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****

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THE SYSTEM

$NiSO_4$ - $CaSO_4$ - H_2O.

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INTRODUCTORY NOTE.

Sometime ago it was noticed by Dr. A. N. Campbell that the solubility of calcium sulphate is considerably greater in a solution of nickel sulphate than in pure water under similar conditions. This was particularly the case at high temperatures.

According to Phase Rule, when the solubility of one salt is increased in the presence of another salt in solution it may generally be inferred that combination occurs between the two salts with the formation of a double salt which is present in contact with that solution.

With this point in view, Phase Rule study was carried out on the solubility of calcium sulphate in nickel sulphate solutions of various concentrations at three different temperatures.

The following narration therefore, is the account of the application of Phase Rule to the investigation of solubility relations between two salts and water, the method employed in this particular problem and the results obtained therefrom.

I wish to express my indebtedness to Dr. A.N. Campbell for his guidance and his valuable advice on many occasions during the progress of this research.

THEORY OF

THREE COMPONENT SYSTEMS

CONSISTING OF

TWO SALTS AND WATER.

THREE COMPONENT SYSTEMS.

The study of equilibria in various systems has been considerably simplyfied by distinguishing the systems according to the number of components existing in them.

Systems[1] are therefore characterised as one, two, three or four component systems.   In the study of one or two component systems no difficulty is experienced in determining the equilibrium between their phases and in the method of representation of their relationships, but in the case of a three component system the problem is somewhat more complex. An increase in the number of components gives rise to a much greater number of systems, and the equilibrium relations of these introduce a number of complications.

On applying the phase rule to a system of three components:-

$$F = C - P + 2$$
$$= 3 - P + 2$$

five phases are necessary to constitute a nonvariant system, four for a monovariant and three for a divariant. Thus a monovariant system exists at a quintuple point.

At an invariant point of a three component system, as in the case of other invariant systems there must be at least one solid phase present, since vapour phase is one, maximum number of liquid layers being three, so that to preserve invariance one solid phase is necessary.

The maximum number of degrees of freedom in
a three component system is four and the minimum number
is zero, in which case not only pressure and temperature but
also the concentration of two of the components must be
fixed to preserve invariance of the system.

Various methods have been suggested to represent
graphically the numerical relationships between the
components of the system.

For two component systems rectangular coordinates
are employed - the concentration of one component expressed
in terms of a fixed amount of the other being measured along
one axis, and the change of another independent variable,
e.g. temperature, measured along the other axis.

In the case of three components one can adhere
to the rectangular system of representation, and this is most
convenient when dealing with systems where the behaviour of
the two of the components with respect to one another is largely
different from their behaviour with respect to the third, e.g.
two salts and water.   Here the concentration of one salt
in a constant weight of water is measured along one axis
and that of the other salt along the axis at right angles
to this, whilst the change of the system with the temper-
ature is represented by the third axes at right angles
to the first two.   This method of representation has a disad-

vantage in that there is no place in the diagram for an
anhydrous double salt nor for solutions containing very
little of the third component. Where the three components
behave in much the same manner towards one another,
rectangular coordinates are not at all serviceable.

Gibbs[2] has suggested the use of a triangular
diagram, where provided the sum of the components is
kept constant, if we take an equilateral triangle of unit
height, the corners of the triangle will represent the pure
components, and any point within the triangle some definite
ternary mixture of the three substances. Any point on
one of the sides of the triangle will give the composition
of a mixture in which only two components, i.e. those which
represent the two angles which this side makes with the
other two lines of the triangle.

By this method it is possible to represent a
mixture of any composition making use of the fact that
"the sum of the concentrations of the three components
will add up to 100% or unity if we work in fractions.
One of the properties of a triangle is that the sum of the
perpendiculars from any point within it unto the sides is
equal to the height of the triangle". Making use of this
fact, it is at once obvious that the composition of a
ternary mixture represented by a point within the triangu-
lar diagram, can be expressed by dropping perpendiculars
to the sides of the triangle from that point. The length

of each of the respective perpendiculars represents the
fractional amounts of the three components present in
the ternary mixture.
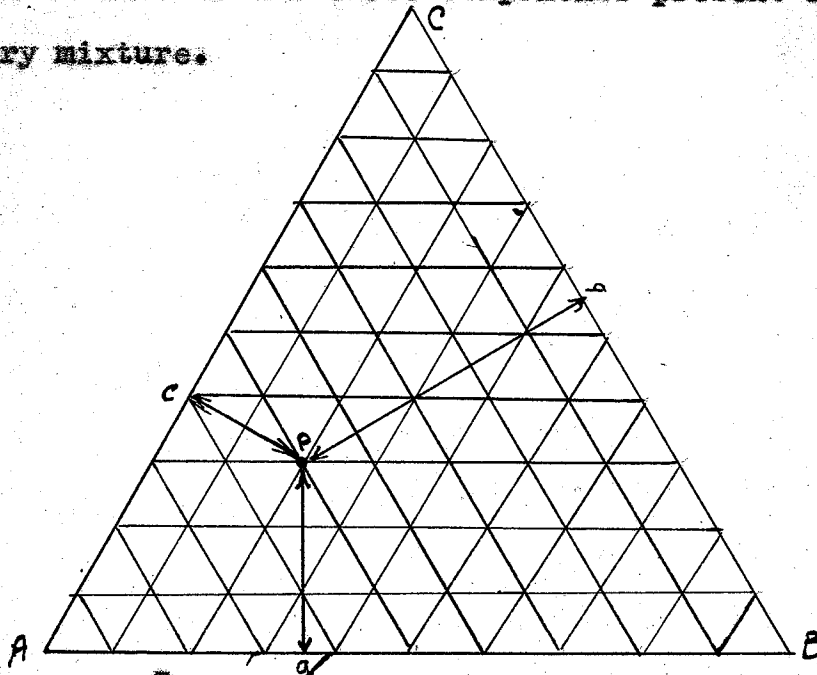
Roozeboom[3] has proposed another form of triangular
diagram which is distinctly superior to that already con-
sidered. It consists of an equilateral triangle with
lines ruled parallel to each side instead of perpendicular.
The length of the side is taken equal to unity or more
often one hundred and the same scale is used for the binary
systems in the side of the triangle as for the ternary
system in the interior. The sum of the fractional or
percentage amounts of the three components is represented
by a side of the triangle. The composition of a ternary
mixture is obtained by determining not the perpendicular
distance of a point from the three sides of a triangle,

but the distance _parallel_ to the sides of the triangle.
Diagram:-
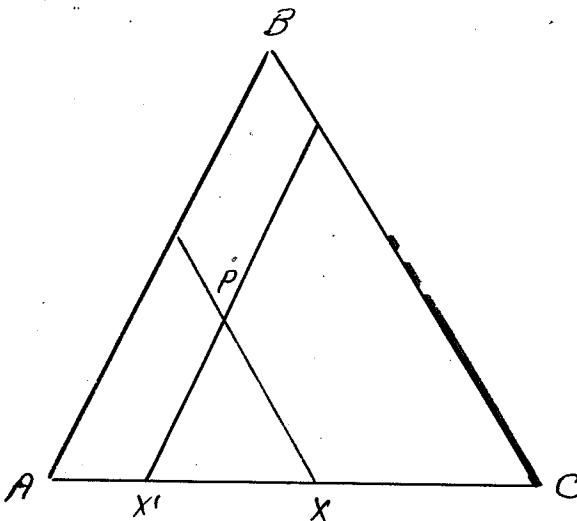
Thus, in order to express the composition of the ternary
mixture of components A, B, and C, represented by the point
P, the portion Bx is measured off and represented percentage
or fractional part of A present.   Similarly Ax' shows the
amount of B component, and the remainder xx' represents the
amount of the third component C.   From the point x, the line
drawn parallel to the side BC of the triangle and similar
one from the point x' parallel to the side AC.   These two
lines meet at the point P.   Hence, from the figure it is
evident that such ternary mixtyre consists of:-

      50% of Component A

      30% of B and

   20% of C, or their fractional parts are 5,3,

and 2 respectively.

In passing it may be well to note an important
property of triangular representation which is that
"a line drawn from one corner of the triangle to the

opposite sides represents the composition of all
mixtures in which the relative amounts of two of the
components remain in fixed proportion - that of their
original composition.

Diagram:-
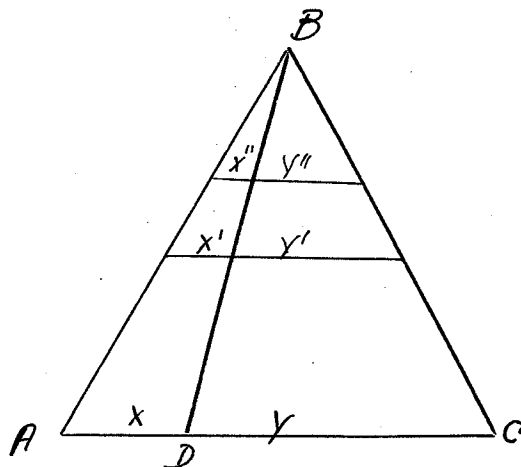
If component B be added to a mixture D of A and
C, every possible ternary mixture will lie on the line BD,
and in every such mixture the proportions of the components
A and C will be in the ratio X:Y.

Thus X:Y::X':Y'::X'':Y'' etc.

In phase rule work it is desired to represent at the
same time the effect of another independent variable, e.g.
temperature, which is done by measuring temperature along
the axes perpendicular to the corners of the triangle.
This results in a right prism and any plane cut through it
parallel to the base represents the behaviour of the three
component systems at the temperature represented by the
plane.   This is known as an <u>isothermal surface</u>.

This method of representation of the relative
behaviour of three components at varying temperatures has

a very wide application in the study of a three component
equilibria. It is useful in the study of solutions of
liquids in liquids, some or all of which are partially
miscible. Their relative miscibility and the change of
such with temperature may be systematically represented
by the above method. It is also very applicable to the
consideration of those ternary systems in which one or
more solid phases can exist with one liquid phase.
Such systems may be divided into two classes:- first,
those systems that are met with in the determination of
freezing point curves of molten metals.

Here, one may represent the change in the
freezing point of a two component system by the addition
of the third component. The change of this in turn with
temperature is clearly represented on a right prism
described above. This includes thermal studies of minerals
and of compounds and materials such as Portland Cement,
produced by fusion of their components.

The systems belonging to the first class have
been mentioned to show the applicability of this method of
representation, but further types of this will not be dis-
cussed as this is not a part of the present problem.

TWO SALTS AND WATER.

This system will be discussed more fully
owing to the fact that the present problem is the study
of equilibria of two salts and water.   When a system
is composed of two salts and water as its components, it
is necessary that the two salts must be salts either of
the same acid or the same base:-
They must be of the types:

$$AB = A^+, \quad B^-$$
$$\text{and} \quad AC = A^+, \quad C^-$$
$$\text{or} \quad AB = A^+, \quad B^-$$
$$DB = D^+, \quad B^-$$

This restriction must be made to have this a three component
system, otherwise the system is one of four components.

Let us consider the meaning of the term "trans-
ition point".   In a binary system when a hydrated salt such
as decahydrate of sodium sulphate is heated to the temper-
ature of 32.50, it undergoes partial liquefaction due to its
decomposition into water and anhydrous sodium sulphate.
The temperature at which this change takes place is known
as the transition temperature for decahydrate.   One form
of this salt is stable above this temperature and the other
below it.

Transition points are also met with in the three
component systems constituted of two salts and water, where
the change may be that of hydration or of the formation of

double salt which is usually accompanied by a change of
hydration.

Several examples of this are known, but only
one or two[4] of such will be quoted to indicate some facts
on which the study of such three component systems is
based.

When d-NaK tartrate is heated to a temperature
of above 55°, it decomposes into its constituent single salts
d-Na tartrate and d-K- tartrate and water.

The change may be represented by the equation:-
$$4NaKC_4O_6H_4 \cdot 4H_2O = 2Na_2C_4O_6 \cdot 2H_2O + 2K_2C_4O_6H_4 \tfrac{1}{2}H_2O + 11H_2O$$

If, on the other hand, the tartrates of Na and K
are mixed in the above proportions above 55°, and temper-
ature allowed to fall, the formation of a double salt will
result. Here, the transition point for this compound is
55°- double salt being stable below it and its two con-
stituent salts above.

A similar instance is found in the behaviour of the
sulphates of sodium and magnesium with formation of the
double salt, astracanite according to the equation.
$$Na_2SO_4 \cdot 10H_2O + MgSO_4 \cdot 7H_2O \underset{}{\overset{22^o}{\rightleftharpoons}} Na_2Mg(SO_4)_2 \cdot 4H_2O + 13H_2O.$$

Here, however, the formation of double salt takes
place above the transition point and decomposition into
constituent salts below it.

Such systems are similar in their behaviour,
and whether the formation of double salt occurs above or
below the transition point may be determined by the

empirical rule that "if the water of crystallization
of the two constituent salts together is greater than
that of the double salt, the latter will be formed on
raising the temperature, but if the double salt contains
more water of crystallization than the two single salts,
raising the temperature will effect the decomposition of
the double salt."

In applying Phase Rule to the study of any
system, the vapour pressure of the system must be considered
in order to determine the degree of freedom of the equilibrium.
Thus, applying Phase Rule in the determination of pressure
- temperature curve of Glauber's Salt

$$F = C - P + 2$$
$$= 2 - 3 + 2 = 1$$

this binary system has one degree of freedom - that is to
every temperature there corresponds a definite vapour
pressure of the system. Similarly, above 32.5 the anhydrous
sodium sulphate in solution constitutes a univariant system
with definite vapour pressure corresponding to each temper-
ature. At 32.5° the two curves intersect and the system
then has four phases, namely:-
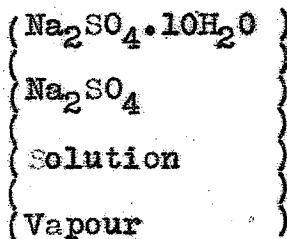
$$\left.\begin{array}{l} Na_2SO_4 \cdot 10H_2O \\ Na_2SO_4 \\ Solution \\ Vapour \end{array}\right)$$ giving $F = 2-4 + 2 = 0$
a non-variant system at a
quadruple point

At this point both systems are in equilibrium and their
vapour pressure is the same. At this point every variable

is defined - and if pressure, temperature or concentration
be altered, one of these phases disappears yielding
$F = 2 - 3 + 2 = 1$, a univariant system.   Since four phases
are present at a quadruple heat, this point is the inter-
section of four univariant systems, which are:

1. Na_2SO_4, Solution, Vapour.

2. $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, Vapour.

3. $Na_2SO_4 \cdot 10H_2O$, Solution, Vapour.

4. $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, Solution.

The equilibrium of each system is shown on the graph:-
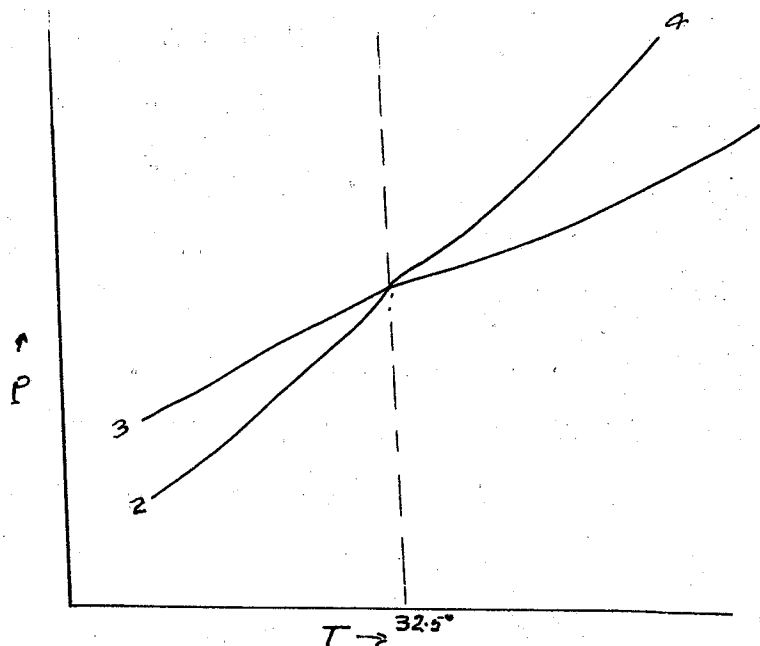
Similar relationships are met with in three
component systems, such as the case of two salts and water
with their formation of double salt.

Thus a mixture of sodium sulphate decahydrate and magnesium sulphate heptahydrate forms an univariant system, i.e.

$$F = 3 - 4 + 2 = 1$$

which means that on heating this mixture to any temperature the vapour pressure is definite. These relative changes are graphically represented by a straight line up to $22°$ where the two single salts give rise to the formation of the third solid phase, astracanite.

Thus _five_ phases are present,- so that the point at which this change occurs is known as a quintuple point. Applying Phase Rule:-

$$F = C - P + 2$$
$$= 3 - 5 + 0$$

The system is _invariant_ - that is, pressure, temperature and concentration must have a definite value to preserve all five phases.

Just as in a binary system the quadruple point is the intersection of four curves, similarly in a ternary system, the quintuple point is where five curves, each representing an univariant system intersect.

The five univariant systems are:-

1. $Na_2SO_4 \cdot 10H_2O$, $MgSO_4 \cdot 7H_2O$, Astracanite, Vapour.

2. $Na_2SO_4 \cdot 10H_2O$, $MgSO_4 \cdot 7H_2O$, Solution,   Vapour.

3. $MgSO_4 \cdot 7H_2O$, Astracanite, Solution   Vapour.

4. $Na_2SO_4 \cdot 10H_2O$, Astracanite, Solution,   Vapour.

5. $Na_2SO_4 \cdot 10H_2O$, $MgSO_4 \cdot 7H_2O$, Astracanite Solution

Representing these on the P-T diagram we get:-
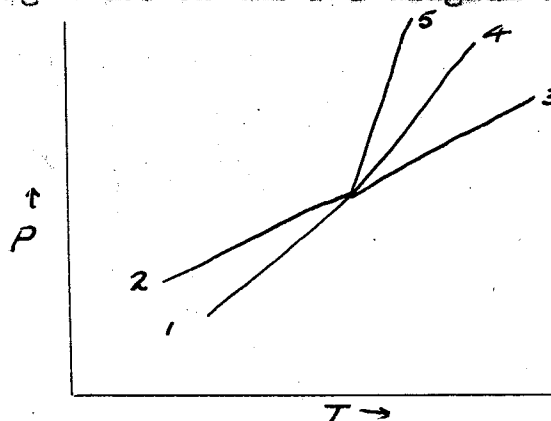
Curve "5", representing the effect of pressure on the

transition point of astracanite, slants to the right showing

that the transition point is raised with the rise in pressure,

hence the formation of astracanite occurs with expansion in

volume.

Curves (2), (3) and (4) represent univariant ternary

systems, in which one of the phases in equilibrium is

solution.   Hence they may also be considered as solubility

curves of various phases in equilibrium.

If the ordinate represent the concentration

of the two constituent salts and the abscissae, temperature

curve (2) is the solubility curve of two $Na_2SO_4 \cdot 10H_2O$

and $MgSO_4 \cdot 7H_2O$.

Similarly curve (3) is the solubility curve of

$MgSO_4 \cdot 7H_2O$ and astracanite at various temperatures.

It should be noted that in a three component system, two solid phases are necessary to make the system univariant and obtain a temperature - concentration curve of these. If, however, the temperature is fixed, then pnly one solid phase must be present in contact with solution to give a univariant system.

Hence, in the ternary system $CaSO_4$-$NiSO_4$-H_2O, we can have varying amounts of $CaSO_4$ in solution with varying amounts of $NiSO_4$ present or vice versa. Thus, if $CaSO_4$ is present as solid phase, the system has one solid, one solution and one vapour phase - three phases and three components giving a univariant system, considering pressure to be constant, as is usually the case in solubility determinations. System is univariant at constant temperature for to every concentration of $NiSO_4$ in solution, there is definite concentration of $CaSO_4$ in that solution. Hence, similar solubility curve is obtained in the P-T, or T-C curves already discussed.

It was already pointed out in the case of sodium sulphate and water, that the solubility curve of the salt undergoes a sudden change in direction at a transition point, and this in invariably accompanied by a change in the solid phase in equilibrium with the solution. The same behaviour is found in the case of double salts. This was pointed out in the discussion of the ternary system $MgSO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$ and water. To illustrate this more fully another example may be given - that of rubidium

dextro and levo tartrates, and the formation of Rb-racemate from them.

Diagram:-
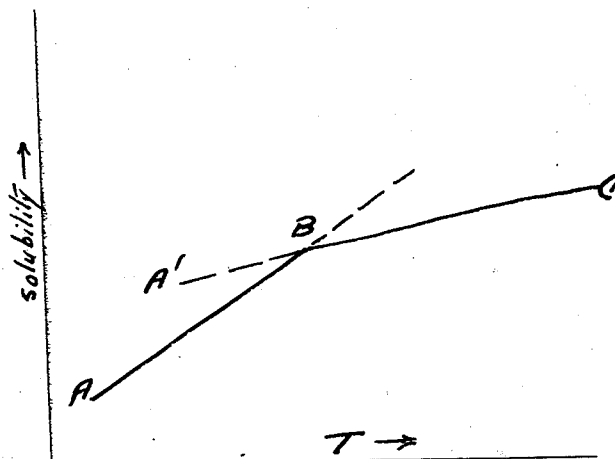
AB represents the solubility of racemate and A'BC that of mixed tartrates.

The graph shows that the solubility of racemate is le s than that of its two constituent salts. Thus solution represented by a point on the curve A'B is saturated with respect to d and l mixture but supersaturated with respect to double salt. Hence, racemate will be deposited, and its final concentration will be represented by the point on the curve AB. Similarly for the solution represented by a point on the metastable prolongation of AB curve. Hence, point B is the transition point for two single salts and a double salt.

The same rule holds for a ternary univariant system where only one solid phase is present and the temperature is fixed. One curve represents the equilibrium of univariant system composed of:-

(One salt as solid phase
(Solution of two salts in water
(Vapour

When there is a break in such a solubility curve
this break is due to a change in the solid phase in
equilibrium with the solution.   This change may be either
the change of hydration of the solid phase or double
salt formation, or, both.

Such curves showing the solubility relations
at constant temperature, are known as isothermal solubility
curves. They show the solubility of one component on the
addition of another component and the conditions of forma-
tion and stable existence of double salts in solution.

For the graphic representation of isothermal
relations in ternary systems, one may employ either the
rectangular or the triangular diagram.   In the latter case
the corners of the triangle represent two salts and water
respectively.

Where no double salt formation takes place in
a ternary system, A, B and H_2O (fig.1), for example, a
two branched curve (acb) is obtained.   In the diagram
(a) represents the solubility of salt A in water, (b) that
of salt B in water, and the curves (ac) and (bc) represent
the three component solutions in equilibrium with solid
salt A and solid salt B respectively.   The point (c) shows
the condition of the existence of invariant system in which
the solution is in equilibrium with both salts as solid
phases.

Diagram:-

FIG I   FIG II
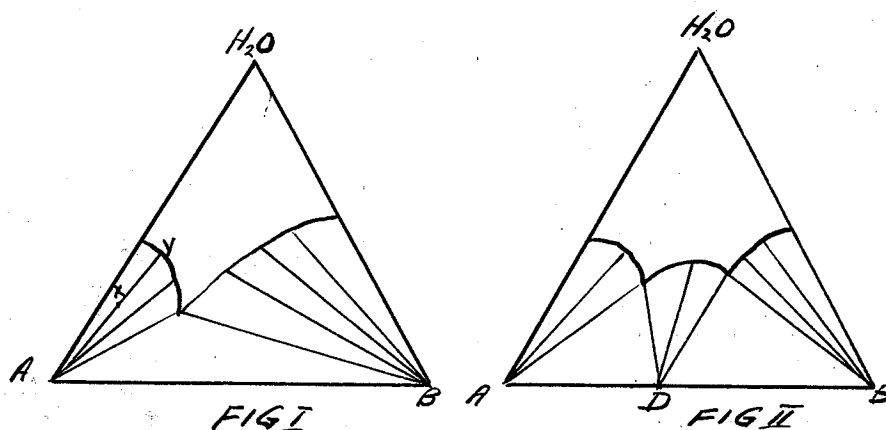
When, however, the ternary system is such that it
gives rise to the formation of double salt at the tempera-
ture at which the equilibrium is investigated, the isother-
mal diagram exhibits three curves (fig.2) where the
middle curve cc' represents the equilibrium between the
ternary solutions and the double salt as solid phase.   Its
composition is represented by the point D - and this may be
determined by the Roozeboom's method as described previously.

If the line joining the point D to the angle of
the triangle representing pure water cuts the curve cc'
then double salt D will be stable and will dissolve in
water without decomposition.   If, however, that line cuts
any one of the other two curves, then the double salt D on
being brought in contact with water will undergo decom-
position into its cinstituent salts.

The three component mixtures represented by the
point (x) gives rise to the heterogeneous system of solid A,
and a saturated solution, the composition of which is re-

presented by the point (y), similarly for the points lying
on the lines joining the points of pure components and
the points of saturation curves cc' and c'b. Thus for a
mixture represented by the point (x), the amount of satur-
ated solution is represented by the length of the line
(Ax) and that of solid phase deposited by the length of (xy).

When the salts in equilibrium with water in a
ternary system are anhydrous, the "tie-lines" converging to
the corner of the system represent the pure salt. If
however, the salt in equilibrium contains water of crystalli-
zation the tie-lines converge to a point on the side of the
triangle representing that salt and water; similarly for the
other salt. In the case of double salt - if the tie-lines
converge to a point on the side AB of the triangle (fig.1)
then the double salt is anhydrous; if, on the other hand, this
point lies within the triangle, then it contains water of
crystallization, the amount of which is computed by Roozeboom's
method pointed out already.

Another method of representing the isothermal rela-
tions in a ternary system is by making use of the rectangular
coordinates.

The composition of the solutions in terms of
grams or gram-molecules of each salt in a fixed amount (say
100 grams or 100 gram-molecules) of water. This method is
applicable to all ternary systems and is widely used but is
not as serviceable as that of triangular representation in
that it does not readily indicate the composition of the

salt if one is formed at that temperature.

In the discussion of the equilibrium relations in ternary systems composed of two salts and water, reference was made to the solubility determinations of one salt by increasing quantities of another at constant temperature.

This consideration may be further extended as an introduction to the case where double salt formation takes place in such system.

Diagram:-
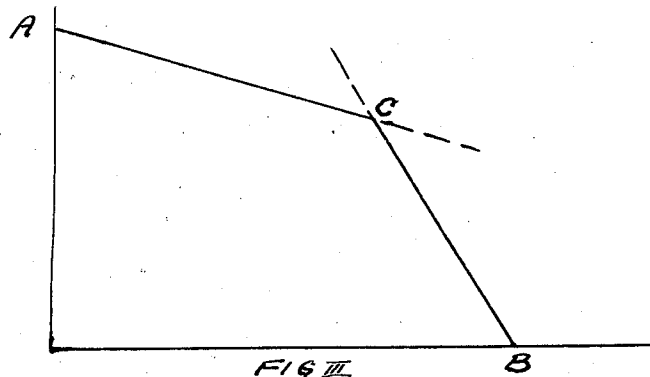
FIG III

In the above diagram the curve AC represents the varying composition of the solution in equilibrium with the solid component A. Similarly the curve BC is that in contact with pure B as solid phases At the intersection of these two curves, C, two solid phases are in contact with the solution, and the system becomes invariant. Here the solution is saturated with respect to A and B - yielding solution of definite composition at a given temperature.

Any point within the area AOBC represents unsaturated solution, whereas, that outside of it, is either supersaturated solution or mixture of saturated

solution and either solid salt A, B, or both.

When the ternary system composed of two salts and water gives rise to double salt - a three branched curve is obtained on the rectangular diagram. If the double salt contains the two constituent salts in equili-molecular proportions, its saturated solution must be represented by a point lying on the line which bisects the angle AOB, the diagram below:-
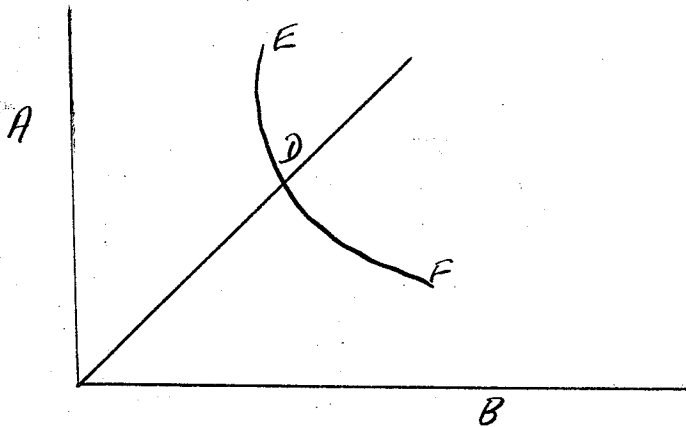
A double salt constituting a single phase, exists in equilibrium with solutions of varying concentra-tions, as shown by the line EDF.

Let the curve AC represent the solution saturated with respect to salt A, and curve BC, the solution saturated with respect to salt B, as solid phase. Diagram:-
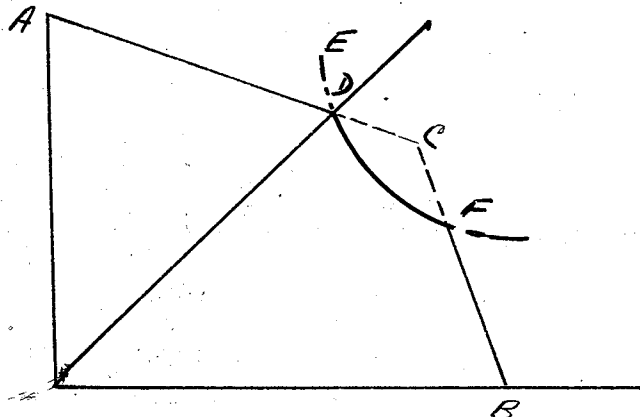
If the temperature is such that it gives rise to the formation of double salt, the solution then which is saturated with respect to the two constituent salts is supersaturated for the double salt. Hence, the curve representing the solubility of double salt cuts the curves AC and BC. The curve EF is the solution saturated with respect to double salt only.

Thus, the above isothermal three branched curve may be interpreted as follows:-

1. Point A - is the solubility of pure component A in water.

2. Curve AE-solubility curve of A in water solution of Component B-A being present as solid phase.

3. Point E- Equilibrium between ternary solution and two solid phases, namely, A and double salt. System invariant at definite temperature, the solution has definite composition.

4. Curve EF- solubility curve of double salt as solid phase.

5. Point F- Equilibrium between ternary solution and the two solid phases - salt F and double salt. This is another nonvariant system.

6. Curve FB is the ternary solubility curve of salt B as Solid Phase.

7. Finally Point B- is the solubility of pure component B in water.

At another temperature the stability of double
salt may be greater or less and accordingly, the solubility
curve for double salts shifts away from or closer to the
point C.

In order to complete information as to
the behaviour of ternary systems of two salts and water at
various temperatures - several such isothermal curves should
be determined.   These may all be represented by space models
measuring temperatures by the third perpendicular axis.   On
such space diagram any surface between two planes will
represent the various solutions in equilibrium with only
one solid phase, that is bivariant ternary system.
A line or curve formed by the intersection of two surfaces
will represent solutions in equilibrium with two solid
phases or univariant systems.   The points formed by the
intersection of three surfaces indicate the existence of the
three solid phases in equilibrium with solutions giving
invariant systems.

Several such systems have been studied and the
relationships between its components at various tempera-
tures indicated by such space models.

Although no single ternary system composed of two
salts has been studied in detail, yet several have been
worked out at experimentally, and their behaviour determined
at various temperatures.   The system, Aluminium sulphate
Copper sulphate and water was studied by R. M. Craven and

T. C. Mitchell.

Their investigation was in part an attempt to
discover a connexion between double salt formation and
difference of electropositiveness between the actions of
component salts.   The equilibrium/in that ternary
mixtures
system are represented in the diagram below:-
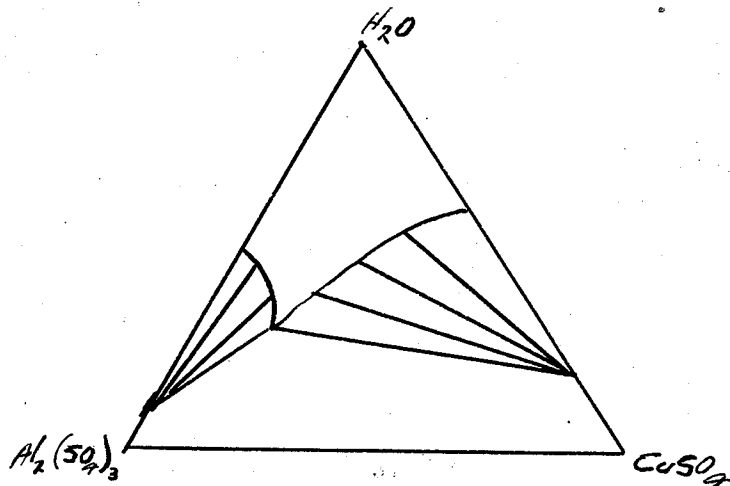
That no combination occurs between Aluminium
sulphare and cupric sulphate is shown by the absence of
the double salt curve and by hhe fact that broken lines
drawn through the solution points and appropriate "rests"
intersect at points corresponding with the composition of
single salts.   If double salts were formed and were stable
at this temperature, a third branch of the isothermal
curve would be shpwn up and the composition of double
salt would be represented by the point where all "tie-
lines" meet.

SOLUBILITY OF

CALCIUM SULPHATE

and

NICKEL SULPHATE

in

WATER.

SOLUBILITY OF CALCIUM SULPHATE IN WATER.

Under ordinary conditions[6] of temperature and in
contact with air, the stable form of calcium sulphate is
Gypsum or $CaSO_4 \cdot 2H_2O$, but there is often found a hemi-
hydrate and two forms of anhydrite as metastable forms.
Their transformation to gypsum is very slow, depending on
temperature and on the origin of the salt.

In water gypsum is said to be stable up to 66^0 at
which temperature it passes to the anhydrous form. Pre-
sence of salts in solution of gypsum are known to lower the
temperature of transformation. However, solubility of gypsum
has been determined up to the temperature of 107^0 - because
its transformation to the anhydrous form is exceedingly
slow.

Because of the existence of various forms of
calcium sulphate, the indefiniteness of the conditions of
their existence, and the slowness of transformation from
the metastable to stable form, much investigation has been
carried on this subject.

These date as far back as to the time of Bezelius
who in his "Traite-dechemie" pointed out that calcium
sulphate is nearly equally soluble in cold and in boiling
water - one part of gypsum dissolves in 46.15 parts of water.
Somewhat similar observations were made by Bucholz, M. Tipp,
and Lecoq de Boisbaudran, but their data do not agree - and
all their results are too high because they were not sure
of the form of salt they dealt with and did not provide
against the great tendency of this salt to form super-

saturated solution.

M. Poggiale[7] made more accurate observations of the solubility of anhydrous calcium sulphate at temperatures 0° to 100°. His results also show too high solubility his error being due to the phenomena of supersaturation which he overlooked. He was the first to note that calcium sulphate has maximum solubility at 35°.

In 1874 Marignac[8] criticized earlier observations on the basis of the supersaturation phenomena, insufficient quantity of solid phase in contact with solution which brings about this condition, and the presence of impurities of salts used in their determinations. He stated that calcium sulphate has a great tendency to form supersaturated solution and that it is very slow to reach equilibrium even in the presence of excess of solid gypsum. In making his determinations he employed artificially prepared samples of gypsum, taking care to have excess of the solid in contact with water and allowed them to stand at constant temperature for a long time agitating them regularly. In this way he claims to have destroyed the supersaturation. He obtained the following data:

Temp:	0°	18°	24°	32°	38°	41°	53°	72°	86°	99°
$CaSO_4.H_2O$	.241	.259	.264	.270	.272	.271	.267	.256	.249	.222
$CaSO_4$.	.190	.205	.209	.213	.215	.214	.211	.202	.189	.175

Hence his solubility curves for both gypsum and for anhydrous calcium sulphate show a maximum solubility between temperatures 32° and 41°.

He also prepared various supersaturated solutions of calcium sulphate and determined the time necessary for the reestablishment of the equilibrium between the solid phase

and the salt in solution.   He found that natural anhydrite
acts similarly to calcium gypsum. The supersaturated solution
of $\frac{1}{351}$ was prepared and allowed to, stand for over eight
months without the solubility coming to its normal value 1/582
but was found to be 1/457. Marignac emphasized the fact that
the state of supersaturation of the solution of calcium sulphate
is very persistent when the excess of dissolved salt is not
too great. When the solution is greatly supersaturated it will
return to its normal value is a short time. Furthermore he
stated that supersaturation is persistent with those salts in
solution where the difference in density between normal and
supersaturated solution is very small. On this basis he ex-
plains the lack of this phenomena in very soluble salts.

He therefore concludes that the solution of calcium
sulphate is in every respect similar to that of a very soluble
salt except that it is extremely slow to cease supersaturation
and the small difference in density of its solutions of various
concentrations.

J.H.Droeze[9] in 1877 in his article "Solubility of
Gypsum in Water and some Salt Solutions" compared data
published by Poggiale, Marignac and other workers such as
Church and Cassa, and found thatbtheir values varied between
wide limits. Values of Poggiale being too high and those of
Church and Cassa too low. He concluded that the former worked
with supersaturated solutions and the latter two with
unsaturated. He agrees with Marignac that "it is of great
importance to take great care to get saturated and not

supersaturated solutions", in determination of solubility
of gypsum.

According to Droeze saturated solutions may be
prepared in many ways.

First - it should stand with water for a long time.

Second - hot solutions can be prepared and cooled
down -. Here one should guard against supersaturation.
In preparation of his solutions by cooling he found that
in order to get it saturated, it was necessary to allow the solid
to stand in contact with water for a long time, such as nine days
itherwise supersaturation will be the result, whereas in
emplyying Marignac's method, that is shaking the solution
with excess of solid phase at constant temperature,-
solution may be saturated within a course of a few hours.
His method of experimenting was quite similar to that of
Marignac's, and his determinations at low temperatures agreed
very well with Marignac's- although at higher temperatures they
deviate somewhat. He found that maximum solubility was at
a little higher temperature than that of Marignac.

He also determined the solubility of gypsum in various
salt solutions of NH_4, K, Mg, Na, and found in general an in-
crease in solubulity with increasing concentrations of the salt.
In the case of K_2SO_4 and $MgSO_4$ - a decrease in solubility
in gypsum was noticed - this he accounted for by the formation
of double and triple salts respectively - the existence of which
is doubtful.

Although the results of Marignac and Droeze are in fair
agreement their values are not accepted as final. In preparing

their solutions they took precautions against supersaturation which previous observers had overlooked, but they did not consider other phenomena such as the effect of the size of particles of a sparingly soluble salt on its normal solubility. Their methods of experimentation such as temperature control during the equilibrium, methods of filtration and analysis, were far inferior to those of later investigators on this subject. It will therefore be more advisable to consider these more in detail.

Perhaps the most accurate work on this subject has been done by Hulett[10] whose data onthe solubility of gypsum are considered most reliable. His extensive investigations revealed a very important relationship between the solubility of certain salts in water, the particle size of the solid phase. According to Hulett's solution in equilibrium with plane surface of solid phase is different from that in equilibrium with curved surface, andtthis the more the greater the curvature of the particles.

He made conductivity measurement of solutions saturated with respect to solid phase of various particles sizes and thus found the relation between the concentration of saturated solution and the actua; size of particles of the solid with which equilibrium has been attained-magnitude of particles being measured by microscope. Solubility of finely grained gypsum is greater than that of coarse-grained solid - solubility increasing 20% by decreasing the size of particles to 0.3u. The solution saturated with respect to fine grains is supersaturated with respect to coarser

particles. <u>He defines normally saturated solution as</u> that where the solution is in equilibrium with the plane surface of the surface or its characteristic.

He observed that if powdered gypsum were left in contact with weather and stirred continually - the concentration of gypsum in solution reaches its maximum value in a short time - and then decreases so that equilibrium is attained only after five days stirring.

This is due to the fact that solution saturated with the fine grains is in an unstable condition, and the coarser grains slowly grow at the expense of the finer ones until the concentration of the solution is in the state of equilibrium, characteristic of one in contact with a plane surface of the solid - which is defined as normally saturated solution.

According to Hulett, normally saturated solution of gypsum is that in which the solution is in equilibrium of solid particles whose average size is 2u. Such solution at 25° contains 15.33 millimoles per litre. Solubility of finely powdered gypsum, the average magnitude of particles being 0.3u gave the contration of 18.2 millemoles per litre. Such solution returns to its normal saturation after five days of stirring during which period its solid particles grow to the magnitude of 2u.

In determination of equilibrium for normally saturated solution with coarse particles of gypsum, care should be taken that in stirring the solid be not agitated

as the gypsum particles by mechanical subdivision will
yield fine powder, which may increase the concentration
from 3% to 5½%, and normally saturated solution will never
be attained.

Marignac and Droeze in preparing theur solutions
took care to have the excess of finely divided gypsum
distributed through the liquid to avoid supersaturation which
is the result of this, but they overlooked the phenomena of
perhaps greater importance than the above, in dealing with
finely divided solid and in their method of attaining the
equilibrium

Their results being high show that they had been
dealing with saturated, but not normally saturated solutions.
Strictly speaking their solutions were supersaturated.

Hulett, having revealed a number of important
facts regarding the solubility of gypsum and obtained some
accurate results, in (1902) undertook the investigations
of the splubility of salt at various temperatures. Here he
emphasizes the need of density determinations, since this
and other magnitudes are necessary to ascertain the relation
of these to the solubility.

To overcome the supersaturation phenomena caused
by the small particles of the solid and too rapid agitation
of this solid which produces small particles, he employed
plates of gypsum of 1.0 to 5 mm. in thickness and over
these the solution was rotated without distributing the
solid below. Solutions so prepared required not more than
1 hour to produce normal saturation. Anglytical methods

were based on the amount of anhydrous calcium sulphate
in 100 cc. of gypsum solution at given temperature. Density
determinations were made by Sprengel-Ostwald pycnometer.
Date:-

Temp.	0°	10°	30°	40°	50°	60°	80°	100°
$CaSO_4$	.1759	.1920	.2090	.2097	.2038	.1996	.1802	.1610
Solid Phase	$CaSO_4 \cdot 2H_2O$						$CaSO_4$	

He showed that in the case of the solubility of
gypsum, the surface tension plays a decided role - Hance
curvature of the particles of solid surface tension, and
solubility of these have similar relationship.

The early workers on the solubility of gypsum
found a change in the direction of the solubility curve.
The results of Marignac and Deorze give 38° as the maxi-
mum solubility. Hulett and Allen give 40° as temperatures
of greatest concentration. From this temperature
the concentration decreases and at 90° it is the same as at
zero - while at 107° it has decreased some 12% further.
Throughout the whole range of curve no abrupt break is
noticed as would be expected at maximum solubility i.e.
40°. This is confirmed by the vappur pressure determinations
of water and gypsum by Von't Hoff and Armstrong who showed
that v.p. gypsum is uniformly increasing from 0 to 85°.
Thus uniformity of vapour pressure curve of gypsum excludes
the idea of explaining the change at 40° (from increasing to
decreasing solubility) by assuming the appearance of a new
solid phase - some different form of calcium sulphate.

Later[12] Hulett reviewed his previous experiments
on solubility of gypsum and added more facts regarding
the nature of solid to be used by the method by which equi-
librium of normally saturated solution may be attained
and the time required for such. He found that the similarity
existing between the vapour pressure of liquids and solution
pressure of solids suggests the analogy as to the size of
particles, of solid particles and their respective behaviour
in contact with the solution. Samll particles have propor-
tionally greater surface, are more soluble and in dissolving
become even more soluble, and this plays the greatest role
in the process of solution. All particles below a certain
size completely disappear, supersaturate the solution and
after a long period are finally deposited on larger particles
yielding normally saturated solution.

According to Hulett solubility is measured by the
concentration of the solution which is in final equilibrium
with the solid and is independent of the rate at which this
equilibrium is established.

Normal saturation of a solution may be approached
from either the unsaturated or supersaturated side. In
the former case the finest particles of a powdered fairly
soluble solid will dissolve first as explained by the
surface energy phenomenon, and after all such particles
have disappeared, the solution is still unsaturated and
the system then slowly approaches concentration that id
in equilibrium with a plane surface from the unsaturated side.

Regarding the latter, the solubility is small, the particles of 2u or less rapidly bring the concentration above the normally saturated solution, and the system then approaches the concentration that is in equilibrium with the plain surface from the unsaturated side. This is assumed to be the case of gypsum when powdered solid is used. Gypsum is very exceptional as regards the time for establishment of equilibrium from the unsaturated side. Finely divided solids of most inorganic substances saturate a solution in an hour or so, whereas, for gypsum half a day or more is necessary.

Hence, the greatest source of error in and difficulty connected with gypsum solubility determinations is the supersaturation, which is accounted for by small particle size. This is confirmed by the facts known from surface energy. Small particles have greater surface curvature, greater solution pressure and therefore greater solubility. Larger particles grow at the expense of smaller ones - but before the small particles settle on the larger ones they go into solution resulting in temporary supersaturation, which is then followed by normal saturation. The most efficient way of preparing normally saturated solution of gypsum is to employ relatively large flat plates of solid, rotate this liquid without disturbing the solid in contact with it. Thus normal saturation is attained from the unsaturated side in relatively short time.

So far have been considered chiefly the facts regarding the solubility of gypsum, the factors that govern the solubility and the precautions that are to be taken

to obtain correct solubility values.   It is learned
that the amount of solid phase present and above all its
physical character plays important role in its solubility.

Little has been said regarding the chemical
nature of calcium sulphate, the conditions of existence
of its various hydrates and anhydrous forms and their
respective solubilities.

Davis[13] investigated the nature of the changes involved
in the dehydration of gypsum. In his determinations on
dehydration of gypsum he observed that when gypsum is heated
at high in a current of dry air, it loses its water of
crystallization and passes from dehydrate to anhydrous form,
which is more soluble than gypsum, thus named "soluble
anhydrate."

Gypsum occurs in two crystalline forms of dehydrate,
alpha, the monosymmetric and beta orthorhombic. The dehy-
dration of ordinary gypsum takes place in various stages
which may be represented by the equation: Alpha $CaSO_4 \cdot 2H_2O$ =
(mono.)
Beta $CaSO_4 \cdot 2H_2O$ = $CaSO_4 \cdot \frac{1}{2}H_2O$ = $CaSO_4 + H_2O$
(ortho.)   (half hydrate) (sol.anhy.)

Thus complete dehydration takes place in two stages, the half
hydrate being formed as intermmediate product of the change.
This latter compound is hygrostatic and will regenerate the
half hydrate if brought in contact with water vapour.

Davis believes that there are Alpha and Beta forms
of a half hydrate and anhydrous salts, and each crystalline
form has its characteristic solubility.

According to Davis, the solubility of salt does not depend on the size of particle as :1. This peculiarity would be shown on an exaggerated scale in the case of highly soluble substances, and 2, if only sufficient time is allowed for equilibrium, small particles first dissolved, forming supersaturated solution will deposit material on larger crystals and thus true solubility of any salt will be reached.

Both Marignac and Hulett found maximum on the solubility curve of gypsum - the values the former point to a maximum at 38°, while Hulett's curve has a bend at the summit.

Although the crystallographic character of gypsum in contact with solution at various temperatures has never been properly determined, it is assumed that the two branches of the curve actually correspond to Alpha and Beta of the dehydrate - their transition being at $38^\circ C$.

From Davis's investigations one may find more reasons to account for the difference in the results obtained on gypsum solubility by earlier workers. The conditions of stable existence of various hydrates and anhydrous forms of calcium sulphate, and the different crystallographic character of each type is not definitely known. It is believed that the difference in their results are due to the differences in the nature of the solid used in dimorphous gypsum or its anhydrous forms.

Although no experiments in this research were carried on at temperatures higher than 90°, it is needless

to dwell on the behaviour of this salt in solution at
higher temperature than that concerned here. But to
complete this discussion it may perhaps be advisable to
consider briefly some facts regarding the nature of changes
taking place in the crystalline forms of the solid and their
respective solubilities at high temperature.

Where Davis' work revealed the existence of
various forms of calcium sulphate and made more or less a
qualitative study of their transformations, Melcher[14] in
1910 undertook to deter mine the solubility and stable
existence of some of these in solutions at high temperatures.
His investigation chiefly consisted in determination of
solubility of calcium sulphate at temperatures 18°, 50°, 100°
150° and 218°. This included the study of the solubility
and existence of three forms of this salt - namely gypsum
soluble anhydrite and ordinary anhydrite. Solubility
values were determined by conductance measurements.

According to Melcher the stability of
anhydrite ranges from 60° up to as high as 218°, the
solubility of this salt being greatest at 60° and decreases
rapidly with rising temperature.

He found the upper limit of existence of
gypsum being 97° which temperature constitutes a transition
point between this salt and soluble anhydrite.

Melcher also showed that judging his results
of specific conductance of solutions saturated with calcium
sulphate, three different solid phases are involved, highest
value for gypsum being 100° that for ordinary hydrite, 156°

abovewwhich temperature another form of anhydrous solid makes its appearance, which he found to be identical with soluble anhydrite.

To leave no doubt as to the possibility of this latter solid being some other form of hydrated calcium sulphate he determined the ratio of solubility of soluble anhydrite and ordinary anhydrite at 100° and 156° and found them to be constant.

This fact follows from the thermo dynamic equation $d \log \frac{S11}{S1} = \frac{}{RT} \cdot dT$ that " when $\frac{S11}{S1}$ the ratio of solubility of two forms is constant, the heat of transition Q is zero. This is found to be the case with calcium sulphate at 156° proving this temperature to be the tramsition point from ordinary to soluble anhydrite and not a hydrate.

Combined results of Melcher and Hulett and Allen may be briefly summarized by the graph shown in figure 1.
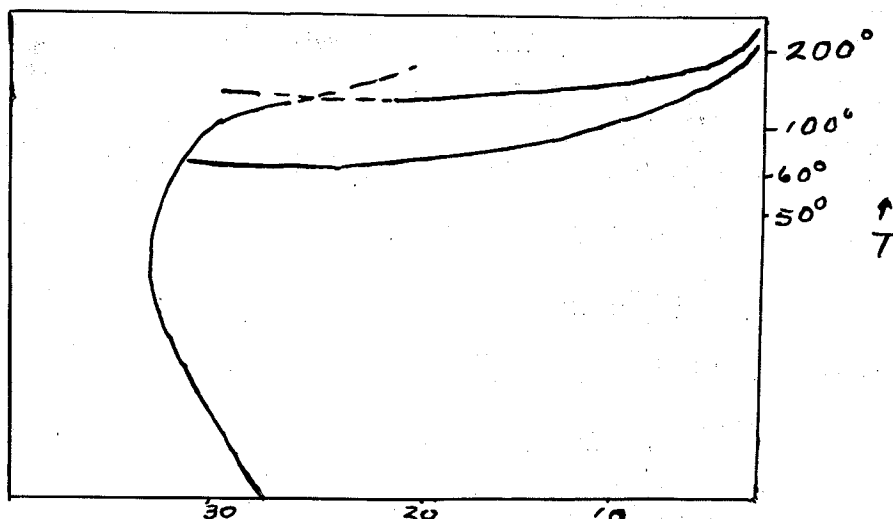
Although Melchor was the only one to carry out the solubility of various forms of calcium sulphate at high temperatures, his results are quite reliable. One may compare his values on the solubility of gypsum at lower

temperatures with those of Hulett and Allen's

Temp.	Melcher's	Hulett and Allen's
i.e. 18^0	29.5	29.6
50^0	30.0	30.1
100^0	23.3	23.8

His results agree almost perfectly with those obtained
by Hulett and Allen by an entirely different method.

Summarizing the facts above, one realizes the
numerous precautions to be taken in correct determination
of solubility of sparingly soluble dimorphous substances
in general of gypsum and of gypsum in particular. Unfor-
seen difficulties are met with if these are not duly observed.
In accrying out determinations in this investigation all
these were dealt with to the best of the apparatus and
material available in this research.

SOLUBILITY OF CALCIUM SULPHATE IN MINERAL
ACIDS AND SOME SALT.

SOLUTIONS[15] :-

Solubility of calcium sulphate is much greater in
acids than in water. Generally this increase with the
increasing concentrations of acid with temperature.
H. Rose found that cold HCl dissolves with $CaSO_4$, but
boiling acid dissolves much more. Lunge determined its
solubility at 25° and 102°, and furnished some data on
solubility values at these two temperatures with increasing
concentrations of HCl. His results show agreement with
statements made by H. Rose, F. K. Cameron and J. F. Breozeale
carried out similar experiments with sulphuric acid at 25°
35° and 43°, and observed considerable increase in solubility
with incr asing concentration of the acid and with temper-
ature.

Considerable work has been done besides that
mentioned above on the solubility of calcium sulphate in
salt solutions, both on common and non-common ion. It is
found to be the general case that "the solubility of
calcium sulphate in water is augmented if a salt with no
common ion is present - and decreased by the addition of
a salt with common ion.

W. A. Tilden and W. A. Shinstone found relationship
existing between the solubility of $CaSO_4$ in a solution of
NaCl of known concentration at various temperatures. Their
results show that presence of NaCl augments the solubility

of $CaSO_4$ and this the more the greater the concentration of NaCl and the higher the temperature. Results of F. K. Cameron who carried out experiments at 23^0 reveal similar facts.

In the solubility of calcium sulphate in various salt solutions such as $MgCl_2.NH_4Cl$, an increase then decrease in solubility is noticed. Plotting the values of conc. of calcium sulphate against that of the salt present solution in each case a maximum is found somewhat similar to that in the solubility of gypsum in water alone at various temperatures.

W. D. Harkins and H. M. Paine and others measured the effect of cupric sulphate in the solubility of calcium sulphate. A decrease is observed in the solubility of calcium sulphate with increasing proportions of cupric sulphate until a minimum is reached. This is an agreement with the general depression of the solubility of the salt produced by the addition of the common ion.

Magnesium sulphate solution affects the solubility of calcium sulphate in a similar way. In the case where maxima are observed the question arises as to whether this change is a result of double salt formation, difference of hydration of gypsum or change of crystalline character of this salt. If so, then, the maximum is the point of intersection of two curves for each form of gypsum or for gypsum and double salt if one is formed.

SOLUBILITY OF NiSO4 IN WATER.

Solubility of nickel sulphate is incomparably greater than that of calcium sulphate. Its behaviour in solutions is entirely unlike that of the salt discussed above - seldom forming supersaturated solutions, and particle size plays no role in its normal solubility as in the case found in calcium sulphate. Nickel sulphate also exists in a number of hydrated and anhydrous forms. These are readily produced when proper conditions for such are brought about.

Under ordinary conditions[16], the most stable form of nickel sulphate is heptahydrate. If a solution of this salt ne evaporated at 50°C to 60°C or allowed to stand after addition of sulphuric acid it loses one molecule of water giving rise to blue tetragonal crystals of hexahydrate. This form may also be obtained by exposing the heptahudrate to light and air that is not saturated with water vapour. The reduction of heptahydrate by this means was at first thought to be due to direct action of sunlight[17], but it was proved by Dobroserdoff[18] to be just a simple case of efflorescence. If, even in the presence of strong light, the atmosphere in contact with the heptahydrate be saturated with water vapour no change in the crystal of this salt will take place. The hexahydrate may also be produced by prolonged exposure of anhydrous salt to moist air. By leaving the heptahydrate in contact with saturated solution at 32° to 52° hexahydrate

crystals are known to be formed and these are diamorphous in character.

Another /form of nickel sulphate was obtained by Dr. Bruyn[16], who prepared this by crystallization of solution of the heptahydrate in sulphuric acid of density 1.4

A solution of any of the above mentioned hydrates be evaporated at temperature of 118^0, di-hydrate will result. Etard obtained this by the action of concentrated sulphuric acid upon the hepta or hexahydrate.

A monohydrate is believed to exist - this being produced by heating the hexahydrate to 100^0 - where five molecules of water are given off.

Lescoeur[16] prepared the same hydrate by adding concentrated H_2SO_4 to a solution of $NiSO_4$ - being precipitated from solution. Ipatief[16] heated a twice normal solution of nickel sulphate to 100^0 under pressure of 100 atnospheres of air and observed the formation of mono-hydrate crystals. All hydrated salts of nickel sulphate when heated at 280^0, yield anhydrous nickel sulphate, which unlike the hydrated forms, is yellow in colour. This latter when brought in contact with air, absorbs moisture from it, yielding the hexahydrate, which ultimately will rehydrate itself into heptahydrate and pass into solution if sufficient water is present.

The above are more or less collected facts
regarding the various forms of nickel sulphate, their
preparation and condition of their stable existence. It is
however, of great importance in this particular discussion
to deal with the actual solubility and of transition
temperatures of some of these hydrates.   This will
therefore, be considered more in detail.

The solubility of nickel sulphate has been
determined at various temperatures by Tobler[19].
His results, however, are neither sufficiently numerous
to indicate the various transition points between
the hydrates encountered in the experiments, nor due
to his experimental methods considered accurate and
will not be discussed at present.

The most reliable work on this subject was done
by Steele and Johnson[20] who in 1904 did some investigation
with the object of determining the conditions of equili-
brium and the composition of the phases in their system-
nickel sulphate-water.

Their solubility determinations extend from -5°C
to 100°C during which temperatures range no other lower
hydrate was observed than that containing six molecules of
water of crystallization.

In preparation of these solutions it was observed that when a heptahydrate is left in contact with its saturated solution for some hours at any temperature between 32^0 and 53^0 it is converted into a blue hexahydrate.

If the heptahydrate or the blue hexahydrate is left in contact with saturated solution above 54^0, it very rapidly becomes converted into bright green monoclinic salt which on analysis was found to be dimorphous hexahydrate of blue tetragonal crystals.

Their numerous solubility determinations at slightly varying temperatures revealed two breaks in the solubility curve, hence, gransition points for different hydrates or dimorphous crystalline forms of the same hydrate.

The first of these was found to be very near 31.5^0 which temperature corresponds with the change:-

$$NiSO_4 \cdot 7H_2O = NiSO_4 \cdot 6H_2O + \text{saturated solution.}$$
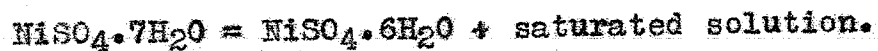
Solubility determinations at temperatures above this indicated the existence of green monoclinic hexahydrate as solid phase.

In the neighbourhood of 53^0 another though very slight break in the solubility curce was noticed. This inflexion was proved to be the transition temperature for the change:-

$$NiSO_4 = \text{Hexahydrate} \quad (53.3^0)$$
blue tetragonal   green monoclinic
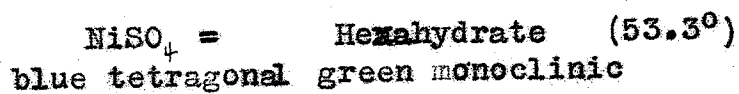
The solubility curves of the rhree salts
$NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$ (blue) and $NiSO_4 \cdot 6H_2O$ (green) lie
very nearly in a straight line so that they were easily
overlooked by Tobler.

The metastable forms were found to exist a certain
range past their transition interval.   Thus the blue
tetragonal hexahydrate often is quite stable below its
transition temperature, i.e. 31.5^o .

The values obtained for solubility of $NiSO_4$ at 45°
75° and 90° which temperatures are concerned with in this
work are:-

90° = 60.78 gms. per 100 gms. of H_2O

75° = .60.28 gms. per 100 gms. of H_2O

45° = 48.26 gms. per 100 gms. of H_2O

These will be referred to later.

VAPOUR PRESSURE

of

HYDRATES.

THEORY.

Phase Rule has a wide application to the study of vapour pressure of equilibria of various systems. As an illustration of this, hydrated copper sulphate may be taken to show the relation between vapour pressure and the various hydrates of this salt.

The study of the equilibria in the two component systems copper sulphate - water revealed the existence of three hydrated and an anhydrous forms of this salt. The equilibria may be represented:-

$$CuSO_4 \cdot 5H_2O = CuSO_4 \cdot 3H_2O + 2H_2O$$

$$CuSO_4 \cdot 3H_2O = CuSO_4 \cdot H_2O + 2H_2O$$

$$CuSO_4 \cdot H_2O = CuSO_4 + H_2O$$

Each case represents a univariant system, i.e.

$$F = C-P + 2$$
$$= 2-3 + 2$$
$$= 1$$

2 solid phases

1 vapour phase

thus, to each temperature there must correspond a definite "dissociation" pressure regardless of the relative or absolute amount of the hydrate which has already undergone dissociation or dehydration. Dissociation pressure at a given temperature is definite only when two solid phases are present.

For exact definition of this pressure, it is necessary to know, not merely what is the substance

undergoing dissociation, but also <u>what is the solid product</u> <u>of dissociation formed.</u>

If copper sulphate pentahydrate be put in a closed vessel at constant temperature connected to a vacuum pump and slowly evacuated, pressure will fall proportionally to the time of pumping until no water vapour but only $CuSO_4 \cdot 5H_2O$ is present in the vessel.

On decreasing the pressure the pentahydrate will commence dissociating into the trihydrate:

$$CuSO_4 \cdot 5H_2O = CuSO_4 \cdot 3H_2O + 2H_2O.$$

The presence of two solid phases and a vapour phase gives an univariant system, and since the temperature is constant, the pressure must also be constant.

Continued evacuation will result merely in the decrease of the pentahydrate and increase of the amount of the trihydrate. When the former has entirely disappeared with only one solid phase remaining, the system again becomes bivariant, the pressure then decreases until the monohydrate is formed and the system again becomes univariant, while the dissociation $CuSO_4 \cdot 3H_2O = CuSO_4 \cdot H_2O + H_2O$ is taking place.

Similar phenomena are met with in the dissociation of the monohydrate into water and anhydrous salt in $CuSO_4 \cdot H_2O = CuSO_4 \cdot H_2O$ as in the first case.

Hence, each dissociation reaction has a definite pressure at constant temperature.

The vapour pressure of a hydrate, therefore, has a definite meaning only when the second solid phase produced by the dissociation is given.

From what has been learned from Phase Rule, the vapour pressure of a hydrated salt has a meaning only on the assumption that the second solid phase, the solid produced by the dehydration of the hydrate into its next lower hydrate, or anhydrous form, exists in contact with the hydrate considered.

This discussion has been introduced because similar phenomena were met with in the investigation of the stable form of calcium sulphate present in solution at different temperatures - in this research. The experimental method and results obtained therefrom will be considered later.

APPARATUS.

THERMOSTAT AND SOLUBILITY APPARATUS.

Solubility determinations,were carried out in
the apparatus shown on figure (1). The solubility flask C
consisted of an ordinary thick-walled bottle of about
200 cc. capacity. The nexk was about five to sic cms. in
diamater so as to provide room for a wide rubber stopper
bearing the stirrer and mercury seal. The mercury seal was
constructed as described in various text books on praätical
physical chemistrt (Findlay's Practical Physical Chem.) The
use of a mercury seal was necessary so as to secure a joint
which while allowing the stirrer to be rotated prevented the
escape of vapour from the solubility bottle.

Care was taken not to allow the pressure to
become so great as to force the air through the mercury.
This was overcome by allowing the bottle with contents to stay
in the thermostat open until its temperature became nearly
that of the bath. The stopper was then inserted into the
neck of the bottle so that no vapour either entered or
escaped from the solubility flask. The type of stirrer used
was the Witt stirrer - water being drawn in at the lower
end of the bulb and thrown out at the sides. It was adjusted
ti the resf of the parts of the mercury seal so that
regardless of the quantity of solid phase present in contact
with solution, the bulb stirrer would be much above the solid .
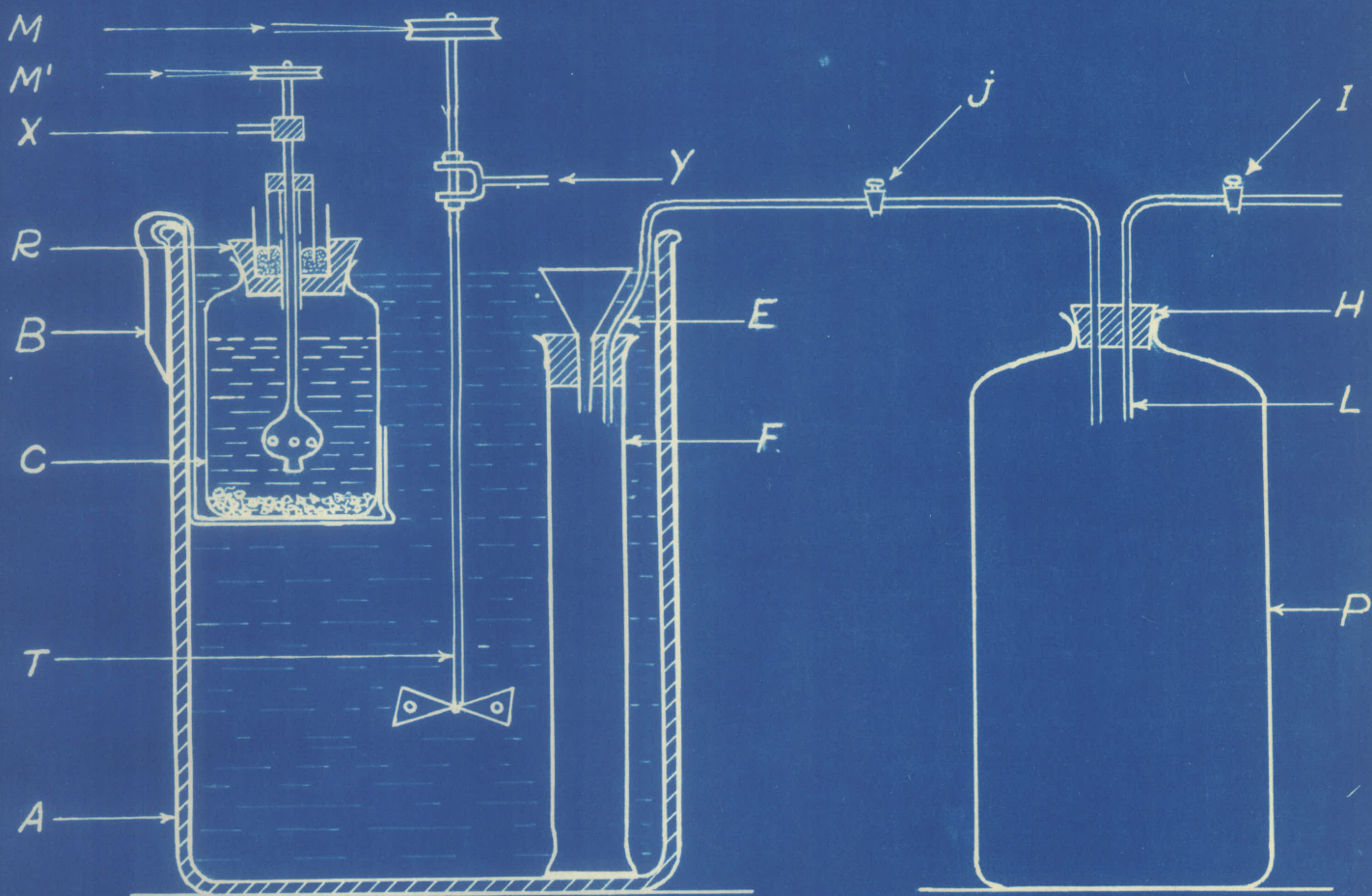
THERMOSTAT AND SOLUBILITY
APPARATUS.

FIG I.

The stirrer while rotating, thus kept the
solution in a slow but steady motion without disturbing
the solid particles to prevent any possible source of
supersaturation.

The thermostat consisted of a large round earthen
ware jar which was covered all around with several thickness-
es of lagging material "A". For high temperatures the
container was provided with a wooden top, lagged with the
same material to prevent radiation as much as possible.

Water was used for lower temperatures while for
higher temperatures this was substituted by light oil of
high flash-point to prevent evaporation during the experi-
ment. The contents of the thermostat was electrically
heated and temperature was controlled also electrically.

T   The ordinary type of insulated immersion heater was
used for higher temperatures and an incandescent electric lamp
for low temperature. The heating current was controlled by
means of an electromagnetic relay in conjunction with an
ordinary toluene-mercury regulator.

In order to maintain a uniform temperature
throughout the bath, it was necessary to stir the water.
This was done by means of an ordinary metal stirrer "T" fitted
with a permenant bearing "Y" the projecting upper end of the
stirrer being attached to a pulley which rested on the edge

of the rod. As a source of power for this stirrer and
that used in the solubility bottle, small electric motors
were used, transmission being carried out by a system
of pulleys.

The bearing for the small solubility stirrer
was made of a piece of glass tubing, this tube being
slightly wider than the stem of the stirrer, the
bearing kept well lubricated by means of vaseline. The
stirrer was adjusted to fit the mercury seal and was held
in its vertical position by means of the clamp "X". The
solubility bottle was wholly immersed in the bath and was
kept in its place by the metal support "B" which was made
to fit the bottle.

FILTRATION APPARATUS.

Since the solubility of nickel sulphate is high, removal of sample of saturated solution for analysis by means employed by others in either cumbersome or not accurate. For example, removing a sample by means of a warmed pipette introduces considerable error due to the fact that a slight error in determination of volume of solution taken by a small pipette would magnify the error appreciably when the solubility of very soluble salt is expressed as parts of salt in 100 parts of water.

Furthermore, in the use of a pipette, there is always a danger of the salt crytallizing in the inner surface during the delivery of the splution. This especially noticeable when concentrated solutions of very soluble salt are dealt with.

Goldschmidt's[21] apparatus has several advantages in that the filtration takes place in the thermostat, but it is too cumbersome where several samples are taken for analysis in comparatively short time.

Accordingly, use was made of the apparatus shown on figure II - this being the modification of one devised by A.N.Campbell[22]. It was constructed as follows:

Through the rubber stopper G, which was large enough to fit tightly the neck of the solubility bottle, there passed two glass tubes B and C of 4 mm. internal diamater.

FILTRATION APPARATUS
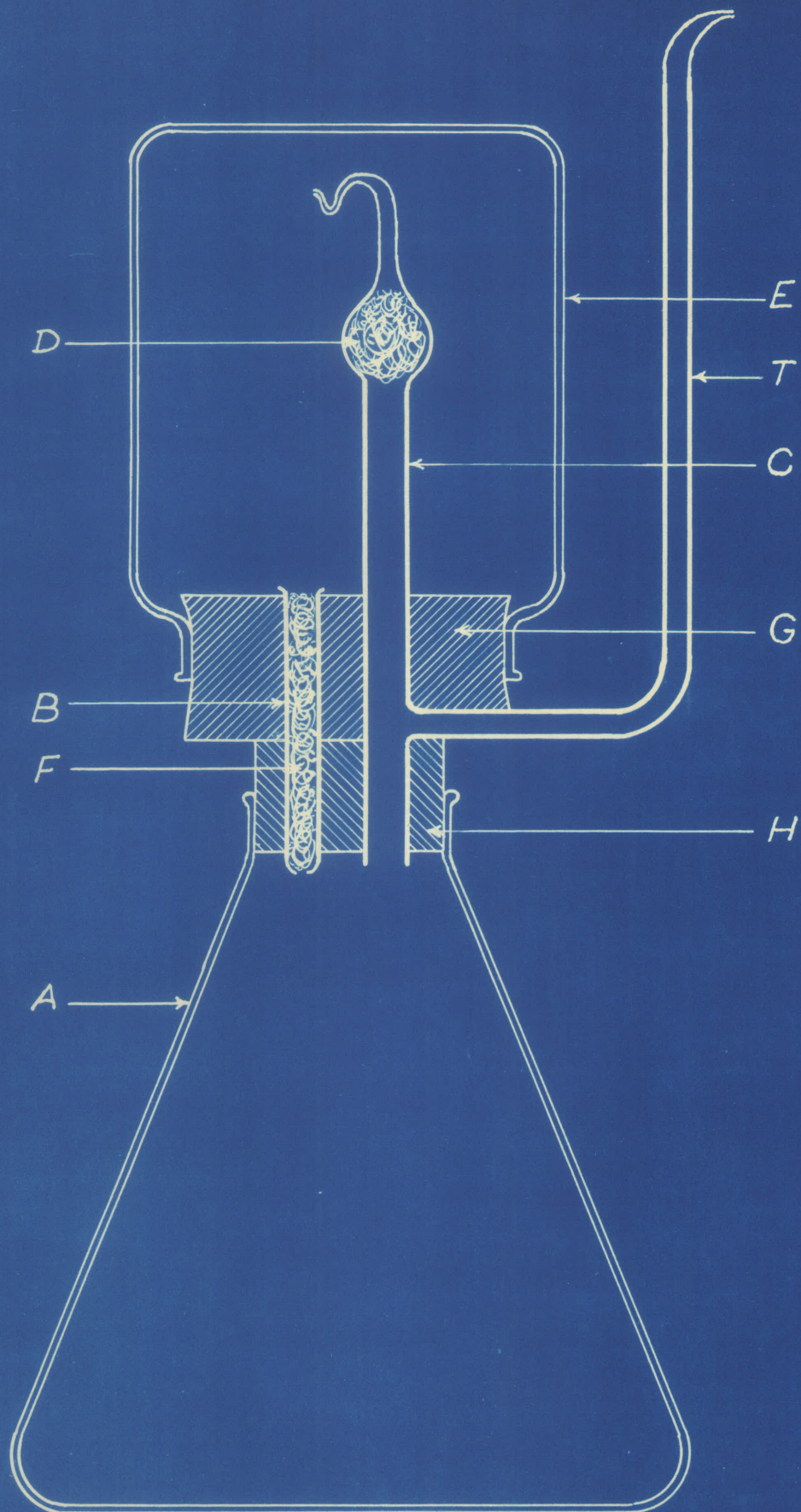

E

T

D

C

G

B

F

H

A

FIG II

One end of the tube was somewhat wider at one end to promote the entrance of the solution through it; at the other end it was constricted and the whole of the tube packed with glass wool and asbestos alternately. The other tube C, is open at the lower end and drawn out to a capillary and bent to an "S" at the other end. The bulb "D" blown in it was packed with glass wool. These tubes were then passed through tightly-fitting holes of the smaller rubber stopper "H", which was mad to fit the neck of the weighing bottle "A". This bottle was of ordinary "conical flask" type of about 250 cc. capacity and weight of approximately 60 grams. It was provided with a ground glass neck and glass stopper ground to fit.

The filtering apparatus, clean and thoroughly dried, was fitted to the weighed bottle A. The constricted end of the tube B is at the lower end to prevent the glass wool being forced into the lower chamber during the process of filtration. When the solution has reached saturation the motor M, (fig. I) is disconnected, clamp X, released and the stopper R, (fig. I) together with stirrer is removed and the filtration apparatus with bottle "A" attached tightly to it immediately inserted into the mouth of the solubility bottle. The amount of evaporation from the solution and possible cooling of the solution during this process is negligible, since the filtration apparatus is inserted almost instantaneously after the stopper "R" is re-

moved. The two bottles thus connected, with both stoppers fitting well into the necks - is then inverted in the thermostat and the solution filters through the tube "B" into the bottle "A". The air in the latter is displaced into the upper chamber through the tube "C". The purpose of the bend S at the end of the tube C and bulb "D" with glass wool in it, is to prevent the entrance of any possible solid matter and the solution into the lower bottle.

If any solid matter enters the capillary of the tube "C" while the filtration apparatus is being fitted to the solubility bottle the small quantity entering would be absorbed by the glass wool in "D" when the apparatus is inverted. Hence only that solution is present in the bottle "A" which filters through the thick layer of glass wool and asbestos.

When all of the solution has filtered into the weighing bottle and nothing but the wet solid phase remains in the upper chamber, the apparatus is removed from the thermostat, the bottle "A" is detached from the rest of the apparatus and its glass stopper immediately inserted.

The surface is washed with alcohol and ether, thoroughly dried and the bottle with its contents weighed. The weight of solution is obtained by difference. The solubility bottle "E" (fig. II) is then opened most of the wet

solid phase being on the surface of the stopper, G.
A sample of this solid is taken into a small clean and
dry weighing bottle, stoppered with ground glass stopper
and weighed.   The amount of the wet solid phase is
determined by difference.   This filtering apparatus works
perfectly and is very suitable for separation of solution
from its solid phase in contact with in at lower tempera-
tures but has to be modified for its use at higher tempera-
atures.   At high temperatures the gas pressure in the
apparatus increases so much as to force out the stoppers
thus causing the leaking in of the thermostat water or oil.
Although the two bottles were held compact by a strong grip
this effect could not be remedied especially at the
temperature of 90°C.

Accordingly a modification of the type[22] was
devised as shown in figure II.

A glass tube "T" of 3 mm. internal diameter was
joined to the tube C of the original apparatus.   It was
made to project to the side of the apparatus through a
depression made in the large rubber stopper.   It was bent
as shown in the diagram, its end being 1 cm. higher than the
top of the solubility bottle when inverted.   Thus, when the
whole of the filtration apparatus is immersed in the bath, the
end of the tube "F" projects above the surface of the water
so as to prevent the leaking of the thermostat water into the

apparatus.

The gas pressure in the apparatus which otherwise would increase is thus passed through the "T" tube resulting in the pressure inside the apparatus being that of the atmosphere.

Another advantage of this modification is that there is no danger of the gas pressure forcing out the bungs and the bottles need not be gripped strongly, thus avoiding the danger of breaking the bottle "A" which is usually of comparatively thin glass

The apparatus described above together with its modification, due to its simplicity and compactness is very suitable for phase rule studies of salts of high solubility - involving the analysis of wet solid phase and can be used at any high temperatures.

Owing to the fact that nickel sulphate exists in relatively large crystals, the solid phase remaining in the solubility bottle after the solution has been filtered off retains relatively small amount of solution in contact with it. The amount of water present besides the water of crystallization is very small. This the analysis of samples of such wet solid phase gives points at considerable distance from the corresponding points for solution when plotted on the triangular diagram.

When, however, the solid phase such as calcium
sulphate is made of exceedingly small crystals, the amount
of solution remaining in contadt with is it considerable.
This is readily understood from the adsorption phenomena.

The amount of adsorption depends on the extent
of the boundary surface, so that finely subdivided particles
such as calcium sulphate in contact with solution possess
a large specific surface thus adsorb relatively large amount
of solution.   This adsorbed solution cannot be filtered off
in the manner above described.

Analysis of wet solid phase of this nature gives
points representing the composition of the solid phase and
its corresponding solution close to each other.   Hence a
small error in the analytical work would shift the "tie-
line" on the triangular diagram considerably.   Furthermore
it was determined experimentally that calcium sulphate has
preferential adsorption towards water.   Solids of this
matter cannot be studied by this method since Phase Rule
takes no account of this phenomenon.   This diagram will
be discussed more fully below.

Accordingly, filtration by suction was necessary
to get rid of this adsorbed solution.   The apparatus for this
purpose is shown in figure I.   It consisted of a long narrow
flask "F" with a rubber stopper fitting tightly to its neck.
Through this stopper passed a small Buchner and a capillary
tube "E" fitted with a stopcock "J" and bent as shown in the
diagram.

The Buchner was so fitted to the bottle that
when the apparatus was immersed in the bath, only the top
of the Buchner was above the surface of the water. The
other end of the tube "E" was passed through another rubber
stopper-this latter being fitted with another capillary
tube "L" which was connected to a vacuum pump. A large
Winchester bottle was fitted then to the stopcock as shown.
The apparatus works as follows:- The flask "F" - all connec-
ted- is allowed to stand in the thermostat for a certain
period before filtration is to take place. Stopcock "J" is
closed, "I" opened, and the air is pumped off from the
bottle "P". Stopcock "I" is then closed and pumping
discontinued.

When nearly all of the solution has filtered by
means of the filtration apparatus shown on figure II, bottle
" (fig. II) is disconnected and stoppered. The solid, phase
and the rest of the solution in contact with it is then
poured into the Buchner and the stopcock "J" opened. The
heated vacuum in the bottle "P" causes rapid filtration -
and in addition the solid in the Buchner is packed to further
remove the water adsorbed to the fine particles of gypsum.
Sample of this is then taken in a weighing bottle and pro-
ceeded with in the usual way.

Since the Buchner is almost wholly immersed in the bath previous to and during the process of filtration and the rapidity of filtration (which takes about 30 seconds) introduces no danger in the solid altering its chemical composition due to possible cooling. This gave very satisfactory results which are shown below.

VAPOUR PRESSURE CURVES OF CALCIUM SULPHATE
AND VAPOUR PRESSURE APPARATUS.

During the progress of solubility determinations
of the present system, it was found necessary to determine
the type of Hydrate of Calcium sulphate that was being
dealt with.   Hence, vapour pressure measurements of $CaSO_4$-
water were made at temperatures at which solubility relations
were investigated.

Gypsum is stable in contact with water at low
temperatures, but at higher temperatures, it may be trans-
formed into a hemihydrate, according to the variety of
gypsum.

Vapour pressure measurements[15] of the system $CaSO_4$.
$2H_2O$ -$CaSO_4.\frac{1}{2}H_2O$ - H_2O vapour by J.H.Vant Hoff and E.F.
Armstrong, show that vapour pressure of this system is lower
than that of pure water, and that the transition point is
at 107^oC.

The vapour pressure corves for systems:-
$CaSO_4.2H_2O$ - $CaSO_4$ (soluble) - H_2O vapour and $CaSO_4.2H_2O$ -
$CaSO_4$ (natural) - H_2O vapour are both above that of water,
the transition point of the former being 95° and that of
the latter 63.5^o.

Thus the higher temperature limit for the

existence of gypsum in contact with water depends on the product of its dehydration.

Accordingly, vapour pressure measurements of gypsum used here were made at temperatures 45°C and 75°C. This was carried out in the apparatus shown in figure III.

About 10 cc. of water were introduced into a bulb "A" and bulb "B" was charged with equal quantities of gypsum and water. The bulbs were then sealed at the top. The tubes leading from the two bulbs were bent so that the bulbs were wholly immersed in the thermostat.

The tubing between the bath and the manometer was covered with a layer of asbestos and wound with fine resistance wire as shown in the diagram. The ends of the wire were connected to a suitable resistance and the main A-C line.

Thermometers at points G and H were bound next to the tubing by means of asbestos to register the temperature at various parts of the apparatus. The purpose of the asbestos layer between the tubing and the heating wire is to distribute the heat throughout and to prevent the possible breaking of the tubing due to high temperature.

VAPOR PRESSURE
APPARATUS

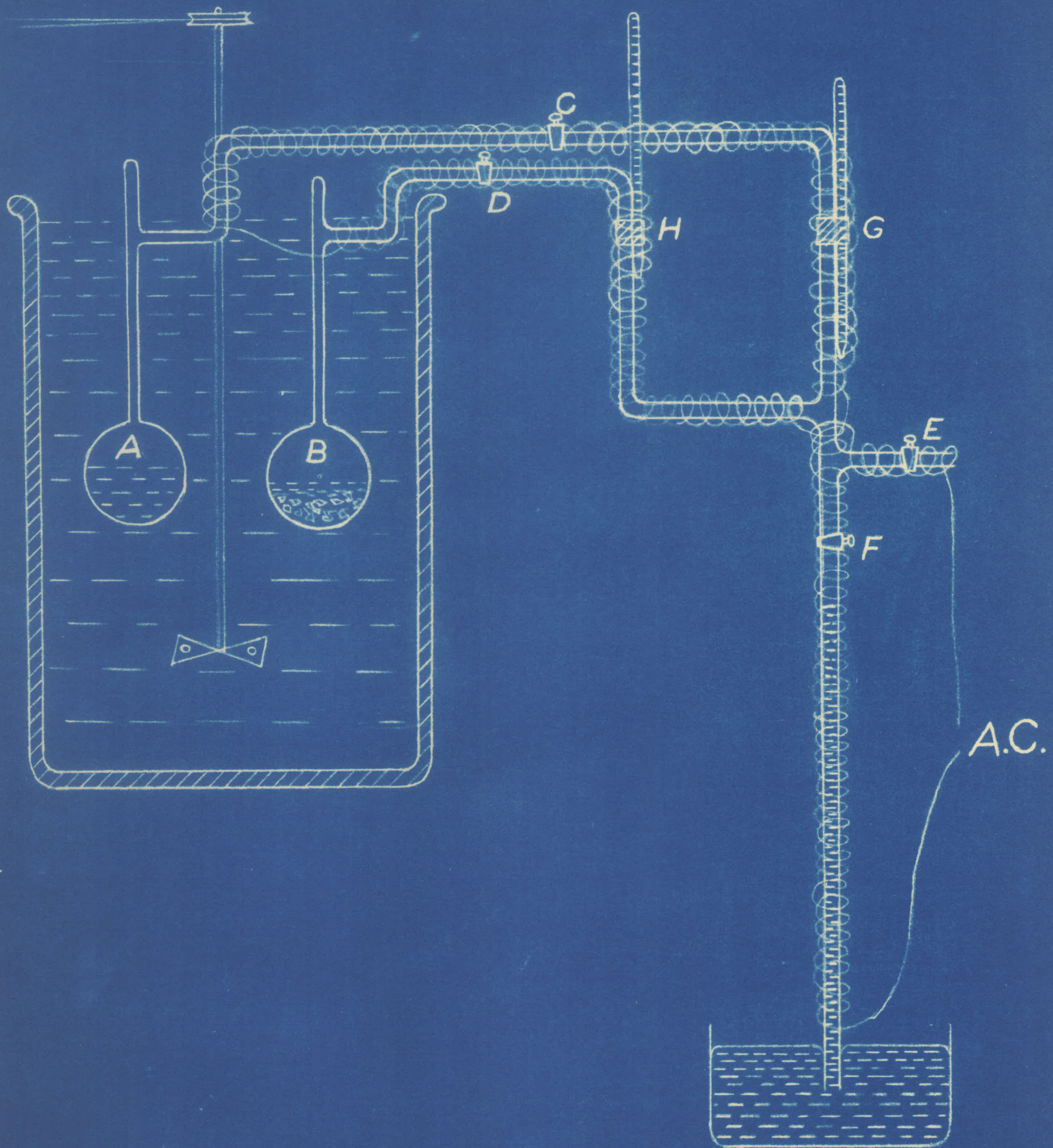A   B   C   D   H   G   E   F   A.C.

FIG. III

The side tube "F" was connected to a high vacuum pump and the lower tube was dipped into the mercury cup.

When the bulbs were immersed in the thermostat all stopcocks were closed. The apparatus was then gradually heated to a temperature above that of the bath. Stopcocks C, D, and F were opened and pumping begun to drive off any possible foreign gases present in the apparatus. While pumping was still continued, stopcocks C and D were closed and F opened. Mercury than rose to the maximum when stopcock F was closed, pumping discontinued and height of mercury in the tube taken. The water vapour from bulb "A" was then allowed to enter the apparatus by opening the stopcock C, thus causing mercury to fall a certain distance The height of mercury was then noted, the difference in the two readings being the vapour pressure of water at that temperature.

Stopcock C was then closed and F opened and pumping begun. Mercury again rose to the same maximum mark, when all the water vapour in the tubing was pumped off. Stopcock F was then closed and D opened. Pumping was continued thus causing the water in contact with gypsum in the bulb B to be driven off.

The vapour pressure of the system in this bulb was determined in the similar way as that of water bulb B.

After pumping for a few minutes the same vapour
pressure reading was ibtained as that of water in bulb "A"
indicating the presence of water yet in contact with salt.
After repeated five minute intervals of pumping and vapour
pressure reading it was found that there was a difference
of about 10 mm. in the pressure. This reading was noted and
immediately the apparatus was removed from the bath, and a
sample of salt was then taken for analysis of water content.
The bulb was then sealed the apparatus again immersed in
the thermostat, and similar operations repeated.

After series of intervals of pumping the contents
of bulb B produced no change in the height of mercury as
that at its maximum, indicating that gypsum was completely
dehydrated. Sample of salt at this stage was taken for
analysis of any possible water content.

Samples taken as described above were kept in a
drying oven at temperatures of 115° and weighed from time to
time-loss in weight dtermined by difference.

after
The first two samples/being exposed to a temperature
of 115°C for 24 hours, proved to have contained 21.95% water
i.e. they were $CaSO_4 \cdot 2H_2O$.

The last two samples treated similarly showed no
loss in weight, being anhydrous calcium sulphate as
pressure
expected. The vapour of/the first hydrate was 61.5 mm.

When these figures are compared with those of

Vant Hoff, whose value for $CaSO_4.2H_2O$ - $CaSO_4$. (nat.) H_2O vapour is 62. mm. shows that $CaSO_4.2H_2O$ was dealt with at 45°. This is confirmed by determination of water content of the first samples.

Similar vapour pressure/determinations of gypsum were made at the temperature of 75°. In this case, however, no difference between the vapour pressure of water and that of calcium sulphate at this temperature was noticed, proving that no hydrate exists at this temperature in contact with water. When after a time of pumping, the contents of the bulb B produced no change in the height of mercury in the tube as that at its maximum, sample of salt was then taken and similarly analyzed for water content. Samples were kept in drying oven for twenty four hours and no loss in weight was detected, proving it to be anhydrous form. This confirms Vant Hoff's figures on the range of stability of gypsum on contact with water. It is possible, however, to have gypsum in contact with water, or other salts in solution at higher tempeeatures than 63.5 which Vant Hoff gives as the transition,point of gypsum-natural anhydrate. In such case gypsum may be considered as in the metastable form. In fact the solubility of this form has been determined to as high a temperature as 107° as discussed in the preeeeding section.

PREPARATION OF MATERIALS

AND

METHODS OF ANALYSIS.

The nickel sulphate used was Mallinckrodt's pure C.P. quality salt. The only traces of impurities were .03% cobalt, .10% alkali metals, and traces of iron and chloride. Calcium sulphate was prepared from calcium carbonate in the following manner:

To a weighed quantity of calcium carbonate was added calculated volume of solution of hydrochloric acid, just sufficient to dissolve the salt. Some silica was found to be present. The solution was therefore filtered a number of times until the silica was removed. To this solution was then added a calculated quantity of dilute sulphuric acid to precipitate calcium sulphate. After the precipitate had settled, it was then filtered through a large Buchner and washed a number of times until the filtrate gave no test for chloride or appreciable sulphates. To get rid of the finest particles of gypsum a large quantity of distilled water was added to the salt in a large beaker and stirred vigorously. It was then allowed to stand for twenty-four hours during which time larger particles settled in the bottom while the finer ones were held in suspension. The supernatant liquid was then removed by suction, hence, getting rid of most of the finer particles in suspension. This operation was repeated three times.

Before individual samples were taken for solubility determinations, they were filtered on a small Buchner to get rid of any possible acid still remaining in the salt.

Duplicate samples of gypsum were analysed for purity and were found to contain the following:

SiO_2 -----------------trace

Mg -----------------.05%

Ba -----------------trace

Fe -----------------absent

Solubility determinations of gypsum in pure water were m made and the results obtained agreed with those of previous workers whose data is considered to be reliable.

The following method was employed in the analysis of solution containing both salts:

The weighed solution was made up to certain definite volume and a-liquit portion taken for analysis. Nickel was first determined electrolytically from the ammoniacal solution containing excess of ammonium sulphate

Calcium was then analyzed for volumetrically by precipitating it with ammonium oxalate, dissolving the precipitate with dilute sulphuric acid and titrating it with standard potassium permanganate solution.

Duplicate samples were made now and again to test the accuracy of the analytical work.

Solid phases were analyzed similarly for both nickel and calcium sulphates.

TABLES

OF

DATA.

ISOTHERMAL

45.0° C.

T A B L E   I.

ISOTHERMAL OF 45.0°C.

Solubility $CaSO_4 \cdot 2H_2O$ in H_2O : .2114 $CaSO_4$ gms. /100 g. $2H_2O$.

Solid Phase   :   74.60% H_2O.

Solubility $NiSO_4 \cdot 6H_2O$. in H_2O : 48.36 $NiSO_4$ gms. /100 g. H_2O

Solid Phase : 49.11% H_2O

	SOLUTION				SOLID	PHASE
Expt.	Solubility $NiSO_4$	Solubility $CaSO_4$	% $NiSO_4$	% $CaSO_4$	% $NiSO_4$	% $CaSO_4$
1	6.23	.220	6.13	.206	1.79	53.10
2	10.61	.223	9.57	.202	4.03	42.54
3	20.42	.243	16.92	.201	3.98	57.61
4	23.50	.236	18.99	.191	6.63	51.20
5.	25.45	.246	20.25	.196	6.05	56.15
6.	26.62	.246	20.98	.194	5.11	59.85
7.	29.43	.255	22.69	.204	8.06	51.97
8	35.03	.252	25.89	.183	9.74	49.02
9	37.99	.257	27.48	.186	8.85	53.34
10	43.54	.242	30.28	.168	10.14	53.66
11	49.31	.200	32.98	.134	48.47	8.69

45.0°C

Gms NiSO₄ per 100 gms H₂O.

Gms CaSO₄ per 100 gms H₂O.

100% H₂O

45.0°C.

100% Ni SO₄

100% Ca SO₄
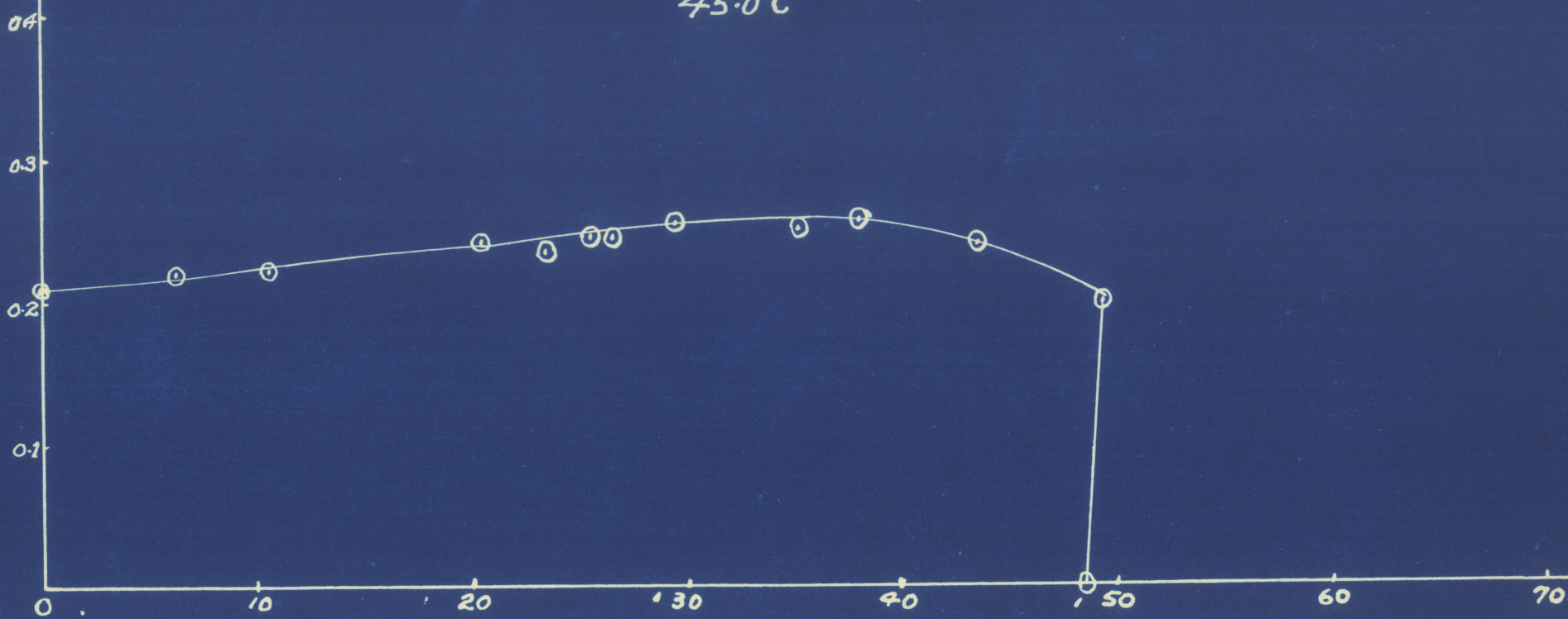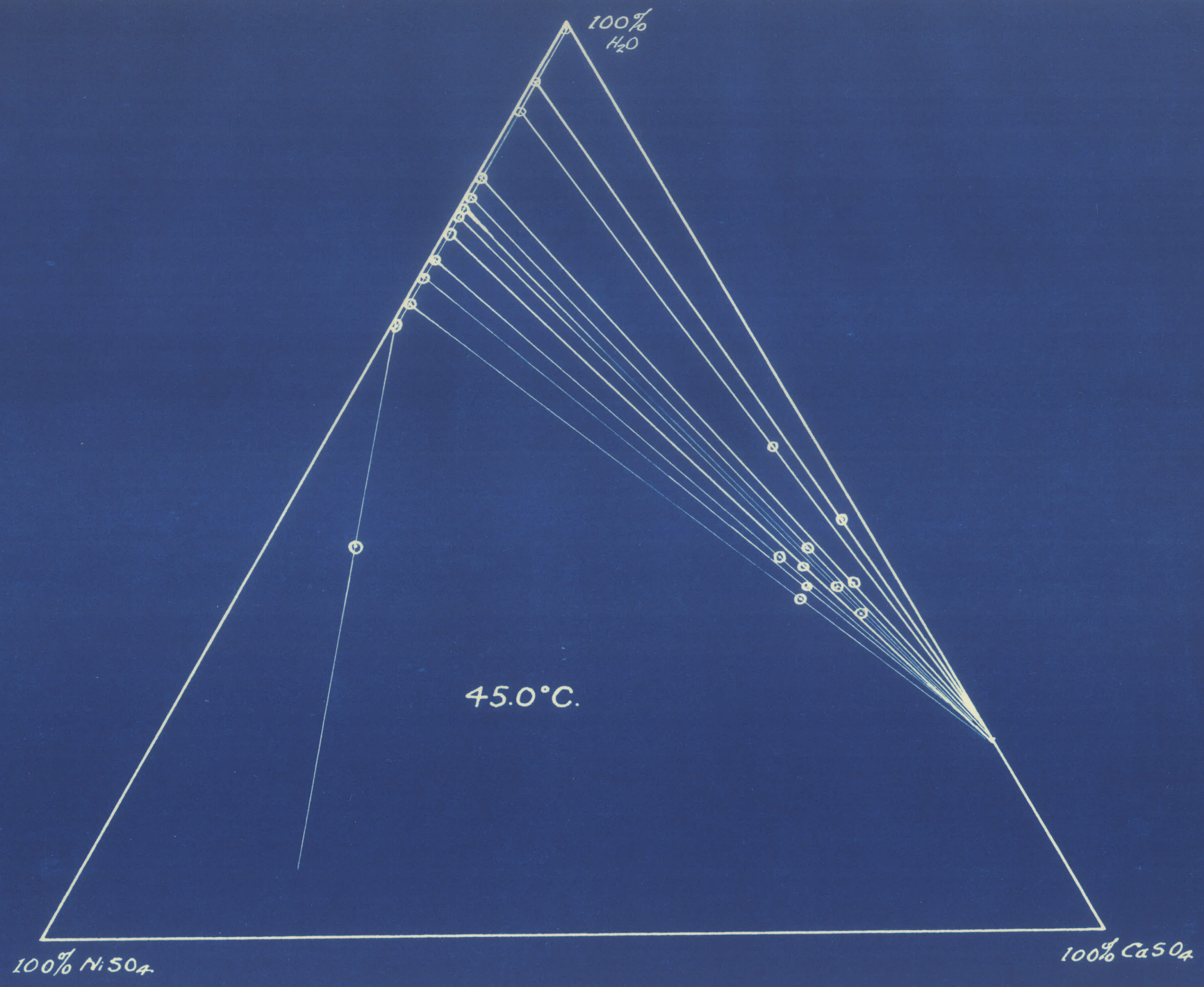
ISOTHERMAL

75.0° C.

TABLE II.

ISOTHERMAL of 75.0 C.

Solubility of Gypsum in H_2O ; .199 gms. $CaSO_4$/100 g. H_2O.

Solubility of $NiSO_4 \cdot 6H_2O$ in H_2O : 60.36 gms. $NiSO_4$/100 g. H_2O.

Expt.	SOLUTION Solubility $NiSO_4$	Solubility $CaSO_4$	% $NiSO_4$	% $CaSO_4$	SOLID PHASE % $NiSO_4$	% $CaSO_4$
1	7.69	.226	7.13	.209	1.77	65.05
2	19.60	.273	16.35	.228	4.83	55.27
3	24.36	.287	19.45	.230	6.30	54.71
4.	33.32	.294	24.94	.220	4.61	64.28
5.	40.16	¾321	28.59	.228	5.41	62.46
6.	40.88	.315	28.96	.223	6.11	61.4
7.	44.59	.302	30.78	.208	10.18	51.39
8.	49.7	.276	33.10	.184	14.29	45.7
9.	58.81	.240	36.97	.150	12.33	52.40
10.	61.25	.220	37.94	.134	47.47	7 .09

100% H₂O

75.0°C

100% Ni SO₄   100% Ce SO₄
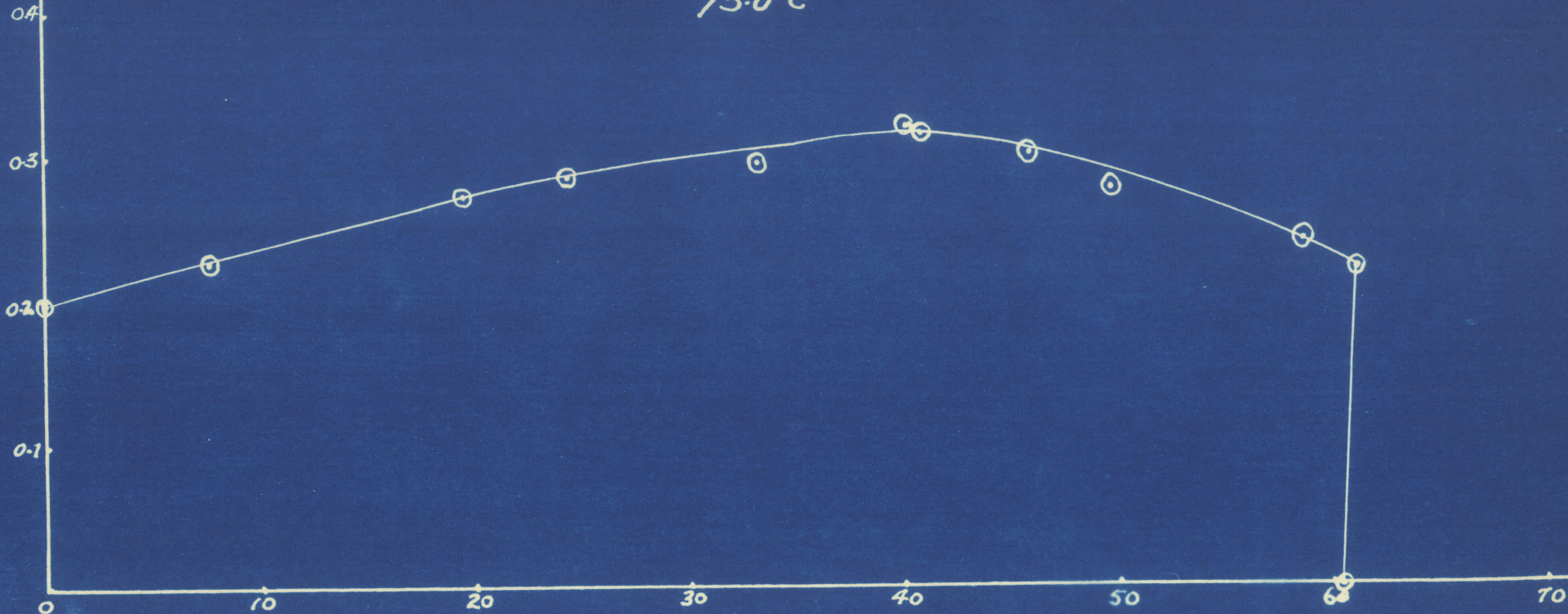
ISOTHERMAL

90.0° C.

TABLE III.

ISOTHERMAL OF 90.0° C.

Solubility of $CaSO_4 \cdot 2H_2O$ in H_2O = .177 gms. $CaSO_4$/100 gms. H_2O.

Solubility of $NiSO_4 \cdot 6H_2O$ in H_2O = 68.70 gms. $NiSO_4$/100 gms. H_2O.

Expt.	SOLUTION				SOLID PHASE	
	Solubility $NiSO_4$	Solubility $CaSO_4$	% $NiSO_4$	% $CaSO_4$	% $NiSO_4$	% $CaSO_4$
1.	7.38	.222	6.75	.199	2.82	43.79
2.	11.15	.268	----	----	----	----
3.	16.23	.309	13.93	.265	3.18	60.15
4.	21.63	.332	----	----	----	----
5.	23.76	.348	19.15	.281	6.40	52.97
6.	24.93	.351	----	----	----	----
7.	29.72	.359	----	----	----	----
8.	31.09	.350	----	----	----	----
9.	31.36	.345	----	----	----	----
10.	34.16	.340	25.40	.253	8.76	51.21
11.	37.24	.337	----	----	----	----
12.	40.06	.335	28.54	.238	9.70	50.8
13.	43.12	.327	30.08	.225	9.12	55.16
14.	44.58	.330	----	----	----	----
15.	46.61	.325	31.72	.221	13.01	46.54
16.	48.95	.291	----	----	----	----
17.	49.56	.299	33.06	.199	12.52	49.58
18.	53.91	.280	----	----	----	----
19.	57.88	.265	36.59	.195	12.76	50.54
20.	61.34	.246	37.94	.191	14.68	48.51
21.	72.40	.185	42.05	.114	45.49	4.55
22.	72.54	.183	42.00	.106	50.98	10.70

100% H₂O

90·0°C

100% NiSO₄   100% CaSO₄
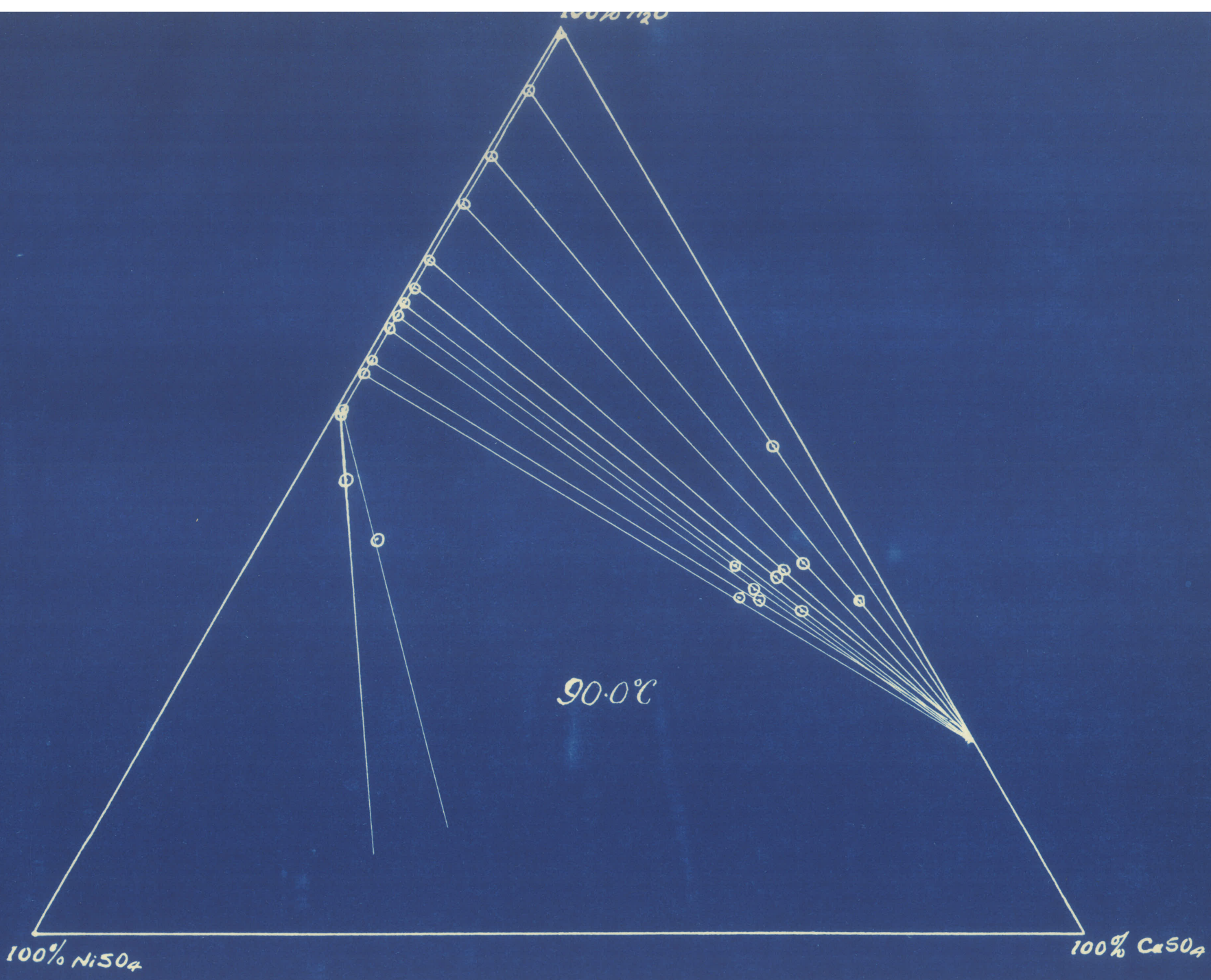
SUMMARY

OF

RESULTS.

Solubility relations between calcium sulphate, nickel sulphate and water were studied at three different temperatures. As is noticed from the graphs that at each isothermal, solubility of calcium sulphate is enhanced due to the presence of nickel sulphate in solution. It first increases then decreases coming to nearly the value of its solubility in pure water when solution of nickel sulphate is nearly saturated. These isothermal curves are somewhat similar to the curve on solubility of calcium sulphate in pure water at various temperatures. It may be noticed that the maximum solubility of gypsum occurs in dilute solution of nickel sulphate at lower temperature, while at high temperature, it is most soluble when the concentration of nickel sulphate in solution is high.

On examining the triangular graphs, it is shown that no double salt formation takes place between calcium sulphate and nickel sulphate in water. All the "tie-lines" meet at a point corresponding to 20.91% H_2O in calcium sulphate proving that throughout the temperature range studied, the form of calcium sulphate present in contact with solution was a dihydrate $CaSO_4 \cdot 2H_2O$. This was confirmed by vapour pressure determinations at 45° as discussed previously.

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