

Measured Relative Enthalpy of Anhydrous Crystalline Aluminum Trifluoride, AlF_3 , from 273 to 1173 °K and Derived Thermodynamic Properties from 273 to 1600 °K¹

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The enthalpy of a high-purity sample of anhydrous crystalline aluminum trifluoride, AlF_3 , relative to that at 0 °C (273.15 °K), was precisely measured with an ice calorimeter and a "drop" method at 18 temperatures starting at 50 °C and proceeding in 50-deg steps to 900 °C (1173.15 °K). Thirty additional enthalpy measurements between 450 and 453 °C revealed a gradual transition. A simple general relation for the progress of transition when impurity is in solid solution is derived. The relation fits the observed transition data and indicates a first-order transition temperature of 455 °C (728 °K). X-ray powder patterns on the sample, measured in the Crystallography Section of the NBS, established the existence of a phase transition by showing not only the known hexagonal structure at room temperature (even after violent quenching from above the transition temperature region) but a new, simple-cubic structure at 570 °C (843 °K). The smooth heat-capacity curve formulated from the data merges very smoothly with that representing published precise low-temperature data. The common thermodynamic properties were derived, and are tabulated at and above 273.15 °K, with extrapolation up to 1600 °K.

Key Words: Aluminum trifluoride, drop calorimetry, enthalpy measurements, high-temperature calorimetry, phase transition, pretransition phenomena, specific heat, thermodynamic properties.

1. Introduction

During the past several years the National Bureau of Standards has conducted a comprehensive program of research to determine accurately the thermodynamic properties of substances that are important in high-temperature applications, such as chemical propulsion, yet for which accurate data have been lacking. Aluminum trifluoride, AlF_3 , is a key example of prime importance in this area. In this research program the heat of formation at room temperature [1]² and the vapor pressures at elevated temperatures [2] of AlF_3 have been accurately measured, and a current thermodynamic study of the AlF_3 – AlCl_3 system involving vaporization equilibrium is in progress. Reliable thermodynamic properties of the solid up to high temperatures are needed, not only to obtain heats of formation and reaction at such temperatures but also to interpret accurately such vaporization data as those just referred to.

Low-temperature heat-capacity measurements (from 54 to 298 °K) on AlF_3 , believed to be accurate,

have been reported by King [3]. Lyashenko [4] measured the high-temperature enthalpy from 290 to 1305 °K. O'Brien and Kelley [5] repeated these measurements and extended them to 1401 °K. Though the results of these investigations did not differ seriously, those of O'Brien and Kelley have been regarded as somewhat more reliable. (For one thing, Lyashenko failed to detect the transition found by O'Brien and Kelley.) However, Frank [6] noted systematic differences between the results of O'Brien and Kelley and those of others for two other substances measured at the same time as the aluminum fluoride, and, concluding that O'Brien and Kelley's recorded temperatures were too high by amounts up to 20° at 1373 °K, made an adjustment of their smoothed data on AlF_3 which leads to corrected heat capacities in poor agreement with King's.

Because of the need for accurate high-temperature enthalpies of AlF_3 and the uncertainties in the existing data, the measurements reported in the present paper were undertaken.

2. Sample

The sample of aluminum fluoride was supplied by the Alcoa Research Laboratories of the Aluminum

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² Figures in brackets indicate the literature references at the end of this paper.

Company of America, New Kensington, Pa., who had purified it by sublimation at 1050 °C in a nickel retort. It was in the form of a fine white crystalline powder.

Specimens were analyzed chemically for aluminum and fluorine in the Applied Analytical Research Section of the NBS, and spectrochemically for a number of heavier chemical elements by a general qualitative method in the Spectrochemistry Section of the NBS. The results of these analyses are given in table 1. The supplier had indicated that the sample would contain "a small amount of aluminum oxide and a spectroscopic amount of nickel," and it will be noted that no analysis for oxygen was made. However, the percentages of aluminum and fluorine in table 1 agree with the theoretical composition within the precision of analysis, and hence no corrections for impurity were made other than adjustment of the enthalpy near the transition temperature as described in section 4.

TABLE 1. Chemical composition of the sample of aluminum trifluoride as determined by chemical and qualitative spectrochemical analysis

Element	Percentage by weight		
	Found		Theoretical
	Individual analysis	Mean	
Al	$\left\{ \begin{array}{l} 32.13 \\ 32.15 \\ 32.17 \end{array} \right\}$	32.15	32.13
F	$\left\{ \begin{array}{l} 68.00 \\ 67.66 \\ 67.61 \end{array} \right\}$	67.76	67.87
Mg	0.01-0.1		0
Ca, Cu, Fe, Mn, Ni, Si	* 0.001-0.01		0
Cr, V	* 0.0001-0.001		0
Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Ga, Ge, Hf, Hg, In, Ir, La, Mo, Nb, Os, P, Pb, Pd, Pt, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, W, Y, Zn, Zr	Undetected		0

* For each of the elements listed.

3. Calorimetric Procedure and Thermal Data

The enthalpy measurements were made by a "drop" method employing a silver-core furnace and a precision ice calorimeter. The temperature of the furnace core, held constant to ± 0.01 deg during a measurement, was measured up to 500 °C by a platinum resistance thermometer (ice-point resistance, about 25 Ω) that had been calibrated at the NBS and whose ice-point resistance was frequently rechecked. Above 500 °C the furnace temperatures were measured by two Pt-Pt-10 percent Rh thermocouples whose independent NBS calibrations were slightly adjusted to make them exactly concordant with the resistance thermometer below 500 °C when compared with it in the furnace of the calorimetric apparatus. The mass of the sample-plus-container was periodically checked for constancy during the series of measurements. Other details of the method and apparatus are discussed extensively in an earlier publication [7].

All the enthalpy measurements were made on a single specimen ("sample") of aluminum fluoride

weighing about 5 g. The cylindrical sample container (wall thickness, about 0.015 in) was fabricated from annealed 99.9 percent-pure silver. One end was drawn down to a narrow neck, and, after introduction of the sample in the air atmosphere of a dry box at room temperature, the container was evacuated and filled with helium to a few torr pressure before pinching the neck and sealing it off with a torch.

The individual enthalpy measurements on the sample-plus-container, the corresponding mean net relative enthalpy of the sample at each temperature, and the deviations of these means from the empirical equations derived to represent them (sec. 5), are given in table 2 for the various furnace temperatures arranged in increasing order. Although the enthalpy measurements at a given furnace temperature are listed in chronological order, the temperatures themselves (particularly from 720 to 726 °K) are not. (The details of the empty-container measurements that were used to complete these calculations are given in another paper [8].) The tabulated values are those after correction for small differences between parts of the sample container and the empty container. The vapor pressure of aluminum fluoride at the highest furnace temperature involved, 900 °C, is only about 1 torr, and it can be shown that at this temperature the heat of evaporation to saturate the 3 cm³ of gas space in the sample container was negligible (about 0.003 cal).

The enthalpy values of table 2 are further treated in sections 4 and 5.

4. Phase Transition

It is known that AlF₃ undergoes a solid-state transition, though the authors are unaware that anyone has previously investigated the nature of the structural change. O'Brien and Kelley's [5] enthalpy measurements showed a small but definite enthalpy increment (150 cal/mol), and over so small a temperature interval that it was attributed to a first-order transition reported to occur at 727 °K.

The present investigation likewise shows a transition with a heat and temperature approximately in agreement with the above values; so, in addition to a series of enthalpy measurements at furnace temperatures every 50 deg from 273 to 1173 °K, a special series of enthalpy values was determined at closely spaced temperatures between 722 and 727 °K, in an effort to distinguish between a first- and a second-order transition and also to define as closely as possible the true (equilibrium) transition temperature (or temperature range).

The individual unsmoothed enthalpy values obtained in this small range are shown in figure 1. The frame of reference which gives these points significance with regard to the transition is afforded by the two solid curves, calculated from the empirical equations derived later (sec. 5). The lower curve is part of that fitting closely all the values at and below 723 °K (except three values approached from higher temperatures, presently to be discussed), and the upper curve similarly fits closely the values from 773 to 1173 °K. Asso-

TABLE 2. High-temperature enthalpy measurements on aluminum trifluoride, AlF₃

Furnace temperature, T ^a	Measured heat (sample plus container) ^{b,c}	H _T - H _{273.15} of AlF ₃ ^{c,d}		
		Individual measurement ^e	Mean observed	Mean observed - smoothed ^f
°K	cal	cal mol ⁻¹	cal mol ⁻¹	cal mol ⁻¹
323.15	90.52	898.6	899.6	+ 3.1
	90.66	901.0		
	90.56	899.3		
373.15	186.12	1873.5	1871.8	+ 2.2
	186.05	1872.3		
	185.89	1869.6		
423.15	285.05	2896.9	2894.4	- 4.1
	284.79	2892.6		
	284.86	2893.8		
473.15	386.95	3963.5	3965.0	- 3.2
	387.08	3965.7		
	387.09	3965.9		
523.15	491.35	5066.0	5069.5	- 0.2
	491.70	5071.9		
	491.63	5070.7		
573.15	598.42	6207.0	6206.8	+ 6.8
	598.39	6206.5		
623.15	706.54	7359.4	7363.1	+ 1.2
	706.85	7364.5		
	706.91	7365.6		
673.15	817.61	8554.4	8556.7	- 7.3
	817.73	8556.4		
	817.90	8559.3		
719.78	* 934.92	* 9892.1		See figure 1. *
721.89	930.44	9788.8		
722.13	931.33	9800.7		
722.16	* 940.87	* 9959.6		
723.06	* 943.25	* 9987.2		
723.59	934.56	9834.9		
723.76	* 943.79	* 9986.9		
723.77	935.01	9840.1		
723.84	936.30	9860.7		
723.90	* 936.22	* 9858.5		
723.91	* 943.27	* 9976.2		
724.04	936.82	9866.7		
724.30	937.62	9876.6		
724.33	938.69	9894.1		
724.40	* 944.03	* 9982.4		
724.52	938.33	9885.4		
724.80	939.72	9905.0		
724.98	941.15	9926.4		
725.18	943.44	9962.1		
725.20	942.77	9950.4		
725.24	943.62	9964.1		
725.27	943.37	9959.6		
725.31	* 947.21	* 10023.3		
725.31	944.01	9969.8		
725.38	943.97	9968.1		

TABLE 2—Continued

Furnace temperature T ^a	Measured heat (sample plus container) ^{b,c}	H _T - H _{273.15} of AlF ₃ ^{c,d}		
		Individual measurement ^e	Mean observed	Mean observed - smoothed ^f
725.44	945.04	9985.2	See figure 1.	
725.54	945.57	9992.7		
725.60	946.56	10008.4		
725.70	947.01	10014.8		
725.89	947.71	10024.0		
726.08	948.73	10038.3		
726.64	949.96	10051.4		
733.00	963.89	10198.6	10198.6	- 0.1
742.00	983.87	10411.2	10411.2	+ 2.3
763.06	1030.64	10908.2	10908.2	+ 6.5
			11140.5	+ 2.2
773.15	1052.60	11138.2		
	1052.92	11143.5		
	1052.69	11139.7		
783.22	1074.69	11370.5	11370.5	- 4.2
793.31	1097.28	11610.5	11610.5	- 1.9
803.20	1118.71	11833.6	11833.6	- 11.2
812.99	1141.13	12074.2	12074.2	- 1.3
818.07	1152.66	12197.2	12197.2	+ 1.8
820.84	1157.74	12244.0	12260.8	- 16.8
			12315.0	- 0.3
823.15	1164.08	12318.2		
	1163.69	12311.7		
	1163.89	12315.4		
873.15	1275.81	13494.3	13494.0	- 5.7
	1275.77	13493.6		
			14691.8	+ 0.8
923.15	1389.25	14690.2		
	1389.31	14691.2		
	1389.48	14694.1		
			15891.1	+ 1.9
973.15	1503.59	15892.2		
	1503.41	15889.2		
	1503.57	15891.9		
1023.15	1619.16	17105.0	17100.0	+ 6.1
	1618.78	17098.7		
	1618.63	17096.2		
			18300.6	- 4.5
1073.15	1734.09	18297.0		
	1734.35	18301.3		
	1734.49	18303.6		
			19521.1	- 1.4
1123.15	1851.71	19523.3		
	1851.41	19518.3		
	1851.61	19521.6		
			20747.1	+ 1.0
1173.15	1969.75	20745.7		
	1970.00	20749.8		
	1969.76	20745.8		

^a International Temperature Scale of 1948, as modified in 1954.
^b 0°C = 273.15 °K.

^c Sample mass = 5.0248 g.

^d 1 cal (defined) = 4.1840 J.

^e Molecular weight = 83.9767.

^f In calculating the net heat due to the sample, the gross heat (column 2) was decreased by the smoothed empty-container heat calculated from the equation

$$H_T - H_{273.15} = 0.76152(T - 273.15) + 2.3649(10^{-5})(T - 273.15)^2 + 0.42246(10^{-7})(T - 273.15)^3 - 8.9987[(T - 273.15)/T] \text{ cal at } T^\circ\text{K}.$$

The observed values which this equation represents are given in table 3 of reference [8].

^g The smoothed values below 728 °K were calculated from eq (14) and those above 728 °K from eq (15).

^h In determining the enthalpy values so indicated in columns 2 and 3, the final sample temperature (column 1) was approached by cooling after first heating above 726 °K. In determining all other enthalpy values in this table, the final sample temperature was approached by heating only.

ciating these two curves with, respectively, the low-temperature (α) and high-temperature (β) forms of AlF₃, it is natural to take the vertical position of any point between as a linear measure (within the experimental precision) of the fraction of the sample which has converted from α to β , provided the sample can be assumed to have always reverted to the same state when cooled in the calorimeter to 273.15 °K.

On this basis the intermediate points approached from lower temperatures ("by heating") indicate a gradual transition between 723 and 726 °K, and it is believed that these represent approximately true equilibrium because two pairs of points involved equilibration times within the furnace which differed by factors of 4 and 10, respectively, without appreciably changing the enthalpy found. On the other hand the points approached by cooling after first heating above 726 °K

(i.e., "by cooling") lie along the upper curve. It is believed that in these latter cases the sample completely converted to the β form but failed to revert partially to α (until quenched in the calorimeter). These points would then not correspond to phase equilibrium, and will not be discussed further.

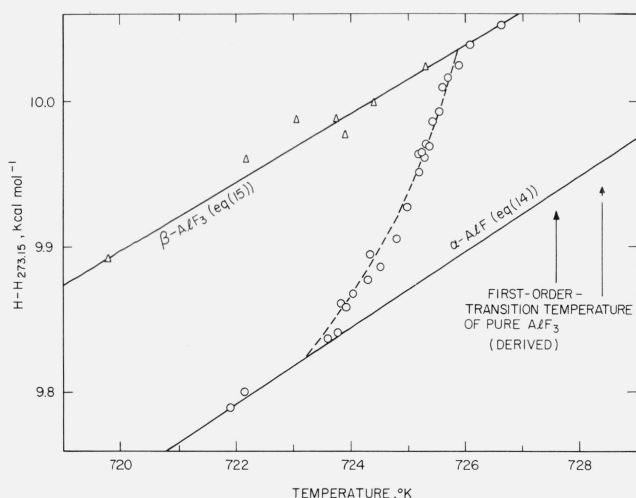


FIGURE 1. *Observed enthalpy of the sample of aluminum fluoride near the transition temperature.*

○ temperature approached by heating only; Δ, temperature approached by cooling after first heating above 726°K. For the derivation of the dotted curve, see text.

It may be noted that the sharp upturn in the enthalpy between 723 and 726 °K, which would correspond to a hump in the heat-capacity curve, is in strong contrast to the gradual upward curvature of the heat-capacity curve over some 200 deg below 723 °K (fig. 3), so that the two phenomena appear to be of different origin. In order to throw light on the nature of the 3-deg upturn, x-ray powder patterns were taken in the Crystallography Section of the NBS on three specimens of the same aluminum-fluoride sample. These specimens were, respectively, one not used in the enthalpy measurements, one that had been heated well above 726 °K and then cooled slowly over two days to room temperature, and one that, after similar heating, had then been quenched in liquid nitrogen (i.e., much more drastically quenched than in the ice calorimeter). All three specimens gave at room temperature the same known pattern associated with the room-temperature hexagonal structure of AlF_3 [9]; it was therefore concluded that in all the enthalpy measurements the sample probably returned to this same form in the calorimeter, and consequently that the points in figure 1 are true measures of the relative enthalpy under the furnace conditions.

Additional x-ray patterns, however, were taken on one of the specimens while at approximately 840 °K, well above the transition region. In these cases the hexagonal pattern was missing, being replaced by a new pattern interpreted as due to a primitive (simple) cubic structure having a cell dimension of 3.580 Å (or possibly some multiple thereof). (TaF₃ is said to show a similar structure at certain temperatures.) From this result it is concluded that the transition in AlF₃ at about 726 °K involves a change in crystal structure. Since a true second-order transition is only compatible with a continuous change in structure not readily conceivable for most pairs of well-defined

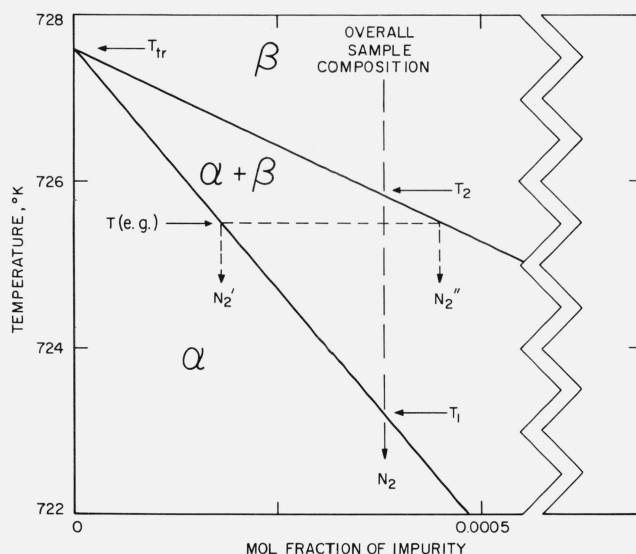


FIGURE 2. Phase-diagram representation of the transition of the sample of aluminum fluoride as affected by impurity.

(See text for definitions of symbols.)

structures, the conclusion is that pure AlF_3 exhibits a true first-order transition. A quantitative explanation of the observed 3-deg transition is offered below after postulating the presence of impurity soluble in both forms of AlF_3 and then treating the sample as a two-component system.

Two-component systems which exhibit both appreciable solid solubility and a first-order transition of one component are very common, and enthalpy data on some such systems have been interpreted in accordance with these characteristics with as much care as the very common treatment of premelting. However, no one treatment is equally appropriate in every case, as in each one approximations must be made that are consistent with the amount and quality of the information available. With this fact in mind, the following very simple treatment was developed for application to the present case; obviously, it can be more generally applied.³

The situation tentatively assumed to exist is illustrated by the type of phase diagram shown in figure 2 (whose specific details are those subsequently derived for the present sample). For simplicity the principal component is assumed to be contaminated with a single component whose overall mole fraction, N_2 , is so small that the temperature-composition phase boundaries may be taken as straight lines in this region. Also for simplicity, maintenance of complete phase equilibrium is assumed. In the example illustrated, the impurity depresses the transition temperature of the pure substance, T_{tr} , to a finite temperature interval T_1 to T_2 , the sample at any intermediate temperature

³ A similar treatment has been published by Mastrangelo and Dornte [12]. Their final equations, while derived for the fusion process only and expressed in terms of slightly less general parameters, can be shown to be equivalent to eqs (9) and (11) below.

T consisting of α and β phases of compositions N'_2 and N''_2 respectively. Though in most known cases of this type the impurity does depress the transition temperature (as in fig. 2), some cases are known where this is elevated, but the following equations are equally applicable to both situations.

The two phase boundaries may be defined by

$$N'_2 = A(T - T_{tr}); \quad (1)^{\dagger}$$

$$N''_2 = B(T - T_{tr}), \quad (2)$$

where A and B are constants. The limits of the two-phase temperature region are then obviously given by

$$T_1 = T_{tr} + N_2/A; \quad (3)$$

$$T_2 = T_{tr} + N_2/B. \quad (4)$$

If at temperature T each mole of the principal component is distributed with n' moles in the α solid solution and n'' moles in the β solid solution, the overall mole balance of each component gives the well-known "lever" relations; on assuming that N_2 , N'_2 , and N''_2 are negligible compared to unity, these relations are

$$n' = \frac{N_2 - N''_2}{N'_2 - N''_2}; \quad (5)$$

$$n'' = \frac{N'_2 - N_2}{N'_2 - N''_2}. \quad (6)$$

It is convenient to define a constant parameter k by

$$B/A = k. \quad (7)$$

From these equations then follow the two relations

$$n'' = \left[\left(\frac{T_2 - T}{T - T_1} \right) k + 1 \right]^{-1}; \quad (8)$$

$$T_{tr} = T_2 + \frac{T_2 - T_1}{k - 1}. \quad (9)$$

If ΔH_{tr} is the molal heat of transition, the molal enthalpy of the sample $n''\Delta H_{tr}$ at T in excess of that of the pure α phase may be calculated from eq (8); eq (9) gives the transition temperature corrected for the impurity. A well-known relation⁴ applicable to dilute solutions exhibiting miscibility in both phases is, in the present notation (and with R as the gas constant),

$$\frac{N'_2 - N''_2}{T - T_{tr}} = \frac{\Delta H_{tr}}{RT_{tr}^2}, \quad (10)$$

and this may be combined with previous equations to give the amount of impurity in the sample, N_2 , causing the transition over the interval T_1 to T_2 :

$$N_2 = \frac{k(T_2 - T_1)\Delta H_{tr}}{(1 - k)^2 RT_{tr}^2}. \quad (11)$$

If T_1 , T_2 , k , and ΔH_{tr} can be evaluated from the thermal data such as that shown in figure 1, eq (9) and (11) may be readily solved.

Close examination of eq (8) shows, however, that some measure of the curvature of the "excess enthalpy" curve in the transition region ($n''\Delta H_{tr}$ versus T) is essential to assigning a value to k and hence using eq (9) and (11) significantly. If the impurity elevates the transition temperature ($T_{tr} < T_1$), then $k < 1$ and this curve is concave downward; but if the transition temperature is depressed ($T_{tr} > T_2$), then $k > 1$ and the curve is concave upward. In either event the curve begins (at T_1) and ends (at T_2) with finite positive slope.

The enthalpy values of figure 1 (excluding the points "by cooling"), though subject to apparently considerable scatter which is a result of the unusually small magnitude of the heat of transition and the correspondingly expanded scale of this plot,⁵ were deemed sufficiently numerous and interconsistent to apply the above relations. An approximation to the best fit to the data gave

$$\left. \begin{aligned} T_1 &= 723.2^\circ \text{K} \\ T_2 &= 725.85^\circ \text{K} \\ k &= 2.5 \end{aligned} \right\}, \quad (12)$$

from which were calculated

$$\left. \begin{aligned} T_{tr} &= 727.6^\circ \text{K} \\ N_2 &= 0.0004 \end{aligned} \right\} \quad (13)$$

and the dashed curve drawn through the transition region in figure 1. This curve fits the points within their precision, and it may be added that a value $N_2 = 0.0004$ is plausible (e.g., if due to MgF_2 , this would correspond to 0.01 weight percent of Mg, which is consistent with table 1). This explanation of the observed transition data is thus regarded as acceptable, with the transition temperature of pure AlF_3 lying above 726°K . Since the value derived above for the transition temperature must be considered uncertain by the order of 1 deg, it will be rounded to 728°K for calculations on pure AlF_3 .

⁴ See, for example, reference [10].

⁵ Note that in figure 1 the total ordinate distance between the two solid curves is equivalent to only about 1.5 percent of the measured relative enthalpy which determines any one point.

TABLE 3. *Thermodynamic functions for aluminum trifluoride, AlF₃, solid phases (in terms of defined calories per mole)*
(1 cal = 4.1840 J; $T^{\circ}\text{K} = t^{\circ}\text{C} + 273.15$; 1 mole = 83.9767 g.)

T	C_p°	$(H_T^{\circ} - H_0^{\circ})$	$(H_T^{\circ} - H_0^{\circ})/T$	S_T°	$-(G_T^{\circ} - H_0^{\circ})$	$-(G_T^{\circ} - H_0^{\circ})/T$
$^{\circ}\text{K}$	cal deg ⁻¹ mol ⁻¹	cal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	cal deg ⁻¹ mol ⁻¹	cal mol ⁻¹	cal deg ⁻¹ mol ⁻¹
Alpha Phase						
273.15	17.045	2340.5	8.569	14.357	1581.2	5.789
298.15	17.957	2778.2	9.318	15.890	1959.4	6.572
300.00	18.021	2811.5	9.372	16.001	1988.9	6.630
325.00	18.828	3272.4	10.069	17.476	2407.5	7.408
350.00	19.526	3752.0	10.720	18.898	2862.3	8.178
375.00	20.119	4247.7	11.327	20.266	3352.0	8.938
400.00	20.623	4757.2	11.893	21.581	3875.2	9.688
425.00	21.053	5278.3	12.420	22.844	4430.6	10.425
450.00	21.426	5809.4	12.910	24.059	5017.0	11.149
475.00	21.754	6349.2	13.367	25.226	5633.1	11.859
500.00	22.054	6896.9	13.794	26.350	6277.9	12.556
550.00	22.625	8013.8	14.571	28.478	7649.2	13.908
600.00	23.258	9160.4	15.267	30.473	9123.5	15.206
650.00	24.071	10343.	15.912	32.365	10695.	16.454
700.00	25.181	11572.	16.532	34.188	12369.	17.656
728.00	25.978	12288.	16.880	35.190	13330.	18.311
Beta Phase						
728.00	23.322	12423.	17.065	35.375	13330.	18.311
750.00	23.392	12937.	17.249	36.071	14116.	18.821
800.00	23.546	14110.	17.638	37.585	15958.	19.947
850.00	23.693	15291.	17.990	39.017	17873.	21.027
900.00	23.833	16480.	18.311	40.375	19858.	22.065
950.00	23.968	17675.	18.605	41.668	21910.	23.063
1000.00	24.099	18876.	18.876	42.900	24024.	24.024
1050.00	24.227	20084.	19.128	44.079	26199.	24.951
1100.00	24.353	21299.	19.363	45.209	28431.	25.847
1150.00	24.476	22520.	19.582	46.294	30719.	26.712
1200.00	24.598	23747.	19.789	47.339	33060.	27.550
1250.00	24.718	24979.	19.984	48.345	35452.	28.362
1300.00	24.837	26218.	20.168	49.317	37894.	29.149
1350.00	24.954	27463.	20.343	50.257	40383.	29.914
1400.00	25.071	28714.	20.510	51.166	42919.	30.656
1450.00	25.187	29970.	20.669	52.048	45500.	31.379
1500.00	25.302	31232.	20.822	52.904	48123.	32.082
1550.00	25.417	32500.	20.968	53.735	50790.	32.767
1600.00	25.531	33774.	21.109	54.544	53497.	33.435

H_0° is the enthalpy of the α form at 0 $^{\circ}\text{K}$ (and 1 atm pressure). Values for temperatures higher than 1150 $^{\circ}\text{K}$ are by extrapolation beyond the measuring range.

APPENDIX. *Thermodynamic functions for aluminum trifluoride, AlF₃, solid phases (in terms of joules per mole)*

(T °K = t °C + 273.15; 1 mole = 83.9767 g.)

T	C_p°	$(H_T^\circ - H_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	S_T°	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
°K	J deg ⁻¹ mol ⁻¹	J mol ⁻¹	J deg ⁻¹ mol ⁻¹	J deg ⁻¹ mol ⁻¹	J mol ⁻¹	J deg ⁻¹ mol ⁻¹
Alpha Phase						
273.15	71.316	9792.6	35.853	60.070	6615.7	24.221
298.15	75.132	11624.	38.986	66.484	8198.1	27.497
300.00	75.400	11763.	39.212	66.948	8321.6	27.740
325.00	78.776	13692.	42.129	73.120	10073.	30.995
350.00	81.697	15698.	44.852	79.069	11976.	34.217
375.00	84.178	17772.	47.392	84.793	14025.	37.397
400.00	86.287	19904.	49.760	90.295	16214.	40.535
425.00	88.086	22084.	51.965	95.579	18538.	43.618
450.00	89.646	24306.	54.015	100.66	20991.	46.647
475.00	91.019	26565.	55.928	105.54	23569.	49.618
500.00	92.274	28857.	57.714	110.25	26267.	52.534
550.00	94.663	33530.	60.965	119.15	32004.	58.191
600.00	97.312	38327.	63.877	127.50	38173.	63.622
650.00	100.71	43275.	66.576	135.42	44748.	68.844
700.00	105.36	48417.	69.170	143.04	51752.	73.873
728.00	108.69	51413.	70.626	147.24	55773.	76.613
Beta Phase						
728.00	97.579	51978.	71.400	148.01	55773.	76.613
750.00	97.872	54128.	72.170	150.92	59061.	78.747
800.00	98.516	59036.	73.797	157.26	66768.	83.458
850.00	99.132	63978.	75.270	163.25	74781.	87.977
900.00	99.717	68952.	76.613	168.93	83086.	92.320
950.00	100.28	73952.	77.843	174.34	91671.	96.496
1000.00	100.83	78977.	78.977	179.49	100520.	100.52
1050.00	101.36	84031.	80.032	184.43	109620.	104.40
1100.00	101.89	89115.	81.015	189.15	118960.	108.14
1150.00	102.41	94224.	81.931	193.69	128530.	111.76
1200.00	102.92	99357.	82.797	198.07	138320.	115.27
1250.00	103.42	104512.	83.613	202.28	148330.	118.67
1300.00	103.92	109696.	84.383	206.34	158550.	121.96
1350.00	104.41	114905.	85.115	210.28	168960.	125.16
1400.00	104.90	120139.	85.814	214.09	179570.	128.26
1450.00	105.38	125394.	86.479	217.77	190370.	131.29
1500.00	105.86	130675.	87.119	221.35	201350.	134.23
1550.00	106.34	135980.	87.730	224.83	212500.	137.10
1600.00	106.82	141310.	88.320	228.21	223830.	139.89

H_0° is the enthalpy of the α form at 0 °K (1 atm pressure). Values for temperatures higher than 1150 °K are by extrapolation beyond the measuring range.

5. Data-Smoothing; Derived Thermodynamic Functions

Pure aluminum fluoride was assumed to have a first-order transition at 728 °K, as derived in section 4, and two separate empirical equations were derived by the method of least squares to fit the observed enthalpy values as functions of temperature below and above this transition temperature. In this fitting, only the mean enthalpy values (given equal weight) at temperatures exactly 50 deg apart, from 323.15 to 1173.15 °K, were used.⁶ After so trying several forms of equation to obtain acceptable smooth fits, the equations selected were as follows (with the enthalpy and standard deviation, σ , in cal mol⁻¹ at T °K, relative to that of the α form at $T_0 = 273.15$ °K). Note that eq (15) is not intended to be applicable down to 273.15 °K.

α -AlF₃ (273–728 °K):

$$H_T - H_{T_0} = -6.27678(T - T_0) + 7.05597(10^{-2})(T^2 - T_0^2) \\ - 8.25715(10^{-5})(T^3 - T_0^3) + 3.93984(10^{-8})(T^4 - T_0^4) \\ \sigma(\alpha) = 5.58 \quad (14)$$

β -AlF₃ (728–1173.15 °K):

$$H_T(\beta) - H_{T_0}(\alpha) = 22.1387(T - T_0) + 1.08571(10^{-3})(T^2 - T_0^2) \\ + 2.1078(10^5)\left(\frac{1}{T} - \frac{1}{T_0}\right) \\ \sigma(\beta) = 4.09 \quad (15)$$

Smooth high-temperature thermodynamic functions of aluminum trifluoride that represent the present work and merge smoothly with those given by King's low-temperature heat capacities [3] are given in table 3 in terms of defined calories, and in the table in the appendix in joules. As a step in generating this table, a smooth heat capacity function was first evaluated from King's results alone, using a computer code which employs four-point Lagrangian interpolation and employing King's combination of Debye and Einstein functions⁷ for temperatures below his range of measurement (below 51 °K). This procedure gave a Third-Law value for $S_{298.15}^\circ$ of 15.890 cal deg⁻¹ mol⁻¹ (King gave 15.89 ± 0.08). The value of $C_p^\circ(298.15)$ given by King (17.95 cal mol⁻¹ deg⁻¹) is the same as that derived from eq (14) (which fits the high-temperature data of the present work alone). The smooth representation of King's heat capacity data was then joined to the high-temperature heat capacity derived from eq (14). In order to ensure a continuous temperature

derivative of heat capacity in the region of joining, minor adjustments were made to the smoothed high-temperature heat capacity data below 360 °K. The net result of these adjustments was to increase the enthalpy increment ($H_{360} - H_{273.15 \text{ °K}}$) by less than 0.02 percent. The thermodynamic functions up to the transition point were generated using King's smoothed heat capacity data and heat capacity values determined from eq (14), adjusted below 360 °K.

Above the transition temperature eq (15) was used, the necessary integration constants being required to be consistent with the heat of transition, 134.6 cal mol⁻¹, given by the difference of eq (14) and (15) at the transition temperature, 728 °K.

6. Discussion

The heat capacities of α - and β -AlF₃ above 145 °K are shown as functions of temperature in figure 3. The high temperature experimental points were calculated in each case from the original enthalpy data employing a curvature correction according to a formula of Osborne et al. [13]. The smoothed results of O'Brien and Kelley were derived from their published enthalpy equation [5]. Lyashenko's smoothed values were derived from an enthalpy function which fit his observed data to 1.5 percent (several equations were tried, but none fit his data more closely). Over most of the temperature range, the solid curve, which represents the smoothed results of the present work (eq (14) or (15), or table 3), lies between that for O'Brien and Kelley's original work [5] and that for their results as adjusted by Frank [6]. King's values merge very smoothly with the authors' curve and nearly as well with O'Brien and Kelley's, but definitely not with Frank's. The authors' curve for the β form is closer to O'Brien and Kelley's than to Frank's. These considerations, taken together with the fact that Frank's adjustment of O'Brien and Kelley's data lowers the apparent α - β transition temperature by 9 °C (whereas the present work predicts a transition temperature essentially in agreement with that of O'Brien and Kelley), lead the authors to conclude that Frank's corrections to the AlF₃ data are completely invalid.

Just previous to the authors' measurements on AlF₃ they made checks on the calorimetric apparatus by repeating measurements of the enthalpy of Calorimetry-Conference standard-sample synthetic sapphire (Al₂O₃) at 373, 773, and 1173 °K relative to 273 °K. At all these temperatures the agreement with earlier work at the NBS using the same sample and the same apparatus was within 0.2 percent, which is within the present precision at 373 and 773 °K but slightly outside it at 1173 °K. Because the calorimetric apparatus used to measure AlF₃ was very recently used also to measure BeO · Al₂O₃ and BeO · 3Al₂O₃ over the same temperature range and with the same high precision, the authors feel that their general discussion of accuracy for the latter two substances [8, 11] is equally applicable to AlF₃. The actually observed enthalpy

⁶ The measurements at 721.89 and 722.13 °K were used to compute the mean enthalpy at 723.15 °K.

⁷ King states that this function fits his heat capacities to within 0.8 percent from 51 to 298 °K.

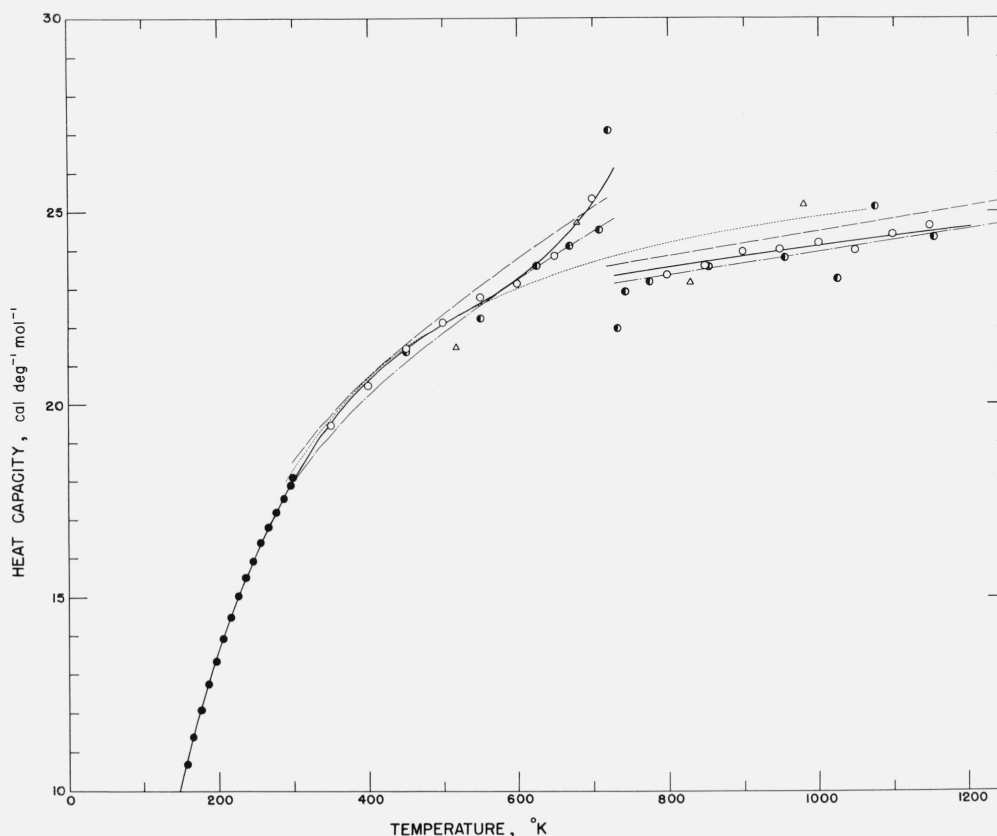


FIGURE 3. Comparison of the heat capacity of α - and β - AlF_3 determined by independent investigations.

For derivation of the curves (which represent smooth values), see text. ●, King, adiabatic method [3]; ○, NBS drop method (this work); —, table 3 (this work); ○—, O'Brien and Kelley [5]; —, O'Brien and Kelley as adjusted by Frank [6]; - - - - -, Δ, Lyashenko [4].

of the sample very near the transition temperature is, of course, subject to additional uncertainty owing to the possibility of incomplete phase equilibrium, but for other temperatures this introduces no uncertainty into the enthalpy and very little into the entropy.

The gradual upturn of the heat-capacity curve for about 200 deg below the transition temperature is interesting (fig. 3). Many solids show this behavior below their melting points or transition temperatures, and it is usually attributed to some type of disorder (of which lattice vacancies form a special case). Despite the x-ray diffraction results summarized in section 4, not enough structural data are presently available on β - AlF_3 to suggest how the lattice may tend to rearrange near the transition temperature.

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NBS, carried out the x-ray examinations and made the structural interpretations of them.

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