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Thermodynamics of the monohydrogen difluorides
IV. The low-temperature heat capacity of NH_4HF_2 [a]

GLENN A. BURNEY[b] and EDGAR F. WESTRUM, JR.[c]

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

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Adiabatic calorimetric results on NH_4HF_2 show its heat capacity to be of a simple sigmate shape from 5 to 300 K. Values of $C_p(T)$, $S°(T) - S°(0)$, $\{H°(T) - H°(0)\}/T$, and $-\{G°(T) - H°(0)\}/T$ at 298.15 K are 25.50, 27.61, 14.23, and 13.38 $cal_{th}\ K^{-1}\ mol^{-1}$.

1. Introduction

Lighter alkali-metal difluorides at ambient conditions are monoclinic or rhombohedral with distorted NaCl-like structures; the potassium and rubidium compounds are tetragonal with a distorted CsCl-like structure which undergo transformations to cubic NaCl-like phases at elevated temperatures. NH_4HF_2, however, has a structure related to that of its potassium analog but differs inasmuch as the two crystallographically distinguishable anions are distorted (from the symmetrical orientation in KHF_2) by NHF hydrogen bonds and has a resultant orthorhombic space group D_{2h}^7–Pman.[1] Two distinguishable NHF groups are also present. Moreover, infrared studies show that the ammonium ion is maintained immobile in the lattice by hydrogen bonding,[2] by an array of NHF collinear bonds.[1]

This paper provides low-temperature heat capacities from 5 to 300 K, extended elsewhere through melting.[3]

2. Experimental

PREPARATION OF NH_4HF_2

The crystalline salt was precipitated by controlled cooling of an aqueous solution prepared by the addition of reagent ammonium carbonate to 48 mass per cent hydrogen fluoride. Crystals of acicular habit about 1 by 4 mm were washed on a

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[b] Current address: E. I. DuPont de Nemours, Savannah River Laboratory, South Carolina, U.S.A.

[c] To whom correspondence concerning this paper should be addressed.

Büchner-type polyethylene filter, dried in an evacuated Fluorothene vessel protected by a liquid nitrogen trap, and then heated for 24 h at 318 K *in vacuo*. Acidimetric determination of hydrogen ion with standard sodium hydroxide and bromthymol blue[4] in polyethylene beakers yielded (100.0±0.2) per cent of theoretical. Gravimetric determination of fluoride by the lead chlorofluoride method[5] indicated (66.6±0.2) mass per cent (theoretical 66.61 mass per cent).

CRYOSTAT AND CALORIMETER

The Mark I adiabatic liquid-helium cryostat employed in these measurements was similar to one described by Westrum, Hatcher, and Osborne.[6] Calibrated resistors, standard cells, and an autocalibrated White potentiometer were employed for these measurements. Duration of the energy input was determined with a vacuum-jacketed tuning fork calibrated against signals from the National Bureau of Standards station WWV. A platinum resistance thermometer (laboratory designation A-3) calibrated by the National Bureau of Standards against IPTS-48 over the range 10 to 705 K and a provisional temperature scale below 10 K were used. The gold-plated copper calorimeter (laboratory designation W-5) has been described elsewhere.[7] Calorimetric measurements were made on a sample of mass 51.4000 g, the thermometer + heater + calorimeter assembly contributed between 25 and 35 per cent of the total heat capacity measured. A small correction was made for the slight differences in the amounts of helium and Lubriseal stopcock grease for thermal contact used in the loaded and the empty calorimeter. Buoyancy correction was made on the sample on the basis of the crystallographic density of 1.50 g cm^{-3}.

3. Results

The experimental heat-capacity determinations are presented in chronological sequence in table 1 so that the approximate temperature increments employed in the

TABLE 1. Heat capacity of NH_4HF_2(c)
(cal_{th} = 4.184 J)

T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}
5.71	0.010	21.79	0.948	75.75	8.886	186.00	18.07
7.34	0.019	23.85	1.232	83.05	9.733	195.81	18.70
8.91	0.038	26.14	1.577	90.83	10.57	205.77	19.30
10.06	0.070	28.70	1.982	91.01	10.59	215.85	19.91
10.92	0.083	31.55	2.454	98.81	11.30	225.94	20.52
11.84	0.112	34.76	2.991	106.83	12.10	236.05	21.14
12.84	0.154	38.43	3.608	115.12	12.86	246.03	21.81
14.06	0.211	42.45	4.262	123.36	13.56	255.97	22.39
15.27	0.288	46.94	4.972	128.53	13.99	265.81	23.09
16.46	0.378	51.85	5.722	137.95	14.74	275.56	23.79
17.87	0.501	56.99	6.463	147.55	15.48	285.18	24.47
16.70	0.399	55.98	6.316	156.90	16.15	294.59	25.21
18.27	0.541	62.04	7.173	166.41	16.80	303.82	25.97
19.94	0.722	68.46	8.002	176.08	17.43		

measurements can be inferred from the differences of the adjacent mean temperatures. These heat capacities are computed on the basis of an ice point of 273.15 K and a molar mass of 57.048 g mol^{-1} for NH_4HF_2, and have been corrected for curvature (*i.e.* for the finite temperature increments employed in the measurements). The standard deviation of the given values above 40 K is approximately 0.04 per cent and test measurements of the Calorimetry Conference sample of benzoic acid confirm

TABLE 2. Molar thermodynamic functions of NH_4HF_2(c)
(cal_{th} = 4.184 J)

T / K	C_s / cal_{th} K^{-1} mol^{-1}	$S°(T) - S°(0)$ / cal_{th} K^{-1} mol^{-1}	$\{H°(T) - H°(0)\}$ / cal_{th} mol^{-1}	$-\{G°(T)-H°(0)\}/T$ / cal_{th} K^{-1} mol^{-1}
10	0.062	0.021	0.156	0.005
15	0.268	0.078	0.892	0.018
20	0.729	0.212	3.284	0.048
25	1.403	0.443	8.539	0.102
30	2.190	0.768	17.506	0.185
35	3.031	1.168	30.542	0.296
40	3.867	1.628	47.799	0.433
45	4.664	2.130	69.14	0.593
50	5.442	2.662	94.42	0.773
60	6.886	3.783	156.14	1.181
70	8.192	4.945	231.68	1.635
80	9.381	6.117	319.61	2.122
90	10.48	7.287	419.04	2.631
100	11.46	8.443	528.8	3.155
110	12.39	9.579	648.1	3.687
120	13.27	10.695	776.5	4.224
130	14.11	11.791	913.4	4.765
140	14.90	12.866	1058.5	5.305
150	15.66	13.920	1211.3	5.845
160	16.37	14.953	1371.4	6.381
170	17.04	15.966	1538.5	6.916
180	17.69	16.958	1712.1	7.446
190	18.33	17.931	1892.2	7.972
200	18.96	18.888	2078.6	8.495
210	19.56	19.827	2271.2	9.012
220	20.17	20.751	2469.8	9.524
230	20.77	21.661	2674.5	10.033
240	21.39	22.558	2885.3	10.536
250	22.02	23.444	3102.3	11.035
260	22.68	24.320	3325.8	11.529
270	23.36	25.189	3555.9	12.019
280	24.08	26.051	3793.1	12.504
290	24.85	26.910	4037.7	12.987
300	25.65	27.765	4290.2	13.464
298.15	25.50	27.608	4243.1	13.377

the absence of significant systematic error. The heat capacities data show a sigmate curve of the type shown by the other monohydrogen difluorides.[7, 8] No evidence of thermal anomalies was detected.

Thermodynamic properties evaluated both by numerical quadrature and by digital computer are summarized at selected temperature in table 2. These smoothed values are probably reliable to the ± 0.03 per cent standard deviation which characterizes them.

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