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THORIUM CERAMICS DATA MANUAL

Volume V - Sulfides

Sigfred Peterson

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Volume V. Sulfides

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ABSTRACT

Physical, chemical, and mechanical properties of thorium sulfides, alone and in combination with other sulfides and other thorium compounds, are compiled from the literature through November 1971. Although the phase equilibria in the thorium-sulfur system are poorly known, the compounds ThS, Th₂S₃, Th₇S₁₂, ThS₂, and ThOS are reasonably well characterized chemically and physically. Mechanical property data are sparse, and very little is known about systems with other compounds except for ThS-US.

SYSTEM INFORMATION

The equilibrium diagram for the thorium-sulfur system is not known, but at least five sulfides of thorium are known. The persulfide has been established as Th₂S₅ by Graham and McTaggart,¹ although earlier work by Strotzer² had suggested Th₃S₇. Since this compound loses sulfur at 600°C and below to form ThS₂, it is of no interest as a ceramic, and its properties will not be reported here. The ceramic sulfides of thorium have been described by Eastman *et al.*^{3,4} The disulfide is probably the most stable sulfide with respect to the elements except at temperatures above 1600°C; Graham and McTaggart¹ indicate that it is the only stable sulfide. However, Samsonov and Popova⁵ suggest that the lower sulfides, ThS and Th₂S₃, are more stable. An intermediate compound has been described as ThS_{1.7} and Th₄S₇ but is usually given the formula Th₇S₁₂ assigned by Zachariasen⁶ on the basis of his crystal structure determination.

The preparation and properties of thorium sulfides have been reviewed by Dell and Allbutt⁷ and Radzikovskaya and Marchenko.⁸

THORIUM MONOSULFIDE SYSTEMS

A. Thorium Monosulfide

1. Composition

The composition of ThS varies little about the stoichiometric proportion.³ Although Strotzer² reported a wide range (all hypostoichiometric) later work

has not confirmed it. Cater *et al.*⁹ indicate a composition ThS_{1.01}. However, Aronson¹⁰ has verified the small difference found by Eastman *et al.*³ in the lattice parameters of thorium monosulfide in thorium-rich and sulfur-rich samples, suggesting that a measurable range of compositions exists for the ThS phase.

2. Preparation

Thorium monosulfide is most easily prepared from the hydride and hydrogen sulfide in stoichiometric proportions, but a purer product can be obtained from ThS₂ and hydride.³ Shalek¹¹ indicates that the latter product is an equimolar mixture of metal and ThS₂, and he converted it to ThS by firing at 1800 to 1900°C. A more traditional preparation is from the powdered elements, but Graham and McTaggart¹ failed to obtain ThS at 800°C; they suggest that oxygen impurity is necessary for the synthesis, but it is more likely that a higher temperature is required to form ThS. Didchenko and Litz¹² prepared the monosulfide by electrochemical reduction of a pressed mixture of anhydrous ThCl₄ and Na₂S with a molten NaCl-KCl eutectic electrolyte.

Pressed and sintered ThS bodies have been prepared by Eastman *et al.*⁴ and by Shalek.¹¹ The former pressed -200 or -300-mesh powder with 5% naphthalene, heated to volatilize the binder, and sintered at 1950 to 2050°C. They reported no effect of Th₂S₃ or ThOS impurities on the sintering. However, Shalek attributed rapid densification at 1900 to 2000°C to the presence of ThOS and formation of a ThS-ThOS eutectic.

Jordan¹³ prepared thorium sulfide samples by reaction of the elements for four to eight days at 350 to 425°C followed by melting under helium. His castings often analyzed richer in thorium than the intended composition, and phases present were not identified.

3. Crystal Properties

Thorium monosulfide has the cubic sodium chloride structure, with the following values reported for the lattice parameter:

Reference	a_0 , Å
Zachariasen ¹⁴	5.683 ± 0.002
Shalek ¹¹	5.684
Cater <i>et al.</i> ⁹	5.6809 ± 0.0009
Aronson <i>et al.</i> ¹⁵	5.680
Tetenbaum ¹⁶	5.682
Aronson ¹⁰	
Thorium-rich	5.681
Sulfur-rich	5.674

The coefficient of thermal expansion is given as $10.1 \times 10^{-6}/^\circ\text{C}$ for 20 to 950°C by Shalek¹¹ and $12.0 \times 10^{-6}/^\circ\text{C}$ for 850 to 1400°C by Aronson *et al.*¹⁵ The latter expansion results are shown graphically in Fig. 4 on p. 80 of Vol. III.

Thorium monosulfide has been described as silvery^{3,9} and dark gray.¹⁷ Sintered bodies are silvery with metallic reflectance.¹¹

4. Thermodynamic Properties

Flotow *et al.*¹⁸ have measured the heat capacity of ThS from 1 to 350°K. Their smoothed results and the other functions derived from them are listed in Table 1. The results include a correction for a small amount of Th₂S₃ in their sample. For the formation of ThS at 25°C, they calculate $\Delta S^\circ = -3.70 \pm 0.11 \text{ cal mole}^{-1} (^\circ\text{K})^{-1}$ or $-15.46 \pm 0.47 \text{ J mole}^{-1} (^\circ\text{K})^{-1}$.

By high-temperature emf measurements on galvanic cells, Aronson¹⁰ found for the reaction $\text{Th} + \text{Th}_2\text{S}_3 \rightleftharpoons 3\text{ThS}$ at 900°C, $-\Delta G^\circ = 19.8 \pm 2 \text{ kcal (83 kJ)}$, $-\Delta S^\circ = 5.9 \pm 2 \text{ cal/}^\circ\text{C (25 J/}^\circ\text{C)}$, and $-\Delta H^\circ = 26.7 \pm 4 \text{ kcal (112 kJ)}$. From the ΔH° and two published^{19,20} heats of formation of Th₂S₃, he derived the 900°C heats of formation for ThS given in Table 2. By correcting to 25°C and to the different standard state of sulfur (rhombic at 25°C, S₂ gas at 900°C), we can estimate the 25°C enthalpies in Table 2; using the above ΔS° , we obtain the free energies of formation. The estimate by Eastman *et al.*³ of $-\Delta H_{298}^\circ = 120 \text{ kcal/mole}$ for formation from gaseous S₂ appears to be too negative.

From measurements of heat of solution in hydrochloric acid, Ader²¹ finds for the heat of formation $-\Delta H_f^\circ = 96.9 \text{ kcal/mole} = 405 \text{ kJ/mole}$ for a composition ThS_{1.029} in good agreement with the better of the two estimates in Table 2.

5. Change of State

Melting point: Shalek¹¹ gives 2335°C in his text but shows 2325°C plotted. Samsonov and Popova⁵ report 2230°C on material of questionable composition.

Vaporization: Cater *et al.*⁹ estimate the vapor pressure to be given by $\log p (\text{atm}) \approx 7.7 - 3.366 \times 10^4/T$ or $\log p (\text{N/m}^2) \approx 12.7 - 3.366 \times 10^4/T$. Eastman *et al.*^{3,4} say the vapor pressure is less than 10^{-3} torr (0.1 N/m²) at 2200°C. Shalek¹¹ gives the rate of evaporation of sintered specimens of unspecified dimensions as negligible up to 1900°C and 2.0%/hr at 2050°C in vacuum.

6. Electrical Properties

Electrical resistivity was measured by Tetenbaum¹⁶ on 85%-dense ThS contaminated with about 5% ThOS. The results are given in Fig. 1. Seebeck coefficients measured on the same material are given in Fig. 2. Similar measurements by Jordan¹³ on poorly characterized material gave a resistivity that varied from about 740 $\mu\Omega\text{-cm}$ at 25°C to 1900 $\mu\Omega\text{-cm}$ at 1000°C and a Seebeck coefficient fluctuating between +30 $\mu\text{V/}^\circ\text{C}$ at 100°C and 19 $\mu\text{V/}^\circ\text{C}$ at 1000°C. Shalek¹¹ found the resistivity at room temperature to increase with firing temperature, varying among specimens from 16 to 43 $\mu\Omega\text{-cm}$. Thorium monosulfide is diamagnetic.^{3,22}

7. Heat and Mass Transport

Kollie *et al.*²³ found for 95.59%-dense ThS thermal conductivity values of 44.8 and 34.3 $\text{W m}^{-1} (^\circ\text{C})^{-1}$ at 75 and 300°C, respectively. Values corrected to theoretical density and estimates to 1000°C based on these values and electrical resistivity are listed in Table 3.

8. Mechanical Properties

In bending strength measurements, Shalek¹¹ found moduli of rupture ranging from 16,000 to 31,000 psi (110 to 214 MN/m^2) for ThS specimens having densities ranging from 85 to 98% of theoretical. The same author found Vickers hardness at a 100-g load varying from 219 to 246 kg/mm^2 . Samsonov and Popova⁵ give microhardnesses in kg/mm^2 of 143.4 ± 29 (5-g load) for powder, 800 ± 81.6 (30-g load) for

Table 1. Thermodynamic Functions of ThS^a

Temperature (°K)	C_P° , Heat Capacity		$H^\circ - H_0^\circ$, Enthalpy		S° , Entropy		$-(G^\circ - H_0^\circ)/T$	
	cal	J	(cal/mole)	(J/mole)	cal	J	cal	J
	mole °K	mole °K			mole °K	mole °K	mole °K	mole °K
5	0.01592	0.0666	0.0257	0.1075	0.00834	0.0349	0.00320	0.0134
10	0.1160	0.4852	0.2916	1.2200	0.04147	0.1735	0.01231	0.0515
15	0.4326	1.810	1.5580	6.5186	0.13989	0.5853	0.03602	0.1507
20	0.9587	4.011	4.9725	20.805	0.33272	1.3921	0.08411	0.3519
25	1.5798	6.610	11.3002	47.280	0.61255	2.5629	0.16054	0.6717
30	2.199	9.200	20.767	86.890	0.95602	4.0000	0.26379	1.1037
35	2.758	11.54	33.176	138.81	1.33750	5.5961	0.38960	1.6301
40	3.241	13.56	48.198	201.66	1.73798	7.2717	0.53301	2.2301
45	3.669	15.35	65.495	274.03	2.1449	8.9743	0.68948	2.8848
50	4.051	16.95	84.811	354.85	2.5516	10.676	0.85538	3.5789
60	4.730	19.79	128.795	538.88	3.3516	14.023	1.2051	5.042
70	5.344	22.36	179.202	749.78	4.1274	17.269	1.5674	6.558
80	5.923	24.78	235.55	985.56	4.8791	20.414	1.9348	8.095
90	6.477	27.10	297.59	1,245.1	5.6090	23.468	2.3026	9.634
100	7.000	29.29	364.98	1,527.1	6.3186	26.437	2.6087	11.166
110	7.488	31.33	437.45	1,830.3	7.0091	29.326	3.0323	12.687
120	7.933	33.19	514.60	2,153.1	7.6800	32.133	3.3917	14.191
130	8.337	34.88	595.98	2,493.6	8.3310	34.857	3.7467	15.676
140	8.700	36.40	681.19	2,850.1	8.9625	37.499	4.0968	17.141
150	9.030	37.78	769.86	3,221.1	9.5741	40.058	4.4417	18.584
160	9.324	39.01	861.66	3,605.2	10.1666	42.537	4.7811	20.004
170	9.591	40.13	956.26	4,001.0	10.7400	44.936	5.1150	21.401
180	9.830	41.13	1053.4	4,407.4	11.294	47.258	5.4429	22.773
190	10.043	42.02	1152.8	4,823.2	11.832	49.506	5.7651	24.121
200	10.232	42.81	1254.2	5,247.4	12.353	51.682	6.0815	25.445
210	10.399	43.51	1357.3	5,679.0	12.856	53.788	6.3922	26.745
220	10.547	44.13	1462.1	6,117.3	13.343	55.827	6.6972	28.021
230	10.686	44.71	1568.2	6,561.5	13.815	57.801	6.9964	29.273
240	10.813	45.24	1675.7	7,011.3	14.272	59.715	7.2901	30.502
250	10.932	45.74	1,784.5	7,466.2	14.716	61.572	7.5782	31.707
260	11.047	46.22	1894.4	7,926.1	15.147	63.376	7.8611	32.891
270	11.154	46.67	2005.4	8,390.6	15.566	65.129	8.1389	34.053
280	11.255	47.09	2117.4	8,859.4	15.974	66.834	8.4113	35.193
290	11.343	47.46	2230.4	9,332.2	16.370	68.493	8.6790	36.313
300	11.420	47.78	2344.3	9,808.4	16.756	70.107	8.9419	37.413
310	11.489	48.07	2458.9	10,288	17.132	71.679	9.2000	38.493
320	11.556	48.35	2574.1	10,770	17.497	73.209	9.4536	39.554
330	11.618	48.61	2690.0	11,255	17.854	74.701	9.7027	40.596
340	11.675	48.85	2806.4	11,742	18.202	76.156	9.9477	41.621
350	11.730	49.08	2923.5	12,232	18.541	77.575	10.1883	42.628
273.15	11.188	46.81	2041	8,538	15.696	65.67	8.224	34.41
298.15	11.405	47.72	2323	9,720	16.685	69.81	8.893	37.21
	±0.057	±0.24	±12	±49	±0.084	±0.35	±0.045	±0.19

^aFrom Flotow *et al.*¹⁸

Fig. 1. Resistivity as a Function of Temperature for Sintered Specimens of Thorium Monosulfide, Uranium Monosulfide, and ThS-US Solid Solutions. Copied from Tetenbaum.¹⁶ Copyright by American Institute of Physics and reproduced with permission.

Fig. 2. Absolute Seebeck Coefficient as a Function of Temperature for Thorium Monosulfide, Uranium Monosulfide, and ThS-US Solid Solutions. Copied from Tetenbaum.¹⁶ Copyright by American Institute of Physics and reproduced with permission.

Table 2. Functions of Formation of ThS

Function	Value Based on Ref. 19		Value Based on Ref. 20		Source
	(kcal/mole)	(kJ/mole)	(kcal/mole)	(kJ/mole)	
ΔH_{1173}	-102.2	-427	-109.0	-456	Ref. 10
ΔH_{298}°	-88	-368	-95	-397	Estimated, see text
ΔG_{298}°	-87	-364	-94	-392	Estimated, see text

Table 3. Thermal Conductivity of Theoretically Dense ThS^a

Temperature (°C)	Conductivity (W m ⁻¹ °C ⁻¹)
0	58.7
75	46.8 ^b
100	44.5
200	39.2
300	35.9 ^b
400	34.5
500	33.4
600	32.8
700	32.1
800	32.1
900	31.7
1000	31.3

^aFrom Kollie *et al.*²³ Except where indicated the values were calculated from two experimental values and electrical resistivity.

^bExperimental values corrected to theoretical density.

sintered material, and 363 ± 39.8 (20-g load) for annealed material.

9. Chemical Properties

After 8 hr in boiling water, ThS acquired only a surface stain.¹¹ It was slowly attacked at room temperature by dilute nitric or sulfuric acid but not by hydrochloric acid at any concentration (Shalek¹¹). Bear and McTaggart¹⁹ report some H₂S evolution from concentrated hydrochloric acid and "Th_{0.6}," but their specimen could have been a mixture of metal and disulfide. Powder samples ignited in the range 460 to 510°C (Shalek¹¹). Eastman *et al.*⁴ found a brown oxide coating on ThS heated in poor vacuum and found a slow reaction with reactive halides up to 1000°C.

Eastman *et al.*⁴ determined the compatibility of ThS crucibles with several molten metals. Cerium, thorium, magnesium, aluminum, and iron were melted satisfactorily in ThS. Platinum reacted at 1900°C with ThS to

form an intermetallic compound and a higher thorium sulfide. Apparently all metals that melt below 1800 or 1900°C can be melted satisfactorily in ThS except for noble metals that form intermetallic compounds with thorium.

10. Surface Properties

No information is available.

B. Thorium-Uranium Monosulfide

1. Composition

The monosulfides of thorium and uranium are completely miscible over the entire range of composition.^{9,11}

2. Preparation

Solid solutions of (Th,U)S were obtained^{9,11,24} by sintering mixed powders of ThS and US at 2050 to 2150°C. Uniformity was not achieved by Shalek¹¹ by sintering at 1805 or 1935°C. However, he did obtain homogeneous solid solutions in 3 hr at 1700 to 1800°C from unfired U-US₂ and Th-ThS₂ powders having the monosulfide composition.

3. Crystal Properties

The lattice parameters in Fig. 3 show a slight positive deviation from Vegard's law by the well homogenized materials of Shalek¹¹ and Cater *et al.*⁹ The deviations by the points from earlier work probably indicate incomplete homogenization, since similar deviations were found by Shalek for materials fired at too low a temperature. On the other hand, substantial negative deviations from Vegard's law were reported by Chechernikov *et al.*²⁴ for material fired under conditions that should have given uniformity.

4. Thermodynamic Properties

No information is available.

Fig. 3. Lattice Parameters of (Th,U)S. Based on Shalek,¹¹ Cater *et al.*,⁹ Zachariasen,¹⁴ and Eastman *et al.*³

5. Change of State

Shalek¹¹ gives the following melting points of (Th,U)S solid solutions:

US, mole %	Observed Melting Point, °C (duplicate determinations)
25	2290, 2310
50	2330, 2350
75	2340, 2350

6. Electrical and Magnetic Properties

Figures 1 and 2 give respectively the electrical resistivity and Seebeck coefficient measured by Tetenbaum¹⁶ on pellets made by pressing a mixture of US and ThS powders and sintering in vacuum or inert atmosphere at about 2000°C. The ThS used contained about 5% ThOS.

Chechernikov *et al.*²⁴ measured magnetic properties over the range US to 98% ThS from 77 to 900°K. Reciprocals of susceptibility are plotted against temperature for many compositions. The results correspond to a uranium moment varying from 2.4 Bohr magnetons for pure US to 3.6 for 90% or more ThS. Solid solutions containing up to 60% ThS are ferromagnetic,

with a Curie point that decreases with increasing ThS content from 180°K for pure US.

7. Heat and Mass Transport

No information is available.

8. Mechanical Properties

Shalek¹¹ reported hardness values (DPH) increasing from 234 for ThS to 277 for $U_{0.5}Th_{0.5}S$ and then decreasing to 184 for US. Modulus of rupture measurements indicated an increase in strength with ThS content.¹¹

9. Chemical Properties

Shalek¹¹ reported

"Solid-solution bodies had less than a linear increase in oxidation resistance from US to ThS. Ignition temperatures for a representative series were 368°C for US, 375° for $U_{0.75}Th_{0.25}S$, 388°C for $U_{0.5}Th_{0.5}S$, 420°C for $U_{0.25}Th_{0.75}S$, and 510°C for ThS."

Despite the reference to "bodies," the ignition temperatures appear to be from an investigation "carried out in air on monosulfide powders using a differential thermal analysis apparatus in which a flow of oxygen was maintained through the sample."

10. Surface Properties

No information is available.

C. Thorium-Plutonium Monosulfides

No information is available.

D. Systems with Nonfuel Sulfides

Eastman *et al.*³ demonstrated miscibility of ThS and CeS, and Zachariasen¹⁴ measured lattice parameters for three of the compositions. Crucibles have been fabricated from the material.⁴

E. Ternary and More Complex Systems with Other Sulfides

No information is available.

THORIUM SESQUISULFIDE SYSTEMS

Systems with other sulfides (parts B through E) and other negative elements (Parts F etc.) have not been studied.

A. Thorium Sesquisulfide

1. Composition

Most investigators accept the finding of Eastman *et al.*³ that the composition range of Th_2S_3 is narrow, but Samsonov and Popova⁵ give a range from 55 to 62 at. % S.

2. Preparation

Eastman *et al.*³ recommend synthesis from metal hydride and H_2S as simplest and from ThS and ThS_2 as giving the purest product; synthesis from the elements is also possible.^{5,13} Although thorium and sulfur or their hydrogen derivatives react at 800°C or below, Th_2S_3 is generally not obtained without heating at or near the melting point. Graham and McTaggart¹ failed to obtain it at 800°C .

Ceramic bodies have been made by pressing mixtures of ThS and ThS_2 and sintering at 1750 to 1850°C ,⁴ by arc melting and casting,¹³ and by hot pressing.⁵

3. Crystal Properties

The structure¹⁴ is orthorhombic, $Pbnm - D_{2h}^{16}$ with lattice parameters $a_0 = 10.99 \pm 0.05 \text{ \AA}$, $b_0 = 10.85 \pm 0.05 \text{ \AA}$, $c_0 = 3.96 \pm 0.03 \text{ \AA}$, theoretical density, 7.87 g/cm^3 . Color: brown.⁵

4. Thermodynamic Properties

For the formation of Th_2S_3 from thorium metal and rhombic sulfur at 25°C , Bear and McTaggart¹⁹ find $\Delta H^\circ = -238 \text{ kcal/mole}$ (-995 kJ/mole) from heat of combustion measurements, while Eyring and Westrum²⁰ find $\Delta H^\circ = -258.6 \text{ kcal/mole}$ (1082 kJ/mole) from heat of solution in hydrochloric acid. The Bear and McTaggart specimen may not have been the Th_2S_3 phase, since later work from the same laboratory¹ showed it absent from similarly prepared material.

Westrum and Grönvold²⁵ estimate an entropy of $20.0 \text{ cal mole}^{-1} (\text{°K})^{-1}$ or $84 \text{ J mole}^{-1} (\text{°K})^{-1}$ corresponding to the formula $\text{ThS}_{1.5}$.

5. Change of State

Eastman *et al.*³ give a melting point of $1950 \pm 50^\circ\text{C}$. Samsonov and Popova estimate a melting point of 2300°C , but they report melting at 2100°C in sintering experiments.⁵ No volatility was observed³ at 1700°C in vacuum.

6. Electrical and Magnetic Properties

Eastman and coworkers³ give a range of 10^{-4} to $10^{-3} \Omega\text{-cm}$ for the electrical resistivity of Th_2S_3 . On

samples of the correct composition but uncertain structure, McTaggart¹⁷ reported a resistivity of $10 \Omega\text{-cm}$ and a Seebeck coefficient of $100 \mu\text{V}/^\circ\text{C}$, and Jordan¹³ measuring specimens of uncertain structure reported $0.260 \Omega\text{-cm}$ and $30 \mu\text{V}/^\circ\text{C}$ (the latter up to 200°C). The compound is diamagnetic.³

7. Heat and Mass Transport

No information is available.

8. Mechanical Properties

Samsonov and Popova⁵ give the following microhardnesses (in kg/mm^2) for Th_2S_3 : Powder, 171.1 ± 29.91 (5-g load); sintered, 539 ± 45 (30-g load); annealed, 227 ± 28 (5-g load).

9. Chemical Properties⁴

The following molten metals react with Th_2S_3 : alkalis, alkaline earths, rare earths, Th, U, and Be. However, the reaction is often slow enough to permit melting in Th_2S_3 crucibles; for example, a 6-min exposure of thorium at 1825°C gave an ingot with a thin ThS coat. Cerium ingots stuck to the crucible after 15 min at 1500°C .

10. Surface properties

No information is available.

Th_7S_{12} SYSTEMS

Systems with other sulfides (parts B through E) and other negative elements (Parts F etc.) have not been studied.

A. Th_7S_{12}

1. Composition

Eastman *et al.*³ report a range of sulfur-to-thorium ratios from 1.71 to 1.76 for the Th_7S_{12} phase.

2. Preparation

Possibly the purest Th_7S_{12} is made by heating ThS_2 in vacuum at 1950°C . Other syntheses are from ThS_2 and hydride or ThS or hydride and H_2S , with firing at high temperature.³ Reaction between the elements at 800°C in the proper proportions failed to give the compound.¹ Another synthesis was from ThO_2 in hydrogen sulfide in the absence of carbon at 1200 to 1300°C .²⁶ Crucibles were prepared⁴ by sintering a mixture of ThS and ThS_2 at 1750 to 1850°C .

3. Crystal Properties

The structure is hexagonal⁶ of type $P 6_3/m$, with parameters given in Table 4. The theoretical density⁶ is 7.88 g/cm³. Color: black.³

Table 4. Lattice Parameters of Th₇S₁₂

Ref.	S/Th	a_0 (Å)	c_0 (Å)
6	1.71	11.064 ± 0.001	3.991 ± 0.001
	1.76	11.087 ± 0.002	4.010 ± 0.002
26	"1.7"	11.069	3.992

4. Thermodynamic Properties

From measurements on high-temperature galvanic cells, Aronson¹⁰ found for the reaction $\text{Th} + \text{Th}_7\text{S}_{12} = 4\text{Th}_2\text{S}_3$ at 900°C, $-\Delta G = 39.7 \pm 2$ kcal (167 kJ), $-\Delta S = 6.3 \pm 3$ cal/°C (26 J/°C), and $-\Delta H = 47.1 \pm 4$ kcal (197 J); for $\text{Th} + 6\text{ThS} \rightleftharpoons \text{Th}_7\text{S}_{12}$, $-\Delta G = 95.2 \pm 4$ kcal (400 J). From these and published^{15,20} heats of formation of Th₂S₃ he estimated $-\Delta H$ of formation at 900°C to be 89.4 kcal/g-atom S (374 kJ/g-atom S) (ref. 19) and 96.2 kcal/g-atom S (403 kJ/g-atom S) (ref. 20). The value of 96.2 does not agree well with the estimate of 55.4 kcal/g-atom S by Eastman *et al.*,³ which apparently was based on the same Th₂S₃ data.

Westrum and Grönvold²⁵ estimate an entropy of 21.6 cal mole⁻¹ (°K)⁻¹ or 88 J mole⁻¹ (°K)⁻¹ at 298°K corresponding to formula ThS_{1.7}.

5. Change of State

Melting point,³ 1770 ± 30°C. No observed volatility at 1700°C in vacuum.³

6. Electrical and Magnetic Properties

For the electrical resistivity, Eastman *et al.*³ reported about 10⁻³ Ω-cm, but Samsonov and Dubrovskaya²⁶ reported 36 to 97 MΩ-cm. On material without phase identification McTaggart¹⁷ reported 25 kΩ-cm and a Seebeck coefficient of 200 μV/°C. The compound is diamagnetic.³

7. Heat and Mass Transport

No information is available.

8. Mechanical Properties

Samsonov and Dubrovskaya report a microhardness of 433 ± 30 kg/mm² (10-g load).²⁶

9. Chemical Properties⁴

The following molten metals react with Th₇S₁₂: alkalis, alkaline earths, rare earths, Th, U, and Be. Metals melting up to 1800°C can be melted in Th₇S₁₂; only a surface reaction is observed with the electropositive metals unless they are also volatile. Uranium and cerium have been melted in Th₇S₁₂; the cerium stuck.

10. Surface Properties

No information is available.

THORIUM DISULFIDE SYSTEMS

Systems of ThS₂ with other sulfides (Parts C, D, and E) have not been studied except for US₂. With other negative elements (Parts F, G), no solid solutions are observed, but several compounds.

A. Thorium Disulfide

1. Composition

Evidence is lacking for any composition range or deviation from stoichiometry for ThS₂.

2. Preparation

Thorium disulfide can be prepared from decomposition of the polysulfide ThS_{2.5}, which is synthesized at 400 to 550°C from the elements.¹ Another preparation is from H₂S and thorium hydride.³ The purest material is prepared from ThO₂ and H₂S at 1300°C or higher in graphite apparatus.^{3,26} In oxide ceramics the reaction stops with ThOS or Th₇S₁₂. Attempts to synthesize lower sulfides without high-temperature homogenization generally lead to a mixture that includes thorium disulfide.¹ Crucibles can be fabricated by pressing and sintering.⁴ Ingots have been arc melted under helium.¹³

3. Crystal Properties

Structure.¹⁴ — Orthorhombic, $Pnmb - D_{2h}^{16}$.

Lattice Parameters. — Reported values are in Table 5.

Theoretical Density.^{14,26} — 7.36 g/cm³.

Color. — Brown^{17,26}, purple,³ purple-brown.¹

4. Thermodynamic Properties

King and Weller²⁷ measured the heat capacities listed in Table 6. From their data they derive $S_{298.15}^\circ - S_{51}^\circ = 20.05$ cal mole⁻¹ (°K)⁻¹ = 83.9 J mole⁻¹ (°K)⁻¹ and

Table 5. Lattice Parameters of ThS₂

Ref.	Parameter (Å)		
	a ₀	b ₀	c ₀
14	4.263 ± 0.002	7.264 ± 0.003	8.618 ± 0.003
1	4.283	7.275	8.617
26	4.267	7.262	8.617

Table 6. Heat Capacity of ThS₂.^a From King and Weiler²⁷

Temperature (°K)	Heat Capacity, C _p	
	(cal mole ⁻¹ °K ⁻¹)	(J mole ⁻¹ °K ⁻¹)
10	(0.16)	(0.67)
25	(1.73)	(7.24)
50	4.61	19.29
75	7.46	31.21
100	9.95	41.63
125	11.86	49.62
150	13.33	55.77
175	14.37	60.12
200	15.12	63.26
225	15.69	65.65
250	16.14	67.53
275	16.51	69.08
298.15	16.80	70.29
523–773 ^b	17.4	73

^aValues in parentheses are extrapolated. The experimental values are probably accurate to 0.3%.

^bAverage over this temperature range reported by Hartman *et al.*²⁸ to ±1.5%.

$S_{298.15}^{\circ} = 23.0 \pm 0.2 \text{ cal mole}^{-1} (\text{°K})^{-1} = 96.2 \text{ J mole}^{-1} (\text{°K})^{-1}$. Combining this with previously published values, they calculated the following functions of formation:

$\Delta S^{\circ}, \text{cal mole}^{-1} (\text{°K})^{-1}$	-5.0 ± 0.3
$\text{J mole}^{-1} (\text{°K})^{-1}$	-21
$\Delta H^{\circ}, \text{kcal/mole}$	-139
kJ/mole	-582
$\Delta G^{\circ}, \text{kcal/mole}$	-137.5
kJ/mole	-575

The enthalpy and free energy are based on the estimate by Eastman *et al.*³ of $-170 \pm 20 \text{ kcal/mole}$ for ΔH° for the formation of ThS₂ from S₂ gas. Hartman *et al.*²⁸ report from heat of combustion measurements a heat of formation at 25°C: $-\Delta H^{\circ} = 195 \text{ kcal/mole} = 820 \text{ J/mole} (\pm 3\%)$.

5. Change of State

*Melting Point.*³ $-1905 \pm 30^{\circ}\text{C}^{\circ}$.

6. Electrical and Magnetic Properties

Pressed powder measured 10,000 MΩ-cm in electrical resistivity.¹⁷ Arc-melted ingots measured only 2.00 Ω-cm, but the specimen was of unknown structure¹³ and may have lost sulfur during melting. The Seebeck coefficient of the arc-melted material¹³ was nearly $-700 \mu\text{V/}^{\circ}\text{C}$ from 300 to 600°C, then dropped to $-200 \mu\text{V/}^{\circ}\text{C}$ at 900°C. Thorium disulfide is diamagnetic.³

7. Heat and Mass Transport

No information is available.

8. Mechanical Properties

No information is available.

9. Chemical Properties

Eastman *et al.*⁴ found that ThS₂ reacts with molten electropositive metals. Because of loss of sulfur, they recommend the use of ThS₂ crucibles be limited to 1500 or 1600°C.

Bear and McTaggart¹⁹ observed the following behavior of ThS₂ with various reactants:

H₂, 3 hr, 950°C, no reaction.

air or O₂, heated, protective layer formed.

water, up to boiling, no reaction.

5 N NaOH, no reaction.

concd. HCl, boiling, complete dissolution.

2 N H₂SO₄, cold, slow, steady reaction.

2 N H₂SO₄, boiling, rapid complete reaction with precipitation of sulfate.

concd. H₂SO₄, cold, evolution of H₂S and formation of white precipitate.

concd. HNO₃, reaction occurs.

titanium powder, sealed in vacuum, 800°C for several days forms "ThS_{1.5}."

10. Surface Properties

No information is available.

B. Thorium-Uranium Disulfides

Jordan¹³ prepared ThS₂-6% US₂ by arc melting the components together. The material had an electrical

resistivity of 1.5 Ω -cm at 400°C and a Seebeck coefficient with a complex temperature dependence.

F. Thorium(IV) Oxide-Sulfide

1. Composition

The only reported intermediate composition between ThO_2 and ThS_2 is the oxide-sulfide, ThOS . No range of compositions has been reported.

2. Preparation

Thorium oxide-sulfide is generally prepared from the reaction of H_2S and ThO_2 in oxide refractories.^{26,29} Use of graphite refractories, particularly if the temperature exceeds 1300°C, leads to formation of ThS_2 . Fabrication of crucibles from the material is described by Eastman *et al.*⁴

3. Crystal Properties.

The oxide-sulfide has the tetragonal PbFCl structure,¹⁴ $P4/nmn - D_{4h}^7$. The lattice parameters¹⁴ are $a_0 = 3.963 \pm 0.002$ Å, $c_0 = 6.747 \pm 0.004$ Å, corresponding to a theoretical density of 8.78 g/cm³. The color is yellow.^{26,29}

4. Thermodynamic Properties

Hartmann *et al.*²⁸ report for ThOS a mean heat capacity of 18.3 cal mole⁻¹ (°C)⁻¹ or 77 J mole⁻¹ (°C)⁻¹ over the range 250 to 500°C and a heat of formation at 25°C of $\Delta H^\circ = -206$ cal/mole = -860

J/mole ($\pm 3\%$). The latter was based on heat of combustion.

5. Change of State

No low-melting eutectics are formed by ThOS with thorium sulfides.²⁹

6. Electrical and Magnetic Properties.

No information is available.

7. Heat and Mass Transport

No information is available.

8. Mechanical Properties

No information is available

9. Chemical Properties

Thorium oxide-sulfide dissolves very slowly in dilute acids and somewhat more rapidly in hot concentrated nitric acid. It reacts with hydrogen sulfide in the presence of graphite at 1500°C to form thorium disulfide.²⁹

10. Surface Properties

No information is available.

G. Other Compounds

Hulliger³⁰ describes the diamagnetic PbFCl -structure compounds Th_2S and ThAsS .

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