THE CONCENTRATION OF RADIUM AND MESOTHORIUM

BROMIDES BY FRACTIONAL CRYSTALLIZATION

by

John Lewis Nierman, B. S., A. B.

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INTRODUCTION

The increased use of radium in cancer therapy,
together with its great scarcity and consequent high
market price,has prompted the investigation of methods
whereby this valuable product can be obtained in greater
quantities and with less expenditure of time and money.
While there is a great diversity of opinion,even among
physicians,as to the value of radium in the treatment
of malignant growths,it seems to have been definitely
established that the main hindrance in successful treat-
ment has been the lack of sufficient radium to make the
treatment effective. The United States Bureau of Mines
in Bulletin No. 104,reports that it knows of no hospital
or individual that has had the privelege of working with
as much as half a gram of radium,that does not report
cures in increasing number or that is not able to treat
even advanced cases with increased assurance of success,
and that two American hospitals,that have 500 milligrams
or more of radium are reporting results daily that will
not be duplicated elsewhere until equal quantities are
available.

The market price of radium is $120,000 and up per

gram of the element. At the outbreak of the European War
sixteen to twenty grams of radium was contracted for abroad,
chiefly by Germany,at a price of $120,000 per gram. As to
the price of the product in the future,it can be said with
safety that the price will not generally decline owing to
the fact that the quantity of radium is exceedingly small.
The market price will therefore depend largely on the ore
supply.

Mesothorium was discovered some years ago by Hahn,but
its chemistry and methods of preparation were until recent-
ly technical secrets. Soddy and Marckwald have shown that (11)
mesothorium is absolutely identical in chemical nature
with radium and cannot be separated therefrom. In con-
sequence,all radium separated from uranium minerals con-
taining thorium,contains also the mesothorium in the miner-
al,and all preparations of mesothorium contain the radium
that is present in the mineral from which the thorium is
derived.

Although mesothorium is itself rayless,its first
product ,which is short-lived and rapidly formed,gives of
a powerful γ and β radiation. Owing to the subsequent
production of radiothorium and its products,mesothorium
acquires an a-radiation with time. Its total radiations
then are identical to those of radium,which permits of

its use as a substitute for radium in luminous watch
dials and other luminous material,thus conserving radium,
which has a life period several hundred times longer than
mesothorium, for therapeutic purposes. Furthermore,as
mesothorium is a byproduct of the gas-mantle industry,its
conservation and subsequent utillization is the more easily
accomplished.

At the Welsbach Plant the mesothorium and any radium
that is present is separated from the thorium by precipita-
tion as mesothorium-radium sulphate. As the quantity of
mesothorium and radium is exceedingly small,and as barium
and radium and mesothorium are always precipitated together,
a small quantity of some salt of barium is added before the
precipitation,so as to increase the weight of the sulphates.
The sulphates are then converted into chlorides and concen-
trated by fractional crystallization until a concentration
of.01 milligrams per gram is reached. They are then convert-
ed into bromides and the fractionation continued.

It is with the fractionation in the form of bromides
that this investigation is chiefly concerned. While it has
been shown that the factor of enrichment is higher for bro-
mides than for chlorides,the effect of the acidity of the
solution of bromides on the factor of enrichment is a prob-
lem yet to be investigated. While most writers on the sub-

ject of the concentration of radium in the form of
chlorides and bromides, express the opinion that the concentration of radium progresses more rapidly in acid than in
neutral solution, this work was undertaken for the purpose
of studying the relationship between crystallization factor,
as hereinafter defined, and the acidity of the solution of
the bromides.   In the course of this study we were led to
the conclusion that the crystallization factor is independent of the acid concentration and varies only with the percent of crystals separating out. Our experimental data form
the basis for this conclusion.

HISTORICAL

The separation of radium from the crude material with which it is usually found has been one of the big problems connected with radium ever since its discovery. In the separation of pure radium chloride from pitch-blende, Mdme Curie (1) resorted to the method of fractional crystallization. She first precipitated the radium and barium chlorides from aqueous solution by the addition of alcohol. The radium chloride was the first to precipitate. This method being somewhat irregular was abandoned by her for the following: "The chlorides of barium and radium were dissolved in pure distilled water, and then crystallized from this aqueous solution. The radium chloride, being less soluble than the barium chloride, more of the radium chloride separated out with the crystals than remained in solution. The solution of the bromides in water was first heated to boiling and then allowed to crystallize by cooling in a closed capsule". Mdme Curie further says, "Beautiful crystals form at the bottom and the supernatant liquor is easily decanted. If part of this liquor is evaporated to dryness the resulting chloride is found to be about five times less active than that which crystallized out". Thus according to Mdme Curie, each crystallization

increases the activity fivefold. At an advanced stage of
the crystallization when the quantity of the material in
solution became small, Mdme Curie (2) added water contain-
ing a known amount of hydrochloric acid. "The advantage
thus gained",she says, "consists in increasing the quanti-
ty of the solution,the solubility of the chlorides being
less in water acidified with hydrochloric acid than in
pure water". She further lays emphasis on the fact that
if water containing much acid is used,excellent separations
are effected,and it is necessary to make only three or four
fractionations. From this one might infer that the crystal-
lization factor is higher for acid solutions of the chlo-
rides than for neutral solutions.

M. Giesel (3) recommends the separation of radium
and barium by fractional crystallization of a mixture of the
bromides. Mdme Curie endorses the advantage of this method
especially in the last stages of the fractionation. Accord-
ing to Giesel the purification of the radium out of the
crude material progresses more rapidly by this method.
After converting the material into bromides ,one crystal-
lization is sufficient to separate the radium and barium
bromide from the bromides of calcium and strontium. In
the course of eight more crystallizations of the mixture of
radium-barium bromides out of water,the radium bromide is
separated from the more soluble barium bromide.

Coehn and Kettembeil (4) carried out extensive experiments in which they showed that the alkaline-earth metals could be separated from each other by electrolysis. Mercury was used as the cathode and a platinum spiral for the anode. They did not conclusively show that this method is applicable to the separation of radium from the metals of the alkaline-earth group.

E. Wedekind (5) conducted experiments showing that by electrolysis of a solution of radium-barium chlorides, using mercury as the cathode and platinum as the anode, an amalgam of radium and barium was obtained, and the activity of the latter showed marked increase. He thus showed that the enrichment of the radium content of a radium-barium chloride solution was possible by electrolysis.

Mdme Curie (6) prepared metallic radium by means of electrolysis and was thus able for the first time to study the properties of the metal.

Ebler and Fellner (7) separated radium by shaking a radium-barium solution with metasilicic acid gel and then volatilizing the silicic acid with hydrogen flouride. They claim that with dilute solutions of radium-barium chloride, 90 - 100 percent was absorbed and concentrated in a preparation $\frac{1}{4}$ to 1/50 of the original weight. With radio-lead 86 to 95 percent was absorbed in preparations 1/3 to 1/100

of the original weight. They claim for this method a
greater concentration of the radioactive material than
by any other method.

Ebler and Bender (8) devised a method for the sep-
aration of radium,which was based on the practical insol-
ubility of barium chloride in 10 N. hydrochloric acid. The
radium is carried down with the barium in the precipitation.
When the aqueous solution is fractionally precipitated by
the addition of hydrogen chloride,practically all the radium
is precipitated with the first two-thirds of the barium
chloride.

Erich Ebler (9) devised a method based on the frac-
tional adsorbtion of radium-barium salts and the fractional
electro-dialysis of the adsorbtion compounds thus obtained.
He used different adsorbtion compounds for different radium
salts. Manganese dioxide hydrate showed marked adsorbtive
power for all radium salts. Basic ferric carbonate acted
similarly toward radium carbonate,so that if a solution
containing radium salts and an excess of ferric salts is
precipitated with sodium carbonate,all the radium is carried
down with the iron precipitate. If this precipitate is
dissolved in the necessary amount of hydrochloric acid,
forming $Fe(OH)_2Cl$,and the solution dialyzed,the radium
salts can be separated. Barium salts pass through the
dialyzer at a different rate than the radium salts and thus

fractionation is brought about.

McCoy(10) invented the hydroxide method of separating radium from barium. This method is also applicable to the separation of mesothorium and thorium X from barium compounds. The separation is effected by converting the barium and other radioactive elements into hydroxides and fractionally separating the barium hydroxide from the solution. McCoy's method differs from other methods in that the concentration of the radium and mesothorium takes place in the liquor rather than in the crystals separating out. The radium and barium are converted into hydroxides, whereupon the barium being the less soluble,greater amounts of the barium hydroxide crystallize out,leaving more of the more soluble radium hydroxide in solution. The liquor when evaporated to dryness gives a product of high radium content.

Soddy and Marckwald have shown (11) that mesothorium and radium have identical chemical properties,and hence the above methods of concentration apply to both. When mesothorium and radium occur together,their ratio is not changed by fractional crystallization.

While various electrolytic and adsorbtion methods of separating radium have been experimented with,they have not come into general use,and fractional crystallization remains the chief method of obtaining radium of high concentration. In the United States Bureau of Mines,radium

is obtained in highly concentrated form by this method.
The procedure is about as follows: (12) To separate the
radium from the original crude material,it is first pre-
cipitated as the sulphate. Barium is first added to in-
crease the quantity of the sulphates. The sulphates
are then converted into sulphides by reduction with
carbon and finally into chlorides by grinding the sul-
phides finely and leaching with chemically pure hydro-
chloric acid. The filtrate which consists of a satur-
ated solution of radium-barium chlorides is now ready
for fractional crystallization. This fractionation is
carried on in silica lined,acid proof,steam jacketed
vessels of from 200 to 250 liters capacity. The sol-
ution is concentrated by heating,so that on cooling one-
half of the barium chloride crystallizes out. The liquor
is then siphoned into another vessel and the process re-
peated. In the last stages of the refinement,the chlorides
are converted into bromides,for the reason that it has been
found that the factor of enrichment is higher for the bro-
mides than for the chlorides. The method of crystallizing
the bromides is similar to that of the chlorides and will
be given in more detail later in this paper.

The U. S. Bureau of Mines (13) seems to favor
the concentration of radium bromides in acid solutions.We

find the following statements: "The degree of acidity to be maintained both in the chloride and bromide crystallizing systems can not be stated definitely,as it depends largely on operating conditions and must be left somewhat to the judgment of the operator. In general it may be stated that the acid concentration should be maintained as high as consistent with the size of the crystal crop to be obtained and the quantity of fumes that can be conveniently liberated". And again," Only when the bromide system is disturbed by the presence of lead or chloride salts or when it contains too little acid,do the bromide crystals fail to form in their characteristic habit. Both disturbing influences should be carefully avoided,as radium concentration is at once retarded if the bromide crystals do not retain their type".

EXPERIMENTAL.

A. CRYSTALLIZATION FACTOR DEFINED.

As in this work we shall attempt to show the relation between crystallization factor and the acidity of the bromide solution at the time of crystallization, it becomes necessary at the outset to define the term, "crystallization factor". In Bulletin 104 of the U. S. Bureau of Mines, pages 75 and 83, the terms "crystalliza- tion factor", "concentration factor", and "factor of enrich- ment" are used. For the crystallization of chlorides from hydrochloric acid solutions a factor of 1.5 to 1.6 is given, while for the bromide system the factor is 2.

According to Dr. Herman Schlundt of the Univer- sity of Missouri, at least three distinct meanings can be given to the term "crystallization factor" :

1. The ratio, $\dfrac{\text{Concentration of Mesth. in Crystals Separated}}{\text{Concentration of Mesth in original crystals}}$ $= \dfrac{C_c}{C_o}$, concentrations being given as milligrams of Mes- othorium, or radium, or mesothorium and radium per gram or kilogram of anhydrous crystals.

2. The ratio, $\dfrac{\text{Total Mesothorium in Crystals}}{\text{Total Mesothorium in mother liquor}} = \dfrac{Q_c}{Q_l}$

3. The ratio, $\dfrac{\text{Conc. of Mesth in crystals separated}}{\text{Conc. of Mesth in crystals from mother liquor}} = \dfrac{C_s}{C_l}$

In the third definition, the term is used in the sense of a partition or distribution coefficient. In the second definition it is regarded as a fractionation coefficient, and appears to be used in this sense in the bulletin of the U. S. Bureau of Mines.

Throughout this discussion the term crystallization factor will be taken to mean:

The ratio, $\dfrac{\text{Conc. of Mesothorium in crystals separated}}{\text{Conc. of Mesothorium in original crystals}} = \dfrac{C_c}{C_o}$,

the concentrations being expressed as in definition 1. This factor serves directly in computing the radium or mesothorium content of the head crystals in "stepping up", as this factor raised to the nth power, $\underline{n}$ being the number of crystallizations, gives the desired multiplier. This factor will also be found serviceable in computing the number of crystallizations necessary to step up to a certain desired concentration, and as a guide to the transfer of liquors and crystals in a crystallizing system.

B. METHOD IN CRYSTALLIZING.

1. Scource of Material.

The material that was used in this study was obtained from the Welsbach Light Company, Gloucester, New Jersey, and consisted of mesothorium-radium-barium bromides, whose radium equivalent measured approximately one-half milligram per gram. This material had previously been

concentrated in the form of chlorides,and had then been con-
verted into bromides and sent to us in this form for fur-
ther concentration by fractional crystallization. During
the year we concentrated approximately $10,000 worth of
mesothorium-radium-barium bromides,of the above concentra-
tion,and ended with a product whose radium equivalent rang-
ed from 150 to 200 milligrams per gram.

2. Method of Treatment.

The underlying principle in the separation
of mesothorium-radium bromides from barium bromide is that
of solubility. The mesothorium-radium bromide is less sol-
uble in water and in acid solutions than is the barium bro-
mide. Consequently when an aqueous solution or an acid sol-
ution of these bromides is concentrated by evaporation,to
the point where by gently blowing a current of air over the
surface of the liquid near the boiling point,small crystals
are made to form on the surface,on removal from the water
bath,a rich crop of crystals will settle out. These crystals
will be richer in mesothorium and radium content than the
salt remaining in the mother liquor. By redissolving the
crystals and repeating the process a sufficient number of
times,the crystals become richer and richer in their meso-
thorium-radium content, while the weight of the crystals
becomes progressively less.

The mesothorium-radium-barium bromides sent us were
sealed in glass tubes, the weight of the bromides ranging
from three to five grams in weight per tube and in activ-
ity equivalent to one to three milligrams of radium, of
which about 4/5 is due to mesothorium and 1/5 to radium.
In order to be able to check up on any losses in the pro-
cess of crystallizing, should any occur, the tubes before
opening, were measured for their radium equivalent by the
gamma-ray method. Each tube was measured separately. In
measuring tubes containing mesothorium and radium, it should
be noted that one milligram of mesothorium is the quantity
whose gamma-ray radiation equals the gamma-ray activity of
one milligram of radium. The mesothorium I must be in equi-
librium with mesothorium II, and the radium must be in equi-
librium with its short-lived product (radium emanation).
Equilibrium between mesothorium I and mesothorium II is
attained in the course of two days, and the radium equilib-
rium after a month. Since mesothorium obtained from mono-
zite sand, the scource of our material, always contains radium,
the activity of commercial mesothorium is measured about a
month after the preparation of the specimen. Its activity
is expressed in terms of radium.

For the first crystallization about twenty-five tubes
were sent. After measuring the radium equivalent of these

tubes they were divided into three groups; those having
the highest mesothorium-radium content were placed in
group ✦ 1,those having the next highest mesothorium-radium
content per gram were placed in group 0,and those having
the lowest mesothorium-radium content per gram were placed
in group - 1.

The tubes were then opened and the contents dis-
solved separately in hot water acidified with a little hy-
drobromic acid. The insoluble matter was removed by filter-
ing. As the material usually contains small quantities of
lead,and as this interferes decidedly with the crystalliza-
tion,it was removed by making the solution slightly alkaline
with ammonium hydroxide and passing in hydrogen sulphide. The
lead is precipitated as lead sulphide and was filtered off.
The solution was again made slightly acid with hydrobromic
acid and is now ready for crystallization.

The crystallizing dishes used in this work were of
fused silica ware and were of different shapes;some with
broad flat bottoms,others with rounded bottoms. For the
lower fractions,the ordinary flat-bottomed,glass crystal-
lizing dishes were used.

The concentration of the liquor was carried out
on a steam bath heated electrically. The water bath contained
distilled water,so that if any losses occurred by spilling,
the material could be recovered in pure form by evaporating

the water to dryness,and thus recovering the material.
The table on which the transfers were made was covered
with glass,so that any liquor spilled could easily be
wiped up. The dishes were numbered on small slips cut
from filter papers,all of which were saved,ignited,and
the residue measured for radium content.

The dishes were placed on the water bath and as
soon as the concentration became such that on blowing
over the surface of the liquor crystals began to form.
on the surface,the dish was removed from the bath,covered
with a watch glass and allowed to cool. Crystals formed
at the bottom of the dish and the clear liquid is easily
decanted. After the dishes had all been removed from the
water bath in this way and allowed to cool,the transfers
were made. The liquor from dish -1 was poured into a new
dish numbered -2. The crystals of dish -1 were moved into
the second series and became dish 0 of that series. Dish
0,second series,received the liquor from dish ∤1 of the
first series. Dish 0,first series,after its liquor had been
poured into dish -1,second series,became dish ∤1,second
series,and received no liquor. The liquor from dish ∤ 1
was poured into dish 0,second series,and the crystals of
dish ∤ 1,first series,became dish ∤2 of the second series.
Crystals in dishes ∤ 1 and ∤ 2,having received no liquor
from any of the other dishes,were dissolved in water. Trans-

fers of liquor and crystals were made in a similar way
for each successive series.

Our first crystallization was made from almost
neutral solution and the following pages give a diagram-
matic scheme of the transfers and a summary of the data.
In the scheme of transfers,the various crystallizing
dishes are represented by circles (zero on typewriter),
and are numbered plus or minus according to their position
in the system. The broken lines represent the course of
the crystals while the solid lines represent the course
of the liquor. An arrow at the end of a broken line
represents the place in the system where the crystals
were removed,dried,and sealed,in glass tubes. An arrow
at the end of a solid line represents the place in the
system where the mother liquor was removed,evaporated to
dryness, and sealed. Several lines converging to the same
arrow indicate a combination of dishes. The letters refer
to these dishes and are used for the sake of brevity in
giving the general summary of the crystallization.

Photograph of Crystallizing System Used
in Concentrating Mesothoriu-Radium-Barium Bromides.
Crystallizing Dishes are shown at the right,the elec-
trically heated Water Bath at the left.

3.   Diagram of Transfers made in the Crystallization of
Mesothorium-Radium Bromides.
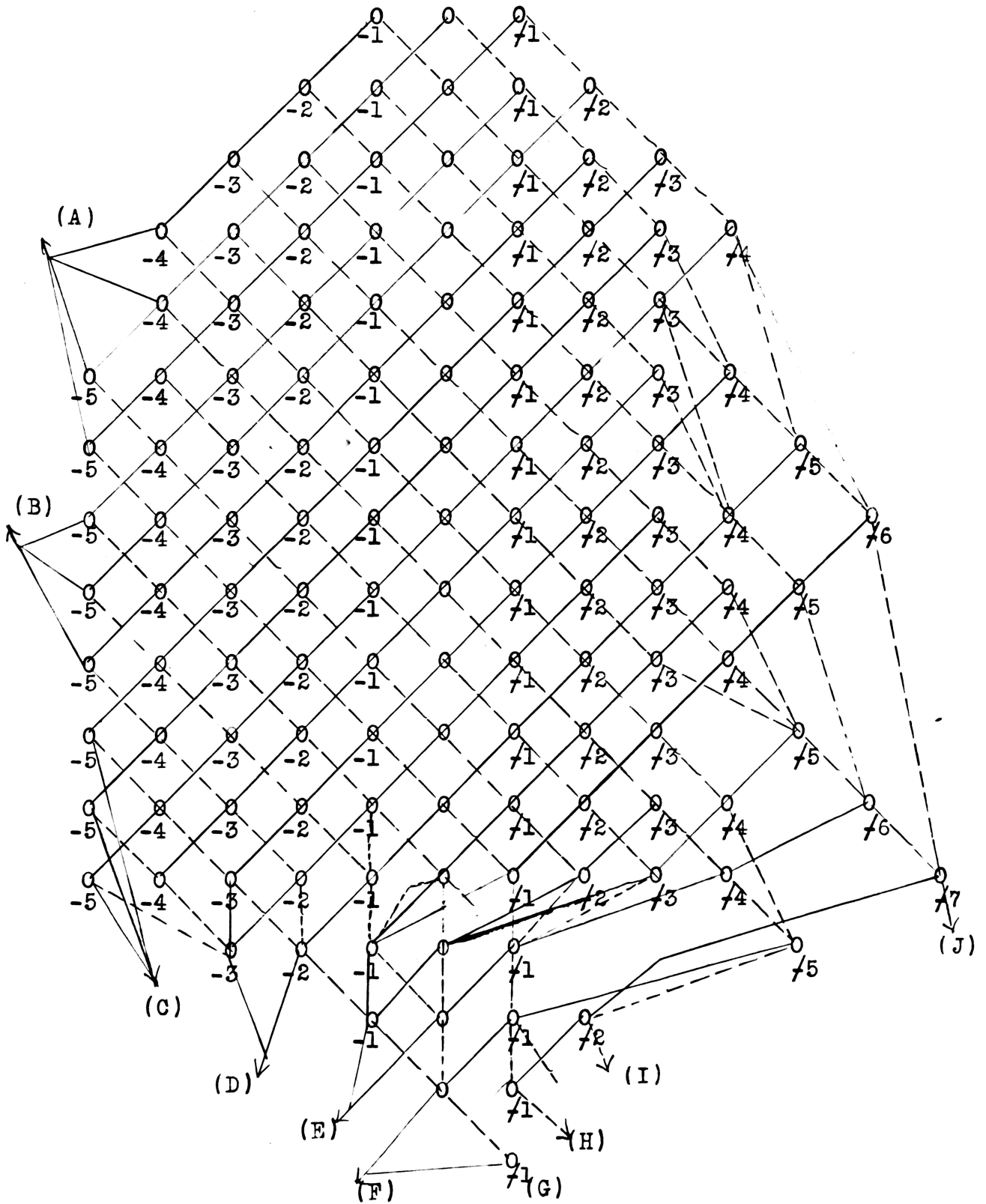
4.   Summary of Data on Preceding Fractionation.

Bromides Before Fractionation.

Dish -1 (see diagram)	24.57 g.
Dish 0 (see diagram)	35.40 g.
Dish /1 (see diagram)	17.62 g.
Total	77.59 g.

Total mesothorium-radium content before fractionation
was 82.93 mg. or approximately 1 mg. per gram. Concentra-
tion of mesothorium-radium in dish /1 was 2.23 mgs per
gram.

Products after Fractionation.

Tube	Weight.	Mesothorium-radium Content.
A (see diagram)	.7.65 g.	.10 mg.
B (" ")	18.45 g.	.05 mg.
C (" ")	15.69 g.	.05 mg.
D (" ")	14.30 g.	.16 mg.
E (" ")	11.48 g.	.58 mg.
F (" ")	7.52 g.	4.98 mg.
G (" ")	1.88 g.	11.73 mg.
H (" ")	.1966 g.	7.27 mg.
I (" ")	.2053 g.	15.33 mg.
J (" ")	.1628 g.	27.31 mg.
Insoluble Residue and H₂S precipitate	.4500 g.	2.25 mg.
Total	77.9847 g.	69.81 mg.

By referring to the summary given on the preceding page, the discrepancy between the total mesothorium-radium content after fractionation and before fractionation becomes apparent. This discrepancy is due to the fact that the radium present in the products after fractionation, had not yet acquired equilibrium. In the course of a month the total gamma-ray activity of the products after fractionation, should total the gamma-ray activity of the bromides before the fractionation was made.

C. FRACTIONATION FROM CONCENTRATED HBr SOLUTIONS.

For the purpose of making a rather rough comparison of the effect of the acidity of the solution of bromides on their crystallization, another fractionation was made. A different quantity of bromides and of different mesothorium-radium concentration was used. The weight of the bromides was 3.3526 grams and the mesothorium-radium content was 31.2 mgs. or 9.30 mgs. per gram. Five series of crystallizations were made. Throughout the fractionation a high concentration of hydrobromic acid was maintained in each dish. The plan of transfers is given on the following page. The significance of lines, arrows, and letters is the same as for the preceding fractionation. A general summary of the fractionation is also given.

Diagram of Tranfers made in Crystallization of
Mesothorium-Radium Bromides.
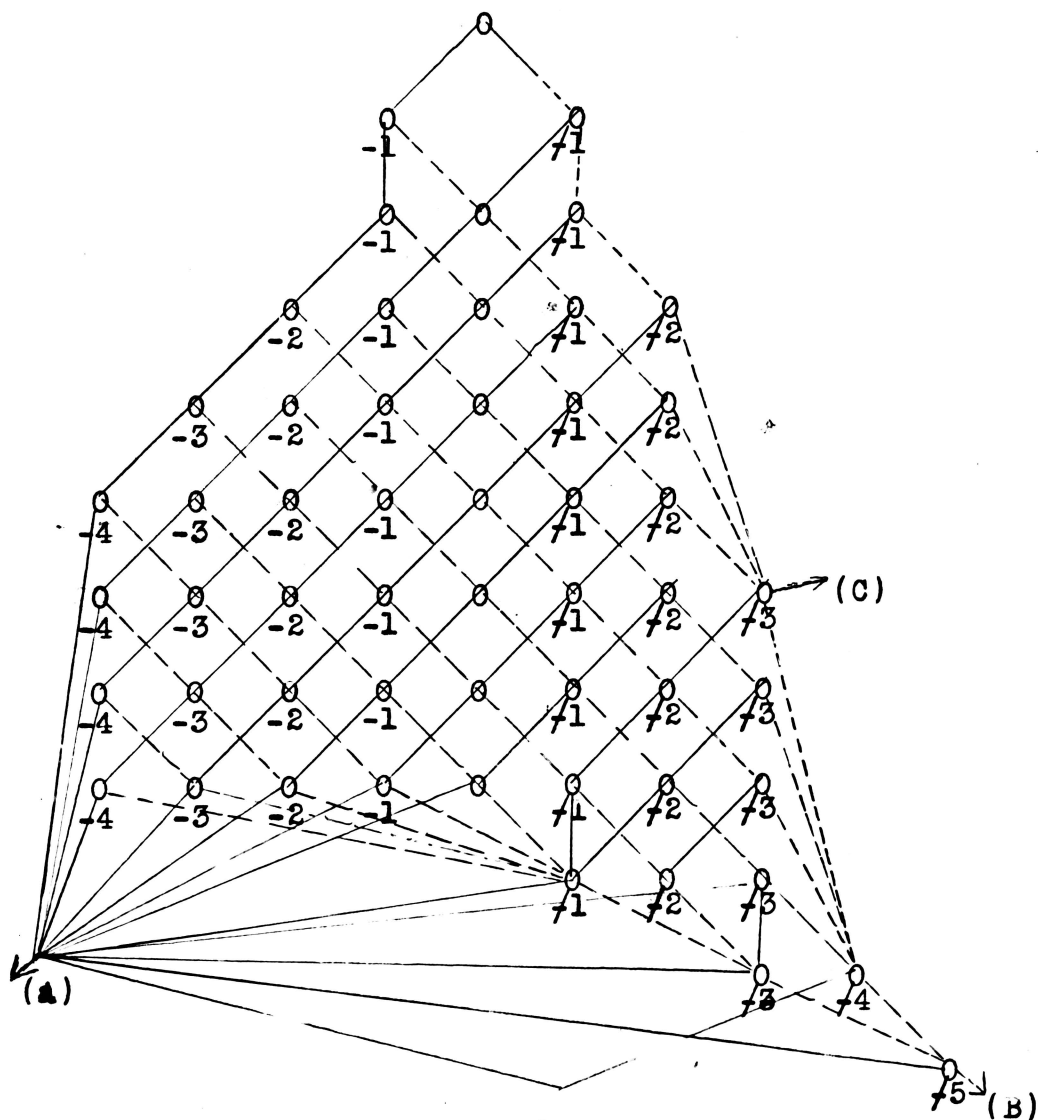

Diagram II.

2. Summary of Data on Second
Fractionation.

Bromides Before Fractionation.

    Weight   3.3526 g.

    Mesth-Ra Content   31.2 mg.

    Mesth-Ra per
        gram   9.30 mg.

Products After Fractionation.

Tube	Weight	Mesth-Ra Content
A	3.0196 g.	3.9 mg.
B	.1938 g	1.9 mg.
C	.2664 g	27.5 mg
Total	3.4798	33.3 mg

Again the discrepancy between the mesothorium-radium content after fractionation and before becomes apparent. This discrepancy is due to a difference in age of the products. The measurement of the products after fractionation,was made about a week after the first measurement,during which time the gamma-ray activity of the product had increased. This fact makes it imperative that material of equal age should be compared in making measurements,if measurements are made before equilibrium is attained.

3. Comparison of Fractionations.

Although the scheme of transfers was not the the same in the two preceding fractionations, nevertheless a comparison of the two reveals some interesting facts: In the first fractionation made in practically neutral solution, the dish #1, first series, contained 17.62 grams of the bromides. The mesothorium-radium content of these bromides was 39.37 milligrams or 2.23 milligrams per gram. After seven crystallizations, the head crystals (represented by J in the diagram on page 19) weighed .1628 g. and its mesothorium-radium content was 27.31 milligrams, or 167.7 milligrams per gram. These bromides had therefore been concentrated 167.7/ 2.23 or 75.2 times. As this was accomplished in seven crystallizations, the crystallization factor X may be obtained from X^7 = 75.2, whence X = 1.852.

In the crystallization of the second lot of bromides from a very concentrated acid solution, the original bromides weighed 3.3526 g. and the mesothorium-radium content was 31.2 milligrams or 9.30 milligrams per gram. After five crystallizations the head crystals (represented by C in the diagram on page 22) weighed .2664 grams and their mesothorium-radium content was 27.5 milligrams or 103.2 milligrams per gram. These bromides had therefore been concentrated 103.2/9.30 or 11.09 times. As this had been accomplished in five crystallizations, the

crystallization factor,X may be obtained from $X^5 = 11.09$, whence $X = 1.617$. These results show that the crystallization factor was no higher for the concentrated acid solutions of the bromides than for the neutral solutions.

D. DETERMINATION OF CRYSTALLIZATION FACTOR.

The two preceding fractionations were made for the purpose of becoming familiar with the technique of fractional crystallization,before beginning the more exact work of determining the crystallization factor. A further study of the relation of the acid concentration to the crystallization factor was now undertaken by the following method: Mesothorium-radium-barium bromides of known weight and known radium equivalent were fused with fusion mixture consisting of equal molecular weights of sodium and potassium carbonates,and thus converted into carbonates. These carbonates,after being well washed,were converted into bromides by dissolving in hydrobromic acid. The clear solution containing the bromides was now made slightly alkaline with ammonium hydroxide,and a few cubic centimeters of aluminium chloride solution,containing one milligram of aluminium per cubic centimeter,was added. This precipitated any radiothorium that was present as radiothorium hydroxide,the aluminium hydroxide forming in the alkaline solution,carrying the radiothorium down with it

in the precipitate. The radiothorium was removed in order
to prevent the formation of thorium X, thorium emanation, and
finally thorium D. The latter gives off a powerful gamma-
ray radiation and would interfere with our gamma-ray meas-
urements later. Hydrogen sulphide was now passed into the
solution and the precipitates of lead sulphide and aluminium-
radiothorium hydroxide filtered off and discarded. The clear
solution of the bromides after having been made neutral or
faintly acid with hydrobromic acid was now ready for crystal-
lization.

The crystallization was carried out on the water
bath as described on page 16. The solution of the bromides
was concentrated by evaporation and a certain weight of
crystals allowed to separate out. The liquor was then de-
canted. The crystals were then thoroughly dried, sealed in
a weighed glass tube, and their weight determined. The de-
gree of acidity of the liquor from which the crystals sepa-
rated was now determined. One cubic centimeter of this
liquor was pipetted into an Erlenmeyer flask, diluted with
a little water, and titrated with half-normal ammonia sol-
ution. Methyl orange was used as the indicator. From the
amount of ammonia solution used, the number of grams HBr
per liter and the normality of the liquor was calculated.
The solution in the Erlenmeyer flask after titration, which
consisted of the bromides of mesothorium, radium, and barium,

together with the ammonium bromide that was formed in the titration was now added to the liquor originally poured off of the crystals,evaporated to dryness,the ammonium bromide smoked off,and the remaining bromides sealed in the same manner as the crystals.

The mesothorium-radium content of the crystals and of the salt obtained by drying the liquor was now determined with a Lind Electroscope by the gamma-ray method. The glass tubing used in sealing the bromides was of uniform diameter and thickness so as to allow of uniform absorbtion by the glass. The tubes were measured at the time of sealing and every twelve hours therafter up to 108 hours from the time of sealing. After a number of measurements had been made in this manner,it was found that after sixty hours the activity became practically constant,or so nearly so that the activity at the end of sixty hours from the time of sealing was taken as a measure of the mesothorium-radium content of the tubes. The curves on page 28 show the relation of the radium equivalent to hours from time of sealing.

All crystallizations were made in flat-bottomed silica dishes,with perpendicular or slightly sloping sides. As much as was possible the same dishes were always used. After the tubes had been measured at constant activity, they were redissolved in as nearly as possible the same concentration of acid,a different quantity of crystals was
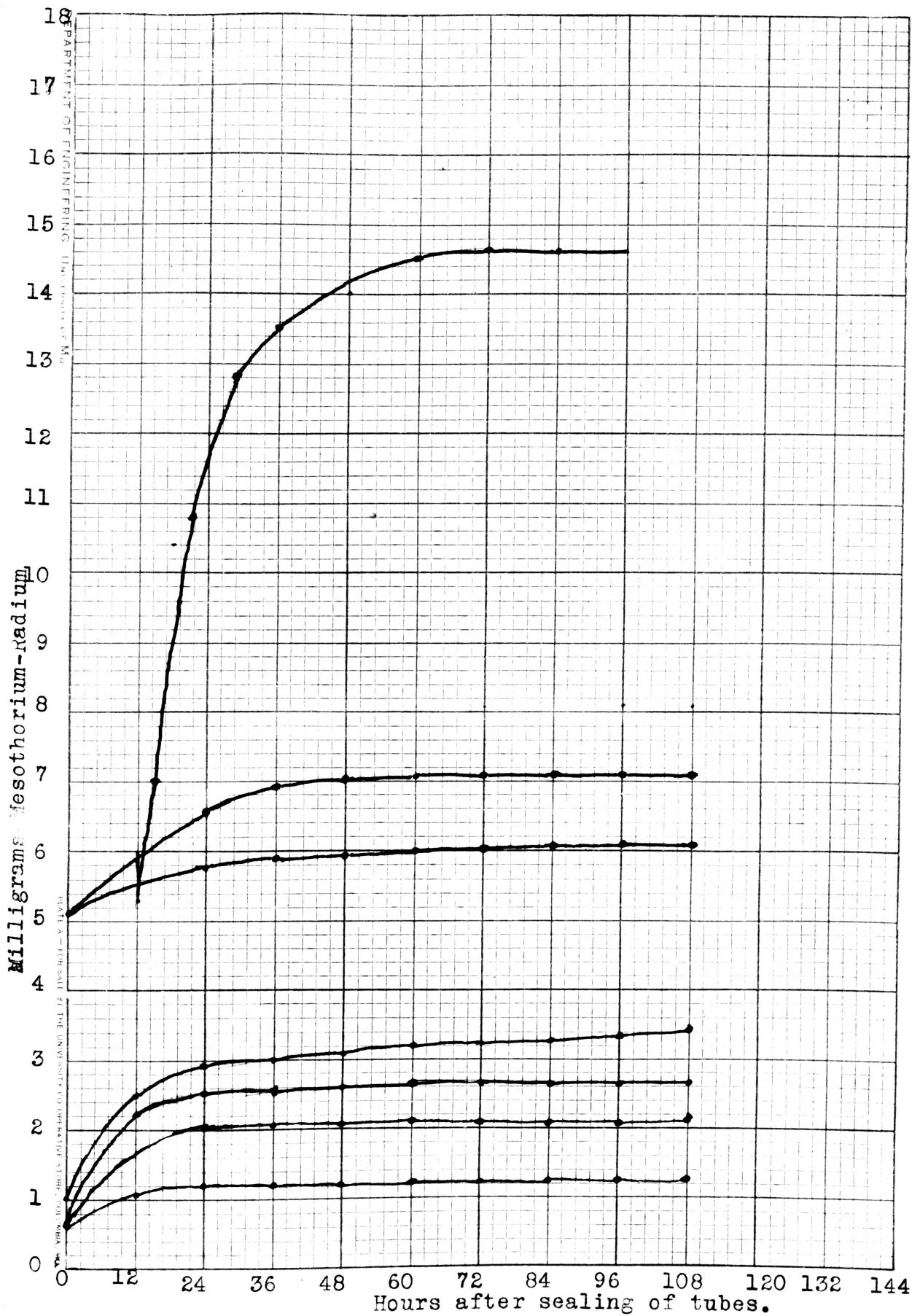
Graph 1.

made to separate out by concentrating the solution further by evaporation,and the entire procedure of drying,sealing, titrating,and measuring repeated. In this way different quantities of crystals were separated from approximately the same acid concentration of liquor. After obtaining different quantities of crystals from a certain acid concentration of the liquor, the acid concentration of the liquor was changed by adding more or less hydrobromic acid. Different quantities of crystals were then separated at this new concentration. In this way different quantities of crystals were obtained from liquor,whose acidity ranged from neutral to six times normal.

The crystallization factor,that is the ratio of the number of milligrams of radium equivalent per gram of material in the crystals,to the number of milligrams radium equivalent per gram of material in the original material before crystallization,was next determined, and plotted along one axis while the percentage of crystals separating out was plotted along the other axis. In this way a comparison of the crystallization factor for different acid concentrations of the solutions of the bromides for different weights of crystals separating out could be made.

This method is subject to considerable error. In the first place as the dry bromides are very hygroscopic, it is difficult to seal them quickly enough to secure absolutely the same degree of dryness in the crystals each time.

Again as a certain amount of organic matter always enters the material from brushes used in handling the material, filtering is necessary and results in small losses when so great a number of crystallizations are made. As the bromides are dried in the crystallizing dishes and the ammonium bromide smoked off, it is impossible to avoid the sticking of small quantities of the bromides to dish and its consequent loss. Then too as all crystallizations were made in open dishes, small losses resulting from "crawling" were inevitable. However as this method of fractionation is the one used commercially, the same method was used in this research, with the end in view that any facts here discovered could the more easily be applied in a commercial way.

Three different lots of bromides were used in these crystallizations. The first tube weighed approximately 5.7850 grams throughout our work and its mesothorium-radium content was approximately 12.25 milligrams. The second tube weighed approximately 9.7318 grams and its mesothorium-radium content was approximately 1.92 milligrams. The third tube weighed approximately 3.6430 grams and its mesothorium-radium content was approximately 1.98 milligrams. We were thus working with different quantities of bromides, and with bromides of different mesothorium-radium content per gram.

Our first crystallizations were made in neutral
solution. Different quantities of crystals were allowed
to separate out;the percentage of crystals separating
was then computed and also the crystallization factor.
The following table shows the data necessary for these
calculations and which is of special interest in this
study.

Table I.

Selected Single Fractionations.

| No.of Tube. | Wt.of original salt | Conc. Mesth per g. | Crystals | | $\frac{C_c}{C_o}$ | % of Crystals | Weight salt |
			Weight	Conc. Mesth C_c per g.			
1	5.785	2.11	2.641	4.08	1.95	46.6	3.148
	5.735	2.11	1.916	5.01	2.35	33.4	3.819
	5.738	2.13	3.269	3.45	1.56	61.9 —	2.469
2	9.710	.19	2.804	.52	2.64	28.8	6.906
	9.833	.19	3.804	.43	2.26	38.7	6.029
3	3.643	.54	1.759	.99	1.83	48.2	1.883 2.0548
	3.634	.54	1.579	1.06	1.96	43.4	

In the above table the concentration of mesothorium
per gram is the total mesothorium content of the original
salt divided by the weight of the original salt. The con-
centration of mesothorium per gram in the crystals (C_c) is

the mesothorium content of the crystals divided by their
weight. The crystallization factor ($\frac{c_c}{c_o}$) is the concen-
tration of mesothorium per gram in the crystals divided by
the concentration of mesothorium per gram in the original
salt. The percent of crystals is the weight of crystals
divided by the weight of the original salt. The concentra-
tion of mesothorium in the mother liquor is similarly the
total mesothorium content of the salt divided by the weight
of the salt. The percent of mesothorium in the mother liquor
is the mesothorium content of the mother liquor divided by
the mesothorium content of both crystals and liquor.

Similar calculations were made for all crys-
tallizations made, but as we are concerned chiefly with two
items of the above table, namely crystallization factor and
percentage of crystals separating out, for the sake of brev-
ity, only these two items will be given in the tables that
follow. The following page gives the different crystalli-
zation factors for different quantities of crystals sepa-
rating in neutral solution.

Table II.

Percentage of Crystals Crystallizing from
Neutral Solutions and the Correspond-
ing Crystallization Factor.
(See Graph No.2)

Percent of Crystals	Crystallization Factor	Product of Percent of Crystals by crystallization factor.
24.3	2.57	62.45
27.9	2.62	73.09
33.4	2.35	78.49
35.1	2.34	82.13
38.3	2.23	85.40
38.7	2.26	87.46
43.4	1.96	85.06
44.8	1.98	88.70
46.6	1.958	90.87
48.9	1.833	89.48
48.2	1.833	88.20
53.6	1.714	91.65
56.9	1.619	91.60
62.3	1.47	91.58
69.0	1.44	99.36

It is evident from the above data that the
crystallization factor varies with the quantity of crystals
separating. As the product of percent of crystals by

Crystallization Curve for Bromides Neutral Solution.
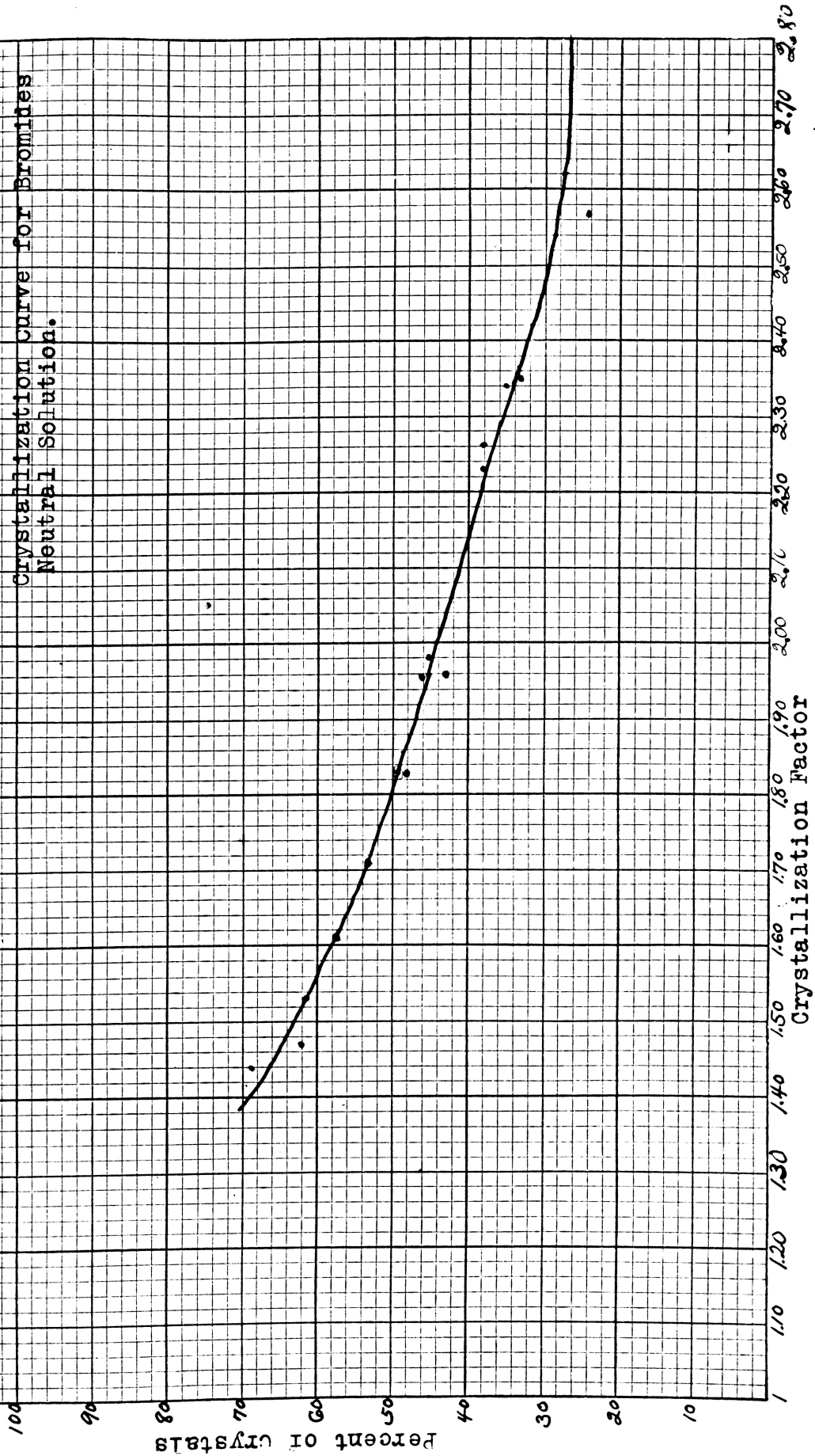
Graph 2.

Crystallization Factor

Percent of crystals

crystallization factor is not a constant this variation
of the crystallization factor with the percent of crystals
separating is evidently not an inverse proportion. This also
becomes more apparent when the curve for the preceding data
is plotted. This curve is shown on the preceding page.

Our attention was next turned to crystallizations
made in acid solutions of different concentrations. As it
was impossible to control absolutely the acidity of the sol-
utions from which the crystals separated, it was done only in
so far as was possible. The bromides were dissolved in water
and a definite amount of hydrobromic acid was added. They were
then crystallized and a certain percent of crystals allowed
to separate out. The crystals were then sealed. The acidity
of the liquor was determined by titration, evaporated to dry-
ness, and the resulting salt sealed, as explained on page 26.
After the interval of 60 hours the crystals and salt obtained
from the liquor were measured and the percent of crystals
and the crystallization factor computed. They were then
ready to be redissolved for another crystallization. They
were again dissolved in water and about the same amount of
hydrobromic acid was added as in the preceding crystalliza-
tion. In this way the acid concentration of the solution
of the bromides was kept approximately the same. Another
crystallization was made and a different amount of crystals
allowed to separate out. The entire procedure of sealing,

titrating and measuring repeated. In this manner we obtained different quantities of crystals from solutions of bromides having approximately the same degree of acidity. The following table gives the data for a number crystallizations made in approximately normal acid solution.

Table III.

Table of Crystallizations
from approximately Normal acid Solution.

| Percent of Crystals	Crystallization Factor	Normality of Liquor.
28	2.73	1.333
28.8	2.64	1.158
29.6	2.66	1.442
36.4	2.19	1.578
38.8	2.22	1.753
53.9	1.59	1.135
66.3	1.36	1.135

It will be noted on referring to the above table that the crystallization factor varies with the percent of crystals separating out, the same as it did for neutral solution. The curve on the following page shows this relation.

Similarly different amounts of crystals were allowed to separate from approximately 2.5 Normal acid

Crystallization Curve for
Bromides from approximately
Normal Acid Solution.

Percent of Crystals.

Crystallization Factor

Graph 3.

DEPARTMENT OF ENGINEERING. UNIVERSITY OF Mo.

PLATE A — FOR SALE AT THE UNIVERSITY CO-OPERATIVE STORE, COLUMBIA, MO.
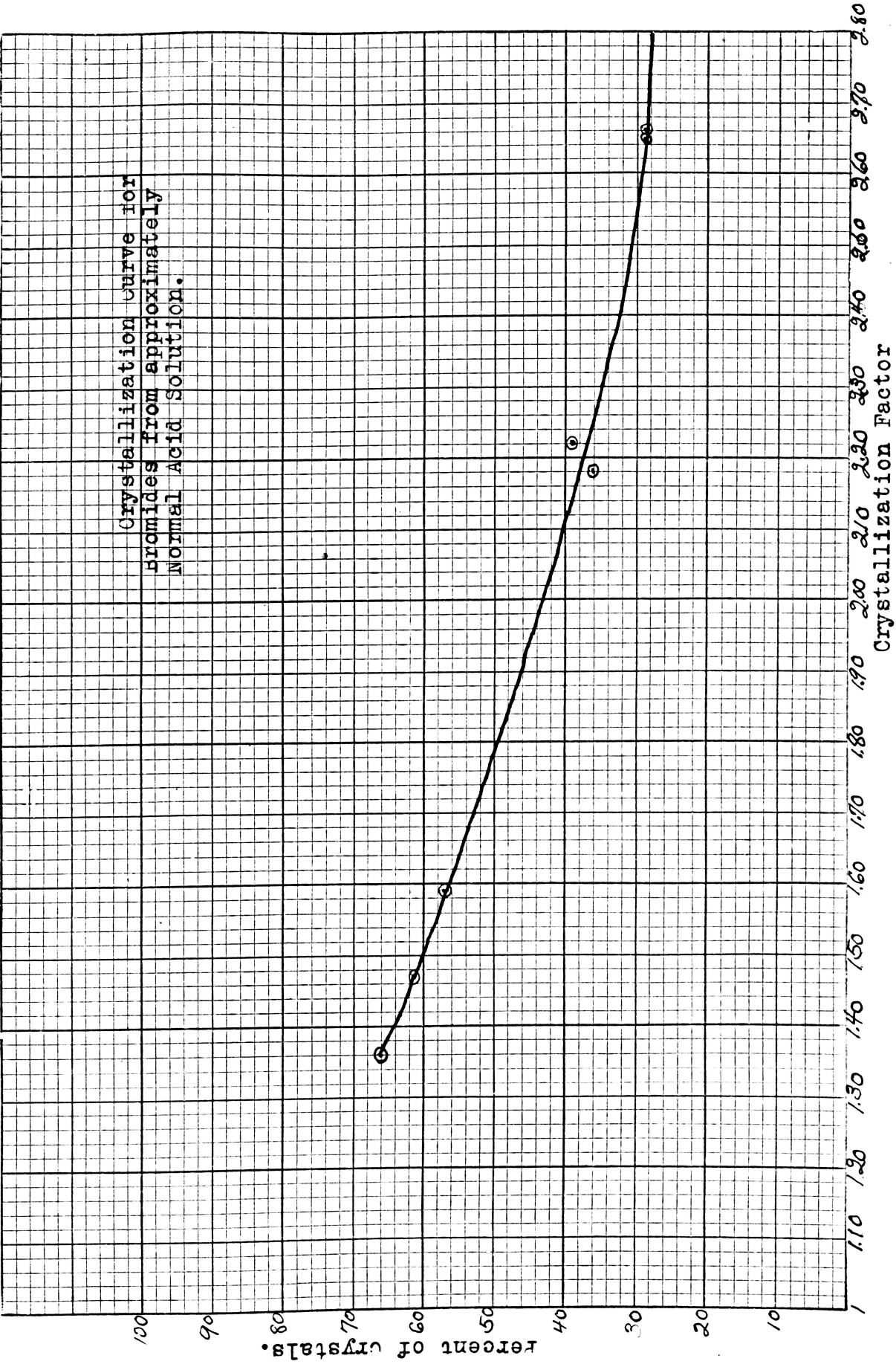
solutions of the bromides and approximately 4 Normal
acid solutions of the bromides. Tables IV and V give
the data obtained while graphs 4 and 5 on pages 39
and 40 show the corresponding curves.

Tables of Crystallizations from
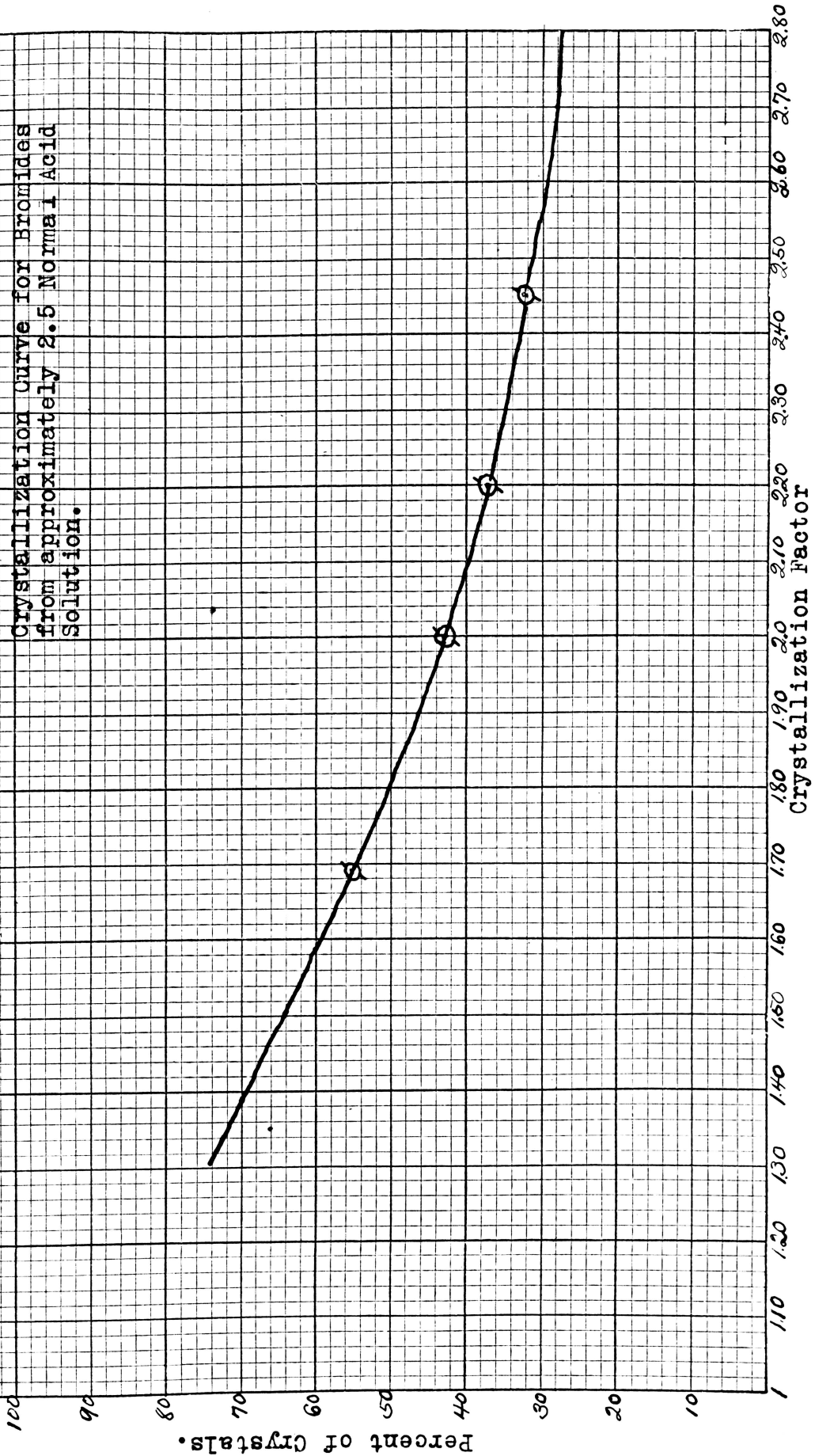approximately 2.5 Normal and 4 Normal Acid Solutions.

Table IV.
Approximately 2.5 Normal Acid Solution.

Percent of Crystals	Crystallization Factor	Normality of Liquor.
32.2	2.45	2.313
37.1	2.19	2.362
43.4	2.00	2.548
55.3	1.68	2.929

Table V.
Approximately 4 Normal Acid Solution

Percent of Crystals	Crystallization Factor	Normality of Liquor.
29	2.60	4.120
34.2	2.34	4.231
48.8	1.81	4.3232
52.8	1.70	4.578
61.7	1.56	4.835
68.2	1.35	4.102

Graph 4.

Crystallization Curve for Bromides
from approximately 2.5 Normal Acid
Solution.

Crystallization Factor

Percent of Crystals.

Crystallization Curve for Bromides
from approximately 4 Normal Acid
Solution.

Crystallization Factor

Graph 5.
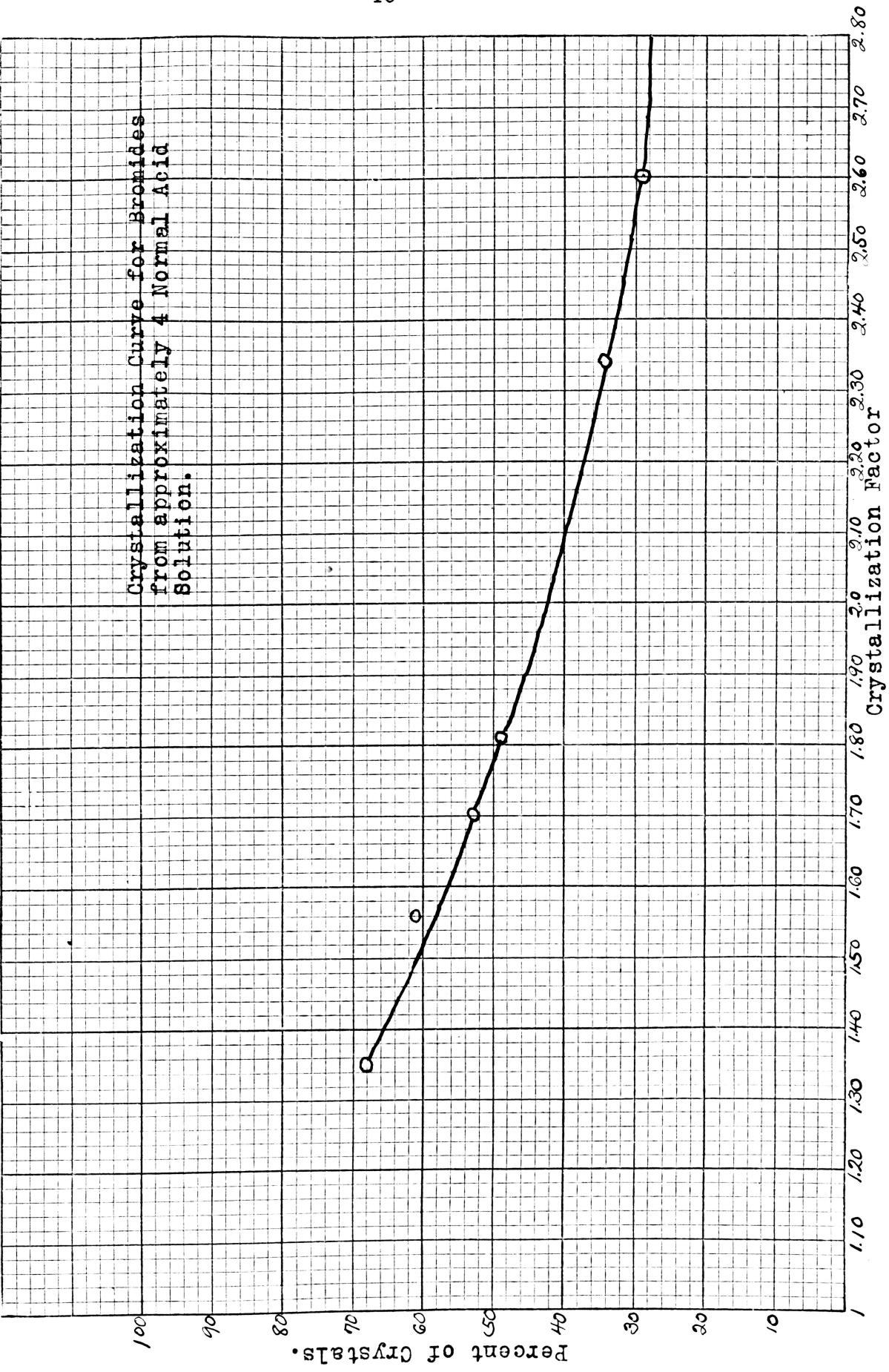
Percent of Crystals.

As the solubility of barium bromide decreases rapid-
ly with increase of acid concentration,it was difficult to
separate the lower percentages of crystals from the solution
of the bromides when the solution became more then four times
normal in acid concentration. However three such separations
were secured and are given in the table below. The corres-
ponding points are plotted in graph 6 and are designated by
an appropriate symbol. These points lie on the composite
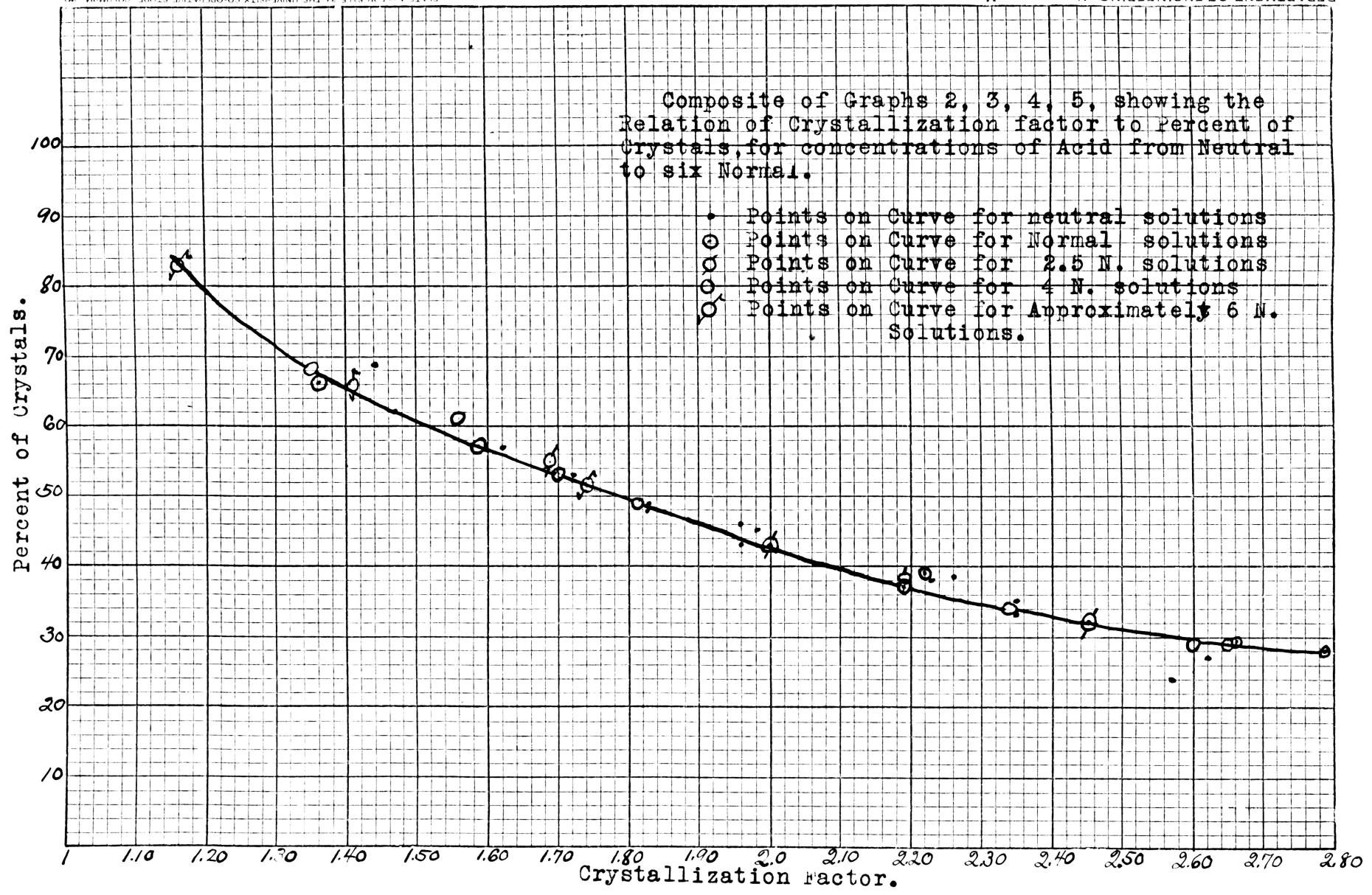of curves drawn for the preceding acid concentrations of
bromides.

Table VI.

Table of Crystallizations from Acid
Solution of the Bromides of High Concentration.

Percent of Crystals.	Crystallization Factor	Normality of Solution.
51.5	1.74	6.907
65.8	1.41	5.519
83.6	1.16	6.879

When Tables II, III, IV, V, and VI are compared,
the same relation between crystallization factor and per-
cent of Crystals separating will be found to exist in all;
namely,that the crystallization factor varies inversely

with the percent of crystals separating out. Again when
graphs 2, 3, 4, and 5 are compared a marked similarity
will be noted. It is evident that the curves obtained
for neutral,approximately normal, 2.5 normal,4 normal,and
6 normal acid solutions of the bromides, occupy nearly the
same position on the different graphs. In fact these cur-
ves can be superimposed and are then practically coincident
throughout,within the limits of experimental error. It
follows then that one curve can be drawn which embodies
within it the relationship between crystallization factor
and percent of crystals separating out that is expressed
separately in graphs 2, 3, 4, and 5. This curve is shown
on page 43. As this curve represents the relation between
crystallization factor and percent of crystals separating
from solutions of bromides whose acidity varied from neutral
to six times normal, we conclude that the crystallization
factor is independent of the acid concentration of the
bromides and varies inversely with the percent of crystals
allowed to separate out.

When the preceding curves are examined it will be
noted that all points plotted do not lie on the curves.
This is due to experimental error as explained on page 29.
The general trend of the curve is evident and sufficient
oasis for the above conclusion.

-43-

Composite of Graphs 2, 3, 4, 5, showing the
Relation of Crystallization factor to Percent of
Crystals, for concentrations of Acid from Neutral
to six Normal.

· Points on Curve for neutral solutions
⊙ Points on Curve for Normal solutions
φ Points on Curve for 2.5 N. solutions
Ọ Points on Curve for 4 N. solutions
Ọ Points on Curve for Approximately 6 N.
      Solutions.

Percent of Crystals. (vertical axis)

100, 90, 80, 70, 60, 50, 40, 30, 20, 10

Crystallization Factor. (horizontal axis)

1, 1.10, 1.20, 1.30, 1.40, 1.50, 1.60, 1.70, 1.80, 1.90, 2.0, 2.10, 2.20, 2.30, 2.40, 2.50, 2.60, 2.70, 2.80

Graph 6.

Having now shown that the crystallization factor is independent of the acid concentration of the solution of bromides when crystallizing, let us next see whether the crystallization factor is in any way influenced by the concentration of mesothorium per gram in the bromides crystallized. On page 30 it was stated that three different lots of bromides were used in these crystallizations and that they were also of different mesothorium-radium content per gram. In the course of our crystallizations made of these different lots of bromides we obtained the data contained in the following table:

Table VII.

Conc.Mesth. per gram C_o	Normality of Solution	Conc. of Crystals C_c	% of Crystals	$\dfrac{C_c}{C_o}$
.55	Neutral	1.23	38.3	2.23
2.23	1.753	4.96	38.8	2.22
.19	Neutral	.43	38.7	2.26

From the above table in will be seen that the concentration of mesothorium per gram of salt in the original material was different in these three crystallizations. The percent of crystals separating was approximately the same. The crystallization factor, within the limits of experimental error, remained constant. From which we may conclude that the crystallization factor is also independent of the mesothorium concentration per gram.

Application of Data Obtained.

We are now concerned with the application of the pre-
ceding data to a crystallizing system conducted on a large
scale. The question arises "Are the best results in crys-
talizing obtained when 40% of the original salt is allowed
to crystallize or when 60% is allowed to separate ?" To
answer this question in a general way, let us take the fol-
lowing example: Suppose we have 1000 grams of the bromides
having an activity of one milligram per gram. For 40% sepa-
rations, we see by referring to graph 6, that the factor is
2.1 . Let us suppose that we desire an 18% product, or 180mgs
mesothorium per gram in the final products. How many crys-
tallizations must be made to obtain this degree of concentra-
tion and how much of the mesothorium will remain in the
liquor ?

It is evident that $(2.1)^n = 180$, where n is the
number of crystallizations. Solving, we have $n = 7$, the
number of crystallizations necessary to obtain a concen-
tration of 180 mgs mesothorium in the head crystals. The
percent of mesothorium passing up in the head crystals is
84. Therefore $1000 \times .84^7 = 294.49$, milligrams mesothorium
in first head crystals after seven crystallizations. The
weight of the first head crystals is expressed by $1000 \times
.4^7 = 1.636$ g. the weight of the first head crystals.

The diagram on page 52   shows the method of making
the transfers throughout this problem. By referring to this
diagram we see that to obtain a concentration of 180 milli-
grams of mesothorium in the head crystals in seven crystal-
lizations, a total of 35 individual crystallization was
necessary.

Let us next consider dish 0 of the third series as
shown in the diagram on page 52. This diagram shows that
dish 0 of the third series, receives no liquor after the
second crystallization. Its mesothorium content must be
stepped up to a concentration of 180 milligrams per gram.
What is the concentration of mesothorium in dish 0 of the
third series, and how many crystallizations will be necessary
to attain a concentration of 180 milligrams per gram ?

Dish 0 receives mother liquor from dish ≠1, series
2, containing .16 X 8 0 or 134 mgs. of mesothorium, and
crystals from dish ≠1 series 2, containing 160 X .84 or
134 mgs. mesothorium. The total mesothorium content of
dish 0, series 3, after the second crystallization is 268
mgs. The weight of salt in dish 0, series 3, is obtained
as follows: From dish ≠ 1 series 2, it receives   400 X
.60 or 240 grams of salt. From dish -1, series 2, it
receives 600 X .40 or 240 grams of salt. The total
quantity of salt in dish 0, second series is then 480 grams,
and the concentration of mesothorium per gram in is there-

fore 268/480 or .56 mgs per gram. Since we desire a con-
centration of 180 mgs in the head crystals, the number of
crystallizations necessary for this concentration will be
expressed by $(2.1)^n = \frac{180}{.56}$, whence n is equal to 8. That
is eight more crystallization after the second will be
necessary to obtain a concentration of 180 mgs mesothor-
ium in dish 0, of series 3. The weight of the salt going
up in this dish after the second crystallization is 480
X $.4^8$ - .315 grams. The mesothorium content of dish /7,
series 10, after eight more crystallizations is 66.37 mgs.
By again referring to the diagram on page 52 we see that
eight more crystallizations after the second, or three more
after the seventh would mean a total of 30 additional, in-
dividual crystallizations (9 inseries 8;10 in series 9;11
in series 10;total 30).

Let us next apply the same computations to dish 0,
series 4. In the process of crystallization, this dish re-
ceives the liquor from dishes /1, /2, /3, /4, and /5, of
series 3, 4, 5, 6, and 7 respectively and the crystals from
dish -1 series 3. After the seventh crystallization it
receives no further liquor. What is the concentration of
mesothorium in dish 0, series 4, after seven crystalliza-
tions have been made and how many more crystallizations
will be necessary to obtain in this dish a concentration
of 180 milligrams per gram ? Also what will be the

mesothorium content after seven crystallization and the
weight of the crystals.?   See diagram page 52

Dish 0,series 4,receives (160 X .16) X .84 or
20.66 mgs.mesothorium from dish -1,series 3. It also
receives (840 X .84) X .16 or 112.89 mgs from dish ≠1
series 3. Total mesothorium in dish 0,series 4 then is
133.5 mgs.   Dish 0,series 4,becomes dish ≠1,series 5,
and receives   from dish 0 133.5 X .84 or 112.18
mgs mesothorium and from dish ≠2,series 4, 592 X .16 or
94.83 mgs of mesothorium. The total mesothorium content
of dish ≠1 series 5 is now 207.1 mgs. This dish now
becomes dish ≠ 2,series 6,and receives from dish ≠1,series
5, 207.1 X .84 or 173.88 mgs Mesothorium and from dish ≠3,
series 5, 497.88 X .16 or 80.56 mgs. The total mesothorium
content of dish ≠2, series 6, is now 254.44 mgs. This dish
now becomes dish ≠3,series 7,and receives from dish ≠2,series
6, 254.44 X .84 or 213.72 mgs.mesothoriumand from dish ≠4,
series 6, 417.32 X .16 or 66.77 mgs mesothorium. The total
mesothorium content of dish ≠3,series 7, is now 280.49 mgs.
This dish now becomes dish ≠4 series 8,and receives from
dish ≠3,series 7, 280.49 X .84 or 235.6 mgs mesothorium and
from dish ≠5,series 7, 350.5 X .16 or 56.08 mgs. The total
mesothorium content of dish ≠4 series 8,is now 291.69 mgs.
It now receives no further liquor.

The weight of the salt in dish 0, of the seventh

crystallization must now be computed. Dish 0,series 4,
receives from dish /1 series 3, 160 X .60 or 96 grams of
salt,and from dish -1,series 3, 360 X .40 or 144 grams of
salt. The total weight of salt in dish 0,series 4,is then
240 grams. This dish now becomes dish /1,series 5,and
receives from dish /2,series 4, 64 X .60 or 38.4 grams
of salt and from dish 0,series 4, 240 X .40 or 96 grams.
The total weight of salt in dish /1,series 5,is 134.4
grams. Dish /1,series 5,now becomes dish /2,series 6 and
receives 25.6 X .60 or 15.36 grams of salt,and from dish
/1 series 5, 134.4 X .40 or 53.75 grams. The total weight
of salt in dish /2,series 6,is then 69.12 grams. This
dish then becomes dish /3,series 7, and receives from
dish /4 series 6, 10.24 X .60 or 6.14 grams of salt,and
dish /2,series 6, 69.12 X.40 Or 27.64 grams. The total
weight of the salt in dish /3,series 7 is 33.78 grams.
Dish /3 series 7, now becomes dish /4,series 8,and re-
ceives from dish /5 series 7, 4.09 X .60 or 2.45 grams
of salt and from dish /3,series 7, 33.78 X.40 or 13.51
grams. The total weight of salt in dish /4,series 8, is
15.96 grams. We saw above that the mesothorium content
of this dish was 291.69 mgs. Its mesothorium concentra-
tion must therefore be 291.69/ 15.96 or 18.2 mgs per
gram. As no more liquor is now added to this dish we can
calculate the number of crystallization that will be re-

quired to obtain in this dish a concentration of 180 mgs.
mesothorium, and the weight of the crystals when this con-
centration is reached. Evidently, $(2.1)^n = \dfrac{180}{18.2}$ or n
is equal to 3. That is three more crystallizations after
the seventh must be made to obtain a concentration of 180
mgs. in dish 0, series 4. As this number of crystallizations
was already made to obtain a concentration of 180 mgs. in
dish 0, series 3, the concentration of dish 0, series 4, to
180 mgs per gram did not add any individual crystallizations
to those already made. The total mesothorium content of
dish ∕6, series 10, after three more crystallizations after
the seventh is expressed by $291.69 \times .84^3 = 173$ mgs. The
weight of the salt in dish ∕6, series 10, after three more
crystallizations after the seventh, is expressed by 15.96
$X .4^3 = 1.018$ grams.

If we assume that liquors from dish -3, series 5,
are removed from the system, the number of milligrams mes-
othorium in first tail liquor is expressed by $1000 \times .16^5$
$= .10$ mgs.

The coputatations of the preceding pages can best
be summarized in the table which is given on the follow-
ing page.

Table VIII.

Summary of Preceding Calculations.
40 % Separating as Crystals.

	Weight of Crystals	Milligrams of Mesth.	No. of Individual Crystallizations
1st Head Crystals Dish/5Ser 7	1.636	294.49	35
2nd Head Crystals Dish /7 series 10	.315	66.37	30
3rd Head Crystals Dish /6 Series 10.	1.020	173.	00
Total	2.971	533.86	65

We thus see that when 40% is allowed to separate out as crystals,after ten series of crystallizations are made,with a total of 65 individual crystallizations,we obtain a concentration of 180 milligrams mesothorium per gram in the final products,the total quantity of the mesothorium being 533.7 mgs. in a total crystal weight of 2.975 grams.

Let us next apply the same calculations to the same material,but this time allow 60% to separate out each time as crystals. We wish to have in the final products a concentration of 180 milligrams mesothorium per gram. How many crystallizations will be required to attain this concentration ? The factor for 60% separations is 1.52. Then as in the preceding problem $1.52^n = 180$,whence n is 12,

Diagram of Scheme of Transfers Used
in Computing Mesothorium Concentration of
Final Products when 40% and 60% Separations
were Made.

(A) First Head Crystals,40%

(B) 2nd Head Crystals,40%

(C) 3rd Head Crystals,40%

(D) 1st Head Crystals
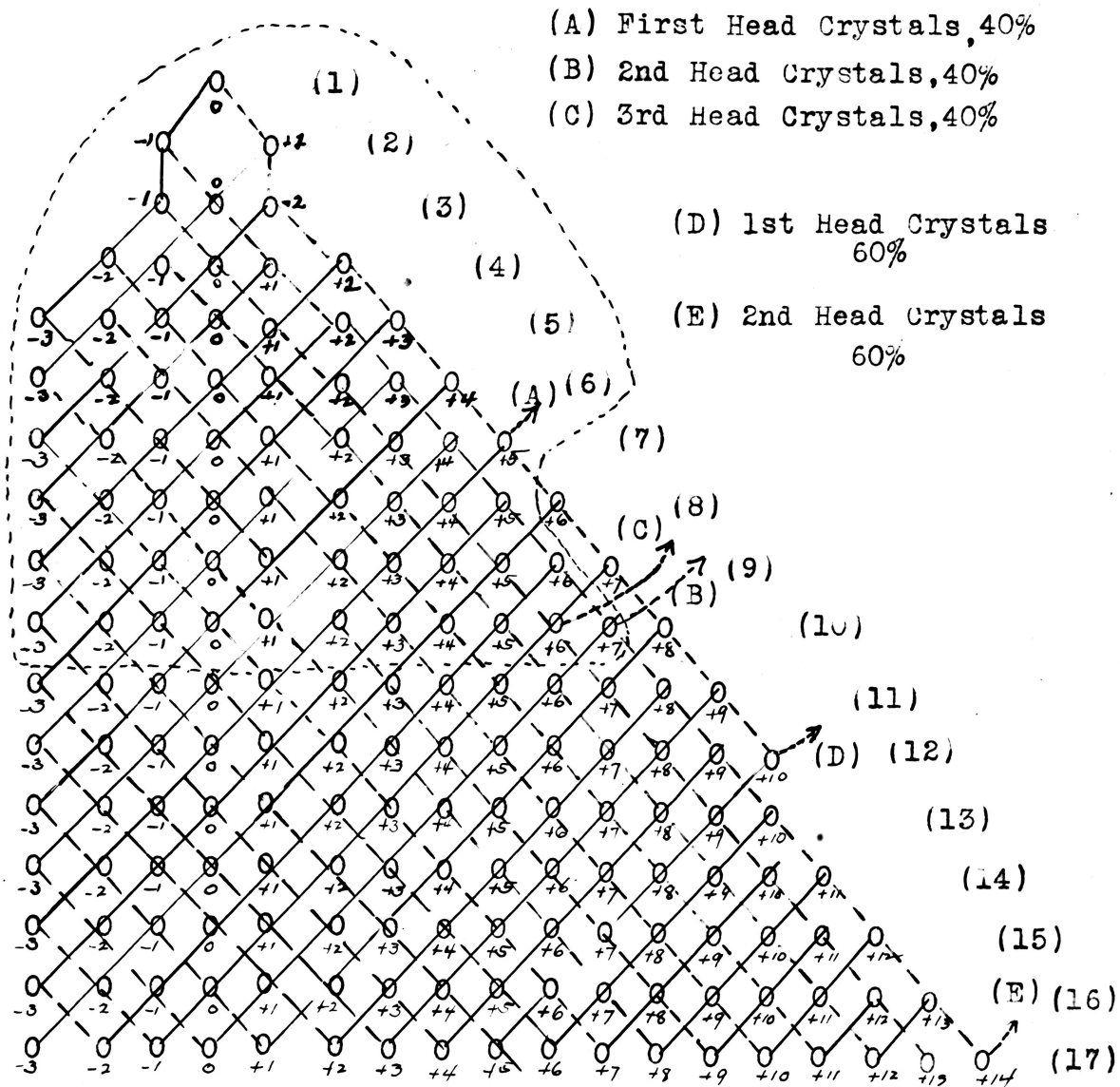60%

(E) 2nd Head Crystals
60%

Diagram III.

the number of crystallizations necessary to obtain a concentration of 180 mgs per gram in the first head crystals. The mesothorium content of the head crystals is 1000 X $.912^{12}$ = 331 mgs. The weight of the first head crystals is 1000 X $.6^{12}$ = 2.178 grams. By referring to the diagram on page 52, we see that 12 crystallizations would mean a total of 95 single crystallizations.

Let us next consider dish 0, series 3, when 60% is again allowed to separate out in each crystallization. From the diagram on page 52 we see that dish 0, series 3, again receives no liquor after the second crystallization. In a manner similar to that for 40% separations, the mesothorium content of dish 0, series 3, is calculated and found to be 160.5 mgs. The quantity of salt in this dish after the second crystallization is also calculated and is found to be 480 grams. The concentration per gram is therefore 165.5/480 or .334 mgs per gram. The number of crystallizations necessary to step this concentration up to 180 mgs. per gram is expressed by $(1.52)^n = \dfrac{180}{.334}$ whence n is 15. That is 15 crystallizations after the second must be made to attain in dish $\neq$14, series 17, a concentration of 180 mgs. mesothorium per gram. The weight of the salt after 15 more crystallizations after the second would be 480 X $.6^{15}$ = .2259. The mesothorium content of dish $\neq$14

series[17] ,after 15 more crystallizations after the second
would be   165.5 X $.912^{15}$ = 41.4 mgs.   By referring to
to the diagram on page 52,we see that 15 more crystalli-
zations after the second,or five more after the 12th would
make a total of 80 additional individual crystallizations.

The number of milligrams mesothorium in dish -3,
after 5 crystallizations is 1000 X $.088^5$ Or.0052 mgs.

Summarizing the data here obtained for 60% sep-
arations we have the following table.

Table IX.

Summary for preceding Calculations
60% Separating as Crystals.

	Weight of Crystals	Milligrams of Mesth	No. of Individual Crystallizations.
1st Head Crystals Dish ⌿10	2.178	331	95
2nd Head Crystals Dish ⌿14 Series 17	.225	41.4	80
Total	2.403	372.4	175

We thus see that when 60% separations are made,
after 17 series of crystallizations are made,with a total
of 175 single crystallizations,we obtain a mesothorium
concentration of 180 mgs.per gram in the final products,
the total quantity of mesothorium in the final products
being 372.4 mgs in a crystal weight of 2.403 grams.

A comparison of results as here computed will be
more easily made from the following table:

Table X

40% and 60% Separations.

	Wt. of Crystals	Mgs. of Mesth	Single Crystallizations.	Mesth content Dish -3,ser.5
40% Separations	2.971	533.86	65	.10 mgs
60% Separations	2.403	372.4	175	.0052 mgs.

It is apparent from the above table that
with 65 crystallizations,40% separating out as crystals,
we obtain 533.86 mgs of mesothorium,of concentration 180
mgs.per gram,while with 60% separations,175 single crys-
tallizations we obtain 372.4 mgs. mesothorium,of concen-
tration 180 mgs.per gram. With 40% separations about 40%
as many crystallizations are required,while the mesothorium con-
tent of the final products is higher,than for 60% separa-
tions. The relative amount of work for the two methods
of crystallizing is shown graphically on page 52. That
portion of the diagram surrounded by a black line repre-
sents the crystallizations made on the basis of 40% sep-
arations.

On the basis of these calculations we conclude
that the concentration of bromides is more rapidly effected

when 40% is allowed to separate out as crystals than when
60% is thus separated. As the quantity of crystals sepa-
rating is greater for concentrated acid solutions than for
weak solutions, we conclude that concentration of the brom-
ides is more rapidly effected in weak acid solutions or
even in neutral solutions(especially since,as has been
shown in this work,the crystallization factor is independ-
of the acid concentration)than in solutions of high acid
concentration.

It should be added here that the number of crys-
tallizations necessary to step up the contents of dish 0,
series 4,by 60% separations,could have been computed. As
the quantity of mesothorium passing from dishes ∤ 1, ∤2,
∤3 etc of series 3, 4, 5, is small, it is not probable
such a calculation would effect the conclusion we have
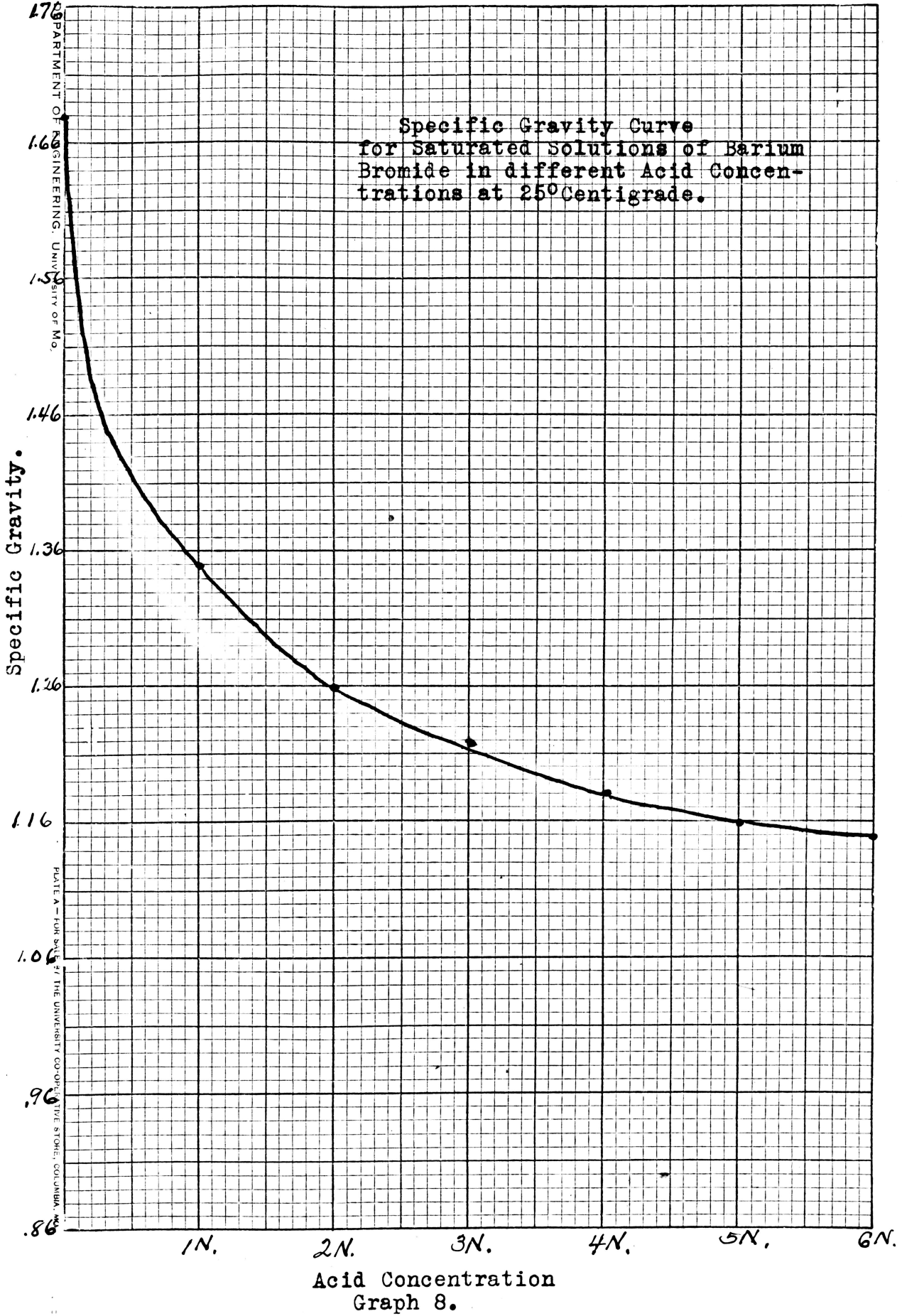drawn.

A METHOD OF CONTROL IN CRYSTALLIZING.

We will next turn our attention to the problem of how to proceed in crystallizing out exactly 40% in each crystallization. For this purpose a solubility curve of barium bromide in different concentrations of hydrobromic acid at 25° C was determined and also a specific gravity curve for saturated solutions of barium bromide in different concentrations of hydrobromic acid at 25°C. These curves are given on the following pages.

Let us suppose then that we have A grams of anhydrous crystals which we wish to dissolve in water and then crystallize out 40% in neutral solution. We would proceed as follows: 1. Obtain the weight of the anhydrous crystals. 2. Get weight of the dish in which crystallization is to take place. 3. Dissolve crystals in water. 4. From the solubility curve for barium bromide we see that 75 grams of anhydrous barium bromide is soluble in 100 g. of water. By referring to the specific gravity curve we find that the specific gravity of this solution at 25°C is 1.685. We then have 75 grams of anhydrous barium bromide soluble in 168.5 grams of solution at 25°C. or 75/168.5 grams per gram of solution. The weight of barium bromide to remain in solution after crystallization, at 25°C is .6A and the weight of solution required to hold this this weight of barium bromide in solution at 25°C is .6A X

Grams BaBr₂ per 100 cc of Solution.
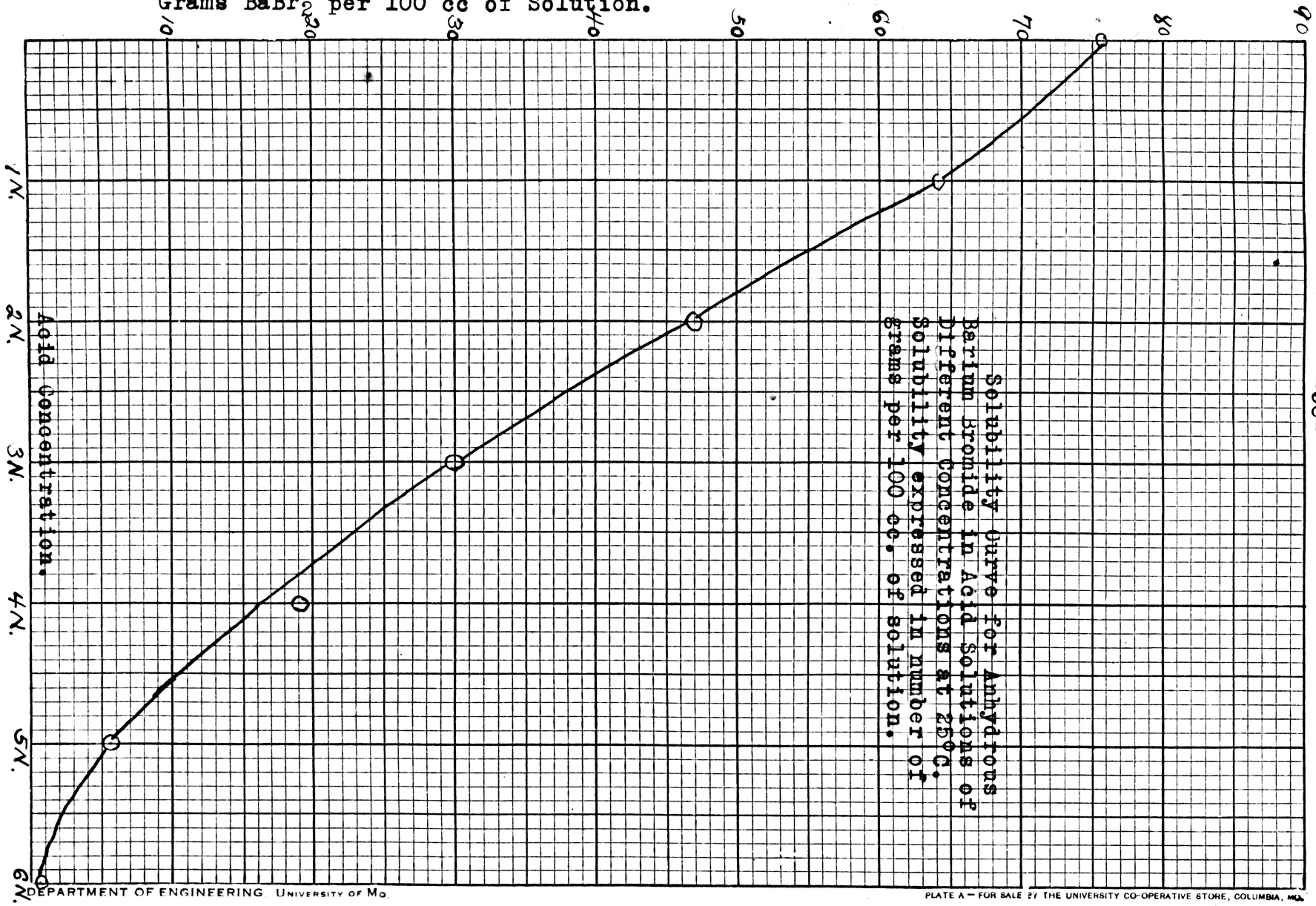
Solubility Curve for Anhydrous
Barium Bromide in Acid Solutions of
Different Concentrations at 25°C.
Solubility expressed in number of
grams per 100 cc. of solution.

-58-

Acid Concentration.

Specific Gravity Curve
for Saturated Solutions of Barium
Bromide in different Acid Concen-
trations at 25⁰Centigrade.

Acid Concentration
Graph 8.

$\frac{168.5}{75}$ grams. 5. Now place dish containing the solution

of bromides on water bath till total weight = Weight of

Dish $\neq \frac{.4A \ BaBr_2.2H_2O}{BaBr_2}$ $\neq \frac{.6A \ X \ 168.5}{75}$. Now cool the sol-

ution and 40% of the original anhydrous salt should crys-

tallize out at 25°C.

Again let us suppose that we have A grams of anhy-

drous salt from which we wish to crystallize 40% in a 2 N.

solution of hydrobromic acid. We would proceed as follows:

1. Get the weight of the anhydrous crystals $\underline{A}$. 2. Obtain

the weight of the dish in which crystallization is to take

place. 3. Dissolve the crystals in water. 4. Add the re-

quired amount of acid to be computed as follows: From the

solubility curve on page 58, we see that in a 2N. hydro-

bromic acid solution 46.8 grams of anhydrous barium bromide

is soluble at 25°C. From the specific gravity curve on

page 59 we see that the specific gravity of this solution

is 1.268 at 25° C. We then have 46.8 grams of barium bromide

in 126.8 grams of solution or 46.8/126.8 grams per gram,

at 25°C. The weight of anhydrous barium bromide to remain

in solution is .6A. The weight of mother liquor required

to hold .6A grams of barium bromide in solution at 25°C is

$\frac{.6A \ X \ 126.8}{46.8}$ grams or $\frac{.6A \ X \ 100}{46.8}$ cc. In $\frac{.6A \ X100}{46.8}$ cc

of a 2N. solution of hydrobromic acid we have .6A X 100 $\underset{\overline{46.8}}{X}$

.1598 grams of HBr. Add this amount of HBr from a standard

hydrobromic acid. 5. Now evaporate until total weight =
Weight of dish $\neq$ $\cdot\dfrac{4A \ BaBr_2 \cdot 2H_2O}{BaBr_2}$ $\neq$ $\dfrac{.6A \ X \ 126.8}{46.8}$ grams.
Now cool,when 40% of the salt should again separate out
as crystals.

Thus it is possible to control the percent of
crystals separating both in neutral and in acid solutions.
While this method of control would hardly be applicable
when working with small quantities of material,when as
much as several liters of solution are concerned, it is
quite possible that this method of control would give
satisfactory results. Mechanical devices for getting
specific gravity and weights are among the possible things
that might be worked out in this connection.

SUMMARY.

I.

By making two fractionations of different lots of mes-othorium-radium-barium bromides, one in neutral and one in concentrated acid solution, technique in fractional crystal-lization was acquired.

II.

A study of the crystallization factor for crystalliza-tions from neutral and from solutions of different acid concentrations was made. It was found that the crystalli-zation factor was independent of the acid concentration and varied only as the percent of crystals separating.

III.

It was found that the crystallization factor does not vary with the concentration of mesothorium per gram of salt, the factor being the same for all concentrations of mesothorium here studied.

IV.

By making a number of calculations for 40% and 60% separations of crystals, it was found that the quantity of mesothorium in the final products is greater and the amount of labor required less, for 40% separations than for 60% separations. We concluded therefore that the concentration of mesothorium-radium-barium bromides is more rapidly effected in weak acid or neutral solutions than in concentrated acid solutions.

V.

The solubility of anhydrous barium bromide in
different acid concentrations of HBr at 25°C was deter-
mined and the corresponding solubility curve plotted.

VI.

The Specific gravity of saturated solutions
of barium bromide in different concentrations of HBr
solutions at 25° C was determined and the corresponding
curve plotted.

VII.

From the computations made in this study it
appears to us that method of making tranfers in a crys-
tallizing system,such as herein described,can be im-
proved on. Such improvement would be based on the
fact that to obtain the most rapid concentration of the
bromides,liquors and crystals of the same concentration
must be poured together.

BIBLIOGRAPHY.

1. Mdme Curie,Thesis "Radioactive Substances" in
   Chemical News,Vol.88,1903,146.

2. Mdme Curie, Thesis,Chemical News,Vol. 88,
   1903, p.147

3. M. Giesel, Berichte der Deutschen Chemischen
   Gesellschaft, 1902,35,3608.

4. Coehn and Kettembeil, Zeitschrift fur Anorganischer
   Chemie, 1904,38, 198.

5. E. Wedekind, Journal of the Chemical Society, 1904,
   Vol. 2,339,Also Chemicker Keitung,1904,28,269-270

6. Mdme Curie,Nature, Vol.84,313,356,478.

7. Ebler and Fellner, Chemical Abstracts,1913,7,2727;
   Also Berichte der Deutschen Chemischen Gesell-
   schaft,46,1577-1586.

8. Ebler and Bender, Berichte der Deutschen Chemischen
   Gesellschaft, 1913,46,1571-1573.

9. Erich Ebler, Eighth International Congress of Applied
   Chemistry,1912,2,91-93. Also chemical Abstracts
   104,Pt.2, 1913,p.659.

10. McCoy,U. S. Patent No.1103600; Journal of the Society
    of Chemical Industry,1914, 33,919.

11. Soddy and Markwald, Chemical Society,1911,99,72.

12. Goverment Bulletin 104,U. S. Bureau of Mines.

13. Government Bulletin 104,U. S. Bureau of Mines

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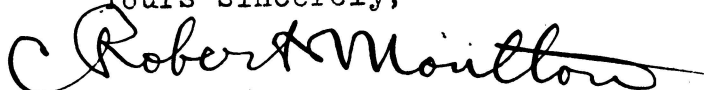
August 19th 1919,

Dean Walter Miller,

Academic Hall,

West Campus.

My dear Dean Miller:

I have read the dissertation submitted by John L. Nierman.   In my opinion this dissertation meets the general standard that has been established in this University for the Masters dissertation.

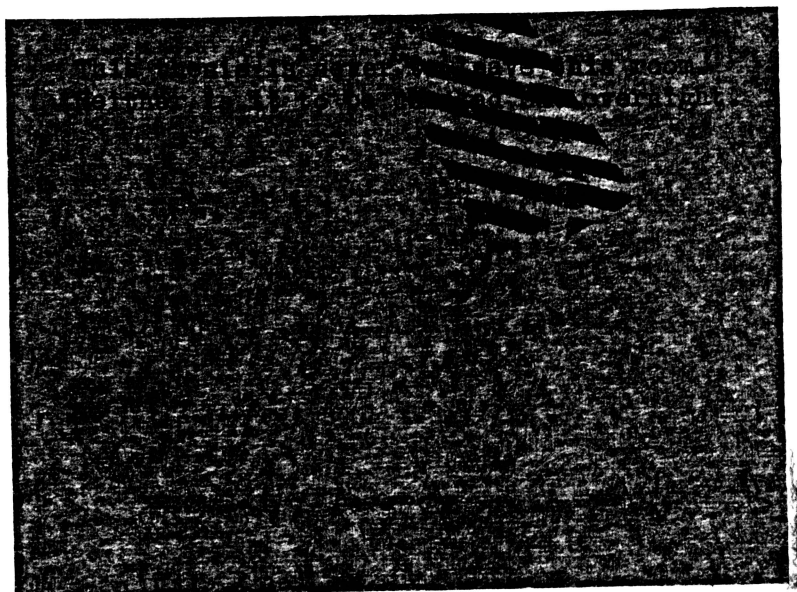Yours sincerely,

Robert Moulton

Professor Agricultural Chemistry.

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