N solution, which contains 0.74552 g. of potassium chloride per liter at 25.0°. This agrees closely with the value, 141.32 ohm^{-1}, as given by Shedlovsky.[5] The results are shown in Table I.

TABLE I

CONCENTRATIONS AND CONDUCTANCES OF SOLUTIONS

Gram formula weights per liter	Resistance of cell in ohms, corrected for resistance of water	Λ in ohms^{-1}	Λ_0 in ohms^{-1}
0.010001	1.0001×10^5	141.37	150.78
.0049986	1.9617×10^5	144.18	150.84
.0025050	3.8731×10^5	146.18	150.89
.0009937	9.6385×10^5	147.62	150.58
.0005130	1.8552×10^6	148.57	150.70

The last column gives the conductances at zero concentration, calculated from the Onsager equation, $\Lambda_0 = \dfrac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}}$. In Fig. 2, the solid line represents the theoretical results. One point is the value 141.37 ohms^{-1} for the 0.01 *N* solution and another is the value for Λ_0 calculated by the Onsager equation from the 0.01 *N* value for Λ. The circles represent our experimental results, which show a general variation of ±0.06%. Using a Leeds and Northrup type K potentiometer, more accurately calibrated resistances and weight normal solutions, it should be possible to make measurements to ±0.01%.

Summary

The equivalent conductances of potassium chloride solutions have been measured from 0.01 to 0.0005 *N*.

A new method of measuring conductances has been presented and is upheld by results of sufficient accuracy to substantiate it.

CHADRON, NEBRASKA RECEIVED DECEMBER 4, 1937

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(5) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Liquidus Surface of the System Sodium, Lithium and Calcium Nitrates

BY ALEXANDER LEHRMAN AND DAVID BRESLOW

The liquidus surface of the ternary system sodium, lithium and calcium nitrates was explored as part of an investigation of the liquidus of the quaternary system potassium, sodium, lithium and calcium nitrates. As was explained in a previous paper[1] it is hoped that this quaternary system will yield a salt bath melting below 100°.

One of the binaries involved here (lithium nitrate–calcium nitrate) has been determined by the apparatus and methods used in the work being reported.[1] A check of the other two binary systems involved (sodium nitrate–calcium nitrate and sodium nitrate–lithium nitrate) by means of time–temperature cooling curves showed eutectic temperatures which differed from those reported in the literature. The liquidus curves of these two binary systems were therefore redetermined. While the melting point of lithium nitrate obtained by us agrees with values previously reported, the melting point of sodium nitrate obtained differs somewhat from previously reported values. Calcium nitrate decomposes before melting and therefore its melting point cannot be directly measured.

Experimental

Materials.—The salts used in the binary and ternary systems were prepared as described in a previous paper.[1]

Temperature Measurements.—Temperatures were measured with a copper–constantan thermocouple of No. 24 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten nitrates by a shield of narrow Pyrex tubing sealed at one end. It was standardized by determining the e. m. f.'s at the boiling point of water, the melting point of U. S. Bureau of Standards tin (231.9°) and the melting point of purified potassium nitrate (333.0°) and plotting the deviations from the standard table of Adams.[2] The deviation curve was a straight line.

Method.—The mixtures, about 20 g. each, were weighed by difference into 2.5 × 20-cm. Pyrex test-tubes, the salt with the highest melting point being the first in the tube. The weights were taken to the nearest centigram.

Two methods were used to obtain the initial crystallization temperatures. The first was that of obtaining time–temperature cooling curves in the manner and in the apparatus described by Lehrman, Selditch and Skell.[3] This method worked well for the pure salts and for those mixtures in the binary systems where lithium or sodium nitrate was the first solid to crystallize. Due, however,

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(1) Lehrman, *et al.*, THIS JOURNAL, **59**, 179 (1937).

(2) Pyrometric Practice, U. S. Bureau of Standards Technological Paper No. 170, p. 309.

(3) Lehrman, Selditch and Skell, THIS JOURNAL, **58**, 1612 (1936).

to the large degree of supercooling when calcium nitrate crystallizes, the method could not be used for calcium nitrate rich mixtures. The method of determining the temperature at which the last crystal could be seen to disappear when a partially crystallized melt was slowly heated was, therefore, used for some of the binary and most of the ternary mixtures. This method will be referred to as the visual method, while the other will be referred to as the cooling curve method. The tube containing the mixed salts was heated in a molten eutectic mixture of calcium, potassium and lithium nitrates (m. p. 117.4°)[1] contained in a wide-mouthed rubber extraction flask (400 ml.). The bath temperature was measured by a thermometer protected by a Pyrex tube sealed at the lower end. The thermometer and shield served also as a stirrer. The bath was heated to about 350° and kept there while stirring the mixed salts in the test-tube with the thermocouple guard tube until they were entirely melted. The bath was then allowed to cool until crystals formed in the tube. During the cooling practically all air bubbles rose to the surface. A microscope lamp throwing a narrow beam onto the molten salt in the test-tube was placed behind the apparatus and the bath slowly heated, both the bath liquid and the salts in the tube being stirred constantly. Some time before the final crystal disappeared the heating was discontinued so that the temperature of the contents of the tube was rising slowly as the last crystal dissolved. This method showed itself to be very convenient and gave values which checked those obtained from cooling curves. The initial crystallization temperatures of most of the ternary and many of the binary mixtures were, therefore, obtained by this procedure. The temperature of disappearance of crystals could be duplicated to within 0.4°. The appended tables indicate the method used for each point. Every reported value by the visual method represents at least two determinations.

For the double purpose of getting the eutectic temperatures and insuring against missing any slight break in the liquidus curves, which would indicate a transition in the solid phase or a peritectic point, time–temperature and time–differential temperature cooling curves were obtained for various melts in the binary and ternary systems. In the ternary system the curves were obtained for four mixtures, one from the center of each of the phase regions and one close to the eutectic point. The same eutectic temperature was found in the four cases.

TABLE I

THE SYSTEM SODIUM NITRATE–LITHIUM NITRATE

c = cooling curve; v = visual.

$NaNO_3$ wt. %	Initial cryst., °C.	Eutectic halt, °C.	Method for detn. of I. C. temp.
100.0	305.5	—	c
84.8	273	191.0	c
74.8	250	—	v
64.5	225	—	v
57.4	208	190.5	c
55.3	206	—	v
52.8	200	—	v
50.4	—	191.2	-
49.8	197	—	v
45.1	204	—	v
40.2	—	191.0	-
33.6	219	—	v
20.7	231	193.1	c
0.0	251.4	—	c

Av. 191.4

TABLE II

THE SYSTEM SODIUM NITRATE–CALCIUM NITRATE

$NaNO_3$ wt. %	Initial cryst., °C.	Eutectic halt	Method for detn. of I. C. temp.
100.0	305.5	—	c
84.6	287	—	c
75.2	273	—	v
69.2	—	223.0	-
68.5	263	222.8	c
65.0	253	—	v
61.6	244	—	v
58.1	236	—	v
57.0	234	—	v
54.7	231	221.1	v
52.2	249	222.4	v
49.6	272	223.1	v
45.2	309	223.5	v
42.9	—	223.5	-
35.8	374	—	v
33.6	—	222.8	-

Av. 222.8

TABLE III

THE SYSTEM SODIUM, LITHIUM AND CALCIUM NITRATES

$NaNO_3$ wt. %	$LiNO_3$ wt. %	Initial cryst., °C.	Eutectic halt. °C.
59.3	19.9	225[a]	169.9
40.2	40.1	194	
19.9	59.8	223[a]	169.5
39.8	19.9	242	
19.8	40.0	274	
19.9	19.9	375[a]	171.6
50.1	30.2	202	
45.2	34.7	186	
40.1	34.7	186	
39.9	29.9	178[a]	170.3
45.1	24.7	189	
50.0	24.8	201	
20.2	69.9	230	
30.0	54.9	214	
30.1	39.8	199	
30.1	25.0	283	
51.8	39.8	199	
33.9	33.0	212	
41.1	32.0	180	
44.1	28.9	188	
40.1	25.9	205	
38.0	29.9	193	
37.1	31.9	193	
42.1	30.0	179	

Av. 170.3

[a] Determined by cooling curves.

The observed initial crystallization temperatures are given in Tables I, II and III and are plotted in Figs. 1 and 2. Figure 3 is a projection of the liquidus surface on the composition triangle. The twenty-four circles indicate the compositions the initial crystallization temperatures

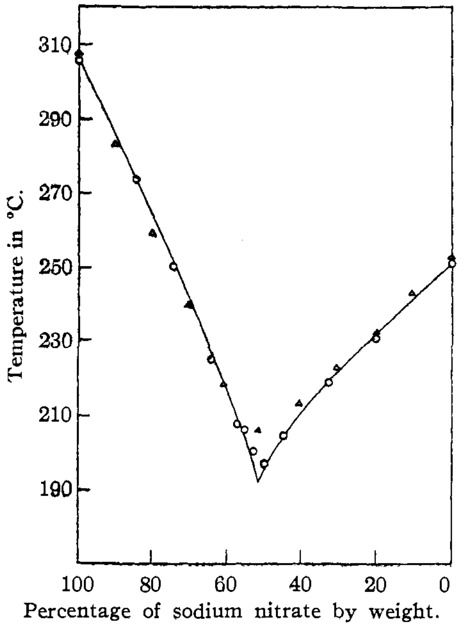

Fig. 1.—The liquidus curve of the system sodium nitrate–lithium nitrate: ○, Lehrman and Breslow; △, Carveth.

of which were determined. These together with the fifty points on the binary systems (not shown in Fig. 3) and the eutectics obtained by cooling curves enable us to fix the liquidus surface. To get somewhat more accurately the phase region boundary lines, vertical sections of the ternary composition–temperature diagram at 20% sodium nitrate, 40% sodium nitrate, 20% lithium nitrate, 40% lithium nitrate and 20% calcium nitrate were plotted. The position of the lowest temperature on these diagrams helped to place the phase region boundary lines on the composition triangle.

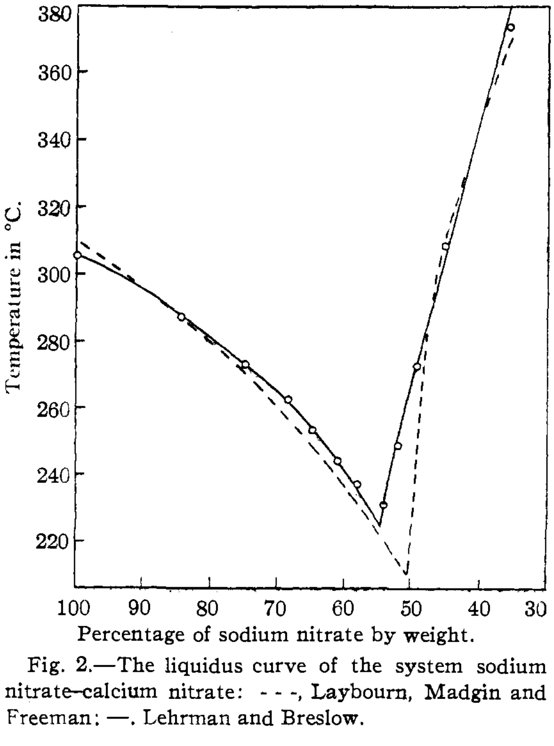

Fig. 2.—The liquidus curve of the system sodium nitrate–calcium nitrate: - - -, Laybourn, Madgin and Freeman; —, Lehrman and Breslow.

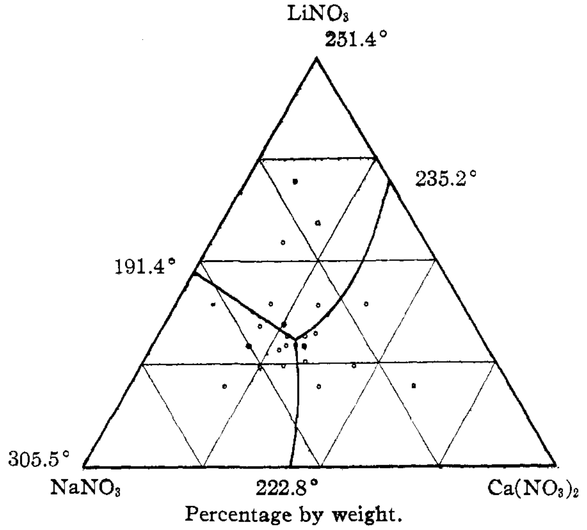

Fig. 3.—Liquidus surface of the system sodium, lithium and calcium nitrates.

Discussion

The melting point observed for lithium nitrate (251.4°) agrees well with that observed by Briscoe, Evans and Robinson (252°).[4] The value for the melting point of sodium nitrate reported here (305.5°) is lower than the values previously reported in the literature.[5,6] Mellor[5] gives 306.8° as a representative value. This was obtained by Stern,[7] who used a platinum resistance thermometer which had been calibrated against an enclosed thermometer of the Anschütz type which had been standardized by the Reichsanstalt. It is interesting to note that Stern obtained 334.5° as the melting point of potassium nitrate. This is 1.5° above the accepted value of 333.0°. If his scale was 1.5° high in this region, his corrected value for the melting point of sodium nitrate would be 305.3°, which agrees very well with the value 305.5 ± 0.5° obtained in this work. The most recent determination, that of Briscoe and Madgin[8] was done by means of a mercury in glass thermometer. Their value of 308.9° was obtained after adding a stem correction of 10.4°.

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[4] (4) Briscoe, Evans and Robinson, *J. Chem. Soc.*, 1100 (1932).

[5] (5) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1922, Vol. II, p. 813.

[6] (6) Menzies and Dutt, THIS JOURNAL, **33**, 1366 (1911).

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

[8] (8) Briscoe and Madgin, *J. Chem. Soc.*, **123**, 1608 (1923).

To see whether further purification would change the melting point of sodium nitrate, three pounds (1.4 kg.) of c. p. sodium nitrate was dissolved in distilled water, filtered and allowed to crystallize. The first crop of about 200 g. was rejected. The second crop of about 150 g. was recrystallized three times from distilled water, the final yield being close to 30 g. The melting point of this was determined by a cooling curve as 305.5 ± 0.5°, and agrees within experimental error with the values obtained for the melting points after one and two recrystallizations. The cooling curves were horizontal for a long period of time at the melting point. This shows the absence of appreciable amounts of impurities.

The only previous determination of the binary system lithium nitrate–sodium nitrate is that of Carveth.[9] His values are plotted in Fig. 1. The agreement with the curve of the present authors is rather good and somewhat unexpected when one considers that Carveth worked in 1898 with a mercury in glass thermometer and used soft glass tubes which, as he was aware, were attacked by the lithium nitrate with an exchange of sodium for lithium. Carveth took the temperature at which the first crystal appeared as the melt cooled. Very little error was introduced by this procedure as practically no supercooling takes place in this system if the melt is stirred.[1] Carveth drew his curve to give a eutectic at 53% sodium nitrate and 204°. His values as plotted in Fig. 1 show that a eutectic point cannot be obtained from them with any reasonable degree of precision.

The binary eutectic for sodium nitrate–calcium nitrate obtained in this work (55% sodium nitrate at 222.8°) does not agree with the value obtained by Laybourn, Madgin and Freeman[10] (50.8% sodium nitrate at 211.3°). These authors do not list the actual values of the initial crystallization temperatures but publish their curve, a copy of which on a different scale is given in Fig. 2. They determined the temperatures at which a crystal first appeared as the melts cooled. The temperature measuring instrument was a chromel–eureka thermocouple "in series with an accurate millivoltmeter." They do not give the details of the calibration of the couple. It should be pointed out that the melts in question supercool especially at the lower temperatures and that the higher the calcium nitrate content the greater will be the supercooling. The fact that these workers determined the temperatures at which the first crystal appeared as the melts cooled would just account for the difference between their curve and the curve obtained by taking the temperatures at which the last crystal disappeared as the melts were slowly heated.

This system was worked out also by Menzies and Dutt[6] as part of the ternary system sodium, potassium and calcium nitrates. Their values, however, have been shown to be unreliable by the work of Rostkovsky[11] and of Laybourn and Madgin.[12] The curve as determined by Menzies and Dutt has a eutectic temperature somewhere about 50% sodium nitrate at 136°. This stated eutectic temperature, however, seems to be a misprint.

The ternary eutectic of the system sodium, lithium and calcium nitrates has not been reported previously. The point as determined in this work is at 40% sodium nitrate, 30.5% lithium nitrate and 29.5% calcium nitrate and a temperature of 170.3°.

The ternary system presented here turns out to be of the simplest type as was to be expected. With the exception of the reluctance of calcium nitrate to crystallize, no difficulties were encountered. It should be pointed out that the calcium nitrate corner of the system is undetermined as calcium nitrate decomposes above 450°. It is surprising that the substitution of sodium nitrate (m. p. 305.5°) for potassium nitrate (m. p. 333.0°) in this system should raise the ternary eutectic temperature from 117.4[1] to 170.3°.

Summary

1. The liquidus surface of the ternary system sodium, lithium and calcium nitrates has been determined.

2. The liquidus curves of the binary systems sodium nitrate–lithium nitrate and sodium nitrate–calcium nitrate have been redetermined.

NEW YORK, N. Y. RECEIVED DECEMBER 29, 1937

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

[10] Laybourn, Madgin and Freeman, *J. Chem. Soc.*, 139 (1934).

[11] Rostkovsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 2055 (1930).

[12] Laybourn and Madgin, *J. Chem. Soc.*, 2582 (1932); 236 (1933).