COMPONENTS:	EVALUATOR:
(1) Lithium chlorate; $LiClO_3$; [13543-71-9] (2) Water; H_2O; [7732-18-5]	H. Miyamoto Department of Chemistry Niigata University, Niigata, Japan and M. Salomon US Army ET & DL Fort Monmouth, NJ, USA August, 1984

CRITICAL EVALUATION:

THE BINARY SYSTEM

Data for the solubility of $LiClO_3$ in water have been reported in five publications (1-5). The data of Mylius and Funk (1) and Treadwell and Ammann (4) can immediately be rejected because of their inconsistencies (low solubilities indicating failure to approach equilibrium), and the fact that many experimental details are absent. Although Mylius and Funk (1) suggest that the anhydrous salt is the solid phase, the value for the solubility is much too low for the experimental temperature of 291 K. Treadwell and Ammann (4) do not report the nature of the solid phases.

The remaining studies (2,3,5) all report complete phase diagrams which qualitatively appear to be in good agreement, but detailed examination of the solubility data show significant differences. All authors agree that the binary system has a tendency to form metastable solutions which probably contributes to the causes in some important differences in solubility data.

Based on the analyses of the three major works (2,3,5), the evaluators agree with Campbell and Griffiths (5) that the various solid phases present in the binary system are:

ice

$LiClO_3.3H_2O$ [66295-75-8]

$LiClO_3.H_2O$

$LiClO_3.1/4H_2O$

β-$LiClO_3$

α-$LiClO_3$

All three major studies agree, in general, on the temperature ranges over which six solid phases exist, but disagreement exists on the composition of several of these phases. Over the temperature range of 262-317 K, Berg (3) claims the solid phase to be $LiClO_3.1/3H_2O$, Kraus and Burgess (2) claim it to be an anhydrous γ-$LiClO_3$, and Campbell and Griffiths (5) have shown it to be $LiClO_3.1/4H_2O$.

In their attempts to determine transition temperatures over the temperature range 262-317 K, Campbell and Griffiths experienced difficulty with metastability. Very careful dilatometric measurements over the range of 308-323 K (5) revealed no transition at 314.7 K which is the temperature claimed by Kraus and Burgess (2) for the γ-$LiClO_3$ β-$LiClO_3$ transition. X-ray diffraction patterns of anhydrous $LiClO_3$ prepared at room temperature and after heating to 353 K showed no change in the X-ray patterns (5). Campbell and Griffiths also found that Berg's photomicrographs of the so-called 1/3-hydrate were identical to the solid phase determined to be (see below) $LiClO_3.1/4H_2O$ (5). The stoichiometry of the 1/4-hydrate was unambiguously proved in (5) by studying the ternary $LiClO_3$ - $LiCl$ - H_2O system. By application of the wet residue method of Schreinemakers, Campbell and Griffiths found that the tie lines (none of which ever crossed) were very reproducible and converged to a single composition of $(LiClO_3)_4H_2O$. The evaluators therefore conclude that the stable solid phase over the temperature range of 293-315 K is the 1/4-hydrate, and that Berg's 1/3-hydrate and Kraus and Burgess' anhydrous γ-$LiClO_3$ are in fact the 1/4-hydrate.

To evaluate the solubility data from (2,3,5), we separately examined each polytherm in the phase diagram, and fitted the data to the smoothing equation (see eq. [1] in the PREFACE)

$$Y_x = A/(T/K) + B\ln(T/K) + C + D(T/K) \qquad [1]$$

where

$$Y_x = \ln\left\{\chi^{v(1-\chi)r}(v+r)^{v+r}/[r^r(1+\chi)^{v+r}]\right\} \qquad [2]$$

COMPONENTS:

(1) Lithium chloride; $LiClO_3$; [13543-71-9]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION:

In eq. [2], r is the hydration number in the solid phase, v is the number of ions produced upon disolution (v = 2 for $LiClO_3$), and χ is the mole fraction solubility (note that for the ice polytherm, v = 0 and r = 1). In general, when applying the solubility data from (2,3,5) to eqs. [1] and [2], a number of solubilities were rejected when the difference in calculated and observed solubilities ($\chi_{calcd} - \chi_{obsd}$) exceeded $2\sigma_x$. σ_x is the standard error of estimate defined in the usual manner by:

$$\sigma_x = [\Sigma(\chi_{obsd} - \chi_{calcd})^2/(N - NC)]^{\frac{1}{2}} \qquad [3]$$

where N is the number of data points, and NC is the number of constants adjusted in eq. [1]. For all the polytherms in the binary $LiClO_3 - H_2O$ system, a four constant fit was used: i.e. NC = 4. The results of fitting the data to eq. [1] are given in Table 1, and additional details are given below. The results of these analyses were used to construct detailed graphs of portions of the polytherms in the regions of phase transitions. From these graphs the evaluators were able to determine the nine observable transition temperatures by graphical interpolation, and the results are given in Table 2. Details on the evaluation of the solubility data for each polytherm follow.

Polytherm For Ice As The Solid Phase

All 16 data points reported in (2) and (5) were used to adjust the constants in the smoothing equation (see Table 1). Mole fraction solubilities at rounded temperatures based on this analysis are designated as *recommended* values, and are listed in Table 3. Based on our graphical interpolation, we find the recommended temperature and solubility at the ice ⟶ $LiClO_3.3H_2O$ transition to be 230.55 K and 0.107, respectively. Both Kraus and Burgess (2) and Berg (3) reported this temperature as 233.2 K, and Campbell and Griffiths (5) reported it as 229.85 K.

Polytherm For $LiClO_3.3H_2O$ As The Solid Phase

Since the polytherm reaches a maximum at the congruent melting point (cmp), we analyzed this system in two parts for $\chi < 0.25$ and for $\chi > 0.25$.

(a) $\chi < 0.25$. Twenty data points from (2) and (5) were fitted to eq. [1]. Only one data point at 281.3 K (8.1°C) from (5) was omitted. The least squares fit to eq. [1] predicts a congruent melting point of 281.16 K.

(b) $\chi > 0.25$. All data points from (2) and (5) were considered, and all four points below 264.2 K were rejected. The resulting fit of 19 data points is given in Table 1, and the congruent melting point as calculated from eq. [1] is 281.12 K.

The solubility at the average cmp of 281.14 K is thus 0.25 mole fraction or 18.503 mol kg^{-1}. Berg (3) reported a cmp of 281.3 K, Kraus and Burgess (2) 281.2 K, and Campbell and Griffiths (5) reported 281.3 K (melting point) and 281.6 K (graphical).

Two metastable transitions involving the trihydrate were found in all three major studies. For the $LiClO_3.3H_2O$ ⟶ $LiClO_3.1/4$ transition (eutectic), the evaluators graphically determined the temperature to be 261.15 K compared to 264 K in (3) and 262.7 K in (5).

For the metastable $LiClO_3.3H_2O$ ⟶ β-$LiClO_3$ eutectic transition, a temperature of 248.5 K was found by the evaluators which is the same value reported in all three major studies (2,3,5).

All calculated solubilities based on the smoothing equation are designated as *recommended*, and values at rounded temperatures are given in Table 3.

COMPONENTS:

(1) Lithium chlorate; $LiClO_3$; [13543-71-9]

(2) Water; H_2O; [7732-18-5]

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CRITICAL EVALUATION:

Polytherm For $LiClO_3.H_2O$ As The Solid Phase.

While there is qualitative agreement between the results in (2,3,5), quantitative agreement does not exist and we are forced to select a preferred set of data. Since Berg's data, particularly at the lower temperatures, are radically different from those in (2,5) we can safely reject these results. We cannot offer convincing evidence favoring either set of data from (2) or (5), and at this time we prefer to use Campbell and Griffiths' results. The smoothed data based on (5) are given in Table 4, and are designated as *tentative* solubilities.

The evaluators have calculated a congruent melting point of 310.5 K at $\chi = 0.500$ (m = 55.508 mol kg^{-1}), but it should be noted that a melting point for $LiClO_3.H_2O$ has not been measured and that it may not melt congruently.

By graphical interpolation the evaluators find the $LiClO_3.H_2O \longrightarrow LiClO_3.1/4H_2O$ transition temperature to be 292.85 K. This transition temperature was reported as 294.2 K, 295.2 K, and 293.65 K in (2,3,5), respectively.

Polytherm For $LiClO_3.1/4H_2O$ As The Solid Phase

The confusion of the composition of this hydrate was discussed above. Summarizing, the evaluators agree with Campbell and Griffiths who accurately and unambiguously determined the composition as the 1/4-hydrate, and that both the γ-$LiClO_3$ phase of Kraus and Burgess and the 1/3-hydrate of Berg are in fact the same phase deduced by Campbell and Griffiths as the 1/4-hydrate.

The 1/4-hydrate easily forms metastable solutions as indicated above and from the fact that its solubility can be experimentally determined down to 261 K. In fitting the solubility data to eq. [1], again Berg's results had to be rejected, and two data points at 305.2 K and 300.8 K (32°C and 27.6°C) from Kraus and Burgess also had to be rejected. The results of fitting the remaining 24 data points to eq. [1] are given in Table 1, and smoothed solubilities designated as *tentative* values are given in Table 4. The smoothed values could not be designated as recommended because the agreement in experimental data from (2) and (5) is not particularly satisfactory as indicated by the large standard errors of estimate (σ values) in Table 1.

By graphical interpolation the evaluators found the 1/4-hydrate $\longrightarrow$ β-$LiClO_3$ transition at 314.85 K. For this transition Berg reported a temperature of 317 K, Kraus and Burgess reported this (eutectic) temperature as 314.7 K, and according to Campbell and Griffiths, this is a peritectic transition occurring at 315.15 K.

Polytherms For Anhydrous $LiClO_3$

The three major studies (2,3,5) all agree that two anhydrous phases (β & α) exist, the latter constituting the higher temperature phase.

β-$LiClO_3$. Forty-three data points reported in (2,3,5) were fitted to eq. [1] and the results are given in Table 1. The β-phase is stable over the range of 314.9-368.5 K (evaluators, see Table 2), but metastable solutions easily form at temperatures as low as 248 K. Because of the large standard errors of estimate obtained for this fit (see Table 1), the solubilities at rounded temperatures given in Table 4 are designated as *tentative* values.

α-$LiClO_3$. Of the 25 data points reported in (2,3), two points from (2) at 102.5°C and 126.7°C had to be rejected. The only data point above 372.1 K reported in (5) was the melting point of 400.6-400.7 K for α-$LiClO_3$, and the value of 400.7 K was used in the least squares fit to eq. [1]. Based on this analysis (Table 1), solubilities at rounded temperatures were calculated and tabulated in Table 4: these solubilities are designated as *recommended* values.

COMPONENTS:	EVALUATOR:
(1) Lithium chlorate; $LiClO_3$; [13543-71-9] (2) Water; H_2O; [7732-18-5]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan Mark Salomon US Army ET & DL Fort Monmouth, NJ, USA August, 1984

CRITICAL EVALUATION:

The temperature of the $\beta \longrightarrow \alpha$ transition has proved somewhat difficult to determine. Direct thermal analyses showed marked hysteresis with transition temperatures ranging from 383 K (rising temp) to 353 K (falling temp), and a best value of 373.0 K was indicated from the falling temperature side (5). Both Berg (3) and Kraus and Burgess (2) report a value of 382 K for this transition. By graphical interpolation the evaluators determined this transition temperature as 368.45 K at a solubility of $\chi = 0.778$. The least squares fit of the data to eq. [1] predicts a melting point of 400.72 K.

The complete phase diagram for the binary system given by Campbell and Griffiths is reproduced below following the data tables.

TERNARY SYSTEMS

The only system reported is that by Campbell and Griffiths (5) for the system $LiClO_3$ - $LiCl$ - H_2O, and for temperatures of 276.0 K, 279.0 K, 281.7 K, and 298.2 K. Some discussion was presented above with emphasis on the confirmation of the 1/4-hydrate solid phase by Schreinemakers' method of wet residues. The four isotherms reported in (5) are reproduced below following the data tables for the binary $LiClO_3$ - H_2O system.

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5. Campbell, A. N.; Griffiths, J. E. *Can. J. Chem.* 1956, *34*, 1647.

COMPONENTS:
(1) Lithium chlorate; $LiClO_3$; [13543-71-9]
(2) Water; H_2O; [7732-18-5]

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CRITICAL EVALUATION:

Table 1. Constants for the smoothing equation[a]

Solid Phase	N	A	B	C	D	σ_y	σ_x
1. ICE	16	-20714.80 (1.32)	-174.9468 (0.00096)	955.5416 (0.0053)	0.372531 (2.1×10^{-5})	0.0051	0.0025
2. $LiClO_3.3H_2O$ (χ < 0.25)	20	29321.07 (2.96)	229.4229 (0.0021)	-1275.480 (0.012)	-0.435711 (4.6×10^{-5})	0.011	0.0030
3. $LiClO_3.3H_2O$ (χ > 0.25)	19	-33115.58 (1.4)	-235.5517 (0.00094)	1324.4436 (0.0053)	0.432482 (1.9×10^{-5})	0.0051	0.0028
4. $LiClO_3.H_2O$	11	208261.78 (0.69)	1454.3290 (0.00043)	-8229.9610 (0.0024)	-2.531326 (8.5×10^{-6})	0.0022	0.0026
5. $LiClO_3.1/4H_2O$	24	63591.78 (7.17)	426.1955 (0.0095)	-2431.857 (0.026)	-0.704569 (9.1×10^{-5})	0.025	0.010
6. β-$LiClO_3$	43	-15101.43 (7.94)	-105.9926 (0.0042)	597.709 (0.024)	0.188232 (7.5×10^{-5})	0.024	0.012
7. α-$LiClO_3$	23	-24948.55 (3.28)	-170.9093 (0.0014)	972.7758 (0.0085)	0.283458 (2.2×10^{-5})	0.0082	0.0068

[a] N is the number of data points fitted to the smoothing equation
σ_y is the standard error of estimate in the function Y (see eq [2])
σ_x is the standard error of estimate for the mole fraction solubilities (see eq [3])

COMPONENTS:	EVALUATOR:
(1) Lithium chlorate; $LiClO_3$; [13543-71-9] (2) Water; H_2O; [7732-18-5]	H. Miyamoto Department of Chemistry Niigata University Niigata, Japan and Mark Salomon US Army ET & DL Fort Monmouth, N.J. USA August, 1984

CRITICAL EVALUATION:

Table 2. Monovariant Equilibria in the Binary System Recommended Transition Temperatures and Solubilities[a]

Transition	T/K	Mole Fraction
ice → $LiClO_3.3H_2O$	230.55	0.107
$LiClO_3.3H_2O$ melt pt[b]	281.14	0.250
$LiClO_3.3H_2O$ → $LiClO_3.H_2O$	271.05	0.350
$LiClO_3.H_2O$ → $LiClO_3.1/4H_2O$	292.85	0.457
$LiClO_3.3H_2O$ → $LiClO_3.1/4H_2O$[m]	261.15	0.406
$LiClO_3.3H_2O$ → β-$LiClO_3$[m]	248.15	0.473
$LiClO_3.1/4H_2O$ → β-$LiClO_3$	314.85	0.558
β-$LiClO_3$ → α-$LiClO_3$	368.45	0.778
α-$LiClO_3$ → melt	400.72[c]	1.000

[a] Results of graphical interpolation by the evaluators except as noted.

[b] Congruent melting point average value obtained from smoothing equation (see discussion in text).

[c] From least squares fit to eq. [1].

[m] metastable points.

COMPONENTS:

(1) Lithium chlorate; $LiClO_3$; [13543-71-9]

(2) Water; H_2O; [7732-18-5]

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CRITICAL EVALUATION:

Table 3. Recommended Solubilities Calculated From the Smoothing Equation (See Table 1)

T/K	ice polytherm mole fraction soly	$LiClO_3.3H_2O$ $\chi \le 0.250$	$LiClO_3.3H_2O$ $\chi \ge 0.250$
228.15	0.1103	0.1036[m]	
233.15	0.1019	0.1071	
238.15	0.0940	0.1119	0.5043[m]
243.15	0.0859	0.1178	0.4797[m]
248.15	0.0769	0.1250	0.4562[m]
253.15	0.0662	0.1334	0.4335[m]
258.15	0.0533	0.1433	0.4111[m]
263.15	0.0377	0.1550	0.3884[m]
268.15	0.0190	0.1688	0.3644[m]
270.65	0.00826	0.1769	0.3513[m]
272.15	0.00140	0.1822	0.3429
273.15		0.1861	0.3371
278.15		0.2104	0.3014
280.15		0.2269	0.2787
281.14[a]		0.2500	0.2500

[a] Average temperatures: range ± 0.02 K (see text for discussion).

[m] Metastable equilibria

COMPONENTS:

(1) Lithium chlorate; $LiClO_3$; [13543-71-9]

(2) Water; H_2O; [7732-18-5]

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CRITICAL EVALUATION:

Table 4. Solubilities at Rounded Temperatures Calculated From Eq. [1] (See Table 1)

T/K	$LiClO_3.H_2O^a$	$LiClO_3.1/4H_2O^a$	β-$LiClO_3{}^a$	α-$LiClO_3{}^b$
248.15			0.473^m	
258.15			0.492^m	
263.15		0.403^m	0.499^m	
273.15	0.352	0.403^m	0.511^m	
278.15	0.362	0.412^m	0.515^m	
283.15	0.382	0.424^m	0.520^m	
288.15	0.413	0.439^m	0.524^m	
293.15	0.462^m	0.457	0.529^m	
298.15		0.478	0.534^m	
303.15		0.501	0.540^m	
308.15		0.525	0.546^m	
313.15		0.549	0.554^m	
323.15			0.573	
328.15			0.585	
338.15			0.614	
348.15			0.653	
358.15			0.706	
368.15			0.776	0.777^m
373.15				0.793
378.15				0.814
383.15				0.841
388.15				0.874
393.15				0.917
398.15				0.969
400.72				1.000

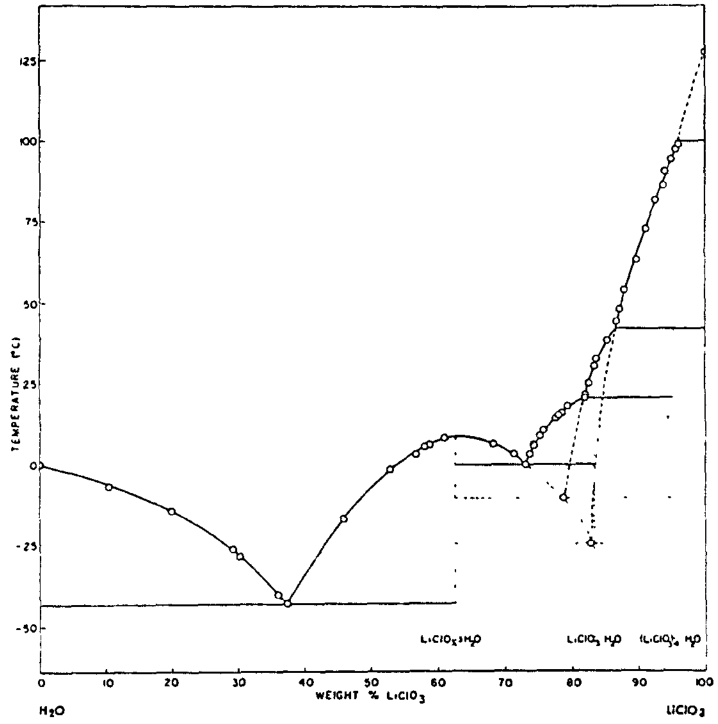
[a] Tentative

[b] Recommended

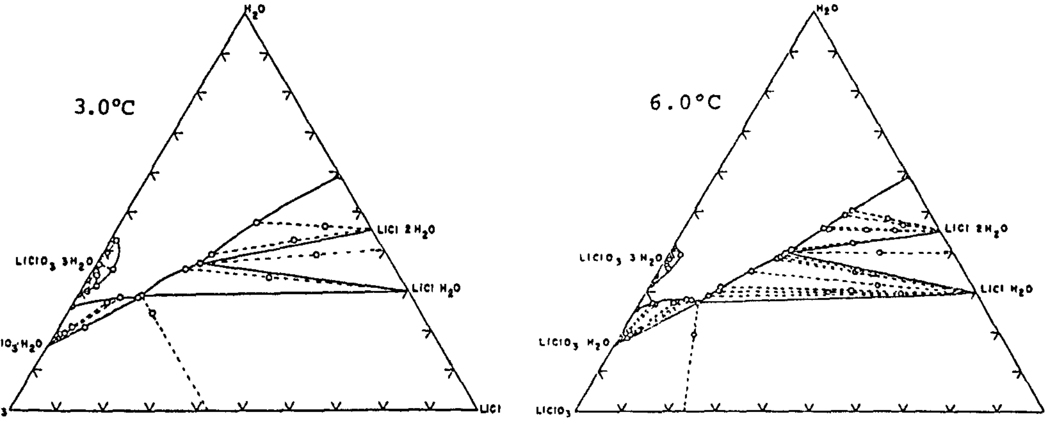
COMPONENTS: (1) Lithium chlorate; $LiClO_3$; [13543-71-9] (2) Water; H_2O; [7732-18-5]	EVALUATOR: Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan August 1984

CRITICAL EVALUATION:

Phase Diagram for the $LiClO_3$ - H_2O System (5)



Phase Diagrams for the $LiClO_3$ - LiCl - H_2O System (5)



COMPONENTS:

(1) Lithium chlorate; $LiClO_3$; [13453-71-9]

(2) Wtaer, H_2O; [7732-18-5]

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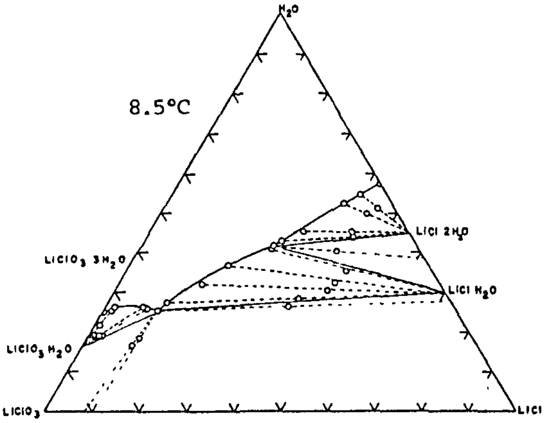
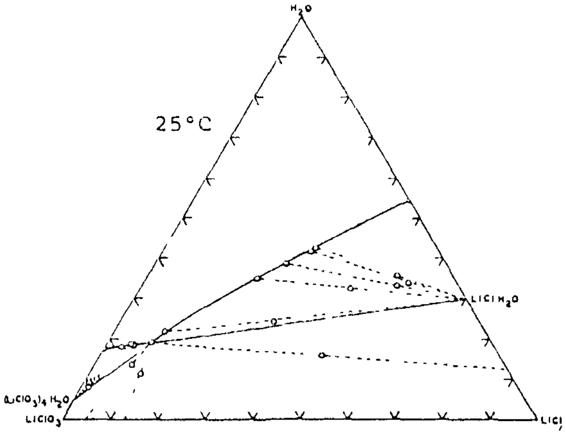
August 1984

CRITICAL EVALUATION:

Phase Diagrams for the $LiClO_3$ - LiCl - H_2O System, continued (5)





Detail of 25°C isotherm