66. *Liquidus and Solidus Studies. Part III. The Ternary System* $Ba(NO_3)_2$–$Ca(NO_3)_2$–KNO_3.

By K. LAYBOURN and W. M. MADGIN.

THE alkaline-earth nitrates and lead nitrate all decompose at low temperatures below the respective fusion points and, consequently, binary systems formed by any two of these salts cannot be investigated by simple thermal analysis. Vegard and Bilberg (*Norske Videnskaps Akad. Oslo*, Avhandl. I, Mat. Naturv. Klasse, 1931, **12**, 1) have shown crystallographically that these four nitrates all belong to the same space group, and Ringdal (*Z. Krist.*, 1932, **82**, 50), using *X*-ray methods, has shown that strontium nitrate forms mixed crystals in all proportions with either barium or calcium nitrate. Vegard and Dale (*ibid.*, 1928, **67**, 148) have shown that barium and lead nitrates are completely miscible in the solid state. From *X*-ray films for calcium nitrate–barium nitrate mixtures, Ringdal (*loc. cit.*) finds weak and diffuse lines, but all measurable lines follow Vegard's additive law for mixed crystals.

It appeared that the authors' method (J., 1932, 2582) of investigating binary systems by the addition of a third component might conveniently be applied to the various binary systems realisable from the four nitrates in question, and the present work concerns the nitrates of barium and calcium. Potassium nitrate was used as a third component, not only because of its own stability, but also because it was thought that it might prove to be an inert solvent giving mixtures of very low melting point (*e.g.*, with lead nitrate it gives a eutectic temp. of 217°; Glass, Laybourn, and Madgin, J., 1932, 874).

Harkins and Clark (*J. Amer. Chem. Soc.*, 1915, **37**, 1816) state that potassium nitrate forms a eutectic system with barium nitrate. Menzies and Dutt (*ibid.*, 1911, **33**, 1366) claim that potassium nitrate and calcium nitrate form a eutectic mixture melting at 210°, but Rostkovski (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 2055) gave the eutectic temperature as 145° and also stated that these two nitrates form an incongruently melting compound, unstable above 174°. The formation of such a compound would not interfere with the present investigation of solid–liquid equilibria, since these have been carried out at much higher temperatures than 174°. It was thought that information concerning this compound might emerge from the present work.

EXPERIMENTAL.

Purification of KNO_3 was effected as previously described (*loc. cit.*); $Ba(NO_3)_2$ was recryst. thrice from H_2O and dried at 120°, and $Ca(NO_3)_2$ (A.R. quality) was recryst. and dehydrated at 130°.

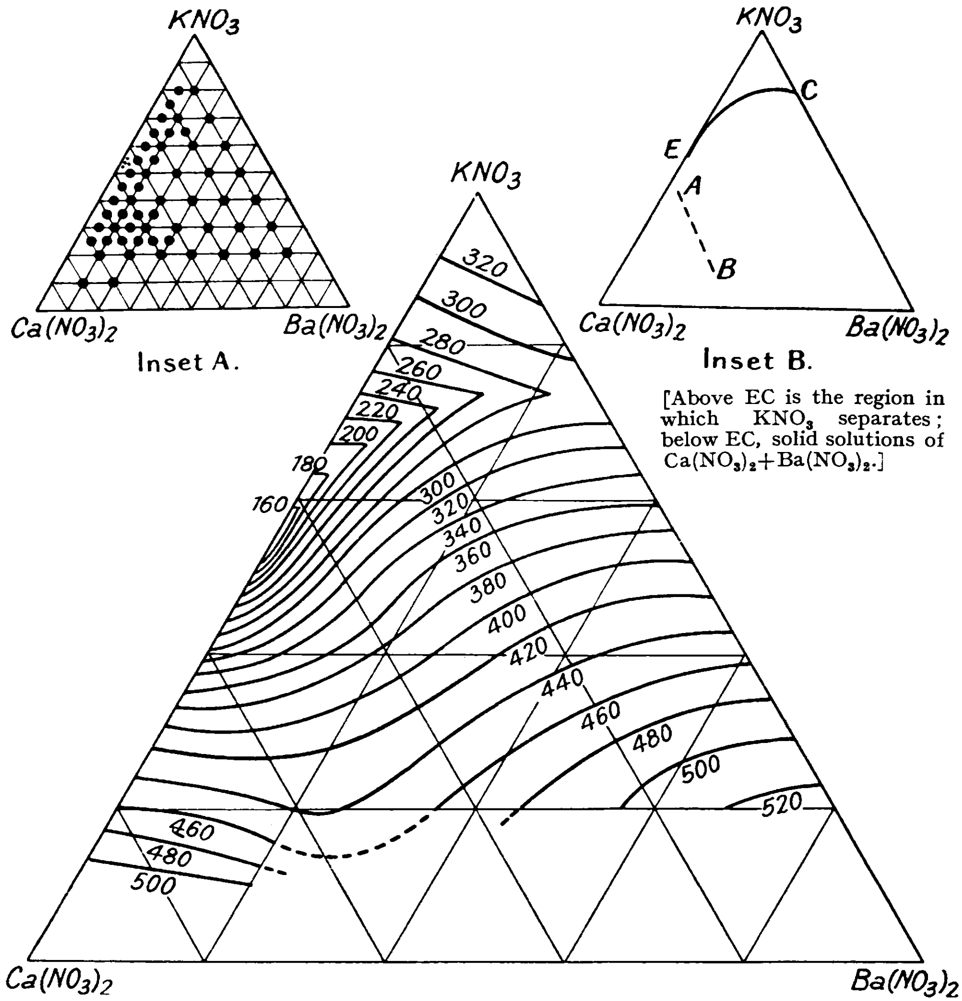
According to Carnelley (J., 1878, **33**, 273), the m. p.'s of $Ba(NO_3)_2$ and $Ca(NO_3)_2$ are both higher than 550°, but we find that decomp. of both salts is violent below 500° (before fusion occurs). However, in ternary mixtures of these two salts with KNO_3 it has been found possible to determine f. p.'s as high as 500°, and the scope of the present investigation has been extended to mixtures containing as much as a total of 80% (by wt.) of the alkaline-earth nitrates. The f. p. data for the two binary systems involving KNO_3 have been redetermined, since much of the earlier work is conflicting.

Freezing Points and Isotherms for Ternary Mixtures.—In addition to the f. p.'s of binary mixtures, those of 60 different ternary mixtures have been found and an isothermal diagram has been constructed (Fig. 1). In deciding the exact form of the isotherms, the essential requirement is a large number of f. p.'s rather than great accuracy in their determination, and in the results now reported, an accuracy of $\pm$ 1° has been considered adequate.

The temp. range of these f. p.'s is very great (529—144°), and therefore a thermocouple (of " chromel–eureka " wire, 30 S.W.G.; made by Foster Instrument Co., Letchworth), in series with an accurate millivoltmeter, was used to determine the f. p.'s. The instrument was calibrated to give temps. to 0·5°.

FIG. 1.

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



F. p.'s were determined by fusing 20 g. of the required mixture in a hard-glass test-tube suspended in a specially constructed electric furnace provided with two small glass observation windows so that the melt could be observed directly without undue heat loss. On cooling the melt, with the thermocouple immersed, the first appearance of solid was easily observed and the corresponding temp. (f. p.) noted. The rate of cooling was very slow (not exceeding 2° per min. for higher temps.), and stirring was done continuously with a glass stirrer.

In mixtures not far removed from the comp. of the eutectic mixture of KNO_3 and $Ca(NO_3)_2$ and having f. p.'s lower than 180° (approx.), viscosity was very great and consequently supercooling was pronounced. For this reason, in addition to cooling expts., these mixtures were re-heated after solidification had commenced, and the temp. (m. p.) at which the last trace of solid disappeared was noted. The mean of the m. p. and the obs. f. p. was regarded as the true f. p. for any one mixture.

Mixture of Lowest Freezing Point.—The present ternary system is peculiar in that no ternary mixture has a f. p. lower than that of the binary eutectic in the system $Ca(NO_3)_2$–KNO_3 (*viz.*, 144°). This fact was obvious from the isotherms (Fig. 1) and was confirmed by determining the f. p.'s of mixtures of comp. differing only slightly from that of the binary eutectic. In every case examined the f. p. was considerably higher than 144°, as is apparent from the results in Table I.

TABLE I.

Mixtures of very low freezing point.

KNO_3, %.	$Ca(NO_3)_2$, %.	$Ba(NO_3)_2$, %.	F. p.	KNO_3, %.	$Ca(NO_3)_2$, %.	$Ba(NO_3)_2$, %.	F. p.
53·5	46·5	0·0	144°	52·0	47·0	1·0	180°
52·5	47·5	0·0	152	54·0	44·0	2·0	208
55·0	44·0	1·0	182	55·0	40·0	5·0	247
54·0	45·0	1·0	180	50·0	45·0	5·0	263
53·0	46·0	1·0	178				

Thus the binary eutectic mixture of KNO_3–$Ca(NO_3)_2$ has the lowest f. p. realisable in the ternary system, and the comp. (wt.) is KNO_3 53·5% and $Ca(NO_3)_2$ 46·5% (cf. Rostkovski, *loc. cit.*, who gave KNO_3 54·3% and f. p. 145°).

Examination of Solid Phases.—Samples of the solid phases separating from mixtures lying on the isothermals 270°, 300°, and 370° were isolated by the method previously described (*loc. cit.*), and samples of liquid in equilibrium with these solids were simultaneously taken. In view of the very deliquescent nature of $Ca(NO_3)_2$, it was necessary to seal all samples immediately in weighed glass tubes. After weighing, the sealed tubes were broken under H_2O and each sample was analysed for K as $KClO_4$ (after removal of Ca and Ba as carbonates) and for Ba as $BaCrO_4$.

TABLE II.

A. Mixtures located on the isotherm 270°.

Liquid phase. $Ba(NO_3)_2$, %.	Liquid phase. KNO_3, %.	Solid phase. $Ba(NO_3)_2$, %.	Solid phase. KNO_3, %.
1·02	43·92	4·16	37·72
1·99	44·42	7·02	38·04
4·72	47·58	12·79	39·20
5·91	50·72	19·22	38·29
7·25	56·40	26·13	40·18
9·96	64·63	33·04	46·55
15·18	72·06	38·88	51·97
15·60	74·14	9·21	84·89
10·65	75·82	6·33	85·71
7·31	76·83	3·97	87·31
2·78	78·09	1·89	86·09

B. Mixtures located on the isotherm 370°.

Liquid phase. $Ba(NO_3)_2$, %.	Liquid phase. KNO_3, %.	Solid phase. $Ba(NO_3)_2$, %.	Solid phase. KNO_3, %.
1·58	33·98	2·02	26·33
4·46	34·44	6·68	25·26
7·42	35·02	12·83	24·19
11·61	36·23	19·45	24·05
14·70	38·10	27·62	22·86
16·82	40·37	31·90	27·14
19·41	45·59	43·36	27·99
20·88	48·66	47·78	30·28
27·09	54·58	54·00	33·92
35·07	57·24	59·01	36·04

C. Mixtures located on the isotherm 300°.

Liquid phase. $Ba(NO_3)_2$, %.	Liquid phase. KNO_3, %.	Solid phase. $Ba(NO_3)_2$, %.	Solid phase. KNO_3, %.
21·17	77·92	14·50	84·83
16·94	79·41	10·76	86·49

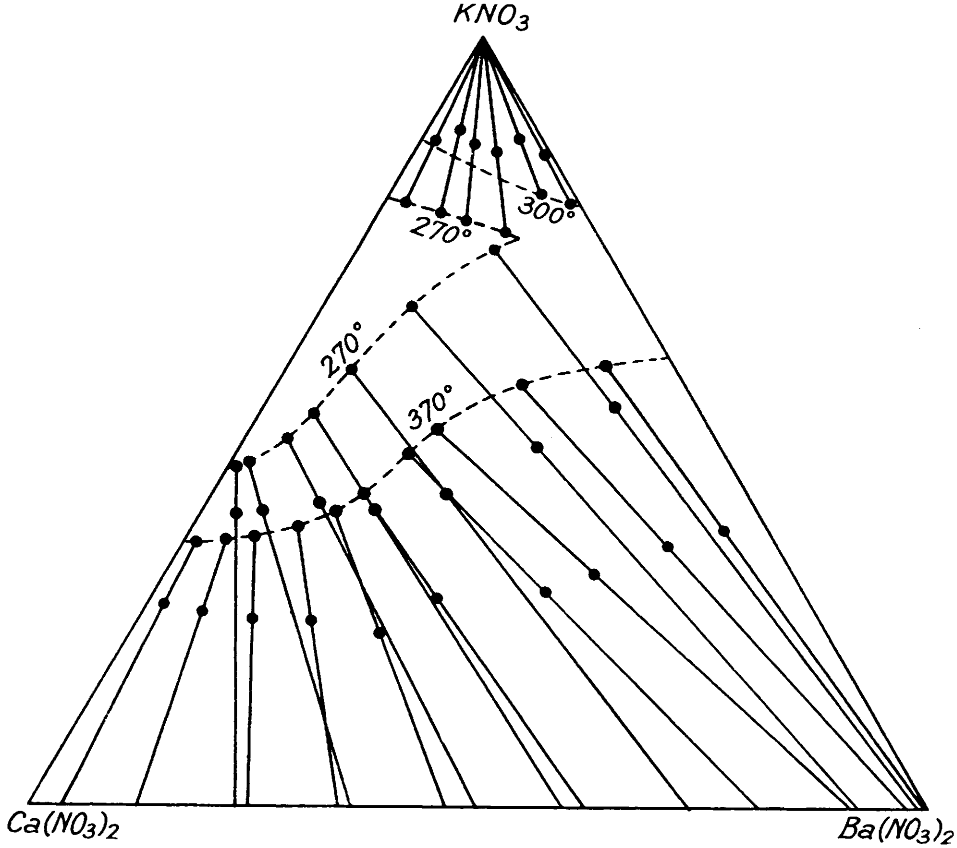
The results of these analyses (Table II) are shown in Fig. 2. Since Rostkovski (*loc. cit.*) claims that a compound, $Ca(NO_3)_2,4KNO_3$, is formed, attempts were made to examine solid phases separating from mixtures within the very small area enclosed by the 180° isotherm. Owing to the very great viscosity and consequent bad drainage of these solid phases, together with the proximity of the liquid and solid phase compositions to the side of the triangle (Fig. 1) corresponding to the two-component system $Ca(NO_3)_2$–KNO_3, the results of these examinations were inconclusive (cf. Browne, *J. Physical Chem.*, 1902, **6**, 305). Consequently it was not possible to determine the nature of the solid phases separating from mixtures of very low f. p.

Discussion of Results.—It appears from the tie lines in Fig. 2 that the two salts $Ca(NO_3)_2$ and $Ba(NO_3)_2$ form a continuous series of solid solutions at the temps. of the isothermals considered. A large number of mixtures, covering a wide range of composition, has been examined in order to explore the possibility of partial miscibility (cf. Glass, Laybourn, and Madgin, this vol., p. 199).

A consideration of Fig. 1 suggests that, if the isothermals could be determined over the whole diagram, the solid solution basin AB (inset B) would be continued to the binary system $Ca(NO_3)_2$–$Ba(NO_3)_2$, but evidently no mixture of these salts can be fused at a sufficiently low temperature to exclude decomposition. However, the present results indicate that, when the m. p.'s of the components are sufficiently lowered by the addition of a third component, so that they can be melted together without decomposition, the two salts do, in fact, form a continuous series of solid solutions. This use of low-temperature systems of molten salts, such as those represented by the isothermals in Fig. 2, to determine the miscibility or otherwise of components which decompose below their m. p.'s and have no stable fusion range, is a valuable experimental technique.

FIG. 2.

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



The authors' previous work (*loc. cit.*) and also Part II of this series (this vol., p. 199) deal with solid–liquid equilibria involving binary systems with definite fusion ranges, and the isothermals there investigated were all for temperatures lying within, or very close to, these ranges. An unusual feature of the present system is that only one eutectic trough appears in the ternary diagram (EC, Inset B, Fig. 1) and no ternary eutectic mixture is formed. It was shown by van Rijn van Alkemade (*Z. physikal. Chem.*, 1893, **11**, 289) that the freezing point of a binary eutectic mixture will be lowered by adding a third component so long as the solid phase separating is a pure component. However, there is no thermodynamic basis for assuming such a lowering of f. p. when the third component forms solid solutions with one component of the eutectic mixture, and, indeed, the f. p. of the eutectic mixture between potassium and calcium nitrates (E, Inset B, Fig. 1) is continually raised along the eutectic trough EC. The solid phase separating along this trough is a eutectic mixture consisting of pure potassium nitrate together with solid solutions of the two other nitrates.

Glasstone and Riggs (J., 1925, **127**, 2846) found that potassium and barium nitrates separate as a compound from aqueous solutions at 50° and 25°, but Rostkovski (*loc. cit.*) was unable to detect this compound in molten mixtures of these two salts. The isothermals (Fig. 2) do not suggest that a compound is formed under the conditions used in the present work.

SUMMARY.

A method is described for investigating the nature of the system $Ca(NO_3)_2$–$Ba(NO_3)_2$, which, owing to decomposition, has no stable fusion range, from a study of the ternary system KNO_3–$Ca(NO_3)_2$–$Ba(NO_3)_2$. The form of the liquidus surface of the ternary system has been determined, and only one eutectic trough appears across the isothermal diagram. No mixture in the ternary system has a lower freezing point than that of the binary eutectic mixture in the KNO_3–$Ca(NO_3)_2$ system. Solid phases from mixtures on the 270°, 300°, and 370° isotherms have been examined, and it appears that calcium and barium nitrates form a continuous series of solid solutions under the conditions of the present experiments.

We are indebted to the Research Committee of this College for a grant.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, January 26th*, 1933.]