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The ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$. Isotherms at −25, −20, −18.2, −10 and 0°C and spatial diagram up to 0°C

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Abstract

A study of the solid–liquid equilibria in the ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$ has been undertaken in order to find an invariant transformation at low temperature.

Five isothermal sections have been established under atmospheric pressure at −25, −20, −18.2, −10 and 0°C. The solid phases observed at these temperatures are: at −25 and −20°C, ice, NH_4NO_3(V) and $Al(NO_3)_3 \cdot 9H_2O$; at −18.2°C, ice, NH_4NO_3(IV) and $Al(NO_3)_3 \cdot 9H_2O$; at −10°C, ice, NH_4NO_3(IV), $Al(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 8H_2O$; at 0°C, NH_4NO_3(IV), $Al(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 8H_2O$.

The X-ray diffraction pattern of the octahydrated aluminium nitrate has been established. The spatial diagram shows four isobaric invariant transformations whose temperatures have been specified by thermal analysis. They correspond to the reactions:

At −33.6°C, $\text{liquid} \rightleftharpoons \text{ice} + NH_4NO_3(V) + Al(NO_3)_3 \cdot 9H_2O$

At −18.6°C, $\text{liquid} + NH_4NO_3(IV) \rightleftharpoons \text{ice} + NH_4NO_3(V)$

$\text{liquid} + NH_4NO_3(IV) \rightleftharpoons NH_4NO_3(V) + Al(NO_3)_3 \cdot 9H_2O$

At −12.3°C, $\text{liquid} + Al(NO_3)_3 \cdot 8H_2O \rightleftharpoons NH_4NO_3(IV) + Al(NO_3)_3 \cdot 9H_2O$

Keywords: Energy storage; Isothermal; SLE; Ternary system

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1. Introduction

Heat energy storage is of great interest in many fields of everyday life and industrial activity, including habitat, agriculture, isothermal transport, food-stuff conservation etc.

Phase change materials are generally used to absorb or evolve heat energy. Their choice depends on their characteristics and must allow for cost, non-toxicity, and chemical and mechanical compatibility with the enclosure. Other constraints must also be fulfilled, in particular the heat storage amount per unit mass, reproducible phenomena during thermal cycles and a well-defined temperature of the transformation.

In this work, we were seeking a stable invariant transformation at about −33°C which might meet these requirements. Following a great number of preliminary investigations, the ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$ was studied at low temperature.

2. Bibliographical analysis

This ternary system has never been described although there have been many reports in the literature about the binary systems water–ammonium nitrate and water–aluminium nitrate. In the first system (Fig. 1), the solid–liquid equilibria are combined with polymorphism phenomena. Seven allotropic forms of ammonium nitrate, labeled (I)–(VII), have been listed but the variety (VI) is stable only from pressures higher than one GPa. Table 1 reports the normal transition temperatures

Table 1
Transition temperatures of ammonium nitrate in °C

VII → V	V → IV	IV → III	IV → II	III → II	II → I	I → liq.	Ref.
	−18	32.3	50	84.2	125.2		[6]
		32.1		84.2	125.2	169.6	[7]
	−18	32.3	50	84.2	125.2	169.5	[8]
	−16	32.1		84.2	125.2	169	[9]
−170	−16.95	32.25					[10]
		32	50	84.5	125	169	[11]
	−18	32.1					[12]
	−18	32.2		84.2			[13]
				84.2			[14]
		32.5		84	125		[15]
		32.1		84.2	125.2	169.6	[16]
	−10.4 ± 6.3	32.1 ± 3.5		84.0 ± 0.1	125.9 ± 0.1		[17]
				82	125		[18]
		32		85	125	170	[19]
	−16.6 ± 1	32.5 ± 0.05		82.26 ± 0.10	125.20 ± 0.06		[20]
		32.7 ± 0.2		83.9 ± 0.2	125.4 ± 0.2		[20]

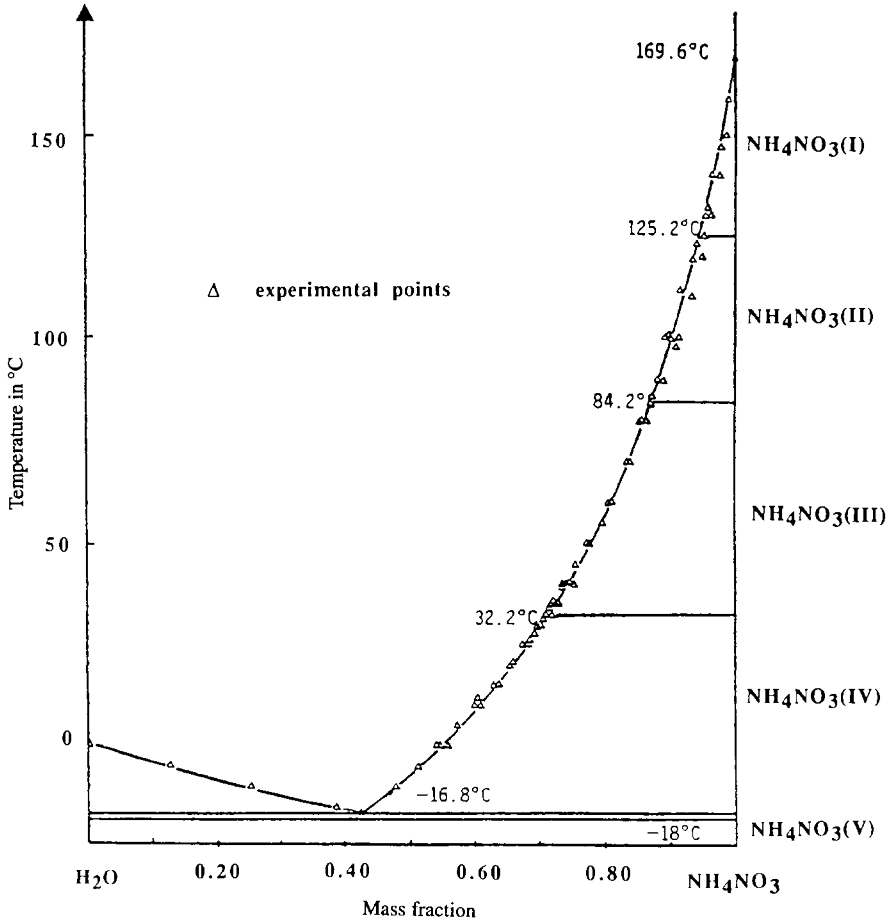

Fig. 1. The binary system H_2O–NH_4NO_3.

determined by different authors. The results relating to the first four crystalline states are in good agreement and the metastable transition (II→IV) is even observed in a reproducible way under particular conditions. The temperature of the transition (IV→V) is rather variable owing to the slow kinetics of the phase transformation.

Fig. 2 shows the solid–liquid equilibria in the binary system H_2O–$Al(NO_3)_3$, established up to 130°C. Four intermediate compounds are indicated in the diagram: the nona-, octa-, hexa- and tetrahydrate of aluminium nitrate. In contrast with the liquidus curve of ice which is well defined, the curves connected with the different hydrates of aluminium nitrate have been poorly determined, so that the nature of the equilibrium is sometimes ambiguous.

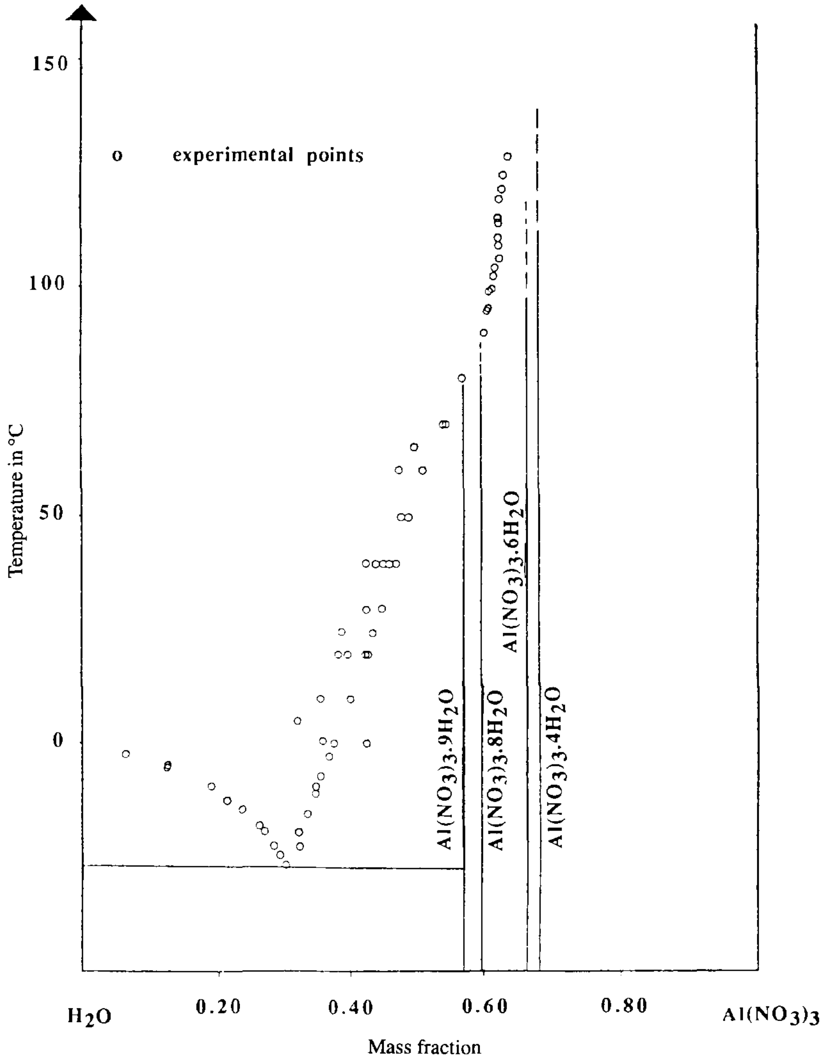

Fig. 2. The binary system H_2O–$Al(NO_3)_3$.

3. Experimental

The isothermal sections of the ternary system have been determined under constant pressure using a conductimetric analysis of the solution; this has been fully described in previous papers [1–3]. Briefly, the method plots the resistivity of the liquid against the volume of a known chemical composition solution added to a salt mixture. The curves present breaks at each phase change and a constant value of resistivity is observed when an invariant equilibrium is analysed. The exploitation of these results permits the nature of the solid phases and their existence fields to be determined.

The thermal analysis of the ternary mixtures was carried out in a constant flow enthalpimeter, built in this laboratory and further described in Ref. [4]. When no phase transformation occurs, the temperature varies linearly on heating or cooling. A simple change of phase involves a break in the temperature versus time curve and when an invariant phenomenon appears the temperature remains constant during a time proportional to the enthalpy of the transformation. The apparatus permits a good determination of the phenomenon temperatures as well as an excellent reproducibility of results and a high separative power.

The purity of the compounds (Prolabo RP) was higher than 98.5%. The solid phases were systematically checked by quantitative chemical analysis. The aluminium ion concentration was determined by plasma spectrometry using a Beckman Spectraspan IV spectrometer (emission line wavelength, 236.705 nm) and the nitrate ion concentration was measured by UV spectrometry in a Cary 15 spectrometer (aqueous solutions of NO_3^- give an absorption band with a maximum at 203 nm).

The accuracy of the results was about 0.2%. Water was twice-distilled before use. X-ray diffraction patterns of the solid compounds were established using a Diffrac 11 diffractometer.

4. Results

The solid–solid equilibria of the ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$ were studied at five temperatures using a conductimetric analysis of the solution.

Table 2
The ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$: isotherm −25°C

Global composition Mass fractions		Nature of the phase change
$Al(NO_3)_3$	NH_4NO_3	
0.2303	0.1158	Ice + liquid/liquid
0.2589	0.0587	Ice + liquid/liquid
0.2854	0	Ice + liquid/liquid
0.2471	0.1312	NH_4NO_3(V) + liquid/liquid
0.2871	0.1158	NH_4NO_3(V) + liquid/liquid
0.2616	0.1945	NH_4NO_3(V) + liquid/$Al(NO_3)_3 \cdot 9H_2O$ + NH_4NO_3(V) + liquid
0.2028	0.0950	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3126	0	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3050	0.1082	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ + liquid

Complementary measurements were undertaken using thermal analysis to clarify the monovariant curves and to define the invariant point co-ordinates under atmospheric pressure.

4.1. Isothermal sections

The isotherms at −25 and −20°C are similar and three crystallization fields are observed, corresponding to ice, NH_4NO_3(V) and $Al(NO_3)_3 \cdot 9H_2O$. Fig. 3 shows,

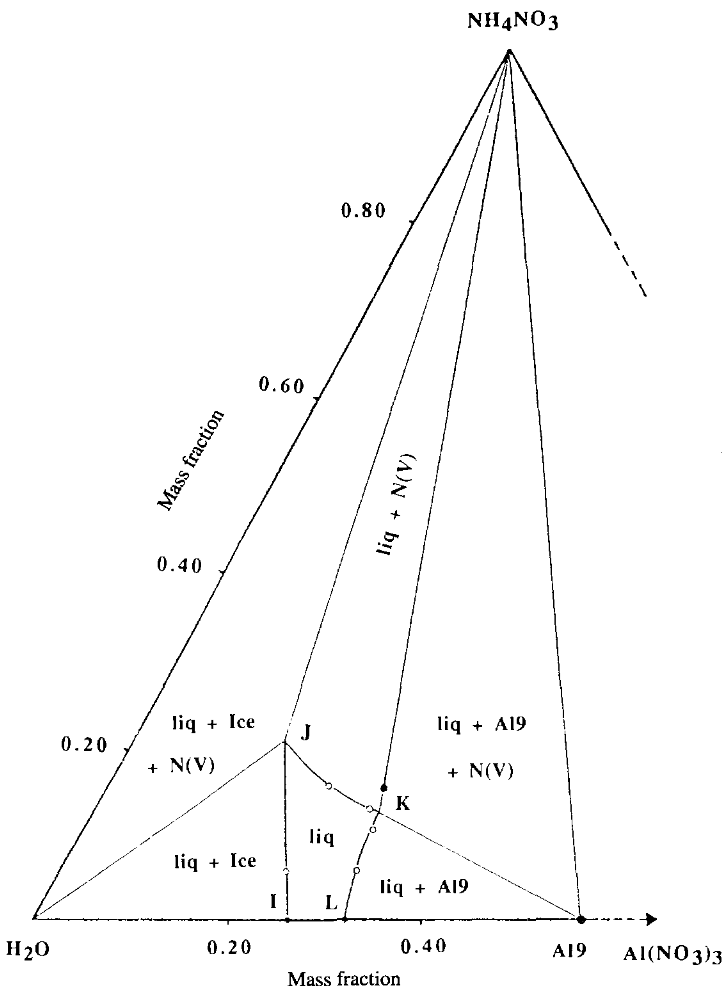

Fig. 3. The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$; isotherm −20°C. N(V), NH_4NO_3(V); Al9, $Al(NO_3)_3 \cdot 9H_2O$; liq, liquid.

Table 3
The ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$: isotherm −20°C

Global composition Mass fractions		Nature of the phase change
$Al(NO_3)_3$	NH_4NO_3	
0.2331	0.0599	Ice + liquid/liquid
0.2633	0	Ice + liquid/liquid
0.2277	0.1645	NH_4NO_3(V) + liquid/liquid
0.2841	0.1347	NH_4NO_3(V) + liquid/liquid
0.2842	0.1562	NH_4NO_3(V) + liquid/$Al(NO_3)_3 \cdot 9H_2O$ + NH_4NO_3(V) + liquid
0.3001	0.1097	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3086	0.0599	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3229	0	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid

as an example, the isotherm at −20°C. Three liquidus curves, which intersect at the single points J and K, are established. The chemical composition of each point was determined either by extrapolation from the liquidus curves or by intersection of the three-phase equilibrium triangle sides. The numerical values are collected in Tables 2 and 3.

The transition temperature of the ammonium nitrate crystalline forms (IV) and (V) is about −18°C, from literature data. A study of adjacent temperatures might provide some information about the precipitation surfaces of these two varieties.

The isotherm at −18.2°C (Fig. 4) does, in fact, show as indicated by X-ray diffraction, a crystallization field of ammonium nitrate (IV), in contrast to what was observed at −20°C, Table 4 presents the experimental results.

Table 4
The ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$: isotherm −18.2°C

Global composition Mass fractions		Nature of the phase change
$Al(NO_3)_3$	NH_4NO_3	
0.1247	0.2380	Ice + liquid/liquid
0.1883	0.1198	Ice + liquid/liquid
0.2517	0	Ice + liquid/liquid
0.1334	0.2546	NH_4NO_3(IV) + liquid/liquid
0.2841	0.1440	NH_4NO_3(IV) + liquid/liquid
0.2841	0.1769	NH_4NO_3(IV) + liquid/$Al(NO_3)_3 \cdot 9H_2O$ + NH_4NO_3(IV) + liquid
0.3001	0.1199	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3081	0.845	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3294	0	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3215	0.1199	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 9H_2O$ + liquid

Table 5
The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: isotherm −10°C

Global composition Mass fractions		Nature of the phase change
$Al(NO_3)_3$	NH_4NO_3	
0	0.2512	Ice + liquid/liquid
0.1824	0	Ice + liquid/liquid
0	0.4710	NH_4NO_3(IV) + liquid/liquid
0.2444	0.1999	NH_4NO_3(IV) + liquid/liquid
0.2518	0.1935	NH_4NO_3(IV) + liquid/liquid
0.2841	0.1662	$Al(NO_3)_3 \cdot 8H_2O$ + liquid/liquid
0.2913	0.1598	$Al(NO_3)_3 \cdot 8H_2O$ + liquid/liquid
0.2976	0.1494	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3236	0.0803	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3423	0	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid

Table 6
The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: isotherm 0°C

Global composition Mass fractions		Nature of the phase change
$Al(NO_3)_3$	NH_4NO_3	
0	0.5499	NH_4NO_3(IV) + liquid/liquid
0.1365	0.3607	NH_4NO_3(IV) + liquid/liquid
0.1996	0.2877	NH_4NO_3(IV) + liquid/liquid
0.2445	0.2475	NH_4NO_3(IV) + liquid/liquid
0.2682	0.2274	NH_4NO_3(IV) + liquid/liquid
0.2852	0.2153	NH_4NO_3(IV) + liquid/liquid
0.2966	0.1911	$Al(NO_3)_3 \cdot 8H_2O$ + liquid/liquid
0.3102	0.1544	$Al(NO_3)_3 \cdot 8H_2O$ + liquid/liquid
0.3148	0.1386	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3344	0.0841	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid
0.3548	0	$Al(NO_3)_3 \cdot 9H_2O$ + liquid/liquid

Table 7
The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: hydration number determination of the octahydrated aluminium nitrate at 0°C

Mixture	Mass fractions		Solid phase	Mass fraction		*n* value excess	*n* value default
	$Al(NO_3)_3$	NH_4NO_3		$Al(NO_3)_3$	NH_4NO_3		
M_1	0.3499	0.1250	R_1	0.5695	0.0234	8.29	7.28
M_2	0.3469	0.1533	R_2	0.3730	0.0172	8.34	7.83

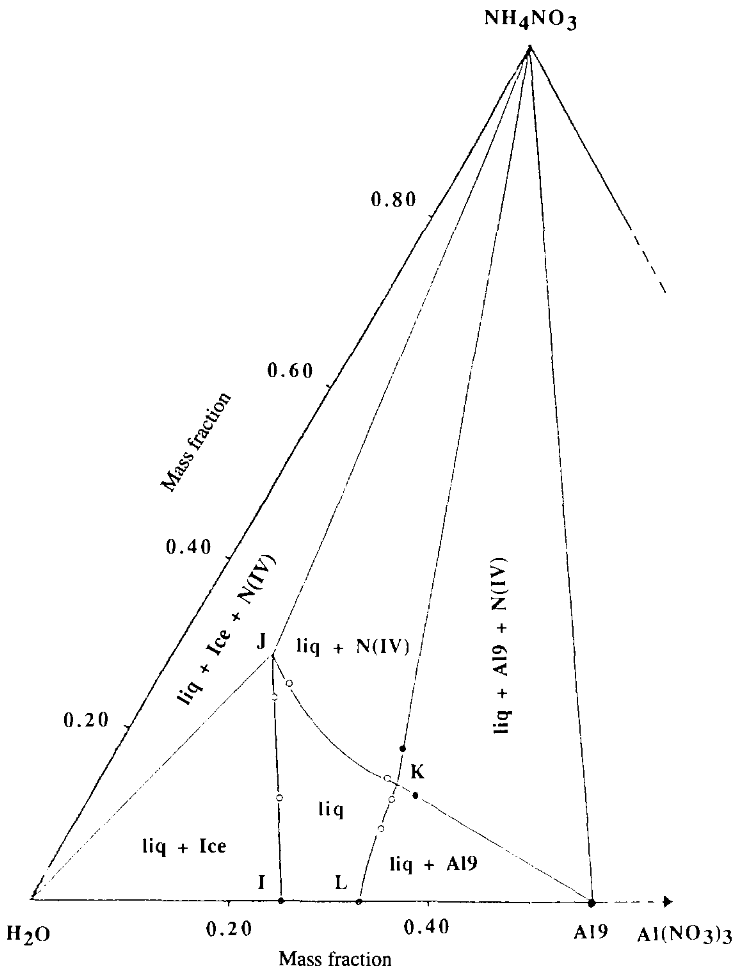

Fig. 4. The ternary system $H_2O-NH_4NO_3-Al(NO_3)_3$; isotherm −18.2°C. N(IV), NH_4NO_3(IV); Al9, $Al(NO_3)_3 \cdot 9H_2O$; liq, liquid.

Two other isothermal sections at −10 and 0°C are plotted respectively in Figs. 5 and 6, the experimental data being listed in Tables 5 and 6. At these two temperatures a new solid phase, the octahydrate of aluminium nitrate, appears in stable equilibrium with the liquid phase.

The hydration number of this compound *n* was determined by quantitative chemical analysis. Two mixtures M_1 and M_2 (Fig. 6) were kept for a week at 0°C under constant stirring. Limited heatings were carried out in order to evaporate slowly the saturated solution so as to form sufficiently massive crystals. Needle-shaped crystals R_1 and R_2 were obtained in this way. After extraction from the mother liquor, they were dried on filter paper. The amount of nitrate and alu-

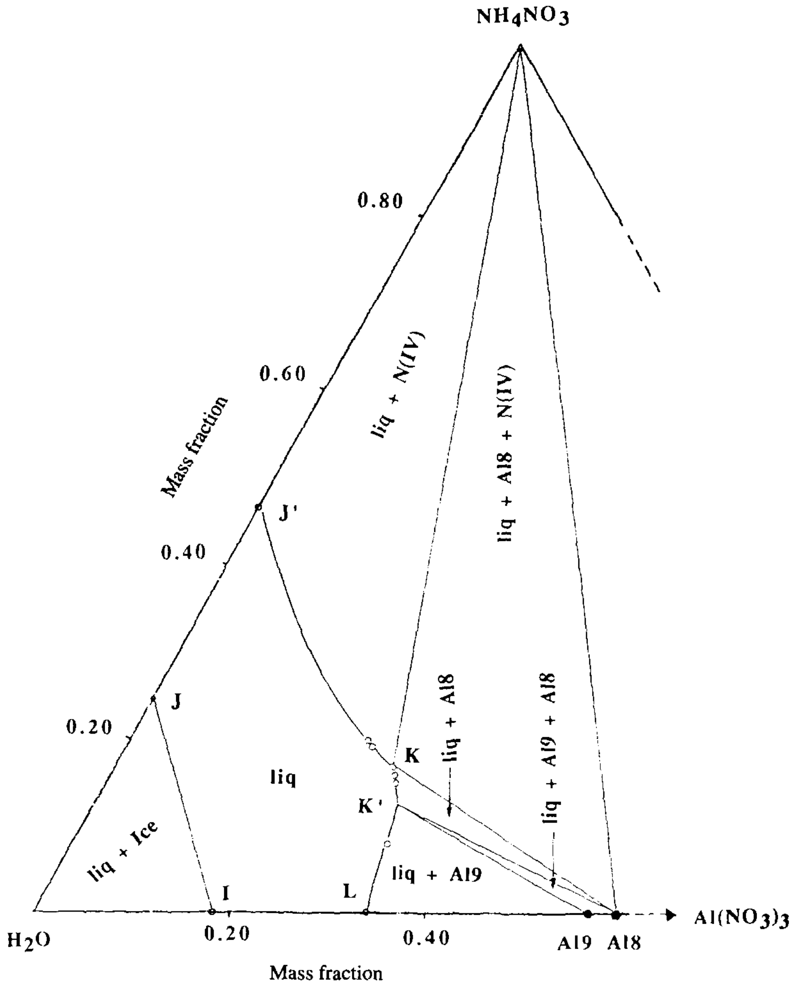

Fig. 5. The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: isotherm −10°C. N(IV), NH_4NO_3(IV); Al9, $Al(NO_3)_3 \cdot 9H_2O$; Al8, $Al(NO_3)_3 \cdot 8H_2O$; liq, liquid.

minium ions, assuming that the solid phase was exclusively a mixture of NH_4NO_3 and $Al(NO_3)_3 \cdot nH_2O$, yielded an n value by excess. However, if the dried crystals were lightly impregnated with mother liquor, the analysis yielded n by default.

The results, see Table 7, are in good agreement according to one or the other assumption, and yield the formula $Al(NO_3)_3 \cdot 8H_2O$. Furthermore, this is corroborated by the morphological appearance of the crystals, previously described by Inamura [5]. Finally, the X-ray diffraction pattern of this compound has been established (Table 8) and is compared with those of NH_4NO_3(IV) and $Al(NO_3)_3 \cdot 9H_2O$ in Fig. 7.

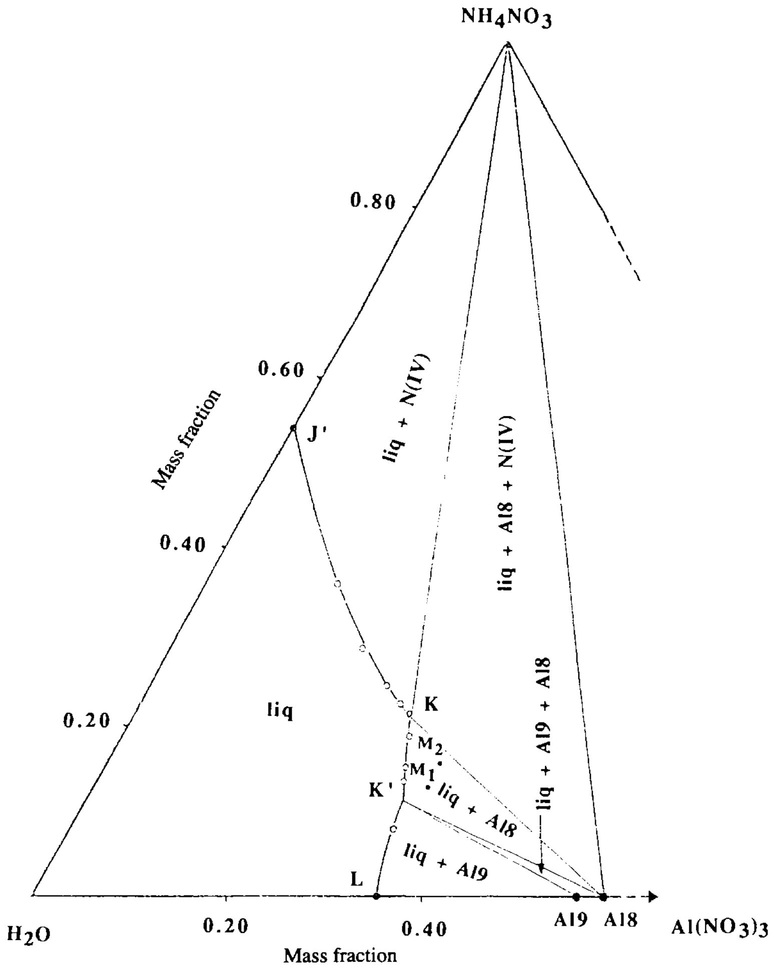

Fig. 6. The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: isotherm 0°C. N(IV), NH_4NO_3(IV); Al9, $Al(NO_3)_3 \cdot 9H_2O$; Al8, $Al(NO_3)_3 \cdot 8H_2O$; liq, liquid.

4.2. Spatial diagram

Four samples (A, B, C and D) were subjected to thermal analysis in a constant flow enthalpimeter. The results, presented in Table 9, suggest four invariant transformations in the ternary system:

(a) A eutectic transformation E at −33.6°C relating to the equilibrium

$$\text{Liquid E} \rightleftharpoons \text{ice} + NH_4NO_3(V) + Al(NO_3)_3 \cdot 9H_2O$$

(b) A transitory transformation T_3 at −12.3°C, relating to the reaction

$$Al(NO_3)_3 \cdot 8H_2O + \text{liquid } T_3 \rightleftharpoons NH_4NO_3(IV) + Al(NO_3)_3 \cdot 9H_2O$$

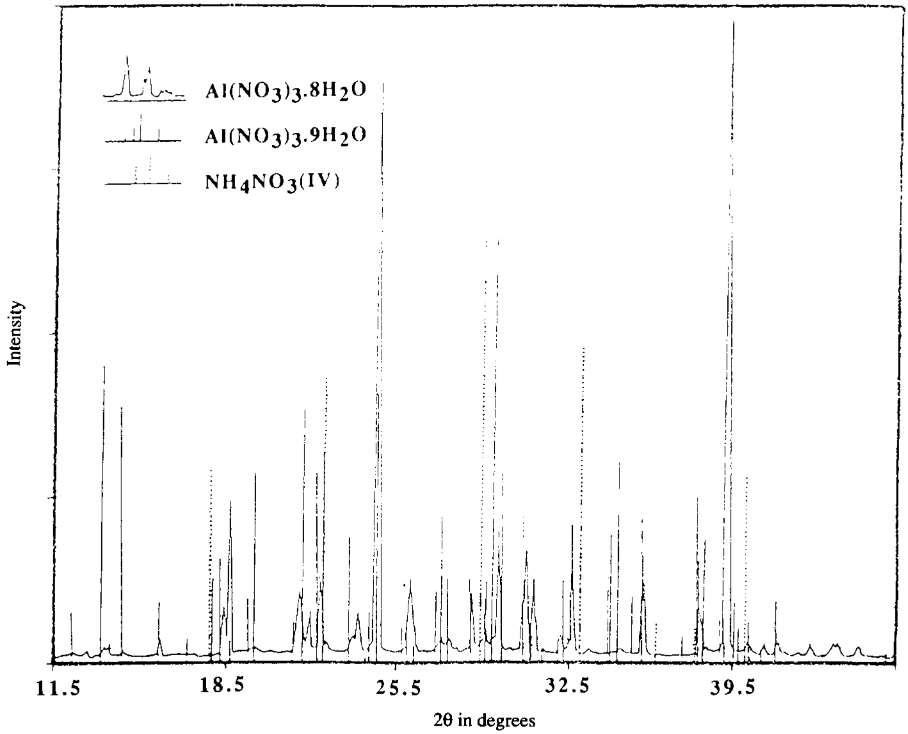

Fig. 7. The X-ray diffraction pattern of $Al(NO_3)_3 \cdot 8H_2O$ and its comparison with those of NH_4NO_3(IV) and $Al(NO_3)_3 \cdot 9H_2O$.

(c) Two transformations T_1 and T_2, related to the thermodynamic equilibrium between varieties (IV) and (V) of ammonium nitrate, at −18.6°C. With regard to the invariant liquids, each of them is a limiting case of a peritectic or transitory transformation. By cooling, the corresponding reactions may be written as

$$NH_4NO_3(IV) + \text{liquid } T_1 \rightleftharpoons \text{ice} + NH_4NO_3(V)$$

$$NH_4NO_3(IV) + \text{liquid } T_2 \rightleftharpoons NH_4NO_3(V) + Al(NO_3)_3 \cdot 9H_2O$$

The co-ordinates of the three-phase equilibrium points are reported in Table 10 and Table 11 gives the characteristics of ternary isobaric invariants.

Fig. 8 shows the monovariant curves projected down upon the composition plane. Five liquidus sheets are so defined; they agree with the precipitation fields of ice, NH_4NO_3(V), NH_4NO_3(IV), $Al(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 8H_2O$.

Fig. 9 shows a perspective drawing of the ternary system under constant pressure up to 0°C, in which are plotted dotted curves corresponding to the experimental isothermal sections.

Table 8
X-ray diffraction pattern of $Al(NO_3)_3 \cdot 8H_2O$

d/nm	I/I_0	d/nm	I/I_0
0.7178	1.2	0.3030	0.7
0.6897	0.6	0.3011	16.3
0.6529	1.1	0.2961	0.7
0.6426	1.3	0.2901	17.9
0.6193	1.2	0.2869	5.8
0.5582	2.1	0.2834	0.7
0.4797	8.5	0.2778	4.0
0.4743	14.9	0.2749	1.8
0.4503	1.4	0.2736	9.2
0.4111	13.0	0.2519	12.8
0.4047	4.0	0.2366	3.4
0.3966	8.1	0.2346	0.8
0.3747	2.5	0.2296	100.0
0.3711	5.1	0.2246	1.8
0.3598	66.1	0.2211	1.3
0.3411	14.8	0.2183	2.3
0.3270	1.9	0.2115	2.0
0.3227	2.3	0.2077	0.9
0.3214	0.8	0.2068	1.1
0.3187	0.9	0.2057	1.0
0.3114	6.3	0.2024	1.1
0.3069	5.4		

5. Conclusion

The isotherms at −25, −20, −18.2, −10 and 0°C of the ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$ have been entirely established. The nature of the solid phases which appear in the diagram has been defined without ambiguity and the crystallization fields have been well demarcated in the studied temperature interval.

The octahydrated aluminium nitrate in stable equilibrium with the liquid phase at −10 and 0°C has been isolated and its X-ray diffraction pattern determined. The hydration number has been confirmed by a spectrometrical analysis of the aluminium and nitrate ions.

Five solid phases have been found to occur at temperatures below 0°C: ice, NH_4NO_3(V), NH_4NO_3(IV), $Al(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 8H_2O$.

The temperatures of the invariant transformations under atmospheric pressure have been precisely measured by direct thermal analysis. The four corresponding reactions are

At −33.6°C, liquid $\rightleftharpoons$ ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$

Table 9
The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$: constant flow thermal analysis by heating

Mass fractions		Temp./°C	Nature of phenomena
$Al(NO_3)_3$	NH_4NO_3		
0.3752	0.0250	−33.7	Ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ → ice + $Al(NO_3)_3 \cdot 9H_2O$ + liquid E
(Point A)		−31.3	Ice + $Al(NO_3)_3 \cdot 9H_2O$ + liquid → $Al(NO_3)_3 \cdot 9H_2O$ + liquid
0.2238	0.0250	−33.7	Ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ → ice + $Al(NO_3)_3 \cdot 9H_2O$ + liquid E
(Point B)		−31.3	Ice + $Al(NO_3)_3 \cdot 9H_2O$ + liquid → ice + liquid
		−16.0	Ice + liquid → liquid
0.1001	0.2997	33.6	Ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ → ice + NH_4NO_3(V) + liquid E
(Point C)		−18.8	Ice + NH_4NO_3(V) + liquid → ice + NH_4NO_3(IV) + liquid T_1
		−16.7	Ice + NH_4NO_3(IV) + liquid → NH_4NO_3(IV) + liquid
0.3361	0.2173	−33.6	Ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ → ice + NH_4NO_3(V) + liquid E
(Point D)		−18.6	NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$ + liquid → $Al(NO_3)_3 \cdot 9H_2O$ + NH_4NO_3(IV) + liquid T_2
		−12.3	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 9H_2O$ + liquid → NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 8H_2O$ + liquid T_3
		11.5	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 8H_2O$ + liquid → $Al(NO_3)_3 \cdot 8H_2O$ + liquid

Table 10
Monovariant solid–liquid equilibria in the ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$

Monovariant lines	Temp./°C	Mass fractions		Solid phases in equilibrium
		$Al(NO_3)_3$	NH_4NO_3	
e_1T_1	−16.6	0	0.4240	Ice + NH_4NO_3(IV)
	−18.2	0.0971	0.2910	Ice + NH_4NO_3(IV)
ET_1	−20.0	0.1560	0.2120	Ice + NH_4NO_3(V)
	−25.0	0.2129	0.1520	Ice + NH_4NO_3(V)
e_2E	−31.3	0.294	0.036	Ice + $Al(NO_3)_3 \cdot 9H_2O$
	−29.9	0.3045 [a]	0 [a]	Ice + $Al(NO_3)_3 \cdot 9H_2O$
ET_2	−25.0	0.2910	0.1136	NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$
	−20.0	0.2967	0.1288	NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$
T_2T_3	−18.2	0.2981	0.1350	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 9H_2O$
PT_3	−10.0	0.3132	0.1260	$Al(NO_3)_3 \cdot 9H_2O$ + $Al(NO_3)_3 \cdot 8H_2O$
	0.0	0.3232	0.1184	$Al(NO_3)_3 \cdot 9H_2O$ + $Al(NO_3)_3 \cdot 8H_2O$
	73.5	0.49 [a]	0 [a]	$Al(NO_3)_3 \cdot 9H_2O$ + $Al(NO_3)_3 \cdot 8H_2O$
T_3K'	−10.0	0.2872	0.1684	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 8H_2O$
	0.0	0.2912	0.2096	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 8H_2O$
	11.5	0.322	0.24	NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 8H_2O$

[a] Literature values.

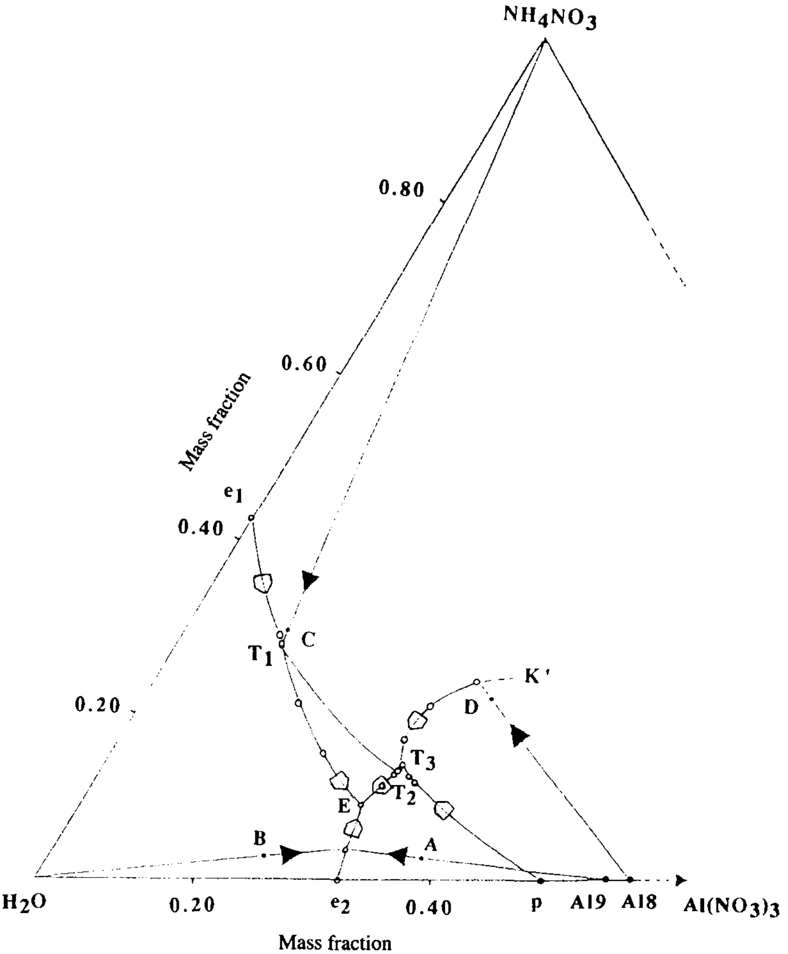

Fig. 8. The ternary system H_2O–NH_4NO_3–$AL(NO_3)_3$: polythermal projection on the composition plane. N(V), NH_4NO_3(V); N(IV), NH_4NO_3(IV); Al9, $Al(NO_3)_3 \cdot 9H_2O$; Al8, $Al(NO_3)_3 \cdot 8H_2O$.

Table 11
Invariant points of the ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$

Temp./°C	Mass fractions		Invariant reactions
	$Al(NO_3)_3$	NH_4NO_3	
−33.6	0.2816	0.0910	Liquid E → ice + NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$
−18.8	0.1040	0.2800	NH_4NO_3(IV) + liquid T_1 → NH_4NO_3(V) + ice
−12.3	0.3000	0.1392	$Al(NO_3)_3 \cdot 8H_2O$ + liquid T_3 → NH_4NO_3(IV) + $Al(NO_3)_3 \cdot 9H_2O$
−18.8	0.2990	0.1370	NH_4NO_3(IV) + liquid T_2 → NH_4NO_3(V) + $Al(NO_3)_3 \cdot 9H_2O$

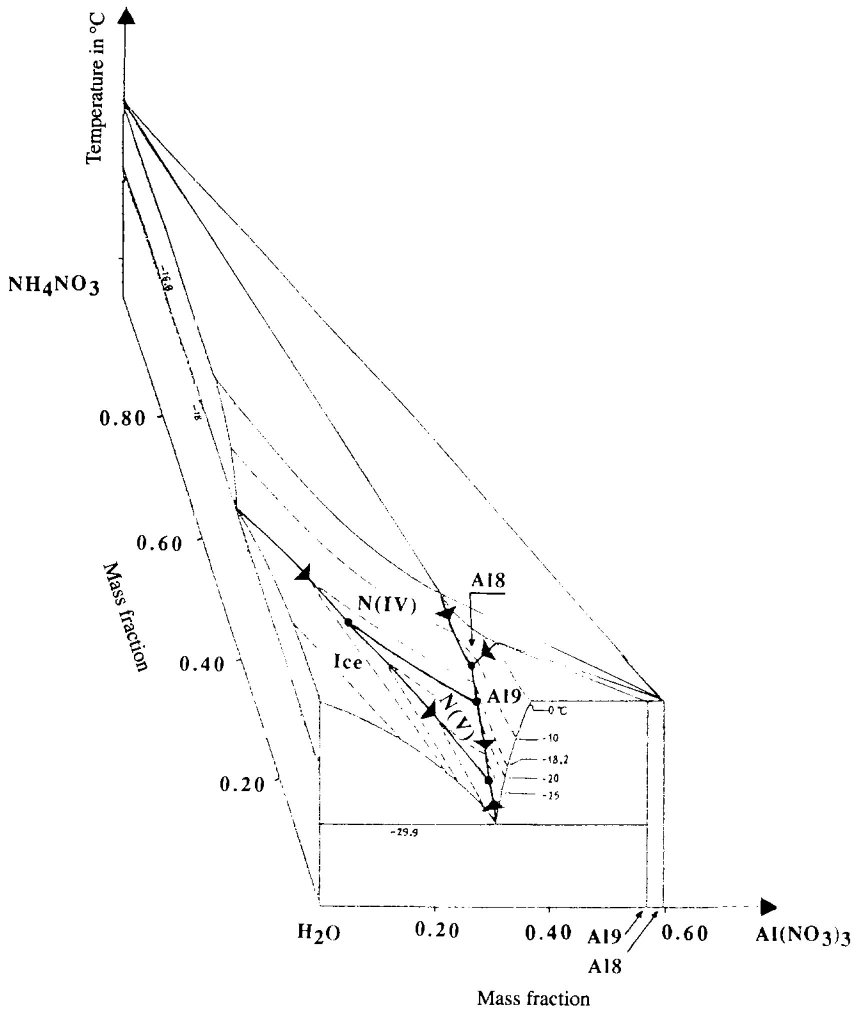

Fig. 9. The ternary system H_2O–NH_4NO_3–$Al(NO_3)_3$; perspective view. N(V), NH_4NO_3(V); N(IV), NH_4NO_3(IV); Al9, $Al(NO_3)_3 \cdot 9H_2O$; Al8, $Al(NO_3)_3 \cdot 8H_2O$.

At −18.6°C, $NH_4NO_3(IV) + \text{liquid} \rightleftharpoons \text{ice} + NH_4NO_3(V)$

$NH_4NO_3(IV) + \text{liquid} \rightleftharpoons NH_4NO_3(V) + Al(NO_3)_3 \cdot 9H_2O$

At −12.6°C, $Al(NO_3)_3 \cdot 8H_2O + \text{liquid} \rightleftharpoons NH_4NO_3(IV) + Al(NO_3)_3 \cdot 9H_2O$

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