THE SYSTEM LITHIUM CHLORATE – LITHIUM CHLORIDE – WATER AT VARIOUS TEMPERATURES[1]

BY A. N. CAMPBELL AND J. E. GRIFFITHS[2]

ABSTRACT

The equilibrium diagram of the system lithium chlorate – water has been determined at all temperatures and that of the system lithium chlorate – lithium chloride – water at the temperatures 3.0°, 6.0°, 8.5°, and 25.0° C.

Lithium chlorate forms three hydrates having the formulae:

(i) $(LiClO_3)_4.H_2O$—stable in contact with solution from 20.5° to 42.0° C.

(ii) $LiClO_3.H_2O$—stable in contact with solution from −0.1° to 20.5° C.

(iii) $LiClO_3.3 H_2O$—melts congruently at 8.4° C.

Hydrate (i) was discovered by Berg but he gave to it the formula $(LiClO_3)_3.H_2O$.

Lithium chlorate and lithium chloride form no double salts at the temperatures of investigation.

Lithium chlorate exists in two enantiotropic forms, namely the α and the β forms. The transition, $\alpha \leftrightarrow \beta$, takes place at 99.8° C. and the α form has the lower density. The γ form, proposed by Kraus and Burgess, does not exist either stably or metastably. The X-ray diffraction pattern of β-$LiClO_3$ has been obtained.

The question of the number and nature of the hydrates of lithium chlorate, after passing through the usual period of ill-founded claims, was attacked in a systematic manner by Kraus and Burgess (5) and by Berg (1), in the period 1926 to 1929. Almost all of the experimental data of these researches are in good agreement but the authors differ, in some respects, regarding their interpretation. Kraus and Burgess claim the existence of three anhydrous modifications, of a trihydrate, and of a monohydrate. Berg claims only two anhydrous modifications and three hydrates, viz. a hydrate with $\frac{1}{3}$ mole water per mole of salt, a monohydrate, and a trihydrate. In short, the two investigators differ in that Kraus and Burgess claim the existence of a γ-anhydrous form, between 22° and 44° C., where Berg claims a hydrate with $\frac{1}{3}$ mole water; in other respects they agree.

In order to decide the conflicting interpretation given above, as well as to verify the formulae of all hydrates, we decided to add a third ion to the binary system $LiClO_3$–H_2O, and to investigate the system $LiClO_3$–$LiCl$–H_2O, at various temperatures. Under these circumstances, the Schreinemakers' "wet rest" method determines the composition of all hydrates without ambiguity. In addition, we thought it well to repeat part of the work of Kraus and Burgess and of Berg, on the binary system. We have also made attempts, more or less successful, to obtain X-ray diffraction patterns of the phases in dispute. Finally, we attempted to determine transition temperatures with the dilatometer since this is the most delicate method of determining transition temperatures, but here again we were not entirely successful because of obstinate metastability.

EXPERIMENTAL

Lithium chlorate was prepared by a method which is essentially that of Potilitzin (6) and of Kraus (5), viz. double decomposition between barium chlorate and lithium sulphate, but the final dehydration to anhydrous salt is a modification of our own. The suppliers' analyses, both of lithium sulphate and of barium chlorate, showed that these salts were very pure; as the method of preparation of the anhydrous salt does not permit recrystallization this is a necessity, as is also the use of exact stoichiometric quantities.

A 1 molar solution of barium chlorate was heated to about 85° C., and a 1 molar lithium sulphate solution was added slowly to this with a dropping funnel until equivalence was reached. The precipitated barium sulphate was removed by repeated filtration. To ensure equivalence of lithium and chlorate ions, the resulting solution was titrated with dilute solutions of barium chlorate and lithium sulphate.

The solution was evaporated slowly, the temperature being kept below 85° C., up to an approximate concentration of 50% lithium chlorate. The filtered solution was transferred to a 250 ml. Claissen flask and dehydration was carried out under a reduced pressure of less than 5 mm. mercury, the distillate being absorbed in concentrated sulphuric acid. The temperature was kept below 85° C., since decomposition begins at this temperature in concentrated solutions. The result of this procedure was a solution containing about 90% lithium chlorate.

On the cooling of the solution to room temperature, the salt crystallized; it was placed under vacuum over phosphorus pentoxide. After about a month, the water content had been reduced to about one per cent. To remove the last trace of water, the salt was placed in a vacuum furnace, over phosphorus pentoxide, and kept at a temperature of 80° C. After several months, no further change was found in the melting point of the salt.

None of the textbook methods for the analysis of lithium chlorate is entirely satisfactory, so we worked out the following method: A weighed sample of lithium chlorate is made up to a volume of 250 ml. A 10, 20, or 25 ml. aliquot is transferred to a 250 ml. iodine flask. To this is added 40 ml. concentrated orthophosphoric acid, followed by the addition of about 0.1 gm. sodium carbonate, to exclude air from the flask. Approximately 25 ml. of iodate-free potassium iodide solution (0.2 gm./ml.) is added and the stoppered flask allowed to stand at room temperature for 60 to 70 min. The free iodine is titrated with sodium thiosulphate. Standardization of the method with pure sodium chlorate indicated an accuracy of ±0.4%.

The chloride content of solutions containing appreciable amounts of chloride was determined volumetrically with silver nitrate solution, using an alcoholic solution of sodium dichlorofluoresceinate as indicator (4). For solutions containing less than five per cent chloride the standard gravimetric method was used.

Solubility determinations were made in the usual way. For temperatures below room temperature a cooled and controlled thermostat was used. Temperature control was good to ±0.05° C. throughout this research

Thermal analysis was used only for the ice curve, the binary eutectics, and $\alpha \leftrightarrow \beta$ transition. After a break had occurred on the cooling curve, a sample of the equilibrium mother liquor was removed for analysis. Temperature was measured with an iron–constantan thermocouple and a good potentiometer.

The technique of X-ray diffraction measurements is now standard but, in the case of anhydrous lithium chlorate, measurements were rendered difficult by the very hygroscopic nature of the substance (it is comparable with that of phosphorus pentoxide). A sample of the anhydrous salt was ground to a fine powder and then returned to the vacuum desiccator and redried for several days. Following this, a very fine and thin-walled capillary tube (outside diameter 0.5 mm. and inside diameter 0.3 mm.) was filled with the sample and immediately sealed at both ends. The intensities of the lines were estimated visually. Powder photographs were taken of a sample that had been in a vacuum desiccator at room temperature for seven months and which we therefore considered to be the form stable at room temperature. A quantity of the same substance was then placed in another vacuum desiccator, held at 80° C. for a week, and then photographed: the results obtained were the same as for the unheated sample.

By means of a high temperature X-ray camera, we were able to take X-ray patterns at 115 ± 5° C. We supposed that, at this temperature, the anhydrous lithium chlorate would have transformed to a different allotrope which would exhibit a different pattern. The result was disappointing; as far as could be judged, the pattern was the same as that at room temperature but the weaker lines of the room temperature picture had vanished and the few lines which did appear were quite broad. This is what would be expected if the lattice structure were the same. The atoms of the lattice would have increased thermal vibration at the higher temperature. A sample of the anhydrous lithium chlorate was sent to the National Research Council at Ottawa for further X-ray study. The work was carried out by Dr. L. D. Calvert, who was able to obtain diffraction patterns of the β form up to the melting point of the salt. Dr. Calvert was unable to detect any change in lattice structure corresponding to the change from the β to the α form, but his apparatus was not susceptible of close temperature control. At higher temperatures, however, he was able to evacuate his camera and this reduces the absorption of X rays by the air. The capillaries used in his work had a wall thickness of 0.007 mm.

The dilatometric work was carried out much in the usual manner. The bulb of the dilatometer had a stoppered side-tube to facilitate filling. The dilatometer was filled in a dry-box. About 100 gm. of anhydrous lithium chlorate, which had been dried for five months, was used to fill the bulb to about three-fourths capacity. The indicator liquid was p-xylene which had been dried over sodium for three days. The bulb of the dilatometer was placed in a thermostat whose temperature was constant to ± 0.1° C. The temperature was raised one degree every 24 hr., but in the range 35° to 50° C., where Kraus and Burgess have claimed an allotropic transformation (5), the rate of increase was reduced to 0.5° per 24 hr. No break occurred on the curve of capillary height versus temperature, up to 106° C., with rising temperature. Since it was still

possible that a very slow transition had been overlooked, the temperature was kept at 60° C. for a week but there was still no indication of an $\gamma \rightarrow \beta$ transition. At higher temperatures an $\alpha \rightarrow \beta$ transition occurred and this was reversible. The formation of the α modification from the β modification is accompanied by a marked expansion but the change, in both directions, showed marked hysteresis.

THE SYSTEM LITHIUM CHLORATE – WATER

Since the part of the diagram where ice and solution were in equilibrium was of little interest, this was outlined by the method of thermal analysis. The compositions of the solutions in equilibrium with ice at various temperatures were determined by chemical analysis. With the exception of a few fixed points the rest of the equilibrium diagram was investigated by isothermal solubility determinations. The solubilities covered the range of composition
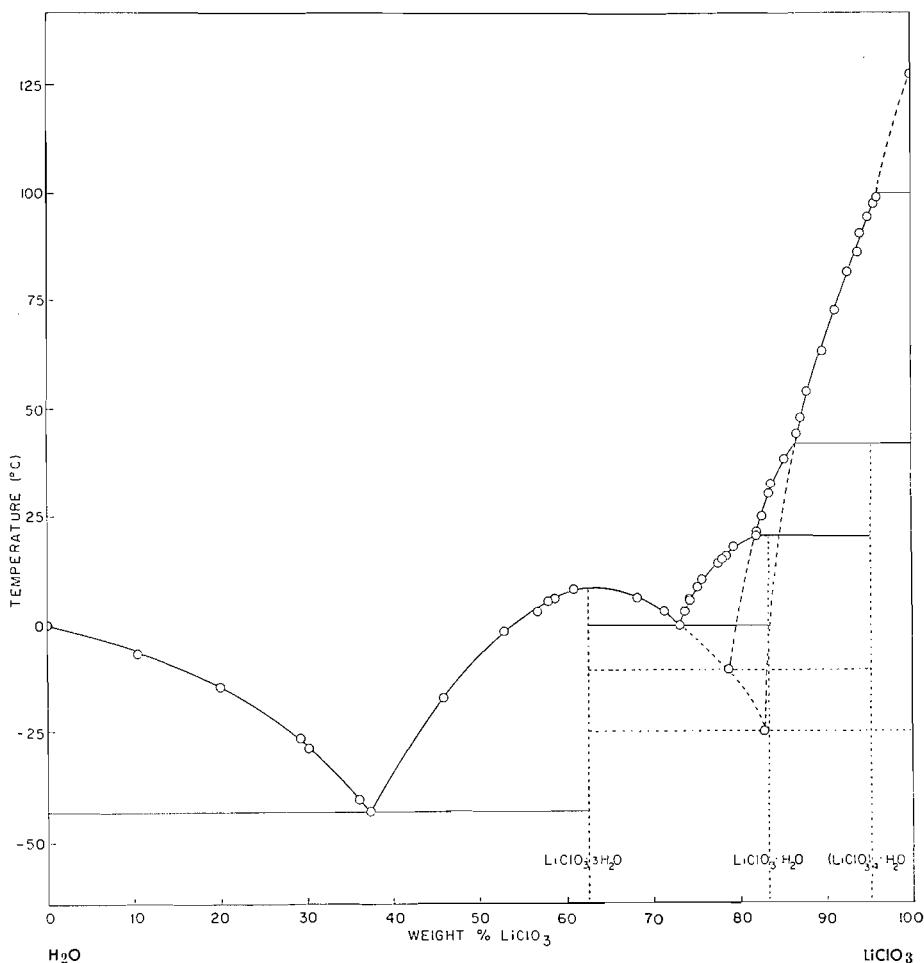

FIG. 1.   System LiClO$_3$–H$_2$O.

from 45.8 to 95.5 weight per cent lithium chlorate. The upper temperature reached was 98.9° C. The determinations were discontinued at this point because the change of solubility per degree rise in temperature had become less than the accuracy of the analysis.

The stable and metastable binary eutectics were determined by thermal analysis in the usual way. The thermal analysis of the anhydrous salt was conducted in an evacuated vessel, with a copper–constantan thermocouple and a Minneapolis–Honeywell recording potentiometer. The temperature was raised slowly to a temperature above the melting point and the melt then allowed to cool slowly. The experiment was repeated many times in the vicinity of 40° C., because of the $\beta \leftrightarrow \gamma$ transition which is said to occur there.

EXPERIMENTAL RESULTS

The solubility relations and the results of thermal analyses are reported in Table I, together with the method used to arrive at them. The equilibrium diagram is shown in Fig. 1. The broken lines indicate solubility curves in the metastable region. A broken vertical line represents the composition of a hydrate. Since the solubility of lithium chlorate in water was not determined at temperatures above 98.9° C., the part of the solubility curve representing α-lithium chlorate in equilibrium with solution from 98.9° C. to 127.5° has been drawn in as a broken line.

TABLE I

THE SYSTEM LiClO₃–H₂O

	Wt. % LiClO₃	Wt. % H₂O	Method	Temperature (° C.)	Nature of the solid phases
1	—	100.0	Thermal analysis	0.0	Ice
2	10.4	89.6	"	− 6.5	"
3	20.0	80.0	"	−14.2	"
4	29.2	70.8	"	−26.2	"
5	30.2	69.8	"	−28.6	"
6	36.0	64.0	"	−40.4	"
7	37.3	62.7	"	−43.3	Ice–LiClO₃.3H₂O (eutectic)
8	45.8	54.2	Solubility	−16.9	LiClO₃.3H₂O
9	52.8	47.2	"	− 1.5	"
10	56.7	43.3	"	3.0	"
11	57.9	42.1	"	5.2	"
12	58.7	41.3	"	6.0	"
13	60.8	39.2	"	8.1	"
14	68.1	31.9	"	6.0	"
15	70.8	29.2	"	3.0	"
16	73.1	26.9	Thermal analysis	− 0.1	LiClO₃.3H₂O–LiClO₃.H₂O (eutectic)
17	73.6	26.4	Solubility	3.0	LiClO₃.H₂O
18	74.2	25.8	"	5.6	"
19	74.1	25.9	"	6.0	"
20	75.1	24.9	"	8.5	"
21	75.7	24.3	"	10.5	"
22	77.5	22.5	"	14.0	"
23	78.0	22.0	"	15.0	"
24	78.5	21.5	"	16.0	"
25	79.3	20.7	"	18.0	"
26	81.9	18.1	"	20.5	LiClO₃.H₂O–(LiClO₃)₄.H₂O (peritectic)

TABLE I (concluded)

	Wt. % LiClO₃	Wt. % H₂O	Method	Temperature (° C.)	Nature of the solid phases
27	82.0	18.0	Solubility	21.5	(LiClO₃)₄.H₂O
28	82.6	17.4	"	25.0	"
29	83.4	16.6	"	30.2	"
30	83.6	16.4	"	32.6	"
31	85.2	14.8	"	38.5	"
32	78.7	21.3	Thermal analysis	−10.5	LiClO₃.3H₂O–(LiClO₃)₄.H₂O (eutectic)
33	82.7	17.3	"	−25.0	LiClO₃.3H₂O–β-LiClO₃ (eutectic)
34	86.7	13.3	Solubility	44.2	β-LiClO₃
35	87.2	12.8	"	47.9	"
36	87.8	12.2	"	54.0	"
37	89.5	10.5	"	63.2	"
38	91.0	9.0	"	72.8	"
39	92.4	7.6	"	81.7	"
40	93.7	6.3	"	86.2	"
41	93.8	6.2	"	90.7	"
42	94.8	5.2	"	94.2	"
43	95.5	4.5	"	97.5	"
44	95.9	4.1	"	98.9	"
45	100.0	0.0	Thermal analysis	127.5	α-LiClO₃

Since Calvert's results for the X-ray diffraction pattern of lithium chlorate at room temperature are in agreement with ours but his are more extensive, we reproduce only Calvert's results, in Table II.

In regard to the dilatometer results, it is sufficient to say that the $\beta \rightarrow \alpha$ transformation took place at 108° and at 106° in two successive cycles with rising temperature, and that the reverse change, $\alpha \rightarrow \beta$, took place at 80° C. and 84.1° C.

The results of the thermal analysis of the anhydrous salt are contained in Table III.

The System Lithium Chlorate – Lithium Chloride – Water

It was found that the time of stirring required for the attainment of equilibrium varies considerably, depending on the nature of the equilibrium solid phase or phases. Because of this uncertainty, equilibrium was always approached from two directions. A mixture of appropriate composition was divided into equal parts and treated as follows. One part was heated until all the solid phase had passed into solution, whereas the other was frozen until all the solution had solidified. These two portions were then stirred in tubes in the thermostat until the compositions of the liquid phases in each portion had become identical. For solutions containing up to 10% lithium chloride, the equilibrium stirring time was found to be from two to three days. When the solutions were more concentrated in lithium chloride, and particularly when the solid phase was the monohydrate or dihydrate of lithium chloride, five or six days were necessary for the attainment of equilibrium.

Solubility isotherms were determined at 3.0°, 6.0°, 8.5°, and 25.0° C., employing the Schreinemakers' method of "wet residues" for the determination of the nature of the equilibrium solid phase.

TABLE II

X-RAY DIFFRACTION PATTERN OF β-LiClO$_3$ (CALVERT)
AT ROOM TEMPERATURE

d (kX)	I	d (kX)	I
3.91	9.5	1.441	4.0
3.79	10.0	1.428	0.4
3.42	9.0	1.416	0.5
2.81	10.0	1.378	1.0
2.71	8.0	1.337	1.4
2.39	3.0	1.331	1.7
2.26	3.4	1.322	0.7
2.13	2.7	1.295	3.0
2.05	0.9	1.255	0.9
1.947	1.1	1.236	1.1
1.879	1.3	1.223	1.0
1.795	0.9	1.213	1.0
1.726	1.1	1.188	1.0
1.665	3.2	1.153	0.9
1.629	1.3	1.140	0.4
1.576	0.9	1.128	0.6
1.549	1.1	1.119	0.8
1.539	1.0	1.078	0.7
1.510	1.1	1.064	0.6
1.500	2.0	1.060	0.9
1.469	0.9	1.040	0.9
1.027	3.5	0.836	1.1
1.025	2.6	0.834	1.0
0.993	1.1	0.831	2.5
0.991	0.9	0.829	2.0
0.985	0.5	0.824	2.1
0.975	0.5	0.822	1.1
0.972	0.5	0.818	1.4
0.969	0.5	0.816	0.4
0.967	0.5	0.812	0.4
0.954	1.6	0.807	0.2
0.933	1.2	0.805	1.7
0.931	1.0	0.803	1.5
0.926	0.2	0.801	1.4
0.923	0.3	0.794	1.6
0.920	0.2	0.792	1.4
0.901	0.8	0.788	1.4
0.898	0.7	0.787	0.6
0.888	0.6	0.784	0.6
0.847	1.0	0.782	2.0
0.844	0.9	0.780	0.5
0.841	0.8	0.774	2.6
0.839	0.6		

TABLE III

THERMAL ANALYSIS OF ANHYDROUS SALT

Rising temperature		Falling temperature	
Transformation	Temperature (° C.)	Transformation	Temperature (° C.)
$\alpha \rightarrow$ Melt	127.4–127.5	Melt $\rightarrow \alpha$	127.4–127.5
$\beta \rightarrow \alpha$	106.1	$\alpha \rightarrow \beta$	98.2
$\beta \rightarrow \alpha$	103.6	$\alpha \rightarrow \beta$	99.8
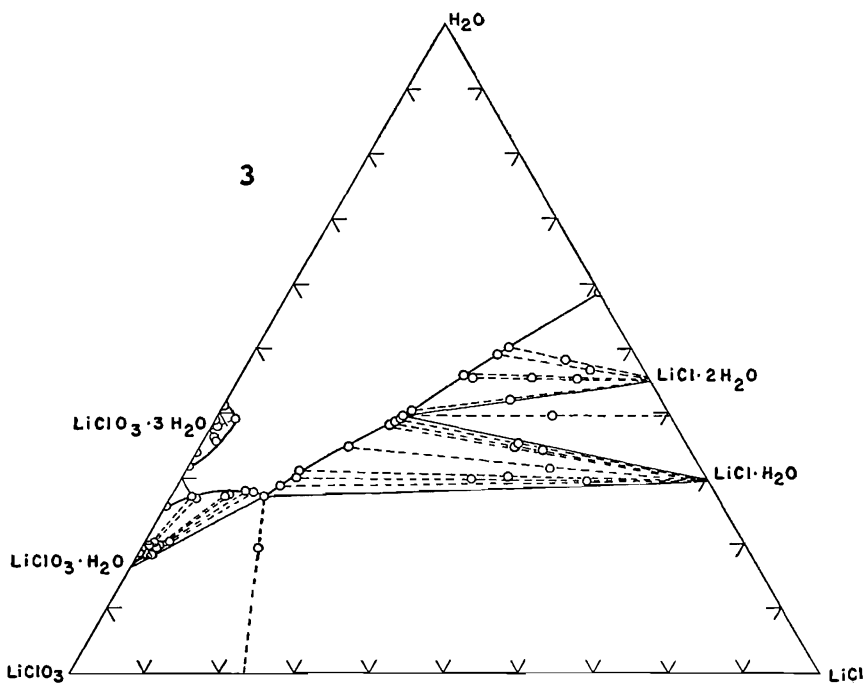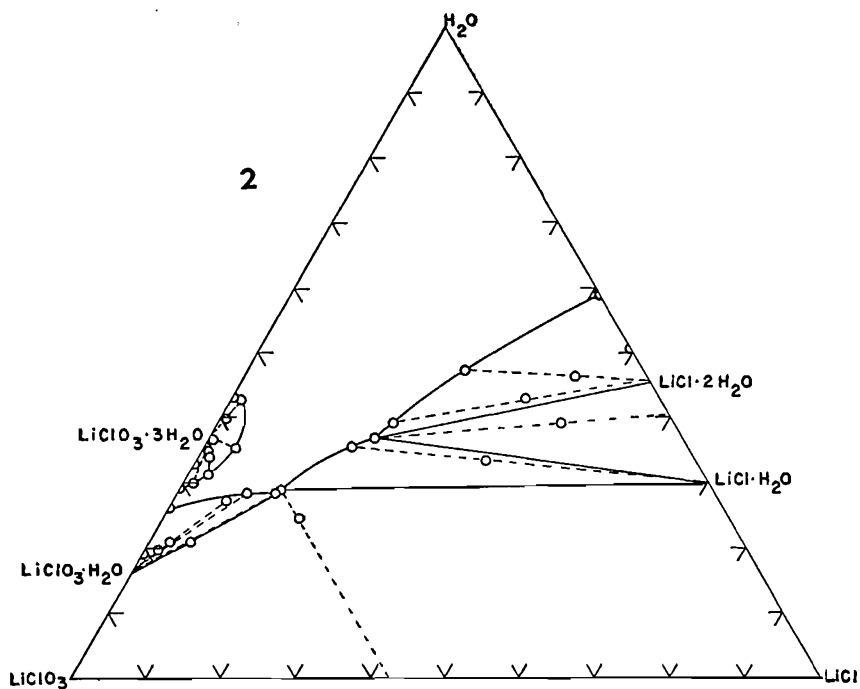
FIG. 2.   System LiClO$_3$–LiCl–H$_2$O at 3.0° C.
FIG. 3.   System LiClO$_3$–LiCl–H$_2$O at 6.0° C.
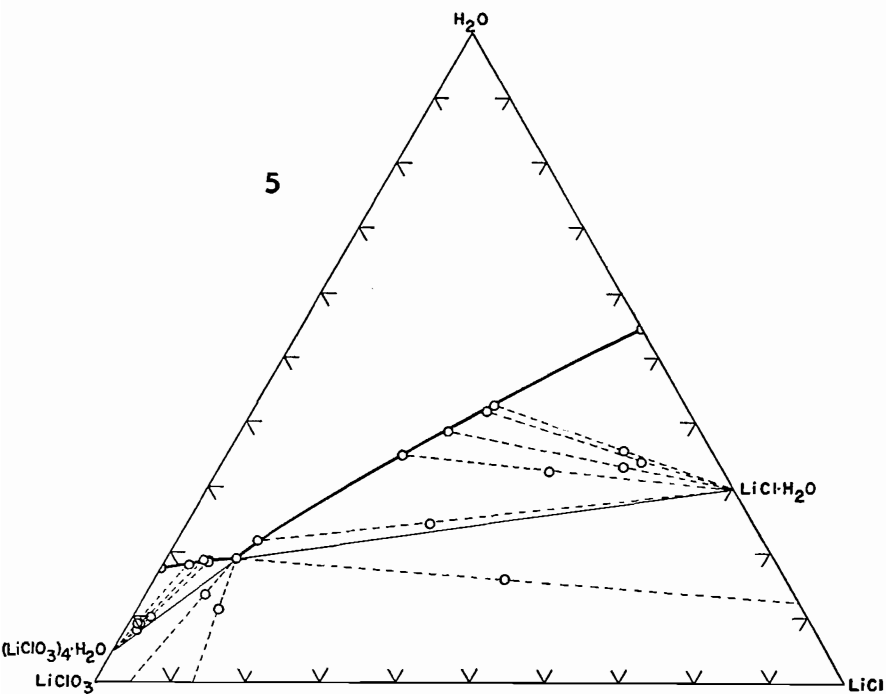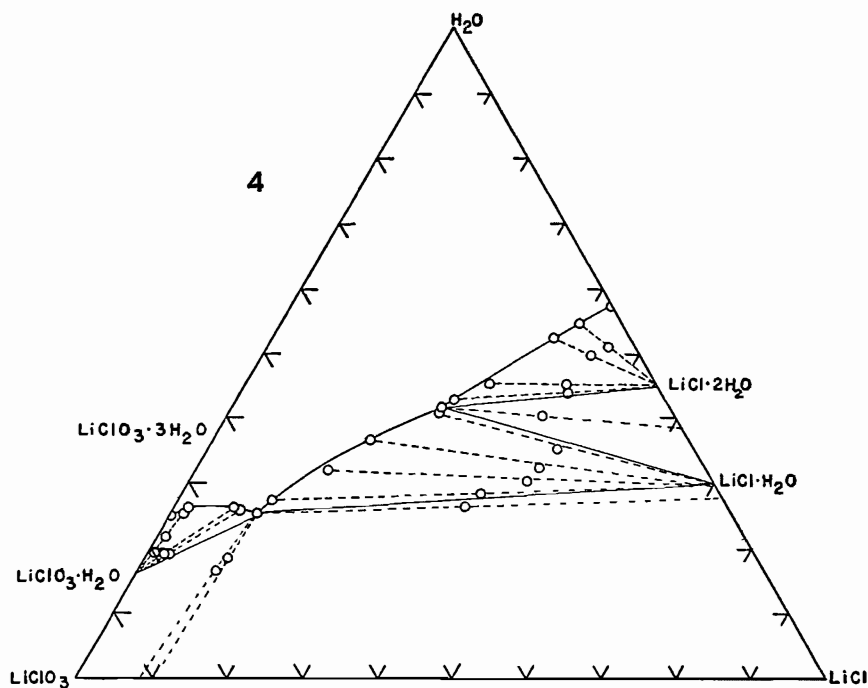
FIG. 4. System $LiClO_3$–$LiCl$–H_2O at 8.5° C.
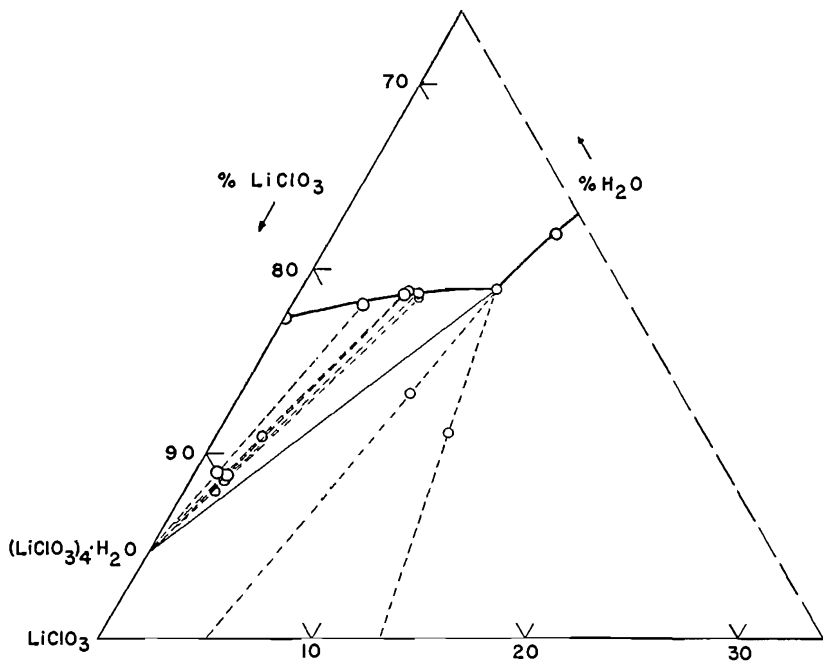FIG. 5. System $LiClO_3$–$LiCl$–H_2O at 25.0° C.

FIG. 6.   Enlarged portion of Fig. 5.

The data for the isothermal ternary studies are given in Tables IV, V, VI, and VII and they are reproduced graphically in Figs. 2, 3, 4, and 5, respectively. Fig. 6 is an enlargement of the lithium chlorate corner of the 25.0° isotherm.

As will be seen later, we believe that the peculiar hydrate which is claimed by Berg (1) to have the formula $(LiClO_3)_3.H_2O$, and which is thought by Kraus and Burgess (5) to be an anhydrous γ form, really has the formula $(LiClO_3)_4.H_2O$. As additional evidence of this, a sample of the wet residue from Expt. 7, Table V, was submitted to microscopic examination. Comparison of these crystals with the photomicrographs of Berg, left no doubt that they represent the same solid phase. A photomicrograph of one of these crystals is reproduced as Fig. 7.

Since, in the ternary system, the stable hydrate of lithium chloride was the dihydrate at temperatures up to and including 8.5° C. and that stable at 25° was the monohydrate, we determined the transition temperature of the reaction

$$LiCl.2H_2O \leftrightarrow LiCl.H_2O + H_2O$$
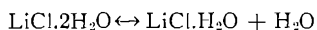
by thermal analysis. We found this temperature to be 12.5°±0.1° C., in agreement with the value of 12.5°, found by Hüttig and Reuscher (3).
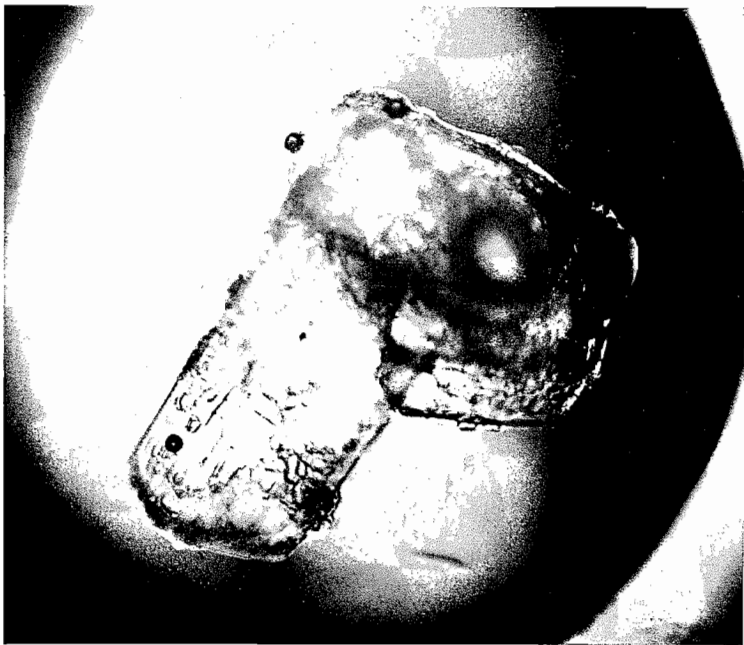
PLATE I

FIG. 7.

RESULTS

TABLE IV

Isotherm for $3.0\pm0.05°$ C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % $LiCl$	Wt. % $LiClO_3$	Wt. % $LiCl$	Nature of the solid phase
1	56.7	—	—	—	$LiClO_3.3H_2O$
2	55.8	1.3	59.4	0.9	"
3	62.2	4.3	62.7	0.7	"
4	66.0	2.8	64.5	1.6	"
5	68.7	1.5	64.1	0.8	"
6	70.8	—	67.0	—	"
7	73.6	—	80.7	—	$LiClO_3.H_2O$
8	65.6	7.1	78.4	1.9	"
9	62.4	9.4	76.2	3.8	"
10	58.5	13.1	73.6	5.6	"
11	57.5	13.7	57.1	18.1	$LiClO_3.H_2O + LiCl.H_2O$
12	44.7	19.9	27.9	38.8	$LiCl.H_2O$
13	40.9	22.1	15.0	46.0	$LiCl.H_2O + LiCl.2H_2O$
14	37.4	23.5	17.8	39.3	$LiCl.2H_2O$
15	23.9	29.1	9.6	44.2	"
16	—	41.0	—	49.3	"

TABLE V

Isotherm for $6.0\pm0.05°$ C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % $LiCl$	Wt. % $LiClO_3$	Wt. % $LiCl$	Nature of the solid phases
1	58.7	—	61.1	—	$LiClO_3.3H_2O$
2	58.3	2.5	61.3	0.8	"
3	62.7	1.8	62.7	1.0	"
4	68.1	—	66.1	—	"
5	74.1	—	81.4	—	$LiClO_3.H_2O$
6	70.0	2.7	79.5	0.9	"
7	69.7	3.4	78.6	1.2	"
8	65.8	7.1	79.9	1.9	"
9	64.9	7.5	78.8	2.0	"
10	62.6	9.6	76.5	3.1	"
11	61.4	10.7	78.0	2.2	"
12	60.4	12.3	65.1	15.6	$LiClO_3.H_2O + LiCl.H_2O$
13	57.5	13.7	16.0	54.3	$LiCl.H_2O$
14	54.8	15.2	31.4	38.9	"
15	53.9	15.0	26.2	43.5	"
16	45.2	20.0	20.0	48.2	"
17	38.2	23.7	23.2	42.0	"
18	37.2	24.0	19.7	46.0	"
19	36.2	24.6	22.2	42.3	$LiCl.H_2O + LiCl.2H_2O$
20	35.7	24.9	16.6	44.8	$LiCl.2H_2O$
21	34.1	25.4	20.0	37.8	"
22	24.4	29.7	15.5	39.0	"
23	23.5	30.0	9.7	45.1	"
24	18.3	32.5	7.1	46.0	"
25	16.3	33.5	7.1	42.0	"
26	—	41.1	—	49.5	"

TABLE VI
ISOTHERM FOR $8.5 \pm 0.05°$ C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phases
1	75.0	—	—	—	$LiClO_3.H_2O$
2	73.4	1.5	77.5	0.9	''
3	72.0	1.9	80.0	0.8	''
4	66.1	7.7	79.0	2.0	''
5	65.6	8.8	78.3	2.5	''
6	64.2	11.2	70.7	11.9	$LiClO_3.H_2O + LiCl.H_2O$
7	63.5	11.2	73.3	11.2	''
8	62.7	11.6	35.1	38.4	''
9	60.5	12.3	31.9	39.7	$LiCl.H_2O$
10	50.8	17.4	24.9	44.9	''
11	31.3	27.7	18.3	46.3	''
12	30.6	27.8	17.8	41.9	$LiCl.H_2O + LiCl.2H_2O$
13	28.2	28.9	12.8	43.4	$LiCl.2H_2O$
14	22.5	32.2	12.2	42.7	''
15	10.4	37.3	6.7	43.7	''
16	5.6	39.7	3.8	45.3	''
17	—	42.7	—	50.3	''

TABLE VII
ISOTHERM FOR $25.0 \pm 0.05°$ C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phases
1	82.6	—	—	—	$(LiClO_3)_4.H_2O$
2	78.7	3.3	90.0	1.0	''
3	76.4	5.0	89.6	1.6	''
4	76.1	5.1	86.9	2.1	''
5	75.7	5.6	89.9	1.5	''
6	75.8	5.7	87.8	2.3	''
7	75.9	5.8	90.7	1.4	''
8	72.3	9.2	78.8	8.0	$(LiClO_3)_4.H_2O + LiCl.H_2O$
9	71.8	9.2	78.1	10.8	''
10	71.6	9.2	37.5	46.7	''
11	67.7	10.7	43.1	32.4	$LiCl.H_2O$
12	41.7	23.3	23.2	44.4	''
13	33.8	27.7	13.0	53.8	''
14	27.0	31.3	10.1	55.7	''
15	25.5	31.7	11.7	52.5	''
16	—	45.5	—	—	''

DISCUSSION OF RESULTS

Apart from a few slight refinements in temperature and composition, the solubility curves in the binary equilibrium diagram, Fig. 1, are essentially the same as those previously obtained by Kraus and Burgess (5) and by Berg (1). In general, the results of previous workers indicate a lower solubility than do our results.

The trihydrate of lithium chlorate melts congruently but the equilibrium curve is very flat and this makes it difficult to read off the exact melting

temperature from the curve. Neither was an attempt to determine the melting point by direct experiment successful, since it is difficult to prepare and maintain the mixture having the exact composition of the trihydrate. We found, experimentally, that the trihydrate exists at 8.1°, while reference to Fig. 4, the 8.5° isotherm, shows that trihydrate is absent. The flat maximum on the equilibrium curve, as well as we could read it, appeared to us to lie at 8.4° C. Kraus and Burgess (5) reported 8.0° and Berg (1) from 8.1 to 8.3°.

The trihydrate participates in four eutectics, two stable ones at −43.3° and −0.1° C. respectively, and two metastable at −10.5° and −25° respectively. The other solid phases at the eutectics are listed in Table I.

The solubility curves of the binary system indicate that two different solid phases are in equilibrium with solution in the temperature ranges −0.1° to 20.5° C. and 20.5° to 42.0°, respectively. The ternary isotherms for 3.0°, 6.0°, 8.5°, and 25.0° show clearly what the phases are. In the lower temperature range, the solid phase is the monohydrate of lithium chlorate, as claimed by Kraus and Burgess and by Berg.

The isothermal ternary study at 25.0° proved to be the most instructive, since it has refuted the claims both of Kraus and Burgess and of Berg. Fig. 6, which is an enlargement of the lithium chlorate corner of the 25° isotherm, shows tie lines running consistently into a composition corresponding to the hydrate $(LiClO_3)_4.H_2O$. Since the existence or non-existence of this hydrate is important, it is well to say a few words about the attainable experimental accuracy in this region. The successful application of the Schreinemakers' method of "wet residues" depends on the accuracy of the chemical analyses employed and on the extent to which mother liquor is removed from the "wet" solid phase. At 25°, we never found more than 11% water in this solid phase; this could hardly be improved upon, since the dry hydrate itself contains 4.7% water. Although the inaccuracy of our chlorate determinations may amount to 0.4%, our gravimetric determinations of chloride were much better than this. In Fig. 6, the tie lines joining the compositions of the liquid phase and the wet residue cross the lithium chlorate reference lines at an angle of about 70°. Hence, if there is an error of 0.4% in the lithium chlorate determination this would lead to an error of about 0.2% lithium chlorate in the composition of the equilibrium solid phase. The consequences of an error in the lithium chloride analysis are far more serious, because the directions of the tie lines and the reference line of lithium chloride approach one another. The fact that none of the tie lines ever crossed, and that they all converged to a single composition when extrapolated, indicates that the analyses were of sufficient accuracy and that equilibrium had been reached in all cases. As a check on the possibility of any consistent error in the procedure, the data were compared with a point which had been determined a month previously. The points all indicated the same solid phase and therefore left no doubt that the hydrate stable at 25° C. has the composition corresponding to the formula $(LiClO_3)_4.H_2O$.

In Fig. 6 there are no experimentally determined solubilities representing solutions containing from 5.8 to 9.16% lithium chloride. In order to prove that

a break did not occur in the solubility curve in this range, the wet residues from the two determinations 7 and 8 were investigated under the polarizing microscope. The solid phase was the same in both cases, although a slight amount of the monohydrate of lithium chloride was present in number 8. Therefore, the invariant solutions 8, 9, and 10 were actually in equilibrium with the one-fourth hydrate of lithium chlorate and the monohydrate of lithium chloride.

The hydrate which Berg claims contains one-third of a mole of water we think contains only one-fourth of a mole of water, but we are referring to the same hydrate. We convinced ourselves of this by comparing our photomicrograph of wet residue 7 with those obtained by Berg of his supposed one-third hydrate. If, therefore, our hydrate contains one-fourth of a mole of water, so does Berg's. Berg deduced the composition of his hydrate by the method of the peritectic halt time and this is far from being a sensitive method. Kraus and Burgess, on the other hand, thought they had eliminated Berg's claim for a hydrate of low water content on the ground that a mixture containing 6.55% water definitely showed the presence of solution between $21.0°$ and $41.5°$ C. If the solid were really the one-third hydrate, which contains 6.2% water, the mixture would not form an observable amount of solution. If, however, the hydrate contains only one-fourth of a mole of water, as we claim, about one-third of the above mixture would liquefy.

At $42.0°$ C., the one-fourth hydrate undergoes a peritectic transition to anhydrous salt and solution. The modification of anhydrous salt formed at $42°$ C. is the first (low temperature) modification of two allotropic forms. This form is the one stable at room temperature and corresponds to the β form of Kraus and Burgess. Of the three methods used to investigate the transition from β to α, viz. thermal analysis, dilatometry, and X-ray diffraction, only the former method gave a really satisfactory result and it indicated that the transition temperature was $99.8°$ C. This value compares favorably with the values obtained by Kraus and Burgess and by Berg. The dilatometer showed a marked increase in volume, accompanying the β to α transition. We have applied the techniques of dilatometry, thermal analysis, solubility, and X-ray diffraction in an attempt to find the supposed β to γ transition, but always without result. The heating and cooling curves of anhydrous salt showed no break and the expansion and contraction of the dilatometer was perfectly regular. Finally, an X-ray diffraction picture was taken of a sample which had never been heated; this was then heated for a week at $80°$ C., allowed to cool, and immediately photographed again. The two patterns were identical.

If the hemihydrate of lithium chlorate claimed by Wächter (8), Troost (7), Potilitzin (6), and Brühl (2) did indeed exist, it would be formed from the monohydrate in a peritectic transformation. This would appear as a break in the solubility curve, in the binary system. No such break occurred between $-0.1°$ and $20.5°$ C. The monohydrate is the solid phase in equilibrium with solution in this temperature interval. Neither was there any break in the solubility curve from $20.5°$ to $42°$ C. In this temperature range, the stable solid phase is the one-fourth hydrate. Therefore, there is no doubt that the

hemihydrate of lithium chlorate does not exist as a stable phase and there have been no indications of its ever appearing as a metastable phase throughout this study.

REFERENCES

1. BERG, L.   Z. anorg. Chem. 155: 311.   1926; 166: 231.   1927; 181: 131.   1929.
2. BRÜHL, H.   Bull. soc. ind. minérale St Étienne, 35: 155.   1912.
3. HÜTTIG, G. F. and REUSCHER, F.   Z. anorg. Chem. 137: 161.   1924.
4. KOLTHOFF, I. M. and SANDELL, E. B.   Quantitative inorganic analysis.   3rd ed.   The MacMillan Co., New York.   1952.   p. 543.
5. KRAUS, C. A. and BURGESS, W. M.   J. Am. Chem. Soc. 49: 1226.   1927.
6. POTILITZIN, A.   J. Russ. Phys. Chem. Soc. 16: 840.   1883.
7. TROOST, L.   Ann. chim. et phys. 51(3): 136.   1857.
8. WÄCHTER, F.   J. prakt. Chem. 30: 322.   1843.