165. *Further Studies on the Formation of Oxynitrates of Lead in Molten Salts.*

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IT has previously been shown (Laybourn and Madgin, J., 1932, 1360) that by dissolving litharge in a molten mixture of lead and potassium nitrates, the compound $PbO,2Pb(NO_3)_2$ could be prepared; and that a new compound, $Pb_3O_4,3Pb(NO_3)_2$, could similarly be obtained from red lead.

It was thought that more exact information concerning the latter compound might be obtained from a study of the three-component system Pb_3O_4–$Pb(NO_3)_2$–KNO_3, including an examination of the form of the liquidus surface and an investigation of solidus–liquidus equilibria (compare Laybourn and Madgin, J., 1932, 2582). In the course of the chemical analyses involved, an interesting geometrical property of the ternary diagram has appeared which is of general application to three-component systems in which the determination of two of the components individually is difficult.

Lead dioxide has not been used hitherto in synthesising oxynitrates, and its behaviour in this respect has been examined. It has been found to yield *lead dioxydinitrate*, $PbO_2,Pb(NO_3)_2$.

System Pb_3O_4–$Pb(NO_3)_2$–KNO_3.—Only a small portion of the liquidus surface could be determined on account of the low solubility of Pb_3O_4 in KNO_3–$Pb(NO_3)_2$ melts, and the decomp. of melts containing high concns. of $Pb(NO_3)_2$. F. p. isotherms were deduced from over 100 f. p.'s measured for ternary mixtures lying within the area ABC (Fig. 1). In determining these f. p.'s, binary fused mixtures of KNO_3 with $Pb(NO_3)_2$ were prepared and known amounts of Pb_3O_4 added, with mechanical stirring; after each addition the f. p. was determined.

That part of the liquidus surface which can be investigated (Fig. 1) shows one eutectic trough and indicates that the solid phases first separating are either KNO_3 or $Pb(NO_3)_2$; it is therefore impossible to determine the compn. of the oxynitrate present in solution by this means.

This was confirmed by analysis of coexisting solid and liquid phases in several ternary mixtures. Determination of Pb_3O_4 in the nitrate-containing phases by available O content was not satisfactory, and the complete analyses were effected by determinations of only K (as $KClO_4$) and total Pb (as $PbCrO_4$). The calculation of the phase compositions from such data is much simplified by the use of the following geometrical construction which we have devised.

The ternary system is represented in Fig. 2 by an equilateral triangle of side 100 units. The corner A represents 100% KNO_3, B represents 100% $Pb(NO_3)_2$, and C 100% Pb_3O_4. A binary mixture of KNO_3 (0% Pb) and $Pb(NO_3)_2$ (62·56% Pb) containing X% Pb is represented by a point X_1 on the side AB such that $AX_1 = 100X/62{\cdot}56$. Similarly a binary mixture of KNO_3 and Pb_3O_4 (90·65% Pb) which contains X% Pb is represented by X_2 on AC, where $AX_2 = 100X/90{\cdot}65$. We find that all points on X_1X_2 represent mixtures containing X% total Pb; this is proved in the following manner.

Consider a three-component system A, B, C, in which A, B, and C contain respectively fractions x, y, and z of an element or radical, R. Take any point P_1 in the ternary diagram ABC (Fig. 3) with co-ordinates a_1, b_1, c_1; the amount of R in the substance represented by P_1 is $xa_1+yb_1+zc_1 = K$. Let P_2 (a_2, b_2, c_2) be another point also containing an amount K of R; then $xa_2 + yb_2 + zc_2 = K$. Then, if P (a, b, c) is any point on the straight line joining P_1 with P_2, it can be shown that the substance represented by P also contains an amount K of R, *i.e.*, $xa + yb + zc = K$. For, let P divide P_1P_2 in the ratio $\alpha : \beta$; then

$$a = PM = (\alpha P_2M_2 + \beta P_1M_1)/(\alpha + \beta) = (\alpha a_2 + \beta a_1)/(\alpha + \beta);$$

similarly $b = (\alpha b_2 + \beta b_1)/(\alpha + \beta)$;

and $c = (\alpha c_2 + \beta c_1)/(\alpha + \beta)$.

Therefore,

$$\begin{aligned} xa + yb + zc &= [x(\alpha a_2 + \beta a_1) + y(\alpha b_2 + \beta b_1) + z(\alpha c_2 + \beta c_1)]/(\alpha + \beta) \\ &= [\alpha(xa_2 + yb_2 + zc_2) + \beta(xa_1 + yb_1 + zc_1)]/(\alpha + \beta) \\ &= (\alpha K + \beta K)/(\alpha + \beta) = K. \end{aligned}$$

This holds for all values of (a, b, c) on the line P_1P_2, and thus all points on this line have the same content of R, *i.e.*, K.

This theorem has been applied in the foregoing investigations in the particular case where $x = 0$; it could be applied to any ternary system in which the same radical occurs in two or three of the components.

FIG. 1.

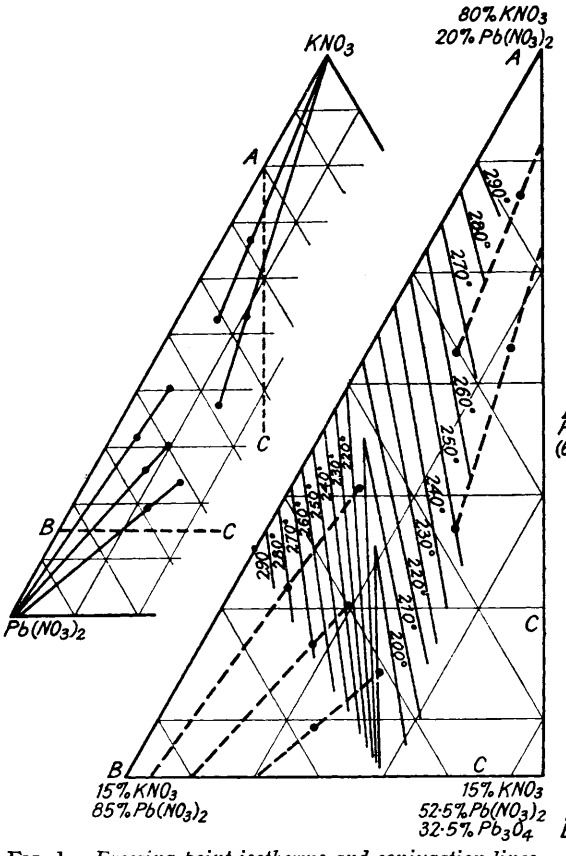

FIG. 2.

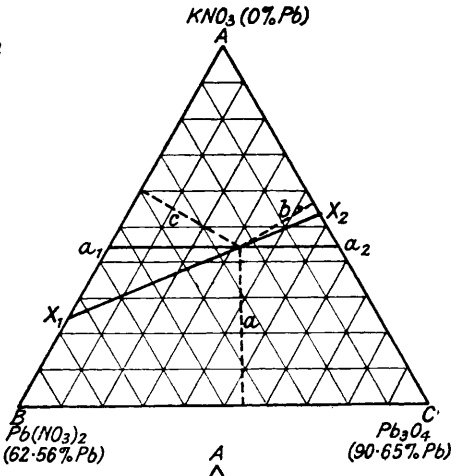

FIG. 1.—*Freezing-point isotherms and conjugation lines in the ternary system* Pb_3O_4–$Pb(NO_3)_2$–KNO_3.

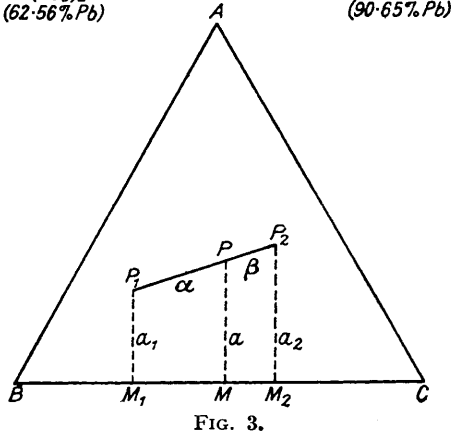

FIG. 3.

In any ternary mixture there will be an amount of KNO_3 (a%) corresponding to the X% total Pb, and all mixtures containing a% KNO_3 lie along the line a_1a_2, which is parallel to BC and at a perpendicular distance a from it. The co-ordinates (a, b, c) of the point of intersection of a_1a_2 and X_1X_2 give the percentages of KNO_3, $Pb(NO_3)_2$, and Pb_3O_4 in the ternary mixture containing a% KNO_3 and X% total Pb.

The analytical results of solid- and liquid-phase expts. are given below, and the corresponding conjugation lines are shown in Fig. 1.

Liquid phase	KNO_3, %	52·60	37·02	40·51	30·10	24·05
	Total Pb, %	31·41	43·35	38·63	46·36	51·62
Solid phase	KNO_3, %	66·94	53·21	31·77	26·49	19·10
	Total Pb, %	21·96	32·25	43·80	48·19	54·04

Synthetic Experiments with Lead Dioxide.—$Pb(NO_3)_2$ and KNO_3, in eutectic proportions to afford melts of low f. p., were fused together in a 250-c.c. Pyrex-glass beaker heated electrically in a furnace lagged with asbestos and provided with observation windows. PbO_2 was added to a series of such melts with mechanical stirring. Dissolution was slow, but, when complete, clear emerald-green melts were obtained. The PbO_2 used was Kahlbaum's (" for analysis "); less pure qualities gave yellow and slightly turbid solutions. The amount of PbO_2 was progressively increased in each melt, but only a comparatively small proportion could be dissolved before the solubility limit was reached. A melt containing equimol. proportions of PbO_2 and $Pb(NO_3)_2$ did not become clear even after 36 hrs.' stirring at 340° [the highest temp. which could be used because of decomp. of $Pb(NO_3)_2$], although a yellow deposit was formed in the liquid, presumably because the latter was saturated with oxynitrate (cf. Laybourn and Madgin, J., 1932, 1360). The clear emerald-green solutions were cooled in desiccators, powdered, and extracted with ice-cold H_2O, whereupon a yellow solid remained. After being separated, washed with EtOH and Et_2O, and dried, the yellow powder was analysed in terms of total Pb (as $PbCrO_4$) and PbO_2 (available O determined by oxalate method). The compn. was found to be independent of the amount of PbO_2 used in preparing the melts (so long as clear melts were obtained), and the following results of typical analyses correspond to a compound of formula $PbO_2,Pb(NO_3)_2$, which requires total Pb, 72·62; PbO_2, 41·94%.

PbO_2, %, in melt	2·5	5·0	10·0
PbO_2, %, in compound	41·80	41·80	41·84
Pb, %, in compound	72·40	72·56	72·50

This *lead dioxydinitrate* is hydrolysed by boiling H_2O: $PbO_2,Pb(NO_3)_2 + H_2O \rightleftharpoons PbO_2 + Pb(OH)NO_3 + HNO_3$. The reaction is not complete even after several days, since the Pb content of the dark brown insol. residue never reaches that required for PbO_2, but the aq. solution contains $Pb(OH)NO_3$ (Found: Pb, 72·35. Calc.: Pb, 72·38%), which crystallises in white needles. Hydrolysis occurs to some extent even at room temp.

On treatment with dil. AcOH, the dioxydinitrate breaks down, $Pb(NO_3)_2$ going into solution and a residue of PbO_2 remaining.

The composition of lead dioxydinitrate is of interest when compared with the two other oxynitrates prepared in molten KNO_3 (Laybourn and Madgin, *loc. cit.*), *viz.*, lead oxytetranitrate, $PbO,2Pb(NO_3)_2$, and lead tetraoxyhexanitrate, $Pb_3O_4,3Pb(NO_3)_2$, and presumably all of the residual valencies of these three compounds are saturated. It would therefore seem necessary to suppose that when 2 mols. of the oxytetranitrate and 1 mol. of the dioxydinitrate are united as in $Pb_3O_4,3Pb(NO_3)_2$, 2 mols. of $Pb(NO_3)_2$ have been liberated in order to free the residual valencies necessary for the union.

SUMMARY.

1. The system Pb_3O_4–$Pb(NO_3)_2$–KNO_3 has been investigated within limits set by decomposition and insolubility. A geometrical property of the ternary diagram has appeared which enables the compositions of the ternary mixtures to be found simply.

2. PbO_2 has been dissolved in a melt of KNO_3 and $Pb(NO_3)_2$; on extraction of the cold melt with ice-cold water, a yellow powder is obtained, lead dioxydinitrate, $PbO_2,Pb(NO_3)_2$.

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[*Received, May 3rd,* 1933.]