traction processes weighed 507 g., 50.7% of the original ore used. Its activity as measured by the emanation method showed that only 4.2% of the radium still remained in the residue.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

BINARY AND TERNARY SYSTEMS OF THE NITRATES OF THE ALKALI AND ALKALINE EARTH METALS.

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In view of the fact that very few complete ternary systems of mixtures of dry salts have been worked out,[1] the following investigations of new systems were made: (1) a study of the complete system comprising barium, sodium, and potassium nitrates; (2) a study of the eutectic and all neighboring points of the system, strontium, sodium, and potassium nitrates; and (3) a study of the system barium, lithium and potassium nitrates as far as the point beyond which marked decomposition prohibited further determinations. The work of Menzies and Dutt on the system calcium, sodium, and potassium nitrates has been utilized for comparison with these systems by means of the respective triangular diagrams.[2]

Method of Procedure.

The freezing points of the various salt mixtures were determined by the usual method. Weighed amounts of the dried salts in the calculated proportion were carefully ground together and then melted with the thermometer bulb immersed. As soon as the melts were perfectly clear, the temperature was lowered at the rate of two degrees per minute, and at the same time the temperature was kept constant through the mixture by constant stirring. Upon the appearance of the first minute crystal, the temperature was carefully noted. Such a method permitted several repetitions so as to obtain a good check on the primary results.

Preparation of the Salts.

The salts used were Kahlbaum's "Zur Analyze" preparations, with the exception of the lithium nitrate which was made by J. T. Baker. Preliminary examinations of the purity of the salts made it clear that nothing was to be gained by recrystallization, except that it was found necessary to recrystallize the lithium nitrate from nitric acid solution because the original salt gave a basic reaction with rosolic acid.

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[1] The following are the ternary systems which have been completely investigated: The system $Ca(NO_3)_2$, KNO_3 and $NaNO_3$ by Menzies and Dutt, THIS JOURNAL, **31**, 1366 (1909). The system $LiNO_3$, KNO_3 and $NaNO_3$ by Carveth, *J. Phys. Chem.*, **2**, 206 (1898). The system Al_2O_3, SiO_2 and CaO in the Geophysical Laboratory, Washington, D. C., by Rankin and Wright, *Am. J. Sci.*, **39**, 1–79 (1915).

[2] Roozeboom, *Z. physik. Chem.*, **15**, 143 (1894); Bancroft, *J. Phys. Chem.*, **24**, 441.

In this work it was essential that the salt should be carefully dried. A test of the effect of the presence of water upon the melting point of pure sodium nitrate showed that 0.231 g. of water produced a lowering[1] of 0.8° when present in 40 g. of perfectly dried salt. All of the salts were finely ground and dried in an electric oven through which a constant stream of pure, dry air was passed. The air was conducted through three wash-bottles of sulfuric acid, a soda lime tube, through absorbent cotton, and finally through a long tube containing a mixture of P_2O_5 and glass beads.

Barium, potassium, and sodium nitrates presented no difficulties and were dried at 140°. In the cases of the strontium and lithium salts, however, gentle desiccation was first necessary before the final heating. From 24–48 hrs., drying was necessary to obtain a sufficiently dry salt.

The components of the mixtures to be examined were weighed out to a thousandth of a gram and then intimately ground together. In the cases where lithium or strontium nitrates were present, this process was carried out in an air-tight box in which calcium chloride and sulfuric acid were used for drying, and in the side of this box were two openings into which two rubber gloves were tightly fitted.

The Apparatus Used.

The heating bath used was similar to that used by Menzies and Dutt, but with some added refinements. A thick, hollow cylinder of concrete formed the base upon which a porcelain tower could rest. It was arranged in this way so that the flame of the Meker burner on the inside could be used at its most effective point. Resting on top of the tower and supported upon it by wire gauze was an iron cylinder, five inches high and three inches in diameter, in which was fitted a small circular shelf of asbestos board, as the base for the support of an ordinary lamp chimney. The test-tubes containing the salts were supported inside this by means of an asbestos rack with close-fitting holes. For the mixtures melting below 300° ordinary soft glass tubes, 1.5 × 16 cm., were used, except when lithium nitrate was used. Owing to its etching effect upon sodium glass, hard glass tubes of the same size were substituted. For the higher temperature measurements, Jena test-tubes, 1.75 × 20 cm., were used and found satisfactory even at 600° when not in direct contact with the flame. A correspondingly large amount of salt was taken in these larger tubes.

In order to give uniform heating from the sides rather than from the bottom, a shield was placed between the flame and the test-tube. This

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[1] The lowering calculated by the van't Hoff equation $\left(\Delta t_{\text{F.P.}} = \frac{RT^2_{\text{F.P.}}}{L_F} \frac{N_1}{N_1 + N_2}\right)$ is less than this experimental value if 3690 calories are taken as the value for the latent heat of fusion as given by Goodwin and Kalmus, *Phys. Rev.*, **28,** 1 (1908).

consisted of a raised clay triangle covered with iron, which also rested on the asbestos shelf inside the lamp chimney. The stirring rod was circular at the bottom so as to loosely circle the thermometer. For temperatures above 500°, insulation with asbestos paper inside and outside the chimney was found advisable, leaving only space enough to observe the formation of crystals.

Methods of Temperature Measurement.

For temperatures below 250°, a small Gerhardt mercury thermometer was employed, and for those from 250–350° a nitrogen-filled mercury thermometer. These were calibrated, immersed always to the same respective levels, against a platinum resistance thermometer of quartz with gold leads for every 5°, in a mechanically stirred crisco bath. This was done several times and the corrections applied. Some measurements were repeated, using the resistance thermometer itself and a good check thus established. For temperatures much above 350°, the nitrogen-filled thermometer proved unsatisfactory in spite of efforts to keep it in close calibration, so a resistance thermometer was used for all temperatures above 350°. In order to protect the fragile platinum coil from the action of the nitrates, the end was covered with a case of platinum foil, brazed with gold. The resistance was determined by a galvanometer and a Wolff box-bridge, which was kept at a temperature of approximately 20°. Corrections were made for the resistance of the copper leads and the temperature determined by means of the Callendar difference formula. Nothing was to be desired in the accuracy of the thermometer in every measurement taken with it. Consequently 595.53° should constitute a value for the freezing point of barium nitrate very close to the true one.

(1) The System Barium, Sodium and Potassium Nitrates.

Eighty-one mixtures corresponding to the points on the triangle shown on Fig. 1 were examined in this system. The three corners represent each of the pure components, the three sides, the three binary systems, and all points within the triangle belong to the ternary system. The sum of the percentages, which are all equivalent rather than weight, is always 100. Points on the intersections, 1 to 66, have percentages of 10 and its multiples, while points 67 to 81 all lie below a barium nitrate concentration of 10% and surround the eutectic (No. 75). Such a triangle, consequently, shows at a glance exactly the composition of all mixtures studied.

For the temperatures below 350° about 20 g. of salt were used, and for the larger test-tubes and longer bulb of the resistance thermometer above 350°, about 30 g. Table I shows the freezing point corresponding to each point represented on the triangle with the equivalent percentages and the actual weights of each of the components.

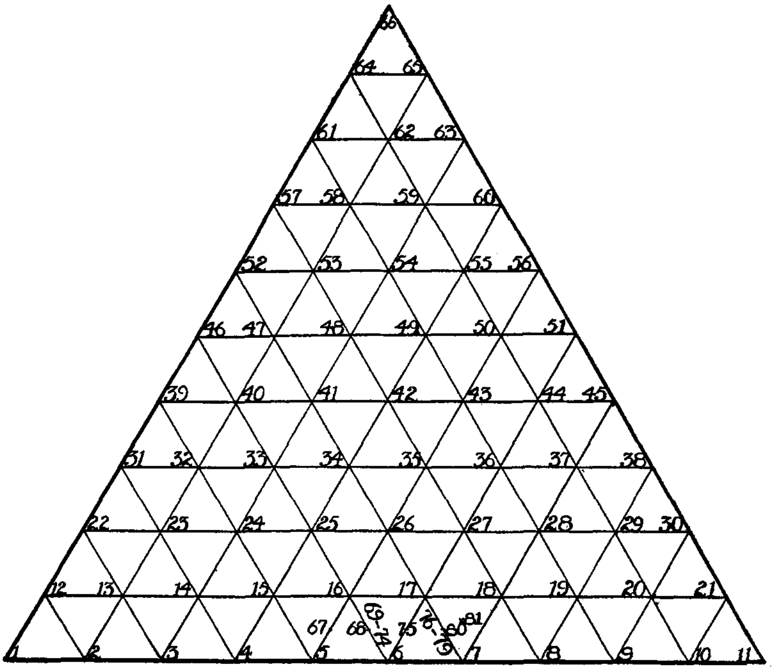

Figure 1

TABLE I.

No.	Eq. % $NaNO_3$.	Eq. % KNO_3.	Eq. % $Ba(NO_3)_2$.	Wt. of $NaNO_3$.	Wt. of KNO_3.	Wt. of $Ba(NO_3)_2$.	Freezing point.
1.	100	0	0	20	0	0	314.1
2.	90	10	0	18	2.38	0	290.9
3.	80	20	0	16	4.76	0	274.1
4.	70	30	0	14	7.14	0	253.8
5.	60	40	0	12	9.51	0	235.2
6.	50	50	0	10	11.89	0	222.4
7.	40	60	0	8	14.27	0	233.8
8.	30	70	0	6	16.63	0	257.5
9.	20	80	0	4	19.01	0	287.3
10.	10	90	0	2	21.39	0	313.7
11.	0	100	0	0	23.78	0	346.3
12.	90	0	10	27	0	4.60	296.6
13.	80	10	10	16	2.38	3.07	285.0
14.	70	20	10	14	4.76	3.07	273.9
15.	60	30	10	12	7.14	3.07	269.4
16.	50	40	10	10	9.51	3.07	257.5
17.	40	50	10	8	11.89	3.07	244.9
18.	30	60	10	6	14.27	3.07	235.2
19.	20	70	10	4	16.63	3.07	260.0
20.	10	80	10	2	19.01	3.07	288.1

TABLE I (*continued*).

No.	Eq. % $NaNO_3$.	Eq. % KNO_3.	Eq. % $Ba(NO_3)_2$.	Wt. of $NaNO_3$.	Wt. of KNO_3.	Wt. of $Ba(NO_3)_2$.	Freezing point.
21	0	90	10	0	21.39	3.07	333.8
22	80	0	20	24	0	9.20	358.3
23	70	10	20	14	2.38	6.14	341.3
24	60	20	20	12	4.76	6.14	334.9
25	50	30	20	10	7.14	6.14	327.2
26	40	40	20	8	9.51	6.14	319.8
27	30	50	20	6	11.89	6.14	310.7
28	20	60	20	4	14.27	6.14	300.9
29	10	70	20	2	16.63	6.14	290.9
30	0	80	20	0	19.01	6.14	311.9
31	70	0	30	21	0	13.80	396.51
32	60	10	30	12	2.38	9.21	384.1
33	50	20	30	10	4.76	9.21	380.1
34	40	30	30	8	7.14	9.21	371.2
35	30	40	30	6	9.51	9.21	364.9
36	20	50	30	4	11.89	9.21	353.3
37	10	60	30	2	14.27	9.21	345.8
38	0	70	30	0	16.63	9.21	350.0
39	60	0	40	18	0	18.40	435.31
40	50	10	40	15	3.57	18.40	429.44
41	40	20	40	12	7.14	18.40	424.72
42	30	30	40	9	10.71	18.40	422.85
43	20	40	40	6	14.28	18.40	410.61
44	10	50	40	3	17.85	18.40	390.20
45	0	60	40	0	14.27	12.28	380.03
46	50	0	50	15	0	23.00	462.98
47	40	10	50	12	3.57	23.00	431.88
48	30	20	50	9	7.14	23.00	453.72
49	20	30	50	6	10.71	23.00	448.67
50	10	40	50	3	14.28	23.00	441.87
51	0	50	50	0	11.89	15.35	433.95
52	40	0	60	12	0	27.60	484.20
53	30	10	60	9	3.57	27.60	483.02
54	20	20	60	6	7.14	27.60	484.20
55	10	30	60	3	10.71	27.60	476.40
56	0	40	60	0	9.51	18.42	474.31
57	30	0	70	9	0	32.20	492.64
58	20	10	70	6	3.57	32.20	489.21
59	10	20	70	3	7.14	32.20	492.04
60	0	30	70	0	10.71	32.20	493.87
61	20	0	80	6	0	36.80	501.69
62	10	10	80	3	3.57	36.80	494.18
63	0	20	80	0	7.14	36.80	495.32
64	10	0	90	3	0	41.40	529.65
65	0	10	90	0	3.57	41.40	514.42
66	0	0	100	0	0	46.05	595.53
67	55	40	5	11	9.51	1.53	225.2
68	50	45	5	10	10.70	1.53	217.1
69	49	46	5	9.8	10.94	1.53	216.5

TABLE I (*concluded*).

No.	Eq. % $NaNO_3$.	Eq. % KNO_3.	Eq. % $Ba(NO_3)_2$.	Wt. of $NaNO_3$.	Wt. of KNO_3.	Wt. of $Ba(NO_3)_2$.	Freezing point.
70...........	48	47	5	9.6	11.18	1.53	216.0
71...........	48	48	4	9.6	11.41	1.23	217.2
72...........	47	48	5	9.4	11.41	1.53	215.5
73...........	46	49	5	9.2	11.65	1.53	214.9
74...........	45	49	6	9	11.65	1.84	217.8
75...........	45	50	5	9	11.89	1.53	214.1
76...........	46	50	4	9.2	11.89	1.23	218.4
77...........	45	51	4	9	12.13	1.23	220.4
78...........	44	53	3	8.8	12.60	0.92	225.5
79...........	44	51	5	8.8	12.13	1.53	215.5
80...........	40	55	5	8	13.08	1.53	217.9
81...........	35	60	5	7	14.27	1.53	229.0

Decomposition was not apparent in any of the melts until a barium nitrate concentration of 80% was reached. In these cases a slight evolution of oxygen began, if the salt was heated too far above the freezing point. By working rapidly, however, and by careful heating, any error produced by the formation of nitrites was reduced to a minimum. When heated for some time these mixtures became yellow in color, showing that even the nitrites break down with sustained heat.[1]

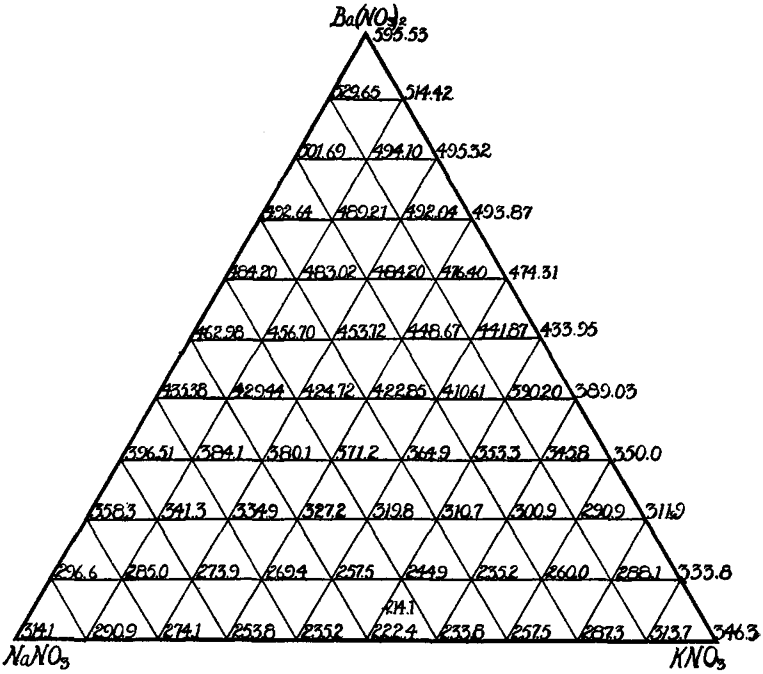

Figure 2

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[1] J. Lang, *Pogg. Ann.*, 118, 282.

As each melting point was determined, it was noted down on a triangular figure upon the point of its corresponding percentage composition. Such an arrangement is shown in Fig. 2. The temperatures for all points are recorded, except for numbers 67 to 74 and 76 to 80, all of which are in the neighborhood of the eutectic. In this figure the temperature is variable in the plane perpendicular to the surface of the page and should it actually be represented, a solid figure would result whose upper surface with its highest point at 595.53° and lowest at 214.1° would represent the true elevation of all temperatures.

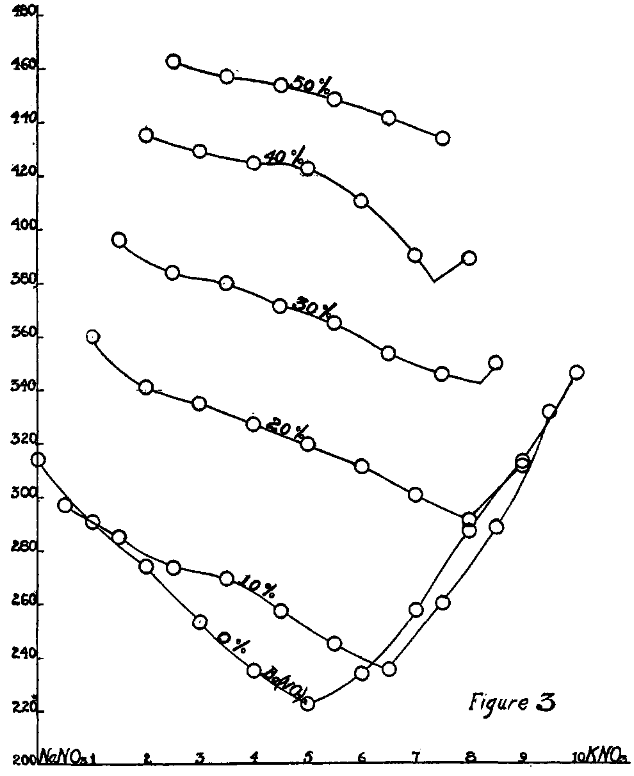
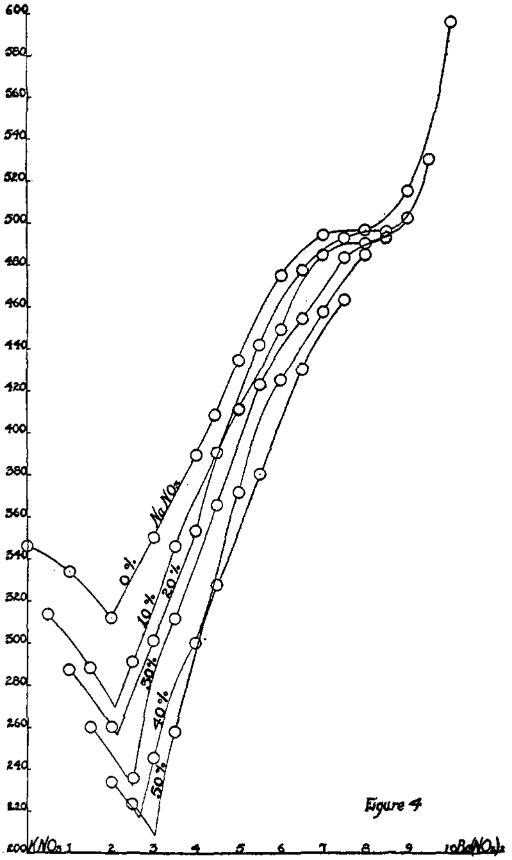


Figure 3

Such a condition is represented on a single plane, of course, by isothermal lines. In order to make the relation of these lines simpler, vertical sections were plotted as in Figs. 3, 4, and 5. In Fig. 3 the curves, drawn directly from the triangle, show in series points 1 to 11, 12 to 21, 22 to 30, 31 to 38, 39 to 45, and 46 to 51 with a fixed percentage of barium nitrate in each case. Similarly, Figs. 4 and 5 show the sections from the basis of the other two sides of the triangle along the lines parallel to those sides. Simple measurements upon these curves make it possible to find the equivalent percentages corresponding to temperatures in round numbers at intervals of 10°, and above 500°, of 50°. Points corresponding to the same temperatures are connected by a smooth line, and the complete liquidus surface contour diagram results which is shown in Fig. 6.

As has already been intimated, the work of others has been repeated in some cases. The melting points of sodium and potassium nitrates and points on the binary curve of the two have been determined many times.[1] The results of Menzies and Dutt were found to be in good accord with the new results, although 314.1° as a value for the freezing point of sodium nitrate, as determined by the writers, is a degree lower than obtained by them, and likewise a difference of 5.7° for a mixture of 50 equivalents each of $NaNO_3$ and KNO_3 is found. The lower part of the curve obtained by the writers is in better agreement with the measurements of Carveth.[2]

For the melting point of barium nitrate, 593° was found by Carnelley[3] and by Le Chatelier,[4] in both cases indirectly. By direct measurement the writers found 595.53°. No record of work upon any ternary mixture of barium, potassium and sodium salts could be discovered. Maumené[5] found a lack of decomposition in mixtures of equal amounts of KNO_3 and $Ba(NO_3)_2$ and of $NaNO_3$ and $Ba(NO_3)_2$. The eutectic of the former was determined by Guthrie[6] to be 278.5° with 29.53% of $Ba(NO_3)_2$ by weight. Although not determined exactly in this work, the curve would show a value approximately 15° higher.



(2) The System Strontium, Sodium and Potassium Nitrates.

With the eutectic point of the system just studied as a guide, the melting points of twelve ternary mixtures of strontium, sodium, and potassium nitrates were determined in the search for the ternary eutectic point. Point number 8 with a composition of 41 equivalent per cent. of $NaNO_3$, 50 of KNO_3 and 9 of $Sr(NO_3)_2$ was found to solidify practically

[1] Menzies and Dutt, *Loc. cit.*, p. 1370.

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

[3] *J. Chem. Soc.*, 33, 273 (1878).

[4] *Bull. soc. chim.*, [2] 47, 300.

[5] *Compt. rend.*, 97, 45, 1215 (1883).

[6] *Phil. Mag.*, [5] 17, 462 (1884).

without change of temperature at 208.4°. This result was further verified by determining the melting point of every possible mixture around it and varying from its own composition by only one equivalent per cent. The twelve points are tabulated as follows:

TABLE II.

No.	Eq. % $NaNO_3$.	Eq. % KNO_3.	Eq. % $Sr(NO_3)_2$.	Wt. of $NaNO_3$.	Wt. of KNO_3.	Wt. of $Sr(NO_3)_2$.	Freezing point.
1	40	45	15	8	10.70	3.74	254.2
2	50	40	10	10	9.51	2.49	221.8
3	41	49	10	8.2	11.66	2.49	210.0
4	40	50	10	8	11.89	2.49	209.5
5	39	51	10	7.8	12.13	2.49	210.5
6	30	60	10	6	14.27	2.49	226.8
7	42	49	9	8.4	11.66	2.24	209.0
8	41	50	9	8.2	11.89	2.24	208.4
9	40	51	9	8	12.13	2.24	209.3
10	42	50	8	8.4	11.89	1.99	210.0
11	41	51	8	8.2	12.13	1.99	211.2
12	45	50	5	9	11.89	1.25	213.8

The freezing points are shown on their proper points in Fig. 7. Their numbers run in order on the triangle from top to bottom and left to right. Only a competent triangle of the complete system triangle is used, the base representing zero concentration of $Sr(NO_3)_2$.

These twelve ternary points involve no repetitions of other work done. Determinations of single binary points of $Sr(NO_3)_2$ with equal weights of $NaNO_3$ and KNO_3, respectively, were made by Maumené[1] and the eutectic mixture with KNO_3 was found by Guthrie[1] to contain 25.81% of $Sr(NO_3)_2$.

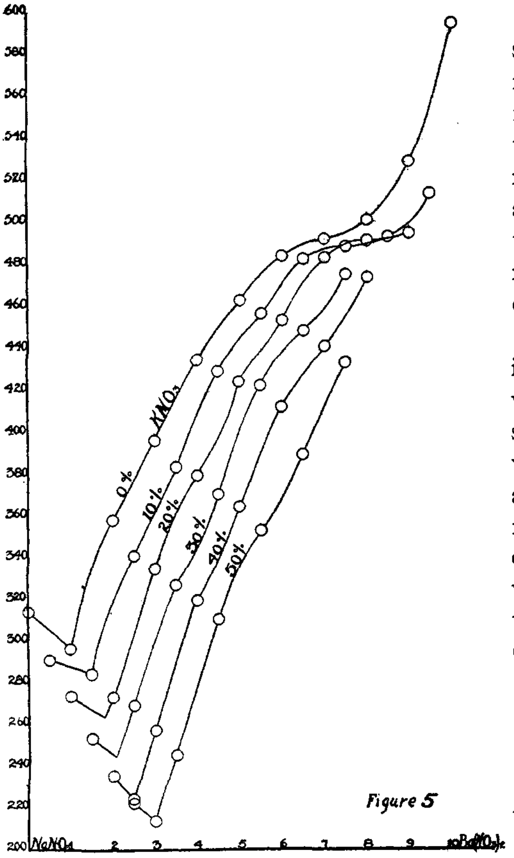


Figure 5

Comparison of the Ternary Systems of Calcium, Barium and Strontium Nitrates with $NaNO_3$ and KNO_3.

We are now in a position to make a comparison of three

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[1] *Loc. cit.*

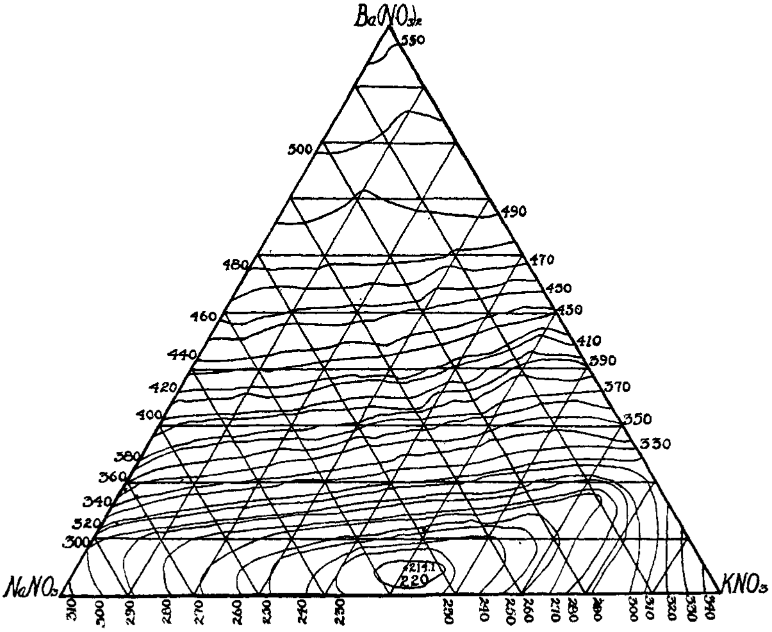

Figure 6

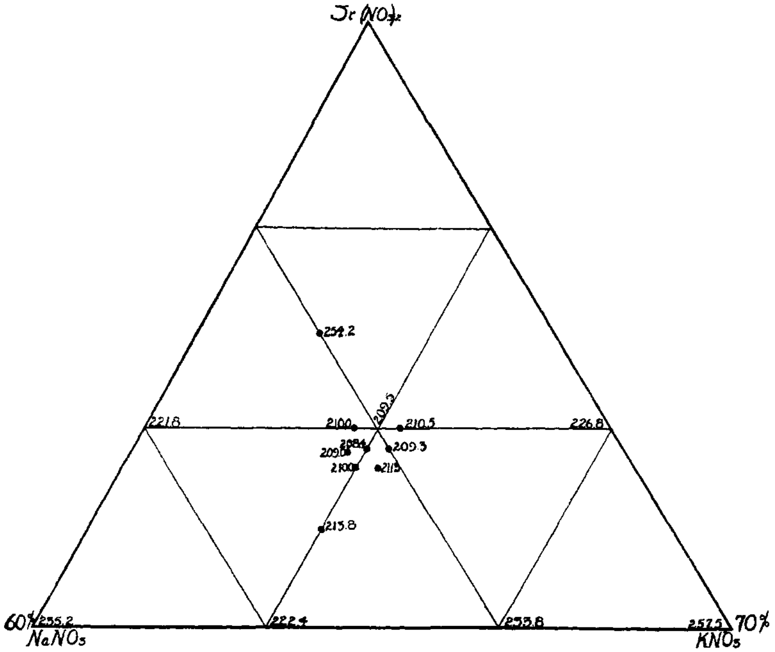

Figure 7

ternary systems, each containing one of the alkaline earth nitrates. The relative position of the three eutectics is best shown diagrammatically as in Fig. 8, using the value obtained by Menzies and Dutt with $Ca(NO_3)_2$. It is to be expected, of course, that this system would show the lowest eutectic point and the barium nitrate one of the highest, judging from the melting points of the pure components. For $Ca(NO_3)_2$, Carnelley[1] obtained 561°; for $Sr(NO_3)_2$, Ramsay and Eumorfopoulois[2] found 570°; and for $Ba(NO_3)_2$ the writer found 595·53°. For these values alone it would be further expected, however, that the eutectic for $Sr(NO_3)_2$ would be much closer to the one found for $Ca(NO_3)_2$. Such a tendency is probably overcome by the fact that strontium and potassium nitrates have a slightly higher eutectic point than even barium nitrate with KNO_2.[3] Consequently the pits in the liquidus surfaces of the systems in which $Ba(NO_3)_2$ and $Sr(NO_3)_2$ are components differ in depth by only 5·3° and in relative position on the triangle by only 4 equivalent per cent. of the two components, respectively. Such facts point to the conclusion that the contour maps of the two must resemble each other very closely indeed.

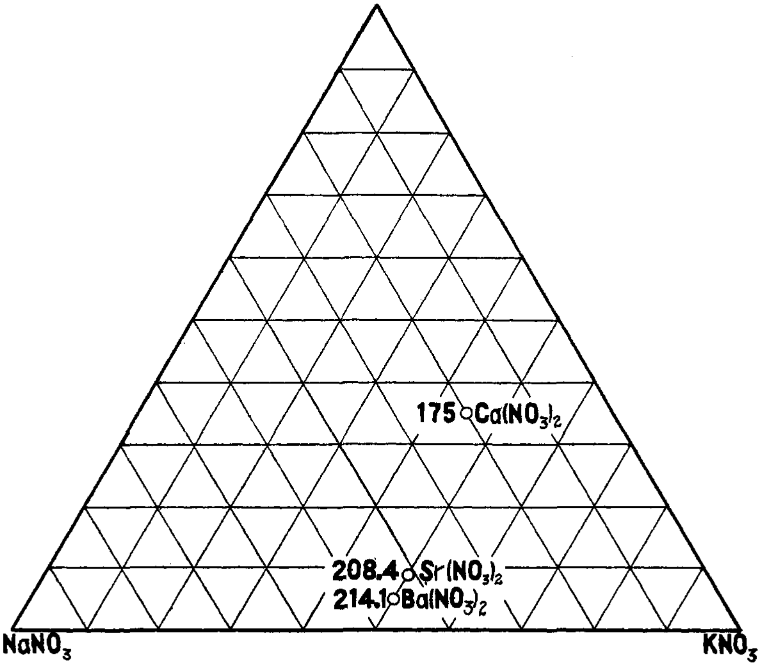

Figure 8

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[1] *Loc. cit.*

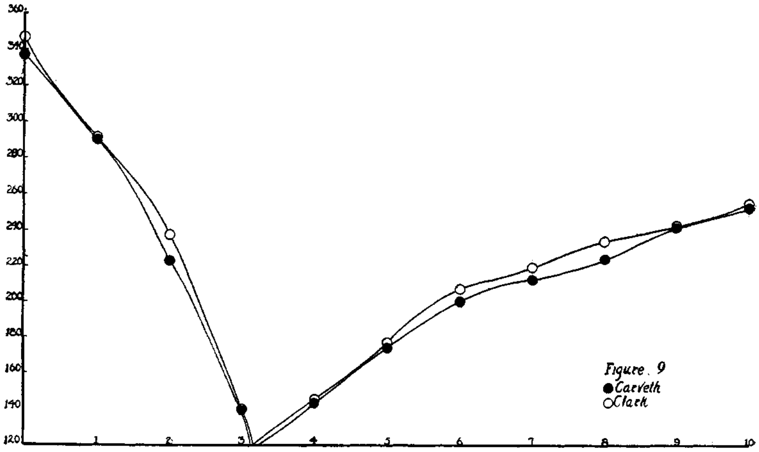
[2] *Phil. Mag.*, [5] 41, 360 (1896).

[3] Guthrie, *Loc. cit.*

(3) The System Barium, Lithium and Potassium Nitrates.

The factor of salt stability enters strongly into determinations upon this system—so strongly in fact that the melts of no three-component mixtures with a higher barium nitrate concentration than 10 equivalent per cent. were attempted. There was no difficulty in determining all points on the $Ba(NO_3)_2$-KNO_3 and $LiNO_2$-KNO_3 sides of the triangle. The eutectic mixtures of lithium and barium nitrates proved to contain only about one equivalent per cent. of the latter, and when 10% was present, the freezing point was observed to be almost 50° higher than the value for pure $LiNO_3$. It was possible to reach a point represented by the concentrations 60 equivalents of $LiNO_3$ and 40 of $Ba(NO_3)_2$, freezing at 436.6° before any great decomposition was noted. Immediately a ternary mixture containing 10% of $Ba(NO_3)_2$ was tried; however, a vigorous evolution of oxygen began long before a completely melted state had been reached, which was most marked when from 10–40% of the $LiNO_3$ was present. The melts rapidly became bright yellow from oxides of nitrogen, and crystallization occurred in stages. Tests showed that practically pure $Ba(NO_3)_2$ would first separate while the remaining liquid would solidify at a point at least 20° lower. To illustrate the power of a mixture of $Ba(NO_3)_2$ and KNO_3 to lower the temperatures where marked decomposition of $LiNO_3$ begins, a mixture containing about 46 equivalent per cent. each of the first two salts and 8 of the latter was melted. At 266° the evolution of oxygen was very marked, while Carveth[1] found that with pure $LiNO_3$ apparent decomposition does not begin until a temperature 24° higher (290°) is reached.

The determination of any more than a small portion of the liquidus surface of the ternary system in open tubes is clearly out of the question



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[1] *Loc. cit.*

when the melted salts show such marked decomposition as that observed. It was deemed advisable, however, to determine the binary curve for $LiNO_3$ and KNO_3. A comparison is made in Fig. 9 with the curve as plotted from the results obtained by Carveth[1] in his work on the system Na, K, and Li, the melting points of which were possibly as high as 2° in error. A recrystallized neutral sample of $LiNO_3$ was used to determine the freezing point of the pure salt. Measurement with the resistance thermometer gave a value of 254.1° as compared with 264° (Carnelley)[1] and 253° (Carveth). In the following table, percentages are equivalent, except for the $LiNO_3$-KNO_3 values which are by weight in order to compare with Carveth's curve. Only points which were determined without great difficulty are given:

TABLE III.

No.	Wt. % KNO_3.	Wt. % $LiNO_3$.	Wt. g. KNO_3.	Wt. g. $LiNO_3$.	Freezing point.
1	100	0	30	0	346.1
2	90	10	27	3	290.9
3	80	20	24	6	237.1
4	70	30	21	9	139.8
5	60	40	18	12	145.2
6	50	50	15	15	177.4
7	40	60	12	18	207.0
8	30	70	9	21	219.8
9	20	80	6	24	234.2
10	10	90	3	27	242.3
11	0	100	0	30	254.1

TABLE IV.

No.	Eq. % KNO_3.	Eq. % $LiNO_3$.	Eq. % $Ba(NO_3)_2$.	Wt. KNO_3.	Wt. $LiNO_3$.	Wt. $Ba(NO_3)_2$.	Freezing point.
1	0	90	10	0	24.79	5.21	303.17
2	0	80	20	0	20.36	9.64	364.4
3	0	70	30	0	16.56	13.44	403.58
4	0	60	40	0	13.26	16.74	436.6
5	10	10	80	3	16.40	3.88	299.09
6	20	10	70	6	14.35	3.88	310.37
7	30	10	60	9	12.30	3.88	317.92
8	40	10	50	12	10.25	3.88	303.70

In conclusion, the writers wish to express their thanks to Mr. W. A. Roberts for assistance in the use of the resistance thermometer.

A grant of two hundred dollars from the Wolcott Gibbs Fund of the National Academy of Sciences has been expended in the purchase of a potentiometer and a galvanometer which will be used in the continuation of the work on fused salts, and also for a study of the lowerings of the freezing points in aqueous solutions of the cobaltamines, and of mixtures of salts. The potentiometer was designed for this work by Dr. W. P. White of the Geophysical Laboratory.

CHICAGO, ILL.

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[1] *Loc. cit.*