36. *Liquidus and Solidus Studies. Part IV.*

By K. LAYBOURN, W. M. MADGIN, and (in part) DOROTHY FREEMAN.

THE graphical thermodynamic treatment of ternary systems involving solid solutions was discussed by Schreinemakers (*Z. physikal. Chem.*, 1904, **50**, 169; 1905, **51**, 547), but few actual examples of such systems were then known. In the present and earlier papers in this series a number of ternary systems, each involving one binary solid solution system, are described, and the forms of the liquidus surfaces, together with a knowledge of solidus–liquidus equilibria, are used to deduce the types of binary systems which could not otherwise be investigated.

In making deductions from the forms of ternary liquidus surfaces it is first necessary to prove that any given surface corresponds to one particular type of binary system, and for this purpose Schreinemakers's theory and methods of representation must be extended, since they do not cover all the particular types of ternary systems examined by us.

Hitherto, water has been used almost exclusively as the third component to determine the types of binary systems of inorganic salts, but such investigations are seriously limited by the impracticability of the determinations of isotherms lying above about 50° under ordinary pressures. In the present work the third component is an inorganic salt, and five ternary systems are now reported involving the nitrates of the alkali metals, the alkaline earths, and lead.

Gibbs ("Collected Scientific Papers," London, 1906) showed that the thermodynamic potential (ζ function) is a minimum for stable equilibrium in a system at constant temperature and pressure, and Alkemade (*Z. physikal. Chem.*, 1893, **9**, 289) described the graphical representation of this function with respect to ternary systems.

In the following we consider systems of three components, A, B, and C. The ζ values of all possible liquid states at a given temperature and pressure are represented on a surface $\alpha\beta\gamma$, those of binary solid solutions of A with B on a curve *ab*, and the ζ value of solid C, the inert third component, on the axis ζ_c [see Fig. 1 (i)]. The graphical treatment of the particular experimental types examined by us, and the derivation of the liquidus forms, may be considerably simplified by considering first a case in which the component C has a very low freezing point in comparison with A or B (as is generally the case in a system formed from water and two salts) so that the only solid phases to be considered are solid solutions of A with B. This is a departure from Schreinemakers's method of treatment and simplifies the application to our particular examples.

I. *The solid solution series A–B is continuous.* In this case the curve *ab* is always convex downwards.

When the binary solid solution system is of Roozeboom's Type I, the curve *ab* cuts through the curve $\alpha\beta$ in a certain manner as temperature is lowered (see Roozeboom, *ibid.*, 1899, **30**, 385); on this assumption the isotherms in the ternary system may be derived as shown in Fig. 1 (i) and (ii), which refer to temperatures respectively above and below the freezing point of the lower-melting component A.

Although *ab* and the surface $\alpha\beta\gamma$ may change in form as temperature alters, it is evident that the liquidus surface in the neighbourhood of A and B will exhibit no marked trough or hump; this is shown by the summary of the isotherms in Fig. 1 (iii).

When the binary solid solution series is of Roozeboom's Type III, the curve *ab* cuts $\alpha\beta$ in two points for a certain temperature range below the melting point of A, and at such temperatures the isotherm of solid solutions is derived as shown in Fig. 2 (i); Fig. 2 (ii) refers to a still lower temperature. It is clear from the method of derivation that, in general, the isotherms will show a marked dip [Fig. 2 (iii)], corresponding to a trough on the liquidus surface, and the occurrence of this type of isotherm might be taken as strong evidence that the binary solid solution system involved is of Roozeboom's Type III.

Three-component salt systems in which the third component C has a freezing point not very different from those of the other two components are the subject of the experimental parts of the present series of papers.

Equilibria of binary solid solutions with solid C are given by points on straight lines joining *c*, the point representing the ζ value of solid C, with points on *ab*. These lines form a surface, as_1bc [Fig. 3 (i)], and, at temperatures where only solid phases can exist in

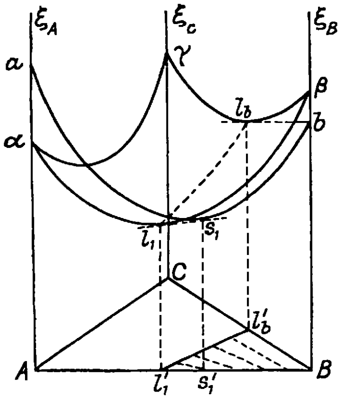


Fig. 1.(i)

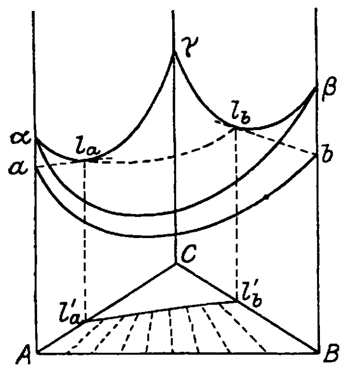


Fig. 1.(ii)

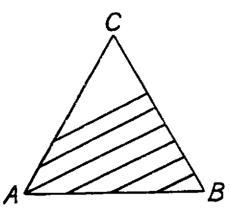


Fig. 1.(iii)

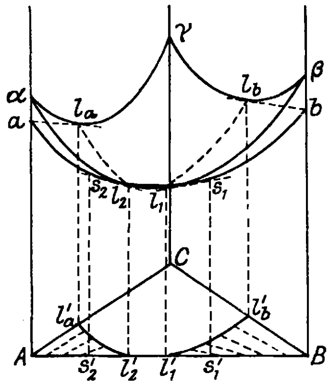


Fig. 2.(i)

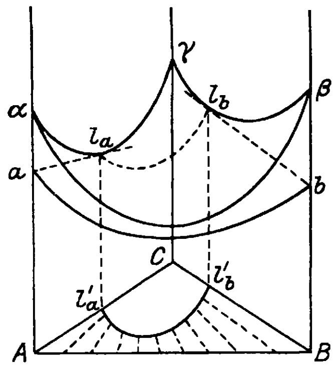


Fig. 2.(ii)

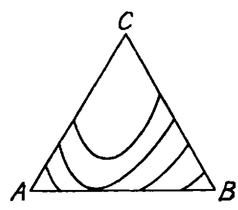


Fig. 2.(iii)

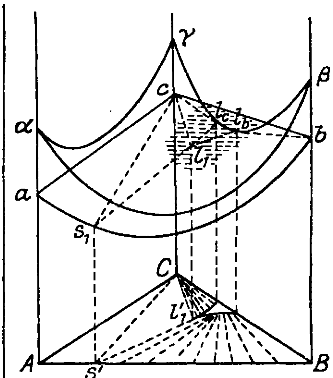


Fig. 3.(i)

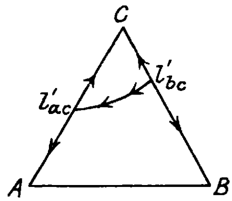


Fig. 3.(ii)

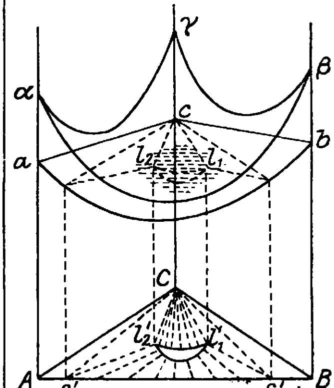


Fig. 4.(i)

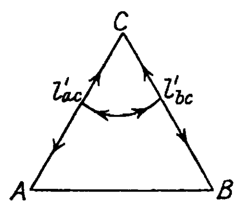


Fig 4.(ii)

the ternary system, this surface must lie entirely below the surface $\alpha\beta\gamma$, but on rise of temperature it will eventually meet it.

When the straight line *bc* is the first conjugation line in the surface as_1bc to touch the surface $\alpha\beta\gamma$ as temperature is raised, and the straight line *ac* is the last, then the touching point of bc with $\beta\gamma$ represents the liquid of lowest freezing point in the ternary system: in this case it is the binary eutectic in the system B–C. At higher temperatures the isotherm shows two branches intersecting in a point, l', which represents a liquid that can exist in equilibrium with both solid C and a solid solution of composition s' [Fig. 3 (i)]. The locus of l' over a range of temperature is shown in projection in Fig. 3 (ii); it extends

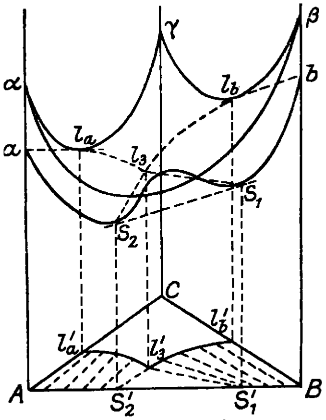


Fig. 5. (i)

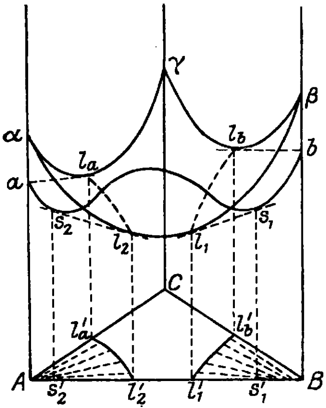


Fig. 5. (ii)

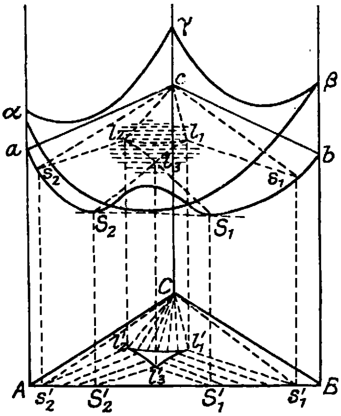


Fig. 5. (iv)

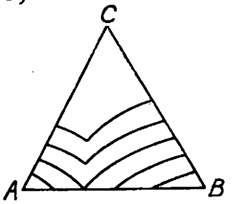


Fig. 5. (iii)

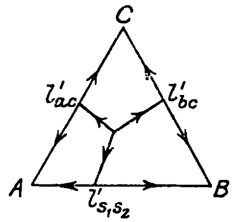


Fig. 5. (v)

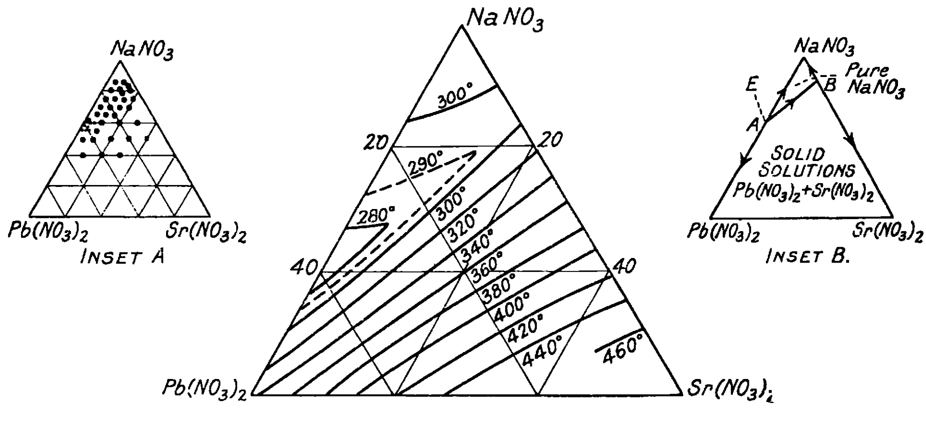


Fig. 6.

from the binary eutectic point l'_{bc} to the binary eutectic l'_{ac}; the freezing points of mixtures represented along this line rise continuously from l'_{ac} to l'_{ac} and this is shown by arrows.

When the first conjugation line in the surface as_1bc to touch the surface $\alpha\beta\gamma$ lies between ac and bc, the point of contact, representing the mixture of lowest freezing point in the ternary system, corresponds to a three-component mixture. At higher temperatures the surface as_1bc cuts $\alpha\beta\gamma$ in a closed curve [shaded in Fig. 4 (i)], and the isotherm consists of two branches which enclose an area within the triangle ABC. The loci of l'_2 and l'_1 [Fig. 4 (i)] form a curve [projected in Fig. 4 (ii)] with a freezing-point minimum.

II. *The solid solution series A–B is not continuous.* The curve ab is now in part concave to AB. Take first the case in which C does not separate as a solid at the temperature considered. When the solid solution series A–B is of the eutectic type, the derivation of the isotherms at two typical temperatures is shown in Fig. 5 (i) and (ii), and Fig. 5 (iii) summarises the isotherms over a temperature range. The locus of l', the point of intersection of the two branches, is a eutectic trough beginning at the binary eutectic in the system A–B.

When C can also separate as a solid phase, the ζ values of complexes of solid C with solid solutions are represented on a surface as_2s_1bc formed by joining c by straight lines to every point on ab. A double touching plane can be drawn to this surface containing the triangle cs_2s_1 and when, as temperature is raised, a point in this triangle first makes contact with the surface $\alpha\beta\gamma$, the touching point, representing the liquid of lowest freezing point in the ternary system, corresponds to a liquid which can exist in equilibrium with three solids, *viz.*, solid C, and the two limiting solid solutions, S'_1 and S'_2. This is thus an invariant point and is, in fact, the ternary eutectic point. At higher temperatures, as_2s_1bc cuts $\alpha\beta\gamma$ in a closed curve, shaded in Fig. 5 (iv), and the isotherm shows three branches. The loci of l'_1 and l'_2 are eutectic troughs extending from the ternary eutectic point to the binary eutectics l'_{bc} and l'_{ac} respectively. Freezing points alter along these curves as shown in Fig. 5 (v).

Similar isotherm forms are obtained even when the two series of solid solutions, As'_2 and s'_1B, are not of the same crystal type (isodimorphism).

EXPERIMENTAL (with DOROTHY FREEMAN).

Of the six binary systems realisable among the nitrates of calcium, strontium, barium, and lead, one has already been reported (Part III, J., **1933**, 236). The nature of the remaining five systems has now been examined by an investigation of five ternary systems. In each case the liquidus surface has been determined within the limits prescribed by decomposition, and in two systems experiments have been made to ascertain the nature of the solid $\rightleftharpoons$ liquid equilibria.

Purification of materials, determination of freezing points, and examination of solid phases were carried out as described in Part III (*loc. cit.*). It was necessary to determine several binary systems and these are reported here.

The System $NaNO_3$–$Pb(NO_3)_2$–$Sr(NO_3)_2$.—In addition to binary points, thirty-six ternary f. p.'s (Fig. 6, inset A) were determined. The mixture of lowest f. p. is the binary eutectic of lead nitrate with sodium nitrate (E, Fig. 6, inset B). Fig. 6 shows the isotherms and Fig. 7 the liquidus–solidus conjugation lines.

Lead and strontium were determined as combined sulphates; lead was then removed as sulphide and strontium determined as sulphate: the analytical figures are in Table I.

TABLE I.

Liquid phase.		Solid phase.		Liquid phase.		Solid phase.	
$Pb(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Pb(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Pb(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Pb(NO_3)_2$, %.	$Sr(NO_3)_2$, %.
A. Isotherm 290°.				B. Isotherm 320°.			
25·02	1·96	14·68	1·29	5·00	18·98	5·13	44·42
19·33	5·61	10·62	3·10	14·72	15·66	16·85	35·40
11·24	10·47	6·31	6·18	21·97	13·08	29·38	32·51
				30·84	9·83	41·75	25·49
				36·69	7·72	51·60	20·17
				42·05	5·70	59·26	14·68
				46·49	3·93	60·71	7·87
				51·10	2·02	69·28	4·34

The System KNO_3–$Sr(NO_3)_2$–$Ba(NO_3)_2$.—Twenty-seven ternary f. p.'s (Fig. 8, inset A) were determined; the mixture of lowest f. p. in the ternary system (260°) has the composition KNO_3, 73·5; $Sr(NO_3)_2$, 23·5; $Ba(NO_3)_2$, 3% (E, Fig. 8, inset B). Fig. 8 shows the isotherms and Fig. 9 the liquidus $\rightleftharpoons$ solidus conjugation lines.

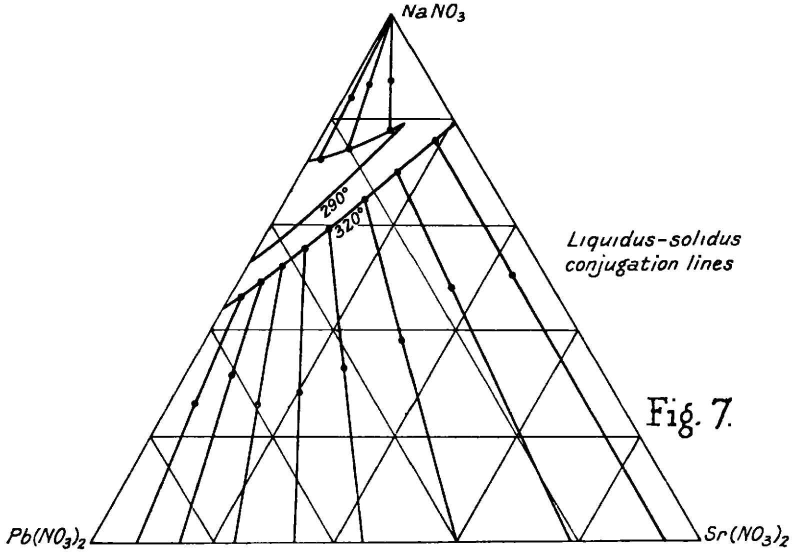


Fig. 7.

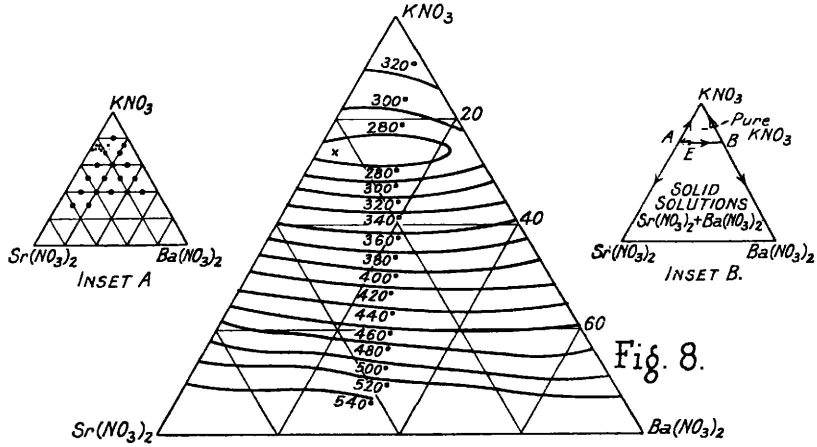


Fig. 8.

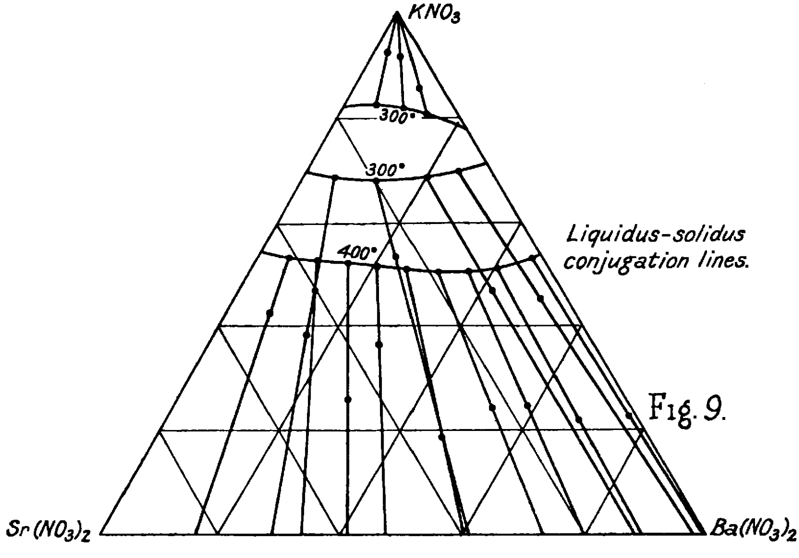


Fig. 9.

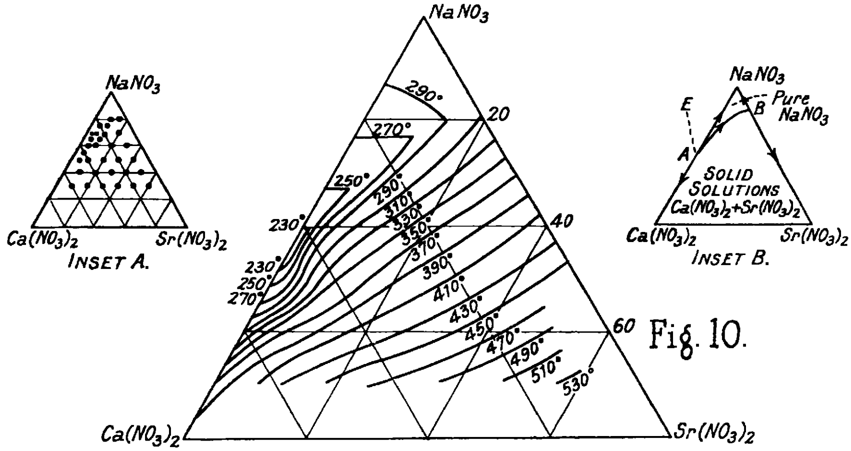


Fig. 10.

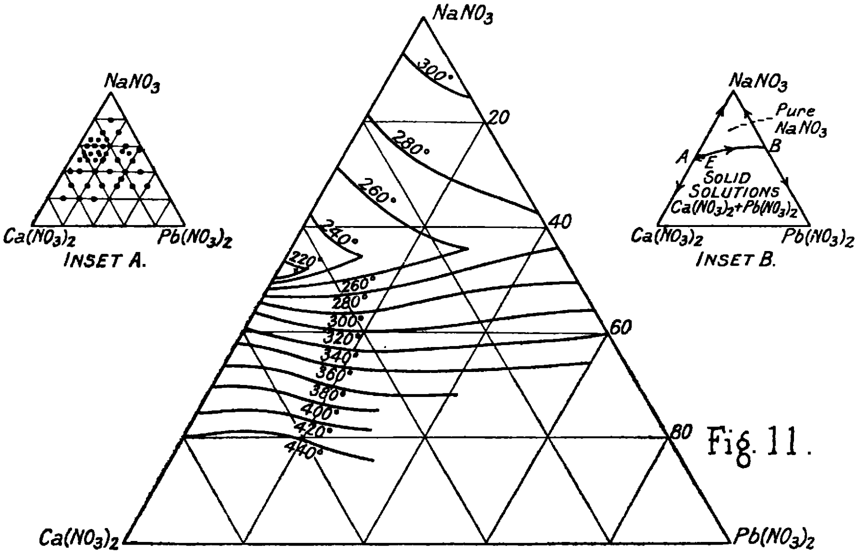


Fig. 11.

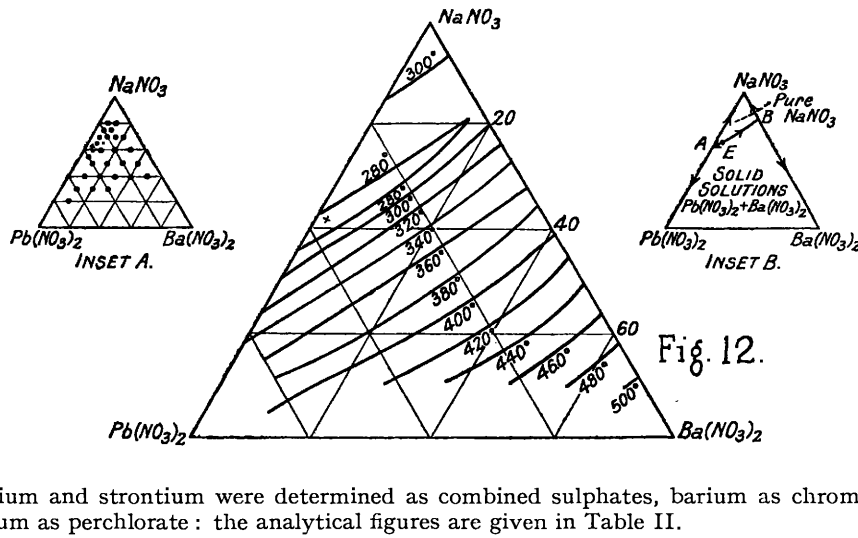


Fig. 12.

Barium and strontium were determined as combined sulphates, barium as chromate, and potassium as perchlorate : the analytical figures are given in Table II.

TABLE II.

Liquid phase.		Solid phase.		Liquid phase.		Solid phase.	
$Ba(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Ba(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Ba(NO_3)_2$, %.	$Sr(NO_3)_2$, %.	$Ba(NO_3)_2$, %.	$Sr(NO_3)_2$, %.
A. Isotherm 300°.				B. Isotherm 400°.			
4·7	26·7	15·8	45·9	5·2	41·7	7·2	50·4
25·3	5·5	50·5	3·7	10·2	37·5	12·4	40·8
20·2	10·9	41·8	11·3	15·3	33·0	27·8	46·0
12·3	19·5	22·5	24·2	20·7	29·5	27·2	35·2
5·2	12·3	2·6	5·1	25·2	33·8	47·8	33·5
10·5	7·3	4·8	3·9	30·9	19·1	52·5	22·3
15·2	4·3	11·1	3·3	35·4	14·6	58·0	17·1
				40·5	7·4	68·1	9·8
				45·1	2·1	75·8	1·0

The System $NaNO_3$–$Ca(NO_3)_2$–$Pb(NO_3)_2$.—Thirty-one ternary f. p.'s (Fig. 10, inset A) were determined. The mixture of lowest f. p. is the binary eutectic of sodium nitrate with calcium nitrate (E, Fig. 10, inset B) : isotherms in Fig. 10.

The System $NaNO_3$–$Ca(NO_3)_2$–$Pb(NO_3)_2$.—Forty-two ternary f. p.'s (Fig. 11, inset A) were determined. There is a minimum f. p. at 202°; composition $NaNO_3$, 51·8; $Ca(NO_3)_2$, 45·2; $Pb(NO_3)_2$, 3% (E, Fig. 11, inset B) : isotherms in Fig. 11.

The System $NaNO_3$–$Ba(NO_3)_2$–$Pb(NO_3)_2$.—Thirty-five ternary f. p.'s determined (Fig. 12, inset A). There is a minimum f. p. at 269°; composition $NaNO_3$, 61·5; $Ba(NO_3)_2$, 2·5; $Pb(NO_3)_2$, 36% (E, Fig. 12, inset B) : isotherms in Fig. 12.

Binary Systems.—Fig. 13 shows the f.-p. curves as obtained for five binary systems. Each system is of the simple eutectic type and the eutectic temperatures and compositions are set out in Table III.

TABLE III.

System.	Eutectic composition, %.	Eutectic temp.
1. $NaNO_3$–$Ba(NO_3)_2$	$NaNO_3$, 82·7; $Ba(NO_3)_2$, 17·3	284·0°
2. $NaNO_3$–$Sr(NO_3)_2$	$NaNO_3$, 84·2; $Sr(NO_3)_2$, 15·8	294·9
3. $NaNO_3$–$Ca(NO_3)_2$	$NaNO_3$, 50·8; $Ca(NO_3)_2$, 49·2	211·3
4. KNO_3–$Ba(NO_3)_2$	KNO_3, 73·0; $Ba(NO_3)_2$, 27·0	285·7
5. KNO_3–$Sr(NO_3)_2$	KNO_3, 33·8; $Sr(NO_3)_2$, 66·2	274·8

DISCUSSION.

On the basis of the theoretical treatment presented in this paper, the various liquidus surfaces realised by us experimentally fall into a few well-defined classes. In each ternary system examined the forms of the isotherms strongly suggest the existence of one binary solid solution system and give a clear indication of the probable type of that system in Roozeboom's classification. An examination of solid $\rightleftharpoons$ liquid equilibria in several of the systems has confirmed these deductions.

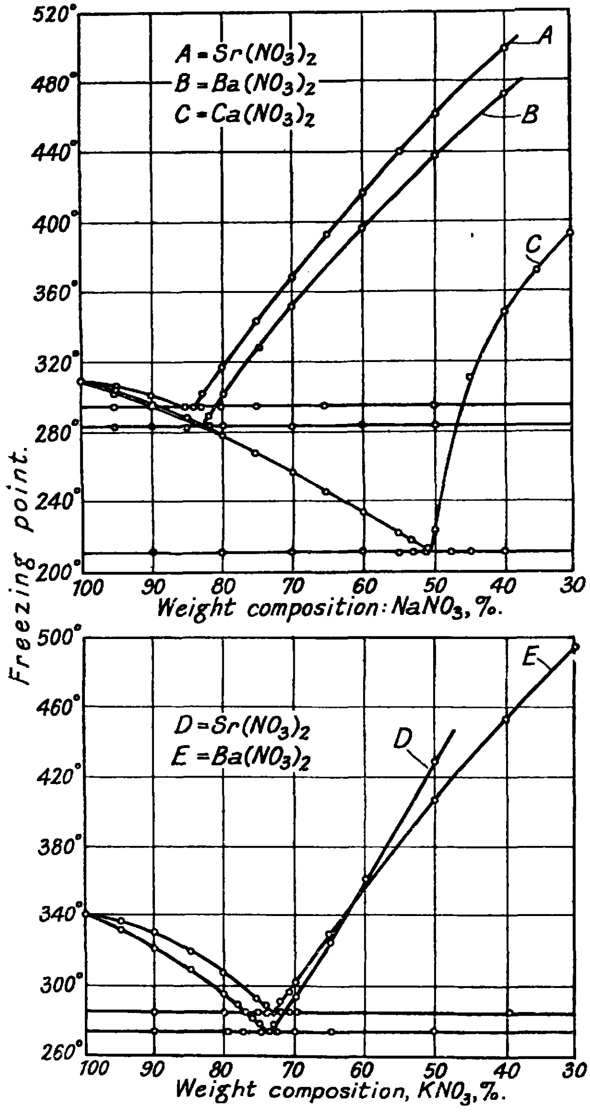
1. *The system* $NaNO_3$–KNO_3–$Pb(NO_3)_2$ (J., 1932, 2582). This system exhibits a ternary minimum point [compare Fig. 4 (ii)] whilst the solid solution isotherms are of the type of Fig. 2 (iii). The binary system $NaNO_3$–KNO_3 is thus probably of Roozeboom's Type III, *i.e.*, the solid solution series has a freezing-point minimum. The conjugation lines obtained experimentally for this system accord with those of Fig. 2 (i) and (ii) and Fig. 4 (i).

2. *The systems* KNO_3–$Sr(NO_3)_2$–$Ba(NO_3)_2$, $NaNO_3$–$Ca(NO_3)_2$–$Pb(NO_3)_2$, *and* $NaNO_3$–$Ba(NO_3)_2$–$Pb(NO_3)_2$. All three systems have the same type of isothermal diagram; there is a ternary minimum point, and the isotherms differ from those in the preceding system in showing no marked dip. It is evident that in each of the three binary systems of the non-alkali metal nitrates a complete series of solid solutions exists, and since the isotherms resemble those of Fig. 1 (iii), the solid solution series are probably of Roozeboom's Type I. The conjugation lines of Fig. 9 are comparable with Fig. 1 (ii).

3. *The systems* KNO_3–$Ca(NO_3)_2$–$Ba(NO_3)_2$ (J., 1933, 236), $NaNO_3$–$Ca(NO_3)_2$–$Sr(NO_3)_2$, *and* $NaNO_3$–$Pb(NO_3)_2$–$Sr(NO_3)_2$. These three systems differ from those immediately preceding only in that the mixture of lowest freezing point is in each case a binary eutectic, *i.e.*, the type is that of Fig. 3 (ii). Like the binary system $Ca(NO_3)_2$–$Ba(NO_3)_2$, the systems $Ca(NO_3)_2$–$Sr(NO_3)_2$ and $Pb(NO_3)_2$–$Sr(NO_3)_2$ evidently represent continuous series of solid solutions. In the system $NaNO_3$–$Pb(NO_3)_2$–$Sr(NO_3)_2$ the isotherms are of the type shown

in Fig. 1 (i) and (ii) and Fig. 3 (i), and the binary system $Pb(NO_3)_2$–$Sr(NO_3)_2$ is therefore probably of Roozeboom's Type I; but the isotherms for the other two ternary systems appear to be transition types, so that the binary systems $Ca(NO_3)_2$–$Ba(NO_3)_2$ and $Ca(NO_3)_2$–$Sr(NO_3)_2$ may be of a type intermediate between Roozeboom's Types I and III. The conjugation lines of Fig. 7 are comparable with those of Figs. 1 (ii) and 3 (i).

FIG. 13.



4. *The system*

KNO_3–NH_4NO_3–$Pb(NO_3)_2$

(J., 1933, 199). This system has a ternary eutectic point and three troughs along which the freezing points rise towards the three binary eutectics [Fig. 5 (v)]. It is clear from the conjugation lines found experimentally that the system

KNO_3–NH_4NO_3

forms a series of solid solutions with a miscibility gap (compare Fig. 5), and the isotherms thus indicate that the binary solid solution series is of the eutectic type.

5. *The binary system*

$Ca(NO_3)_2$–$NaNO_3$.

The great temperature lowering at the eutectic composition in this system is comparable with that in the system $Ca(NO_3)_2$–KNO_3, reported by Rostkovski (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 2055), who regarded the abnormal lowering as evidence of compound formation. Cooling curves have failed to give any indication of a compound in the present system, which is comparable with

KNO_3–$Pb(NO_3)_2$,

where a great temperature lowering at the eutectic composition was not accompanied by evidence of compound formation.

SUMMARY.

The graphical thermodynamic treatment of certain heterogeneous systems, involving solid solutions, has been extended to elucidate the experimental results obtained by us for ternary systems. The liquidus surfaces have been determined for five ternary systems involving nitrates of the alkali metals, the alkaline earths, and lead, and in two cases solid $\rightleftharpoons$ liquid equilibria have been investigated analytically. Information concerning five binary systems, not hitherto reported, has emerged incidentally. The experimental results, together with those given in earlier parts of this series, have been discussed collectively in the light of our extended graphical treatment.

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