + (-28.2) + 0\\ &= -258.6 \text{ kcal. mole}^{-1}\end{aligned}$$

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 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 presented[8] and need not be repeated here. An attempt by Warf to prepare the trivalent thorium fluoride was not successful[9] although Hayek and Rehner[10-11] and Anderson and D'Eye[12] claim to have prepared thorium(III) iodide.

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