THE TERNARY SYSTEM LITHIUM

CHLORATE - LITHIUM

CHLORIDE - WATER

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By

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To the memory

of my Father

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ABSTRACT

The phase diagram of the system lithium chlorate - water was determined. The phase diagrams of the system lithium chlorate - lithium chloride - water at 3.0, 6.0, 8.5 and 25.0°C. were determined.

Lithium chlorate forms three hydrates having the following formulae :

    (i) $(LiClO_3)_4 \cdot H_2O$ - stable from 20.5 to 42.0°C.

    (ii) $LiClO_3 \cdot H_2O$ - stable from -0.1 to 20.5°C.

    (iii) $LiClO_3 \cdot 3H_2O$ - melts at 8.4°C.

The hydrate having the formula $(LiClO_3)_3 \cdot H_2O$, proposed by Berg, was shown to have the formula $(LiClO_3)_4 \cdot H_2O$. The transition temperature of the transformation

$$LiCl \cdot 2H_2O \rightleftharpoons LiCl \cdot H_2O + solution$$
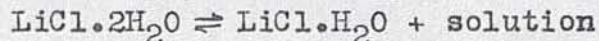
was found to be 12.5 ± 0.1°C. confirming the results of Hüttig and Reuscher. Lithium chlorate and lithium chloride do not form any double salts at 3.0, 6.0, 8.5, or at 25.0°C.

Lithium chlorate can exist in two enantiotropic forms, α and β, and the transformation, $\alpha \rightleftharpoons \beta$, takes place at 99.8°C., the α form having the lower density. The γ form, proposed by Kraus and Burgess, does not exist as a stable or metastable form. The X-ray diffraction pattern of β $LiClO_3$ was obtained and a method for obtaining the diffraction pattern of α $LiClO_3$ was proposed. A crystal structure of $LiClO_3 \cdot 3H_2O$ was also proposed.

A modification of the standard iodometric analysis of (XO_3) was developed and successfully applied to lithium chlorate, where (X) is any halogen.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Up to the present time, the natures of the hydrates
and anhydrous modifications of lithium chlorate have been
somewhat controversial. There have been reported in the
literature a trihydrate, a monohydrate, a hemihydrate and
a one-third hydrate as well as three allotropic modifica-
tions of the anhydrous salt. Several of these reports were
based on unsound experimental techniques as well as on
analytical methods that were not very accurate.

Much of the earlier work involved the preparation
of the salt followed by a chemical analysis to determine
the composition of the prepared sample. A crystallographic
study indicated that three enantiotropic allotropes of the
anhydrous salt and a hemihydrate were capable of stable
existence. The analysis used in this latter study was not
sufficiently accurate to make any such claim. As an added
complication, the anhydrous salt as well as the hydrates
were extremely hygroscopic, which would render some of the
conclusions, based on the weighing of various samples, invalid.

In the period from 1926 to 1929, Kraus and Burgess
(17), and Berg (3,4,5,) published some excellent work on
the phase relations of the binary system lithium chlorate
and water. Almost all of the experimental data in these
works compared quite favourably with each other but their
respective interpretations differed slightly. Kraus and

Burgess reported the existence of three anhydrous modifi-
cations of the anhydrous salt as well as a trihydrate and a
monohydrate. Berg, however, reported only two anhydrous
modifications and three hydrates containing one-third,
one, and three molecules of water per molecule of lithium
chlorate. The conclusions, therefore, were the same,
except that Kraus and Burgess claimed the existence of a gamma
anhydrous form whereas Berg claimed a one-third hydrate
existed in the temperature interval from $22^{o}C$. to $44^{o}C$.

It was apparent that a definite uncertainty still
existed concerning the nature of the hydrates and anhydrous
modifications of lithium chlorate, even though a substantial
amount of work had been carried out on the subject. The
object of the present work, therefore, was to remove all
uncertainty involved in the composition of the hydrates of
lithium chlorate as well as to investigate the supposed
allotropic modifications of the anhydrous salt.

The determination of the complete binary phase
diagram by thermal analysis and isothermal solubility
measurements seemed advisable. This study would not deter-
mine accurately the composition of the hydrates, but it
would indicate the temperature interval in which they were
stable. It would also indicate the temperature intervals
in which the allotropic forms of the anhydrous salt were

stable. The temperature at which a phase change took place would appear as a break in the solubility curves in the phase diagram, provided that the change took place with the formation of another phase. In the case where a compound melts, the solubility curve exhibits a smooth maximum and the composition of the compound would correspond to the maximum on the curve.

To determine the composition of the hydrates, it was decided to carry out several isothermal ternary investigations of the system lithium chlorate - lithium chloride - water at appropriate temperatures by the Schreinemaker method of "wet residues" (23). This method was capable of higher accuracy in the determination of the composition of incongruently melting binary compounds than direct chemical analysis because of the difficulty of obtaining a sample without occluded mother liquor. Since each allotropic form of a compound has a characteristic crystal structure, an attempt to obtain an X-ray diffraction pattern of each form was carried out. To determine the transition temperatures of the anhydrous forms, the method of thermal analysis and the dilatometer method were used. The dilatometer was selected because its accuracy is limited only by the relative amounts of salt and indicator liquid and by the diameter of the capillary used. Therefore, if the ratio of anhydrous salt to indicator liquid was made sufficiently

large, and the bore of the capillary fine enough, the slightest change in lattice dimensions between two allotropic modifications could be detected.

The experimental methods mentioned above are all proven techniques in problems of this type, and therefore, should be capable of removing the uncertainty which exists in the literature on the system lithium chlorate and water.

THEORETICAL DISCUSSION

(a) The Phase Rule

In heterogeneous systems all states and changes
of equilibrium can be described qualitatively by the use
of Gibbs' Phase Rule and Le Chatelier's Theorem. Gibbs'
deduction of the Phase Rule (12) is quite complicated, and
many alternative methods are now found. Any good text on
thermodynamics will have some method suggested. All,
however, give the Phase Rule in the following form:

$$F = C - P + 2$$

where F = number of degrees of freedom.

  C = number of components.

  P = number of Phases.

A comprehensive treatment of the applications and limitations
of the Phase Rule is given by Findlay, Campbell and Smith (9).

(b) Types of Systems

Since the results of this research are based to
a large extent on the graphical expression of the phase rule
in terms of two types of systems, these are considered
briefly here.

(i) Binary systems, or systems of two components,
when they exist in one phase would constitute a tervariant
system, in which pressure, temperature and concentration
must be known to completly define the system. When the
system is under atmospheric pressure, the pressure is

constant and the system becomes bivariant. Then, two phases could exist in stable equilibrium. Binary systems are usually represented on a plane diagram with temperature as ordinate and concentration as abscissa, the pressure being constant. The graphical expression is known as a temperature-concentration curve, or a t - x diagram.

Binary systems are usually classified according to the phases present in order to give a better means of discussion of the equilibria concerned.

(ii) Ternary Systems, or systems of three components, by application of the phase rule require the simultaneous presence of five phases for invariance. Representation of these systems graphically is somewhat difficult. Most methods use a solid figure with temperature as one axis. The development of methods was followed by Findlay (10), and while several of those he mentions are still used, the most common is the triangular diagram developed by Roozeboom (22). It consists of an equilateral triangle with reference lines ruled parallel to each side. The sides are divided into 100 parts, and the same scale is used for the binary systems on the side of the triangle. The co-ordinates of a ternary point are then measured parallel to the sides.

There are many types of ternary systems, but none will be discussed here since this study was an isothermal one, and hence simple in conception.

(c) Isothermal Curves

In three component systems, the solubility
relationships at constant temperature show clearly the
conditions of formation and stable existence of binary
compounds in the presence of three components, as well
as the existence of any ternary compounds.

Several graphical methods can be employed for the
representation of the isothermal solubilities in a ternary
system. Three of these are discussed by Findlay (11), one
of which is the triangular diagram mentioned above. This
undoubtedly is the most useful in this research because the
compositions of the solid phases saturating the solutions
become apparent. In all cases, the "tie-line" which
joins the composition of the liquid phase and the solid
phase will indicate, in the direction liquid to solid, what
solid component or compound is saturating the liquid. Since
it is impossible to separate completely the mother liquor
from the solid phase, the tie-line will have to be extra-
polated to give the actual composition of the solid phase.

(d) Methods of Determining the Equilibrium Curve

For determining the equilibrium curve of binary
and ternary systems many methods may be employed. The
most common are isothermal solubility measurements, and
thermal analysis. In the case of the isothermal solubility

method, it is necessary to analyse the liquid and solid
phases in order to arrive at the composition of the liquid
and solid phases. The liquid phase analyses will give the
curve of solubility. The method used to determine the compo-
sition of the solid phases, in a three component system, is
due originally to Schreinemakers (23) but was developed further
by Bancroft (1,2). Since it is important in this research,
it will be explained briefly here.

Consider that we are dealing with an aqueous
solution of two salts having a common ion (a three component
system) which does not form any double salts. Representing
the solubility relations in a system of triangular
co-ordinates, we would obtain an isotherm _acb_ (Fig.1).
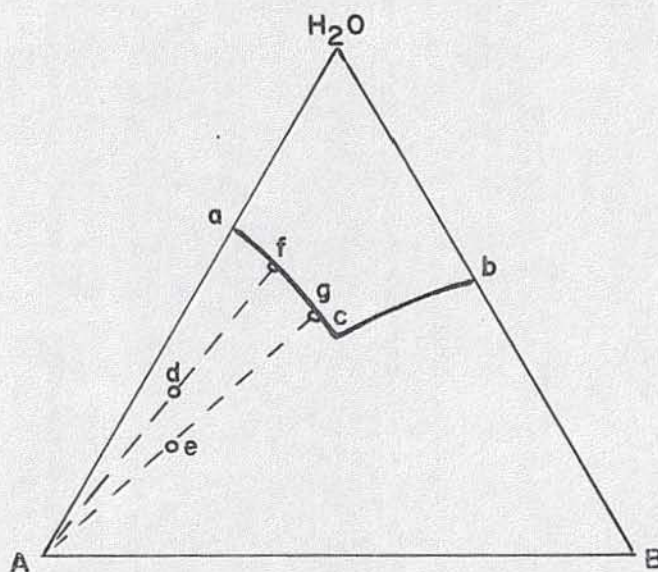
Figure 1. A Typical Isotherm

In Fig.1, <u>a</u> represents the solubility of salt A
in water, <u>b</u> the solubility of salt B, and <u>c</u> represents the
solution in equilibrium with pure A and B.

Consider, then, that pure A is in equilibrium
with a solution, at the temperature of this isotherm,
having the composition of point (f). The bulk of the
solution is separated from the solid phase, and the latter,
together with any adhering mother liquor, is analysed. The
composition of this wet residue will correspond to the point
<u>d</u> on the line (fA), where A represents the composition of
pure A. Similarly, the analysis of a solution of different
composition in equilibrium with A, will lead to the points
(e) and (g) and hence the line (gA). The method of finding
the composition of an unknown binary compound reduces to
finding the position of two lines such as (fd) and (ge).
The point where these lines intersect represents the
composition of the solid compound saturating the solution.
In the case where the solid phase is a hydrate of A or B the
lines will intersect at a point on the A - H_2O or B - H_2O
side of the triangle.

In certain cases, the graphical solution may not
be sufficiently accurate to determine the composition of the
equilibrium solid phase. Since the tie-lines intersect at
the composition of the solid phase, an analytical solution
to the problem can be used. By the geometry of Fig.1, for

each of the two tie-lines the change in per cent A will be
directly proportional to the change in per cent B. Let the
compositions of (f) and (g) be given h%A, k%B and r%A and
s%B respectively, and let the compositions of (d) and (e)
be given by h'%A, k'%B and r'%A, s'%B respectively. Also
let the point of intersection of the tie-lines be given by
x%a and y%B. For (df), therefore,

$$\frac{h' - h}{k' - k} = \frac{x - h}{y - k}$$

and for (eg)

$$\frac{r' - r}{s' - s} = \frac{x - r}{y - s}$$

Solving these two simultaneous equations for x and y will
give the composition of the equilibrium solid phase. If
the equilibrium solid phase is known to be anhydrous or to
be one of the binary hydrates, this information is equiva-
lent to knowing the position of one of the tie-lines, so
that only one tie-line must be determined experimentally,
and only one equation in one unknown need be solved. In
practice, however, it is better to have more than the
minimum number of tie-lines.

Since the method of thermal analysis was used
extensively by Kraus and Burgess (17), and Berg (5), in
their work on the binary system lithium chlorate - water,
a discussion of the method and its practical limitations

will be given here. The principle on which the method of thermal analysis is based is the fact that a phase change normally takes place with the evolution of heat with falling temperature and the absorption of heat when the phase change takes place with rising temperature.

When a pure substance is cooled and no change in state occurs, a graph of its temperature against time will be exponential and continuous, when the surroundings are maintained at constant temperature in accordance with Newton's law of cooling. If, however, a change of state occurs, then the curve will show a "break" at the temperature at which the change began to take place. When this change involves the crystallization of a pure component from its melt, the curve will be horizontal until complete crystallization has taken place, provided that the rate of crystallization is fast in comparison to the rate of cooling.

A different form of the curve results when the substance being cooled is a liquid mixture of two components which are completely miscible in the liquid state and form no compounds or solid solutions in the solid state. This mixture will cool until primary separation of one solid component occurs. Since a solution does not freeze at one temperature, the curve will exhibit a change in slope at the temperature of primary separation. Cooling will proceed at a lower rate until an invariant temperature is reached, where

the temperature remains constant until complete solidifi-
cation of the solution takes place.

A typical cooling curve representing the above
process is shown in Fig. (2) where ab represents cooling of
the solution, b is the temperature of primary separation,
cd represents the crystallization of a solution having the
eutectic composition and de represents further cooling of
the solid mixture.
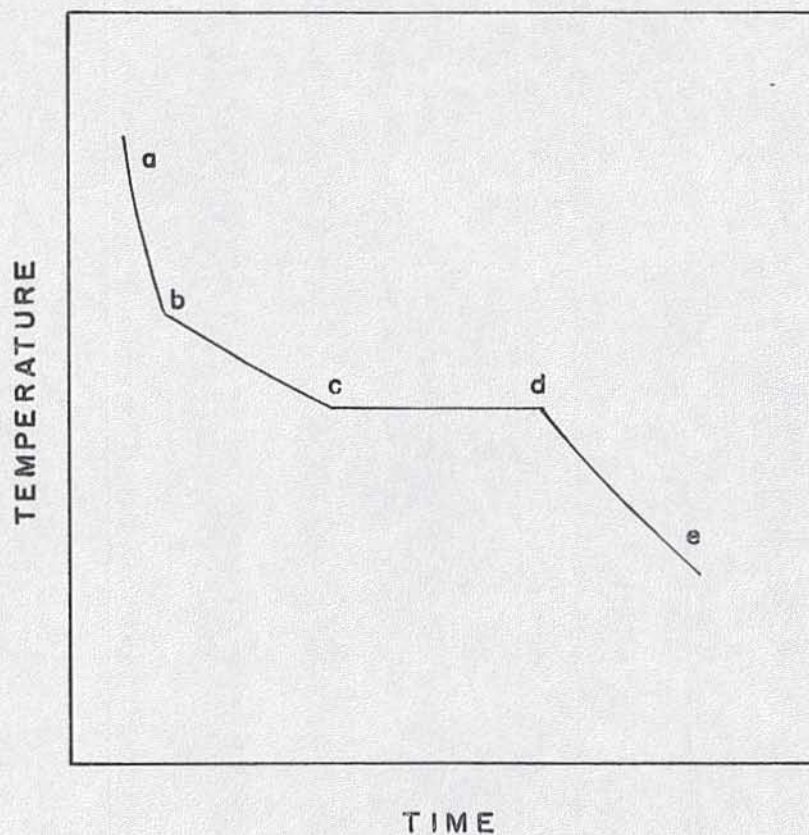
Figure 2. A Typical Cooling Curve

For a particular weight of mixture, the length of <u>bc</u> will be inversely proportional to the excess of either component over the eutectic composition. Therefore, the length of <u>bc</u> will increase as the composition of the liquid mixture approaches the eutectic composition and will be a maximum for a mixture having the eutectic composition.

In more complex systems such as when congruently and incongruently melting compounds are formed, this method is applicable to the determination of their respective compositions. In all cases, the cooling curve gives the temperature at which primary separation takes place, and if a sample of the solution at this temperature is analysed, the solubility of the separating component in the second component is also obtained. The eutectic temperature can also be obtained if cooling is carried out to a low enough temperature. When incongruently melting compounds are formed, there will be a peritectic halt for mixtures having a composition richer in the higher melting component than that of the peritectic solution. In a binary system, an incongruently melting compound decomposes to form another solid phase and a liquid at a temperature below the congruent melting point of the compound. The composition of the liquid is different from that of the compound and the point at which this transition takes place is called an incongruent melting point or a peritectic point. Therefore,

the peritectic halt time is the time required for this
type of transition to be completed.

To determine the composition of any incongruently
or congruently melting compounds, the peritectic halt times
or the eutectic halt times respectively are plotted against
composition. The peritectic halt time will be a maximum and
the eutectic halt time will be zero at the composition of
any incongruently melting compounds . In the case of congru-
ently melting compounds the halt time will be zero at the
composition of the compound and for the pure components.
The above principle is represented in Fig.3. The above
mentioned method is due to Tammann (24), but it is not used
extensively now because of the many sources of error in
determining the halt times accurately. Errors in this measure-
ment often, as in the case of $LiClO_3$ investigated by Berg (5),
give misleading results. The triangular curves obtained in
this way are often referred to as Tammann triangles.
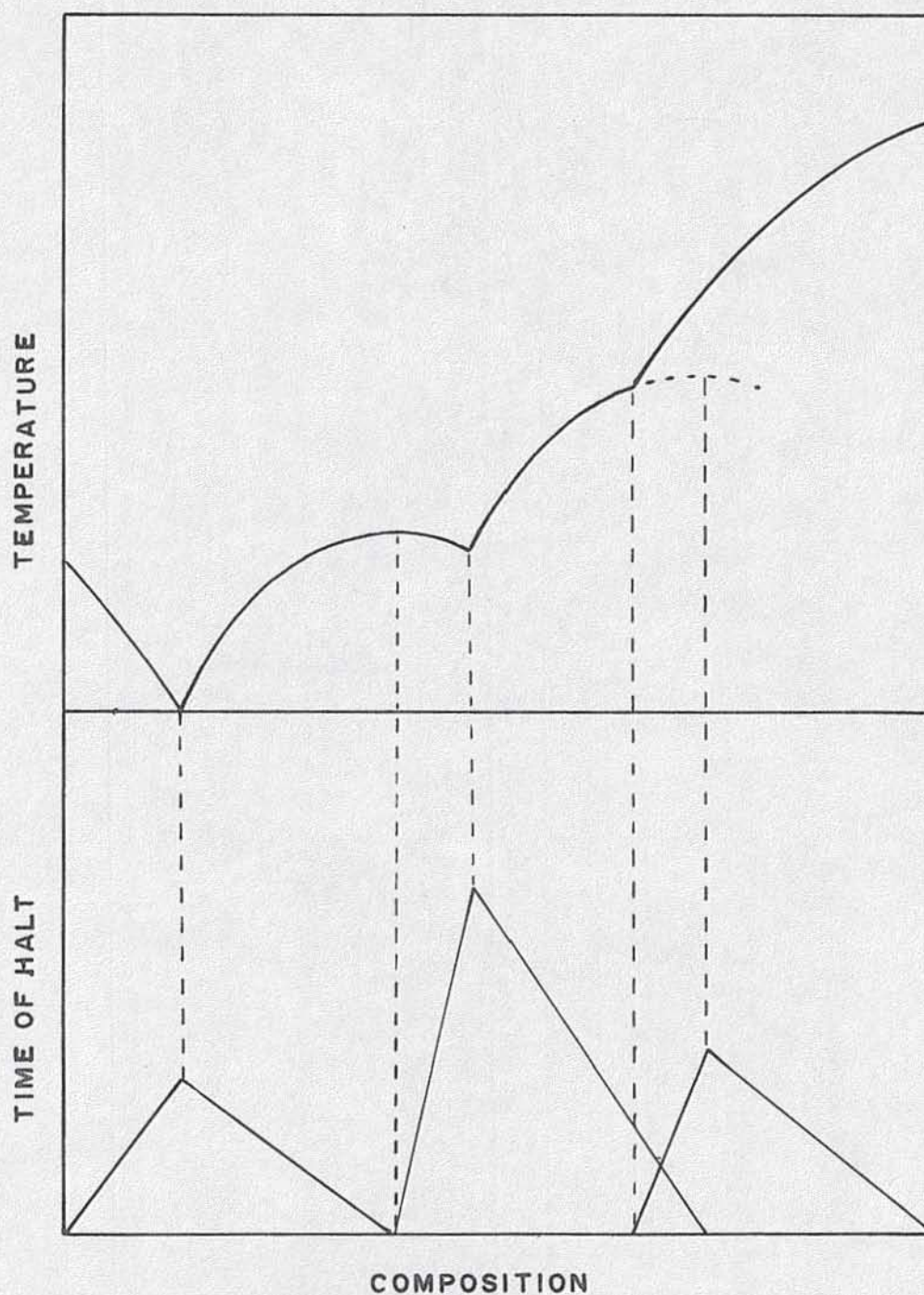
Figure 3. Determination of the Composition of Compounds
by Eutectic and Peritectic Halt Times

REVIEW OF LITERATURE

Lithium Chlorate

This salt appears to have been first prepared
in 1843 by Wächter (26) by the action of chloric acid on
lithium carbonate. It crystallizes as long rhombic needles
and, according to Wächter, has the composition of a hemi-
hydrate, $LiClO_3.\frac{1}{2}H_2O$. Troost (25), who prepared the salt
in 1857, agreed on the composition of the hydrate and stated
that it melted at $50^{\circ}C$. and decomposed at $100^{\circ}C$. He claimed,
however, that the hydrate crystallized as regular tetrahedrons
or octahedrons. In 1883, Potilitzin (20), prepared the salt
by treating barium chlorate with lithium sulphate. This
method was particularly suitable because the barium
sulphate formed could be readily separated leaving a solution
of lithium chlorate. On evaporating this solution, he
was able to obtain the anhydrous salt which melted at
$124^{\circ}C$. and the hemihydrate which melted at $50^{\circ}C$. and lost
water at $90^{\circ}C$. He claimed, however, that if the evapora-
tion was carried out at too high a temperature, then
decomposition would occur to a slight extent giving rise
to a product that contained lithium chloride as an impurity.
In 1887 Mylius and Funk (19) determined its solubility in
water; they found that no hydrate existed. They reported
that at $18^{\circ}C$. a saturated aqueous solution contained 75.8
per cent lithium chlorate. Retgers (21), in 1890, also

reported that no hydrate was found. In 1912 Mlle. Brühl (7) investigated the salt by crystallographic methods and reported three allotropic modifications of the anhydrous form A, B, and C, and a hemihydrate D. She prepared the salt by the method of Potilitzin, removing impurities with alcohol in which lithium chlorate is soluble. The alcoholic solution proved to be explosive when hot, thereby making it necessary to evaporate the alcohol at $50^{\circ}C$. She then crystallized the strong aqueous solution in a dessicator over sulfuric acid or phosphorus pentoxide. To determine the composition of the hydrate, several samples were weighed and placed in a vacuum dessicator over phosphorus pentoxide at $100^{\circ}C$. for one day. Weighing back the samples and averaging the results, she found a composition corresponding to the hemihydrate. This method, however, is open to criticism.

It is shown in the present work, that the dehydration time of one day is far too short for complete removal of the water of hydration. The salt obtained in this way could quite conceivably be a mixture of anhydrous salt and occluded solution, or one of anhydrous salt and some undesignated higher hydrate each in such proportions that it would indicate the presence of a hemihydrate. Therefore, if a hydrate does indeed exist, it must have a higher degree of hydration than the hemihydrate.

TABLE I

Temperature ($^{\circ}C$)	Remarks
125 – 127.5	Melting Point of A
63 – 65	Melting Point of D
105	Stable form is A
72	Stable form is B
28 – 60	Stable form is C
22	Stable form is D

L. Berg, in a series of two papers (3,4), took up the investigation of the hydrates of lithium chlorate. He prepared the salt and made up mixtures corresponding in composition to that of the one-third hydrate, the hemihydrate, and integral hydrates containing one, two, three and five molecules of water respectively. On cooling these mixtures, he found that crystals separated from those having the composition of the one-third, the mono and the trihydrate. He was unable, however, to find any evidence in support of the existence of the hemihydrate. As a check on the composition of the crystals which had separated, he subjected them to analysis and confirmed his observations.

The method of analysis, used by Berg, involved the action of sulfuric acid on the sample, and evaporation to

To investigate the optical properties of the anhydrous and hydrated forms, Mlle. Brühl used a polarizing microscope and coated the very hydroscopic lithium chlorate with an oil to prevent the taking up of water from the air. Her results are listed below.

A - Very birefringent, uniaxial negative and most often found in spherolites, either dextro or laevo about the optical axis.

B - Spherolites are produced with contraction. Optically negative with weak birefringence. There is an angle of about 90° between axes.

C - Small losange shaped crystals. Very birefringent, quasiternary and optically negative.

D - Less birefringent than C. Gives polarization colours. Very different from C, because of numerous hemitropic lamellae that can be formed by compression of the crystals.

In addition to the optical properties, she also reported the melting points and temperature ranges in which the various forms are stable. These are listed in Table I.

dryness. The residue was weighed as lithium sulphate.
He claimed an accuracy of better than ± 0.2 per cent.

The results obtained by Berg on the transition
temperatures and melting points of the various hydrates,
together with the transformations occuring at these
temperatures, are listed in Table II.

TABLE II

Hydrate	Temperature(^{O}C)	Transformation
$LiClO_3 \cdot 3H_2O$	8.1	$LiClO_3 \cdot 3H_2O \rightarrow$ Melt
$LiClO_3 \cdot H_2O$	22.0	$LiClO_3 \cdot H_2O \rightarrow (LiClO_3)_3 \cdot H_2O +$ sol'n.
$(LiClO_3)_3 \cdot H_2O$	44.0	$(LiClO_3)_3 \cdot H_2O \rightarrow LiClO_3 +$ sol'n.

In 1927, Kraus and Burgess (17) claimed the existence
of three anhydrous modifications, α, β and γ, and two hydrates
containing one and three molecules of water respectively.
These conclusions were based on thermal analysis and
solubility measurements. In Table III are given the ten
invariant points which were observed, together with the concen-
tration of the solutions in weight per cent of salt, the
temperature, and the nature of the transformation. The trans-
formations in parentheses were in the metastable region. The
graphical representation of their data is shown in Figure 4.

TABLE III

Phases	% LiClO$_3$	Temp.	Transformation
α - LiClO$_3$ - Melt	100.0	127.6°C.	Fusion
β - LiClO$_3$ - α LiClO$_3$ - sol'n	94.9	99.0	Peritectic
γ - LiClO$_3$ - β LiClO$_3$ - sol'n	86.6	41.5	Peritectic
γ - LiClO$_3$ - LiClO$_3 \cdot$H$_2$O - sol'n	81.2	21.0	Peritectic
β - LiClO$_3$ - LiClO$_3 \cdot$3H$_2$O - sol'n	81.0	-25.0	(Eutectic)
γ - LiClO$_3$ - LiClO$_3 \cdot$3H$_2$O - sol'n	75.7	- 9.0	(Eutectic)
LiClO$_3 \cdot$3H$_2$O - LiClO$_3 \cdot$H$_2$O - sol'n	71.1	1.5	Eutectic
LiClO$_3 \cdot$3H$_2$O - Melt	62.6	8.0	Fusion
LiClO$_3$3H$_2$O - Ice - sol'n	37.0	-40.0	Eutectic
Ice - Water	00.0	0.0	Fusion

They determined the solubility of the salt by
noting the temperature at which the solid phase of a
mixture disappeared in the solution. Therefore, any
break appearing in the solubility curves indicated a change
in the solid phase at that temperature. One such break
was observed at 99°C. and this was checked by thermal analysis.
This technique was not too successful because the trans-
formation was always a suspended one. The transition was

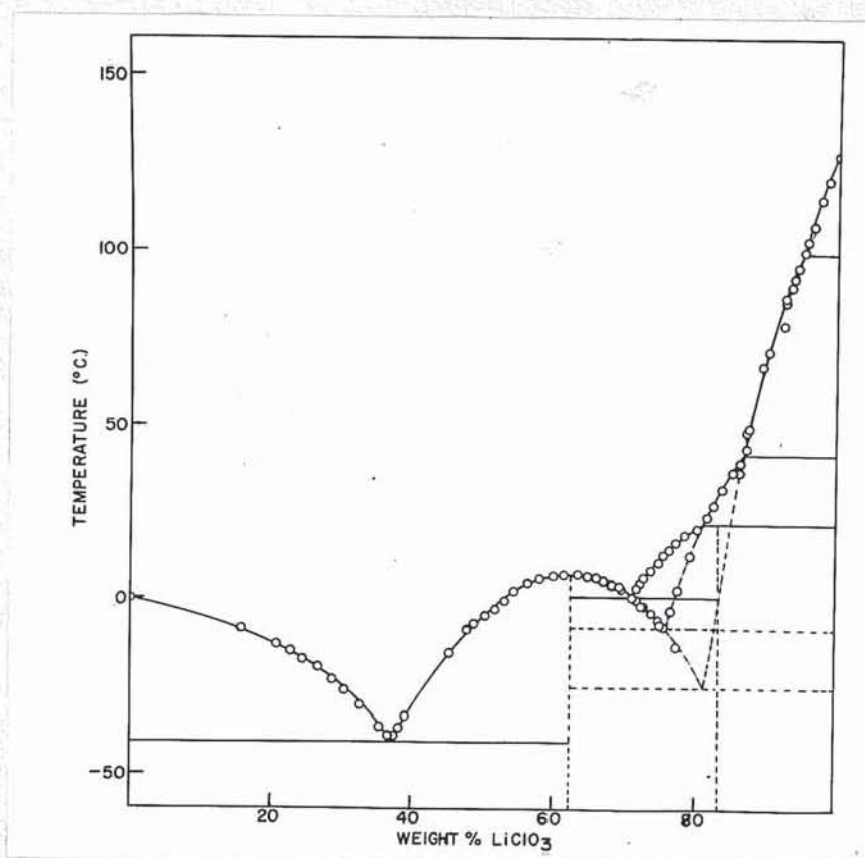observed to be reversible, and to lie between 93°C. and 100°C.

Figure 4. The System: Lithium Chlorate — Water,

by Kraus and Burgess

A third modification, $\gamma LiClO_3$, was also claimed
to exist as a stable phase, although Berg (3,4) had
published fairly conclusive experimental evidence that the
solid phase was actually a one-third hydrate. Kraus and
Burgess, however, ruled out the possibility of this proposed

hydrate by claiming that a mixture which contained 6.55 per cent water showed the presence of solution between the temperatures of 21.0 and 41.5°C. The one-third hydrate would contain by calculation, 6.19 per cent water; therefore, if it were the solid phase, it would not supply enough solution to be observable in this temperature range. In addition, they claimed a $\gamma \longrightarrow \beta$ transition, but only in the presence of a solution of the salt and water. They were unable to obtain the transformation in either direction with the pure salt. This, they claimed, was positive evidence for the existence of the γ form.

To show that the mono-hydrate actually contained one molecule of salt per molecule of water, they cooled mixtures containing less than 16.6 per cent water, which is the composition of $LiClO_3 \cdot H_2O$, to below 21.0°C. and observed that no solution was present. The trihydrate, from the shape of the phase diagram, requires no further comment.

In 1929 Berg (5) took up the problem again, utilizing the same experimental methods, solubility and thermal analysis, that Kraus and Burgess had used. His phase diagram was essentially the same as that of Kraus and Burgess, but the conclusions reached were the same as in his previous works.

He was not able to detect any phase transformation of the type $\gamma \rightarrow \beta$ with the anhydrous salt in the temperature

region of $41.5^{\circ}C$. When water was added, however, he obtained
a definite halt by thermal analysis at $43.5^{\circ}C$. to $44.5^{\circ}C$.
Several thermal analyses were carried out on samples of the
salt containing progressively larger amounts of water,
whereby he was able to obtain a Tammann triangle which
indicated the presence of the one-third hydrate. He further
argued that if the gamma form were actually real, it would
be impossible for the gamma and beta forms to exist together
except at the transition temperature. He prepared samples
of the beta form, the one-third hydrate, and a mixture of
the two, and let them remain at a temperature less than
$44^{\circ}C$. and greater than $22^{\circ}C$. for some time. Later, he
obtained photomicrographs of these samples and showed that
the beta form and the one-third hydrate indeed could exist
together. Therefore, the species stable between $22^{\circ}C$. and
$44^{\circ}C$. was $(LiClO_3)_3 \cdot H_2O$ and not the gamma form. His work
on the rest of the system agreed with that of Kraus and
Burgess.

Lithium Chloride

In this research, lithium chloride appears only
as the monohydrate and the dihydrate. The temperature at
which the dihydrate decomposes to form the monohydrate with
the loss of a molecule of water was reported by Bogorodsky (13)
to be $21.5^{\circ}C$. Hüttig and Reuscher (13), however, reported
that this transition took place at $12.5^{\circ}C$.

MATERIALS AND ANALYSIS

(a) <u>Preparation and Purification of Lithium Chlorate</u>

The salt was prepared by a method which was
essentially that of Potilitzin (20) and Kraus (17), in which
barium chlorate was treated with lithium sulphate. Because
of the difficulty in removing impurities, it was necessary
to use materials as pure as possible.

Barium chlorate was obtained from the British Drug
Houses limited, and was used without further purification.
A solution of the salt did not show any trace of chloride
when tested with a solution of silver chlorate. The lithium
sulphate was obtained from the Fischer Scientific Company,
and also was used without further purification. The analyses
of these chemicals are listed in Tables IV and V.

A one molar solution of barium chlorate was heated
to about 85°C., and a one 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, keeping the
temperature below 80°C., up to an approximate concentration

TABLE IV

Impurities in Barium Chlorate

Chloride(Cl) ---- 0.002%
Alkalis --------- 0.3 %

TABLE V

Impurities in Lithium Sulphate

Acidity (H_2SO_4) ---------None
Alkalinity (Li_2CO_3) ----0.029%
Ammonia (NH_3) ------------0.001
Chloride (Cl) ------------0.000
Heavy Metals (Pb) -------0.0005
Insoluble Matter --------0.000
Nitrate (NO_3) -----------0.000
Iron (Fe) ---------------0.0005
Magnesium ---------------0.001
Other Alkalis -----------0.5
Phosphate (PO_4) ---------0.000

of 50 per cent lithium chlorate. To remove all traces of dust and barium sulphate, the solution was filtered twice through a sintered glass filter funnel of medium porosity. The filtered solution was transferred to a 250 mls. Claissen flask, and dehydration was carried out under a reduced pressure of less than 5 mms. of mercury, taking up the distillate in concentrated sulphuric acid. Care was taken to keep the temperature below 85°C. since decomposition began to take place at this temperature when the solution became very concentrated. By this procedure it was possible to obtain a product containing about 90 per cent lithium chlorate, the rest being water.

On cooling to room temperature, the salt crystallized quite rapidly, and was placed under a vacuum over phosphorus pentoxide. After about a month, the water content had been reduced to about one per cent. To remove the last traces of water, the salt was rapidly pulverized to a fine powder and was transferred to a special apparatus which had been built for the purpose. It consisted of two cylindrical glass tubes, each being 25 cms. long and having a diameter of 4 cms., joined by a stopcock. Each could be opened by means of a ground glass joint located near the end of each tube. The tube that contained the lithium chlorate was closed off at one end, whereas the one containing the phosphorus pentoxide had small tubular openings at both ends. The lithium chlorate tube was maintained at a temperature of

about 80°C. and the whole system evacuated. After several
months, no further change was found in the melting point
of the salt.

(b) Analysis of Lithium Chlorate

Several methods, reported in the literature and
in standard textbooks of analysis, were attempted and shown
to be unsatisfactory. These methods gave non-reproducible
analyses and results indicating incomplete reduction of the
chlorate. Finally, the following procedure was adopted.
A weighed sample of lithium chlorate was taken and diluted
to a volume of 250 mls. A ten, twenty, or twenty-five mls.
aliquot was placed in a 250 mls. iodine flask. To this
was added 40 mls. of concentrated ortho-phosphoric acid
(0.11 per cent impurities), followed by the addition of about
0.1 grams of sodium carbonate to exclude air from the flask.
Then, approximately 25 mls. of iodate free potassium iodide
solution (0.2 gms./ml.) was added, and the stoppered flask
allowed to stand at room temperature for 60 to 70 minutes.
The free iodine was titrated with sodium thiosulphate (0.012
per cent impurities) using starch solution as indicator.

Standardization of this method, using sodium
chlorate (0.0015 per cent impurities) which had been dried
at 130°C. for several days, indicated an accuracy of better
than ± 0.4 per cent. The precision was found to be far
superior to the accuracy of the method.

(c)   Analysis of Lithium Chloride

Samples containing more than five per cent lithium chloride were titrated with silver nitrate solution. A seventy per cent alcoholic solution of sodium dichlorofluorosceinate was used as an indicator (15). The silver nitrate was obtained from the British Drug Houses Limited and subjected to two recrystallizations from water, followed by drying over sulphuric acid. Pure, dry sodium chloride was used to standardize the silver nitrate solution by the adsorption indicator method (15).

For samples containing less than five per cent of lithium chloride, the standard gravimetric method of precipitation as silver chloride was chosen (16).

The volumetric method gave a maximum error of $\pm$ 0.1 per cent when checked against the gravimetric method.

(d)   Mixed Chlorate and Chloride Analysis

A sample containing lithium chlorate and sodium chloride was weighed and diluted to 250 mls. The previously described methods were applied separately to various aliquots. Tables VI and VII represent an actual analysis and indicate the applicability of the method. A sample low in chlorate content was made up because it is in this range of concentration that the method itself was found to have the least accuracy.

TABLE VI

LITHIUM CHLORIDE ANALYSIS

Aliquot (mls.)	Wt. of NaCl (gms.)	$AgNO_3$ (mls.)	% NaCl Found	% NaCl Sought
25	0.221	38.08	97.01	96.98
25	0.221	38.06	96.97	96.98
20	0.177	30.43	96.90	96.98
20	0.177	30.45	96.94	96.98

TABLE VII

LITHIUM CHLORATE ANALYSIS

Wt. of $LiClO_3$ (gms.)	H_3PO_4 (mls.)	KI (gms.)	Time (mins.)	$Na_2S_2O_3$ (mls.)	%$LiClO_3$ Found	%$LiClO_3$ Sought
0.069	40	5	60	41.01	2.74	3.02
0.069	40	5	65	40.52	2.71	3.02
0.069	40	5	70	40.21	2.69	3.02

APPARATUS AND GENERAL PROCEDURE

(a) Determination of Solubility

In order to give accurate data on any system, isothermal determinations require a very exact temperature control. Hence it was necessary to ascertain and maintain the temperature within narrow limits during the attainment of equilibrium by any binary or ternary system.

A cylindrical glass vessel containing water was used as a thermostat. To reduce heat losses due to radiation, the walls of the thermostat were covered with one and a half inches of heavy felt. At temperatures far removed from that of the room, a three quarter inch wood cover, with holes for apparatus, was also used. The thermostat liquid was stirred by means of a motor driven metal stirrer.

For solubility determinations below 20°C. a secondary thermostat containing a kerosene and diesel oil mixture was maintained at temperatures about 10°C. lower than that of the main thermostat. To accomplish this, a cooling coil was immersed in the oil and connected to a refrigerating unit. A metal thermo-regulator placed in the oil, was used to control the intermittent cooling of the bath.

The main thermostat was fitted with a coil of one quarter inch copper tubing, which in turn was linked

through a circulatory pump to the colder oil bath. As a
heating source, a twenty-five watt light bulb was used.

The intermittent heating and cooling was
controlled by a two way mercury relay, which was actuated
by a mercury thermo-regulator. The two way relay was
connected to the lamp and to the circulatory pump in such
a way, that one of the two was always in operation. This
arrangement of the apparatus reduced the time lag suffi-
ciently to make it possible to control the temperature to
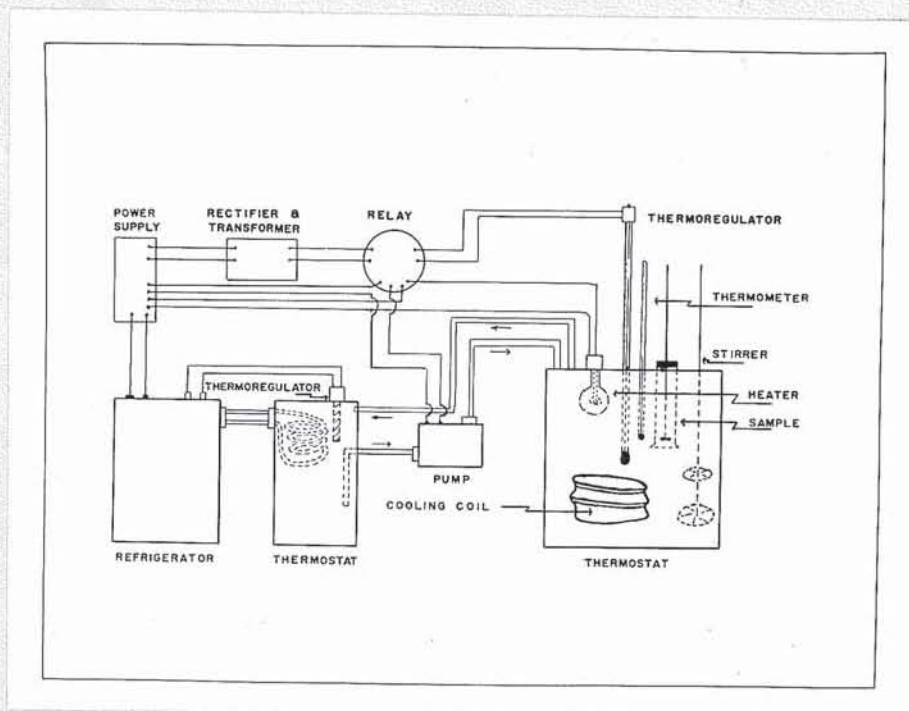$\pm 0.05^{\circ}C$. A diagram of the above apparatus is shown in
Figure 5.

Figure 5. Constant Temperature Apparatus

For temperatures above 20°C. and below 30°C. the secondary thermostat was replaced by a coil of very small copper tubing, through which ordinary tap water was passed continually. The rate of flow, and hence the rate of cooling, could be controlled quite easily. In the temperature interval from 30°C. to 100°C. atmospheric cooling was used. Evaporation of the water became more appreciable as the temperature was raised. To counteract this, the water content of the bath was progressively decreased and mineral oil was added. In addition, the wattage of the heating lamps was increased, until at 85°C. a 100 watt bulb was on continually and another 100 watt bulb was connected to the mercury relay for the intermittent heating as required, in order to maintain the desired temperature.

The actual temperature was measured with a mercury in glass thermometer, graduated in tenths of a degree, and calibrated against a standard platinum resistance thermometer. With this arrangement of apparatus, the temperature was controlled to ±0.05°C. throughout the research.

The container used to hold the binary and ternary systems, was a glass cylinder of 250 mls. capacity, with an inside diameter of one and one quarter inches, and an inside tapered ground glass top. With this apparatus, a mercury seal stirrer, or an ordinary glass stirrer through a closely fitted rubber stopper, could be used.

This glass cylinder was part of an all-glass unit constructed especially for efficient separation of liquid and solid phases (Fig. 6)

SUCTION
TUBE

RECEIVER

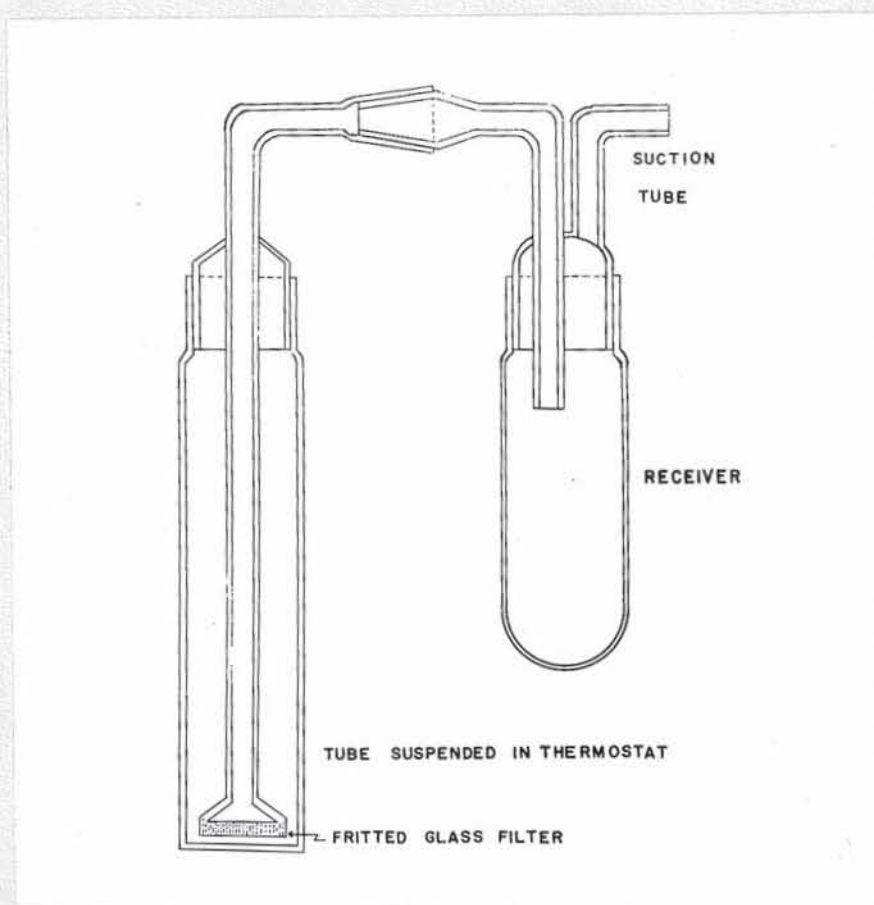TUBE SUSPENDED IN THERMOSTAT

FRITTED GLASS FILTER

Figure 6. Sampling Apparatus

All joints were of standard taper ground glass. When
suction was applied, the liquid phase was drawn up
through the sintered glass plug into the receiver. The
solid phase remaining in the cylinder, could be sucked
quite dry in a very short time. Usually about sixty seconds
were required to complete the operation, but in more dilute
samples about thirty seconds were required.

A sample of the liquid phase in the receiver was
poured into a tared weighing bottle provided with a ground
glass stopper. The wet solid phase was immediately removed
from the equilibrium vessel by means of a long glass rod
with one end flattened in the shape of a spoon. This sample
was placed in another tared weighing bottle, also provided
with a ground glass stopper. The samples obtained in this
way, were diluted to 250 mls. and appropriate aliquots were
subjected to analysis.

(b) Thermal Analysis

The method of thermal analysis was not considered
to be good enough for the binary system because of the reluct-
ance of some of the solid phases to appear. This was
particularly true for the hydrates of lithium chlorate.
For this reason, thermal analysis was used only for the
ice curve, the binary eutectics, and the $\alpha \rightleftharpoons \beta$ transition
temperature.

A thin walled glass tube having a length of 12 cms. and an inside diameter of 3.0 cms. was used to contain the solutions. Into the neck of this tube was fitted a rubber stopper, through which were placed a coiled glass hand stirrer, a sampling device, and a thermocouple encased in a thin walled glass tube. The sampling device was merely a glass tube in which was placed a small amount of glass wool. Then, at any desired time a sample of the solution could be withdrawn for analysis by application of suction. The glass wool prevented the sucking up of any crystals in the solution at the time of sampling.

The solution container was jacketed by another glass tube, thereby providing a dead air space between the inner tube and the cooling bath.

A solution was then made up to the approximate desired concentration and placed in the container, which in turn was placed in its jacket. The whole apparatus was then placed in an appropriate cooling mixture. The temperature of the solution was taken every minute by means of a calibrated iron-constantan thermocouple in conjunction with a sensitive Leeds and Northrup type K potentiometer. During the cooling process, the solution was stirred vigorously until a break in the E.M.F. - time readings, indicated that a solid phase had begun to separate. When this occured, suction was applied to the sampling tube. The sample obtained

in this way represented the solution at that temperature
in equilibrium with the particular solid phase that had
separated. The thermal analysis of a mixture of lithium
chlorate and water is represented graphically in Figure 7
where the composition of the sample taken at -14.2°C. is
that of the solution in equilibrium with ice at that
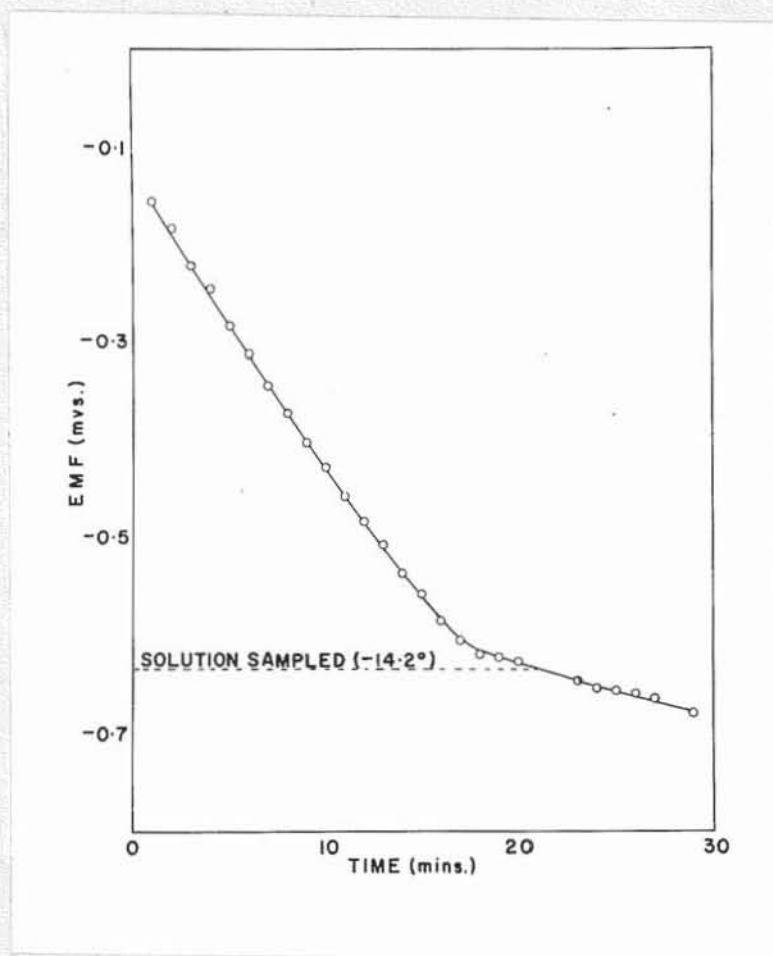temperature.

Figure 7. Thermal Analysis of a Lithium Chlorate
and Water Mixture

The iron-constantan thermocouple used in this
research was calibrated against the freezing points of
pure mercury ($-38.87^{\circ}C.$), pure carbon tetrachloride
($-22.9^{\circ}C.$) and pure water ($0.0^{\circ}C.$). During all thermal
analyses, the cold junction of the thermocouple was kept
in a bath of melting ice.

(c) X-Ray Powder Photography

X-ray diffraction photographs serve as a means
of identifying different crystalline substances. A given
pure substance will give rise to its own unique diffraction
pattern, if both the position and the intensity of the lines
or spots in the photograph are considered. Such a unique
pattern is therefore sufficient evidence for the identifi-
cation of the substance as a separate crystalline individual.

The theory underlying the various aspects of
X-ray powder photography can be found in any textbook on
crystallography (8). In practice, a monochromatic beam of
X-rays is passed through a small specimen of the powdered
sample. Numerous cones of diffracted beams emerge from the
specimen, and these are recorded as arcs on a strip of film
encircling the specimen. Each arc on the film represents
the combined diffracted beams from all the crystals in the
powder specimen which happen to be suitably oriented for
reflecting the primary X-ray beam from one particular set

of planes. The fundamental equation of X-ray diffraction
by crystalline solids is known as Bragg's law and is of the
form

$$d = \frac{n\lambda}{2\sin\theta}$$

where λ - is the wave length of the X-rays in Angstrom units.

    d - is the distance between successive identical
       planes of atoms in the crystal in Angstrom units.

    θ - is the angle between the primary X-ray beam
       and these atomic planes.

    n - is any whole number, from one upwards.

A measure of linear distance between corresponding
arcs on either side of the primary beam direction permits
an evaluation of the angles of diffraction. Since the
value of λ is known and constant for all of the lines in
any one photograph, it is then possible to calculate the
lattice spacings d of the powder specimen under investiga-
tion. If the crystal structure of the
substance is known, it is possible from d values to calcu-
late the unit cell dimensions. Since this has not been
determined for anhydrous lithium chlorate, this calculation
has not been carried out here.

During this phase of the investigation, special
precautions were taken to protect the salt as much as

possible from the atmosphere. A sample of the anhydrous
salt was taken from the vacuum dessicator and reground to
a very fine powder. It was then returned for drying for
several days. Following this, a very fine and thin walled
capillary tube of outside diameter 0.5mm. and inside diameter
of 0.3 mms. was filled with the sample and sealed immediately
at both ends with a torch. The sample prepared in this way,
was mounted in the camera and irradiated with X-rays for
three hours.

The position of each line in the resulting
photograph was measured and the spacing (d) of the corres-
ponding set of lattice planes was obtained from tables
provided for use with the camera employed. The relative
intensity (I), of each line was estimated visually. This
intensity estimation was carried out by assigning the
arbitrary value 10 to the strongest line. The intensities
of all other lines were compared to this and were assigned
values that were proportional to their intensities. For
example, a line one half as intense as the strongest, would
have been assigned the value five, etc. The lattice
spacings were expressed in kX units (6), one kX unit being
equal to 1.002 Angstrom units.

Powder photographs were taken of a sample that
had been in a vacuum dessicator at room temperature for
seven months, and hence was considered to be the form stable

at room temperature. The ($\underline{d}$) and ($\underline{I}$) values for this form were calculated and are listed in TABLE VIII. A quantity of this form was then placed in another vacuum dessicator, and held at 80°C. for a week and then photographed. The results obtained were the same as for the unheated sample.

A high temperature camera was available for use and it was decided to obtain a diffraction pattern of any other form stable at higher temperatures. A small nichrome wire coil was embedded in an asbestos mat surrounding the the sample. A space of about 5 mms. was left between two of the loops of the coil to enable the X-rays to enter and be diffracted. In order that the film or the camera dimensions might not be affected by the higher temperatures, a fine coil of copper tubing was mounted around and coaxial with the heating element. Cold water was passed through this coil. Of necessity, the camera was somewhat bulkier than the standard X-ray camera; but, the specimen to film distance was only 0.03 cms. larger. Suitable resistances were used to control the temperature of the specimen at 115 ± 5°C.

In theory this method was excellent, but in practice it had serious shortcomings. It was expected that most of the weaker lines normally obtained in room temperature photographs would not appear at elevated temperatures. This proved to be the case. In addition, the few lines that did appear were quite broad, and hence were unsatisfactory for interpretation. These characteristics
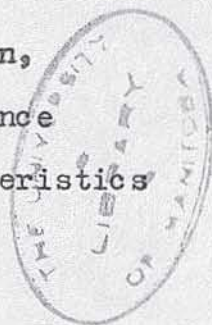
TABLE VIII

X-RAY POWDER DATA

Substance ...... $LiClO_3$

Radiation ...... Copper

Filter .... Nickel

$\underline{d}$ (kX)	$\underline{I}$
3.92	10.0
3.39	8.0
2.81	9.0
2.70	6.0
2.41	2.0
2.27	1.5
2.14	1.2
1.510	0.6
1.439	0.9
1.305	0.7

were explained on the basis of increased thermal vibrations
of the atoms at higher temperatures.

This problem, however, does not necessarily have
to remain unsolved. At room temperature, several photographs
were taken of specimens mounted in capillaries of various
wall thicknesses. It was found that the thinner the wall
of the capillary, the better the photograph. Obviously,
this should apply at higher temperatures also. Then, if
a dry box were available, it would be possible to work
without fear of the sample taking up moisture from the air.
As a result, greater care could be taken in loading a
capillary, and hence, it would be possible to work with
much thinner walled capillaries. This proposed solution,
however, is beyond the scope of this research.

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
and he was able to obtain diffraction patterns of the beta
form up to the melting point of the salt. By this technique
he was not able to detect any change in lattice structure
corresponding to the transition from the beta to the alpha
form. The apparatus used by Dr. Calvert was not capable
of close temperature control. At higher temperatures, however,
he was able to evacuate the camera which reduced the absorp-
tion of X-rays by the air. The capillaries used in his work
had a wall thickness of 0.007 mms. His results are listed
in Table IX.

TABLE IX

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

$\underline{d}$ (kX)	I	$\underline{d}$ (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

TABLE IX (continued)

d (kX)	I	d (kX)	I
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		

(d) Dilatometry

In an attempt to substantiate Kraus' (17) conten-
tion that a gamma form of lithium chlorate exists at room
temperature and that it exhibits a transition to the beta
form at 41.5°C., use was made of the fact that, if such a
transition did occur, it would undoubtedly be accompanied
by a change in volume. This fact was also used to attempt
to substantiate the claim of both Kraus and Burgess (17)
and of Berg (5) that a beta to alpha transition occurred
at 99°C. A dilatometer was constructed to measure these
changes in volume. This dilatometer was constructed in the
usual manner, a long capillary tube attached to a bulb
containing the lithium chlorate. In addition to this, a
small standard tapered stopper was built into the bulb to
facilitate loading.

The dilatometer was placed into a dry-box which
was not as efficient as could be desired. Commercial
nitrogen which had been passed over calcium chloride,
phosphorus pentoxide and silica gel was used to flush out
the dry-box for one hour. The dry-box also contained dishes
of phosphorus pentoxide in an attempt to reduce the water
content of the air as much as possible. About 100 grams
of anhydrous lithium chlorate, which had been dried vigor-
ously for five months, was used to fill the dilatometer
bulb to about three-fourths of its capacity. The indicator

liquid was para-xylene which had been dried with sodium for three days. The height of the indicator liquid was measured with a cathetometer,

The bulb of the dilatometer was placed in a large oil thermostat. The temperature was controlled to $\pm 0.1^{\circ}C$. by means of a regulating thermometer connected to a mercury relay. The heating elements were standard light bulbs and heaters and were connected to the mercury relay. Atmospheric cooling was used. The thermostat oil was stirred by means of a motor driven double blade stirrer and a screw type stirrer. Temperatures were recorded with a mercury in glass thermometer which had been calibrated against a certified platinum resistance thermometer.

The temperature was raised one degree every twenty-four hours, but in the range from $35^{\circ}C.$ to $50^{\circ}C.$ this increment was reduced to $0.5^{\circ}C.$ per twenty-four hours. There were no breaks occurring in the curve of capillary height versus temperature. The possibility of a very slow transformation was not overlooked. The temperature of the bath was held at $60^{\circ}C.$ for as long as a week and no indications of a gamma to beta transition were observed.

At higher temperatures an alpha to beta transition occurred and was shown to be reversible. A marked expansion took place on formation of the alpha modification from the beta, and conversely a contraction was observed in the

alpha to the beta transformation. These changes, however, were accompanied by prolonged hysteresis effects. With rising temperatures, the transformation took place at $108^{\circ}C$. and $106^{\circ}C$. in two cycles, whereas with falling temperatures the reverse process took place at $80^{\circ}C$. and $84.1^{\circ}C$. respectively. This evidence shows that the alpha to beta transition temperature lies between $84.1^{\circ}C$. and $106^{\circ}C$.

As a further complication in the dilatometric study, the lithium chlorate slowly decomposed, giving gaseous products, when the temperature was kept above $90^{\circ}C$. for any appreciable period of time. The gaseous decomposition products caused such fluctuations in the height of the indicator liquid that further cycling procedures had to be abandoned.

(e) The System: Lithium Chlorate - Water

The phase relations have been studied by thermal analysis and solubility determinations. The range of composition, which contains from seventy-five to one hundred per cent lithium chlorate was of primary interest in this research. It was felt, however, that a complete investigation of the phase relations in the binary system might be of advantage.

Various experimental techniques were used in the hope that the results obtained would be superior to those

of previous investigators (3,4,5,17). Since the part of the
phase diagram where ice and solution were in equilibrium
was of little interest, it 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 phase diagram was determined by
isothermal solubility determinations.

The solubilities covered the range of composition
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 the temperature was less than
the accuracy of the analysis.

The stable and metastable binary eutectics were
determined by thermal analysis in the usual way.

For the investigation of the anhydrous salt by
thermal analysis, a special unit was used. A glass tube, about
10 cms. long and having a diameter of about 2 cms. was used
to contain the salt. This tube could be sealed off from
the atmosphere by means of a standard ground glass cap.
Into the top of this cap, a thin walled glass thermocouple-
well and a glass tube were built. The system could be
evacuated through the glass tube, which had a stopcock
in it. A calibrated copper-constantan thermocouple was

used in conjunction with a Minneapolis-Honeywell recording
potentiometer to record the heating and cooling curves of
the anhydrous salt.

After the salt was placed in the glass tube and
the system evacuated, it was subjected to slow heating from
room temperature to temperatures above the melting point
of the salt. Following this, the molten salt was subjected
to slow cooling and resulting temperature versus time plots
were interpreted. This process was repeated several times
to reduce the hysteresis effects. The results of this
investigation are given in Table X. In Figure 8, a thermal
analysis curve from the above study is shown.

There was no indication of any other type of
transformation except as reported in the Table IX. A great
deal of care was taken to try and find some change taking
place in the vicinity of $40^{\circ}C$. but none was found.

TABLE X

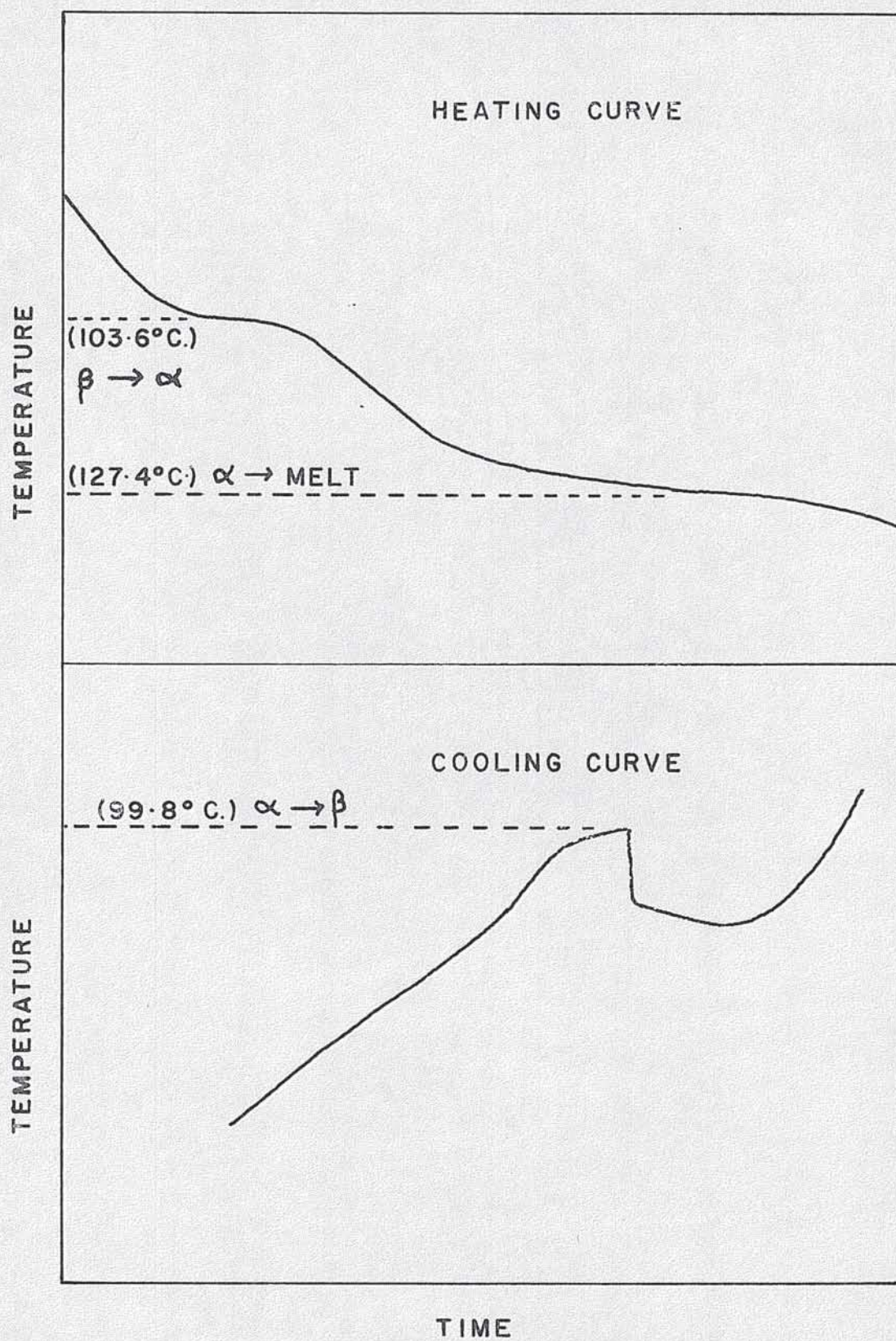| RISING TEMPERATURE		FALLING TEMPERATURE	
Transformation	Temperature $(^{\circ}C.)$	Transformation	Temperature $(^{\circ}C.)$
$\alpha \rightarrow$ Melt	127.4-127.5	Melt $\rightarrow \alpha$	127.4-127.5
$\beta \rightarrow \alpha$	106.1	$\alpha \rightarrow \beta$	98.2
$\beta \rightarrow \alpha$	103.6	$\alpha \rightarrow \beta$	99.8

Figure 8.   Thermal Analysis of Lithium Chlorate

The solubility relations and the results of thermal analyses are listed in Table XI together with the method used to arrive at them. The phase diagram is shown in Figure 9, where the solubilities in weight per cent lithium chlorate are plotted as abscissae, from left to right, and temperatures are plotted as ordinates. The broken lines indicate solubility curves in the metastable region. A broken vertical line represents the composition of a compound. Since the solubility of lithium chlorate in water was not determined at temperatures above 98.9°C., the region of the solubility curve representing alpha lithium chlorate in equilibrium with solution from 98.9°C. to 127.5°C. was drawn in as a broken line.

TABLE XI

The System $LiClO_3 - H_2O$

Wt. % $LiClO_3$	Wt. % H_2O	Method	Temperature ($^oC.$)	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 - $LiClO_3 \cdot 3H_2O$ (eutectic)
8	45.8	54.2	Solubility	-16.9	$LiClO_3 \cdot 3H_2O$
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	$LiClO_3 \cdot 3H_2O - LiClO_3 \cdot H_2O$ (eutectic)
17	73.6	26.4	Solubility	3.0	$LiClO_3 \cdot H_2O$
18	74.2	25.8	"	5.6	"

TABLE XI (continued) 54

	Wt. % $LiClO_3$	Wt. % H_2O	Method	Temperature (°C.)	Nature of the Solid Phases
19	74.1	25.9	Solubility	6.0	$LiClO_3 \cdot H_2O$
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	$LiClO_3 \cdot H_2O - (LiClO_3)_4 \cdot H_2O$ (peritectic)
27	82.0	18.0	"	21.5	$(LiClO_3)_4 \cdot H_2O$
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	$LiClO_3 \cdot 3H_2O - (LiClO_3)_4 \cdot H_2O$ (eutectic)
33	82.7	17.3	" "	-25.0	$LiClO_3 \cdot 3H_2O - \beta\, LiClO_3$ (eutectic)
34	86.7	13.3	Solubility	44.2	$\beta\, LiClO_3$
35	87.2	12.8	"	47.9	"

TABLE XI (continued)

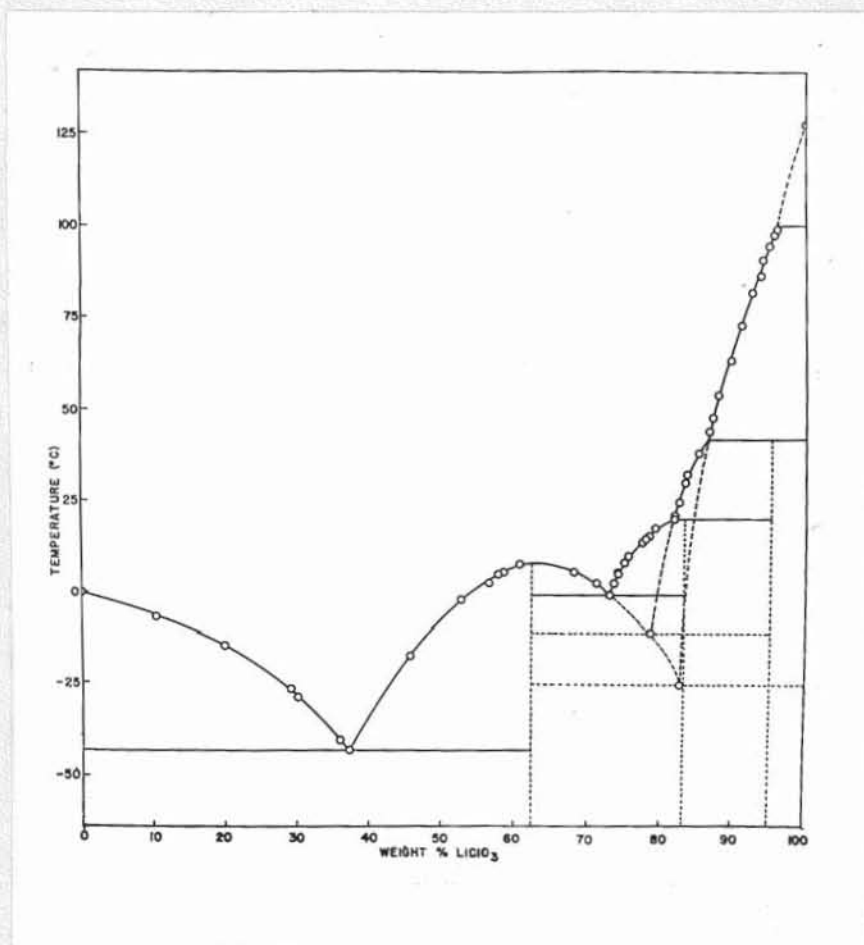|	Wt. % LiClO$_3$	Wt. % H$_2$O	Method	Temperature (°C.)	Nature of the Solid Phases
36	87.8	12.2	Solubility	54.0	β LiClO$_3$
37	89.5	10.5	"	63.2	"
38	91.0	9.0	"	72.8	"
39	92.4	7.6	"	81.7	"
40	93.7	6.3	"	86.2	"
41	93.8	6.2	"	90.7	"
42	94.8	5.2	"	94.2	"
43	95.5	4.5	"	97.5	"
44	95.9	4.1	"	98.9	"
45	100.0	0.0	Thermal Analysis	127.5	α LiClO$_3$

Figure 9. The System: $LiClO_3$ - Water

(f) The System: Lithium Chlorate - Lithium Chloride - Water

For the determination of the isothermal solubility curves of lithium chlorate in aqueous lithium chloride, the solutions were saturated by stirring in contact with the solid phase in tubes suspended in the thermostat. The stirring time required for equilibrium to be reached varied considerably depending primarily on the solid phase with which the solution was in equilibrium.

To show that equilibrium had been reached, it was approached from two directions. A mixture of appropriate composition was divided into equal parts and was treated as follows. One was heated until all of the solid phase had passed into solution whereas the other was frozen until all of the solution had solidified. These portions were then stirred in tubes in the thermostat, and the time required for the two liquid phases to become identical in composition was determined. This interval was considered to be the time required for a state of equilibrium to be reached. Another method found to give equally satisfactory results was to continue the stirring until the tie-line joining the composition of the liquid phase and the "wet residue" did not deviate from the composition of the solid phase when extrapolated.

For solutions up to ten per cent lithium chloride, the stirring time was found to be from two to three days

before equilibrium was reached. When the solutions were more concentrated with respect to lithium chloride, and particularly when the solid phase in equilibrium with the solution was the monohydrate or dihydrate of lithium chloride, equilibrium was reached only when the sample had been stirred for five or six days.

The solubility isotherms were determined at $3.0^\circ C.$, $6.0^\circ C.$, $8.5^\circ C.$, and $25^\circ C.$, employing Schreinemakers' method of "wet residues" for the determination of the equilibrium solid phase. The familiar Roozeboom equilateral triangle method was used to represent the experimentally determined solubilities.

The data for the isothermal ternary studies are listed in Tables XII, XIII, XIV, and XV, and the data corresponding to these tables are plotted in Figures 10, 11, 12, and 13, respectively. In Figure 14 the lithium chlorate corner of the $25^\circ C.$ isotherm has been enlarged to show more distinctly the composition of the equilibrium solid phase.

As additional evidence that the one-third hydrate proposed by Berg was actually the one-fourth hydrate of lithium chlorate, a sample of the wet residue from number 7, Table XV, was prepared for a microscopic examination. On comparing these crystals with the photo-micrographs of Berg (5), there was no doubt that they represent the same

solid phase. A photomicrograph of one of these crystals from the wet residue of number 7, Table XV, is reproduced in Figure 15.

Since the dihydrate of lithium chloride was the stable hydrate in the binary system: lithium chloride - water at 3.0°C., 6.0°C., and 8.5°C., and the monohydrate was the stable hydrate at 25°C., the transition temperature between the two must be between these two limits. A sample of $LiCl.H_2O$ and water, having the composition of the dihydrate, was cooled until the dihydrate formed. The sample was heated and cooled several times and the point where the temperature remained constant in this cycling procedure was noted. This corresponded to the transition temperature between the two hydrates. It was $12.5 \pm 0.1^{\circ}$C. which corresponds to the value of 12.5°C. found by Hüttig and Reuscher (13).

TABLE XII

ISOTHERM FOR $3.0 \pm 0.05°C.$

	Solution		Wet Residue		Nature of the Solid Phase
	Wt. % $LiClO_3$	Wt.% LiCl	Wt. % $LiClO_3$	Wt.% LiCl	
1	56.7	-	-	-	$LiClO_3 \cdot 3H_2O$
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	-	$LiClO_3 \cdot H_2O$
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	$LiClO_3 \cdot H_2O + LiCl \cdot H_2O$
12	44.7	19.9	27.9	38.8	$LiCl \cdot H_2O$
13	40.9	22.1	15.0	46.0	$LiCl \cdot H_2O + LiCl \cdot 2H_2O$
14	37.4	23.5	17.8	39.3	$LiCl \cdot 2H_2O$
15	23.9	29.1	9.6	44.2	"
16	-	41.0	-	49.3	"
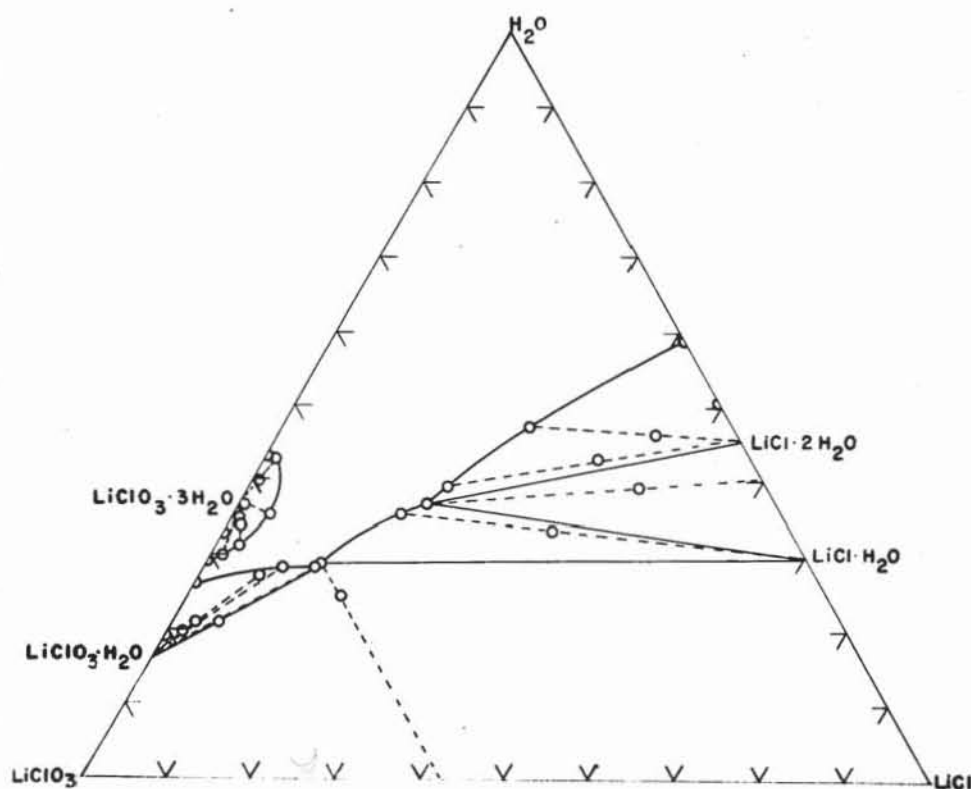
Figure 10. The System: $LiClO_3$ - $LiCl$ - H_2O
Isotherm for $3.0^{\circ}C$.

TABLE XIII

ISOTHERM FOR $6.0 \pm 0.05^{\circ}C$.

	Solution		Wet Residue		Nature of the Solid Phases
	Wt. % $LiClO_3$	Wt.% LiCl	Wt. % $LiClO_3$	Wt.% LiCl	
1	58.7	-	61.1	-	$LiClO_3 \cdot 3H_2O$
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	-	$LiClO_3 \cdot H_2O$
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	$LiClO_3 \cdot H_2O + LiCl \cdot H_2O$
13	57.5	13.7	16.0	54.3	$LiCl \cdot H_2O$
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	"

TABLE XIII (continued)

ISOTHERM FOR $6.0 \pm 0.05^{\circ}C$.

	Solution		Wet Residue		Nature of the Solid Phases
	Wt. % $LiClO_3$	Wt.% $LiCl$	Wt. % $LiClO_3$	Wt.% $LiCl$	
18	37.2	24.0	19.7	46.0	$LiCl.H_2O$
19	36.2	24.6	22.2	42.3	"
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	"
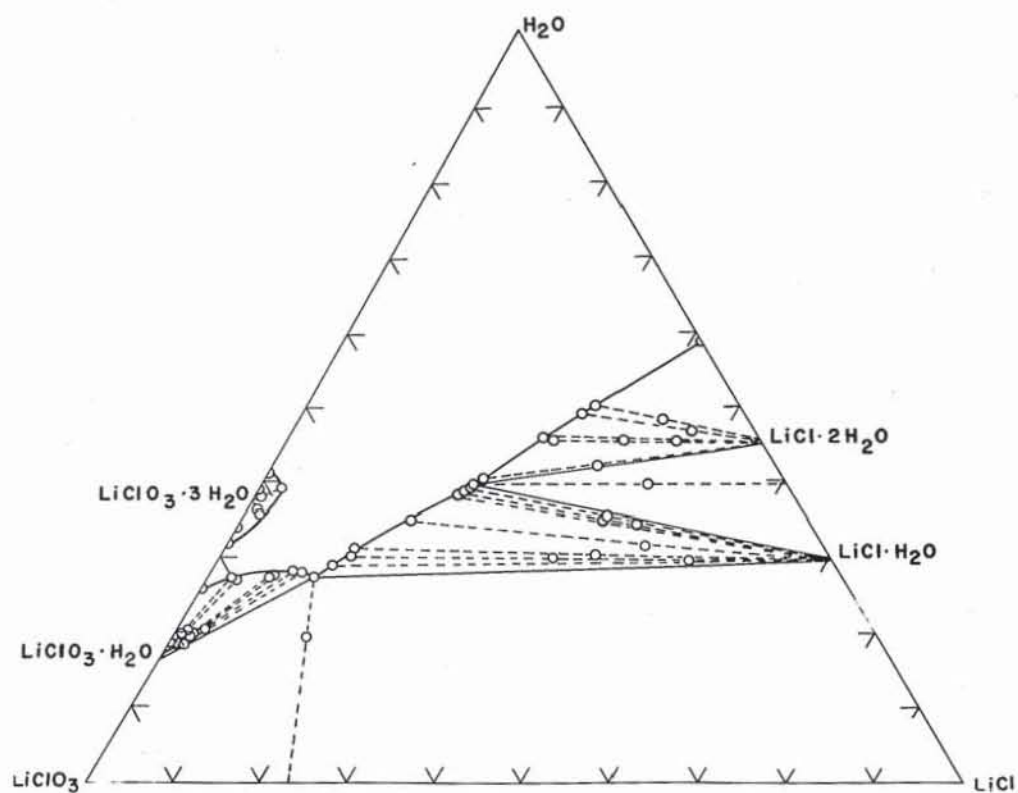
Figure 11. The System: $LiClO_3$ - $LiCl$ - H_2O
Isotherm for $6.0^{\circ}C$.

TABLE XIV

ISOTHERM FOR 8.5 $\pm$ 0.05°C.

	Solution		Wet Residue		Nature of the Solid Phases
	Wt. % $LiClO_3$	Wt.% $LiCl$	Wt. % $LiClO_3$	Wt.% $LiCl$	
1	75.0	-	-	-	$LiClO_3 \cdot H_2O$
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	$LiClO_3 \cdot H_2O + LiCl \cdot H_2O$
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	$LiCl \cdot H_2O$
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	$LiCl \cdot H_2O + LiCl \cdot 2H_2O$
13	28.2	28.9	12.8	43.4	$LiCl \cdot 2H_2O$
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	"
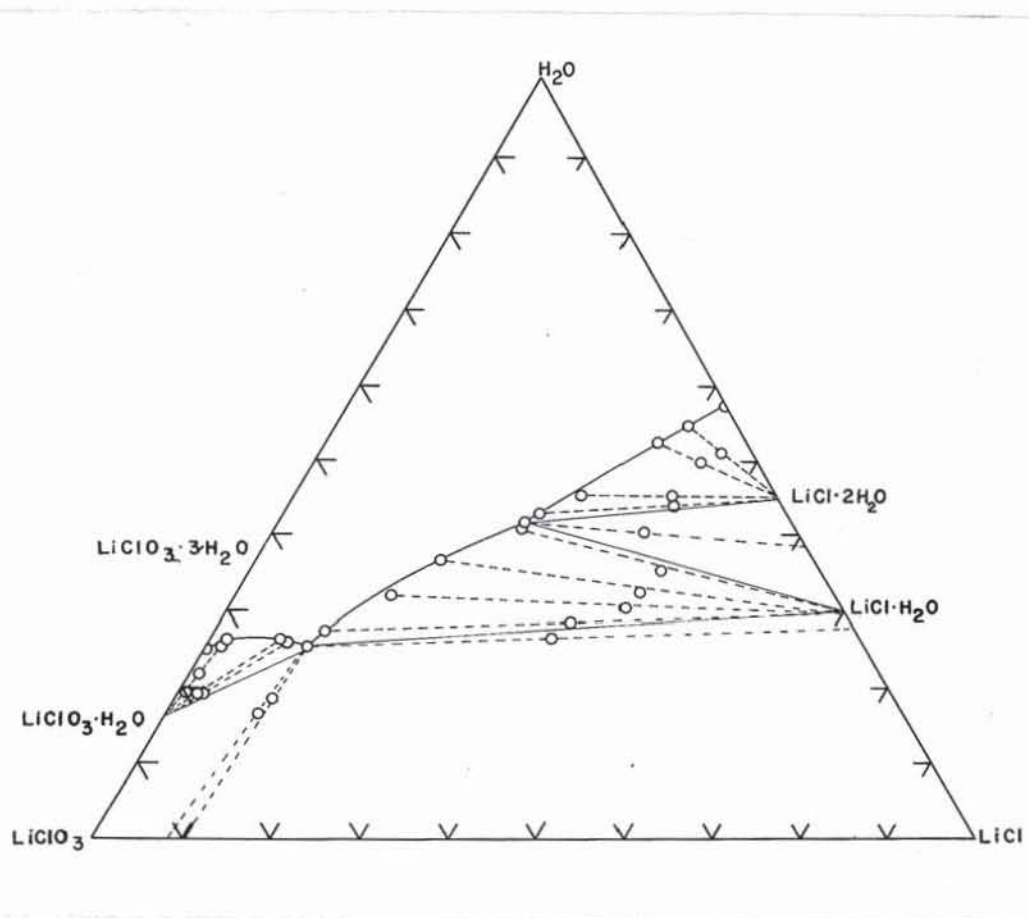
Figure 12.   The System: $LiClO_3$ - $LiCl$ - H_2O
Isotherm for 8.5°C.

TABLE XV

ISOTHERM FOR $25.0 \pm 0.05^{\circ}C$.

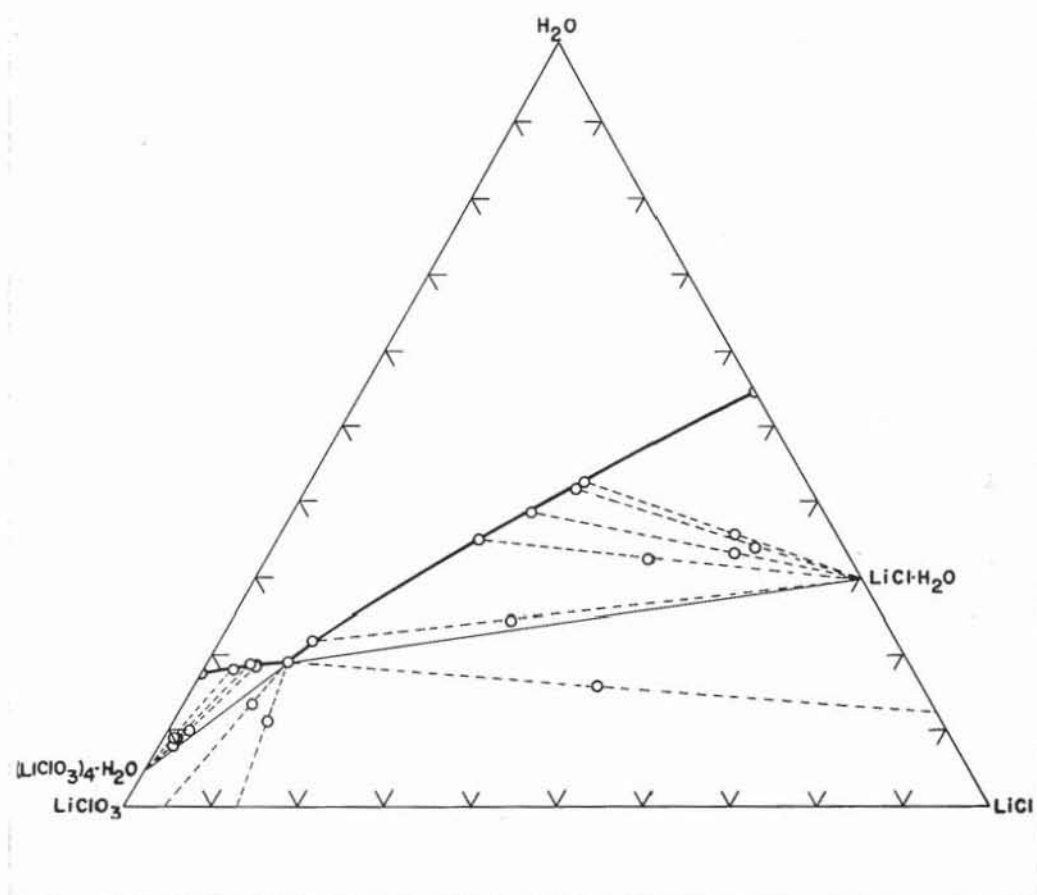|	Solution		Wet Residue		Nature of the Solid Phases
	Wt. % $LiClO_3$	Wt.% LiCl	Wt. % $LiClO_3$	Wt.% LiCl	
1	82.6	-	-	-	$(LiClO_3)_4 \cdot H_2O$
2	78.7	3.3	90.0	1.0	"
3	76.4	5.0	89.6	1.6	"
4	76.1	5.1	86.9	2.1	"
5	75.7	5.6	89.9	1.5	"
6	75.8	5.7	87.8	2.3	"
7	75.9	5.8	90.7	1.4	"
8	72.3	9.2	78.8	8.0	$(LiClO_3)_4 \cdot H_2O + LiCl.H_2O$
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	-	-	"

Figure 13.   The System: $LiClO_3$ - $LiCl$-H_2O
Isotherm for $25.0^{\circ}C$.
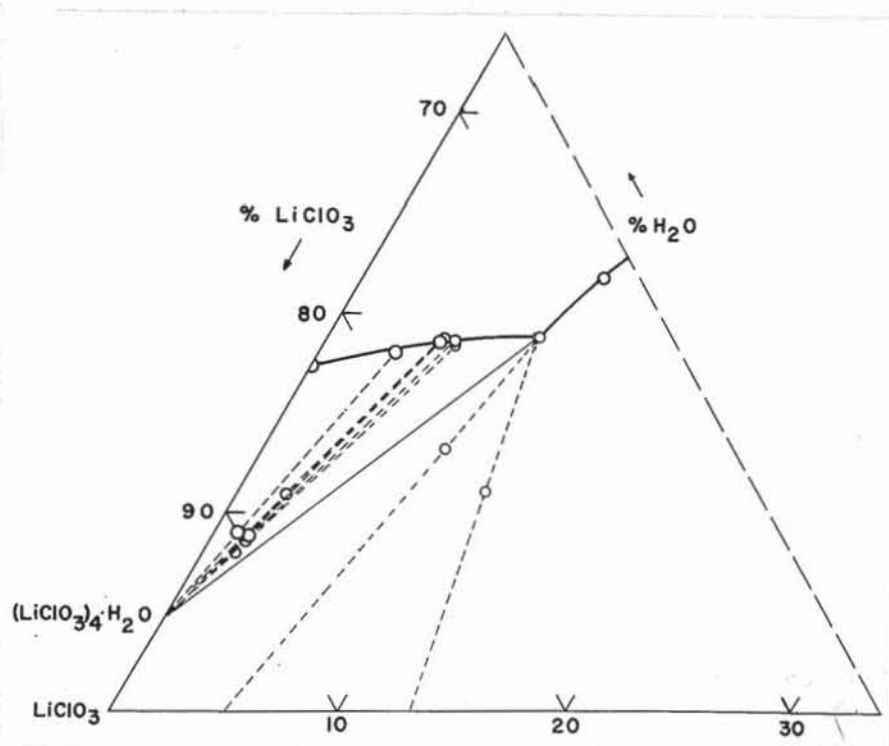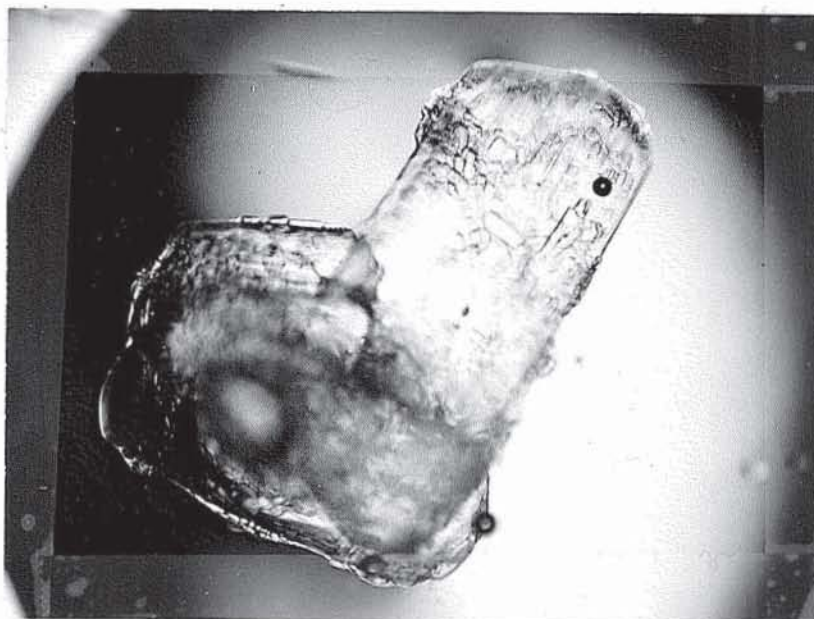
Figure 14. Enlarged Portion of Figure 13.

Figure 15. Photomicrograph of $(LiClO_3)_4 \cdot H_2O$

DISCUSSION OF RESULTS

With the exception of a few slight refinements
in temperature and composition, the solubility curves in
the binary phase diagram, Figure 9, were essentially the
same as those previously determined by Kraus and Burgess (17),
and by Berg (5). In general, their results indicated a
lower solubility of lithium chlorate in water than that of the
present work. This was most probably due to their not
allowing sufficient time for equilibrium conditions to
be set up.

The existence of the trihydrate was fairly
obvious from the shape of the phase diagram because it
was a congruently melting compound. The flatness of the
solubility curve, however, did not lend itself to an
accurate determination of the melting point. A direct
determination of the melting point was not successful
either, because of the difficulty involved in preparing
and maintaining a mixture having the exact composition
of the trihydrate.

In an attempt to solve this problem, the three
isothermal ternary investigations of the system lithium
chlorate - lithium chloride — water, at $3.0^{\circ}C.$, $6.0^{\circ}C.$,
and $8.5^{\circ}C.$ were carried out.

Then, because lithium chlorate trihydrate is

a congruently melting compound, the curve representing

solutions in equilibrium with this solid phase, at these

temperatures, appears as a peninsula on the respective

phase diagrams. The solutions, on each of these peninsulas,

having a lithium chlorate content of 62.6 per cent, which

is the composition of the trihydrate, would also have a

certain percentage of lithium chloride. These percentages

of lithium chloride then could be plotted as abscissae and

the corresponding temperatures as ordinates. The resulting

curve, on extrapolation to zero per cent lithium chloride,

would intersect the temperature axis at the melting point of

the trihydrate.

The trihydrate, however, melted at a temperature

less than 8.5°C. The extrapolation of the line joining the

two figures at 3.0°C., and 6.0°C., indicated a melting point

of 8.7°C. Obviously this method was not suitable.

In the binary study, however, the trihydrate was

found to exist at 8.1°C. and also did not exist at 8.5°C.

The maximum on the binary solubility curve of the trihydrate

indicated the melting point to be 8.4°C. Kraus and Burgess (21)

reported 8.0°C. and Berg (5) reported from 8.1°C. to 8.3°C.

as the melting point of the trihydrate.

The trihydrate also formed four eutectics, two

stable at -43.3°C., and -0.1°C., and two metastable at -10.5°C.

and -25°C. The solid phases in equilibrium with solution

at these eutectics were listed in Table XI.

It was realized, however, that a binary investigation of the phase relations, by solubility measurements, would not lead to an accurate determination of the composition of any incongruently melting compounds. It would merely indicate at what temperature a change in phase had occurred. In a binary study of this type, involving a salt and water, the composition of any incongruently melting compound could only be determined by direct analysis, or by the method of the peritectic halt time (24). Both of these methods are open to serious criticism. The former almost always gives misleading results, especially if two possibilities are very close to each other in composition, because of the difficulty in removing all the adhering mother liquor from the hydrates. There is also the possibility of removing some of the water of hydration in the process of drying the sample. The latter method, which involves the plotting of the peritectic halt time against the composition of the mixture being analysed, gives two curves intersecting at the composition of the incongruently melting compound. The success of this method depends on the accuracy with which the composition of the sample is known and on the determination of the halt time. Because of the many possible sources of error in the latter determination, the method is seldom used except to obtain a rough approximation of the composition of the solid phase undergoing change, or being formed at this temperature.

The solubility curves indicated that two different solid phases existed in stable equilibrium with solutions in the temperature intervals from -0.1°C. to 20.5°C., and from 20.5°C. to 42.0°C. The compositions of these phases were determined by isothermal ternary studies of the system: lithium chlorate - lithium chloride - water, at 3.0°C., 6.0°C., 8.5°C., and 25°C. The phase diagrams at the three lower temperatures showed beyond doubt that the solid phase in the lower temperature interval actually was the monohydrate of lithium chlorate. This, therefore, substantiates the work of Kraus and Burgess (17), and Berg (5).

The isothermal ternary study at 25°C. proved to be the most fruitful of the four. The interpretation of this study refuted the claims of Kraus and Burgess and of Berg, and yet it was also consistent with their experimental data.

It is well known that the successful application of Schreinermakers' method of "wet residues" depends largely on the accuracy of the chemical analyses employed as well as on the ability to remove as much solution from the wet residue as possible. In the 25°C. isotherm, the hydrated lithium chlorate residue never contained more than 11 per cent water. This, by normal standards, could hardly be improved upon since about 4.7 per cent water was present in the hydrate.

Although the chlorate analysis was claimed to

be accurate to within ± 0.4 per cent, the accuracy was
considered to be better than ± 0.2 per cent, in samples
very rich in lithium chlorate. The standard gravimetric
method of determining chloride, however, was capable of far
better accuracy than this. Therefore this method was used
in this study for the analysis of lithium chloride.

In Figure 14, 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
seventy degrees. Therefore, if there were a maximum possible
error of ± 0.2 per cent lithium chlorate in the analysis
of the wet residue, this would not lead to an error of
greater than ± 0.1 per cent lithium chlorate in the composi-
tion 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 each other.
The standard gravimetric method was chosen for this reason.

The fact that none of the tie-lines ever crossed
and that they all converged to a single composition when
extrapolated, indicated 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 about a month before. These points indicated

the same solid phase and therefore left no doubt that the
hydrate stable at $25^{\circ}C$. had the composition corresponding
to $(LiClO_3)_4 \cdot H_2O$.

In Figure 14, there are no experimentally
determined solubilities representing solutions containing
from 5.8 to 9.16 per cent 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 with a polarizing microscope.
The solid phase in both cases was the same, although a
slight amount of the monohydrate of lithium chloride was pre-
sent 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.

Berg's claim for the existence of a one-third
hydrate has been refuted on the evidence found in this
ternary study at $25^{\circ}C$. In addition, photomicrographs of
wet residue 7 and those obtained by Berg of his proposed
one-third hydrate were the same. Therefore, since the
hydrate in this work had the composition of a one-fourth
hydrate, the hydrate isolated by Berg must also have had this
composition. The method of the peritectic halt time, used
by him, was obviously not sensitive enough to determine
the exact composition of the hydrate. Kraus and Burgess,

on the other hand, had apparently eliminated Berg's claim
for the one-third hydrate on the grounds that a mixture
containing 6.55 per cent water definitely showed the
presence of solution between $21.0^{\circ}C$. and $41.5^{\circ}C$. If the
solid phase was the one-third hydrate, containing 6.2 per
cent water, the mixture would not supply an observable amount
of solution. A mixture of this composition, in which the solid
phase was the one-fourth hydrate, however, would supply
the observed solution.

At $42.0^{\circ}C$., the one-fourth hydrate underwent
a peritectic transition to the anhydrous salt and solution.
The anhydrous salt formed at $42^{\circ}C$. is the first of two
allotropic modifications. This form was the one stable
at room temperature and corresponds to the beta form
previously found by Kraus and Burgess. The X-ray diffraction
pattern of this modification was determined and the character-
istic $\underline{d}$ and $\underline{I}$ values are listed in Tables VIII and IX.

The transition from the beta to the alpha form
was investigated by thermal analysis, dilatometry and by
X-ray diffraction. The former was the only method that
yielded satisfactory results, indicating that the transition
took place reversibly at $99.8^{\circ}C$. This value compared
favourably with those reported by Kraus and Burgess and
by Berg. The latter two methods were found to be unsuccessful,
although the dilatometer showed a marked increase in volume

when the beta to alpha transition took place, in the range from 84.1°C. to 106°C.

If the hemihydrate of lithium chlorate prepared by Wächter (26), Troost (25), Potilitzin (20), and Brühl (7) did indeed exist, it would undoubtedly be formed from the monohydrate in a peritectic transformation. The phenomenon would appear as a break in the solubility curve on the binary phase diagram. No such break occurred between -0.1°C. and 20.5°C. The monohydrate was shown to be the solid phase in stable equilibrium with solutions in this temperature interval. There was no break in the solubility curve from 20.5°C. to 42°C. either. The one-fourth hydrate was shown to be the stable phase in this temperature interval. Therefore, there is no doubt that the hemihydrate of lithium chlorate does not exist as a stable solid hydrate and there have been no indications of it ever appearing as a metastable phase in this study.

Kraus and Burgess claimed that anhydrous lithium chlorate could exist in three enantiotropic forms. Two of these, the alpha and beta, were confirmed by Berg and also in the present work. Neither Kraus and Burgess nor Berg could offer any evidence indicating that a gamma to beta transformation had ever occurred.

In the present work, the techniques of dilatometry, thermal analysis, solubility, and X-ray diffraction were

used to try and detect the presence of the gamma form or the supposed gamma to beta transition. The first two of these methods were applied with great care and no such phenomenon was detected. The solubility curves showed no break that would indicate the presence of a gamma to beta transition. Finally the X-ray diffraction technique was used to eliminate the possibility of a monotropic modification. This was accomplished by obtaining a diffraction pattern of a sample that had never been heated. The sample was then heated to $80^{\circ}C$. for one week and allowed to cool before obtaining another diffraction pattern of the same sample. These two patterns were the same.

If the anhydrous salt had been a monotropic modification, prolonged heating would have caused this form to change to that of the stable form. Since the change would have been irreversible, the stable form would remain when the temperature was lowered. Then, the second diffraction pattern would have been different from the first because the unit cells of the respective forms would of necessity have had different dimensions.

This work, therefore, refuted the claim of Kraus and Burgess that gamma lithium chlorate existed as a stable allotropic modification of the anhydrous salt. It also eliminated the possibility of the gamma form existing as a monotropic modification.

The isothermal ternary study of the system lithium chlorate, lithium chloride, water, at 3.0, 6.0 and 8.5°C, indicated that the stable phase, at these temperatures, in the binary system lithium chloride and water was the dihydrate of lithium chloride. The addition of lithium chlorate to the binary system caused this hydrate to lose one molecule of water when the solutions reached the compositions of the invariant points shown in the phase diagrams. At 25.0°C, the stable phase in the binary system was the monohydrate of lithium chloride.

The transition temperature from the monohydrate to the dihydrate of lithium chloride was determined to be 12.5 ± 0.1°C. This corresponded to the value given by Hüttig and Reuscher (13).

CONCLUSIONS

1. The phase diagram of the system lithium chlorate and water has been determined.

2. The isothermal phase diagrams of the system $LiClO_3$ - $LiCl$ - H_2O at $3.0^{\circ}C.$, $6.0^{\circ}C.$, $8.5^{\circ}C.$, and $25^{\circ}C.$ have been determined.

3. Lithium chlorate forms three hydrates having the following formulae:

    (i) $(LiClO_3)_4 \cdot H_2O$ - stable from $20.5^{\circ}C.$ to $42^{\circ}C.$

    (ii) $LiClO_3 \cdot H_2O$ - stable from $-0.1^{\circ}C.$ to $20.5^{\circ}C.$

    (iii) $LiClO_3 \cdot 3H_2O$ - melts at $8.4^{\circ}C.$

The hydrate having the formula $(LiClO_3)_3 \cdot H_2O$ proposed by Berg (4,5) was shown to have the formula $(LiClO_3)_4 \cdot H_2O$.

4. The transition temperature between the mono and dihydrates of lithium chloride has been determined to be $12.5 \pm 0.1^{\circ}C.$, confirming the results of Hüttig and Reuscher (13).

5. Lithium chlorate and lithium chloride do not form any double salts at $3.0^{\circ}C.$, $6.0^{\circ}C.$, $8.5^{\circ}C.$, and $25^{\circ}C.$

6. Lithium chlorate can exist in two enantiotropic forms, alpha and beta, and the transition, $\alpha \rightleftharpoons \beta$, has been shown to take place at $99.8^{\circ}C.$ The alpha form has the lower density. The gamma form proposed by Kraus and Burgess (17),

6. does not exist as a stable or metastable modification of the anhydrous salt.

7. The X-ray diffraction pattern of beta $LiClO_3$ has been obtained and a method for obtaining the diffraction pattern of alpha $LiClO_3$ has been proposed.

8. A modification of the standard iodometric analysis of (XO_3) has been developed and successfully applied to lithium chlorate, where (X) is any halogen.

BIBLIOGRAPHY

The convention used in compiling this bibliography
is the same as in the Canadian Journal of Chemistry.

1. Bancroft, J. Physical Chem., 6, 179 (1902).

2. Ibid., Z. anorg. Chem., 40, 148 (1904).

3. Berg L., Z. anorg. Chem., 155, 311 (1926).

4. Ibid., 166, 231 (1927).

5. Ibid., 181, 131 (1929).

6. Bragg W.L., "Atomic Structure of Minerals," Cornell
    University Press, New York (1937).

7. Brühl H., Bull. soc. ind. minerale, 35, 155 (1912).

8. Bunn C.W., "Chemical Crystallography," Clarendon
    Press, Oxford (1948).

9. Findlay A., Campbell A.N., and Smith N.O., "The Phase
    Rule and its Applications," Ninth edition, Dover
    Publishing Inc. (1951).

10. Ibid., pp. 277 - 281.

11. Ibid., pp. 340 - 342.

12. Gibbs J.W., Trans. Conn. Acad. (1874 - 8).

13. Gmelins Handbuch der anorganischen Chemie, Teil 20,
    Lithium, Verlag Chemie G.m.b.H., Berlin (1926), p. 125.

14. Hazlewood E.A., Z. Krist., 98, 439 (1938).

15. Kolthoff I.M., and Sandell E.B., "Quantitative Inorganic
    Analysis," MacMillan, Third edition (1952), p. 543.

16. Ibid., p.303.

17. Kraus C.A. and Burgess W.H., J. Am. Chem. Soc., 49, 1226 (1927)

18. Macgillavry C.H. and van Eck C.L.P., Rec. Trav. Chim., 62, 729 (1943).

19. Mylius and Funk, Ber. 30, 1716 (1887).

20. Potilitzin, J. Russ. Phys. Chem. Soc., 16, 840 (1883).

21. Retgers, Z. physik. chem., 5, 449 (1890).

22. Roozeboom, Z. physical. chemie., 15, 145 (1894).

23. Schreinemakers, Ibid., 11, 76 (1893).

24. Tammann, Z. anorg. chem., 37, 303 (1903).

25. Troost, Ann. Chim. phys., [3], 51, 136 (1857).

26. Wächter, J. prakt. chem., 30, 321 (1843).

27. West C.D., Z. Krist., 88, 198 (1934).