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PHYSICO-CHEMICAL STUDIES OF THE
$Ni(4\text{-methylpyridine})_4(SCN)_2 \cdot$ TOLUENE CLATHRATE SYSTEM

by

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DIPLOMA, TAIPEI INSTITUTE OF TECHNOLOGY

A Thesis
Submitted in Partial Fulfillment of the
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School of Graduate Studies
Northern Michigan University
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August 1971

PHYSICO-CHEMICAL STUDIES OF THE
Ni(4-methylpyridine)$_4$(SCN)$_2$ · TOLUENE CLATHRATE SYSTEM

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This thesis is recommended for approval
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ABSTRACT

A brief outline of the history of clathrate compounds is presented. A study of the clathration reaction utilizing $Ni(4\text{-mepy})_4(SCN)_2$ as host and benzene, toluene, and p-xylene as guests was carried out under various conditions. Evidence obtained in this study indicates that the clathration reaction is not a first order, reversible reaction for toluene as the guest component. The Freundlich adsorption isotherm equation was found to "fit" the clathration reaction involving benzene but apparently does not fit when toluene or p-xylene are employed as guests. It is suggested that this is due to the larger size of the latter two guest molecules. The evidence would indicate that the critical size of a guest molecule is about 6Å; that is somewhere between the length of a benzene molecule (~5.1Å) and a toluene molecule (~7.6Å).

ACKNOWLEDGEMENTS

The author wishes to express her appreciation to Dr. Gerald D. Jacobs for his enthusiastic guidance throughout the research by providing helpful suggestions and corrections in the preparation of this thesis; to the faculty members and graduate students of the Chemistry Department for their criticism of the experiments.

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HISTORICAL BACKGROUND

HISTORICAL BACKGROUND

About twenty years ago, H. M. Powell named the cage-like molecular compounds, in which one component fits into a cavity in the other, "clathrates". The term was first introduced into the literature following Powell's X-ray studies on a series of molecular compounds (38). Following this work, intensive studies on this new type of compound were made by Mandelcorn (32). Work was divided among the following three areas:

1. Gas hydrates
2. Quinol complexes
3. $Ni(CN)_2NH_3 \cdot M$(M=organic adduct)

1. Gas hydrates

A gas or low-boiling-point liquid is dissolved in water under pressure and upon cooling forms the complex we now call gas hydrates. The first complex, formed from chlorine and water, was reported by Davy in 1810 (10). Faraday proposed the formula $Cl_2 \cdot 10H_2O$ (18). Brown (6) separated gas hydrates into two groups; one contains six guest molecules combined with 46 water molecules; the guests are small molecules such as Cl_2, Br_2, SO_2, H_2S, CH_4, etc., and the other group contains one guest molecule for each 17 water molecules. The guests in the latter complexes are slightly larger and include $CHCl_3$, C_2H_5Cl, C_3H_8 etc..

The crystal structure was studied by Pauling and Marsh (37) and they reported that all gas hydrate crystals are cubic structures, guest molecules being situated in cavities formed by a framework of water molecules (the host) linked together by hydrogen bonds.

2. Quinol complexes

By means of hydrogen bonds, six hydroquinone molecules are linked together in the shape of a hexagon to form cages. The hydroquinone cage forms "the host" thereby allowing the guest molecule to become trapped. The first report of these complexes was made by Wohler (49) and Clemm (9). More recent work in this area, based upon X-ray analysis, was reported by Powell and coworkers (35,36) (38-44).

Thermodynamic and other related properties have been determined by Evans and Richards (15-17) and many other workers (12-14).

3. $Ni(CN)_2NH_3 \cdot M$(M=benzene)

This is the first clathrate which was formed from an inorganic complex and an organic compound. The crystal structure was determined by Rayner and Powell using X-ray analysis (45). More detailed work was reported by Bhatnager (5).

Following these early investigations a large number of Werner complexes have been shown to function as host. Schaeffer and William's (46,48) reported a large number of these compounds. The clathrate for which $Ni(4\text{-mepy})_4(SCN)_2$ serves as host, was studied by Hart, Minton, and Smith (23,24,33,34) and thermodynamic constants, kinetic rate data, infrared spectra and phase diagrams reported. The crystal structure of this clathrate was studied by Belitskus, et. al. (4). The work by Lok (31), showed that there is a definite size relationship between host and guest. More recent work by Vasantha (47), using $Ni(4\text{-}mepy)_4(SCN)_2$ as the host and benzene as the guest molecule, has shown that the clathration process is apparently not a first order, reversible reaction.

It was found that not all of the substances under study were "clathrates" as originally defined by Powell. A classification scheme was needed and the following was proposed:

I. Complex molecules
  A. Coordination compounds
  B. Inorganic polymers
  C. Molecular compounds
    1. Inclusion compounds
      a. Urea and Thiourea Adducts
      b. Zeolite Complexes
      c. Graphite and Silica Complexes
      d. Dextrin - Iodine Type Complexes
      e. Clathrates

Inclusion Compounds are stable crystalline solids that result from the combination of complete molecules united spatially without effecting the bonding system of the components and could be distinguished by the nature of the cavity.

Recent developments in this field indicate that this classification system is not inclusive and will need further modification. (50)

INTRODUCTION

INTRODUCTION

Since 1957, when Schaeffer and coworkers published a paper entitled "Separation of Xylene, Cymenes, Methylnaphthalenes, and Other Isomers by Clathration with Inorganic Complexes". (46), a large number of clathrates have been prepared and their physical and chemical properties studied. According to the paper by Schaeffer et.al., most of the complex compounds that proved to have clathration properties had four molecules of a nitrogen base coordinated with a central metal atom. Substituted pyridines and quinolines were suitable basic nitrogen compounds and transition elements were suitable metals for forming these clathrates. The clathrates were prepared by two different methods, the suspension process and the solution process. Only the suspension process was utilized for the present work. The work by Schaeffer was concerned exclusively with the enrichment of petroleum fractions and was only analytical in nature. Further work by Lok (31) indicated that several complexes, listed in Schaeffer's paper failed to form clathrates using the suspension process. Up to now, the $Ni(4\text{-mepy})_4(SCN)_2$ is the complex which has been studied in greatest detail. In 1962, Hart (24) presented infrared spectra, phase diagrams, calorimetric and X-ray data for clathrates of $Ni(4\text{-mepy})_4(SCN)_2$. In 1967, Minton (33) presented the results of further kinetic, phase and calorimetric studies. The configuration of the complex is octahedral as proven by Belitskus' single crystal X-ray studies (4) and was further confirmed by magnetic susceptibility measurements and visible absorption spectra.

In Minton's thesis (33) clathration is considered a first order, reversible process for p-xylene and ethylbenzene as guests. However, research by Lok (31) indicated that clathration is apparently not a first order, reversible reaction. In 1969, Allison (1) assumed the clathration to be an adsorption process. Work by Vasantha (47) also indicates that the clathration is not a first order, reversible reaction and might be simple adsorption for benzene as guest.

Additional experiments were designed in this laboratory using larger guest molecules; toluene was chosen first for testing various factors which will effect the rate of clathration. These factors are (i) temperature (ii) particle size of the host crystals (iii) the rate of stirring of the mixture (iv) concentration of the host and (v) concentration of the guest. Allison's assumption was further tested by kinetic rate studies of clathration using $Ni(4\text{-mepy})_4(SCN)_2$ as host and benzene, toluene, and p-xylene as guests.

INSTRUMENTATION

INSTRUMENTION

Analytical Measurements

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

Spectral Measurements

Beckman silica cells and a Beckman DB-G Grating Spectrophotometer were used to obtain the ultraviolet spectra which were recorded on a Sargent Model SR Recorder.

Temperature

All the kinetic rate studies were carried out in a constant temperature bath with regulation ±0.2°C. The temperature was monitered with a thermometer calibrated and certified by the United States National Bureau of Standards.

X-Ray Measurements

The X-ray powder diffraction patterns were obtained using copper K-alpha radiation and a Siemens Kristalloflex 4, X-Ray Diffractometer. The line measurements were made with a coincidence scale having an accuracy of ±0.01 mm.

EXPERIMENTAL

EXPERIMENTAL

Preparation of $Ni(4\text{-mepy})_4(SCN)_2$

After 0.228 mole of $NiCl_2 \cdot 6H_2O$ and 0.456 mole of KSCN were completely dissolved in three liters of water, 0.910 mole of 4-methylpyridine was added slowly with constant stirring. This mixture was stirred for one hour before filtering. During filtering, a large amount of water was used to remove the excess thiocyanate. The precipitate was allowed to air dry for several hours and was then transferred to desiccator and dried over solid potassium hydroxide for approximately one week. After drying, the purity of the complex was determined using quantitative analyses for the percent of nickel. The chemicals used in this preparation were Reagent Grade.

Purification of Solvent

Reagent Grade heptane was purified before it was used as a suspension medium in the kinetic rate studies.

The procedure involved transferring the heptane to a large separatory funnel and shaking with concentrated sulfuric acid. The heptane was then neutralized by shaking with a 10% sodium carbonate solution, followed by salting-out with saturated sodium chloride solution. Twenty four hours of contact with each reagent was used. The heptane was dried by passing it through a column of anhydrous calcium chloride and finally it was fractionally distilled. The purity of the heptane was determined from ultraviolet spectra and it was shown to have the same purity as commercially available "spectroquality" grade.

Kinetic Rate Studies

A one liter volumetric flask containing 300 ml of purified heptane and 10 ml of toluene was placed in the thermostat and stirred with a magnetic stirrer which was placed beneath the bath. After thermal equilibrium was reached, one milliliter of the sample solution was withdrawn by means of a filter stick. A micropipet was then used to accurately measure 0.1 ml of the withdrawn sample and this solution was introduced into a 25 ml volumetric flask and diluted with purified heptane.

Following the withdrawal of the initial sample, the inorganic complex, in powder form, was introduced into the flask. The initial time for the kinetic run was taken as the time the complex was added to the solution. At pre-determined time intervals, samples of the solution were withdrawn.

Each study was allowed to proceed for no less than 48 hours. The decrease in the concentration of toluene was determined by a Beckman DB-G Spectrophotometer operating in the ultraviolet region between 380 mu and 240 mu with a maximum absorbance at 263 mu.

After the reaction reached equilibrium, the contents of the volumetric flask were filtered and the precipitate was allowed to dry. This solid was used for X-ray powder diffraction studies and quantitative analyses.

X-Ray Diffraction Patterns

Samples of the complex and the material which formed in the kinetic run were used for X-ray powder diffraction patterns. First, the samples were ground to a fine powder and mixed with collodion. Then, the partially dried sample was extruded from a 0.5 mm capillary tube. Patterns were obtained using a Siemens two radian camera, copper k-alpha radiation and an exposure time of one hour.

Quantitative Analyses

The percent of nickel in the complex and in the clathrate was determined by a standard method (51,52). Dilute hydrochloric acid was used to break down the complexes and clathrates.

The procedure followed in the volumetric analysis was to titrate the nickel solution with EDTA solution using murexide as indicator; the color changing from yellow to purple. The purity of the complex was indicated by the percent of nickel in the complex.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Kinetic Studies

Kinetic rate studies on gas hydrates have been reported by Barrer and Ruzika (3), and for hydroquinone clathrates by Lahr and Williams (28). The first kinetic's report on Werner complex clathrates was made by Gawalek and Könnecke in 1963 (21); they reported that the time for clathrate formation was less than fifteen minutes in most cases and that the rate of formation was effected by the solubility of the complex in the hydrocarbon suspension medium. The work by Minton and Smith (34) indicated that the clathration reaction was completed in four to six hours and that there was an initial rise in the guest concentration caused by either adsorption or absorption of the guest by the complex. The initial rise can be eliminated by extracting with 6N HCl, as was reported by Lok (31), and this suggested that the initial rise was due to the existence of free 4-methylpyridine in solution.

An equation representing the clathration process can be written as follows:

$$\text{Complex } (\alpha) \longrightarrow [\text{Complex } (\beta)] \longrightarrow \text{Clathrate}$$

The symbol α represents the lattice of the complex and β the "empty" lattice of the clathrate. This equation is based on Hart and Smith's report (23), that a lattice change occurs during the clathration process. The process described by Minton (33) is: "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." Minton also indicated that the reaction followed first order, reversible kinetics with respect to the guest. However, the work by Jacobs and Lok (25) indicated that the clathration is not a first order, reversible reaction using p-xylene as the guest. Further studies by Vasantha (47), also indicated that the reaction is not a first order, reversible reaction for benzene as the guest. Allison's work (1) indicated that clathration might be a simple adsorption process and this was further tested by Vasantha (47). In order to extend these studies, the larger size guest molecule, toluene, was used. The factors which are thought to influence the rate of clathration are:

(i) Temperature
(ii) Particle size of the host crystals
(iii) Rate of stirring of the mixture
(iv) Concentration of the guest component
(v) Concentration of the host complex

Temperature

This effect was studied at 5°C, 15°C, 25°C, and 35°C using two different host concentrations; specifically 30 and 40 grams of $Ni(4\text{-mepy})_4(SCN)_2$ with 10 ml of toluene. The results are presented in Table I through IV and Figures 1 through 4. Tables I and II present the analytical data and the change in guest concentration (measured as a decrease in absorbance) with time for the case of 40 grams of complex. Table's III and IV present data for the case of 30 grams of complex. Figure's 1 and 3 show absorbance as a function of time for the two complex concentrations. These figures show an initial rise which, in general, increased with temperature. This could be due to increased adsorption or absorption of solvent molecules. The period required for first observing a decrease in guest concentration using toluene is found to be larger than was the case using benzene as the guest (47). A reasonable explanation would be the larger size of the toluene molecule. Figure's 2 and 4 are plots of log(At - Ae) vs. time at various temperatures for 40 and 30 grams of complex respectively. From these curves it would appear that the clathration reaction utilizing toluene is not a first order reaction except in a small region. It is also observed that the higher the temperature, the lower the value of At - Ae. This would imply that the Guest/Host ratio decreases as the temperature increases. The variation in absorbance was estimated to ±0.005 units. Clathration is an exothermic reaction as shown by the decrease in rate with increasing temperature.

The difference between using 30 and 40 grams of complex at different temperatures can be found from Figures 1 through 4 and Tables I through IV. The results indicate that (1) The decrease in the concentration of the guest with higher

TABLE I

VOLUMETRIC ANALYSES FOR Ni IN THE COMPLEX Ni(4-mepy)$_4$(SCN)$_2$ AND TOLUENE CLATHRATE

		PERCENT NICKEL			
TRIAL	COMPLEX	CLATHRATE I*	II*	III*	IV*
1	10.71	9.77	9.68	10.02	9.91
2	10.69	9.75	9.72	10.08	9.91
AVERAGE	10.70	9.76	9.70	10.05	9.91
THEORETICAL	10.73				
MOLE RATIO[+] (GUEST/HOST)		0.625	0.664	0.438	0.529

[+] The values are reliable to an extent of ±0.06 units.

*Clathrate I, II, III, and IV refers to the clathrate formed at 5°C, 15°C, 25°C, and 35°C respectively for 40 grams of complex and 10 ml of toluene.

TABLE II

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

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.3181	0.3096	0.3096	0.3139
3	0.3139	0.3096	0.3096	0.3263
6	0.3096	0.3054	0.3284	0.3284
10	0.2833	0.3054	0.3222	0.3381
12	0.2923	0.3010	0.3050	0.3324
24	0.2001	0.2227	0.2122	0.3464
26	0.1875	0.2014	0.1973	0.3361
29	0.1673	0.1875	0.2001	0.3096
34	0.1644	0.1747	0.2001	0.2799
36	0.1553	0.1732	0.2001	--
48	0.1523	0.1673	0.2001	0.2292
50	0.1523	0.1673	0.2001	0.2279
52	0.1523	0.1673	0.2001	0.2279

*Sample I, II, III, and IV refers to clathrate formed at 5°C, 15°C, 25°C, and 35°C respectivity for 40g of complex and 10 ml of toluene.

TABLE III

VOLUMETRIC ANALYSES FOR Ni IN THE TOLUENE CLATHRATE

		PERCENT NICKEL			
TRIAL	CLATHRATE	I*	II*	III*	IV*
1		9.97	9.86	10.08	9.97
2		9.79	9.76	10.08	9.93
AVERAGE		9.88	9.81	10.08	9.95
MOLE RATIO+(GUEST/HOST)		0.548	0.596	0.420	0.503

*Clathrate I, II, III, and IV refers to the clathrate formed at 5°C, 15°C, 25°C, and 35°C respectively for the 30g of complex and 10 ml of toluene.

+The values are reliable to an extent of ±0.06 units.

TABLE IV

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

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu			
	SAMPLE I*	SAMPLE II*	SAMPLE III*	SAMPLE IV*
0	0.3096	0.3139	0.3096	0.3181
3	0.3139	0.3181	0.3171	0.3171
6	0.3139	0.3100	0.3171	0.3181
10	0.3096	0.3100	0.3424	0.3324
12	0.3010	0.3100	0.3171	0.3345
24	0.2480	0.2504	0.2989	0.3464
26	0.2253	0.2292	0.2911	0.3464
29	0.2148	0.2073	0.2648	0.3424
34	0.2068	---	0.2367	0.3365
36	0.1903	0.2068	---	---
48	0.1903	0.1903	0.2253	0.2765
50	0.1804	0.1903	0.2214	0.2672
52	0.1804	0.1903	0.2214	0.2516
54	0.1804	0.1903	0.2214	0.2455

*Sample I, II, III, and IV refers to clathrate formed at 5°C 15°C, 25°C, and 35°C respectively for 30 g of complex and 10 ml of toluene.

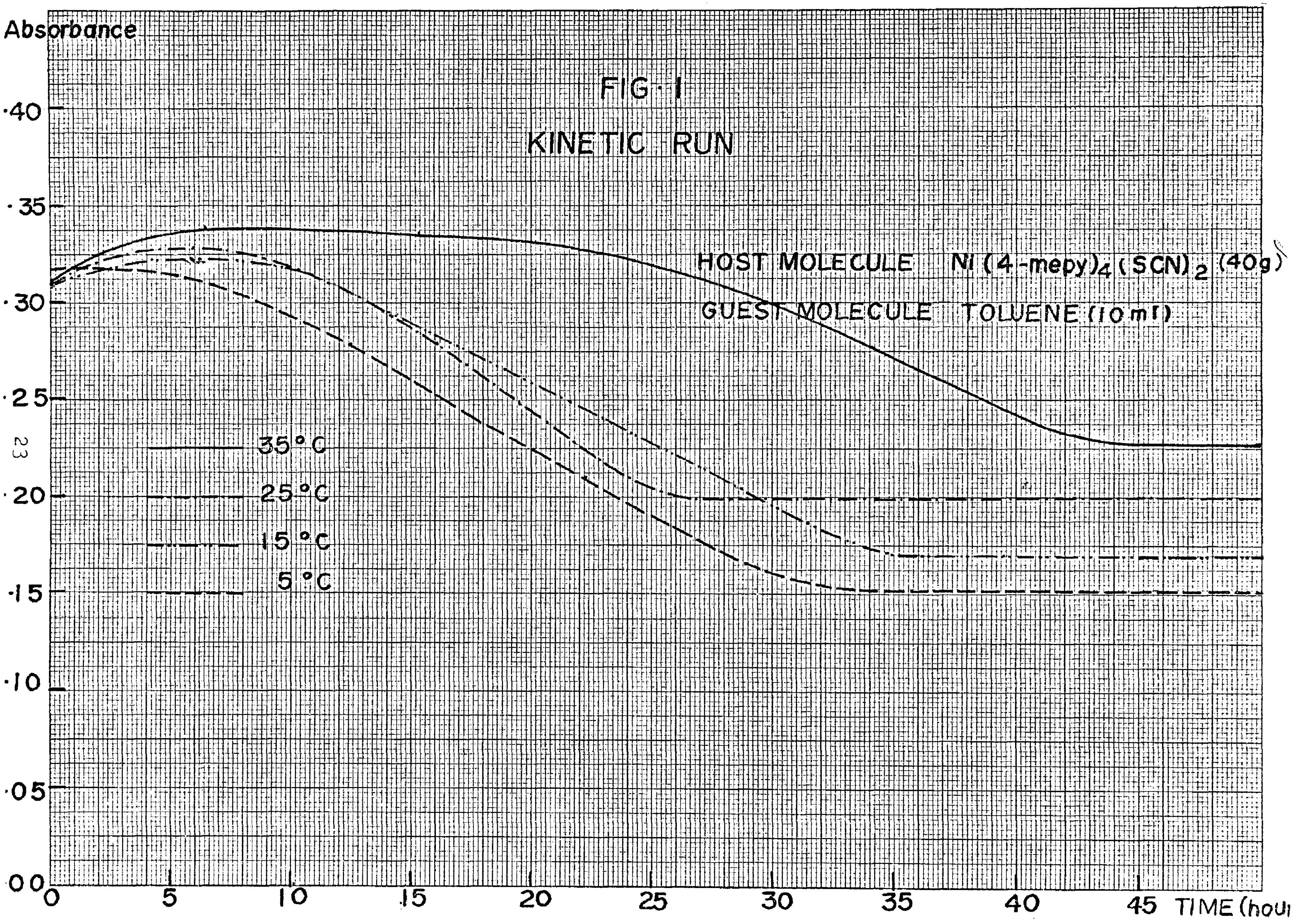
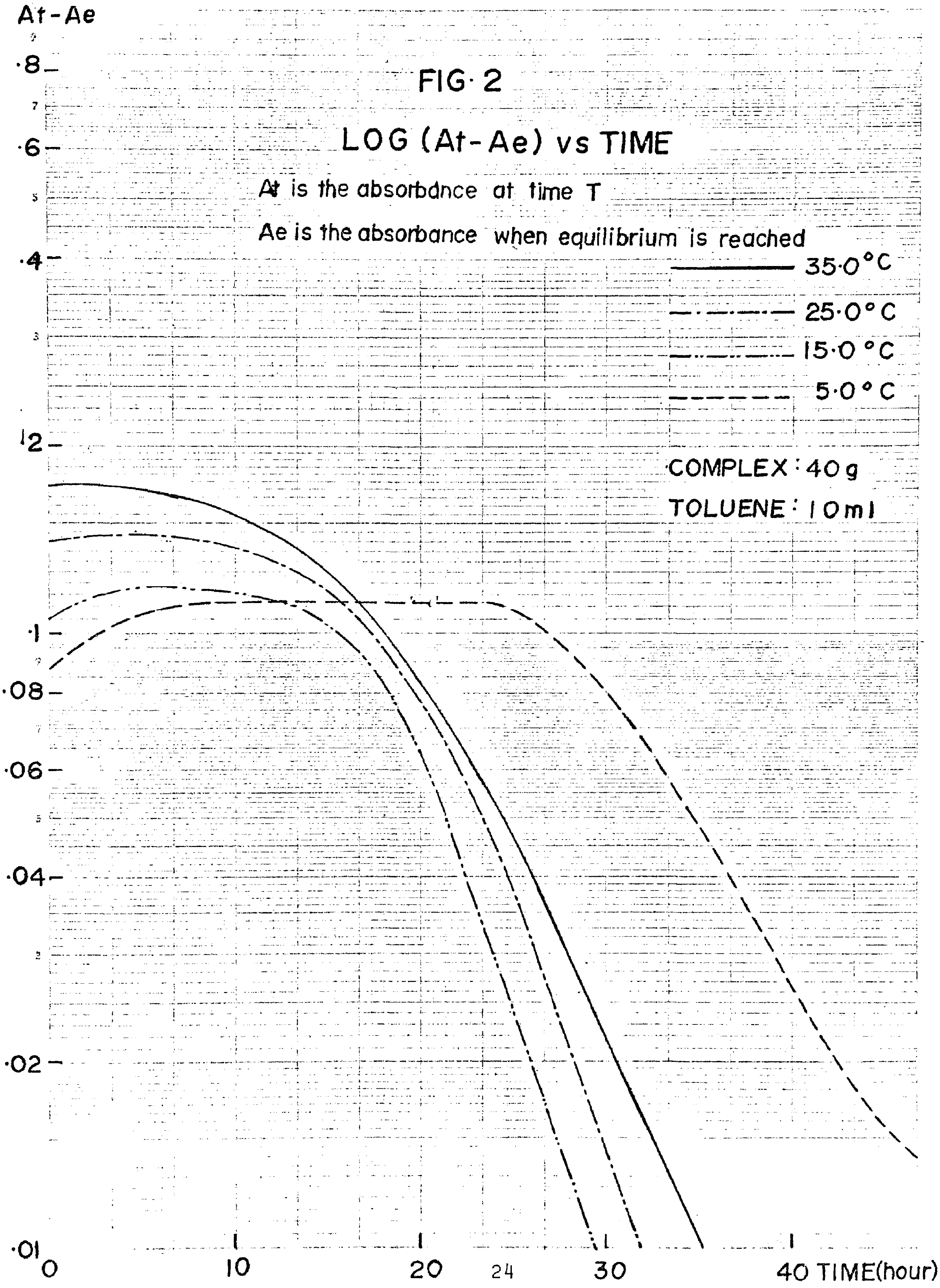


FIG. I

KINETIC RUN

HOST MOLECULE Ni(4-mepy)$_4$(SCN)$_2$ (40g)

GUEST MOLECULE TOLUENE (10 ml)



FIG· 2

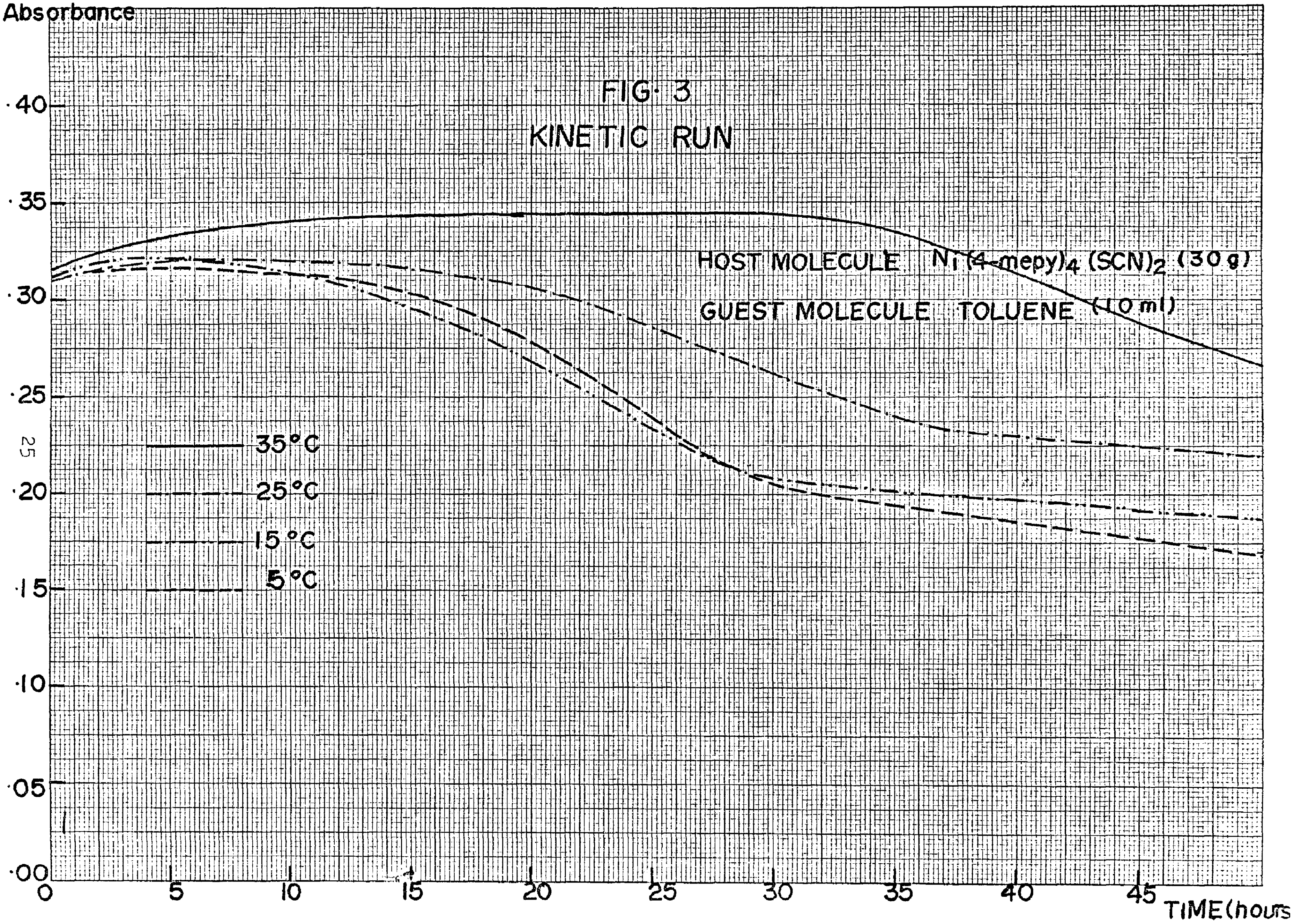
LOG (At-Ae) vs TIME

At is the absorbance at time T

Ae is the absorbance when equilibrium is reached

FIG. 3

KINETIC RUN



FIG·4

LOG (At-Ae) vs TIME

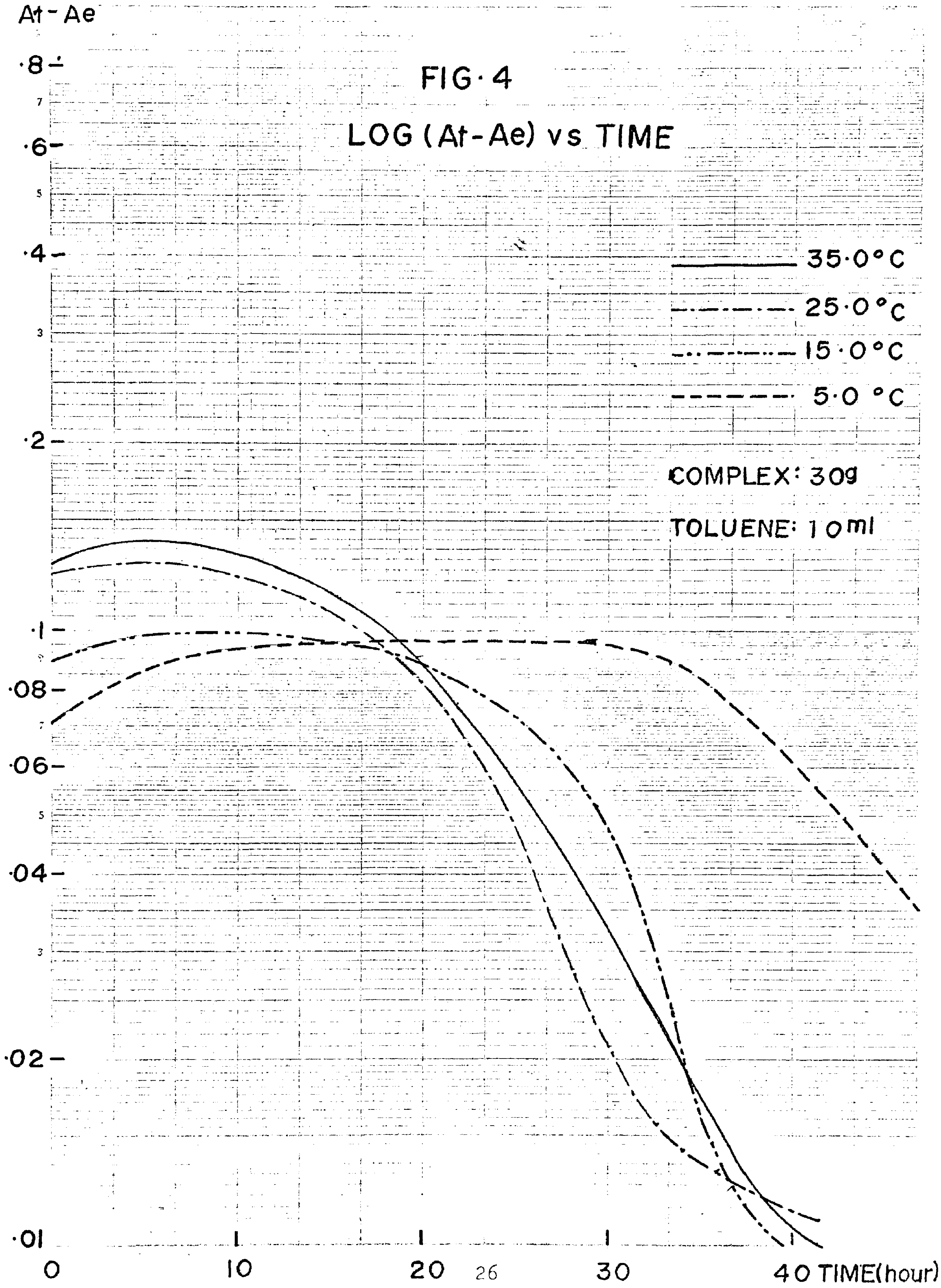


TABLE V

VOLUMETRIC ANALYSES FOR Ni IN THE TOLUENE CLATHRATE

TRIAL	CLATHRATE	PERCENT NICKEL I*	 II*	 III*
1		10.10	9.60	10.02
2		10.10	9.68	10.08
AVERAGE		10.10	9.64	10.05
MOLE RATIO+	(GUEST/HOST)	0.406	0.703	0.438

*Clathrate I, II, and III refers to clathrate formed with the complex of variable size and complex which passes seives of 150 and 250 mesh respectively.

+The values are reliable to an extent of ±0.06 units.

TABLE VI

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu		
	SAMPLE I*	SAMPLE II*	SAMPLE III*
0	0.3365	0.3365	0.3096
½	0.3365	0.3304	0.3096
1	0.3365	0.3304	0.3284
2	0.3365	0.3464	0.3284
4	0.3424	0.3560	0.3284
6	0.3404	0.3560	0.3284
12	0.3204	0.3365	0.3050
24	0.1903	0.2209	0.2122
36	0.1903	0.2209	0.2001
48	0.1903	0.2209	0.2001

*Sample I, II, and III refers to clathrate formed with the complex of size, variable, 150 and 250 mesh respectively.

TABLE VII

VOLUMETRIC ANALYSES FOR Ni IN THE TOLUENE CLATHRATE

TRIAL	CLATHRATE	PERCENT NICKEL I*	 II*
1		10.04	10.04
2		10.08	10.06
AVERAGE		10.06	10.05
MOLE RATIO+ (GUEST/HOST)		0.433	0.438

*Clathrate I and II refers to clathrate formed at maximum and minimum speed of stirring.

+The values are reliable to an extent of ±0.06 units.

TABLE VIII

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE AT 263 mu	
	SAMPLE I*	SAMPLE II*
0	0.3139	0.3181
2	0.3222	0.3222
5	0.3385	0.3181
7	0.3181	0.3139
10	0.2967	0.2923
13	0.2672	0.2672
22	0.2148	0.2148
26	0.2148	0.2122
28	0.2041	0.2068
36	0.2041	0.2068
48	0.2041	0.2068

*Sample I and II refers to clathrate formed at maximum and minimum speed of stirring.

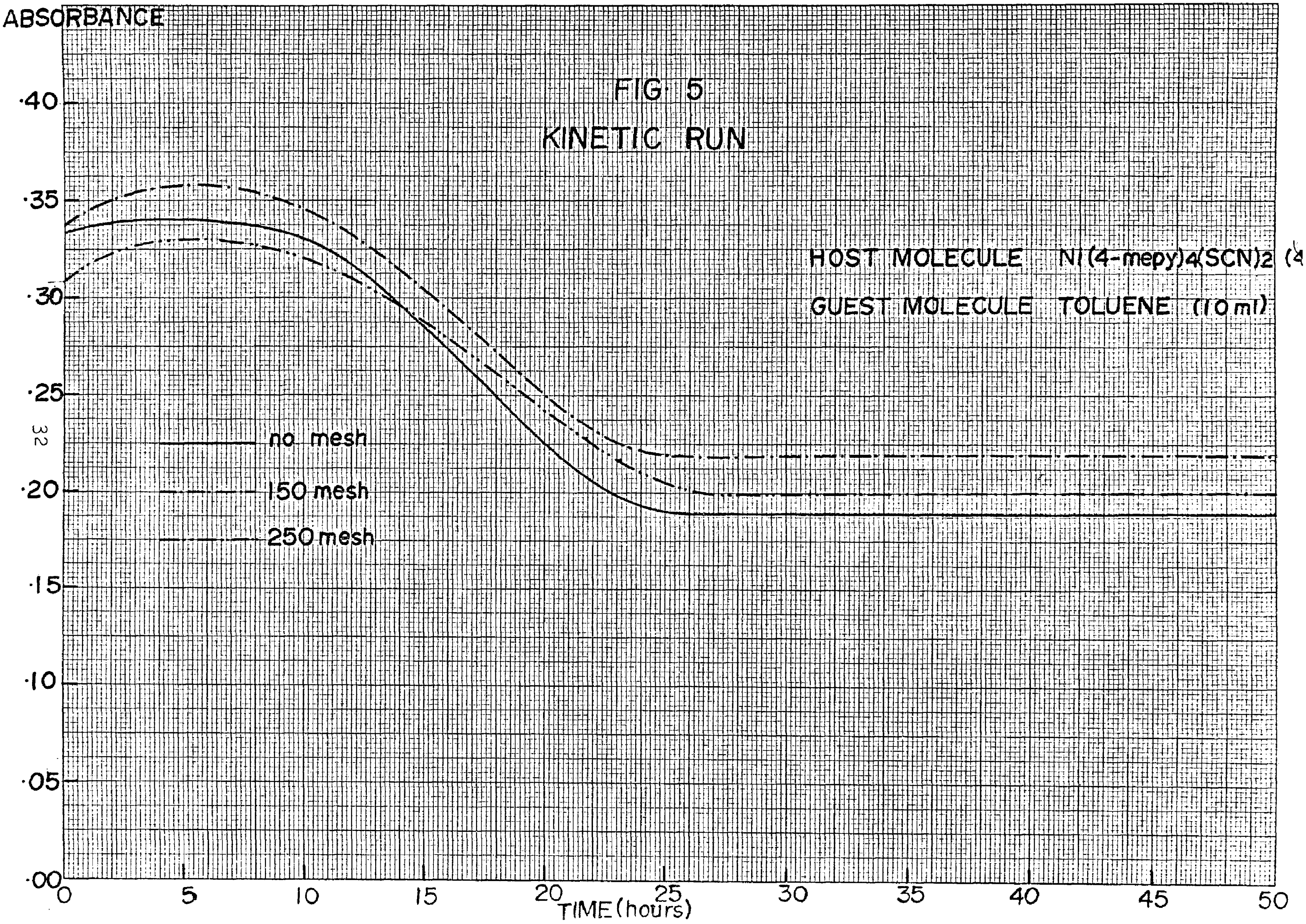


FIG 5

KINETIC RUN

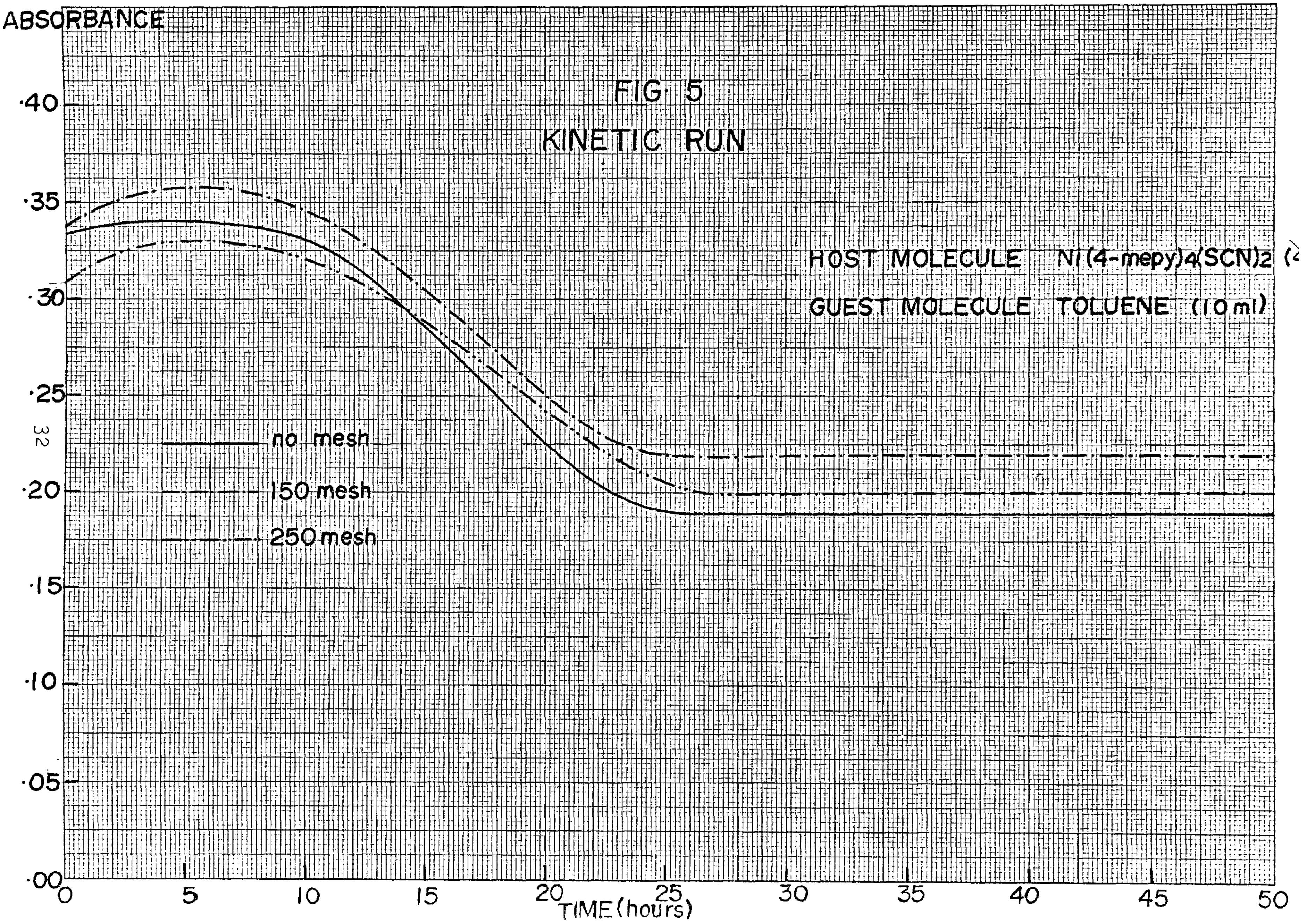


FIG 5

KINETIC RUN

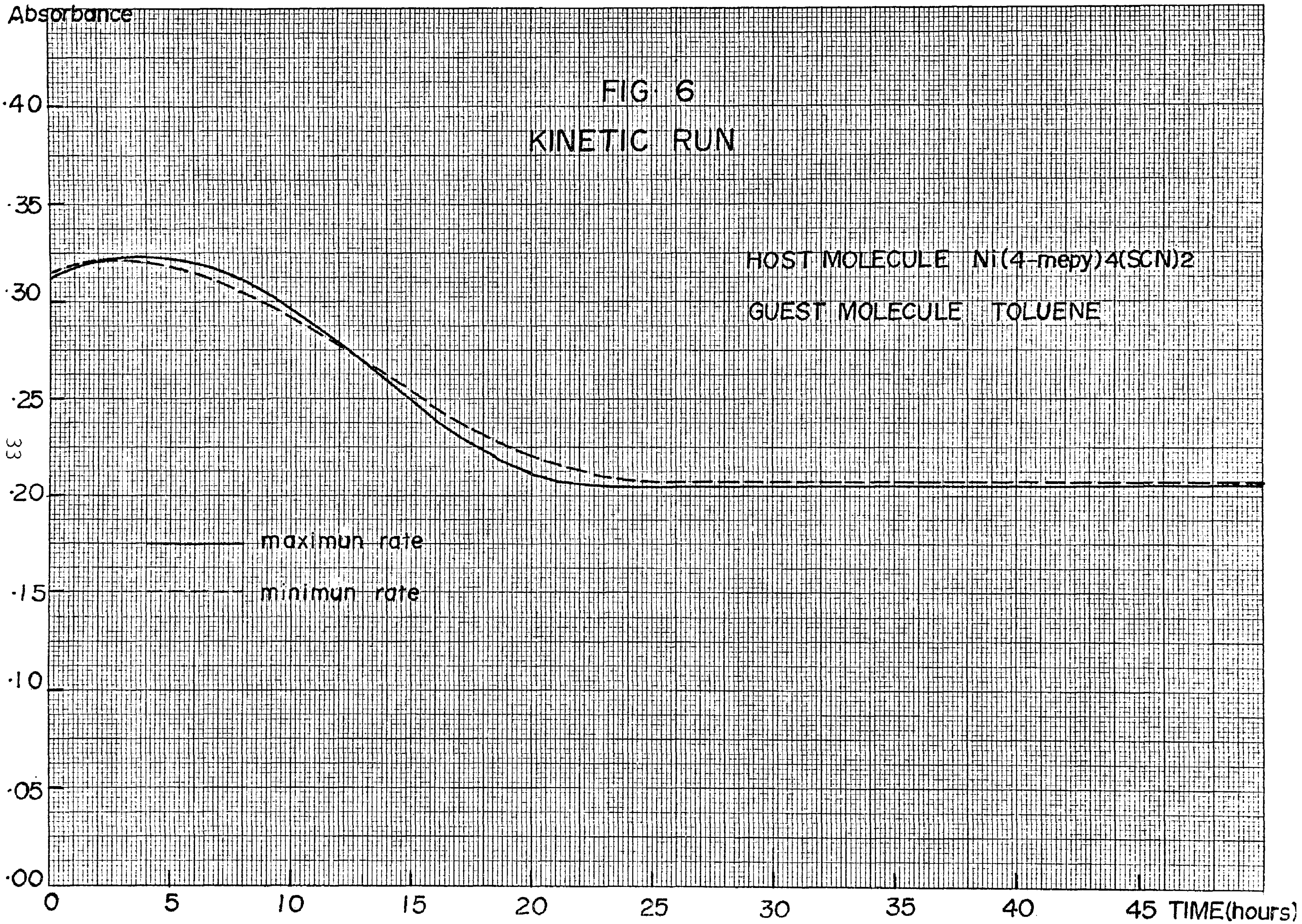


FIG 6

KINETIC RUN

Concentration of the guest component

In this study the guest concentration was varied from 1.66 to 6.66% by volume using 40 grams of complex of particle size 250 mesh. The temperature was maintained at 25°C. The results are presented in Tables IX and X and in Figures 7 to 9. Figure 9 is an expanded plot of the 1.66% by volume case. As observed from the graphs, the higher the concentration of guest, the less time needed for completing the clathration reaction. This is undoubtedly due to the large excess of guest molecules competing with the solvent molecules to dissolve the complex. This result is in agreement with Gawalek's (21), that the rate of clathrate formation is affected by the solubility of the complex in the hydrocarbon. Again, it is observed that the reaction is not first order at the lower concentration, but appears to be pseudo first order at higher concentration.

Two different complex/toluene ratios were run for comparison; one used 40 grams of complex with 20 ml toluene, the other 30 grams of complex with 20 ml toluene. From Tables XI and XII and Figure 10, the results show that the 30 grams of complex took somewhat longer to formaa clathrate. In addition, there is an initial rise for the case of 30 grams of complex. It would appear from this study that 40 grams of complex and 20 ml of guest is the best ratio for the clathration reaction.

Concentration of the host complex

The host concentration was varied from 3.66×10^{-2} to 7.32×10^{-2} moles, keeping the guest concentration constant

TABLE IX

VOLUMETRIC ANALYSES FOR Ni IN THE TOLUENE CLATHRATE

		PERCENT NICKEL		
TRIAL	CLATHRATE	I*	II*	III*
1		9.74	10.04	10.58
2		9.72	10.06	10.58
AVERAGE		9.73	10.05	10,58
MOLE RATIO+ (GUEST/HOST)		0.645	0.438	0.097

*Clathrate I, II, and III refers to clathrate formed with toluene concentrations of 6.66, 3.66 and 1.66% respectively.

+The values are reliable to an extent of ±0.06 units.

TABLE X

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-}mepy)_4(SCN)_2$ AND TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu		
	SAMPLE I*	SAMPLE II*	SAMPLE III*
0	0.6385	0.3181	0.1584
2	0.6128	0.3222	0.1732
5	0.4886	0.3181	0.1732
7	----	0.3139	0.1732
10	0.4669	0.2923	0.1732
13	0.4683	0.2672	0.1832
22	0.4650	0.2148	0.1832
26	0.4624	0.2122	0.1832
28	0.4624	0.2068	0.1832
36	0.4624	0.2068	0.1832
48	0.4624	0.2068	0.1820
57	0.4624	0.2068	0.1774
72	0.4624	0.2068	0.1553
90	0.4624	0.2068	0.1255
93	0.4624	0.2068	0.1239
96	0.4624	0.2068	0.1239

*Sample I, II, and III refers to clathrate formed with toluene concentrations of 6.66, 3.66, and 1.66% respectively.

TABLE XI

VOLUMETRIC ANALYSIS FOR Ni IN THE TOLUENE CLATHRATE

	PERCENT NICKEL	
TRIAL CLATHRATE	I*	II*
1	9.74	9.64
2	9.72	9.70
AVERAGE	9.73	9.67
MOLE RATIO+(GUEST/HOST)	0.645	0.684

*Clathrate I and II refers to clathrate formed with 40g and 30 g of complex in 20 ml of toluene.

+The values are reliable to an extent of ±0.06 units.

TABLE XII

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-}mepy)_4(SCN)_2$ AND TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu SAMPLE I*	 SAMPLE II*
0	0.6385	0.6385
⅓	----	0.6435
1⅓	0.6301	0.6385
1	0.6025	0.6609
2	0.6128	0.6191
4	0.5119	0.5763
5	0.4886	0.5231
6	0.4757	0.5403
9	0.4669	0.5020
12	0.4683	0.4942
24	0.4624	0.4886
36	0.4624	0.4886
48	0.4624	0.4886

*Sample I and II refers to clathrate formed with 40g and 30g of complex in 20 ml of toluene.

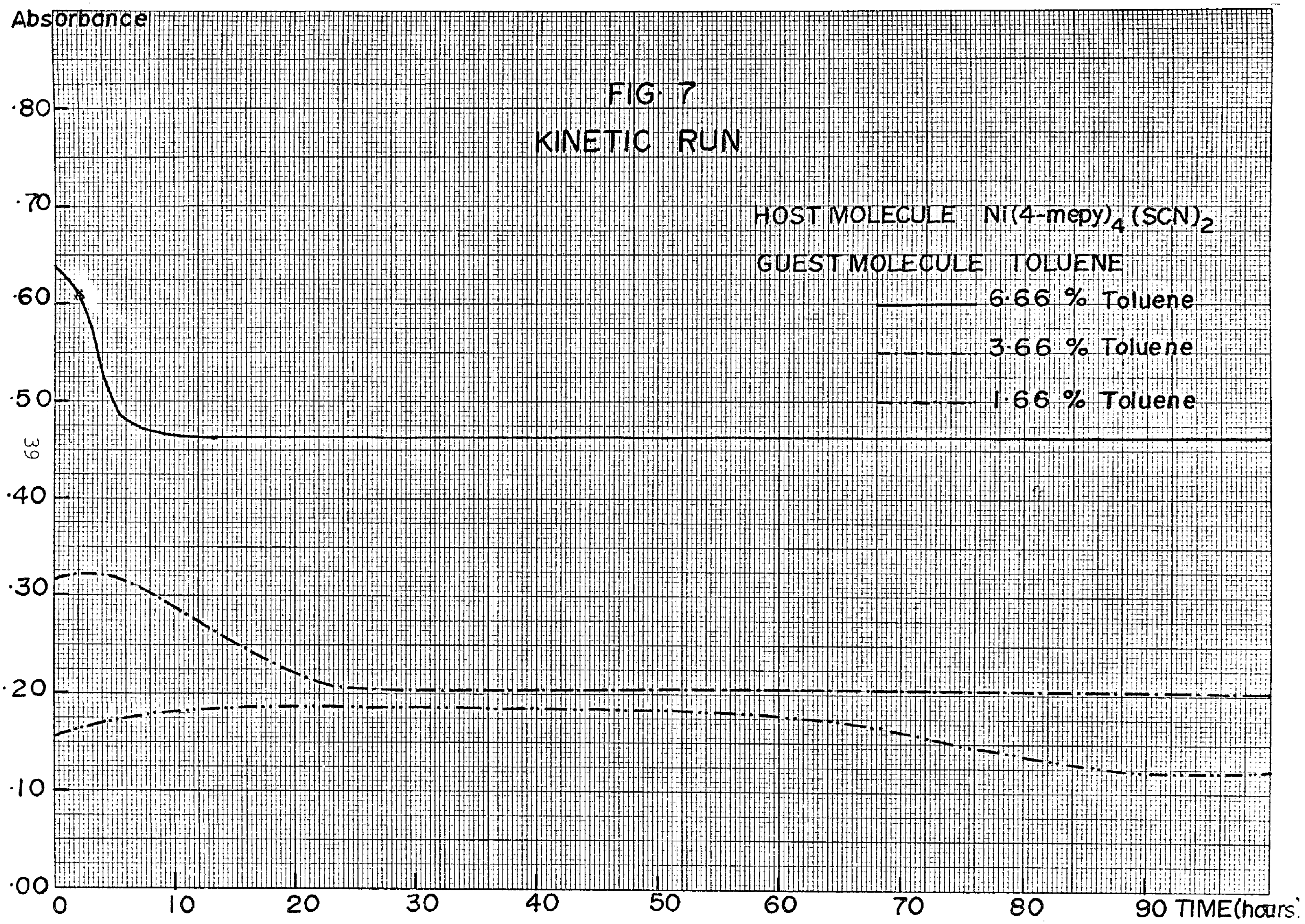
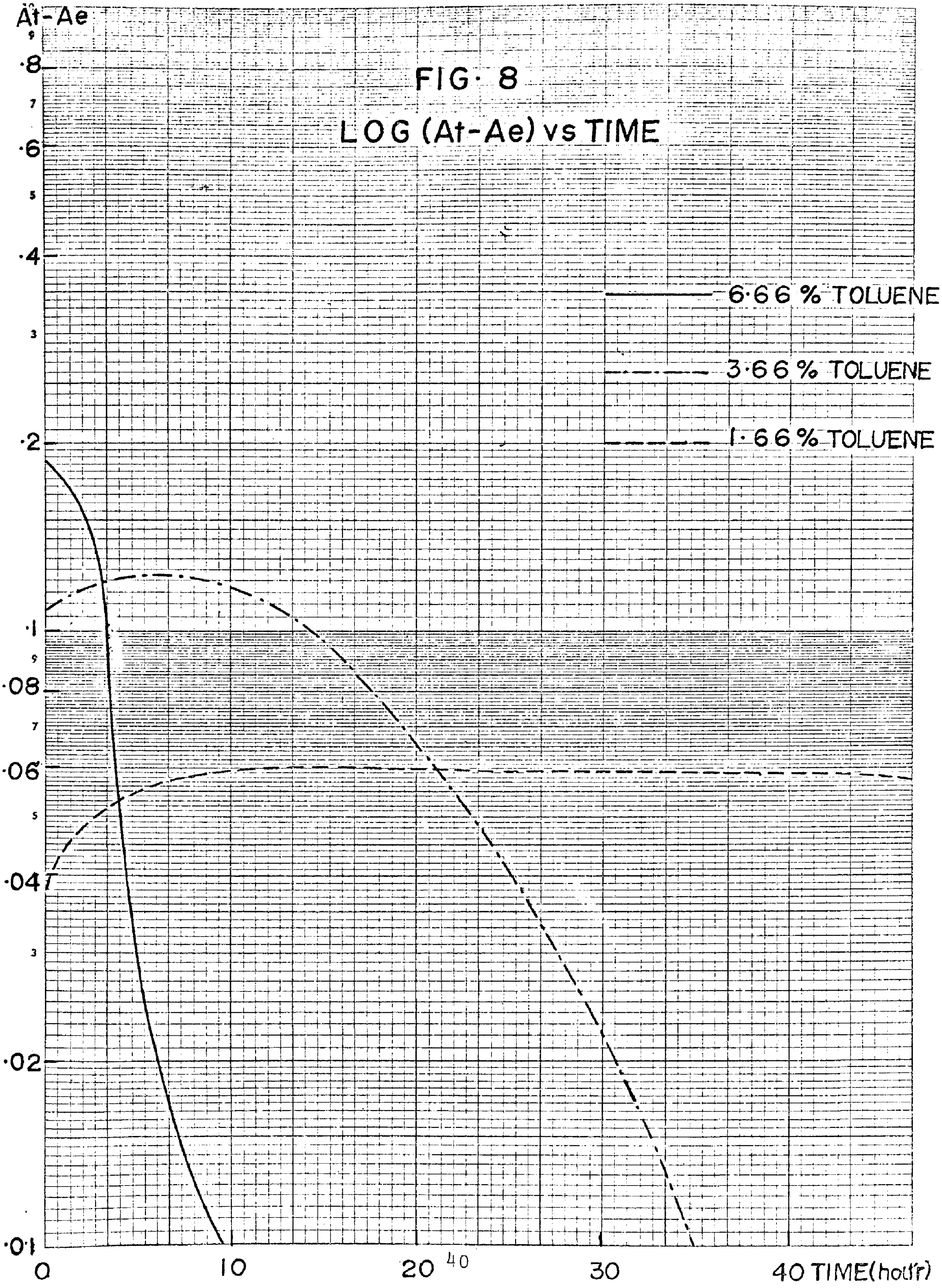


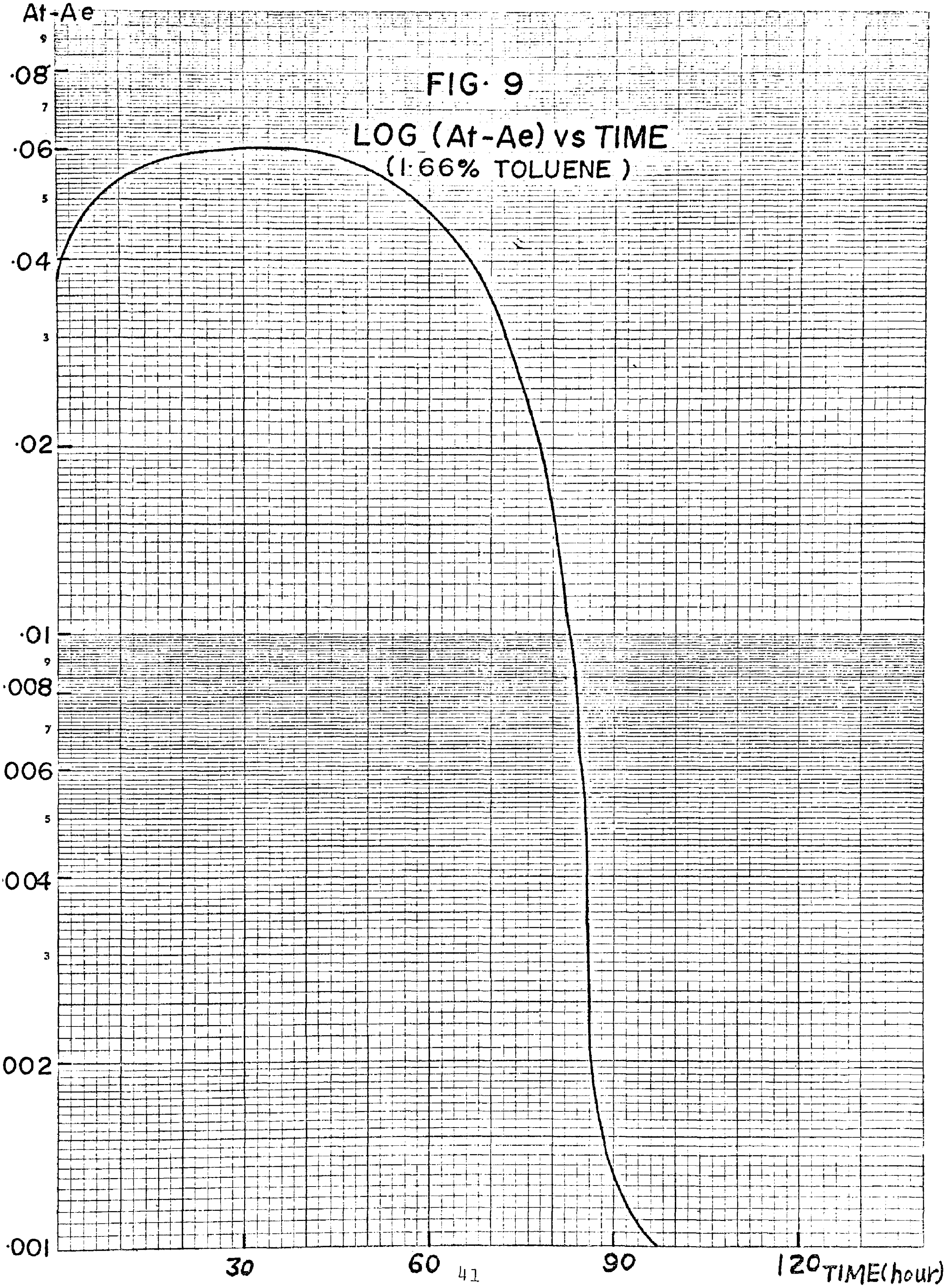
FIG 7

KINETIC RUN



FIG· 8

LOG (At-Ae) vs TIME



FIG· 9

LOG (At-Ae) vs TIME

(1·66% TOLUENE)

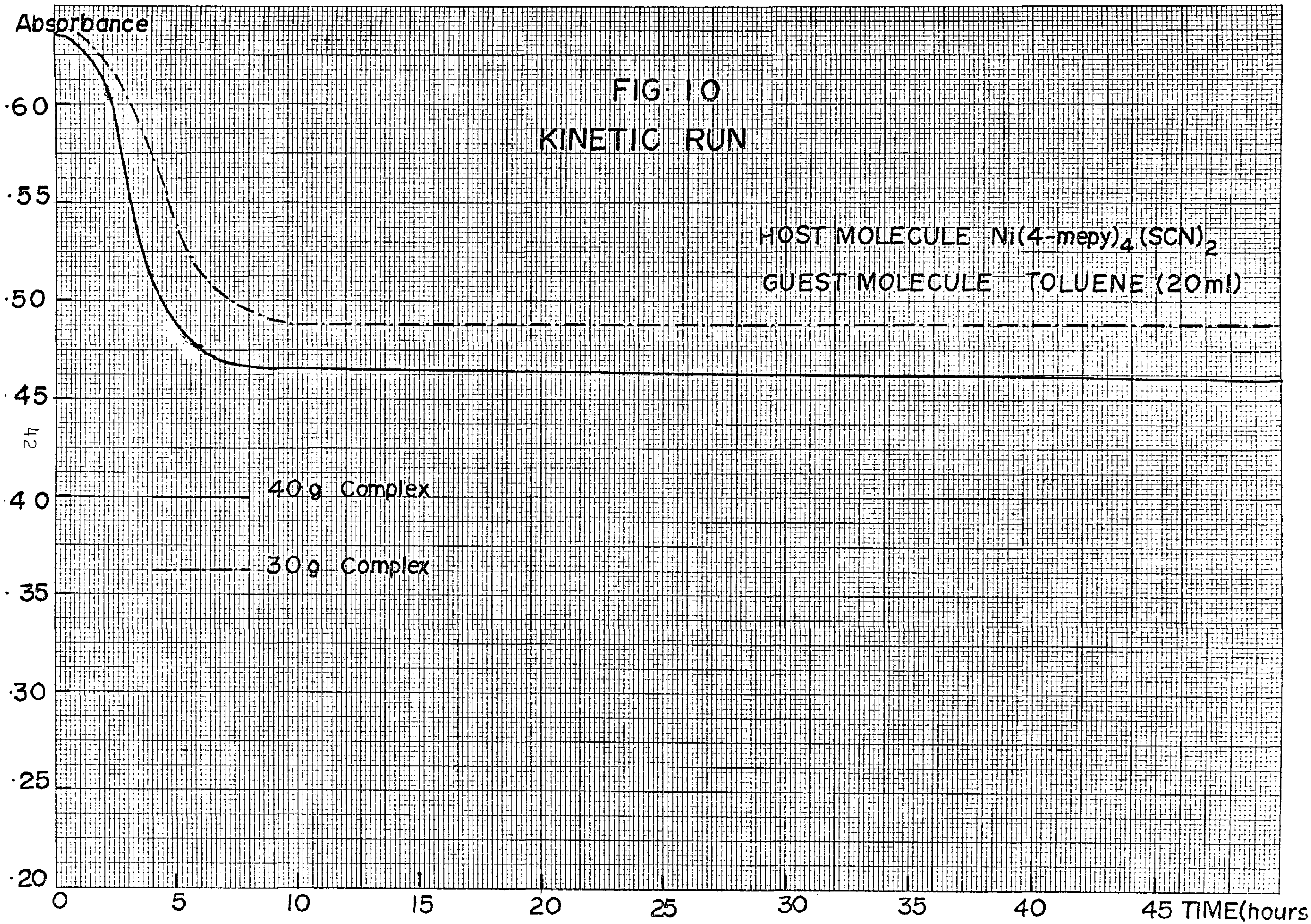


FIG 10

KINETIC RUN

TABLE XIII

VOLUMETRIC ANALYSIS FOR Ni IN THE TOLUENE CLATHRATES

	PERCENT NICKEL		
TRIAL CLATHRATE	I*	II*	III*
1	10.04	10.08	10.17
2	10.06	10.08	10.13
AVERAGE	10.05	10.08	10.15
MOLE RATIO+ (GUEST/HOST)	0.438	0.420	0.374

*Clathrate I, II, and III refers to the clathrate formed with 40, 30, and 20 grams of complex respectively.

+The values are reliable to an extent of ±0.06 units.

TABLE XIV

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-}mepy)_4(SCN)_2$ AND TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE OF TOLUENE AT 263 mu		
	SAMPLE I*	SAMPLE II*	SAMPLE III*
0	0.3181	0.3096	0.3096
2	0.3222	0.3171	0.3181
4	0.3181	0.3171	0.3222
7	0.3139	0.3171	0.3222
10	0.2923	0.3424	0.3324
12	0.2764	0.3171	----
23	0.2136	0.2989	0.3096
26	0.2122	0.2911	0.3010
29	0.2122	0.2643	0.2878
35	0.2068	0.2367	0.2601
48	0.2068	0.2253	0.2553
50	0.2068	0.2214	0.2553
52	0.2068	0.2214	0.2553

*Sample I, II, and III refers to the clathrate formed with 40, 30, and 20 grams of complex respectively.

TABLE XV

VOLUMETRIC ANALYSES FOR Ni IN THE SOLID BEFORE AND AFTER REVERSIBILITY STUDY

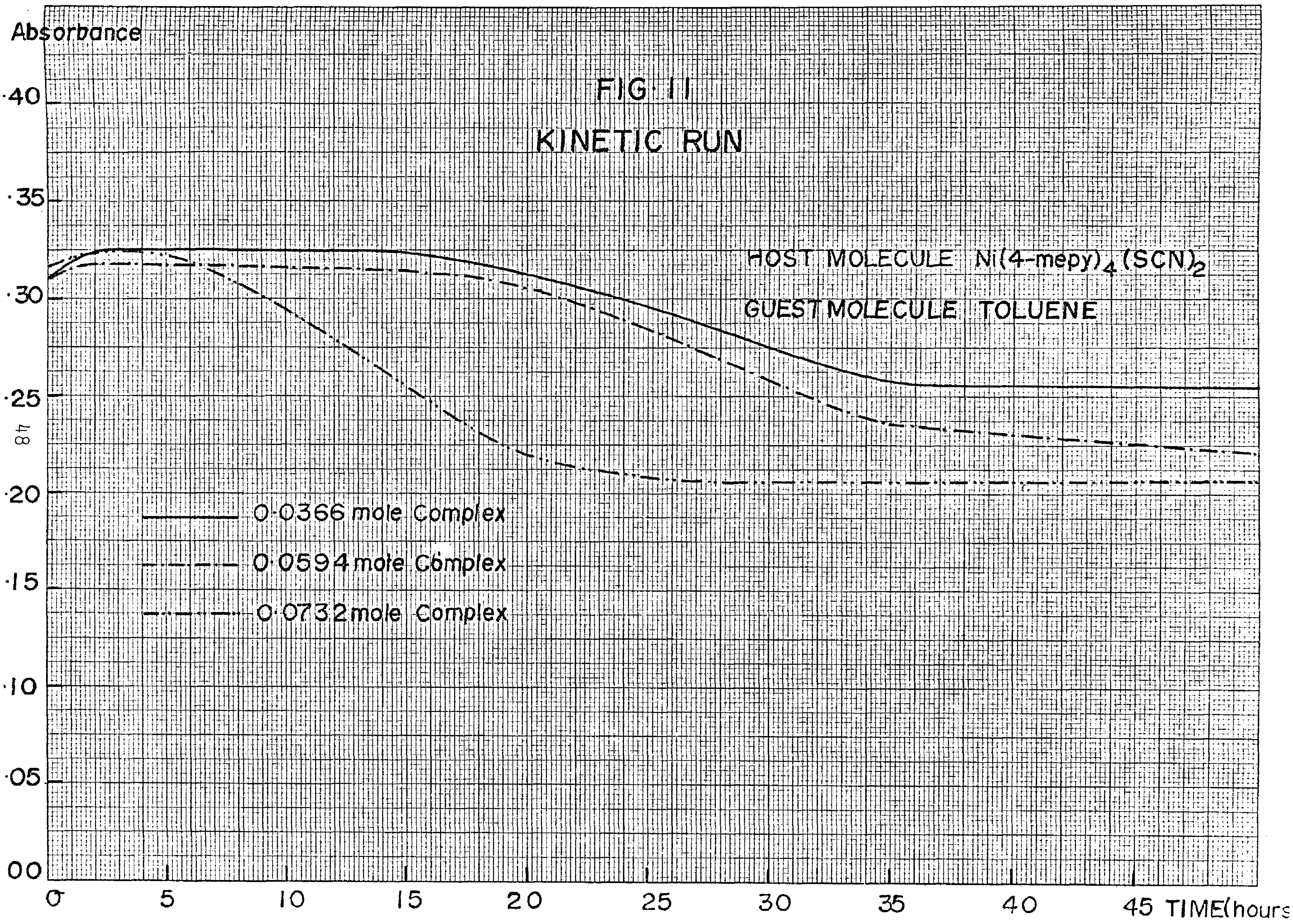
	PERCENT NICKEL	
TRIAL	BEFORE	AFTER
1	10.12	10.16
2	10.12	10.16
AVERAGE	10.12	10.16
MOLE RATIO+(GUEST/HOST)	0.394	0.368

+The values are reliable to an extent of ±0.06 units

TABLE XVI

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE REVERSIBILITY STUDY WITH $Ni(4\text{-}mepy)_4(SCN)_2$ TOLUENE AT 25°C

TIME (HOURS)	ABSORBANCE AT 263 mu
0	0.1004
½	0.0719
1½	0.0490
3	0.0453
5	0.0415
7	0.0414
12	0.0414
24	0.0394
36	0.0380
47	0.0414
48	0.0414



FIG·11

KINETIC RUN

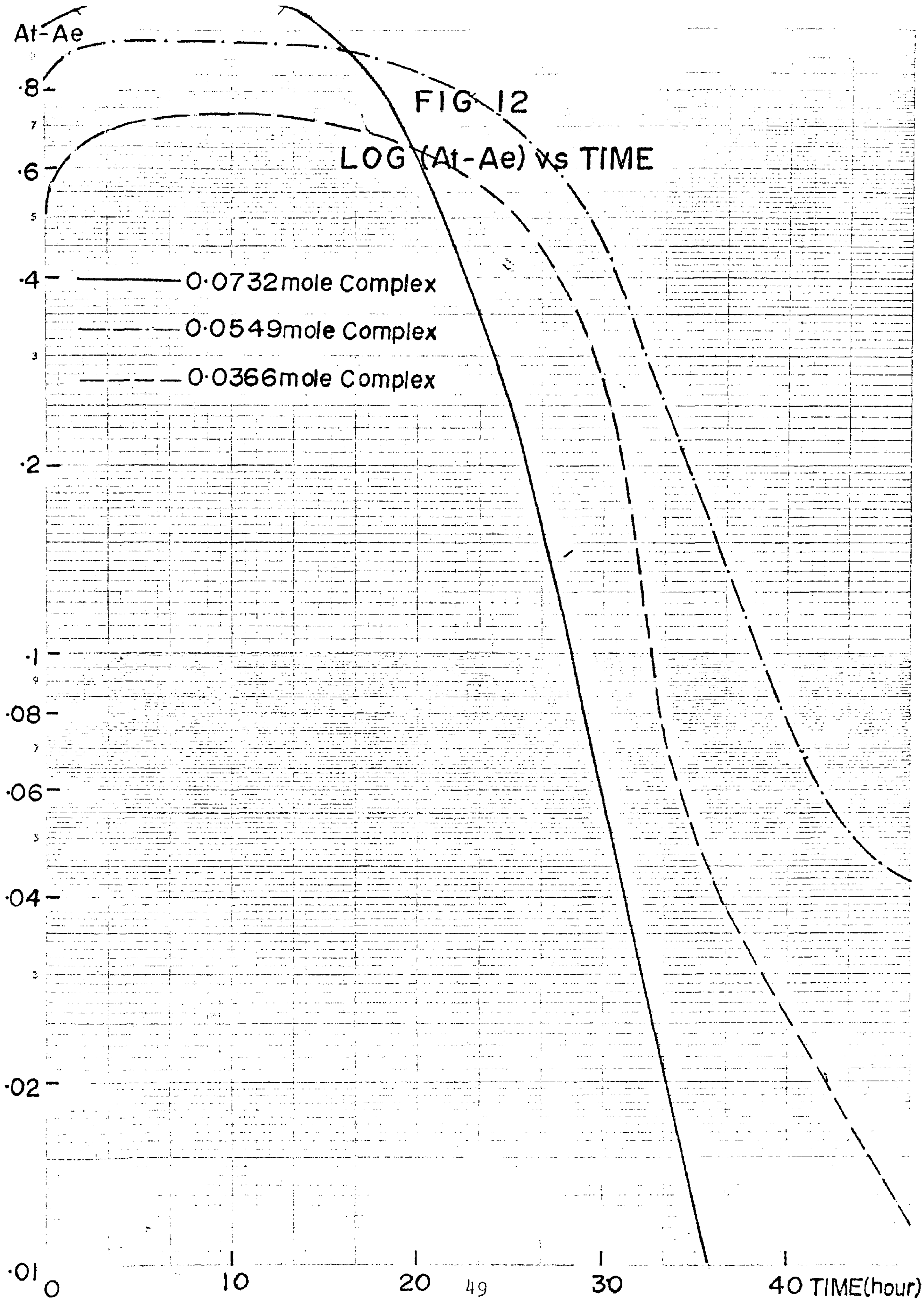


FIG 12

LOG (At-Ae) vs TIME

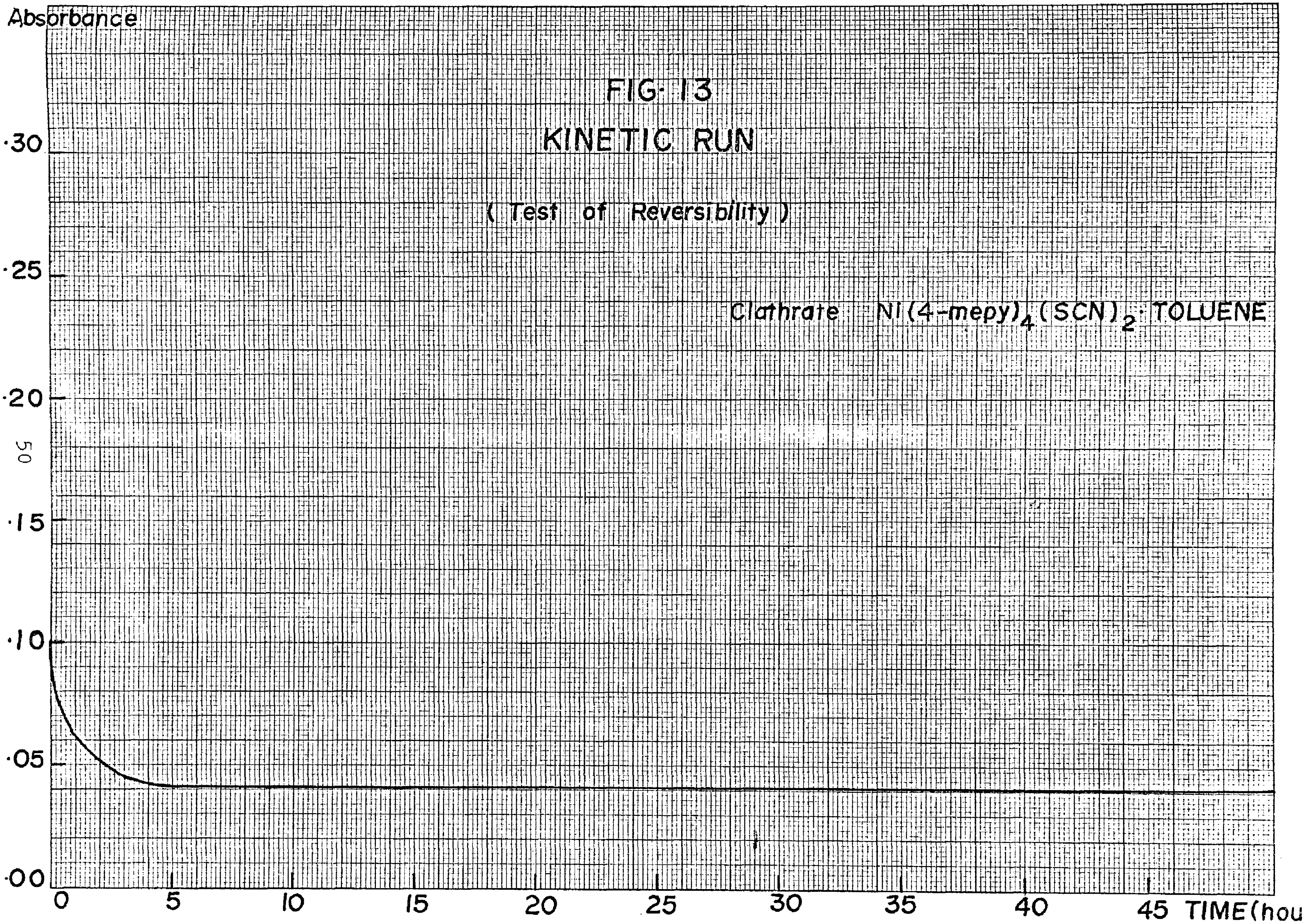


FIG. 13

KINETIC RUN

(Test of Reversibility)

Clathrate Ni$(4\text{-mepy})_4(SCN)_2$·TOLUENE

TABLE XVII

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-}mepy)_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX		CLATHRATE
obsd	Lit*	
	8.64s	12.70m
8.45s	8.37vs	8.17s
	7.56m	
7.43w	7.34w	5.85w
	5.17w	
	5.03s	5.06m
4.96w	4.98m	
	4.85m	
	4.50s	4.49m
4.34s	4.36s	
	4.27s	4.23w
	4.08m	
4.05w	4.05m	
3.90w	3.90m	
	3.85m	
	3.65w	
	3.55w	3.55w
	3.15w	

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

Based on the results which have been presented on the previous pages, a clathration mechanism can be proposed as follows:

$$\text{Complex } (\alpha) \rightleftharpoons \text{Complex } (\beta) \qquad (1)$$

$$\text{Complex } (\beta) + \text{Guest} \longrightarrow \text{Clathrate} \qquad (2)$$

Equation (1) represents a lattice change in the crystal structure of the complex which is brought about by the guest; it is greatly effected by variables such as temperature, particle size of the host, rate of stirring or solvent. The lattice change from α to β has been proven by X-ray analyses as presented in Tables XVII, XVIII, and XIX for the benzene, toluene and p-xylene clathrate respectively. These results agree with the work of Hart and Smith (23). 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 the host concentration alone. From the previous discussion and results, the reaction is found to depend on the guest concentration and is less effected by the host concentration. At higher concentrations of the guest, the reaction depends only on the guest concentration and is a pseudo first order reaction. However, at lower concentrations of the guest, the reaction may depend on both the guest concentration and the host concentration and be of second order. Thus, the reaction may be in fact somewhere between first and second order for most of the kinetic run.

Adsorption

In 1969, Allison published a paper entitled "Sorption in

TABLE XVII

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-}mepy)_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX		CLATHRATE
obsd	Lit*	
	8.64s	12.70m
8.45s	8.37vs	8.17s
	7.56m	
7.43w	7.34w	5.85w
	5.17w	
	5.03s	5.06m
4.96w	4.98m	
	4.85m	
	4.50s	4.49m
4.34s	4.36s	
	4.27s	4.23w
	4.08m	
4.05w	4.05m	
3.90w	3.90m	
	3.85m	
	3.65w	
	3.55w	3.55w
	3.15w	

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

TABLE XVIII

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE Ni(4-mepy)$_4$(SCN)$_2$ COMPLEX AND THE TOLUENE CLATHRATE

COMPLEX		CLATHRATE
obsd	Lit*	
	8.64s	12.70s
8.45s	8.37vs	7.97s
	7.56m	
7.43w	4.34w	5.80w
	5.17w	
	5.03s	5.03m
4.96w	4.98m	
	4.85m	
	4.50s	4.45m
4.34s	4.36s	
	4.27s	
	4.08m	
4.05w	4.05m	
3.90w	3.90m	
	3.85m	3.87w
	3.65w	
	3.55w	3.53w
	3.15w	

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

TABLE XIX

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE Ni(4-mepy$_4$(SCN)$_2$ COMPLEX AND THE P-XYLENE CLATHRATE

COMPLEX		CLATHRATE		
obsd	Lit*	obsd	Lit*	Calcd**
	8.64s	13.08m	13.34m	13.43
8.45s	8.37vs	88.19vs	8.36vs	8.39
	7.56m	7.08w	7.14s	7.12
7.43w	7.34w			
	5.17w	5.21m	5.41s	5.43
	5.03s		5.23s	5.23
4.96w	4.98m			
	4.85m		4.86w	4.80
	4.50s	4.24s	4.60s	4.66, 4.56
4.34s	4.36s			
	4.27s			
	4.08m			
4.05w	4.05m	4.00s	4.02w	4.01
3.90m	3.90m		3.95m	3.95
	3.85m	3.84s	3.80m	3.85, 3.75
	3.65m		3.65s	3.57
	3.55w		3.62m	3.56
		3.32w	3.32w	3.32
	3.15w	3.14m	3.19w	3.22, 3.16

*M. I. Hart and N. O. Smith, J. Am. Chem. Soc. 84, 1816 (1962).
**D. Belitskus, et. al., Inorg. Chem., 2, 873 (1963).

β-phase of Transition Metal (II) Tetra-(4-methylpyridine) Thiocyanates and Related Compounds" (1). The assumption was made that the clathration reaction is in reality an adsorption phenomenon.

The process by which atoms or molecules of one material become attached to the surface of another is called adsorption. Adsorbility increases as solubility decreases in a given solvent and adsorbility further 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 character. The force in physical adsorption, is of the van der Waals type and the adsorption is reversible, that is, the amount adsorbed at a given concentration and temperature is the same whether the final concentration is obtained by dilution of a strong solution or by concentrating a weaker one. 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. 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 belong to the van der Waals type and thus the adsorption was considered as a physical adsorption.

Several adsorption equations have been developed, since 1918, when Langmuir (29,30) published the equation now known as the Langmuir isotherm. This equation was derived for adsorption of gases on solids and assumed that the adsorption is limited to a monolayer and further that it occurs on a uniform surface. While the equation fits experimental data in only a limited number of cases, it is important in further development of adsorption theory. In 1938, Brunauer, Emmett, and Teller (7) developed a theory of multimolecular adsorption now known as the BET theory. The BET theory utilized the polarization theory of DeBoer and Zwicker (11) 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. Because of the assumptions employed in the derivation, the BET isotherm has been critized by many. Further modifications have been made by Freukel (19) and other workers (2,26). However, 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 equation (20) 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.

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 material adsorbed versus the number of moles of material unadsorbed at constant temperature, is called an adsorption isotherm. Brunauer, Deming, Deming, and Teller (8) have classified physical adsorption isotherms into five types as shown in Figure 14.

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 great.

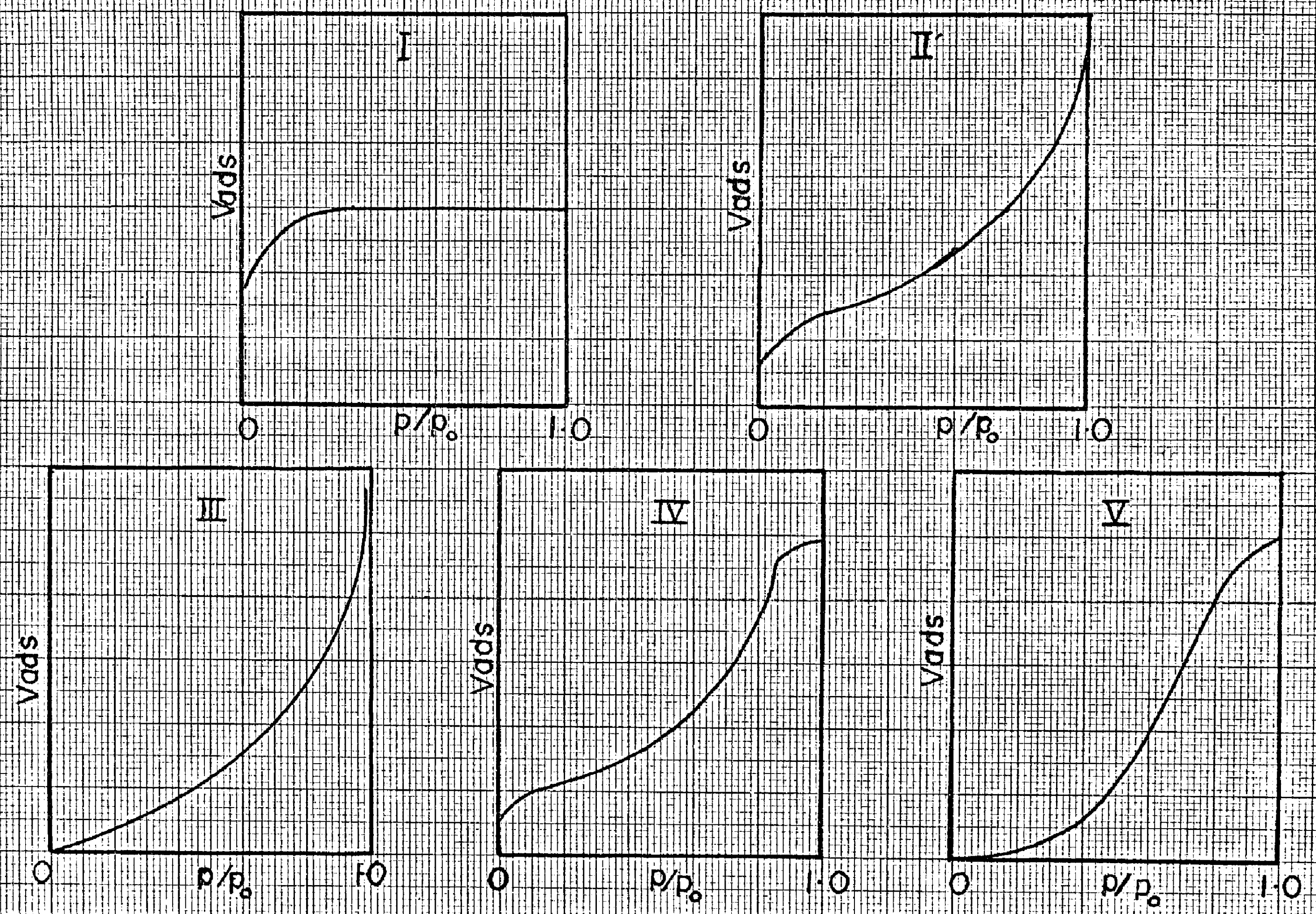
Type IV and Type V have been explained by extending the theory of multimolecular adsorption to include condensation in the capillaries at pressures below the saturation value.

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 (27) 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 substance adsorbed by the

FIG. 14

BRUNAUER'S ADSORPTION ISOTHERMS



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 (22), and is shown in Figure 15.

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 substance structure.

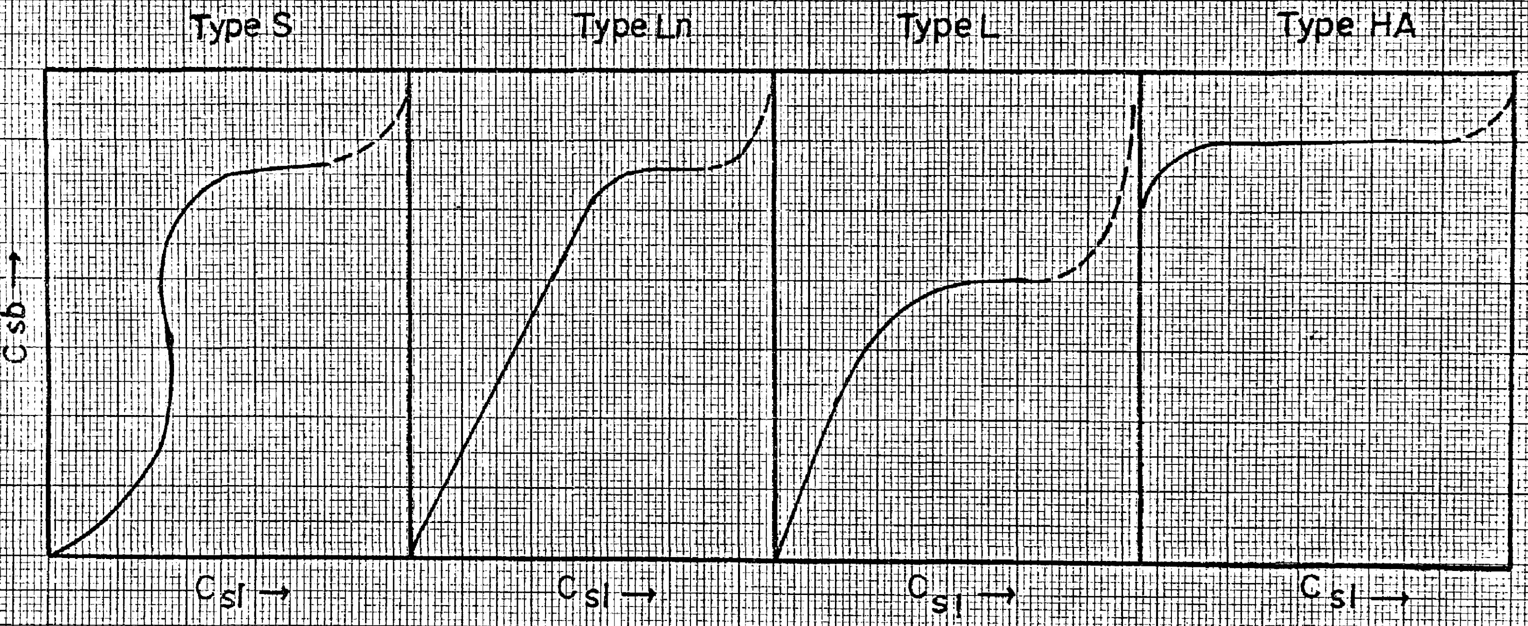
Type HA stands for high affinity. It is a special form of the L curve in which a solute with very high affinity for the solid, in a solvent of low affintiy, is completely adsorbed from dilute solutions.

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

FIG· 15

ADSORPTION ISOTHERMS TYPE



C sb is the equilibrium concentration of the adsorbed solute on the substrate

C sl is the equilibrium concentration of the solute in solution it appeared to give the best fit for clathration.

Data on the clathration reaction between $Ni(4\text{-}mepy)_4(SCN)_2$ as host and benzene, toluene, and p-xylene as guests was subjected to adsorption analysis. Plots of the Freundlich Isotherm for each of the above pairs were made and are shown in Figures 16, 17, and 18. As will be noted from the figures a straight line is obtained in the case of benzene suggesting that the following equation is applicable:

$$X = kc^{1/n}$$

where, x = the number of moles of material adsorbed.
c = the number of moles of material unadsorbed when equilibrium is reached.
k and n = empirical constants.

However, in the case of toluene a slighty curved line is obtained while using p-xylene produces a plot which is far from linear.

From these plots, one may draw the conclusion that "clathration" is perhaps simply an adsorption process for benzene, but apparently not for toluene or p-xylene as guest. This could be explained as simply due to the larger size of the latter two guest molecules. It would further indicate that the critical dimension of a guest molecule is about 6Å.

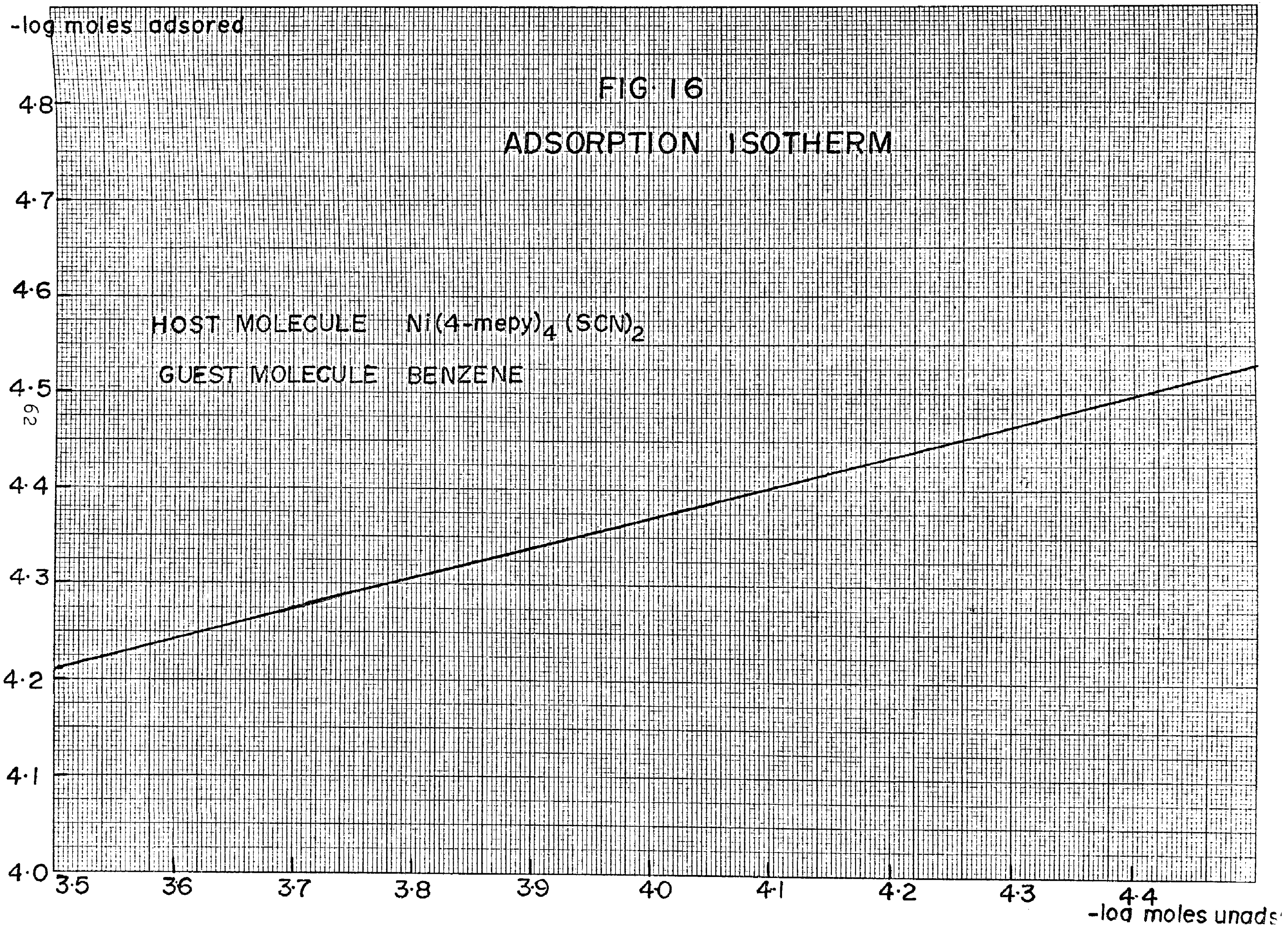


FIG 16

ADSORPTION ISOTHERM

HOST MOLECULE Ni(4-mepy)$_4$ (SCN)$_2$

GUEST MOLECULE BENZENE

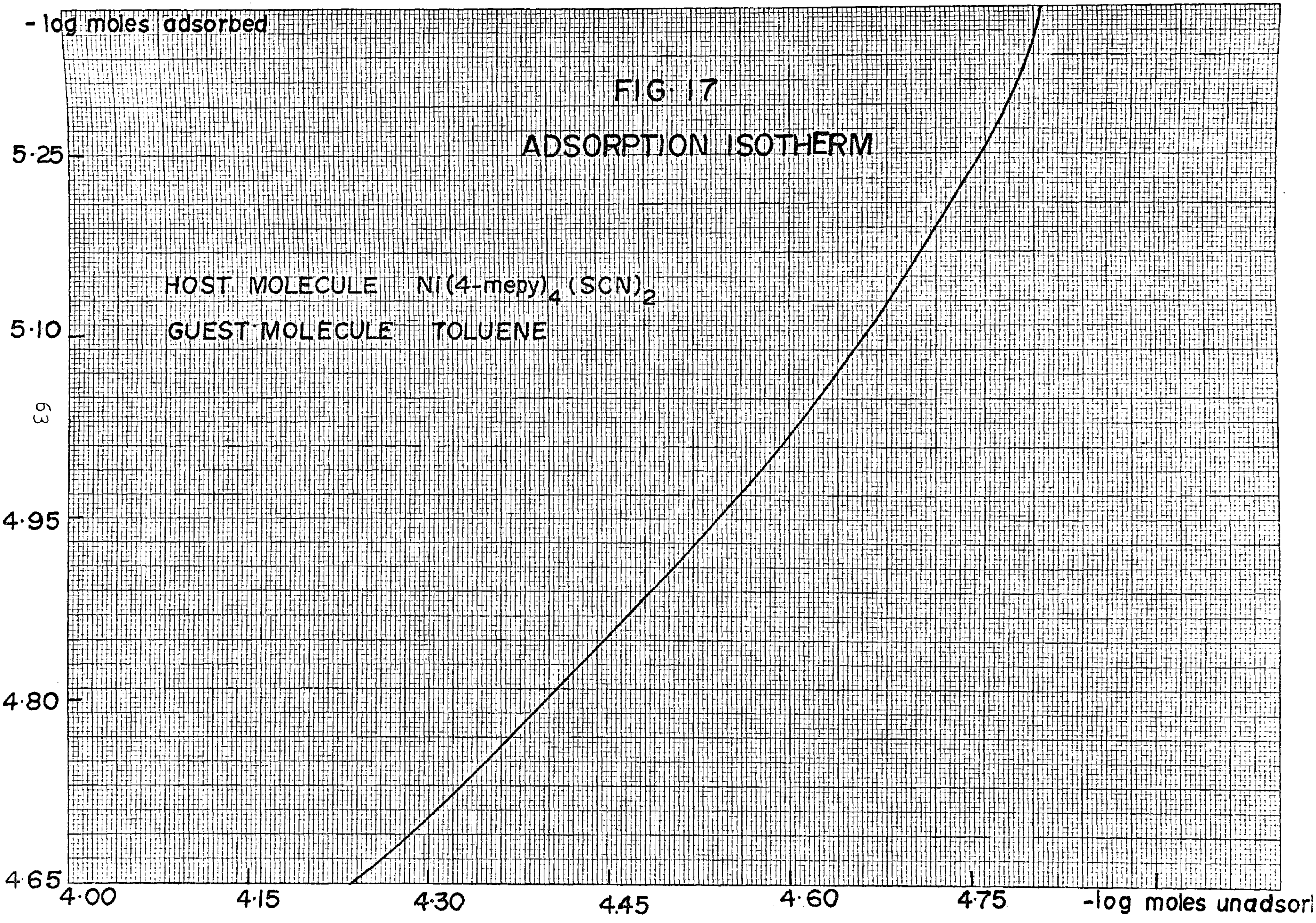
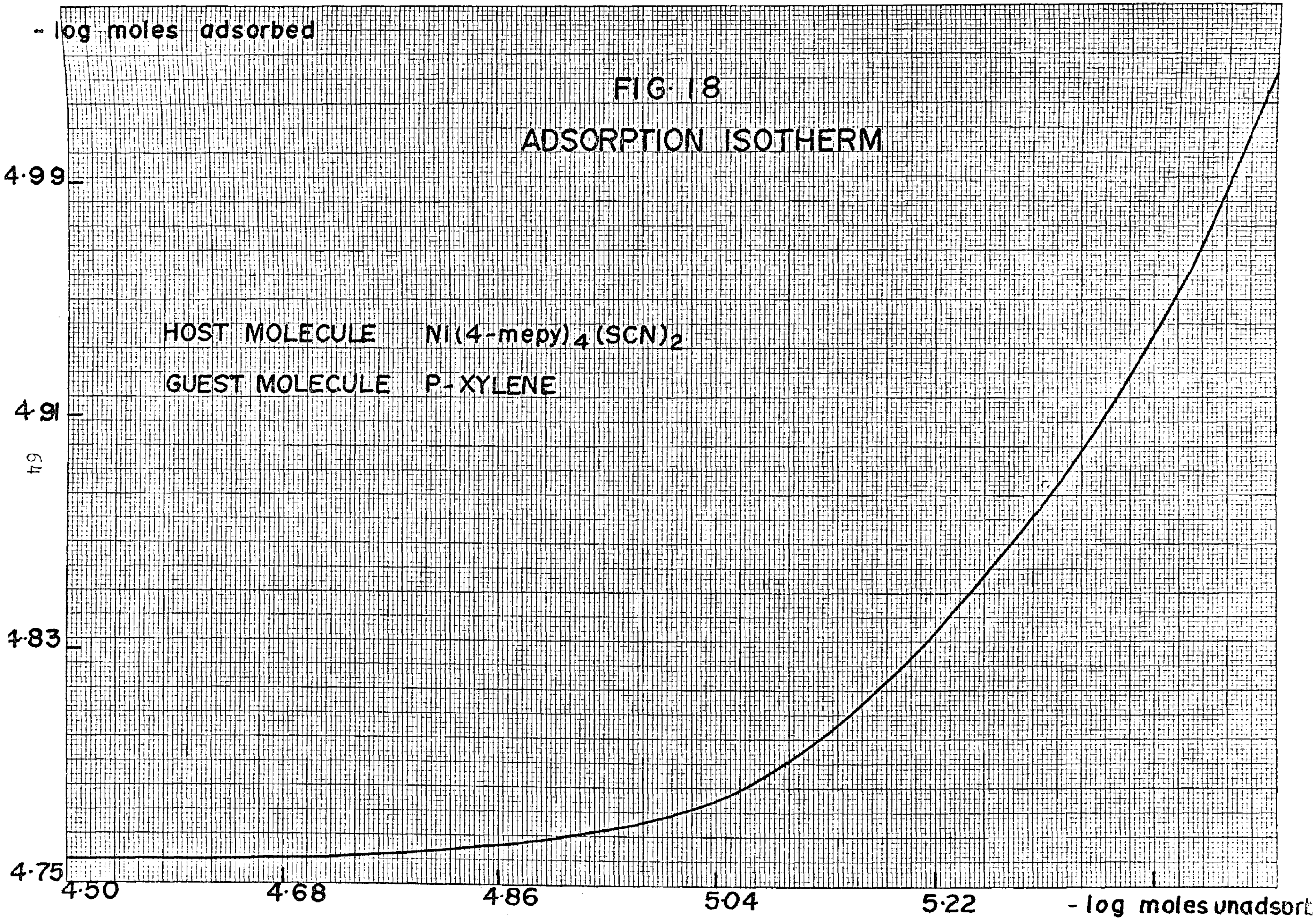


FIG 17

ADSORPTION ISOTHERM

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

GUEST MOLECULE   TOLUENE



FIG· 18

ADSORPTION ISOTHERM

HOST MOLECULE Ni(4-mepy)$_4$(SCN)$_2$

GUEST MOLECULE P-XYLENE

GENERAL SUMMARY

GENERAL SUMMARY

Previous work in this laboratory has involved studying the kinetics of the clathration process in an attempt to resolve the conflict between the results obtained in other laboratories (33) and observations made in this laboratory (31), using $Ni(4\text{-mepy})_4(SCN)_2$ as the host structure and benzene as the guest component. The factors which have been studied, are temperature, stirring rate, particle size of the complex, concentration of the host complex and concentration of the guest component. In order to further test the mechanism of clathration proposed by Jacobs and Vasantha (53) the above factors were tested using toluene as the guest molecule. The results of these studies revealed that the clathration reaction between $Ni(4\text{-mepy})_4(SCN)_2$ and toluene is other than a first order, reversible reaction, and the proposed mechanism would still apply. In addition, it is shown that 40 grams of complex with 20 ml of guest is the best ratio for the clathration reaction.

Published work in the literature (1) has assumed clathration to be an adsorption process. In order to further test this theory, kinetic rate studies of clathration were carried out using $Ni(4\text{-mepy})_4(SCN)_2$ as the host and benzene, toluene, and p-xylene as guests. Plots of the Freundlich isotherm for each of the above combinations of host and guest were made. A straight line was obtained in the case of benzene, and a slightly curved line in the case of toluene. However, the plot for p-xylene was far from linear. The conclusion was drawn that the clathration reaction may be simply an adsorption process for the case of benzene but apparently not for toluene or p-xylene as guests. The reason could be due to the larger size of the guest molecules toluene and p-xylene. It would further indicate that the critical dimension of a guest molecule lies somewhere between the length of the benzene molecule (~5.1Å) and the length of the toluene molecule (~7.6Å); that is about 6Å.

The lattice change in going from complex (α) to clathrate (β) was confirmed by X-ray powder diffraction patterns for all the guest molecules used in this work.

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