

CCCIV.—*The Hydrates of Lithium Sulphate and their Solubility in Water between -16° and $+103^{\circ}$.*

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ANHYDROUS lithium sulphate and its monohydrate are described in the literature, the hydrate constituting the stable phase in contact with water from 0° to 100° . Nevertheless, data hitherto published on its solubility in water at various temperatures show considerable lack of agreement, as is evident from Fig. 1. Even the more recent data appear to be as discordant as the earlier, for whilst the four determinations of Schreinemakers and Jacobs agree well with Kremers's curve, the results of Etard and Massink stand alone. Further, the exceptionally steep fall in solubility observed by Etard as the temperature falls from -4° to -20° seems inherently improbable. It was decided, therefore, to study the problem afresh.

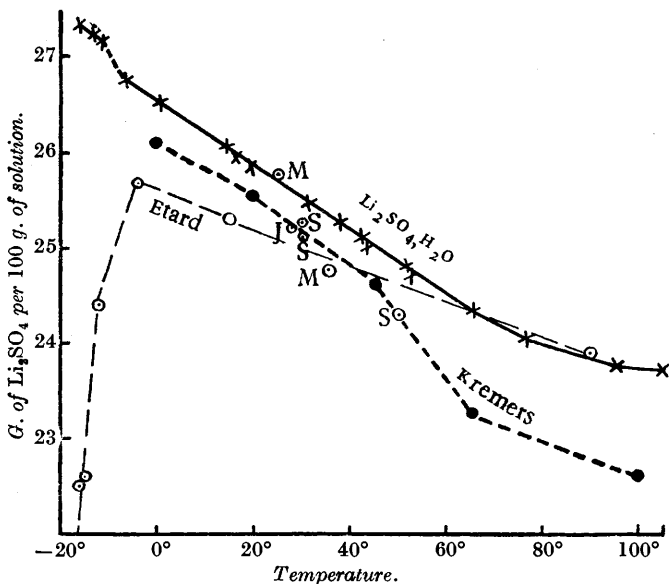
Lithium sulphate was prepared by dissolving the pure carbonate in dilute sulphuric acid, and crystallising the solution. Spectroscopic examination showed that any impurities could only be present in the merest traces. Gravimetric analysis confirmed Röhrig's observation (*J. pr. Chem.*, 1888, **37**, 225) that, on precipitating the sulphate ion with barium chloride, the barium sulphate is contaminated with appreciable quantities of lithium, unless very special precautions are taken. The lithium is readily detected spectroscopically and the results may be several units % too high.

The lithium sulphate solution was stirred continuously in contact with the finely crushed salt for about 2 hours, a portion being then withdrawn by suction from the saturation flask through a Büchner funnel with a glass filter disc into a receiving flask, the usual precautions for submersion in the thermostat being taken to ensure complete uniformity of temperature. The solution was evaporated to dryness on the water-bath in a platinum dish, heated to 140° in an electric oven, and finally raised for a few moments to dull redness over a Bunsen flame to ensure complete expulsion of the last traces of water. The weight of anhydrous lithium sulphate was thus obtained directly and accurately. The saturated solution in

contact with excess of salt boiled at $103.2^{\circ}/756$ mm. (Kremers gives 105°).

The solubilities shown in Fig. 1 are given in Table I as g. of anhydrous salt per 100 g. of solution. Between -6.5° and $+65^{\circ}$ the curve is linear, the solubility being given by the expression $S = 26.52 - 0.0335t$. Of previous work, only two data are in harmony with the present, namely, those of Massink at 25.79° and

FIG. 1.



● Kremers, *Pogg. Annalen*, 1855, **95**, 468.

○ Etard, *Ann. Chim. Phys.*, 1894, **2**, 547.

S Schreinemakers and co-workers, *Z. physikal. Chem.*, 1907, **59**, 645; *Chem. Weekblad*, 1918, **15**, 121.

J Jacobs, Dissertation, Leiden, 1914.

M Massink, *Z. physikal. Chem.*, 1918, **92**, 355.

× Present research.

of Etard at 90° . All the other data are lower, and the explanation is not obvious. Etard (*loc. cit.*, p. 514) appears to have determined the lithium sulphate gravimetrically by precipitation as barium sulphate—a method that gives uncertain results; but so enormous a difference at the lower temperatures between his results and the author's seems hardly explicable on this ground alone. Kremers's results give curves of the same general shape as the author's, but the data are always appreciably lower, although the same method of estimating the salt was adopted. His method of filtration, however,

TABLE I.

Temp.	S.	Temp.	S.	Temp.	S.	Temp.	S.
-16.0°	27.32	14.0°	26.07	38.0°	25.28	65.7°	24.34
-13.0	27.24	16.5	25.96	42.2	25.12	77.0	24.05
-11.5	27.18	16.7	25.96	43.7	25.00	94.8	23.76
- 6.5	26.73	19.6	25.85	51.6	24.82	103.0	23.72
+ 0.6	26.51	31.8	25.47	52.4	24.71	103.0	23.72

appears to have been crude, and in itself would suffice to account for the difference noted.

Below 0° the solution became increasingly viscous and the solubility curve appeared to break at about the same temperature as was noted by Etard, namely - 8° (Etard gave - 9°), but with this difference, that the rapid fall in solubility recorded by Etard was not confirmed. The break in the curve was taken to indicate the existence of a higher hydrate and the solid phase at various temperatures was removed and analysed. The results, in the order in which they were obtained, are as follows: - 6.5°, H₂O, 30.8, 25.54; - 11.5°, H₂O, 29.76; - 16°, H₂O, 25.66; - 10°, H₂O, 28.95, 28.91 (Calc. for Li₂SO₄.2H₂O, 24.69; for Li₂SO₄.3H₂O, 32.96%).

The results do not harmonise as closely as one could wish. It is difficult to free the crystals from mother-liquor without incurring simultaneous decomposition of the crystals to monohydrate. In all cases except the last the crystals were rapidly pressed between filter-papers to effect the removal of mother-liquor, but in the last experiment, at - 10°, one batch of crystals was dried between filter paper, and the second batch on a Büchner filter with glass filter disc. The two results agree well. It appears probable, therefore, that at low temperatures a higher hydrate, possibly the dihydrate, Li₂SO₄.2H₂O, is capable of existence.

Kremers states that the monohydrate heated at 100° still retains water of crystallisation, apparently implying its almost complete retention. Gmelin took this view; but such is not the case. Pettersson ("Untersuchungen," etc., Upsala, 1873) is more correct in stating that the salt becomes anhydrous, or partly so, at this temperature. This was proved as follows: a solution containing approximately 2 g. of anhydrous lithium sulphate was evaporated to dryness in a platinum dish on the water-bath, and the heating continued for 8 hours. The salt lost in weight fairly rapidly at first, but very slowly later, and finally retained only 0.0210 g. of water. This was expelled on warming for a few moments over a Bunsen flame, the original weight of anhydrous salt being then recovered. Upon exposure to moist air the anhydrous salt takes up moisture, rapidly at first, until the monohydrate is formed. No

break in the rehydration-time curve could be detected which was suggestive of a hemihydrate. In a very humid atmosphere the salt absorbs slightly more water than corresponds to the monohydrate, but rapidly yields up the excess in a desiccator over calcium chloride. In two rehydration experiments, the product contained H_2O , 14·14, 13·96; mean 14·05 (Calc. for $Li_2SO_4 \cdot H_2O : H_2O$, 14·08%).

In conclusion, the author desires to acknowledge the assistance of Mr. Eric G. K. Pritchett, who determined six of the solubilities between 0° and 60° .

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