383. *Liquidus and Solidus Studies in the Ternary System Composed of the Nitrates of Potassium, Sodium, and Lead.*

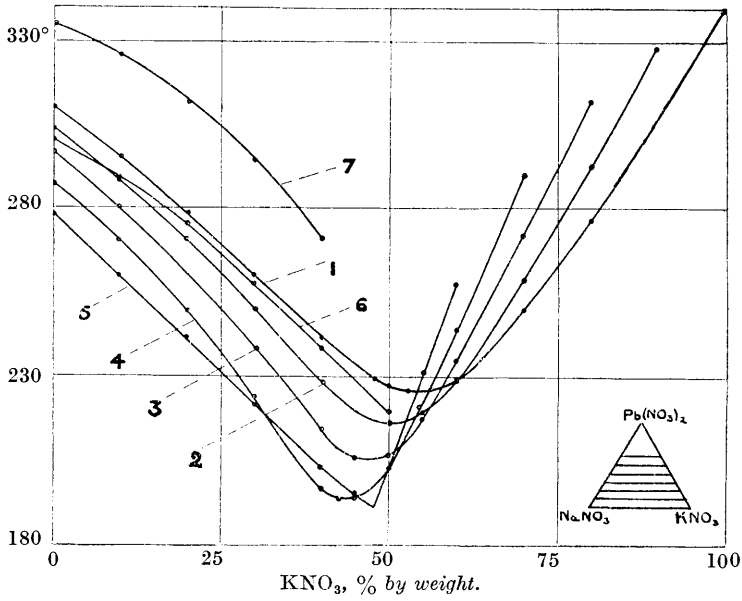
By KENNETH LAYBOURN and WALTER M. MADGIN.

THE binary system KNO_3–$NaNO_3$ has been shown to form a complete series of solid solutions (Madgin and Briscoe, J., 1923, **123**,

1608, 2914). Earlier workers (see *idem*, *ibid.*) have disagreed with this view, and, more recently, Freeth (*J. Physical Chem.*, 1925, **29**, 497) has stated that thermal analysis is inconclusive in deciding the nature of the binary system. Tammann (*Z. anorg. Chem.*, 1931, **197**, 65) has since concluded that a complete series of solid solutions is formed at higher temperatures, but that segregation occurs on cooling.

FIG. 1.

Freezing point–composition diagrams for the system $Pb(NO_3)_2$–KNO_3–$NaNO_3$.



KNO_3, % *by weight.*

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; *No.* 7, 60.

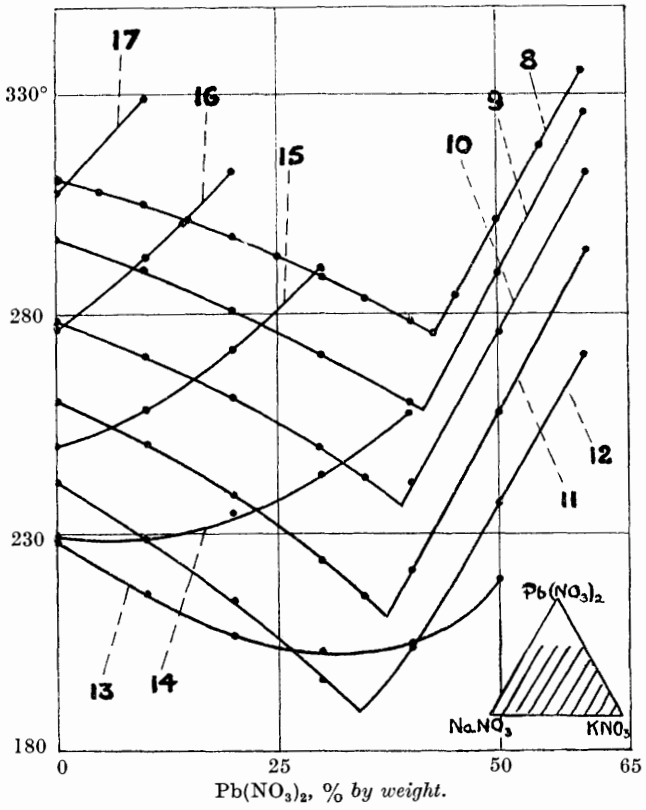
The principle of Schreinemakers (see Bancroft, *J. Physical Chem.*, 1902, **6**, 178) could be applied in determining the nature of the solid phases separating from this binary system by the addition of a third inert substance. It has been shown recently (Glass, Laybourn, and Madgin, this vol., p. 874) that lead nitrate is inert towards the two alkali nitrates, and, accordingly, a study of the ternary system of all three nitrates has been undertaken.

Ternary systems involving sodium and potassium nitrates have been investigated by Menzies and Dutt (*J. Amer. Chem. Soc.*, 1911, **33**, 1366) and by Harkins and Clark (*ibid.*, 1915, **37**, 1816), but the diagrams of these authors agree with those of Carveth (*J. Physical*

Chem., 1898, **2**, 209) in showing eutectic minima for the binary system $NaNO_3$–KNO_3. It was therefore considered desirable to determine the positions of the various isotherms and the nature of the liquidus surface before proceeding to the investigation outlined above. The method employed to determine the liquidus surface

FIG. 2.

Freezing point–composition diagrams for the system $Pb(NO_3)_2$–KNO_3–$NaNO_3$.



$Pb(NO_3)_2$, % *by weight.*

Contents (%) *of* KNO_3 :

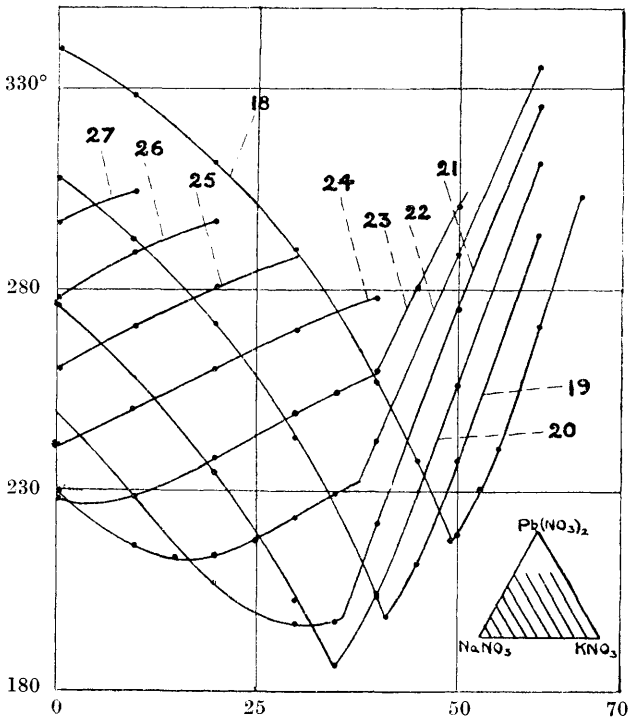
Graph No. 8, 0; *No.* 9, 10; *No.* 10, 20; *No.* 11, 30; *No.* 12, 40; *No.* 13, 50; *No.* 14, 60; *No.* 15, 70; *No.* 16, 80; *No.* 17, 90.

was essentially the same as that of Menzies and Dutt (*loc. cit.*) and involved the determination of a series of curves each of which gives the freezing points of mixtures containing a constant percentage of one component with varying proportions of the other two components (see, *e.g.*, Figs. 1, 2, and 3). A very large number of freezing points has been determined with the object of defining exactly the

forms of the individual curves, since insufficient attention has hitherto been given to this important matter : for instance, Harkins and Clark (*loc. cit.*) were probably misled by the insufficiency of their data in their series of curves for constant percentages of barium nitrate (*loc. cit.*, p. 1822). From the freezing-point curves now

FIG. 3.

Freezing point–composition diagrams for the system $Pb(NO_3)_2$–KNO_3–$NaNO_3$.



$Pb(NO_3)_2$, % *by weight.*

Contents (%) *of* $NaNO_3$:

Graph No. 18, 0; *No.* 19, 10; *No.* 20, 20; *No.* 21, 30; *No.* 22, 40; *No.* 23, 50; *No.* 24, 60; *No.* 25, 70; *No.* 26, 80; *No.* 27, 90.

determined, the various isothermal lines for the ternary system have been deduced, and, in addition, the solid phases separating under several isothermal conditions have been examined in order to settle the nature of the three possible binary systems.

EXPERIMENTAL.

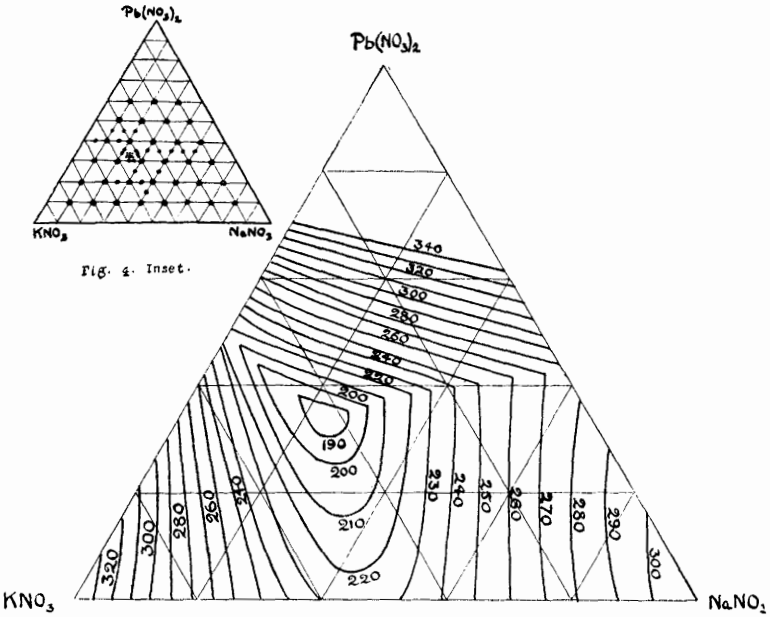
Purification of materials and determinations of f. p.'s for various mixtures were carried out as described by Glass, Laybourn, and Madgin (*loc. cit.*). The

decomp. of $Pb(NO_3)_2$ (*ibid.*) limited the present investigations to mixtures containing no more than 60% of this salt.

Freezing Points and Isotherms for Ternary Mixtures.—The f. p.'s of 70 different ternary mixtures have been investigated. The compositions of these mixtures were chosen from the crossing points on a triangular diagram similar to that used by Menzies and Dutt (*loc. cit.*, p. 1370), but in the present work the number and dispositions of the points were different and were chosen with special reference to the objects of this investigation, *viz.*, the nature of the

FIG. 4.

Freezing point isotherms in the ternary system
$Pb(NO_3)_2$–KNO_3–$NaNO_3$.
(10° Intervals.)



binary systems. A small triangular diagram, showing the points, is inset in Fig. 4. The f. p. data now determined are shown in Figs. 1, 2, and 3, which are vertical sections of a solid model of the liquidus surface.

Isothermal lines were drawn across Figs. 1, 2, and 3, and thus the curves were intersected by each line in a succession of points giving the composition of mixtures having the same f. p.'s. The data thus obtained are translated into an isothermal diagram in Fig. 4.

Mixture of Lowest Freezing Point.—By plotting the temps. and compositions corresponding to the min. points on Figs. 1, 2, and 3, three distinct lines are obtained intersecting in a point. These lines represent the two eutectic troughs *AE* and *BE* (Fig. 5, inset) and the min. points in the solid solution basin *CE* ; the point *E* represents the mixture of lowest f. p. in the ternary system. With the composition of this mixture thus approx. deter-

mined, the f. p.'s of 12 mixtures, differing from it only slightly in composition, were investigated, and in this way the lowest ternary f. p. and the corresponding composition were accurately located. A melt of the composition thus determined gave on freezing a solid phase of practically the same composition (see table)—a characteristic of a pure eutectic.

Liquid phase.		Solid phase.		Liquid phase.		Solid phase.	
$Pb(NO_3)_2$, %.	KNO_3, %.	$Pb(NO_3)_2$, %.	KNO_3, %.	$Pb(NO_3)_2$, %.	KNO_3, %.	$Pb(NO_3)_2$, %.	KNO_3, %.
A. *Mixtures located on the isotherm* 200°.				B. *Mixtures located on the isotherm* 230°.			
37·62	37·23	76·21	13·86	26·28	57·52	13·01	75·07
37·41	37·20	75·60	15·18	10·21	60·89	4·32	71·98
40·80	44·13	78·36	16·03	49·12	43·20	82·10	15·21
40·63	44·14	75·97	18·21				
25·20	44·81	10·10	48·39	C. *Mixtures located on the isotherm* 260°.			
28·22	38·90	15·11	36·57				
28·22	38·71	14·01	36·99	44·26	15·57	76·97	6·31
30·71	49·65	14·25	65·00	15·06	22·42	5·96	13·81
				50·16	31·24	80·14	12·63
D. *Mixture of minimum f. p.*, 185·6°.				36·41	11·26	19·02	7·03
33·07	44·10	33·78	44·36				

Examination of Solid Phases.—The compositions of the solid phases separating from mixtures lying on the isothermals 200°, 230°, and 260° have been determined by a modification of the method described by Madgin and Briscoe (*loc. cit.*), their apparatus having been altered in the following respects: (*a*) A nest of Pyrex beakers, wound with resistance wire, replaced the one beaker A, and the innermost beaker contained the melt. This furnace gave an improved temp. control. (*b*) A closely-fitting, thick (1″) asbestos stopper replaced the double lid *F*. (*c*) The tube *G* was replaced by a plunger tube with a draining platform and two gutters, to run off mother-liquor; such a platform is necessary to prevent deposited solid from sliding back into the melt.

When in use, the whole of this apparatus was enclosed by an asbestos cupboard provided with two small doors through which to observe the melt and read the thermometers. In this way loss of heat was minimised and a const. temp. ($\pm$ 0·5°) could be maintained.

For each solid-phase determination, 500 g. of melt were prepared in the innermost beaker, exactly as described by Laybourn and Madgin (this vol., p. 1361). The composition of such a melt was made up exactly to conform to the appropriate isotherm (200°, 230°, or 260°) so that, on cooling, solid did not separate until the required temp. was reached. Since this temp. was maintained const. only a small amount of solid could separate. In each expt., the temp. was first raised to some 30° above the f. p. of the melt, and the plunger was slowly lowered into the melt until the surface of the liquid just covered the platform. By regulating the external resistance, the temp. was now allowed to fall very slowly (3° per hr.) until the f. p. was reached. The temp. was then maintained const. for 6 hrs. so that a very small ring of solid separated on the platform, and the plunger was then raised until the tips of the gutters just remained in contact with the melt surface. The temp. was raised by 4—5°. Under these conditions, efficient drainage of mother-liquor from the solid occurs, due largely to surface-tension effects caused by the tips of the draining platform just touching the liquid surface. After draining for about 12 hrs., the plunger was removed from the apparatus and allowed to cool in a desiccator.

Simultaneously, a duplicate sample of the melt was withdrawn in previously heated glass tubes. The amount of solid deposited on the plunger never exceeded 4 g., and as this could have no appreciable effect on the composition of the 500 g. of melt, true equilibrium may be considered to have existed. The use of more than one heated beaker prevented a deposit from forming on the walls of the inner beaker concurrently with the deposition on the plunger.

Both the melt samples (liquid phase) and the solid from the plunger (solid phase) were analysed for K (as $KClO_4$, Pb being first removed by pptn. as PbS), and for Pb (as $PbCrO_4$); Na was calc. by difference. The results of these analyses are given in the table and plotted in Fig. 5, which shows, for

FIG. 5.

Liquidus–solidus conjugation lines in the ternary system $Pb(NO_3)_2$–KNO_3–$NaNO_3$.

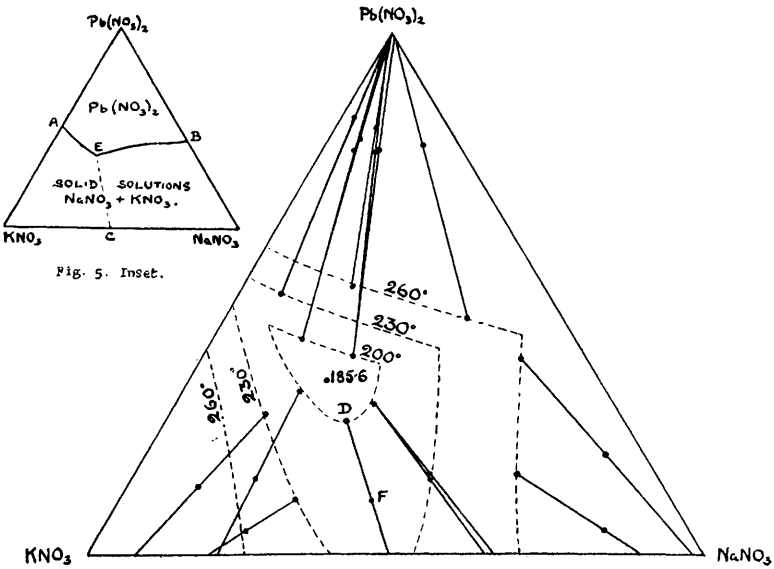


Fig. 5. Inset.

the three isothermals examined, the conjugate solid- and liquid-phase compositions joined by tie lines.

Results.—The forms of the curves (Figs. 1, 2, and 3) and of the isothermals in Fig. 4 give valuable information as to the nature of the three binary systems formed by the salts under consideration. Figs. 2 and 3 confirm the views of Glass, Laybourn, and Madgin (*loc. cit.*) that the systems containing $Pb(NO_3)_2$ are eutectic in type, whilst Fig. 1 especially suggests that solid solutions are formed by $NaNO_3$ and KNO_3 mixtures as supposed by Madgin and Briscoe (*loc. cit.*). These conclusions receive further support from a consideration of Fig. 4, where two eutectic troughs and a solid solution basin are very evident.

Conclusive proof as to the type of all three binary systems is seen in Fig. 5, where the tie lines show that all mixtures rich in $Pb(NO_3)_2$ give only this component as a solid phase whereas mixtures rich in KNO_3 or $NaNO_3$ give solid solutions of these two components as solid phases. The mixtures examined

cover a wide range of composition and temp. In view of Hissink's opinion (*Z. physikal. Chem.*, 1900, **32**, 537), that $NaNO_3$ and KNO_3 form a limited series of solid solutions with a miscibility gap, a mixture in the solid solution basin (D, Fig. 5) was examined, and the direction of the conjugation line *DF* is definite evidence that such a miscibility gap does not exist in the solid state at temps. above the lowest ternary f. p. (185°).

Summary.

(1) The three-component system $Pb(NO_3)_2$–KNO_3–$NaNO_3$ has been investigated, and isothermal lines on the liquidus surface determined at 10° intervals.

(2) The ternary mixture of lowest freezing point has been found to have the following composition (weight %): $Pb(NO_3)_2$ 33, KNO_3 44, and $NaNO_3$ 23. The f. p. is 185·6°.

(3) Solid phases from various mixtures on the 200°, 230°, and 260° isotherms have been examined and it has been concluded that : (*a*) KNO_3 and $NaNO_3$ form a continuous series of solid solutions, and (*b*) $Pb(NO_3)_2$ forms eutectic systems with each of the other two components. This confirms the thermal analyses of Glass, Laybourn, and Madgin (*loc. cit.*) and of Madgin and Briscoe (*loc. cit.*).

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