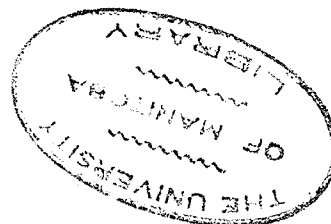EQUILIBRIUM STUDIES IN THE SYSTEM
LITHIUM NITRATE - ETHANOL - WATER

by

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A Thesis submitted to the Faculty
of Graduate Studies and Research
of The University of Manitoba in
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ABSTRACT

The system lithium nitrate - water was investigated by thermal analysis. The only hydrate found was the trihydrate; no evidence of the hemihydrate claimed by Donnan and Burt was found by thermal analysis or by x-ray powder diffraction studies. The x-ray powder diffraction pattern of lithium nitrate trihydrate was determined.

Thermal analysis was also applied to the system ethanol - water, giving results in general agreement with previous work, but low temperature x-ray powder diffraction photographs gave the first definite evidence for the existence of a solid hydrate of ethanol. The construction of the low temperature camera is described.

The system lithium nitrate - ethanol was studied at low salt concentrations by thermal analysis and at higher concentrations by solubility determinations. An important intermediate range could not be investigated because of high viscosity and supercooling. No alcoholates were found.

Freezing points of lithium nitrate in the solvents 27.2, 42.0, 49.7, 66.4, and 78.2 weight percent ethanol in water were determined, as well as freezing points of lithium nitrate trihydrate in ethanol. No definite evidence of a ternary compound was found, but some inconclusive indications of one were obtained in solvents of 66.4 and 78.2 weight percent ethanol. Data from the above were used to plot isothermal solubility diagrams for the ternary system at 25°C, 15°C, 10°C, 0°C, -15°C, -35°C, and -60°C.

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INTRODUCTION

Interest in the phase study of the system lithium nitrate – ethanol – water arose from the results of conductance studies of lithium nitrate in ethanol and in ethanol – water mixtures carried out by Campbell and Debus (1). In applying the Stokes – Wishaw equation to their results, these authors found that the value of the constant term $\overset{o}{a}$, the so-called "distance of closest approach of the ions," increased considerably as the ethanol content of the solutions increased. A rather large change in $\overset{o}{a}$ was found in the region between thirty and seventy weight percent ethanol. This fact was explained on the assumption that the solvation sheath of the lithium ions changed progressively from water to ethanol with most of the change taking place in this concentration range.

It is generally admitted that the lithium ion in aqueous solution is very strongly hydrated, and an indication of the strength of this hydration may be given by the frequency with which solid hydrates of lithium salts are formed. Lithium nitrate itself is well-known to form a trihydrate. It was thus of interest to find out whether lithium nitrate forms a solid alcoholate analogous to its hydrate and, if so, whether the water was replaced all at once or in a step-wise fashion, leading to mixed hydrate – alcoholates. The

existence of solid alcoholates would imply an appreciable attraction between the lithium ion and the ethanol molecules.

The system lithium nitrate - ethanol - water involves the three binary systems lithium nitrate - water, ethanol - water, and lithium nitrate - ethanol. Previous work on the first two of these binaries was not entirely satisfactory. The system lithium nitrate - water had received only one comprehensive study, that by Donnan and Burt (2). These authors reported a hemihydrate that could not be found by Campbell and Kartzmark (3). The second system, ethanol - water, also involved considerable uncertainty. Although some evidence for the existence of solid hydrates of ethanol had been put forward, no definite proof had been forthcoming. It was thought advisable, therefore, to repeat the investigation of these systems as well as to study the remaining binary system and the ternary one. Nothing was known about the latter two below 25°C.

Most of the investigations in this study were made by the method of thermal analysis, although some isothermal solubility determinations were carried out. X-ray diffraction studies of some of the solid phases were also made.

THEORETICAL CONSIDERATIONS

A. The Phase Rule

The phase rule as developed by Gibbs (4) is
commonly expressed by the relation

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

Here, F represents the number of degrees of freedom, or
the variance, of the system -- i.e. the number of variables
that must be specified to define the system completely.
C stands for the minimum number of components required to
give the composition of the system, and P represents the
number of phases present.

In general, the degrees of freedom involve the pres-
sure, temperature, and concentration of the system. For
condensed systems the effect of pressure is usually small,
so that such cases may be studied under atmospheric
conditions assuming the pressure, and hence one degree of
freedom, to be fixed.

B. Types of Systems

This discussion will deal with only two and three
component systems involving simple liquid - solid equilibria.
These lead to freezing point or solubility diagrams.

The freezing point of any substance is in most instances
lowered when a second substance is dissolved in it.

Further, rather than freezing at a fixed temperature as
does a pure substance, a range of temperature is observed
in which a solid is in equilibrium with liquid solution.
A freezing point or solubility curve indicates the composi-
tion of solution in equilibrium with solid phase as a
function of temperature.   Since this applies to both
components of a binary system, it follows that at the
intersection of the two freezing point curves there must
exist a point where two solids are in equilibrium with
solution, and this point is the lowest temperature at which
liquid can exist.   Such a point is referred to as a
eutectic.   Although it is evident that a solution having
the eutectic composition must freeze at a fixed temperature,
this fact is without significance in regard to interactions
between the components.   If a stable compound is formed
between the two substances an increase in the freezing point
curve must occur after a eutectic is reached.

We have the freezing point diagrams 'a' and 'b' of
Figure 1, which show a plot of freezing point against
composition for the case of a simple eutectic and a con-
gruently melting compound respectively.   A third simple
case exists, shown in Figure 1 'c'.   If a solid compound
forms which decomposes below its melting point (an incon-
gruently melting compound) we have a peritectic point

(also called meritectic point) P on the diagram.   At the
peritectic temperature the compound decomposes to give
solution and solid component B.
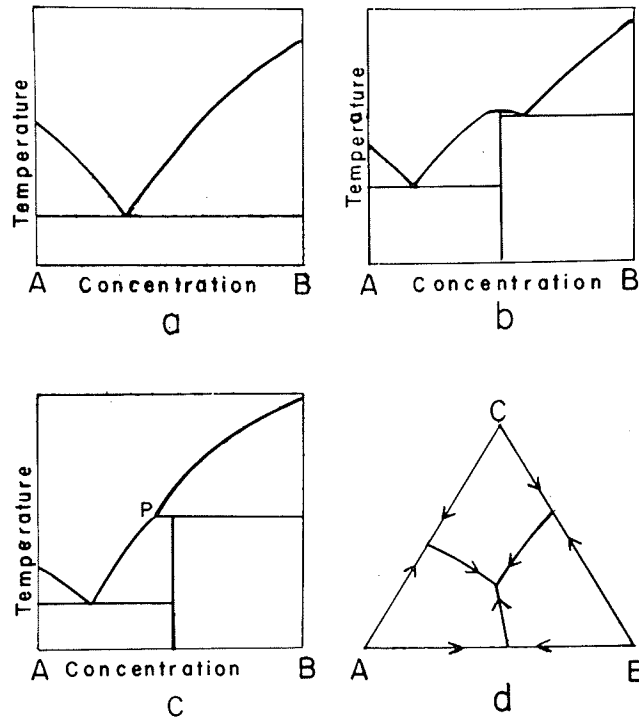
Typical Phase Diagrams
Figure 1

From the phase rule it may be seen that when three
phases are present, as at a eutectic or peritectic point,
the variance is zero (assuming fixed pressure).   Such

a point is referred to as an invariant point. When two
phases are in equilibrium, as along the freezing point
curve, there is one variable not fixed; either tempera-
ture or concentration may be chosen arbitrarily and the
other will then be determined.

Three component systems are completely analogous,
but an additional concentration variable is involved.
This factor makes graphical representation difficult if
we wish to show the effect of temperature. Of the
several methods that have been proposed, the one most
commonly employed involves plotting concentration on an
equilateral triangle. Each apex represents a pure
component, and compositions are plotted parallel to the
sides. Temperature may be represented on an axis per-
pendicular to the triangle, giving a solid model. For
planar representation, the temperature variation may be
projected onto the triangular base. Figure 1 'd' shows
the simplest projection diagram for a system of which the
three components are A, B, and C. The binary systems
involve only simple eutectics and no ternary compounds
form. The arrows indicate the direction of decreasing
temperature. Alternatively, a series of isothermal lines
may be plotted on the one triangle to show the effect of
temperature. From the phase rule it is clear that with

pressure fixed, four phases must be in equilibrium for
invariance, as at a ternary eutectic point.

C. Methods of Determining Freezing Point Diagrams Used in
this Investigation:

The two methods used in this investigation for the
determination of freezing point diagrams were thermal
analysis of solutions of known concentration, and iso-
thermal solubility measurements.   These methods have
been most widely used in work of this type.   The former
lends itself most readily to two component systems,
although its application to ternary systems is possible.
Under conditions where supercooling is pronounced, it is
less accurate than the method of solubility measurements,
but this is somewhat offset by its simplicity and speed,
particularly at temperatures far removed from room.
In addition, supercooling can often be eliminated by
inoculating the solution with a crystal of the solid
phase when the temperature reaches the freezing point.

Thermal analysis involves cooling a solution and
measuring the fall of temperature with time.   Normally,
for a binary system, a plot of temperature as ordinate
against time as abscissa gives an exponentially
decreasing curve according to Newton's law of cooling.
This shows a more or less sharp change in slope at the

temperature at which crystals first appear, followed by a
horizontal at an invariant point provided a suitable rate
of cooling is used.   Figure 2 shows typical cooling
curves, 'a' idealized and 'b' showing supercooling.
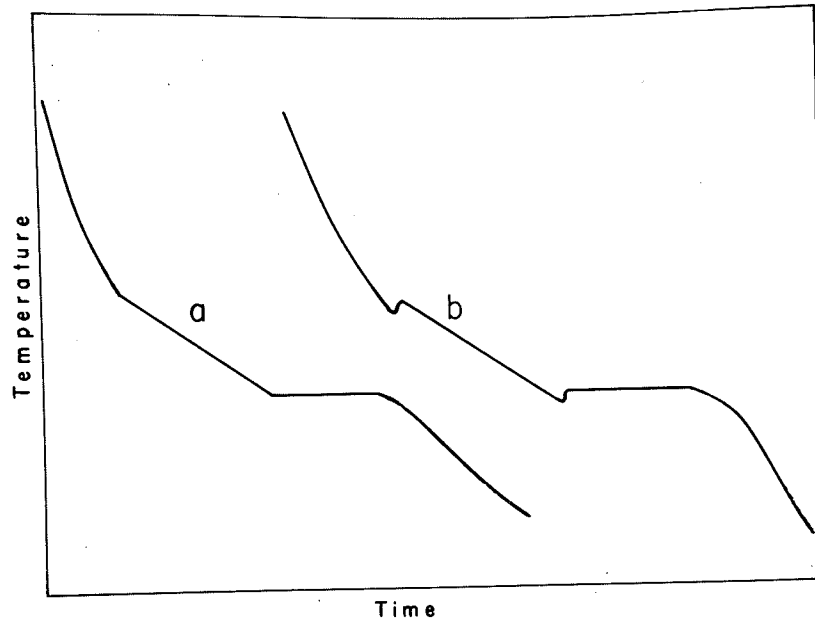
Typical Cooling Curves

Figure 2

When supercooling is encountered, the cooling curve
goes below the true freezing point, then rises again as
crystals deposit and heat is evolved.   At an invariant
point the curve will rise to the true temperature of this
point, and it will normally show a horizontal here.   If
the freezing point is not an invariant, the cooling curve

will not rise to the proper temperature of this point,
but to some lower temperature whose exact value will
depend on the degree of supercooling and the rate of
fall of temperature as well as on the rate of crystal-
lization. A precise determination of the freezing point
in such a case becomes rather difficult; it is discussed
by Weissberger (5) and more thoroughly by Andrews et.
al. (6).

Nevertheless, a fairly accurate value can usually
be obtained for the true temperature of first crystalli-
zation by simply extrapolating that portion of the cooling
curve immediately succeeding the maximum that follows
supercooling back to the point at which it cuts the cooling
curve for the unfrozen solution. The point of inter-
section is taken as the true temperature of freezing. If
a large temperature difference exists between the sample
and its surroundings (6) or if the supercooling is not
excessive and the cooling curves are fairly straight, such
a procedure yields results that are sufficiently accurate
for all but the most exacting investigations.

The above method is illustrated graphically in Figure
3. A B C D E represents a cooling curve for which ABC
indicates cooling of liquid, and D^E cooling with crystalli-
zation. If B is the true freezing point of the solution

and C is the point at which crystallization begins, the extent of supercooling is BC. The temperature increase CD after crystallization is less than BC, but B can be found by a straight line extrapolation of DE. Clearly, the accuracy with which B can be determined depends on the form of the cooling curve and the distance over which the extrapolation must be made.
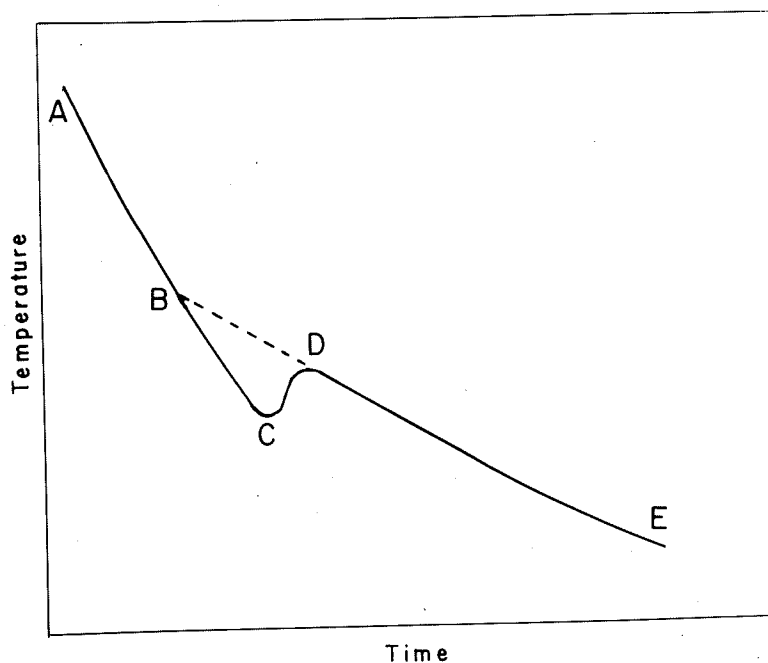
True Freezing Point from a Cooling Curve
Exhibiting Supercooling

Figure 3

Solubility measurements of a solid in a liquid are made by stirring together a mixture of the solvent and solute until equilibrium is reached, and then analyzing a portion of the solution that has been filtered from the residual solid.

A long time may be required to reach equilibrium, and thus the problem of maintaining constant temperature for extensive periods of time is encountered. The temperature must be constant both during the stirring and during the filtering. The problem of sampling may be considerable if the solution is viscous, but if such difficulties are overcome this method is capable of good accuracy.

D. X-Ray Diffraction:

It is well-known that when a crystalline substance is exposed to a beam of monochromatic x-rays, a diffraction pattern characteristic of the substance can be obtained photographically. For a single crystal this pattern consists of a series of spots, but if we take a crystalline powder in which the crystals are present in all possible orientations we obtain rather a series of concentric cones of diffracted rays. These may be recorded as a set of arcs on a cylindrical strip of photographic film surrounding the specimen, which normally is mounted in the form of a rod coaxial with the film. Each such arc represents the combined diffracted rays from all crystals in the specimen that are suitably oriented to reflect the x-rays from some particular set of atomic planes. This forms the basis of the standard Debye – Scherrer – Hull or

powder method.

The diffraction from a crystal is governed by the
Bragg relation

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

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

      d is the spacing, also in Angstroms, between
        successive identical planes of atoms in the
        crystal.

      θ is the angle between the primary x-ray beam and
        the diffracting planes.

      n is a positive integer.

Measurement of the linear distance between the arcs
on the film and the direction of the primary beam permits
an evaluation of θ , and, if λ is known, of d , the
lattice spacing.   The spacings and relative intensities
of the lines of the diffraction pattern are unique for
any pure solid and for different solid phases of the
same substance.   This makes it possible to use this
method to identify solids and to differentiate between
various solid phases.

REVIEW OF THE LITERATURE

A. The Binary Systems

The system lithium nitrate – ethanol – water involves the three binary systems lithium nitrate – water, ethanol – water, and lithium nitrate – ethanol. No reference to the latter could be found in the literature, but the first two have been the subjects of several investigations, none completely satisfactory.

1. The System Lithium Nitrate – Water

The system $LiNO_3$ – H_2O was first studied in detail by Donnan and Burt (2) in 1903. They reported an ice – lithium nitrate trihydrate eutectic at -17.8°C and 33 weight percent $LiNO_3$, a trihydrate – hemihydrate eutectic at 29.6°C and 59 weight percent $LiNO_3$, and a hemihydrate – anhydrate peritectic point at 61.1°C and 65 weight percent $LiNO_3$. The phase diagram for this system proposed by these authors is shown in Figure 4.
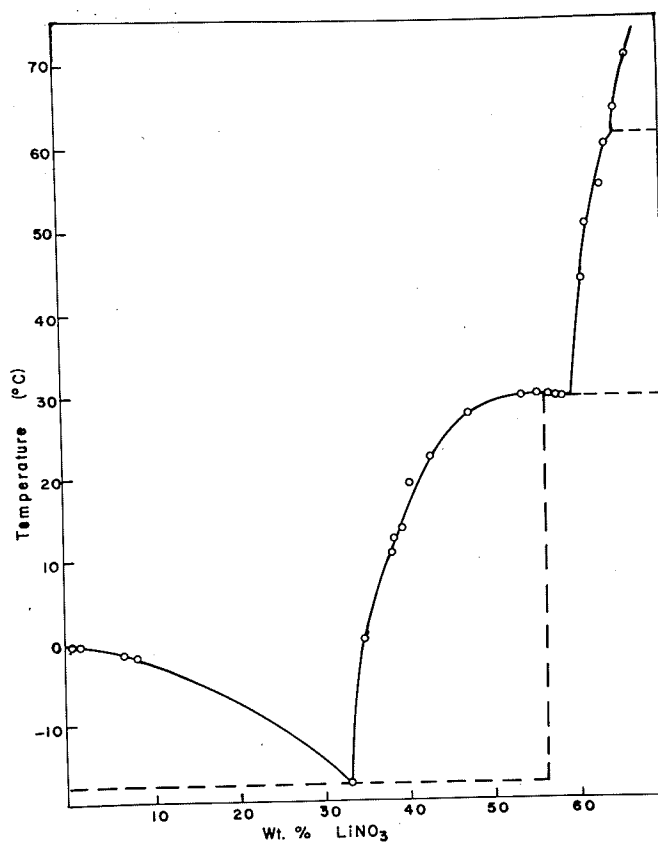
The System LiNO$_3$ — H$_2$O by Donnan and Burt

Figure 4

The ice curve and lower eutectic were given only a cursory investigation by Donnan and Burt. They used freezing point measurements for this. The higher temperature regions were studied by solubility measurements and by dilatometry, and it was the latter procedure that gave the evidence for the existence of the hemihydrate.

Campbell and Kartzmark (3), in 1956, repeated the dilatometric experiments of Donnan and Burt but were unable to find evidence of the reported hemihydrate. It did not appear either in their isothermal study at 25°C.

Gropp (7), in 1915, made a study of the conductance of a six normal lithium nitrate solution. From this he concluded that the point of complete solidification -- i.e. the eutectic, lay in the neighbourhood of $-24^{\circ}C$. He also reported evidence for a eutectoid at $-58.9^{\circ}C$.

2. The System Ethanol - Water

A great deal of attention has been focussed on the system ethanol - water, but until now much uncertainty has surrounded it. This system is well-known for its anomalous physical behaviour, and consequently the large deviations from ideality shown by its physical properties have often been put forward as evidence of compound formation. Maxima, minima, and discontinuities on curves of various physical properties vs. concentration gave numerous formulae for the proposed hydrates. The following are typical.

Mendeleef (8), in 1887, plotted the rate of change of density with concentration against concentration for various alcohol - water mixtures and obtained a series of straight lines. He maintained that the intersections of these lines corresponded to definite hydrates, namely $C_2H_5OH.12H_2O$, $C_2H_5OH.3H_2O$ and $C_2H_5O\ H.\frac{1}{3}H_2O$.

Pickering (9), repeated this plot, using various published density values, and obtained a smooth curve. He therefore contended that Mendeleef's conclusions were invalid.

Schmattola (10), in 1902, also using density measurements, plotted concentration against the change in volume of ethanol on adding water. He obtained numerous discontinuities in this curve, and from their positions he concluded that the hydrates $C_2H_5OH \cdot \frac{1}{2}H_2O$, $C_2H_5OH \cdot \frac{1}{8}H_2O$, $C_2H_5OH \cdot \frac{1}{3}H_2O$ and $C_2H_5OH \cdot H_2O$ were present.

Varenne and Godefroy (11), in 1903, plotted viscosity against composition, and obtained a distinct maximum that they believed was due to the hydrate $C_2H_5OH \cdot 3H_2O$. They also reported some evidence for the compounds $C_2H_5OH \cdot \frac{2}{3}H_2O$, $C_2H_5OH \cdot 2H_2O$, $C_2H_5OH \cdot 6H_2O$, and $C_2H_5OH \cdot 22H_2O$.

The results obtained by the above and other authors from this type of investigation were not in agreement, and it is now generally recognized that no reliable indication of compound formation is provided by such methods. In the case of ethanol and water, where interactions due to hydrogen bonding might be expected to lead to a complex structure in the solution, such physical properties could not be expected to yield information on the composition

of solid phases freezing out. Anomalous physical properties can only indicate that interaction is taking place; they cannot give quantitative information about the nature of such interaction.

The soundest method of dealing with such cases is that of the phase rule. This has been applied through the technique of thermal analysis by several workers. The first systematic freezing point determinations in concentrated alcohol solutions were carried out in the late nineteenth century by Pictet (12) and by Pickering (13). However, these earlier workers were interested only in the point of first crystallization and made no attempt to obtain complete cooling curves.

In 1915, Pushin and Glagoleva (14) made the first comprehensive thermal analysis study of this system and concluded that no compounds were in fact formed. They obtained only a eutectic point at -118°C, at 85 mole percent ethanol. These authors suggest that solid solutions of ice in ethanol up to nearly 15 mole percent water exist on the basis of the following observations: (a) a eutectic halt never appeared in this region; and (b) the cryoscopic constant of ethanol as determined by them was abnormal when water was the solute. The curves joining the freezing points of the pure

components to the eutectic were very nearly straight lines when composition was expressed in mole percent. Considerable supercooling was encountered; this was a difficulty that appears to have beset all investigators. It is particularly extensive in the region around 80 mole percent ethanol, and although Pushin and Glagoleva were able to reduce it somewhat by slow cooling and the use of large volumes of solution, they could not eliminate it here.

In 1928 Tarassenkov (15) repeated these thermal analysis measurements up to 75 weight percent ethanol. He obtained an inflection on the freezing point curve that he interpreted as evidence for a solid hydrate, but he failed to obtain a peritectic halt on any cooling curve. The inflection fell at about 42 weight percent ethanol and at $-33^{\circ}C$.

In 1935 Shalberov et. al. (16) also studied ethanol in solutions of concentrations up to 53 mole percent. They studied as well the ternary system ethanol - water - lithium chloride, and in both systems they found an inflection point that, in the case of ethanol and water, fell at 34 weight percent ethanol. Again, no peritectic halt was obtained but these authors nevertheless used the inflection as evidence for compound formation. Using the rather unreliable method of determining the formula of this supposed hydrate from physical properties of the solution, they used the rate of

change of viscosity with temperature and the coefficient of expansion of the mixture to suggest the formula $C_2H_5OH \cdot 5H_2O$.

Ross (17), in 1954, determined the freezing points of a number of ethanol - water mixtures and also obtained an inflection on the freezing point curve which fell at $-30^{\circ}C$, 42 weight percent ethanol.

Physical property - composition data of solutions are no criteria of compound formation in the solid state and certainly cannot be relied upon to give the formulae of any compounds that may be formed. The strongest indication of compound formation in the system ethanol - water is the occurrence of the point of inflection or break in the freezing point curve, but even this, without the presence of a peritectic halt on the cooling curve, cannot be accepted as truly significant unless there is further evidence that a second solid phase separates beyond this point. The failure to obtain a peritectic halt if this is a true peritectic point is difficult to explain, but the reason may lie in the persistent supercooling of alcohol - water mixtures. It is possible that the peritectic halt is somehow hidden by the metastability of the system.

Of the freezing-point data available for this system, the values of Pushin and Glagoleva become significantly lower at higher ethanol concentrations. However, their value for

the freezing point of pure ethanol, -110.5°C, is about four degrees higher than the value presently accepted. It is probable that all of their temperatures in this region are incorrect, perhaps due to faulty calibration of their thermocouple.

Some studies of liquid ethanol at low temperatures have been carried out, and these serve to throw some light on the physical anomalies and metastability of the system. It is well-known that concentrated alcohol solutions, including the constant boiling 96 percent solution normally encountered, supercool readily and eventually form a rigid glass near -190 C. Prietzschk (18) studied the x-ray scattering at -150°C, as well as at -75°C, of liquid ethanol; in the first instance supercooled. From Fourier analysis he derived a radial intensity distribution curve of the pattern and from this he was able to deduce an average distribution of atoms. The structure thus determined is applicable to cold absolute alcohol as well as to cold alcohol containing a few percent water, and may be expected to give a qualitative indication of interactions in any alcohol solution.

Prietzschk found that at -150°C every oxygen atom is linked to two others, presumably by hydrogen bonding. We thus have the structure shown in Figure 5, where the oxygen atoms are linked through hydrogen to form long zig-zag chains; the C_2H_5 groups lie at right angles to this chain.
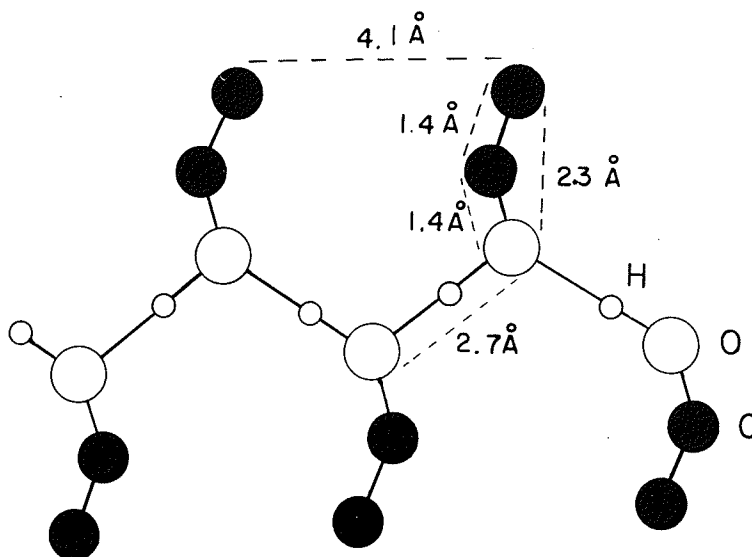
Chain Formation by Ethanol Molecules at
Low Temperature
Figure 5

Harvey's (19) investigation of ethanol at -75°C gave
the same result as that by Prietzschk.   The number of nearest
neighbours of each oxygen atom is found to be only 1.2 at
this temperature.   This shows that the hydrogen bonding is
becoming less as the temperature increases, as would be
expected, but it is still quite appreciable at this temperature.

It has been found by many workers that perfectly dry
ethanol is readily crystallized, although it can also be
supercooled to a pronounced extent.   The addition of small
amounts of water, however, renders crystallization extremely
difficult.   Furthermore, it is found that at a given tempera-
ture the viscosity is sharply increased by small amounts of
water and that the lower the temperature the less water is
required for an increase of the same degree.

Bernal and Fowler (20) have shown that at low tempera-
tures the oxygen atom of a water molecule can be surrounded
by four others that are linked to it by hydrogen bonds. It
is evident that the oxygen of water might equally well be
surrounded by four oxygens of ethanol. Therefore, in an
alcohol solution of low water content, we might expect that
each water molecule could form the point of linkage of four
alcohol chains if the temperature were low enough. At
higher temperatures dissociation would be greater and perhaps
only three, or two, alcohol chains would be attached to each
water. Moreover, the average length of these chains would
be less as the temperature increased. Figure 6 is a planar
diagram of three ethanol chains linked to a water molecule.
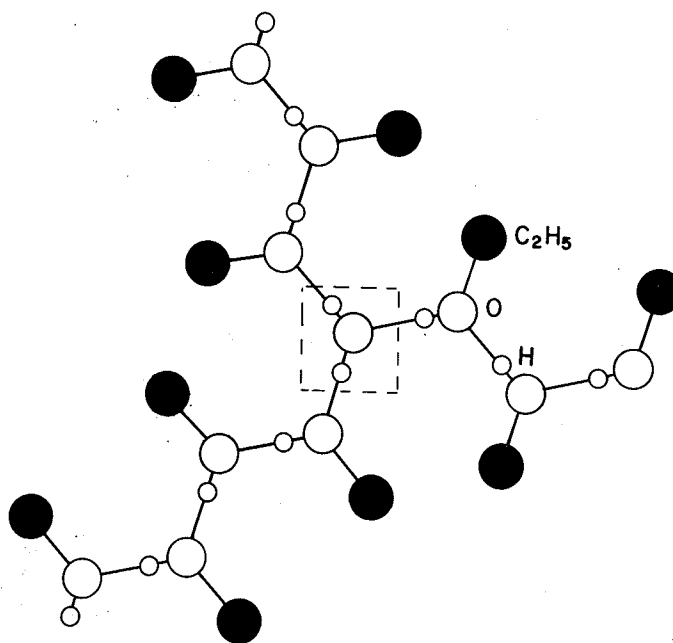
Linkage of Three Ethanol Chains to a Central
Water Molecule

Figure 6

Prietzschk, using the viscosity data of Tammann and Hesse (21), has calculated the average length of the alcohol chains linked by water at -130°C. Assuming that the viscosity will increase sharply as water is added until all the alcohol chains present are linked through the water, and that then the viscosity should level off, he finds that there are about 25 molecules of ethanol for each molecule of water. The alcohol chains are then six or eight molecules long, depending on whether four or three chains are linked by each water at this temperature.

It is evident that there is a fundamental difference between absolute alcohol and "wet" alcohol at low temperatures. Pure alcohol is linked only in the form of linear chains, while, when water is present, an irregular three-dimensional network is formed which is analogous to the structure in silicate glasses. The lack of three-dimensional linking in pure ethanol accounts for the comparative ease with which this material is crystallized.

Prietzschk found no difficulty in obtaining the powder diffraction pattern of solid ethanol. He found it to be extremely simple, consisting only of a very broad, intense line flanked very closely on each side by a sharper but weaker line.

Wahl (22), from direct observation, concluded that the crystals of ethanol belong to one of the low symmetry classes, but he found that crystallization was so imperfect that no definite information could be obtained about them.

B. ## The Ternary System

The ternary system has been studied only by Campbell and Kartzmark (3), who in an isothermal investigation at 25°C found no evidence of compound formation between lithium nitrate and ethanol.

PURITY OF MATERIALS

The lithium nitrate used was Fisher "Certified Reagent" material. This was dried when necessary, but was not subjected to any other additional purification. A significant amount of water was present in this chemical, and this was removed by fusing at least twice in a platinum dish. The fused material was retained in a desiccator over concentrated sulfuric acid or phosphorus pentoxide. Grinding and transferring were done in a dry-box when very dry salt was required.

The dry-box was constructed of wood and had a glass top, hinged for access, which closed tightly on a sponge rubber gasket. All cracks were filled with a filling compound and the inside was coated with a "Glyptol" paint to seal all pores in the wood. Attached rubber gloves permitted manipulation of objects in the box. Open dishes of desiccant kept a fairly dry atmosphere inside and a stream of dry nitrogen gas could be admitted when very dry conditions were desired.

The ethanol used when absolute ethanol was not required was purified by distillation through a Podbelniak type fractionating column. The middle third was the only fraction retained.

Absolute ethanol was prepared from commercial material by prolonged refluxing with quicklime, followed by treatment of the distillate with magnesium according to the method described by Fieser (23). The final distillation from magnesium was done in the column mentioned above with careful exclusion of moist air. Absolute ethanol was retained in a glass stoppered flask and stored in the dry-box; it was transferred only here.

As a convenient check on the dryness of the absolute ethanol, it was tested with aluminum ethoxide, according to the method of Henle (24), whenever a solution was made up with it. This test is claimed to show as little as .05 percent water in the ethanol, and any sample giving a negative test with this reagent would certainly be dry enough for the purposes of this investigation. In additon, the density was determined for each batch of ethanol so prepared. The results were always in good agreement with the literature values.

METHODS OF ANALYSIS

Analysis of solutions was extremely simple. To determine $LiNO_3$, a weighed amount of solution was evaporated to dryness in a platinum dish; the residue was fused, cooled in a desiccator, and rapidly weighed. The fusion was repeated at least once, and since $LiNO_3$ is hygroscopic, it was necessary to carry out the final weighing as rapidly as possible. Accuracy of about .1 percent could be obtained.

Ethanol — water mixtures were readily analyzed by density, which was determined at $25.00^{o}C$ by means of a Weld type pycnometer of about 25 ml. capacity. The concentration was then determined from the published tables.

APPARATUS

A. Apparatus for Thermal Analysis

Thermal analysis was carried out in glass cells equipped with a stirrer and closed from the atmosphere. Temperatures were measured with a copper-constantan thermocouple whose E.M.F. was recorded by a Brown recording potentiometer. The components will be discussed individually.

1. The Recorder

The Brown recording potentiometer used is an instrument operating on the basic potentiometer principle, but having the very great advantage of being self-balancing and giving a continuous record of the voltage measured. In a potenticmeter the unknown E.M.F. is opposed by a known E.M.F. which may be varied by a variable resistance such as a slidewire contact until it is equal to the unknown. When this condition is reached no current flows in the circuit, and the instrument is said to be balanced.

The recording potentiometer is shown schematically in Figure 7. A difference exists between the applied E.M.F. from the thermocouple and the known E.M.F. from the battery when the contact is at all positions save the balance point. Thus a d.c. voltage whose polarity depends on the direction of unbalance will appear across AA. This is converted by
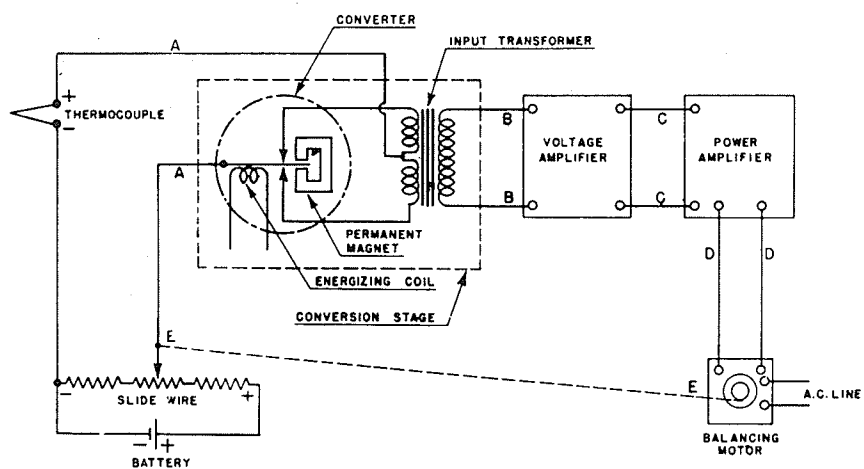
Schematic Circuit Diagram of the Brown Recording
Potentiometer

Figure 7

the "conversion stage" to an alternating voltage (at BB) which is amplified by the "voltage amplifier."   This controls the output of the "power amplifier" which in turn drives the "balancing motor" which fixes the position of the slidewire contact and the recording pen.   The working battery is automatically standardized against a standard cell at frequent intervals.

The accuracy attainable with such an instrument is limited.   For the model used, which had a range of zero to 10 millivolts, the chart could not be read to better than ± .05 mv.   A simple copper-constantan thermocouple has a temperature coefficient of about .04 mv. per degree C., and thus temperatures could not be obtained with an accuracy better than about $1^{o}C$ with a simple thermocouple. One can of course increase the sensitivity by using a multi-junction thermocouple, but then one is restricted by the range of temperature to be covered.   A triple junction thermocouple of the above metals, for example, is limited to a range of about $90^{o}C$.

This recorder gives the required plot of temperature (in terms of millivolts) against time directly and automatically, and results in a great saving of labor and time.

2. The Thermocouples:

The thermocouples used were constructed of copper and constantan, a well-known combination for work at low temperatures.   For all work on the $LiNO_3 - H_2O$ system, and for nearly all points in the ternary system lying above zero degrees centigrade, a triple junction couple was used, while for all other measurements a double junction thermocouple was employed.

The thermocouples (and at the same time the recorder) were calibrated at low temperatures from the freezing points of purified, redistilled mercury, "spectro" grade carbon tetrachloride, reagent grade toluene, and "spectro" grade diethyl ether.   The freezing points of these substances are $-38.87^{\circ}C$, $-22.8^{\circ}C$, $-95.0^{\circ}C$, and $-116.3^{\circ}C$ respectively.   Since Roeser and Wensel (25) suggest that calibration points need be no closer than $50^{\circ}C$ apart, this is clearly adequate.   The triple junction couple was not used at very low temperatures, so only the first two substances named were used for its calibration.   Calibration above $0^{\circ}C$ was made by comparison with a previously calibrated mercury in glass thermometer reading to $.1^{\circ}C$.

The E.M.F. for each temperature used was obtained from the National Bureau of Standards Circular 508.   The difference between this tabulated E.M.F. and the observed E.M.F. was found in each case, and plotted against the

observed E.M.F. according to the method of Roeser and

Wensel (25). Provided that the corrections are small,

as they were found to be, a straight line interpolation

between the calibration points may be used to give the

correction to be applied to any observed E.M.F.

The reference junction of the thermocouples was

maintained in a well-stirred mixture of ice and water

in a dewar flask.

3. The Freezing Point Cells:

Two types of cell were used which differed funda-

mentally only in the method of stirring. Both consisted

of an inner glass tube containing the solution and surrounded

by an outer jacket which could be evacuated as required to

reduce the rate of cooling. A well for the thermocouple

extended into the solution near the stirrer.

The first type of cell, shown in Figure 8 a, was

stirred by a glass spiral attached to a glass-covered iron

slug which was moved up and down by means of an external

magnet driven by an electric motor from an automobile

windshield wiper. Filling of the cell was accomplished

through a ground glass joint; when this was capped the

solution was completely isolated from the atmosphere.

The outer jacket was also fitted by means of a ground

glass joint, making these cells ideal for use with solutions

freezing above room temperature.   Such solutions could
be rapidly warmed by placing the inner tube directly in
a beaker of hot water.   The usual volume of solution
placed in these cells was about 15 ml.

The second type of cell, shown in Figure 8b, was
used when viscosity effects prevented the rather weak
magnetic stirring of the previous cells from being effective.
Most low temperature work was done in these.   Stirring
was performed mechanically through a mercury seal.   An
outlet was provided to equalize pressures on both sides
of the seal, since considerable contraction of the air in
the cell occurred on cooling.   To this outlet was attached
a tube of desiccant, either drierite or magnesium perchlorate.
These cells were somewhat larger than the previous type, and
held about 40 ml. of solution; larger volumes could not be
stirred effectively.

Cooling was attained by immersing the cell in a
dewar flask containing a suitable cooling agent.   Usually
either a dry-ice - acetone mixture or liquid nitrogen was
used.

B. <u>Apparatus for Solubility Determinations</u>:
A few solubility determinations of lithium nitrate
in absolute ethanol were carried out.   The solubility
cell, a glass vessel containing about 150 ml. of solute and
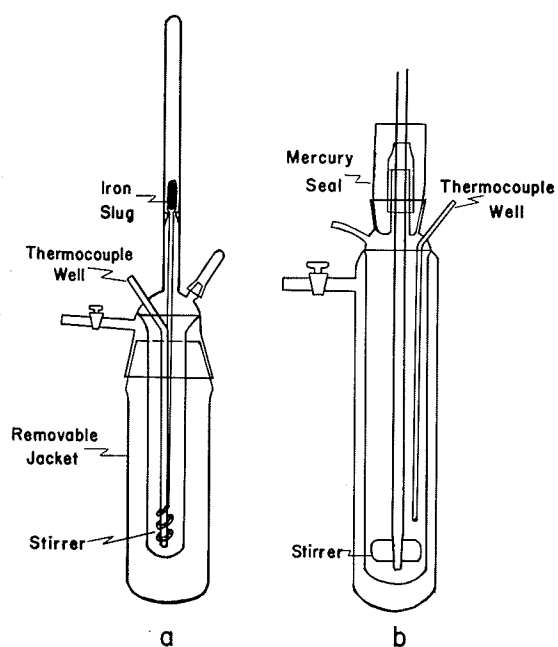
Freezing Point Cells (a) with Magnetic Stirring;
(b) with Mechanical Stirring

Figure 8

solvent, was placed in a constant temperature bath and the contents stirred through a mercury seal. When equilibrium was established, some solution could be withdrawn for analysis through a sintered glass filter-stick that replaced the stirrer. The filtrate was collected in a receiver attached by a ground glass joint. The solubility cell and sampling apparatus are shown in Figure 9.
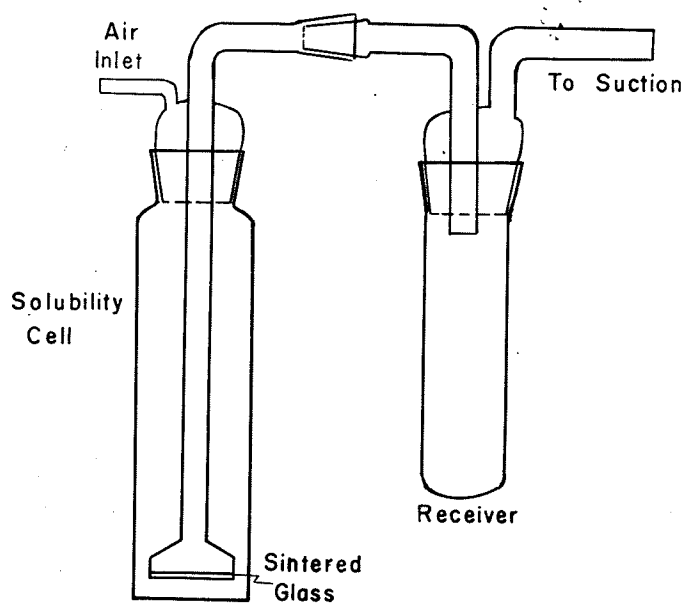
The Solubility Cell and Sampling Apparatus

Figure 9

The constant temperature bath used above 0°C was a simple thermostat of a conventional type, controlled to better than ± .05°C. Colder baths were suitable freezing mixtures (crushed ice and water, ice, salt, and water, or dry-ice and acetone) kept in a four litre wide-mouth dewar flask which was packed in a case lined with cotton waste and wrapped with heavy felt. About two inches of felt covered the top. The temperatures were constant to within one degree.

C. The X-Ray Diffraction Cameras:

Although x-ray diffraction photographs present little problem at room temperature, pictures above or below room temperature require special equipment (26). A high temperature camera was available and was used in the investigation of the system $LiNO_3 - H_2O$, but for the study of solid phases in the system $C_2H_5OH - H_2O$ a low temperature camera was required. It was found possible to construct a simple modification of the high temperature camera that was able to be operated at low temperatures. These were both based on the standard cylindrical camera design, and are described in detail below.

1. The High Temperature Camera

The high temperature camera was a copy of the Buerger camera (27)(28), available commercially, in which the specimen was mounted at the centre of an asbestos tube

containing a small coil of nichrome wire which served
as the heater.   A space of about 5 mm. width between
two loops of this coil permitted passage of the x-rays.
To protect the film a coil of copper tubing through which
water could be circulated surrounded the heater, and
this combination formed a cylinder which was mounted co-
axially with the film case.   A metal framework covered
with black paper protected the film from light while the
entire outer film case was demountable.   A thermometer
inserted in the open end of the inner cylinder gave the
temperature of the specimen.

The diameter of the film case was nominally 57.3
mm.   Therefore, a 1 mm. distance measured on the film
would represent a diffracting angle θ of one degree.

Temperature could be controlled by supplying
power through a variable transformer.   The temperature
fluctuated by about $\pm 10^{\circ}C$ unless constant supervision was
exercised; this was chiefly due to variation in the flow
of cooling water.   No closer control was required for
this investigation.

Figure 10 shows the high temperature camera with
the furnace tube in place.   The film case and film cover
are shown beside it.
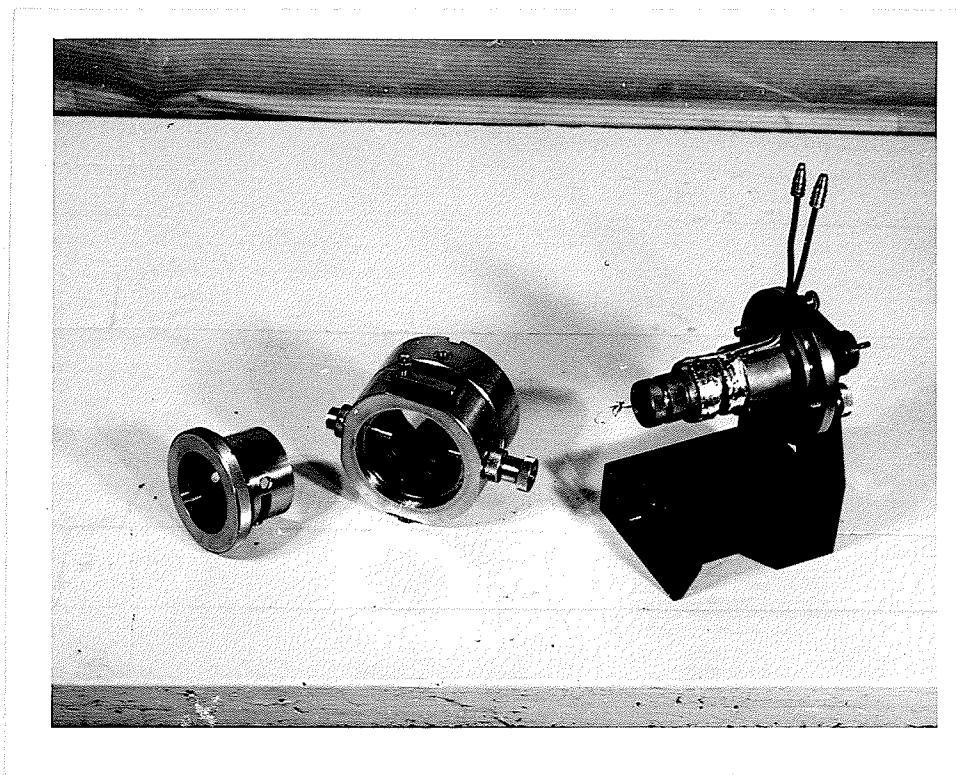
The High Temperature Camera, Partially Assembled

Figure 10

2. <u>The Low Temperature Camera:</u>

This camera was constructed from the high temperature camera by replacing the heater tube with a cylinder that permitted a cold atmosphere to be kept around the specimen. This consisted of a brass cylinder heavily lined with sheet cork. A cellophane covered slit extending most of the way around this tube permitted passage of the x-rays, while a slotted glass tube fitted about the cylinder behind the slit served as a defroster. A stream of dry nitrogen gas from a cylinder passed through this defrosting tube and swept across the cellophane covered slit, carrying away moist air and hence preventing frost formation. This nitrogen then passed out through the open face of the camera.

As a cooling agent, boiling liquid nitrogen was used. The boiler was somewhat similar to that described by Cioffi and Taylor (29). A four litre wide-mouth dewar flask was fitted with an insulated metal top attached by a mixture of beeswax and resin, softened by a little turpentine. The top contained three holes fitted with rubber stoppers. Through one passed the lead wires to the heater, which was a coil of nichrome wire wound on a glass rod bent in a circular shape and placed near the bottom of the dewar. This heater had a resistance of

about 15 ohms at room temperature.   The second hole
was used for filling, while the third contained the
outlet tube.   This was first of copper, later of glass
with a rubber joint to permit flexibility when inserting
into the camera.   It was insulated only with a layer of
cotton waste.   The boiler is shown in Figure 11.
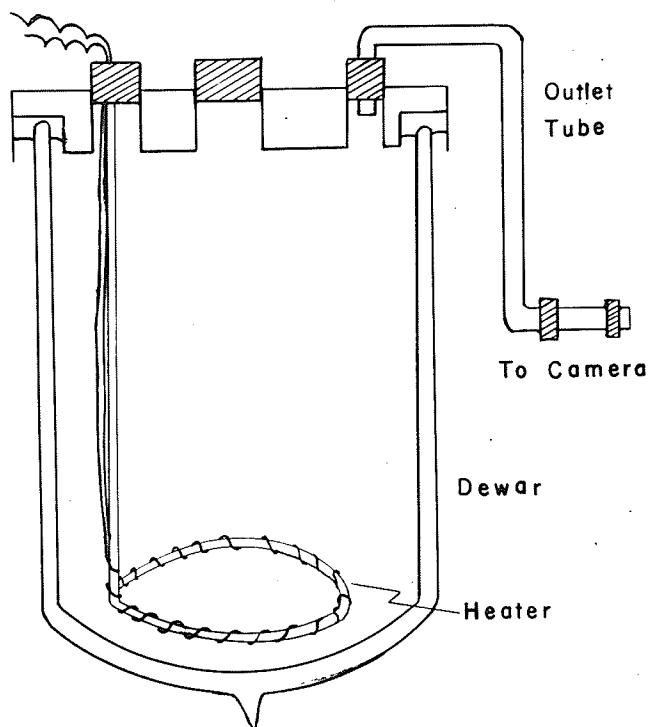
The Liquid Nitrogen Boiler of the Low
Temperature Camera

Figure 11

The outlet tube was inserted into the open end
of the cork-lined brass cylinder, and the cold nitrogen
gas emerged directly on the specimen.   After passing
over the sample, the cooling gas escaped through a hole

originally designed to contain a screw for centering the specimen. This screw was of course absent during the runs.

Temperature was measured by means of a copper-constantan thermocouple, placed just behind the specimen. This junction was led in through the slot in the outer film case provided for the cooling coil of the high temperature camera.

Temperature was controlled by controlling the rate of boiling of the liquid nitrogen by means of a variable transformer. With reasonable attention a temperature constant to within $\pm 5^{\circ}C$ could be attained easily and the desired temperature could be reached very rapidly.

The low temperature camera is illustrated in Figures 12, 13 and 14. Figure 12 shows the components of the camera, Figure 13 shows the camera partially assembled, and Figure 14 shows the camera ready for operation.
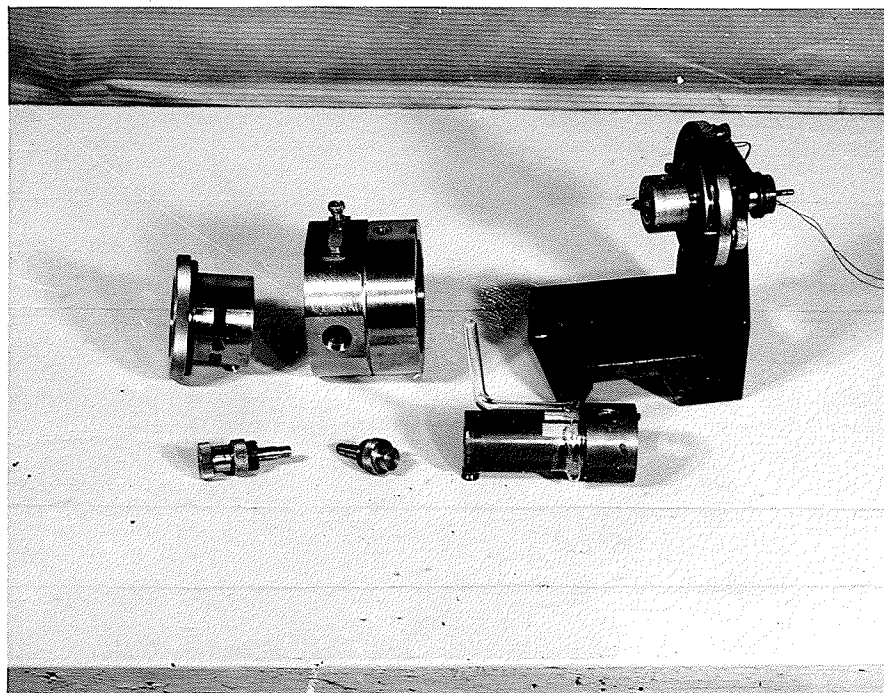
The Low Temperature Camera, Showing Components

Figure 12
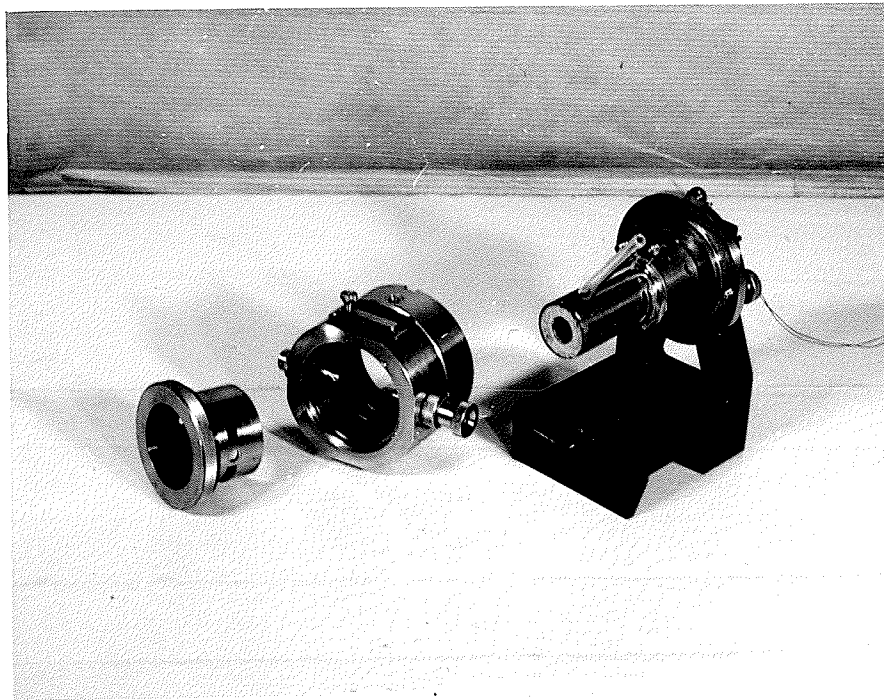
The Low Temperature Camera, Partially Assembled

Figure 13
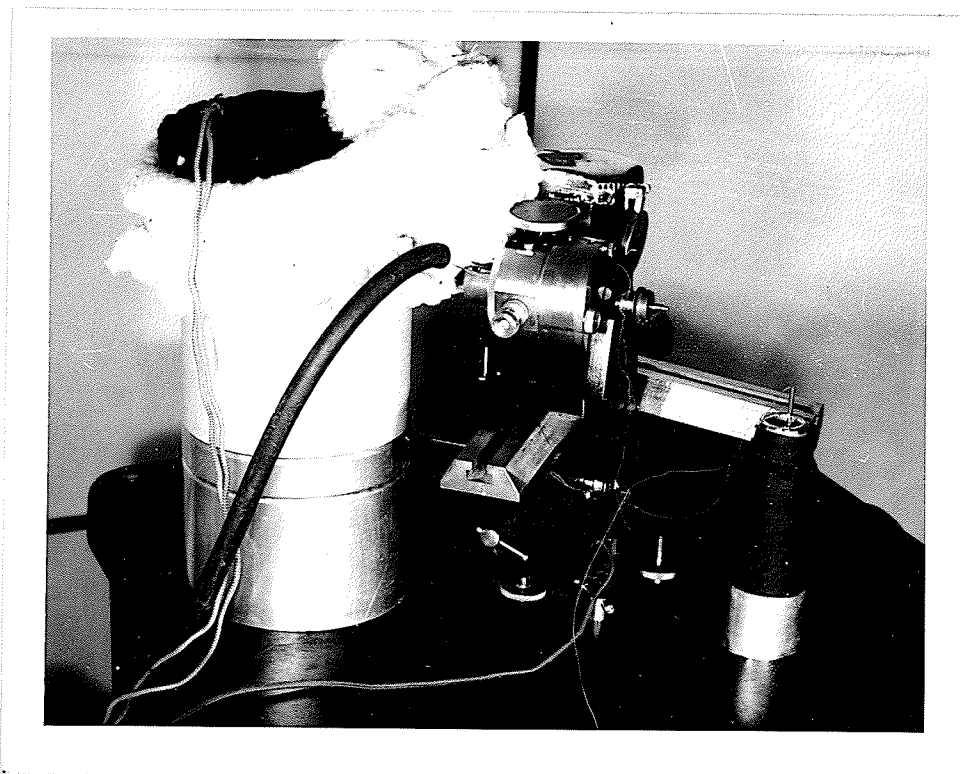
The Low Temperature Camera in Operation

Figure 14
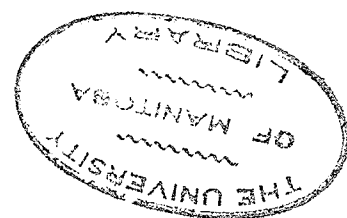
The performance of the camera with regard to temperature was better than anticipated. Four litres of liquid nitrogen were sufficient to reach and maintain a temperature of -80°C for about two hours, while at -120°C the rate of boiling was about three litres per hour. During refilling of the boiler, the camera lost its temperature, but only for a few moments.

The defrosting device used prevented formation of frost on the slit and on the paper covering of the film at all temperatures attained. At temperatures approaching -80°C much frost tended to form on the outside of the camera, but this did not interfere with its operation. The minimum temperature at which this camera could be operated satisfactorily for a reasonable length of time was about -130°C.

Pictures taken at low temperatures should be sharper than those taken at room temperature because thermal vibration of the atoms is less. In this camera, however, this was offset by extraneous scattering of the x-rays, firstly from the cellophane covering of the slit, and secondly from the glass capillaries in which the samples were placed. Absorption by the paper film cover required that the exposure time be longer than for room temperature pictures with standard cameras, and this contributed to an increase in the general background darkening.

A more serious fault of this camera lay in the presence of stray lines which appeared on the diffraction pattern. Some of these were due to the collimating system, and were present also in the high temperature camera, but a few broad bands existed that had an inexplicable origin. These varied in intensity in an apparently irregular manner from one run to another. All of these lines fell at fixed places, however, and could be eliminated by reference to a photograph taken with no specimen present. Moreover, their appearance differed greatly from lines from the samples, so that there was little chance of confusion.

EXPERIMENTAL PROCEDURE

A. The System Lithium Nitrate - Water

Solutions of lithium nitrate in water first were made up to approximately known concentrations. When complete solution took place below room temperature, a comparatively large volume of solution was made up; part of this was placed in the freezing point cell and the remainder was analyzed. If the freezing point of the solution was above room temperature, it was usually the practice to add the dry, powdered solid and the water to the cell separately; this was immersed in hot water and stirred until complete solution took place. After the completion of the cooling curves the mixture was warmed again and the solution poured out for analysis. A ground glass cap on the cell prevented evaporation from the warmed solution.

Cooling was usually slowed to about 1°C per minute near the freezing point by evacuation of the outer jacket. Considerable supercooling was encountered, particularly in more concentrated solutions, but this was reduced by "seeding" the solution at the freezing point with a small amount of solid taken directly from the reagent bottle. The solution was melted and refrozen until at least two freezing points were obtained that agreed within the experimental error, which was estimated as $\pm.2$°C.

To determine the composition of the ice-trihydrate eutectic, a sample of solution remaining when a mixture showed the eutectic halt was withdrawn through a tube containing a glass-wool plug and analyzed.

No trace of the peritectic point reported by Donnan and Burt (2) could be found by thermal analysis, and the work of Campbell and Kartzmark (3) had strongly indicated that it did not exist. However, as an additional check, some x-ray diffraction work was done. If the break in the freezing point curve really did exist, it could be due either to a second hydrate, as Donnan and Burt suggested, or to an allotropic modification of the anhydrous salt. Both of these possibilities were investigated.

A sample of anhydrous $LiNO_3$ was finely ground in a dry-box and sealed into a fine glass capillary tube. X-ray diffraction pictures were taken in the high temperature camera at room temperature, 45°C, and 100°C. A second picture was taken at the latter temperature after prolonged heating in case any phase transformation occurred slowly. A second sample was made up to have a composition closely corresponding to that of the hemihydrate. This, too, was sealed into a capillary, and after it had been maintained at 45°C for some time, x-ray diffraction photograph was taken

of it. By comparing the positions of the lines in these pictures it is possible to determine if a different solid phase was present in any of them.

No diffraction pattern for $LiNO_3 \cdot 3H_2O$ is listed in the A.S.T.M. index of diffraction patterns, so this compound was photographed at room temperature on the standard camera. The melting point of this substance lies at about $30^\circ C$ and it was found impossible to grind it to the required fine powder at room temperature because of the soft nature of the crystals. The mortar and pestle were therefore thoroughly chilled and the grinding carried out in the cold, where no difficulty was encountered. It was even possible to load a capillary tube under such conditions. The photograph in the capillary was taken only to be sure that no loss of water from the trihydrate occurred during the exposure. This was considered possible since a few lines in the pattern of the trihydrate were nearly identical with some of the lines given for the anhydrous salt, but no such loss occurred.

For all pictures copper $K\alpha$ radiation was used. The standard camera had a diameter of 57.3 mm.

B. The System Ethanol - Water:

Solutions for thermal analysis were made up from
redistilled 96 percent ethanol and water, or from abso-
lute ethanol and water when concentrations greater than
96 percent by weight ethanol were desired.   The exact
concentration was determined from the density.   Little
supercooling was encountered in dilute solutions, but as
the alcohol content was increased, the supercooling also
increased until beyond 75 weight percent ethanol it
became extremely difficult to obtain a freezing point
at all.   On cooling, solutions in this region became
extremely syrupy and were usually opaque due to the
presence of air bubbles.   The use of mechanical stirring
was imperative here.   Little difficulty from supercooling
was encountered with absolute ethanol, but as water was
added supercooling increased rapidly.

To investigate the solid phases separating, x-ray
diffraction photographs were taken of frozen solutions.
In all cases the solution was placed in a capillary tube
drawn out from large diameter Pyrex tubing so as to have
very thin walls.   The ends of these capillaries
could not be sealed in a flame when filled with solution,
so the ends were closed with plasticine.   It was found
that a fairly wide capillary was necessary to prevent
separation of the liquid column during cooling.   This
was especially true for samples rich in ethanol.

Diffraction photographs were taken first of ice at temperatures from $-20^{\circ}C$ to $-80^{\circ}C$, as a basis of comparison. A series of pictures were also taken of solutions containing less than 40 percent by weight ethanol at various temperatures, particularly above the suspected peritectic temperature of $-30^{\circ}C$. If any new phase appeared it was expected to do so beyond 40 weight percent ethanol, and photographs were taken in this region at a series of temperatures and compositions. The composition was not taken beyond 65 percent ethanol, since the sample often refused to crystallize beyond this point. The temperature was not taken below $-100^{\circ}C$. All of these pictures were taken with copper $K\alpha$ radiation with an exposure time of about 1.5 hours. Diffraction photographs were also taken of absolute ethanol, both with copper and with iron radiation, at temperatures between $-120^{\circ}C$ and $-130^{\circ}C$.

C. The System Lithium Nitrate - Ethanol

This system was first attacked by the method of thermal analysis. The solutions were made up directly by putting weighed quantities of freshly fused lithium nitrate and absolute ethanol into bottles equipped with ground glass caps. All manipulations, including filling of the freezing point cells, were carried out in the dry-box. All solutions of lithium nitrate in ethanol were very viscous and supercooled extensively. Seeding of these solutions with anhydrous crystalline lithium nitrate did not help, and freezing points

could be determined only in solutions containing less than about six percent salt.

In order to obtain information in higher concentration regions, solubility measurements were made at a series of temperatures. These were 50°C, 30°C, 20°C, 0°C and -21°C. An attempt was made to obtain the solubility at -80°C, but the extreme viscosity made sampling impossible. The procedure of this method consisted of stirring together absolute ethanol and excess lithium nitrate until equilibrium was established -- usually for from four to six days. Solution was then withdrawn and analyzed. During the sampling, which often took considerable time, the air inlet of the sampling device was attached to a drying tube containing a good desiccant. The receiver was chilled to reduce evaporation from the filtrate.

In order to be certain that equilibrium had been reached when the mixture was sampled, in two cases (20.1°C and 0.0°C) samples were withdrawn on successive days and the concentrations of each determined. Since no change was found, it was apparent that equilibrium had been reached. This test was not applied to the other runs, but since all of the results lie on a smooth curve, it is evident that equilibrium was at least closely approached in all cases. At low temperatures,

the lithium nitrate — ethanol mixture was chilled
before stirring in order to eliminate any possibility
of supersaturating (perhaps with alcoholate) a solution
saturated at a higher temperature.

D. The Ternary System Lithium Nitrate — Ethanol — Water

The first approach to the ternary system involved
an attempt to follow the eutectic troughs inward from
the lithium nitrate — water edge of the diagram.
Solutions were made up having a composition near expected
positions of the troughs. These solutions were cooled
until the eutectic halt appeared, and some of the
remaining liquid was withdrawn for analysis through a
glass tube containing a plug of glass wool. This gives
a composition lying on the eutectic trough at the tem-
perature of sampling, but the high viscosity of the
solutions made sampling impossible at low temperatures
and difficult at higher ones, and the metastability
encountered also presented difficulty. Consequently,
this method was abandoned.

The only suitable alternative available was to
study the ternary as a number of pseudo-binary systems
in each of which the ratio of two of the components was
kept fixed while the concentration of the third in this
mixture was varied. The simplest of such pseudo-binaries

used a fixed ethanol – water solution as solvent for
anhydrous lithium nitrate, and five pseudo-binaries
of this type were investigated.   The procedure applied
was identical with that applied to the lithium nitrate
– water system, but with particular care being taken
to prevent any change in the alcohol – water ratio of
the solutions.   Such changes could have been brought
about by evaporation or by the use of lithium nitrate
containing water.

When considered in relation to the graphical
expression of the ternary system as a whole, the freezing
points on such pseudo-binary systems lie on straight
lines radiating from the lithium nitrate apex and cutting
the ethanol – water edge at the composition of the
solution used as solvent.   Only the point of first
crystallization may be used since, in general, the path
of crystallization of the solution does not lie along
the line of the pseudo-binary "cut" and so the composi-
tion of the liquid freezing at a eutectic trough does
not have the alcohol – water ratio of the pseudo-binary
system.   Therefore, pseudo-binary eutectic temperatures
could be found accurately only if the original solution
happened to have the composition of the eutectic.   If,
however, the original composition were close to that of

the eutectic, the temperature of the eutectic halt
obtained would be at most a very few degrees below the
true temperature.   Since it was not considered worth-
while for the purposes of this investigation to prepare
samples having the exact pseudo-binary eutectic composi-
tion, the eutectic halt of a solution near this point
was taken.

In cases where the solid phase separating was the
anhydrous salt, the path of crystallization would
follow the line of the pseudo-binary "cut."   True
eutectic temperatures could be obtained in such cases.
It is clear that everything said above about eutectic
halts applies to peritectic halts under the same conditions.

In addition to pseudo-binary systems having a fixed
ethanol - water ratio, systems having a fixed lithium
nitrate - water ratio can be treated without great diffi-
culty.   Accordingly, the hydrate $LiNO_3.3H_2O$ was made up
and freezing points with increasing amounts of ethanol
were determined.   In order to avoid the experimental
difficulties associated with absolute ethanol, the tri-
hydrate was dissolved in a solvent of 96 weight percent
ethanol in water and containing sufficient anhydrous
$LiNO_3$ to give a lithium nitrate - water ratio in this
solvent of one mole to three.   This system must behave
as a true binary system between the compounds $LiNO_3.3H_2O$
and C_2H_5OH as long as the trihydrate is the stable solid
separating.

It is interesting to note that alcoholic solutions
could usually be induced to crystallize at their
freezing point by seeding with anhydrous lithium nitrate.
This was true even when the anhydrous salt was not the
solid phase separating.   The effect was not always
instantaneous.   After a solution had been frozen once,
it could usually be frozen subsequently with much less
supercooling.   Anhydrous lithium nitrate was often used
to obtain the first crystallization.   Its effect,
however, was reduced or absent in solutions of higher
alcohol content.

In pseudo-binary systems of high ethanol content,
some inconclusive evidence for the existence of a "solvate"
of lithium nitrate other than the trihydrate was obtained
from thermal analysis.   In one case, that of the "cut"
using 66.4 weight percent ethanol as solvent, a peritectic
point appeared to exist, as well as the maximum that
was present on "cuts" for lower alcohol content.   In
order to determine if the peritectic, which was based on
somewhat uncertain evidence, really existed, it was
decided to examine by x-ray powder diffraction the solids
separating above and below this point.   Therefore,
solutions were made up firstly having the concentration
of the maximum on the freezing point curve, and secondly,

with a concentration less than that of the peritectic
point.   These were filtered at a temperature between
 17°C and 13°C in the first case, and at 0°C in the
second case.   The solids were sucked as dry as possible,
and ground in the cold for x-ray analysis.

Pictures were taken with the specimens exposed to
the air, and also in sealed capillaries.   It was found,
however, that the crystals obtained below the apparent
eutectic point were so fibrous and melted so readily
that they defeated all attempts to load a capillary with
them.   Part of the ease with which they were found to
melt may have been due to occluded alcohol.

In solvents of greater alcohol content, where
additional indications of alcoholate formation were
found, the viscosity made the normal procedure of
filtering through sintered glass impossible at the tem-
peratures required.   It was felt, therefore, that further
work along this line with the facilities at hand would
not be worthwhile.   Some consideration was given to
freezing solutions "in situ" in the low temperature
camera, but since it was observed that crystallization
could never be obtained without vigorous stirring or
scratching of the glass, this method did not promise to
be fruitful either.

EXPERIMENTAL RESULTS

The experimental data are collected
in the following tables, which list
the freezing points, solubilities
and x-ray diffraction patterns of the
systems investigated.

TABLE I

Thermal Analysis data of the system lithium nitrate —water

Wt. % $LiNO_3$	Freezing Point °C	Invariant Point °C	Solid Phases Present at Freezing Point
10.7	-7.4	-22.8	ice
16.0	-11.3	-23.4	"
22.3	-17.7		"
24.5		-22.9	ice + $LiNO_3 . 3H_2O$
30.1	-7.9	-22.9	$LiNO_3 . 3H_2O$
35.1	1.5	-22.9	"
40.1	14.5		"
41.8	17.5		"
42.1	20.2		"
43.7	20.6		"
51.3	28.4		"
55.2	29.4		"
56.0	29.6		"
57.8	29.5		"
58.0	29.5		"
59.6	28.8	27.9	"
62.3	33.6	27.9	$LiNO_3$
63.4	41.3	27.9	"
63.6	47.1	27.9	"
64.6	53.7	27.9	"
66.4	70.0	27.9	"
66.9	75.6	27.9	"

TABLE II

X-Ray Powder Diffraction Pattern of $LiNO_3.3H_2O$

Relative Intensity	Lattice Spacing (A°)
2	6.13
7	4.20
3	3.47
10	2.99
2	2.79
2	2.68
1	2.53
5	2.37
8	2.13
1	2.02
1	1.90
2	1.80
3	1.71
2	1.54
	1.36

TABLE III

Thermal Analysis Data of the System $C_2H_5OH-H_2O$

Composition Wt. % C_2H_5OH	Freezing Point °C	Invariant Point °C
8.1	-3.8	
14.8	-7.4	
21.4	-12.7	
27.1	-17.9	
32.1	-22.4	
38.1	-28.3	
40.4	-30.3	
41.6	-30.8	
43.2	-31.8	
45.1	-33.1	
48.3	-34.2	
53.0	-38.6	
56.3	-40.8	
62.5	-45.7	
64.0	-46.5	
67.1	-52.6	
71.3	-56.1	
75.5	-64.0	
75.8	-64.6	
81.1	-	-124.1
82.7	-	-124.4
83.9	-	-124.1
85.6	-	-124.1
86.8	-	-124.1
87.4	-	-124.6
88.1	-	-123.8
93.6	-122.9	
95.4	-118.6	
97.8	-115.7	
100.0	-114.4	

TABLE IV

X-Ray Powder Diffraction Pattern of Ice

Observed Values (Mean of 4 Pictures)		Literature Values	
Lattice Spacing d (A°)	Relative Intensity	Lattice Spacing d (A°)	Relative Intensity
4.14	v. weak	3.92	10
3.92	medium	3.67	100
3.55	strong	3.44	20
2.70	medium	2.67	15
2.30	medium	2.26	10
2.11	strong	2.07	50
1.95	strong	1.92	10
1.45	v. weak	1.52	15
1.39	weak	1.37	2
1.27	v. weak	1.30	3
		1.25	3
		1.17	5

TABLE V

X-Ray Powder Diffraction Pattern of Frozen Solutions Containing less than 40 wt. % Ethanol at Temperatures above -30°C. (Mean of 8 pictures)

Lattice Spacing d (A°)	Relative Intensity	Number of Times Observed
4.18	v. weak	3
3.92	weak	4
3.76	v. weak	3
3.54	strong, diffuse	8
2.69	medium	8
2.30	strong	5
2.13	medium	6
1.39	weak	5

TABLE VI

X-Ray Powder Diffraction Pattern of Frozen Solutions Containing more than 40 wt. % Ethanol at Temperatures from $-30^\circ C$ to $-90^\circ C$. (Mean of 10 pictures)

Lattice Spacing d (A°)	Relative Intensity	Number of Times Appearing
3.61	weak, diffuse	6
3.32	strong	10
2.97	strong	8
2.64	v. weak	2

TABLE VII

Thermal Analysis Data of the System $LiNO_3-C_2H_5OH$.

Composition Wt. % $LiNO_3$	Freezing Point $^\circ C$
0.0	-114.4
0.8	-115.8
2.1	-116.7
3.8	-118.2
5.5	-118.6
6.3	-124.

TABLE VIII

Solubility Data of the System $LiNO_3-C_2H_5OH$.

Temperature $^\circ C$	Solubility Wt. % $LiNO_3$
50.0	25.6
30.1	24.7
20.1	24.0
0.0	23.0
-21.	21.9

TABLE IX

Thermal Analysis Data of the Pseudo-Binary System
$LiNO_3$ - 27.2 wt. % C_2H_5OH.

Composition wt. % $LiNO_3$	Freezing Point °C	Pseudo-Invariant Point °C
0.0	-17.8	
8.5	-25.0	
10.2	-27.1	
12.7	-30.1	
15.0	-35.3	
17.6	-26.9	-41.1
20.3	-16.6	
24.3	-4.6	
35.4	13.0	
48.6	25.0	
52.2	25.3	
57.9	50.6	22.1
56.7	38.7	22.3

TABLE X

Thermal Analysis Data of the Pseudo-Binary System $LiNO_3$ -42.0 wt. % C_2H_5OH.

Composition wt. % $LiNO_3$	Freezing Point °C	Pseudo-Invariant Point °C
0.0	-30.6	
5.6	-38.8	
9.7	-44.9	
12.5	-41.8	-51.0
14.1	-34.7	
33.8	15.5	
39.6	21.3	
40.3	(~21.)	
42.8	22.4	
47.0	22.1	
48.7	21.6	
51.0	21.3	
52.3	35.6	20.7
54.0	46.2	21.0

TABLE XI

Thermal Analysis Data of the Pseudo-Binary System
LiNO$_3$ - 49.7 wt. % C$_2$H$_5$OH.

Composition Wt. % LiNO$_3$	Freezing Point °C	Pseudo-Invariant Point °C
0.0	-36.0	
5.0	-43.4	
8.0	-48.7	
10.4	-54.2	-58.9
14.1	-33.7	
19.7	-12.4	
36.0	18.8	
37.0	19.2	
38.5	20.1	
43.7	21.8	
45.7	21.3	
48.5	23.6	19.8
48.8	30.1	19.5

TABLE XII

Thermal Analysis Data of the Pseudo-Binary System
LiNO$_3$ - 66.4 wt. % C$_2$H$_5$OH.

Composition Wt. % LiNO$_3$	Freezing Point °C	Pseudo-Invariant Point °C
0.0	-47.4	
4.9	-57.9	
6.8	-63.2	
9.0		-73.0
10.2	-62.0	
13.8	-27.0	
15.5	-18.2	
18.3	-7.8	
23.2	4.4	
26.6	10.3	
27.0	11.0	
29.6	13.8	
29.7	14.1	12.1
30.9	15.6	12.5
35.6	17.5	
35.7	17.3	
40.0	16.6	
43.0	31.1	15.0
43.9	43.1	14.6

TABLE XIII

Thermal Analysis Data of the Pseudo-Binary System
$LiNO_3$ - 78.2 wt. % C_2H_5OH.

Composition wt. % $LiNO_3$	Freezing Point °C	Pseudo-Invariant Point °C
16.6	-13.2	
17.9	-6.3	
21.5	-1.3	
24.4	0.8	
26.2	1.6	
27.4	2.5	
30.6	5.4	
31.4	5.6	
32.6	(~5.2)	
32.8	11.3	
34.5	24.0	(~5)
35.1	28.8	5.7
35.2	31.9	
36.2	43.5	5.1

TABLE XIV

Thermal Analysis Data of the System $LiNO_3 \cdot 3H_2O$ - C_2H_5OH.

Composition wt. % C_2H_5OH	Freezing Point °C
0.0	29.6
14.2[a]	24.2
24.4[a]	22.4
30.0[a]	20.2
32.9	18.8
40.9	16.3
41.1	16.1
46.8[a]	14.5
52.6	9.7
54.4	7.7
59.0	1.7
61.8[a]	-1.0
67.3	-5.2
72.2	-25.0

[a] Values interpolated from pseudo-binary cuts

DISCUSSION OF RESULTS

A. The System Lithium Nitrate - Water

The results obtained for this system, as listed in
Table I and shown graphically in Figure 15, are not in
complete agreement with those of Donnan and Burt (2).
The ice - trihydrate eutectic lies at $-22.9^{\circ}C$ and 24.5
weight percent lithium nitrate; this is at both a lower
temperature and a lower concentration than reported by
Donnan and Burt ($-17.8^{\circ}C$; 33 wt. % LiNO3). The higher
eutectic, at 27.9°C and 61.5 weight percent lithium
nitrate, is also different from the value previously
accepted (29.6°C; 59 wt. % LiNO3). Here, trihydrate is
in equilibrium with anhydrous lithium nitrate and not
with hemihydrate as the previous study had supposed.
The melting point of lithium nitrate trihydrate was found
to be 29.6°C.

All of the x-ray diffraction photographs taken in
the high temperature camera previously described were
fundamentally identical, although at higher temperatures
the lines became broader and some of the fainter ones
disappeared. From this it is apparent firstly that
only one phase of the anhydrous salt exists in the tempera-
ture range from room to 100°C, and secondly that a mixture
having the composition of the hemihydrate at temperatures

above that of the higher eutectic contains only anhydrous lithium nitrate as the solid phase.   This evidence, together with the observations of Campbell and Kartzmark (3), decisively refutes the claim that a hemihydrate exists.

The x-ray powder diffraction pattern for $LiNO_3 \cdot 3H_2O$ is listed in Table II.   The lattice spacing gives the separation of the atomic planes in Angstrom units. Relative intensities of the lines were estimated visually, with the strongest line being assigned an intensity of 10. The trihydrate pattern has many lines in common with that of the anhydrous salt, but care was taken to ensure that no water was lost from the trihydrate; the pattern is not that of a mixture.
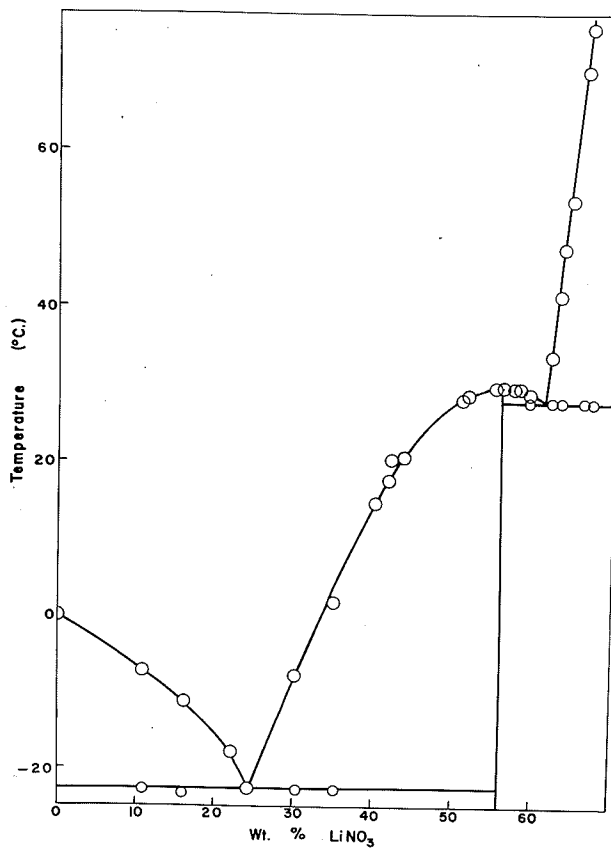
The System LiNO$_3$ — H$_2$O

Figure 15

B. The System Ethanol - Water

The results from the thermal analysis study of this system are listed in Table III and the phase diagram is shown in Figure 16. It was found that supercooling increased with ethanol content, becoming extremely persistent beyond 75 weight percent ethanol where it became impossible to detect an initial freezing point, although eutectic halts could be obtained with solutions having up to the eutectic composition. Even on warming a completely frozen solution no definite melting point could be obtained. This was perhaps because the very viscous mixture then present could not be stirred adequately even with fairly high speed stirring. On the alcohol side of the eutectic, supercooling and viscosity increased with increasing water content, but reasonably good freezing points could be observed up to the eutectic point. No eutectic halts were obtained in this region, and this may be an indication that the solid solution formation reported by Pushin and Glagoleva (14) does indeed exist.

Solid solution formation is most common between substances having similar crystal structures. Ice crystallizes in the hexagonal system, and although the structure of the ethanol molecule is known, nothing is known as to the crystal structure of solid alcohol, but the direct observations of Wahl (22) indicate that it has a very unsymmetrical form. This could easily result if the crystal

were made up from the irregular chains of ethanol molecules that Prietzschk has shown to be present in the cold liquid. It could then be possible for water to enter such a crystal lattice as part of an alcohol chain, or even as the point of linkage of two or more chains, since Prietzschk indicates that such linkage certainly takes place in the liquid. Formation of solid solutions of ice in ethanol thus may be accounted for readily without the need of similar crystal structures.

The freezing point curve shows the inflection found by Tarassenkov (15) and by Shalberov et. al. (16), but no peritectic halt could be obtained. The inflection falls at $-30^{\circ}C$ and 39.5 percent by weight ethanol. The eutectic was obtained at $-124.1^{\circ}C$, and at about 93.0 weight percent ethanol, whereas Pushin and Glagoleva (14) reported the values 93.5 weight percent ethanol and $-118^{\circ}C$ for this point. The freezing point of absolute ethanol was found to be $-114.4^{\circ}C$, within experimental error equal to the most generally accepted value of $-114.6^{\circ}C$.
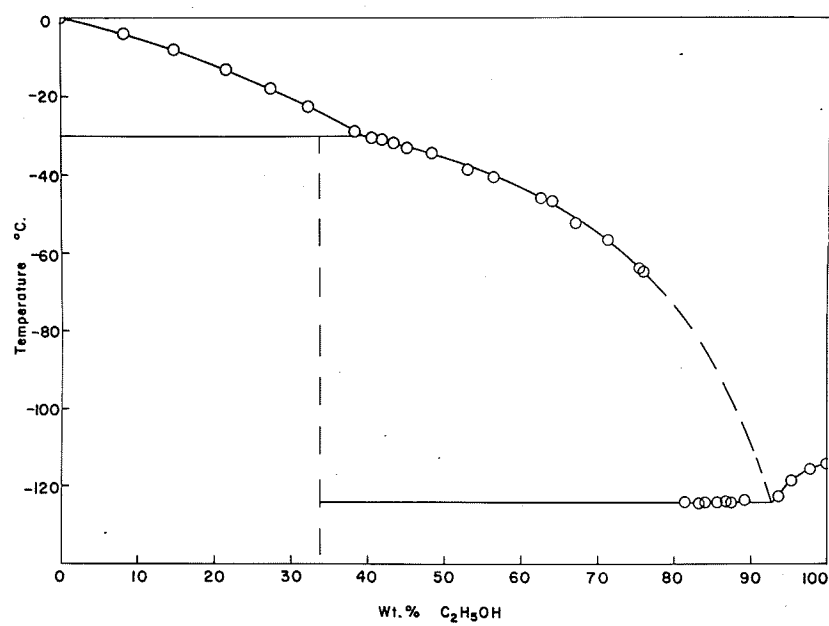
The System $C_2H_5OH - H_2O$

Figure 16

Results of the x-ray diffraction studies at low
temperatures are collected in Tables IV, V and VI, which
list the spacings and intensities of the lines from
diffraction photographs of ice, of dilute ethanol solu-
tions (i.e. solutions containing less than 30 percent
by weight ethanol), and of more concentrated ethanol
solutions, respectively. The pictures in all cases con-
tained much background darkening, and the lines were quite
broad since it was necessary to use wide capillaries to
prevent separation of the liquid column on cooling, so
that no great accuracy in the measurement of the spacings
could be obtained. Although the nominal diameter of the
camera was 57.3 mm., the fact that the ice pattern, the
mean of four pictures, has spacings consistently larger
than those listed in the A.S.T.M. index and determined by
Dennison (30) and by Barnes (31), indicates either that
the camera is slightly smaller than this or that shrinkage
of the film occurred. No attempt was made to calibrate
the camera, since only comparative results were desired
and the discrepancy was not large in any case.

From Table IV it is evident that the values of the
spacings for ice agree quite reasonably with those of the
literature (30) but are all somewhat larger as indicated
above. Neither the strong line of spacing $d = 3.67A^\circ$ nor

the weaker line at $d = 3.44A^\circ$ could be found, but a strong line was obtained at $d = 3.55A^\circ$, and it is probable that this is equivalent to the two missing lines. Considering the small camera used and the width of the lines obtained, it is not surprising that resolution of this line into its components was not obtained. A very weak line at $d = 4.14A^\circ$ which does not appear in the literature tabulation also occurred.

The diffraction patterns of dilute alcohol solutions taken under such conditions that no compound could be formed (i.e. at temperatures above that of the inflection point) were not good. The lines were quite diffuse, largely due to unfrozen liquid in the samples. As expected, the results here also agree fairly well with the literature tabulation for ice, although an additional line at $d = 3.76A^\circ$ appeared in three cases, and many of the weaker lines were absent. The additional line cannot be explained. The results are shown in Table V. The spacings are the mean of eight pictures.

The pattern given by solutions containing more than 40 percent by weight ethanol is listed in Table VI. A total of ten pictures containing distinguishable lines were used. These pictures were little better than those taken in dilute solutions and the lines were particularly broad,

since in general wider capillaries were required for such
solutions. Few lines were obtained -- really only three
that appeared at all consistently. Of these, the first,
at $d = 3.61A^{\circ}$, lies close to the position of a strong line in
the ice pattern. Since this line is both weak and diffuse,
there is the possibility that it is due to ice deposited on
the outside of the capillary from moisture present in the
camera at the beginning of the run, but it is difficult to
see how enough ice could be deposited in this way to give
an observable line, and it is most probable that it is a
true line from the specimen.

The other two lines, both strong and both nearly
always present, are quite far removed from any ice lines.
This is particularly true of that falling at $d = 2.97A^{\circ}$.
These two lines were predominant on the diffraction patterns
of solutions of alcohol exceeding 40 weight percent ethanol
and taken at temperatures between $-35^{\circ}C$ and $-90^{\circ}C$.   In no
case was the temperature taken to the freezing point of
ethanol or below, so they could not be due to solid alcohol.
Moreover, they did not appear on any picture taken of ice
at any temperature, or of more dilute solutions of alcohol
at temperatures above $-30^{\circ}C$. They can be explained only if
they are caused by a new solid phase freezing from the solu-
tion. They indicate that there is an incongruently melting

hydrate of ethanol formed, and that the inflection point on the freezing point curve is a true peritectic point.

A few solutions of roughly the expected composition of the hydrate, $C_2H_5OH \cdot 5H_2O$, were made up and photographed at temperatures well below the supposed peritectic temperature. These pictures showed only the ice pattern, whereas, if a compound is formed, they should show lines from it as well. This can be explained only if the system cools metastably past the peritectic temperature, and the reaction ice + solution $\longrightarrow$ compound does not take place. The absence of a peritectic halt on the cooling curves indicates that such is the case.

It should be pointed out again that the spacings measured from these diffraction patterns are not highly accurate and that any one picture by itself would be of doubtful value because of the broad lines and the generally dark background against which they were measured. However, as a group the results are consistent and any errors in the listed spacings are not nearly great enough to invalidate the conclusions drawn from them.

The question of the composition of this hydrate of ethanol cannot be answered satisfactorily. The position of the inflection corresponds to an alcohol - water ratio of 1 to 3.98. The compound must contain more water than this,

Although the formula $C_2H_5OH.4H_2O$ is possible, it is unlikely, since this is so extremely close to the position of the inflection. The most probable formula may be taken as that proposed by Shalberov et. al. (16); namely $C_2H_5OH.5H_2O$.

The diffraction photographs of absolute ethanol were disappointing. Only a single broad line of strong intensity was obtained. This had a spacing of $d = 3.89A^\circ$. This is the result from two pictures, one taken with copper, the other with iron, radiation. The latter was used in the hope that it would result in the resolution of the single line into the closely spaced triplet observed by Prietzschk (18). It did not. The position of the single line obtained appeared to be similar to that of the triplet in the photograph published by Prietzschk, but unfortunately, he does not indicate any spacings.

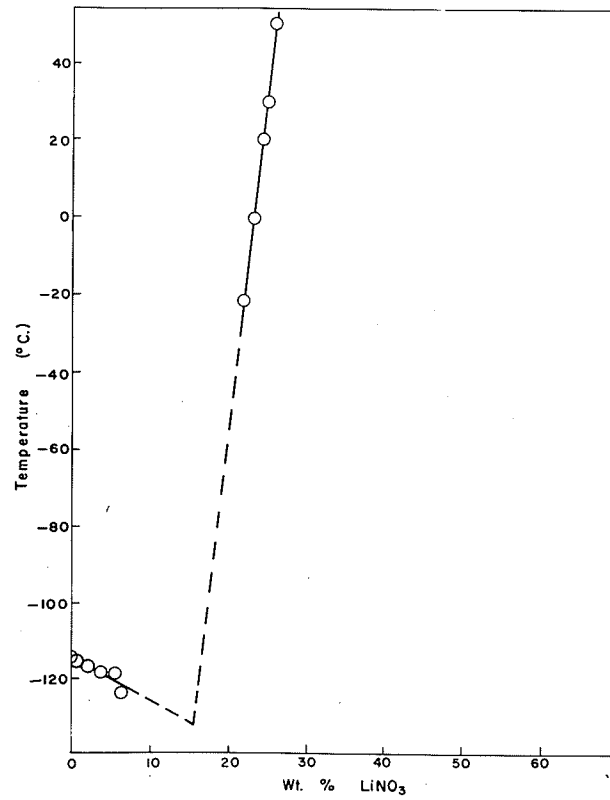C. The System Lithium Nitrate – Ethanol

The results obtained by thermal analysis for the system $LiNO_3$-C_2H_5OH are shown in Table VII. Only quite dilute solutions could be frozen, and for these it was found that supercooling increased with lithium nitrate content. The viscosity of such solutions appeared to be much greater than that of any alcohol – water mixture at the same temperature. Solutions containing about ten percent lithium nitrate at temperatures of about $-100^\circ C$ formed a sticky semi-solid

mass that refused to crystallize, while more concentrated
solutions reached this state at higher temperatures.   The
supercooling encountered here made accurate determination
of the freezing points of solutions that did freeze impos-
sible.   No eutectic halt could be detected.

Solubility measurements are summarized in Table VIII.
These solutions, even near room temperatures, were quite
viscous.

A plot of freezing point and solubility data, as seen
in Figure 17, shows that, in order that the two curves should
intersect without compound formation, the eutectic point
must lie unusually far into the diagram.   For systems
involving substances whose melting points are as dissimilar
as are those of ethanol and lithium nitrate, it is seldom
that the eutectic lies more than a very little distance from
the axis of the lower melting component.   It is quite
possible, then, that an alcoholate of lithium nitrate exists
in the solid state.   If congruently melting, such a com-
pound would have a composition between $LiNO_3 \cdot 7C_2H_5OH$, and
$LiNO_3 \cdot 3\frac{1}{2}C_2H_5OH$.

The very great viscosity of alcoholic lithium nitrate
solutions at low temperatures indicates some sort of inter-
action between ethanol and lithium nitrate.   It is extremely
probable that the strongly electropositive lithium ion and

The System LiNO$_3$ - C$_2$H$_5$OH

Figure 17

the electronegative oxygen of the alcohol exhibit strong
electrostatic attraction for one another, just as do
lithium ions and water.   Since at low temperatures the
ethanol molecules are linked in chains, the lithium ions
would be solvated by a number of these chains, and would
in effect form the point of linkage of them.

It is also conceivable that hydrogen bonding could take
place between the oxygen atoms of the nitrate radical and
the oxygen of the ethanol molecule.   This bonding would
become stronger as the temperature decreased, and this
would readily explain the viscosity effects noted.
Either or both of these attractions could operate.

The only quantitative viscosity data available for
lithium nitrate in ethanol solution are those of Campbell
and Debus (1), at 25°C.   These are plotted in Figure 18.
The relative viscosity of lithium nitrate in absolute
alcohol is much greater than than of lithium nitrate in
water (32) at the same concentration.   This is true to
a lesser degree for solutions in 70 weight percent ethanol
also, but the relative viscosities of lithium nitrate in
water and in 30 weight percent ethanol are nearly the same,
although the absolute viscosity of the alcohol solutions
is greater than that of the solutions in water.

The shapes of the viscosity-concentration curves for lithium nitrate in water and in ethanol are quite different as well.   In water and in solutions of 30 weight percent ethanol the viscosity rises slowly until the concentration of the salt becomes fairly large, and then increases very sharply, whereas in absolute alcohol the viscosity rises steeply at once in an almost linear manner.

It is impossible to draw definite conclusions regarding solvation from viscosities in these mixed solvents. If we concede, however, that the increase in the viscosity of such solutions is due to interaction between solute and solvent, it is evident that even at $25^\circ C$ considerable interaction takes place between lithium nitrate and ethanol.

O = LiNO₃ in H₂O
● = LiNO₃ in 30% C₂H₅OH
▲ = LiNO₃ in 70% C₂H₅OH
△ = LiNO₃ in 100% C₂H₅OH
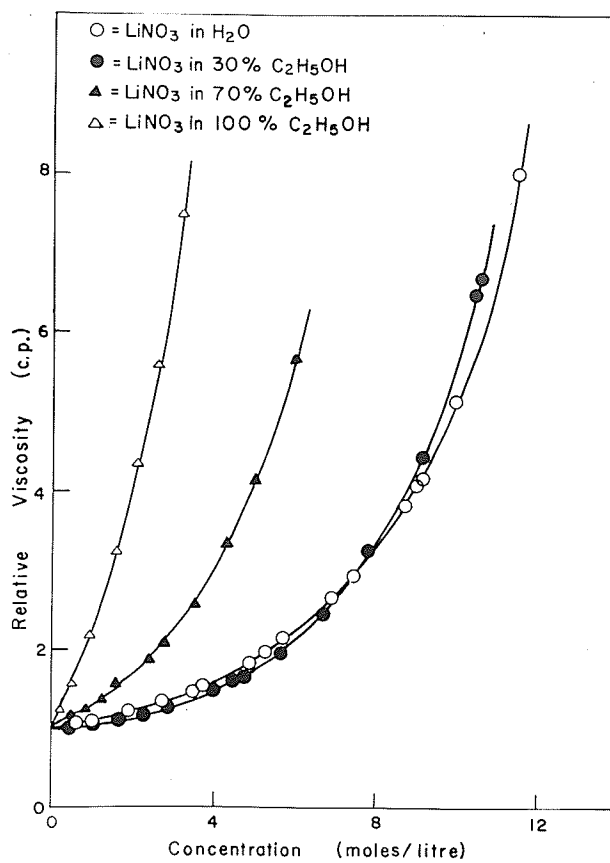
Relative Viscosities of Solutions of
LiNO₃ in Water and in Ethanol

Figure 18

D. The Ternary System Lithium Nitrate - Ethanol - Water

Five pseudo-binary "cuts" in which lithium nitrate was dissolved in solvents of fixed ethanol - water ratio were made through the ternary system. The solvents were 27.2, 42.0, 49.7, 66.4 and 78.2 weight percent ethanol. Tables IX to XIII list the thermal analysis data, while Figures 19 to 23 show the freezing point curves which were obtained. It was found that super-cooling increased with alcohol content except when an-hydrous lithium nitrate was the solid phase, when it was nearly negligible even in solutions containing consider-able alcohol. Supercooling was especially pronounced with solutions in 78.2 percent ethanol where freezing points below -20°C could not be obtained satisfactorily.

The first three pseudo-binary systems, those where solutions were of lower ethanol content, showed no trace of any solid phases of lithium nitrate except the tri-hydrate and the anhydrous salt, but the "cut" in 66.4 percent ethanol exhibited a halt, on some of the cooling curves, which is explicable only if a peritectic point is present. This fell at 12.3°C, about 5°C below the maximum on the freezing point curve, and at 29 weight percent lithium nitrate. Considerable metastability was encountered in this region, making investigation of

the apparent peritectic point difficult. Moreover,
since the solution which would be present at a peritectic
halt in this region does not have the ethanol – water
ratio of the pseudo-binary system, the true significance
of the halts must be considered somewhat uncertain.

The "cut" in a solvent of 78.2 weight percent
ethanol shows (Figure 23) that no congruently melting
compounds exist here. A definite peritectic point exists
at 5.4°C, 33 weight percent lithium nitrate. A distinct
inflection on the freezing point curve at 3°C and 28
weight percent lithium nitrate also exists, but no peri-
tectic halt was obtained to indicate that it is really
significant. As mentioned above, this system showed
extreme metastability, which could account for the failure
to obtain a peritectic halt. Such supercooling made the
study of systems of higher ethanol content practically
impossible.

The system lithium nitrate trihydrate – ethanol is
shown in Figure 24 and the thermal analysis data are given
in Table XIV. Some of these points are taken from the
freezing point curves of the pseudo-binary systems
described above. A slight inflection appears to exist
at about 30 weight percent ethanol, but nothing was ob-
served to indicate that this is a peritectic point.

The x-ray diffraction studies yielded no definite results. Photographs of solid exposed to the atmosphere gave only the pattern of the trihydrate, but this would be the expected result if the specimen were some other solvated phase that tended to lose alcohol. Any anhydrous salt thus formed would undoubtedly absorb moisture from the air to become hydrated.

Material crystallizing from the maximum on the pseudobinary cut in 66.4 percent alcohol, when photographed in a glass capillary tube, showed relatively few lines. These could have belonged either to the trihydrate or to the anhydrous salt. Thus, again, the possibility of an alcoholate decomposing below room temperature arises.

Figures 25 and 26 show the ternary system as a whole. In Figure 25, a series of isothermal solubility lines are depicted. These were obtained from the various pseudobinary cuts by reading off the compositions corresponding to each temperature. The isothermal at 25°C is fundamentally the same as that determined by Campbell and Kartzmark (3), but since a limited number of points were available it is less exact. A minor difference exists in the region of 50 to 70 percent ethanol where anhydrous lithium nitrate is the solid phase. A distinct curvature of this line is obtained, whereas Campbell and Kartzmark draw a straight

line here.   This is attributable to their widely spaced
points in this region.   Isothermals at 20°C, 15°C, 10°C,
0°C, -15°C, -35°C, and -60°C are also shown, as well as the
line in the ice region at -20°C.

In Figure 26, only the eutectic and peritectic troughs
are shown.   Again, the composition data were obtained from
the pseudo-binary cuts.   It may be observed that the
eutectic trough where trihydrate and anhydrous salt are in
equilibrium is a straight line until about 30 percent
ethanol is added; curvature then begins.   It is possible
to link this point and the points at which inflections were
noted on the pseudo-binary cuts and on the lithium nitrate
trihydrate - ethanol cut to give a plausible peritectic
trough in the system.   The evidence available, however,
really does not justify its inclusion.

It is apparent from the above discussion that the ex-
istence of a ternary compound, perhaps having a formula
such as $LiNO_3 \cdot 2C_2H_5OH \cdot H_2O$, is possible, but the evidence for
it is extremely inconclusive.   It is reasonably certain that
no alcoholates of lithium nitrate crystallize from a solvent
of less than fifty weight percent ethanol, but in more concen-
trated alcohol solutions the nature of some of the solid
phases is uncertain.   In cases where the solvent contained
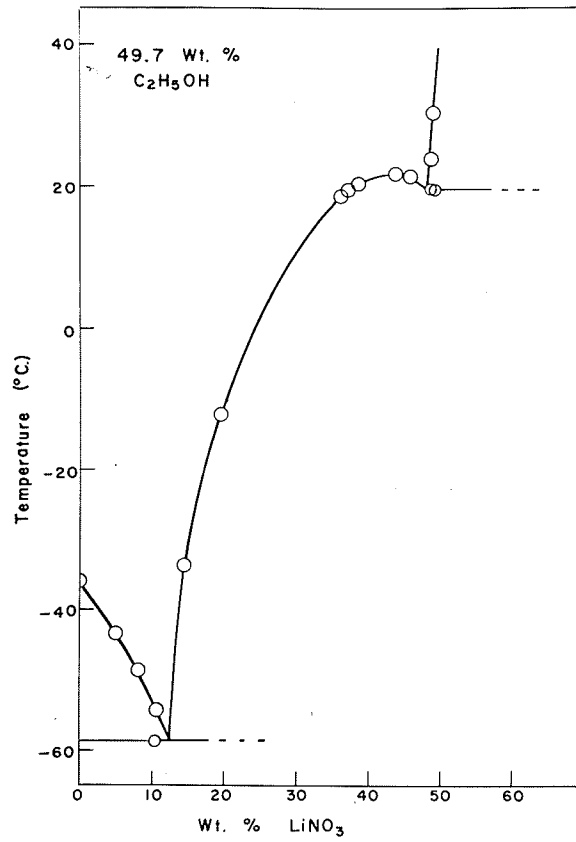more than 80 percent ethanol, pronounced supercooling prevented
an adequate study.
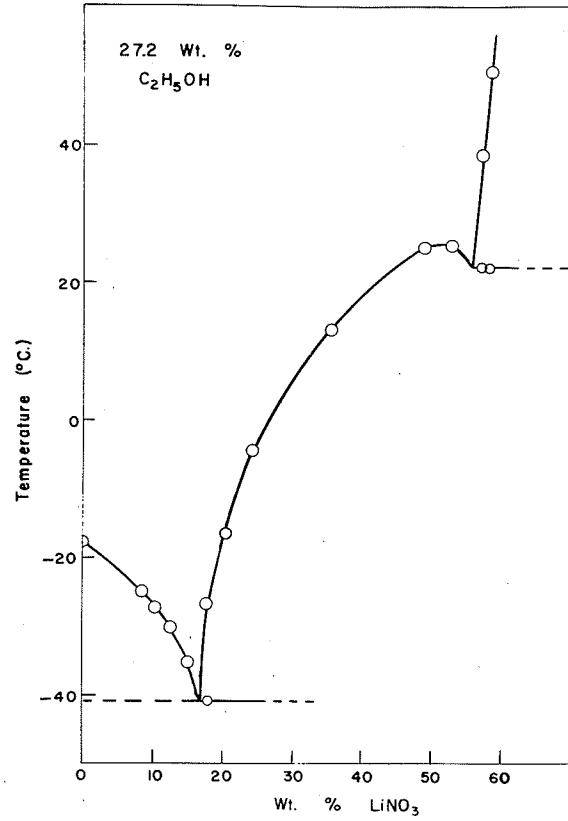
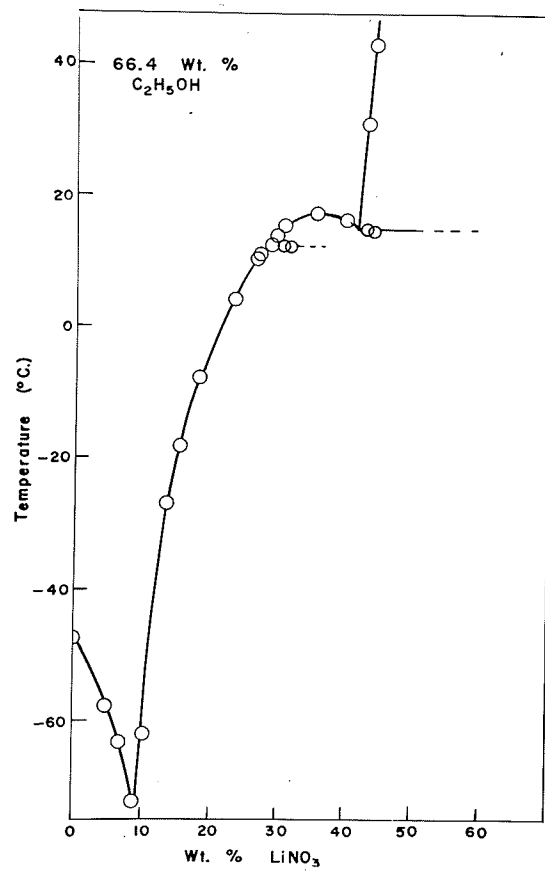The Pseudo-Binary System
$LiNO_3$ – 22.7 Wt. % C_2H_5OH

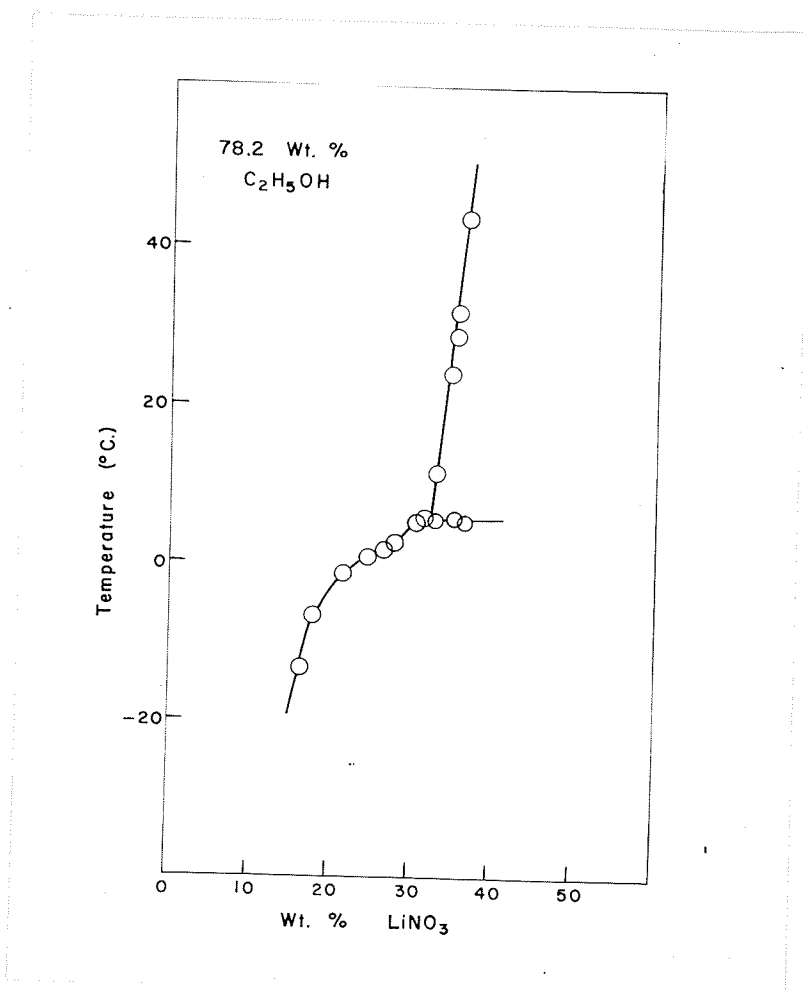Figure 19
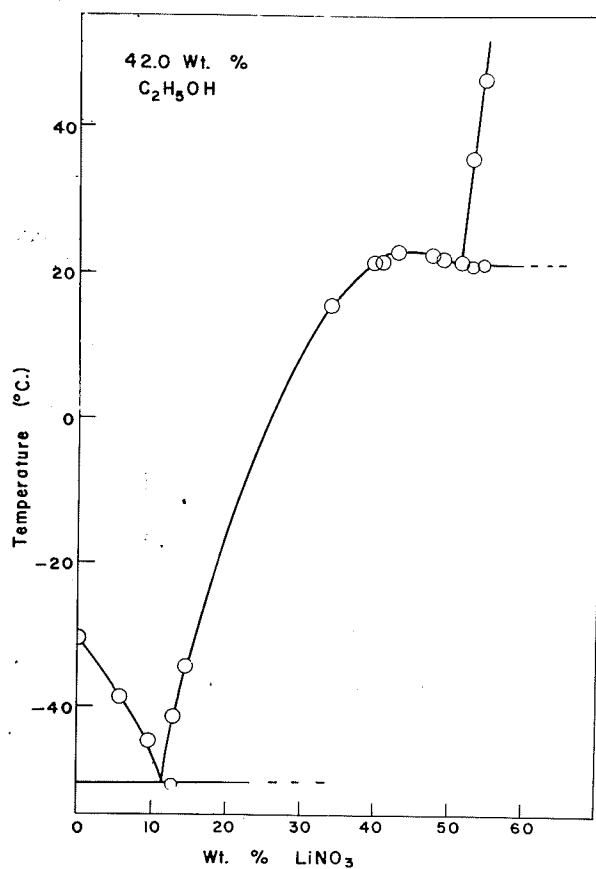
The Pseudo-Binary System
LiNO$_3$ - 42.0 Wt. % C$_2$H$_5$OH

Figure 20

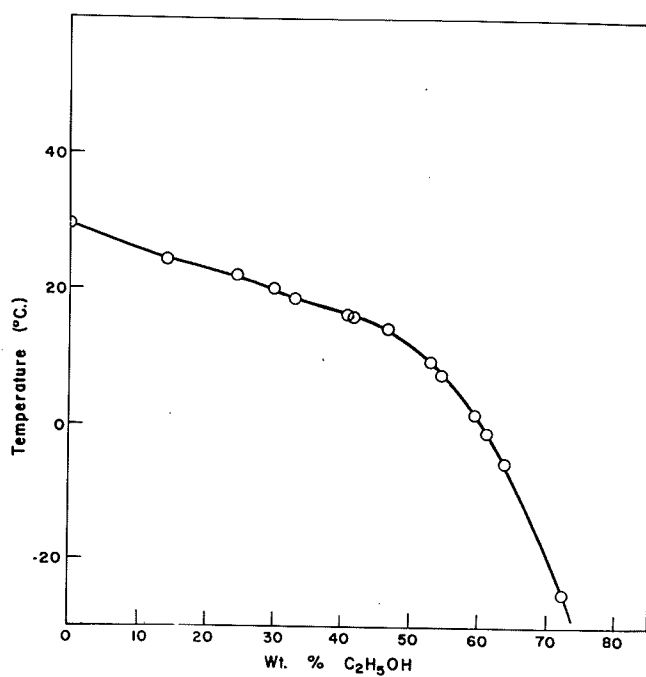The Pseudo-Binary System
$LiNO_3 - 49.7$ Wt. % C_2H_5OH

Figure 21

The Pseudo-Binary System
LiNO$_3$ – 66.4 Wt. % C$_2$H$_5$OH

Figure 22

The Pseudo-Binary System
$LiNO_3$ — 78.2 Wt. % C_2H_5OH

Figure 23

The System $LiNO_3 \cdot 3H_2O - C_2H_5OH$

Figure 24
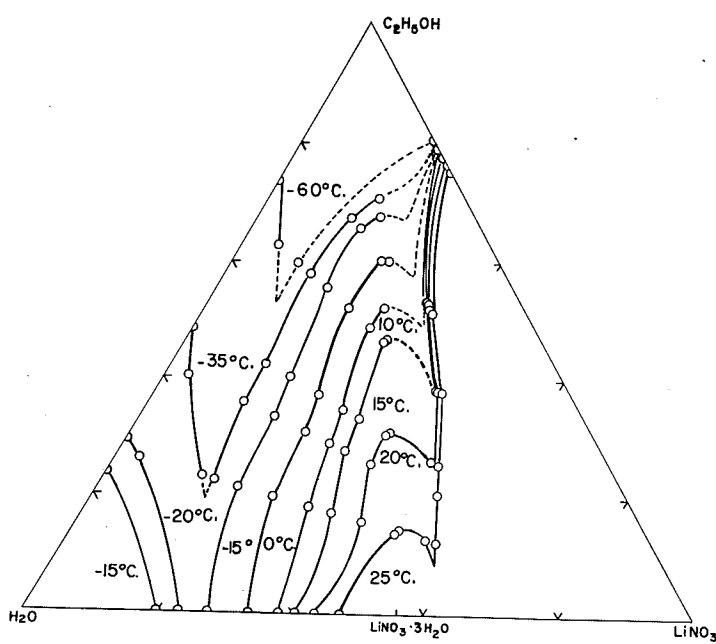
Solubility Isotherms in the System LiNO$_3$ – C$_2$H$_5$OH – H$_2$O

<u>Figure 25</u>
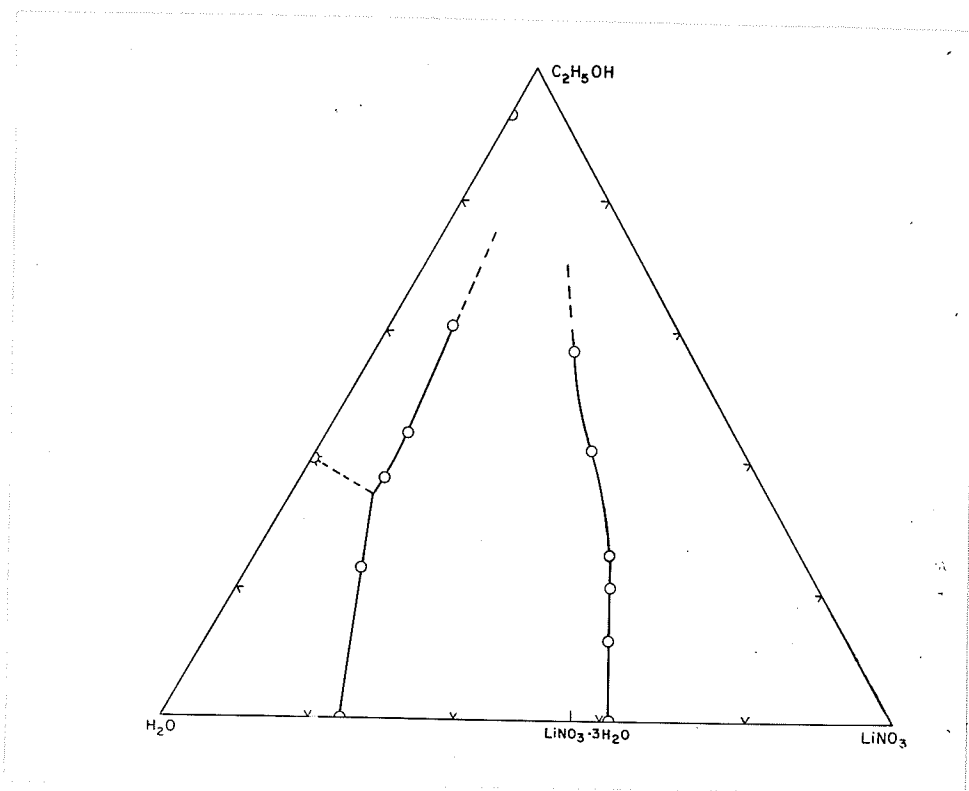
Eutectic Troughs in the System $LiNO_3 - C_2H_5OH - H_2O$

<u>Figure 26</u>

SUMMARY AND CONCLUSIONS

The system lithium nitrate - water was investigated by thermal analysis and by x-ray powder diffraction studies. Two eutectics were found, one at -22.9°C and 24.5 weight percent lithium nitrate where ice and trihydrate are the solid phases, and the other at 27.9°C and 61.5 weight percent salt, where trihydrate and anhydrous lithium nitrate are the solids present. No trace of the hemihydrate reported by Donnan and Burt (2) could be found by thermal analysis, and no solid phase but the anhydrous salt was indicated by x-ray powder diffraction. The x-ray powder diffraction pattern of $LiNO_3 \cdot 3H_2O$ was determined for the first time.

The system ethanol - water was also studied by the above methods. Thermal analysis showed an inflection at -30°C, 40 weight percent ethanol. This is almost certainly a true peritectic point. The formula of the hydrate formed remains uncertain, but is probably $C_2H_5OH \cdot 5H_2O$. The eutectic lies at -124.1°C, 93 weight percent ethanol.

Low temperature x-ray powder diffraction studies of frozen ethanol solutions provided the only evidence that the inflection mentioned above is a true peritectic point. The powder pattern of solutions containing more than 40 weight percent ethanol, at temperatures between -30°C and -90°C, was distinctly different from that of ice. This difference can

be explained only if a solid hydrate exists in this region.

A very simple low temperature modification of the Buerger (27)(28) high temperature x-ray camera was used in the above study, and this has been described.

The system lithium nitrate - ethanol was studied by thermal analysis and by isothermal solubility determinations. High viscosity and extreme supercooling permitted the study of only very dilute solutions and those near room temperature, but a large gap between these regions could not be investigated. No evidence of alcoholate formation was found, although strong interactions between solute and solvent were indicated.

The ternary system lithium nitrate - ethanol - water was investigated by thermal analysis. Freezing points of lithium nitrate in a series of solvents each of fixed ethanol - water ratio were determined. These formed a series of pseudo-binary systems. The solvents used were 27.2, 42.0, 49.7, 66.4, and 78.2 weight percent ethanol. In the latter two, some very inconclusive indications of the existence of a ternary compound were obtained. The system $LiNO_3 \cdot 3H_2O$ - C_2H_5OH was also investigated.

The data from the pseudo-binary systems were used to plot isothermal solubility diagrams for the ternary system and to plot the eutectic troughs over part of their range. No indication of solid alcoholates of lithium nitrate were found

in solvents containing less than 50 weight percent ethanol, and there can be little doubt that none are formed here. The situation in solutions of higher ethanol content is uncertain; evidence for alcoholate formation was obtained, but it is not conclusive.

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