

a passage of only 4 liters of dry air before it began to dry efficiently. Meyers<sup>6</sup> believes that when boric oxide is prepared at a temperature above 800°, molecular complexes are formed whose rate of reaction with water is much slower than the reaction of the boric oxide prepared at lower temperatures. The existence of such complexes would explain the "period of induction."

While an absolute comparison of the drying efficiency of the boric acid anhydride is difficult to make, these experiments indicate that this material is more efficient than sulfuric acid and calcium chloride but is somewhat inferior to phosphorus pentoxide and magnesium perchlorate.

With a drying column 40 cm. long and 7 mm. in diameter the boric oxide absorbed all the moisture from 88 liters of air saturated with moisture at 23° and flowing at the rate of 2 liters per hour.

### Summary

1. In preparing boric oxide for drying purposes the boric acid should be dehydrated at about 800°. If prepared above this temperature, the product shows an induction period which decreases its efficiency.

2. The formation of a hard glass on cooling may be partly avoided by pouring the fused boric oxide into carbon tetrachloride at 0°. The resulting fragments are fairly easy to powder and the product is a very satisfactory drying agent.

3. The boric oxide was found to be an efficient drying agent until its moisture content rose to about 25% of its own weight.

MADISON, WISCONSIN

---

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF NEW YORK UNIVERSITY]

## THE SYSTEM LITHIUM PERCHLORATE-WATER

BY JOHN P. SIMMONS AND CLARENCE D. L. ROPP<sup>1</sup>

RECEIVED MARCH 27, 1928

PUBLISHED JUNE 5, 1928

According to A. Potilitzin,<sup>2</sup> aqueous solutions of lithium perchlorate give the trihydrate,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , which loses approximately two-thirds of its combined water when heated between 98 and 100°, changing to monohydrate, and all of its water between 130 and 150°. The approximate nature of these data makes apparent the need of a more careful study of this system.

### Preparation of Lithium Perchlorate

Anhydrous lithium perchlorate was made by the method of Richards and Willard.<sup>3</sup> The purity of the salt was proved by a modification of a

<sup>1</sup> The results of this investigation were submitted by Clarence D. L. Ropp as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **19**, 339 (1887); **20**, 541 (1888).

<sup>3</sup> Richards and Willard, *THIS JOURNAL*, **32**, 4 (1910).

method by Lamb<sup>4</sup> for the analysis of perchlorates. This consists in heating a weighed amount of lithium perchlorate in a Pyrex test-tube loosely plugged with asbestos. The loss in weight is assumed to be due to the oxygen driven off. As an illustration, two such determinations gave 100.10 and 100.15% of lithium perchlorate.

### Procedure

In order to establish accurately the number and composition of the hydrates of lithium perchlorate capable of existing between 0° and the temperature where the anhydrous salt is stable, the following experiments were made.

(1) Saturated solutions of lithium perchlorate were cooled from temperatures between 0 and 90°, approximately. As a result, long, needle shaped crystals formed which, after careful drying between filter paper, showed upon analysis a water content of 33.90%, which agrees well with the corresponding theoretical value for the trihydrate, 33.68%.

(2) A quantity of this trihydrate was powdered and placed in a desiccator over anhydrous lithium perchlorate and kept thus for a period of six weeks. This experimental arrangement causes the trihydrate to change to the next lower hydrate. Determinations of the water content of the specimen were made at frequent intervals and the percentage of water finally became constant at 14.52%. The theoretical value for  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  is 14.48%.

(3) A synthetic lithium perchlorate monohydrate was made and this was used as a desiccating agent for crystals obtained by cooling solutions saturated between 0 and 90° and which by experiment<sup>2</sup> were proved to be  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ . The latter showed constancy in water content at 33.66%, which agrees with the corresponding value for  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , 33.68%.

The results of these three sets of experiments indicate that lithium perchlorate forms two hydrates,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  and that evidence of the existence of a dihydrate does not exist. The system was not investigated below 0°.

To obtain more precise information regarding the transition points involved in this system, solubility measurements were made over a temperature range from 0 to 170°. These measurements were made at the lower temperatures by agitating an excess of anhydrous salt with water in a solubility tube kept at constant temperature in a thermostat until constancy in concentration was reached. These determinations were supplemented by results obtained by sealing in a tube known quantities of anhydrous lithium perchlorate and water, immersing the tube in water and gradually heating until the solid phase disappeared. The tube was

<sup>4</sup> Lamb and Marden, *THIS JOURNAL*, **34**, 812 (1912).

then cooled until the hydrate, stable at the temperature being used, crystallized out. The tube was then heated carefully one-tenth of a degree at a time with constant agitation and the temperature noted at which the last trace of solid phase disappeared. The solubility measurements at the higher temperatures were all made by the second method. Solubility data for the temperatures indicated are given in Table I.

TABLE I  
SOLUBILITY OF  $\text{LiClO}_4$  IN GRAMS PER 100 OF SOLUTION

Temp., °C.	Concn.	Temp., °C.	Concn.	Temp., °C.	Concn.
0 <sup>a</sup>	29.90	92.3	62.5	108.9	72.8
10	32.88	94.3	65.0	120.7	75.0
20	35.95	95.1	66.32	136.9	80.0
25	37.48	94.8	66.67	144.0	82.5
30	38.87	93.2	70.0	148.5	85.0
40	41.97	92.7	70.3	149.3	87.5
64.6	50.0	92.53	70.33	144.2	90.0
77.9	55.0	93.2 <sup>b</sup>	70.5	167.5 <sup>c</sup>	91.04
89.2	60.0	97.3	71.0	172	91.11

<sup>a</sup> Trihydrate is solid phase.

<sup>b</sup> Monohydrate is solid phase.

<sup>c</sup> Anhydrous salt is solid phase.

Density values of the saturated solutions at the lower temperatures were made by weighing a known volume and are given in Table II.

TABLE II  
DENSITIES OF SATURATED SOLUTIONS OF  $\text{LiClO}_4$

0°	10°	20°	25°	30°	40°
1.215	1.236	1.258	1.269	1.277	1.300

H. H. Willard and G. F. Smith<sup>5</sup> determined the solubility of lithium perchlorate in water at 25°, obtaining a value of 37.385% and a density of 1.268, which agree very well with our values of 37.48% and a density of 1.269.

The melting point of anhydrous lithium perchlorate was determined by Potilitzin<sup>2</sup> and by Richards and Willard<sup>3</sup> as 236°, and this value was used in the construction of the solubility curve in Fig. 1. An inspection of the solubility curve of lithium perchlorate, Fig. 1, indicates clearly two transition temperatures and two congruent melting points. The melting point of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  from the curve is 95.1°, which agrees well with Potilitzin's<sup>2</sup> value of 95°. The melting point of  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  from the curve is 149° for a content of 86.5% of  $\text{LiClO}_4$ . The theoretical value is 85.52°.

In order to determine the transition points with greater accuracy than could be attained by use of the solubility data, cooling experiments were

<sup>5</sup> Willard and Smith, *THIS JOURNAL*, **45**, 286 (1923).

performed. Marked halts in temperature drop were observed at 92.53 and 145.75°. These temperature points indicate the transition points for  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{LiClO}_4 \cdot \text{H}_2\text{O}$  and  $\text{LiClO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{LiClO}_4$ , respectively.

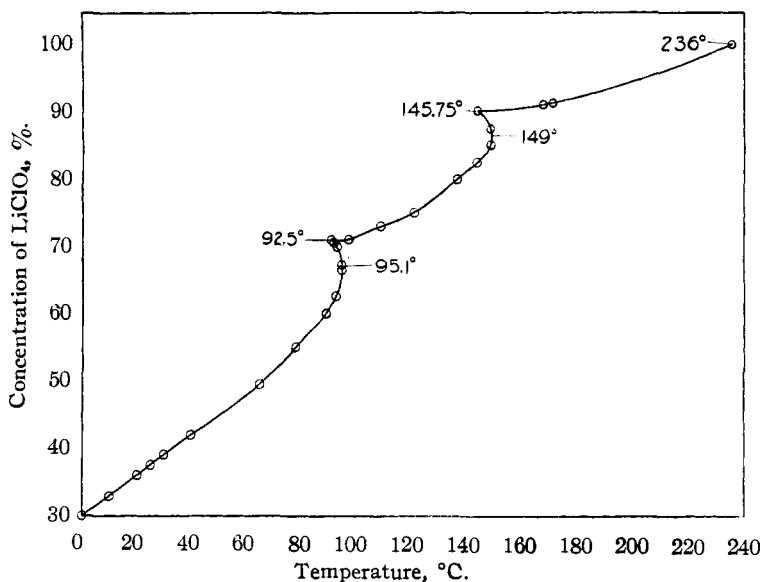


Fig. 1.

### Summary

1. Solubility measurements of  $\text{LiClO}_4$  in water over a temperature range from 0 to 170° have been made.
2. Density values of the saturated solutions over a temperature range from 0 to 40° have been made.
3. The existence of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  is definitely established.
4. No evidence of the existence of a dihydrate was observed.
5. The transition point  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{LiClO}_4 \cdot \text{H}_2\text{O}$  is 92.53°.
6. The transition point  $\text{LiClO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{LiClO}_4$  is 145.75°.
7. The melting point of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  is confirmed at 95.1°.
8. The melting point of  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  is 149°.

NEW YORK CITY