

Thermodynamics of the monohydrogen difluorides

VI. Heat capacities of RbHF₂ and CsHF₂ from 300 to 530 K, transitions and melting^a

EDGAR F. WESTRUM, JR.,^b C. P. LANDEE,^c Y. TAKAHASHI,^d and MONIQUE CHAVRET^e

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

(Received 19 September 1977; in revised form 6 January 1978)

The heat capacities of RbHF₂ and CsHF₂ were determined from 5 to 533 K, and hence into the molten-salt region by adiabatic calorimetry. The thermodynamics of the transitions were determined. The entropy of transition ΔS_t of the II-to-I transition in RbHF₂ is $(5.59 \pm 0.04) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ and the corresponding entropy of melting ΔS_m is $(2.31 \pm 0.03) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. Both entropy values are comparable to those in the isostructural compound KHF₂. For CsHF₂, ΔS_t (III-to-II), ΔS_t (II-to-I), and ΔS_m are (1.74 ± 0.07) , (2.20 ± 0.08) , and $(1.62 \pm 0.09) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. The occurrence of the II-to-I transition was first reported on the basis of these studies. At 500 K the standard entropies S° are (47.91 ± 0.05) and $(50.63 \pm 0.05) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ for RbHF₂ and CsHF₂.

1. Introduction

The structure and the phase transitions of the alkali-metal hydrogen difluorides have attracted considerable attention from both theorists and experimentalists. Although initially interest was focused mainly on the single-minimum potential-energy curves for the proton in the strong hydrogen bond of the FHF⁻ ion, originally established by thermophysical calorimetry^(2,3) and later confirmed by other techniques,⁽⁴⁻⁷⁾ more recently interest has centered on the structural and ionic orientational disorder of these interesting ionic crystals consisting of spherical cations and cylindrical (linear) anions and the comparison and correlation of their thermophysical properties and phase behavior with those of the azides.⁽⁸⁻¹²⁾ Interest in the nature of the hydrogen bond in alkali and related substances continues unabated.⁽¹³⁻¹⁶⁾

^a Supported initially by Division of Research, U.S. Atomic Energy Commission and subsequently by Chemical Thermodynamics Program, Chemistry Division, National Science Foundation under Contract No. CHE-77-10049. The previous paper in this series is reference 1.

^b To whom correspondence concerning this paper should be directed.

^c Present address: Department of Chemistry, Washington State University, Pullman, Washington 99163, U.S.A.

^d Present address: Department of Nuclear Engineering, University of Tokyo, Hongo, 7-chome, Bunkyo-ku, Tokyo, Japan.

^e Present address: Laboratoire de Chimie Analytique 1, Université Claude Bernard Lyon-1, 43 Boulevard du 11 Novembre 1918, 69621 Villeurbanne, France.

From the isostructural (tetragonal) phases of these alkali difluorides⁽¹⁷⁾ transitions to phases of KHF_2 ,^(3,18) of RbHF_2 ,⁽¹⁹⁾ and of CsHF_2 ^(19,20) stable at higher temperatures are known. The higher-temperature phases of KHF_2 and RbHF_2 are isostructural (NaCl-type); that of CsHF_2 is of the CsCl-type structure.

In the ambient-temperature phases the FHF^- ion is in an ordered array in the plane perpendicular to the tetragonal axis.⁽¹⁷⁾ The work of Kruh *et al.*⁽¹⁹⁾ has shown that in the higher-temperature phases the FHF^- anions are aligned along the cube diagonals for the potassium and rubidium compounds and along the Cartesian axes for the cesium salt. A randomly oriented hydrogen difluoride ion rather than a freely rotating ion is characteristic of the ionic motion in these salts. Unfortunately, extensive thermophysical investigation has been hitherto achieved only on the transition in crystalline KHF_2 .⁽¹⁸⁾

Structural differences between the high-temperature phases of KHF_2 and CsHF_2 introduce differences in the thermodynamic characteristics of transition and melting. Hence, the present study of the phase transitions and melting of RbHF_2 and CsHF_2 by precise heat-capacity measurements clarifies the behavior of the rod-shaped anions at the transitions involved and extends the low-temperature heat-capacity studies presented elsewhere.⁽²¹⁾

2. Experimental

SAMPLE PROVENANCE

The high-purity samples synthesized by Burney and Westrum⁽²¹⁾ for low-temperature calorimetry has been stored in Teflon and were utilized for this study. Full details of the preparation are reported in their paper and purities higher than 99.92 moles per cent are claimed. Fractional melting studies of this investigation are consistent with purities of 99.9 moles per cent if account is taken of the decomposition pressure of hydrogen fluoride.

CALORIMETRIC MEASUREMENTS

All measurements were taken in the silver calorimeter of laboratory designation W-22-o in the Mark IV adiabatic calorimetric thermostat described elsewhere.⁽²²⁾ This apparatus is provided with an electronic shield-control system consisting of three channels of recording circuitry with proportional, rate, and reset modes. These controls maintain the temperature difference between calorimeter and adiabatic shield within 1 mK and reduce heat interchange with the calorimeter to a negligible amount. Platinum resistance thermometer A-5, in the re-entrant well of the calorimeter, was calibrated by the National Bureau of Standards against the IPTS-48. All measurements of mass, time, potential, current, and resistance are referred to standards maintained by the National Bureau of Standards.

The heat capacity of the empty calorimeter was determined separately; its volume is 83.77 cm³. The heat capacities of RbHF_2 and CsHF_2 represented 72 per cent and 76 per cent of the total measured heat capacity of the sample plus calorimeter. Helium gas (7.2 kPa at 300 K) was added to facilitate thermal equilibration.

3. Results

The experimental heat capacities for RbHF₂ and CsHF₂ are presented in table 1 in chronological sequence so that the temperature increments used in the measurements may usually be deduced from the differences in the adjacent (mean) temperatures. These results have been adjusted for curvature, *i.e.* for the difference between $\Delta H/\Delta T$ and the corresponding derivative. The results in the transition and melting regions are presented in figures 1 to 3. Comparisons of enthalpy-type determinations with values obtained by integration of the smoothed curve in both transition and normal heat-capacity regions are shown in tables 2 and 3.

The smoothed heat capacities and the thermodynamic functions derived from them are presented in table 4 at selected temperatures. The smoothed heat capacities were obtained by a digital-computer program and checked by comparison with large-scale plots. The integrations also were performed by digital computer. For the entropies at 298.15 K, the results of Burney and Westrum⁽²¹⁾ were used. The higher-temperature functions have a standard deviation of less than 0.1 per cent. Adjustment

TABLE 1. Experimental heat capacity determinations on RbHF₂ and CsHF₂
(cal_{th} = 4.184 J)

$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹
Cesium hydrogen difluoride (CsHF ₂)							
Series I		448.91	94.7	331.44	3900	320.28	22.58
303.83	21.18	450.08	398.9	331.80	134.6	325.99	23.27
322.80	22.92	450.36	2330	333.72	23.21		
329.40	75.0	450.37	6290	336.84	23.33		
331.44	445	450.39	2240				
336.09	269	450.65	272.9				
345.78	23.77	451.45	123.5	Series VI			
355.86	23.99	452.29	225.4	322.80	22.92		
365.80	24.35	452.75	371.8	$\Delta H_t(\text{III-to-II})$ detn. D			
375.63	24.64	455.08	433.5				
385.36	24.95	455.68	31.17	Series VII			
394.98	25.27	460.86	27.78	320.27	22.56		
405.05	25.59	466.25	27.86	$\Delta H_t(\text{III-to-II})$ detn. E			
415.56	25.90						
423.94	26.33	Series III		Series VIII			
434.06	27.52	431.10	26.81	433.65	27.64		
443.61	35.66	$\Delta H_t(\text{II-to-I})$ detn. A		$\Delta H_t(\text{II-to-I})$ detn. F			
449.19	189.7	ΔH_m detn. B		450.41	901		
450.25	4132			450.53	242		
451.28	197	Series IV		450.84	101.8		
452.76	353	$[\Delta H_t(\text{II-to-I})$		451.40	121.5		
457.95	34.2	+ $\Delta H_m]$ detn. C		451.86	164.2		
468.20	27.75			452.20	216.9		
		Series V		Series IX			
		331.13	165.2	292.96	20.44		
Series II		331.41	5422	298.44	20.87		
428.72	26.84	331.42	19000	303.86	21.21		
441.78	31.11	331.43	13940	309.21	21.53		
446.09	42.18						
						Series XII	
						306.20	21.24
						307.49	21.34
						308.78	21.47
						310.07	21.60
						311.35	21.59
						312.63	21.79

TABLE 1—*continued*

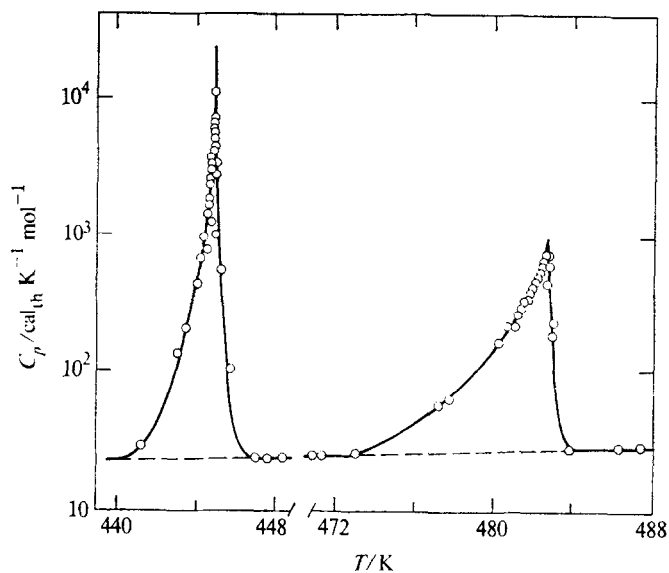
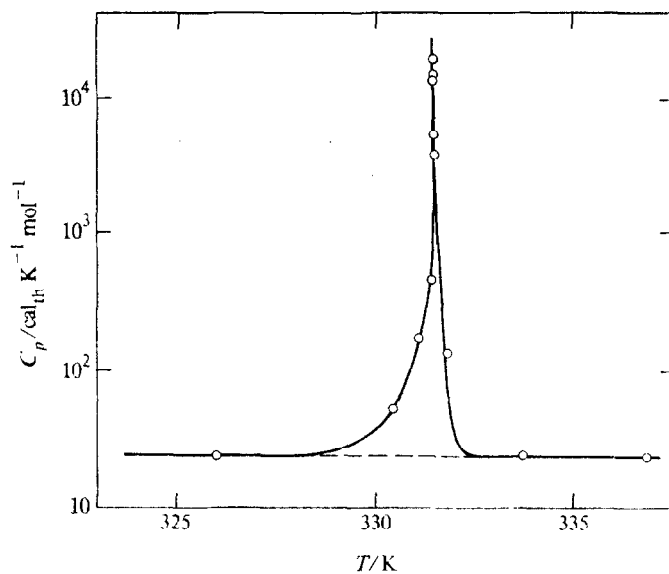
$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal _{th} K ⁻¹ mol ⁻¹
Rubidium hydrogen difluoride (RbHF ₂)							
Series I		397.65	22.23	444.71	3610	522.66	28.71
307.88	19.33	406.85	22.91	448.32	113.4	530.16	28.79
318.30	19.59	415.90	22.99				
328.60	19.86			Series VIII		Series XIII	
338.55	20.10	Series V		415.90	22.99	481.02	214
348.62	20.40	429.90	23.84	392.11	21.82	481.25	271
358.56	20.68	438.21	27.44	398.34	22.20	481.47	324
368.37	20.99	442.99	136.8	401.36	22.40	481.68	334
378.07	21.27	444.12	422	404.33	22.76	481.84	329
398.87	22.37	444.40	823	407.31	23.01	481.99	368
409.22	23.12	444.55	1410	410.28	22.68	482.14	406
419.41	23.24	444.64	1750	413.24	22.71	482.26	451
429.45	24.07	444.71	2430	416.22	23.05	482.38	541
		444.77	3250	419.19	23.18	482.47	600
		444.81	4980			482.56	643
Series II		444.85	4130	Series IX		482.64	719
437.74	26.19	444.88	5364	ΔH_t detn. B		482.72	707
443.50	201.0	444.91	11000	Series X		482.80	591
444.26	633	444.93	4420	ΔH_t detn. C		482.99	186.3
444.43	914	444.96	937	462.15	23.05	483.88	27.79
444.54	1380	444.98	4390	470.91	24.50		
444.63	1650	445.03	2770	477.31	56.70	Series XIV	
444.69	2320	445.74	104.5	480.30	154.6	473.07	24.93
444.75	2270	447.59	22.68	481.57	313	ΔH_m detn. D	
		450.54	22.68	482.28	476	Series XV	
Series III				483.15	229	464.39	23.13
444.76	1211	Series VI		487.48	28.99	471.28	24.89
444.83	2890	394.23	21.98	495.03	28.36	ΔH_m detn. E	
444.87	4320	401.08	22.22			Series XVI	
444.89	5690	404.06	22.56	Series XI		Series XVI	
444.91	6350	407.02	22.78	477.74	61.40	ΔH_m detn. F	
444.93	6680	409.96	22.75	480.75	212	Series XVII	
444.96	5320	412.93	22.76	481.89	368	ΔH_t (II-to-I) detn. G	
444.99	4980	415.88	22.79	482.67	434	445.26	535
445.03	3230	418.83	22.92	486.35	40.07	Series XVIII	
448.32	22.82	421.75	23.16	Series XII		ΔH_t (II-to-I) detn. H	
				492.40	28.19	447.84	23.03
Series IV		Series VII		500.01	28.32	Series XIX	
378.70	21.32	ΔH_t (II-to-I) detn. A		507.60	28.39	ΔH_t (II-to-I) detn. J	
388.25	21.70	444.09	84.6	515.16	28.48		

has not been made for isotope-mixing nor for nuclear-spin contributions to $\{S^\circ(T) - S^\circ(0)\}$ or to $-\{G^\circ(T) - H^\circ(0)\}/T$; hence, these values are practical ones for use in chemical thermodynamic calculations.

4. Discussion

TRANSITION AND MELTING OF RbHF₂

Corresponding RbHF₂ and KHF₂ phases are isostructural and both compounds have phase transitions from the tetragonal structure (phase II) with the space group

FIGURE 1. The heat capacity of RbHF₂ near the II-to-I and melting transitions.FIGURE 2. The heat capacity CsHF₂ near the III-to-II transition.

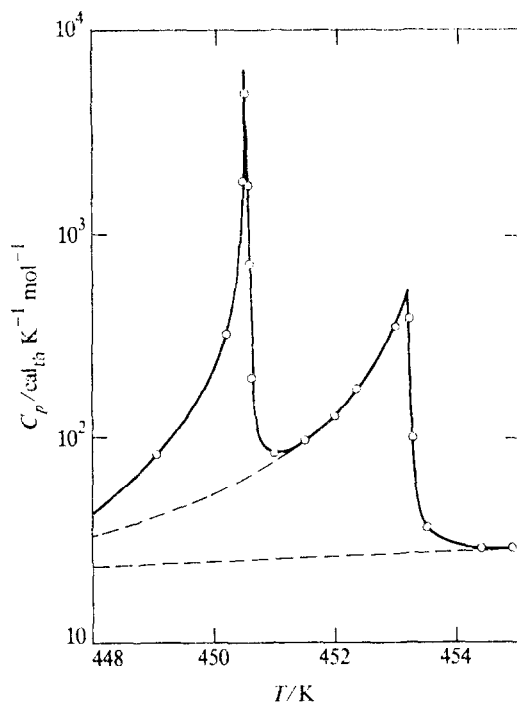


FIGURE 3. The heat capacity of CsHF_2 near the II-to-I and melting transitions.

TABLE 2. Thermodynamics of transition II-to-I and melting of RbHF_2
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

	No. of detns.	T_2 K	T_1 K	$\frac{H^\circ(T_2) - H^\circ(T_1)}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{H^\circ(452 \text{ K}) - H^\circ(420 \text{ K})}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
TRANSITION II-to-I					
Series V	20	451.53	425.51	3103	3249 ^a
Series VII	4	451.82	424.95	3114	3236
Series XVIII	2	449.34	437.66	2740	3228
Series XIX	1	464.83	434.39	3183	3230
Average value $\{H^\circ(452 \text{ K}) - H^\circ(420 \text{ K})\}$: 3232 ± 2					
Lattice contribution $\{H^\circ(452 \text{ K}) - H^\circ(420 \text{ K})\}$: 746 ± 4					
$\Delta H_t(\text{II-to-I})/\text{cal}_{\text{th}} \text{ mol}^{-1} = 2486 \pm 5$					
$\Delta S_t(\text{II-to-I})/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 5.59 \pm 0.4$					
$T_t(\text{II-to-I})/\text{K} = 444.93 \pm 0.03$					

TABLE 2—continued

No. of detns.	T_2 K	T_1 K	$\frac{H^\circ(T_2) - H^\circ(T_1)}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{H^\circ(496 \text{ K}) - H^\circ(460 \text{ K})}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
MELTING ^b				
Series X	8	491.22	457.66	1941
Series XIV	2	491.22	470.54	1634
Series XV	2	490.18	467.05	1692
Average value $\{H^\circ(496 \text{ K}) - H^\circ(460 \text{ K})\}$: 2020 ± 3				
Lattice contribution $\{H^\circ(496 \text{ K}) - H^\circ(460 \text{ K})\}$: 903 ± 4				
$\Delta H_m/\text{cal}_{\text{th}} \text{ mol}^{-1} = 1117 \pm 5$				
$\Delta S_m/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 2.31 \pm 0.03$				
$T_m/\text{K} = 482.67 \pm 0.04$				

^a Rejected from average because of uncertainties in the drift corrections.

^b Melting determinations include "bump" 481.1 to 481.6 K which has 32.4 cal_{th} mol⁻¹ of excess enthalpy.

TABLE 3. Thermodynamics of transitions III-to-II and II-to-I and melting for CsHF₂ (cal_{th} = 4.184 J)

No. of detns.	T_1 K	T_2 K	$\frac{H^\circ(T_2) - H^\circ(T_1)}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{H^\circ(340 \text{ K}) - H^\circ(315 \text{ K})}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
TRANSITION III-to-II				
Series I	4	318.15	340.72	1099.2
Series VI	2	316.76	337.25	1044.8
Series VII	2	316.35	337.12	1051.5
Average value $\{H^\circ(340 \text{ K}) - H^\circ(315 \text{ K})\}$: 1150.6 ± 0.7				
Lattice contribution $\{H^\circ(340 \text{ K}) - H^\circ(315 \text{ K})\}$: 570.3 ± 2				
$\Delta H_t(\text{III-to-II})/\text{cal}_{\text{th}} \text{ mol}^{-1} = 580.3 \pm 2$				
$\Delta S_t(\text{III-to-II})/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 1.74 \pm 0.07$				
$T_t(\text{III-to-II})/\text{K} = 331.42 \pm 0.02$				
No. of detns.	T_1 K	T_2 K	$\frac{H^\circ(T_2) - H^\circ(T_1)}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{H^\circ(470 \text{ K}) - H^\circ(420 \text{ K})}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
TRANSITION II-to-I AND MELTING				
Series I	9	418.77	473.72	3122.3
Series II	15	439.34	468.96	2437.7
Series III	3	428.30	460.45	2509.1
Series IV	3	419.88	460.16	2721.9
Average value $\{H^\circ(470 \text{ K}) - H^\circ(420 \text{ K})\}$: 2995.8 ± 0.3				
Lattice contribution $\{H^\circ(470 \text{ K}) - H^\circ(420 \text{ K})\}$: 1349 ± 4				
$\{\Delta H_t(\text{II-to-I}) + \Delta H_m\}/\text{cal}_{\text{th}} \text{ mol}^{-1} = 1646 \pm 4$				
(TRANSITION II-to-I)				
$\Delta H_t(\text{II-to-I})/\text{cal}_{\text{th}} \text{ mol}^{-1} = 991 \pm 4$				
$\Delta S_t(\text{II-to-I})/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 2.20 \pm 0.08$				
$T_t(\text{II-to-I})/\text{K} = 450.36 \pm 0.02$				
(MELTING)				
$\Delta H_m/\text{cal}_{\text{th}} \text{ mol}^{-1} = 655 \pm 4$				
$\Delta S_m/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 1.62 \pm 0.09$				
$T_m/\text{K} = 453.20 \pm 0.08$				

^a Rejected from average because of magnitude (12 cal_{th} mol⁻¹) of drift corrections.

TABLE 4. Thermodynamic properties of RbHF₂ and CsHF₂
 (cal_{th} = 4.184 J)

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	$S^\circ(T) - S^\circ(0)$ cal _{th} K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(0)$ cal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
Rubidium hydrogen difluoride (RbHF ₂)				
CRYSTAL II				
298.15	19.03	28.70	3932	15.51
300	19.07	28.82	3967	15.59
325	19.65	30.36	4451	16.67
350	20.36	31.85	4951	17.70
375	21.34	33.28	5472	18.69
400	22.35	34.69	6018	19.65
425	23.58	36.08	6590	20.57
444.93 ^a	(11000)	37.16	7060	21.29
CRYSTAL I (Transition II-to-I)				
444.93 ^a	(11000)	42.73	9545	21.29
475	26.47	44.25	10245	22.68
482.67 ^a	(720)	44.60	10415	23.02
LIQUID				
482.67 ^a	(720)	46.91	11531	23.02
500	28.29	47.91	12020	23.87
525	28.75	49.30	12732	25.05
Cesium hydrogen difluoride (CsHF ₂)				
CRYSTAL III				
298.15	20.83	32.30 ^b	4199 ^b	18.22 ^b
300	20.93	32.43	4238	18.30
325	23.08	34.18	4784	19.46
331.42 ^a	(≈ 20000)	34.63	4929	19.76
CRYSTAL II (Transition III-to-II)				
331.42 ^a	(≈ 20000)	36.38	5509	19.76
350	23.85	37.66	5946	20.67
375	24.63	39.31	6552	21.84
400	25.42	40.92	7178	22.97
425	26.32	42.50	7823	24.09
450.36 ^a	(≈ 8000)	44.03	8497	25.16
CRYSTAL I (Transition II-to-I)				
450.36 ^a	(≈ 8000)	46.23	9488	25.16
453.2 ^a	(≈ 600)	46.38	9566	25.27
LIQUID (Melting)				
453.2 ^a	(≈ 600)	48.00	10222	25.27
475	27.91	49.19	10828	26.39
500	28.14	50.63	11529	27.57
525	28.43	51.94	12236	28.63

^a Assuming the transitions involved to be entirely isothermal.

^b These values have been revised on better knowledge of the heat capacity near 300 K but differ from those reported in reference (20) by less than 0.05 per cent.

D_{4h}¹⁸-I 4/mcm stable at 300 K into a NaCl-type cubic structure (phase I), O_h⁵-Fm3m,⁽¹⁹⁾ stable at higher temperatures until melting occurs. For KHF₂ Phase I is a soft translucent wax-like solid at 469.8 K. The entropy increment of 5.69 cal_{th} K⁻¹ mol⁻¹ for the II-to-I transition is nearly twice that of melting.^{(17)†}

The temperatures of transition and melting of RbHF₂ were determined by the present study as $T_i = 444.93$ K and $T_m = 482.67$ K, both of which differ considerably from the values reported by Kruh *et al.*,⁽¹⁹⁾ ($T_i = 449$ K and $T_m = 461$ K, determined by using a polarizing microscope equipped with Kofler hot stage). Prideaux and Webb⁽²³⁾ reported T_m as 477 to 478 K. Very recently, White and Pistorius⁽⁹⁾ found the values of T_i and T_m at atmospheric pressure as (448.2 ± 1) K and (476 ± 1) K, respectively, with a high-pressure d.t.a. apparatus. These discrepancies are probably due in part to the purity of the samples and in part to the methods of determination of the transition and melting temperatures.

Entropies of transition and melting of RbHF₂ (5.59 and 2.31 cal_{th} K⁻¹ mol⁻¹, respectively) are comparable to well known values for KHF₂ (*i.e.* 5.69 and 3.09 cal_{th} K⁻¹ mol⁻¹).⁽¹⁸⁾ The ΔV_i for the transition of RbHF₂ is calculated from the X-ray data⁽¹⁹⁾ as 7.53 cm³ mol⁻¹, which also corresponds with that of KHF₂, calculated as 5.6 cm³ mol⁻¹ from p, V data,⁽¹⁰⁾ 4.2 cm³ mol⁻¹ from X-ray diffraction data,⁽¹⁹⁾ and determined directly by dilatometry as (4.2 ± 0.1) cm³ mol⁻¹ in this laboratory.⁽²⁷⁾ The large entropy and volume increments accompanying the transitions of KHF₂ and RbHF₂ are not easy to explain. Kruh *et al.*⁽¹⁹⁾ suggested that in phase I each hydrogen difluoride ion would randomly occupy positions along the body diagonals of the unit cell. The expected disordering entropy increment would be close to $R \ln 4$ (2.75 cal_{th} K⁻¹ mol⁻¹). The experimental values of entropy increments, 5.69 and 5.59 cal_{th} K⁻¹ mol⁻¹ for KHF₂ and RbHF₂, respectively, are much larger. The large entropy increments are not easily explained but may accompany the structural changes as well as the considerable volume increments which is larger for the former (4.2 cm³ mol⁻¹ for KHF₂,^(19,27) and 3.8 cm³ mol⁻¹ for RbHF₂)⁽¹⁰⁾ as is the ΔS_i . This suggests that phase I has additional degrees of orientational freedom, that the structural change itself is enhancing the transitional entropy, and that other contributions are involved, *e.g.* $(\partial S/\partial V)_T$.

TRANSITION AND MELTING OF CsHF₂

Although it has been known that CsHF₂ has a transition near 330 K,^(19,20) the present investigation shows that, in addition to this first transition at 331.42 K, a second sharp heat-capacity anomaly occurs at 450.36 K only 2.8 K below the melting temperature of 453.2 K. The two heat-capacity anomalies are nearly separate and thus clearly indicate the existence of a second transition, phase II \rightarrow phase I, in CsHF₂.

The lower temperature (III-to-II) transition was first reported by Windsor and Cady⁽²⁰⁾ at 330 K and confirmed by Kruh *et al.*⁽¹⁹⁾ but at 334 K. In an extensive high-temperature X-ray diffraction study, they concluded that phase III of CsHF₂ was isostructural with phase II of KHF₂ and transforms to the CsCl-type, cubic structure with the space group O_h¹-Pm3m.

† Throughout this paper cal_{th} = 4.184 J.

The structural features of the CsHF₂ (III-to-II) transition are very similar to those of univalent azides such as RbN₃, CsN₃, TlN₃, *etc.*,^(11,12) which have linear N₃⁻ anions instead of HF₂⁻ anions. Furthermore, the entropy increment of 1.75 cal_{th} K⁻¹ mol⁻¹ for this CsHF₂ transition as obtained in the present study, is in good accord with the entropy increments of 1.9 and 1.8 cal_{th} K⁻¹ mol⁻¹ reported for RbN₃ and CsN₃.⁽⁹⁾ The small ΔV_t is calculated as 0.59 cm³ mol⁻¹ from the X-ray data and is also comparable to the values for these azides: ΔV_t(RbN₃) = 0.5; ΔV_t(CsN₃) = 0.3 cm³ mol⁻¹.⁽⁸⁾ Thus, taking into account both thermodynamic and X-ray diffraction data, the nature of the III-to-II transition of CsHF₂ can be regarded as essentially the same as that of the transition in these azides. Mueller and Joebstl⁽²⁴⁾ pointed out that the entropy increment at these azide transitions, assuming completely random orientation of the N₃⁻ anions parallel to the edges of the unit cell for the high-temperature phase, is expected to be $R \ln 3$ (2.18 cal_{th} K⁻¹ mol⁻¹).⁽²⁴⁾ Experimental values of ΔS_t would be less than $R \ln 3$ if the length of the linear anion is large enough relative to the unit-cell dimensions to make collinear alignment of two or three ions

TABLE 5. Transition and melting thermodynamics for some alkali dihydrogen fluorides (cal_{th} = 4.184 J)

Substance	Phase change	T_t K	$\frac{\Delta H_t}{\text{cal}_{th} \text{ mol}^{-1}}$	$\frac{\Delta S_t}{\text{cal}_{th} \text{ K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta V_t}{\text{cm}^3 \text{ mol}^{-1}}$
KHF ₂	II-to-I	469.8 ^a	2671 ^a	5.69 ^a	4.2 ^e
		± 0.05	± 14	± 0.06 [5.64] ^b	4.2 ^d
RbHF ₂	II-to-I	444.93	2486	5.59	[3.8] ^e
		± 0.03	± 5	± 0.04 [5.49] ^b	
CsHF ₂	III-to-II	331.42	580.3	1.74	[0.24] ^b
		± 0.02	± 2	± 0.07 [3.10] ^b	[1.0] ^f < 0.59 ^e
CsHF ₂	II-to-I	450.36	991	2.20	[3.2] ^b
		± 0.02	± 4	± 0.08 [2.0] ^b	to [4.9]
Substance	Phase change	T_m K	$\frac{\Delta H_m}{\text{cal}_{th} \text{ mol}^{-1}}$	$\frac{\Delta S_m}{\text{cal}_{th} \text{ K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta V_m}{\text{cm}^3 \text{ mol}^{-1}}$
KHF ₂	melting	511.8 ^a	1582 ^a	3.09 ^a	[0.8] ^f
		± 0.1	± 6	± 0.05 [3.09] ^b	
RbHF ₂	melting	482.67	1117	2.31	[0.96] ^b
		± 0.04	± 5	± 0.03 [2.80] ^b	
CsHF ₂	melting	453.2	665	1.62	[1.9] ^b
		± 0.08	± 4	± 0.09 [1.60] ^b	

^a Reference 18. ^b Values in brackets [], are from high-pressure phase studies summarized in reference 10. ^c Reference 19. ^d Reference 27. ^e At 160 kPa, reference 10. ^f At 220 kPa, reference 10.

HEAT CAPACITIES OF RbHF₂ AND CsHF₂

in adjacent cells improbable for steric reasons—as is also the case for the alkali azides. A calculation of the correlation energy for succino-nitrile has been made by Descamps and Coulon,^(25,26) but the CsHF₂ case has not been evaluated.

Our detection of the II-to-I transition in CsHF₂ near 450 K was subsequently confirmed by White and Pistorius⁽⁹⁾ by d.t.a. They found that this transition occurs at atmospheric pressure, but that at 1.3 MPa and higher pressures only melting was observed. Although their measured T_1 (II-to-I) is lower (447.4 K) and that of melting (459 K) is higher than the present values, other features are essentially the same.

White and Pistorius⁽⁹⁾ estimated the volume change associated with this transition from our ΔS_t and ΔS_m of 2.20 and 1.45 cal_{th} K⁻¹ mol⁻¹, respectively, and the trend of the melting curve with pressure, to be between 3.2 and 4.9 cm³ mol⁻¹. The large ΔS_t and ΔV_t suggest that a part of the increments is due to structural randomness. Many CsCl-type crystals undergo transition into a NaCl-type structure at high temperatures and/or low pressures, with a decrease in coordination from 8- to 6-fold. Direct structural analysis of this phase by high-temperature X-ray diffraction is an obvious desideratum, but the temperature range in which CsHF₂ phase I exists is so narrow the X-ray study will not be convenient. Hence, we assume following the arguments of White and Pistorius⁽¹⁰⁾ based on the large ΔV_t (II-to-I) that phase I of CsHF₂ may have an NaCl-type cubic structure with the space group O_h²-Fm3m, as is characteristic of phase I KHF₂ and RbHF₂.

It will be noticed in table 5 that the calorimetrically determined ΔS_t and ΔS_m values are typically in good accord with the less accurately determined quantities from high-pressure phase-equilibrium studies. Although one finds increasing evidence of interest in the comparisons between the linear anionic orientational disorder and thermophysical parameters in the alkali azides and the hydrogen difluorides^(9,10-12) and in the related thermodynamic characteristics, pressures, and mechanisms of the decomposition processes in the alkali (and alkaline earth) hydrogen difluorides⁽²⁸⁾ much work remains to be done before a comprehensive appreciation of these compounds is achieved.

The authors acknowledge with gratitude the partial financial support of the Division of Research, U.S. Atomic Energy Commission and the continuing support of Chemical Thermodynamics Program, Chemistry Division, National Science Foundation. We appreciate the assistance of Dr Harmas Kiwia with the measurements.

REFERENCES

1. Carling, R. W.; Westrum, E. F., Jr. *J. Chemical Thermodynamics* **1976**, *8*, 269.
2. Westrum, E. F., Jr.; Pitzer, K. S. *J. Am. Chem. Soc.* **1949**, *71*, 1940.
3. Westrum, E. F., Jr.; Pitzer, K. S. *J. Chem. Phys.* **1949**, *15*, 1526.
4. Ketelaar, J. A. A.; Vedder W. *J. Chem. Phys.* **1951**, *19*, 654.
5. Peterson, S. W.; Levy, H. A. *J. Chem. Phys.* **1952**, *20*, 704.
6. Ibers, J. A. *J. Chem. Phys.* **1964**, *40*, 402.
7. Ibers, J. A. *J. Phys. Paris* **1964**, *25*, 474.
8. Pistorius, C. W. F. T. *J. Chem. Phys.* **1969**, *51*, 2604.
9. White, A. J. C.; Pistorius, C. W. F. T. *J. Chem. Phys.* **1972**, *56*, 4318.
10. Pistorius, C. W. F. T. *Prog. Solid State Chem.* **1976**, *11*, 1, 1.
11. Carling, R. W.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1976**, *8*, 565.

12. Carling, R. W.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* in the press.
13. Opalovskii, A. A.; Fedotova, T. D.; Sobolev, E. V.; Grankina, Z. A. *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk* **1968**, 1, 107.
14. Fedotova, T. D.; Opalovskii, A. A.; Gabuda, S. P. *Radiospektrosk. Kvantovokhim. Metody Strukt. Issled.* **1967**, 213.
15. Ruchkin, E. D.; Opalovskii, A. A.; Fedotova, T. D. *Izv. Sib. Otd. Akad. Nauk. SSSR Ser. Khim. Nauk* **1968**, 4, 22.
16. Fedotova, T. D.; Opalovskii, A. A.; Grankina, Z. A.; Sobolev, E. V. *Zhur. Strukt. Khim.* **1967**, 8, 258.
17. Helmholtz, L.; Rogers, M. T. *J. Am. Chem. Soc.* **1939**, 61, 2590.
18. Davis, M. L.; Westrum, E. F., Jr. *J. Phys. Chem.* **1961**, 65, 338.
19. Kruh, R.; Fuwa, K.; McEver, T. E. *J. Am. Chem. Soc.* **1956**, 78, 4256.
20. Winsor, R. V.; Cady, G. H. *J. Am. Chem. Soc.* **1948**, 70, 1500.
21. Burney, G. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1976**, 8, 21.
22. West, E. D.; Westrum, E. F., Jr. In *Experimental Thermodynamics*, Vol. 1. McCullough, J. P.; Scott, D. W.: eds. Butterworths: London. 1968. p. 333.
23. Prideaux, F. B. R.; Webb, K. R. *J. Chem. Soc. London* **1937**, 1.
24. Mueller, H. J.; Joebstl, J. A. *Z. Krist.* **1965**, 121, 385.
25. Descamps, M.; Coulon, G. *Chem. Physics* **1975**, 10, 199.
26. Descamps, M.; Coulon, G. *Chem. Physics* **1977**, 19, 347.
27. Fink, R. W.; Westrum, E. F., Jr. *J. Phys. Chem.* **1956**, 60, 801.
28. Nikolaev, A. V.; Opalovskii, A. A.; Fedorov, V. E.; Fedotova, T. D. *J. Therm. Anal.* **1974**, 6, 461.