THE UNIVERSITY OF MANITOBA

THE TERNARY SYSTEMS:-

LITHIUM SULPHATE - LITHIUM BROMATE - WATER

POTASSIUM SULPHATE - POTASSIUM BROMATE - WATER

AND

LITHIUM BROMATE - SODIUM BROMATE - WATER

AT 25°C.

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A Thesis

Submitted to

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by

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TO MY PARENTS

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ABSTRACT

The equilibrium diagrams of the systems K_2SO_4-$KBrO_3$ - H_2O, Li_2SO_4-$LiBrO_3$-H_2O and $NaBrO_3$-$LiBrO_3$-H_2O have been determined at $25^{\circ}C$.

The $KBrO_3$-K_2SO_4-H_2O diagram is relatively simple - no double salt or solid solution being formed.

In the system Li_2SO_4-$LiBrO_3$-H_2O a monohydrate $LiBrO_3.H_2O$ was found to exist and the X-ray powder picture has been determined.

A series of solid solution of $LiBrO_3.H_2O$ in $Li_2SO_4.H_2O$ exists, extending from 2.2% to 45% $LiBrO_3.H_2O$. There is no corresponding solid solution of $Li_2SO_4.H_2O$ in $LiBrO_3.H_2O$.

The existence of the solid solution results from the character of the tie-lines and has also been proved by X-ray analysis.

This system appears to represent another example of Ricci's sixth type of solid solution formation (1) (in the Roozeboom classification).

A complex of the form $(2Li_2SO_4.LiBrO_3)3H_2O$ may exist in the region of the solid solution but the X-ray pattern does not indicate this.

The $NaBrO_3$-$LiBrO_3$-H_2O diagram is simple, $NaBrO_3$ and $LiBrO_3.H_2O$ being the only solid phases.

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THEORETICAL INTRODUCTION

1. THE PHASE RULE

In heterogeneous systems all states and changes at equilibrium can be described qualitatively by the use of Gibb's Phase Rule and Le Chatelier's Theorem.

The phase rule derived from thermodynamic principles in 1879 by J. Willard Gibbs (2) has the usual form

$$F = C-P + 2.$$

Where F = number of degrees of freedom which is defined as the number of variable factors, temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.

P = number of phases. A phase is defined as a homogeneous part of the system bounded by distinct surfaces and separable in principle by mechanical means.

C = number of components. The total number of components is the smallest number of independent composition variables necessary to define the composition of every phase in the system.

The phase rule is applicable only when true equili-

brium exists throughout the system.

Under constant temperature and pressure conditions two of the variables are fixed and with reservations a modified phase rule equation may be used viz F = C-P.

2. THREE COMPONENT SYSTEMS

At constant temperature and pressure the composition of ternary systems can be represented on an equilateral triangle by Roozeboom's method.

The apices of the triangle represent the pure components A, B and C. The length of each side is made equal to one hundred and the components are plotted in weight per cent or mole per cent of each component.

A point on the side of the triangle represents the composition of a binary system and a point within the triangle represents a composition of the ternary system.
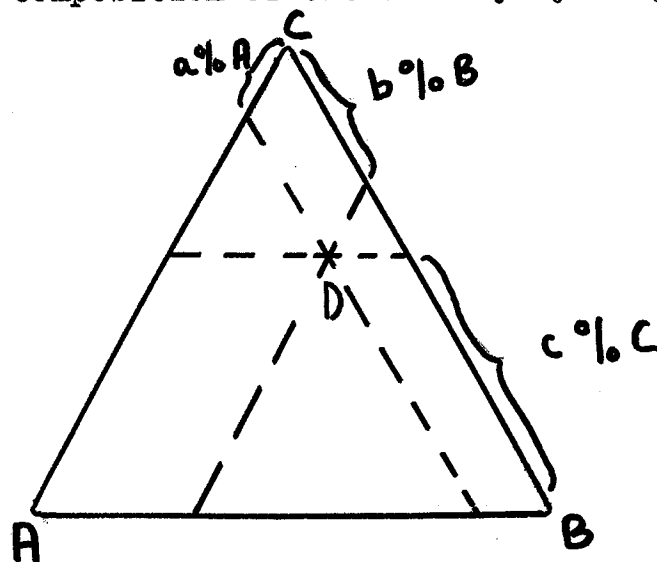
FIGURE I

A Point on a Triangular Graph

Thus a point D in Figure I represents a system of
a%A, b%B and c%C.

From the modified form of the phase rule viz F=C-P
it is readily seen that for invariance i.e. F=0 in a ternary
system, three phases must be present in an aqueous system
at 25°C, a solution and two solids.

In three component systems, the solubility relation-
ships at constant temperature and pressure 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 compound.

A. An example of the simplest three component system is
shown in Figure II.
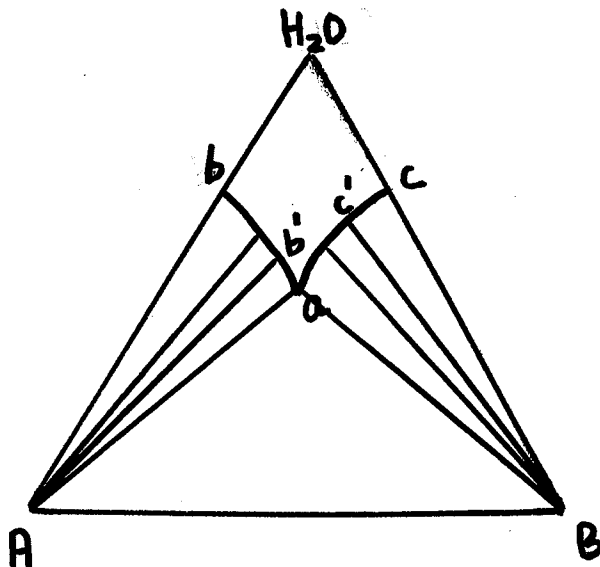
FIGURE II

A Simple Three Component System

The area H_2O-b-a-c represents unsaturated solution of the salts in water. The curve ab represents the compositions of solutions in equilibrium with solid A; ac gives the compositions of solutions in equilibrium with solid B and point 'a', the isothermally isobaric invariant point gives the composition of the saturated solution in equilibrium with both A and B. F the variance is zero at the invariant point.

The triangle AaB is called an invariant triangle. Any system plotting inside this triangle will break up into solution of composition a, solid A and solid B.

The lines Ab', BC' are called tie-lines; they indicate the compositions of saturated solutions in equilibrium with the pure solid phases.

B. If one of the components A or B exists as a hydrate at room temperature and the pure components are the only solid phases, i.e. there is no compound formation or solid solution the equilibrium diagram will resemble Figure III.

In Figure III triangle aBAxH_2O is the invariant triangle.

C. In some cases the hydrate may be dehydrated by the other component and the equilibrium diagram will resemble Figure IV.
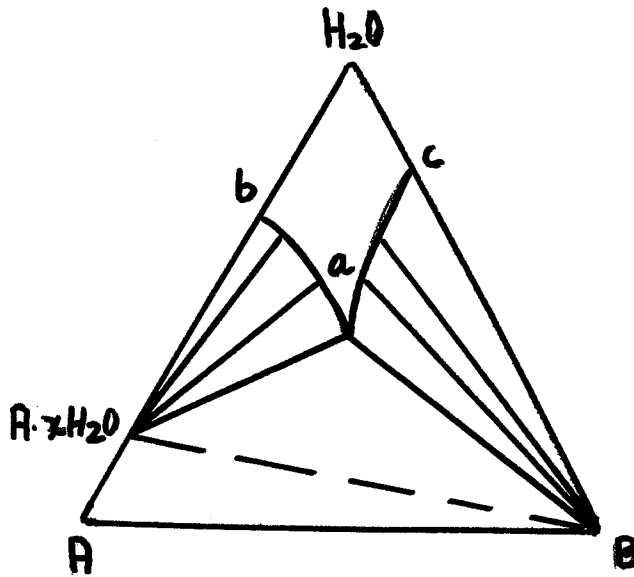
FIGURE III

Typical Three Component System Showing Hydrate
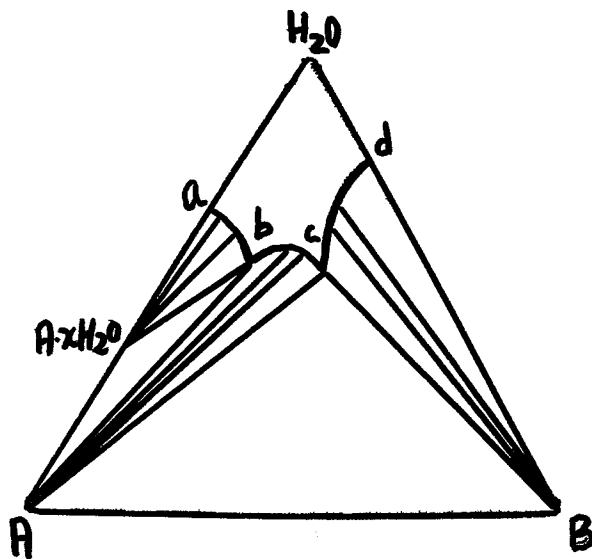
FIGURE IV

System Showing Hydrate Dehydrated by Second Salt

There are now two invariant triangles, AcB and AbAxH$_2$O.

The equilibrium solid phases will be:- AxH$_2$O along ab, anhydrous A along bc and anhydrous B along cd.

D. If a binary compound is formed depending on whether it is congruently saturating or incongruently saturating the phase diagrams will resemble Figure V and Figure VI.
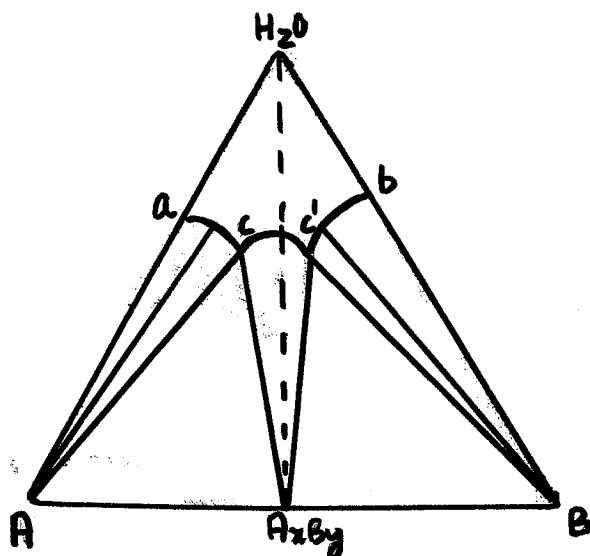
FIGURE V

System Showing Congruently
Saturating Compound
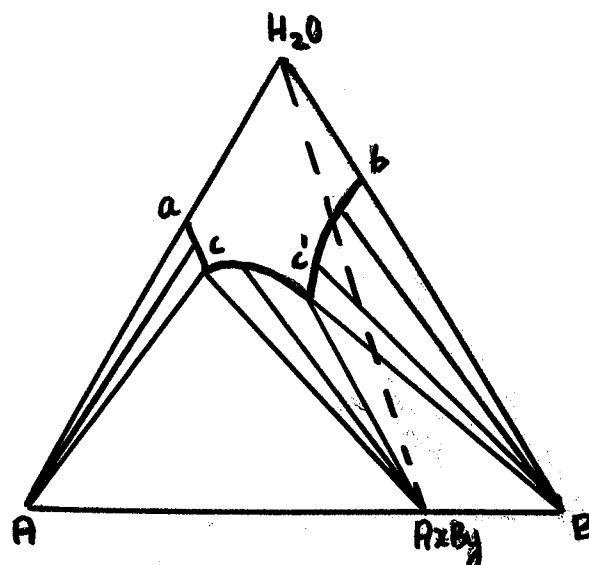
FIGURE VI

System Showing Incongruently
Saturating Compound

Figure V gives the case where the complex is congruently saturating, i.e. addition of water to AxBy does not decompose it but it dissolves to form a solution of the same composition. In this case the line joining the point AxBy to the

H_2O corner cuts the curve cc', the solubility curve for

AxBy.

Figure VI gives the case where the complex is

incongruently saturating, i.e. addition of water to AxBy

decomposes it into, in this case, the pure component A

and liquid c'. The complex cannot coexist in contact with

a liquid where the proportion of A to B is the same as

in itself. In this case the line joining the point AxBy to

the H_2O corner does not cut the curve cc^1.

E. In some systems solid solutions are formed. When there

is limited solid solubility it is assumed, according to the

Roozeboom classification of solid solution, that a pair of

conjugate solid solutions exists. A system where there is

incomplete solid miscibility will have an equilibrium

diagram resembling Figure VII.
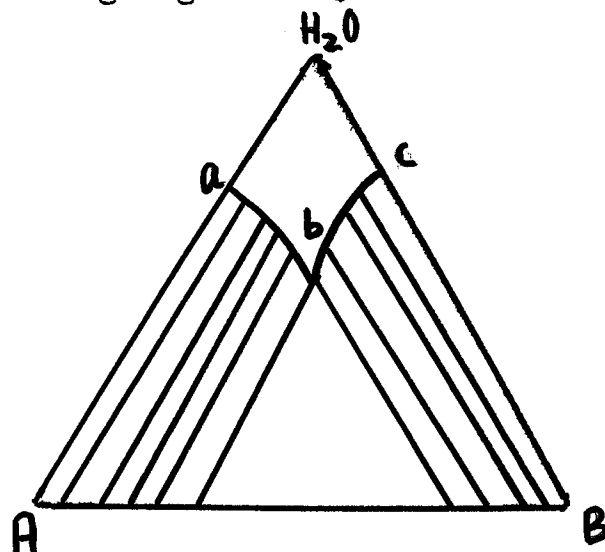
FIGURE VII

Three Component Systems Showing Two
Conjugate Solid Solutions

Experimentally however it has been found that there are systems where the two salts are incompletely miscible but which give only one series of solid solution for example, the system Na_2SO_4-$NaBrO_3$-H_2O at 37.5°C/and 52°C (1). The 45°C equilibrium diagram at these temperatures where the solid solution exists resembles Figure VIII.
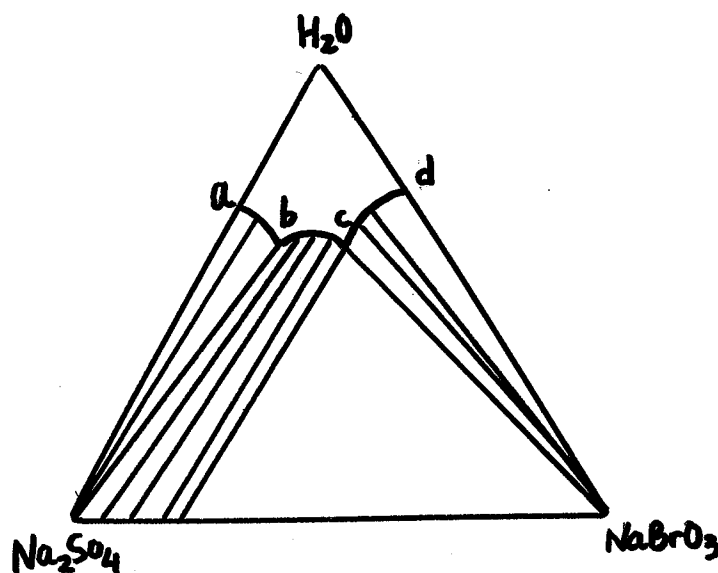
FIGURE VIII

System Showing Only One Series of Solid Solution

Another example is the system Li_2SO_4-Na_2SO_4-H_2O at 25°C (3) studied by Campbell and Kartzmark. The equilibrium diagram is represented by Figure IX.
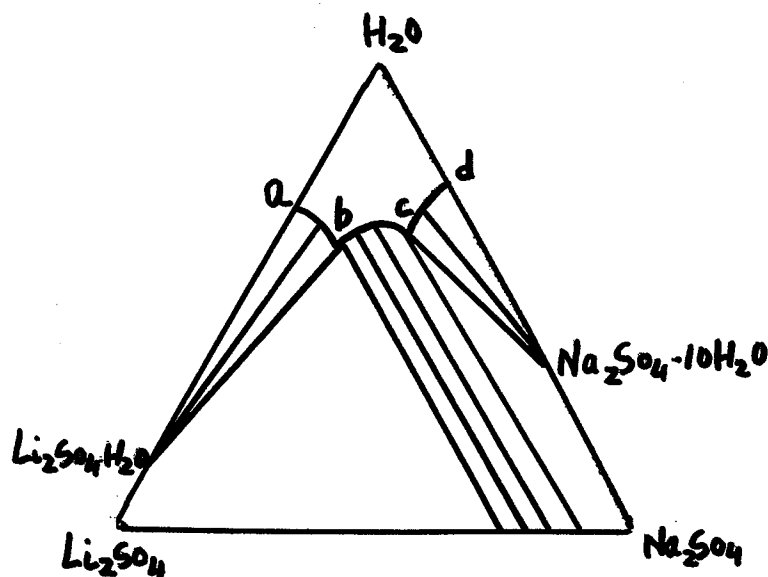
FIGURE IX

The System Li_2SO_4-Na_2SO_4-H_2O at $25^{\circ}C$ (3).

These last two systems have been classified as a sixth type of solid solution formation in the Roozeboom classification by Ricci (1).

3. DETERMINATION OF SOLUBILITY FOR PHASE DIAGRAMS

The curves in three component diagrams trace out the compositions of solutions saturated with respect to one or more salts. Thus if any mixture of water and the two salts is taken, which leaves some crystals undissolved, the analysis of the solution must give a point on one of the solubility curves.

By taking a range of mixtures, a number of saturated solutions can be obtained and a sufficient number of points determined to draw all the curves in the diagram. To complete the diagram it is necessary to know with what salt or salts each solution is saturated and it is then necessary to determine the composition of the undissolved crystals.

By filtering and analysing the crystals an approximate idea may be formed but this is not sufficiently accurate as some mother liquor will be left in the filtered crystals. As it is practically impossible to remove all the mother liquor, a method is used which allows for the presence of mother liquor and therefore no attempt is made to remove it.

This method introduced by F.A.H. Schreinemakers in 1893 is known as the method of "wet residues" (4). This method depends on the fact that if any complex is marked on the diagram it lies on the straight line joining its solution with its pure solid.

Take for example a point 'a' in Figure X and let the solution pt be 'b'. Joining b to a and producing gives the pure solid phase as A. The composition of the 'wet residue' must lie on the same straight line but nearer to the pure solid. The composition of the 'wet residue' is represented by 'c' in Figure X.
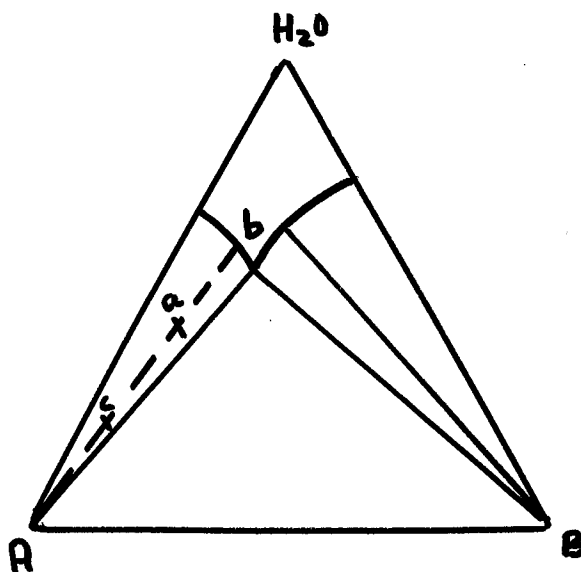
FIGURE X

Illustrating the 'Wet Residue' Method

By analysing a solution and its 'wet residue' two
points can be plotted on a diagram and a straight line
drawn through them. The composition of the solution
gives a point on the curve; the composition of the solid
phase must lie somewhere on the straight line beyond the
position of the 'wet residue'.

If several solutions and their wet residues are
analysed and plotted, the tie lines will be found to meet

at points representing solid compounds while others meet
at the point representing solution. Different wet resi-
dues will be found in equilibrium with the same solution
depending on the amount of each solid phase present.
The resulting lines fan out from the invariant solution
as shown in Figure XI. This is the best evidence for
the invariant solution.
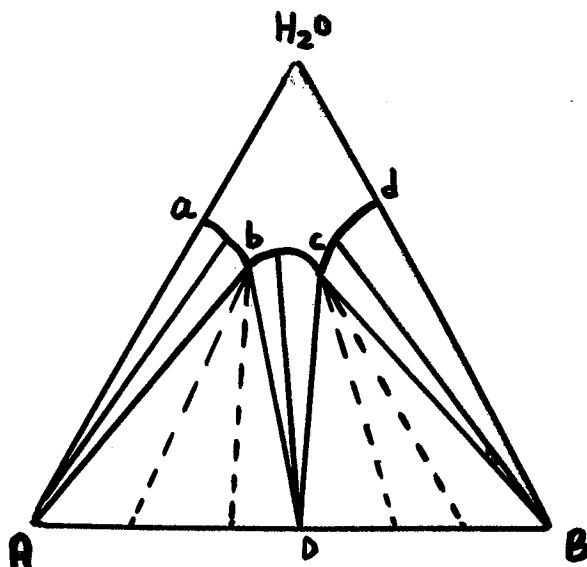
FIGURE XI

System Showing Compound Formation

In Figure XI it can be seen how the tie lines meet
at D indicating formation of a binary compound. If the tie
lines do not intersect as in Figure VIII or Figure IX solid

solution is indicated. In no case however should the tie lines cross.

Another method which has been found to be quite accurate is a modification of the above, known as the Synthetic Complex Method. Instead of analysing the wet residue a complex is prepared of known composition and the solution only is analysed. This again gives two points on the equilibrium diagram: the solution point on the curve and the complex point which replaces the wet residue point.

Hill and Ricci (5) claim that this method may be more accurate than the residue method if algebraic extrapolation of the tie-lines is used.

I used both methods thereby obtaining three points through which the straight line was drawn in my study of the various systems.

4. APPLICATION OF X-RAY ANALYSIS TO PHASE RULE PROBLEMS

It is well known that when a beam of monochromatic X-rays is directed at a crystalline substance, a characteristic diffraction pattern is obtained. If a crystalline powder is used, the pattern will appear as a series of arcs on a strip of film mounted coaxially with the specimen. The conditions under which diffraction occurs are defined by the Bragg relation

$$n\lambda = 2d \sin\theta$$

where n = a positive integer denoting the 'order'
of the reflection

λ = the wavelength of the monochromatic radiation in Angstrom units

d = the distance between two successive lattice planes in Angstrom units

θ = the angle between the incident beam and the lattice plane (the glancing angle)

Since every crystalline substance has a characteristic pattern, X-ray powder photographs can be used as a means of identifying crystalline substances.

The presence of a hydrate of a crystalline substance can be demonstrated by X-ray analysis.

The X-ray pattern of the hydrate can be compared with that of the anhydrous substance obtained by heating and drying in vacuum. There normally should be a marked difference in the two patterns.

Compound formation between two salts can be confirmed by X-ray analysis. The pattern of the new compound will be different from that of either of the components; new lines will appear and others may disappear.

Solid solution formation can also be confirmed by X-ray analysis. The X-ray pattern will be that of the

primary lattice but the lines will be slightly displaced
due to the presence of the other components.

X-ray analysis helps to distinguish between solid
solution and a heterogeneous mixture of the two salts.
The X-ray pattern of a heterogeneous mixture of two com-
ponents will be a mixture of that of each component -
the pattern will include lines from each component.

To conclude it should be emphasized that detection
by X-ray analysis is limited to about 5 per cent. If less
than 5 per cent of one component is present in the mixture,
the X-ray pattern of the mixture will not show any lines
of that component.

INTRODUCTION

The system Li_2SO_4-$LiBrO_3$-H_2O has been studied as an analogue to the system Na_2SO_4-$NaBrO_3$-H_2O studied by J. E. Ricci (1).

Ricci claimed the existence of an additional type of solid solution, which he called 'the sixth type', to the five types of solid solution in the Roozeboom classification.

Roozeboom (6) showed that five different types of solid solution are possible. These types depend upon the mutual solubility of the two salt components in the solid phase or phases possible. Three of these types are concerned with complete miscibility of the solid components. The other two types refer to systems in which the miscibility is incomplete and in which there are always two series of solid solutions (conjugate solid solutions).

Type I includes systems in which the miscibility is complete and the concentration of one of the two salts in the liquid phase exceeds that of the same salt in the solid phase for all concentrations.

Type II includes systems in which the miscibility is unlimited but the concentration of one of the salts in the liquid phase exceeds that of the same salt in the solid phase for lower total concentrations and is less for higher total concentrations.

Type III includes systems in which the miscibility
is unlimited but the concentration of one of the salts
in the liquid phase is less than that of the same salt in
the solid phase for lower total concentration and is more
for higher total concentration.

In Type IV one of the two solid solutions contains a
larger concentration of one of the salts than the coexisting
liquid and the other solid solution contains a smaller
concentration of that same salt than in the coexisting
liquid. The equilibrium diagram for a system of Type IV
will resemble Figure XII.
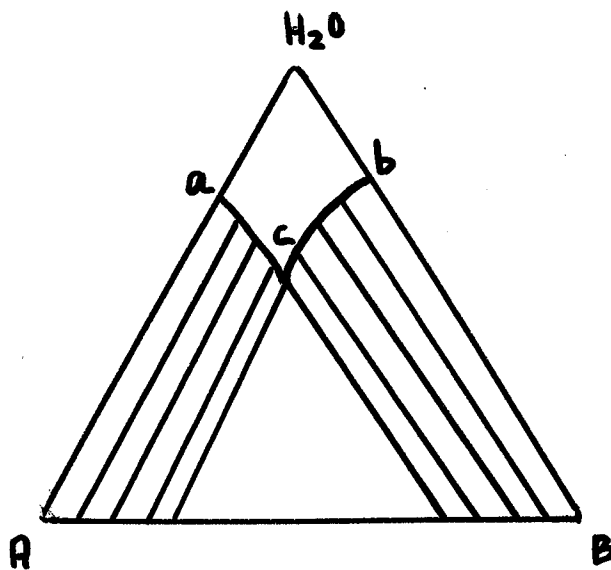
FIGURE XII

System Showing Type IV Solid Solution Formation
in Roozeboom's Classification

In Type V also we have two series of solid
solution but the concentration of one of the salts is
always greater in the liquid than in the coexisting solid.
A system of Type V is given in Figure XIII.
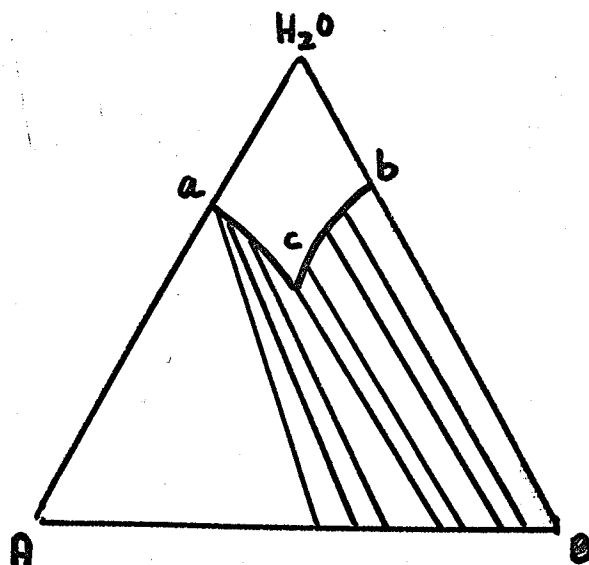
FIGURE XIII

System Showing Type V of Solid Solution in
Roozeboom's Classification

To the above five types of solid solution, a sixth
type claimed by J. E. Ricci (1) may now be added. He
studied the system $Na_2SO_4-NaBRO_3-H_2O$ at $10^{\circ}C$, $25^{\circ}C$, $30^{\circ}C$,
$37.5^{\circ}C$, $45^{\circ}C$ and $52^{\circ}C$.

At 10°C, 25°C and 30°C Ricci obtained relatively simple equilibrium diagrams. No complex formation or solid solution was obtained; the only solid phases were $NaBrO_3$ and $Na_2SO_4 \cdot 10H_2O$. The system at 25°C is shown below in Figure XIV.
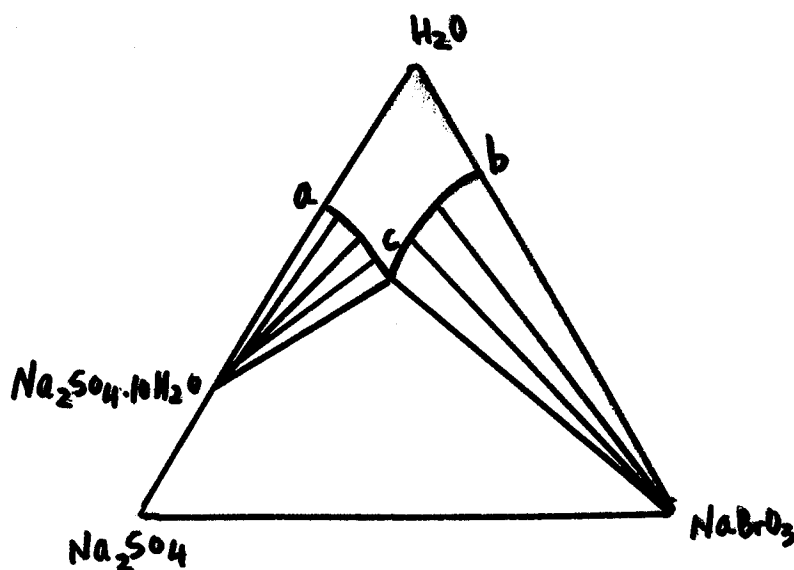
FIGURE XIV

The System Na_2SO_4-$NaBrO_3$-H_2O (1) at 25°C.

It should be noted that, though the transition temperature for the reaction

$$Na_2SO_4 \cdot 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$$
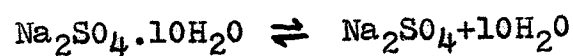
is only 32.5°C, it has not been lowered to 25°C by as much

as 11 per cent NaBrO$_3$, i.e. no anhydrous Na$_2$SO$_4$ appears.

At 37.5^{o}C, 45°C and 52°C the system Na$_2$SO$_4$-NaBrO$_3$-H$_2$O can be represented by Figure XV which gives the 45°C isotherm.
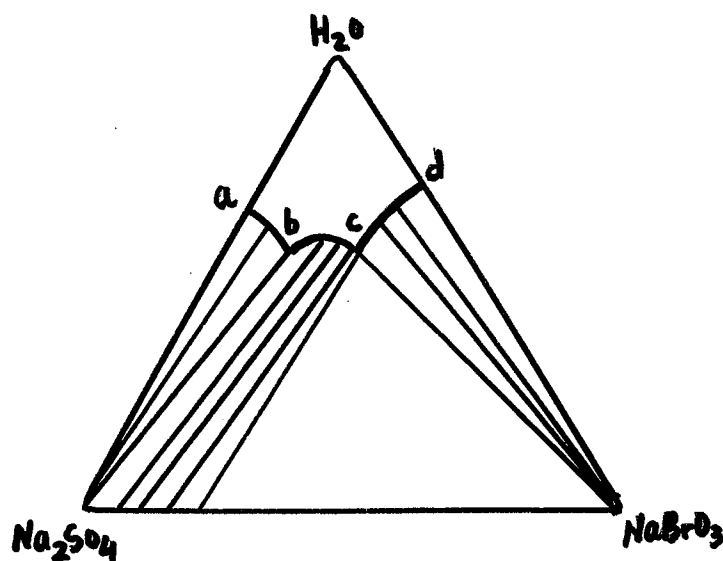
FIGURE XV

The System Na$_2$SO$_4$-NaBrO$_3$-H$_2$O (1) at 45°C.

At these higher temperatures the stable solid phases are: anhydrous Na$_2$SO$_4$ for solutions between a and b; solid solution (anhydrous) for solutions b-c; and NaBrO$_3$ for solutions c-d.

That the phase in equilibrium with solutions on the curve bc of Figure XV is a solid solution (a homogeneous

solid phase of varying composition) is seen from the behaviour of the tie lines in that region.

The limits found for the solid solution do not correspond to any definite stoichoimetric ratio of the two salts which make it impossible to consider this phase as a solid solution of Na_2SO_4 in any complex.

At those temperatures at which the solid solution exists the following sequence of solid phases is observed on an isotherm: Pure component Na_2SO_4, anhydrous solid solution (not corresponding to any stoichoimetric compound) and the other pure component, $NaBrO_3$. This means that in binary system Na_2SO_4-$NaBrO_3$ at these temperatures, the miscibility is incomplete and yet there is no pair of conjugate solid solutions but a single limited phase of solid solution.

Though this 'sixth type' of solid solution is not included in the Roozeboom classification, experimentally there are many binary systems where the miscibility is incomplete but there is only one series of solid solution.

The following ternary systems serve as examples:

1. Na_2SO_4-K_2SO_4-H_2O at 25°C (7)
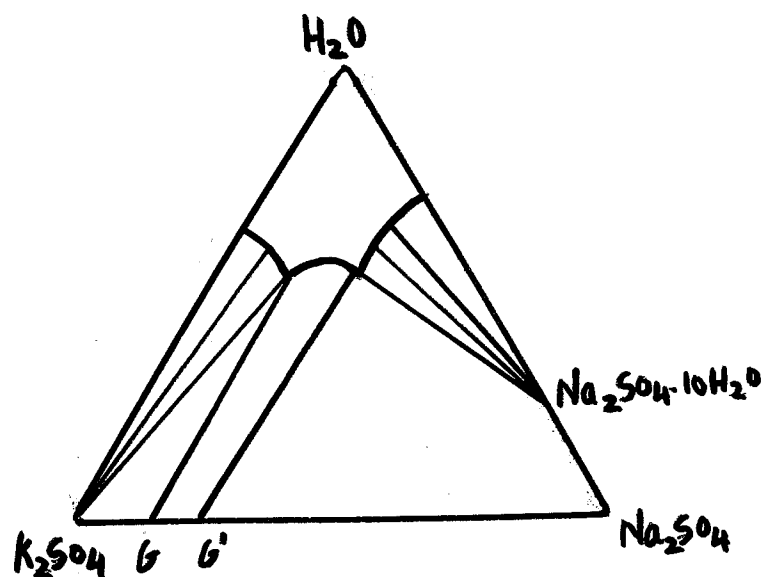
FIGURE XVI

The System $Na_2SO_4-K_2SO_4-H_2O$ at $25^{\circ}C$

The point G represents the composition of pure
glaserite $3K_2SO_4 \cdot Na_2SO_4$. The point G^1 represents the
maximum amount of sodium sulphate which glaserite can
dissolve at $25^{\circ}C$, 3.3 per cent according to Hamid (7).
There is no corresponding solid solution of glaserite in
Na_2SO_4.

2. $Na_2CO_3-K_2CO_3-H_2O$ at $20^{o}C$ (8)

Here there is a single solid solution phase inside the triangle, consisting of a solution of $K_2CO_3 \cdot 6H_2O$ and $Na_2CO_3 \cdot 6H_2O$
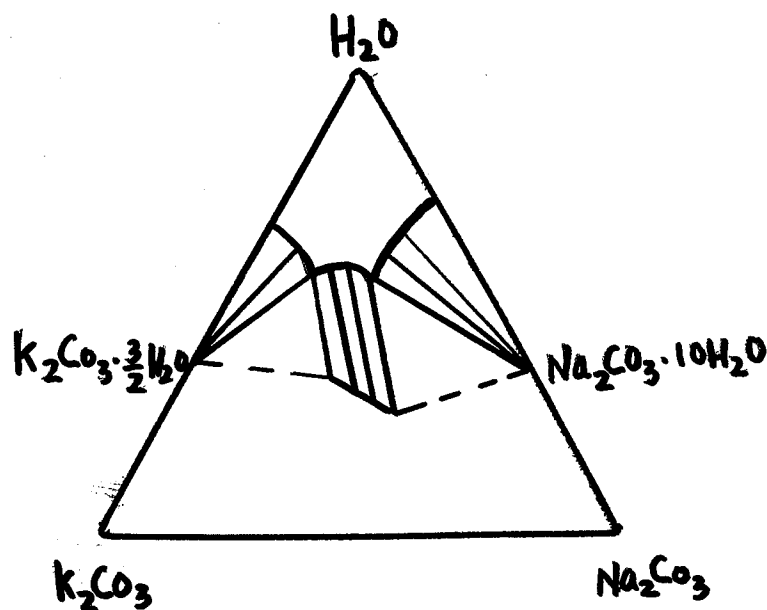
FIGURE XVII

The System $Na_2CO_3-K_2CO_3-H_2O$ at $25^{o}C$

3. $Li_2SO_4-Na_2SO_4-H_2O$ at $25^{o}C$ (3)

Figure XVIII shows extensive solid solubility of lithium sulphate in sodium sulphate but no corresponding solid solution of sodium sulphate in lithium sulphate.
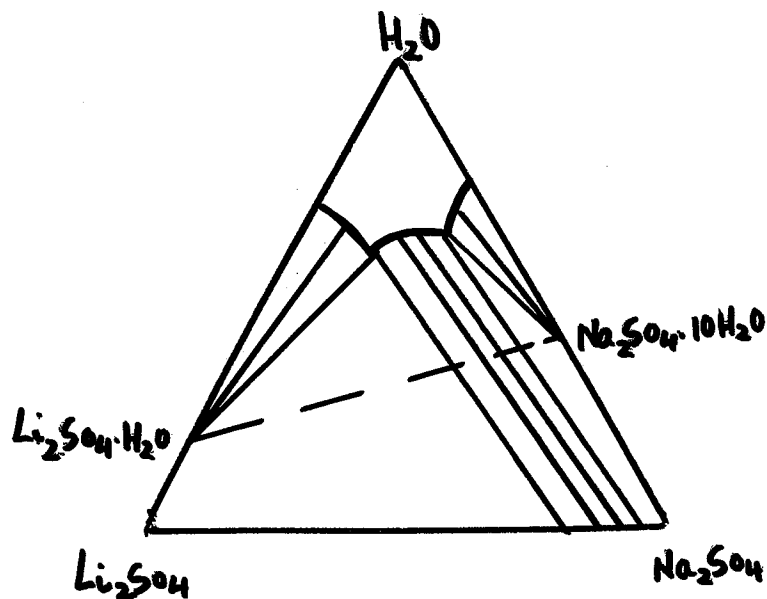
FIGURE XVIII

The System Li_2SO_4-Na_2SO_4-H_2O at 25°C.

The main objection to this type of behaviour exhibiting only one series of solid solution was put by Rivett (9). Rivett argued that since the composition of a pure component is always the same even at different temperatures, it cannot be in equilibrium with varying solutions at different temperatures. But the argument is fallible since chemical composition is not a thermodynamic variable required by the phase rule; the three thermodynamic variables used in

the derivation of the phase rule are temperature, pressure and concentration. Chemical composition does not necessarily give the true concentration.

Thermodynamically however it can be shown that a pure component can be in equilibrium with a varying solid solution. Since specific volume changes with temperature the chemical potential of a pure component does change with temperature and therefore the same component (chemically) can be in equilibrium at different temperatures with solutions of varying compositions. Hence thermodynamically the 'sixth' type of solid solution is not impossible.

The system Li_2SO_4-$LiBrO_3$-H_2O investigated by me also showed only one series of solid solution at $25^{o}C$.

The investigation was carried further using the potassium salts, i.e. K_2SO_4-$KBrO_3$-H_2O but in this case there was no solid solution whatsoever. That was in line with the general observation that potassium salts do not favour solid solution formation.

LITERATURE REVIEW

The only systematic work on lithium bromate has been carried out by I.N. Averko Antonowich (10). He checked the solubility of lithium bromate in water for the temperature range -45°C to 143°C. At 24.9°C he gave a value of 65.54 for the solubility in water. He confirmed the existence of a monohydrate at room temperature and determined the transition temperature for the reaction $LiBrO_3 \cdot H_2O \rightleftharpoons LiBrO_3 + H_2O$. He found the transition temperature to be 52°C. He also noted that the anhydrous form exists metastably down to 0°C.

EXPERIMENTAL METHOD

1. PURITY OF MATERIALS

All the chemicals were used as supplied by the manufacturer without further purification. All the salts with the exception of lithium sulphate were kept in an oven whose temperature was kept constant at $100^{\circ}C$.

I did not attempt to dry the lithium sulphate since it would have dehydrated easily.

The reagents used are listed in Table I.

TABLE I.

	Salt.	Supplier	Grade
1.	$NaBrO_3$	Fisher Scientific Co.	Certified reagent
2.	$KBrO_3$	Fisher Scientific Co.	Certified reagent
3.	$Li_2SO_4.H_2O$	Mallinckrodt Chemical Works	Analytical reagent
4.	$LiBrO_3$	City Chemical Corporation	Purified
5.	K_2SO_4	British Drug Houses Ltd.	Analar.

2. EXPERIMENTAL DETERMINATION OF SOLUBILITY

Both the Schreinemakers' method of wet residues and the synthetic complex method were used in the determination of the solubility curves.

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The apparatus used is shown in Figure XIX. A complex of known weights of each salt A and B and water was stirred for forty-eight hours in a constant temperature bath kept at 25.00 $\pm$ 0.01°C. The composition of the complex was calculated to weight percentages and plotted on the diagram.

The mixture was then allowed to settle while still maintained at 25°C and some of the clear liquid was filtered off, weighed, diluted with a known amount of water and then analysed. This analysis gave a point on the solubility curve.

For the analysis of the wet residue on clear liquid was filtered off leaving the solid phase as dry as possible. Some of the crystals sticking to the filter were scraped off into a weighing bottle, weighed, dissolved in a known volume of water and then analysed. This analysis gave another point on the triangular diagram.

These three points: the complex point, the solution point and the wet residue point must be in one straight line; if they are not then either there has been some mistake in the analysis or the system had not yet reached equilibrium when the analysis was carried out.

The line joining the solution point, the complex point and the wet residue point must pass through the true solid phase.

Figure XIX   Solubility Apparatus   29A

MERCURY SEAL STIRRING APPARATUS

GROUND GLASS JOINTS

FOR SUCTION APPARATUS WET RESIDUE ANALYSIS

← FRITTED GLASS FILTER
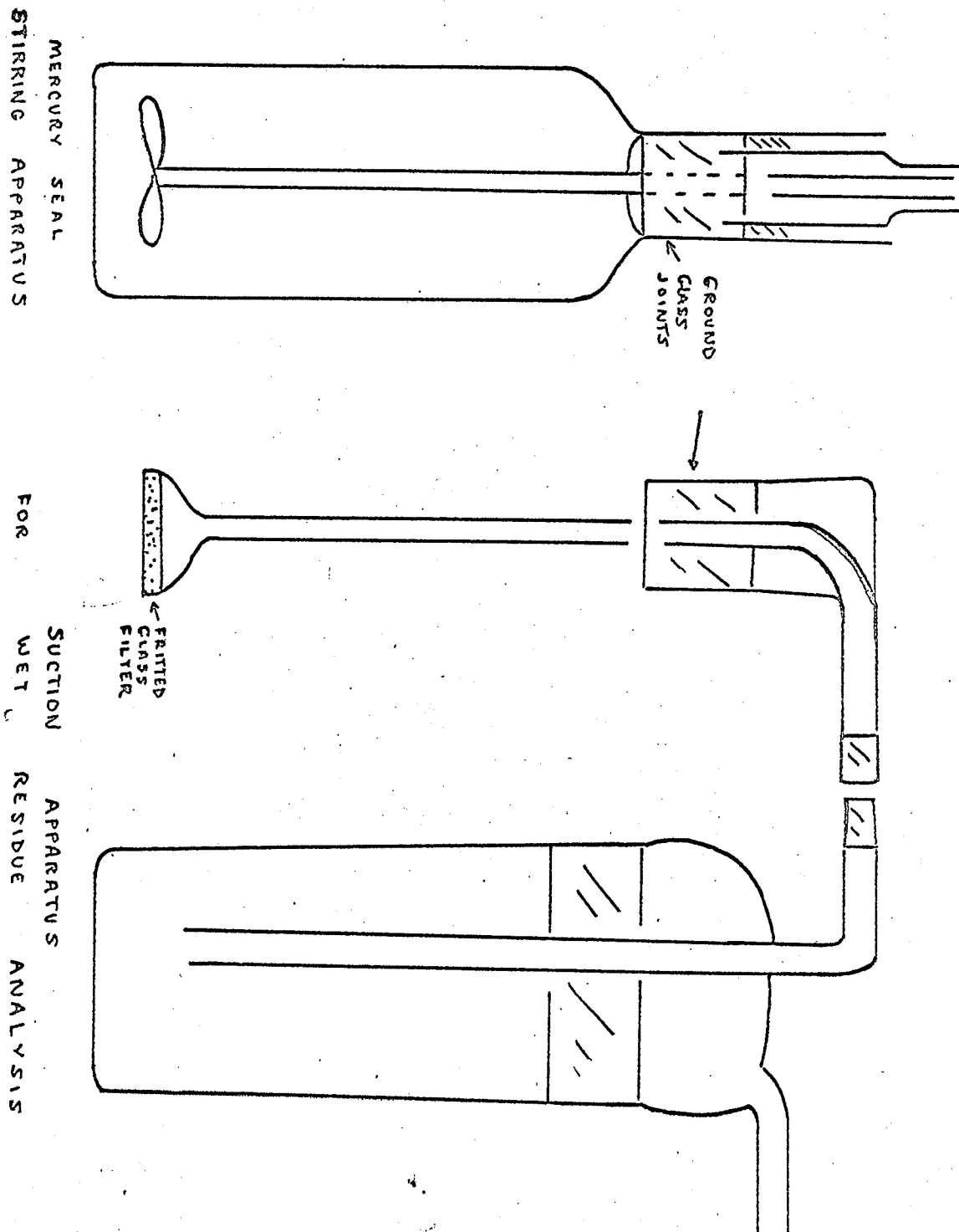
3. CHEMICAL ANALYSIS

The solutions made by diluting the weighed amount of
clear liquid in a known volume of water and by dissolving
the weighed amount of wet residue in a known volume of water
were analysed for each radical. The volumetric apparatus
used was initially standardised.

A. ESTIMATION OF ANIONS

In this case the bromate radical was estimated
iodometrically using the method adopted by Vogel (11) and
Kolthoff and Sandell (12).

I did not attempt to estimate the sulphate radical
by the barium sulphate precipitation method since this method
has been found by Campbell and Kartzmark (3) to be very un-
reliable in the presence of alkali ions.

In the estimation of the bromate radical 25 ml of the
dilute solution was treated with 2 grs of iodate-free potass-
ium iodide and 5 ml of 4N hydrochloric acid in a conical
flask, tightly corked and left standing for 2-3 minutes.
The liberated iodine was then titrated against standard
sodium thiosulphate solution using starch as indicator.

This method of estimating the bromate radical gave
very reliable results when the analysis was carried out
using known weights of lithium bromate. In an actual

standardisation experiment the following results were
obtained.

Wt.of LiBrO$_3$ (grs)	Vol.of Na$_2$SO$_3$ (ml)	Normality of thio	Wt. of LiBrO$_3$ found	% error
2.9710	33.05	0.1001N	2.9720	0.04
2.701	30.01	0.1001N	2.704	0.10

The applicability of the method of analysis is shown
by the low percentage error.

B. ESTIMATION OF CATIONS

Analysis of the phases for cations was made using
the flame photometer. The flame photometer is an instrument
designed for the rapid determination of the alkali and
alkaline earth metals in solution. It measures quantitatively
the light emitted by the various metals when atomized from
solution, fed to a propane burner and excited to spectral
emission in a flame. Because the intensity of light
emitted by each element depends upon the concentration of
atoms of the element in the flame at a given instant, a
measure of the light intensity produced makes possible the
quantitative determination of that element.

In Figure XX a diagram of the Perkin-Elmer (model 146)
flame photometer is shown. The liquid samples are intro-
duced into the atomizer where they are blown into the

PRISMS

ENTRANCE
SLIT

REED

BEAM
SPLITTER

MOVABLE
SLIT

FIXED
SLIT

PHOTOTUBES
RED

PHOTO-
TUBE

MAIN
AMPLIFIER

BLUE

COMPRESSED
AIR

DRAIN

FUEL

INTERNAL
STANDARD
AMPLIFIER

AMPLIFIER
FOR
UNKNOWN

SOLUTION

INTERNAL
STANDARD

COARSE FINE

OFF-ON

ELEMENT SELECTOR

METER

SIGHT TUBE
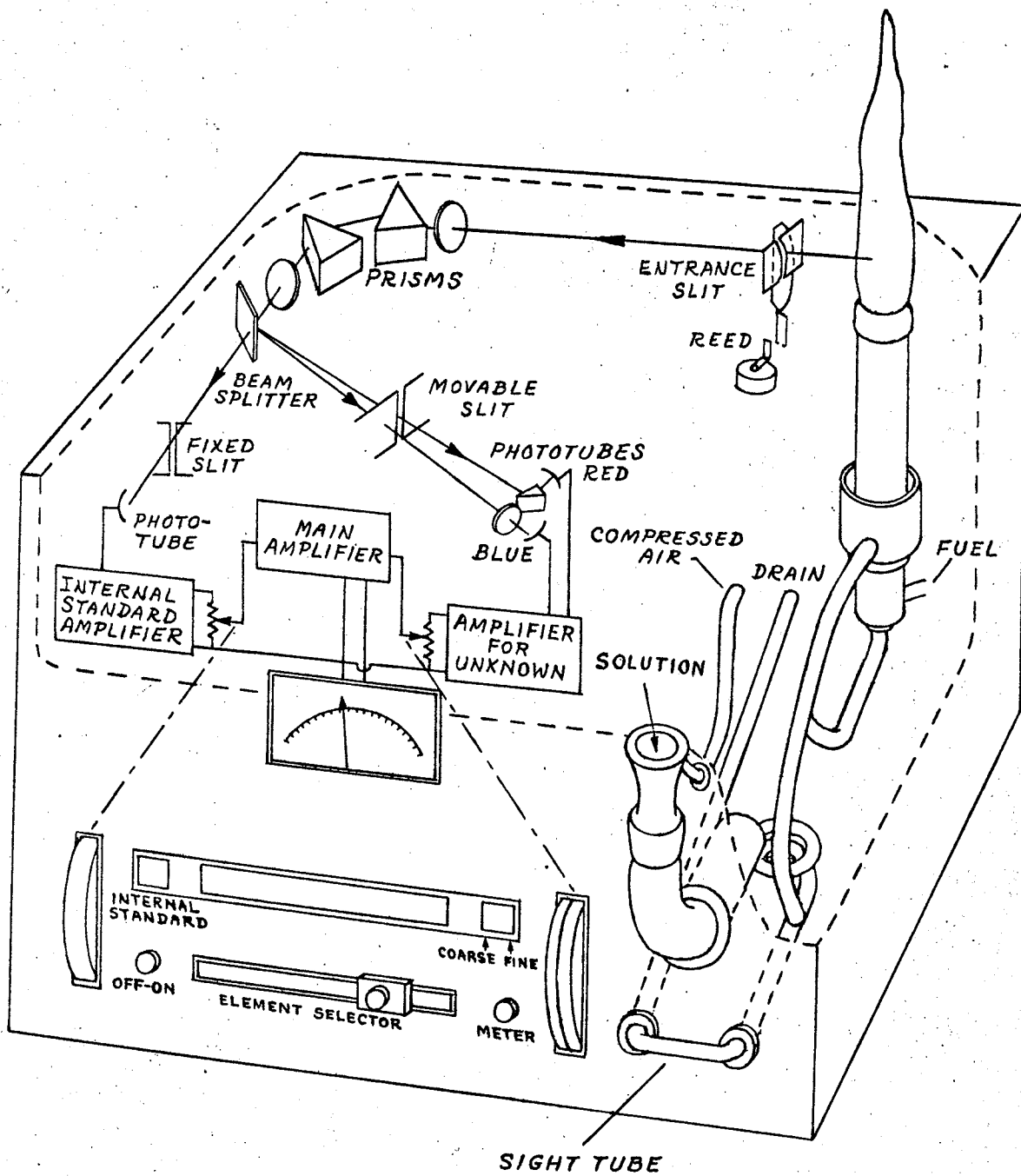
Fig. XX.   Flame Photometer, cutaway view

atomizer chamber by a stream of compressed air and thence into the base of the Meker-type burner. The atomizer is designed to retain the large liquid particles and to pass the fine liquid mist to the burner causing spectral emission by the following rapid steps:

1. The water evaporates leaving minute particles of salt.

2. At the elevated temperature of the flame, decomposition or chemical reaction may take place.

3. The salts or their decomposition products vaporise and may also dissociate into constituent atoms or radicals.

4. The vapours of the metal are then excited by the thermal energy of the flame.

The process of excitation results in the raising of an electron to a higher energy level followed by the loss of a discrete amount of energy in the form of radiation energy as the excited electron returns to a lower state.

The entrance slit allows a beam of light from the flame to fall upon a monochromator, where it is dispersed into a spectrum by a prism. Another slit is used to limit the bandwidth of radiation passed on to the phototube detectors. The phototube converts the selected wavelength to an electric current, which is amplified and indicated on

the meter.

Standard solutions for lithium, sodium and potassium were made from fused salts of these metals in concentrations of 10, 20, 30 etc., parts per million of the alkali metal. These were used to draw a calibration curve of intensity against concentration of ions from which the experimental solutions diluted to the proper range could be found graphically.

With the flame photometer it is advisable to use very dilute solutions because:

1. Flame emission tends to saturate at high concentrations.

2. Interference effects fall off markedly with dilution.

3. High concentrations of salts affect instrument operation by deposition, corrosion, burner or atomizer clogging or by introducing a memory effect from sample to sample.

The direct intensity method was used; this assumed that the atomizer delivery was constant, the portion of the sample nebulized remained the same and the flame characteristics did not vary for both the standard and experimental solutions. But these assumptions are not strictly valid and the accuracy obtained is around two per cent.

Relative interferences among the three alkali metals as well as the interferences due to sulphate and bromate in the solution are negligible.

4. EXAMPLE OF A CALCULATION

In a typical experiment for the system Li_2SO_4-$LiBrO_3$-H_2O the original complex was found to have the following weight percentages:

$$\text{Weight \% water} = 44.88$$
$$\text{Weight \% } Li_2SO_4 = 3.45$$
$$\text{Weight \% } LiBrO_3 = 51.67$$

The sodium thiosulphate solution was standardised using standard potassium iodate solution.

The normality of the sodium thiosulphate solution was found to be 0.1238N.

A. THE LIQUID PHASE

20.7719 grs of clear saturated solution were filtered off and diluted to 1 litre for the bromate analysis.

25 ml of the above solution were used for each titration.

It was found that 87.50 ml of standard (0.1238N) thiosulphate solution were required for neutralization of the liberated iodine.

But 1 ml of N - $Na_2S_2O_3$ = 0.0225 grs $LiBrO_3$

∴87.5 ml of 0.1238N-$Na_2S_2O_3$ = 0.0225x0.1138x87.5

= 0.2437 grs $LiBrO_3$

But this weight of $LiBrO_3$ is present in

$$\frac{20.7719}{40}$$ grs of solution, i.e. in

0.5193 grs of solution.

∴ weight % $LiBrO_3$ = $\frac{0.2437}{0.5193}$ x 100 = 46.93

% Li^+ due to 46.93% $LiBrO_3$ = 46.93 x$\frac{6.94}{134.86}$ = 2.405

Using the Flame photometer it was found that the solution contained 2.773 parts Li^+

∴ % Li^+ due to Li_2SO_4 = 2.773-2.405

= 0.368

And % Li_2SO_4 = 0.368 x $\frac{109.95}{13.88}$ = 2.915%

Therefore the solution point is:

Weight % $LiBrO_3$ = 46.93

Weight % Li_2SO_4 = 2.92

This point was plotted on the triangular diagram.

B. THE SOLID PHASE

Weight of wet residue taken = 1.0335 grs.

The solid was dissolved in 1 litre of water and analysed for lithium content using the flame photometer.

It was found that it contained 5.012 pts Li^+.

From the titration it was found that 25 ml of the above solution were neutralized by 7.10 ml of 0.1238N sodium thiosulphate solution.

$$\therefore \quad \text{Weight \% LiBrO}_3 = \frac{7.10 \times 0.0225 \times 0.1238 \times 100}{\frac{1.0335}{4}}$$

$$= 76.67$$

$$\text{\% Li}^+ \text{ due to LiBrO}_3 = 76.67 \times \frac{6.94}{134.86} = 3.946$$

$$\therefore \text{ \% Li}^+ \text{ due to Li}_2\text{SO}_4 = 5.012 - 3.946$$

$$= 1.066$$

$$\text{And \% Li}_2\text{SO}_4 = 1.066 \times \frac{109.95}{13.88}$$

$$= 8.44$$

This point (76.67% $LiBrO_3$ and 8.44% Li_2SO_4) was plotted on the triangular diagram.

EXPERIMENTAL RESULTS

The experimental results are collected in Table II, III and IV.

Table II lists the compositions of the original complex, saturated solution and wet residue for the system Li_2SO_4-$LiBrO_3$-H_2O.

Table III lists the compositions of the original complex, saturated solution and wet residue for the system K_2SO_4-$KBrO_3$-H_2O.

Table IV lists the compositions of the original complex, saturated solution and wet residue for the system $NaBrO_3$-$LiBrO_3$-H_2O.

The equilibrium diagrams are shown in Figures XXI, XXII and XXIII respectively.

Tables V, VI and VII give the X-ray powder data for $Li_2SO_4.H_2O$, $LiBrO_3$ (anhydrous) and $LiBrO_3.H_2O$ respectively.

Tables VIII and IX give the X-ray powder data for the wet residue at the two extremes of the solid solution region.

TABLE II. The System Li_2SO_4–$LiBrO_3$–H_2O at 25°C. The compositions are Given as Weight Percentages.

Original Complex		Saturated Solution		Wet Residue		Nature of Solid
Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	Phase
0	0	25.50	0	-	-	$Li_2SO_4 \cdot H_2O$
		0	65.64	-	-	$LiBrO_3 \cdot H_2O$
3.45	51.67	2.72	46.93	8.44	76.67	$LiBrO_3 H_2O + S.S$
5.52	49.08	2.68	46.84	27.91	59.51	$LiBrO_3 H_2O + S.S$
2.40	49.86	2.72	46.93	6.00	72.13	$LiBrO_3 H_2O + S.S$
16.93	45.87	2.72	46.82	35.01	45.10	$LiBrO_3 H_2O + S.S$
41.21	6.86	18.58	10.63	58.06	3.52	$Li_2SO_4 \cdot H_2O + S.S$
35.49	8.47	18.42	10.64	54.63	6.67	$Li_2SO_4 \cdot H_2O + S.S$
28.96	3.06	21.48	3.59	78.01	0.94	$Li_2SO_4 \cdot H_2O$
39.98	5.94	19.79	7.90	80.21	0.68	$Li_2SO_4 \cdot H_2O$
2.24	54.27	2.16	48.02	0.55	75.01	$LiBrO_3 \cdot H_2O$
0.85	59.02	1.00	53.01	0.56	70.04	$LiBrO_3 \cdot H_2O$
26.86	14.53	14.11	16.47	60.07	12.66	$S.S$

TABLE II CONTINUED

Original Complex		Saturated Solution		Wet Residue		Nature of Solid Phase
Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	
35.02	19.04	10.22	23.50	71.21	14.12	S.S
21.38	35.98	5.05	38.04	46.86	32.78	S.S
34.33	28.50	7.52	31.75	50.36	27.59	S.S
30.10	21.64	9.99	24.44	65.01	16.47	S.S
14.90	27.14	8.66	27.81	39.92	22.67	S.S

TABLE III. The System K_2SO_4–$KBrO_3$–H_2O at $25^{\circ}C$. The Compositions are Given as Weight Percentages.

Original Complex		Saturated Solution		Wet Residue		Nature of Solid Phase
K_2SO_4	$KBrO_3$	K_2SO_4	$KBrO_3$	K_2SO_4	$KBrO_3$	
35.10	1.204	10.05	1.78	68.30	0.560	K_2SO_4
36.20	2.52	9.79	3.44	80.04	0.780	K_2SO_4
-	0	10.62	0	-	-	K_2SO_4
0	-	0	7.41	-	-	$KBrO_3$
2.07	27.56	2.70	5.72	0.98	79.95	$KBrO_3$
4.01	29.98	5.25	5.00	1.00	83.01	$KBrO_3$
24.12	20.52	9.36	4.00	39.20	33.04	$KBrO_3$ + K_2SO_4
20.01	4.22	9.34	4.00	63.02	8.02	$KBrO_3$ + K_2SO_4
7.01	30.23	9.34	4.00	3.11	75.02	$KBrO_3$

TABLE IV. The System $NaBrO_3$–$LiBrO_3$–H_2O at 25°C. The compositions are given as weight percentages.

Original Complex		Saturated Solution		Wet Residue		Nature of Solid
$NaBrO_3$	$LiBrO_3$	$NaBrO_3$	$LiBrO_3$	$NaBrO_3$	$LiBrO_3$	Phase
⌐	0	28.43	0	—	—	$NaBrO_3$
0	⌐	0	65.64	—	—	$LiBrO_3 \cdot H_2O$
41.12	14.99	12.52	22.40	95.40	1.63	$NaBrO_3$
49.13	3.75	23.17	4.99	100.00	trace	$NaBrO_3$
30.09	34.13	3.69	47.18	92.52	3.79	$NaBrO_3$
1.48	67.36	1.21	53.91	0.464	72.60	$LiBrO_3 \cdot H_2O$
2.01	65.02	3.02	49.98	0.99	76.12	$LiBrO_3 \cdot H_2O$
4.12	61.52	3.02	49.90	4.99	75.04	$LiBrO_3H_2O+NaBrO_3$
10.52	56.52	3.02	49.97	19.24	63.22	$NaBrO_3+LiBrO_3H_2O$
19.12	49.84	3.02	49.94	35.03	50.24	$LiBrO_3H_2O+NaBrO_3$
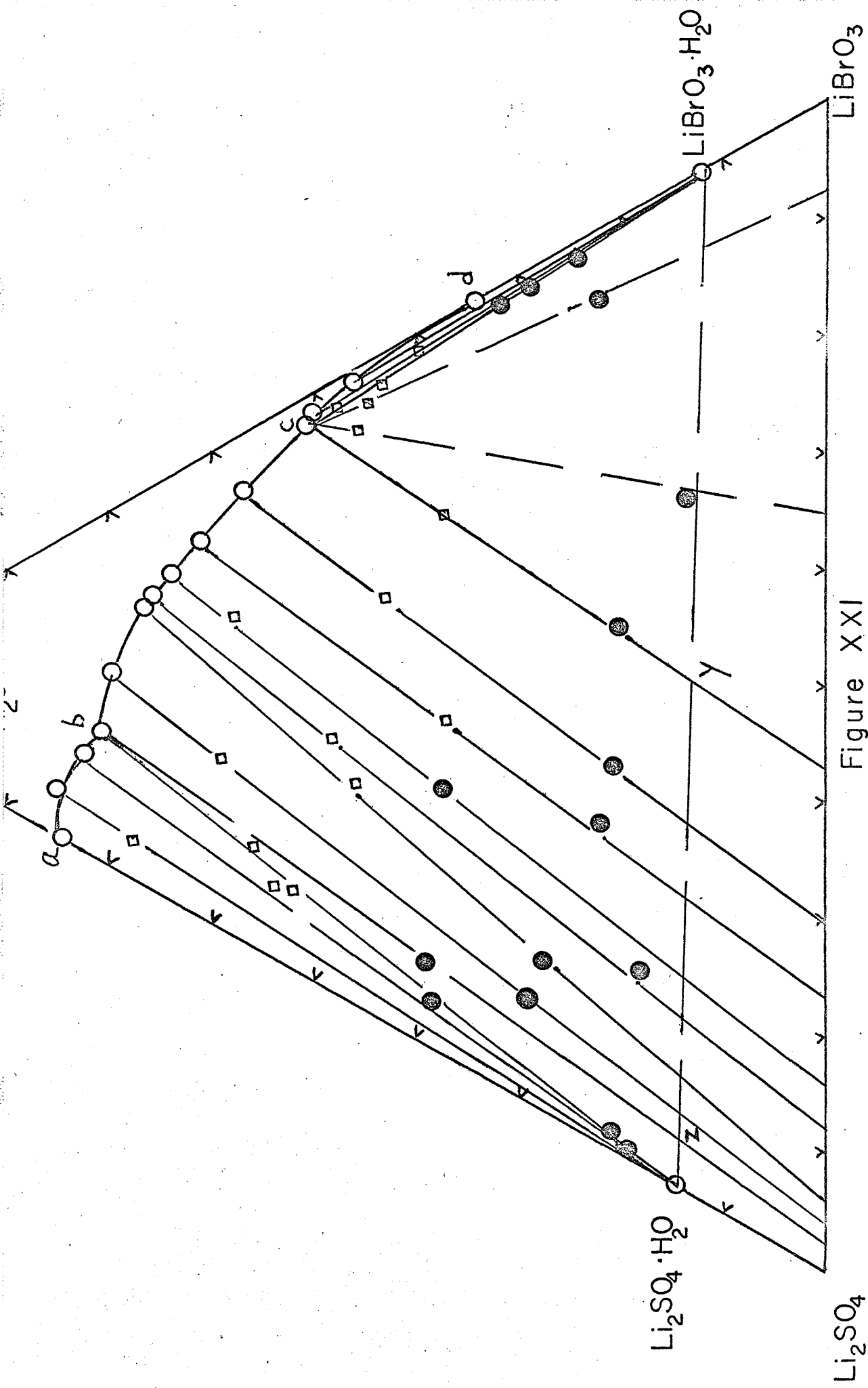
Figure XXI

The System Lithium Sulphate–Lithium Bromate–Water at 25°C

Figure XXII

KBrO₃

K₂SO₄
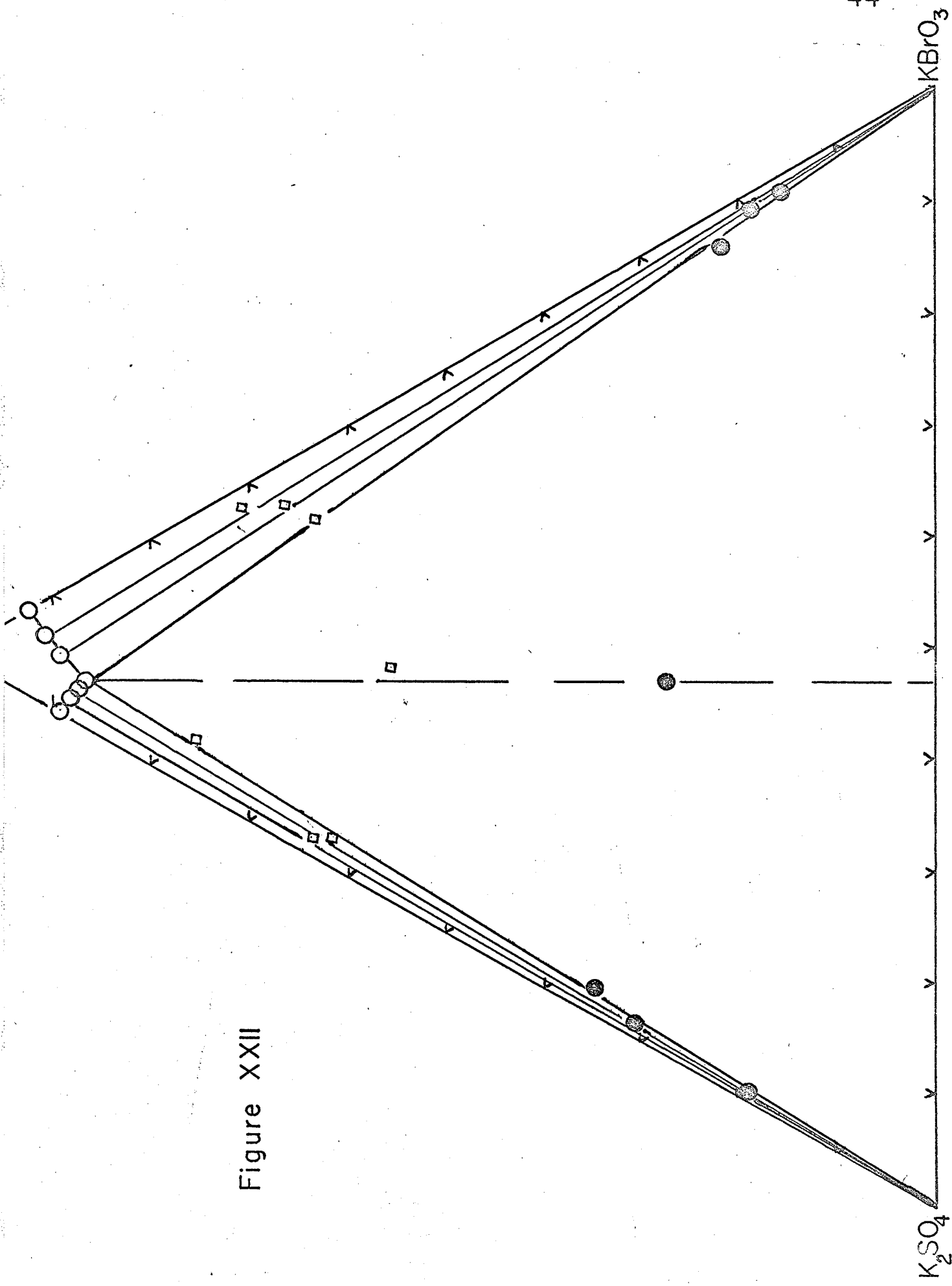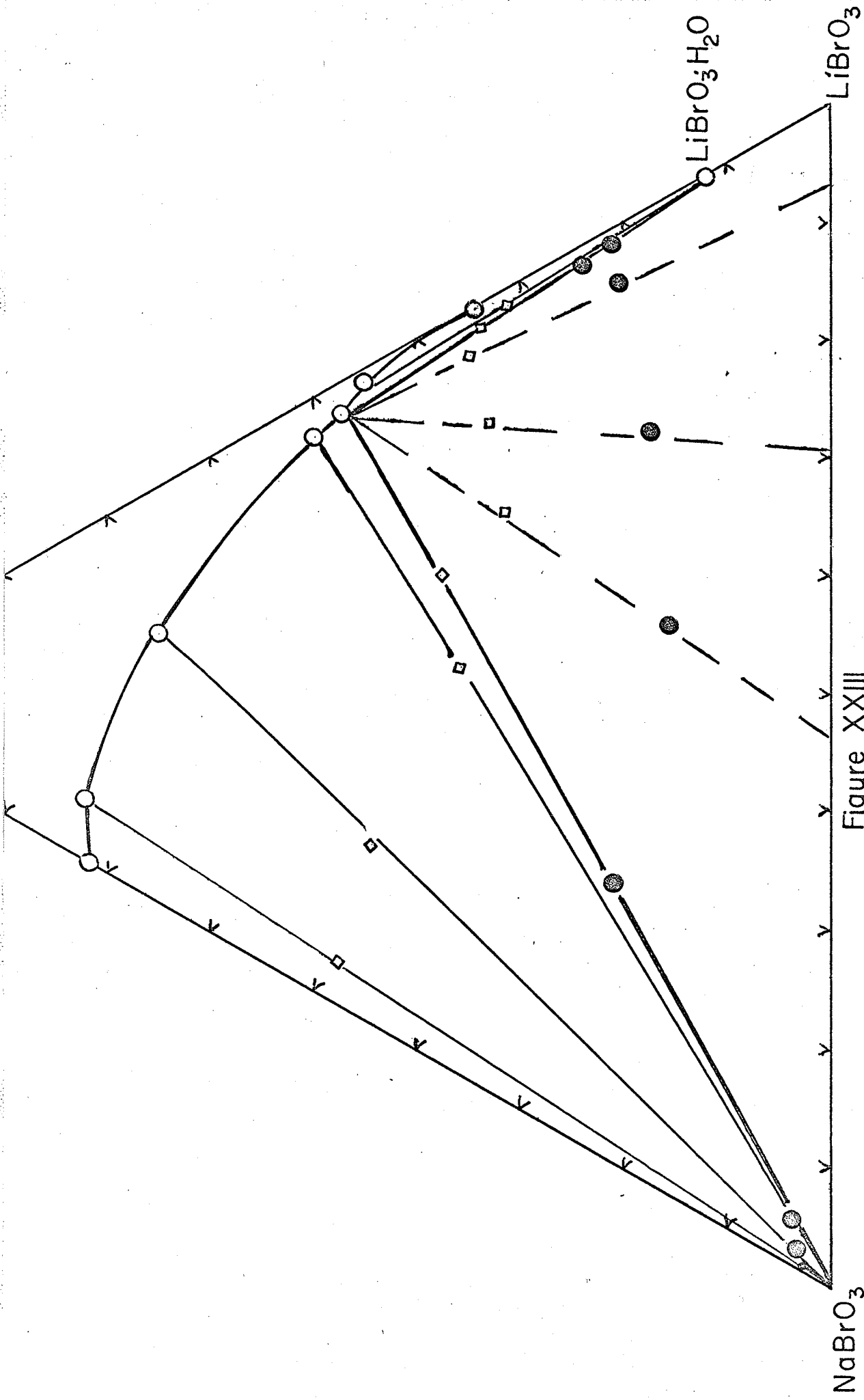
Figure XXIII

The System Sodium Bromate – Lithium Bromate – Water at 25°C.

TABLE V. X-ray Powder Data for Lithium
Sulphate Monohydrate

Radiation: Copper $K\alpha$	Filter:Nickel	
	Literature	Measured
I/I_0	$d\mathring{A}$ (14)	$d\mathring{A}$
4	7.8	8.0
10	5.1	5.1
10	4.12	4.13
9	3.84	3.84
4	3.68	3.68
9	3.54	3.55
7	3.02	3.03
7	2.93	2.95
6	2.72	2.72
3	2.65	2.65
5	2.41	2.40
2	2.33	2.34
2	2.28	2.29
3	2.18	2.20
2	2.04	2.06
2	1.91	1.92
2	1.81	1.81
2	1.72	1.72
2	1.70	1.70
2	1.59	1.59
2	1.55	1.55
2	1.49	
2	1.38	

TABLE VI.   X-ray Powder Data for Lithium
Bromate Anhydrous.

Radiation: Copper $K\alpha$ I/I_0	Filter:Nickel	
	Literature dÅ (13)	Measured dÅ
<1	4.26	
3	3.92	
10	3.86	3.86
3	3.47	3.47
2	2.99	2.99
3	2.796	2.796
4	2.754	
4	2.527	2.527
1	2.448	
2	2.376	2.376
<1	2.327	2.327
<1	2.23	2.230
<1	2.153	
<1	2.124	2.124
<1	1.961	1.961
3	1.930	1.930
<1	1.875	
<1	1.856	
<1	1.836	
<1	1.807	1.807
1	1.749	
1	1.733	1.733
3	1.678	1.678
<1	1.640	1.640
<1	1.622	1.622
<1	1.588	
<1	1.551	1.551
<1	1.514	
1	1.500	1.501
<1	1.472	

TABLE VII. X-ray Powder Data for Lithium
Bromate Monohydrate $LiBrO_3 \cdot H_2O$

Radiation:Copper Kα I/I_0	Filter:Nickel $d\overset{\circ}{A}$ (measured)
8	7.25
7	5.52
7	5.31
2	4.87
2	4.406
2	4.135
10	3.837
5	3.693
5	3.441
5	3.280
3	3.164
5	3.083
9	2.919
3	2.848
2	2.720
8	2.644
4	2.388
2	2.247
2	2.205
2	2.149
2	2.122
2	1.997
2	1.933
2	1.880
2	1.851
2	1.809
2	1.784
2	1.750
2	1.713
2	1.687
2	1.647
2	1.622
2	1.589
2	1.544
2	1.501

TABLE VII CONTINUED

Radiation:Copper Kα I/I$_0$	Filter:Nickel d$\overset{\circ}{A}$ (measured)
2	1.464
2	1.434
2	1.394
2	1.355
2	1.328
2	1.294
2	1.264
2	1.250
2	1.236
2	1.218
2	1.200
2	1.182

TABLE VIII. X-ray Powder Data for the
Wet Residue at One Extreme
of the Solid Solution Region

Radiation:Copper Kα I/I$_o$	Filter:Nickel dÅ (measured)
4	8.2
10	5.15
10	4.20
10	3.88
5	3.70
8	3.60
8	3.05
8	2.98
6	2.72
3	2.69
5	2.48
2	2.36
2	2.32
2	2.22
2	2.08
2	2.00
2	1.86
2	1.76

TABLE IX. X-ray Powder Data for the
Wet Residue at the Other
Extreme of the Solid-
Solution Region

Radiation:Copper -Kα	Filter:Nickel
I/I_o	d$\overset{\circ}{A}$
4	8.2
10	5.20
10	4.24
10	3.88
5	3.72
8	3.60
8	3.05
8	2.98
6	2.72
3	2.69
5	2.48
2	2.36
2	2.32
2	2.22
2	2.08
2	2.00
2	1.86
2	1.76

DISCUSSION OF RESULTS

The equilibrium diagram for the system Li_2SO_4-$LiBrO_3$-H_2O at 25°C shown in Figure XX has many interesting features.

There are two invariant triangles: $Li_2SO_4 \cdot H_2O$-b-z and C-Y-$LiBrO_3 \cdot H_2O$. The compositions of the saturated solution, original complex and wet residue for the two invariant points b and c are given below in Tables X and XI respectively.

TABLE X

Original Complex		Saturated Solution		Wet Residue	
Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$
41.21	6.86	18.58	10.63	58.06	3.52
35.49	8.47	18.42	10.64	54.63	6.67
35.02	11.01	18.54	10.62	54.21	11.14
45.32	9.22	18.48	10.59	62.34	7.99

TABLE XI

Original Complex		Saturated Solution		Wet Residue	
Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$	Li_2SO_4	$LiBrO_3$
3.45	51.67	2.72	46.93	8.44	76.67
5.52	49.08	2.68	46.84	27.91	59.51
2.40	49.86	2.72	46.93	6.00	72.13
16.93	45.87	2.72	46.92	35.01	45.10

In the first triangle the three phases are: lithium sulphate monohydrate, solution of composition b and solid solution of composition z. In the other triangle the three phases are lithium bromate monohydrate, solution of composition c and solid solution of composition y.

The solid phases stable in the ternary system at 25°C are: lithium sulphate monohydrate for solutions between points a and b; solid solution for solutions b-c and lithium

bromate monohydrate for solution c-d.

That the phase in equilibrium with solutions on the curve b-c in Figure XX is a solid solution – a solid phase of varying composition – is seen from the behaviour of the tie lines in that region. The existence of the solid solution was confirmed by X-ray analysis of the wet residues. Tables VIII and IX give the X-ray powder data of the wet residues at the two extremes of the solid solution region. Comparing the data from Tables VIII and IX with those from Tables V and VII it can be seen that no new lines have appeared in the X-ray pattern of the wet residues – the pattern is identical with that of lithium sulphate monohydrate except that the 'd' values have become slightly bigger due to the presence of lithium bromate monohydrate as part of its lattices.

It should be pointed out at this stage that the single seriesof solid solution exists only between the points Y and Z. From Z to $Li_2SO_4.H_2O$ there is heterogeneity and any system inside the invariant triangle $Li_2SO_4.H_2O$-b-z will break up into $Li_2SO_4.H_2O$, liquid of composition b and solid solution of composition Z.

Algebraic extrapolation of the tie-lines gives the following limits in percentage by weight of $LiBrO_3.H_2O$ for the solid solution at $25^{\circ}C$: 2.2 per cent to 45.2 per cent. Because of the very different crystal structures of $LiBrO_3$.

H_2O and $Li_2SO_4.H_2O$ ($LiBrO_3.H_2O$ is rhombic and $Li_2SO_4.H_2O$ is monoclinic) it was very surprising that there should be any solid solution at all.

The analysis of the solutions and wet residues which lie in the region of the solid solution were carefully verified after the complexes had been stirred for at least two days. In a few cases the complexes were stirred for one week to ensure true equilibrium before analysing the solution and wet residue. Hence there was no doubt about the existence of the solid solution. There was no evidence of the existence of a compound; there was no tendency for the tie lines to intersect.

The equilibrium diagram for the system Li_2SO_4-$LiBrO_3$-H_2O at $25^{\circ}C$ as given in Figure XX is difficult to explain. Only one series of solid solution is obtained between Z and Y; no compound has been found to exist using X-ray analysis. Stoichoimetrically however two compounds could exist in the region of the solid solution, i.e. between Z and Y; a compound of the form $(8Li_2SO_4.LiBrO_3)8H_2O$ having the following weight percentages: Li_2SO_4 75.74%, $LiBrO_3$ 11.72% and H_2O 12.54 could exist at Z and a compound of the form $(2Li_2SO_4.LiBrO_3)3H_2O$ having the following weight percentages: Li_2SO_4 53.80%, $LiBrO_3$ 32.99% and H_2O 13.21% could exist near the other extreme of the solid solution region. But as has been said earlier X-ray analysis does not indicate the

existence of any compound.

The system $Li_2SO_4-LiBrO_3-H_2O$ at $25^{\circ}C$ is very similar to the system $Li2SO_4-Na_2SO_4-H_2O$ studied by Campbell and Kartzmark (3). The system $Li_2SO_4-Na_2SO_4-H_2O$ at $25^{\circ}C$ is represented by Figure XXIV.
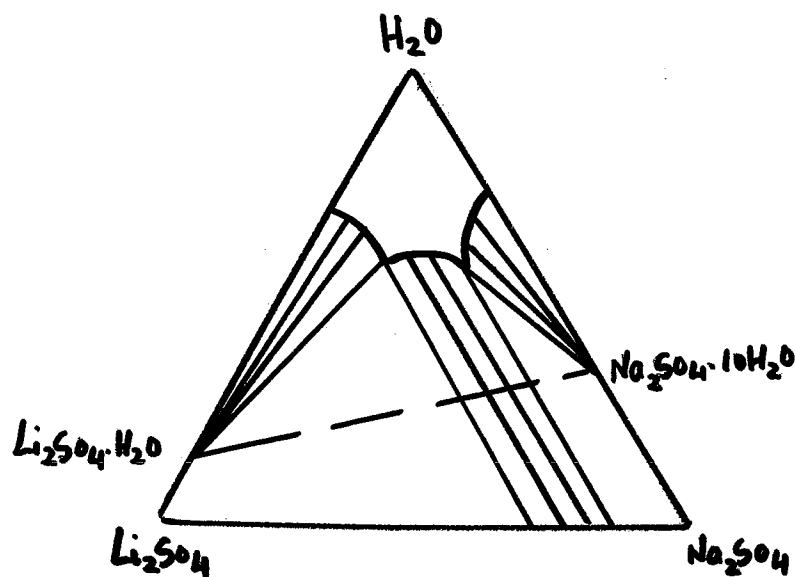
FIGURE XXIV

The System $Li_2SO_4-Na_2SO_4-H_2O$ at $25^{\circ}C$.

Here again there is only one series of solid solution and no compound has been found to exist at $25^{\circ}C$. Stoichoi-metrically however a compound of the form $Li_2SO_4 \cdot Na_2SO_4$ can

exist in the region of the solid solution. This compound $Li_2SO_4 \cdot Na_2SO_4$ has indeed been found to exist at and above $39.5^{\circ}C$.

The system $Na_2SO_4-NaBrO_3-H_2O$ at $45^{\circ}C$ studied by J. E. Ricci (1) is also very similar to the above two systems. The equilibrium diagram for this system is shown in Figure XXV.
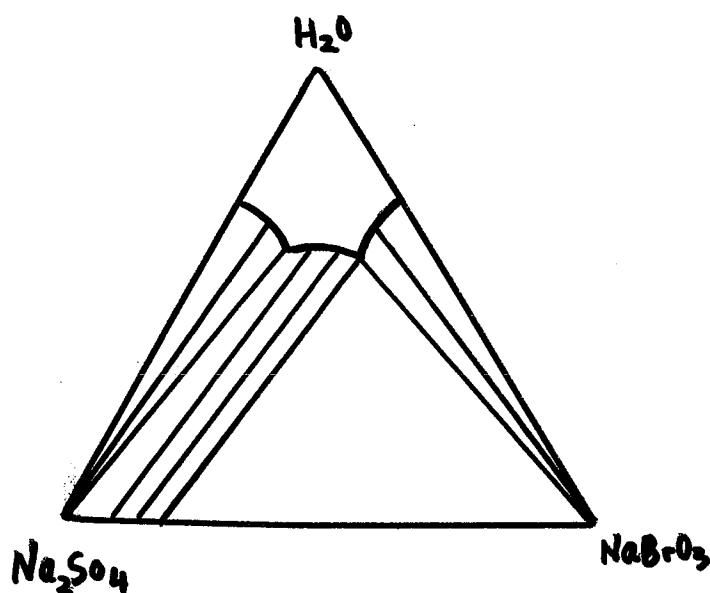

FIGURE XXV

The System $Na_2SO_4-NaBrO_3-H_2O$ at $45^{\circ}C$.

Only one series of solid solution has been found to exist extending from 2.5 per cent to 17 per cent $NaBrO_3$.

There is no evidence of compound formation and/no hypothetical

compound could be 'pinned' down in the region of the solid

solution.

In all these systems viz Li_2SO_4-$LiBrO_3$-H_2O at $25^{\circ}C$,

Li_2SO_4-Na_2SO_4-H_2O at $25^{\circ}C$ and Na_2SO_4-$NaBrO_3$-H_2O at $45^{\circ}C$

the following sequence of solid phases are observed on an

isotherm: first a pure component, second an anhydrous solid

solution (hydrated in the first system) and third the other

pure component. This means that in the binary systems

Li_2SO_4-$LiBrO_3$, Li_2SO_4-Na_2SO_4 and Na_2SO_4-$NaBrO_3$ at those

temperatures at which the solid solutions are observed

the miscibility is incomplete and yet there is not a pair

of conjugate solid solutions but a single limited phase

of solid solution. As has been mentioned in the introduc-

tion such a binary system does not belong to any of the five

types of binary systems forming solid solutions in the

Roozeboom classification. Three of the five types are con-

cerned with complete miscibility of the solid components.

The other two types refer to systems in which the miscibility

is incomplete and in which there are always two series of

solid solutions (conjugate solid solutions). In other

words it is assumed that if the mutual solubility is not

unlimited solid solutions always exist in conjugate pairs.

Experimentally however it has now been proved that

the last statement is not true (cf the Introduction). It

is quite possible to have limited miscibility but with only one series of solid solution. Thermodynamically also it has been proved that a pure component can coexist with a solid solution. Hence what has been called the sixth type of solid solution by J. E. Ricci (1) is not impossible.

The main difference between the system Na_2SO_4-$NaBrO_3$-H_2O and the systems Li_2SO_4-$LiBrO_3$-H_2O and Li_2SO_4-Na_2SO_4-H_2O lies in the fact that in the latter systems a hypothetical complex exists in the region of the solid solution but in the system Na_2SO_4-$NaBrO_3$-H_2O no complex could be formulated. In the system Li_2SO_4-Na_2SO_4-H_2O the existence of a complex of the form Li_2SO_4-Na_2SO_4 was proved at 39.5^oC. In the system Li_2SO_4-$LiBrO_3$-H_2O at 25^oC which I studied two complexes of the form $(2Li_2SO_4.LiBrO_3)3H_2O$ and $(8Li_2SO_4.LiBrO_3)8H_2O$ could exist in the region of the solid solution but their existence could not be confirmed by X-ray analysis. The X-ray diffraction patterns of the wet residues do not indicate the existence of such complexes - they indicate the existence of a solid solution.

The X-ray diffraction patterns of some of the wet residues lying in the region of the solid solution were taken and the results for the wet residues at the two extremes of the solid solution region are given in Tables VIII and IX. The patterns are identical with that of lithium sulphate monohydrate except that the 'd' values are slightly bigger.

Such a result is unusual, i.e. since no solid solution occurs in the pure components it would be expected that the lattice of the solid solution region would be different from that of either component. It became of interest to ascertain the analogous behaviour in the Li_2SO_4-Na_2SO_4-H_2O system.

For this reason the X-ray picture of a wet residue lying in the region of the solid solution for the system Li_2SO_4-Na_2SO_4-H_2O at $25^{\circ}C$ (3) was taken.

The pattern obtained was that of Na_2SO_4; there were no new lines to indicate the existence of a compound. That was in agreement with my results; I did not obtain any new lines in the X-ray patterns of the wet residues lying in the solid solution region.

One point which is common to all the three systems mentioned earlier viz Li_2SO_4-$LiBrO_3$-H_2O, Li_2SO_4-Na_2SO_4-H_2O and Na_2SO_4-$NaBrO_3$-H_2O is that there is no solid solution of Li_2SO_4 in $LiBrO_3$, Na_2SO_4 in $NaBrO_3$ while there is solid solution of $LiBrO_3$ in Li_2SO_4, Li_2SO_4 in Na_2SO_4 and $NaBrO_3$ in Na_2SO_4.

I find it difficult to explain the fact that one of the components can have the other component as part of its lattice but the reverse does not happen.

Another perplexing point is why $LiBrO_3$.H_2O should dissolve in Li_2SO_4.H_2O only when the concentration of

$LiBrO_3 \cdot H_2O$ is between 2.2 per cent and 45.0 per cent. Why does not $Li_2SO_4 \cdot H_2O$ dissolve smaller amounts of $LiBrO_3 \cdot H_2O$? I am completely certain of the fact but am unable to offer an explanation.

It would not have been very difficult to explain the existence of the solid solution if it were a continuous one starting from 0 per cent $LiBrO_3 \cdot H_2O$. The same difficulty arises in the system $Na_2SO_4 - NaBrO_3 \cdot H_2O$ at $45^\circ C(1)$ and in the system $Li_2SO_4 - Na_2SO_4 - H_2O$ at $25^\circ C$ (3).

That lithium bromate exists as a monohydrate was shown by I.N. Averko Antonowich (10). He determined the transition temperature for the reaction $LiBrO_3 \cdot H_2O \rightleftharpoons LiBrO_3 + H_2O$ and found it to be $52.0^\circ C$.

Burns (13) using a hot X-ray camera obtained the X-ray pattern of lithium bromate at $52^\circ C$. His results are given in column I of Table VI. I used the anhydrous powder sealed in a capillary tube for the X-ray analysis. My results are given in column II of Table VI.

I also determined the X-ray pattern of lithium bromate monohydrate. The results are given in Table VII. To be quite certain that I had the monohydrate, the anhydrous powder was kept in contact with water for a week. After that period of time the crystals were dried in between filter papers and an X-ray picture was taken. Comparison of Tables VI and VII will show that the two substances are quite

different. While $LiBrO_3$ has its strongest line at $d = 3.86\text{Å}$, $LiBrO_3 \cdot H_2O$ has strong lines at $d = 3.83\text{Å}$ and $d = 2.92\text{Å}$ and two other moderately strong lines at $d = 7.25\text{Å}$ and $d = 2.38\text{Å}$. The X-ray powder data of the two substances are given on pages 47 and 48.

The system K_2SO_4-$KBrO_3$-H_2O represented by Figure XXII has only one invariant point and the invariant liquid has the following composition 9.34 per cent K_2SO_4 and 4.00 per cent $KBrO_3$.

The system $NaBrO_3$-$LiBrO_3$-H_2O represented by Figure XXIII also has only one invariant point and the invariant liquid has the following composition: 3.02 per cent $NaBrO_3$ and 49.96 per cent $LiBrO_3$.

CONCLUSIONS

1. The equilibrium diagrams for the ternary systems Li_2SO_4-$LiBrO_3$-H_2O, K_2SO_4-$KBrO_3$-H_2O and $NaBrO_3$-$LiBrO_3$-H_2O have been determined at 25°C.

2. The existence of a monohydrate of lithium bromate has been proven and its X-ray powder data have been determined.

3. The system Li_2SO_4-$LiBrO_3$-H_2O at 25°C shows extensive solid solubility of $LiBrO_3.H_2O$ in $Li_2SO_4.H_2O$.

4. The system Li_2SO_4-$LiBrO_3$-H_2O at 25°C seems to belong to the 'sixth type' of solid solution formation mentioned by J. E. Ricci (1).

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