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PHASE INVESTIGATIONS OF THE SYSTEM Na_3AlF_6 - NaCl

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ABSTRACT

The paper represents the phase diagram of the system NaCl-Na_3AlF_6 together with enthalpies of mixing of liquid mixtures in this system.

INTRODUCTION

Mixtures in the system NaCl-Na_3AlF_6 belong to the ternary reciprocal system

$$3\ NaCl + AlF_3 = 3\ NaF + AlCl_3$$

Phase examinations in the system NaCl-NaF-AlF_3 by Kuvakin and Kusakin [1] show that the system NaCl-AlF_3 acts as a stable diagonal in the ternary reciprocal system. From the change in Gibbs free energy and enthalpy for the above reaction it is clear that the equilibrium is shifted strongly to the left. According to available thermodynamic data [2] ΔG^o_{1300} as well as ΔH^o_{1300} should be of the order of 290 kJ for the metathetical reaction. Mixtures in the system NaCl-NaF-AlF_3 may therefore be treated as if they belonged to the ternary additive system. In the following the phase diagram of the system NaCl-Na_3AlF_6 will be presented together with enthalpies of mixing of liquid mixtures in the system. The ΔH^M-data have been determined directly by high-temperature calorimetry.

EXPERIMENTAL

1. Chemicals. Na_3AlF_6, cryolite, and AlF_3, aluminium fluoride, were the same as described in a previous paper [3]. NaCl, sodium chloride, reagent grade, fusum, from Merck, Germany, was used in the examinations of the phase diagram, while NaCl, reagent grade, from Fisher Scientific Co., USA, was used for the calorimetric work. The sodium chloride was premelted and clear crystals were selected from the sample.

2. Thermal analysis. The equipment used in the present work for the cooling curve investigations was the same as described in a previous papers [3] and [4]. A graphite crucible, 55 mm in diameter and of 120 mm height, containing 40-100 g melt, was placed inside a "thermal gradient free" standard type

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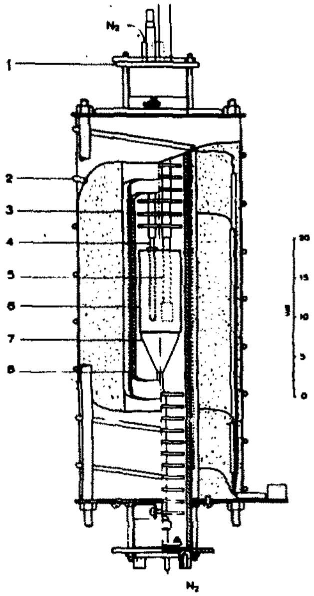
furnace [5]. The temperature was recorded by a Pt/Pt10%Rh thermocouple calibrated at the melting points of silver, 960.5^{o}C, and NaCl, 800.5^{o}C. The experimental set-up for the thermal analysis, furnace and crucible, are shown in Fig. 1. Supercooling of the melt was prevented by stirring and by seeding with small cryolite or sodium chloride crystals. The uncertainty in determining temperatures by this method is $\pm$ 0.2^{o}C. However, due to supercooling effects the uncertainty in some experiments could be as large as $\pm$ 0.5^{o}C.

3. Calorimetry. The mixing experiments were performed in the same high-temperature calorimeter as described in a previous paper [4]. The same equipment and technique as for the mixing of NaF and Na_3AlF_6 was used.

RESULTS

Results obtained by thermal analysis (cooling curve method) and DTA, are given in Table 1 and plotted in a phase diagram in Fig. 2. Here the results obtained by Kuvakin and Kusakin [1] are also given. As can be seen the liquidus curve obtained by the Russians is somewhat lower than the curve obtained inthis work.

The results from the high-temperature calorimetric mixing experiments are given in Table 2 and plotted in Fig. 3. All experiments were performed at 1014$\pm$1^{o}C.



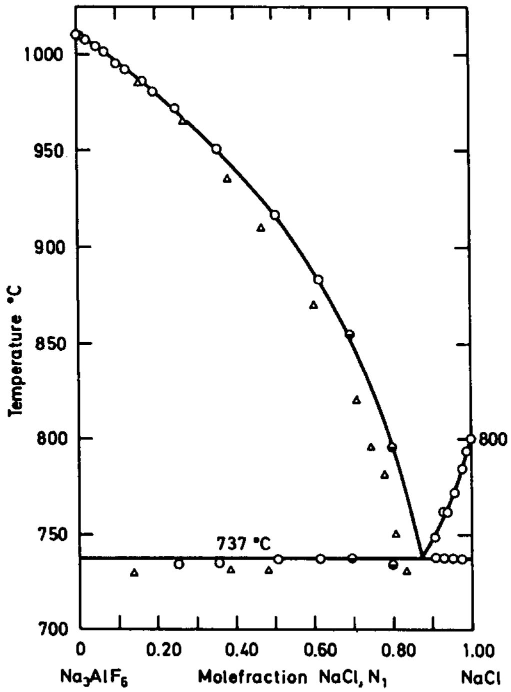
Experimental set-up (furnace and crucible) for thermal analysis.
1. nickel lid; 2. copper mantel with copper cooling tubes; 3. kanthal windings; 4. Pt/Pt10%Rh thermocouple; 5. screw shaped graphite stirrer; 6. graphite crucible; 7. alundum supporter; 8. Pythagoras tube.

Fig 1

Table 1. The system NaCl-Na_3AlF_6. Temperatures obtained by thermal analysis.
T_1 = melting temperature
T_2 = binary eutectic temperature

*) Found by DTA.

Molefraction Na_3AlF_6, N_0	T_1 °C	T_2 °C	Molefraction Na_3AlF_6, N_0	T_1 °C
0.0000	800.5		0.8007	980.5
0.0107	792.8		0.8276	984.7
0.0213	784.0	736.6	0.8331	985.8
0.0412	771.5	737.4	0.8953	994.4
0.0619	761.3	737.5	0.8978	995.5
0.0907	748.0	737.6	0.9265	1001.1
0.2000	795 *	735 *	0.9508	1003.6
0.2996	857 *	736 *	0.9577	1004.0
0.3833	882.4	736.5	0.9745	1007.4
0.4902	917.2	736.6	0.9890	1009.6
0.6419	950.7	734.7	0.9960	1010.3
0.7474	971.3	732.9	1.0000	1010.8

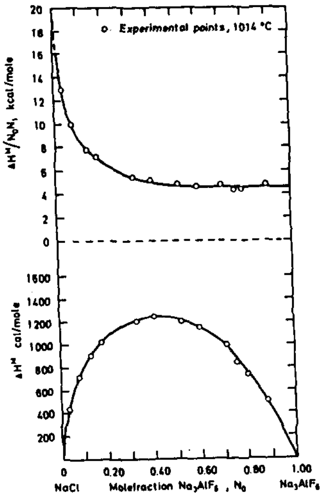


The phase diagram of the system Na_3AlF_6-NaCl.
o, points obtained by thermal analysis.
●, points obtained by DTA.
△, points from Kuvakin and Kusakin[1].

Fig. 2

Table 2. Enthalpy of mixing in liquid mixtures of cryolite and sodium chloride.

Molefraction Na_3AlF_6 N_0	Molefraction NaCl N_1	ΔH^M kcal/mole	$\Delta H^M/N_0N_1$ kcal/mole
0.0338	0.9662	0.422	12.921
0.0776	0.9224	0.712	9.947
0.1328	0.8672	0.901	7.828
0.1703	0.8292	1.022	7.284
0.3321	0.6679	1.209	5.451
0.4043	0.5957	1.245	5.170
0.5237	0.4763	1.200	4.812
0.6000	0.4000	1.148	4.783
0.7064	0.2936	0.981	4.730
0.7509	0.2491	0.827	4.472
0.7961	0.2039	0.723	4.455
0.8812	0.1188	0.500	4.776



Enthalpies of mixing in liquid mixtures of Na_3AlF_6 with NaCl.

Fig. 3

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