57. *Liquidus and Solidus Studies. Part II. The Ternary System* KNO_3–NH_4NO_3–$Pb(NO_3)_2$.

By H. M. GLASS, K. LAYBOURN, and W. M. MADGIN.

STUDYING the system potassium nitrate–ammonium nitrate, Perman and Saunders (J., 1923, **123**, 841) found a mixture of minimum f. p. (13·6% KNO_3 by weight); they examined solids separating from various mixtures, and stated: "By analysis the crystals separating have been shown to be ammonium nitrate below 13·6% potassium nitrate, and a little above that concentration mixed crystals of the two nitrates with about 45% of the potassium salt." Such a system seems remarkable in showing complete solid immiscibility in mixtures rich in ammonium nitrate (55—100%), although the two component salts are isomorphous.

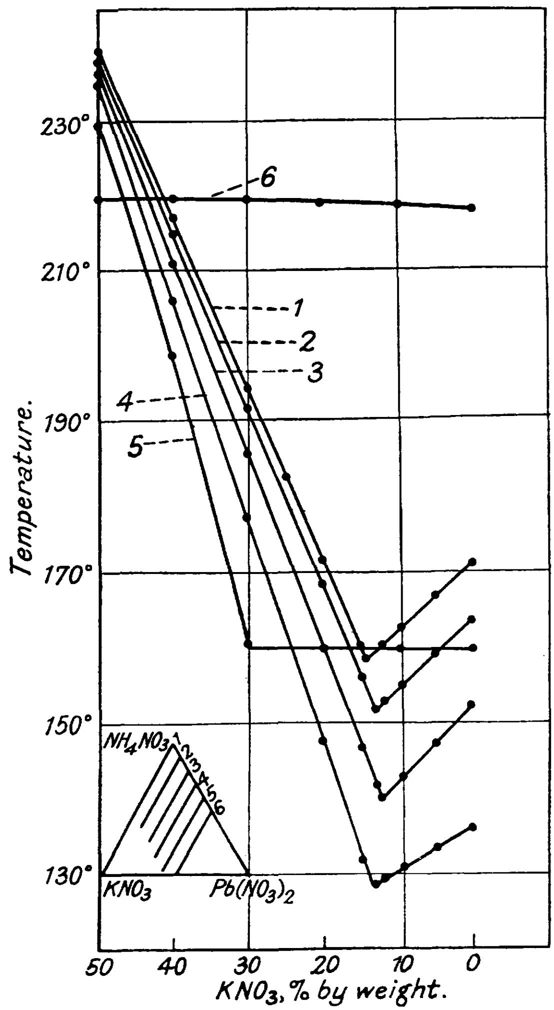
Jänecke (*Z. angew. Chem.*, 1928, **41**, 916) found that the system showed partial solid miscibility, with a large miscibility gap between 92·5% and 1·5% ammonium nitrate, but later Jänecke, Hamacher, and Rahlfs (*Z. anorg. Chem.*, 1932, **206**, 357) concluded that the extent of solid miscibility is much greater, their limits being 92% and 60% ammonium nitrate.

The conclusions of all of the foregoing authors were formed from the study of binary systems.

Recently, Laybourn and Madgin (J., 1932, 2582) investigated the system potassium nitrate–sodium nitrate by studying a ternary system involving these salts, and this method seemed applicable to the system potassium nitrate–ammonium nitrate; accordingly, the ternary system of this salt pair in lead nitrate has been investigated. Lead nitrate was chosen as the third component since it appears to be inert towards both potassium nitrate (Glass, Laybourn, and Madgin, J., 1932, 874) and ammonium nitrate (Bogitsch, *Compt. rend.*, 1915, **161**, 790), and is thus a suitable solvent.

FIG. 1.

Freezing point–composition diagrams for the system KNO_3–NH_4NO_3–$Pb(NO_3)_2$.



Contents (%) *of* $Pb(NO_3)_2$.
Graph No. 1, 0; *No.* 2, 10; *No.* 3, 20; *No.* 4, 30; *No.* 5, 40; *No.* 6, 50.

EXPERIMENTAL.

Purification of KNO_3 and $Pb(NO_3)_2$ was carried out as previously described (*loc. cit.*). NH_4NO_3 (A.R. quality) was recryst. thrice from H_2O and dried in an air-oven at 120°.

The scope of the present investigation is limited by the volatility of NH_4NO_3, but as this is considerably diminished by dilution with other nitrates (cf. Bogitsch, *loc. cit.*), it was possible to investigate ternary mixtures of f. p. up to 250°. Below this temp., the decomp. of $Pb(NO_3)_2$ (Laybourn and Madgin, J., 1932, 1360) need not be considered.

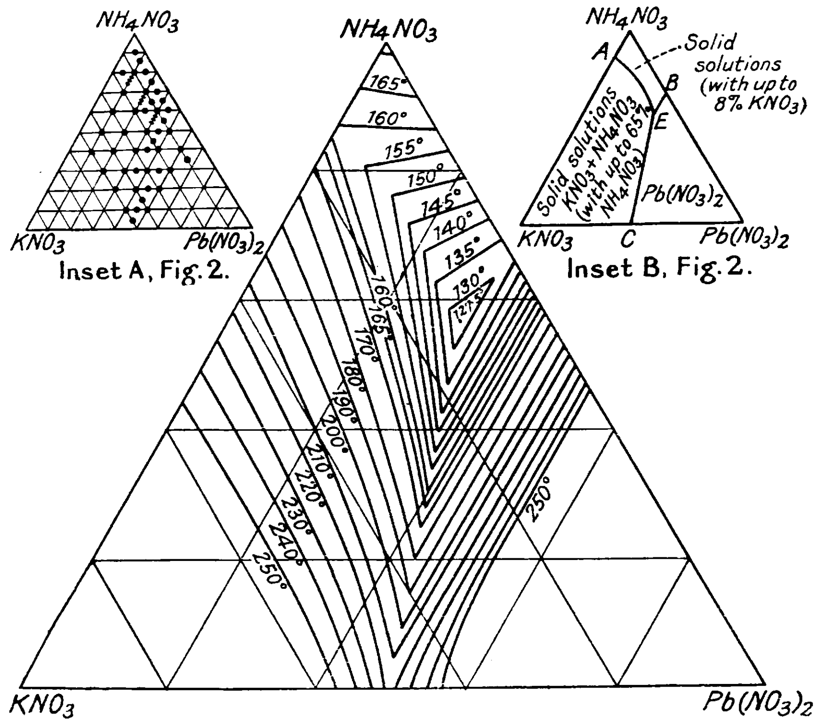
The f. p. data for the three binary systems were required: results previously determined for KNO_3–$Pb(NO_3)_2$ (*loc. cit.*) have been used, but redeterminations have been made for the other two systems.

Freezing Points and Isotherms for Ternary Mixtures.—The f. p.'s of 64 different ternary mixtures (see inset A, Fig. 2) have been found as described by Laybourn and Madgin (J., 1932, 2582) and the isothermal diagram has been constructed (Fig. 2). Fig. 1 shows a series of curves, representing the f. p.'s of mixtures containing various const. percentages of $Pb(NO_3)_2$, and is included as additional evidence of the nature of the system KNO_3–NH_4NO_3.

The comp. of the mixture of lowest f. p. was found to be 12% KNO_3, 32% $Pb(NO_3)_2$, and 56% NH_4NO_3 (f. p. 127·5°).

FIG. 2.

Freezing-point isotherms in the ternary system KNO_3–NH_4NO_3–$Pb(NO_3)_2$.



Examination of Solid Phases.—Samples of the solid phases separating from mixtures lying on the isothermals 150°, 160°, and 190° were isolated by the method of Laybourn and Madgin (*loc. cit.*), and samples of the liquids in equilibrium with these solids were also obtained. All of these samples were analysed by determining NH_4 by Kjeldahl's method, Pb as $PbCrO_4$, and K as $KClO_4$. These analytical results are shown in Table I and plotted in Figs. 3 and 4, where the conjugate solid and liquid phase compositions are joined by tie lines.

The isotherms 150° and 160° were chosen in view of the results reported by Jänecke, Hamacher, and Rahlfs (*loc. cit.*), who found a eutectic point at 157°, and it was anticipated that the isotherms should give valuable information concerning the limits of the miscibility gap near to the eutectic temp. As a high-temp. example the isotherm 190° was studied.

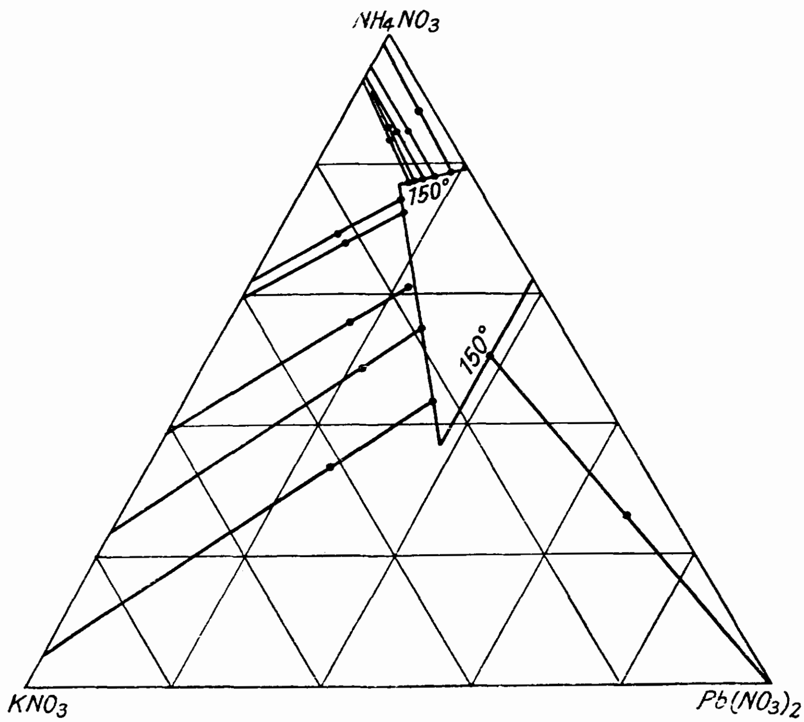
Discussion of Results.—The nature of the binary system NH_4NO_3–KNO_3 was the primary problem under consideration. Fig. 1 shows that the well-defined minima are of the usual type for two substances which form a eutectic system; Fig. 2 similarly shows a well-defined eutectic trough (AE, inset B). Figs. 3 and 4 show very definitely that the system NH_4NO_3–KNO_3 is of the solid-solution type, and it must be concluded that the

TABLE I.

Liquid phase.		Solid phase.		Liquid phase.		Solid phase.	
$Pb(NO_3)_2$, %.	NH_4NO_3, %.	$Pb(NO_3)_2$, %.	NH_4NO_3, %.	$Pb(NO_3)_2$, %.	NH_4NO_3, %.	$Pb(NO_3)_2$, %.	NH_4NO_3, %.
A. Mixtures located on the isotherm 150°.				B. Mixtures located on the isotherm 160°.			
18·92	78·54	9·92	88·10	11·52	86·54	7·24	91·03
16·91	78·02	10·04	84·93	7·27	86·88	4·96	90·33
15·92	77·19	8·98	84·84	3·53	87·01	2·64	89·09
14·87	77·28	7·09	85·60	1·96	87·02	1·29	89·31
13·96	77·14	8·49	83·52	2·49	81·76	1·97	76·02
14·11	74·24	8·01	69·00	4·03	79·98	3·10	73·42
15·41	72·07	9·99	67·48	17·06	63·09	12·23	57·20
21·89	60·99	16·29	55·40	34·46	38·71	25·81	28·60
26·13	54·52	21·40	48·82	40·01	36·62	61·71	23·70
33·52	43·47	24·98	33·41	40·02	46·41	63·79	28·49
38·12	50·30	68·07	26·11	40·00	55·66	62·31	34·89
C. Mixtures located on the isotherm 190°.							
8·32	62·03	5·92	50·94	44·93	23·12	64·49	15·01
26·46	39·97	18·01	29·50	45·02	47·98	61·62	33·51
40·13	21·87	26·56	14·82				

FIG. 3.

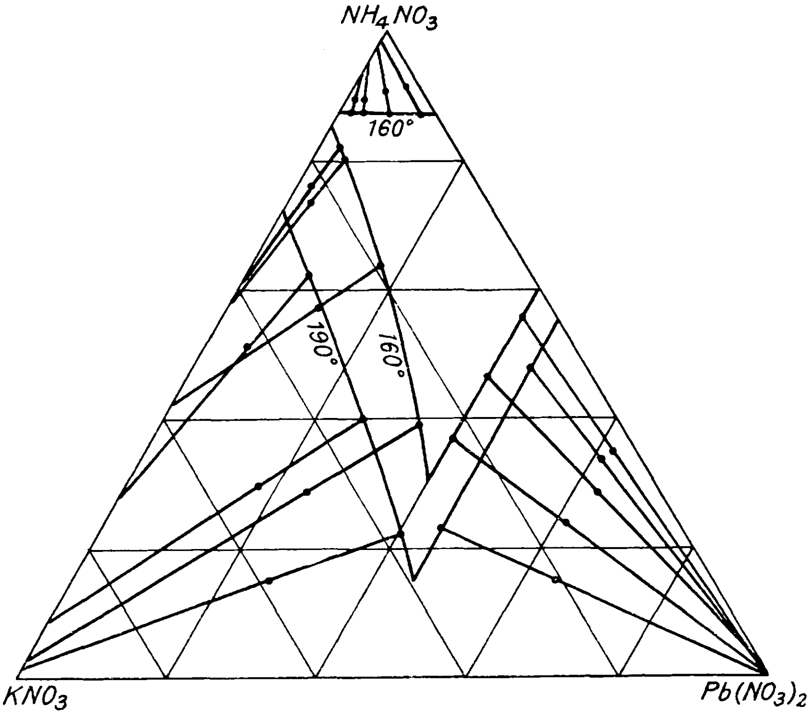
Liquidus–solidus conjugation lines in the ternary system KNO_3–NH_4NO_3–$Pb(NO_3)_2$. (*Isotherm* 150°.)



eutectic minima are due to partial miscibility of solid solutions. In Fig. 3 it is evident that there is a wide range of solid miscibility extending from 100% KNO_3 to about 35% KNO_3 on the one side, whilst in NH_4NO_3-rich mixtures the degree of miscibility is small, only 100—92% NH_4NO_3. The other results (Fig. 4) support these conclusions, and in particular, the 160° isotherm results confirm the extent of the miscibility gap. It is considered that this interpretation of the present results affords strong support for the conclusions of Jänecke, Hamacher, and Rahlfs (*loc. cit.*), and it appears that the miscibility gap is of practically the same extent at both 150° and 160°. There is no evidence that pure ammonium nitrate separates from molten mixtures rich in this salt, as claimed by Perman and Saunders (*loc. cit.*), and it seems probable that their method of analysing the crystals separating from binary mixtures is unsatisfactory. Evidently the Schreinemakers principle as here applied is a more satisfactory means of investigating binary systems, and a high degree of accuracy is claimed for the present results. A large number of mixtures, covering a wide range of composition, has been examined, and this enhances the value of the results now reported.

FIG. 4.

Liquidus–solidus conjugation lines in the ternary system KNO_3–NH_4NO_3–$Pb(NO_3)_2$. (*Isotherms* 160° *and* 190°.)



The simple eutectic nature of the other two binary systems KNO_3–$Pb(NO_3)_2$ and NH_4NO_3–$Pb(NO_3)_2$ involved in this investigation is very evident from Figs. 2, 3, and 4, and calls for no further comment.

SUMMARY.

(1) The liquidus surface of the system KNO_3–NH_4NO_3–$Pb(NO_3)_2$ has been investigated. The ternary mixture of lowest freezing point has the following composition (weight %) : KNO_3, 12 ; $Pb(NO_3)_2$, 32 ; NH_4NO_3, 56. The f. p. is 127·5°.

(2) Solids separating from various mixtures on the 150°, 160°, and 190° isotherms have been analysed, and it has been concluded that potassium and ammonium nitrates form a discontinuous series of solid solutions with a break in the solid miscibility between 8% and 35% of the former. This agrees with the thermal analysis of Jänecke, Hamacher, and Rahlfs (*loc. cit.*) on the binary system.

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TABLE OF ATOMIC WEIGHTS ISSUED IN 1932 BY THE INTERNATIONAL UNION OF CHEMISTRY

	Symbol.	At. No.	At. wt.
Aluminium	Al	13	26·97
Antimony	Sb	51	121·76
Argon	A	18	39·944
Arsenic	As	33	74·93
Barium	Ba	56	137·36
Beryllium	Be	4	9·02
Bismuth	Bi	83	209·00
Boron	B	5	10·82
Bromine	Br	35	79·916
Cadmium	Cd	48	112·41
Cæsium	Cs	55	132·81
Calcium	Ca	20	40·08
Carbon	C	6	12·00
Cerium	Ce	58	140·13
Chlorine	Cl	17	35·457
Chromium	Cr	24	52·01
Cobalt	Co	27	58·94
Copper	Cu	29	63·57
Dysprosium	Dy	66	162·46
Erbium	Er	68	167·64
Europium	Eu	63	152·0
Fluorine	F	9	19·00
Gadolinium	Gd	64	157·3
Gallium	Ga	31	69·72
Germanium	Ge	32	72·60
Gold	Au	79	197·2
Hafnium	Hf	72	178·6
Helium	He	2	4·002
Holmium	Ho	67	163·5
Hydrogen	H	1	1·0078
Indium	In	49	114·8
Iodine	I	53	126·932
Iridium	Ir	77	193·1
Iron	Fe	26	55·84
Krypton	Kr	36	83·7
Lanthanum	La	57	138·90
Lead	Pb	82	207·22
Lithium	Li	3	6·940
Lutecium	Lu	71	175·0
Magnesium	Mg	12	24·32
Manganese	Mn	25	54·93
Mercury	Hg	80	200·61
Molybdenum	Mo	42	96·0

	Symbol.	At. No.	At. wt.
Neodymium	Nd	60	144·27
Neon	Ne	10	20·183
Nickel	Ni	28	58·69
Niobium (Columbium)	Nb (Cb)	41	93·3
Nitrogen	N	7	14·008
Osmium	Os	76	190·8
Oxygen	O	8	16·0000
Palladium	Pd	46	106·7
Phosphorus	P	15	31·02
Platinum	Pt	78	195·23
Potassium	K	19	39·10
Praseodymium	Pr	59	140·92
Radium	Ra	88	225·97
Radon	Rn	86	222·00
Rhenium	Re	75	186·31
Rhodium	Rh	45	102·91
Rubidium	Rb	37	85·44
Ruthenium	Ru	44	101·7
Samarium	Sm	62	150·43
Scandium	Sc	21	45·10
Selenium	Se	34	79·2
Silicon	Si	14	28·06
Silver	Ag	47	107·880
Sodium	Na	11	22·997
Strontium	Sr	38	87·63
Sulphur	S	16	32·06
Tantalum	Ta	73	181·4
Tellurium	Te	52	127·5
Terbium	Tb	65	159·2
Thallium	Tl	81	204·39
Thorium	Th	90	232·12
Thulium	Tm	69	169·4
Tin	Sn	50	118·70
Titanium	Ti	22	47·90
Tungsten	W	74	184·0
Uranium	U	92	238·14
Vanadium	V	23	50·95
Xenon	Xe	54	131·3
Ytterbium	Yb	70	173·5
Yttrium	Y	39	88·92
Zinc	Zn	30	65·38
Zirconium	Zr	40	91·22