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Enthalpies of Fusion of the Alkali Cryolites Determined by Drop Calorimetry

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Enthalpies of the alkali cryolites have been determined in the fusion region with an aneroid, inverse drop calorimeter with adiabatic shields. The values for the enthalpy of fusion are Li_3AlF_6: 21.0 ± 0.3; Na_3AlF_6: 27.1 ± 0.5; K_3AlF_6: 29.3 ± 0.4; Rb_3AlF_6: 31.5 ± 0.8; Cs_3AlF_6: 29.3 ± 0.9 kcal mol^{-1}. Measurements carried out on sodium chloride and sodium fluoride for comparison purposes are also reported.

Investigations of systems connected with the electrolytic production of aluminium have been carried out at the Institute of Inorganic Chemistry, The Technical University of Norway, during a number of years. In the course of these investigations, knowledge of the enthalpies of fusion of the alkali cryolites became of importance. Of these enthalpies of fusion, only the ones for lithium cryolite [1–3] and sodium cryolite [4,5] had then been measured calorimetrically. Values for potassium cryolite had been calculated from phase diagrams.[6,7] Some of the systems chosen for the calculations show extensive solid solubility, and the derived values are therefore rather unreliable. It was therefore decided to determine the enthalpy of fusion of all the alkali cryolites by drop calorimetry. Results of these determinations are presented in this work, together with data obtained for sodium chloride and sodium fluoride for comparison purposes.

EXPERIMENTAL

A. Materials. The sodium cryolite, Na_3AlF_6, was natural, hand-picked crystals from Ivigtut, Greenland. Aluminium trifluoride (AlF_3, technical grade, Riedel de Haën AG, Germany) was purified by repeated sublimations. Clear hexagonal crystals were picked from the samples. Sodium chloride (NaCl, *p.a. fusum* E. Merck AG, Germany), lithium fluoride (LiF, Fisher Certified Reagent, Fisher Scientific Co., USA), sodium fluoride (NaF, sample 1, min. 99 %, Baker & Adamson, USA, sample 2, (used for synthetic Na_3AlF_6) *p.a.*, E. Merck AG, Germany), rubidium fluoride (RbF, min. 99.8 %, Koch-Light Laboratories Ltd., England), cesium fluoride (CsF, sample 1, min. 98 %, The

British Drug House Ltd., England, sample 2, 99.9 %, Koch-Light Laboratories Ltd., England), were all melted in platinum crucibles and clear crystals were selected for use. The alkali cryolites were made by fusing alkali fluoride and aluminium trifluoride in stoichiometric proportions. The compositions were checked by differential thermal analysis (DTA). If the sample was deficient in AlF_3 due to evaporation, more AlF_3 was added, and the process was repeated until no eutectic reaction could be observed by DTA.

All high-temperature work was carried out in an inert atmosphere of 99.99 % nitrogen.

B. Apparatus and method of operation. The determinations were carried out in a previously described[8] apparatus of the inverse drop type, operated with adiabatic shields. The finely crushed samples were loaded into platinum capsules, which were then evacuated inside a glove-box filled with purified nitrogen. After evacuation the capsules were filled with purified argon and the top lid was welded shut. The amount of sample used ranged from 2.9 to 5.3 g, and the mass of the empty platinum capsule was about 12 g.

The calorimetric measurements and calculations were carried out as described in the earlier paper.[8] The reported temperatures are in terms of the International Practical Temperature Scale of 1968. Steady state conditions were usually present after 10–25 min, depending on the sample studied and on the furnace temperature. The calorimeter temperature during the experiments ranged from 300 to 340 K with an estimated mean of 315 K. The heat capacities at 315 K, used in the adjustment of the enthalpies to 298 K, are given in Table 1.

Table 1. C_p values at 315 K.

	C_p/cal mol^{-1}K^{-1}	Reference
NaCl	12.01	JANAF [9]
NaF	11.31	»
Li_3AlF_6	49.05	»
Na_3AlF_6	52.50	»
K_3AlF_6	53.94	»
Rb_3AlF_6	54.9	[a]
Cs_3AlF_6	55.9	[a]

[a] Estimated.

Table 2. Enthalpy increments, experimental and calculated from $H_T - H_{298.15} = a + bT$.

T/K	$H_T - H_{298.15}$/cal mol^{-1} exp.	$H_T - H_{298.15}$/cal mol^{-1} calc.	T/K	$H_T - H_{298.15}$/cal mol^{-1} exp.	$H_T - H_{298.15}$/cal mol^{-1} calc.
		NaF, 3.3413 g; 1 mol $\triangleq$ 41.9882 g			
1195.1	11984	11989	1277.2	19090	–
1212.7	12256	12258	1288.5	21468	21450
1231.7	12556	12555	1296.5	21637	21588
1247.7	12805	12805	1307.6	21674	21772
			1315.6	21844	21905
		NaCl, 3.1698 g; 1 mol $\triangleq$ 58.4428 g			
1002.0	9568	9590	1082.1	16522	–
1028.7	9800	–	1085.4	17426	–
1039.1	10221	10171	1106.3	18005	17953
1049.3	10357	10331	1107.4	17860	17972
1058.4	10419	10474	1135.3	18513	18447
			1136.4	18462	18466

Table 2. Continued.

Li_3AlF_6; 1 mol ≙ 161.7889 g

Sample 1, 3.1566 g

974.7	44290	44364
994.3	45664	45668
1011.9	47046	46838
1035.1	48672	48381
1069.5	72071	71960
1086.1	73632	73491
1098.8	74771	74661
1113.1	76033	75980

Sample 2, 3.8094 g

985.6	44122	–
1017.0	47065	47178
1041.2	48480	48787
1073.2	72056	72301
1092.2	73995	74053
1119.6	76466	76579

Na_3AlF_6; 1 mol ≙ 209.9413 g

Sample 1, natural cryolite, 3.4344 g

1173.1	59616	59528
1184.0	60650	–
1196.8	61837	–
1203.0	61039	–
1216.2	63164	–
1223.1	63825	–
1223.2	63750	–
1234.7	64865	–
1241.5	66012	–
1290.3	95626	94857
1298.0	95296	95588
1303.3	95850	96091
1309.3	97533	–
1310.4	96542	96765
1317.6	97368	97448
1325.2	98516	98169
1329.5	99562	–

Sample 2, natural cryolite, 4.0912 g

1198.6	61821	–
1212.3	63001	–
1226.8	64424	–
1249.4	67010	–
1293.6	95076	95170
1307.4	95684	–
1319.5	97493	97628
1333.1	99137	98919

Sample 3, synthetic cryolite, 3.4140 g

1081.8	53379	53232
1102.7	54911	54673
1122.2	55913	56018
1122.8	55725	56059
1130.3	56560	56577
1139.6	57080	57218
1148.0	57817	57797
1156.2	58028	58362
1167.2	59558	59121
1189.7	61355	–
1214.3	63319	–
1293.3	94788	95142
1295.4	95605	95341
1303.0	95992	96062
1307.7	96295	96509
1308.9	96346	96622
1311.6	96775	96879
1319.2	97795	97600

K_3AlF_6, 3.1380 g; 1 mol ≙ 258.2779 g

1126.2	56608	56763
1145.4	58111	58141
1162.9	59414	59396
1177.1	60481	60415
1190.1	61294	61348
1290.5	98122	98264
1298.7	99042	99034
1305.9	99694	99709
1313.7	100684	100441
1316.6	100719	100713

Rb_3AlF_6; 1 mol ≙ 397.3819 g

Sample 1, 5.2556 g

1053.6	49272	50016
1064.4	50101	50771
1083.2	51327	52086
1095.9	52836	52974
1107.1	54192	53758
1135.0	60784	–

Sample 2, 2.8822 g

1066.7	51178	50932
1084.0	52846	52142
1099.6	54161	53233
1115.8	55812	–
1144.5	60453	–
1203.7	92566	–

Table 2. Continued.

1166.9	65078	–	1223.4	94169	93907
1216.1	93231	93226	1238.7	95421	95336
1224.5	93811	94010	1253.6	96878	96728
1234.4	94778	94935			
1249.4	96186	96335			
		Cs_3AlF_6; 1 mol ≙ 539.6869 g			
Sample 1, 5.3079 g			Sample 2, 5.1218 g		
946.2	43203	43398	952.9	43777	43851
962.9	44229	44528	963.8	44895	44588
974.9	45757	–	974.3	45506	45299
994.2	47660	–	983.1	45874	45894
1013.5	49986	–	993.5	46671	46597
1047.5	56682	–	1103.8	83491	83915
1094.1	83838	83014	1111.9	83868	84668
1108.1	85052	84315	1127.1	85259	86080
1122.8	86228	85680	1143.5	86803	87603
1133.3	87222	86656			
1143.7	86151	–			
1156.6	89088	88820			

RESULTS AND DISCUSSION

The results of the enthalpy measurements are given in Table 2, and plotted in Figs. 1 – 3 together with some literature values. The measured values were fitted to equations of the type

$$H_T - H_{298.15} = a + bT$$

by a least squares treatment. Here b corresponds to the heat capacity, C_p, and is assumed constant over the limited temperature range in question.

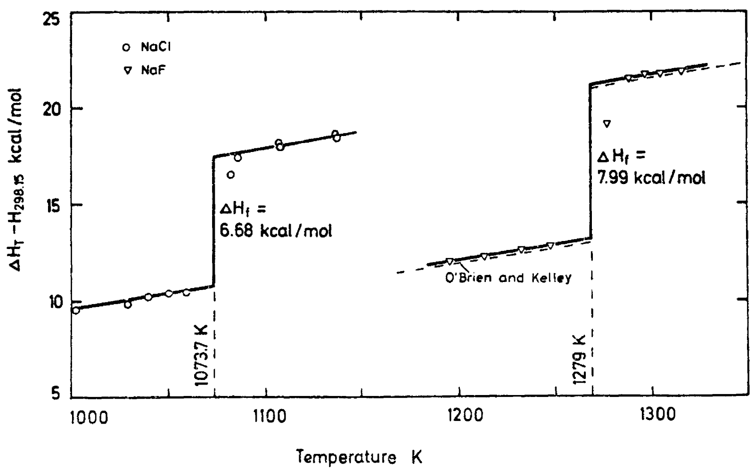

Fig. 1. The enthalpy and enthalpy of fusion of NaCl and NaF, ○ NaCl; ▽ NaF.

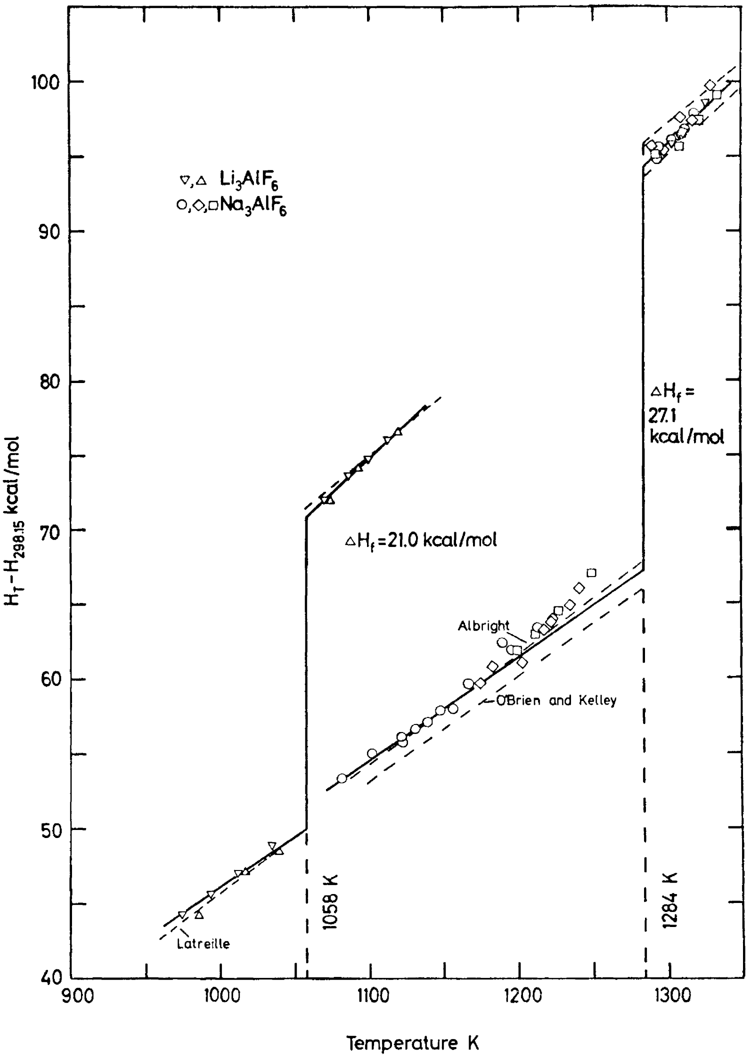

Fig. 2. The enthalpy and enthalpy of fusion of Li_3AlF_6 and Na_3AlF_6. ▽ Li_3AlF_6, sample 1; △ Li_3AlF_6, sample 2; ◇ Na_3AlF_6, sample 1, natural cryolite; □ Na_3AlF_6, sample 2, natural cryolite; ○ Na_3AlF_6, sample 3, synthetic cryolite.

Values which gave unreasonable C_p values were not included in the calculations of the straight lines. As is clearly seen from Figs. 2 – 3, the alkali cryolites exhibit a strong tendency to pre-melting. The exception seems to be Li_3AlF_6, which did not show deviations from the straight line up to 1040 K (melting point 1058 K). Na_3AlF_6 followed the straight line only up to 1170 K (melting point 1284 K), in very good agreement with the observations of

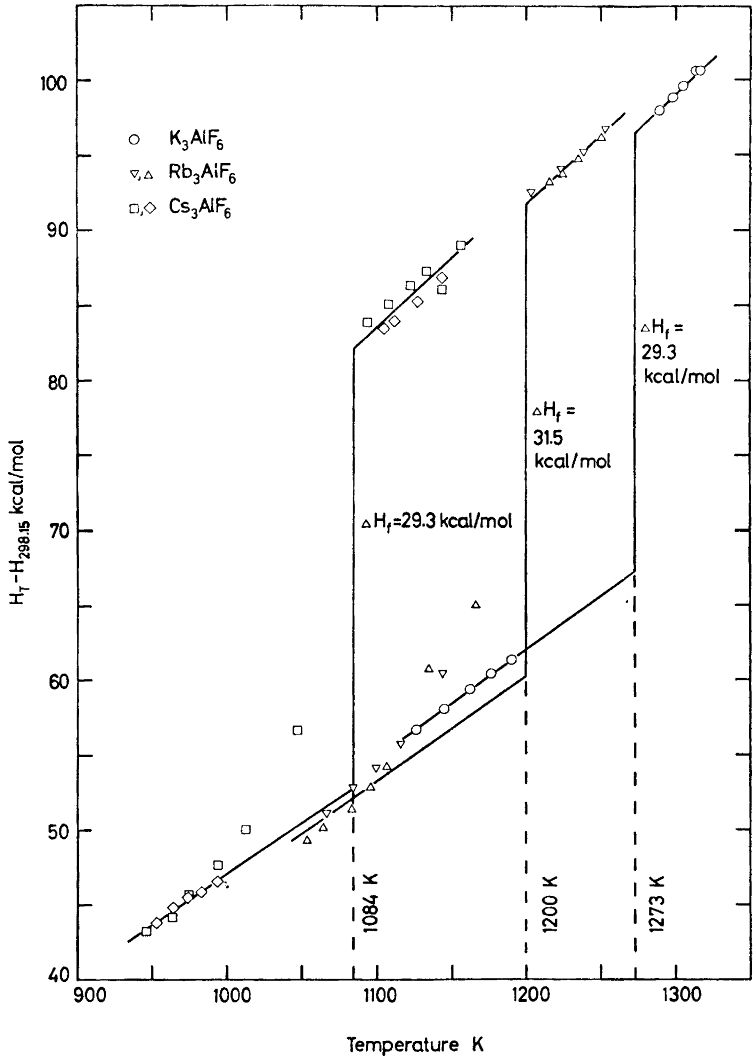

Fig. 3. The enthalpy and enthalpy of fusion of K_3AlF_6, Rb_3AlF_6, and Cs_3AlF_6. ○ K_3AlF_6; △ Rb_3AlF_6; sample 1; ▽ Rb_3AlF_6, sample 2; □ Cs_3AlF_6, sample 1; ◇ Cs_3AlF_6, sample 2.

Albright.[4] For this compound measurements were made on samples of both the natural mineral and of synthetic Na_3AlF_6, made from NaF and AlF_3. Within the experimental errors, no systematic differences could be detected between the results for the various samples. The enthalpy of K_3AlF_6 was not measured between 1190 K and 1290 K (melting point 1273 K). No pre-melting effects were observed below 1190 K, but DTA investigations [10] indicate that pre-melting does indeed take place in K_3AlF_6. The results for Rb_3AlF_6 and

Cs_3AlF_6 indicate pre-melting from approximately 1110 K and 990 K, respectively (melting points 1200 K and 1084 K). The constants in the enthalpy equations for the various compounds, and the temperature range in which the measurements were made, are given in Table 3.

Table 3. The constants in the equation $H_T - H_{298.15} = a + bT$.

Compound	Solid phase			Liquid phase		
	Temperature range T/K	a cal mol^{-1}	$b = C_p$ cal mol$^{-1}K^{-1}$	Temperature range T/K	a cal mol^{-1}	$b = C_p$ cal mol$^{-1}K^{-1}$
NaF	1180 – 1260	– 6694	15.63	1280 – 1330	57	16.61
NaCl	990 – 1070	– 6123	15.68	1080 – 1150	– 870	17.02
Li_3AlF_6	960 – 1050	– 20462	66.51	1065 – 1130	– 26645	92.20
Na_3AlF_6	1070 – 1175	– 21661	68.95	1290 – 1340	– 27605	94.91
K_3AlF_6	1120 – 1200	– 24030	71.74	1280 – 1330	– 22842	93.84
Rb_3AlF_6	1045 – 1100	– 23671	69.94	1205 – 1260	– 20334	93.38
Cs_3AlF_6	935 – 995	– 20598	67.64	1090 – 1170	– 18622	92.90

The enthalpy equations were extrapolated to the melting point, and the enthalpy of fusion was calculated. In cases were pre-melting occurs, this extrapolation was done from below the pre-melting region. The enthalpies of fusion are given in Table 4, together with literature values. The melting points were determined by thermal analysis or by DTA.[10]

Table 4. Enthalpies and entropies of fusion.

	Melting point T/K	ΔH_f/kcal mol^{-1}			ΔS_f cal mol^{-1}K^{-1} this work
		This work	Other calorimetric work	Calculated from phase diagrams	
NaF	1269	7.99 ± 0.05	8.03 [5]		6.22
NaCl	1073.7	6.68 ± 0.14	6.69,[11] 6.76 [12]		6.30
Li_3AlF_6	1058	21.0 ± 0.3	20.2,[1] 21.5 [2-3]	20.7,[6,13] 21.1,[14] 22.0,[2-3] (24.5 [7])[a]	19.8
Na_3AlF_6	1284	27.1 ± 0.5	27.91,[4] 27.64 [5]	27.4 [6]	21.1
K_3AlF_6	1273	29.3 ± 0.4		27.6 [6] (44.4 – 44.7 [7])[a]	23.0
Rb_3AlF_6	1290	31.5 ± 0.8			26.2
Cs_3AlF_6	1084	29.3 ± 0.9			27.0

[a] From phase diagrams with solid solubility.

As can be seen from Fig. 1 and Table 4 the agreement between our results for NaCl and those reported in earlier work [11,12] is very good. Dworkin and Bredig [11] do not give the actual enthalpies or the heat capacities, only the enthalpy of fusion, while the results of Dawson *et al.* are practically coinciding with ours. The agreement between the results from this work and those of O'Brien and Kelley [5] for NaF and Na_3AlF_6 is also satisfactory. The heat capacity values reported for Li_3AlF_6 by Latreille [2] and for Na_3AlF_6 by Albright [4] are, however, somewhat different from those found in this work, while their enthalpy of fusion values are in fairly good agreement with ours. On the basis of comparing the heat capacities for all the alkali cryolites, and also taking into consideration the heat capacities of the alkali fluorides (JANAF [9]) and of AlF_3 (Douglas and Ditmars [15]), we judge our heat capacity values to be more accurate than those obtained earlier.

In Table 4 are also included the entropies of fusion of the alkali cryolites, $\Delta S_f = \Delta H_f / T_f$. These entropies can be seen to increase with increasing size of the alkali ion. Except for Rb_3AlF_6, a plot of $\Delta S_f(Me_3AlF_6)$ *versus* r_{Me^+} or $r_{Me^+}^2$ (Me = Li, Na, K, Rb, Cs) gives a smooth curve (Fig. 4).

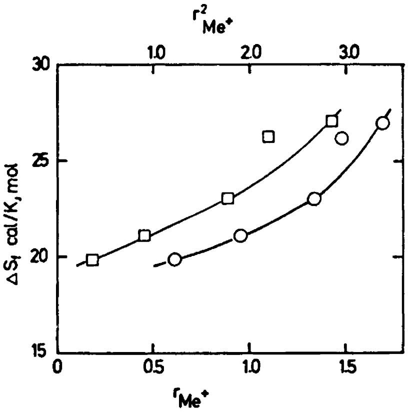

Fig. 4. The entropy of fusion of the alkal cryolites, *versus* the size of the alkali ion ○ ΔS_f *vs.* r_{Me^+}; □ ΔS_f *vs.* $r_{Me^+}^2$.

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