XXXV.—*The Solubilities and Transition-Points of Lithium Nitrate and its Hydrates.*

By FREDERICK GEORGE DONNAN and BRYCE CHUDLEIGH BURT.

THE object of the experiments described in this paper was to examine the various solid phases which can separate from the two-component system, water—lithium nitrate, and to determine the conditions of their existence in contact with the saturated solution.

As the first member of its group, lithium shows many analogies with the elements of the succeeding series, in particular with calcium. In agreement with this, lithium nitrate is a very deliquescent and extremely soluble salt. It is also characterised by a tendency to form supersaturated solutions, resembling calcium chloride in this respect.

The first experiments on the hydrates of lithium nitrate appear to have been those of Kremers (*Jahresberichte*, 1854, 324; *Pogg. Ann.*, 92, 520), who mentions that he obtained a hydrate crystallising in needles and also another form crystallising in rhombohedra which he assumed to be the anhydrous salt. The former he regarded as the hydrate $\text{LiNO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. The same formula was assigned to it by Troost (*Jahresberichte*, 1857, 140). Both observers obtained this salt by crystallisation below 20° .

According to Dott, however (*Pharm. J.*, 1893, 124, [iii], 215), the hydrate obtained by Kremers and Troost possesses the formula $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$.

Solubility measurements were carried out by Kremers at a few temperatures, but these do not agree well with the results recorded below. Similar discrepancies have been observed in many other cases of this sort, and are chiefly due to the fact that not enough attention was paid by the earlier observers to the securing of constant temperature and complete saturation.

Crystallisation Experiments.

The salt used in the following experiments was obtained from Kahlbaum and purified by recrystallisation. When a strong solution was cooled down to the ordinary temperature and allowed to crystallise, delicate deliquescent needles were obtained. These were filtered by suction and rapidly dried between folds of filter paper. They proved on analysis to consist of the trihydrate, as shown by the following results:

Found $\text{H}_2\text{O} = 44.1$; $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ requires 43.9 per cent.

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On allowing a more concentrated solution to crystallise at a temperature above 30° , crystals were obtained having an entirely different appearance. It was found difficult to obtain specimens giving constant results on analysis by simply filtering off and drying in the usual way, probably owing to the rapid solidification of the adherent mother liquor to a mixture of the two hydrates (see p. 339). However, on crystallising in an air-bath at a constant temperature of 40° and allowing the selected crystals to dry on filter paper while remaining in the bath, a hydrate was obtained in a state of purity, as shown by the following analyses:

Found $\text{H}_2\text{O} = 11.6, 11.8$; $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires 11.5 per cent.

Isothermal crystallisation, at a temperature of 90° , yielded a salt which on examination under the microscope appeared to differ in crystalline form from the preceding hydrates. This was evidently the anhydrous nitrate, although the specimens analysed appeared to contain quantities of water varying from 1 to 2 per cent. As the salt is, however, exceedingly deliquescent, this small and variable amount of water may safely be ascribed to the difficulty in obtaining a really dry sample.

Solubilities of the Trihydrate.

These determinations were carried out by stirring the salt with water, using an apparatus of the form employed by van't Hoff. The arrangements, which were of the usual description, included a water-thermostat, an Ostwald toluene thermo-regulator, with a small Heinrici hot-air motor to drive not only the thermostat-stirrer but also the stirrers of two solubility vessels. The thermometer employed was divided into tenths, and standardised by comparison with Travers' hydrogen thermometer.

Usually, the solutions were rapidly stirred for 24—30 hours to attain saturation-equilibrium. The stirrer was then stopped, and after the particles of salt had been given a short time to settle, a portion of the solution was withdrawn by means of a previously warmed pipette, to the lower end of which a small filtering tube containing glass wool was attached by indiarubber tubing. The solution thus removed was at once poured into one or more small weighed Erlenmeyer flasks of Jena glass. These were placed in an air-bath maintained at 180° , and connected to a water-pump through a drying bottle containing strong sulphuric acid. The evaporation, which was thus carried out in a vacuum desiccator at 180° , was continued until the anhydrous salt was of constant weight.

The analyses recorded in this paper were all carried out in this way.

Each solubility result contained in the following, as well as in the other tables, is the mean of two concordant determinations (carried out simultaneously in different solubility vessels.

1. *Solubilities of* $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$.

Temperature	0·10°	10·50°	12·10°	13·75°	19·05°	22·10°
Concentration (parts by weight of dry anhydrous salt in 100 parts by weight of solution)	34·8	37·9	38·2	39·3	40·4	42·9

The lowest temperature was obtained in a bath of ice and water.

On attempting to make solubility measurements with this hydrate at higher temperatures, the solubility was found to increase very rapidly, evidently indicating its rapid approach to a point of infinite solubility, that is, to the true melting point of the trihydrate.

An approximate preliminary estimate of this temperature was obtained by melting the salt in a tube and observing the melting point with an ordinary thermometer; the trihydrate was found to melt at about 30° to a perfectly clear liquid.

The exact position of this point and the course of the curve on either side were determined as follows.

Solutions corresponding to the upper portion, *BC*, of the solubility curve of the trihydrate contain less water than the crystallised salt. They are therefore obtained most readily by melting the trihydrate and driving off a portion of the water. The amount of water expelled in this operation must be controlled by frequent weighing in order to avoid reaching the point *C*, which would cause the separation of the next phase. Solutions corresponding to points on the right of *BC* and below *C* will deposit the trihydrate on cooling. A weighed amount of such a solution of known concentration being placed in a Beckmann freezing-point tube fitted with thermometer and stirrer, the tube was allowed to cool until the solution was slightly supercooled, after which the tube was inserted in the air jacket, the latter being packed round with sheep's wool contained in a large beaker. Crystallisation having been started by the introduction of a minute crystal of the trihydrate, the mixture was kept constantly stirred and the maximum temperature noted, observations being made for 20—30 minutes, during which time the temperature remained practically constant.* After a preliminary observation, more accurate experiments were made by employing a

* The technique of measurements of this kind has been recently developed by F. A. Lidbury (*Zeit. physikal. Chem.*, 1902, **39**, 453).

constant supercooling of 0.5° . The first point thus determined was quite close to *C*. Lower points on the curve were obtained by successive dilutions made *in situ*. For this purpose, very thin sealed glass bulbs containing small weighed quantities of water were introduced into the tube and broken by means of the stirrer. The temperatures thus determined on the arbitrary scale of the Beckmann thermometer were referred to the standard thermometer by comparison of the two scales immediately before and after the observations.

The melting point of the trihydrate (see point *B* in the figure)

corresponds with a point on the curve where the tangent is vertical, and could now be determined graphically, since points on either side in its immediate neighbourhood were known; it was found to be 29.88° , a value agreeing sufficiently well with the direct determination of this temperature. The following table contains the results of the experiments made in the manner described above. These data enable the form of the solubility curve of the trihydrate in the neighbourhood of its melting point to be determined with considerable precision.

2. *Temperature-Concentration Data for $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ in the Neighbourhood of its Melting Point.*

Temperature	27.55°	29.47°	29.78°	29.87°	29.86°	29.64°	29.55°
Concentration (parts LiNO_3 per 100 parts of solution) ..	47.30	53.67	55.09	56.42	56.68	57.48	58.03

Solubilities at Temperatures above 30°.

In the case of solubility measurements carried out at higher temperatures it was unsafe to employ a pipette in withdrawing the saturated solution, so the latter was blown over into a small weighed Erlenmeyer flask of Jena glass. To the end of the connecting tube which passed through the rubber stopper of the solubility vessel a small filtering tube containing glass-wool was attached by indiarubber tubing, the whole apparatus being completely immersed in the thermostat.

The solid phase employed in these determinations was the semihydrate obtained as described previously by isothermal crystallisation at 40°. As before, stirring was continued for a long time, in order to ensure complete saturation and also to allow time for any changes occurring in the solid phase. As will be seen, such changes did actually occur at the higher temperatures. The solubilities thus determined are given in the following table :

3. *Solubilities at Higher Temperatures.*

Temperature	43.6°	50.5°	55.0°	60.0°	64.2°	70.9°
Concentration	60.8	61.3	63.0	63.6	64.9	66.1

Concentration is expressed in the same units as before, and the numbers in the lower line are the means of independent determinations. On plotting these data it was apparent that a break existed at about 61° (see point *D* in the figure. Owing to a slight error in "adjustment" of the curve *CD* shown in the diagram, the point *D* is represented as corresponding to a rather higher temperature).

In order to confirm the existence of this transition-point and to obtain an independent determination of its position, measurements

were made with a van't Hoff dilatometer, the arrangements for filling being such that both dilatometer and paraffin were well exhausted before the latter was introduced into the capillary. As we had reason to suppose that the break in the solubility curve corresponded with a transition to the anhydrous salt, a little of the latter was added to the slightly moist semihydrate contained in the dilatometer bulb. The following is a brief record of the observations made:

Slow heating up to 62.5° in thermostat. Regular expansion at 62.5° sudden increase of expansion.

Rapid cooling to 60.7° . Ascending value not recovered; remained overnight at this temperature; meniscus returned to original (ascending) point.

Slow heating up to 62° ; expansion (isothermal) occurs.

Contents of dilatometer brought to the state of half transition as recommended by van't Hoff; neither expansion nor contraction at 61° during 48 hours. At 61.4° an expansion of about 5 mm. in the course of several hours.

The transition-point therefore lies between 60.7° and 61.4° , the mean of which, 61.05° , agrees very well with the value obtained from the solubility curves. We may therefore take 61.1° as being a fairly close approximation to the transition-temperature.

No evidence of any further transition was observed, even when the dilatometer was heated up to 90° . As the isothermal crystallisation at temperatures of 75 — 90° invariably yielded the anhydrous salt, there is no doubt that the above transition-point corresponds with the change, semihydrate $\rightarrow$ anhydrous salt + saturated solution.

Determination of Point C.

The composition of the solution corresponding to the maximum temperature point *B* of the curve *ABC* is the same as that of the trihydrate. A corresponding maximum-temperature point for the semihydrate would lie on the metastable portion of *CD* beyond *D*. The composition of the solution represented by the point *C* lies therefore between the compositions of the two hydrates. Hence if heat be removed from a solution the composition of which corresponds with *C* it will solidify gradually (provided supersaturation is guarded against) to a mixture of the trihydrate and semihydrate. In this way an independent determination of the position of *C* was carried out (its position being already known approximately from the solubility-curves).

A saturated solution of $\text{LiNO}_3, \frac{1}{2}\text{H}_2\text{O}$, contained in a tube insulated by a vacuum-vessel packed round with sheep's wool, was allowed to cool

slowly to a temperature below the approximate position of C , crystallisation being then started by dropping in small crystals of both hydrates. The thick paste thus obtained was stirred vigorously and the steady maximum temperature noted. In this way the temperature corresponding with C was found to be 29.6° .

Cryohydrate-Point and Ice-Curve.

The lower portion of the ice-curve OA (from zero to -2.5°) was determined in the ordinary way in the Beckmann apparatus. Owing to the highly deliquescent nature of the lithium nitrate, weighed quantities of a solution of known concentration contained in thin sealed glass bulbs were added to a known weight of water, and the bulbs broken by the stirrer.

The position of the cryohydrate-point A was fixed by ascertaining the steady temperature assumed by a mixture of finely powdered ice and $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, contained in a tube well protected from external heating by a packing of ice. The corresponding solution was also analysed. The thermometer employed was standardised at 0° , and its scale calibrated from 0° to -20° . The cryohydrate-temperature determined in this manner was found to be -17.8° .

The following is a summary of the quadruple-points, melting-points, and equilibrium-curves of the lithium nitrate—water system. The letters refer to the diagram accompanying this paper.

I. *Quadruple-points* :

A . Cryohydrate-point of the trihydrate (-17.8°).

C . Transition-point, trihydrate + semihydrate $\rightleftharpoons$ saturated solution (29.6°).

D . Transition-point, semihydrate $\rightleftharpoons$ anhydrous salt + saturated solution (61.1°).

II. *Melting-points* :

O and B . Melting-points of ice and trihydrate (29.88°) respectively.

III. *Equilibrium-curves* :

OA , ABC , CD , and DE , correspond with the solid phases, ice, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and LiNO_3 respectively.

A determination of the solubility of the trihydrate at 10° (made at an early stage of our work) which did not agree with any subsequent determinations suggested the possible existence of another phase. Thermometric experiments gave no indication, however, of any break in the cooling-curve of the system, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ + saturated solution. Furthermore, the cryohydrate-point and the point corresponding with 0° lie on a curve continuous with the solubility-determinations at higher temperatures. The solubility-determination in question must

therefore have been vitiated by some large error, and accordingly it has not been shown on the diagram.

In conclusion, we desire to express our thanks to Professor Ramsay for the interest which he has taken in our work.

CHEMICAL LABORATORY,
UNIVERSITY COLLEGE, GOWER STREET, W.