as does $(\gamma\pm)_{Na_2SO_4}$[3] for pure sodium sulfate solutions (Fig. 2). The assumption the $(g_{H^+}{}^2g_{SO_4^-})$ is similarly dependent on I in sulfuric acid–sodium sulfate solutions leads to calculated dissociation behavior which is in reasonable agreement with available experimental information. Finally, $(\gamma\pm)_{NaHSO_4}$ values calculated with the additional assumption that $(g_{Na^+}{}^2g_{SO_4^-}) = (g_{H^+}{}^2g_{SO_4^-})$ are found to be consistent with published isopiestic results. This additional assumption is a reasonable extension of the first and, in view of the consistent $(\gamma\pm)_{NaHSO_4}$ values which result, is probably justified.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High Temperature Heat Contents of Cryolite, Anhydrous Aluminum Fluoride and Sodium Fluoride

BY C. J. O'BRIEN AND K. K. KELLEY

RECEIVED JUNE 6, 1957

High temperature heat content measurements of cryolite, anhydrous aluminum fluoride and sodium fluoride were conducted from 298.15°K. to 1370, 1401 and 1746°K., respectively. Cryolite has a crystalline transformation at 845°K. and melts at 1300°K. Aluminum fluoride has a minor crystalline transformation at 727°K. Sodium fluoride melts at 1285°K. Heat absorptions for these phase changes were extracted from the measurements. A table of heat content and entropy increments above 298.15°K., for use in thermodynamic calculations, is included.

Introduction

Despite the importance of cryolite and its constituent fluorides in aluminum metallurgy, thermodynamic data for these substances have been either lacking or inadequate. A recent paper from this Laboratory by King[1] reported the results of low temperature heat capacity measurements and entropy evaluations at 298.15°K. for cryolite, anhydrous aluminum fluoride and sodium fluoride. The present paper gives the results of high temperature heat content measurements of the same substances. The heats of formation will be the subject of a subsequent paper.

Materials.—The present work was conducted with the same samples as King[1] used in low temperature heat-capacity measurements. His paper gives the results of chemical and spectrographic analyses. It will suffice to say here that the sodium fluoride was reagent-grade material, the anhydrous aluminum fluoride was especially prepared for thermodynamic measurements, and the cryolite was hand-picked natural mineral from Greenland. The cryolite was deficient in sodium fluoride and was considered by King to be $Na_{2.959}AlF_{5.959}$, for the purpose of correcting his results to stoichiometric composition. The same consideration is applied in the present work, and the reported results for cryolite have been corrected for the sodium fluoride deficiency. This correction is small in net amount, altering the results for the crystalline range by only 0.01 to 0.06% and those for the liquid range by 0.1%.

Measurements and Results.—The measurements were conducted with previously described apparatus.[2] The samples were enclosed in platinum-rhodium capsules, the heat contents of which were determined by separate experiments. After being filled with sample, each capsule was evacuated, filled with helium and sealed by platinum welding. During the course of the measurements the furnace thermocouple was calibrated frequently against the melting point of gold. Electrical calibrations of the calorimeter were in precise agreement with earlier calibrations.

The experimental heat content values are listed in Table I and plotted in Fig. 1. They are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Corrections to vacuum weighing were made and the employed molecular weights accord with the 1953 International Atomic Weights.[3] The definition, 0°C. = 273.15°K., was employed. The heat content values are considered accurate to within ±0.2%.

TABLE I

EXPERIMENTAL HEAT CONTENTS ABOVE 298.15°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$
		Na_3AlF_6 (mol. wt. 209.95)			
401.3	5,570	839.9	33,970[a]	1263.5	67,550[b]
507.8	11,740	846.7	36,000	1285.5	74,470[b]
600.2	17,410	901.4	39,600	1289.4	79,290[b]
704.1	24,090	1008.8	46,830	1296.6	85,830[b]
753.3	27,330	1052.8	49,860	1301.1	95,100
790.7	29,950	1099.8	53,070	1322.4	97,040
809.7	31,360	1152.6	57,140	1340.7	98,850
835.5	33,340[a]	1200.5	60,730	1370.5	101,650
		AlF_3 (mol. wt. 83.98)			
401.3	1,970	728.1	9,550	1045.7	17,000
500.4	4,090	736.3	9,730	1104.6	18,480
603.0	6,370	749.4	10,030	1200.4	20,810
648.4	7,440	801.6	11,240	1301.5	23,270
704.0	8,780	904.5	13,660	1379.9	25,210
714.2	9,030	1007.0	16,100	1401.2	25,800
724.9	9,320				
		NaF (mol. wt. 41.99)			
406.1	1,240	1105.1	10,480	1298.0	21,460
498.1	2,360	1200.5	11,910	1313.9	21,710
602.8	3,660	1252.6	12,740	1366.3	22,580
705.2	4,970	1264.4	12,930	1428.9	23,610
800.7	6,230	1272.9	13,300	1541.9	25,490
903.6	7,610	1282.2	19,510[b]	1651.3	27,220
1003.2	9,020	1287.6	21,270	1746.5	28,780

[a] Shows pretransition effect. [b] Shows premelting effect.

---

(1) E. G. King, THIS JOURNAL, **79**, 2056 (1957).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(3) E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

Cryolite undergoes two phase changes in the measured temperature range: a crystalline transformation at 845°K., and melting at 1300°K. These are the temperatures at which the phase change is complete upon heating. The accompanying heat absorptions are 2,160 and 27,640 cal./mole, respectively. The latter value corresponds to an entropy of fusion of 21.26 cal./deg. mole, which is lower on a gram-atom basis than the average for previously studied halides. On the other hand, the heat capacity of liquid cryolite per gram-atom is higher than usual for halides. Only 70° of the liquid range could be studied because of damage to the platinum–rhodium capsules. (At temperatures near 1400°K., small leaks developed and small weight losses occurred, making it advisable to discontinue measurements). Over this range, the heat capacity of the liquid is 93.4 cal./deg. mole or 9.34 cal./deg. g. at. It is suggested that the low heat of fusion and high heat capacity of the liquid are inter-related and possibly associated with the presence in the liquid state of larger than usual atomic groups (such as complex ions) which further dissociate with increasing temperature.

As the natural cryolite was deficient in sodium fluoride, as previously mentioned, the sample showed premelting effects over the range 1263–1300°K. (points labeled *b* in Table I). Pretransition effects also were evident between 835 and 845°K. (points labeled *a* in Table I).

The literature contains three previous sets of heat-content data for cryolite—Krestovnikov and Karetnikov[4] (288–1273°K.), Lyashenko[5] (290–1217°K.), and Roth and Bertram[6] (293–1371°K.). These previous measurements are quite discordant, especially in the β-range (between the transformation and melting points) where deviations run up to 11%. The present measurements for the crystals intermediate those of Krestovnikov and Karetnikov and those of Lyashenko, thus confirming that Roth and Bertram's results for the β-range are in serious error. Previous measurements in the liquid range consist only of two widely discrepant points by Roth and Bertram.

Aluminum fluoride undergoes a minor crystalline transformation at 727°K., which to our knowledge has not been reported previously and which escaped detection in the heat content measurements of Lyashenko.[5] The heat effect is only 150 cal./mole which is too small to be readily apparent in Fig. 1 but the location of the point is indicated by the arrow. Lyashenko's results are otherwise in fair agreement with the present work up to 1100°K., the average deviation being about 0.8%.

The results for sodium fluoride in both the crystalline and liquid states appear entirely normal in comparison with previously studied halides. The melting point is 1285°K. and the heat of fusion is 8,030 cal./mole, leading to an entropy of fusion of 6.25 cal./deg. mole. The earlier measurements of sodium fluoride—Krestovnikov and Karetnikov[4] (288–1073°K.) and Lyashenko[5] (290–1287°K.)—were considered by Kelley[7] in compiling his table of "best values." The present results deviate by an average of about 3% from this table. In addition to being of higher accuracy, the present work adds 460° to the measured temperature range for this substance.

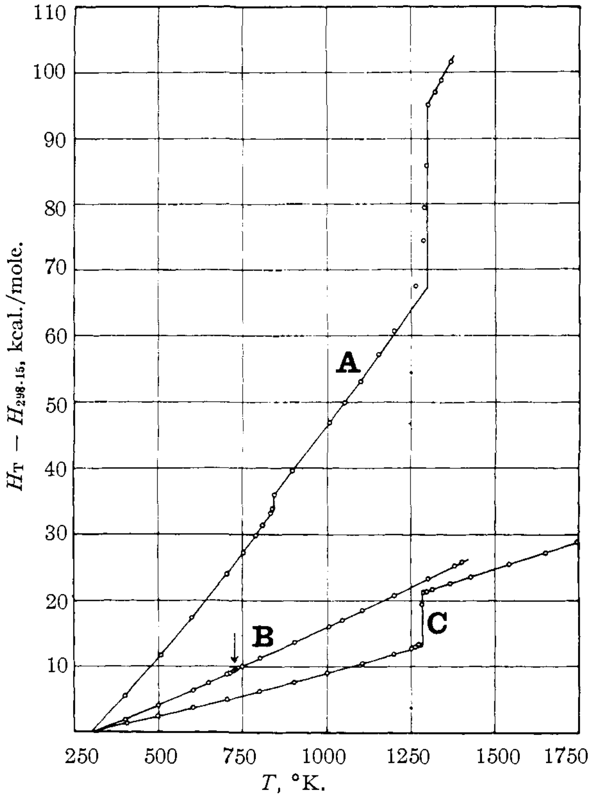

Fig. 1.—Heat contents above 298.15°K.: curve A, Na_3AlF_6; curve B, AlF_3; curve C, NaF.

Table II contains smooth heat content and entropy increments above 298.15°K. for the three substances at even 100° temperature intervals and at transition and melting points.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.15°K.

	Na_3AlF_6		AlF_3		NaF	
T, °K.	$H_T - H_{298.15}$	$S_T - S_{298.15}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$
400	5,510	15.86	1,950	5.61	1,180	3.40
500	11,270	28.70	4,070	10.33	2,380	6.08
600	17,380	39.83	6,310	14.41	3,620	8.34
700	23,820	49.76	8,680	18.06	4,900	10.31
727	....	...	9,360(α)	19.02	....	...
727	....	...	9,510(β)	19.22	....	...
800	30,590	58.79	11,200	21.43	6,220	12.07
845	33,730(α)	62.61	....	...	....	...
845	35,890(β)	65.17	....	...	....	...
900	39,520	69.33	13,550	24.20	7,570	13.66
1000	46,240	76.41	15,930	26.71	8,970	15.13
1100	53,120	82.96	18,340	29.01	10,410	16.50
1200	60,160	89.09	20,780	31.13	11,900	17.80
1285	....	...	....	...	13,210(c)	18.85
1285	....	...	....	...	21,240(1)	25.10
1300	67,360(β)	94.85	23,250	33.11	21,490	25.30
1300	95,000(1)	116.11	....	...	....	...
1400	104,340	123.03	25,740	34.95	23,130	26.51
1500	....	...	....	...	24,770	27.64
1600	....	...	....	...	26,410	28.70
1700	....	...	....	...	28,050	29.70
1800	....	...	....	...	29,690	30.64

---

(4) A. N. Krestovnikov and G. A. Karetnikov, *Legkie Metal.*, **3**, 29 (1934).

(5) V. S. Lyashenko, *Metallurg.*, **10**, 85 (1935).

(6) W. A. Roth and W. W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

(7) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

The results in Table II are represented (to within the average deviations indicated) by the equations

$Na_3AlF_6(\alpha)$

$$H_T - H_{298.15} = 45.95T + 14.73 \times 10^{-3}T^2 + 2.78 \times 10^5T^{-1} - 15{,}942$$

(0.2%, 298–845°K.)

$Na_3AlF_6(\beta)$

$$H_T - H_{298.15} = 52.15T + 7.93 \times 10^{-3}T^2 - 13{,}840$$

(0.1%, 845–1300°K.)

$Na_3AlF_6(l)$

$$H_T - H_{298.15} = 93.40T - 26{,}420$$

(0.2%, 1300–1400°K.)

$AlF_3(\alpha)$

$$H_T - H_{298.15} = 17.27T + 5.48 \times 10^{-3}T^2 + 2.30 \times 10^5 \cdot T^{-1} - 6408$$

(0.2%, 298–727°K.)

$AlF_3(\beta)$

$$H_T - H_{298.15} = 20.93T + 1.50 \times 10^{-3}T^2 - 6500$$

(0.1%, 727–1400°K.)

NaF(c)

$$H_T - H_{298.15} = 10.40T + 1.94 \times 10^{-3}T^2 + 0.33 \times 10^5 \cdot T^{-1} - 3384$$

(0.3%, 298–1285°K.)

NaF(l)

$$H_T - H_{298.15} = 16.40T + 170$$

(0.1%, 1285–1800°K.)

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Heat Capacity, Heat of Fusion, Heat of Transition and Heat of Vaporization of Chlorodifluoromethane between 16°K. and the Boiling Point[1,2]

BY ELEANOR F. NEILSON AND DAVID WHITE

RECEIVED JUNE 11, 1957

The heat capacity of 99.98 mole % pure chlorodifluoromethane has been determined from 16–230°K. A λ-type transition in the solid was observed at approximately 59°K. with a heat of transition of 16 ± 2 cal. The heat of fusion at the melting point, 115.73 ± 0.01°K., was found to be 985.47 ± 1.82 cal./mole. The heat of vaporization at the normal boiling point, 232.50 ± 0.07°K., was found to be 4832.5 ± 12.5 cal./mole. Thermodynamic functions of chlorodifluoromethane have been computed from 0 to 232.5°K. The entropy of the ideal gas at the normal boiling point, from the calorimetric measurements, is 63.92 ± 0.28 e.u. as compared with the spectroscopic value of 64.03 ± 0.02 e.u. The large uncertainty of the calorimetric entropy was due to difficulty in evaluating the Debye θ ($\theta = 70 \pm 5$) which was necessary for the extrapolation of the data to 0°K. From an agreement of the calorimetric and spectroscopic entropy it can be concluded that there is no appreciable hydrogen bonding in the gas phase.

Introduction

The thermodynamic properties of chlorodifluoromethane have in part been investigated over the past few years. Benning and McHarness have obtained P-V-T data,[3] vapor pressures[4] and the heat capacity of the liquid and gas[5] above the normal boiling point. Gelles and Pitzer[6] have calculated the heat capacity of the ideal gas from spectroscopic data. Their calculations agree with those of Benning and McHarness at high temperatures, but not at lower temperatures. The possibility of hydrogen bonding in the gas phase, as in the case of hydrogen fluoride, may result in discrepancies between calorimetric and spectroscopic values of the thermal functions. Recent investigations[7] of the vapor pressure of fluorocarbon mixtures indicates that large positive deviations from Raoult's Law are due to hydrogen bonding in the liquid. Whether these hydrogen bonds manifest themselves in the gas phase as they do in the liquid phase will be reflected in the agreement between the spectroscopic and calorimetric entropies. The object of this research was therefore to determine experimentally the heat capacity of chlorodifluoromethane so that such a comparison of the calorimetric and spectroscopic entropies could be made.

Material.—The chlorodifluoromethane was supplied through the courtesy of the General Electric Research Laboratories at Schenectady, New York. It was a high purity sample from the General Chemical Division of Allied Chemical and Dye Corporation at Morristown, New Jersey.

From the variation of the melting point with amount of sample melted the purity of the sample was estimated to be 99.98 mole %. The weight of sample was 92.9426 g. (1.0743 moles).

Apparatus.—The apparatus used in this research is similar to the condensed gas calorimeter system which has been described by Johnston and co-workers.[8] A high pressure calorimeter system[9] also was used for several heat of vaporization measurements, supplementing those made using the condensed gas calorimeter.

Experimental Procedures.—The experimental procedure for the determination of the heat capacity, heat of vaporization and the heat of fusion is identical to that described by Johnston and co-workers[8] in their paper on condensed gas calorimetry.

Experimental Data

I. Heat Capacities of the Solid and Liquid.—The experimental heat capacities are summarized in Table I and plotted in Fig. 1 along with the data of Benning and McHarness[4] for the heat capacity of the liquid above the normal boiling point. Three series of determinations were made: series

---

[1] This work was supported in part by the General Electric Company, Schenectady, New York.

[2] This article contains in part material abstracted from a dissertation presented by Eleanor F. Neilson to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Master of Science.

[3] A. F. Benning and R. C. McHarness, *Ind. Eng. Chem.*, **31**, 912 (1939).

[4] A. F. Benning and R. C. McHarness, *ibid.*, **32**, 497 (1940).

[5] A. F. Benning, R. C. McHarness, W. H. Markwood, Jr., and W. J. Smith, *ibid.*, **32**, 976, 1074 (1940).

[6] E. Gelles and K. S. Pitzer, THIS JOURNAL, **75**, 5259 (1953).

[7] N. Thorp and R. L. Scott, *J. Phys. Chem.*, **60**, 670, 1441 (1956).

[8] H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, **72**, 3933 (1950).

[9] E. B. Rifkin, E. C. Kerr and H. L. Johnston, *ibid.*, **75**, 785 (1953).