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High-Temperature Enthalpy and X-Ray Powder Diffraction Data for Aluminum Sulfide (Al_2S_3)

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HIGH-TEMPERATURE ENTHALPY AND X-RAY POWDER DIFFRACTION DATA FOR ALUMINUM SULFIDE (Al_2S_3)

by

M. J. Ferrante [1] and R. A. McCune [1]

ABSTRACT

High-temperature enthalpy and X-ray powder diffraction studies were conducted on aluminum sulfide (Al_2S_3) as part of the Bureau of Mines effort to provide new data for the advancement of mineral technology consistent with environmental preservation and energy conservation. Relative enthalpies were measured with a copper-block calorimeter from 298.15 to 879 K. Tabulated values are listed for heat capacity, entropy, Gibbs energy functions, and relative enthalpies between 298.15 and 900 K. Enthalpies were also given in the form of an equation and combined with published data to calculate standard enthalpies of formation and Gibbs energies of formation for reactions of crystalline aluminum with crystalline, liquid, and gaseous diatomic sulfur. The hexagonal, rhombohedral, and cubic phases of Al_2S_3 were identified by X-ray powder diffraction studies, and the indexed powder diffraction patterns of these phases are given. The hexagonal phase was stable to about 852 K and was partially converted to the rhombohedral form at 879 K.

INTRODUCTION

The use of aluminum in the world during recent years was reported by Stamper (18)[2] to exceed that of all other metals except iron. Because of the continued significance of aluminum in virtually all industries, the present investigation is one of a series by the Bureau of Mines to provide new and reliable thermodynamic data for important compounds of aluminum. Such thermodynamic data can be used as guidelines for the efficient utilization of the Nation's mineral resources with minimal energy consumption and environmental degradation.

The only thermodynamic property of Al_2S_3 measured prior to 1976 was the standard enthalpy of formation, and reported values differed by as much as 51 kcal/mole (13, 16-17). A new value for the enthalpy of formation was measured at the Bureau of Mines by Ko (15) in 1976; Ko also reported low-temperature heat capacities that were measured for the first time. The

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

present investigation was carried out to obtain high-temperature relative enthalpies because these data were not available in the literature. This investigation also included X-ray powder diffraction studies to identify the crystal phases of Al_2S_3. Unless designated otherwise, Al_2S_3 refers to the hexagonal crystal form that is the stable polymorph in the temperature range of 0 to about 850 K. The hexagonal form is also referred to as the α-phase.

The investigation of high-temperature enthalpies was made with a copper-block calorimeter. These enthalpy values were combined with the thermodynamic data previously reported by Ko and with auxiliary data from the literature to calculate standard enthalpies of formation and Gibbs energies of formation as functions of temperature. This investigation also involved X-ray powder diffraction studies with a high-angle, vertical diffractometer in order to identify and calculate diffraction patterns for the phases of the Al_2S_3.

MATERIALS

Details of the preparation of Al_2S_3 were given by Ko. While only a summary of the preparation is given here, complete analyses are shown for convenience. Aluminum sulfide was made by reacting aluminum foil of 99.99+ pct purity with an excess of sublimed sulfur in an evacuated and sealed glass vessel. This glass vessel was opened in a glove box under dry argon because of the reactive nature of Al_2S_3 with moisture. Chemical analyses by ignition of the Al_2S_3 to Al_2O_3 showed 64.07 and 64.03 pct S compared with the theoretical value of 64.06 pct S. Optical emission spectroscopy revealed that the Al_2S_3 contained only about 200 ppm Si. X-ray powder diffraction analyses of the Al_2S_3 showed the major phase to be the hexagonal α-phase with trace amounts (<1 pct) of the high-temperature rhombohedral γ-phase and the face-centered cubic phase. The patterns for the X-ray powder diffraction analyses of these three phases were calculated from the crystal data reported by Donnay (3) and then compared with the pattern of the Al_2S_3 prepared in this investigation. The X-ray powder diffraction patterns of these phases are given in the section on X-ray results.

EXPERIMENTAL WORK AND RESULTS

High-Temperature Enthalpy

Enthalpies relative to 298.15 K were measured with a drop calorimeter. This isothermal-jacketed calorimeter has a copper-block with a heat capacity of about 1.51 kcal/deg. The design and operation of the calorimeter were as described by Douglas (5), except for two modifications. The present apparatus incorporates a more sensitive potentiometer and null detector system that can resolve temperature changes equivalent to ±50 μK. The second difference was the addition of a furnace with a silver core to provide a near-isothermal zone for heating the encapsulated sample. The construction of the furnace was similar to that at the National Bureau of Standards (8). The temperature of the Al_2S_3 sample in the silver-core furnace was measured with a platinum versus platinum-10 pct rhodium thermocouple, which was frequently calibrated against the melting point of pure gold. Temperatures refer to the International Temperature Scale of 1968 (2).

Relative enthalpies that were measured with the drop calorimeter are expressed in terms of the thermochemical calorie (1 cal = 4.1840 j). Before and after a series of enthalpy measurements for a substance, the calorimeter was calibrated electrically and the entire system was checked for accuracy by measuring the enthalpy of MgO (periclase). These MgO measurements agreed to within 0.1 pct with values given by Victor (19).

The sample container for experimental measurements was a clear glass capsule of pure SiO_2. After the capsule was filled with powdered Al_2S_3 in a glove box filled with dry argon, it was transferred to a vacuum system without exposure to air. The neck of the evacuated capsule was fusion-sealed with a flame while the portion of the capsule containing the Al_2S_3 was immersed in ice water. A mass of 9.55890 g of Al_2S_3 was sealed in 5.28368 g of SiO_2. This amount of SiO_2 contributed approximately 40 pct of the total enthalpy measured for the Al_2S_3 and SiO_2 capsule. Relative enthalpies of the empty capsule were measured in separate experiments. The empty capsule had an internal volume of 8.35 cu cm. The volume of Al_2S_3 was calculated to be 4.10 cu cm, based on the density of 2.33 g/cu cm. The mass of the Al_2S_3 and SiO_2 was periodically checked for constancy by weighing between enthalpy measurements. All weighings were corrected to vacuum. The molecular weight of 150.143 for Al_2S_3 conforms to the 1977 Table of Atomic Weights (11). Results of experimental measurements are listed in table 1 in chronological order as standard enthalpies relative to 298.15 K ($H°-H°_{298}$). Table 1 also shows the percent deviation between the experimental and smoothed values. The deviation of the smoothed enthalpies is given in the Discussion section.

TABLE 1. - High-temperature experimental enthalpies of Al_2S_3(c)

T, K	$H°-H°_{298}$, kcal/mole	Deviation,[1] pct	T, K	$H°-H°_{298}$, kcal/mole	Deviation,[1] pct
403.1	2.788	0.38	652.7	10.004	-0.03
452.9	4.174	.18	703.4	11.541	.01
403.0	2.783	.30	753.5	13.067	-.03
452.9	4.167	.02	802.6	14.588	.01
502.7	5.593	.11	852.1	16.139	.06
553.2	7.054	.01	[2]878.5	17.140	1.06
603.3	8.531	.00			

[1]Deviation, pct = 100 (experimental enthalpy - smoothed enthalpy)/experimental enthalpy.

[2]Partial conversion from the α-phase to the metastable γ-phase.

X-Ray Powder Diffraction

The powdered samples of Al_2S_3 for X-ray diffraction were loaded into either double bottles or silica capsules in a glove box under dry argon. The sample container was later opened in the helium-filled glove box of the X-ray laboratory. A flat sample holder was loaded by pressure packing from the top, placed on a diffractometer spindle, and covered with a gastight cap fitted with a 2-mil-thick Mylar window. The spindle, sample, and cap were removed from the glove box as a unit and positioned on the diffractometer. Identification scans were made with nickel-filtered copper radiation at 45 kv and

35 ma. A scintillation detector was used with pulse-height discrimination, solid state electronics, and a strip chart recorder. The diffractometer scan rate for identification was 1° 2 θ/min, and the chart speed was 1/2 in/min.

The Powder Diffraction File (PDF) (10) lists three patterns for Al_2S_3 on card numbers 1-726, 24-14, and 26-37. Card 1-726 shows very early data, includes several extraneous lines, and is not indexed. Card 24-14 lists data indexed in the tetragonal system and did not appear to be pertinent to the experimental data. Card 26-37 shows data for a compound formed under 40 kbar at 400° C and also did not appear to be pertinent. Therefore, the lattice parameters for the Al_2S_3 phases listed in Donnay's "Crystal Data Determinative Tables" (3) were used as a basis for identifying and indexing the phases in the experimental diffraction patterns for the α, γ, and cubic phases of Al_2S_3.

The indices (hkl), the interplanar spacing (d), and the relative line intensities (I) of these phases are listed in table 2.

TABLE 2. - X-ray diffraction patterns of Al_2S_3

α-Al_2S_3 (hexagonal)			γ-Al_2S_3 (rhombohedral)			[1]Al_2S_3 (face-centered cubic)		
hkl	d, A	I	hkl	d, A	I	hkl	d, A	I
						111	5.73	20
101	5.31	21	101	5.33	18			
102	4.72	23	012	4.70	39			
104	3.48	8						
			104	3.42	10			
110	3.21	100	110	3.24	100			
006	2.97	81						
			015	2.94	2			
			006	2.88	100			
113	2.84	93	113	2.82	37			
201	2.75	3	021	2.77	5			
202	2.66	4	202	2.67	20			
						400	2.48	100
204	2.36	2	024	2.35	2			
107	2.32	2						
			107	2.26	5	331	2.28	5
116	2.18	34	205	2.18	2			
			116	2.15	30			
211	2.09	2	211	2.10	2			
212	2.05	3	122	2.06	12			
			018	2.014	21	422	2.03	75
117	2.00	2						
214	1.902	3						
109	1.870	6						
			300	1.868	37			
300	1.850	61						
301	1.810	2	125	1.805	3			
208	1.739	2				440	1.755	75

See footnote at end of table.

TABLE 2. - X-ray diffraction patterns of Al_2S_3--Continued

α-Al_2S_3 (hexagonal)			γ-Al_2S_3 (rhombohedral)			[1]Al_2S_3 (face-centered cubic)		
hkl	d, A	I	hkl	d, A	I	hkl	d, A	I
216	1.716	2						
			208	1.710	16			
119	1.685	45						
			119/					
305	1.645	1	1•0•10	1.650	8			
217	1.621	2	220	1.618	5			
220	1.606	8						
306	1.573	30						
			306	1.567	22			
223	1.550	6						
218	1.529	2						
			128	1.512	13	533	1.514	15
						622	1.497	15
			0•2•10	1.470	2			
314	1.458	1						
						444	1.433	15
226	1.413	5						
1•1•12	1.349	1						
229	1.247	13						

[1]The face-centered cubic phase was observed only as a trace amount in the presence of both the α- and γ-phases. Some possible lines of the cubic phase that are not shown have been obscured by lines of other phases.

DISCUSSION

High-Temperature Enthalpy

No enthalpy measurements of Al_2S_3 could be found in the literature to compare with the data of the present investigation. Enthalpy measurements of the present investigation were computer-fitted with polynomial functions to obtain the best fit of smooth curves to these data. The fitting process was described by Justice (12). During this process, care was taken to smoothly merge the high-temperature enthalpies with the low-temperature data reported by Ko. The polynomials were used to calculate smooth values of enthalpies at the temperatures of the experimental measurements. These smooth enthalpies were then compared with the experimental values as the percent deviation shown in table 1. The polynomials were also used to derive smoothed values of relative enthalpy ($H°-H°_{298}$), heat capacity ($C_p°$), and entropy ($S°$), and Gibbs energy function $[-(G°-H°_{298})/T]$. These data are shown in table 3 at selected temperature intervals. The absolute uncertainty of the smoothed enthalpies was estimated to be ±0.4 pct. The standard deviation of the enthalpy measurements from the smoothed values was 0.2 pct. The standard deviation is calculated from the following equation, where d is the percent deviation of a measurement from the smoothed curve, and n is the total number of measurements:

$$\text{Standard deviation, pct} = \sqrt{\frac{\Sigma d^2}{n-2}}$$

TABLE 3. - High-temperature thermodynamic properties of Al_2S_3(c)

T, K	cal/deg mole			$H°-H°_{298}$, kcal/mole
	$C_p°$	S°	$-(G°-H°_{298})/T$	
298.15	25.111	27.927	27.927	0
300	25.163	28.082	27.927	.047
350	26.522	32.071	28.239	1.341
400	27.473	35.678	28.947	2.692
450	28.192	38.957	29.880	4.085
500	28.768	41.958	30.940	5.509
550	29.251	44.723	32.069	6.960
600	29.669	47.287	33.232	8.433
650	30.043	49.677	34.406	9.926
700	30.384	51.916	35.577	11.437
750	30.701	54.023	36.738	12.964
800	30.999	56.014	37.881	14.507
850	31.284	57.902	39.003	16.064
[1]900	(31.558)	(59.698)	(40.103)	(17.635)

[1]Values in parentheses are extrapolations.

The relationship between the experimental and smoothed enthalpies is shown graphically in figure 1 as the mean heat capacity, $(H°-H°_{298})/(T-298.15)$ versus T. Enthalpy experiments were discontinued when it became apparent that the last valid measurement on the smooth curve was 852 K. A significant change in the Al_2S_3 occurred after it was heated at 879 K for 2 1/2 hours for the next measurement. This measurement had an abnormally high thermal effect equivalent to 1.1 pct above the smooth curve. X-ray powder diffraction analysis of the sample showed the abnormal effect was caused by a partial conversion from the α-phase to the γ-phase. Because the temperature at which the α-structure transforms into the γ-structure is not precisely known, the smoothed data of table 3 were extrapolated from 852 to 900 K.

The smoothed enthalpies were also expressed by an equation to better meet the needs of various users, especially in engineering applications. Kelley (14) described the method of derivation for the equation. The temperature range of validity and the average deviation from the experimental data are shown in parentheses after the following equation:

$$H°-H°_{298}, \text{ kcal/mole} = 28.170 \times 10^{-3}T + 2.143 \times 10^{-6}T^2 + 385.7T^{-1} - 9.883$$

(298 - 900 K; <0.1 pct)

Because the equation is an excellent fit to the smoothed values (average deviation of <0.01 pct), little accuracy is lost in using enthalpies calculated from this equation instead of those from table 3.

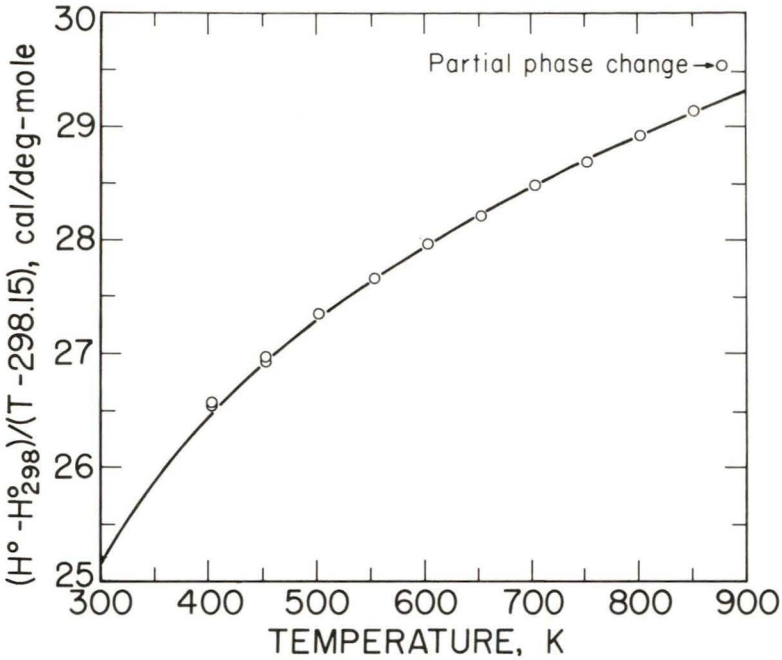

FIGURE 1. - High-temperature mean heat capacities of Al_2S_3(c).

Standard enthalpies of formation ($\Delta Hf°$), Gibbs energies of formation ($\Delta Gf°$), and logarithms to the base 10 of the equilibrium constants of formation (log Kf) were calculated as functions of temperature for Al_2S_3. This was done by combining enthalpy values from the present investigation with supplementary data from the literature. Similar calculations were also made for the reaction of Al(c) with S_2(g). Ko was the source of the remaining data for Al_2S_3(c). CODATA (1) was the source for the standard heat of formation at 298.15 K for S_2(g) and the entropy at 298.15 K for both S(c, ℓ) and Al(c). The low-temperature data for S(c, ℓ) and Al(c) were taken from the JANAF tables (6). The other thermodynamic data necessary for S_2(g) and S(c, ℓ) were obtained from the JANAF tables (7) and West (20), respectively. High-temperature values above 298.15 K for Al(c) were taken from Hultgren (9). The data of Hultgren and West were adjusted to the International Practical Temperature Scale of 1968 as described by Douglas (4).

The results of these calculations for the formation data are listed in table 4. Data for the reaction involving S_2(g) are shown in table 5.

TABLE 4.- Formation data for $2Al(c) + 3S(c,\ell) = Al_2S_3(c)$

T, K	kcal/mole		Log Kf	T, K	kcal/mole		Log Kf
	$\Delta Hf°$	$\Delta Gf°$			$\Delta Hf°$	$\Delta Gf°$	
298.15	-155.600	-153.034	112.175	400	-157.453	-152.055	83.078
300	-155.605	-153.017	111.471	500	-158.698	-150.559	65.809
[1]368.54	-155.782	-152.410	90.380	600	-159.647	-148.836	54.213
368.54	-156.070	-152.410	90.380	700	-160.407	-146.971	45.886
[1]388.36	-156.129	-152.209	85.655	[2]717.80	-160.527	-146.626	44.643
388.36	-157.359	-152.209	85.655				

[1]Transition point of S.
[2]Boiling point of S.

TABLE 5. - Thermodynamic data for the reaction $2Al(c) + 1.5\ S_2(g) = Al_2S_3(c)$

T, K	kcal/mole		Log Kr
	ΔHr°	ΔGr°	
298.15	-201.665	-181.574	133.096
300	-201.661	-181.449	132.184
400	-201.409	-174.749	95.477
500	-201.081	-168.119	73.484
600	-200.730	-161.558	58.847
700	-200.382	-155.057	48.410
800	-200.057	-148.603	40.596
900	-199.769	-142.193	34.529

X-Ray Powder Diffraction

X-ray powder diffraction studies identified the α, γ, and cubic phases in the Al_2S_3 by indexing their powder diffraction patterns based on the lattice parameters given by Donnay. X-ray diffraction analysis of the sample heated at 879 K for 2-1/2 hours and quenched in the copper-block calorimeter showed a partial conversion from the α-phase to the metastable γ-phase. This phase-change was also shown by X-ray analyses of separate samples heated at 100° intervals between 920 and 1,320 K for about 3 hours or at 1,500 K for 1 hour and quenched on an aluminum brick to simulate quenching in the copper-block calorimeter. These analyses revealed that the amount of γ-phase changed from trace to major while heating from room temperature to 920 K. At the same time, the amount of α-phase changed from principal to minor, and the cubic phase disappeared. Continued heating to 1,320 K decreased the amount of α-phase to a trace, which remained at 1,500 K. The original amounts of the three phases were restored by heating the sample for several hours at slightly below 850 K. This restoration does not take place in the copper-block calorimeter, because the sample is in effect quenched from the furnace temperature to near 298 K in the calorimeter.

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