Thermochimica Acta, 6 (1973) 375–398

PHASE RELATIONS AND THERMODYNAMIC PROPERTIES IN THE TERNARY RECIPROCAL SYSTEM $LiF–NaF–Na_3AlF_6–Li_3AlF_6$

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(Received 13 January 1973)

ABSTRACT

The ternary reciprocal system $LiF–NaF–Na_3AlF_6–Li_3AlF_6$ has been investigated by thermal analysis, differential thermal analysis, quenching, X-ray diffraction, microscopy, and calorimetry. The phase diagrams of the following systems are given: LiF–NaF (revised), $LiF–AlF_3$, $Na_3AlF_6–LiF$, and $LiF–NaF–Na_3AlF_6–Li_3AlF_6$. Some values of heat of mixing and heat content in the system have been measured.

It is shown that molten mixtures in this system can be treated as consisting of the following species: Li^+, Na^+, AlF_6^{3-}, AlF_3, and F^-. At high contents of alkali fluoride the dissociation of the AlF_6^{3-} ion to AlF_3 and F^- will, however, be negligible.

On the basis of the calorimetric data, heats of mixing and dissociation, together with the degree of dissociation of AlF_6^{3-}, in the systems $LiF–AlF_3$ and $LiF–Na_3AlF_6$ have been calculated. The partial Gibbs free energy, enthalpy and entropy of Na_3AlF_6 in the system $LiF–Na_3AlF_6$ have also been calculated. Finally the activity of Na_3AlF_6 in the latter system has been calculated by treating it as a part of the ternary reciprocal system

$$3LiF + Na_3AlF_6 \rightarrow Li_3AlF_6 + 3NaF$$

A satisfactory agreement between the Flood, Førland and Grjotheim theory and the experimental values is obtained at small Na_3AlF_6 concentrations.

INTRODUCTION

In this paper the thermodynamic properties of melts within the system $NaF–LiF–Li_3AlF_6–Na_3AlF_3$ will be considered. This system, besides being a part of the ternary *additive* system $LiF–NaF–AlF_3$, can also be treated as a ternary *reciprocal* system according to

$$3LiF + Na_3AlF_6 \rightarrow Li_3AlF_6 + 3NaF.$$

As shown by several authors, however, the cryolite anion is partly dissociated. Holm[1] concluded from enthalpy of mixing data in the system $NaF–AlF_3$ that in sodium fluoride-rich melts cryolite is dissociated according to

$$Na_3AlF_6(l) = 3NaF(l) + \text{“}AlF_3\text{”}(l)$$

where "AlF_3" denotes solvated AlF_3, $AlF_6^{3-} = (AlF_3)3F^-$, and not as often thought

$$Na_3AlF_6(l) = 2NaF(l) + NaAlF_4(l)$$

This is shown by the fact that the equilibrium

$$Na_3AlF_6(l) + 2AlF_3(l) = 3\text{"}NaAlF_4\text{"}(l)$$

is shifted to the left, $\Delta H_{1273} = +12$ kcal. This has now been verified by some new calorimetric data[2,3] in the system NaF–AlF_3.

Molten mixtures within the system LiF–Na_3AlF_6 would therefore consist of the following ions or species: Li^+, Na^+, AlF_6^{3-}, "AlF_3", and F^-. This makes the theoretical treatment more complicated. However, as shown by calculations in the NaF–Na_3AlF_6 system[1,3], the degree of dissociation of AlF_6^{3-} is small at high contents of alkali fluoride. For instance, at temperatures of about 1000°C and concentrations smaller than 10 mol% Na_3AlF_6, the dissociation reaction

$$AlF_6^{3-} = \text{"}AlF_3\text{"} + 3F^-$$

will be shifted strongly to the left ($\alpha = 0.06$ at $N_0 = 0.10$). Thus it may be justified to treat molten mixtures at these concentrations as ternary reciprocal mixtures consisting of Li^+, Na^+, F^-, and AlF_6^{3-} ions. In the theoretical treatment of the cryolite-rich mixtures, however, one also has to consider the dissociation of the AlF_6^{3-} complex.

In the first part of this paper a description of equipment, methods and techniques, which have been used by the present authors in studies of the complicated phase equilibria in the ternary reciprocal system will be given.

EXPERIMENTAL

Chemicals

Na_3AlF_6, sodium cryolite, was hand-picked, natural cryolite from Ivigtut, Greenland, of the type described previously[1,2]. LiF, lithium fluoride, reagent grade (Fisher Scientific Co., U.S.A.) and NaF, sodium fluoride, reagent grade (Merck, Germany) were dried in a vacuum furnace at 400°C before use. Lithium fluoride for calorimetric work was melted, and clear crystals were selected from the samples. AlF_3, aluminium fluoride, anhydrous (MacKay, U.S.A.) was sublimated twice in a vacuum furnace at 910°C. The method used has been described by Henry and Dreisbach[4]. For the preparation of Li_3AlF_6, stoichiometric amounts of LiF and AlF_3 were melted together in a platinum crucible in a purified nitrogen atmosphere.

Thermal analysis

A graphite crucible, 55 mm in diameter and 120 mm high, containing 40–100 g melt, was placed inside a "thermal gradient free" standard type furnace[5]. The temperature was recorded by a Pt/Pt10%Rh thermocouple calibrated at the melting points of silver, 960.5°C, and NaCl, 800.5°C.

The e.m.f. of the thermocouple was determined with a precision potentiometer (Tinsley and Co., Ltd.) in connection with a mirror galvanometer (Multiflex Galvanometer, Dr. B. Lange, Berlin, Germany). Supercooling of the melt was prevented by stirring and by seeding with small cryolite or alkali fluoride crystals. The uncertainty in determining temperature by this method is ±0.2°C. However, due to supercooling effects the uncertainty in some experiments could be as large as ±0.5°C. The equipment has been described in more detail in a previous paper[6].

Differential thermal analysis (DTA)

The arrangement for DTA has been described in detail elsewhere[7]. The sample and reference material are in platinum crucibles mounted symmetrically in a nickel block. The block is covered by a nickel lid with two bores for the differential thermocouple. Both the block and the lid are grounded. The differential temperature was measured with a Pt/Pt10%Rh/Pt thermocouple. The two junctions were immersed directly into the sample and the reference to obtain the highest sensitivity and no time delay in the reaction. The actual temperature was measured with a Pt/Pt10%Rh thermocouple placed in a bore in the nickel block, symmetrically with respect to the crucibles. The thermocouples were protected from contact with the block and lid by alumina tubes.

The nickel block is mounted in a vertical Kanthal-wired laboratory furnace. The inner tube of the furnace has a diameter of 50 mm, and is 45 cm long.

The DTA curves were recorded either by an XY recorder (Speedomax G, Leeds & Northrup, U.S.A.) or by a Varian G 2022 Dual Channel Recorder. In both cases the differential signal was amplified by use of a d.c. Microvolt Amplifier, range 50–2000 μV (Leeds & Northrup, U.S.A.). When the XY recorder was used, the exact reaction temperatures were measured with a potentiometer, with an accuracy of ±1 degree. With the dual channel recorder the reaction temperatures were read directly from the curves with the same accuracy, ±1 degree.

The sample size was 1.5–2 g. The reference material used was fired Al_2O_3. The heating rate was 7–8°C/min and the cooling rate 3.5–5.4°C/min. Highly purified nitrogen (99.99% N_2, Norsk Hydro, Norway) was passed through the furnace during experiments.

Quenching

Samples for quenching were powdered and placed in platinum capsules. After equilibration under inert atmosphere in a laboratory furnace, the samples were quenched by dropping into kerosene oil. The quenched samples were examined by X-ray powder diffraction and by microscopy.

X-ray equipment

The X-ray diffraction experiments were carried out in a metal ribbon furnace, similar to the type described by Smith[8]. The combined sample holder and heating element was a flat strip made from platinum–10% rhodium. The temperature was recorded with a Pt/Pt10%Rh thermocouple welded to the strip, and was constant within ±1 °C with time. Calibration at the transition point of Na_3AlF_6 ($\alpha \rightarrow \beta$) at 560 °C showed the recorded temperature to be correct to within ±5 °C. The radiation used was nickel-filtered Cu K_α, and the X-ray diagrams were recorded by a Philips diffractometer (basic unit, PW 1353/00).

Calorimetry

Enthalpy of mixing and enthalpy of solution

This part of the investigations was carried out at the James Franck Institute, The University of Chicago. The calorimetric experiments were performed in a single-unit micro-calorimeter. This has been described in detail elsewhere[1,2,9]. The temperature-sensing element of the unit is a thermopile which consists of 54 Pt/Pt13%Rh thermocouples connected in series. The temperature of the calorimeter is measured with reference to the inside wall of a heavy cylindrical Nichrome jacket which completely surrounds the calorimeter assembly, except for a 1-in.-diameter entrance "port". The output of this thermopile is amplified by means of a Leeds and Northrup amplifier and recorded by means of a Leeds and Northrup Recorder, type H-Azar. The furnace assembly which surrounds the calorimeter consists of a cylindrical main heater in the middle and two separately wired heaters, one at the top and one at the bottom. The experimental arrangements inside the calorimeter were the same as described previously[1,2,9]. The temperature during the experiments was 1287±1 K.

The calorimeter was calibrated by the "platinum drop method", *i.e.*, by means of the heat effect associated with dropping pieces of 2-mm-diameter platinum wire into the calorimeter from room temperature. This heat effect was calculated from the heat-content equation given by Kelley[10]. During its fall into the calorimeter, the platinum wire picks up some heat, largely by radiative heat transfer. The magnitude of this effect was determined in separate experiments by carrying out calibrations with platinum wires of different diameters. Extrapolation to zero area showed that this pickup for 2 mm wires represents 1.3% of the heat content at 800 °C, and 3.9% at 1000 °C. A correction of 4% was used in the present work at 1014 °C.

Drop calorimetry

This part of the investigations was carried out at the Institute of Chemistry, The University of Oslo. Two samples of each of the compounds were loaded into platinum containers of known mass. The containers were evacuated carefully inside a glove box to get rid of the air. The glove box was filled with purified nitrogen. After evacuation, the containers were filled with purified argon. They were then sealed by arc-welding a cup-shaped platinum lid to the rim of the container.

The sample was equilibrated in a vertical laboratory furnace and lifted into the silver calorimeter, which was placed above the furnace. The calorimeter was surrounded by silver shields, electrically heated to maintain quasi-adiabatic conditions. The furnace temperature was measured by a Pt/Pt10%Rh thermocouple and the calorimeter temperature by a quartz thermometer.

The calorimeter proper, the calibration of the calorimeter and the method of calculating the enthalpy increments $H_T - H_{298\cdot15}$ have been described in detail by Grønvold[11]. Steady state conditions were usually obtained after 10–20 minutes, depending on the furnace temperature. The calorimeter temperature during the period of experiments ranged from 298 to 330 K with a mean of 315 K. The heat capacity values at 315 K, which were used for adjusting the enthalpies to 298 K, are listed in Table 1.

TABLE 1

VALUES OF THE HEAT CAPACITY AT 315 K (JANAF[12]) (1 cal$_{th}$ = 4.184 J)

Compound	C_p *(cal$_{th}$ K^{-1} mol^{-1})*
LiF	10.19
AlF_3	18.43
Li_3AlF_6	49.05

RESULTS

Phase studies

The system LiF-NaF

The phase diagram of this system, which is given in Fig. 1, was determined by thermal analysis. The observed eutectic point in the system is at 39 mol% NaF and 649 °C, which is in good agreement with the data reported by Bergman and Dergunov[13]. In an earlier study of the system by Holm[14] a solid solution of about 5 mol% LiF in NaF at the eutectic temperature was established. New examinations confirm this, but the solid solubility seems to be somewhat larger, namely somewhere between 7 and 9 mol% LiF. Theoretical calculations confirm this new limit of crystalline solubility. These new results are also in better agreement with the results obtained by Short and Roy[15], who found that 8 ± 1 mol% LiF was present in solid NaF at 625 °C.

The system LiF–AlF_3

The phase diagram of the system LiF–AlF_3 has been determined by DTA and TA. The obtained liquidus and solidus temperatures in the system are given in Table 2 and the phase diagram of the system is presented in Fig. 2. The compound Li_3AlF_6 melts at 785 °C, and the two eutectics are at 14.5 mol% AlF_3, 710 °C and 35.5 mol% AlF_3, 709 °C. This is in good agreement with other works, as can be seen from Table 3. There was no indication that $LiAlF_4$ is stable in the solid phase, although this compound is known to exist in the gas phase[25–28]. There was no sign of solid solubility in the system. In most of the runs on the LiF side of the system, the temperature curve was not recorded below the eutectic temperature.

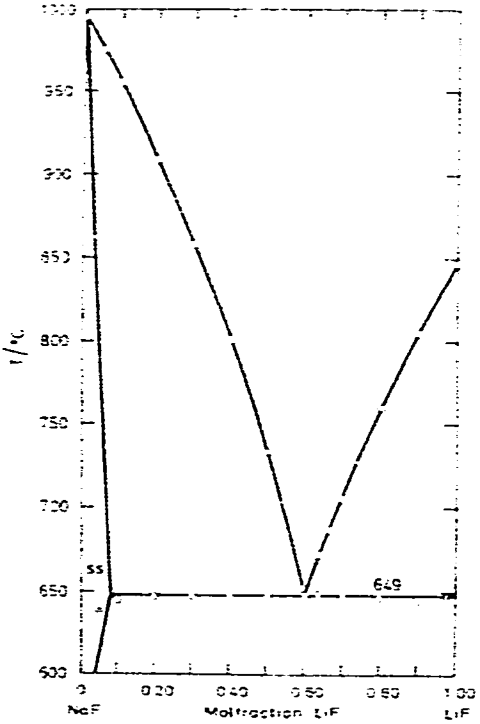

Fig. 1. The phase diagram of the system NaF–LiF, from Holm[14], and revised.

TABLE 2
THE SYSTEM $LiF-AlF_3$

Temperatures (in °C) obtained by Differential Thermal Analysis: T_1 = melting temperature, T_2 = eutectic temperature, T_3 = phase transition γ-$Li_3AlF_6 \rightarrow \delta$-$Li_3AlF_6$ (cf. Holm and Jenssen[16]), T_4 = phase transition β-$Li_3AlF_6 \rightarrow \gamma$-$Li_3AlF_6$ (cf. Holm and Jenssen[16]), T_5 = phase transition α-$AlF_3 \rightarrow \beta$-AlF_3, and T_{max} = maximum temperature during experiment.

Mol fraction AlF_3	T_1	T_2	T_3^a	T_4^a	T_5	T_{max}
0.00	848					
0.0377	832	711				
0.0832	798	710				
0.1289	739	711				
0.1700	730	709				
0.1981	763	709				
0.2282	775	710	597	505		
0.2500	785^a		597	510		
0.2770	773^a	706	597	511		
0.3244	724^a	705	597	512		
0.3657	718^a	708	600	514		
0.4309	(815)	709	604	517	452	980
0.4660	(900)	711	608	513	454	1030
0.5000	(975)	710	598	511	454	1035
0.5057	(975)	710	607		450	1065

[a] Temperatures taken from heating curve.

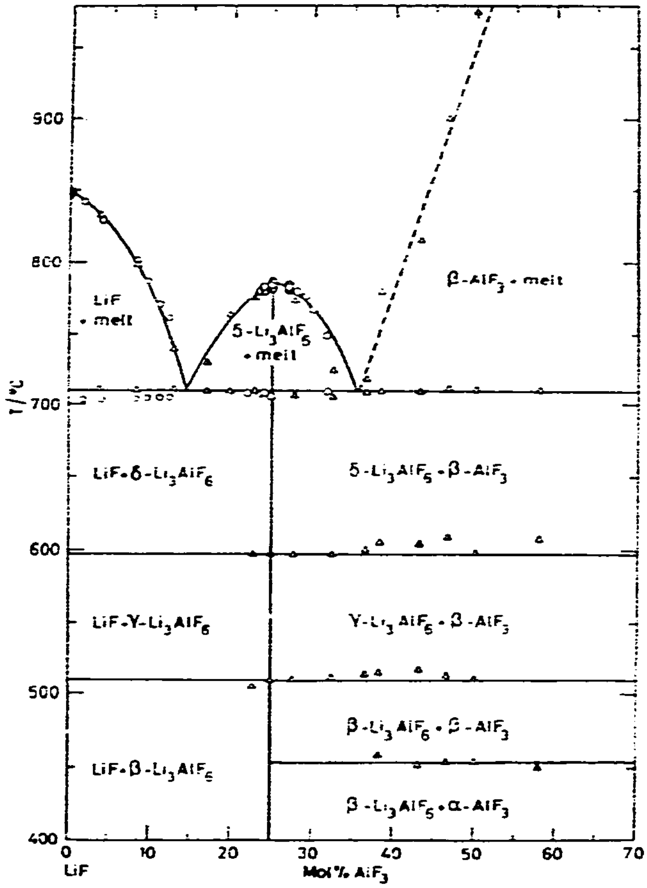

Fig. 2. The phase diagram of the system LiF–AlF$_3$, from this work. ○, points obtained by thermal analysis; △, points obtained by DTA.

TABLE 3

SURVEY OF STUDIES ON INVARIANT POINTS AND MELTING POINTS OF THE COMPOUND Li$_3$AlF$_6$ IN THE SYSTEM LiF–AlF$_3$

Congruent melting		*Eutectic*		*Congruent melting*		*Eutectic*		*Ref.*
Mol% AlF$_3$	*T (°C)*	*Mol% AlF$_3$*	*T (°C)*	*Mol% AlF$_3$*	*T (°C)*	*Mol% AlF$_3$*	*T (°C)*	
0	870	14.5	705	25.0	800	37	690	[a]
0	860	15	715	25.0	790	36	710	[b]
0	845	16.5	706	25.0	792			[c]
				25.0	783	35.5	711	[d]
0	848	14.5	711	25.0	785	36.0	710	[e]
0	847	15	711	25.0	782	35	708	[f]
0	847	15.5	711	25.0	782			[g]
0	848	14.5	710	25.0	785	35.5	709	[h]

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[a] Puschin and Baskow[17]. [b] Fedotieff and Timofeeff[28]. [c] Dergunov[19]. [d] Rolin and Muhlethaler[20]. [e] Thoma et al.[21]. [f] Malinovsky et al.[22]. [g] Rolin, Latreille and Pham[23,24]. [h] this work.

The system Na_3AlF_6–Li_3AlF_6

The results of the phase examinations in this system have been published recently[29]. The phase diagram was established from very extensive phase examinations using DTA, low- and high-temperature X-ray examinations, microscopy, and equilibration and quenching techniques.

Two intermediate compounds, corresponding to Na_2LiAlF_6 and $Na_3Li_3Al_2F_{12}$ were found, the latter identical with the cubic mineral cryolithionite. Na_2LiAlF_6 was found to be monoclinic at room temperature. On heating, the monoclinic α-Na_2LiAlF_6 modification changes to cubic β-Na_2LiAlF_6.

TABLE 4

THE SYSTEM Na_3AlF_6–LiF

Temperatures (°C) obtained by TA and DTA: T_1 = melting temperature, T_2 = second thermal arrest, T_3 = third thermal arrest, T_4 = fourth thermal arrest, and T_5 = fifth thermal arrest.

Mol fraction Na_3AlF_6	T_1	T_2	T_3	T_4	T_5	*Method*
0.0000	848.0					DTA
0.0264	811.5	693.7				TA
0.0450	790.4	693.2				TA
0.0681	768.6	693.8				TA
0.0884	747.8	693.6				TA
0.1071	731.0	694.0			556	TA
0.1200	718					DTA
0.1400	702	690	625		553	DTA
0.1600	698		628		554	DTA
0.1801	719	691	628		553	DTA
0.1980	732	692	629		553	DTA
0.2993	827	689	629		555	DTA
0.3993	881	682	629		552	DTA
0.4728	911.7	680.2			556	TA
0.5000	919		629		554	DTA
0.6026	943	664	628			DTA
0.6135	951.1	666			556	TA
0.6993	964	641	627		554	DTA
0.7500	975.6				555	TA
0.7989	978		629		555	DTA
0.8059	983.7				556	TA
0.8159	988	635			553	DTA
0.8500	992.2				555	TA
0.8800	999	660	630		554	DTA
0.9000	998.2		630		556.8	TA
0.9160	1000.3				557.6	TA
0.9200	1000	713		590	557	DTA
0.9542	1005.5			559		TA
0.9550	1005	777		561	554	DTA
0.9720		807		564	554	DTA
0.9880	1009.0					TA
0.9911	1009.6					TA
1.0000	1010.8				560.2	TA
1.0000	1010				565	DTA

No solid solution was found at room temperature, while extensive formation of solid solutions was observed at higher temperatures.

The liquidus curve has its minimum at 710°C and 64 mol% Li_3AlF_6. One new phase, of tetragonal structure, was found in the region between 560 and 660°C, 90 and 99 mol% Li_3AlF_6.

The system Na_3AlF_6–LiF

The phase diagram of this system has been determined by TA, DTA and quenching experiments. The quenched samples were examined by microscopy and X-ray diffraction. The obtained liquidus and solidus temperatures in the system are given in Table 4, and the results from the quenching experiments are summarized in Table 5. The phase diagram is presented in Fig. 3. Two microphotographs of quenched samples of composition 60 mol% Na_3AlF_6 are shown in Figs. 4a and 4b.

TABLE 5

RESULTS OF QUENCHING EXPERIMENTS IN THE SYSTEM LiF–Na_3AlF_6

Mol fraction Na_3AlF_6	*Temperature (°C) quenched from*	*Phases present*	*Method*[a]
60	705	α-Na_3AlF_6 + melt	m
60	680	α-Na_3AlF_6 + LiF + melt	m + X
85	705	α-Na_3AlF_6 + melt	m
90	705	α-Na_3AlF_6 + melt	m
90	680	α-Na_3AlF_6 + LiF	X

[a] Abbreviations: m = microscopy, X = X-ray investigation.

As the enthalpy changes associated with the formation of solid solutions are small, they are often hard to detect. The DTA equipment and techniques developed by the present authors have proved well suited for this purpose. In addition to the present system, the technique has been used with success in the systems NaCl–KCl[29], $MgCl_2$–$CaCl_2$[30], and Li_3AlF_6–Na_3AlF_6[29]. The heating and cooling curves for the composition 2.8 mol% LiF are shown in Fig. 5.

In the subsolidus region below 550°C the system is a pseudobinary one, since LiF and α-Na_3AlF_6 are the only phases present. In the solid–liquid region the system becomes a part of the ternary reciprocal system

$$3\,LiF + Na_3AlF_6 \rightarrow Li_3AlF_6 + 3\,NaF$$

due to formation of solid solutions between Li_3AlF_6 and Na_3AlF_6. The observed depression in the second thermal arrest T_2 is due to this solid solubility. The crystallization does not end in the pseudobinary eutectic point at 694°C, but rather at 628°C, in the ternary eutectic point in the system NaF–LiF–Na_3AlF_6. To check on this assumption, thermal analysis was made of some samples in this ternary system. The results of these experiments are given in Table 6, and confirm the explanation of the observed temperature depression and the third thermal arrest.

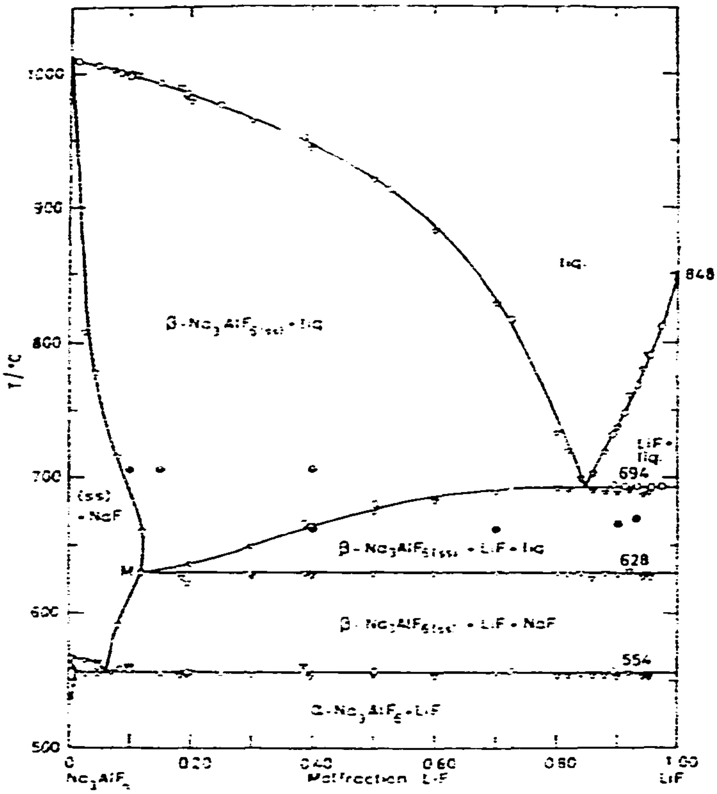

Fig. 3. The phase diagram of the system Na_3AlF_6–LiF, from this work. ○, points obtained by thermal analysis; ∇, points obtained by DTA; ●, from quenching experiments; ⊖, one solid phase+liquid present; ○, two solid phases+liquid present.

The ternary system LiF–NaF–Na_3AlF_6–Li_3AlF_6

The phase diagram of this system is presented in Fig. 6. The isotherms have been drawn on the basis of the four binary systems discussed above and some examinations of compositions in the ternary system. As can be seen, the system has two ternary eutectic points, one in the system LiF–NaF–Na_3AlF_6 at 628 °C and one in the system LiF–Li_3AlF_6–Na_3AlF_6 at 684 °C. The temperature of the latter was established by DTA of a sample containing 66 mol% LiF, 27 mol% Na_3AlF_6, and 7 mol% Li_3AlF_6. Because of the formation of solid solutions in the system, crystallization of compositions within the triangle $(NaF)_3$–Na_3AlF_6–P will not end in the ternary eutectic point. Instead the crystallization will end somewhere along the phase boundary curve e_1E_1, with the phases NaF(ss) and Na_3AlF_6(ss).

Calorimetry

Enthalpies of mixing of molten LiF and Na_3AlF_6 were measured near the 50:50 composition at 1014 °C. The results are summarized in Table 7.

The enthalpy content of two mixtures, one of 74.3 mol% LiF and 25.7 mol% AlF_6 and another of 60.6 mol% Li_3AlF_6 and 39.4 mol% AlF_3 were measured by drop calorimetry. The results of the enthalpy measurements are given in Tables 8 and 9

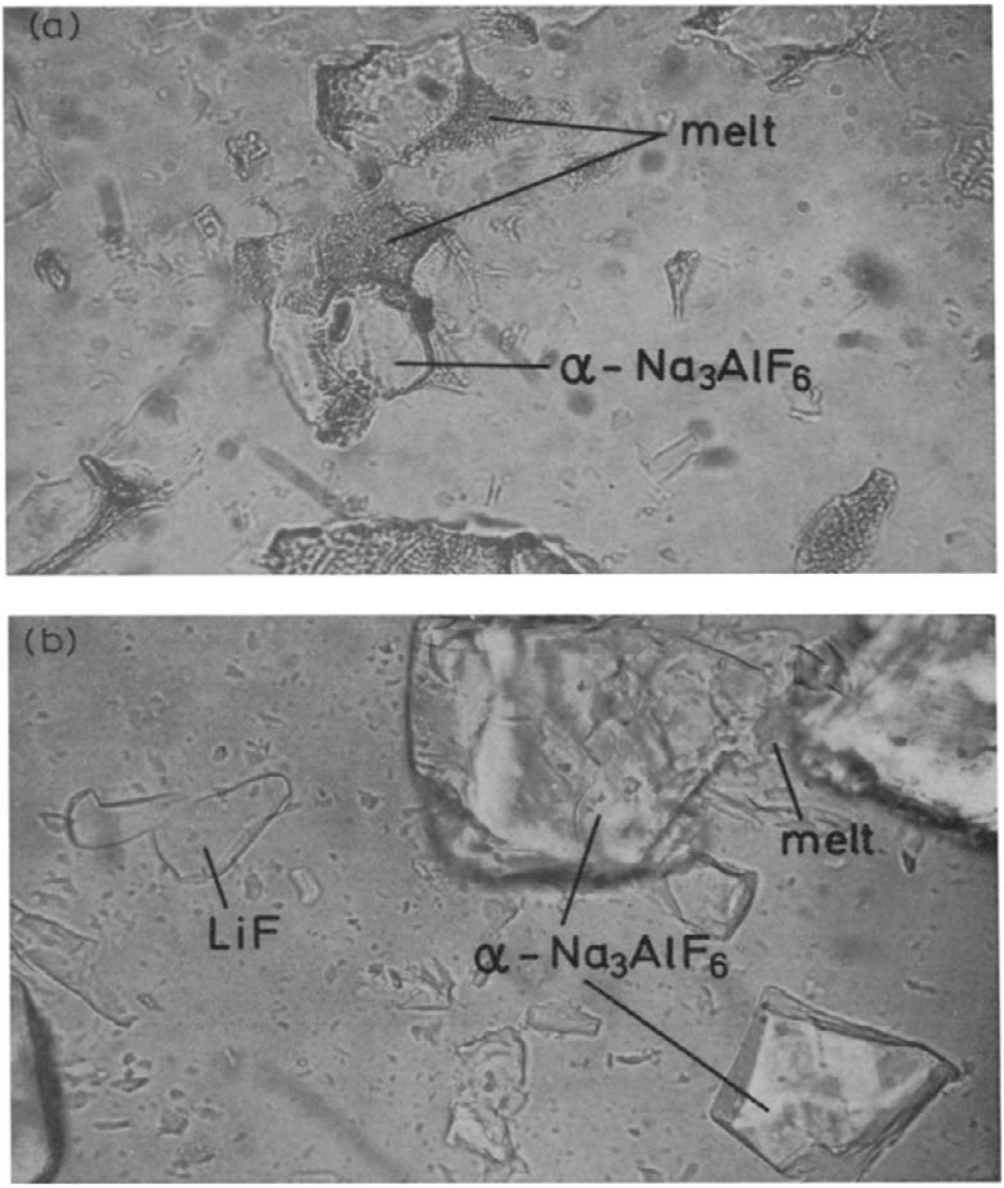

Fig. 4. Photomicrograph of the phases in a mixture of 60 mol% Na_3AlF_6 + 40 mol% LiF. Magnification, × 200. (a), quenched from 705 °C, showing primary crystals of Na_3AlF_6 and quenched liquid; (b), quenched from 670 °C, showing co-existing crystals of Na_3AlF_6 and LiF, and quenched liquid.

and plotted in Figs. 7 and 8. The data were fitted by a least squares treatment to equations of the type

$$H_T - H_{298 \cdot 15} = a + bT$$

where b corresponds to the heat capacity of the solid or the liquid and is assumed constant over the limited temperature ranges in question (Table 10).

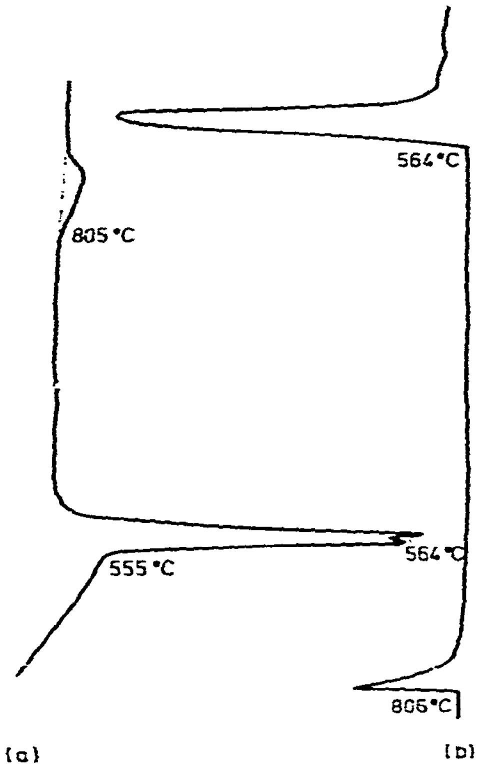

Fig. 5. DTA heating and cooling curves for a sample of composition 97.2 mol% Na_3AlF_6 + 2.8 mol% LiF, showing the phase transition $\alpha \rightleftharpoons \beta$-$Na_3AlF_6$(ss) at 555 °C and 564 °C, respectively, and the reaction NaF(ss) + Na_3AlF_6(ss) ⇌ melt + Na_3AlF_6(ss) at 806 °C.

TABLE 6

THERMAL ANALYSIS OF SAMPLES IN THE TERNARY SYSTEM LiF–NaF–Na_3AlF_6

Composition (mol fractions)			*Thermal arrests (°C)*		
N_{LiF}	N_{NaF}	$N_{Na_3AlF_6}$	T_1	T_2	T_3
0.5935	0.3815	0.0250		645	637
0.5659	0.3638	0.0703	694.3	649	634
0.5402	0.3472	0.1126	698.7	651	634
0.4866	0.3128	0.2006		648	634

TABLE 7

ENTHALPIES OF MIXING IN THE SYSTEM LITHIUM FLUORIDE–CRYOLITE AT 1014 °C

Composition (mol fraction)		ΔH^M *(cal$_{th}$ mol^{-1})*	$\Delta H^M/N_0N_1$ *(cal$_{th}$ mol^{-1})*
N_{LiF}	$N_{Na_3AlF_6}$		
0.5000	0.5000	+90.3	360
0.5005	0.4995	+82.6	346
0.4999	0.5001	+99.0	396

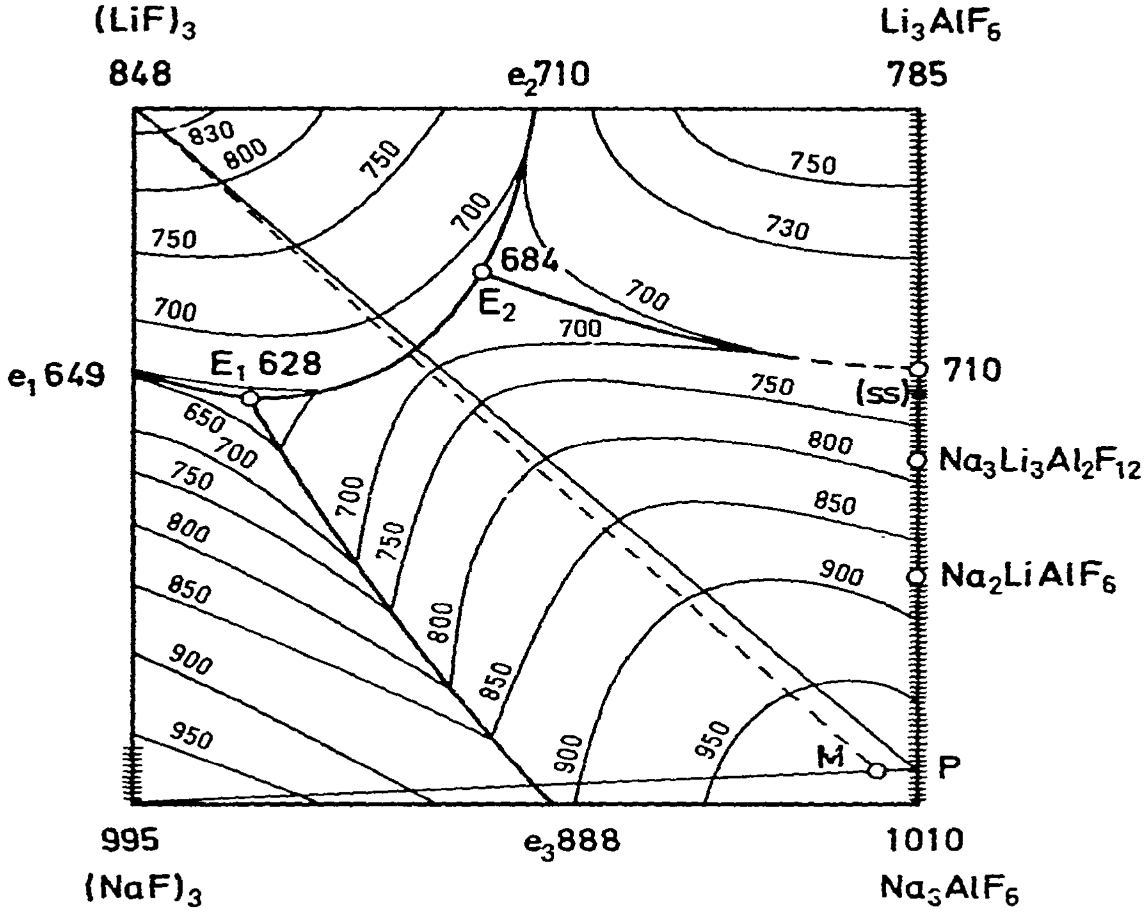

Fig. 6. The phase diagram of the ternary reciprocal system $3LiF + Na_3AlF_6 = Li_3AlF_6 + 3NaF$.

TABLE 8

EXPERIMENTAL AND CALCULATED ENTHALPY INCREMENTS FOR THE SOLID AND LIQUID MIXTURE 0.743 LiF+0.257 Li_3AlF_6

T (*K*)	$H_T - H_{298.15}$ (cal_{th} mol^{-1})		*T* (*K*)	$H_T - H_{298.15}$ (cal_{th} mol^{-1})	
	Expt.	*Calc.*		*Expt.*	*Calc.*
Solid			Liquid		
864.9	14595	14540	1034.9	28265	28299
872.7	14727	14762	1056.9	29076	29095
885.7	15078	15131	1073.6	29696	29676
902.3	15627	15602	1085.5	30078	30089
918.2	16090	16053	1098.3	30544	30534
932.3	16400	16453	1107.5	30896	30854
952.2	17040	17017	1122.1	31430	31362
			1144.2	32111	32130
			1163.7	32752	32808

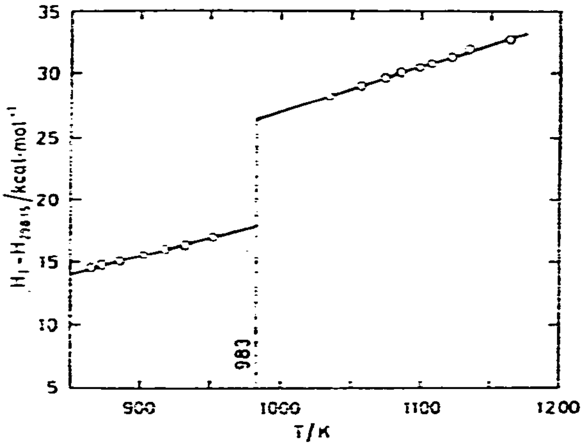

Fig. 7. Enthalpy increments $H_T - H_{298.15}$ and enthalpy of fusion of the eutectic mixture 74.34 mol% LiF + 25.66 mol% Li_3AlF_6.

TABLE 9

EXPERIMENTAL AND CALCULATED ENTHALPY INCREMENTS FOR THE SOLID AND LIQUID MIXTURE 0.6056 Li_3AlF_6 + 0.3944 AlF_3

Solid			*Liquid*		
T (K)	$H_T - H_{298.15}$ (cal_{th} mol^{-1})		*T (K)*	$H_T - H_{298.15}$ (cal_{th} mol^{-1})	
	Expt.	*Calc.*		*Expt.*	*Calc.*
925.1	30043	30112	1012.6	51973	52002
925.9	30100	30154	1012.8	52074	52018
926.0	30151	30159	1013.8	51952	52096
926.1	30084	30164	1013.9	51934	52104
927.7	30359	30249	1015.3	52211	52213
927.8	30104	30254	1015.9	52114	52260
928.2	30165	30275	1016.5	52309	52306
944.2	31089	31119	1034.6	53717	53718
944.3	31158	31124	1034.8	53666	53734
944.7	31190	31145	1034.9	53636	53741
944.8	31145	31150	1035.3	53721	53773
945.6	31298	31193	1035.6	53652	53796
946.2	31120	31224	1036.1	53757	53835
955.5	31656	31715	1036.2	53789	53843
955.8	31772	31730	1053.0	55299	55153
964.3	32289	32179	1054.3	55396	55254
966.0	32126	32268	1054.7	55463	55285
966.1	32331	32274	1055.9	55543	55379
966.6	32304	32300	1057.8	55554	55527
			1057.9	55545	55535
			1057.9	55496	55535
			1058.4	55526	55574
			1074.2	56580	56806
			1074.5	56817	56830
			1078.8	57033	57165
			1079.4	57101	57212
			1152.3	62946	62897
			1187.5	65302	65642

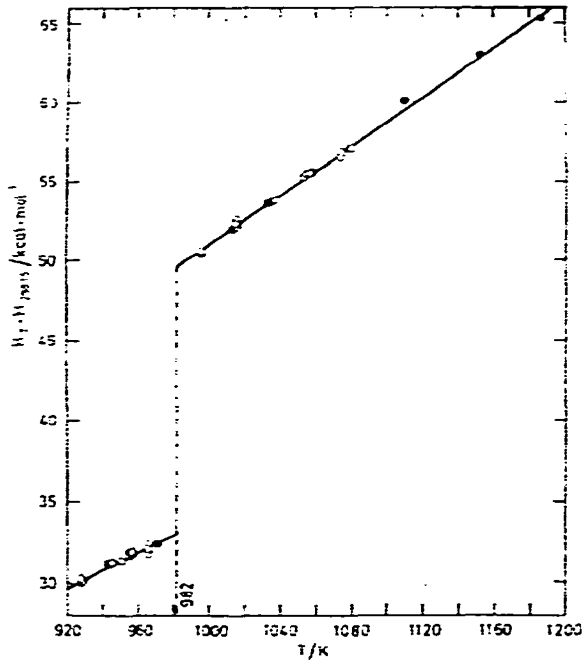

Fig. 8. Enthalpy increments $H_T - H_{298.15}$ and enthalpy of fusion of the eutectic mixture 60.56 mol% Li_3AlF_6 + 39.44 mol% AlF_3.

TABLE 10

ENTHALPY INCREMENTS $H_T = H_{298.15} = a + bT$ AS A FUNCTION OF TEMPERATURE, AND STANDARD DEVIATION σ

Mixture	$H_T - H_{298.15}$ (*cal*$_{th}$ *mol*$^{-1}$)	σ (*cal*$_{th}$ *mol*$^{-1}$)
$(0.743LiF + 0.257Li_3AlF_6)$ (s)	$-9999 + 28.37T$	50
$(0.743LiF + 0.257Li_3AlF_6)$ (l)	$-7655 + 34.77T$	24
$(0.6056Li_3AlF_6 + 0.3994AlF_3)$ (s)	$-17852 + 51.90T$	103
$(0.6056Li_3AlF_6 + 0.3994AlF_3)$ (l)	$-26851 + 77.89T$	171

CALCULATIONS AND DISCUSSION

The system LiF–AlF$_3$

The enthalpy of the reaction between molten LiF and molten AlF_3 to Li_3AlF_6 can be calculated from a thermochemical cycle:

Cycle 1

$$\begin{tikzcd}
Li_3AlF_6(s) \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_f(Li_3AlF_6)"] & 3LiF(s) \arrow[d, "3\Delta H_f(LiF)"] & + & AlF_3(s) \arrow[d, "\Delta H_f(AlF_3)"] \\
Li_3AlF_6(l) \arrow[r, "\Delta H_1^M"] & 3LiF(l) & + & AlF_3(l)
\end{tikzcd}$$

According to the cycle

$$\Delta H^{\mathrm{M}} = \Delta H_{\mathrm{f}}(\mathrm{Li_3AlF_6}) - 3\Delta H_{\mathrm{f}}(\mathrm{LiF}) - \Delta H_{\mathrm{f}}(\mathrm{AlF_3}) - \Delta H_1 \tag{1}$$

By inserting the different enthalpies given in Table 11, the enthalpy of mixing, ΔH^{M}, has been calculated at 850°C. The following value is obtained: $\Delta H_1^{\mathrm{M}} = -13.3 \pm 1$ kcal mol^{-1}. This corresponds to an enthalpy of mixing 0.75 mol LiF+0.25 mol $\mathrm{AlF_3}$ of $\Delta H^{\mathrm{M}} = -3.3$ kcal mol^{-1} at 850°C with an estimated uncertainty of ± 0.5 kcal mol^{-1}. The change in the heat capacity for this reaction is

$$\Delta C_{\mathrm{p,m}} = C_{\mathrm{p}}(\mathrm{Li_3AlF_6}) - 3C_{\mathrm{p}}(\mathrm{LiF}) - C_{\mathrm{p}}(\mathrm{AlF_3})$$

TABLE 11

ENTHALPIES OF FUSION AND REACTION, AND HEAT CAPACITIES, FOR MOLTEN COMPOUNDS IN THE $\mathrm{AlF_3}$-LiF SYSTEM

	ΔH (cal$_{\mathrm{th}}$ mol^{-1})		*Reference*
	850°C	*1000°C*	
ΔH_1	6.9	8.1	Greene, Gross and Hayman[31]
$\Delta H_{\mathrm{f}}(\mathrm{Li_3AlF_6})$	22.7	26.5	Jenssen Holm and Grønvold[32]
$\Delta H_{\mathrm{f}}(\mathrm{AlF_3})$	10.6	11.3	Holm[2]
$\Delta H_{\mathrm{f}}(\mathrm{LiF})$	6.47	6.64	Douglas and Dever[33] and Kelley[10]
ΔH_2	9.6		this work

By inserting the following values: $C_{\mathrm{p}}(\mathrm{Li_3AlF_6}) = 92.2$ cal mol^{-1} K^{-1} (Jenssen Holm and Grønvold[32]), $C_{\mathrm{p}}(\mathrm{LiF}) = 15.5$ cal mol^{-1} K^{-1} (Kelley[10]) and $C_{\mathrm{p}}(\mathrm{AlF_3}) = 29.1$ cal mol^{-1} K^{-1} (Holm[2]) one obtains $\Delta C_{\mathrm{p,m}} = 14$ cal mol^{-1} K^{-1}. Hence ΔH_1^{M} at 1273 K is

$$\Delta H_1(1273) = -13300 + 2300 = -11000 \text{ cal mol}^{-1}$$

Cycle 2

$$\begin{tikzcd}
0.743\,\mathrm{LiF(s)} \arrow[d] & + & 0.257\,\mathrm{Li_3AlF_6(s)} \arrow[d] \arrow[r, dash] & {} \arrow[d, "\Delta H_2"] \\
0.743\,\mathrm{LiF(l)} & + & 0.257\,\mathrm{Li_3AlF_6(l)} \arrow[r, "\Delta H_2^{\mathrm{M}}"] & \text{mixture}
\end{tikzcd}$$

According to cycle 2

$$0.743\,\Delta H_{\mathrm{f}}(\mathrm{LiF}) + 0.257\Delta H_{\mathrm{f}}(\mathrm{Li_3AlF_6}) + \Delta H_2^{\mathrm{M}} = \Delta H_2. \tag{2}$$

By inserting the values given in Table 11 one obtains $\Delta H_2^{\mathrm{M}} = -1.0$ kcal mol^{-1} with an estimated uncertainty of ± 0.2 kcal mol^{-1}. This corresponds to an enthalpy of the reaction

$$0.855\,\mathrm{LiF(l)} + 0.145\,\mathrm{AlF_3(l)} = \text{mixture}$$

of $\Delta H_2^{\mathrm{M}} = -2.5 \pm 0.2$ kcal mol^{-1}.

The theoretical enthalpy of mixing, ΔH_C^M, of LiF and Li_3AlF_6 has been calculated by using an equation similar to the one used by Holm[1,3] for calculation of the enthalpies of mixing of NaF and Na_3AlF_6

$$\Delta H_C^M = -\Delta H^{diss} N_0(\alpha_0 - \alpha_1). \tag{4}$$

The enthalpy curves are presented in Fig. 9 for one value of ΔH^{diss}, namely 14000 cal. The best curve seems to be the one calculated for a degree of dissociation for molten Li_3AlF_6 of $\alpha_0 = 0.30$ and 850°C.

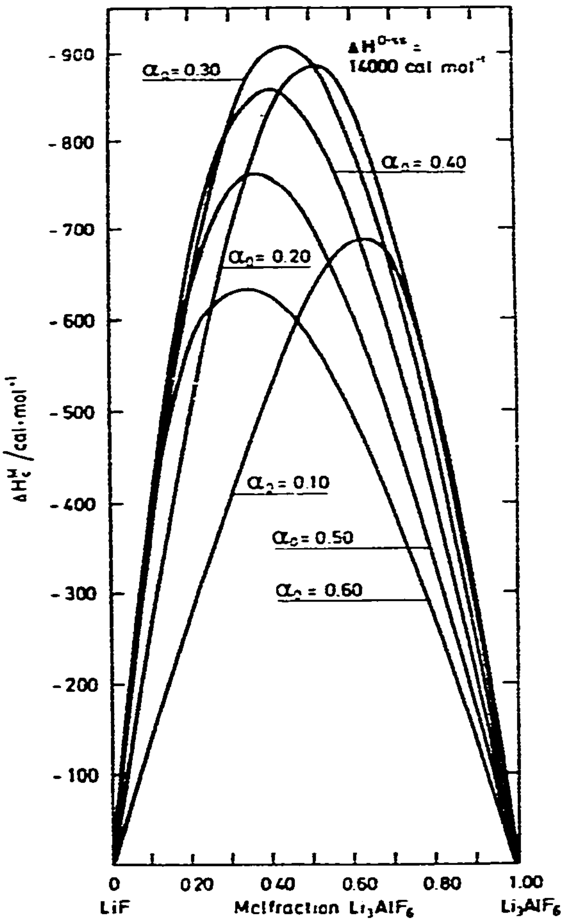

Fig. 9. Calculated ΔH_C^M curves for liquid mixtures of LiF and Li_3AlF_6 at 850°C assuming a dissociation $Li_3AlF_6 = 3LiF + AlF_3$, $\Delta H^{diss} = 14000$ cal for different degrees of dissociation.

In Table 12 are given the changes in the heat capacity on mixing:

$$\Delta C_{p,m} = C_p\,(\text{mixture}) - C_p\,(\text{compound}) \tag{4}$$

for three different mixtures in the system LiF–AlF_3. As can be seen, $\Delta C_{p,m}$ increases with increasing content of AlF_3 in the melt. This means that the enthalpy of mixing, ΔH^M, will become more and more temperature-dependent as the AlF_3 content in the melt increases.

TABLE 12

CHANGES IN HEAT CAPACITY ON MIXING IN MOLTEN MIXTURES OF LiF AND AlF_3: $\Delta C_{p,m} = C_p$ (mixture) $- C_p$ (compound).

Mol fraction AlF_3	*C_p (cal_{th} K^{-1} mol^{-1})*		*$\Delta C_{p,m}$ (cal_{th} mol^{-1} K^{-1})*
	compound	*mixture*	
0	15.5	19.6	0
0.15	17.7		+1.9
0.25	19.0	23.0	+4.0
0.35	20.3	27.5	+7.2
1.0	29.5		0

The system $LiF–Na_3AlF_6$

Enthalpy of mixing

The enthalpy for the process 0.5 $Na_3AlF_6(l) + 0.5\ LiF(l) \rightarrow Mix$ was measured calorimetrically, and found to be $\Delta H^M = +90 \pm 9$ cal mol^{-1} (Table 7). This ΔH^M value can be compared with the enthalpies of solution of Na_3AlF_6 in molten LiF at 900°C[1]. By subtraction of the enthalpy of fusion for Na_3AlF_6, the enthalpies of mixing given in Table 13 are found. Here N_0 and N_1 are the weighed-in mol fractions of Na_3AlF_6 and LiF, respectively. The calculated $\Delta H^M/N_0N_1$ values from these three experiments are in good agreement with the results from the liquid–liquid experiments at 1014°C (Table 7). It is therefore assumed that the enthalpy of mixing in the system $LiF–Na_3AlF_6$ follows the simple symmetrical expression

TABLE 13

CALCULATED ENTHALPIES OF MIXING OF LiF AND Na_3AlF_6 AT 900°C

Mol fraction LiF	*ΔH^M (cal_{th} mol^{-1})*	*$\Delta H^M/N_1N_0$ (cal_{th} mol^{-1})*
0.9694	+10	+337
0.9430	+18	+335
0.9236	+24	+340

$$\Delta H_C^M = +360\, N_0 N_1 \tag{5}$$

As a first approximation it is assumed that the enthalpy of mixing is due to a reaction of Na_3AlF_6 to Li_3AlF_6, and that the enthalpy of mixing can be expressed by

$$\Delta H_C^M = \{N_0(\alpha - \alpha_0) + \tfrac{1}{3} N_1 (1-\alpha)\}\, \Delta H_1^{diss} - \{\tfrac{1}{3} N_1 (1-\alpha)\}\, \Delta H_2^{diss} \tag{6}$$

The first term is the enthalpy loss due to the dissociation of Na_3AlF_6, while the second term is the enthalpy gain due to formation of Li_3AlF_6. Introducing $\Delta H_1^{diss} = 22000$ cal, the enthalpy of dissociation of $Na_3AlF_6(l) = 3NaF(l) + AlF_3(l)$ (Holm[1,3])

$\Delta H_2^{\text{diss}} = 11000$ cal as calculated from this work, and also $\alpha_0 = 0.31$, the degree of dissociation for pure molten cryolite (Holm[1,3]), one obtains at $N_0 = 0.5$, and by setting $\Delta H_C^M = 90$, a degree of dissociation of AlF_6^{3-} in the mixture of $\alpha = 0.19$. Due to the interaction between NaF and LiF a third term should also be added in eqn (6), namely

$$\Delta H_3^M = N_{LiF} N_{NaF} \lambda(Li^+, Na^+)\, F^- \tag{7}$$

The mol fractions are here given by

$$N_{LiF} = N_{Li^+} N_{F^-} = \frac{N_1}{3N_0+N_1} \cdot \frac{3N_0\alpha+N_1}{1+3N_0\alpha}$$

$$N_{NaF} = N_{Na^+} N_{F^-} = \frac{3N_0}{3N_0+N_1} \cdot \frac{3N_0\alpha+N_1}{1+3N_0\alpha}$$

and λ, the interaction parameter, is -1900 cal mol^{-1} as given by Holm and Kleppa[9].

Thus one arrives at the following expression for the enthalpy of mixing in the system LiF–Na_3AlF_6 at 1010°C

$$\Delta H_C^M = N_0(\alpha-\alpha_0)\, 22000 + \tfrac{1}{2} N_1(1-\alpha)\, 11000 - 5700 \frac{N_0 N_1}{(3N_0+N_1)^2} \left[\frac{3N_0+N_1}{1+3N_0\alpha}\right]^2 \tag{8}$$

from which α can be calculated if ΔH_C^M is known. For instance, by setting $\Delta H_C^M = 90$ at $N_0 = 0.5$, eqn (8) gives $\alpha = 0.206$, a value which is only slightly higher than that calculated from eqn (6). The degree of dissociation of AlF_6^{3-} at different compositions has been calculated from eqn (8) by assuming that the enthalpy ΔH_C^M follows eqn (5). The calculated values are given in Table 14.

TABLE 14

PARTIAL GIBBS FREE ENERGY, ENTHALPY AND ENTROPY OF Na_3AlF_6, AND DEGREE OF DISSOCIATION OF AlF_6^{3-}, IN MIXTURES OF Na_3AlF_6 WITH LiF

Mol fraction cryolite, N_0	α	$\bar{G}$ *(cal$_{th}$)*	$\bar{H}$ *(cal$_{th}$)*	$\bar{S}$ *(eqn (12)) (cal$_{th}$ mol^{-1} K^{-1})*	$\bar{S}$ *(eqn (14)) (cal$_{th}$ mol^{-1} K^{-1})*
0.9000	0.306	−253	+4	0.20	0.38
0.8000	0.295	−687	+14	0.55	0.63
0.7000	0.276	−1009	+32	0.84	1.01
0.6000	0.248	−1415	+86	1.21	1.46
0.5000	0.206	−1900	+90	1.67	2.04
0.4700	0.185	−2030	+101	1.79	2.22
0.4000	0.120	−2581	+130	2.71	2.71

Calculations from phase diagram data

The low enthalpy of mixing means that mixtures in the system can be considered to be close to ideal with a nearly random distribution of the cations, Na^+ and Li^+, on the Alk^+ sites.

The mol fraction of Na_3AlF_6 in the system can be expressed by

$$N_{Na_3AlF_6} = kN^3_{Na^+}N_{AlF_6{}^{3-}} \tag{9}$$

In pure molten cryolite $N_{Na_3AlF_6} = 1, N_{Na^+} = 1$ and $N_{AlF_6^{3-}} = (1-\alpha_0)/1+3\alpha_0$. By use of the dissociation degree for the best scheme $AlF_6^{3-} = $ "AlF_3"$+3F^-$, $\alpha_0 = 0.31$ at 1011 °C[1–3], one finds $k = 2.80$ and therefore

$$N_{Na_3AlF_6} = 2.80\, N^3_{Na^+}N_{AlF_6^{3-}}$$

The partial Gibbs free energy of Na_3AlF_6 has been calculated from the phase diagram data, using

$$\bar{G}_{Na_3AlF_6} = -\Delta H_f\left(1-\frac{T}{T_f}\right)+\frac{\Delta C_p(\Delta T)^2}{2T} \tag{10}$$

Here it has been assumed that there is no solid solubility of LiF in Na_3AlF_6. As seen from the phase diagram of the system Na_3AlF_6–LiF there is, however, a limited solid solubility on the Na_3AlF_6 side. One should therefore use the expression

$$\bar{G}_{Na_3AlF_6(l)} = \bar{G}_{Na_3AlF_6}-\bar{G}_{Na_3AlF_6(ss)} \tag{11}$$

where $\bar{G}_{Na_3AlF_6(ss)}$ is the partial Gibbs free energy of Na_3AlF_6 in the solid phase. In the calculations this term has been neglected, not only because the solid solubility is small, but also because the partial enthalpy term $\bar{H}_{Na_3AlF_6(ss)}$ is not known.

The partial entropy of Na_3AlF_6 has been calculated from

$$\bar{S}_{Na_3AlF_6} = \frac{\bar{H}_{Na_3AlF_6}-\bar{G}_{Na_3AlF_6}}{T} \tag{12}$$

In this calculation it has been assumed that the partial enthalpy of cryolite will be given by the simple regular solution model, eqn (5).

$$\bar{H}_{Na_3AlF_6} = 360N_1^2 \tag{13}$$

The partial entropy of cryolite will according to this model (eqn (9)) be given by

$$\bar{S}_{Na_3AlF_6} = -R'\log N_{Na_3AlF_6} = -R'\log\left[2.8\left(\frac{3N_0}{3N_0+N_1}\right)\frac{3N_0(1-\alpha)}{1+3N_0\alpha}\right] \tag{14}$$

where N_0 and N_1 again are the weighed-in mol fractions of Na_3AlF_6 and LiF.

The experimental and calculated data are summarized in Table 14. Here is also given the degree of dissociation of AlF_6^{3-} in the mixture, which has been calculated by a combination of eqns (5) and (8).

The entropy obtained from the experimental data, (eqn (12)), is somewhat lower than that calculated from eqn (14). One of the reasons for this discrepancy is that the solid solubility has not been taken into consideration in the calculations. Somewhat better agreement between the calculated and the experimental entropy would probably have been obtained if data for $\bar{G}_{Na_3AlF_6(ss)}$ had been available.

4. *Ternary reciprocal mixtures*

The theories of reciprocal molten salt systems were first discussed and put in a form which could be used in calculations by Flood, Førland and Grjotheim (FFG)[34], the so-called FFG theory. Later this first approximation theory was extended to a second approximation theory by Førland[35] and by Scrosati, Flood and Førland[36]. Blander and Yosim[37] have shown that the conformal solution theory may also be applied to these types of ternary mixtures.

In the so-called first approximation of the FFG theory the activity coefficient of LiF in a mixture with Na_3AlF_6 is given by

$$\ln \gamma_{\mathrm{LiF}} = N'_{\mathrm{Na^+}} N'_{\mathrm{AlF_6^{3-}}} \frac{\Delta G^\circ}{RT}. \tag{15}$$

Here the equivalent fractions have been introduced, since the mixture contains ions of different charge. These fractions are given by:

$$N'_{\mathrm{Na^+}} = N_{\mathrm{Na^+}} = \frac{N_{\mathrm{Na^+}}}{N_{\mathrm{Li^+}}+N_{\mathrm{Na^+}}} = \frac{3N_0}{3N_0+N_1}$$

$$N'_{\mathrm{AlF_6^{3-}}} = \frac{3N_{\mathrm{AlF_6^{3-}}}}{3N_{\mathrm{AlF_6^{3-}}}+N_{\mathrm{F^-}}} = \frac{3N_0}{3N_0+N_1}$$

In these expressions the degree of dissociation α has been set equal to zero.

ΔG° is the standard Gibbs free energy for the exchange reaction

$$\mathrm{LiF(l)} + \tfrac{1}{3}\mathrm{Na_3AlF_6(l)} = \tfrac{1}{3}\mathrm{Li_3AlF_6(l)} + \mathrm{NaF(l)}.$$

The enthalpy change for this reaction can be calculated from the enthalpies of the two reactions as given before:

$$\mathrm{Na_3AlF_6(l)} = 3\mathrm{NaF(l)} + \mathrm{AlF_3(l)}, \qquad \Delta H_{1300} = +22000\ \mathrm{cal}$$
$$3\mathrm{LiF(l)} + \mathrm{AlF_3(l)} = \mathrm{Li_3AlF_6(l)}, \qquad \Delta H_{1300} = -11000\ \mathrm{cal}$$

The standard enthalpy for the exchange reaction becomes

$$\Delta H^\circ = \tfrac{1}{3}(22000-11000) = 3500\ \mathrm{cal.}$$

The change in entropy, ΔS°, is not known. It is reasonable to assume that $\Delta S^\circ \simeq 0$. Thus, by setting $\Delta G^\circ = 3500$ cal, one obtains the following expression for the activity coefficient of LiF:

$$\ln \gamma_{\mathrm{LiF}} = \left(\frac{3N_0}{3N_0+N_1}\right)^2 \frac{3500}{RT} \tag{16}$$

The activity of LiF in the mixture is given by

$$a_{\mathrm{LiF}} = N_{\mathrm{Li^+}} N_{\mathrm{F^-}} \gamma_{\mathrm{LiF}} = \left(\frac{N_1}{3N_0+N_1}\right)^2 \gamma_{\mathrm{LiF}} \tag{17}$$

The activity of LiF has been calculated from the phase diagram data, using the equation

$$\log a_{\mathrm{LiF}} = \frac{\Delta H_{\mathrm{f}}(\mathrm{LiF})}{R'}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{f}}}\right) + \frac{\Delta C_{\mathrm{p}}(\mathrm{LiF})}{2R'}\left(\frac{\Delta T}{T}\right)^2 \tag{18}$$

In Fig. 10 the experimental activities are compared with those calculated by use of eqns (16) and (17).

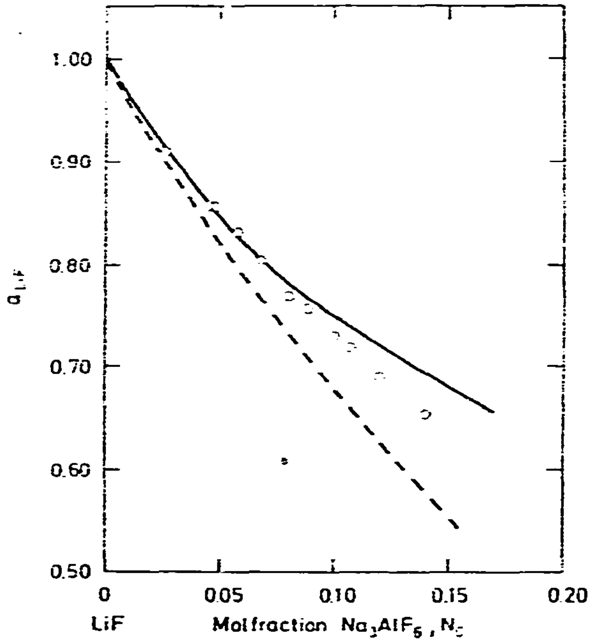

Fig. 10. Experimental and calculated activities of LiF in liquid mixtures of LiF with Na_3AlF_6. O, experimental points; dashed line, ideal curve; full line, I. approximation equation according to the Flood, Førland and Grjotheim theory, with $\Delta G^\circ = 3500$ cal.

As can be seen the first approximation formula gives a good fit with the experimental values up to about 10 mol% Na_3AlF_6. At higher cryolite concentration the calculated activities are more positive than the experimental ones.

Better agreement between theoretical and experimental values could probably be obtained by allowing for the additional binary terms which have not been taken into consideration in the first approximation formula. These additional terms are

$$\begin{aligned} RT \ln \Delta\gamma_{\mathrm{LiF}} = {} & N'^{2}_{\mathrm{Na^+}} \lambda'_{\mathrm{F^-,AlF_6^{3-}}} + N'_{\mathrm{AlF_6^{3-}}} \lambda'_{\mathrm{Na^+,Li^+}} + \\ & + N'_{\mathrm{Na^+}} N'_{\mathrm{AlF_6^{3-}}} [N'_{\mathrm{Li^+}}(\lambda'_{\mathrm{F^-}} - \lambda'_{\mathrm{AlF_6^{3-}}}) + N'_{\mathrm{F^-}}(\lambda'_{\mathrm{Li^+}} - \lambda'_{\mathrm{Na^+}})] \end{aligned} \tag{19}$$

where the λ's are equivalent interaction parameters. Here $\lambda'_{\mathrm{F^-}}$ and $\lambda'_{\mathrm{AlF_6^{3-}}}$ are related to deviations from ideality in the $(Li^+–Na^+)F^-$ and $(Li^+–Na^+)AlF_6^{3-}$ systems, respectively, and $\lambda'_{\mathrm{F^-,AlF_6^{3-}}}$ accounts for the same type of long-range interaction as $\lambda'_{\mathrm{F^-}}$ and $\lambda'_{\mathrm{AlF_6^{3-}}}$, but in mixtures containing both F^- and AlF_6^{3-} ions. Similarly,

λ'_{Li^+} and λ'_{Na^+} are related to the deviations from ideality in the $\mathrm{Li}^+(\mathrm{F}\text{–}\mathrm{AlF}_6^{3-})$ and $\mathrm{Na}^+(\mathrm{F}^-\text{–}\mathrm{AlF}_6^{3-})$ systems, respectively, while in mixtures containing both Li^+ and Na^+, $\lambda'_{\mathrm{Li}^+,\mathrm{Na}^+}$ refers to the same type of interactions.

Most of the parameters λ' are of the order of -1.3 to -4.0 kcal mol^{-1}. Some of the terms in eqn (19) will partly balance each other. The deviation between the calculated and experimental curve at 15 mol% $\mathrm{Na_3AlF_6}$ corresponds to -120 cal. This is equivalent to a total interaction parameter of

$$\lambda = -120/N'^2_{\mathrm{Na}^+} = -1000\ \mathrm{cal}$$

Thus there seem to be good reasons to believe that one would obtain a better agreement between the two curves by taking into account the additional terms as given by the second approximation formula, eqn (19).

ACKNOWLEDGEMENTS

Financial support has been received from the following Norwegian sources and is gratefully acknowledged: Norges Teknisk-Naturvitenskapelige Forskningsråd, Norges Almenvitenskapelige Forskningsråd, and Kaltenborn Griegs Stipendiefond. During one of the authors' (J.L.H.) stay at the James Franck Institute, The University of Chicago, the work was supported by grants from "The National Science Foundation" (GP-5015 and GP-7782) and by the Army Research Office, Durham, N.C. to Professor O. J. Kleppa. It also benefitted from the general support to Materials Science at the University of Chicago provided by the Advanced Research Projects Agency, Depart of Defense, U.S.A.

Thanks are due to Professor K. Grjotheim for laboratory facilities at the Institute of Inorganic Chemistry, Trondheim, to Docent F. Grønvold, The University of Oslo, for his guidance and help with the drop calorimeter work, and to Professor O. J. Kleppa, The University of Chicago, for his kind permission to use one of his high temperature calorimeters.

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