Low Temperature Thermodynamic Properties of Aluminum Trichloride

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The low temperature heat capacity of $AlCl_3$ has been measured in the range 13° to 310° K. A vacuum adiabatic calorimeter with automatic data recording was used. The values of C_p°, S_T°, $(H_T^\circ - H_0^\circ)/T$, and $-(G_T^\circ - H_0^\circ)/T$ found at 298.15° K. are 21.75, 26.12, 13.61, and 12.51 cal./deg. mole (±0.5%).

AS PART OF A PROGRAM to measure and tabulate the thermodynamic properties of rocket exhaust products the heat capacity of $AlCl_3$ was determined in the range 13° to 310° K. Experimental interests in the equilibrium between gaseous $AlCl_3$ and its dimer (*11*) are better expedited with a reliable entropy for the solid. The entropy estimate of Brewer *et al.* (*1*) of 40 cal./deg. mole for $AlCl_3$ is tabulated by Rossini *et al.* (*8*). Preliminary measurements in this laboratory were communicated to Kelley and King (*5*) as well as Wagman *et al.* (*12*). Additional measurements led to the definitive presentation given here.

EXPERIMENTAL

Sample. The sample was doubly sublimed reagent grade $AlCl_3$. After the last sublimation the material was ground up in a dry box, and the material which passed through a 20-mesh screen was used for calorimetry. The quantitative analyses for aluminum and chloride (quadruplicate determinations for each) indicated that the sample was of $99.9_4\%$ purity. The chloride content was determined as the silver salt and found to be 79.74% (theoretical 79.77%), while aluminum was weighed as the oxine and accounted for 20.20% (theoretical 20.23%) of the sample. Therefore it was not necessary to correct for impurities.

Calorimetric Apparatus. The adiabatic calorimeter used has been described (*3, 6, 9*). The automatic recording of temperatures (thermal drifts) and energies (the voltage across and current through the calorimeter heater) facilitated data procurement. The measuring circuits were recalibrated prior to the measurements, and the heat capacity of benzoic acid was determined to test the calibration. The entropy of benzoic acid was found to be 40.01 cal./

Table I. Experimental Low Temperature Heat Capacity of Aluminum Chloride

T, ° K.	Cp, Cal./ Deg. Mole
Series I	
13.64	0.300
16.83	0.470
19.41	0.621
21.77	0.838
24.20	1.058
26.74	1.310
29.30	1.613
32.46	1.958
35.96	2.322
39.38	2.800
43.24	3.354
47.42	3.919
51.88	5.541
57.07	5.301
62.94	6.180
69.04	7.107
75.88	8.059
83.77	9.226
92.23	10.36
100.68	11.32
108.94	12.24
116.70	13.10
124.08	13.81
131.17	14.48
128.00	15.10
144.63	15.62
151.09	16.10
157.41	16.52
163.59	16.98
169.66	17.29
175.63	17.62
Series II	
13.26	0.317
16.22	0.432
19.53	0.663
22.61	0.891
24.97	1.112
27.44	1.409
30.02	1.652
32.87	2.016
36.09	2.387
39.62	2.834
47.97	4.010
52.73	4.693
57.81	5.422
63.59	5.339
70.06	7.252
76.96	8.238
84.76	9.365
93.17	10.48
101.71	11.43
109.76	12.40
117.86	13.24
126.09	13.93
133.93	14.73
141.50	15.44
148.83	16.00
155.96	16.52
162.93	17.00
169.74	17.42
176.44	17.81
183.02	18.21
191.21	18.60
200.96	19.06
210.54	19.42
219.96	19.81
229.24	20.34
238.39	20.42
248.03	20.63
258.12	20.95
268.11	21.29
276.90	21.41
284.54	21.57
292.10	21.78
299.62	21.93
307.09	22.13
Series III	
111.86	12.55
120.74	13.51
129.88	14.40
138.60	15.21
147.01	15.98
155.13	16.46
163.03	16.99
170.76	17.43
178.32	17.84
185.74	18.25
193.05	18.60
200.25	18.95
208.60	19.23
218.07	19.62
227.39	19.97
237.15	20.38
247.36	20.50
257.44	20.77
267.43	21.09
277.31	21.26
287.09	21.44
294.64	21.65
299.96	21.77
305.26	21.88
Series IV	
104.46	11.71
113.34	12.77
121.61	13.58
130.23	14.44
139.24	15.25
147.90	15.91
156.28	16.53
165.09	17.13
174.34	17.62
183.37	18.14
192.22	18.62
200.91	18.94
209.47	19.34
211.90	19.36
221.39	19.74
230.73	20.24
239.95	20.33
249.09	20.53
258.14	20.83
266.82	21.07
275.42	21.27
284.24	21.36
292.97	21.64
Series V	
287.53	21.47
296.24	21.66
303.27	21.84
308.64	22.00
313.99	21.98
Series VI	
227.41	19.92
232.06	20.69
239.58	20.29
249.94	20.55
260.18	20.86
270.31	21.13
280.35	21.38
290.27	21.65
300.11	21.77
309.86	21.99

deg. mole, which compares favorably with 40.055 cal./deg. mole reported by Furukawa *et al.* (*2*) and 40.11 cal./deg. mole reported by Oetting and McDonald (*6*).

A gold-plated copper calorimeter (laboratory designation CU-3) of about 70-cc. internal volume was used for the determinations. A 90-ohm platinum resistance thermometer (laboratory designation PRT 8) was permanently fixed in the calorimeter, as was the 100-ohm radial heater. The calorimeter empty heat capacity was measured in a separate set of determinations. Both sample and empty were measured in the presence of 1 atm. of helium gas. Corrections were applied for the differences in solder and helium observed from the two loadings of the cryostat. The sample heat capacity varied from 54% of the total at 14° K. down to 39% at 75° K. and back to 46% at 310° K. The sample mass (in vacuo) was 86.563 grams, and the molecular weight was taken as 133.3405. The density used for buoyancy corrections was 2.44 grams per cc. All handling and transfer of $AlCl_3$ were done in a nitrogen dry box, although weighings were taken outside the dry box.

The ice point was taken as 273.15° K., and one defined calorie as 4.1840 joules. The measurements of mass, time, electromotive force, resistance, and temperature can be traced to standards maintained at the National Bureau of Standards.

Table II. Thermodynamic Functions of Aluminum Chloride[a]

T, ° K.	Cp	$S°$	$H° - H°_0$	$-(G° - H°_0)/T$
13	0.287	(0.086)	(0.852)	(0.021)
14	0.324	0.109	1.157	0.026
15	0.369	0.133	1.502	0.032
20	0.688	0.279	4.083	0.075
25	1.131	0.478	8.587	0.135
30	1.661	0.730	15.54	0.212
35	2.256	1.030	25.30	0.307
40	2.899	1.373	38.17	0.418
45	3.579	1.753	54.35	0.545
50	4.288	2.167	74.01	0.686
60	5.759	3.078	124.2	1.008
70	7.244	4.077	189.2	1.374
80	8.681	5.139	268.9	1.778
90	10.03	6.240	362.5	2.212
100	11.26	7.361	469.1	2.671
110	12.39	8.488	587.4	3.148
120	13.43	9.612	716.6	3.640
130	14.39	10.73	855.8	4.143
140	15.27	11.82	1004.1	4.652
150	16.07	12.91	1160.9	5.166
160	16.78	13.97	1325.2	5.683
170	17.41	15.00	1496.2	6.201
180	17.97	16.01	1673.1	6.718
190	18.47	17.00	1855.4	7.234
200	18.93	17.96	2042.4	7.746
210	19.35	18.89	2233.8	8.255
220	19.73	19.80	2429.3	8.759
230	20.06	20.69	2628.3	9.258
240	20.36	21.55	2830.4	9.752
250	20.63	22.38	3035.3	10.241
260	20.89	23.20	3242.9	10.724
270	21.15	23.99	3453.1	11.200
280	21.39	24.76	3665.8	11.671
290	21.60	25.52	3880.8	12.135
298.15	21.75	26.12	4057.5	12.509
300	21.79	26.25	4097.7	12.594
310	22.02	26.97	4316.7	13.046

[a] Units. Cal., g.f.w., ° K.

RESULTS AND DISCUSSION

Heat Capacities and Thermodynamic Functions. The six series of measured heat capacity points of $AlCl_3$ are given in Table I in chronological order. Temperature increments approximated 10% of the absolute temperature up to 100° K. and 10° K. thereafter. The gross heat capacities were corrected for curvature (*10*), whereupon the heat capacity of the empty calorimeter was deducted.

The smoothed heat capacities and thermodynamic functions at selected temperatures are given in Table II. The functions were derived from polynomial approximations of the heat capacity data on a digital computer (*4*). This allowed the calculations to be analytical. The values of $S°_{13}$ and $(H°_{13} - H°_0)$ were derived from Debye θ of 255° K. in four degrees of freedom. This is a good approximation of the data from 13° to 20° K. The experimental heat capacities generally deviated less than 0.5% from the smooth curve above 30° K. The precision decreased to about 10% of the heat capacity at 13° K. because of the decreasing sensitivity of the thermometer and thermocouples. The thermodynamic functions are expected to have an error no greater than 0.5% above 100° K.

Gibbs Energy of Formation. The value of $\Delta Hf°_{298.15}$ of $AlCl_3$ is tabulated as $-168.5_8 \pm 0.20$ kcal. per mole (*10*). The value of $\Delta Sf°_{298.15}$ is found to be $-60.5_8 \pm 0.1_3$ cal./deg. mole. This is calculated from the reported entropy of $AlCl_3$ and the JANAF Thermochemical Tables (*10*). The Gibbs energy of formation is found to be $-150.5_2 \pm 0.2_5$ kcal. per mole.

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LITERATURE CITED

(1) Brewer, L., Bromley, L.A., Gilles, P.W., Lofgren, N.F., Paper 6, National Nuclear Energy Series IV-19B, L.L. Quill, Ed., McGraw-Hill, New York, 1950.
(2) Furukawa, G.T., McCoskey, R.E., King, P.J., *J. Res. Natl. Bur. Std.* **47**, 256 (1951).
(3) Hildenbrand, D.L., Kramer, W.R., McDonald, R.A., Stull, D.R., *J. Am. Chem. Soc.* **80**, 4129 (1960).
(4) Justice, B.H., "Calculation of Heat Capacities and Derived Thermodynamic Functions from Thermal Data with a Digital Computer," U. S. At. Energy Comm., Rept. **TID-12722** (1961).
(5) Kelley, K.K., King, E.G., "Contributions to the Data on Theoretical Metallurgy," U. S. Bur. Mines, Bull. **592** (1961).
(6) Oetting, F.L., McDonald, R.A., *J. Phys. Chem.* **67**, 2737 (1963).
(7) Osborne, N.S., Stimson, H.F., Sligh, T.S., Cragoe, C.S., Natl. Bur. Stand., Sci. Paper **20**, 65 (1924).
(8) Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stand., Circ. **500** (1952).
(9) Stull, D.R., *Anal. Chim. Acta* **17**, 133 (1957).
(10) Stull, D.R., Ed., "JANAF Thermochemical Tables," Clearinghouse Fed. Sci. Tech. Inform. Doc. **PB-168370-1-2.**
(11) Vrieland, G.E., Stull, D.R., J. CHEM. ENG. DATA **12**, 532 (1967).
(12) Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M., Schumm, R.H., "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stand., Tech. Note **270-3** (1968).

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