113. *The Two-component Salt Mixtures of Lead Nitrate with Sodium or Potassium Nitrate.*

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The two binary systems, lead nitrate with sodium or potassium nitrate, have been investigated as a preliminary to further studies involving all three nitrates, because of the inadequacy of the existing data. Guthrie (*Phil. Mag.*, 1884, **17**, 462) has reported eight freezing points for mixtures containing potassium nitrate, but only the composition of the mixture of minimum freezing point for the system with sodium nitrate. He also reports that lead nitrate, admixed with 30% (by weight) of potassium nitrate, decomposes in the region of the m. p. of the mixture (335°) and this composition thus represents a limiting mixture in the investigation of this system. However, it is also stated (*loc. cit.*, p. 477): "Mixtures consisting of . . . 80% and even . . . 90% nitrate of lead fuse together into clear liquids without decomposition but I have not determined the melting points."

The freezing point–composition diagrams have now been determined for the two binary systems, and the results show that each is a eutectic system. More precise information is also given concerning limiting mixtures in both systems, and it would appear that these are those mixtures which fuse at so high a temperature that the rate of decomposition of lead nitrate is rapid enough to prevent the determination of a steady and reproducible freezing point. The authors now find that such a decomposition temperature is conditioned by the concentration of lead nitrate in a mixture, and that the temperature rises as the concentration falls.

A photomicrographic examination of the system lead nitrate–sodium nitrate is now reported, and this confirms the existence of a eutectic system. Glasstone and Saunders (J., 1923, **123**, 2134) find that these salt mixtures behave as eutectic systems in the two ternary systems formed by solution in water.

EXPERIMENTAL.

Purification of Materials.—The salts used were of pure quality and were recrystallised three times from water. The sodium and potassium nitrates were fused after the first recrystallisation and any scum formed was removed from the surface of the melt.

The lead nitrate was dried by the process of Baekeland (*J. Amer. Chem. Soc.*, 1904, **26**, 391), who showed that its decomposition occurs at a much decreased temperature if a trace of moisture is present.

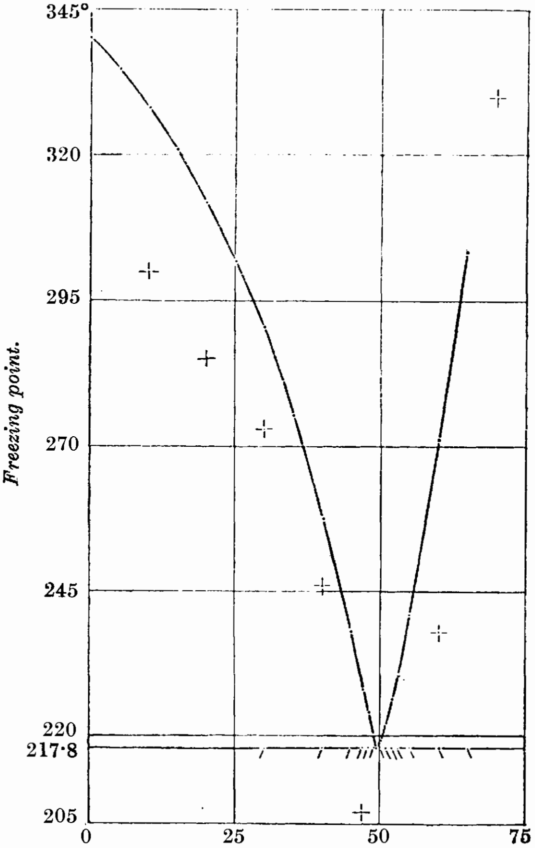
Freezing-point Determinations.—Freezing points were determined by the cooling-curve method for two series of synthetic mixtures of pure lead nitrate with sodium and potassium nitrates respectively. The synthetic mixtures were prepared by weighing the requisite amounts of the appropriate salts and intimately mixing these in a dry warm mortar, whence they were transferred to a moisture-freed Jena glass test-tube. The tube and its contents were heated in an air oven at 110° for 2 hours, and then placed in an electric furnace and heated slowly, with very frequent stirring, until the salt mixture was completely fused. This required 2—3 hours because of the slowness with which lead nitrate dissolves. Bogitch (*Compt. rend.*, 1915, **161**, 790) has observed similar behaviour with lead nitrate in ammonium nitrate. The furnace used was similar to that employed by Briscoe and Madgin (J., 1923, **123**, 1608), except that it was made much deeper so that the fusion tube could be completely immersed. Preliminary investigations with this furnace showed that, when it was combined with an external resistance, the rate of cooling could be adjusted to almost any desired slowness. The approximate freezing points were first obtained so that the various synthetic mixtures could be fused without undue heating above the temperatures of complete fusion.

The actual freezing points were determined by fusing 20 g. of the required mixture in a test-tube, and closing the mouth of the tube with a cork carrying two thermometers and a length of glass tubing, through which small particles of solid could be introduced to inoculate against supercooling. One of the thermometers (" melt thermometer ") was immersed in the melt to a depth of 1", and the other (" furnace thermometer ") was 1" above the surface of the melt so that the mean temperature of the exposed melt thermometer stem, within the furnace, could be obtained and applied in correcting observed freezing points. They were nitrogen-filled mercury thermometers graduated in degrees, the former having a range 150° to 450°, and the latter 0° to 400°. The melt thermometer was directly compared with a precisely similar instrument, which had been standardised by the National Physical Laboratory, the two thermometers being immersed together in fusible metal and the temperature controlled electrically. Corrections were of a similar nature to those applied by Briscoe and Madgin (*loc. cit.*). The melt was first raised to 15° above the freezing point, and the furnace then set for 180°; a convenient rate of cooling was thus obtained under standardised conditions. Stirring of the melt was done continually by using the melt thermometer, and the time for each 1° fall in temperature was taken. In this way the arrests corresponding to the freezing point and the eutectic temperature were easily identified.

The differences between the "furnace" and "melt" thermometers, at the times of freezing-point determinations, showed a maximum of 35° and a minimum of 20° for all the results now reported. With the aid of a sliding lens, attached to the melt thermometer, the temperature could be read to 0·1°. The means of three closely-agreeing values (within less than 0·2°) were taken for the freezing point and the eutectic temperature, and in most cases the first three determinations conformed to these limits. The results of these temperature determinations are plotted in Figs. 1 and 2, corrected temperatures being used, and in each case two branches of the curve intersect in a point corresponding to the eutectic mixture. The

FIG. 1.

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

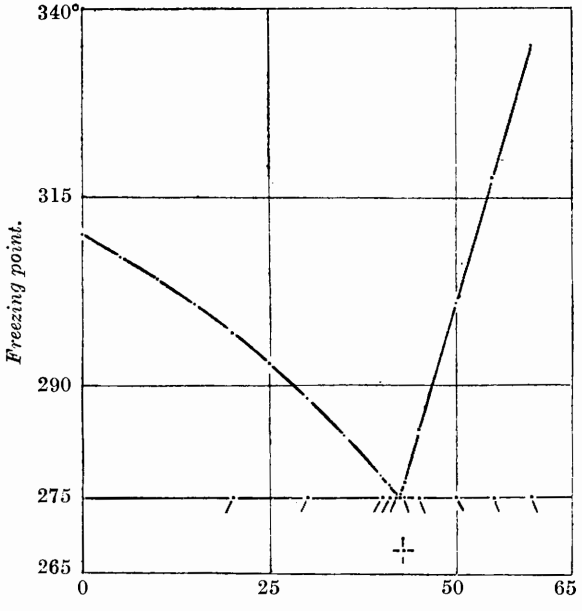


$Pb(NO_3)_2$, % *by weight.* (*Crosses show Guthrie's results.*)

composition of each such mixture was found from a separate large-scale plot of the results. Supercooling was very marked with mixtures near the eutectic composition and containing excess lead nitrate. It was entirely prevented, however, by inoculation with one or two minute crystals introduced through the glass tube provided. The crystals were always introduced when the melt was 2° above the previously ascertained freezing point; exact agreement for successive determinations was often obtained, and differences of as much as 0·2° were very rare.

FIG. 2.

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



$Pb(NO_3)_2$, % *by weight.* (*Cross shows Guthrie's result.*)

Separate observation showed that the rate of dissolution of these added crystals was very slow and was not complete before the freezing point was reached.

Important confirmatory evidence of the eutectic compositions was obtained by direct observation of the cooling of mixtures with freezing points not more than 1° above the eutectic temperatures. On observing the freezing-point arrests for such mixtures, cooling was stopped and the temperature slowly raised, thus preventing the formation of eutectic solid. By removing the test tube from the furnace, before complete re-fusion occurred, it was possible to detect which pure component was present as a solid, since sodium or potassium nitrate always floats while lead nitrate, being denser than any melt, always sinks.

TABLE I.

Experimental data for freezing points and eutectic arrests of mixtures containing lead nitrate.

(Compositions are expressed as percentages of lead nitrate by weight.)

Series I. $Pb(NO_3)_2$ with KNO_3.			Series II. $Pb(NO_3)_2$ with $NaNO_3$.		
$Pb(NO_3)_2$, %.	F. p., obs.	F. p., corr.	$Pb(NO_3)_2$, %.	F. p., obs.	F. p., corr.
0·0	334·0°	340·0°	0·0	305·0°	310·0°
5·0	329·3	335·0	5·0	302·6	307·2
10·0	322·8	328·2	10·0	299·9	304·1
15·0	316·0	320·8	15·0	296·4	300·7
20·0	307·6	311·9	20·0	292·9	297·0
25·0	297·8	301·7	25·0	288·9	292·8
30·0	286·7	290·4	30·0	284·2	288·0
35·0	272·0	275·2	35·0	279·5	283·1
40·0	254·8	257·6	40·0	274·6	278·0
45·0	235·0	238·0	41·0	273·5	276·8
47·0	224·9	228·0	42·0	272·5	275·6
48·0	221·0	224·1	(E_2) 42·3	271·8	275·0
49·0	217·0	219·7	42·5	272·4	275·7
(E_1) 49·5	215·2	217·8	43·0	273·9	277·2
50·0	216·5	219·2	45·0	280·5	284·1
51·0	219·4	222·4	50·0	296·9	300·9
52·0	223·3	226·4	55·0	312·6	317·6
53·0	227·0	230·2	60·0	329·2	335·3
55·0	237·9	240·7			
60·0	267·9	271·0			
65·0	299·5	303·4			

(E_1) and (E_2) = Eutectic compositions.

Series III. Eutectic temperatures (corrected) from cooling curves :

A. Mixtures containing KNO_3.

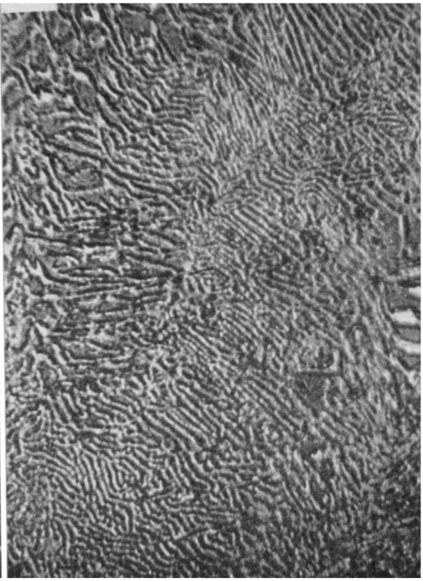
$Pb(NO_3)_2$, %	30·0 40·0 47·0 48·0 49·0 49·4 50·0 53·0 60·0	45·0 51·0 52·0 55·0	65·0
Temp. ...	217·9°	217·8°	217·7°

B. Mixtures containing $NaNO_3$.

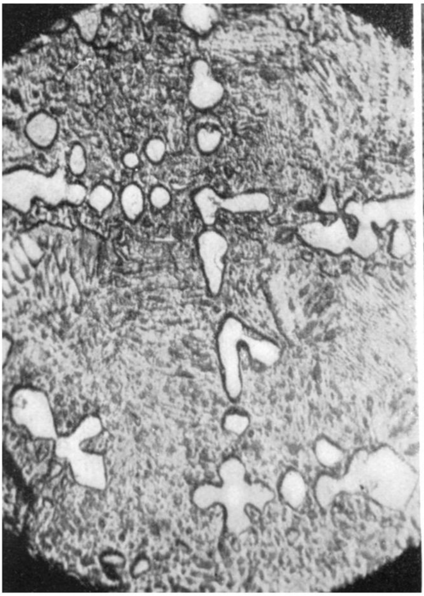
$Pb(NO_3)_2$, % ...	40·0 41·0 42·0 43·0 45·0 55·0	30·0 60·0	20·0	50·0
Temp.	275·0°	274·9°	274·8°	275·1°

The results of the freezing-point determinations are shown in Table I (Series I and II). The eutectic mixtures were synthesised according to the compositions deduced from Figs. 1 and 2, and the experimentally determined freezing points (E_1 and E_2, Table I) were found to agree exactly with those shown by the diagrams. Additional confirmation was obtained from the cooling curves, which were continued to the eutectic temperature in many cases. For mixtures containing potassium nitrate, 14 such determinations were made, and the extremes among these results only differed by 0·2°, while for mixtures with sodium nitrate, 10 results differed by 0·3°. These results are shown in Figs. 1 and 2, in the usual manner for such data, and in Table I, Series III.

5% $Pb(NO_3)_2$.



42·3% $Pb(NO_3)_2$.



50% $Pb(NO_3)_2$.

50% $Pb(NO_3)_2$.

[*To face p.* 879.

Photomicrographs.—In the photomicrographic examination of the system lead nitrate–sodium nitrate, the specimens were prepared in a similar manner to that adopted with mixtures containing potassium nitrate (Madgin, J., 1930, 458). The hygroscopic nature of sodium nitrate caused some difficulty during polishing of the specimens, but if the specimen was rubbed by a rotating wheel, covered with Selvyt cloth on which benzene was dropping, then a highly polished surface was obtained. Mixtures of the following compositions (weight % of lead nitrate) were examined : 5%, 42·3% (eutectic composition), and 50%.

Under vertical illumination they presented features identical with those previously found in mixtures containing potassium nitrate (Madgin, *loc. cit.*), but the sodium nitrate mixtures could only be photographed satisfactorily after staining with hydrogen sulphide, as was done with potassium nitrate mixtures. The lead sulphide thus formed on the polished surfaces appears white on photographs in vertical illumination, while the sodium nitrate appears dark grey or black (Plate I). Banded eutectic structure is easily recognisable in all cases but in the 5% mixture only small areas of this structure occurred between very large primary crystals of sodium nitrate. The latter mixture was chosen to support the conclusion that there was no partial solid miscibility even at very low concentrations.

The 50% mixture shows a striking similarity to the potassium nitrate mixture of comparable composition, since the large primary crystals of lead nitrate appear to be surrounded by an area of pure sodium nitrate. Doubtless, segregation is the cause of the phenomenon in this case also.

Decomposition of Lead Nitrate, and Limiting Mixtures.—Melts used to determine the freezing points (Table I) were all clear liquids, unaltered on remelting for repeat determinations. The highest temperatures reported on the lead nitrate branch are (1) 303·4° for 35% KNO_3 melted at 320°, and (2) 335·3° for 40% $NaNO_3$ melted at 350°.

Mixtures containing greater percentages of lead nitrate gave brown fumes before complete fusion, and attempted repeat freezing points differed by as much as 3°. This absence of reproducibility shows that the figures just quoted are to be regarded as those for limiting mixtures.

An investigation has been made to ascertain whether all mixtures containing lead nitrate decompose at these same limiting temperatures. Fused mixtures were prepared in the usual way and contained 50%, 30%, and 10% of lead nitrate with 50%, 70%, and 90% of potassium nitrate respectively. The temperature of the melts was slowly raised at such a rate that a 5° rise occurred in less than 1 hour and the temperature was then kept constant for the remainder of that hour.

The melt was examined for signs of decomposition (brown fumes and yellow coloration) at every temperature halt. Temperatures at which decomposition was first observed are given below and are seen to rise progressively as the concentration of lead nitrate decreases. Sodium nitrate was examined similarly.

	System $Pb(NO_3)_2$–KNO_3.				System $Pb(NO_3)_2$–$NaNO_3$.			
$Pb(NO_3)_2$, %	70	50	30	10	60	40	20	10
Decomp. temp. ...	335°	355°	370°	400°	355°	380°	400°	415°

These partially decomposed melts were finally dissolved in cold water and some insoluble pale yellow residue always remained, thus contrasting with the melts used for the results in Table I, which were completely soluble in cold water.

A possible explanation of the rise in decomposition temperature with dilution is that the rate of decomposition decreases with dilution, and consequently it becomes necessary to raise the temperature of such melts to obtain a rate which is rapid enough to be detectable and is comparable with that of a more concentrated melt at a lower temperature.

If the graph of the decomposition temperature–composition is produced, it will cut the freezing-point curve at the conditions of the limiting mixture.

Summary.

(1) The freezing-point curves for binary mixtures of lead nitrate with sodium nitrate and potassium nitrate have been determined; each system is of the eutectic type.

(2) A photomicrographic study of the system involving sodium nitrate has been made, surfaces stained with hydrogen sulphide being used.

(3) Limiting compositions have been found beyond which freezing points cannot be determined because of decomposition of lead nitrate, and the variation of decomposition temperature with concentration has been investigated.

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