Thermodynamics of the monohydrogen difluorides

V. Melting thermodynamics of NH$_4$HF$_2$ [a,b]

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The heat capacity of ammonium hydrogen difluoride was extended from 300 to 450 K by adiabatic calorimetry in order to study the melting phenomenon and provide thermodynamics into the liquid region. The corrected enthalpy of melting at the triple-point temperature, 399.6 K, was found to be (4564 ± 2) cal$_{th}$ mol^{-1} and the corresponding entropy increment is (11.42 ± 0.01) cal$_{th}$ K^{-1} mol^{-1}. Our enthalpy of melting is at variance with a published value (3940 cal$_{th}$ mol^{-1}) derived from cryoscopic measurements and is large compared with the sum of transition and melting enthalpies for the nearly isostructural alkali hydrogen difluorides. Heat capacities in excess of 10^4 cal$_{th}$ K^{-1} mol^{-1} in the essentially isothermal region and significant premonitory thermal effects were observed.

1. Introduction

Enthalpies of melting, ΔH_m, of ionic materials obtained by direct adiabatic calorimetry are scarce and often difficult to determine because of the usually high melting temperatures of ionic compounds. To obtain such data, method of mixtures, enthalpy determinations, and cryoscopic experiments are often employed, and often provide good results, but do not reveal the trend of the heat capacity in the vicinity of the melting temperature. Ammonium hydrogen difluoride (NH$_4$HF$_2$), an ionic compound with a melting temperature in the range of our intermediate thermostat, provided us with the opportunity to test the reliability of the enthalpies of fusion derived from cryoscopic measurements made previously[2–4] and supplement earlier cryogenic data.[5]

Since ΔH_m's of NH$_4$HF$_2$ cited in two papers from the same laboratory[2,3] were at variance with each other (15.68 and 3.94 kcal$_{th}$ mol^{-1}) and with a third (preliminary) cryoscopic value (14.0 kcal$_{th}$ mol^{-1}) from this laboratory,[4] the determination of ΔH_m from the heat-capacity measurements was a desideratum.

Ammonium hydrogen difluoride is structurally similar to KHF$_2$, RbHF$_2$, and CsHF$_2$ in that all have distorted CsCl-like structures at ambient temperatures.[6]

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The alkali metal hydrogen difluorides are tetragonal, however, while NH_4HF_2 is orthorhombic. The structure of NH_4HF_2 is completely determined by hydrogen bonding with the ammonium ion displaced from the normal sites by NHF bonds.

2. Experimental

CALORIMETRIC APPARATUS

Measurements were made in the Mark IV adiabatic thermostat previously described[7] using a silver calorimeter (laboratory designation W-22). Measurements on the 38.46 g calorimetric sample were made to 450 K, approximately 50 K beyond fusion. The heat capacity of the calorimetric sample always exceeded 73 per cent of the total heat capacity. Buoyancy corrections were based on a sample density of 1.50 g cm^{-3} calculated from the lattice parameters of the unit cell (compare table 1). Helium gas (93 Torr at 302 K) was used to enhance thermal contact between the sample and calorimeter.† All measurements of mass, temperature, resistance, potential, and time are referred to calibrations performed at the National Bureau of Standards.

TABLE 1. Structural data for orthorhombic NH_4HF_2

a/nm	b/nm	c/nm	Reference
0.8170	0.8416	0.3676	ASTM 12-302[9]
0.833	0.814	0.368	Hassel and Luzanski[10]
0.8180	0.8426	0.369	Rogers and Helmholtz[11]
0.8175	0.8414	0.368	This research ^{a}

^{a} Guinier, Cu K$_{\alpha 1}$. Calculated from a least-squares fit of 24 indexed lines. The uncertainties (three standard deviations) are considered to be ± 0.0003 nm for all three lattice parameters.

PREPARATION AND CHARACTERIZATION OF THE SAMPLE

The calorimetric sample was prepared by Burney[5] in 1953. Purity determinations at that time were made by acidimetric titration to a bromothymol-blue end-point with sodium hydroxide, and gravimetric analysis for fluoride (as lead chlorofluoride) and nitrogen (Kjedahl method). After the heat capacity was determined from 7 to 300 K,[5] the sample was placed in a screw-capped polyethylene bottle stored in a desiccator.

Further characterization of the sample was done after the heat capacity from 300 to 450 K had been determined, primarily because of the extensive premelting region found in the heat capacity. An X-ray powder diffraction photograph yielded lattice parameters given in table 1 in excellent accord with previous determinations. A potentiometric fluoride titration was done with an Orion lanthanum fluoride membrane electrode with lanthanum nitrate as the titrant. The standardization of the electrode and titration procedure have been described elsewhere.[8] Results of the titration yielded fluoride content of (100.04 ± 0.02) mass per cent of theoretical.

† Throughout this paper Torr = (101.325/760) kPa; cal$_{th}$ = 4.184 J.

TABLE 2. Molar heat capacity of NH$_4$HF$_2$
($cal_{th} = 4.184$ J)

$\dfrac{T}{K}$	$\dfrac{\Delta T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{\Delta T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{\Delta T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$
Series I			399.47	0.075	4930	Series VI		
308.05	10.32	26.61	399.52	0.020	18600	381.99	8.58	34.35
318.24	10.06	27.52	399.54	0.026	14100	ΔH_m Determination B		
328.20	9.86	28.22	399.56	0.013	28400	408.83	8.30	34.00
337.94	9.62	29.13	399.58	0.031	12100			
347.47	9.43	30.10				Series VII		
356.75	9.14	31.10	Series IV			381.62	8.58	34.30
365.77	8.90	32.14	382.47	8.43	34.34	ΔH_m Determination C		
374.57	8.69	33.17	393.09	12.79	148.6	408.72	8.34	33.99
383.14	8.46	34.32	399.50	0.046	8300			
391.32	7.91	37.37	399.52	0.022	17000	Series VIII		
397.12	3.71	91.71	399.52	0.024	15800	372.16	6.93	32.82
			399.55	0.046	8200	380.28	9.31	34.11
Series II			399.58	0.030	12500	391.96	14.05	67.34
366.54	8.58	32.46	399.61	0.016	23900	399.19	0.41	2650
375.05	8.45	33.10	399.63	0.028	13600	399.43	0.066	16400
383.38	8.20	34.37	399.66	0.041	9200	399.48	0.043	25800
391.28	7.62	37.75	401.17	3.00	115.5	399.51	0.013	62200
396.95	3.72	88.54	406.91	8.47	33.99	403.08	7.12	56.32
399.04	0.51	713.1				411.96	10.66	34.04
			Series V			422.55	10.56	34.36
Series III			382.19	8.52	34.43	433.09	10.50	34.60
398.70	0.99	364.2	ΔH_m Determination A			443.53	10.41	34.93
399.28	0.19	1900	417.02	8.23	34.26			
399.40	0.078	4770						

3. Results

HEAT CAPACITY

The experimental heat capacities at the mean temperatures of each determination are listed in chronological order in table 2 and are displayed in figure 1. These results have been adjusted for "curvature" and are considered to have a probable error of less than 0.1 per cent. The values are based upon an ice point of 273.15 K, a molar mass of 57.0433 g mol^{-1} for ammonium hydrogen difluoride, and the IPTS-48.

MELTING

During the course of the heat-capacity measurements, five sets of determinations were made through the melting region (compare table 3).

The interpretation of the lattice contribution to the heat capacity presented a problem over the region 320 to 400 K due to seemingly extensive premelting. The lattice heat-capacity curve used for the calculation of ΔH_m is the dotted line deviating from the experimental curve at 375 K as shown in figure 1. The dashed line in this figure is an alternative estimate of the lattice contribution from a plot of effective θ_D against T. The alternative interpretation based on these values is presented in table 3.

TABLE 3. Enthalpy of melting of NH_4HF_2
($cal_{th} = 4.184$ J)

Designation	Number of determinations	$\dfrac{H(415\ K) - H(375\ K)}{cal_{th}\ mol^{-1}}$	$\dfrac{\Delta H_m}{cal_{th}\ mol^{-1}}$ [a]
Series IV	12	6.099.2 [b]	4563.6
ΔH_m Determination A	1	6101.0	4565.4
ΔH_m Determination B	1	6098.7	4563.1
ΔH_m Determination C	1	6097.6	4562.0
Series VIII	12	6101.3 [b]	4565.7

Mean: 4564 ± 2 [c]

$\Delta S_m = (11.42 \pm 0.01)\ cal_{th}\ K^{-1}\ mol^{-1}$ [c]

[a] A "lattice" enthalpy of 1535.6 $cal_{th}\ mol^{-1}$ over the range 375 to 415 K has been subtracted.
[b] Corrected for drift.
[c] Utilization of an alternative lower "lattice" (dashed) curve of figure 1 (based on Debye θ extrapolations) would involve a "lattice" enthalpy of 3017 $cal_{th}\ mol^{-1}$ over the range 321 to 415 K. The $\Delta H'_m$ and $\Delta S'_m$ including this premonitory region are then (4620 ± 2) $cal_{th}\ mol^{-1}$ and (11.55 ± 0.01) $cal_{th}\ K^{-1}\ mol^{-1}$, respectively.
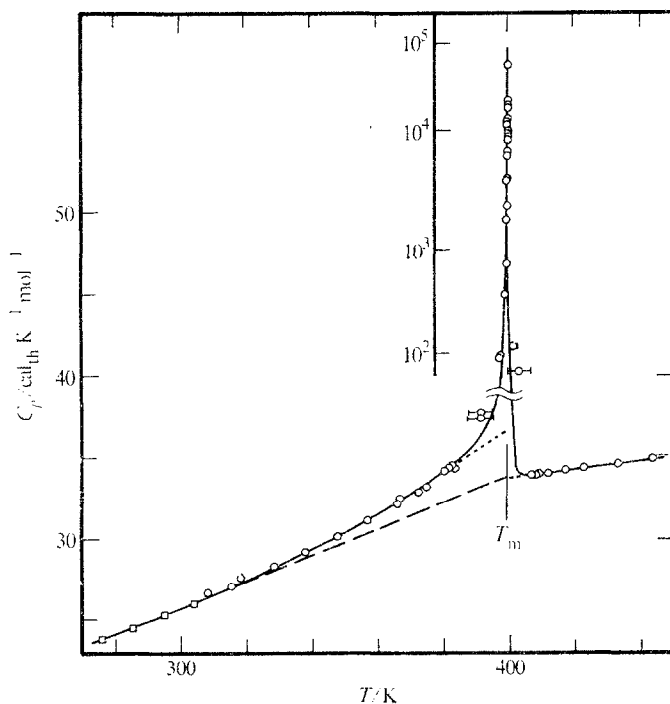

FIGURE 1. Intermediate-temperature heat capacities of NH_4HF_2. ○, Experimental values from this research; □, Burney.[4] See text for explanation of lattice curves.

The amount of solid-insoluble liquid-soluble impurity was estimated from a plot of the observed temperature T_m against the reciprocal of the fraction melted, F. The extrapolated temperature T_1, corresponding to $1/F = 1$, is the triple-point temperature of the calorimetric sample; the temperature corresponding to $1/F = 0$ is the triple-point temperature T_{tp} of the pure sample. The mole fraction x_2 of impurity is given[12] by $x_2 = \Delta H_m(T_{tp} - T_m)/RT_{tp}^2$. Values of T_1, T_{tp}, and x_2, respectively are (399.52 ± 0.02) K, (399.60 ± 0.01) K, and 0.0012.

THERMODYNAMIC FUNCTIONS

The molar thermodynamic functions are listed in table 4 at selected temperatures. The values of the derived thermal properties have been calculated with a high-speed digital computer by integration of a least-squares polynomial fitted through the

TABLE 4. Intermediate-temperature thermodynamic functions of NH$_4$HF$_2$
(cal$_{th}$ = 4.184 J)

$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{\{S°(T) - S°(0)\}}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{\{H°(T) - H°(0)\}}{\text{cal}_{th}\,mol^{-1}}$	$\dfrac{-\{G°(T) - H°(0)\}/T}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
		Crystal		
300 [a]	25.73	27.77	4292	13.466
320	27.51	29.49	4824	14.414
340	29.43	31.21	5393	15.35
360	31.51	32.95	6002	16.28
380	33.80	34.72	6655	17.20
399.6 [b]	(6×10^4)	36.47	7339	18.106
		Liquid		
399.6 [b]	(6×10^4)	47.89	11903	18.106
400	33.61	47.93	11917	18.14
420	34.24	49.58	12596	19.59
440	34.90	51.19	13286	20.99

[a] Based on reference 5.
[b] Assuming the transition to be isothermal.

experimental points. Estimated probable errors in the thermodynamic functions are less than 0.1 per cent. Nuclear spin and isotopic mixing contributions have not been included.

4. Discussion

The disparities in the reported ΔH_m's require discussion, although the earliest reported value[2] of 15.68 kcal$_{th}$ mol^{-1} can be dismissed since the authors provide neither details nor source. The other two[3, 4] were derived from cryoscopic measurements with NH$_4$F adduct by use of the equation $d \ln(\gamma_1 x_1)/d(1/T) = -\Delta H_m/R$ involving the mole fraction x_1 of NH$_4$HF$_2$. Hence, ΔH_m may be deduced from the figure 2 (showing both sets of data to be essentially in accord) provided it is assumed[13] that the activity coefficient γ of NH$_4$HF$_2$ is unity, that no dissociation
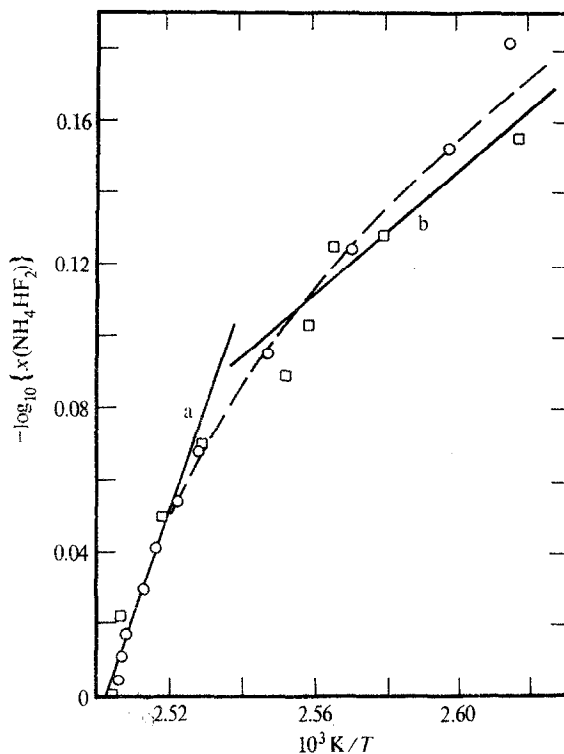
FIGURE 2. Cryoscopic measurements on $NH_4HF_2 + NH_4F$. $\square$, Benjamins;[3] $\bigcirc$, Sudarikov *et al.*[2] The dashed curve represents the combined data. The solid chords are discussed in the text: a, $\Delta H_m = 14$ kcal$_{th}$ mol^{-1}; b, $\Delta H_m = 3.9$ kcal$_{th}$ mol^{-1}.

or association occurs in the melt, and that equilibrium is attained. Benjamins'[4] value of 14 kcal$_{th}$ mol^{-1} corresponds to the limiting slope as $x_1 \rightarrow 1$. Derivation of Sudarikov *et al.*'s[3] value from these data is less certain: ΔH_m may have been deduced from the slope (shown) at large x_2's. The presumed dissociation occurring on fusion precludes acceptance of either value (for reasons cited below); Sudarikov's value appears fortuitous.

Moreover, initial slopes of the plots of $\ln x_i$ against $1/T$ for congruent melting peaks do yield ΔH_m values for $NH_4H_3F_4$ and for NH_4HF_2 in reasonable accord with direct calorimetric determinations (compare table 5). However, a deviation of γ_1 from unity by only 8 per cent at $x_1 = 0.9$ would be required to account for the 14 kcal$_{th}$ mol^{-1} we obtain from the combined data of Benjamins[4] and Sudarikov *et al.*[3] with NH_4F adduct. Further study on the possibility of solid-solution complications on the NH_4F-rich side of the congruent NH_4HF_2 peak and of the species in the melt are obvious desiderata.

For the unusually long range of premonitory excess heat capacity, defect formation is a frequently summoned explanation. For NH_4HF_2 one may postulate that the rupture of NHF hydrogen bonds may well herald onset of reorientation of the NH_4^+

TABLE 5. Comparison of enthalpies of melting of ammonium hydrogen fluorides
($cal_{th} = 4.184$ J)

Compound	Adduct	$\dfrac{\Delta H_m}{kcal_{th}\ mol^{-1}}$	
		cryoscopic	calorimetric [a]
$NH_4H_3F_4$	NH_4HF_2	4.5 [b]	
	$NH_4H_5F_6$	5.7 [b]	4.53 [b]
NH_4HF_2	$NH_4H_3F_4$	3.6 [b]	
	NH_4F	14,[c] 3.9 [d]	4.5 [e]
	KHF_2	4.3 [d]	

[a] On pure substances. [b] Reference 14. [c] Reference 4. [d] Reference 3. [e] This research.

ion or of the FHF⁻ ion and, hence, initiate the trend to a more ionic phase behavior. Proton nuclear magnetic resonance line widths at half height over the range 298 to 423 K on NH_4HF_2 in Teflon-lined tubes taken in a 100 MHz JEOL model JNM-PFT/100 unit are depicted in figure 3. The temperatures were measured using a copper-to-constantan thermocouple calibrated with a standard ethylene glycol sample. The temperatures are reliable to ± 2 K. The narrowing is consistent with this interpretation, and may thus explain the premonitory heat-capacity effect.
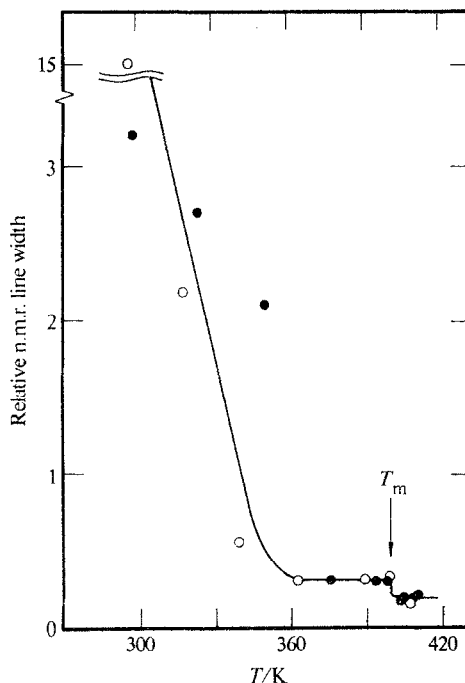

FIGURE 3. Proton nuclear magnetic resonance measurements on NH_4HF_2. The different types of circles indicate distinct series of experiments on different samples.

Utilization of the initial slope of the T against p melting curve of White and Pistorius[15] and our measured ΔH_m in the Clapeyron equation yields a $\Delta V_m = 11.5 \text{ cm}^3 \text{ mol}^{-1}$ for the volume change on melting. This apparent 30 per cent volume increment on melting may indicate, as suggested by these authors (on the basis of other data—as well as on the anomalously high compressibility of the liquid) that liquid NH_4HF_2 may differ significantly from the crystalline phase at 300 K and may be ionic, $i.e.$ without significant interionic hydrogen bonding. The results shown in figures 2 and 3 are consistent with this model.

Our triple-point temperature is seen to be higher than the (397.75 ± 0.3) K melting-temperature of Ruff and Staub[16] but is in good accord with Sudarikov $et\ al.$'s[3] value (399.35 ± 0.2) K, and with the (398.35 ± 1.6) K value of White and Pistorius.[15]

REFERENCES

1. Part IV. Burney, G.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1976**, 8, 21.
2. Sudarikov, B.; Cherkasov, V.; Rakov, E.; Bratishko, V. *Tr. Mosk. Khim.-Tekhnol. Inst.* **1967**, 56, 228.
3. Sudarikov, B.; Cherkasov, V.; Rakov, E.; Bratishko, V. *Tr. Mosk. Khim.-Tekhnol. Inst.* **1968**, 58, 37.
4. Benjamins, E. Ph.D. Thesis, The University of Michigan, Ann Arbor, Michigan. **1953**. cf. *Diss. Abst.* 15, 715, 1955.
5. Burney, G. A. Ph.D. Thesis, The University of Michigan, Ann Arbor, Michigan. **1953**. cf. *Diss. Abst.* 14, 1027, 1954.
6. Landee, C. P.; Westrum, E. F., Jr. To be published.
7. West, E. D.; Westrum, E. F., Jr. In *Experimental Thermodynamics*, Vol. 1, p. 333. McCullough, J. P.; Scott, D. W.; editors. Butterworths: London. **1968**.
8. Lingane, J. *J. Anal. Chem.* **1967**, 39, 881; *Ibid.* **1968**, 40, 935.
9. *Catalog of X-ray Powder Data*, American Society for Testing and Materials, No. 12-302.
10. Hassel, O.; Luzanski, N. *Z. Krist.* **1932**, 83, 448.
11. Rogers, M. T.; Helmholz, L. *J. Amer. Chem. Soc.* **1940**, 62, 1533.
12. Westrum, E. F., Jr.; McCullough, J. P. Thermodynamics of organic crystals. In *Physics and Chemistry of the Organic Solid State*, Vol. 1, p. 32. Fox, D.; Labes, M. M.; Weissberger, A.; editors. Interscience: New York. **1963**.
13. Kelley, K. K. Heats of fusion of inorganic substances. *U.S. Bur. Mines Bull.* 393. **1936**.
14. Euler, R. D.; Westrum, E. F., Jr. *J. Phys. Chem.* **1961**, 65, 1291.
15. White, A. J. C.; Pistorius, C. W. F. T. *J. Solid State Chem.* **1972**, 4, 195.
16. Ruff, O.; Staub, L. *Z. Anorg. Chem.* **1933**, 212, 399.