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Physico-Chemical Studies of Some Werner-Complex Clathrates

S. W. K. Chick

Northern Michigan University

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PHYSICO-CHEMICAL STUDIES OF SOME
WERNER-COMPLEX CLATHRATES

by

S. W. K. CHICK

B. S., Hong Kong Baptist College

A Thesis

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Arts in Chemistry

School of Graduate Studies
Northern Michigan University
Marquette, Michigan

May 1973

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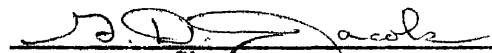
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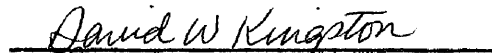
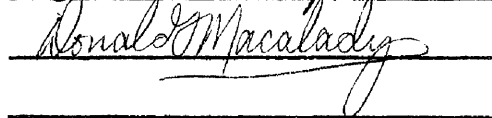
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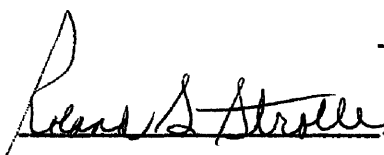
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Submitted in partial fulfillment of the
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Master of Arts

Northern Michigan University

Marquette, Michigan

May 1973

Abstract

A brief outline of the history of clathrate compounds is presented. A study of the clathration reaction utilizing Ni(II), Co(II) and Fe(II) complexes as the hosts and benzene, toluene, and p-xylene as guests was carried out under various conditions. Evidence obtained in this study indicates that the clathration reactions are not first order, reversible reactions for benzene, toluene, and p-xylene as the guest components.

Crystal lattice changes in going from complexes to clathrates are confirmed by X-ray powder diffraction patterns.

The Freundlich adsorption isotherm equation was found to "fit" the clathration reaction involving benzene but to show large deviations when toluene and p-xylene are employed as guests.

In addition to the conventional $\log (A_t - A_\infty)$ vs. time plots, an attempt was made to fit the kinetic rate data by plotting \ln (guest concentration at any time) vs. \ln time in accordance with the expression proposed by Lahr and Williams (34).

Reversibility tests were carried out and it was found that none of the clathration reactions are reversible.

Thermogravimetric analyses were carried out with the hope of correlating the results with the adsorption studies being carried out in this laboratory; however, further work is needed before any conclusions can be drawn.

TO MY DEAREST PARENTS
WHOSE LIVES GUIDED MINE

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It is with a feeling of sincere gratitude that the author wishes to extend his deepest appreciation to Dr. Gerald D. Jacobs for his constant encouragement, guidance, invaluable advice and whole-hearted support which he so generously rendered during this entire research project. Special thanks go to Dr. David W. Kingston for his help and advice in making available the thermobalance he constructed, which the author has utilized as part of his research project.

Finally, the author would like to acknowledge the less specific, but no less important, contributions of his teachers and graduate students of the Chemistry department, who will be aware of their influence in the development of the ideas in this thesis.

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HISTORICAL BACKGROUND

HISTORICAL BACKGROUND

Compounds of the type which are now called "clathrates" have been known for over one hundred years. The term "clathrates" was first introduced into chemistry by H. M. Powell following his X-ray studies on a series of molecular compounds (44-51). Powell defined 'clathrates' (from the Latin word clathratus, which means enclosed or protected by the cross-bars of a grating) as "compounds in which molecules may be firmly united to each other without the operation of strong attractive forces between them but through the enclosure of one by the other, of both by the other, or in more complex ways, in a suitable frame work formed by another" (44-51).

Following Powell's pioneering work, other investigators began intensive studies on this new type of compound and the early investigations were concentrated in three main areas:

- I. Gas hydrates
- II. Quinol complexes
- III. $\text{Ni}(\text{CN})_2\text{NH}_3\cdot\text{M}$ (M = organic adduct)

I. Gas hydrates

A gas hydrate is essentially the complex formed by dissolving a gas or low boiling liquid in water under pressure with subsequent cooling. The first gas hydrate of chlorine and water was reported by Davy in 1810 (13). Faraday proposed the formula $\text{Cl}_2\cdot 10\text{H}_2\text{O}$ (22). Further investigations by M. von Stackelberg and others (60,61) clarified

the nature of these compounds. More recent work by M. Broneman (7), G. Chancel and F. Parmentier (11), and others demonstrated that this type of hydrate can be formed with a large number of gases or volatile liquids such as Cl_2 , Br_2 , H_2S , SO_2 , Kr, Xe, Ar, CH_4 , CH_3Cl , and CHCl_3 .

Brown (6) classified gas hydrates into two main categories; one containing six comparatively small guest molecules such as Cl_2 , Br_2 , SO_2 , etc., combined with 46 water molecules and the other containing one relatively large molecule such as CHCl_3 , $\text{C}_2\text{H}_5\text{Cl}$, C_3H_8 , etc. for each 17 water molecules.

X-ray structural studies by L. Pauling and Marsh (43) revealed that all gas hydrates crystallize in the cubic system, believed to be solid solutions, with the guest molecules positioned in cavities formed by a framework of host water molecules bound together by hydrogen bonds.

II. Quinol Complexes

The first report of these complexes was made by Wohler and Clemm (63) more than a century ago. More recent work by Powell and coworkers (44-51) utilizing X-ray analysis provides convincing proof that hydroquinone molecules are linked together by means of hydrogen bonds to form a pair of three dimensional networks. However, the networks do not completely fill the available space and the resulting cavities, bounded by two circles of six hydrogen bonded hydroxyl groups and by benzene rings of six quinol molecules, provide spaces for the guest molecules within the cavities.

Thermodynamic values, as well as other physical and chemical properties for quinol complexes have been determined by Evans and Richards (19), van der Waals (56-59), J. C. Platteeuw (52,53) and others.

Indeed, conclusive proof that clathrate formation depends on molecular "form" rather than on chemical bonding is indicated by the fact that even the inert gases Ar, Kr, and Xe are capable of forming stable quinol complexes.

III. $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{M}$ (M = benzene)

The clathrate formed between the $\text{Ni}(\text{CN})_2\text{NH}_3$ complex and benzene was first reported in 1897 (28) and was the first clathrate formed between an inorganic complex and an organic compound. The structure of this compound remained a mystery until 1952 when Rayner and Powell elucidated its crystal structure by X-ray analysis (51). The $\text{Ni}(\text{CN})_2\text{NH}_3$ has a cage like structure in which guest molecules such as benzene, thiophene, furan, pyrrole, aniline or phenol are enclosed. A more detailed and vivid structural analysis of $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{benzene}$ was later worked out and reported by Bhatnager (5). It was reported that the crystal structure of the clathrate is tetragonal ($I4_1/a$), with the unit cell containing atoms corresponding to twice the formula. When benzene is enclosed in the cavity provided by the complex, each benzene molecule is comparatively remote from any Ni ion. It is contained in a cavity where it makes contacts at van der Waal's distances with other benzene molecules and with cyanide and ammonia groups.

Since these pioneering investigations were reported, large numbers of other Werner complexes have been prepared and shown to function as hosts for various clathrates. Schaeffer and Williams (54,62) listed as many as 40 complexes of the first row transition metals that were reported to serve as host molecules. M. I. Hart, M. J. Minton and N. D. Smith (27,28,39,40) utilizing $\text{Ni}(4\text{-methylpyridine})_4(\text{NCS})_2$ as the host, investigated and reported the thermodynamic constants, kinetic rate data, infrared spectra, X-ray analyses and phase diagrams for several of these clathrates. Belitskus, et. al. (4), undertook single crystal x-ray analyses of the clathrates formed by cobalt and nickel tetra-4-methylpyridine diisothiocyanate. Recent work by Lok (30,37), Vasantha (55), and Chou (12) showed that there are definite relationships between guest/host sizes, temperature, guest concentration, and particle sizes of the host molecules during the clathration process.

A survey of published literature indicates that not all of the substances under investigation are "clathrates" as originally defined by Powell. A classification scheme became necessary and the following was proposed:

- I. Complex molecules
 - A. Coordination Compounds
 - B. Inorganic Polymers
 - C. Molecular Compounds
 1. Inclusion Compounds

	<u>Nature of Cavity</u>
a. Urea and thiourea adducts	Channels
b. Zeolite Complexes	Channels
c. Graphite and Silica Complexes	Layers
d. Dextrin-Iodine Type Complexes	Solution
e. Clathrates	Cages

Indeed, inclusion compounds possess characteristic cavities and are distinguished by the nature of the cavity.

At the present time there is indication that this scheme of classification is not inclusive and will require further modification (64).

INTRODUCTION

Introduction

In 1957, Schaeffer and co-workers published a paper entitled "Separation of Xylenes, Cymenes, Methyl-Napthalenes and Other Isomers by Clathration with Inorganic Complexes" (54). This marked the beginning of a new series of inorganic complexes which can be used as hosts in the process of clathration. Since that time, a large number of inorganic Werner complexes have been prepared and their physico-chemical properties, including unit cell dimensions for the crystals, studied. According to Schaeffer's article (54), more than 40 complexes utilizing first row transition metals are capable of forming clathrates and most of the complexes that proved to have clathration properties had four molecules of a nitrogen base co-ordinated with a central metal ion. Indeed, Schaeffer's paper indicated that the three constituents of these complexes (the metal atom, a basic nitrogen compound and the anion) all contribute to the ability of the complexes to form clathrates as well as determining the type of organic molecules that will be clathrated. Typical nitrogen base compounds employed in these investigations were substituted pyridines and quinolines, whereas the anion may be a simple monoatomic ion such as chloride or bromide, or it may be a polyatomic ion such as thiocyanate, formate, cyanate, cyanide, or nitrite. Furthermore, Schaeffer listed two general methods for the preparation of clathrates; the suspension

method and the solution technique. In the present work, only the 'suspension' method was used. Apparently, Schaeffer's work was analytical in nature only, since his paper dealt exclusively with the enrichment of petroleum fractions.

Further work in this laboratory by Lok (30,37) revealed that not all the complexes listed in Schaeffer's paper form clathrates, at least by the suspension technique. Until recently, $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ was the sole complex which had been thoroughly investigated. (4-mepy is an abbreviation used throughout this thesis for 4-methylpyridine.) Hart in his dissertation (28) presented infrared spectra, phase diagrams, calorimetric and X-ray data for the $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ clathrate system. Minton (39,40) working in the same laboratory later presented the results of further kinetic, phase and calorimetric studies in her dissertation on the same subject matter. Casellato and Casu in their article (10), attempted further investigation of the infrared spectra of the clathrates of $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$. X-ray data presented by Hart (27,28) indicated a profound change in the crystal structure of the complex before and after the clathration process. The suspected octahedral configuration of the complex was confirmed by magnetic susceptibility measurements and visible absorption spectra. Subsequent single crystal X-ray studies by Belitskus (4) further confirmed the existence of an octahedral configuration (point group $I4_1/a$).

Minton in her dissertation (39) presents evidence to show that clathration is apparently a first order, reversible

process for p-xylene and ethylbenzene as guests. Work in this laboratory by Chou (12), Lok (30,37) and Vasantha (55) indicated that clathration is not a first order, reversible reaction. Therefore, it became necessary to investigate further the rate processes involved in clathration. The various factors expected to affect the rate of clathration are (i) size of the host crystals, (ii) concentration of the host, (iii) concentration of the guest compound, (iv) temperature, and (v) rate of stirring. However, work by Chou (12) and Vasantha (55) indicated that the particle size of the host crystals and rate of stirring, do not affect the reaction rate of the $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ system significantly. On the other hand, reports by Chou (12) and Vasantha (15) also suggested that for the $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ system, the optimum ratio for the clathration reaction is 40 gms of complex to 10 ml of the guest component.

In this thesis, experiments were designed to study the kinetics of the clathration reactions using Ni, Co, and Fe with the same ligands, NCS^- and 4-mepy and different guest molecules, that is, benzene, toluene and p-xylene. All the kinetic runs were carried out under the assumptions that (i) the rate of stirring has a negligible effect on the clathration reaction and (ii) the optimum ratio for the clathration reaction is indeed 40g of complex to 10 ml of guest. Hence, the only factors that were varied included (i) temperature, and (ii) particle size of the host crystal.

In addition, thermogravimetric experiments on the Ni and Fe complex system were carried out using a thermobalance with the intention of correlating the results with the data obtained on adsorption studies currently being carried out in this laboratory.

Finally, in addition to the conventional $\log(A_t - A_\infty)$ vs. time plots, a plot was made of $\ln(\text{Guest})$ vs. $\ln(\text{time})$ following the kinetic rate expression suggested by Lahr and Williams, (62) to test whether such an expression is valid for the systems studied in this research project.

The kinetic rate expression suggested by Lahr and Williams is:

Rate = $k \times (\text{Guest}) / (\text{Host}) \times \text{Time}$, where k =
rate constant.

INSTRUMENTATION

Instrumentation

Temperature

All kinetic rate studies were carried out in a constant temperature bath capable of regulation to $\pm 0.2^{\circ}\text{C}$. Temperature measurements were made with a thermometer calibrated and certified by the National Bureau of Standards.

Spectral Measurements

Ultraviolet spectra were obtained on a Beckman DB-G Grating Spectrophotometer, using Beckman silica cells. A Beckman Model 1005 Recorder was used to record the spectra.

X-ray Measurements

The X-ray powder diffraction patterns were obtained on a Siemens Kristalloflex 4, X-ray Diffractometer, using copper k-alpha radiation. A Siemens two radian camera was used and line measurements were made with a coincidence scale having an accuracy of ± 0.01 mm.

Analytical Measurements

An Ainsworth Type 21N single pan automatic balance was used for all weighings.

Thermogravimetric Analysis Measurements

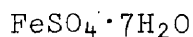
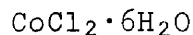
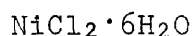
All thermogravimetric analyses were carried out in a thermobalance constructed by Kingston (32).

EXPERIMENTAL

Experimental

Preparation of M (4-mepy)₄(SCN)₂ (M = Ni, Co and Fe)

To 0.228 moles of each of the following hydrates dissolved in 3 liters of water was added 0.456 moles of KSCN



After complete solution of the metal salt and thiocyanate, 0.910 mole of 4-methylpyridine was added slowly with constant stirring. The mixture was then stirred for an additional half hour before filtering. The precipitate was air dried for four to six hours and then transferred to a dessicator and stored over solid potassium hydroxide. Removal of all moisture required approximately one week. All chemicals used in this preparation were of analytical Reagent Grade. A large excess of water was used in the precipitation in order to prevent the co-precipitation of thiocyanate.

An indication of the purity of the complexes was obtained by quantitative analysis for the percent of metal in each of the compounds.

Purification of Solvent

It was necessary to purify Reagent Grade heptane before it was used as a suspension medium in the kinetic rate studies. Ultraviolet spectral studies revealed that the purified heptane was of equal purity as commercially marketed 'Spectro-quality Grade' heptane.

The purification procedure was as follows: First, heptane was transferred to a large separatory funnel containing concentrated sulphuric acid. The extraction process was then accomplished with periodic shaking of the mixture over a period of twenty four hours. The heptane layer in the mixture was then neutralized with 10% sodium carbonate solution, followed by a salting-out process using saturated sodium chloride solution. The heptane was dried by passing it through a column of anhydrous calcium chloride and then fractionally distilled. Purity of the resultant heptane was checked using ultraviolet spectra with 'Spectroquality Grade' heptane as reference.

Kinetic Rate Studies

All kinetic rate studies were carried out in a thermostat capable of regulation to $\pm 0.2^{\circ}\text{C}$.

A one liter volumetric flask containing 300 ml of purified heptane was placed in the thermostat and allowed to come to equilibrium. Ten milliliters of the guest component (benzene, toluene, or p-xylene) was then introduced and the solution stirred by means of a magnetic stirrer located beneath the thermostat. After thermal equilibrium was reached, approximately one milliliter of the solution was withdrawn by means of a filter stick. A micro-pipet was then used to transfer exactly 0.1 ml of each of the samples to a 25 ml volumetric flask and the resultant mixture diluted to the mark with purified heptane.

Following the withdrawal of the initial sample, the Werner complex was then introduced into the reaction flask. An amount slightly less than required for a 1:1 ratio of guest to host was employed and the initial time for the kinetic run was taken as the time the complex was introduced into the solution.

At pre-selected time intervals, 1.0 milliliter samples of solution were withdrawn from the reaction vessel by means of filter sticks and exactly 0.1 ml of each of these samples was transferred to a 25 ml volumetric flask and diluted to the mark with purified heptane.

Each of the kinetic rate studies was allowed to proceed for not less than 48 hours. The change in guest concentration present as a function of time was determined by a Beckman DB-G Spectrophotometer operating in the ultraviolet region at pre-selected wavelengths.

At the completion of each kinetic run, contents of the reaction vessels were emptied, filtered, and the solid component air dried. The solid material was then analysed quantitatively for the metal content and also used in obtaining X-ray powder diffraction patterns.

X-Ray Diffraction Patterns

Samples of each of the complexes and the solid contents obtained from each of the kinetic runs were used for X-ray powder diffraction studies. Samples were prepared by mixing the powdered samples with collodion and then extruding the

partially dried samples from capillary tubes of 0.5 mm diameter.

X-ray diffraction patterns were obtained with a Siemens two radian camera using filtered copper k-alpha radiation and exposure times of 1 to 2 hours depending on the samples employed.

Quantitative Analysis

The percentages of metals in the complexes and clathrates under investigation were determined by standard analytical procedures. Dilute hydrochloric acid was used to dissolve the clathrates and complexes of Fe and Ni, whereas heat was utilized for clathrates and complexes of Co.

The percent of Ni(II) in the complexes and clathrates was determined volumetrically by titrating the nickel solution with standardized EDTA solution using murexide as indicator.

The percent of Fe(II) in the complexes and clathrates was determined by igniting preweighed samples of iron in a crucible, dissolving the residue with 6N HCl, and then reducing the Fe(III) ions to Fe(II) using SnCl₂ solution. HgCl₂ and MnSO₄ solutions were then added sequentially and the final solution titrated with standardized KMnO₄ solution.

The percent of Co(II) in the complexes and clathrates was determined by treating preweighed samples of cobalt with α -nitroso β -naphthol and then dissolving the resulting precipitate in a small amount of hydrochloric acid, nitric

acid, and 5 ml of 1:1 sulphuric acid. The solution was then evaporated, neutralized with ammonium hydroxide (with 40 ml in excess) and the final solution electrolyzed at 2 amp for 1 hour using a rotating Pt electrode.

Thermogravimetric Analysis

The isothiocyanatopyridine compounds investigated in this study were prepared by the reaction between a salt (sulfate or chloride) of the appropriate transition metal, potassium thiocyanate and 4-methylpyridine in aqueous solution. The products were dried in a dessicator until constant weight was attained.

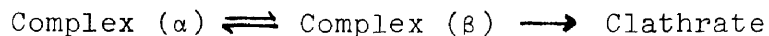
A thermobalance constructed by Kingston (32) was used. The experimental technique was the same as that previously reported (64). All decompositions were carried out under an oxygen atmosphere at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Results and Discussion

Kinetic Studies

Kinetic rate studies on gas hydrates have been reported by Barrer and Ruzika (3) and for the hydroquinone clathrates by Lahr and Williams (34). The first kinetic rate studies on Werner complex clathrates were reported by Gawalek et.al. (25); they revealed that the time for clathrate formation was less than fifteen minutes and that the solubility of the complex in the hydrocarbon suspension medium greatly effects the rate of formation of the clathrates. Further kinetic rate investigations by Minton and Smith (39,40) indicated that the clathration reaction was completed in four to six hours and was characterized by an apparent initial increase in guest concentration. They attributed this increase to either adsorption or absorption of heptane by the complex. They also reported that the reaction appeared to follow first order, reversible, kinetics. Lok (30,37) attributed this initial rise in concentration to an excess of 4-methylpyridine and suggested that this can be eliminated by extracting the solution with 6N HCl. Based on their research, Hart and Smith (27,28) proposed an equation to represent the clathration process:



where the symbol α represents the lattice of the complex and β the "empty" lattice of the clathrate. According to the

proposed equation, it suggests that a lattice change occurs during the clathration process. Minton (39,40) described the process of clathration as: "the clathration reaction would not begin until the guest molecule could displace solvent molecules, come in contact with the complex, dissolve it to some extent and bring about the lattice change by precipitation. Then, when the lattice change was at least partially accomplished the guest molecules could move into the host."

Contrary to the findings of Minton et.al, work in this laboratory by Jacobs and Lok (30), Chou (12) and Vasantha (55) all suggest that the clathration process is not a first order, reversible reaction using benzene, toluene and p-xylene as the guests. It has also been shown conclusively by Chou and Vasantha (12,55) that factors like the rate of stirring and particle size of host crystals have little or no effect on the reaction rate. In addition, it has been shown that the optimum host to guest ratio for clathrate formation is 40 g of complex to 10 ml of guest.

Utilizing the above findings with the assumptions that (i) stirring rate has a negligible effect on the kinetic rate, and (ii) the optimum host to guest ratio is 40 g of complex and 10 ml of guest, a re-determination of the published data on the rates of clathrate formation between $\text{Ni(4-mepy)}_4(\text{NCS})_2$ and benzene, toluene, and p-xylene was then undertaken. The results from the rate studies, X-ray powder patterns, and gravimetric metal analyses were in total agreement with the

earlier work of Minton (39,40), Belitskus (4), Chou (12), Lok (30,37), and Vasantha (55) which support clathrate formation.

Further kinetic runs were then carried out at different temperatures (5°C, 15°C, 25°C, 35°C) on the Werner complexes $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ and $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ utilizing different guest molecules and varying the host crystals' particle sizes.

Temperature

This effect was studied at 5°C, 15°C, 25°C, and 35°C using 40g of host and 10 ml of guest.

(I) $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$: the change in guest concentration (measured as a decrease in absorbance) with time during the clathration process is shown in Tables I through III. The results of gravimetric analyses are presented in Tables IV, and V and the X-ray powder patterns in Table VI. Figures I through III represent the results of the kinetic rate studies. Tables I through III present the change in guest concentration (measured as a decrease in absorbance) with time using 40g of complex and 10 ml of guest in each case. Figures I through III show the absorbance as a function of time. These figures show that when benzene is used as the guest molecule, all show an initial rise in absorbance except the case at 5°C, whereas when toluene is used, every case shows an initial rise in absorbance and when p-xylene is used as the guest, the kinetic runs at 5°C and 35°C show an initial rise in absorbance. Such behaviour could be due to

TABLE I

CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ AND BENZENE

TIME (HOURS)	ABSORBANCE OF BENZENE AT 255 nm			
	SAMPLE I ^a	SAMPLE II ^a	SAMPLE III ^a	SAMPLE IV ^a
0	0.240	0.200	0.278	0.234
½	0.238	0.230	0.308	0.302
½	0.215	0.233	0.330	0.308
1	0.200	0.252	0.300	0.316
2	0.187	0.262	0.289	0.218
3	0.185	0.242	0.277	0.185
4	0.150	0.219	0.268	0.185
6	0.148	0.191	0.262	0.152
8	0.138	0.180	0.240	0.152
10	0.140	0.180	0.238	0.150
12	0.138	0.162	0.234	0.130
24	0.134	0.150	0.225	0.128
28	0.114	0.144	0.212	0.104
32	0.114	0.130	0.200	0.126
36	0.115	0.120	0.203	0.114
48	0.113	0.115	0.189	0.113

^aSamples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40 g of complex and 10 ml of benzene in 300 ml heptane.

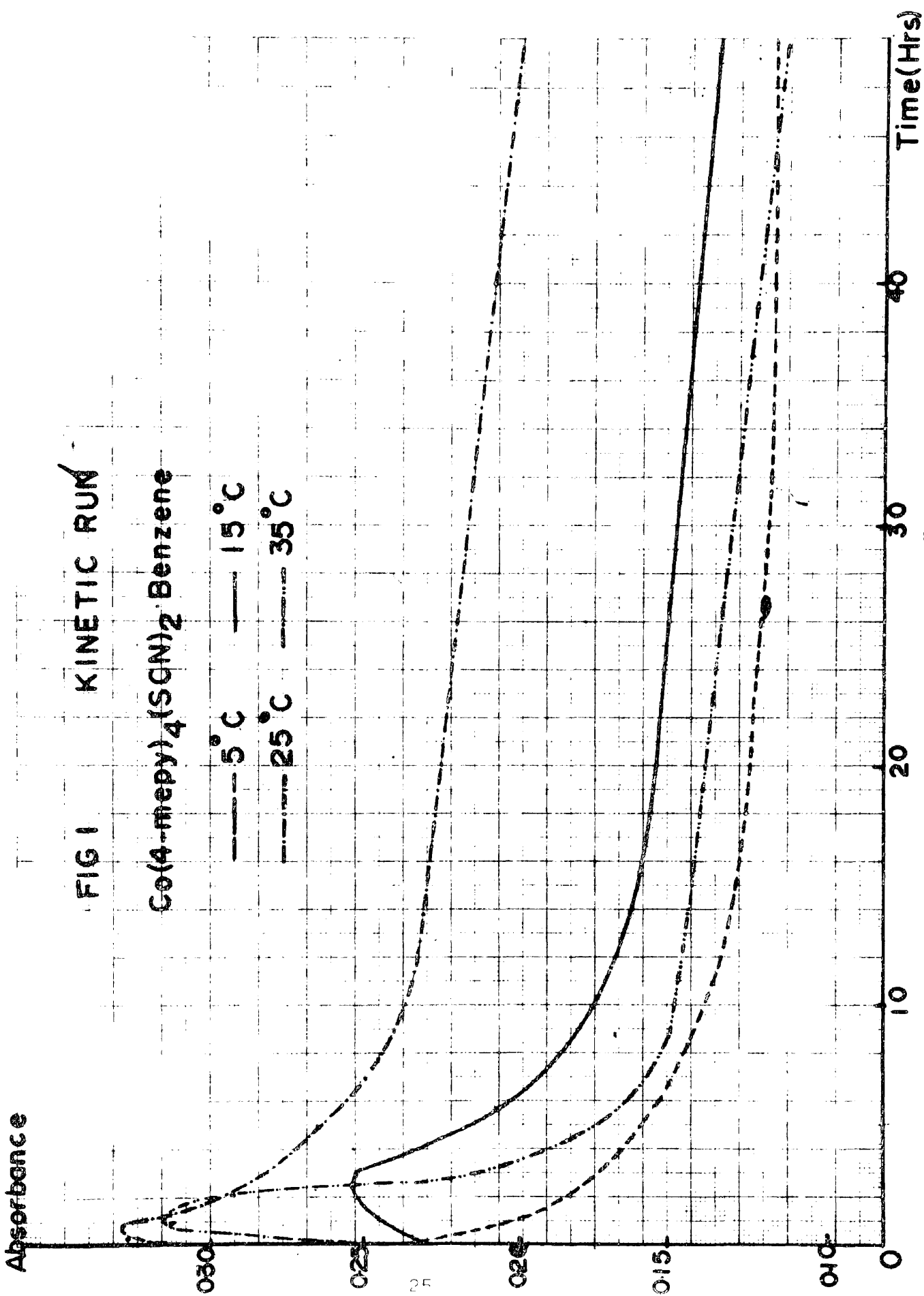
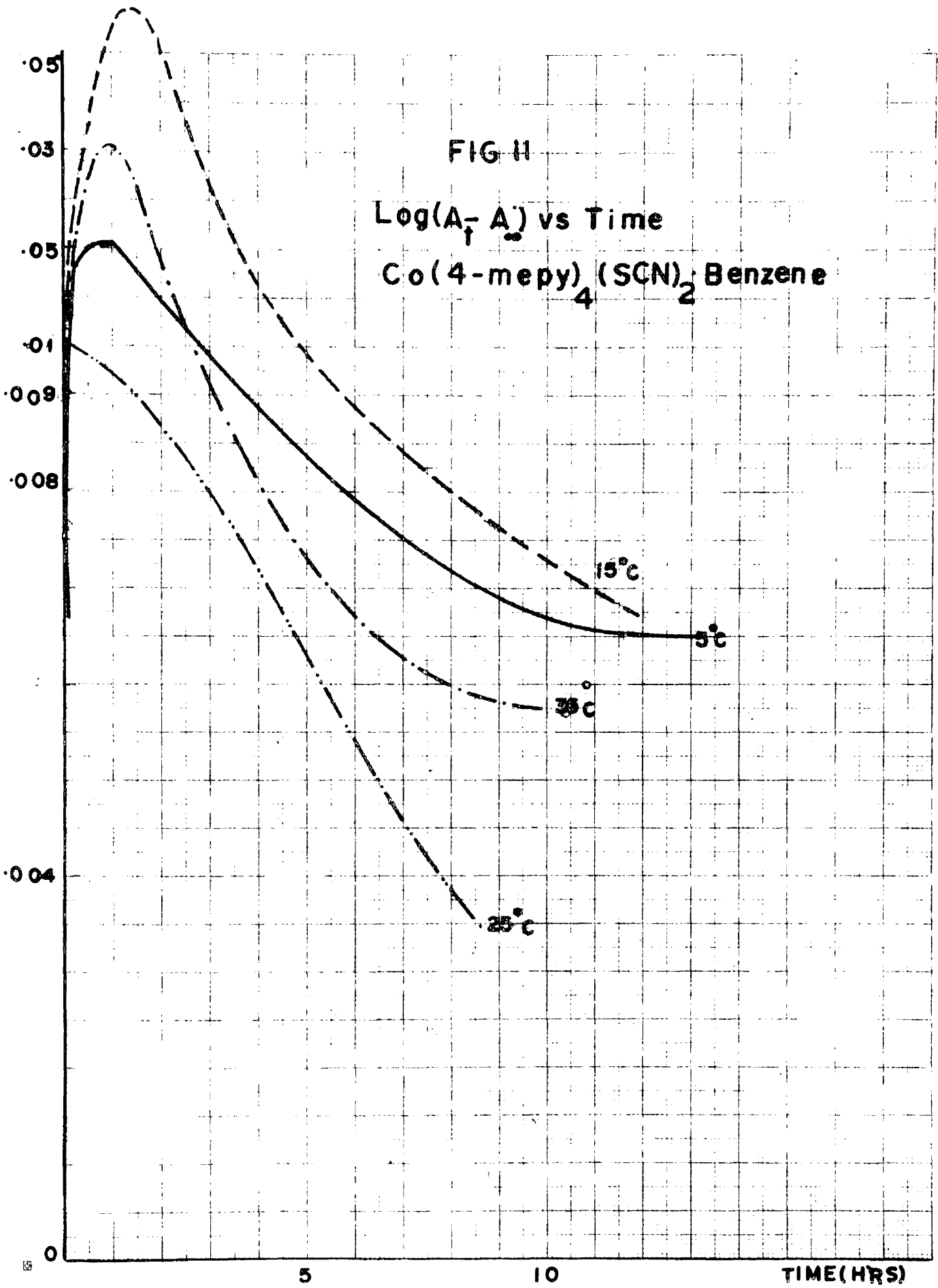


FIG II

Log(A_t - A_∞) vs Time

Co(4-mepy)₄(SCN)₂ Benzene



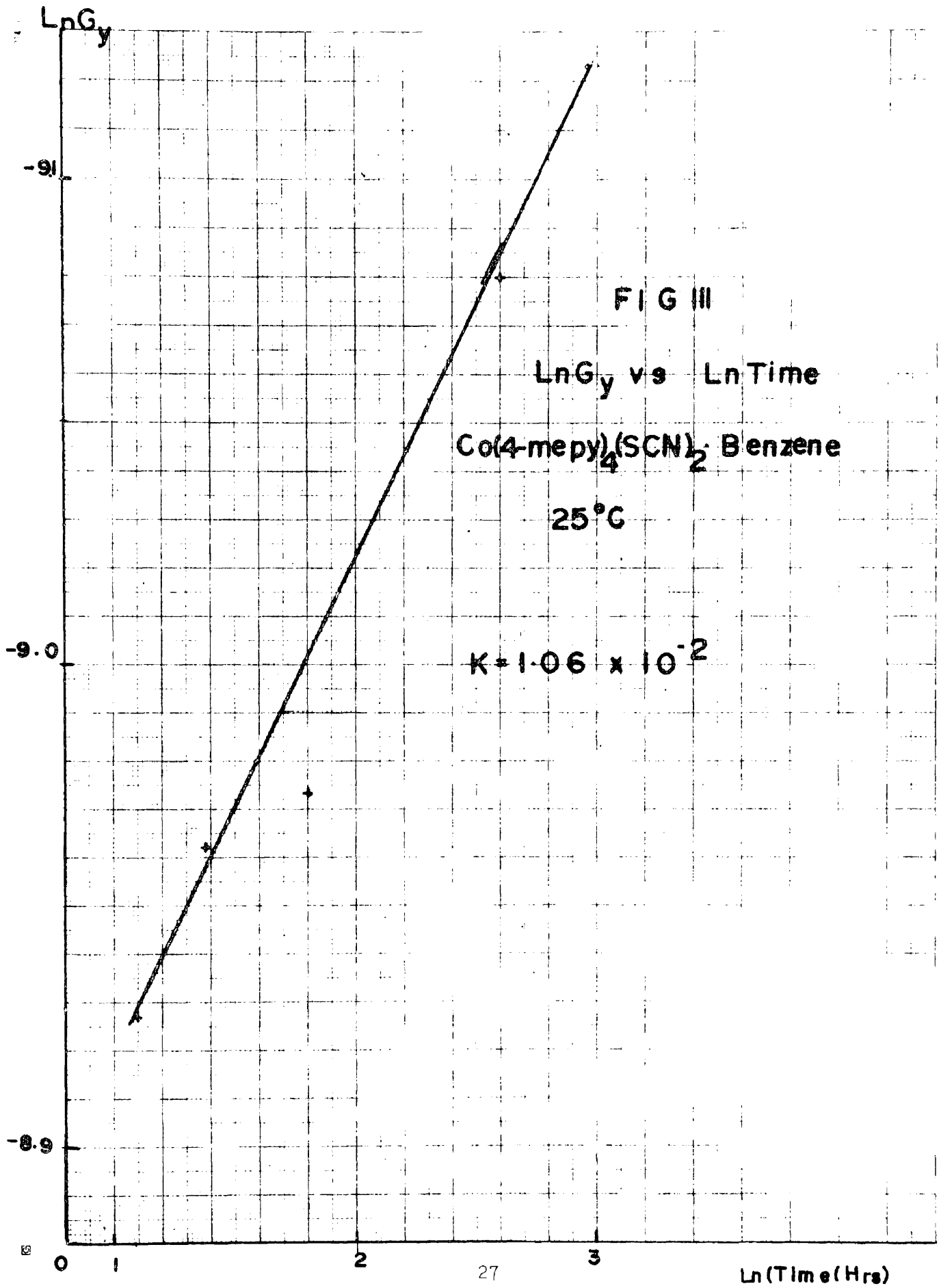


TABLE II

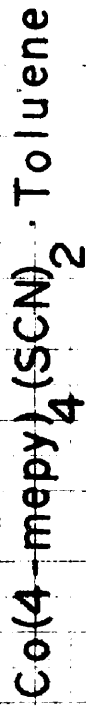
CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ AND TOLUENE

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.270	0.275	0.274	0.296
$\frac{1}{4}$	0.273	0.279	0.301	0.322
$\frac{1}{2}$	0.278	0.281	0.315	0.323
1	0.281	0.290	---	0.323
2	0.281	0.282	0.322	0.301
3	0.268	0.250	0.298	0.270
4	0.254	0.249	0.288	0.270
6	0.240	0.248	0.264	0.259
8	0.222	0.250	0.250	0.260
10	0.212	0.243	0.240	0.260
12	0.209	0.235	0.230	0.259
24	0.185	0.216	0.227	0.258
28	0.180	0.210	0.212	0.259
32	0.178	0.185	0.202	0.259
36	0.176	0.200	0.182	0.256
48	0.164	0.190	0.187	0.240

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40 g of complex and 10 ml of toluene in 300 ml heptane.

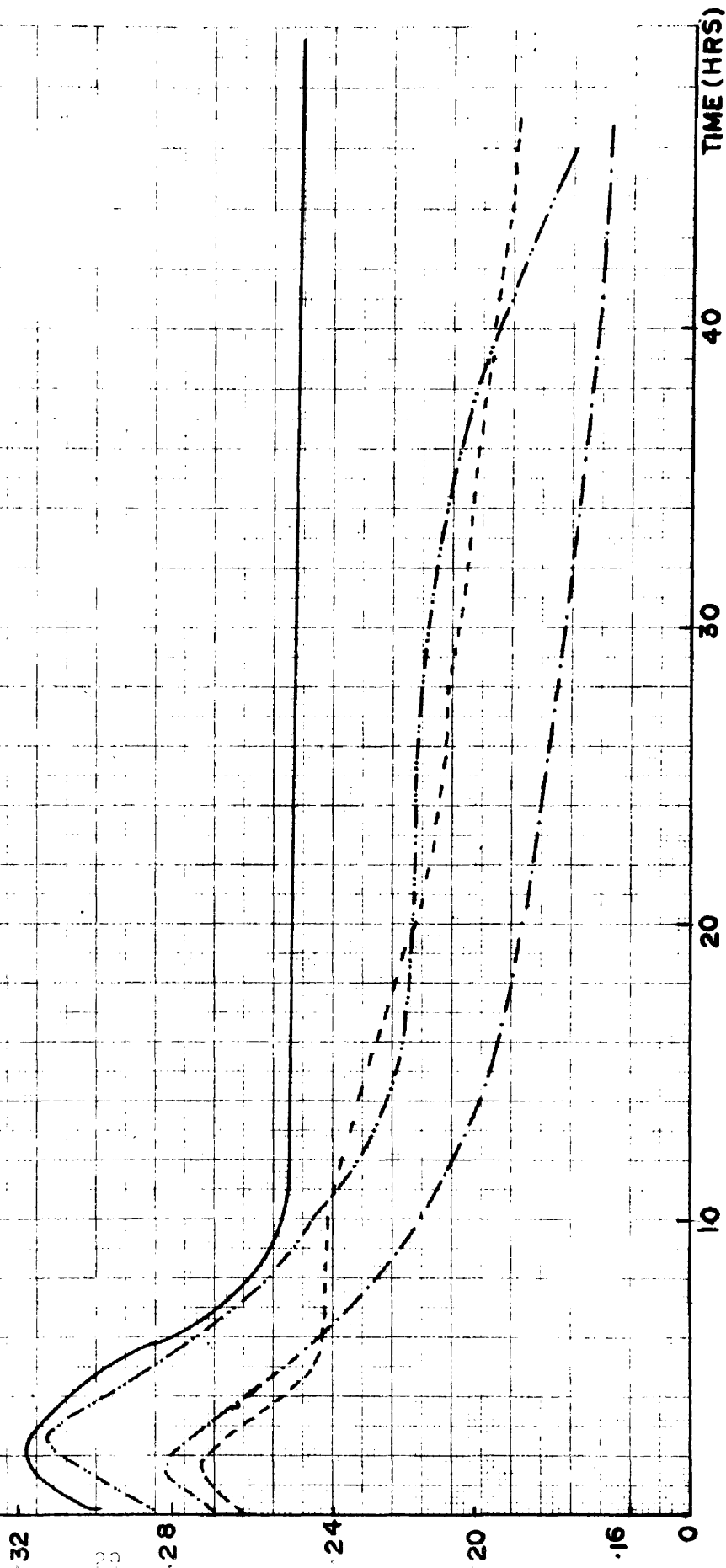
Absorbance

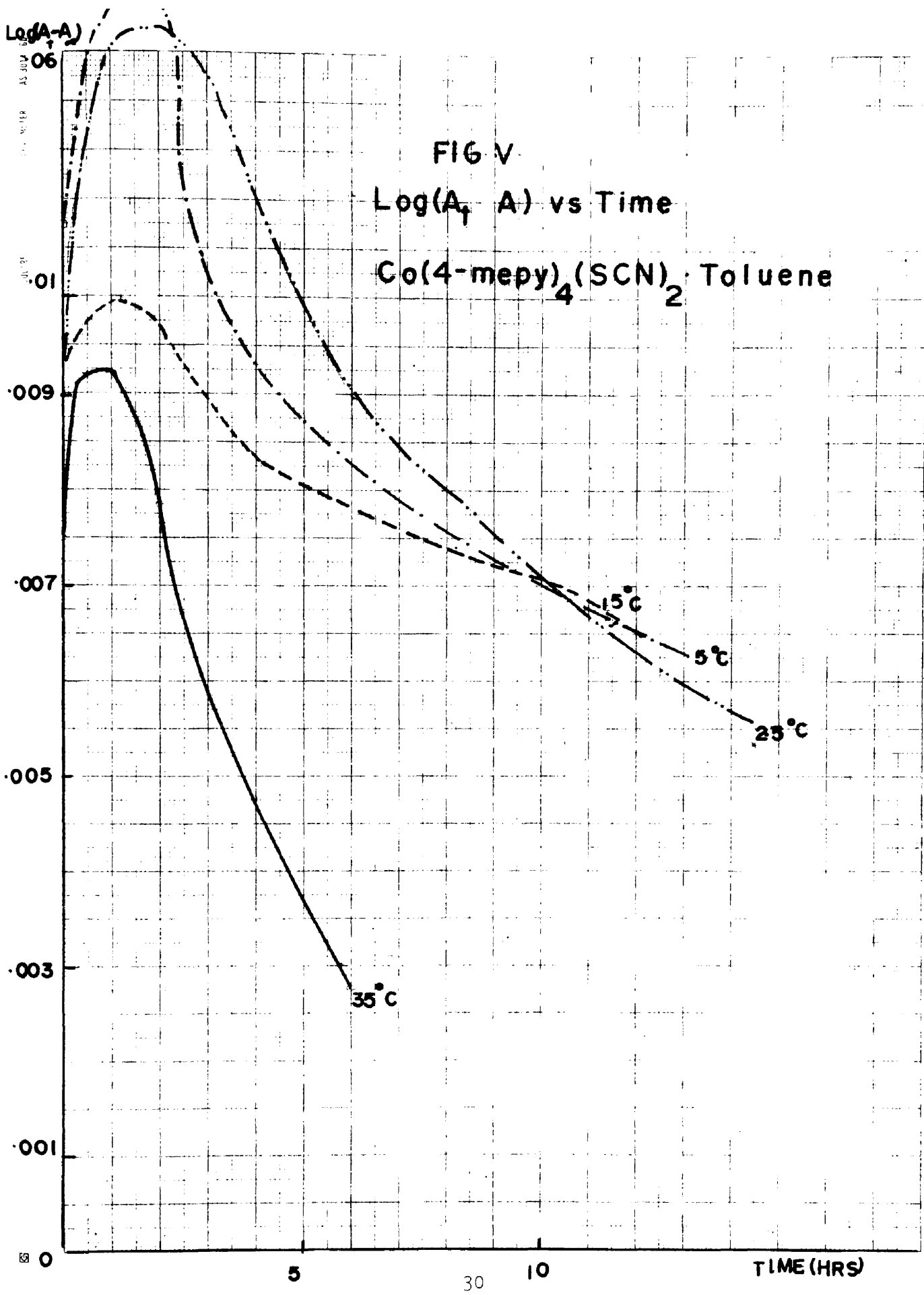
FIG IV KINETIC RUN



--- 5°C --- 15°C

— 25°C — 35°C





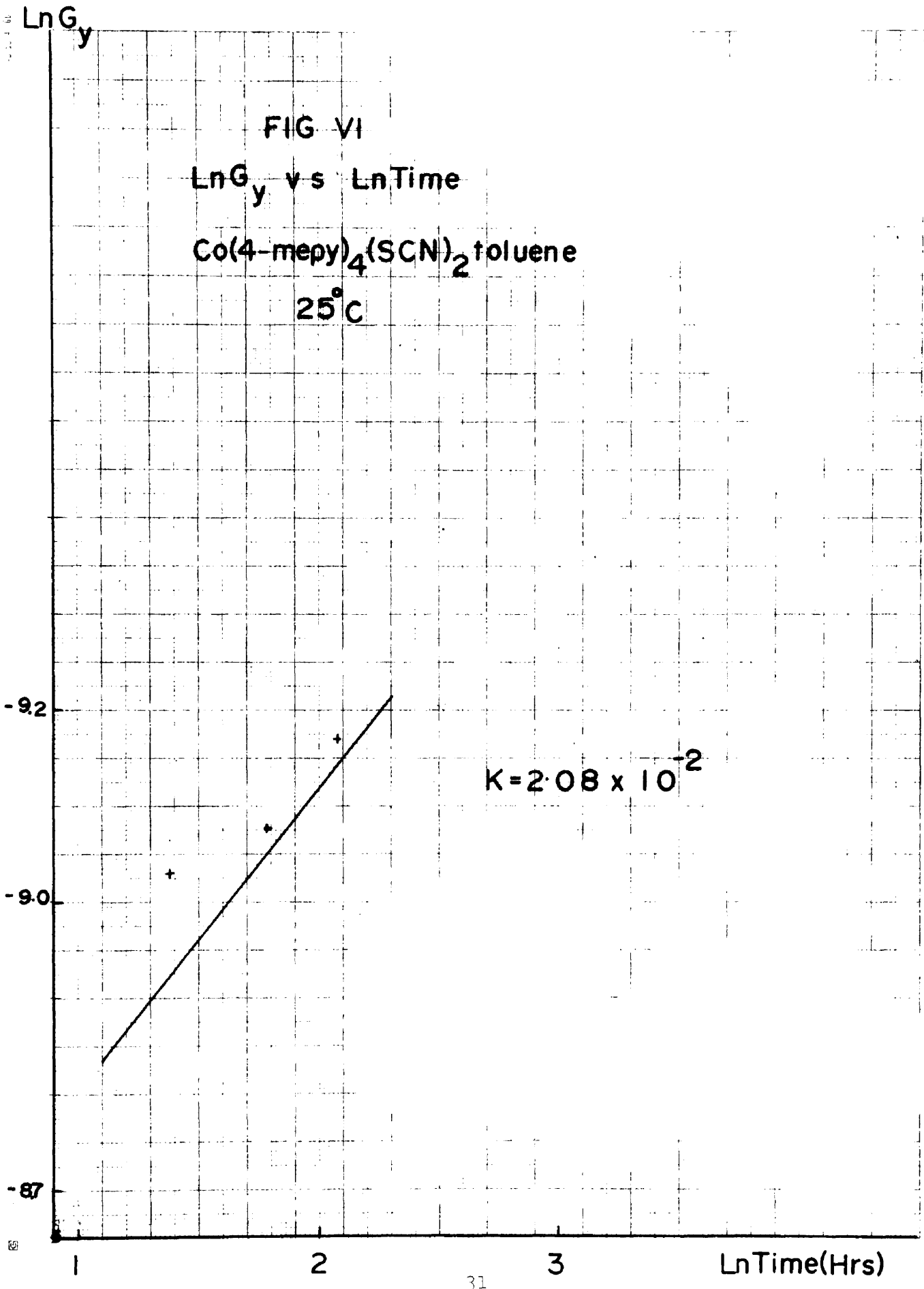


TABLE III

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION
REACTION BETWEEN $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ AND p-XYLENE

TIME (HOURS)	ABSORBANCE OF p-XYLENE AT 275 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.5900	0.5780	0.5800	0.5900
¼	0.6400	0.5600	0.5600	0.5600
½	0.6000	0.5180	0.5430	0.5380
1	0.5830	0.4700	0.5030	0.4380
2	0.5300	0.3900	0.4460	0.3220
3	0.5600	0.3420	0.4440	0.2780
4	0.4040	0.3200	0.4440	0.2440
6	0.3400	0.2880	0.3900	0.2260
8	0.3300	0.2600	0.3640	0.1980
10	0.2300	0.2380	0.3480	0.1850
12	0.2020	0.2220	0.3440	0.1750
24	0.1640	0.2020	0.2820	0.1690
28	0.1430	0.1940	0.2620	0.1650
32	0.1260	0.1930	0.2600	0.1650
36	0.1190	0.1950	0.2490	0.1600
48	0.1190	0.1860	0.2280	0.1540

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40 g of complex and 10 ml of p-xylene in 300 ml heptane.

Absorbance

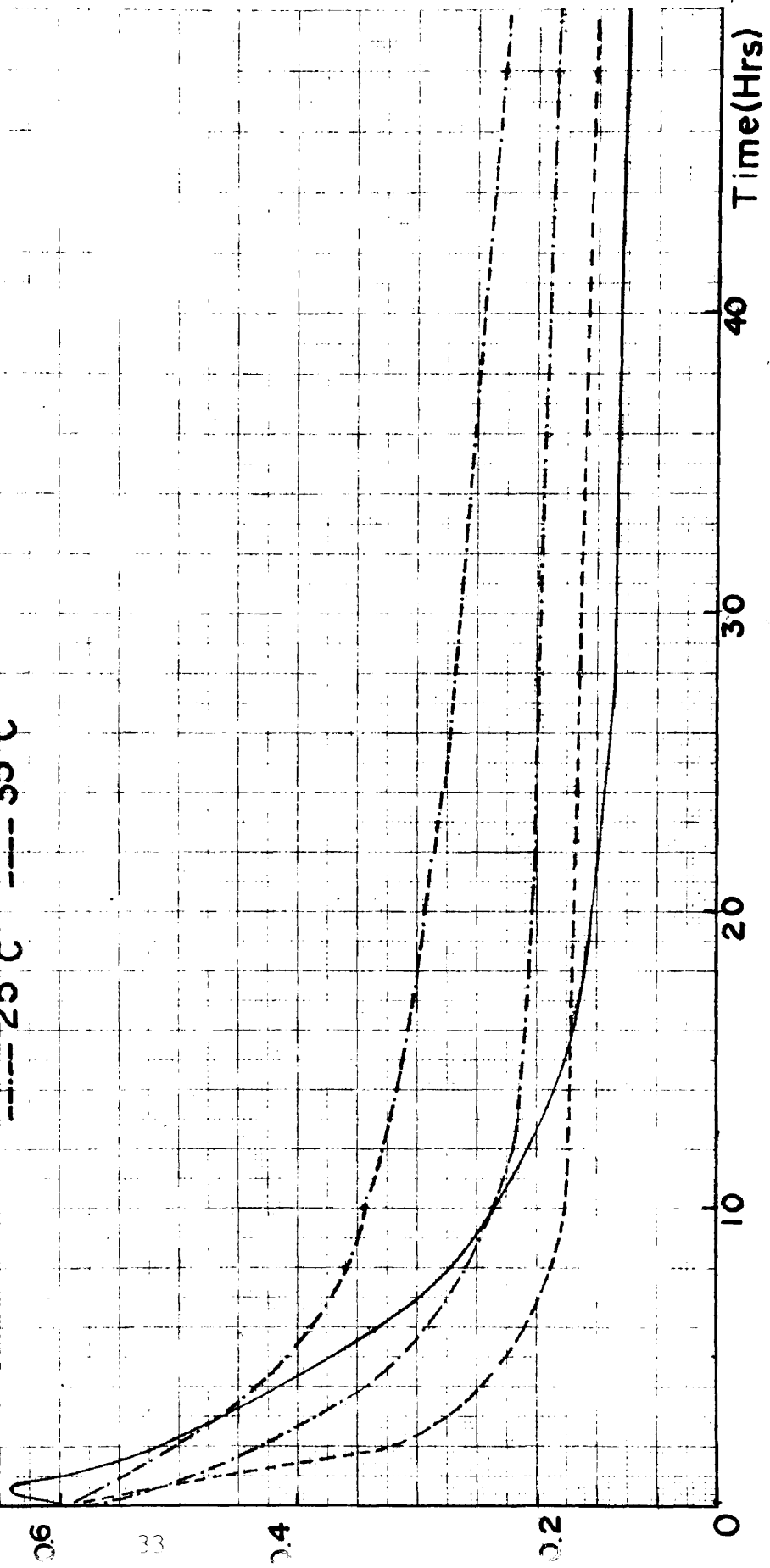
FIG VII KINETIC RUN

HOST MOLECULE $\text{Co}(\text{4-mepy})_4 (\text{SCN})_2$

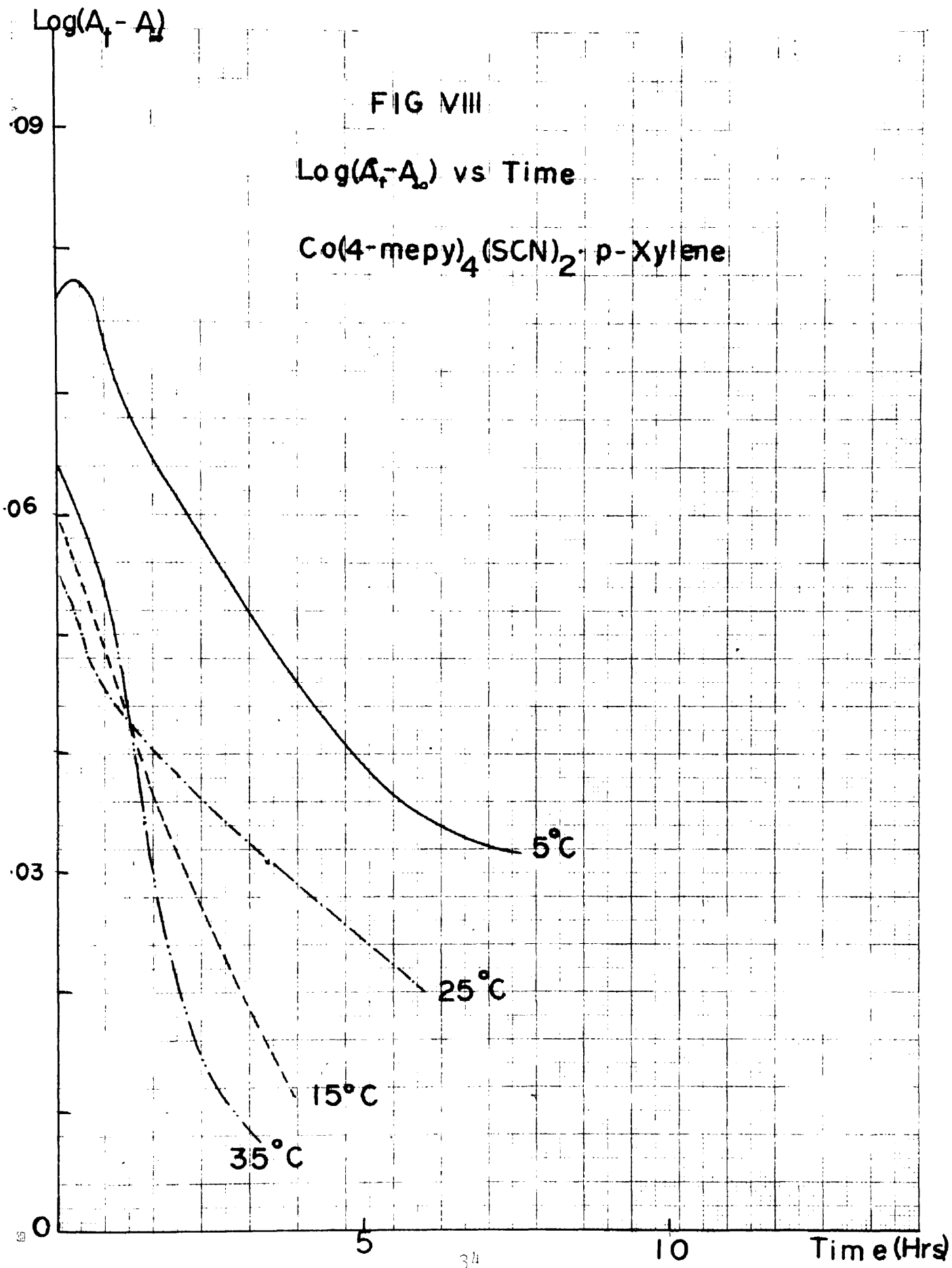
GUEST MOLECULE p-xylene

— 5°C - - - 15°C

- · - · 25°C - - - - 35°C



Time(Hrs)



$\ln G_y$

FIG (X)

$\ln G_y$ vs \ln Time

(G_y = Concentration of Guest
at time t)

$\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ / p -xylene

25°C

-9.5

$K = 0.51 \times 10^{-2}$

-90

1

2

3

3

4

\ln Time (Hrs)

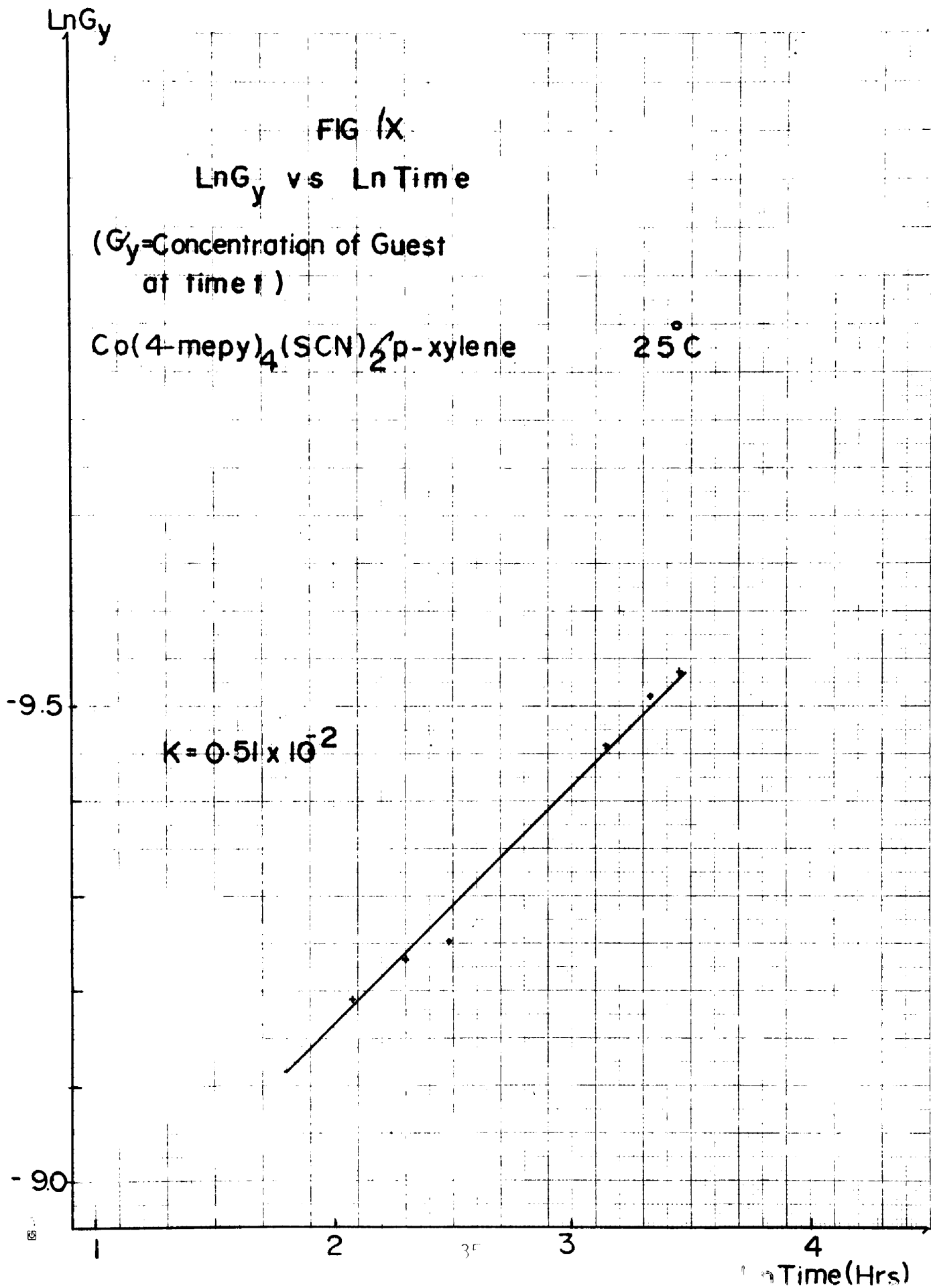


TABLE IV

GRAVIMETRIC ANALYSES FOR Co IN THE COMPLEX $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$
AND THE BENZENE AND TOLUENE CLATHRATES

BENZENE CLATHRATE

TRIAL	COMPLEX	BENZENE CLATHRATE	PERCENT Co			
			I*	II*	III*	IV*
1	10.74		10.28	10.10	9.60	9.50
2	10.70		10.30	10.08	9.58	9.48
AVERAGE	10.72		10.29	10.09	9.59	9.49
THEORETICAL	10.76					
MOLE RATIO (GUEST/HOST)			0.318	0.469	0.823	0.895

TOLUENE CLATHRATE

TRIAL	COMPLEX	TOLUENE CLATHRATE	PERCENT Co			
			I*	II*	III*	IV*
1	10.74		9.85	9.70	9.78	9.65
2	10.70		9.88	9.72	9.76	9.63
AVERAGE	10.72		9.86	9.71	9.82	9.64
THEORETICAL	10.76					
MOLE RATIO (GUEST/HOST)			0.581	0.509	0.607	0.723

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively with 40g of complex and 10 ml of benzene or toluene as guest in 300 ml of heptane.

TABLE V

GRAVIMETRIC ANALYSES FOR Co IN THE COMPLEX $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$
AND THE p-XYLENE CLATHRATE

TRIAL	COMPLEX	CLATHRATE	PERCENT Co			
			I*	II*	III*	IV*
1	10.74		9.74	9.68	9.54	9.40
2	10.70		9.70	9.62	9.50	9.43
AVERAGE	10.72		9.72	9.67	9.52	9.41
THEORETICAL	10.76					
MOLE RATIO (GUEST HOST)			0.597	0.624	0.710	0.773

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively with 40g of complex and 10 ml of p-Xylene in 300 ml of heptane.

TABLE VI

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS
FROM THE $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ COMPLEX AND THE BENZENE,
TOLUENE, AND p-XYLENE CLATHRATES

COMPLEX		CLATHRATE		
OBSD	LIT*	BENZENE	TOLUENE	p-XYLENE
		13.86		
8.38	8.58	8.43	8.50	8.39
7.02	7.69		7.05	7.16
5.71	6.88			5.84
5.21		5.23	5.34	5.25
5.01	5.09			4.90
4.63	4.55	4.62	4.61	4.57
4.26	4.37			
	4.10	3.97	3.96	3.98
	3.88			3.92
	3.61	3.63	3.62	3.35
	3.14	3.11		3.11
	2.99			

*Lok, M. T., M. A. thesis, Northern Michigan University,
January, 1970

increased adsorption or absorption of solvent molecules or due to the existence of free 4-methylpyridine in solution. The period required for first observing a decrease in guest concentration using p-xylene is found to be shorter than was the case using benzene as the guest. This is contrary to the case where $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ was used as the host (12). Figures I, II, V, and VIII are plots of $\log(A_t - A_\infty)$ vs. time at various temperatures and different guest molecules. From these curves it would appear that the clathration reaction, utilizing different guest molecules, is not a first order reaction except perhaps in a very small region. Utilizing the expression proposed by Lahr and Williams (34), it is further found that there is indeed a small region in which the reaction appears to follow a first order rate law and this is shown in the \ln (concentration of guest at t time) vs. \ln Time plots in Figures III, VI, and IX. From these curves, the rate constants were calculated.

(II) $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$: the change in guest concentration (measured as a decrease in absorbance) with time during the clathration process is shown in Table VII through Table IX. The results of gravimetric analyses are presented in Tables X and XI and the X-ray powder patterns in Table XII. Figures X, XI, and XII represent the results of kinetic rate studies. Tables VII through IX show the change in guest concentration with time using 40g of complex and 10 ml of guest in each case. Figures X, XI and XII show the absorbance as a function

of time. These figures show that when benzene and toluene are the guest molecules, there is a continuous rise in absorbance with time suggesting that no clathrates are formed. X-ray analyses confirm that no clathrates were formed, contrary to the findings of Lok (30,37). However, when p-xylene is the guest molecule, a plot of absorbance vs. time shows a decrease in absorbance with time and X-ray analyses show that there is indeed a lattice change confirming the formation of clathrates. The failure of benzene and toluene to form clathrates with the $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ complex could be attributed to the size factor of the guest molecules employed in clathration as previously shown in this laboratory (30,37). Gravimetric analyses for Fe(II) are shown in Tables X, XI. However, the results are unfruitful probably due to the presence of a mixture of Fe(II) and Fe(III) present in the final residue. Indeed, negligence in preparing the complex could also contribute to the failure of clathration with benzene and toluene molecules. The anomalous behaviour of a constant rise in absorbance with time in the cases of benzene and toluene suggest continuous adsorption or absorption of solvent molecules by the complex. However, such an explanation is not entirely satisfactory and will require further clarification. A plot of $\log (A_t - A_\infty)$ vs. time is shown in Figure XIII and such a plot implies that clathration reactions are not first order except in a small region.

TABLE VII

CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ AND BENZENE

TIME (HOURS)	ABSORBANCE OF BENZENE AT 255 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.184	0.270	0.161	0.318
¼	0.196	0.275	0.234	0.354
½	0.204	0.280	0.234	0.368
1	0.200	0.282	0.235	0.365
2	0.229	0.294	0.235	0.414
3	0.238	0.320	0.258	0.449
4	0.244	0.321	0.259	0.458
6	0.267	0.320	0.267	0.498
8	0.268	0.320	0.272	0.498
10	0.268	0.322	0.278	0.524
12	0.268	0.325	0.313	0.550
24	0.301	0.331	0.345	0.599
28	0.362	0.335	0.355	0.624
32	0.431	0.340	0.375	0.623
36	0.444	0.378	0.409	0.624
48	0.480	0.342	0.449	---

*Samples I, II, III, and IV refer to kinetic runs at 5°C, 15°C, 25°C, and 35°C respectively for 40 g of complex and 10 ml of benzene in 300 ml heptane.

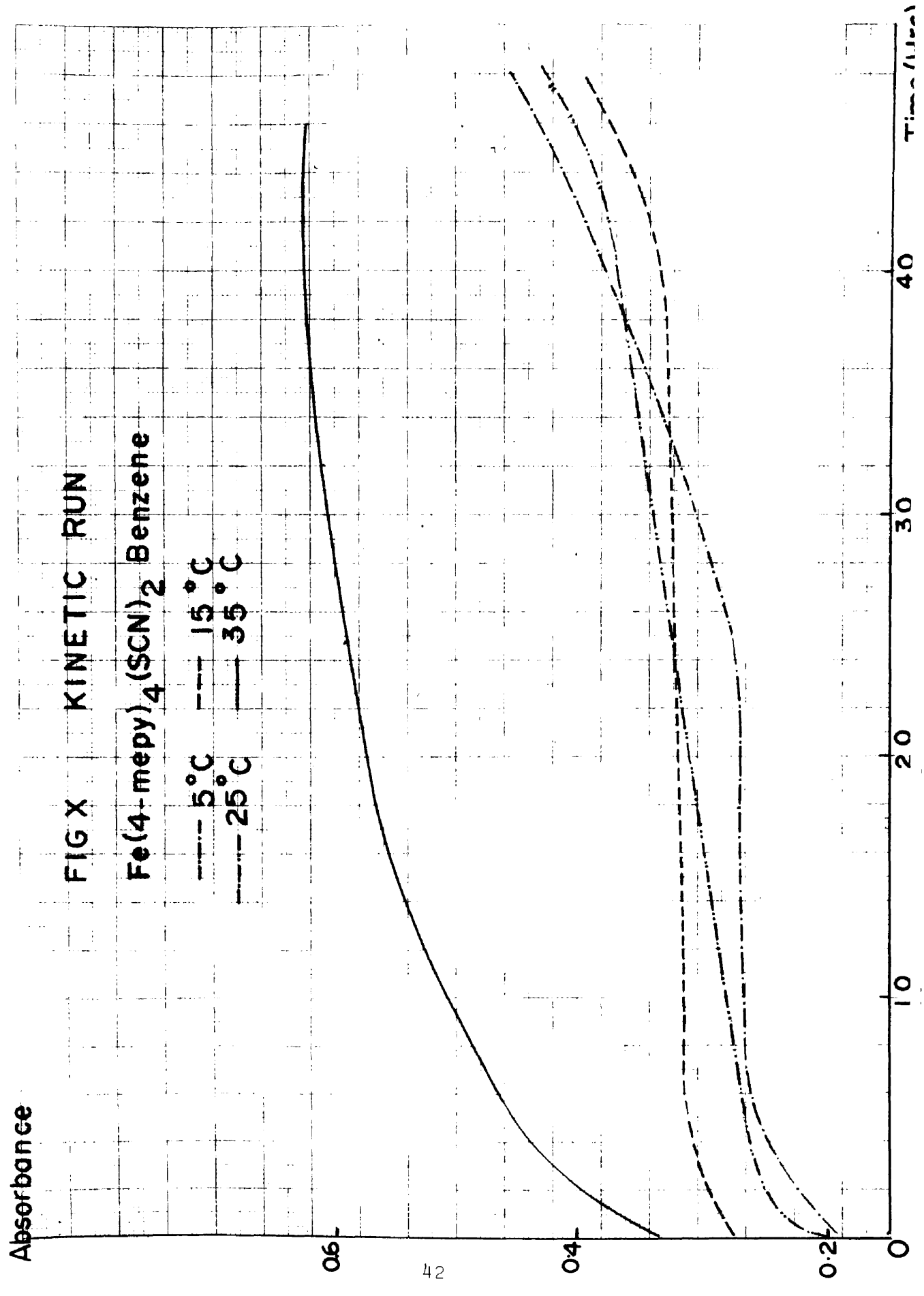


TABLE VIII

CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ AND TOLUENE

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.259	0.274	0.310	0.310
¼	0.278	0.310	0.316	0.339
½	0.283	0.315	0.359	0.348
1	0.289	0.317	0.359	0.359
2	0.293	0.316	0.360	0.362
3	0.292	0.316	0.380	0.362
4	0.300	0.317	0.385	0.373
6	0.302	0.317	0.410	0.377
8	0.302	0.318	0.430	0.375
10	0.304	0.319	0.435	0.378
12	0.303	0.320	0.435	0.400
24	0.304	0.322	0.464	0.442
28	0.305	0.325	0.445	0.435
32	0.308	0.322	0.442	0.384
36	0.309	0.322	0.442	0.440
48	0.308	0.320	0.422	0.443

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, 35°C respectively for 40g of complex and 10 ml of toluene in 300 ml of heptane.

Absorbance

FIG XI KINETIC RUN

$\text{Fe}(\text{4-mepy})_4 (\text{SCN})_2 \cdot \text{Toluene}$

— 5°C --- 15°C

- - - 25°C - - - 35°C

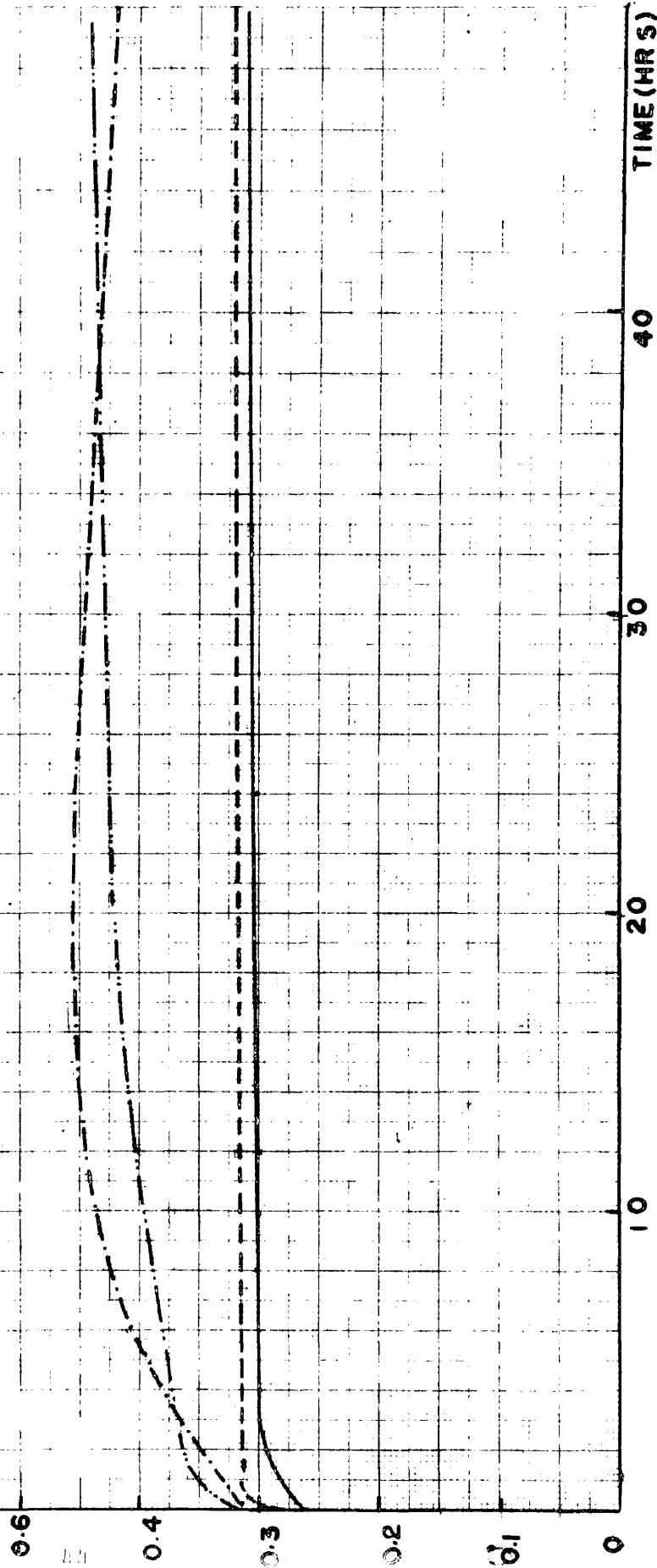


TABLE IX

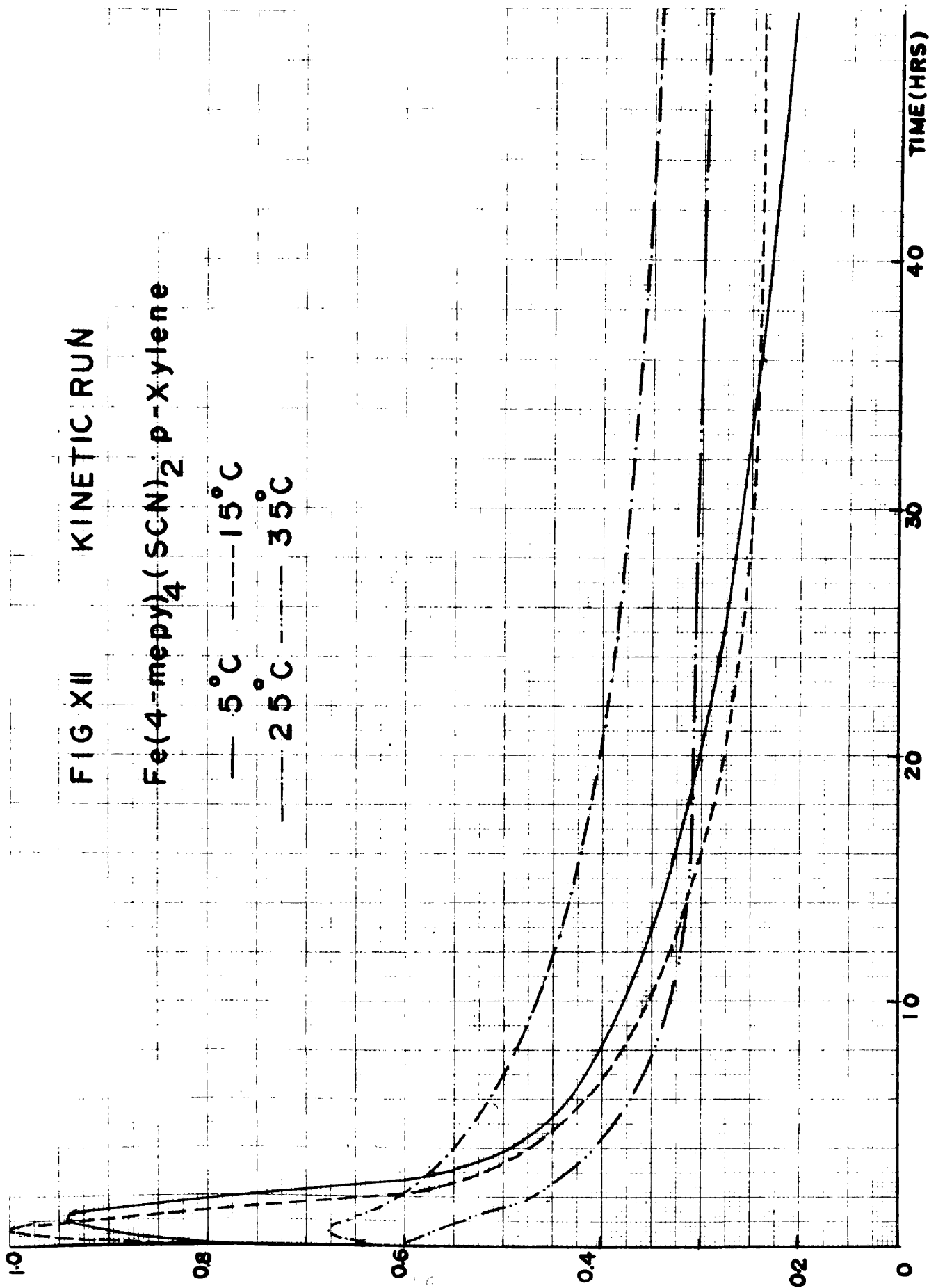
CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ AND p-XYLENE

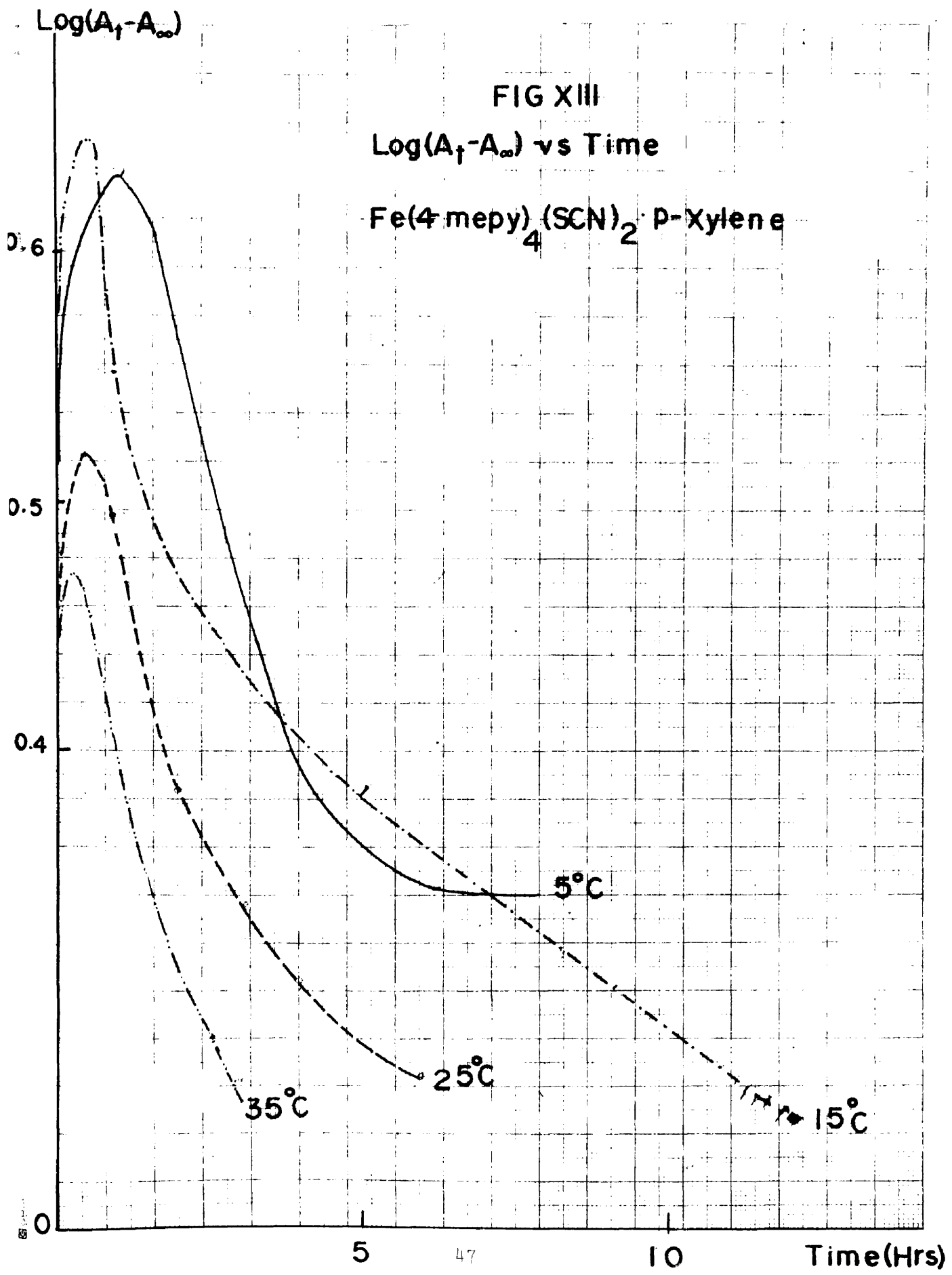
TIME (HOURS)	ABSORBANCE OF p-XYLENE AT 275 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.638	0.758	0.637	0.600
¼	0.638	0.758	0.637	0.644
½	0.900	1.000	0.678	0.580
1	0.940	0.616	0.658	0.570
2	0.760	0.568	0.578	0.455
3	0.540	0.524	---	0.424
4	0.562	0.455	0.540	0.424
6	0.407	0.432	0.524	0.369
8	0.402	0.400	0.489	0.366
10	0.393	0.360	0.413	0.330
12	0.388	0.328	0.440	0.340
24	0.283	0.292	0.413	0.310
28	0.270	0.255	0.393	0.310
32	0.259	0.248	0.362	0.298
36	0.240	0.240	0.360	0.297
48	0.210	0.239	0.343	0.294

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40 g of complex and 10 ml of p-xylene in 300 ml heptane.

Absorbance

FIG XII KINETIC RUN
 $\text{Fe}(\text{4-mepy})_4(\text{SCN})_2$ p-Xylene
— 5°C --- 15°C
— 25°C - - - 35°C





LnG_y

FIG XIV

LnG_y v \checkmark Ln Time
Fe(4-me \checkmark py)₄(SCN)₂ p-xylene
25 ^\circ C

-9.2

$K = 5.6 \times 10^{-2}$

-9.1

-9.0

-8.9

-8.8

2

3

LnTime(Hrs)

TABLE X

GRAVIMETRIC ANALYSES FOR Fe IN THE COMPLEX $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$
AND THE BENZENE AND TOLUENE CLATHRATE

		BENZENE CLATHRATE			
		PERCENT Fe			
TRIAL	COMPLEX	CLATHRATE I*	II*	III*	IV*
1	12.05	9.87	9.78	9.73	9.97
2	11.00	10.10	9.54	9.65	10.17
3	11.93	8.99	9.60	9.89	9.91
AVERAGE	11.65	9.65	9.64	9.75	10.02
THEORETICAL	10.26				
MOLE RATIO (GUEST/HOST)		0.47	0.48	0.39	0.2

		TOLUENE CLATHRATE			
		PERCENT Fe			
TRIAL	COMPLEX	CLATHRATE I*	II*	III*	IV*
1	12.05	9.87	9.97	9.73	10.22
2	11.00	9.65	9.91	9.82	10.26
3	11.93	9.87	10.21	9.79	10.18
AVERAGE	11.65	9.79	10.03	9.78	10.22
THEORETICAL	10.26				
MOLE RATIO (GUEST/HOST)		0.31	0.15	0.32	0.026

*Samples I, II, III, and IV refer to kinetic runs at 5°C, 15°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of benzene or toluene in 300 ml of heptane.

TABLE XI

GRAVIMETRIC ANALYSES FOR Fe IN THE COMPLEX $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$
AND THE p-XYLENE CLATHRATE

TRIAL	COMPLEX	PERCENT Fe			
		CLATHRATE I*	II*	III*	IV*
1	12.05	9.50	9.75	8.82	9.80
2	11.00	9.43	9.30	9.58	9.61
3	11.93	8.30	8.46	9.45	9.80
AVERAGE	11.65	9.07	9.17	9.29	9.70
THEORETICAL	10.26				
MOLE RATIO (GUEST/HOST)		0.71	0.65	0.57	0.33

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of benzene or toluene in 300 ml of heptane.

TABLE XII

INTERPLANAR SPACINGS (\AA) FOR THE MORE PROMINENT REFLECTIONS
FROM THE $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ COMPLEX AND THE p-XYLENE
CLATHRATE

COMPLEX		CLATHRATE	
OBSD	LIT*	OBSD	LIT*
	13.94		13.92
			10.07
8.23	8.53	8.25	8.16
7.41	7.30	7.10	6.96
5.89	6.01		5.66
	5.35	5.26	5.27
	4.95	4.88	4.91
4.69	4.65	4.59	4.60
4.36	4.01		4.20
3.91	3.81	3.96	
3.70	3.64	3.78	
3.49	3.39	3.60	
3.21	3.14	3.32	
2.99		3.18	
		3.09	

*M. T. Lok, M. A. Thesis, Northern Michigan University,
January, 1970.

Utilizing the expression proposed by Lahr and Williams (34), it is found that a small region does indeed appear to be first order, as shown in the \ln (concentration of guest at time t) vs. \ln Time plot in Figure XIV.

(III) $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$: in general, the results are in exact agreement with the work of Lok (30), Chou (12) and Vasantha (55) and the results are presented in Tables XIII and XIX, Figures XV through XXII. However a plot of \ln (concentration of guest at time t) vs. \ln time was also attempted and the plot suggests non-linearity of the clathration reaction except in a selected portion and this is shown in Figure XXII. The rate constant was also calculated.

Test of Reversibility

This test was performed in order to resolve the apparent conflict between the results of Minton (39,40), in which the clathration reaction is described as a first order, reversible reaction, and the results of Chou (12), Lok (30,37) and Vasantha (55) which indicate that the reaction is not first order and is not reversible. Experiments were carried out to test the reversibility of the clathration reaction with Co and $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ as host and benzene, toluene and p-xylene as guests. Reversibility experiments were performed by adding clathrate to pure heptane and following the change in guest concentration. The results are presented in Tables XX and XXI and Figures XXIII through XXVI. From the plotted data it is apparent that the clathration processes studied in this project are also irreversible.

TABLE XIII

CHANGE OF GUEST CONCENTRATION* WITH TIME DURING THE CLATHRATION
REACTION BETWEEN $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ AND BENZENE

TIME (HOURS)	ABSORBANCE OF BENZENE AT 255 nm			
	SAMPLE I**	SAMPLE II**	SAMPLE III**	SAMPLE IV**
0	0.300	0.298	0.298	0.301
¼	0.290	0.295	0.289	0.301
½	0.297	0.287	0.298	0.305
1	0.296	0.270	0.289	0.310
2	0.290	0.270	0.290	0.312
3	0.283	0.259	0.280	0.298
4	0.273	0.250	0.271	0.290
6	0.242	0.240	0.244	0.249
8	0.220	0.221	0.240	0.240
10	0.211	0.210	0.231	0.228
12	0.190	0.205	0.221	0.228
24	0.190	0.204	0.2100	0.210
28	0.193	0.204	0.2080	0.210
32	0.188	0.201	0.2060	0.205
36	0.186	0.200	0.2060	0.201
48	0.188	0.190	0.2050	0.200

*For calibration curve see Appendix II

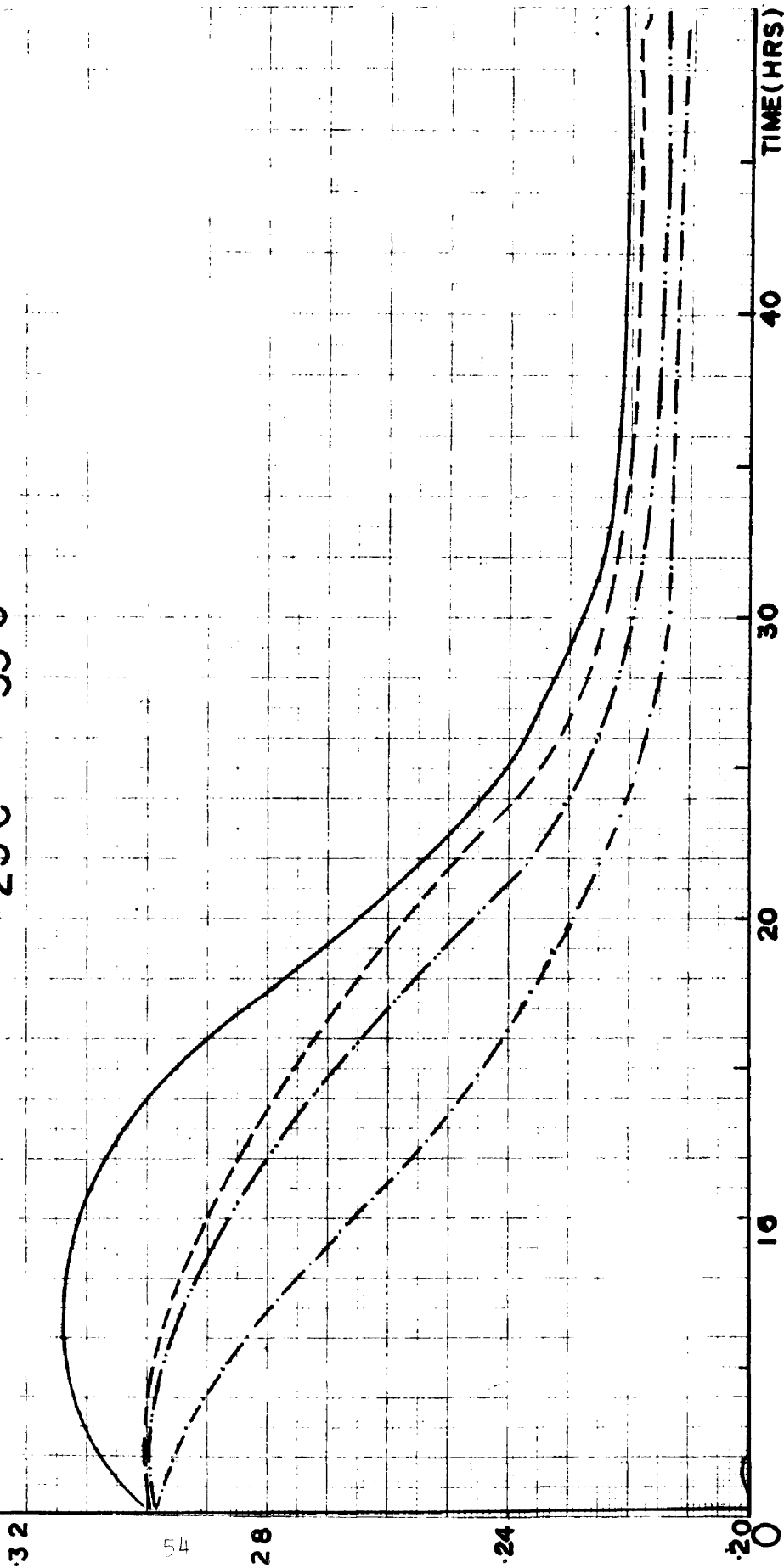
**Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of benzene in 300 ml heptane.

Absorbance

FIG XV KINETIC RUN
Ni(4-mepy)₄(NCS)₂ Benzene

----- 5°C ----- 15°C

--- 25°C --- 35°C

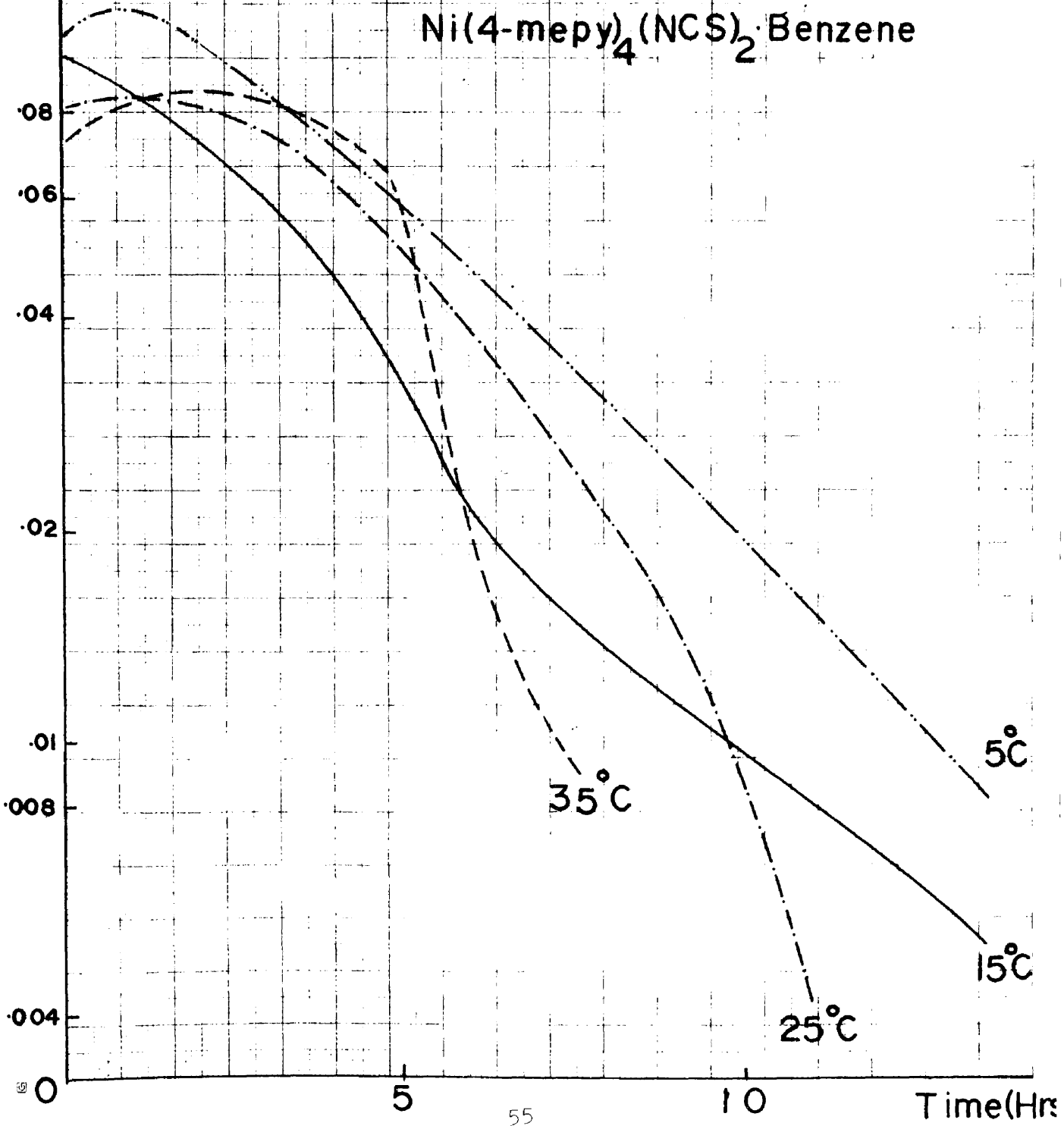


$\text{Log}(A_f - A_\infty)$

FIG XVI

$\text{Log}(A_f - A)$ vs Time

$\text{Ni}(\text{4-mepy})_4(\text{NCS})_2 \cdot \text{Benzene}$



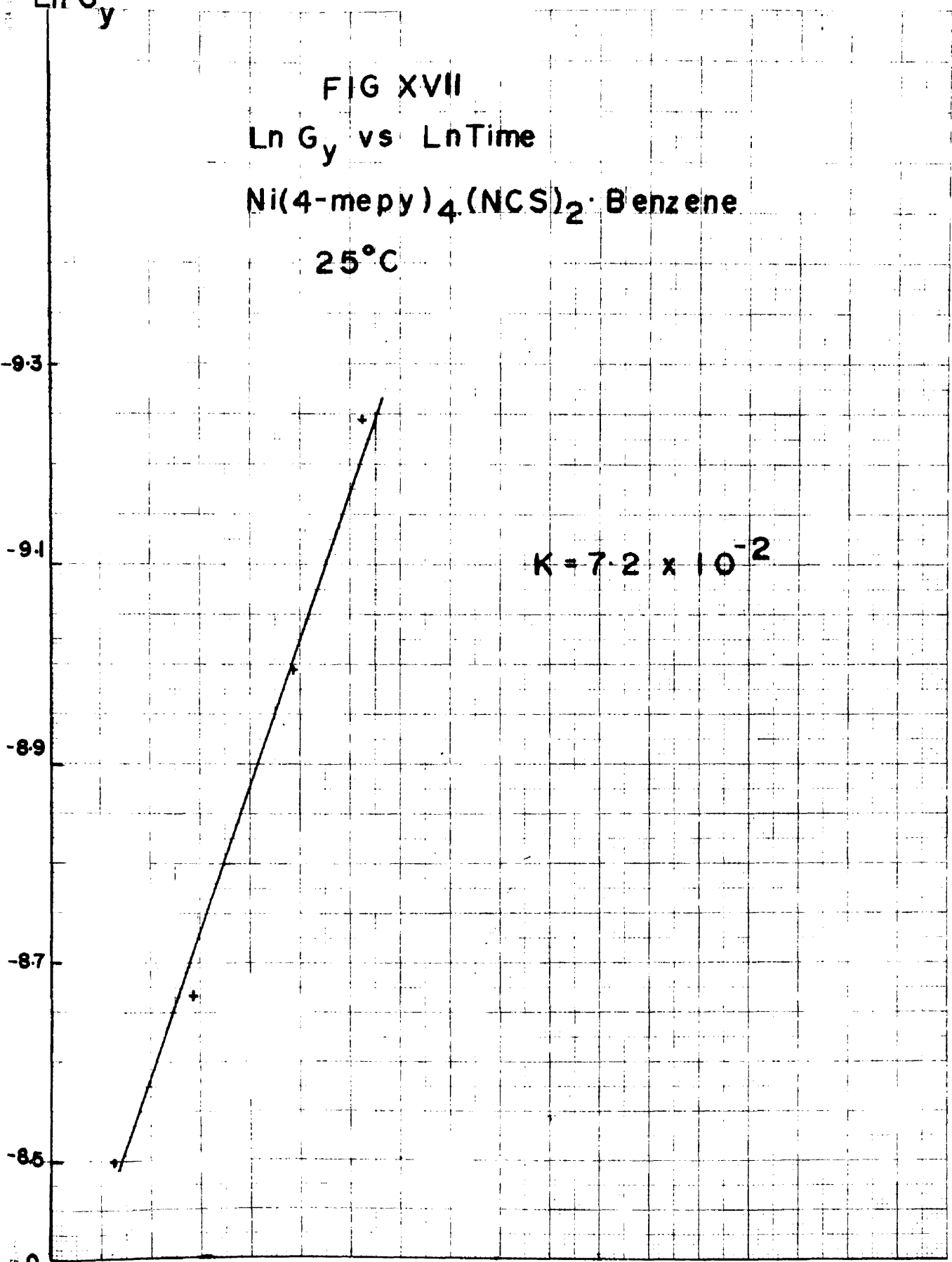
Ln G_y

FIG XVII
Ln G_y vs LnTime
Ni(4-mepy)₄(NCS)₂ · Benzene
25°C

-9.3
-9.1
-8.9
-8.7
-8.5
0

$K = 7.2 \times 10^{-2}$

1 2 3 LN(TIME)



1

2

3

LN(TIME)

TABLE XIV

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION
REACTION BETWEEN $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ AND TOLUENE

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.3180	0.3150	0.3155	0.3155
¼	0.3180	0.3154	0.3154	0.3180
½	0.3178	0.3133	0.3150	0.3183
1	0.3150	0.3100	0.3140	0.3195
2	0.3140	0.3090	0.3100	0.3200
3	0.3140	0.3090	0.3100	0.3300
4	0.3100	0.3058	0.3300	0.3320
6	0.3089	0.3050	0.3320	0.3340
8	0.3085	0.3058	0.3280	0.3352
10	0.2850	0.3040	0.3200	0.3328
12	0.2845	0.3000	0.3075	0.3460
24	0.2200	0.2400	0.2320	0.3350
28	0.2000	0.1905	0.2090	0.3109
32	0.1805	0.1780	0.2000	0.3060
36	0.1650	0.1750	0.2030	0.2840
48	0.1520	0.1665	0.2028	0.2254

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of toluene in 300 ml heptane.

Absorbance

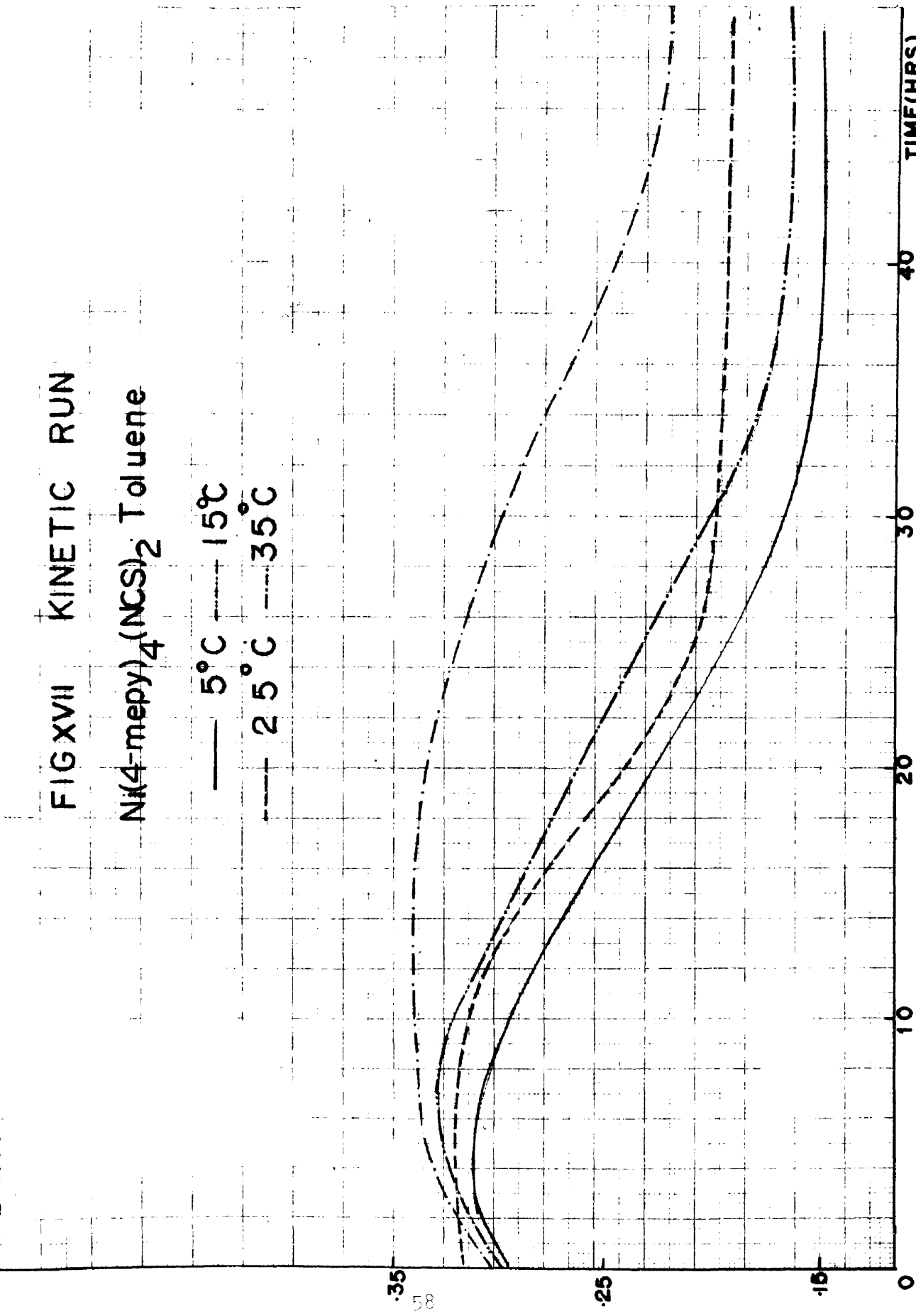
FIG XVII KINETIC RUN

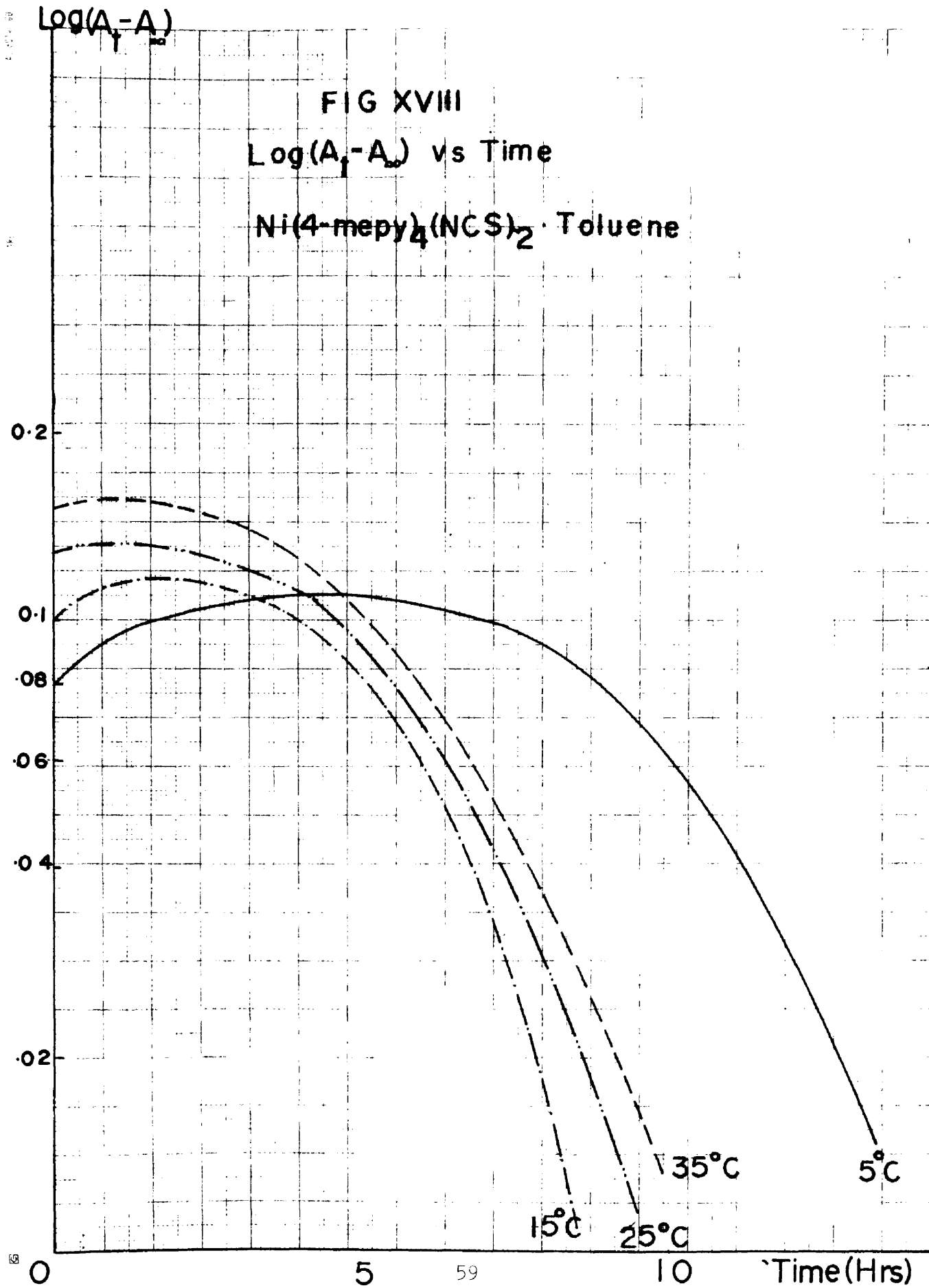
$\text{Ni}(\text{4-mepy})_4(\text{NCS})_2$ Toluene

— 5°C — 15°C

- - - 25°C - - - 35°C

TIME(HRS)





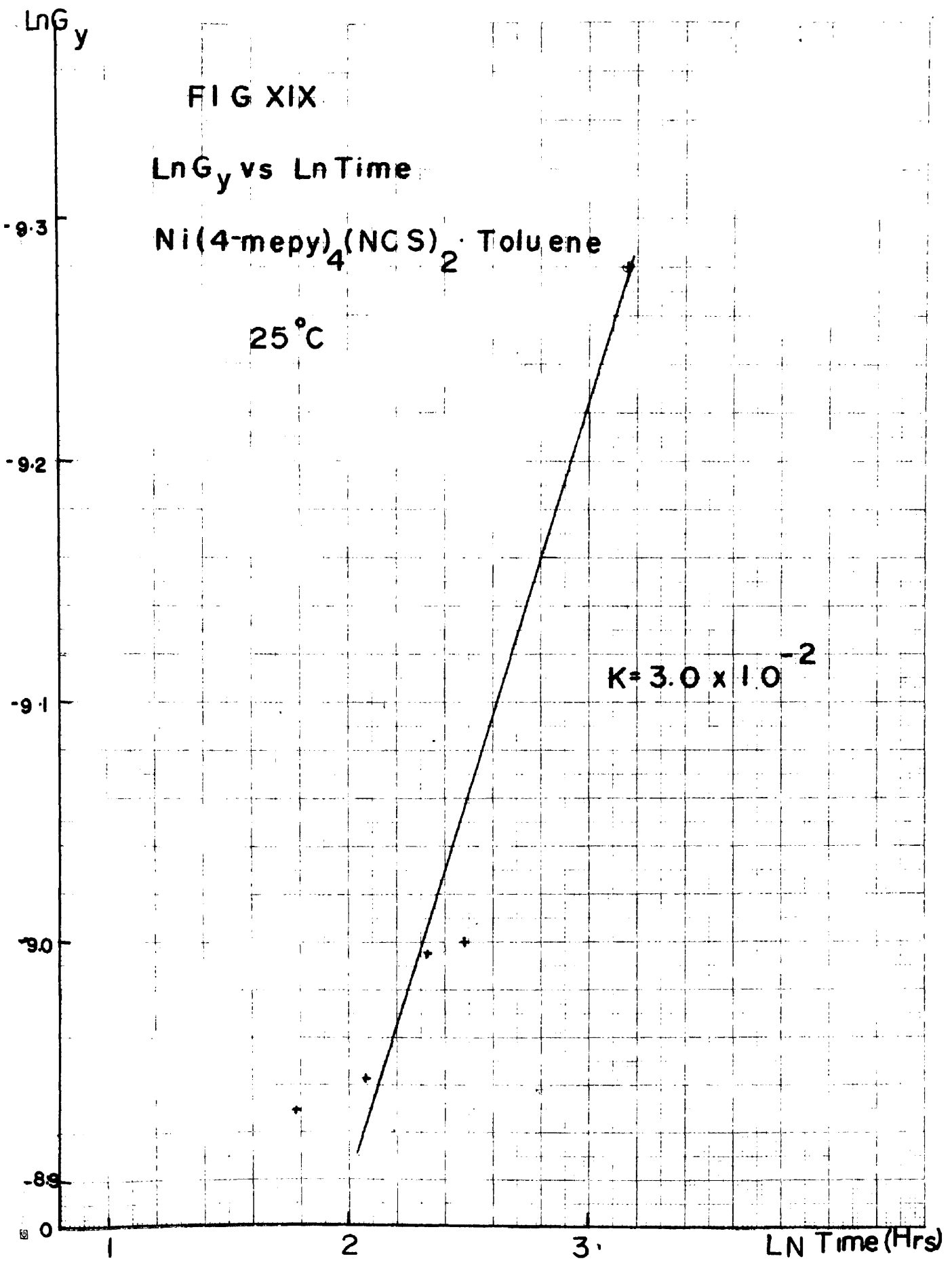
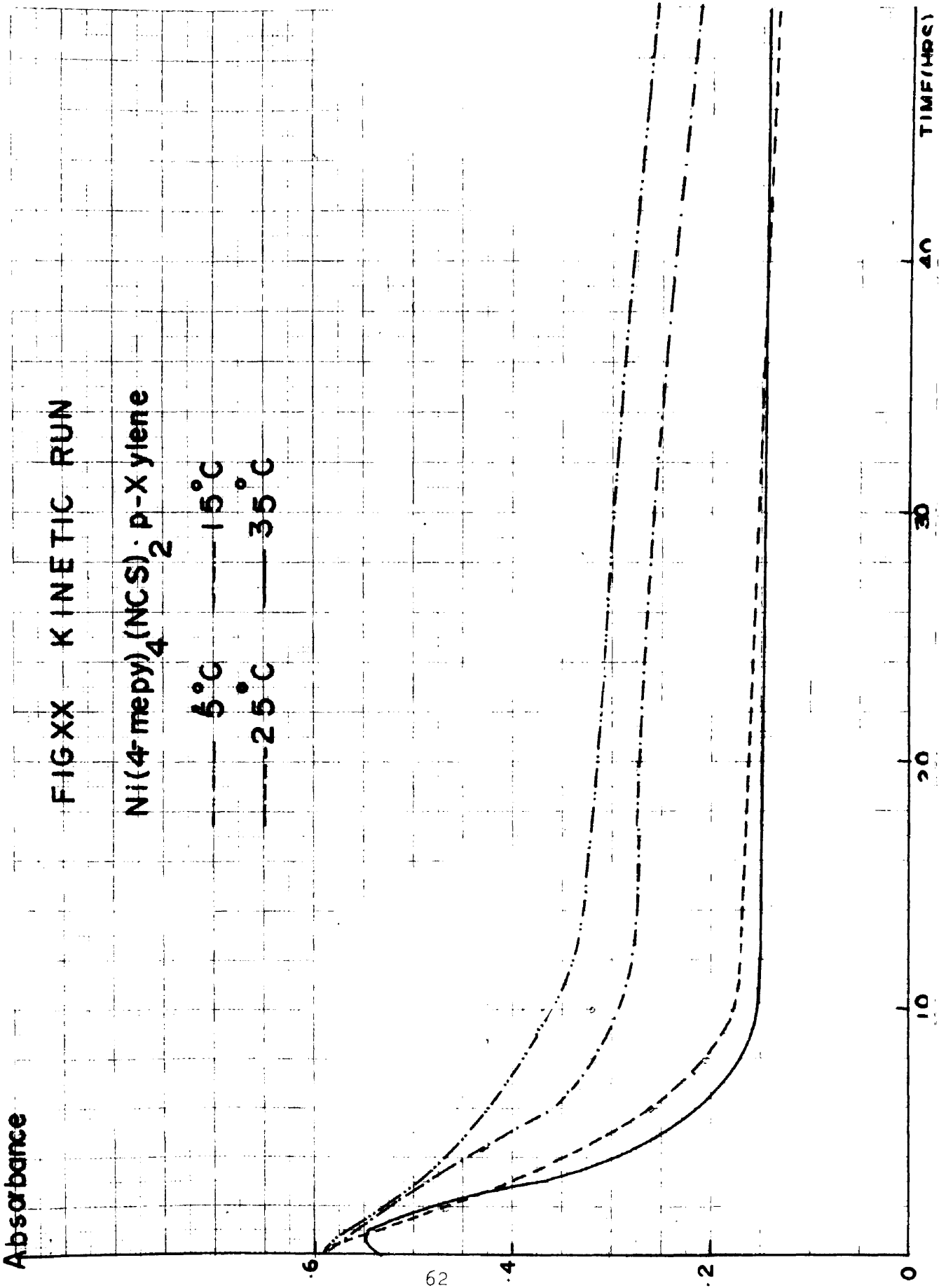


TABLE XV

CHANGE OF GUEST CONCENTRATION WITH TIME DURING CLATHRATION
REACTION BETWEEN $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ AND p-XYLENE

TIME (HOURS)	ABSORBANCE OF p-XYLENE AT 275 nm			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.598	0.598	0.594	0.528
$\frac{1}{4}$	0.580	0.564	0.582	0.521
$\frac{1}{2}$	0.570	0.560	0.578	0.540
1	0.570	0.558	0.578	0.520
2	0.564	0.550	0.568	0.470
3	0.490	0.485	0.418	0.370
4	0.470	0.440	0.362	0.325
6	0.425	0.360	0.262	0.212
8	0.390	0.319	0.202	0.178
10	0.370	0.322	0.192	0.162
12	0.330	0.270	0.175	0.150
24	0.310	0.273	0.164	0.155
28	0.300	0.262	0.143	0.149
32	0.291	0.250	0.147	0.150
36	0.280	0.225	0.145	0.149
48	0.264	0.220	0.143	0.140

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, 35°C respectively for 40g of complex and 10 ml of p-xylene in 300 ml of heptane.



$\text{Log}(A_t - A_\infty)$

FIG XXI

$\text{Log}(A_t - A_\infty)$ vs Time

$\text{Ni}(\text{4-mepy})_4(\text{NCS})_2$ p Xylene

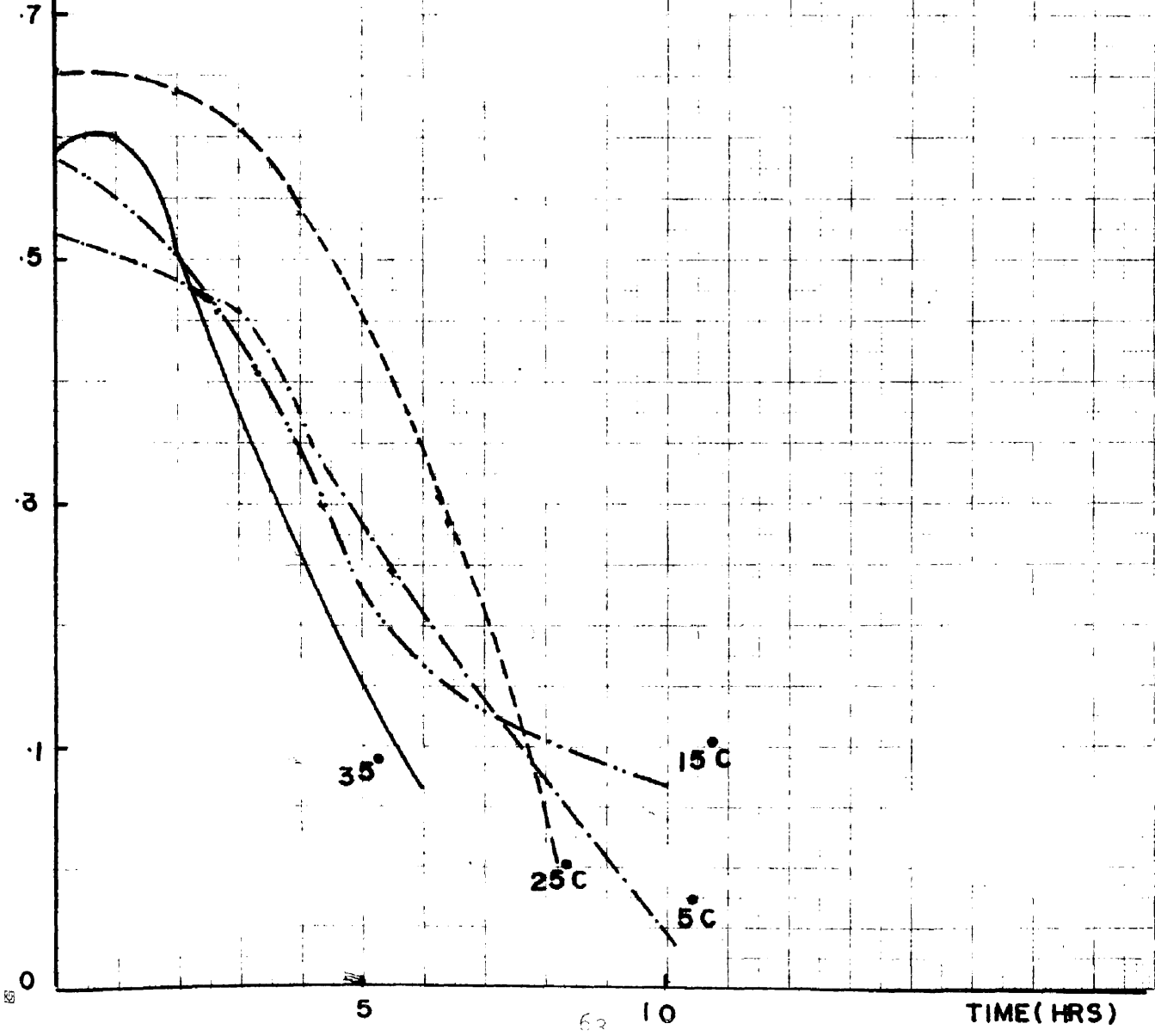


FIG XXII

LnG_y vs LnTime

$\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ p-xylene 25°C

$$K = 1.29 \times 10^{-2}$$

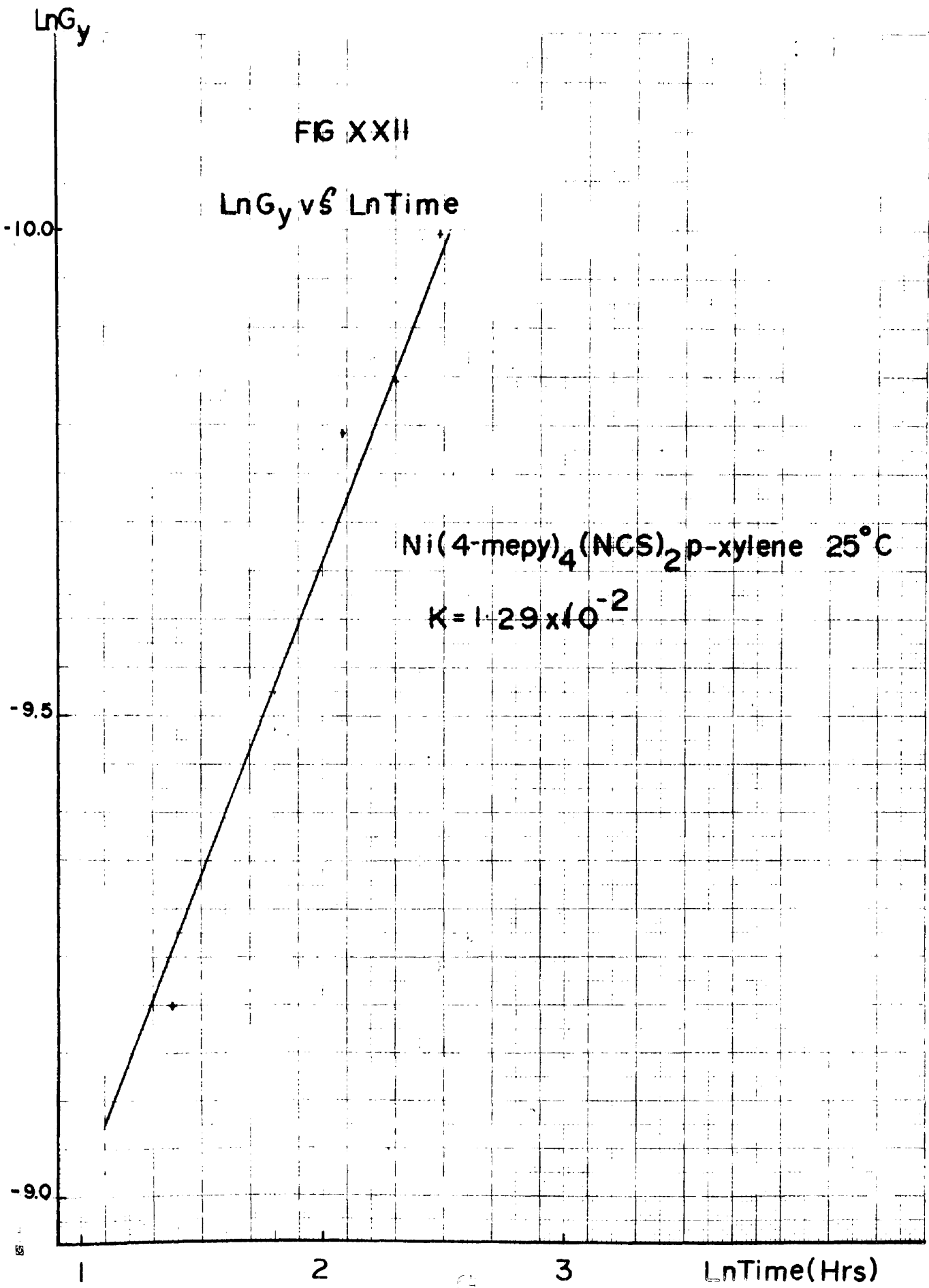


TABLE XVI

VOLUMETRIC ANALYSIS FOR Ni IN THE COMPLEX $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$
AND BENZENE CLATHRATES

TRIAL	COMPLEX	CLATHRATE	PERCENT Ni			
			I*	II*	III*	IV*
1	10.95		10.52	10.32	10.12	10.02
2	10.95		10.50	10.36	10.14	9.98
AVERAGE	10.95		10.51	10.34	10.13	10.00
THEORETICAL	10.73					
MOLE RATIO (GUEST/HOST)**			0.164	0.291	0.447	0.545

*Clathrates I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of benzene in 300 ml heptane.

**For calculations of GUEST/HOST mole ration see Appendix I.

TABLE XVII

VOLUMETRIC ANALYSIS FOR Ni IN THE COMPLEX $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$
AND TOLUENE CLATHRATE

TRIAL	COMPLEX	PERCENT NICKEL			
		CLATHRATE I*	II*	III*	IV*
1	10.95	9.80	9.70	10.07	9.99
2	10.95	9.76	9.74	10.10	10.01
AVERAGE	10.95	9.78	9.72	10.08	10.0
THEORETICAL	10.73				
MOLE RATIO** (GUEST/HOST)		0.613	0.652	0.419	0.471

*Clathrates I, II, III, and IV refer to the clathrates formed at 5°C, 10°C, 25°C, and 35°C respectively for 40g of complex and 10 ml of toluene in 300 ml heptane.

**The values are reliable to an extent of 0.06 units.

TABLE XVIII

VOLUMETRIC ANALYSES FOR Ni IN THE COMPLEX $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$
AND THE p-XYLENE CLATHRATE

TRIAL	COMPLEX	PERCENT Ni			
		CLATHRATE I*	II*	III*	IV*
1	10.95	9.24	9.20	9.15	9.06
2	10.95	9.27	9.23	9.17	9.08
AVERAGE	10.95	9.25	9.21	9.16	9.07
THEORETICAL	10.73				
MOLE RATIO (GUEST/HOST)		0.84	0.86	0.89	0.94

*Samples I, II, III, and IV refer to clathrates formed at 5°C, 15°C, 25°C and 35°C respectively for 40g of complex and 10 ml of p-Xylene and 300 ml of heptane.

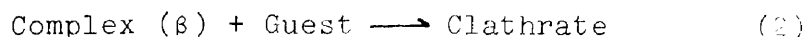
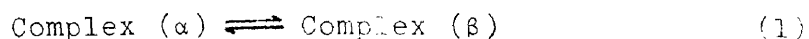
TABLE XIX

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS
FROM THE $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ COMPLEX AND THE BENZENE,
TOLUENE, AND p-XYLENE CLATHRATES

COMPLEX		CLATHRATES		
OBSD	LIT*	BENZENE	TOLUENE	p-XYLENE
8.72	8.64	13.12	12.74	13.08
	8.37	8.44		8.39
	7.56		7.87	
7.37	7.34	6.80	6.60	7.30
5.85	5.17	5.80	5.75	5.49
5.47	5.03	5.43	5.03	5.25
5.34	4.98	5.10		
5.73	4.85	4.77		4.61
	4.50	4.61	4.58	
4.31	4.36		4.40	
	4.27			4.24
	4.08		4.09	
	4.05			
3.89	3.90	3.98		3.99
3.73	3.85	3.79	3.81	3.83
	3.65	3.70		
3.49	3.55		3.49	3.65
	3.15			3.14
2.98				

*M. I. Hart and N. O. Smith, J. Am. Chem. Soc. 84, 1816 (1962)

From the results presented on the previous pages, the following mechanism for the clathration process is proposed:



Equation (1) represents a lattice change in the crystal structure of the complex which is brought about by the guest; it is greatly affected by variables such as temperature, and concentration of guest. The lattice change from α to β has been proven by X-ray analyses as presented in Tables VI, XIII, and XIX for the benzene, toluene, p-xylene clathrates respectively. Equation (2) would appear to be a second order, irreversible reaction. If it is to be a first order reaction then it must depend on only the guest concentration or host concentration alone. Previous work by Chou (12) and Vasantha (55) has shown that such reactions depend on the guest concentration and are less affected by the host concentration. At higher concentrations of the guest, the reaction depends only on the host concentration and is a pseudo first order reaction. However, at lower guest concentrations, the reaction may depend on both the guest concentration and the host concentration and be of second order. Thus, the reactions may be in fact somewhere between first and second order for most of the kinetic run.

Adsorption Studies

Allison et.al. (1) reported in an article entitled "Sorption in β -Phases of Transition Metal (II) Tetra-(4-

TABLE XX

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE REVERSIBILITY
STUDY WITH $\text{Co}(4\text{-mepy})_4(\text{SCN})_2\text{X}$
(X=BENZENE, TOLUENE, p-XYLENE) AT 25°C

TIME (HOURS)	ABSORBANCE		
	BENZENE AT 255 nm	TOLUENE AT 263 nm	p-XYLENE AT 275 nm
0	0.0025	0.005	0.005
½	0.0740	0.095	0.074
1	0.0770	0.097	0.075
2	0.0780	0.094	0.076
4	0.0720	0.098	0.075
8	0.0760	0.098	0.077
12	0.0740	0.097	0.076
24	0.0740	0.098	0.075
36	0.0750	0.097	0.074
48	0.0760	0.096	0.073

Absorbance

FIG XXIII
 KINETIC RUN (TEST OF REVERSIBILITY)
 $\text{Co(4-mepy)}_4(\text{SCN})_2 \cdot \text{X}$ (X = benzene or toluene)
 25°C

TOLUENE

BENZENE

0.10

0.5

0

10

20

30

40

MINUTES

Absorbance

FIG XXIV

KINETIC RUN (TEST OF REVERSIBILITY)

Co(4-mepy)₄(SCN)₂ p-xylene

25°C

1.0
0.75
0.5
0.25
0

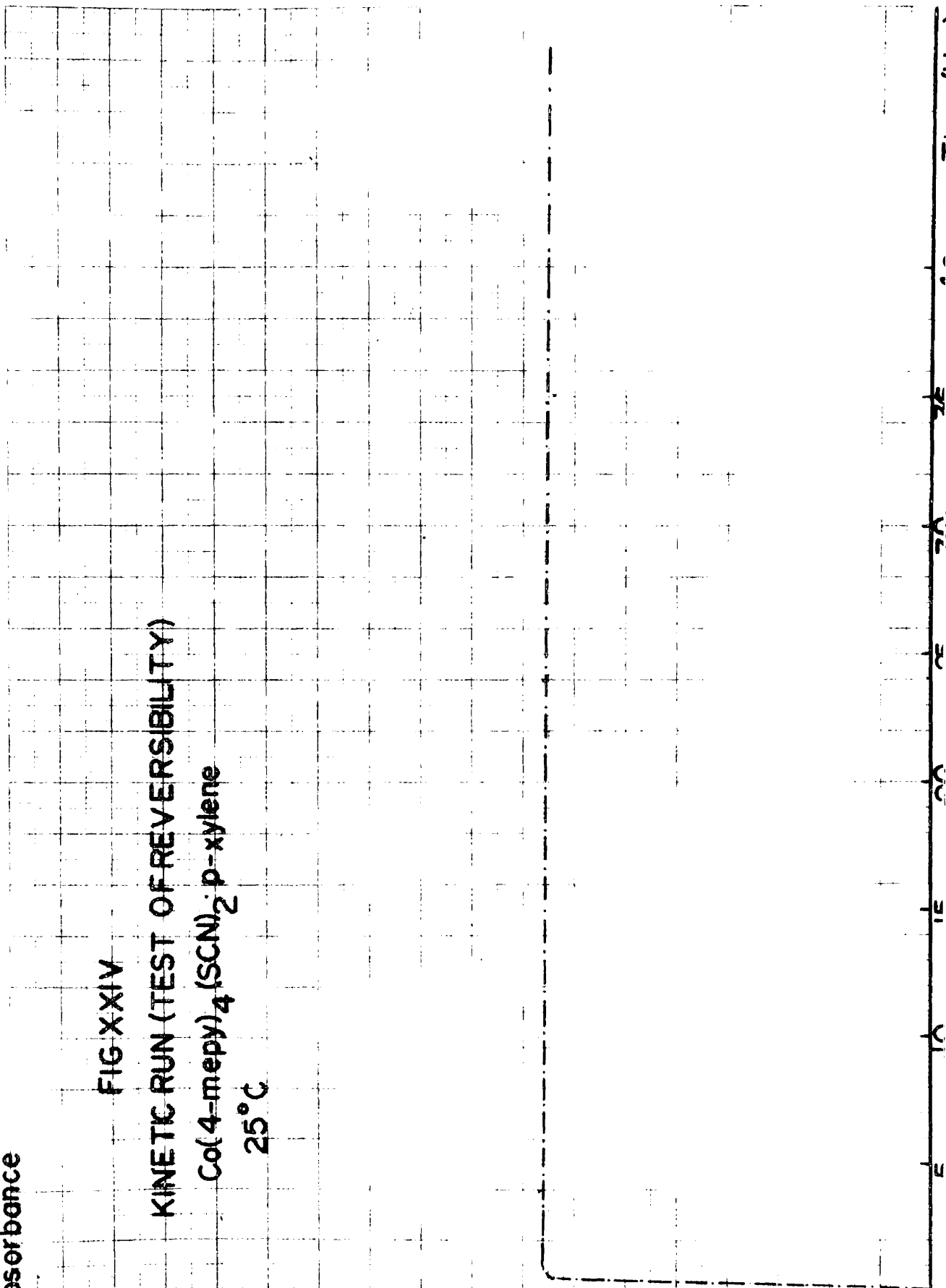


TABLE XXI

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE REVERSIBILITY
STUDY WITH $M(4\text{-mepy})_4(\text{SCN})_2$ p-XYLENE
(M=NICKEL, IRON) AT 25°C

TIME (HOURS)	ABSORBANCE (p-XYLENE at 275 nm)	
	Ni CLATHRATE	Fe CLATHRATE
0	0.005	0.005
¼	0.077	0.076
½	0.075	0.074
1	0.075	0.079
2	0.076	0.075
4	0.073	0.076
8	0.074	0.075
12	0.073	0.075
24	0.075	0.075
36	0.073	0.075
48	0.075	0.074

Absorbance

FIG XXV

KINETIC RUN (TEST OF REVERSIBILITY)

Fe(4-mepy)₄(SCN)₂p-xylene

25 °C

10

05

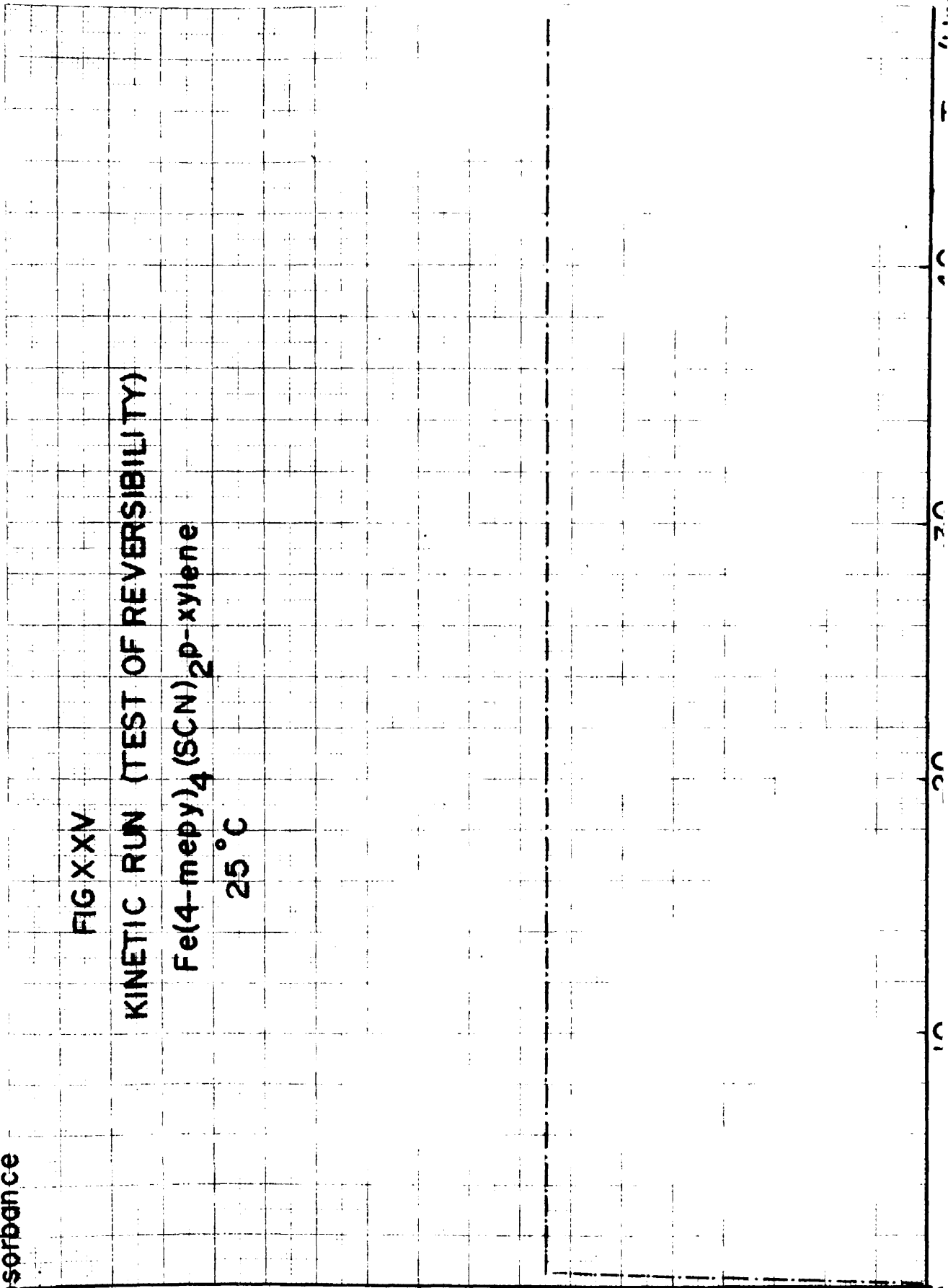
10

20

30

40

50



Absorbance

FIG XXVI

KINETIC RUN (TEST OF REVERSIBILITY)

Ni(4-mepy)₄(NCS)₂ p-xylene

25°C

10
75

05

0

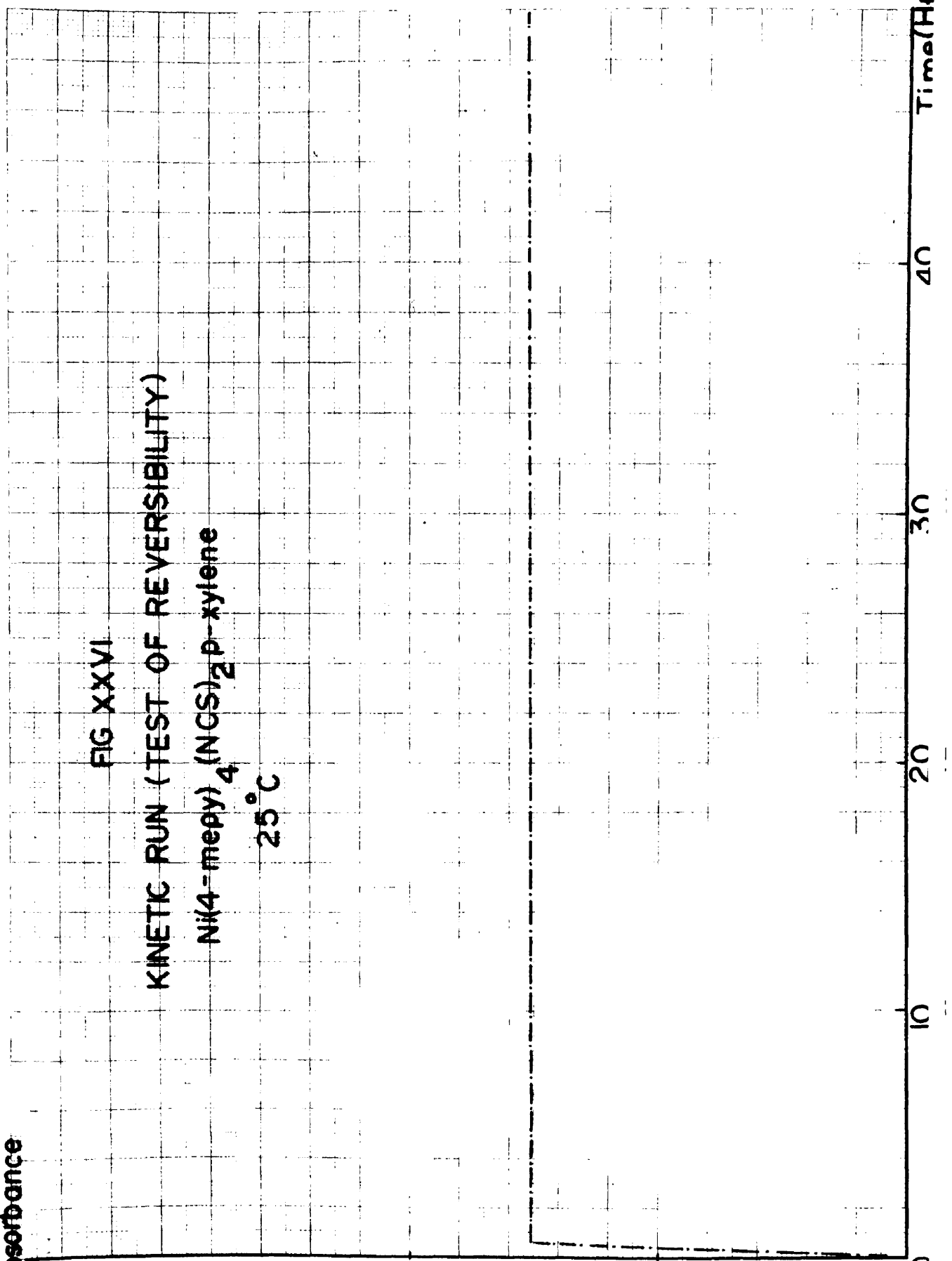
10

20

30

40

Time(Hrs)



methylpyridine) Thiocyanates and Related Compounds" that the clathration reaction is in reality an adsorption reaction.

In general the process by which atoms or molecules of one material become attached to the surface of another is called adsorption. The extent of adsorption increases as solubility decreases in a given solvent and the extent of adsorption furthermore depends on the velocity of diffusion in the adsorbent. There are two main classes of adsorption depending on whether the forces between adsorbate and adsorbent are physical or chemical in nature. The force in physical adsorption, is of the van der Waal's type and the adsorption is a reversible process, that is, the amount adsorbed at a given concentration and temperature is the same whether the final concentration is obtained by dilution of a concentrated solution or by concentration of a weaker one. On the other hand, chemical adsorption or chemisorption involves forces of a chemical nature similar to those encountered in chemical combination. Chemisorption is irreversible, and the adsorbate cannot be washed off the surface by treatment with the solvent. However, in both types the adsorption process is exothermic and the extent of adsorption decreases as the temperature is raised. The forces found in clathrates appear to be of the van der Waals type and thus any adsorption was considered as a physical adsorption.

Several adsorption equations have been developed and refined since Langmuir (35,36) published what is now known

as the Langmuir isotherm in 1918. This equation was derived for adsorption of gases on solids and assumed that adsorption is limited to a monolayer and that the surface is uniform. However, the shortcoming of the Langmuir isotherm equation is that it fits experimental data in only a limited number of cases.

In 1938, Brunauer, Emmett and Teller (8,9) developed a theory of multimolecular adsorption now known as the BET theory. The BET theory utilized the polarisation theory of DeBoer and Zwicker (14) and is an extension of Langmuir's treatment of monomolecular adsorption. The theory postulates that the heat of adsorption for all layers beyond the first is equal to the latent heat of condensation of the adsorbate. The BET method is frequently used for measuring surface area but because of the assumptions employed in its derivation, it has been criticized by many. Further modifications have been made by Frenkel (23) and other workers. Nonetheless, the modified BET isotherm involves algebraic variations and it is difficult to know how much physical significance should be attached to its ability to fit data.

For a heterogeneous surface, the Freundlich isotherm (24) is often applied. Unlike the Langmuir isotherm, this equation does not become linear at lower concentration but remains concave to the concentration axis. A constant value will be obtained by plotting the log of the number of moles adsorbed versus the log of the number of moles unadsorbed. An attempt was made to fit the data in this thesis to the Freundlich isotherm.

Indeed, phenomena which are often involved in physical adsorption are monomolecular adsorption, multimolecular adsorption and condensation in capillaries or pores. A plot of the number of moles of materials adsorbed versus the number of moles of material unadsorbed at constant temperature, is called an adsorption isotherm. Brunauer, Deming, et.al. (9) have classified physical isotherms into five categories as shown in Figure XXVII.

Type I is a typical adsorption isotherm which approximates monomolecular adsorption and is frequently referred to as the Langmuir type.

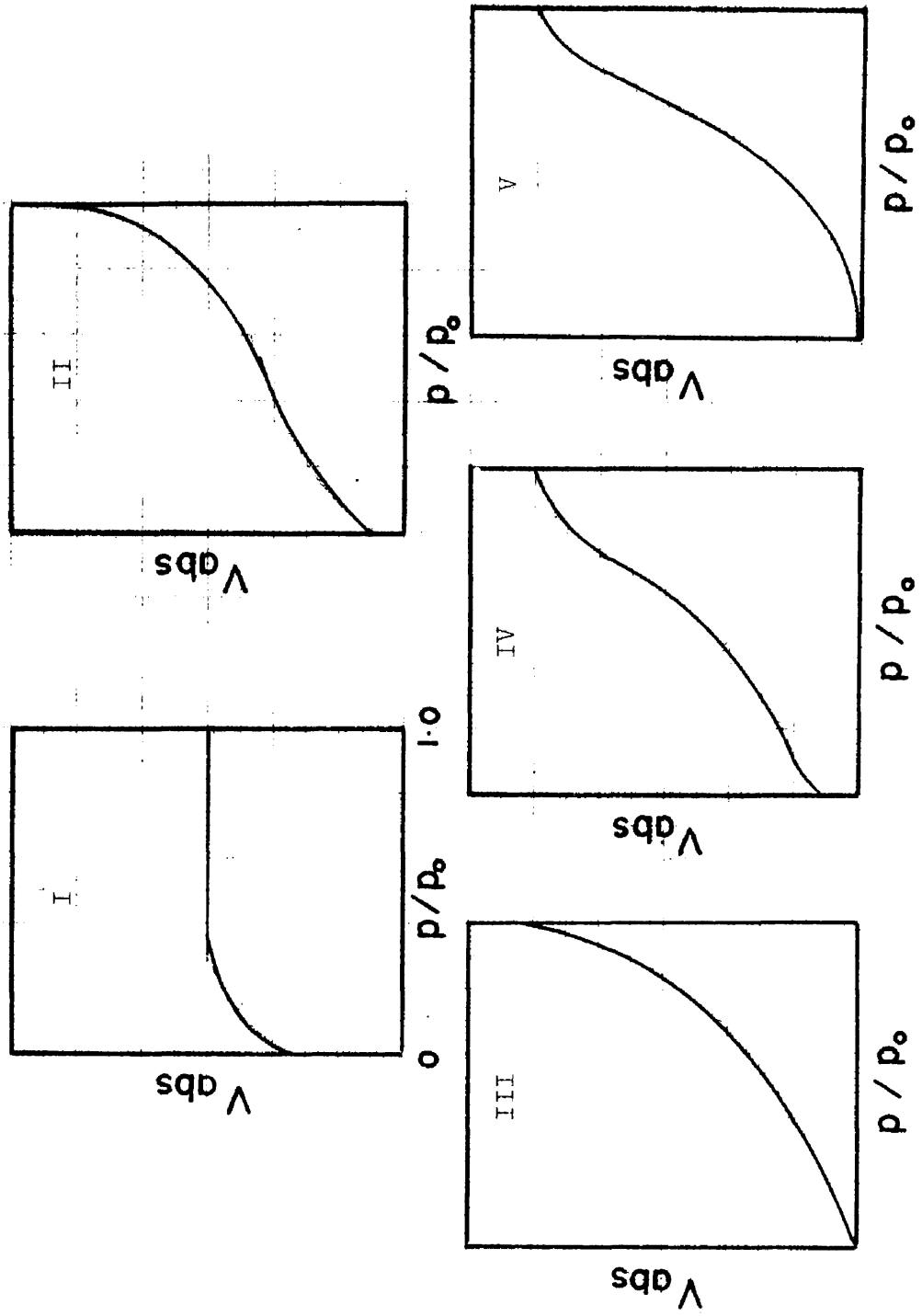
Type II and Type III are derived from the BET equation; the linear region is not very extensive.

Type IV and V have been explained by extending the theory of multimolecular adsorption to include condensation in the capillaries at pressures below the saturation value.

Type III and V occur only when the forces of monomolecular adsorption are small. They are rarely encountered. Type II is the most frequently encountered adsorption isotherm.

The above classification was developed for adsorption from the gas phase. Additional isotherms were developed for adsorption from solution and these are the ones which apply in this thesis. Kipling (33) has emphasized the necessity for distinguishing the term 'adsorption' as applied in studies with gases and with solutions. The isotherm of adsorption of a gas refers to the actual amount of one

FIG XXVII
BRUNAUER'S ADSORPTION ISOTHERMS



substance adsorbed by the unit mass of a solid. However, the adsorption isotherm which refers to adsorption from solution refers to a change in concentration in the solution and is a measure of the difference in the solution and solvent adsorbed. Adsorption from solution is a very complex phenomenon. It depends on the nature of solute-solvent interaction in the solution phase and in the interfacial region, as well as on their interaction with the adsorbent. Classification into four main types was made by Giles and MacEwan (26) and is shown in Figure XXVIII.

Type L or the Langmuir type is the same as Brunauer's Type I and is the one usually encountered in adsorption from dilute solutions.

Type S is the same as Brunauer's Type V.

Type Ln stands for linear. It appears to represent a condition where the number of sites for adsorption remains constant even though the amount of solute adsorbed increases. This will occur when the solute can swell and penetrate the adsorbent structure.

Type HA stands for high affinity. It is a special form of the L curve in which a solute with very high affinity for the solid, in a solvent of low affinity, is completely adsorbed from dilute solutions.

Type L is the most common type of adsorption which has been found to occur from solution.

From the above discussion, it is apparent that there are many types of adsorption isotherms and equations derived for

adsorption. The Freundlich equation was applied here because it appeared to give the best fit for clathration.

Data on the clathration reactions between $M(dmpy)_4(SCN)_2$, where M is Ni(II), Co(II), and Fe(II), as host and benzene, toluene, and p-xylene as guests were subjected to adsorption analysis.

Plots of the Freundlich isotherm for each of the above pairs were made and are shown in Figures XIX through Figure XXXVI.

As will be noted from the Figures, none of the cases studied above gave a straight line except for the case of benzene. Closer examination of the adsorption isotherm plots reveals that they are more similar to the Adsorption Isotherm Type Ln and Type L shown in Figure XXVIII than the Freundlich isotherm.

Indeed, from such plots, one may draw the conclusion that "clathration" is not a simple adsorption process, in other words, more sophisticated adsorption isotherms may be needed to fit the data obtained in this study. Indeed, more detailed studies are needed to conclusively prove that 'clathration' processes are 'adsorption' in nature.

Thermogravimetric Studies

The isothiocyanatopyridine compounds of Ni and Fe were investigated. The resultant thermograms are presented in Figures XXXIV and XXXV. Calculations based on the thermograms are in good agreement with the results reported

Log (moles adsorbed)

FIG XXIX

Adsorption Isotherm

$\text{Co}(\text{4-mepy})_4(\text{SCN})_2$ benzene

25°C

4.3

83

4.5

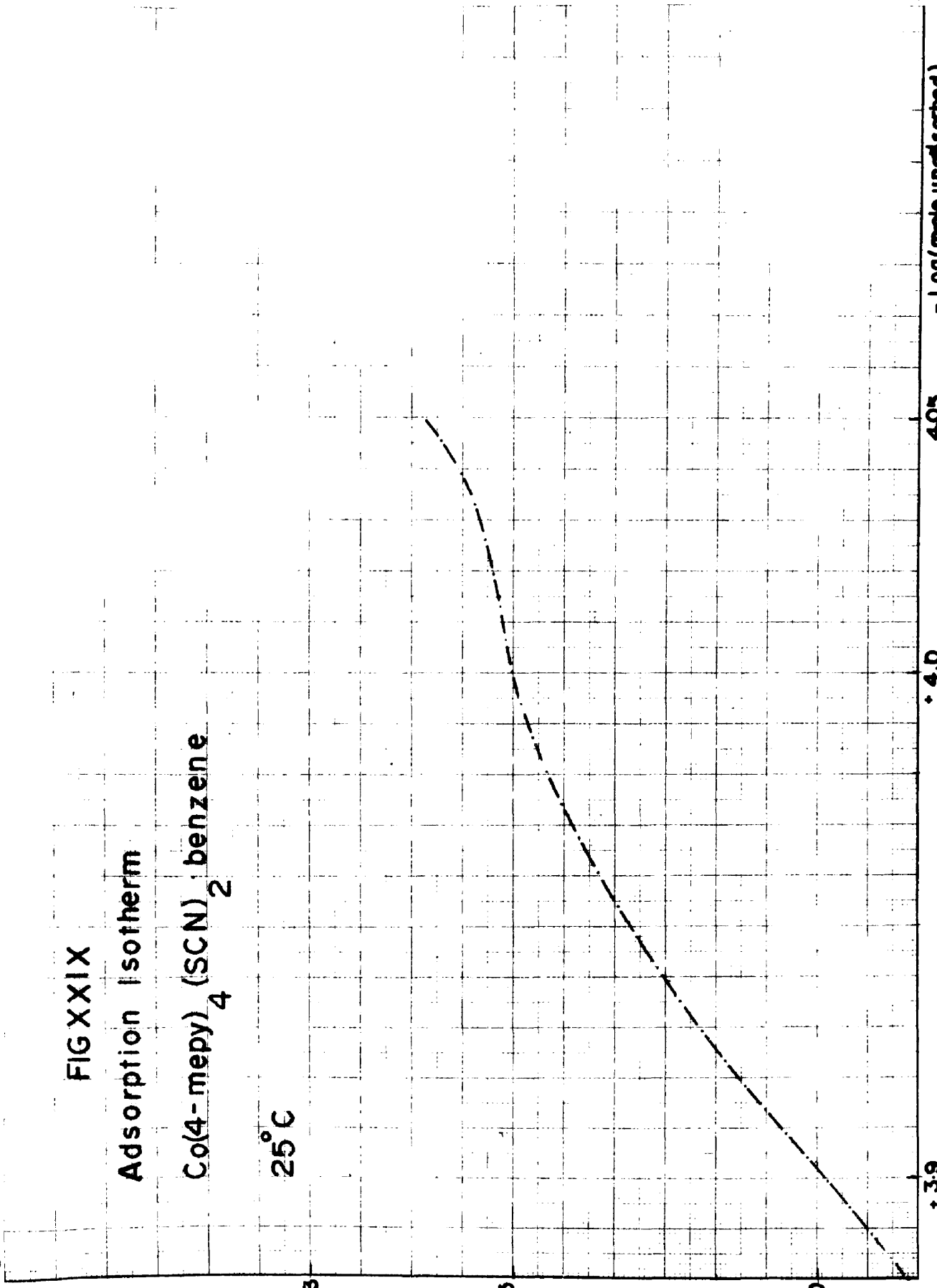
5.0

+ 3.9

+ 4.0

405

- Log (mole undisorbed)



Log(mole adsorbed)

FIG. XXX

Adsorption Isotherm

Co(4-mepy)₄(SCN)₂·toluene

25°C

4.07

-4.8

84

-5.0

-5.2

-5.3

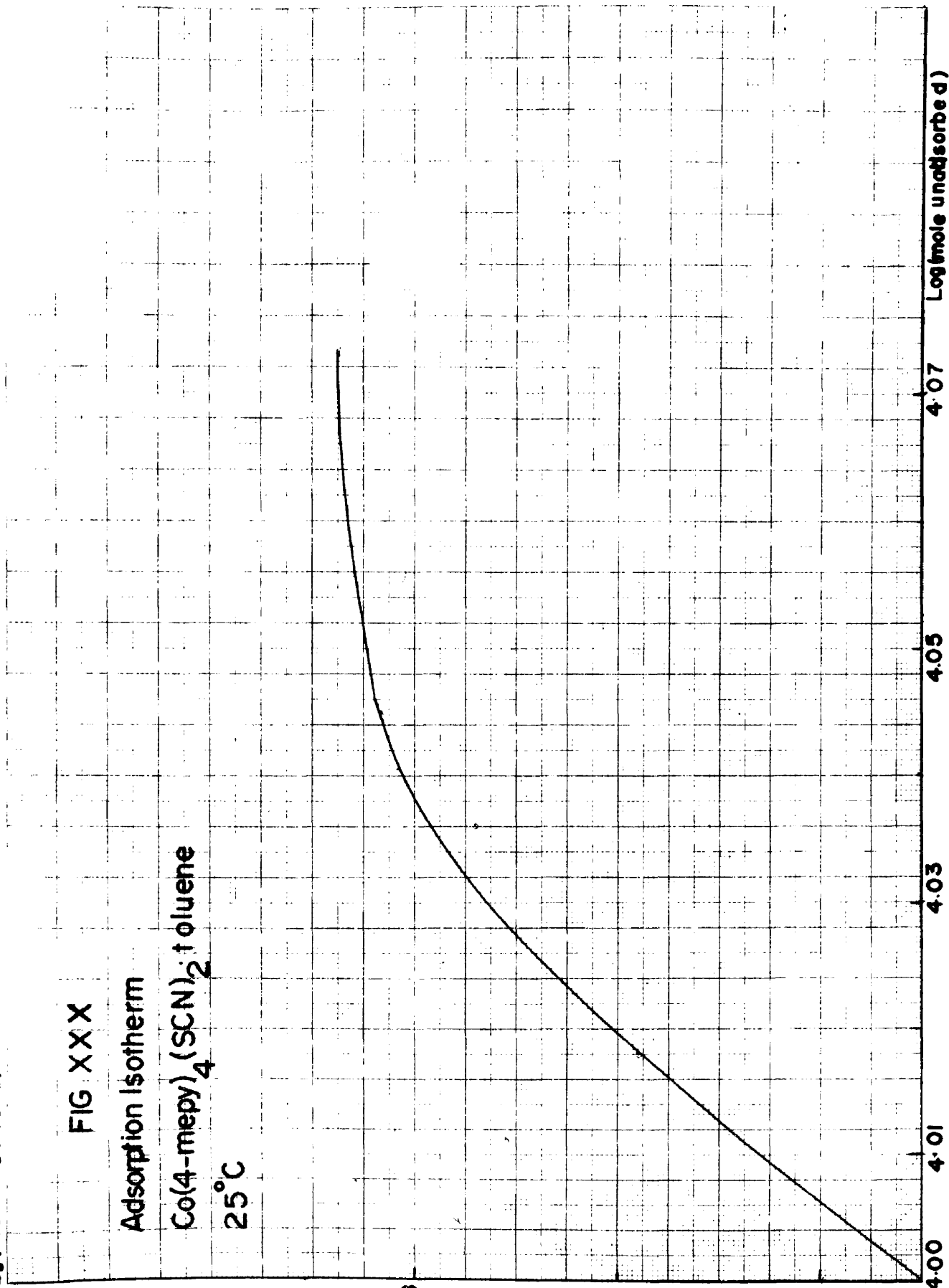
4.01

4.03

4.05

4.07

Log(mole unadsorbed)



Log(mole adsorbed)

-4.2

-4.5

85

-5.0

-5.4

3.8

3.9

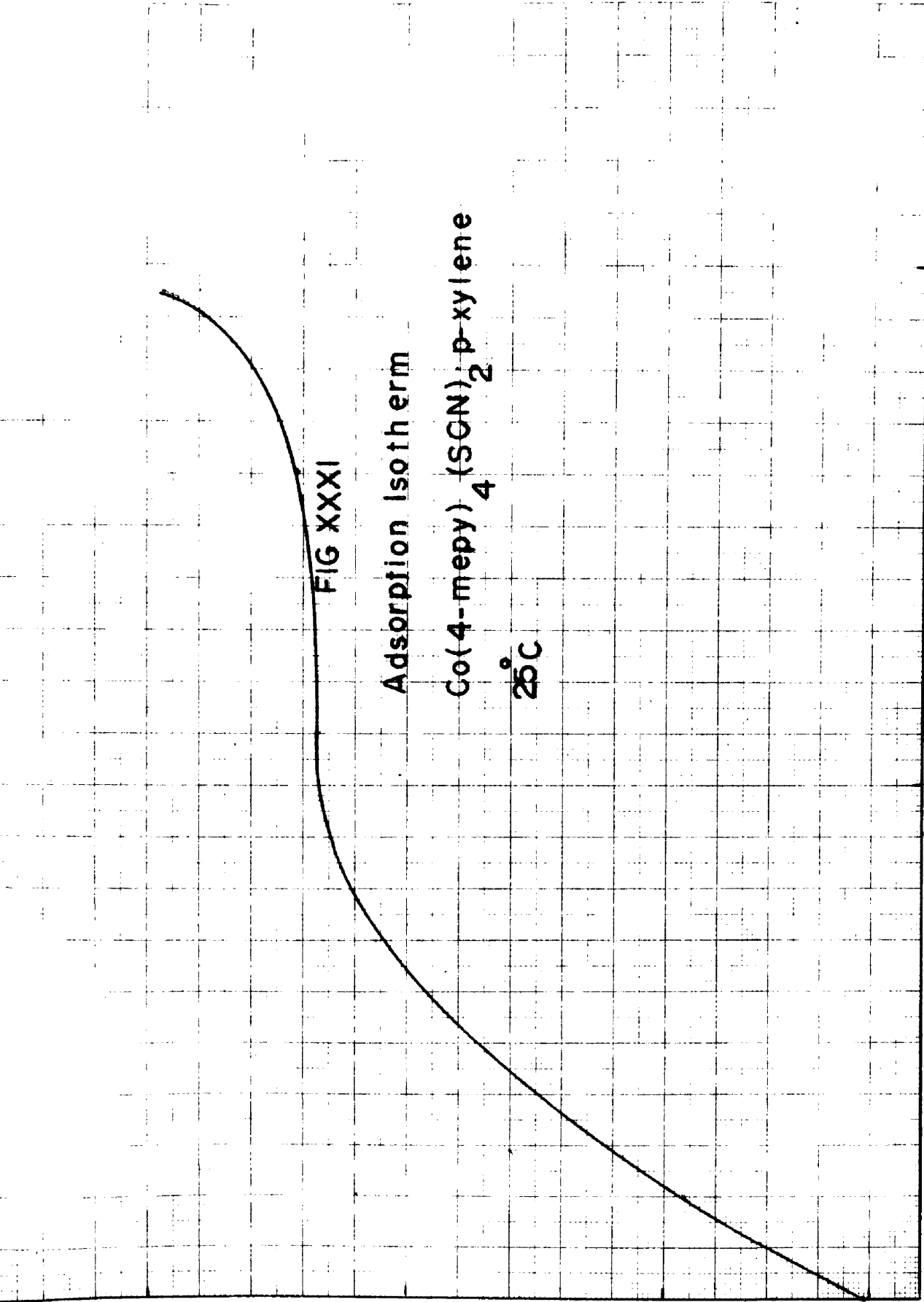
4.0 - Log(mole unadsorbed)

FIG XXXI

Adsorption Isotherm

Co(4-mepy)₄(SCN)₂p-xylene

25°C



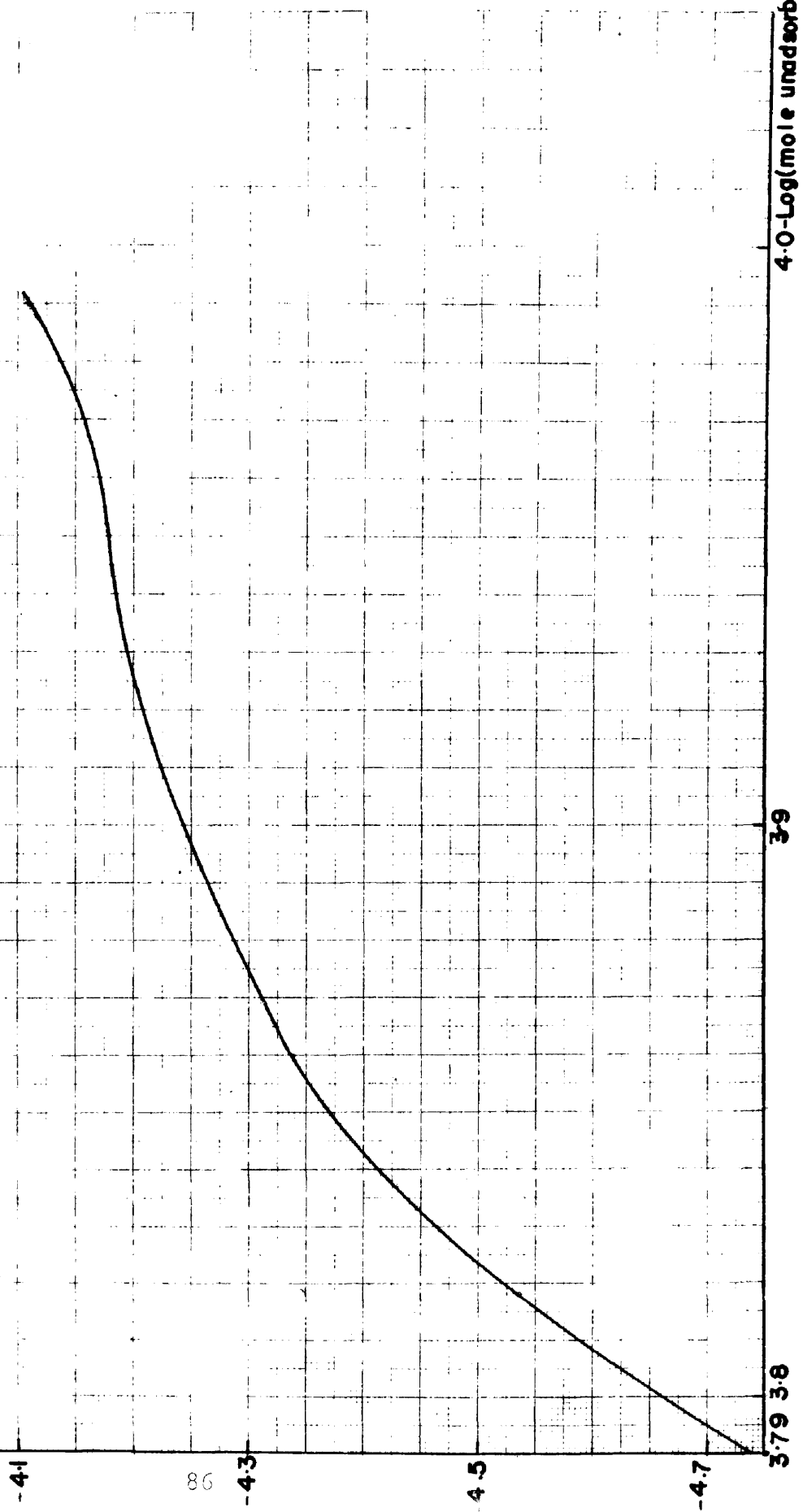
Log(mole adsorbed)

FIG XXXII

Adsorption Isotherm

Fe(4-mepy)₄(SCN)₂·p-xylene

25°C



3.7 3.8

3.9

4.0-Log(mole unadsorbed)

Log (mole adsorbed)

FIG XXXIII

Adsorption Isotherm

Ni(4-mepy)₄ (SCN)₂ p-xylene

25°C

-40

87

5.0

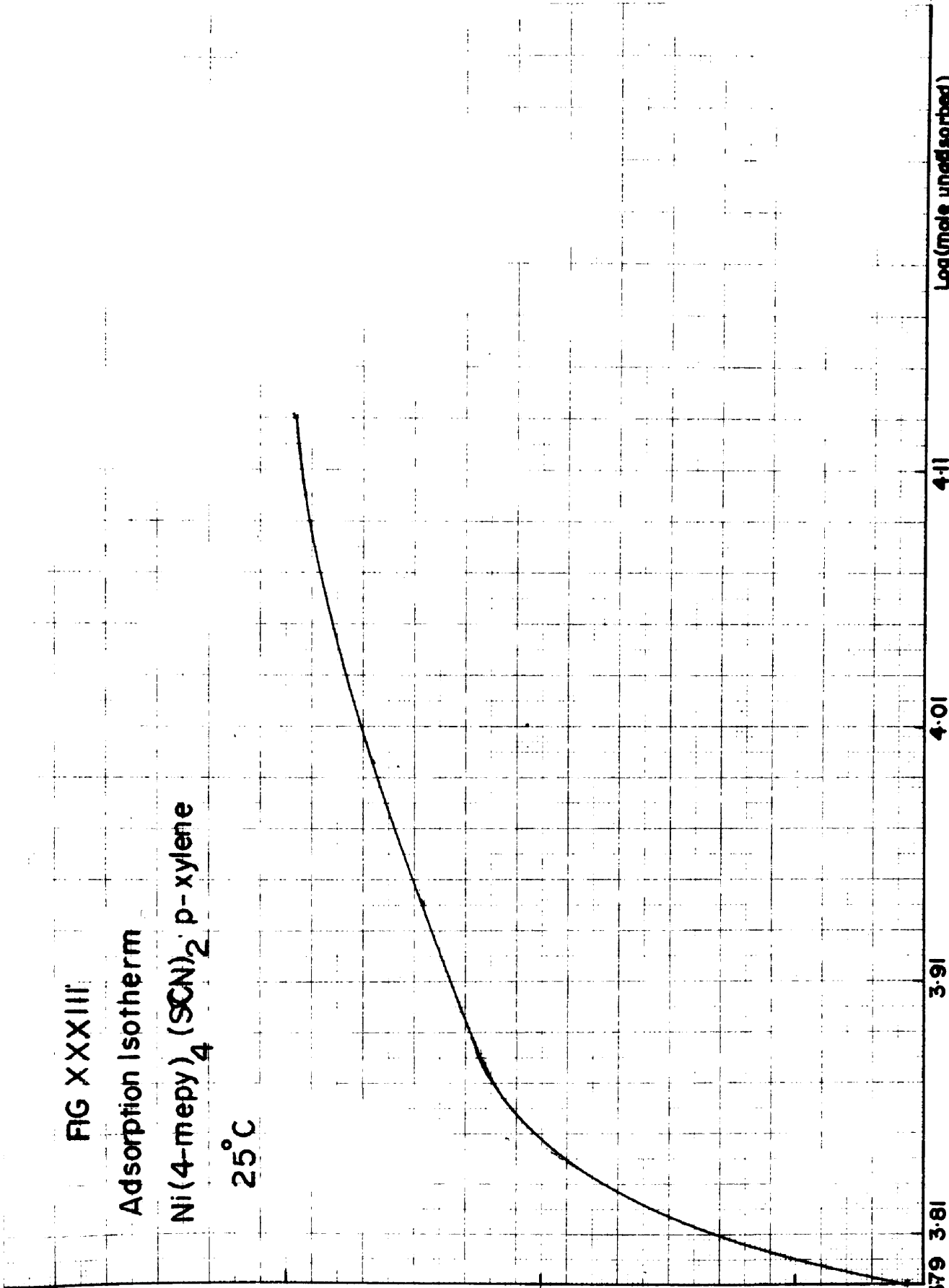
3.79 3.81

3.91

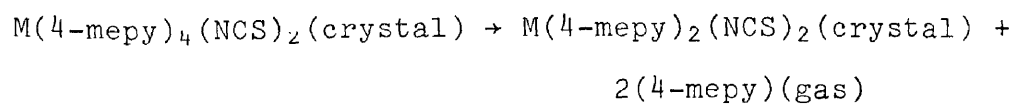
4.01

4.11

Log (mole unadsorbed)



by Beech and Kauffman (67) who suggested the decomposition reaction as



where M is the Metal, 4-mepy is 4-methylpyridine.

However, up to this stage there is not enough data gathered in this study to offer any definite conclusions.

Weight (mg)

Temp °C

40

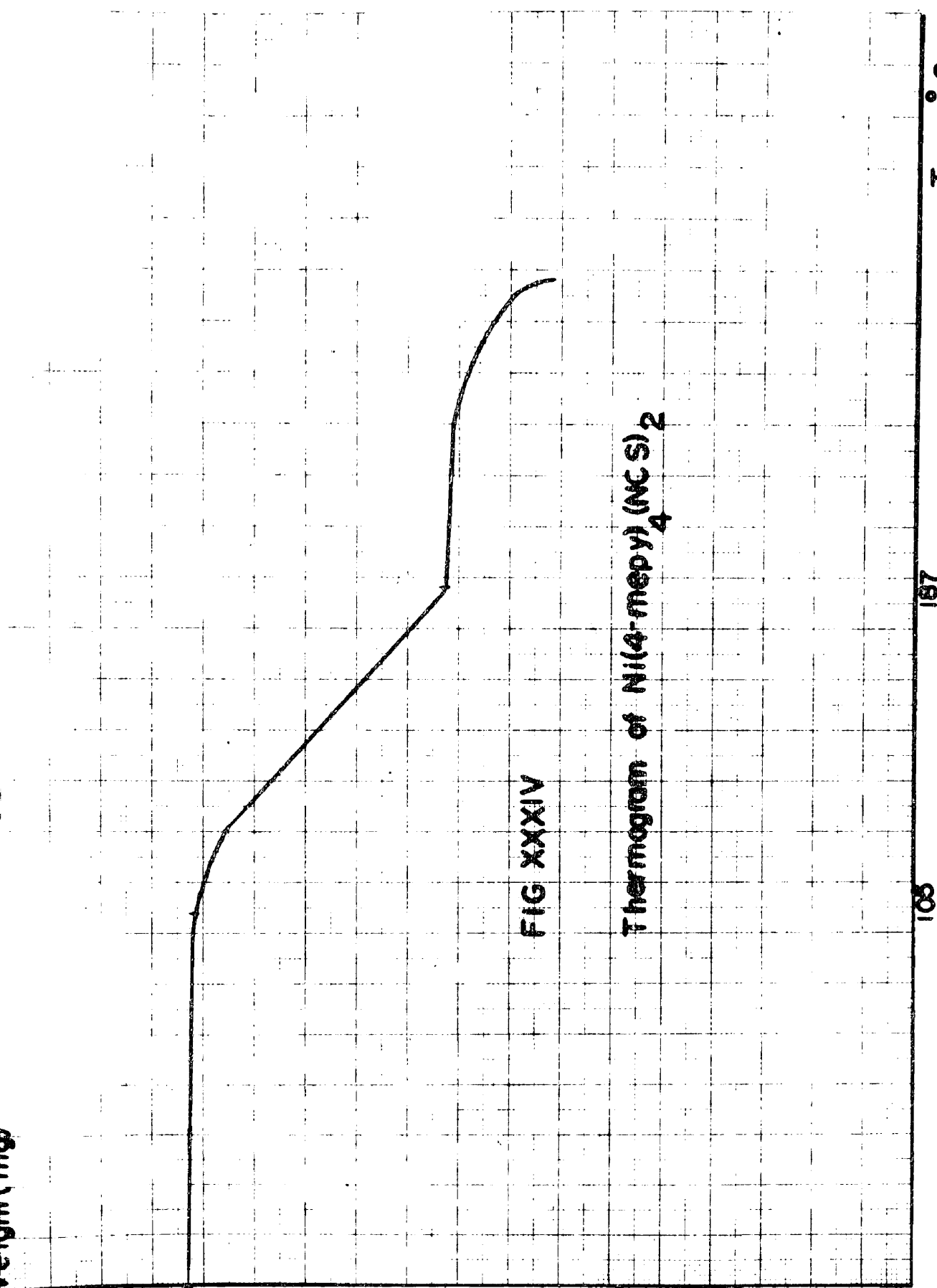
80
27

108

187

FIG XXXIV

Thermogram of Ni(4-mepy)₄(NC S)₂



Weight (mg)

31.5

90

21

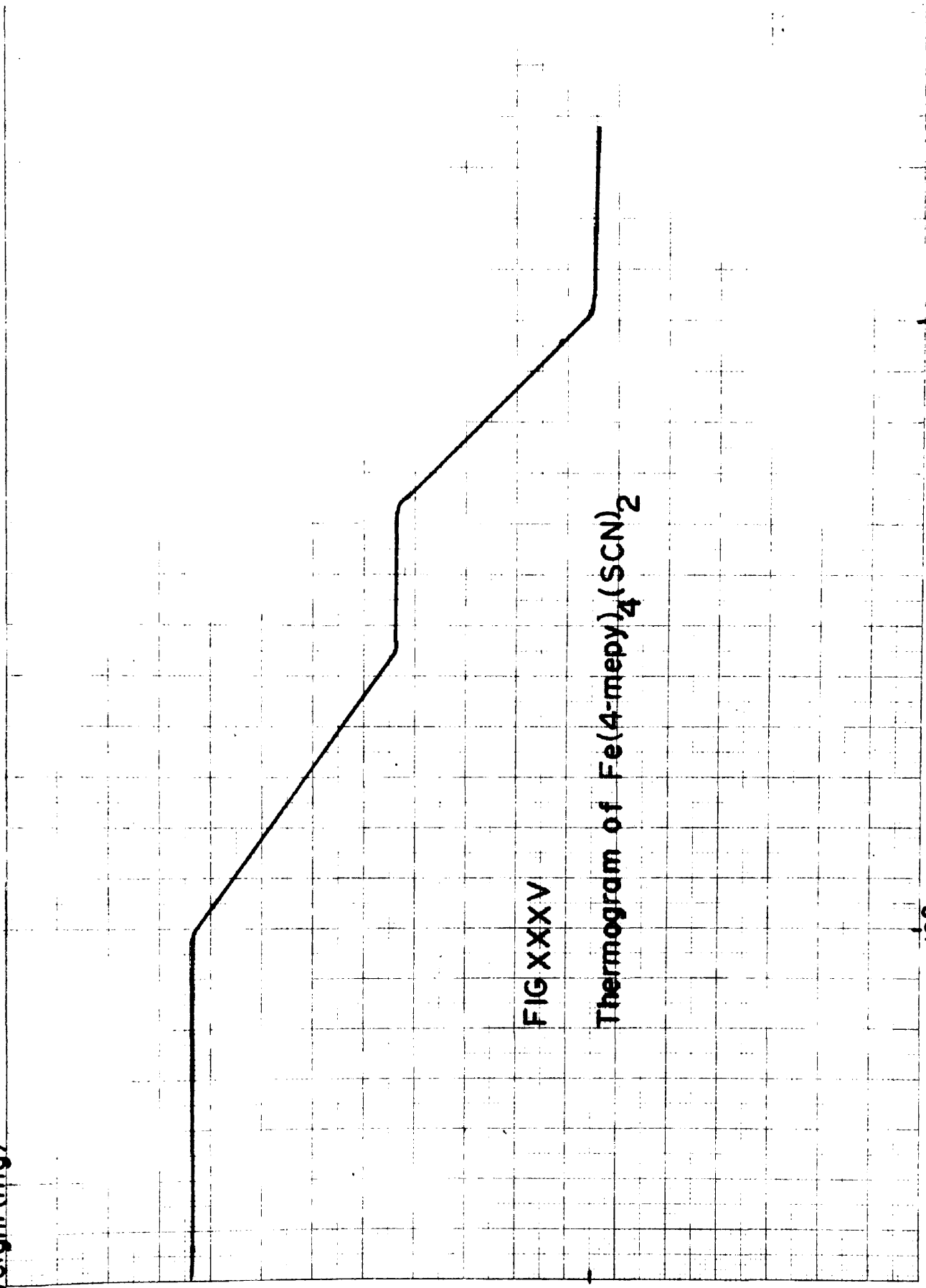
FIG XXXV

Thermogram of $\text{Fe}(\text{4-mepy})_4(\text{SCN})_2$

102

205

Temp °C



GENERAL SUMMARY

General Summary

Clathrates of Werner complexes have been studied mainly because of their ability to separate various isomers. Previous work in this laboratory has included the preparation and kinetic studies of a number of clathrates utilizing complexes formed by the first row transitional metals. The study presented here consists of further investigation of the kinetics of the clathration reaction under various experimental conditions and with the assumption as shown previously (12) that the optimum clathration condition obtains by using 40g of complex with 10 ml of guest and that stirring rate and particle size of host crystal have a negligible effect on the kinetic rate.

Extensive studies were carried out on the $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ and $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ Werner complexes using benzene, toluene, and p-xylene as guests. The results of these studies showed that the clathration reaction between $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ and the respective guests is not a first order, reversible reaction. For the other case, clathration is found to occur between $\text{Fe}(4\text{-mepy})_4(\text{SCN})_2$ and p-xylene only and there is no indication of the formation of clathrates between the Fe(II) complex and benzene or toluene as previously predicted by Lok (30,37) in this laboratory. This behaviour could be due to the size factor of the guests and/or the anomalous nature of Fe(II) which may be oxidized to Fe(III) during the preparation process. Re-runs of the clathration reaction

using $\text{Ni}(4\text{-mepy})_4(\text{NCS})_2$ as host and benzene, toluene and p-xylene as guests are in total agreement with the work performed by Chou (12) and Vasantha (55) in this laboratory.

It was postulated in the literature that the clathration reaction may in fact be a simple adsorption process (1). To test such a hypothesis plots of the Freundlich isotherm for each of the above combinations of host and guest were made. A near straight line is obtained in the case of benzene but with toluene and p-xylene all plots are non-linear suggesting that clathration may not be a simple adsorption process as has been hypothesised. Such results are suggestive of the critical dimension of the guest molecules essential in bringing about an adsorption process.

Plots of \ln (concentration at time t) vs. \ln time were attempted in addition to the conventional $\log (A_t - A_\infty)$ plots to test whether the clathration process is indeed first order or not. The results show that clathration follows a first order kinetic rate law in only a very narrow region.

Reversibility tests were carried out on all systems using various guests and from the plots of absorbance vs. time, it appears that none of the systems studied were reversible.

The results of X-ray powder diffraction measurements confirm the lattice change ($\alpha \rightarrow \beta$) in going from complex to clathrate.

Preliminary thermogravimetric analyses were also carried out on the Ni(II) and Co(II) complexes; however, more detailed investigations are required in order to establish any meaningful conclusion.

BIBLIOGRAPHY

Bibliography

1. Allison, S. A., and R. M. Barrer, J. Chem. Soc., (Sec. A) 1717 (1969)
2. Anderson, R. B., and W. K. Hall, J. Am. Chem. Soc., 70, 1727 (1948)
3. Barrer, R. M., and D. J. Ruzicka, Trans. Faraday Soc., 58, 2262 (1962)
4. Belitskukus, D., Jeffery, G. A., McMulan, R. K., and N. C. Stephenson, Inorganic Chem., 2, 873 (1963)
5. Bhatnager, V. M., Sepa. Sci., 4 (4), 287-98 (1969)
6. Brown, J. F. Jr., Scientific Am., 82 (July, 1962)
7. Broneman, M., Ann., 189, 183 (1877)
8. Brunauer, S., Emmett, P. H., and E. Teller, J. Am. Chem. Soc., 60, 309 (1938).
9. Brunauer, S., Deming, L. S., Deming, W. E., and E. Teller, J. Am. Chem. Soc., 62, 1723 (1940)
10. Casellato, F., and B. Casu, Spectrochimica Acta, 25, No. 8, 1407 (1969)
11. Chancel., G., and F. Paramentier, C. R., Acad. Sci. Paris, 100, 27 (1885)
12. Chou, Y. L., M. A. Thesis, Northern Michigan University (1971)
13. Davy, H., Phil. Trans. Roy. Soc., 101, 155 (1811)
14. DeBoer and Z. Zwicker, Physik, Chem., B3, 407 (1929)
15. Dryden, J. S., and K. J. Meakins, Nature, 169, 324 (1952)
16. Dryden, J. S., and K. J. Meakins, J. Chem. Soc., 3295 (1950)
17. Dryden, J. S., Trans. Faraday Soc., 49, 1333 (1953)
18. Duval, C., Inorganic Thermogravimetric Analysis, Second and Revised Edition, Elsevier Publishing Co., 1963
19. Evans, D. F., and R. E. Richards, Nature, 170, 246 (1952)

20. Evans, D. F., and R. E. Richards, J. Chem. Soc., 3932 (1952)
21. Evans, D. F., and R. E. Richards, Pro. Roy. Soc., 223A, 238 (1954).
22. Faraday, M., Quart. J. Sci., 15, 71 (1823)
23. Frenkel, J., Kinetic Theory of Liquids, Oxford, Oxford University Press, 1946
24. Freundlich, H., Colloid and Capillary Chemistry, Methuen, London, 1926.
25. Gawalek, G., and H. G. Konnecke, Revue. de Chemie Academie de la Republique Populaire Roumaine, 7, 875 (1962)
26. Giles, C. H., and T. H. MacEwan, Proc. Intern. Congr. Surface Activity, 2nd, Vol. 3, p. 457, London, 1957
27. Hart, M. I. Jr., and N. O. Smith, J. Am. Chem. Soc., 84, 1816 (1962)
28. Hart, M. I. Jr., Ph.D. Dissertation, Fordham University, (1962)
29. Honda, K., Sci. Rept. Tohoku University, 4, 97, (1915)
30. Jacobs, G. D., and M. T. Lok, Inorganic Chem., 10, 1823, (1971)
31. Keenan, A. G., J. Am. Chem. Soc., 70, 3947 (1948)
32. Kingston, D. W., Private Communication
33. Kipling, J. J., Proc. Intern. Congr. Surface Activity, 2nd, London, 1957
34. Lahr, P. H., and H. L. Williams, J. Phys. Chem., 63, 1432 (1959).
35. Langmuir, I., J. Am. Chem. Soc., 40, 1361 (1918)
36. Langmuir, I., J. Chem. Soc., 511 (1940)
37. Lok, M. T., M. A. Thesis, Northern Michigan University, (1970)
38. Mandelcorn, L., Chem. Revs., 59, 827 (1959)

39. Minton, M. J., Ph.D. Dissertation, Fordham University, (1966)
40. Minton, M. J., and N. O. Smith, J. Phys. Chem., 71 (II) 3618-22 (1967)
41. Palin, D. E., and H. M. Powell, J. Chem. Soc., 208 (1947)
42. Palin, D. E., and H. M. Powell, J. Chem. Soc., 815 (1948)
43. Pauling, L., and R. E. Marsh, Proc. Nat. Acad. Sci. U. S., 38, 112 (1952)
44. Powell, H. M., Research, I, 353 (1948)
45. Powell, H. M., and P. Riesz, Nature, 161, 52 (1948)
46. Powell, H. M., and M. Guter, Nature, 164, 240 (1949)
47. Powell, H. M., Endeavour, 9, 154 (1950)
48. Powell, H. M., J. Chem. Soc., 298 (1950)
49. Powell, H. M., J. Chem. Soc., 468 (1950)
50. Powell, H. M., Rec. Trav. Chim., 75, 885, (1956)
51. Powell, H. M., and J. H. Rayner, J. Chem. Soc., 319 (1952)
52. Platteeuw, J. C., Rec. Trav. Chim., 77, 403 (1958)
53. Platteeuw, J. C., and J. H. Van der Waals, Mol. Phys., I, 91 (1958)
54. Schaeffer, D., S. Dorsey, D. A. Skinner, and C. G. Christian, J. Am. Chem. Soc., 79, 5870 (1957)
55. Vasantha, K., M. A. Thesis, Northern Michigan University, (1971)
56. Van der Waals, J. H., Trans. Faraday Soc., 52, 182 (1956)
57. Van der Waals, J. H., and J. C. Platteeuw, Rec. Trav. Chim., 75, 912 (1956)
58. Van der Waals, J. H., J. Phys. Chem. Solids, 18, 82 (1961)
59. Van der Waals, J. H., and J. C. Platteeuw, Adv. Chem. Phys., 2, I (1959)

60. Von Stackelberg, M., and H. R. Muller, J. Chem. Phys., 19, 1319 (1951)
61. Von Stackelberg, M., Proceedings of International Congress on Co-ordinating Compounds, 408 (1955)
62. William, F. V., J. Am. Chem. Soc., 79, 5876 (1957)
63. Wohler, K., Ann., 69, 294 (1849)
64. Zuccherò, R., M. A. Thesis, Northern Michigan University, June, 1972
65. Physical Methods in Chemical Analysis, editor W. G. Berl, VI, IV, Academic Press, N.Y., p. 223, 1961
66. Thermal Analysis, editors R. F. Schwenker Jr. and P. D. Garn, Vol. II, Academic Press, N.Y., 1969
67. Thermochimica Acta, editor W. W. Wendlandt, Vol. I, No. I, p. 93-102, 1970

APPENDICES

Appendix I

Calculation of Guest-Host Mole Ratio in Clathrates

$$\% \text{ of Ni in Ni(4-mepy)}_4(\text{NCS})_2 = (58.71/547.34) \times 100 = 10.73$$

% of Ni in Benzene Clathrates

$$\text{Ni(4-mepy)}_4(\text{NCS})_2 \cdot \text{C}_6\text{H}_6 = (58.71/625.45) \times 100 = 9.39$$

(assuming 1:1 ratio of guest:host)

% of benzene in the clathrate

$$\text{Ni(4-mepy)}_4(\text{NCS})_2 \cdot \text{C}_6\text{H}_6 = (78.11/625.45) \times 100 = 12.49$$

(assuming 1:1 ratio of guest:host)

If, for example, 10.20% of Ni is then found in a clathrate, then 'x', the guest to host mole ratio is given by:

$$\frac{10.73 - 9.39}{1} = \frac{10.73 - 10.20}{x}$$

$$x = 0.53/1.34 = 0.40.$$

A similar procedure is applied to other clathrates by substituting appropriate values for the various 'Metal' and 'Guest' molecules considered.

Appendix II

Calibration Curves

The absorbances of benzene, toluene and p-xylene were obtained on the Beckman DB-G Spectrophotometer using matched silica cells. Spectroquality benzene, toluene and p-xylene were used while the purity of the solvent, n-heptane, was obtained spectrophotometrically and gave a straight baseline from 320 nm to 245 nm.

Data Plotted

(p-Xylene)

Number of λ 's* of p-xylene per 100 ml of heptane	Concentration**	Absorbance
40	32.44	1.900
10	8.11	0.550
2.5	2.02	0.130
0.625	0.51	0.035
0.125	0.17	0.010

(Toluene)

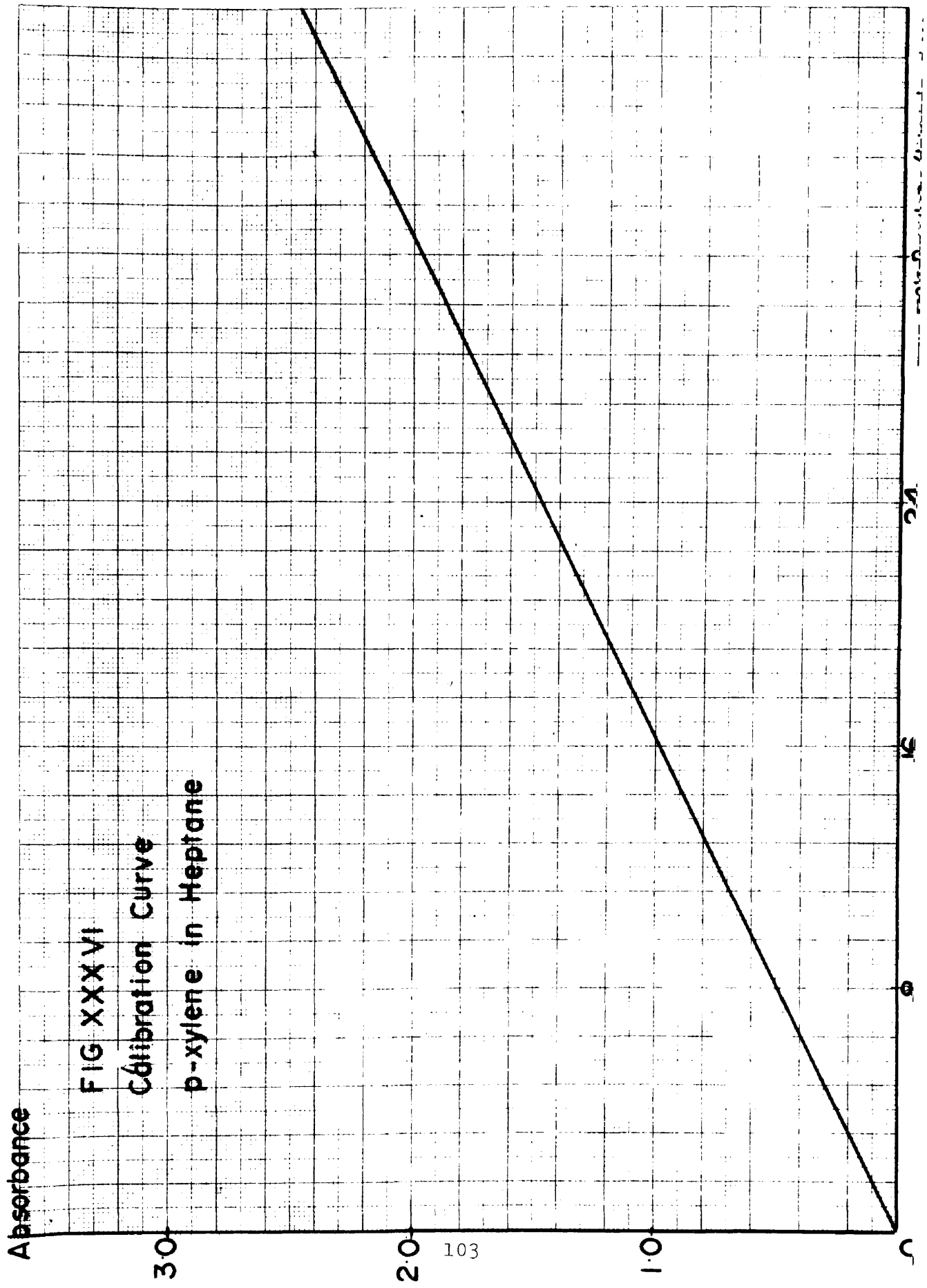
Number of λ 's* of Toluene per 100 ml of heptane	Concentration**	Absorbance
40	37.59	0.880
10	9.34	0.247
2.5	2.35	0.056
0.625	0.58	0.033
0.125	0.15	0.010

(Benzene)

Number of λ 's* of Benzene per 100 ml of heptane	Concentration**	Absorbance
40	44.98	0.915
10	11.25	0.248
2.5	2.81	0.075
0.625	0.70	0.058
0.125	0.14	0.018

* $1\lambda = 0.001$ ml

** moles of benzene, toluene, or p-xylene per liter of
heptane $\times 10^4$



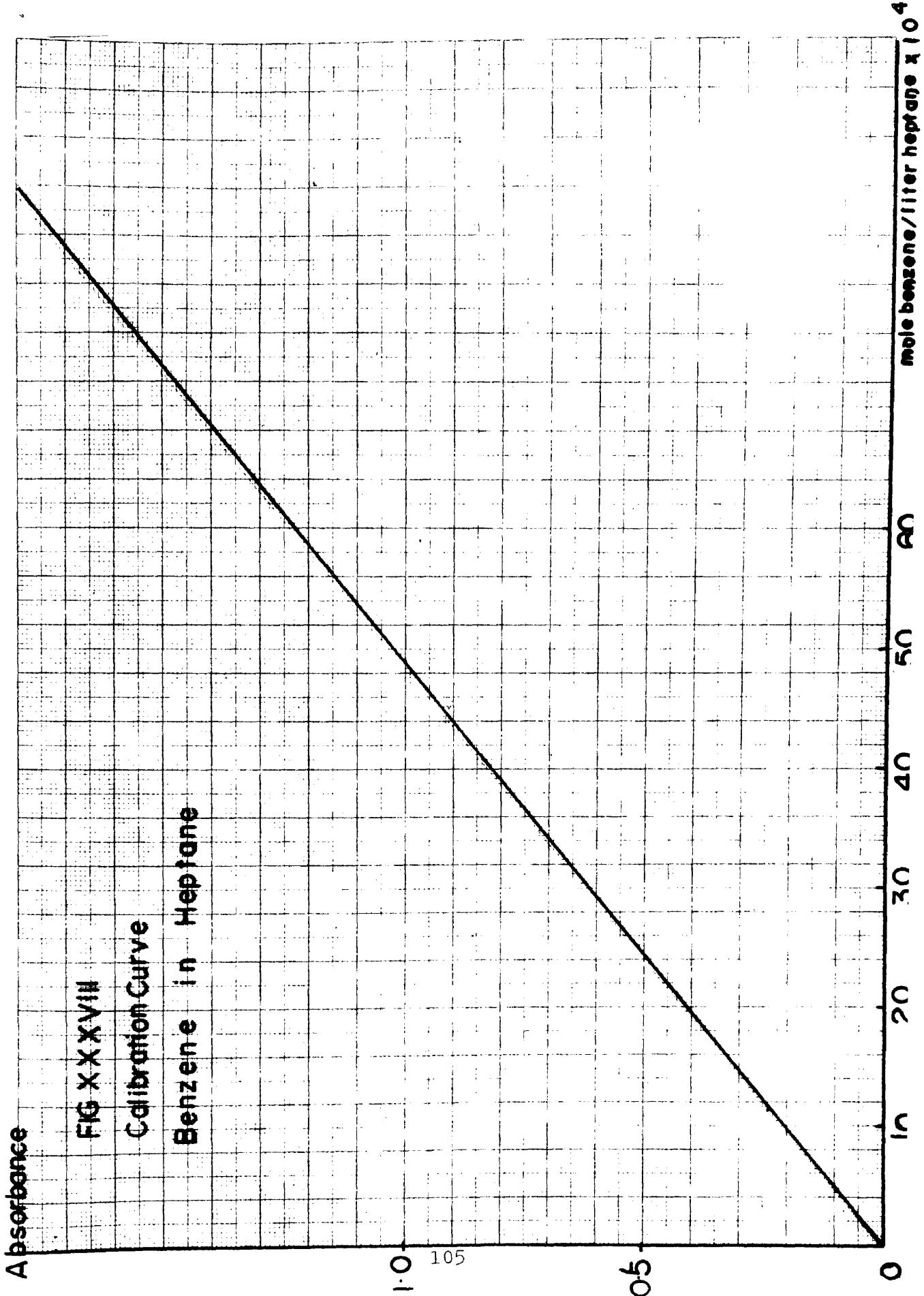


FIG XX XVIII
Calibration Curve
Benzene in Heptane