[redacted]

1171

x CN-1863

( A-2690 ) 11A

Metallurgical Project

A.H. Compton, Project Director

* * *

Clinton Laboratories

M.D. Whitaker, Director
R.L. Doan, Associate Director for Research

* * *

Chemistry Division

W.C. Johnson, Division Director
H.S. Brown, Assistant Director
C.D. Coryell, Section Chief, Section C-II
G.E. Boyd, Section Chief, Section C-III
T.H. Davies, Associate Chief, Section C-III

N. Sugarman, Acting Section Chief, Section C-III (Chicago)

* * *

DECLASSIFIED
CLASSIFICATION CHANGED TO:
BY AUTHORITY OF: Ltd 1152
BY: [illegible] 1-30-58

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

FINAL REPORT

# THE SOLUBILITY OF $BiPO_4$ IN $HNO_3$

Joint Report of Section C-III (Clinton) and Section C-III (Chicago)

This work was carried out under Problem Assignment
202-X59C Solubility and Rate of Solution of $BiPO_4$ in $HNO_3$

July 30, 1944

Report Prepared By: G.R. Leader
Experimental Work By: G.R. Leader and O.K. Neville (Clinton)
E. Mapp and H. Evans (Chicago)
Supervisors Responsible: T.H. Davies (Clinton)
Wm. Rubinson (Chicago)

Received Clinton: AUG 11 1944
Received Chicago: AUG 11 1944
Series A Issued:
Series B Issued:

RECEIVED
AUG 12 1944
TNX CLASSIFIED FILES
U. S. ENGINEER OFFICE
OAK RIDGE, TENN.

[redacted]

[redacted]



## ABSTRACT

Bismuth phosphate has been shown to exist in at least two allotropic forms, differing in crystal structure and in solubility in $HNO_3$. As ordinarily precipitated under conditions of the $BiPO_4$ process, $BiPO_4$ comes down as hexagonal crystals, moderately soluble in 10N $HNO_3$. Upon prolonged digestion at 75° these hexagonal crystals are converted to a monoclinic structure only about 40% as soluble in 10N $HNO_3$.

The existence of these two forms of $BiPO_4$ is a complication in determining $BiPO_4$ solubilities which was not realized during the earlier studies on solubility. In the present report new data are presented for the solubility of the hexagonal or $\alpha$-form of $BiPO_4$ in various concentrations of $HNO_3$ at four temperatures. These new solubilities were determined by a method involving approach to equilibrium from the undersaturated side, in which case there is less interference from conversion to the monoclinic or $\beta$-form than was encountered in previous work.

In agreement with earlier work, the new data show $BiPO_4$ solubility in $HNO_3$ to depend on the 2.35 power of the $HNO_3$ concentration at 25°. Very nearly the same power dependence is also observed at 10°, 50° and 75°. Temperature is shown to have little effect on the solubility of $BiPO_4$ in the range 2 - 6N $HNO_3$, but at 8 and 10N $HNO_3$ a steady decrease in solubility with increasing temperature is observed. At 1N $HNO_3$, the solubility was found unchanged between 25° and 50°, about 10% higher at 1° and about 20% higher at 75°.

The available information concerning the $\beta$ (monoclinic) form of $BiPO_4$ is discussed and data are given for the solubility of the $\beta$-form in various concentrations of $HNO_3$ at 25°. The solubility of the $\beta$-form is found to show nearly the same power dependence upon $HNO_3$ concentration as does the $\alpha$-form and is about 40% as great at a given acidity. The solubility of the $\beta$-form in 10N $HNO_3$ is shown to decrease with increasing temperature as does the solubility of the $\alpha$-form.

In order to determine what chemical reaction occurs when $BiPO_4$ dissolves in $HNO_3$, the solubility of $\alpha$- $BiPO_4$ in various concentrations of $HClO_4$ and in solutions containing mixtures of $HClO_4$, $NaNO_3$ and $NaClO_4$ has been determined. These studies have shown that nitrate ion plays an important part in the solution of $BiPO_4$ in $HNO_3$ because of the low degree of dissociation of $Bi(NO_3)_3$ in $HNO_3$ solutions.

The solubility of $\alpha$-$BiPO_4$ in 10N $HNO_3$ containing various concentrations of HF has been determined. The presence of 1N HF in 9.6N $HNO_3$ was shown to increase the solubility of $BiPO_4$ from 82 gr./l. to 100 gr./l.

[redacted]

[redacted]



Table of Contents


1. Introduction. 5

2. The Two Forms of $BiPO_4$. 6

   A. The $\alpha$ Form. 6

   B. The $\beta$ Form. 6

   C. Interconversion of the two forms. 6

3. Methods of Solubility Determination. 7

4. Methods of Analysis. 8

   A. Gravimetric bismuth determination. 8

   B. Volumetric " " . 9

   C. Colorimetric " " . 9

   D. Acid determination. 9

5. Solubility of $\alpha$ $BiPO_4$ in $HNO_3$. 9

   A. Equilibrium approached from below. 9

   B. Equilibrium approached from the supersaturated side. 16

6. The Solubility of $\beta$ $BiPO_4$ in $HNO_3$. 18

7. Interpretation of Solubility Data for $BiPO_4$ in $HNO_3$. 21

   A. Introduction. 21

   B. The solubility of $BiPO_4$ in $HClO_4$. 22

   C. Solubility of $BiPO_4$ in mixtures of $HNO_3$ and $HClO_4$. 24

   D. Effect of $NO_3^-$ concentration on solubility at constant $H^+$ concentration. 25

   E. Effect of $H^+$ concentration on solubility at constant $NO_3^-$ concentration. 26

   F. Effect of $H_3PO_4$ on solubility of $BiPO_4$ in 10N $HNO_3$. 27

   G. Discussion. 27


[redacted]

8. The Effect of Temperature on $BiPO_4$ Solubility. 30

A. The $\alpha$ Form. 30

B. The $\beta$ Form. 31

9. The Effect of HF on the Solubility of $\alpha$-$BiPO_4$ in 10N $HNO_3$. 32

10. The Density of $HNO_3$ Solutions of $BiPO_4$. 33

11. Bibliography. 34

## 1. INTRODUCTION

The present report is intended to augment the data on $BiPO_4$ solubility in $HNO_3$ already available in CN-933, CN-989, CN-1044, CN-1141, and CN-1214. It covers the work on the two forms of $BiPO_4$ and their solubility behavior done since January 1, 1944 by members of Chemistry Section C-III at Chicago (Sugarman) and of Chemistry Sections C-II and C-III at Clinton (Coryell, Boyd).

The $BiPO_4$ solubility data already reported includes the solubility of the ordinary (hexagonal) form of $BiPO_4$ in various concentrations of $HNO_3$ and at various temperatures. The effect of uranyl ion and of ferric ion has also been investigated. Subsequent work has revealed the existence of complicating factors which affect the solubility determination of $BiPO_4$, namely the existence of a second form of $BiPO_4$ and the slow rate at which $HNO_3$ solutions supersaturated with $BiPO_4$ come to equilibrium. The present studies are intended to utilize this information to make available more accurate $BiPO_4$ solubility data by detailed redetermination of the solubility by the method previously employed of approaching equilibrium from the supersaturated side and by the alternative method of approaching equilibrium from the undersaturated side.

2. The Two Forms of $BiPO_4$.

A. The $\alpha$-Form.

When $BiPO_4$ is precipitated from 1N $HNO_3$ at 75° with low concentrations of $H_3PO_4$ (e.g. .1 - .6 molar) and is digested at that temperature for short periods, the crystals obtained are readily soluble in 10N $HNO_3$ and have been shown by R.C.L. Mooney to have a hexagonal crystal structure (CN-1457). When prepared from a known weight of bismuth metal and thoroughly dried in high vacuum at 25°, the weight of $\alpha$-$BiPO_4$ obtained is such as to indicate the formula $BiPO_4$ (CN-1214 and CC-1683). It was at one time thought that $\alpha$-$BiPO_4$ might contain water of hydration or might be $BiOH_2PO_4$, but subsequent experiments have shown that all water can be removed without affecting the crystal structure. Chemical analysis of $\alpha$-$BiPO_4$ shows Bi and P present in 1:1 ratio (CN-1446). The density of $\alpha$-$BiPO_4$ has been found to be 5.5 (CN-1214).

$BiPO_4$ precipitated from $HClO_4$ solution in the complete absence of nitrate ion also comes down as the $\alpha$-form.

B. The $\beta$-Form.

The possible existence of a second form of $BiPO_4$ of lower solubility was first mentioned in CN-1141 as a plausible explanation of the way in which the solubility of $BiPO_4$ in 10N $HNO_3$ was observed to steadily decrease when the solution was held at 75° or at 50°. This supposition was subsequently supported by an X-ray study of the $BiPO_4$ precipitated from 10N $HNO_3$ by heating the solution to 75° and then digested at 75° for 10 hours or more in the strong acid. Such $BiPO_4$ was found to show an X-ray diffraction pattern different from that of the ordinary $\alpha$-form, and to have a higher density (6.3). More recent work has shown this new form of $BiPO_4$ to be monoclinic (CP-1576, CP-1728).

When dry $\alpha$-$BiPO_4$ is heated in air at 250°, the resulting powder shows the X-ray diffraction pattern of both the $\alpha$ and of the new form of $BiPO_4$ which we shall call the $\beta$ form. By sufficiently prolonged heating complete conversion to the $\beta$ form can be effected. This indicates a close relationship of the two forms and since the $\alpha$-form has been shown to be anhydrous $BiPO_4$ it is likely that the $\beta$-form is a different crystalline modification of the same formula. Analysis of $\beta$-$BiPO_4$ shows Bi and P present in 1-1 ratio.

C. Interconversion of the Two Forms of $BiPO_4$.

Under the usual conditions of the $BiPO_4$ process, the $BiPO_4$ precipitates consist almost entirely of the $\alpha$-form, especially

when working in stainless steel equipment or in the presence of $Fe^{+3}$ since the presence of even low concentrations of iron in solutions from which $BiPO_4$ precipitates has been shown to inhibit formation of the $\beta$-form (CN-1214). However, when $BiPO_4$ is precipitated from 1N $HNO_3$, 0.6M $H_3PO_4$ at 75° in the absence of iron, increasing amounts of $\beta$ $BiPO_4$ are found in the precipitate the longer the time of digestion (5% $\beta$ after 4 hours, 10% after 8 hours, complete conversion to $\beta$ upon prolonged digestion CP-1376).

Conversion of $\alpha$-$BiPO_4$ to $\beta$-$BiPO_4$ is also observed at 25° when $\alpha$-$BiPO_4$ is stirred for long periods with 10N $HNO_3$. After 440 hours, the solid $BiPO_4$ in contact with the acid was found by X-ray diffraction to be about 50% $\beta$-form and after 1400 hours it was found to be entirely $\beta$ (CC-1683). At 75°, the conversion of $\alpha$ to $\beta$-$BiPO_4$ in 10N $HNO_3$ is much more rapid - about 95% conversion to $\beta$ occurring within one hour. After 6 hours, conversion to $\beta$ is complete (CC-1394, CP-1376).

No conversion of $\beta$-$BiPO_4$ to $\alpha$-$BiPO_4$ upon standing as dry powder or as solid in contact with saturated $HNO_3$ solutions has been observed, and it appears highly probable that the $\beta$-form is the thermodynamically more stable form of $BiPO_4$ throughout the temperature range of interest to the $BiPO_4$ process.

$\beta$-$BiPO_4$ dissolved in $HNO_3$ and then reprecipitated comes down as the $\alpha$-form. For example, when a sample of $\beta$ $BiPO_4$ was treated with 9.6N $HNO_3$, only 24.2 gr. of $BiPO_4$/l. dissolved in 23 hours stirring. When the resulting $HNO_3$ solution was diluted to 1N heated to 75°, made 0.1M in $H_3PO_4$ and digested one hour at 75°, the resulting $BiPO_4$ was found to be soluble in 9.0N $HNO_3$ to the extent of 70 gr./l., a value characteristic of the $\alpha$ form at this acid concentration.

3. Methods of Solubility Determination

In approaching equilibrium from the undersaturated side, solutions of $\alpha$ and $\beta$ $BiPO_4$ were prepared by stirring the solid $BiPO_4$ with the desired concentration of $HNO_3$ in 3-necked glass-stoppered flasks, fitted with stirrers and thermometers and held in a thermostat at the desired temperature. After suitable intervals of stirring, samples were withdrawn for analysis until a nearly constant value was reached. In studying solubilities at 50° and 75° by this method, solid $BiPO_4$ was added to the acid, already heated to the desired temperature. The solutions were separated from excess solid $BiPO_4$ by centrifuging (at 25°), by letting the solid settle under gravity, or by drawing the liquid through a tube containing a sintered glass plate (at 0°, 50° and 75°). In all cases where solubilities were

measured at temperatures other than 25°, the saturated solutions after being separated from the solid $BiPO_4$ were cooled or warmed to 25° before being sampled for analysis. The solubilities given, therefore, are all in terms of volumes of $HNO_3$ measured at 25°. The 0° samples remained supersaturated during the time required to warm to 25° and take a sample.

In approaching equilibrium from the supersaturated side (in the case of $\alpha$ $BiPO_4$ only) a solution of $\alpha$ $BiPO_4$ in the strongest acid concentration to be studied was prepared at 0° and analyzed. It was then raised to 25° and stirred until the amount of dissolved $BiPO_4$ fell to a nearly constant value; similarly at 50° and 75°. To study the solubility in lower acid concentrations, the original saturated solution was diluted to the desired acidity, then stirred successively at 0°, 25°, 50°, and 75° until apparent equilibrium values were obtained. The same solution was used at a given acidity for each of the four temperatures.

At 50° and 75°, particularly in strong nitric acid solutions, it is necessary to take samples over a comparatively short period of time soon after starting the experiment because of the conversion to $\beta$ form which occurs under these conditions, thereby causing low results. This precaution was observed in the experiments in which equilibrium was approached from below, but was not observed in the experiment in which equilibrium was approached from above (Table III), in which case the solutions were held at elevated temperatures for long periods of time, resulting in some cases in a large and undetermined amount of conversion to $\beta$-form.

The solubilities of $BiPO_4$ in solvent mixtures other than $HNO_3 + H_2O$ which are reported here were not determined as carefully as were the solubilities in various $HNO_3$ concentrations. In general, the solutions were shaken at room temperature for what was thought to be sufficient time to achieve saturation, but the attainment of true equilibrium was not proved. The experiments were performed merely to aid in interpretation of the $HNO_3$ solubility data and while the results appear to be reliable because of their internal consistency, no great accuracy is claimed for them.

## 4. Methods of Analysis

### A. Gravimetric Bismuth Determination

Solutions of $BiPO_4$ in $HNO_3$ or $HClO_4$ containing relatively large amounts of $BiPO_4$ (> 10 gr. $BiPO_4$/l.) were analyzed by diluting to about 0.5N acid, heating to 75°, and making the solution .1M in phosphate with $(NH_4)_2HPO_4$ solution. After about an hour's digestion on the steam bath, the precipitated $BiPO_4$ was

filtered off through a sintered glass crucible, washed with .01M $H_3PO_4$, then with water. It was finally dried at 250° for at least 3 hours and weighed as $BiPO_4$.

B. Volumetric Bismuth Determination

Solutions containing smaller amounts of Bi than 10 gr. $BiPO_4$/l. were analyzed by the volumetric "Oxine" method described in CC-934. This method gives very satisfactory accuracy (about 1%) even on amounts of Bi as small as 1 mg. The procedure involves precipitating the bismuth as the 8-hydroxyquinoline addition compound of the bismuth iodide complex.

The precipitate is dissolved in HCl and titrated to a starch end point with standard $KIO_3$ solution in the presence of KCN. It was found convenient to carry out the precipitation in 50 or 100 cc. centrifuge tubes and to wash the precipitate by centrifugation rather than by filtering as recommended in the original procedure.

C. Colorimetric Bismuth Determination

Solutions containing very low concentrations of Bi were analyzed by means of a colorimetric method based on the color of the bismuth iodide complex. (E.B. Sandell, "Colorimetric Determination of Traces of Metals" p. 161)

D. Acid Determination

The $HNO_3$ or $HClO_4$ content of the solutions studied was determined by dilution with water and direct titration with standardized NaOH solution. The $BiPO_4$ present precipitates before the end point is reached and does not hydrolyze sufficiently to affect the results.

5. Solubility of $\alpha$-$BiPO_4$ in $HNO_3$

A. Equilibrium Approached from the Undersaturated Side.

$BiPO_4$ was prepared for these studies by slow addition of concentrated $H_3PO_4$ to a solution of $Bi(NO_3)_3$ in 1N $HNO_3$ at 70°. The $BiPO_4$ was allowed to settle and was washed by decantation with 0.5M $HNO_3$ several times to remove excess $H_3PO_4$. Finally it was washed into a centrifuge bottle, and freed as well as possible from wash liquid by centrifugation.

The freshly prepared sludge of $BiPO_4$ was added to the $HNO_3$ solution to be studied and the mixture was then stirred and sampled at intervals. An ample excess of $BiPO_4$ over that required to saturate the solutions was used in all cases, but the ratio of solid $BiPO_4$ to volume of solution was not controlled and hence few conclusions can be drawn from this data as to the rate of solution of $BiPO_4$ in $HNO_3$.

The results obtained by this method of approach to equilibrium are presented in Tables I and II and in Figures 1 and 2. In the graphs, the solubility results obtained by both methods of approaching equilibrium are plotted together for comparison.

It is thought at present that the results by method A are most nearly correct, but it is of interest to note that the results obtained by method B in the experiment reported in Table III are in many cases not greatly different. In more recent experiments in which solubilities at a given acidity were determined by both methods of approach to equilibrium, much larger discrepancies have been observed (CC-1767).

Table Ia

Solubility of $\alpha BiPO_4$ at Various $HNO_3$ Concentrations

(Equilibrium approached from undersaturated side. Best values picked from results in Table II.)

1°

| $HNO_3$ Normality | Gr. $BiPO_4$/l. |
|---|---|
| 1.06 | .50 |
| 3.03 | 5.36 |
| 6.60 | 31.5 |
| 8.81 | 83.0 |
| 12.3 | 150.0 |

Table Ib

25°

| $HNO_3$ | Gr. $BiPO_4$/l. |
|---|---|
| 0.98 | .37 |
| 3.0 | 4.73 |
| 5.9 | 26.5 |
| 7.4 | 44.3 |
| 9.6 | 78.9 |
| 9.7 | 83.9 |
| 13.1 | 127.6 |

50°

| $HNO_3$ | Gr. $BiPO_4$/l. |
|---|---|
| 1.00 | .41 |
| 3.05 | 4.70 |
| 5.10 | 17.55 |
| 7.40 | 43.30 |
| 10.0 | 74.0 |

75°

| $HNO_3$ | Gr. $BiPO_4$/l. |
|---|---|
| 1.0 | .535 |
| 3.0 | 4.28 |
| 5.08 | 17.33 |
| 7.35 | 38.7 |
| 9.9 | 62.5 |

Table IIa

Effect of Time of Stirring on Observed $\alpha$ $BiPO_4$ Solubilities in Various Concentrations of $HNO_3$ and at Various Temperatures (Equilibrium approached from undersaturated side.)

1°

| $HNO_3$ | TIME | | Gr. $BiPO_4$/l. |
|---|---|---|---|
| | Hrs. | Min. | |
| 1.06 | 1 | 30 | .500 |
| | 21 | 0 | .498 |
| | 22 | 30 | .509 |
| | 43 | 30 | .484 |
| 3.03 | 2 | 30 | 5.40 |
| | 23 | 30 | 5.36 |
| | 26 | 0 | 5.33 |
| | 44 | 30 | 5.12 |
| | 50 | 30 | 5.15 |
| 6.60 | 2 | 45 | 24.0 |
| | 25 | 0 | 31.4 |
| | 27 | 30 | 31.5 |
| | 46 | 0 | 25.4 (?) |
| 8.8 | | 45 | 81.4 |
| | 2 | 0 | 83.0 |
| | 27 | 45 | 82.2 |
| | 34 | 15 | 81.3 |

Table II-b

25°

| $HNO_3$ | TIME Hrs. | TIME Min. | Gr. $BiPO_4$/l. |
|---|---|---|---|
| .98 | 1 | 20 | .368 |
| | 17 | 50 | .367 |
| | 22 | 5 | .361 |
| | 41 | 5 | .375 |
| | 48 | 20 | .308 |
| 3.0 | 1 | 20 | 4.43 |
| | 17 | 50 | 4.51 |
| | 22 | 5 | 4.65 |
| | 41 | 5 | 4.67 |
| | 48 | 20 | 4.73 |
| 5.9 | | 30 | 26.5 |
| | | 75 | 26.2 |
| 7.4 | 2 | | 44.08 |
| | 4 | | 44.04 |
| | 6 | | 44.16 |
| | 8 | | 44.31 |
| 9.7 | | 55 | 83.2 |
| | 2 | 10 | 83.9 |
| | 4 | 40 | 82.0 |
| | 20 | | 81.7 |
| 13.1 | | 30 | 127.5 |
| | | 75 | 127.6 |

Table II-c

50°

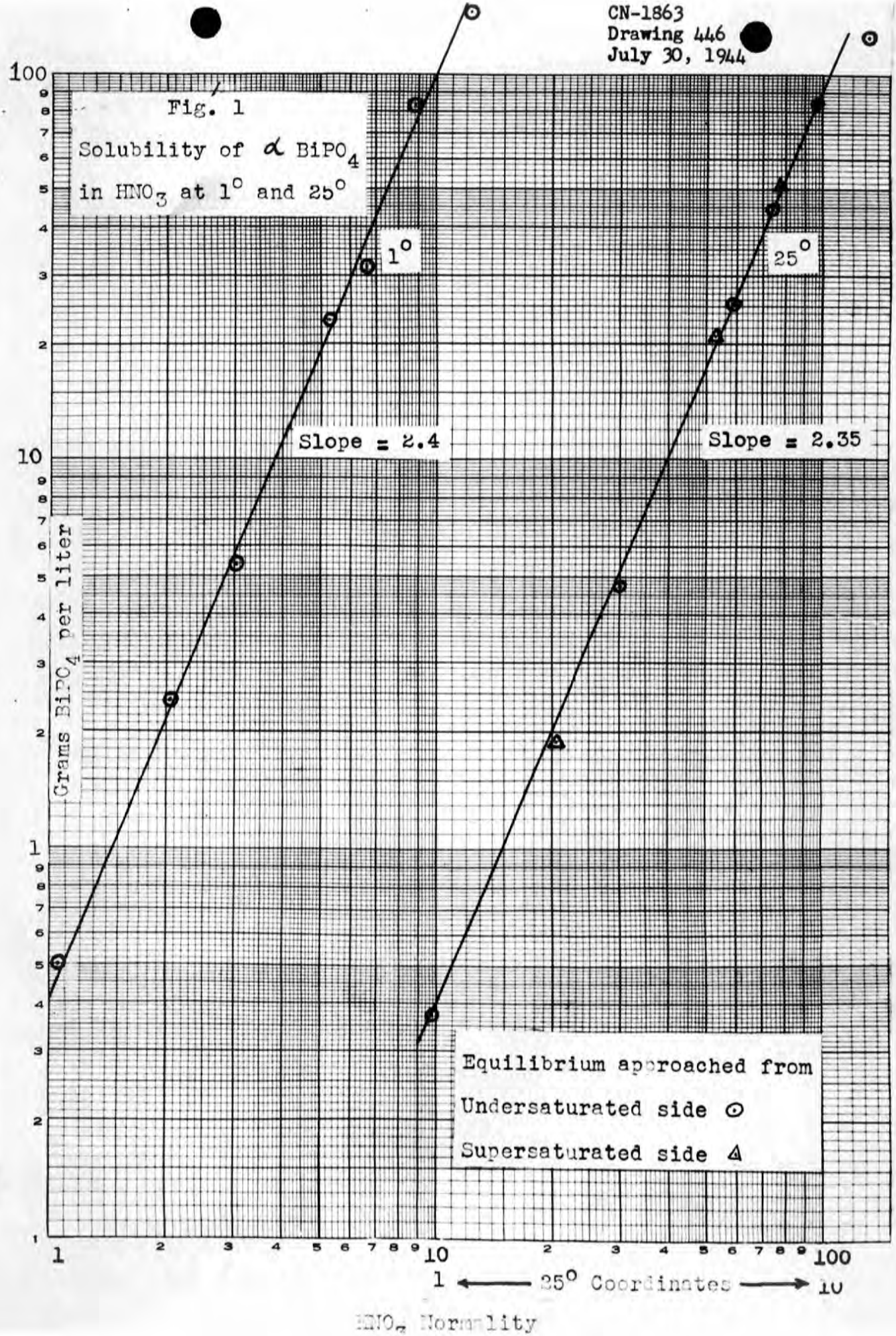
| $HNO_3$ | TIME Hrs. | TIME Min. | Gr. $BiPO_4$/1. |
|---|---|---|---|
| 1.02 | 1 | 30 | .414 |
| | 3 | 15 | .414 |
| | 19 | | .412 |
| | 24 | | .425 |
| 3.05 | | 35 | 4.25 |
| | 1 | 50 | 4.68 |
| | 3 | 15 | 4.69 |
| | 4 | 15 | 4.80 |
| | 20 | 45 | 5.10 |
| 5.10 | | 35 | 17.89 |
| | 1 | 50 | 17.56 |
| | 3 | 15 | 17.50 |
| | 4 | 15 | 17.61 |
| | 20 | 45 | 17.60 |
| 7.4 | | 35 | 43.8 |
| | 1 | 50 | 43.3 |
| | 3 | 15 | 43.2 |
| | 4 | 15 | 42.8 |
| 10.0 | | 15 | 75.7 |
| | | 30 | 74.4 |
| | 1 | 15 | 74.0 |
| | 2 | | 73.6 |
| | 3 | | 74.1 |

Table II-d

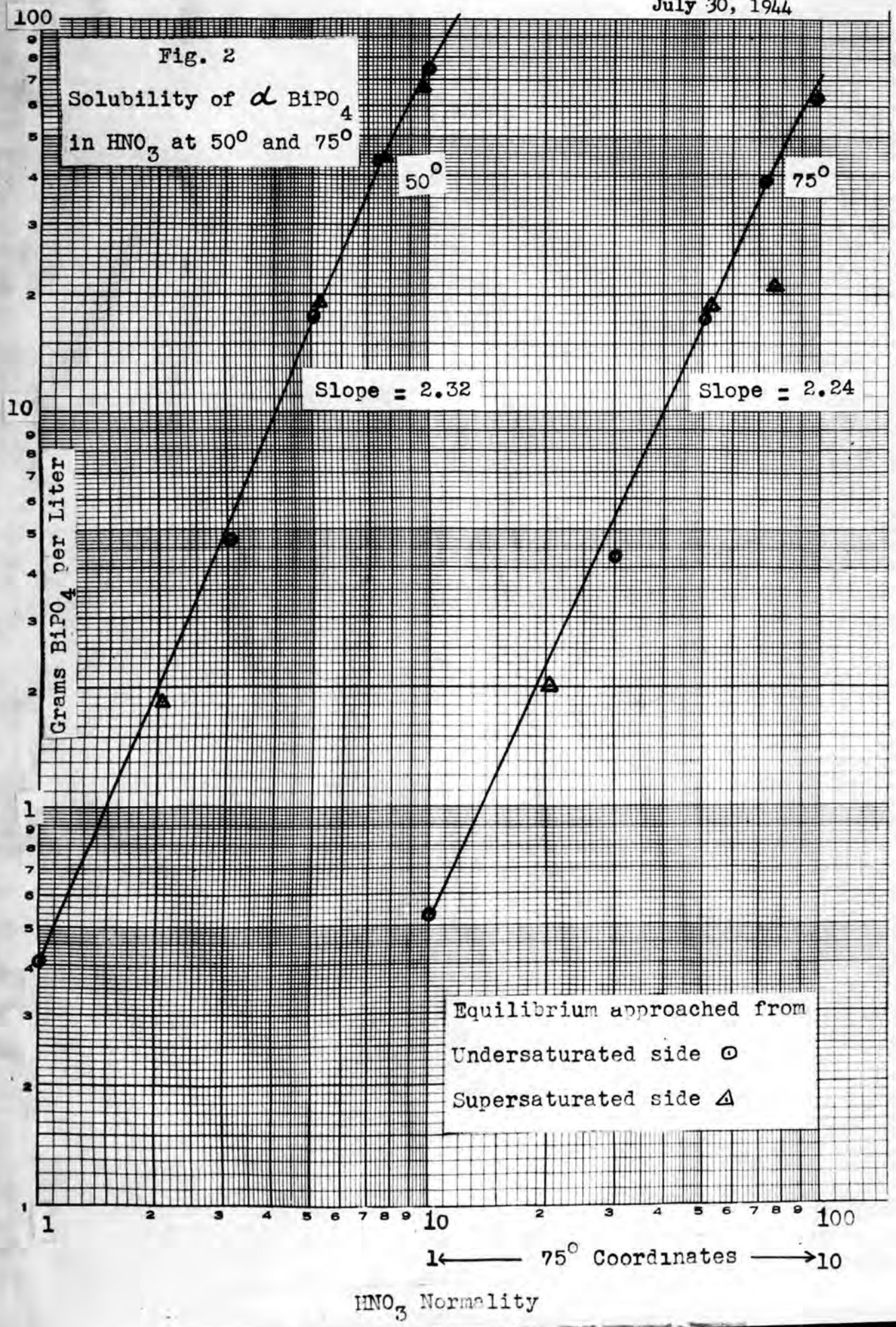
$75^{o}$

| $HNO_3$ | TIME Hrs. | TIME Min. | Gr. $BiPO_4$/l. |
|---|---|---|---|
| 1.00 | | 55 | .531 |
| | 2 | 5 | .535 |
| | 3 | 10 | .525 |
| | 3 | 45 | .509 |
| 3.0 | | 40 | 4.28 |
| | 1 | 30 | 4.28 |
| | 2 | 30 | 4.26 |
| | 3 | 20 | 4.36 |
| 5.08 | | 40 | 17.33 |
| | 1 | 30 | 17.33 |
| | 2 | 30 | 17.30 |
| | 3 | 20 | 17.10 |
| 7.35 | | 40 | 39.4 |
| | 1 | 30 | 38.7 |
| | 2 | 30 | 38.7 |
| | 3 | 20 | 38.8 |
| 9.9 | | 11 | 63.0 |
| | | 20 | 62.5 |
| | | 32 | 62.3 |
| | | 47 | 62.4 |
| | | 75 | 62.3 |

CN-1863
Drawing 446
July 30, 1944



CN-1863
Drawing 447
July 30, 1944



B. Equilibrium Approached from the Supersaturated Side

In the earlier studies on $BiPO_4$ solubility in $HNO_3$, the technique employed involved diluting a saturated $BiPO_4$ solution in strong $HNO_3$ to the desired lower acid concentration, whereupon $BiPO_4$ present in excess of the solubility at that acidity was expected to precipitate out. The results reported in CN-933 and CN-1044 were obtained by this method. Subsequent more elaborate determinations of solubility by the same method showed that when the solubilities were followed as a function of time of stirring that a steady decrease in the amount of $BiPO_4$ found in the solution was observed, especially at 50° and 75° (CN-1141).

In Table III a set of results obtained by this method is presented. The solubilities at a given acidity were determined first at 1° and then at the successively higher temperatures using the same solution. Thus, in all cases (with the exception of the strongest acid at the lowest temperature) the solution was initially supersaturated and $BiPO_4$ precipitated as it came to equilibrium. It can be seen from Table III that the solubilities observed at a given acidity are very markedly a function of the time of stirring and that a decrease in solubility with increasing temperature occurs. It is now known that the pronounced steady decrease in solubility observed upon stirring the more strongly acid solutions at 50° and 75° is due partly to transformation of the solid $BiPO_4$ present to a $\beta$ modification which is only about 40% as soluble as the ordinary hexagonal form and which is very slow in coming to equilibrium with solutions containing more $BiPO_4$ than corresponds to the $\beta$ equilibrium solubility.

The results of solubility determinations by this method plotted on the same graphs as the results obtained by approaching equilibrium from the undersaturated side (Figures 1-2) show that in most cases the two methods give fairly concordant results. A serious difficulty in interpreting the results for solubilities approached from the undersaturated side lies in the fact that a steady decrease in amount of dissolved $BiPO_4$ with time occurs. One cannot be sure whether the decreasing trend of the solubility time curve at any given point is due to the solution being still supersaturated or to the fact that appreciable conversion to the less soluble $\beta$ form is occurring.*

Whether a true equilibrium value is obtained or not for a given solution depends on the relative rates of approach to equilibrium and of conversion to $\beta$ form for that particular solution and temperature.

---

*One would suppose that the decrease in amount of dissolved $BiPO_4$ associated with conversion to the $\beta$ form would occur only after all the solid phase present was changed to $\beta$ form. However, it has been observed that the solubility falls below the equilibrium value upon continued stirring even while ample amounts of $\alpha$-$BiPO_4$ are still present in the solid phase. We are unable at present to explain this anomaly.

Table III

Solubility of $BiPO_4$ in $HNO_3$ at Various Temperatures
(Equilibrium approached from supersaturated side)

| $HNO_3$* Normality | Time of Stirring Hours | Observed Solubility $BiPO_4$/1. | | | |
|---|---|---|---|---|---|
| | | 1° | 25° | 50° | 75° |
| 2.04- | 4 | 2.60 | 1.99 | 1.86 | 1.96 |
| 2.07 | 8 | 2.45 | 1.86 | 1.83 | 2.00 |
| | 12 | 2.42 | 1.88 | 1.84 | 2.03 |
| | 16 | | | | 2.03 |
| 5.29- | 4 | 33.0 | 21.9 | 19.2 | 18.5 |
| 5.35 | 8 | 22.9 | 21.3 | 18.9 | 18.5 |
| | 12 | 22.9 | 21.0 | 18.7 | 18.8 |
| 7.72- | 4 | 67.0 | 56.1 | 44.5 | 39.9 |
| 7.83 | 8 | 64.3 | 51.3 | 44.1 | — |
| | 12 | 64.0 | 50.8 | 44.0 | 22.9 |
| | 16 | | | | 20.7 |
| | 20 | | | | 20.2 |
| 9.68- | 4 | 98.9 | 86.3 | 68.5 | 35.3 |
| 9.75 | 8 | 98.1 | 81.5 | 66.2 | 28.8 |
| | 12 | 98.1 | 81.2 | 67.0 | 28.1 |
| | 16 | | | | 27.2 |
| 12.26- | 4 | 149.8 | 133.9 | 81.1 | 37.0 |
| 12.46 | 8 | 150.0 | 127.9 | 68.1 | 34.2 |
| | 12 | | 124.6 | 62.8 | 33.5 |
| | 16 | | 114.5 | 57.6 | 38.8 |
| | 20 | | | 54.6 | 33.1 |
| | 24 | | | 52.8 | 34.2 |

*The acid concentration was determined frequently during these runs, and was observed to increase gradually as the run progressed through the range indicated.

At 1°, the rate of conversion to $\beta$ is slow, but the rate of approach to equilibrium is also very slow so that the solubilities appear to level off at values slightly greater than those obtained by approaching equilibrium from the other side. It can be seen in Figure I that the points for solubilities determined from supersaturated solutions lie slightly above the curve drawn through the points for solubilities determined by approaching equilibrium from below.

At 25° and especially at 50°, the rate of approach to equilibrium is favorable relative to the rate of formation of $\beta$ form and consequently good agreement is obtained between the two methods of solubility determination. Even at 25° however, it can be seen from Table III that in 12.3N $HNO_3$, conversion of $BiPO_4$ to the $\beta$ form appears to go on at a fairly rapid rate.

At 75°, the values observed at 2 and 5N $HNO_3$ are in fairly good agreement with the values determined by the other method, but at higher acid concentrations so much conversion to $\beta$ form is now known to occur when experiments extend over such a long period of time (at 75°) that the results as given are meaningless in respect to the solubility of the $\alpha$ form.

$BiPO_4$ solubility determinations at 24-28° have been made by the Clinton Plant Assistance group and are reported in CN-1446. Their data extend to higher acid concentrations and their solubilities at a given acidity are considerably higher than those reported here, possibly due to their method of analysis which involved evaporating off $HNO_3$ and $H_2O$ and weighing the residual $BiPO_4$.

The solubilities of $BiPO_4$ precipitates prepared under process conditions have been studied by Section C-I (Chicago) and are reported in CN-1700.

6. <u>The Solubility of $\beta$-$BiPO_4$.</u>

The solubility of $\beta$ $BiPO_4$ in $HNO_3$ can best be determined by approach to equilibrium from the undersaturated side since the precipitation of $BiPO_4$ in supersaturated solutions on solid $\beta$ $BiPO_4$ is an extremely slow process.

$\beta$-$BiPO_4$ was prepared for these solubility studies by heating a saturated solution of $\alpha$-$BiPO_4$ in 10N $HNO_3$ at 90° for about 20 hours. The resulting precipitate of $\beta$-$BiPO_4$ was washed several times with 10N $HNO_3$; then an excess of the solid was stirred with the desired concentration of $HNO_3$ and samples were taken at suitable intervals, usually until approximate constancy was reached.

The equilibrium solubilities observed for various concentrations of $HNO_3$ at 25° are listed in Table IV and graphed in Fig. 3. Table V contains

the solubilities observed at various times of stirring and gives a rough idea of the rate of solution. Since the relative amounts of solid $BiPO_4$ and acid used for determinations of both $\alpha$ and $\beta$ forms were approximately the same, one can see by comparison of Table V with Table II that the rate of solution of the $\beta$ form is appreciably less than that of the $\alpha$-form.

In Fig. 3 it will be noted that the log-log plot of $\beta$ $BiPO_4$ solubility versus $HNO_3$ concentration is a straight line as in the case of the $\alpha$-form. The slope of the straight line (2.2) is nearly the same as that observed for solubility of the $\alpha$ form (2.3), suggesting that the solution reaction is the same for both as would be expected if the two substances are allotropes. The equation describing $\beta$ $BiPO_4$ solubility in $HNO_3$ at 25° is

$$S = .21\ C^{2.2}$$

where S = Solubility in Gr. $BiPO_4$ per liter.
C = Normality of $HNO_3$.

Table IV

Solubility of $\beta$ $BiPO_4$ at Various $HNO_3$ Concentrations (Equilibrium approached from undersaturated side). 25°

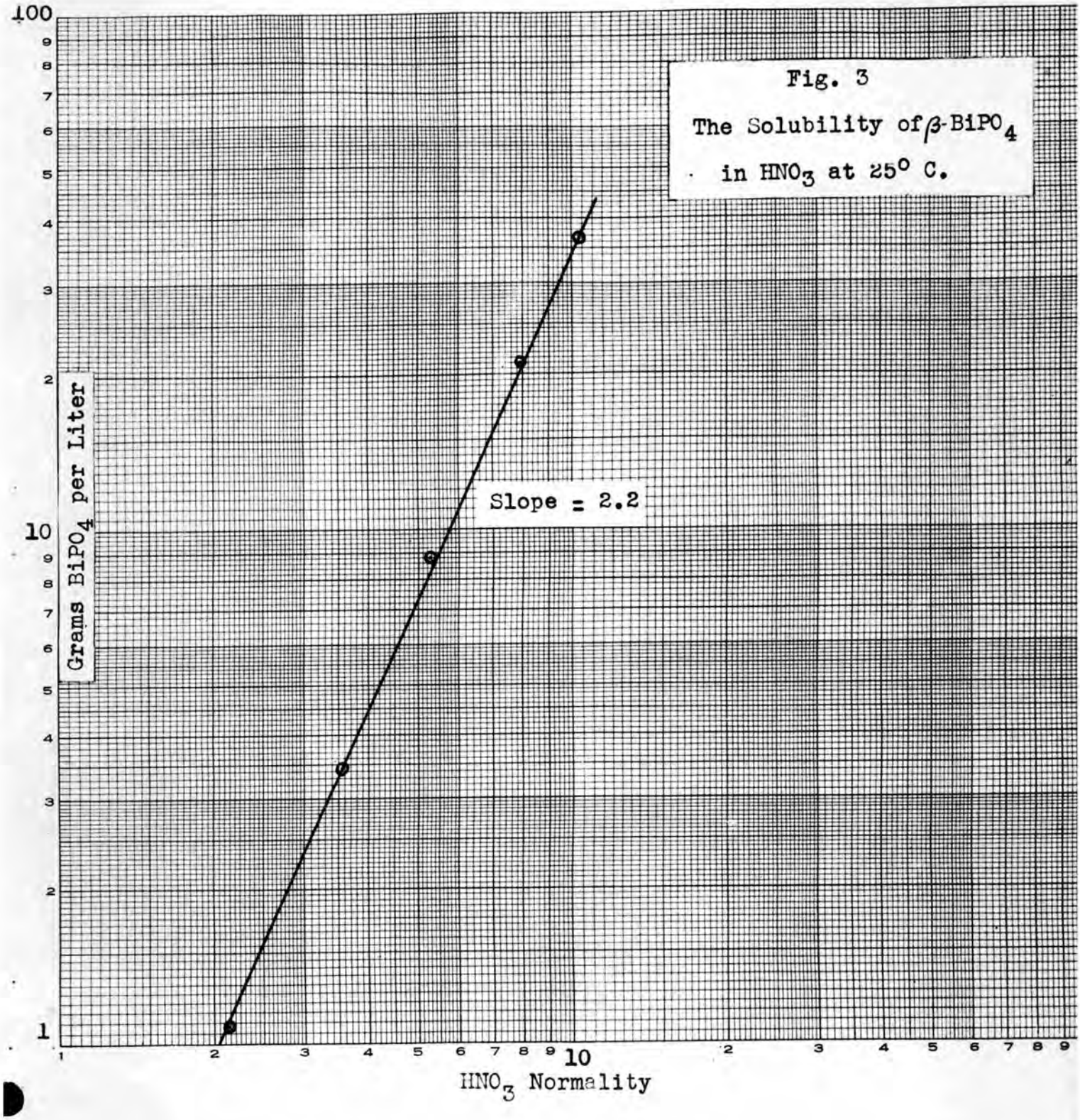
| $HNO_3$ Normality | Gr. $BiPO_4$/l. |
|---|---|
| 2.14 | 1.08 |
| 3.57 | 3.42 |
| 5.25 | 8.8 |
| 7.3 | 20.6 |
| 7.9 | 21.0 |
| 10.4 | 36.8 |

Table V

Effect of Time of Stirring on Observed $\beta BiPO_4$ Solubilities in Various Concentrations of $HNO_3$ and at Various Temperatures (Equilibrium approached from undersaturated side.)

| Temp. | $HNO_3$ | Time Hrs. | Time Min. | Gr. $BiPO_4$/l. |
|---|---|---|---|---|
| 25° | 2.14 | 2 | 40 | .99 |
| | | 43 | 30 | 1.08 |
| 25° | 3.57 | 1 | 20 | 3.12 |
| | | 2 | | 3.26 |
| | | 7 | 45 | 3.42 |
| 25° | 5.25 | | 35 | 7.48 |
| | | 1 | 35 | 8.4 |
| | | 18 | 50 | 8.8 |
| 25° | 7.3 | 1 | 15 | 18.4 |
| | | 2 | 45 | 19.7 |
| | | 5 | 45 | 20.6 |
| 25° | 7.9 | | 30 | 12.72 |
| | | 1 | 30 | 14.52 |
| | | 18 | 10 | 20.96 |
| 25° | 10.4 | 1 | | 32.34 |
| | | 3 | | 36.24 |
| | | 5 | | 36.24 |
| | | 24 | | 36.76 |
| 1° | 10.0 | 1 | 30 | 16.1 |
| | | 3 | 30 | 33.1 |
| | | 6 | 15 | 37.6 |
| 1° | 10.2 | 45 | | 36.56 |
| 50° | 10.4 | 6 | 35 | 32.0 |
| 75° | 10.4 | 4 | 45 | 28.6 |

CN-1863
Drawing 448
July 30, 1944



## 7. Interpretation of Solubility Data for $BiPO_4$ in $HNO_3$.

### A. Introduction

It can be seen in Figures 1 and 2 that the solubility of $BiPO_4$ varies approximately as the 2.3 power of the $HNO_3$ concentration and that the power dependence is practically constant from 0 - 75° in the range 1 - 10N $HNO_3$. In CN-933, it was shown that the same power dependence held even down to 0.1N $HNO_3$ at 30°. The solubility of $\alpha$-$BiPO_4$ in $HNO_3$ at the temperatures studied can be expressed approximately by the following equations:

$$1^\circ \quad S = 0.41C^{2.4} \tag{1}$$

$$25^\circ \quad S = 0.40C^{2.35} \tag{2}$$

$$50^\circ \quad S = 0.40C^{2.32} \tag{3}$$

$$75^\circ \quad S = 0.51C^{2.24} \tag{4}$$

where S = Solubility in Gr. $BiPO_4$ per liter
C = Normality of $HNO_3$

At 50 and 75°, the equations are not valid at high acidities.

We have heretofore assumed that the dissolution reaction for $BiPO_4$ in $HNO_3$ was essentially:

$$BiPO_4 + 3H^+ \rightleftharpoons Bi^{+3} + H_3PO_4 \tag{5}$$

and the solubility product for $BiPO_4$ has been calculated by Coryell (CN-1205 p. 50) on the basis of the data in CN-933 and using the expression:

$$K_{sp} = \frac{(Bi^{+3})\ (H_3PO_4)}{(H^+)^2} \quad \frac{K_{H_3PO_4}\ (\gamma_{Bi})}{(\gamma_H)^3} \tag{6}$$

a value of $6.1 \times 10^{-30}$ for $K_{sp}$ was obtained.

According to equation (5), one would expect $BiPO_4$ solubility to vary as the 1.5 power of the $HNO_3$ concentration. Coryell was able to show, assuming that reaction (5) is correct, that the variation in ratio of bismuth to hydrogen ion activity coefficients with increasing ionic strength is such that one would predict an increase in the power dependence of 1.0 arising from this factor. To determine whether equation (5) is the correct solution reaction for $BiPO_4$ in $HNO_3$, a number of special experiments have been performed which are described in the following sections.

B. The Solubility of $BiPO_4$ in $HClO_4$

The solubility of $BiPO_4$ in perchloric acid at 25-30° C. was determined by stirring or shaking $HClO_4$ solutions of various concentrations with solid $BiPO_4$ washed free of $H_3PO_4$ and $HNO_3$. Successive samples were taken after suitable stirring periods to insure attainment of equilibrium, and dissolved $BiPO_4$ was determined volumetrically or colorimetrically.

Table VI

Solubility of $BiPO_4$ in $HClO_4$

| $HClO_4$ Conc. | mg. $BiPO_4$/l. | $HClO_4$ Conc. | mg. $BiPO_4$/l. |
|---|---|---|---|
| .1 | 4.3* | 4.9 | 353 |
| .2 | 10.9* | 5.5 | 450 |
| .4 | 27.6* | 6.3 | 380** |
| .8 | 72* | 6.8 | 393 |
| 1.08 | 98 | 7.24 | 406 |
| 1.65 | 185* | 7.6 | 393 |
| 2.03 | 226 | 8.03 | 583** |
| 3.94 | 372 | 10.35 | 1890 |
| 4.16 | 380** | 10.4 | 2150 |

* Analyzed colorimetrically.

**Equilibrium approached from supersaturated side.

CN-1869
Drawing 449
July 30, 1944

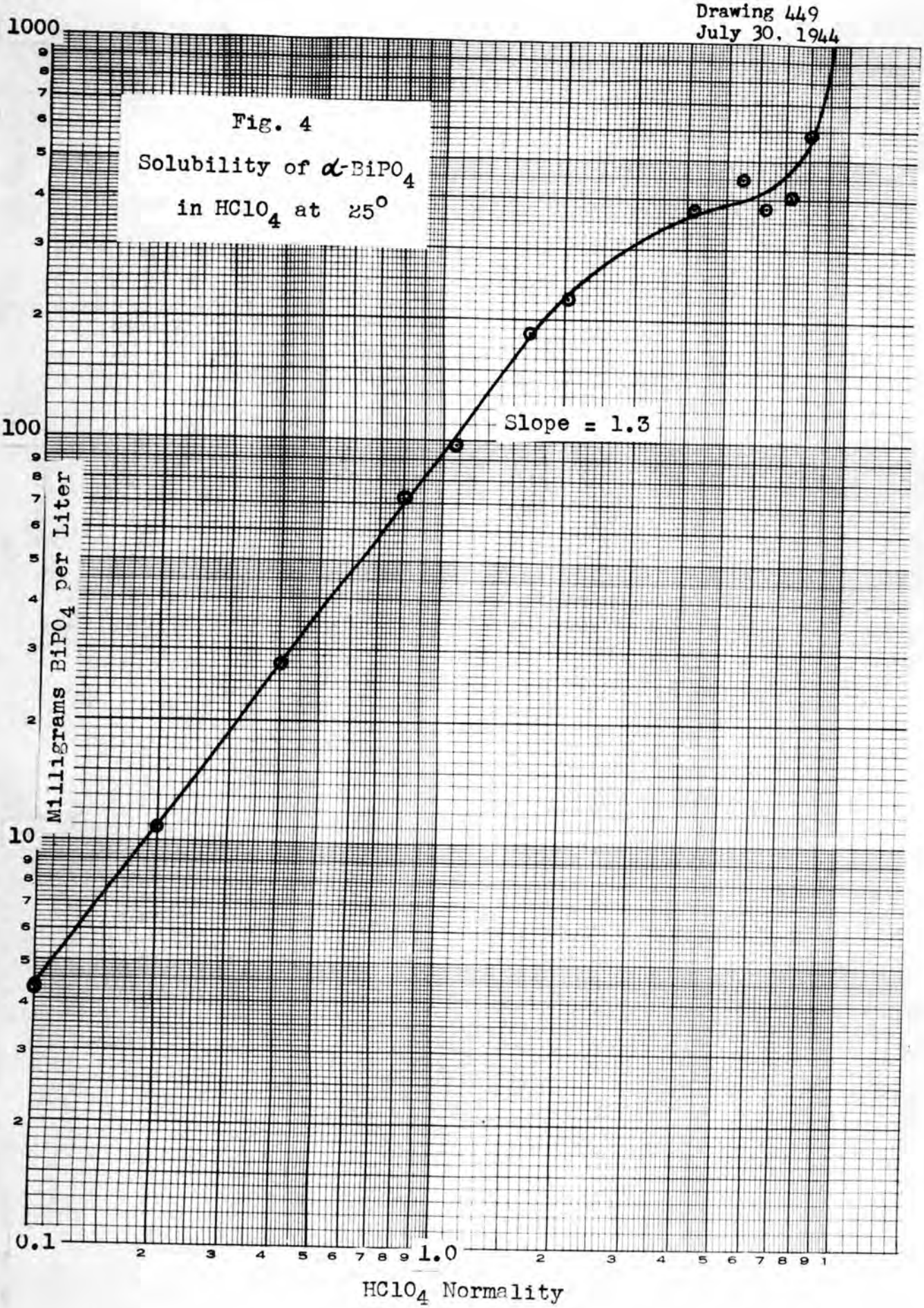


Table VII

Effect of $H^+$ Concentration on Solubility of $BiPO_4$ at Constant $ClO_4^-$ Concentration

| $HClO_4$ Molarity | $NaClO_4$ Molarity | mg. $BiPO_4$ per liter |
|---|---|---|
| .197 | 1.8 | 11.5 |
| .49 | 1.5 | 35 |
| .98 | 1.0 | 89 |
| 1.48 | 0.5 | 163 |
| 2.0 | 0.0 | 248 |

The results obtained are presented in Tables VI and VII and in Fig. 4. It will be noted that much lower solubilities are observed for $BiPO_4$ in $HClO_4$ and that the log-log plot of solubility versus acidity is linear up to about 2 or 3M$HClO_4$, but shows rather strange behavior at higher acid concentrations. The peculiar shape of the curve above 4N is probably due in part to the large deviations from unity of the mean activity coefficient of $HClO_4$ at high concentrations (Landolt Bornstein Tabellen III p.2144). Below 2N, the solubility of $BiPO_4$ in $HClO_4$ varies as the 1.3 power of the $H^+$ concentration and is independent of the $ClO_4$ concentration (Table VII). This suggests that when $BiPO_4$ dissolves in $HClO_4$ below 2N, the reaction occurring is principally:

$$BiPO_4 + 2H^+ + H_2O \rightleftharpoons BiOH^{++} + H_3PO_4 \qquad (7)$$

Most significant for the present purpose is the fact that $HClO_4$ gives much lower solubilities than $HNO_3$ even at low concentrations at which their activity coefficients are nearly the same. This cannot be due to limited solubility of $Bi(ClO_4)_3$ in $HClO_4$ since in 1N $HClO_4$, $Bi(ClO_4)_3$ is soluble to the extent of $>62$ gr./l.

The lower solubility obtained in $HClO_4$ suggests that in $HNO_3$ the nitrate ion plays an important part in solution of the $BiPO_4$. To determine the effect of nitrate ion, the solubility of $BiPO_4$ in mixtures of $HNO_3$ and $HClO_4$, and in 2N $HClO_4$ containing various amounts of $NaNO_3$ was determined as described in sections C and D below. To determine the effect of the ($H^+$) at constant nitrate

concentration, the solubility of $BiPO_4$ in mixtures of $HNO_3$ and $NaNO_3$ was determined as described in section E. The effect of $H_3PO_4$ on the solubility of $BiPO_4$ in 10N $HNO_3$ is described in section F.

C. Solubility of $BiPO_4$ in Mixtures of $HNO_3$ and $HClO_4$

Solutions of $HNO_3$ and $HClO_4$ of equal normality were made up (~10N). Various mixtures of the two were made to give solutions of constant total acidity, and varying nitrate concentration. Excess, freshly precipitated $\alpha$ $BiPO_4$, washed free of $H_3PO_4$ was added to each, and the solutions allowed to stand at 25° for 24 hours with frequent shaking, then analyzed for Bi.

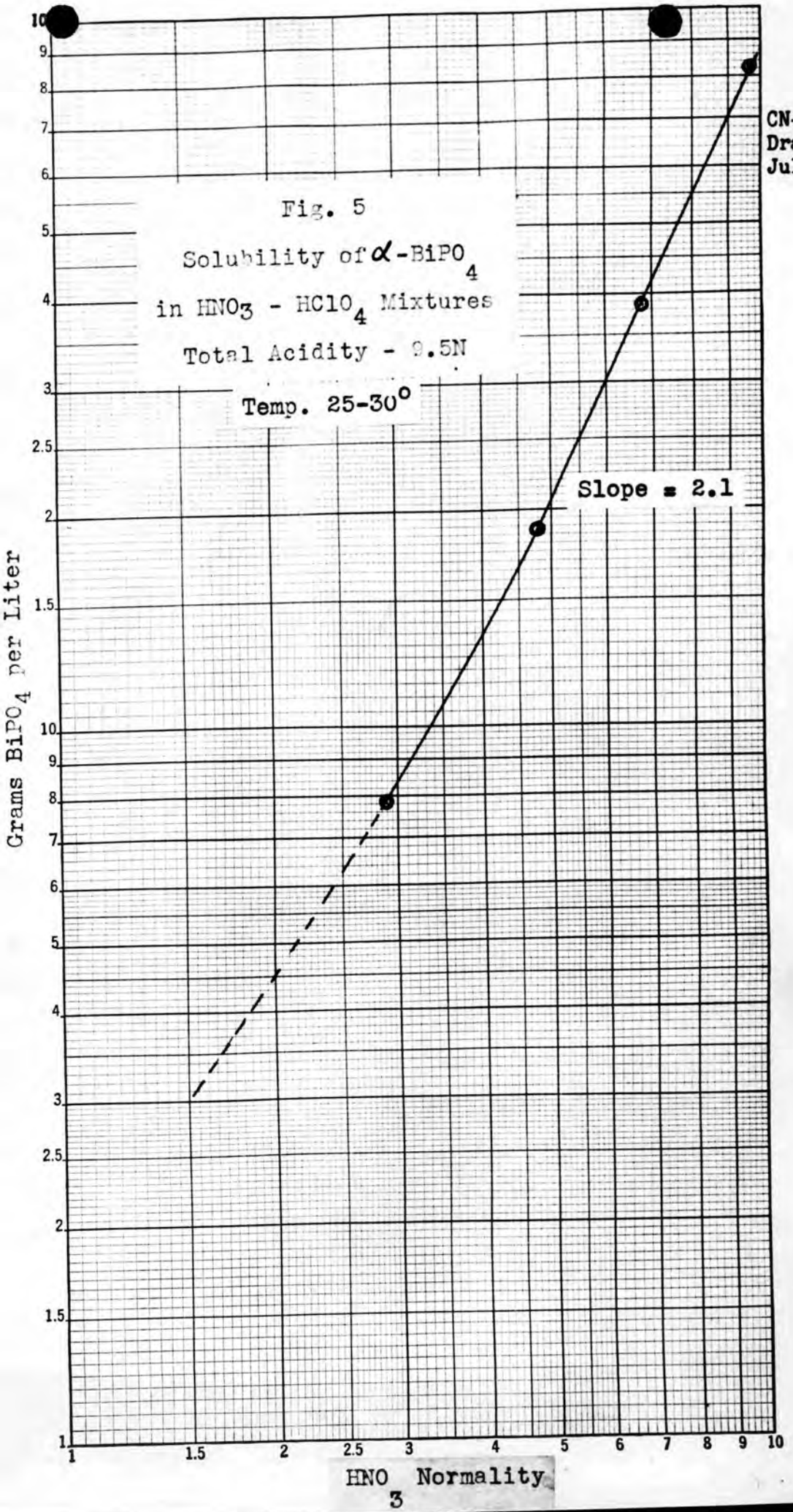
The results obtained are shown in Table VIII and in Fig. 5.

Table VIII

Solubility of $BiPO_4$ in $HNO_3$ - $HClO_4$ Mixtures

| Total Acidity | $NO_3^-$ Normality | Gr. $BiPO_4$ per liter |
|---|---|---|
| 9.65 | 0 | 1.75 |
| " | 2.9 | 7.85 |
| " | 4.8 | 18.7 |
| " | 6.8 | 38.7 |
| " | 9.65 | 82.5 |

On log-log paper, a plot of solubility vs. $NO_3^-$ gives a straight line of slope 2.11.




CN-1863
Drawing 450
July 30, 1941

Logarithmic, 1 × 2 Cycles.
MADE IN U. S. A.

D. Effect of $NO_3^-$ Concentration on $BiPO_4$ Solubility at Constant $H^+$ Concentration.

Mixtures of $HClO_4$, $NaClO_4$ and $NaNO_3$ solutions were prepared so as to give final solutions all 2N in $HClO_4$, with a total ionic strength of 4, and containing various concentrations of $NaNO_3$. Excess freshly prepared $\alpha$ $BiPO_4$, washed free of $H_3PO_4$ and $HNO_3$, was added to each and after standing 6 days with frequent shaking at room temperature the solutions were analyzed for Bi by the volumetric "oxine" method.

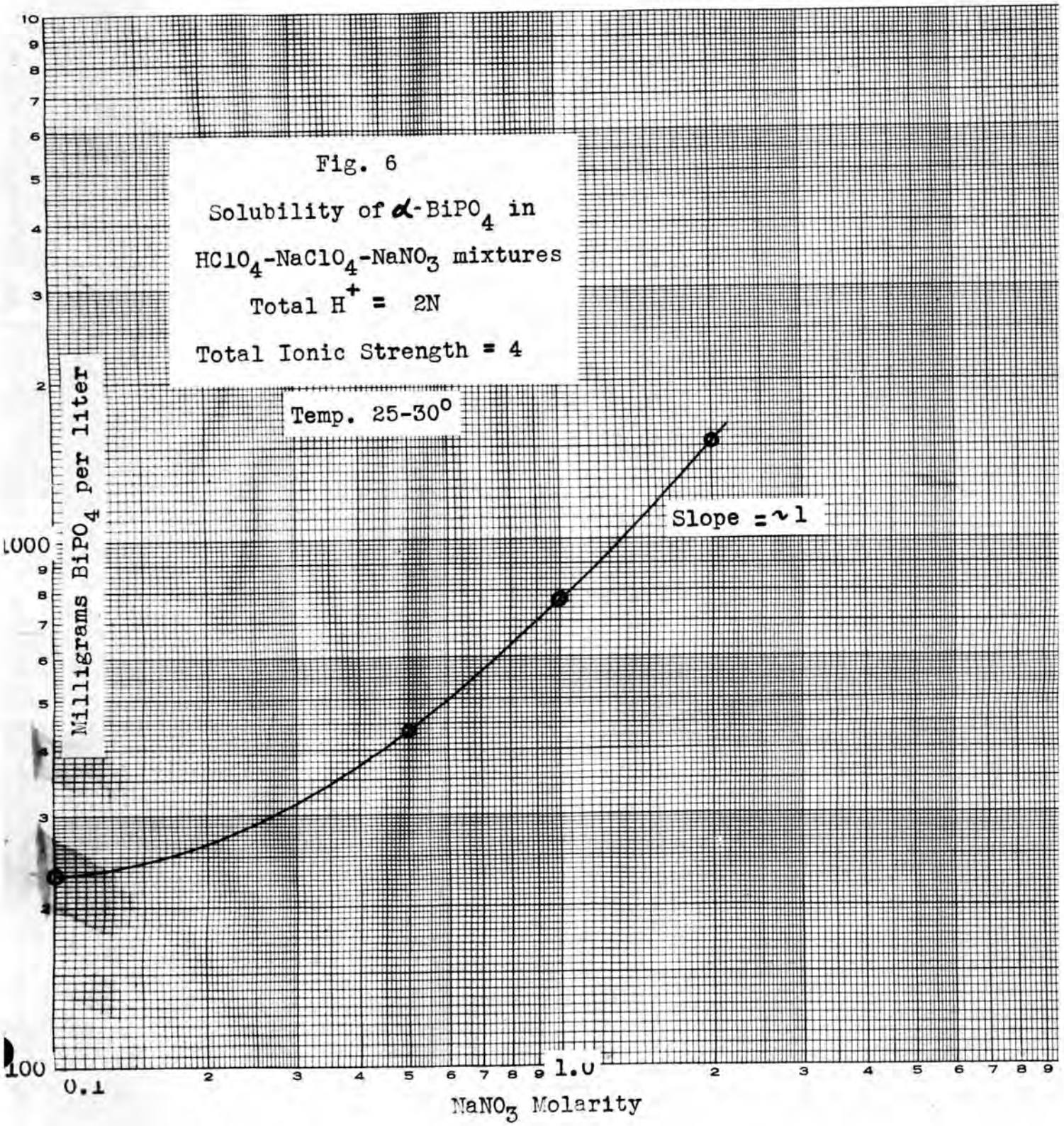
The results obtained are shown in Table IX and in Fig. 6. It was not known whether the solid phase in contact with the solutions remained entirely $\alpha$ $BiPO_4$ during the time allowed to reach equilibrium.

Table IX

Effect of $NO_3^-$ Concentration on Solubility of $BiPO_4$

| $HClO_4$ M | $NaClO_4$ M | $NaNO_3$ M | Mg. $BiPO_4$ per liter |
|---|---|---|---|
| 2 | 2 | 0 | 183 |
| 2 | 1.9 | .1 | 230 |
| 2 | 1.5 | .5 | 434 |
| 2 | 1.0 | 1.0 | 763 |
| 2 | 0 | 2 | 1540 |

CN-1863
Drawing 451
July 30, 1944

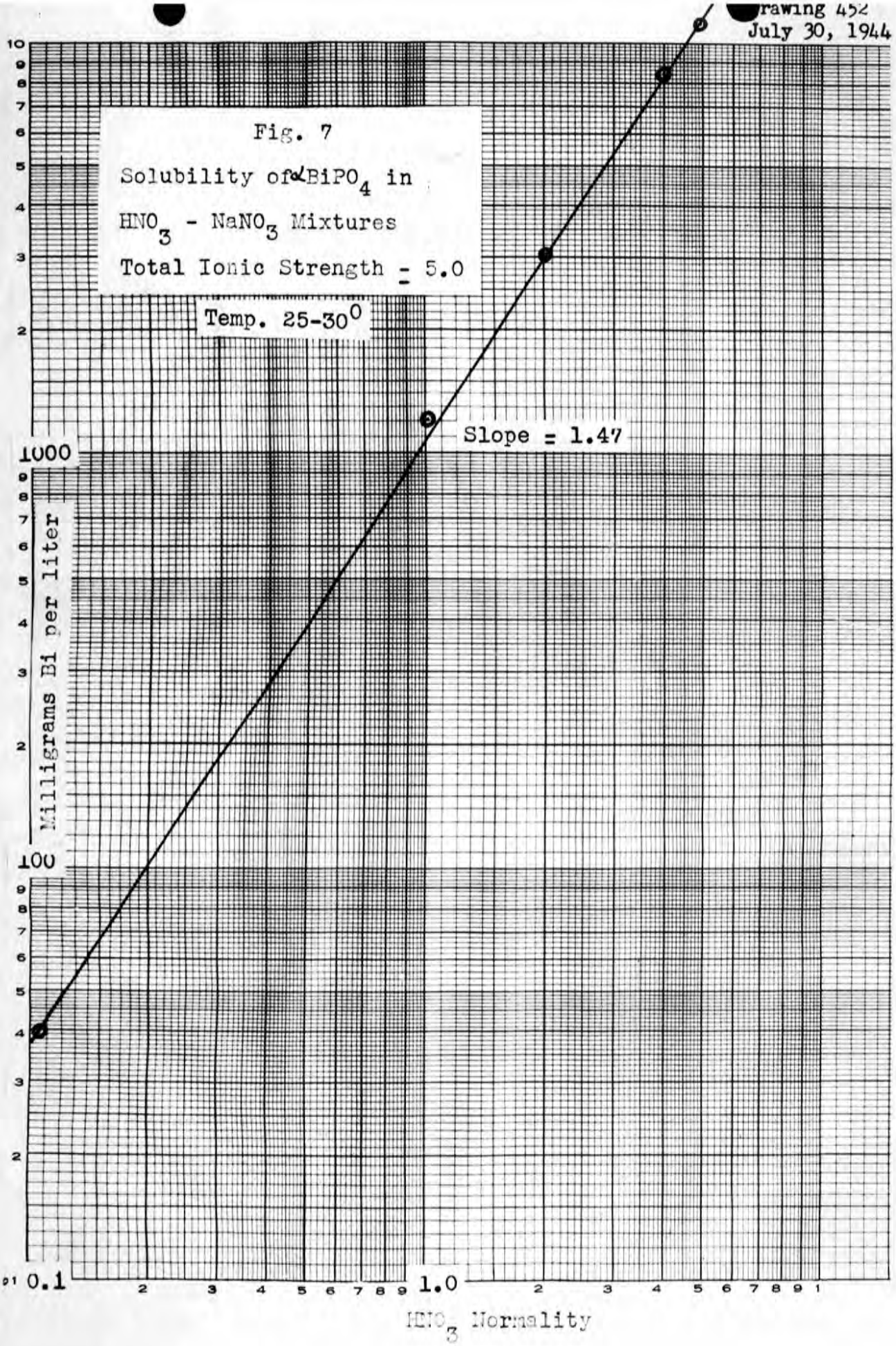


E. Effect of $H^+$ Concentration on $BiPO_4$ Solubility at Constant $NO_3^-$ Concentration

Since the preceding experiment has shown that at constant $H^+$ concentration, $BiPO_4$ solubility increases directly with the nitrate concentration, it is evident that both the $H^+$ and $NO_3^-$ from $HNO_3$ contribute to the 2.4 power dependence on $HNO_3$ concentration observed for solubility of $BiPO_4$ in $HNO_3$. To determine the power dependence on $H^+$ only, various mixtures of $HNO_3$ and $NaNO_3$ solution were prepared to give solutions of total ionic strength five, total nitrate = 5M, and $H^+$ from .1 to 4N. Excess freshly prepared and washed $BiPO_4$ was added to each and after standing two days at 25° with frequent shaking the solutions were analyzed for Bi by the volumetric "oxine" method.

The results obtained are shown in Table X and in Fig. 7.

Drawing 452
July 30, 1944



F. Effect of $H_3PO_4$ on Solubility of $\alpha$ $BiPO_4$ in 10N $HNO_3$.

It has already been shown (CN-933) that in 1N $HNO_3$ the solubility of $BiPO_4$ is markedly decreased by $H_3PO_4$.

To determine whether the same thing is true in 10N $HNO_3$, the solubility of $\alpha$ $BiPO_4$ in 9.94N $HNO_3$ containing .29M $H_3PO_4$ was determined. Excess $BiPO_4$ was added to the mixture of $HNO_3$ and $H_3PO_4$ and after 24 hours at 25° with occasional hand shaking, the observed solubility was 55.1 gr. $BiPO_4$/1. as compared with 89 gr./1. in the absence of the $H_3PO_4$.

G. Discussion

It is evident from the foregoing results that the dissolution mechanism previously assumed for $BiPO_4$ in $HNO_3$ is incorrect. Nitrate ion plays a part in the solution of $BiPO_4$ in $HNO_3$, and the reason for its effect is probably the low degree of dissociation of $Bi(NO_3)_3$. The much lower solubility of $BiPO_4$ in $HClO_4$ than in $HNO_3$ can be interpreted as due to the fact that $Bi(ClO_4)_3$ is much more highly dissociated at a given $HClO_4$ concentration than is $Bi(NO_3)_3$ at a corresponding $HNO_3$ concentration.

D.F. Smith (Section 11-E) has studied the solubility of $BiONO_3$ in $HNO_3$ and the conductance of $Bi(NO_3)_3$ in various concentrations of $HNO_3$. He concludes from his results that Bi in such solutions exists largely in the form of partially ionized $Bi(NO_3)_3$.

Applying this conception to the solution of $BiPO_4$ in $HNO_3$, makes it seem likely that the reaction occurring when $BiPO_4$ dissolves in $HNO_3$ is of the following type:

$$BiPO_4 + 3H^+ + NO_3^- \rightleftharpoons Bi(NO_3)^{++} + H_3PO_4 \qquad (8)$$

$$BiPO_4 + 3H^+ + 2NO_3^- \rightleftharpoons Bi(NO_3)_2^+ + H_3PO_4 \qquad (9)$$

$$BiPO_4 + 3H^+ + 3NO_3^- \rightleftharpoons Bi(NO_3)_3 + H_3PO_4 \qquad (10)$$

$$BiPO_4 + 3H^+ + 4NO_3 \rightleftharpoons Bi(NO_3)_4^- + H_3PO_4 \qquad (11)$$

Reaction 9 above predicts $BiPO_4$ solubility dependent on the 1.5 power of the $H^+$ and the 1.0 power of the $NO_3^-$ concentration (neglecting activity coefficients). See equation 13. Separate determinations of the effect of $H^+$ and $NO_3^-$ ion concentration on $BiPO_4$ solubility (Figures 6 and 7) have actually shown a 1.5 power dependence on $H^+$ and a 1.0 power dependence on $NO_3^-$ under conditions of constant ionic strength.

It seems reasonable to assume that the degree of dissociation of $Bi(NO_3)_3$ would vary considerably in going from weak to concentrated $HNO_3$ and that consequently one of the foregoing reactions

would occur predominantly in one range of acidity and some other reaction in another range. If this occurred, the power dependence of solubility on $NO_3^-$ (and consequently on $HNO_3$) concentration would change in going from low to high acidity. Actually one observes a fairly uniform 2.3 power dependence throughout the range .1 to 10N $HNO_3$. From this one might be tempted to conclude that reaction (9) occurred at all acidities. It is more likely, however, that all of the reactions play a part, and that the changes in activity coefficients of the ions involved that occur upon going from low to high acid concentration largely counteract the increasing dependence on $NO_3^-$ concentration which occurs as we go from reaction (8) to reaction (11).

In Fig. 5 it will be noted that at $H^+ = 9.6$, the $BiPO_4$ solubility varies about as the 2.1 power of the $HNO_3$. This can be interpreted as indicating that reaction (11) is involved at this acidity if one assumes that the activity coefficients of $HClO_4$ and $HNO_3$ are the same in all the solutions.

The effect of temperature upon the solubility of $BiPO_4$ is different for 10N $HNO_3$ than for 5.0N $HNO_3$ (Fig. 8). This also tends to indicate that the type of reaction occurring between $BiPO_4$ and $HNO_3$ changes as we go to higher acidities.

If one assumes that solution of $BiPO_3$ in $HNO_3$ occurs according to reaction (9), then an equilibrium constant for the reaction can be expressed as follows:

$$K_R = \frac{[Bi(NO_3)_2^+][\gamma_{Bi(NO_3)_2^+}][H_3PO_4]}{(BiPO_4)[H^+]^3[NO_3^-]^3[\gamma_{H^+}]^3[\gamma_{NO_3^-}]^2} \quad (12)$$

When $BiPO_4$ dissolves in $HNO_3$, $Bi(NO_3)_2^+ = H_3PO_4$

hence

$$Bi(NO_3)_2^+ = \sqrt{K_R}\,[H^+]^{3/2}[NO_3]\frac{[\gamma_H]^{3/2}[\gamma_{NO_3}]}{[\gamma_{Bi(NO_3)_2^+}]^{1/2}} \quad (13)$$

or

$$Bi(NO_3)_2^+ = \sqrt{K_R}\,[HNO_3]^{5/2}\frac{[\gamma_H]^{3/2}[\gamma_{NO_3}]}{[\gamma_{Bi(NO_3)_2^+}]^{1/2}} \quad (14)$$

This equation agrees closely with the observed 2.3 power dependence of $BiPO_4$ solubility in $HNO_3$ if one assumes that the ratio of the

activity coefficients involved remains nearly constant throughout the range .1 to 10N $HNO_3$.

Regardless of which of the reactions (8-11) one uses to describe the solubility of $BiPO_4$ in $HNO_3$, the effect of $H_3PO_4$ on the solubility will be given by the following expression:

$$S' = \frac{\sqrt{K_K}\,[H^+]^3\,[NO_3^-]^n}{[H_3PO_4 + S']} \; \frac{[\gamma_H]^3\,[\gamma_{NO_3}]}{[\gamma_{Bi(NO_3)_n^{+3-n}}]} \qquad (15)$$

where S' is the solubility of $BiPO_4$ in the presence of $H_3PO_4$.

Comparison of this equation with the corresponding expression for the solubility in the absence of added $H_3PO_4$, namely:

$$S = \frac{\sqrt{K_R}\,[H^+]^3\,[NO_3^-]^n}{S} \; \frac{[\gamma_H]^3\,[\gamma_{NO_3}]}{[\gamma_{Bi(NO_3)_n^{+3-n}}]} \qquad (16)$$

where S = solubility in the absence of $H_3PO_4$ in moles/liter

enables us to derive the following equation for the effect of $H_3PO_4$ on the solubility of $BiPO_4$

$$\frac{S}{S'} = \frac{H_3PO_4 + S'}{S}$$

$$\text{or } S^2 = S'(H_3PO_4 + S') \qquad (17)$$

In an analogous way, one can show that the solubility (S'') of $BiPO_4$ in $HNO_3$ containing low concentrations of $Bi(NO_3)_3$ is related to the solubility in the same concentration of pure $HNO_3$ (S) by the equation

$$S^2 = S''(S'' + C_{Bi}) \qquad (18)$$

where $C_{Bi}$ represents the concentration of added $Bi(NO_3)_3$. In CN-933, the solubility of $BiPO_4$ in 1.3N $HNO_3$, 0.1M $H_3PO_4$ is given as 18.5 mg. $BiPO_4$/l. at 25° as compared with 700 mg./l. in the absence of $H_3PO_4$. Using equation (17) one would predict a solubility of 16.3 mg./l.

In the present report (section 7-F) the solubility of $BiPO_4$ in 9.94N $HNO_3$ containing .29M $H_3PO_4$ is found to be 55.1 gr./l. at 25° as compared with 89 gr./l. in the absence of $H_3PO_4$. Using equation (17) one would predict the solubility to be 56.3 gr./l.

Whereas $H_3PO_4$ reduces the solubility of $BiPO_4$ in $HNO_3$, it does not affect the solubility of $BiPO_4$ in HCl. K.A. Jensen (11-C) has shown from a study of the solubility of $BiPO_4$ in solutions containing $Cl^-$, $H^+$ and $H_3PO_4$ that the solubility is proportional to the square of the $H^+$, the cube of the $Cl^-$ concentration, and is independent of the $H_3PO_4$ concentration. He attributes this to the fact that the reaction occurring when $BiPO_4$ dissolves in HCl is mainly

$$BiPO_4 + 2H^+ + 3Cl^- \rightleftharpoons \left[Bi \begin{matrix} Cl_3 \\ H_2PO_4 \end{matrix}\right]^- \qquad (19)$$

## 8. The Effect of Temperature on $BiPO_4$ Solubility

### A. The $\alpha$-Form.

In Table XI are presented the solubilities of $BiPO_4$ at various acidities and temperatures, read off from the graphs in Figures 1 and 2. The curves drawn on these graphs are determined by the points representing solubilities determined by approach to equilibrium from the undersaturated side.

It can be seen in Table XI and in Fig. 8 that in the range of acidity from 2 - 6N the solubility of $BiPO_4$ is practically unaffected by temperature in the range 0 - 75°. In 1N, the solubility curve has a flat minimum, being practically constant from 25-50°, about 10% higher at 0° and about 20% higher at 75°. In 8 and 10N $HNO_3$, there is a steady downward trend of solubility with increasing temperature.

Table XI

Effect of Temperature on the Solubility of $\alpha$-$BiPO_4$ in Various Concentrations of $HNO_3$. (Using values obtained by approaching equilibrium from the undersaturated side.)

| $HNO_3$ Normality | Gr. $BiPO_4$/l. at* | | | |
|---|---|---|---|---|
| | 1° | 25° | 50° | 75° |
| 1.0 | .42 | .38 | .39 | .54 |
| 2.0 | 2.1 | 2.0 | 1.80 | 2.0 |
| 4.0 | 10.0 | 10.0 | 9.5 | 9.7 |
| 6.0 | 26.0 | 27.0 | 25.0 | 25.5 |
| 8.0 | 59.0 | 54.0 | 47.0 | 45.0 |
| 10.0 | 100.0 | 90.0 | 74.0 | 64.0 |

* Interpolated values from Figures 1 - 2.

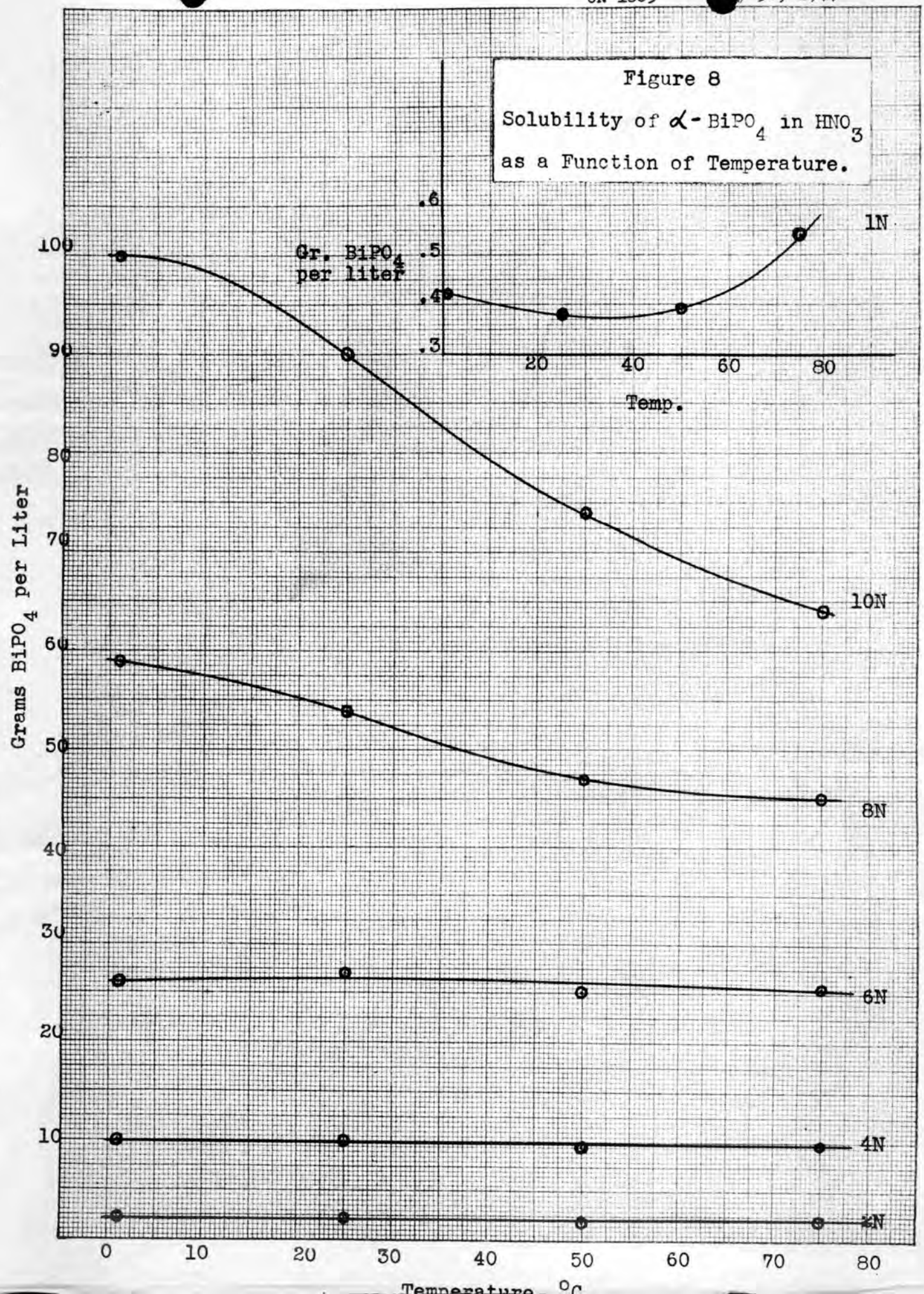



Figure 8
Solubility of $\alpha$-$BiPO_4$ in $HNO_3$ as a Function of Temperature.

Form No. 990—10 Millimeters to Centimeter
AMERICAN PAD & PAPER CO., HOLYOKE, MASS.

B. The $\beta$-Form

The effect of temperature on the solubility of the $\beta$-form has been studied only in 10N $HNO_3$. The results are listed in Table XII and shown graphically in Figure 9. It will be noted that just as with the $\alpha$-form the solubility steadily decreases with increasing temperature.

Table XII

Solubility of $\beta$-$BiPO_4$ in 10.0N $HNO_3$ as a Function of Temperature. (Corrected to 10.0N from the observed values, assuming that the rate of variation of solubility with acid concentration is the same at all temperatures).

| Temperature | Gr. $BiPO_4$/l. |
|---|---|
| $1^o$ | 36.3 |
| $25^o$ | 33.6 |
| $50^o$ | 29.8 |
| $75^o$ | 25.4 |

CN-1863
Drawing 454
July 30, 1944

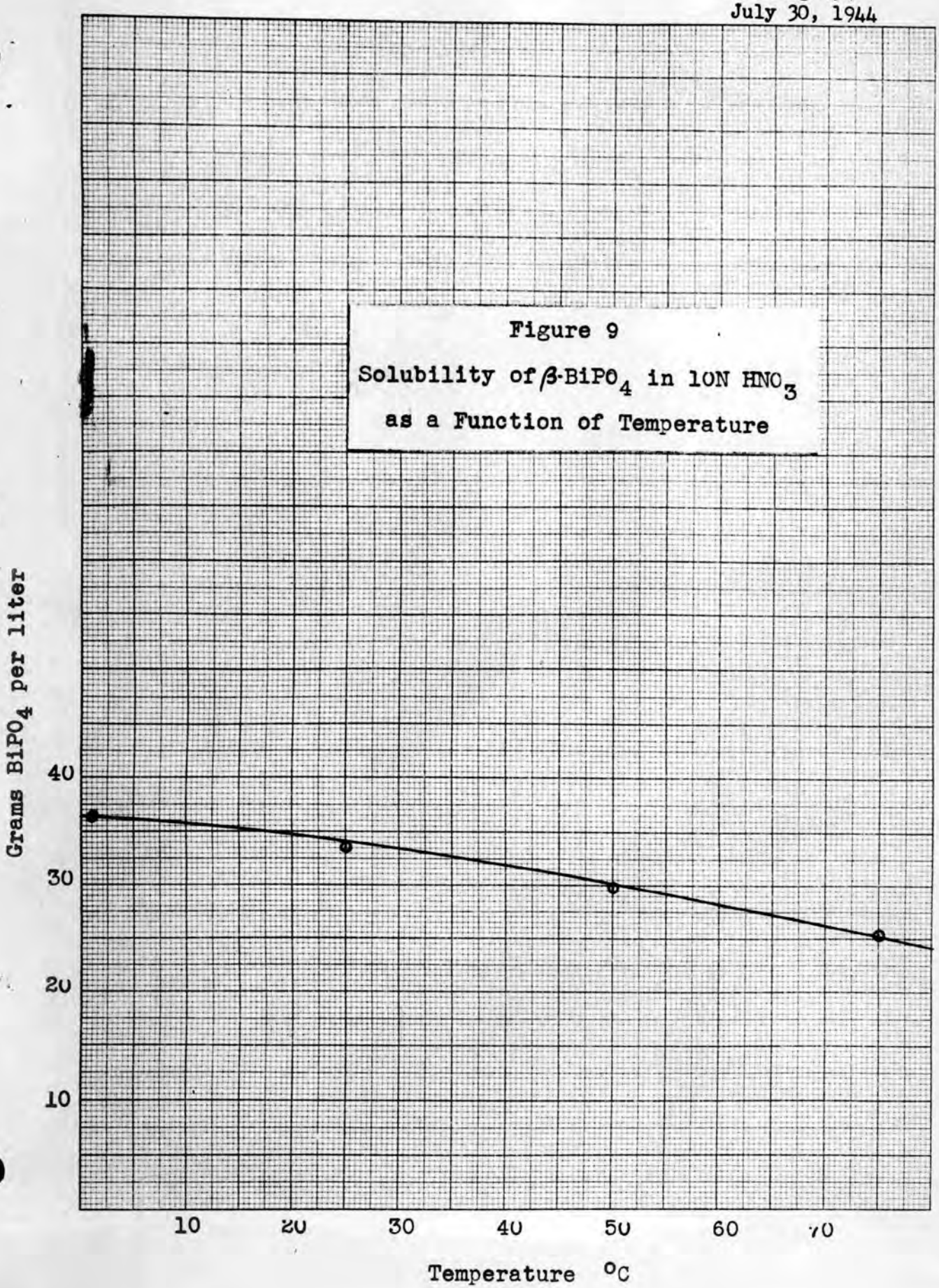



Figure 9

Solubility of $\beta$-$BiPO_4$ in 10N $HNO_3$ as a Function of Temperature

9. The Effect of HF on Solubility of $\alpha$ $BiPO_4$ in 10N $HNO_3$.

Mixtures of $HNO_3$ and HF (e.g. 10N $HNO_3$, 1N HF) have been reported by J. McBride (private communication) to dissolve $\beta$ $BiPO_4$ more rapidly than does $HNO_3$ alone. Since the presence of fluoride ion in the solutions may permit formation of more soluble complexes it was thought to be of interest to determine the extent to which the solubility of $\alpha$ $BiPO_4$ in 10N $HNO_3$ is increased by the presence of various amounts of HF.

Freshly precipitated and washed $BiPO_4$ was dissolved in $HNO_3$ until the solution was nearly saturated. The acid strength was then found to be 9.62N. To three separate portions of the solution in lusteroid tubes, sufficient 27N HF was added to make the solutions 1, 0.5 and 0.1N in HF. Additional solid $BiPO_4$ was then added and the amount of dissolved $BiPO_4$ present in each of the solutions after two hours stirring at 25° was determined (volumetric oxine method). The results obtained are given in Table XIII.

Table XIII

Effect of HF on Solubility of $\alpha$ $BiPO_4$ in 9.6N $HNO_3$
(2 hrs. stirring at 25°)

| HF Normality | Gr. $BiPO_4$ per liter |
|---|---|
| 0 | 82.0 |
| 0.1 | 87.0 |
| 0.5 | 91.8 |
| 1.0 | 99.5 |

The solubilities were followed as a function of time, and showed a slight decrease with continued stirring, possibly attributable to conversion to $\beta$ $BiPO_4$, e.g. after 22 hours the observed solubilities were: 1.0N HF - 97.2 gr. $BiPO_4$/l.; 0.5N HF - 90.2 gr./l.; 0.1N HF - 85.5 gr./l.

10. The Density of $HNO_3$ Solutions of $BiPO_4$.

The effect of dissolved $BiPO_4$ on the density of $HNO_3$ solutions of various concentrations are shown in Table XIV in which the densities of $HNO_3$ solutions nearly saturated with $BiPO_4$ are given at 25° and compared with the density of the same concentration of pure $HNO_3$.

Table XIV

Densities at 25° of $HNO_3$ Solutions of $BiPO_4$
(Saturated with $BiPO_4$ at 25°)

| $HNO_3$ Normality | Grams $BiPO_4$ per liter | Density at 25° gr./cc. | Density at 25° of $HNO_3$ - $H_2O$ Mixture only * |
|---|---|---|---|
| 2.01 | 2.39 | 1.062 | 1.070 |
| 5.10 | 23.42 | 1.179 | 1.162 |
| 7.94 | 58.98 | 1.287(28.5°) | 1.242 |
| 9.98 | 95.68 | 1.376 | 1.297 |
| 11.95 | 132.25 | 1.449 | 1.341 |

* I. C. T. Vol. III, p. 58.

The temperature coefficient of density of a $BiPO_4$ solution in $HNO_3$ has been studied by the Plant Assistance Group of Section S-I. The density of a 5N $HNO_3$ solution containing 14.4 gr. $BiPO_4$/l. was found to vary from 1.175 at 25°, to 1.157 at 50° and to 1.151 at 60°. (R.S. Apple, Private Communication).

11. Bibliography of Published Non-Project Literature on $BiPO_4$ and Related Subjects

A. Determination of Bismuth as Phosphate.
W.C. Blasdale and W.C. Parle, Ind. Eng. Chem. Anal. Ed., 8 352 (1936)

B. Crystal Structure of $BiPO_4$.
A. DeSchulten Bull, Soc. Chem. (3) 29 723 (1903)

C. Solubility of $BiPO_4$ in HCl.
K.A. Jensen Z. Anorg. U. Allgem. Chemie 219 238 (1934).

D. Bismuth Oxychloride and Bismuth Chloride Complexes.
A.A. Noyes and W. Hall, J. A. C. S. 39 2526 (1917).

E. Bismuth Nitrate - Conductivity of Solutions in $HNO_3$.
D.F. Smith, J. A. C. S. 45 360 (1923).

F. Bismuth Nitrate - Solubility in $HNO_3$.
G.M. Rutten Z. Anorg. U. Allgem. Chemie 28 210 (1901); 30 386 (1902)

G. Bismuth Oxynitrate - Solubility in $HNO_3$.
D.F. Smith, J. A. C. S. 45 360 (1923).

H. Bismuth Perchlorate.
D.F. Smith, J. A. C. S. 45 360 (1923).
F. Fichter and E. Jenny, Helvetica Chem. Acta 6 225-31 (1923).

I. Bismuth Oxalate - Solubility in $HNO_3$
A. Keschan, Z. Anal. Chemie 67 81 (1925).