

Stability of AlCl_3NH_3 in Chloroaluminate Melts

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The decomposition of AlCl_3NH_3 into AlCl_3 and NH_3 has been investigated in basic $\text{MCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ mixtures ($\text{M}=\text{Na},\text{K}$) in the temperature range 500–600 °C. The results indicate that AlCl_3NH_3 is relatively stable in $\text{NaCl}-\text{AlCl}_3$ melts. Due to a substantially lower activity of AlCl_3 in $\text{KCl}-\text{AlCl}_3$ melts, up to 70 % AlCl_3NH_3 may be decomposed in these mixtures. The degree of decomposition increased with increasing temperature. Formation of $\text{AlN}(\text{s})$ was detected in all experiments, in increasing amounts with increasing temperature.

1. INTRODUCTION

In an extraction process for direct dehydration of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ the last intermediate compound is assumed to be AlCl_3NH_3 .¹ Hence, the decomposition of the ammine into AlCl_3 and NH_3 is a prerequisite for a successful dehydration process. Possible equilibria involving AlCl_3NH_3 are given with equilibrium constants in Table 1.

Raman spectroscopic studies of molten AlCl_3NH_3 have confirmed that the ammine exists mainly as AlCl_3NH_3 .² Weak dissociation into AlCl_4^- and $\text{AlCl}_2(\text{NH}_3)_2^+$ was found. The equilibrium constant for the reaction



was found to be $3 \cdot 10^{-3}$ (Ref. 2).

In acidic chloroaluminate melts ($X_{\text{AlCl}_3}/X_{\text{MCl}} > 1$) the association reaction



is also observed.^{2,3} The equilibrium constant for reaction (8) is ≈ 1 at ≈ 600 K.

A straight forward thermal decomposition of AlCl_3NH_3 into AlCl_3 and NH_3 is not feasible, as the reaction



is energetically more favorable^{4,5} than the desired decomposition reaction⁶



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The equilibrium constant of eqn. (10) is expressed by

$$K_{10} = \frac{a_{\text{AlCl}_3(l)} \cdot P_{\text{NH}_3}}{a_{\text{AlCl}_3\text{NH}_3(l)}} \quad (11)$$

which shows that a reduction of the AlCl_3 activity will favor the decomposition of the ammine, as it causes the partial pressure of $\text{NH}_3(\text{g})$ to increase. Hence, a melt which dissolves AlCl_3NH_3 and effectively reduces the activity of AlCl_3 might be used.

The Alcoa process for production of aluminium is based on electrolysis of a mixture of alkali-, earth alkali-, and aluminium chloride,⁷ where the aluminium chloride is produced by chlorination of alumina. The activity of AlCl_3 in chloroaluminate melts varies over a wide range depending on composition, thus rendering these mixtures interesting candidates as media for solution and decomposition of AlCl_3NH_3 . The production of AlCl_3 by decomposition of AlCl_3NH_3 also suggests utilization of other mineral sources than bauxite for aluminium production.

2. EXPERIMENTAL

2.1. Chemicals. The chemicals used were AlCl_3 (99.992 %, Fluka, AG, Buchs, FRG), KCl (*p.a.*, J.T. Baker Chemicals, Deventer, Holland), LiCl , NaCl (*p.a.*, E. Merck, AG, Darmstadt, FRG), NH_4Cl (*p.a.*, J.T. Baker Chemicals, Deventer, Holland) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (99.99 % E. Merck, AG, Darmstadt, FRG).

Aluminium chloride was purified by three times distillation in closed, evacuated silica tubes at 200 °C.

Aluminium chloride monoammine was prepared by reacting AlCl_3 and NH_4Cl in closed, evacuated silica cells at 320 °C. The reaction product, AlCl_4NH_4 , was transferred to a distillation cell equipped with a tube for collection of AlCl_3NH_3 and a liquid nitrogen cold trap for condensation of HCl . At 300 °C, AlCl_4NH_4 decomposes according to the reaction⁸



Aluminium chloride monoammine was distilled three times by this procedure to ensure complete decomposition of AlCl_4NH_4 .

Potassium chloride, NaCl and LiCl were purified by three times recrystallization from the melt. Only clear crystals were used for preparation of salt mixtures.

Prior to use, NH_4Cl was purified by three times sublimation in closed evacuated quartz tubes at 310 °C.

Anhydrous NiCl_2 was prepared by dehydrating $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a stream of dry HCl , at temperature gradually increasing from 100–450 °C over three days.

The cells were thoroughly cleaned before use, and residual carbon impurities were burned away with a torch and removed with a stream of oxygen in the cell. All handling of

Table 1. AlCl_3NH_3 -equilibria and equilibrium constants.

(i) Equilibrium	$\log K_i (\text{T})$	Ref.
(1) $\text{AlCl}_3\text{NH}_3(\text{l}) = \text{AlCl}_3\text{NH}_3(\text{g})$	$5.45 - 3760(\text{T/K})^{-1}$	8
(2) $\text{AlCl}_3\text{NH}_3(\text{l}) = \text{AlN}(\text{s}) + 3\text{HCl}(\text{g})$	$17.25 - 14320(\text{T/K})^{-1}$	4,5
(3) $\text{AlCl}_3\text{NH}_3(\text{g}) = \text{AlN}(\text{s}) + 3\text{HCl}(\text{g})$	$11.8 - 10560(\text{T/K})^{-1}$	
(4) $\text{AlCl}_3\text{NH}_3(\text{l}) = \text{AlCl}_3(\text{g}) + \text{NH}_3(\text{g})$	$13.36 - 12490(\text{T/K})^{-1}$	6
(5) $\text{AlCl}_3\text{NH}_3(\text{g}) = \text{AlCl}_3(\text{g}) + \text{NH}_3(\text{g})$	$7.91 - 8730(\text{T/K})^{-1}$	
(6) $\text{AlCl}_3(\text{g}) + \text{NH}_3(\text{g}) = \text{AlN}(\text{s}) + 3\text{HCl}(\text{g})$	$3.89 - 1830(\text{T/K})^{-1}$	

the salts was done in a glove box with a H_2O content (volume) less than 5 ppm. Between experiments, the salts were stored in closed, evacuated quartz ampules in the glove box.

2.2. Experimental procedure. The decomposition of AlCl_3NH_3 to AlCl_3 and NH_3 was performed in closed, evacuated quartz cells. A quartz frit separated the two compartments of the cell; one of these contained AlCl_3NH_3 dissolved in a chloroaluminate melt, the other contained NiCl_2 which absorbed the evolved $\text{NH}_3(\text{g})$.⁹⁻¹³ In all experiments, the total amount of alkali chloride, AlCl_3 and AlCl_3NH_3 was approximately 20 g. An excess amount of NiCl_2 (1–2g) relative to the amount of AlCl_3NH_3 was always used.

The furnace was a kanthal wound quartz tube with two heating zones. The current through the zone where the NiCl_2 part of the cell was situated during the experiments was limited by a resistor in parallel. The temperature in this part of the furnace was varied in the range 250–330 °C, and the temperature in the part of the furnace which contained the chloroaluminate melt was between 500 °C and 600 °C. The temperature in each zone was monitored by thermocouples.

The charged cell was placed in the furnace and heated to the experimental temperature over 6 h. The cell was held at this temperature in periods ranging from 1.5 to 16 h. During melting, the furnace was moved up and down by a motor to ensure complete mixing of the salts. The experiments were terminated by cooling the cell containing the melt in a stream of cold air, while the NiCl_2 compartment was cooled in the furnace to 100 °C before the cell was removed. This was done in order to prevent condensation of the AlCl_3 containing gas components in the nickel chloride compartment.

The chloroaluminate mixture and the NiCl_2 were dissolved in distilled water, and the content of NH_3 in each solution was determined by the Kjeldahl method. For some of the experiments the amount of Al^{3+} , K^+ , Na^+ were determined by atomic absorption, and Cl^- by precipitation with AgNO_3 . The analyses were carried out by the Division of Analytical Chemistry at SINTEF, Trondheim, Norway.

Vapour pressures above $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts were determined as described by Linga *et al.*¹⁴

3. RESULTS

3.1. Solubility of AlCl_3NH_3 in molten salts. Aluminium chloride monoammine has very low solubility in molten alkali chloride melts. The solubility of AlCl_3NH_3 in molten LiCl/KCl (58.1/41.9 mol %) is less than 1 weight %. The solubility increases by adding 5 mol % AlCl_3 to the LiCl/KCl mixture.

Considerable solubility of AlCl_3NH_3 was observed in acidic chloro-aluminate melts.³ Table 2 shows some qualitative results for basic $\text{KCl}-\text{AlCl}_3$ mixtures.

3.2. Partial pressures of AlCl_3NH_3 above basic chloroaluminate melts containing AlCl_3NH_3 . Some experiments were carried out to obtain approximate activities of AlCl_3NH_3 in basic chloroaluminate melts containing AlCl_3NH_3 . The total pressure above these melts is mainly due to the vapour species AlCl_3NH_3 . This may be observed in Fig. 1. The total

Table 2. Phase relations in some basic chloroaluminate melts containing AlCl_3NH_3 .

Melt	Composition (mol %)	T (°C)	Number of phases
$\text{AlCl}_3/\text{KCl}/\text{AlCl}_3\text{NH}_3$	43.5/46.5/10	400	1
$\text{AlCl}_3/\text{KCl}/\text{AlCl}_3\text{NH}_3$	40.5/50/9.5	520	1
$\text{AlCl}_3/\text{KCl}/\text{AlCl}_3\text{NH}_3$	36.6/54.9/8.5	575	1
$\text{AlCl}_3/\text{KCl}/\text{AlCl}_3\text{NH}_3$	32.5/60/7.5	650 ^a	2(melt+KCl(s)) ^b

^a The cell exploded at this temperature due to the pressure of $\text{AlCl}_3(\text{g})+\text{Al}_2\text{Cl}_6(\text{g})+\text{NH}_3(\text{g})$. ^b A white precipitate, which is assumed to be $\text{KCl}(\text{s})$, was observed before the cell exploded.

pressure over the $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ (45–45–10(mol %)) melt is around two orders of magnitude higher than the pressures above the NaAlCl_4 melt as shown by Linga *et al.*¹⁴ and by Dewing (49.5 mol % AlCl_3).¹⁵

3.3. *Decomposition of AlCl_3NH_3 .* A limited number of initial experiments were performed in order to single out the most promising mixture for the decomposition of AlCl_3NH_3 . Two methods were used:

1. Decomposition of AlCl_3NH_3 dissolved in the melt.
2. Decomposition of $\text{AlCl}_3\text{NH}_3(\text{g})$ by bubbling the gas through the melt.

The results of these experiments showed that AlCl_3NH_3 decomposes readily in a basic $\text{KCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melt. Decomposition of $\text{AlCl}_3\text{NH}_3(\text{g})$ by bubbling the gas through pure liquid alkali chlorides or basic chloroaluminate melts (bubble diameters ≈ 0.5 mm) did not work properly, presumably due to a too small melt/gas contact surface.

The final decomposition experiments were carried out by dissolving AlCl_3NH_3 in $\text{KCl}-\text{AlCl}_3$ melts, as described in Section 2.2. The results from these experiments are presented in Table 3. Detail observations are given below.

Evolution of NH_3 was observed in each experiment by the changes in color of NiCl_2 which was kept at approximately 300 °C in each run. At the onset of an experiment, the color was light yellow; after an experiment it was brownish yellow. In experiments 6–10, part of the NiCl_2 was green after cooling, which indicates formation of $\text{NiCl}_2 \cdot 2\text{NH}_3$.⁹

A white deposit was formed on the hot/cold zone interface of the cell wall. The amount of the deposit increased with increasing duration of the experiment and temperature. The deposit was soluble in strong base, and chemical analysis of the basic solution showed excess Cl over Al and N. This may be due to absorbed KCl. X-ray analysis of the deposit (Debye-Scherrer) identified AlN, which contained some KCl. No traces of AlOCl or Al_2O_3 were found in the sample.

4. DISCUSSION

4.1. *Experimental procedure.* The experimental results are presented in Table 3, which shows that no AlCl_3NH_3 decomposes in acidic chloroaluminate melts. However, decomposition does occur in the basic melts, and to a larger extent in the potassium than in the sodium chloroaluminate mixtures. Samples of the NiCl_2 used in experiments 4 and 7 were analyzed for Al content, which averaged 0.08 weight %. The low content of Al indicates that condensation of AlCl_3NH_3 and AlCl_3 in the NiCl_2 compartment was prevented.

Aluminium trichloride reacts with $\text{NiCl}_2(\text{s})$ to give the gaseous complex $\text{NiAl}_2\text{Cl}_8(\text{g})$.^{16–19} The amount of NiCl_2 which is complexed is small, as the partial pressure of $\text{NiAl}_2\text{Cl}_8(\text{g})$ under the experimental conditions is estimated to $\approx 10^{-6}$ atm.

As seen from Table 1, decomposition of AlCl_3NH_3 into $\text{AlN}(\text{s})$ and $\text{HCl}(\text{g})$ is more favorable thermodynamically than the direct decomposition into $\text{AlCl}_3(\text{g})$ and $\text{NH}_3(\text{g})$. Eqn. (3) has an equilibrium constant of 1 at 895 K, whereas the equilibrium constant of eqn. (5) is 1 at 1104 K.

The partial pressure of $\text{HCl}(\text{g})$ in equilibrium with AlCl_3NH_3 at 1 atm is given in Table 4 for different temperatures. This shows that the decomposition reaction should be carried out at a low temperature (300–400 °C) in order to limit the amount of $\text{AlN}(\text{s})$ formed. The

Table 3. Decomposition of AlCl_3NH_3 dissolved in chloroaluminate melts.

Exp. No.	NaCl (mol %)	KCl (mol %)	AlCl_3 (mol %)	AlCl_3NH_3 (mol %)	Melt temperature (°C)	Duration of experiments (h)	Rel. rest conc. NH_3 in melt $100m_{\text{NH}_3}/r_{\text{NH}_3}^0$ (mol %)	Rel. amount NH_3 absorbed in NiCl_2 $100m_{\text{NH}_3}(\text{NiCl}_2)/r_{\text{NH}_3}^0$ (mol %)	NH_3 not accounted for (mol %)
1		50	40	10	410		—	38	
2		50	40	10	500		—	50	
3		50	40	10	580		—	60	
4	53.5	—	42.9	3.6	590	4.0	89	9	2
5	52.7	—	43.4	3.9	600	6.5	98	3	-1
6	35.9	18.1	43.1	2.9	605	7.0	88	10	2
7	—	51.5	43.0	5.5	525	4.0	66	25	9
8	—	50.3	43.9	5.8	555	1.5	—	49	—
9	—	52.2	45.3	2.5	570	3.0	45	54	1
10	—	52.2	45.5	2.3	550	4.0	26	70	4
11	—	53.5	43.4	3.1	590	4.5	25	70	5
12	—	53.4	43.6	3.0	578	16.0	32	61	7
							≈ 100	0	

^a Acidic melts $X_{\text{MCl}} < X_{\text{AlCl}_3}$.^a Ref. 3.

Table 4. Equilibrium partial pressures of HCl(g) in 1 atm AlCl₃NH₃(g).

T (°C)	P _{HCl} (atm)
300	0.06
500	0.24
700	2.07

liquidus temperature for basic chloroaluminate melts containing alkali chlorides demand experimental temperatures of 500–600 °C. Thus formation of AlN(s) will occur.

4.2. *Activities of AlCl₃ in chloroaluminate melts.* The activity of AlCl₃ is an important parameter for the decomposition of AlCl₃NH₃ in molten chloroaluminate mixtures. The vapor pressure of pure AlCl₃ is high at the temperature in question.²⁰ However, large negative deviations from ideality effectively reduce the total pressure of chloroaluminate mixture.¹⁴ It has been shown that MCl–AlCl₃ (M=Li, Na, K) mixtures with X_{AlCl₃} < 0.5 successfully can be described as anion mixtures of Cl[–] and AlCl₄[–] with the common cation M⁺. When an asymmetrical regular solution model is used to describe the mixture, the activity coefficients of MCl(1) and MAIAlCl₄(2) can be expressed by¹⁴

$$\ln \gamma_1 = \frac{\alpha\beta}{RT} \left[\frac{X_2}{X_1 + \beta X_2} \right]^2 \quad (12)$$

$$\ln \gamma_2 = \frac{\alpha}{RT} \left[\frac{X_1}{X_1 + \beta X_2} \right]^2 \quad (13)$$

where X₁ and X₂ are the mole fractions of MCl and MAIAlCl₄, respectively. In eqns. (12) and (13) α is an interaction parameter while β is related to the ratio of the molar volumes, and both parameters are assumed to be independent of temperature. The complex MAIAlCl₄ dissociates to some extent in the molten mixture, according to the reaction



which has to be considered when the activity of AlCl₃ in the chloroaluminate mixture is calculated.

Table 5. Activity and activity coefficient of AlCl₃NH₃ in basic NaCl–AlCl₃–AlCl₃NH₃ melts.

Mol % NaCl– AlCl ₃ –AlCl ₃ NH ₃	T (K)	P _{tot} (Torr)	P ^o _{AlCl₃NH₃}	a _{AlCl₃NH₃}	γ _{AlCl₃NH₃}
45-45-10	579.4	14.7	69.4	0.212	2.12
	608.2	26.8	140.8	0.190	1.90
	642.3	54.7	299.8	0.182	1.82
	693.4	142.6	809.6	0.176	1.76
	693.2	136.9	806.7	0.170	1.70
47-43-10	737.4	330.3	1705.4	0.194	1.94
	738.0	290.4	1721.7	0.169	1.69
	767.5	514.0	2702.7	0.190	1.90
	798.2	725.0	4170.8	0.174	1.74

Reaction (10) describes the decomposition of AlCl_3NH_3 into AlCl_3 and NH_3 , with the equilibrium constant, K_{10} [eqn. (11)]. The numerical value of K_{10} is low for temperatures below 600 °C. In order to achieve a high degree of decomposition of AlCl_3NH_3 at relatively low temperatures, it is imperative that the activity of AlCl_3 is as low as possible. Activity data are not known for the $\text{MCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ mixtures. The amount of AlCl_3NH_3 is, however, small (<6 mol %) in all experiments. Hence, by setting $X_{\text{AlCl}_3\text{NH}_3}=0$, the thermodynamic model developed for the binary alkali chloride – aluminium chloride may be employed to give a rough estimate of the AlCl_3 -activities in the ternary melts.

In order to compare the activity of AlCl_3 in $\text{NaCl}-\text{AlCl}_3$ and $\text{KCl}-\text{AlCl}_3$ melts, a_{AlCl_3} is calculated as function of melt composition for the temperatures 450, 525 and 600 °C and the results are shown in Fig. 2. Extrapolation below the liquidus temperature is shown with dotted lines.

Fig. 2 demonstrates that the activity of AlCl_3 in the $\text{NaCl}-\text{AlCl}_3$ mixtures is roughly ten times higher than in the $\text{KCl}-\text{AlCl}_3$ systems. For both systems, the activity of AlCl_3 increases with increasing temperature.

4.3. Equilibrium pressure of NH_3 above $\text{MCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts. The activity of AlCl_3NH_3 in chloroaluminate melts is not known, but may be estimated from the vapor pressure data of pure $\text{AlCl}_3\text{NH}_3(\text{l})$,^{3,6} and the total vapor pressures above chloroaluminate-monoammine melts. In a rough estimation of this activity the contribution from gas species like AlCl_3 , Al_2Cl_6 and MAlCl_4 to the total vapor pressure can be neglected as can be seen from Fig. 1. Table 5 shows calculated activity coefficients for AlCl_3NH_3 based on this assumption at two compositions in the $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melt. The Table 5 shows that $\gamma_{\text{AlCl}_3\text{NH}_3}$ is close to 2, and decreases with increasing temperature.

The partial pressure of $\text{NH}_3(\text{g})$ above these melts can be estimated when the following assumptions are made:

1. a_{AlCl_3} in $\text{MCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ systems can be estimated from the equilibrium constant of eqn. (14) and the activity coefficients of MCl and MAlCl_4 given by eqns. (12) and (13).¹⁴
2. $\gamma_{\text{AlCl}_3\text{NH}_3}$ is set equal to 2.

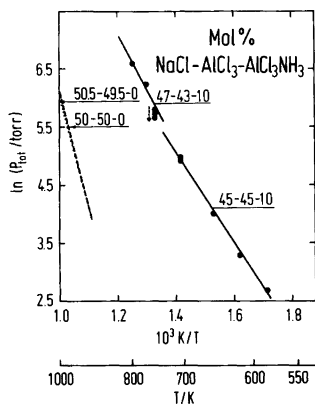


Fig. 1. Vapour pressure above $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts. ○: Present work, arrow indicates vapour pressure decrease with time for the basic melt. ----: Linga *et al.*¹⁴: Dewing¹⁶.

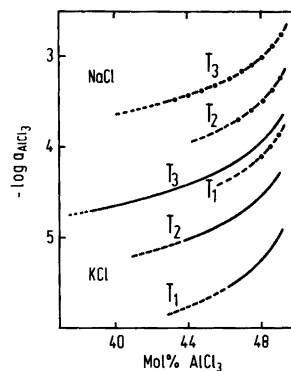


Fig. 2. Calculated activity of AlCl_3 in $\text{MCl}-\text{AlCl}_3$ melts. $\text{M}=\text{Na}$ or K . T_1, T_2, T_3 : 450, 525, 600 °C.

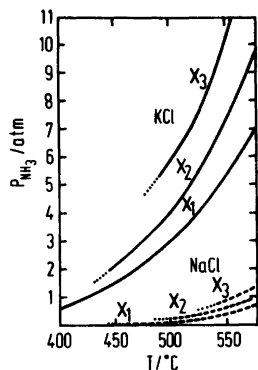
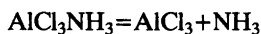


Fig. 3. Estimated vapour pressure of NH_3 above $\text{MCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts. $\text{M}=\text{Na}$ or K . X_1, X_2, X_3 : $X_{\text{AlCl}_3}^\circ=0.475, 0.465, 0.450$.

The partial pressure of $\text{NH}_3(\text{g})$ above $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ and $\text{KCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts containing 3 mol % AlCl_3NH_3 is shown as function of temperature in Fig. 3. In the calculation, X_{AlCl_3} is calculated from the content of AlCl_3 and MCl in the melt. Recently, the presence of $\text{Al}_2\text{Cl}_6\text{NH}_3$ has been detected in acidic $\text{KCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts where equilibrium (8) is established.² As the activity of Al_2Cl_6 is very low, the mole fraction of $\text{Al}_2\text{Cl}_6\text{NH}_3$ is negligible for the present melts. Dotted lines indicate extrapolation below the liquidus temperature. P_{NH_3} increases with increasing temperature, due to the fact that the increase in the equilibrium constant K_{10} overrules the effect of the increasing AlCl_3 - activity. The partial pressure of $\text{NH}_3(\text{g})$ also increases with decreasing AlCl_3 content. Due to a 10 times lower AlCl_3 activity in KCl - than in NaCl - mixtures, the partial pressure of $\text{NH}_3(\text{g})$ is 10 times higher above $\text{KCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ than above $\text{NaCl}-\text{AlCl}_3-\text{AlCl}_3\text{NH}_3$ melts. Again, this reflects that the basic $\text{KCl}-\text{AlCl}_3$ melts will be more effective as solvents for the decomposition of AlCl_3NH_3 than the LiCl and NaCl chloroaluminate mixtures.

4.4. Concluding remarks. The experiments have shown that it is possible to decompose AlCl_3NH_3 dissolved in chloroaluminate melts through the reaction



when NH_3 is removed by absorption in $\text{NiCl}_2(\text{s})$. In basic $\text{NaCl}-\text{AlCl}_3$ mixtures, less than 10 % AlCl_3NH_3 is decomposed, whereas 70 % was decomposed in the corresponding $\text{KCl}-\text{AlCl}_3$ melts due to the low activity of AlCl_3 . The degree of decomposition and the formation of $\text{AlN}(\text{s})$ increase with increasing temperature.

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