The density of vitreous selenium was also determined. In order to ensure that the sample might consist, as far as possible, entirely of vitreous selenium, liquid selenium was quenched in a steel mold. It was found possible only to determine the density of this form at room temperature because at higher temperatures, e. g., 90°, the velocity of conversion to the stable metallic form was appreciably great. The result obtained was: $d^{21.8}_4 = 4.2524$.

Discussion

The formula obtained by Dobinski and Wesolowski for the density of liquid selenium is

$$D = 3.987 - 0.0016(t - 220)$$

The close agreement of Dobinski and Wesolowski's results with ours shows the suitability of the methods employed by both. The conclusion is that the results of Dobinski and Wesolowski are equally reliable throughout their range of measurement, i. e., up to 345°. The linear relationship between density and temperature indicates that as far as density is concerned the behavior of both solid and liquid selenium is quite regular, i. e., unaccompanied by a shifting internal equilibrium.

From our results, the change in volume on melting results as +0.03737 cc. per gram. Taking the heat of fusion as 13.4 cal. per gram,[3] we obtain for the change in fusion temperature with pressure +0.033° per atmosphere. This seems abnormally large and might make selenium an interesting subject for pressure experiments.

Summary

The densities of selenium (metallic and liquid) have been measured over the range 20–277°. In agreement with the conclusion of Dobinski and Wesolowski[1] these measurements give no indication of a shifting internal equilibrium. The rise of the melting point with pressure has been calculated.

(3) Mondain and Monval, Bull. soc. chim., [4] 39, 1349 (1926).

The Systems: LiNO₃-NH₄NO₃ and LiNO₃-NH₄NO₃-H₂O

BY A. N. CAMPBELL

The system LiNO₃–NH₄NO₃ is interesting as one of the series of binary systems consisting of NH₄NO₃ and the nitrates of the univalent metals, viz., TlNO₃, AgNO₃, LiNO₃, NaNO₃, KNO₃, all which have been studied. In some of these systems, compound formation occurs, in others solid solution, and in others again, the equilibrium diagram is of the simple eutectic form, unaccompanied by solid solution. This appears to be the case with lithium nitrate, according to Perman and Harrison,[1] who investigated the system up to a content of 45% LiNO₃.

Certain of the observations of Perman and Harrison are important in the present work and I quote: "On increasing the proportion of lithium salt, the stability was reduced, so that the range of the experiments at higher temperatures was very limited." I have not found this to be the case; on the contrary, measurements were carried as high as 230° (in presence of LiNO₃) before decomposition invalidated the results.

"The curve shows the usual two branches, with a eutectic at 97° and 25% LiNO₃. There is,

however, a marked break in the left branch at 122° indicating a change (on cooling) from the δ to the γ-form of NH₄NO₃.

"A cooling curve was obtained for LiNO₃ (in a separate experiment) between 265° (its melting point) and 80°. It showed no breaks, thus proving that this salt exists in but one crystalline form between these limits of temperature."

I have repeated the work of Perman and Harrison, using a refined technique, and have carried the measurements to a higher content of lithium nitrate. The technique used was that of metallurgical practice, and consisted essentially in the use of a neutral body and two thermocouples in opposition: very small thermal changes in the system are thus rendered evident by large displacements of a sensitive galvanometer: the method is due to Roberts-Austen.[2] In the course of this investigation I frequently detected a point of recalescence which led me to suspect either limited solid solubility or the existence of a compound with incongruent melting point. I there-

(1) Perman and Harrison. J. Chem. Soc., 125, 1709 (1924).

(2) Fifth Report, Alloys Research Committee. Proc. Inst. Mech. Engrs. (London), (1899).

fore investigated the ternary system LiNO₃–NH₄NO₃–H₂O at 90, 60, 31 and 25° and have thus shown that neither compound nor solid solutions exist.

Experimental

Two large hard glass test-tubes were placed symmetrically in an electric furnace. One tube contained the LiNO₃–NH₄NO₃ mixture, in weighed proportions (from 60 to 100 g.), and the other the neutral body of silica, of such a weight as to have nearly equal thermal capacity. Each test-tube carried an iron–constantan thermocouple, connected in opposition through a delicate reflecting galvanometer. Temperatures were read directly on mercurial thermometers inserted in the system and in the neutral body. The thermometers were calibrated in boiling benzene, water, toluene, m-xylene, aniline, nitrobenzene and naphthalene and in freezing lead; an exposed stem correction was also applied. Systems consisting of mixtures of salts are at a disadvantage in comparison with similar systems consisting of metals, because of the low thermal conductivity of the former. It is, therefore, important to make provision for adequate stirring and in the present case this was achieved by means of a fine stream of compressed air passing through a capillary immersed in the melt. Unfortunately, no system of stirring is of any value after solidification, or even partial solidification, has taken place, and the full effect of poor thermal conductivity then comes into play.

In conducting the thermal analysis, the Plato method of graduated cooling[3] was applied; i. e., the temperature of the furnace was reduced by equal decrements per unit of time, by increasing the resistance in the circuit. The lithium nitrate and ammonium nitrate used were British Drug Houses A. R. chemicals. To ensure their dryness, the ammonium nitrate was kept over sulfuric acid, with frequent grinding, and the lithium nitrate was fused just before use; lithium nitrate must not be kept fused for any length of time, or the temperature raised much above the melting point, lest decomposition become appreciable.

To ensure homogeneity of the mixtures, the following procedure was adopted: The ammonium nitrate was first weighed out and brought to the temperature of incipient fusion; the powdered and weighed lithium nitrate was then added, little by little and with constant stirring, until a completely clear and homogeneous melt was obtained. This was then placed in the furnace, which had previously been raised to a temperature above the freezing point of the mixture.

The observation of Lowry[4] that melts rich in ammonium nitrate invariably cracked the test-tube on cooling was confirmed. He attributes this to the transformation NH₄NO₃ II → NH₄NO₃ III at 82°, which occurs with expansion on cooling: the transformation III → IV at 32° is accompanied by a contraction.

Results

The results of the thermal analysis are given in Table I (in duplicate runs, the results were repro-

(3) Z. physik. Chem., **55**, 721 (1906).

(4) Early and Lowry. J. Chem. Soc., **115**, 1387 (1919).

TABLE I
TEMPERATURE-COMPOSITION DATA FOR THE SYSTEM: LiNO₃–NH₄NO₃

% LiNO₃	Freezing point, °C.	Peritectic, °C.	Eutectic, °C.
100	270		
75	218		
70	212		
65	205		
60	196	116–113 (indistinct)	
55	182	118	
50	171	120	95
45	151	119	97
40	135	117	96
35	121	...	96
30	110	...	97
25	97	...	97
20	106	...	97
15	119	...	97
10	133	126 (NH₄NO₃ transition)	97
5	153	128	93
0	169	126	

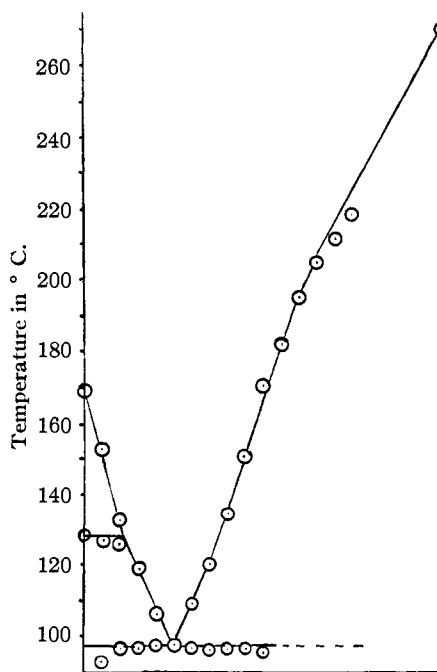ducible to ±0.5°). These figures are expressed graphically in Fig. 1.

Fig. 1.

Discussion

The figures entirely confirm the results of Perman and Harrison. The only new observation is the so-called "peritectic point." A recalescence on the lithium nitrate curve, for mixtures between 60 and 40% LiNO₃, was frequently observed, at a temperature of about 110–120°. No explanation

TABLE II
System LiNO₃-NH₄NO₃-H₂O

Wt. % NH₄NO₃	Wt. % LiNO₃	Wt. % NH₄NO₃	Wt. % LiNO₃	Wt. % NH₄NO₃	Wt. % LiNO₃	Wt. % NH₄NO₃	Wt. % LiNO₃	Wt. % NH₄NO₃	Wt. % LiNO₃
90°		**60°**		**31°**		**31° (contd.)**		**Solid phase: LiNO₃ anhyd.**	
Solid phase: NH₄NO₃ II		Solid phase: NH₄NO₃ III		Solid phase: NH₄NO₃ IV		14.8	51.8		
						9.1	53.9	36.9	39.5
*88.5	0.0	*81.0	0.0	*71.5	0.0	5.1	56.0	33.8	41.0
70.0	10.6	68.5	9.2	70.0	0.6	3.1	56.7	32.2	41.8
66.7	20.8	63.0	14.9	68.2	1.6	1.5	57.7	29.0	43.3
66.0	23.3	60.2	18.7	66.2	2.9	0.0	*58.5	20.8	47.3
Invariant Point:		57.0	25.9	60.5	7.7	* Literature Values: NH₄NO₃ = 71.0 (I. C. T.); LiNO₃ = 57.8 at 29.6° (Donnan and Burt).		19.6	48.0
65.5	29.3	57.1	27.4	56.5	11.4			14.3	50.5
Solid phase: LiNO₃ anhyd.		Invariant Point:		47.3	22.9	**25°**		Invariant Point 2:	
60.7	32.0	56.4	31.2	43.8	32.9	Solid phase: NH₄NO₃ IV		14.0	51.0
56.3	34.6	Solid phase: LiNO₃ anhyd.		42.3	34.5	*69.2	0.0	Solid phase: LiNO₃·3H₂O	
52.2	36.9	56.9	31.5	Invariant Point:		55.8	9.9	12.5	49.0
45.0	41.5	32.2	44.3	42.0	38.7	49.1	17.4	11.5	47.5
38.5	45.0	30.2	45.5	41.9	38.4	43.6	25.7	7.0	45.0
38.0	45.5	19.2	51.5	Solid phase: LiNO₃ anhyd.		40.2	31.5	3.8	45.0
26.5	52.2	14.4	54.0	39.9	39.3	38.5	35.0	2.8	45.3
23.2	54.2	9.0	56.6	39.3	39.9	Invariant Point 1:		1.0	45.6
17.6	57.8	0.0	*62.2	38.4	40.5	37.5	39.0	0.0	*46.0
10.1	61.8	* Literature Values: NH₄NO₃ = 80.8 (I. C. T.); LiNO₃ = 63.6 (Donnan and Burt).		37.7	41.1	37.7	38.9	* Literature Values: NH₄NO₃ = 68.7 (I. C. T.); LiNO₃ = 45.24 (Interpolated from Donnan and Burt).	
0.0	*68.0			32.2	43.0				
* Literature value: NH₄NO₃ = 89.3 (I. C. T.). LiNO₃ = not previously determined.				31.5	43.5				
				24.0	47.0				

has been found for this observation. It may be the result of some unknown experimental trouble; or it may indicate a polymorphic transition of lithium nitrate, although this could not be confirmed by the cooling curve of pure lithium nitrate. It does not seem to be the transition temperature of a compound of the two salts, since the ternary system revealed neither compound nor solid solution formation.

LiNO₃-NH₄NO₃-H₂O.—This system was investigated at 90, 60, 31 and 25°. Using a small thermostat, a low-lag electrical heating unit, and a sealed mercury arc relay, it was possible to maintain temperature constant to within 0.01° even at 90°. All solutions were stirred for twenty-four hours before analyzing them. In order to obtain a solid phase as free as possible from mother liquor, an all-glass apparatus was designed, incorporating a sintered glass filter and filtration by suction at the temperature of the thermostat. Ammonia was estimated by distillation and lithium by conversion to sulfate in a platinum dish. The accuracy of the ammonia estimation is high, certainly as high as 0.1%; that of the lithium determination not so high, 0.2% at best. The reproducibility

was checked by taking solutions close together in composition: the analytical results lie on a smooth curve. Occasional discrepancies were due to insufficient time of stirring: these solutions attain equilibrium very slowly. The results are in Table II, and plotted in Figs. 2, 3, 4 and 5.

Since the hydrate, LiNO₃·¹/₂H₂O, described by Donnan and Burt,[5] nowhere occurs as solid phase in any of these systems, a dilatometric investigation of the transition points of hydrated lithium nitrate was carried out. The dilatometer contained anhydrous lithium nitrate to which water was added in amount more than sufficient to convert all the salt to hemihydrate but insufficient to convert it entirely to the trihydrate; the indicator fluid was m-xylene. The dilatometer was kept at room temperature overnight to ensure hydration and it was obvious to the eye that this had occurred. According to Donnan and Burt, the bulb should have contained a mixture of tri- and hemihydrates. A marked transition point was found at 28.8°. Donnan and Burt give 29.6° as the temperature of the transition
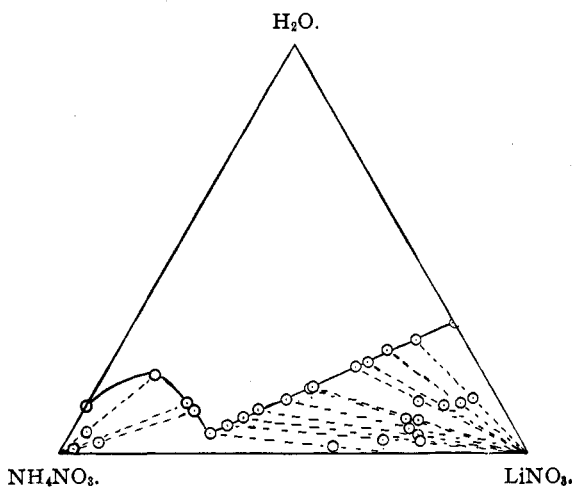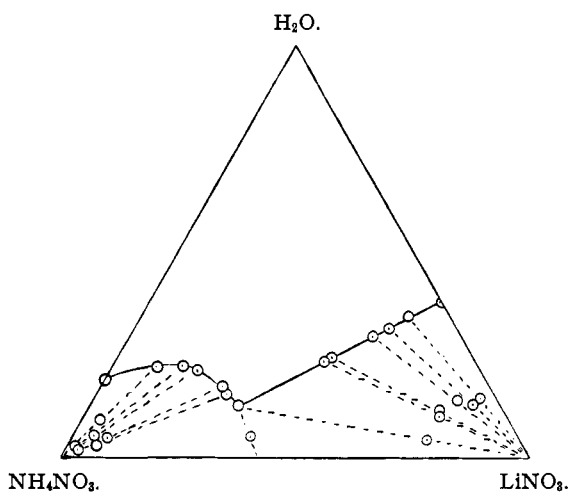
$$LiNO_3 \cdot 3H_2O \rightleftharpoons LiNO_3 \cdot {}^1/_2H_2O + 2{}^1/_2H_2O$$

(5) Donnan and Burt, J. Chem. Soc., 83, 335 (1903).

These authors also give 61.1° as the temperature of the transition

$$LiNO_3 \cdot {}^1/_2H_2O \rightleftarrows LiNO_3 + {}^1/_2H_2O$$
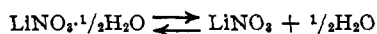
I observed no second transition up to 78.8°.

Fig. 2.—90°.

Fig. 3.—60°.

Discussion

It is apparent from the isotherms that no compound is formed between ammonium nitrate and lithium nitrate and that, in the solid state, ammonium nitrate is insoluble in lithium nitrate (up to 90°) and lithium nitrate insoluble in all four crystalline modifications of ammonium nitrate. It is well known that ammonium nitrate forms solid solutions with potassium and cesium nitrates, but not with sodium nitrate. It is pointed out by Tutton[6] that in some cases similarity in crystalline form alone, even when it is

(6) "Crystalline Structure and Chemical Constitution," Macmillan, London, 1910, p. 128.
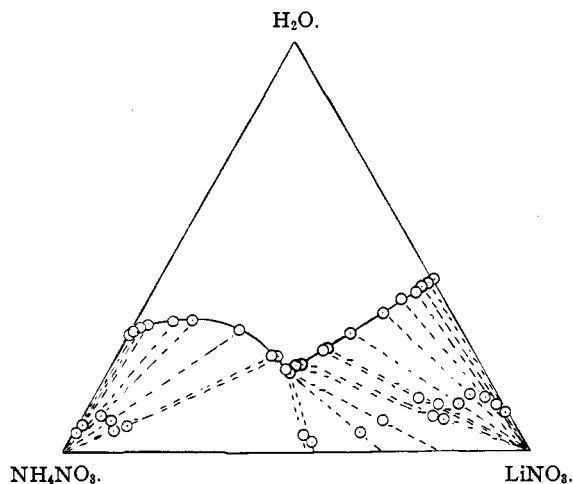
Fig. 4.—31°.
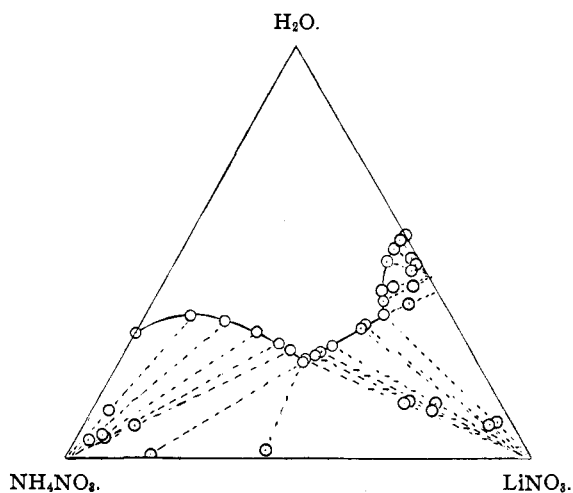
Fig. 5.—25°.

very marked, is not sufficient to cause miscibility in the solid state, but that the molecular volumes of the two substances must also be almost equal. The molecular volumes of the nitrates in cc. are

NH₄NO₃	KNO₃	CsNO₃	LiNO₃	NaNO₃
46.5	48.0	52.8	29.6	35.8

Another striking feature of the isotherms is that the hemihydrate, $LiNO_3 \cdot {}^1/_2H_2O$, nowhere occurs as stable solid phase. A similar observation was made by Massink,[7] working on a system comprising LiNO₃, who found that, with the exception of one experiment, anhydrous LiNO₃ always occurred as the solid phase, where the results of Donnan and Burt[5] would lead one to expect the hemihydrate. Donnan and Burt base their evidence for the existence of the hemihydrate on a direct determination of transition point in the dilatometer and on the occurrence of a break in

(7) Massink, Z. physik. Chem., **92**, 356 (1916–1918).

their solubility curve for lithium nitrate in water. I have been unable to obtain the transition point dilatometrically and, if the solubility figures of Donnan and Burt are plotted, there seems no reason to give the curve the shape drawn by them; their figures are better represented by a smooth curve: in any case, their determinations are too far apart to settle the matter definitely. I conclude that the existence of the hydrate, $LiNO_3 \cdot {}^1/_2H_2O$, is doubtful.

Summary

1. The system $LiNO_3$–NH_4NO_3 has been investigated by thermal analysis. The results of Perman and Harrison are confirmed and extended.

2. The system $LiNO_3$–NH_4NO_3–H_2O has been investigated at 90, 60, 31 and 25° by the usual solubility technique.

3. No compound occurs, under any of the above conditions; neither is solid ammonium nitrate soluble in solid lithium nitrate (up to 90°), nor lithium nitrate in any of the four crystalline modifications of ammonium nitrate.

4. Lithium nitrate exists in but one crystalline form between room temperature and its melting point, in accordance with Perman and Harrison.

5. The hydrate, $LiNO_3 \cdot {}^1/_2H_2O$, described by Donnan and Burt, nowhere exists as stable solid phase. A direct investigation of transition point with the dilatometer failed to reveal the transition: $LiNO_3 \cdot {}^1/_2H_2O \rightleftharpoons LiNO_3 + {}^1/_2H_2O$, which is said to occur at 61.1°. The existence of this hydrate is doubtful.

Spectroscopic Evidence of Intermolecular Transfer of Protons

BY DUDLEY WILLIAMS[1] AND W. DAVID STALLCUP[2]

The high degree of association exhibited by pure liquids and by liquid mixtures in which the molecules contain hydrogen atoms attached to atoms of the electronegative elements fluorine, oxygen or nitrogen has been explained, qualitatively at least, in terms of proton bonds or hydrogen bridges formed between neighboring molecules. According to the proton-bond theory, protons are "shared" between adjacent molecules in somewhat the following manner

$$R—O{\overset{H}{\underset{H}{\diagdown \diagup}}}O—R'$$
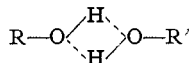
In the case of water and other liquids having especially strong proton bonds, the proton can be transferred from one molecule to another when the molecules are separated. Whether actual intermolecular transfer of protons can occur in all liquid mixtures having association of the type indicated above is not entirely clear. The purpose of the present paper is to report a method for detecting intermolecular transfer and to give the results for a single binary mixture.

The method is rather simple: the hydrogen in one liquid is replaced by deuterium. Then the two liquids are mixed. After mixing, the liquids are separated by distillation and the liquid originally containing no deuterium is tested for the presence of deuterium. The changes in physical constants produced by the presence of deuterium are, in most cases, so slight that it was decided to use the infrared absorption of the liquids as a test for the presence of deuterium. The separation of OH and OD bands in alcohols is approximately 830 cm.$^{-1}$; the OH and OD absorption bands appear at 3.0 μ and 4.0 μ, respectively. The two liquids chosen for study were methanol and heavy butanol.

Experimental Results

Anhydrous methanol was prepared by treating a suspension of magnesium methylate in methanol with freshly distilled methanol and then separating the methanol from this mixture of magnesium oxide and magnesium methylate by distillation. The methanol thus prepared had the following physical constants: b. p. 64.5°, $n^{25}D$ 1.3268, and d^{25}_4 0.7896.

The deuterium butoxide was prepared by adding deuterium oxide to n-butyl borate. After standing a few hours, the precipitated boric acid was removed by filtration. The filtrate was then fractionated in order to separate the deuterium

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