THE LIQUIDUS SURFACE OF THE TERNARY SYSTEM COMPOSED OF THE NITRATES OF POTASSIUM, SODIUM AND CALCIUM.

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The cases are not yet numerous in which the liquidus surface of a ternary system has been explored throughout the entire range of possible concentration. In many cases where the results promised to be of direct utilitarian value in the arts, portions of such surfaces have been intensively studied, especially in the case of metallic alloys. In the latter case, however, wide regions of concentration fall outside the composition of the commercially useful alloys, and have therefore remained uninvestigated as possessing merely scientific interest. The present work has had its ulterior object in the search for a low-melting bath liquid for use in the laboratory that should, among other qualifications, be stable, transparent, non-volatile, uninflammable, cheap, applicable over wide ranges of temperature, and without harmful action upon glass or metal. Fused nitrates have already been used in this laboratory as elsewhere with some success for this purpose; and, to extend our knowledge of nitrate mixtures in respect of fusibility, one step is here made by a study of the complete liquidus surface for ternary mixtures of the nitrates of potassium, sodium and calcium. It is hoped that further steps in the same direction may be undertaken later.

The Degree of Accuracy Aimed At.—When the temperatures measured are much above 200°, determinations of the freezing and melting points even of ostensibly pure substances by different observers are notoriously discordant. Selecting, for example, as a case in which better concordance might well be expected, the lowest melting of the three components of the system here studied, namely potassium nitrate, we find the melting point of this so well defined and easily purified substance given by the several observers as 339°; 338.3°; 342°; 353° ± 1; 339° ± 2; 320°; 327° (see p. 1375).

In the case of two-component systems, where the solid phase separating on freezing differs in composition from the liquid phase that forms the mother liquor, it is very obvious that such a high degree of concordance cannot be expected as in the case of a single pure substance, for the reason that, in general, the liquid phase varies progressively in concentration as the freezing-out process proceeds. In the presence of still a third component it would seem to be altogether futile to expect the same degree of accuracy in freezing point measurement, especially in view of the added opportunities of error in synthesizing directly the ternary mixtures from materials each of which is a possible contributor of impurity. For the purposes of the study contemplated, therefore, it was considered unprofitable to aim at an accuracy of freezing point measurement higher than ± 1°, as this is amply sufficient to adequately characterize the liquidus surface. The proposed degree of accuracy having been thus decided upon in advance, it became possible to avoid the labor of unnecessary and disproportionate refinements in all of the subsequent work. In this, as in other normal cases, higher precision of measurement would be attainable only by the expenditure of much more than a proportional amount of time and labor.

The Material Employed, and Its Purity.—All three nitrates were the purest preparations of Kahlbaum. Qualitative examination demonstrated the absence of chloride, chlorate, perchlorate, sulfate and of heavy metals. Calcium was absent from the potassium and sodium nitrates. The nitrates were then dried. The potassium and sodium nitrates required nothing but grinding and maintaining at 150° until the weight was constant. The calcium nitrate, which contained four molecules of water of hydration, was gradually desiccated by gentle heating and the drying completed at 150° until constant weighings were obtained.

Quantitative examination of each of the three nitrates was made as follows:

Potassium Nitrate.—Quantities of about 5 grams were converted into sulfate in a platinum crucible in the usual way. In the results here tabulated all weights are stated in grams:

	Nitrate taken.	Sulfate found.	Sulfate expected.	Difference.
(1)............	5.1434	4.4298	4.4312	0.0014
(2)............	5.1423	4.4276	4.4303	0.0027

If the difference in the last column is attributed solely to the presence of sodium nitrate, then this impurity is present to the extent of (1) 0.19 per cent.; (2) 0.36 per cent.

An estimate of the effect of impurities upon the melting point may be obtained by a consideration of the "molecular depression" for fused potassium nitrate regarded as a cryoscopic solvent. Using, in van't Hoff's formula, the latent heat of fusion observed by Person,[1] Stern[2] computes for potassium nitrate the molecular depression 16°.

Sodium Nitrate.—The results obtained by a similar treatment were:

	Nitrate taken.	Sulfate found.	Sulfate expected.	Difference.
(1)............	5.1746	3.6759	3.6758	0.0001
(2)............	5.1646	4.6689	3.6688	0.0001

Calcium Nitrate.—Portions of about 2 grams were converted to oxide by ignition in platinum crucibles over the blast-lamp. The following results were obtained:

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[1] *Pogg. Ann.*, 10, 300 (1847).

[2] *Z. physik. Chem.*, **65**, 667 (1909).

	Nitrate taken.	Oxide found.	Oxide expected.	Difference.
(1)............	1.9529	0.6654	0.6673	0.0019
(2)............	1.8498	0.6305	0.6322	0.0017

If the difference be attributed to presence of water in the nitrate taken, the amount of this impurity would be (1) 0.09 per cent. and (2) 0.3 per cent., respectively.

An approximate estimate of the effect of impurities on the freezing points of each of the three nitrates may be obtained directly from an inspection of Table I below, from which it may be seen, for example, that the presence of one molecule of sodium nitrate among 99 molecules of potassium nitrate would lower the freezing point of the latter by less than 3°; or that one equivalent of calcium nitrate in 99 equivalents of sodium nitrate would lower its freezing point by about 1°. In view of the degree of accuracy aimed at, therefore, the degree of purity of the materials used may be considered adequate.

The Method Employed.—About 20 grams of each of the mixtures investigated were prepared by synthesis, weighings being made to the nearest centigram. After grinding in a mortar, each mixture was transferred to a 130 × 12 mm. test tube, which was then heated in a suitable bath. After melting was complete, the temperature was slowly lowered, with constant stirring, until the first fine crystals appeared; the temperature was then noted upon a thermometer immersed directly in the melt. By slowly raising the temperature again, the point at which the last crystals vanished was likewise noted. The process could be repeated with concordance within 0.2°, provided the stirring was sufficiently vigorous.

The Heating Bath and Stirrer.—In the earlier experiments, stirred paraffin and other transparent baths were used with success. It was later found, however, that results of adequate accuracy could be much more quickly obtained by the use of an air bath constructed as follows. A glass lamp chimney (250 mm. long, 37 mm. internal diameter) rests on a wire gauze, which is supported by a stoneware tower of the type so often used to protect Bunsen burners from draughts. A chimney was selected whose upper end was broken in such a way as to leave two proecting triangular apices of equal height on opposite sides. A sheet of asbestos (130 mm. square, 7 mm. thick) clamped in a ring stand, by engaging the two apices in two corresponding holes, maintained the chimney in a vertical position and served also to support, by a close-fitting hole, the test tubes containing the nitrate mixtures.

The stirrer consisted of a glass rod (2 mm. diameter) bent in a circle at its lower end so as to loosely embrace the thermometer. A slender cord passing from the top of the stirrer, through a "pulley" formed of a bent glass tube, to a pin set eccentrically in a rotating disc imparted to the stirrer a vertical reciprocating motion. The amplitude of this motion could be varied at will by altering the distance of the pin from the axis of the disc, which was driven by a small three-speed electric motor.

The Temperature Measurement.—A nitrogen-filled thermometer of Jena resistance glass 59^{III} and graduated in whole degrees from 180°–550° over a length of 250 mm. was employed throughout, except in the case of two or three of the lowest temperatures which fell below 180°. The ice-point of this thermometer was determined every working day by the help of the short range of graduations for the purpose, with which the thermometer was provided. A perfectly regular and continuous rise of zero was observed amounting in all to 0.2°. No trouble was experienced from distillation of mercury within the stem.

As the depths of the melt contained in the test tube were not greater than 80 mm., it is obvious that complete immersion of the mercury thread in this liquid was not attainable except for the lower temperatures. It is well known that, for temperatures above 300°, correction for "exposed thread" based on the usual method of computation is far from satisfactory. To overcome this difficulty, the thermometer was standardized with the same amount of exposed thread and with other conditions the same as when it was used.

For purposes of standardization a platinum resistance thermometer of the form devised by Haagen was employed. The quartz-embedded platinum wire forming the "bulb" of this thermometer had an electrical resistance at 0° of about 50 ohms. In comparison with this large resistance, changes of resistance in the gold leads connecting the bulb with the head of the thermometer were negligible, where an accuracy of only 0.1° was aimed at. The resistance measurements were made upon a dial-form Wheatstone bridge whose resistance coils had been previously calibrated. With the arrangement employed, the galvanometer used was sufficiently sensitive to indicate fiftieths of a degree over the whole temperature scale.

As standard points of temperature for use in determining the scale of the platinum thermometer were used the boiling points of sulfur (assumed as 445° on the thermodynamic scale) and the boiling and freezing points of water. The ice-water used in obtaining the ice-point of the thermometer left on subsequent evaporation a residue of 1 part in 10,000, an amount which would not vitiate the accuracy to tenth degrees, which was aimed at in this standardization.

The difference formula of Callendar was utilized in the reduction of resistance to temperature. The other precautions observed have been discussed on another occasion.[1]

[1] THIS JOURNAL, **32**, 1422 (1910).

The Mixtures Examined.—In order sufficiently to cover the field, 70 different mixtures, in all, were examined. It was found that about 10 of the mixtures containing the largest proportions of calcium nitrate yielded, on melting, slightly opalescent instead of perfectly clear liquids. The point at which these mixtures began to deposit crystals was therefore somewhat more difficult to determine than in cases where the liquid was entirely clear. With the very flexible heating arrangement described, however, frequent repetition in cases of doubt is an extremely simple matter, while the speed of cooling can be made as slow as desired. In all cases the temperatures recorded are those at which the first separation of crystals became visible in a briskly stirred liquid cooling not faster than 1 degree per minute.

Tabulation of Results.—With a view to subsequent convenient tabulation, the composition of the mixtures synthesized was chosen so as to fall on the crossing points of the triangular diagram shown in Fig. 1. It

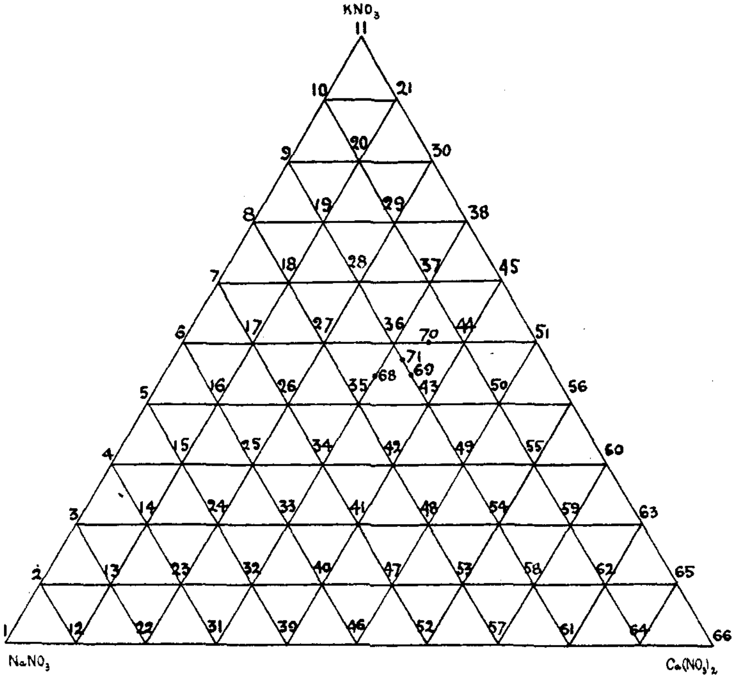

Fig. 1.

will be recalled that in such a diagram each of the three vertices of the triangle represents one of the three chosen substances, considered as 100 per cent. pure. The sum of the three perpendiculars from any selected point within an equilateral triangle upon the three sides is constant and may be considered equal to 100. Accordingly, if percentage composition of each component is taken as represented by the length of the perpendicular from the selected point upon the side opposite to the vertex occupied by that component, it is clear that, with a ruled diagram such as Fig. 1, the percentage composition in each of the three components may, for any crossing point, be read off by inspection.

It was considered more rational to represent equivalent percentages rather than percentages by weight of the three components; for example, point number 25 in Fig. 1 represents the composition of a mixture containing the three nitrates in the proportion of 30 equivalents of potassium nitrate (KNO_3), 50 equivalents of sodium nitrate ($NaNO_3$), and 20 equivalents of calcium nitrate $^1/_2[Ca(NO_3)_2]$; in all, one hundred equivalents.

The number of crossing points obtained by a division of the three sides of the triangle into ten parts, as shown, was considered sufficient for the present purpose. A few additional mixtures were studied in the neighborhood of the ternary eutectic.

The adjoining table, in which the number of each mixture refers to a composition which may be read off from Fig. 1, contains the complete record of all freezing points observed. The position of points numbers 67, 68, 70, and 71 is intended to be exactly midway between the neighboring points; the point 69 lies midway between 36 and 43.

TABLE I.

Point No.	Equivalent percentage.			Freezing point.
	$NaNO_3$.	KNO_3.	$\frac{1}{2}[Ca(NO_3)_2]$.	
1	100	0	0	315.1°
2	90	10	0	290.1
3	80	20	0	274.5
4	70	30	0	255.0
5	60	40	0	237.6
6	50	50	0	228.1
7	40	60	0	242.9
8	30	70	0	262.5
9	20	80	0	289.3
10	10	90	0	316.7
11	0	100	0	346.3
12	90	0	10	303.9
13	80	10	10	284.2
14	70	20	10	260.4
15	60	30	10	234.5
16	50	40	10	225.0
17	40	50	10	222.0
18	30	60	10	240.0
19	20	70	10	268.5
20	10	80	10	291.2
21	0	90	10	318.5
22	80	0	20	285.6
23	70	10	20	263.3

TABLE I—(*Continued*).

Point No.	Equivalent percentage.			Freezing point.
	$NaNO_3$.	KNO_3.	$\frac{1}{2}[Ca(NO_3)_2]$.	
24	60	20	20	240.9°
25	50	30	20	219.8
26	40	40	20	206.3
27	30	50	20	196.2
28	20	60	20	225.0
29	10	70	20	255.0
30	0	80	20	295.2
31	70	0	30	272.9
32	60	10	30	241.0
33	50	20	30	225.0
34	40	30	30	211.6
35	30	40	30	199.3
36	20	50	30	180.0
37	10	60	30	220.7
38	0	70	30	262.2
39	60	0	40	249.8
40	50	10	40	227.0
41	40	20	40	217.2
42	30	30	40	207.6
43	20	40	40	195.2
44	10	50	40	205.3
45	50	60	40	210.5
46	50	0	50	136.5
47	40	10	50	221.5
48	30	20	50	208.7
49	20	30	50	197.8
50	10	40	50	214.8
51	0	0	50	221.9
52	40	0	60	284.1
53	30	10	60	258.2
54	20	20	60	231.2
55	10	30	60	247.8
56	0	40	60	263.3
57	30	0	70	355.4
58	20	10	70	345.3
59	10	20	70	318.3
60	0	30	70	345.3
61	20	0	80	421.0
62	10	10	80	428.0
63	0	20	80	450.0
64	10	0	90	490.0
65	0	10	90	508.4
66	0	0	100	[561.0][1]
67	25	50	25	184.0
68	25	45	30	183.0
69	80	45	35	175.0
70	15	50	35	186.0
71	20	47.5	32.5	176.0

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[1] Carnelley. This point was not determined by us.

The Solid Figure, Its Surfaces, and Its Vertical Sections.—If we agree to represent temperature along an axis perpendicular to the plane of the paper, we have, in Table I, the requisit coördinates in three-dimensional space of 70 points which may be joined smoothly by continuous surfaces. The outlines of vertical sections of these surfaces by three series of planes parallel to the three sides of the triangle were now obtained by direct plotting of the observations. For example, regarding Fig. 1 as a plan, the vertical section on 4–60 should show the curve obtained by plotting the several temperatures observed along 4–60 against the corresponding concentrations. From the sets of curves so obtained, the concentrations could be located graphically at which various mixtures froze at selected round numbers of degrees. By smoothly joining the sets of points representing concentrations of mixtures of identical freezing point the series of isotherms shown in Fig. 2 were obtained. These isotherms are contour lines of the liquidus surface, and are shown for each 10° interval to 300°, and for each 50° interval above that temperature.

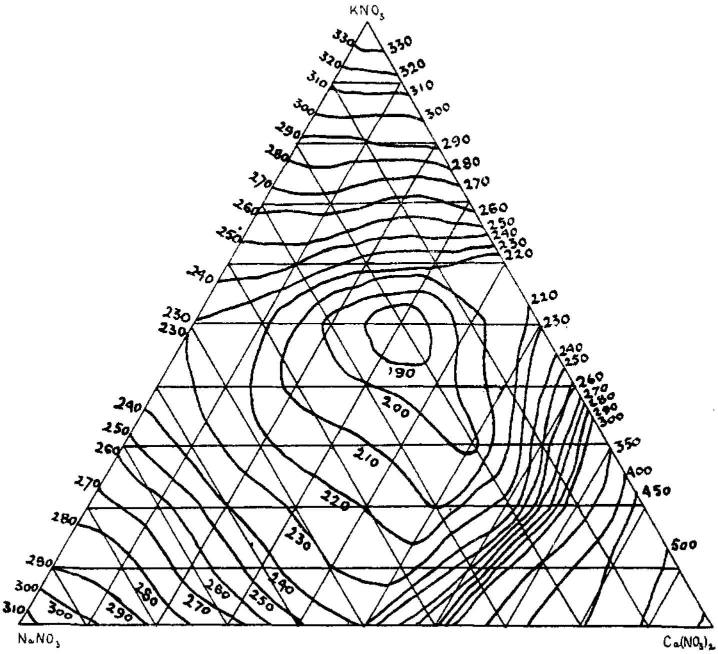

Fig. 2.

Comparison of Values Obtained with those of Other Observers.—The present work overlaps that of others in that, (1) the individual melting points of sodium and potassium nitrates have already been determined by several investigators; (2) points on the freezing point curve of binary mixtures of potassium and sodium nitrates have been determined by three observers; (3) one observer[1] determined the freezing point of a single mixture of calcium and sodium nitrates.

The various values obtained are quoted below, but without critical discussion on account of the want of precision in the thermometry of the older measurements. In the case of the comparatively recent measurements of Carveth,[2] however, the thermometers used were compared with what would seem to be thermometers verified at the Reichsanstalt,[3] and the readings were doubtless corrected for exposed thread, zero creep, etc.

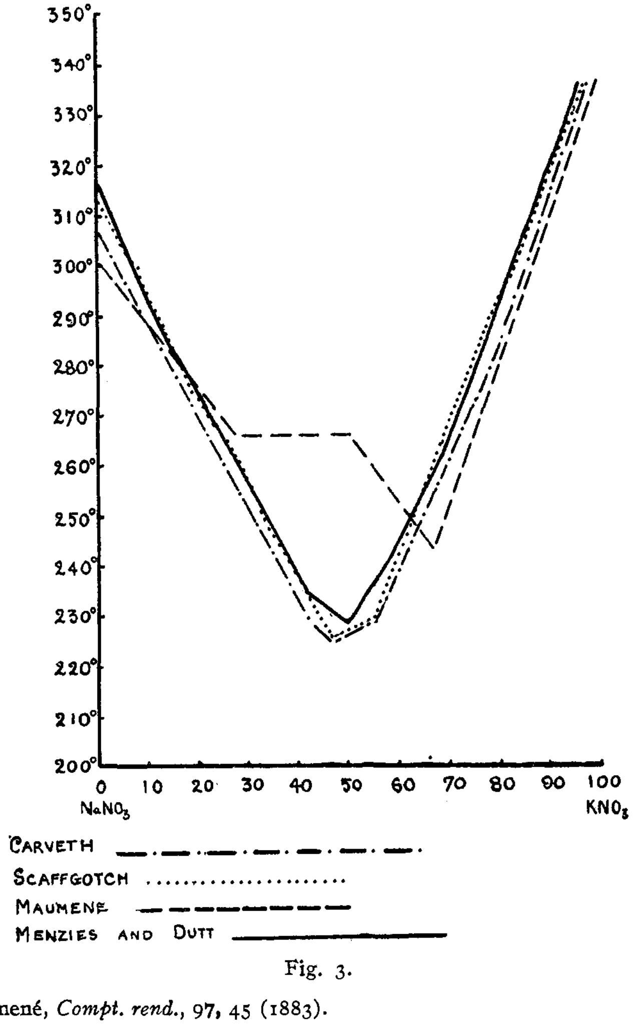

Fig. 3.

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[1] Maumené, *Compt. rend.*, 97, 45 (1883).

[2] *J. Physic. Chem.*, 2, 209 (1898).

[3] *Loc. cit.*, p. 211.

The test tubes containing the melted material were cooled in air at room temperature and were stirred with the thermometer until the first crystals appeared. It is stated that "with the use of such small amounts of material and this method of measurement, there is possibly an error of 2° as a maximum."

For the melting point of sodium nitrate the following values have been obtained: Person (1849), 310.5°; Braum (1875), 342°; Carnelley (1876–78), 319°, 316°, 330° ± 2; Guthrie, 305°; Maumené (1883), 298°; Carveth (1898), 308°. We found 315.1°.

For potassium nitrate, the following are the melting points obtained by others: Person, 339°; Schaffgotsch (1857), 338.3°; Braum, 342°; Carnelley, 353° ± 1, 332° ± 5, 339° ± 2; Guthrie, 320°; Maumené, 327°; Carveth, 337°. We found 346.3°.

For the freezing point curve for binary mixtures of potassium and sodium nitrates, the four curves shown in Fig. 3 embody the results obtained by Schaffgotsch,[1] Maumené, Carveth and ourselves. Percentage by weight is represented on the axis of abscissas. The usual large discrepancies between the results of different observers are here again in evidence.

For the freezing point of the mixture represented by [$NaNO_3$, $Ca(NO_3)_2$], Maumené obtained 235°. Interpolation on the appropriate curve would lead us to 261°.

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THE MECHANICAL STIMULUS TO CRYSTALLIZATION. II.

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In a previous paper[2] by one of us it has been pointed out that mechanical impacts produced within supercooled liquids and solutions are capable of stimulating these to crystallization, and that further, the sensitiveness of the supercooled system increases with the degree of supercooling, and that to stimulate crystallization in very slightly supercooled systems requires very large mechanical stimulus. It was also pointed out that there seems to be no justification for dividing the supercooled field into metastable and labil fields as the whole supercooled field appears to be labil in such a sense that crystallization may be forced at any point within it by sufficient mechanical stimulus.

It has long been held that foreign particles, such as dust and the like, exert under some circumstances an influence upon the production of crystals in supercooled liquids. No very definit ideas concerning the influence of such particles have been advanced up to the present time,

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[1] *Pogg. Ann.*, **102**, 293 (1857).

[2] THIS JOURNAL, **33**, 148.