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STUDY OF THE REACTION OF PENTABORANE WITH HYDRAZINE AND SUBSTITUTED HYDRAZINES

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A REPORT TO

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CHEMICAL PRODUCTS DIVISION
VON KARMAN CENTER
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

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STUDY OF THE REACTION OF PENTABORANE WITH HYDRAZINE AND SUBSTITUTED HYDRAZINES

Prepared by

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Chemical Products Division
Von Karman Center
AEROJET-GENERAL CORPORATION
Azusa, California
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

FOREWORD

This final technical report is submitted in fulfillment of the contract and covers the period from 1 March 1962 through 28 February 1965.

The work was performed under the basic contract and Supplemental Agreements No. 1 and 2, and covered Project No. 9751, Task No. 37510, and Project-Task No. 9751-01.

The principal investigators were Drs. H. V. Seklemian (since May 1964), R. W. Lawrence (May 1963 - May 1964), and S. D. Rosenberg (March 1962 - May 1963). Drs. Lawrence and Rosenberg have also served as technical advisors, as has Dr. G. A. Guter. A chronological bibliography of publications resulting from this work is presented at the end of the text.

AEROJET-GENERAL CORPORATION

E. M. Wilson

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ABSTRACT

Pentaborane and hydrazine were found to react in solution according to the following equation:

$$B_5H_9 + 2\ N_2H_4 \longrightarrow B_5N_4H_{16} + 0.5\ H_2$$

The process includes an initial fast reaction followed by a slow reaction that evolves hydrogen and an insoluble solid product. The hydrogen evolution was found to be a first-order process with a rate constant of $1.74 \pm 0.1 \times 10^{-4}$ sec^{-1} at 25°C.

The rate-determining step was found to be dependent only on the hydrazine concentration. Traces of hydrazine are believed to catalyze the decomposition of a postulated soluble intermediate so that an ionic-type mechanism involving acid-base catalysis is proposed. The reaction in the gas phase yields the same reaction products; however, the reaction is considerably faster.

When monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine were used in place of normal hydrazine, the respective reactions were as follows:

$$B_5H_9 + 4\ CH_3NHNH_2 \longrightarrow B_5N_8H_{20}(CH_3)_4 + 0.5\ H_2$$

and

$$B_5H_9 + 2\ H_2NN(CH_3)_2 \longrightarrow B_5N_4H_{13}(CH_3)_4$$

The hydrogen from the reaction involving MMH also evolved by a first-order process, and the postulated mechanism is the same.

The products of the pentaborane-hydrazine and pentaborane-MMH reactions are insoluble in nonpolar solvents. They thermally decompose, evolving hydrogen. It is believed that the products are polymeric substances.

Attempts to obtain a definitive structure for the insoluble products by nuclear-magnetic-resonance techniques and high-resolution infrared analysis were unsuccessful.

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CONTENTS (cont.)

I. OBJECTIVES

The objectives of this program were to determine (a) the overall kinetics for the reaction of pentaborane with hydrazine, (b) the most likely mechanism for this reaction, (c) the effect of solvent on the reaction and the effect of substitution on the hydrazine nucleus, and (d) a postulated structure of the reaction product consistent with the observed physical and chemical data.

II. SUMMARY

Hydrazine and pentaborane, which have been found to react in a ratio of 2 moles of hydrazine to 1 mole of pentaborane, were allowed to react in an inert solvent (cyclohexane) under dilute conditions. High dilution was adopted to slow the reaction so that the reaction rate could be readily measured, but even under these conditions the initial reaction occurred too rapidly to permit spectrophotometric measurements. The initial reaction was followed by a slower reaction that was characterized by the evolution of hydrogen and the formation of a precipitate. The amount of hydrogen evolved was found to be 0.5 mole per mole of pentaborane used, so that the overall reaction may be written as follows:

$$B_5H_9 + 2\ N_2H_4 \longrightarrow B_5N_4H_{16} + 0.5\ H_2$$

The rate of hydrogen evolution was followed manometrically. At pentaborane concentrations of 16.1 mmoles/liter or less, the gas-evolution process was observed to be a first-order reaction with a rate constant of $1.74 \pm 0.1 \times 10^{-4}$ sec^{-1} at 25°C. A competitive, zero-order reaction was observed at higher concentrations; it is much slower and appears to be diffusion-controlled rather than chemically controlled. Further experiments were confined to dilute solutions, in which only the first-order reaction occurs.

It was found that the initial rate of hydrogen evolution is independent of the concentration of B_5H_9 and is first-order with respect to N_2H_4, indicating that the rate-determining step is dependent only on hydrazine. It was hypothesized that a soluble intermediate undergoes base-catalyzed decomposition in the rate-determining step.

An effort was made to isolate the soluble intermediate by filtering off the solution from the insoluble product that had formed after the hydrogen-evolution process was partially completed. A trace quantity of hydrazine was added to the filtrate. Hydrogen was evolved, and the insoluble product formed; the quantity formed was considerably greater than could be accounted for by the added hydrazine, indicating that hydrazine acted as a basic catalyst. The following mechanism consistent with these facts is proposed:

$$B_5H_9 + 2\ N_2H_4 \rightleftharpoons B_5H_9 \cdot 2\ N_2H_4 \qquad (1)$$

$$B_5H_9 \cdot 2\ N_2H_4 + N_2H_4 \rightleftharpoons B_5N_4H_{16}\text{--}H\text{--}N_2H_4 \qquad (2)$$

$$B_5N_4H_{16} \longrightarrow B_5N_4H_{15} + 0.5\ H_2\ \text{(slow)} \qquad (3)$$

$$B_5N_4H_{15}\text{--}H\text{--}N_2H_4 \rightleftharpoons B_5N_4H_{16} + N_2H_4 \qquad (4)$$

In this mechanism the hydrazine acts as a basic catalyst, accepting a proton from the intermediate as illustrated in Reaction (2).

Reaction-rate constants were obtained for temperatures from 20 to 35°C. These data were used to determine activation energy. Below 30°C, where there is greater interest, the activation energy is 26,400 cal/mole and the activation entropy is 17.4 cal/°C per mole of pentaborane used. Both values are within the normal limits expected of gas-elimination reactions, except that the entropy of activation is positive (probably because the activated state is a less ordered configuration, e.g., a linear polymer). The data obtained above 30°C were not consistent with data obtained at other temperatures; it is believed that a different mechanism is involved at higher temperatures.

The effect of different solvents on the reaction was determined. It was observed that the rate constant and reaction order were the same when other hydrocarbon solvents were used. When diethyl ether (a weak base) was used, the reaction rate was observed to increase, because the base was acting as a catalyst.

The reaction was investigated in the gas phase. The stoichiometry was found to be the same as in the solution phase, but the reaction occurred too rapidly to be measured.

The effect of substitution on the hydrazine nucleus was also investigated; in this work, monomethylhydrazine (MMH) and unsym.-dimethylhydrazine (UDMH) were used in the reaction with pentaborane. The respective reactions were as follows:

$$B_5H_9 + 4\ CH_3NHNH_2 \longrightarrow B_5N_8H_{20}(CH_3)_4 + 0.5\ H_2$$

and

$$B_5H_9 + 2\ H_2NN(CH_3)_2 \longrightarrow B_5N_4H_{13}(CH_3)_4$$

Both products were insoluble, and did not react in most solvents. The reaction kinetics with MMH resembled those of the reaction involving hydrazine, and a similar reaction mechanism is proposed. The latter reaction occurred too rapidly for its kinetics to be determined.

Deuterated hydrazine was used in an effort to determine the reactant from which the evolved hydrogen was obtained. It was found that the quantity of gas evolved was approximately one-third the amount found when pentaborane reacts with undeuterated hydrazine. Analysis of the gas showed that 51.3 mol% was HD, 35% H_2, and 13.7% D_2; thus, the gas was found to be 61% hydrogen and 39% deuterium. An analysis showing three products in random quantities indicates that the overall reaction may be a competitive sum of several reactions, or that the gas-evolution process involves a hydrogen-deuterium exchange during a gas-elimination reaction postulated to occur at the apex position of pentaborane.

The properties of the insoluble product were also investigated. It was found that the products of the pentaborane-hydrazine and pentaborane-MMH reactions were insoluble or dissolved upon reaction with a number of potential solvents. The products were thermally decomposed and were found to evolve hydrogen. Differential thermograms of products from the first- and zero-order pentaborane-hydrazine reactions differ, indicating different products. In either case, the decomposed product did not evolve all its hydrogen, even when heated to 960°C for 48 hours. Two to three hydrogen atoms out of the original 16 remained.

A chronological bibliography of publications resulting from the work performed is presented after the list of references following the text.

III. BACKGROUND

Pentaborane and hydrazine are known to react with explosive violence when mixed at ambient temperature. The reaction products include hydrogen, boron nitride, and unidentified miscellaneous substances. The reaction can be slowed by carrying it out in a dilute solution of diethyl ether or cyclohexane, but attempts to follow the rate of consumption of the reactants by infrared absorption were unsuccessful. Most of the experiments were conducted with pentaborane and hydrazine. Monomethylhydrazine and UDMH were also used (see Section IV,E, below). Most of the experiments were conducted with very dilute cyclohexane solutions yielding hydrogen gas and an insoluble solid as the products.

By observing the amount of reactants consumed, it was found that the product was formed from 1 mole of pentaborane and 2 moles of hydrazine. Any hydrazine in greater concentration could be separated from the product, along with the solvent, by vacuum evaporation. It was concluded that the product composition is that of the 1-to-2 molar-ratio $B_5H_9 \cdot 2\ N_2H_4$. The kinetics of the reaction and the thermal decomposition of the insoluble product are described below. Previous work in this field was limited to diborane with hydrazine and pentaborane with amines.

Emeléus and Stone (Ref. 1) have found that diborane and hydrazine form an adduct. Steindler and Schlesinger (Ref. 2) found that the reaction of diborane with hydrazine in ether solution forms a 1-to-1 adduct that is stable to about 50°C and has the structure $H_3BNH_2NH_2BH_3$. Burg (Ref. 3) found that, when pentaborane is heated with methyl-substituted amines, volatile compounds $\left\{\text{i.e., } \left[(CH_3)_2N\right]_3B_3H_3 \text{ and } \left[(CH_3)_2N\right]_2B_4H_6\right\}$ are formed along with polymeric solids having boron-to-boron linkages. Zhigach and co-workers (Ref. 4) reported that pentaborane reacts with secondary amines, yielding an intermediate that decomposes and evolves volatile compounds ($B_2H_5NH_2$ and BH_2NR_2), polymers, and hydrogen.

IV. EXPERIMENTAL PROCEDURES AND RESULTS

A. MATERIALS

Hydrazine, MMH, and UDMH were obtained from the Olin Mathieson Corporation, and were purified by vacuum distillation over barium oxide (Ref. 5). The purified compounds were analyzed by gas-phase chromatography and were stored in a desiccator over Drierite. Pentaborane was obtained from the same source, and was purified by high-vacuum, low-temperature fractionation in a vacuum rack. The purified pentaborane was stored in a vacuum system and was used as needed. Spectro-grade cyclohexane was obtained from the Matheson, Coleman and Bell Division of the Matheson Company and was not further purified because this grade is of excellent purity. Baker and Adamson diethyl ether, benzene, and n-hexane were obtained from the General Chemical Division of Allied Chemical Corporation and were dried over sodium.

B. STOICHIOMETRY OF PENTABORANE-HYDRAZINE REACTION

It was found that the reaction of 1 mole of pentaborane and 2 moles of hydrazine in cyclohexane solution evolved a gas and produced an insoluble solid product. The gas was identified by mass spectrography as hydrogen. The total quantity of hydrogen evolved was determined by conducting experiments in which the reactants were placed in a flask to which was attached a Fischer & Porter Company needle valve. After the substances were allowed to react for 7 days to ensure completion of the reaction, the evolved gases were found by mass spectrography to be 99% hydrogen. The results are given in Table 1. The average amount of hydrogen evolved was 0.505 mole per mole of pentaborane used. Thus, the overall stoichiometry of the reaction may be written

$$B_5H_9 + 2\ N_2H_4 \longrightarrow B_5N_4H_{16} + 0.5\ H_2$$

It was observed that, at the higher concentrations, the hydrogen evolution was completed in approximately 20 hours. At more-dilute concentrations, the completion time required was as little as 4 hours (see Figure 1). Thus, if it is not possible to observe the rate of disappearance of reactants, rate data for the above stoichiometric equation can be obtained by observing the rate of appearance of hydrogen.

C. KINETICS OF PENTABORANE-HYDRAZINE REACTION

1. Spectrophotometric Method

Spectrophotometric observation of the rate of disappearance of reactants was attempted. Ultraviolet and visible spectra of pentaborane and hydrazine were obtained with a Beckman Model DK-2 spectrophotometer. It was observed that hydrazine absorbed at 290 millimicrons (Figure 2) and pentaborane at 212 millimicrons (Figure 3) when in cyclohexane solution.

For the reaction-rate determination, hydrazine in cyclohexane was placed in a cell fitted with a serum stopper and pure solvent was placed in the reference cell. The spectrophotometer was set for 290 millimicrons (the absorption frequency of hydrazine). Pentaborane in cyclohexane solution was added to the hydrazine in stoichiometric amounts with a tuberculin syringe and a hypodermic needle. It was planned to obtain the rate of disappearance of the hydrazine by observing the rate of change in absorption, but in all cases the spectral absorption line disappeared too quickly. As a result, all the rate data obtained were from the slower hydrogen-evolution process.

2. Manometric Method

a. Apparatus

The apparatus used in the manometric rate study is illustrated in Figures 4 and 5. It consists of a round-bottom flask to which is attached, by standard-taper fittings, a dropping funnel containing a side arm. Both the funnel and the side arm have stopcocks with pressure fittings. Attached to the upper end of the dropping funnel, by a standard-taper fitting, is an adaptor containing a pressure stopcock. The adaptor is fitted on the other end to a 1/16-in.-ID Tygon tube attached to a mercury manometer. The manometer has a three-way stopcock at the upper end, with attachments to vacuum and argon inlets. The procedure used was as described below.

The round-bottom flask, dropping funnel, and adaptor were placed in a constant-temperature bath that rested on a magnetic stirring motor. Water was filled to the level of the stopcock on the adaptor. A knife-edge heater, a mercury temperature regulator, and a mechanical stirrer were placed in the bath.

Fifty milliliters of solvent was pipetted into the round-bottom flask, to which a magnetic stirring bar had been added. The flask was attached to a vacuum rack, and the desired amount of hydrazine was vacuum-distilled into the flask. The flask and its contents were flushed with argon, and the dropping funnel was attached. Fifty milliliters of solvent was pipetted into a separate round-bottom flask, which was attached to a vacuum rack. The desired amount of pentaborane was vacuum-distilled into the flask, and the flask was flushed with argon. The contents of this flask were then pipetted into the argon-flushed dropping funnel, with care taken to assure than an argon blanket was maintained during pipetting. The adaptor, with the pressure stopcock in the closed position, was then placed on the dropping funnel. All glass joints in the apparatus were greased with Apiazon N lubricant. The Tygon tube from the mercury manometer was attached to the end of the adaptor, and the apparatus was lowered into the bath, which had been set at the desired temperature. By means of alternate evacuation and argon flushing, the air within the manometer and Tygon tubing was replaced by argon.

The stopcock on the adaptor was opened, and the gas pressure within the system was noted. The magnetic stirring motor was started, to bring the contents of the flask into temperature equilibrium with the bath. When the system temperature reached the bath temperature, the manometer no longer registered a pressure change. The lower stopcock on the dropping funnel was opened, and the contents (the pentaborane solution) were allowed to pass into the round-bottom flask. This step required about 30 sec. Pressure measurements were made periodically following the release of the pentaborane solution into the hydrazine solution in the round-bottom flask.

This procedure was altered as desired for changes in the concentration of reactants, temperature, solvent, and stirring speed. For reactions requiring more than 4 hours for completion, the manometer was photographed at short intervals with an automatic camera.

Rate measurements in solutions were made at several concentrations of reactants, at several temperatures, with different solvents, and at two different stirring speeds. The latter was done because hydrazine has a limited solubility in cyclohexane (1.79 moles/100 ml at 25°C), and the possibility exists that the reaction is diffusion-controlled.

b. Effect of Concentration

In determining the effect of concentration, rate measurements were made at 25°C and at the following stoichiometric concentrations of pentaborane and hydrazine (in millimoles per 100 ml of cyclohexane solvent): 1.07 and 2.14, 2.14 and 4.28, 1.61 and 3.21, 4.28 and 8.45, and 2.68 and 5.35. The effect of temperature was determined from measurements made at 20, 23, 25, 28, 30, 32, and 35°C, using 1.07 mmoles of pentaborane and 2.14 mmoles of hydrazine per 100 ml of solvent. The effect of solvent was determined at 25°C from measurements made using n-hexane, diethyl ether, and benzene in place of cyclohexane. The concentrations used for these reactions were 1.07 mmoles of pentaborane and 2.14 mmoles of cyclohexane in 100 ml of solvent. Manometric data are given in Tables 2, 3, and 4, and in Figures 6 and 7. The degree of precision of the rate is approximately ±10% in terms of the volume of hydrogen evolved (Figure 1).

It was observed that a change in the stirring speed did not change the reaction rate when the reactants were in low concentration. It was therefore concluded that diffusion is not rate determining at low concentrations. Stirring speed does influence the rate at higher reactant concentrations.

It was observed that the data fit a first-order rate plot at concentrations below 1.61 mmoles of pentaborane per 100 ml of cyclohexane solvent at 25°C (see Figure 8, where the data-point symbols relate to four separate runs). At higher concentrations of reactant, a competitive zero-order process was observed. This is a slower process that continues after the first-order process is complete (Figures 1 and 6). The amount of hydrogen remaining after the first-order process was determined by taking the difference between the amount evolved from the zero-order process and the total hydrogen evolved. The rate constant of the first-order process from the dilute solution is $1.74 \pm 0.1 \times 10^{-4}$ sec^{-1}. The zero-order process is assumed to be diffusion-controlled rather than chemically controlled. To eliminate the zero-order reaction, all further experiments were conducted at concentrations below 1.61 mmoles of pentaborane and 3.21 mmoles of hydrazine per 100 ml of cyclohexane.

c. Effect of Solvent

Changing the solvent did not alter the reaction rate except when diethyl ether was used, as shown in Table 4. The rates observed with benzene or n-hexane are first-order and have approximately the same values as those obtained for cyclohexane; this was expected because all are hydrocarbons. Diethyl ether, however, has a single-bonded oxygen and is slightly basic. The rate of hydrogen evolution was difficult to reproduce, but was several times greater than with the three hydrocarbon solvents.

d. Effect of Temperature

The temperature effect from 20 to 35°C is shown in Table 3. The reciprocal of the absolute temperature is plotted against the log of the rate constant in Figure 9, an Arrhenius plot. The plot is linear from 20 to 30°C, above which there is a sudden plateau. A slow decomposition of the product begins above 35°C, and complicates the gas-evolution rate.

The activation energy was obtained from the data below 30°C. According to the Arrhenius equation,

$$\log k = - \frac{\Delta E'}{2.3\ RT} + C$$

where k is the rate constant, $\Delta E'$ the activation energy, R the gas constant (1.987 cal/°C), and C a constant. The slope ($\Delta E'/2.3R$) may be obtained from the plot of $10^3/T$ vs log k (Figure 9). On the basis of this slope, the value of $\Delta E'$ at temperatures below 30°C is 26,400 cal/mole. For most reactions, $\Delta E'$ is between 15,000 and 50,000 cal; hence, this magnitude is not exceptional.

The entropy of activation may be obtained from the energy of activation. From statistical thermodynamics and transition-state theory (Ref. 6),

$$k_1 = \frac{kT}{h} \exp\left(-\Delta F^{\ddagger}/RT\right)$$

where k_1 is the rate constant at temperature T, h is Planck's constant (6.6×10^{-27} erg-sec), k is Boltzmann's constant (1.38×10^{-16} erg/°C), $\Delta F^{\ddagger}$ is the free energy of activation, and R is the gas constant. Since $\Delta F = \Delta H - T\Delta S$,

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively. Then,

$$k_1 = \frac{kT}{h} \exp\left(\Delta S^{\ddagger}/R\right) \exp\left(-\Delta H^{\ddagger}/RT\right)$$

and

$$\Delta H^{\ddagger} = \Delta E' RT$$

Knowing $\Delta E'$, k_1 at 25°C, and the constants R, h, and k, it is possible to calculate $\Delta S^{\ddagger}$. A value of 17.4 cal/°C mole is obtained; it is exceptional only in that it is a positive quantity.

3. Ostwald Isolation Method

In order to establish whether the rate-determining step is dependent upon the concentration of reactants, the concentration of pentaborane (or the concentration of hydrazine) was changed while the other reactant was held constant. If the rate-determining step should actually be dependent upon the concentration of pentaborane, the initial rate of reaction would increase with increasing initial pentaborane concentration, or would decrease with decreasing initial pentaborane concentration. Pentaborane (2.14 mmoles in 50 ml of cyclohexane) was added in about 30 sec to a well-stirred mixture of 2.14 mmoles of hydrazine in 50 ml of cyclohexane. The initial rate of reaction for this system was the same as for the one in which 1.07 mmoles of pentaborane was used, as may be seen in Table 5. When 1.07 mmoles of pentaborane in 50 ml of cyclohexane was added to 0.55 mmole of hydrazine in 50 ml of cyclohexane, the initial reaction rate was about half the rate for the reaction in which 2.14 mmoles of hydrazine was used. The measured reaction rate is therefore independent of the pentaborane concentration but is first-order with respect to hydrazine. These rates are shown in Table 5; they were measured after 20% of the reactions had been completed. No runs were made with an excess of hydrazine.

4. Reverse-Addition Method

In the kinetic studies, pentaborane was added to hydrazine and an insoluble product was immediately obtained. The reverse order of addition was then tried. Hydrazine (2.14 mmoles in 50 ml of cyclohexane) was added in 2 min to 1.07 mmoles of pentaborane in 50 ml of cyclohexane, with stirring. A precipitate was not observed to form until approximately half of the hydrazine solution was added. It was therefore concluded that a precipitate does not form at any particular instant unless the hydrazine concentration is in excess. In the normal addition (pentaborane to hydrazine), hydrazine is always in excess for the 30 sec required for the addition. It was hypothesized that hydrazine and pentaborane react to form a product that is soluble at the concentration of the above reaction, and that hydrazine in excess of this intermediate product reacts additionally with the intermediate, producing the insoluble final product.

To test this hypothesis, an experiment was conducted in which some of the reaction solution was passed through a filter; the resulting clear solution was observed for further reaction. In this experiment, a pentaborane solution (2.14 mmoles in 50 ml of cyclohexane) was added to 4.28 mmoles of hydrazine in 150 ml of cyclohexane. After 20 min of reaction, approximately half of the reaction solution containing some precipitate was forced through a filter by argon pressure, yielding a clear solution. No further precipitate was observed to form in this solution, nor was any gas observed to evolve. When a trace quantity of hydrazine (0.002 ml) was added to this filtrate, a precipitate formed and hydrogen was evolved. The amount of precipitate formed was 4 times as much as could be accounted for by the hydrazine used if the added hydrazine entered into the stoichiometry of the reaction. Weak organic bases such as ethers did not visibly produce this effect. The addition of platinum black to a solution yielded hydrogen but no insoluble product. The platinum probably causes a decomposition by a different mechanism. The experiment indicates that the process is probably a base-catalyzed decomposition of a 2-to-1 addition product of 2 moles of hydrazine and 1 mole of pentaborane. Vacuum evaporation of the filtrate yielded no residue. This indicates that the intermediate reaction product can dissociate reversibly to hydrazine and pentaborane.

5. Gas-Phase Determinations

The effect of solvent was determined indirectly by observing the reaction in the gas phase without the influence of any solvent. If the solvent is involved in the reaction, the effect should be observed as a change in the reaction rate.

The reaction was conducted at 25°C in an all-glass system composed of two interconnected flasks separated by a 6-mm stopcock. A manometer was attached to each flask. The two flasks, one 3 liters and the other 500 ml, were evacuated. Hydrazine vapor was passed into the larger flask until its 25°C vapor pressure was reached (12 mm Hg). Pentaborane was passed into the smaller flask until a pressure of 42 mm was reached; argon was then added, bringing the total pressure to 442 mm. This amount of pentaborane is equal to that necessary for reaction with the hydrazine in the other bulb (36-mm pressure), plus the amount needed to maintain an equal pressure of pentaborane in both flasks when the stopcock is opened. The stopcock between the two flasks was opened, and the contents of the small flask under a pressure of 442 mm surged into the larger flask.

Immediate reaction occurred as the larger flask became cloudy. No further pressure change was observed on the attached manometer. The cloudy dust in the flask began to settle and eventually coated the inner surface of the flask. The contents of the flask were analyzed by mass spectrometry and were found to be argon carrier gas and hydrogen. The amount of hydrogen was very nearly 0.5 mole per mole of pentaborane used, and it is interesting to note that the amount of hydrogen evolved was the same as in the solution reaction.

Because of hydrogen evolution during the first few seconds of the reaction, it was not possible to determine the kinetics by this method. It was possible only to observe that the reaction was very much faster than the solution reactions, despite the low concentrations employed.

D. DEUTERATED-HYDRAZINE STUDIES

Hydrogen gas is evolved during the reaction of pentaborane and hydrazine in solution. It was desired to determine the source of the evolved hydrogen in order to obtain an insight into the structure of the product. If all the hydrogen of one of the reactants was deuterium, an analysis of the gas evolved would establish the source.

Anhydrous, deuterated hydrazine was purchased from the U.S. Nuclear Corporation. The specifications of 98% deuteration and 1% water content (deuterium oxide) were checked by infrared analysis and gas chromatography, respectively. It was found that the degree of deuteration was greater than 90% and the deuterium oxide content was 0.57%. The deuterated hydrazine was vacuum-distilled on a small scale over barium oxide (Ref. 5) in order to render the hydrazine as anhydrous as possible and to remove traces of impurities such as amines. A product containing 0.17% deuterium oxide was obtained.

The purified, anhydrous, deuterated hydrazine was added to a solution of pentaborane in cyclohexane. The initial concentrations of pentaborane and deuterated hydrazine were 1.07 and 2.14 moles, respectively, in 100 ml of solvent. The solution was allowed to react, with stirring, for 3 days at ambient temperature. The gas evolved was analyzed and was found to be approximately one-third of the amount that had been found for the reaction of normal hydrazine and pentaborane.

Analysis indicated that the gas consisted of 51.1 mol% HD, 35.1% H_2, and 13.8% D_2 (see Table 6). This is equivalent to a gas containing 61 mol% hydrogen and 39% deuterium. If the gas evolved in a completely random manner, 53% would come from pentaborane and 47% from hydrazine, because there are 9 atoms of hydrogen in a pentaborane molecule and 8 atoms of hydrogen in 2 molecules of hydrazine. The analysis shows that 61% of the gas evolved from pentaborane and 39% from hydrazine.

Two possibilities exist that can account for this analytical observation: (1) There are several competing reactions, some evolving hydrogen and some evolving deuterium, and (2) the rapid exchange of hydrogen and deuterium. Heretofore, the most favorable mechanism postulated for adduct formation assumed that the apex hydrogen of the pentaborane molecule is eliminated in the formation of product. Such a mechanism would require all the eliminated gas to be hydrogen when the reactants are pentaborane and deuterated hydrazine. If there is an exchange between hydrogen and deuterium during the reaction, some of the eliminated gas will be deuterium because a portion of the pentaborane entering the reaction will have deuterium at the apex position.

According to Koski (Ref. 7), isotopic exchange between pentaborane and deuterated diborane occurs most readily with pentaborane at the apex position and least readily on the bridge positions. If the hydrogen-deuterium exchange were complete and the gas eliminated during the reaction originated from the apex of the pentaborane, 47 mol% of the gas would be deuterium. If the exchange did not occur, all the gas evolved would be hydrogen. Because the deuterium concentration (39 mol%) is between these two, the degree of exchange is assumed to be appreciable. A degree of exchange of 83% would yield 39% deuterium. Several competing gas reactions would be very unlikely to yield what would appear to be a single, overall, first-order, gas-elimination reaction. The rates and orders of the various competing reactions would be different, and the resulting data would not fit the scheme of a single first-order reaction.

E. STUDIES OF SUBSTITUTED HYDRAZINES

The effect of methyl substitution on the hydrazine nucleus was determined by using the two substituted hydrazines, MMH and UDMH, in the reaction. Because the use of deuterated hydrazines was rendered ineffective by the rapid exchange reaction, the use of substituted hydrazine might help to elucidate the structure. In addition, the final product of the reaction when substituted hydrazines are used might be soluble in a number of unreactive solvents.

Because MMH and UDMH differ from hydrazine, the stoichiometry of 2 moles of hydrazine to 1 mole of pentaborane does not necessarily apply. The stoichiometry of the reaction between MMH and pentaborane was obtained. An excess of pentaborane, 8.56 mmoles (obviously a greater amount than stoichiometry would suggest was needed), was reacted with 2.14 mmoles of MMH in a 100-ml cyclohexane solution. The reaction was accomplished by dissolving the pentaborane in 50 ml of cyclohexane and adding this to a solution of MMH in 50 ml of cyclohexane, with stirring, as was done before in the kinetic studies with hydrazine. Hydrogen was evolved and a precipitate formed. The excess pentaborane was determined by removing a 25-ml aliquot from the cyclohexane solution after the reaction had been allowed to proceed overnight and analyzing the aliquot for pentaborane by gas chromatography. The reverse process, using an excess of substituted hydrazine, could not be used, inasmuch as the hydrazines are soluble only to a limited degree and adhere to surfaces such as the precipitate that forms during the reaction; therefore, withdrawing an aliquot with an excess of the hydrazines would not yield a representative sample.

Analysis of the aliquots showed a greater excess of pentaborane than a 2-to-1 stoichiometry could account for. The results of three runs (in moles per mole of MMH) are

B_5H_9 Added	B_5H_9 Recovered	Difference
4	3.73	0.27
4	3.73	0.27
4	3.75	0.25

The average difference is 0.26 for the three runs, or 3.85 moles of MMH to 1 mole of pentaborane. The assumed stoichiometry is therefore 4 moles of MMH per mole of B_5H_9. Analysis of the gas evolved showed that the molar amount of evolved hydrogen was very nearly the same as with unsubstituted hydrazine - namely, 0.5 mole (Table 7). The overall reaction may then be written

$$B_5H_9 + 4\ CH_3NHNH_2 \longrightarrow B_5N_8H_{20}(CH_3)_4 + 0.5\ H_2$$

The solid final product from the reaction is insoluble in pyridine, dimethyl formamide, dioxane, and diethyl ether, in which solubility tests were conducted. It reacted with water, alcohols, and acetonitrile.

The same procedure for determining the overall stoichiometry was used with UDMH. An excess of pentaborane (8.56 mmoles) was reacted with 2.14 mmoles of UDMH in 100 ml of cyclohexane solvent. As was done for the MMH-stoichiometry determination, the pentaborane was dissolved in 50 ml of cyclohexane and was added to a solution containing UDMH in 50 ml of cyclohexane, with stirring. The excess UDMH was analyzed by the aliquot procedure described above. No hydrogen was observed to form during the reaction; however, a precipitate similar in appearance to the product of the pentaborane-MMH reaction was observed.

Analysis of the aliquots showed an excess of pentaborane equal to that of a 2-to-1 stoichiometry for the reaction. The results of four runs (in moles per mole of UDMH) are

B_5H_9 Added	B_5H_9 Recovered	Difference
4	3.81	0.19
4	3.54	0.46
4	3.54	0.46
4	3.55	0.45

The average difference is 0.46 for the three final runs (neglecting the first run), or 2.17 moles of UDMH to 1 mole of pentaborane. The assumed stoichiometry is therefore 2 moles of UDMH per mole of B_5H_9. The overall reaction may be written

$$B_5H_9 + 2\ H_2NN(CH_3)_2 \longrightarrow B_5N_4H_{13}(CH_3)_4$$

The solid final product is a true adduct in this case, because no gas is formed, and is similar in appearance to the products of the reactions involving unsubstituted hydrazine and MMH. This adduct is insoluble in pyridine, dimethyl formamide, dioxane, benzene, and diethyl ether, in which solubility tests were conducted.

Investigation of the effect of increased substitution on the hydrazine nucleus in the reaction with pentaborane was continued with tetramethyl hydrazine. The product of the reaction of pentaborane and tetramethyl hydrazine was an adduct similar in appearance to that produced in the pentaborane-UDMH reaction. No gases were observed to evolve.

F. KINETICS OF PENTABORANE-MMH REACTION

As with pentaborane and hydrazine, the initial reaction of pentaborane and MMH in cyclohexane was too fast to measure. The kinetics were therefore investigated by following the rate of hydrogen evolution in the same manner as the pentaborane-hydrazine kinetics. Stoichiometric quantities of pentaborane and MMH in cyclohexane were used. Pentaborane (1.07 mmoles) dissolved in 50 ml of cyclohexane was added to a stirred mixture of 4.28 mmoles of MMH in 50 ml of cyclohexane in a constant-temperature bath at 25°C. The pressure increase due to hydrogen evolution was observed and was found to fit a first-order rate plot with a rate constant of 2.07×10^{-4} sec^{-1} (as shown in Table 8). This compares closely with the value obtained for the hydrazine reaction under these conditions (1.74×10^{-4} sec^{-1}). The reaction is similar to the hydrazine reaction in another respect as well; it is independent of the pentaborane concentration and is first-order with respect to the concentration of MMH.

G. THERMAL DECOMPOSITION

1. Insoluble Product of Pentaborane-Hydrazine Reaction

The properties of the insoluble product of the pentaborane-hydrazine reaction were also investigated. Quantities of insoluble product were prepared for various experiments. The insoluble product was isolated from reactions in which the reactant concentrations before mixing were 128 mmoles of hydrazine in 50 ml of cyclohexane and 65 mmoles of pentaborane in 50 ml of cyclohexane; at such concentrations, most of the hydrogen evolves by the zero-order process. The total yield in this case was slightly less than 4 g.

The insoluble product was also isolated from a first-order, chemically controlled reaction conducted under dilute conditions. Pentaborane (10.7 mmoles) in 500 ml of cyclohexane was added, with stirring, to 21.4 mmoles of hydrazine in 500 ml of cyclohexane. In this reaction all the hydrogen evolved by the first-order process. In each case a white precipitate was formed. Upon completion of the reaction, the solvent was filtered off and the product was collected as a solid.

An attempt was made to find suitable solvents for the products of these reactions so that their molecular weights and structures could be determined by means of nuclear magnetic resonance and high-resolution infrared spectroscopy. Dioxane, carbon tetrachloride, chloroform, and acetonitrile were tried. The products would not dissolve in any of the first three, and they reacted with acetonitrile. The infrared spectrum of the product of the "dilute-solution" reaction was obtained in the solid phase by the Nujol-mull method (Figure 10). Absorption bands due to B-N, B-H, and N-H may be observed.

The insoluble products produced from the dilute solution and the concentrated solution were subjected to thermal-decomposition studies. Quantities of each were placed in Vycor tubes, which were evacuated and heated. Hydrogen was evolved in both cases; however, when the two products were heated to 960°C, they changed in appearance as the temperature was increased. The dilute-solution product remained white until 700°C, when it became a dark gray-brown. The concentrated-solution product changed from white to violet to yellow to gray. Differential thermograms of these products were also different (Figure 11). A single broad exotherm was observed with the dilute-solution product, but two pronounced exotherms were observed with the concentrated-solution product.

The insoluble products are very similar in their other physical and chemical properties. Similar infrared spectra were obtained for both products, as was the case for the final decomposition products. Nearly the same amount of hydrogen was evolved during heating for the two products: 13 out of 16 gram-atoms of hydrogen for the dilute-solution product and 14 out of 16 gram-atoms of hydrogen for the concentrated-solution product. A trace of nitrogen was found to evolve from the concentrated-solution product when the decomposition temperature was 960°C. The relative amounts of hydrogen evolved (moles per mole of adduct) are shown below as a function of temperature for the product of the dilute-solution reaction.

25 to 80°C	80 to 130°C	130 to 240°C	240 to 960°C	Total
1.07	2.35	2.99	0.342	6.75
1.20	2.27	1.64	1.54	6.65
1.30	2.20	1.50	Exploded	-
1.35	3.60	0.61	1.55	7.11

The product heated at 960°C was analyzed for nitrogen and hydrogen, and boron was obtained by difference. Because only trace amounts of gases other than hydrogen were found to be evolved when the reaction product was heated, and because the observed boron/nitrogen atomic ratio was 5.0 to 3.76, it was concluded that the presumed ratio of 5.0 to 4.0 in the unheated product was correct.

2. Pentaborane-MMH Reaction Product

The product of the pentaborane-MMH reaction was separated from the solvent and was dried under vacuum. The sample was heated under vacuum to temperatures of 80, 350, 500, and 980°C. Gas samples were removed after heating at each temperature and were analyzed by mass spectrometry for gas content.

		Mol%			
Temp, °C	Gas Volume ml	H_2	CH_4	C_2H_6	Color of Product
80	20	98	-	-	Yellow
350	12	86	13	-	Orange-yellow
500	10	84	15	1	Purplish black
980	10	95	3.5	1	Black

The weight of the sample was 6.328 mg; on the basis of the above gas-evolution data, 58% of the methyl groups of the sample evolved as methane and ethane. All the hydrogen of the product was evolved, leaving carbon (which accounts for the black color of the product). Like the product of the pentaborane-hydrazine reaction, which lost most of its hydrogen even when heated to 980°C for 24 hours, this product lost all its hydrogen after heating to 980°C for 24 hours.

The colors of the products heated to the temperatures given above are similar to the colors noted when the pentaborane-hydrazine product was thermally decomposed.

V. DISCUSSION OF RESULTS AND CONCLUSIONS

A. INITIAL REACTION RATE

It was observed that the reaction of pentaborane and hydrazine occurred too fast to be measured by following the decomposition of either reactant spectrophotometrically. The spectrophotometric procedure was complicated by the appearance of precipitate when pentaborane was added to hydrazine in solution. It was observed, however, that the hydrazine peak at 290 millimicrons disappeared immediately, before the transmittance became inappreciable. This indicates that the initial reaction of hydrazine and pentaborane is very fast - too fast to be measured by the spectrophotometer.

Such an observation is expected from the nature of the reactants. Hydrazine is a basic substance containing an unbonded pair of electrons on each nitrogen. Pentaborane, on the other hand, is electronically deficient and is consequently a Lewis acid. Thus, pentaborane and hydrazine react as any acid and base - very quickly.

B. RATE OF HYDROGEN EVOLUTION

The hydrogen evolution is much slower, indicating a slower subsequent step in comparison with the initial fast reaction. This process is first-order with respect to the hydrogen evolved. This is expected from unimolecular-decomposition processes and not from bimolecular processes. The hydrogen-evolution step is dependent upon the reactant concentrations in solution. Above a critical concentration (1.61 mmoles of pentaborane and 3.21 mmoles of hydrazine per 100 ml of cyclohexane), two competitive reactions are observed (one first-order and one zero-order, the latter being slower). The zero-order process could be diffusion-controlled, and probably represents the decomposition of insoluble material. Although most first-order processes are homogeneous, a number are shown to be heterogeneous as well. Because in this case a zero-order process is concurrently observed, that zero-order process would be the heterogeneous diffusion-controlled process leaving the first-order process to proceed homogeneously. This postulate lends credence to the hypothesis that the decomposing substance is an intermediate that is slightly soluble in cyclohexane. The dissolved portion decomposes by a first-order process, and the undissolved excess decomposes by the slower zero-order process.

C. MECHANISM OF REACTION WITH HYDRAZINE

It was observed that the insoluble final product did not immediately form when hydrazine was added to pentaborane (the reverse of conventional addition). The precipitate appeared only when nearly half of the hydrazine had been added. With conventional addition, precipitate is observed almost immediately. In the latter case, hydrazine is always in excess during the addition; in the former, there is a deficiency of hydrazine until the end of the addition. It is therefore inferred that excess hydrazine is necessary for the formation of final product (and evolution of hydrogen) from the postulated, partially soluble intermediate.

This process may occur in either of two ways: (1) The intermediate is a 1-to-1 addition product that takes up another hydrazine to yield the final product and hydrogen, or (2) the intermediate is a 1-to-2 addition product ($B_5H_9 \cdot 2\ N_2H_4$) that requires hydrazine to catalyze the decomposition by an acid-base mechanism.

These hypotheses were tested in the experiment in which a filtered aliquot was taken from the reaction medium, after approximately one-third of the reaction had been completed, and was passed into a vessel to which a trace quantity of hydrazine was added. The clear aliquot solution stood indefinitely without change, but the addition of 0.02 g of hydrazine resulted in the formation of an insoluble product and the evolution of hydrogen. The amount of product was 4 times more than could be accounted for by the stoichiometry of the reaction. Weak organic bases such as ethers did not produce this effect. The addition of platinized platinum to a solution yielded hydrogen but no insoluble product. The platinum, a good hydrogen-reaction catalyst, probably causes decomposition by a different mechanism. The experiment indicates that the process is a base-catalyzed decomposition of a 2-to-1 addition product of hydrazine and pentaborane.

The greatly increased reaction rate when a mildly basic solvent (diethyl ether) is used instead of a hydrocarbon solvent may be explained in this manner. The solvent itself weakly catalyzes the decomposition of the intermediate.

This conclusion was verified by the Ostwald isolation method of reaction-order determination (Ref. 8). It was found that the initial rate was first-order with respect to hydrazine concentration, but was independent of the pentaborane concentration. Such is the case with acid-base catalysis. The reaction rate is catalyst-concentration-dependent. The slow, rate-determining step, however, is independent of the concentration of reactants that have undergone an initial fast reaction.

On the basis of the foregoing experiments, the following mechanism may be postulated:

$$B_5H_9 + 2\ N_2H_4 \rightleftharpoons B_5H_9 \cdot 2\ N_2H_4$$

$$B_5H_9 \cdot 2\ N_2H_4 + N_2H_4 \rightleftharpoons B_5N_4H_{16}\text{--H--}N_2H_4$$

$$B_5N_4H_{16} \longrightarrow B_5N_4H_{15} + 0.5\ H_2 \text{ (slow)}$$

$$B_5N_4H_{15}\text{--H--}N_2H_4 \rightleftharpoons B_5N_4H_{16} + N_2H_4$$

In this mechanism an initial fast reaction of pentaborane with hydrazine occurs in a stoichiometric manner, yielding the slightly soluble $B_5H_9 \cdot 2\ N_2H_4$ intermediate. In turn, the intermediate undergoes decomposition by a base-catalyzed mechanism to yield hydrogen and the final product, the insoluble $B_5N_4H_{16}$. The base-catalyzed steps are shown in the foregoing mechanism with the base, N_2H_4, accepting a proton from the intermediate rather than in the usual ionic pattern, because the solvents used were nonionic.

D. MECHANISM OF REACTION WITH MONOMETHYLHYDRAZINE

Because the reaction of MMH and hydrazine is similar to the pentaborane-hydrazine reaction in that it also features a fast reaction followed by a slow hydrogen-evolution step and is also base-catalyzed, a similar mechanism may be given:

$$B_5H_9 + 4\ N_2H_3CH_3 \rightleftharpoons B_5H_9 \cdot 4\ N_2H_3CH_3$$

$$B_5H_9 \cdot 4\ N_2H_3CH_3 + N_2H_3CH_3 \rightleftharpoons B_5N_8H_{20}(CH_3)_4\text{--H--}N_2H_3CH_3$$

$$B_5N_8H_{20}(CH_3)_4 \longrightarrow B_5N_8H_{19}(CH_3)_4\ \text{(slow)} + 0.5\ H_2$$

$$B_5N_8H_{19}(CH_3)_4\text{--H--}N_2H_3CH_3 \rightleftharpoons B_5N_8H_{20}(CH_3)_4 + N_2H_3CH_3$$

E. ACTIVATION ENERGY AND ENTROPY

The activation energy and activation entropy are obtained from the Arrhenius plot of log k vs 1/T (Figure 9). The activation energy (26,400 cal/mole) is not exceptional; for most chemical reactions, it ranges between 15,000 and 50,000 cal/mole. Nor is the value of the activation entropy unusual (17.4 cal/°C-mole), except that it is a positive quantity. The activation entropy of most reactions is negative, especially for bimolecular reactions (Ref. 6). Because this reaction has a positive entropy of activation, it is inferred that the rate-determining step is unimolecular.

It is also possible that the positive activation entropy results from the formation of a product of a less-ordered species in the activated state of the slow step of the reaction. The product was found to be insoluble without reaction in several solvents used, was shown by X-ray analysis to be amorphous, and is believed to be polymeric. With regard to the structure of the final product of the reaction, the positive entropy of activation provides evidence that this product is a polymeric substance. Such a polymeric material was found as one of the products from the reaction of pentaborane and substituted amines (Ref. 3). Pentaborane, which has an ordered and coordinated pyramidal structure, upon reaction breaks into a polymeric material having a linear structure. The linear polymer would have a less-ordered structure, and the process would consequently show a positive entropy change. This could easily be noted if the pentaborane pyramid is broken during the formation of the activated complex in the slow step.

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TABLE 1

MOLES OF HYDROGEN EVOLVED PER MOLE OF PENTABORANE USED

Concentration mmoles/100 ml solvent		H_2 Evolved	
B_5H_9	N_2H_4	mmoles	moles/mole B_5H_9
1.07	2.14	0.55	0.51
1.07	2.14	0.51	0.48
4.28	8.56	2.31	0.54
4.28	8.56	2.10	0.49
4.28	8.56	2.11	0 49

TABLE 2

RATE OF HYDROGEN EVOLUTION

Run No.	Temp °C	Concentration mmoles/100 ml solvent		H_2 Total Pressure mm Hg	H_2 Evolved mmoles	Rate Constant	
		B_5H_9	N_2H_4			First Order $k \times 10^4$, sec^{-1}	Zero Order $k \times 10^6$, moles/sec
20	35	4.28	8.45	127	2.23	2.8	2.3
22	35	4.28	8.45	139	2.43	1.28	2.9
24	30	4.28	8.45	122.5	2.15	1.48	3.37
26	30	4.28	8.45	108	1.90	0.77	2.78
35	25	2.14	4.28	53	0.93	3.42	2.22
37	25	2.68	5.35	80	1.41	1.92	2.77
38	25	2.68	5.35	70.5	1.23	1.01	2.77
42	25	2.14	4.28	61	1.00	1.05	2.30
43	25	1.07	2.14	27	0.485	1.60	--
44	25*	1.07	2.14	31	0.545	1.92	--
45	25	1.07	2.14	26	0.458	1.90	--
46	25*	1.07	2.14	27	0.485	1.82	--
47	25	1.07	2.14	28	0.492	1.65	--
48	25	1.07	2.14	28	0.492	1.61	--
49	25*	1.07	2.14	26	0.458	1.61	--
50	25	1.61	3.21	43	0.756	1.78	--
51	25	1.61	3.21	40	0.705	1.74	--
52	25	1.61	3.21	44	0.773	1.85	--

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*Slow stirring rate.

TABLE 3

TEMPERATURE DEPENDENCE OF GAS-EVOLUTION KINETICS
(2.14 mmoles N_2H_4 and 1.07 mmoles B_5H_9 per 100 ml of Solvent)

Temp °C	H_2 Evolved mmoles		Rate Constant $k \times 10^4$, sec^{-1}
20	0.366		0.682
20	0.406		0.684
		Av	0.684
25	0.485		1.60
25	0.545		1.92
25	0.458		1.90
25	0.492		1.65
25	0.492		1.61
		Av	1.74
28	0.366		2.84
30	0.432		3.33
30	0.445		3.60
30	0.353		3.70
30	0.353		3.57
		Av	3.57
32	0.445		3.28
32	0.432		3.50
32	0.445		3.50
		Av	3.41
35	0.423		3.58
35	0.366		3.25
35	0.445		3.33
35	0.445		3.59
		Av	3.39

TABLE 4

RATE OF HYDROGEN EVOLUTION, PENTABORANE-HYDRAZINE REACTION USING VARIOUS SOLVENTS (25°C)

(2.14 mmoles N_2H_4 and 1.07 mmoles B_5H_9 per 100 ml of Solvent)

Solvent	H_2 Total Pressure mm Hg	First-Order Rate Constant $k \times 10^4$, sec^{-1}
n-Hexane	27	2.39
n-Hexane	28	2.38
n-Hexane	25	2.28
Benzene	30	2.38
Benzene	30	2.18
Ether	22	17.1
Ether	23	3.93
Ether	24	9.0
Ether	22	7.8

TABLE 5

EFFECT OF CONCENTRATION ON INITIAL REACTION RATE (AT 25°C)

Concentration mmoles/100 ml solvent		Rate After 1/5 of Reaction Completed mmoles H_2/hour
N_2H_4	B_5H_9	
2.14	2.14	27.5
2.14	2.14	35
2.14	1.07	35
2.14	1.07	27
1.07	1.07	14
0.55	1.07	10

TABLE 6

ANALYSIS OF GAS EVOLVED, PENTABORANE-DEUTERATED HYDRAZINE REACTION

Run No.	Analysis, mol% H_2	HD	D_2	Gas Evolved moles/mole B_5H_9
2	41	47.8	11.2	0.32
3	40	50	10	0.11
4	29	51.5	19.5	0.25
5	35.7	54.2	10.1	0.16
6	33.1	49.3	17.6	0.22
7	32.3	53.2	14.5	0.18
Av	35.1	51.5	13.8	0.21

TABLE 7

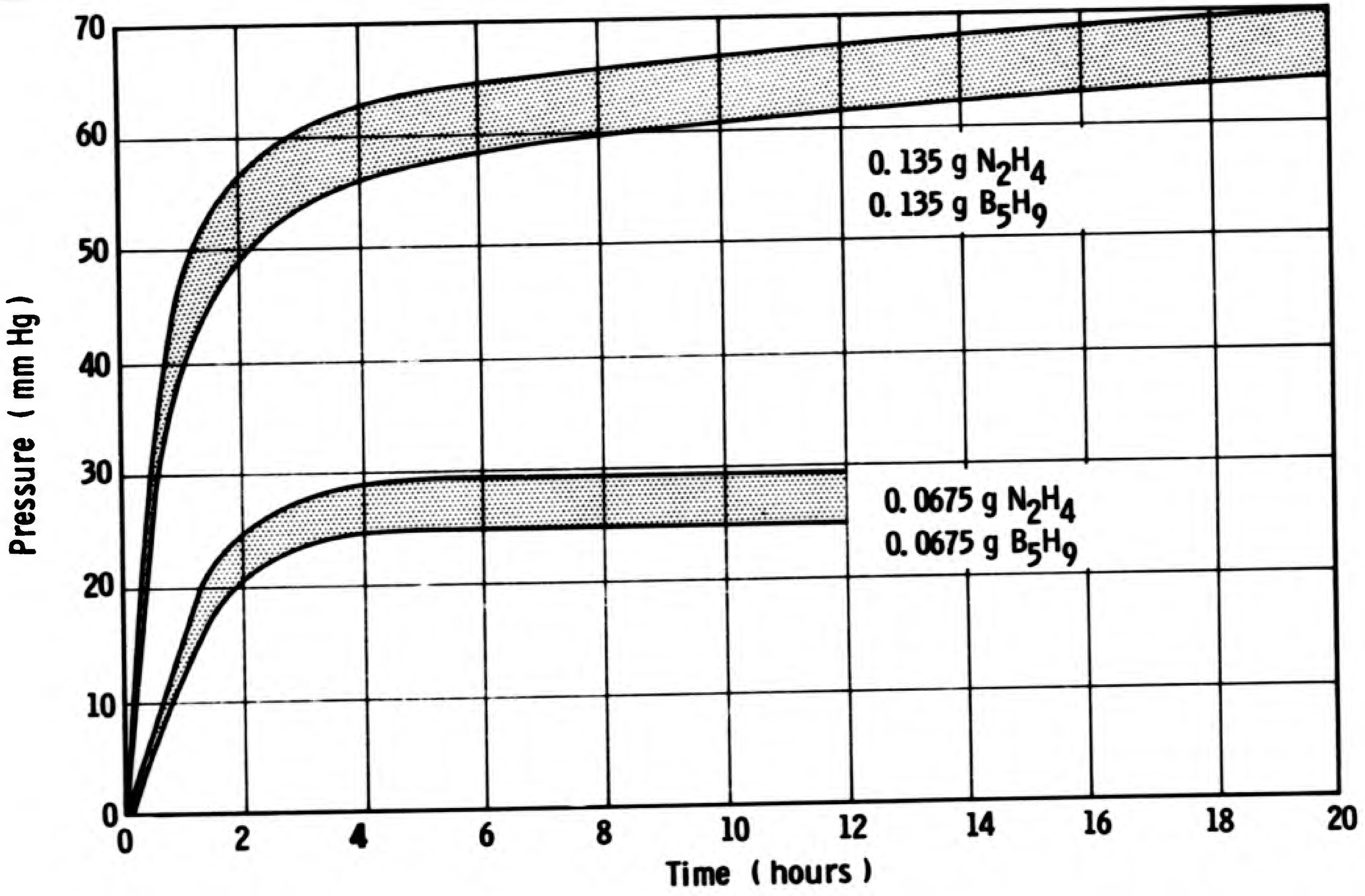
EVOLUTION OF HYDROGEN, PENTABORANE-MONOMETHYLHYDRAZINE REACTION

Total Gas Evolved mmoles	H_2 Evolved vol%	mmoles	mmoles/mole B_5H_9
0.56	95	0.532	1.0
0.53	97	0.515	0.96
0.428	55	0.235	0.44
0.216	90	0.193	0.36
0.417	90	0.375	0.70
0.437	27	0.118	0.22
0.252	85	0.214	0.40
0.29	92	0.267	0.50
0.264	77	0.203	0.38

TABLE 8

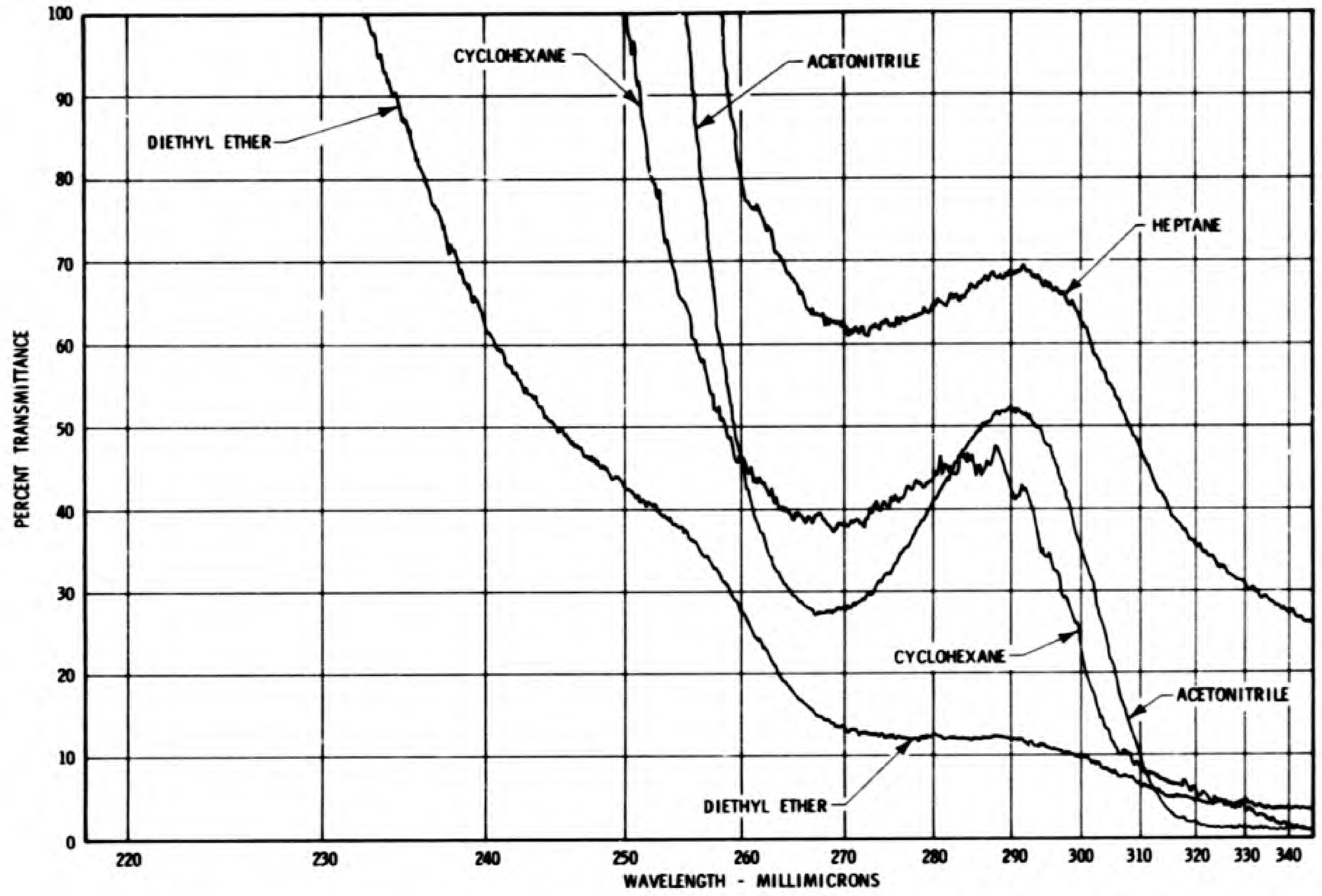
RATE OF HYDROGEN EVOLUTION, PENTABORANE MONOMETHYLHYDRAZINE REACTION (AT 25°C) (4.28 mmoles $N_2H_3CH_3$ and 1.07 mmoles B_5H_9 per 100 ml of Solvent)

Run No.	H_2 Total Pressure mm Hg	First-Order Rate Constant, $k \times 10^4$, sec^{-1}
40	27	2.03
42	26	2.04
43	29	1.98
44	27	1.97
46	27	2.08



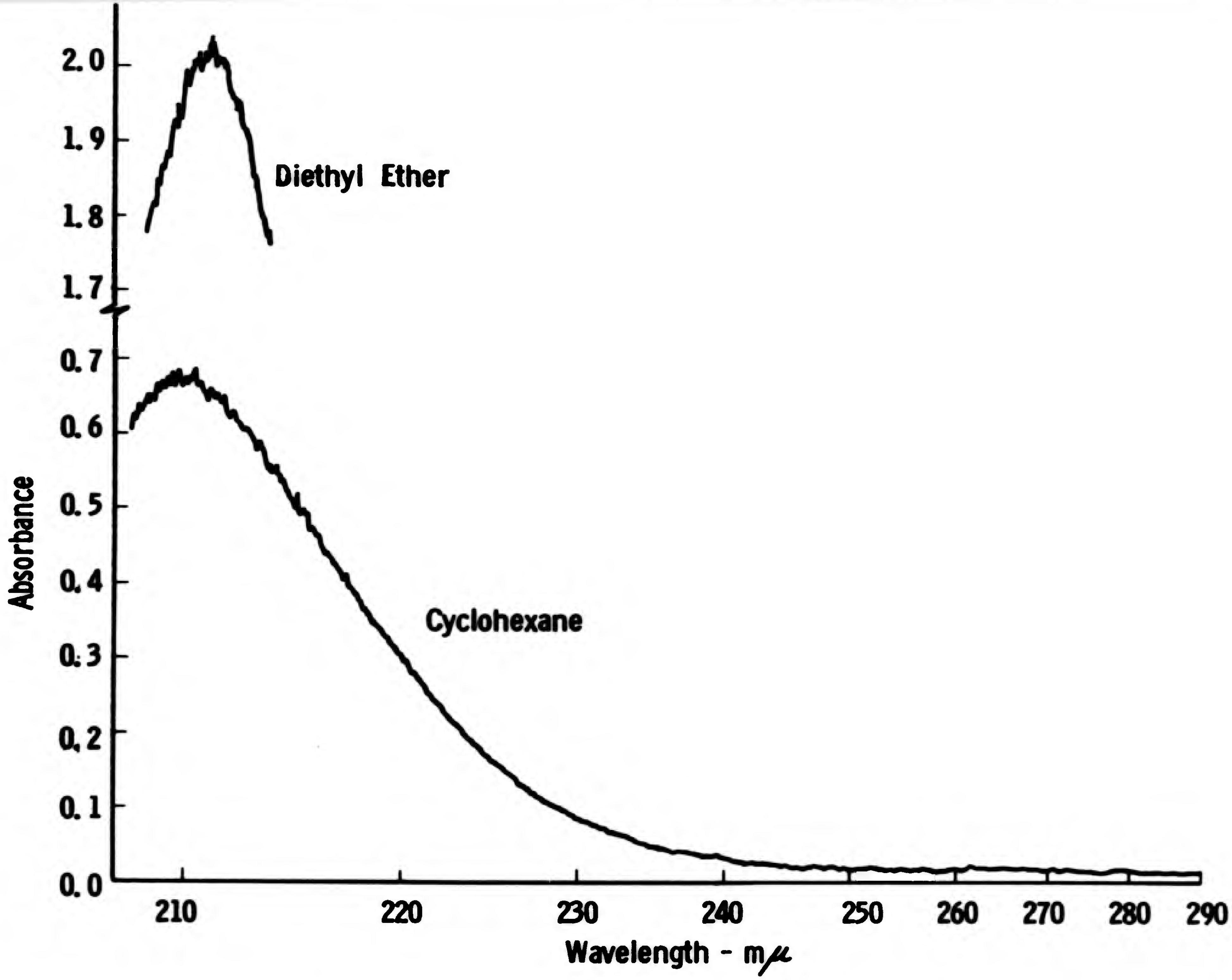
Degree of Precision, Reaction of Pentaborane and Hydrazine

Figure 1



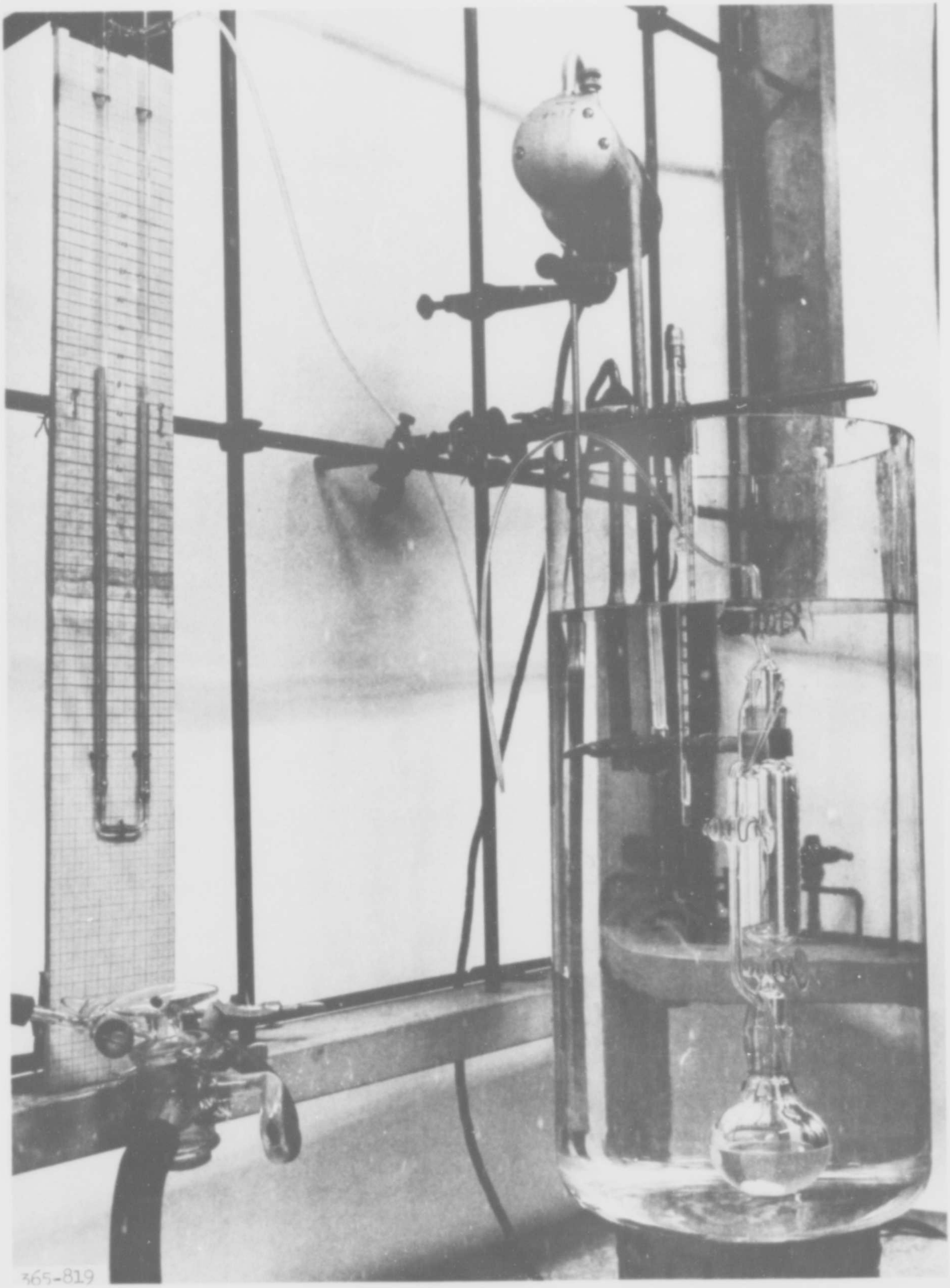
Spectrum of Hydrazine in Several Solvents

Figure 2



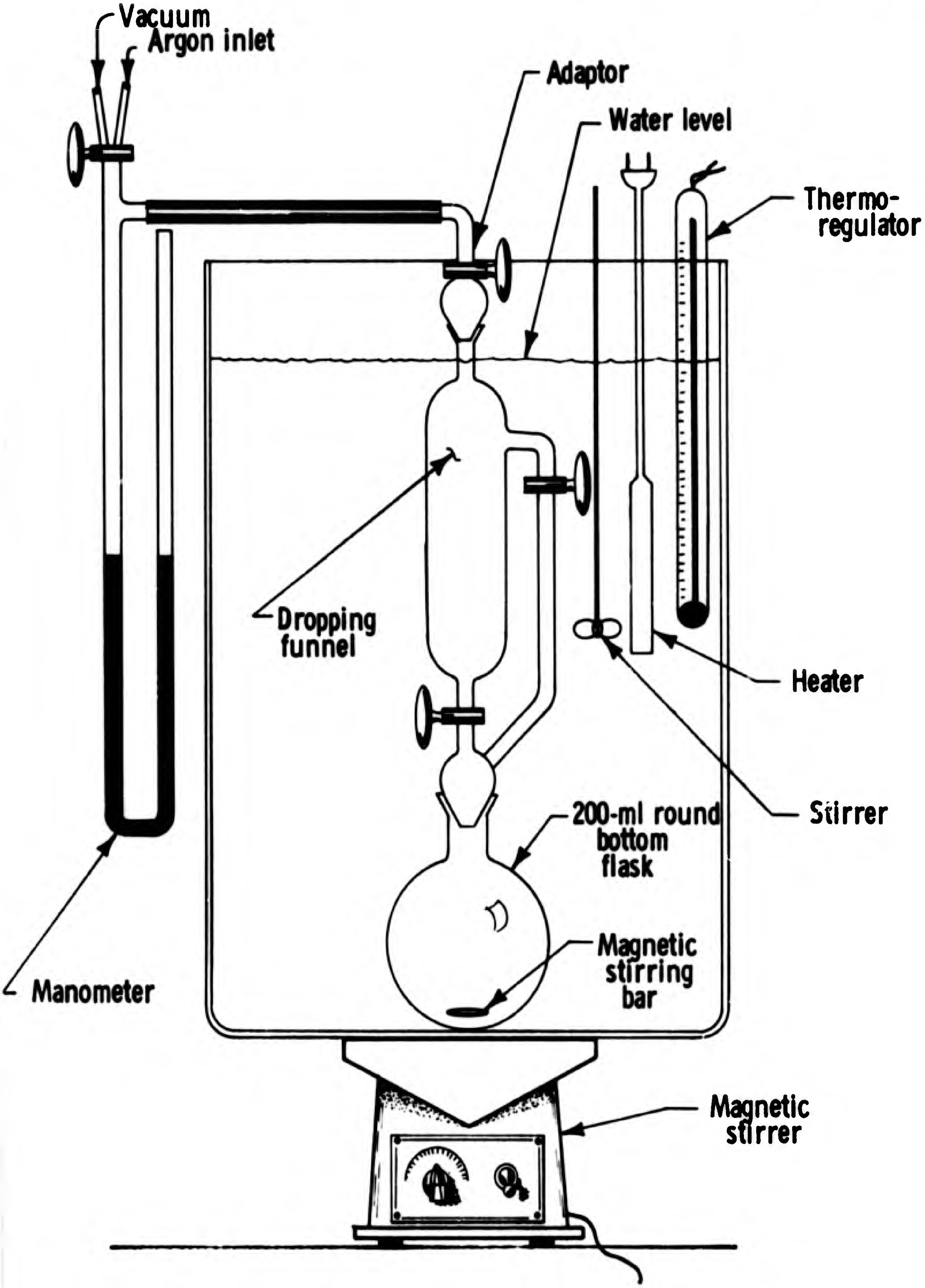
Spectrum of Pentaborane in Cyclohexane and Diethyl Ether

Figure 3



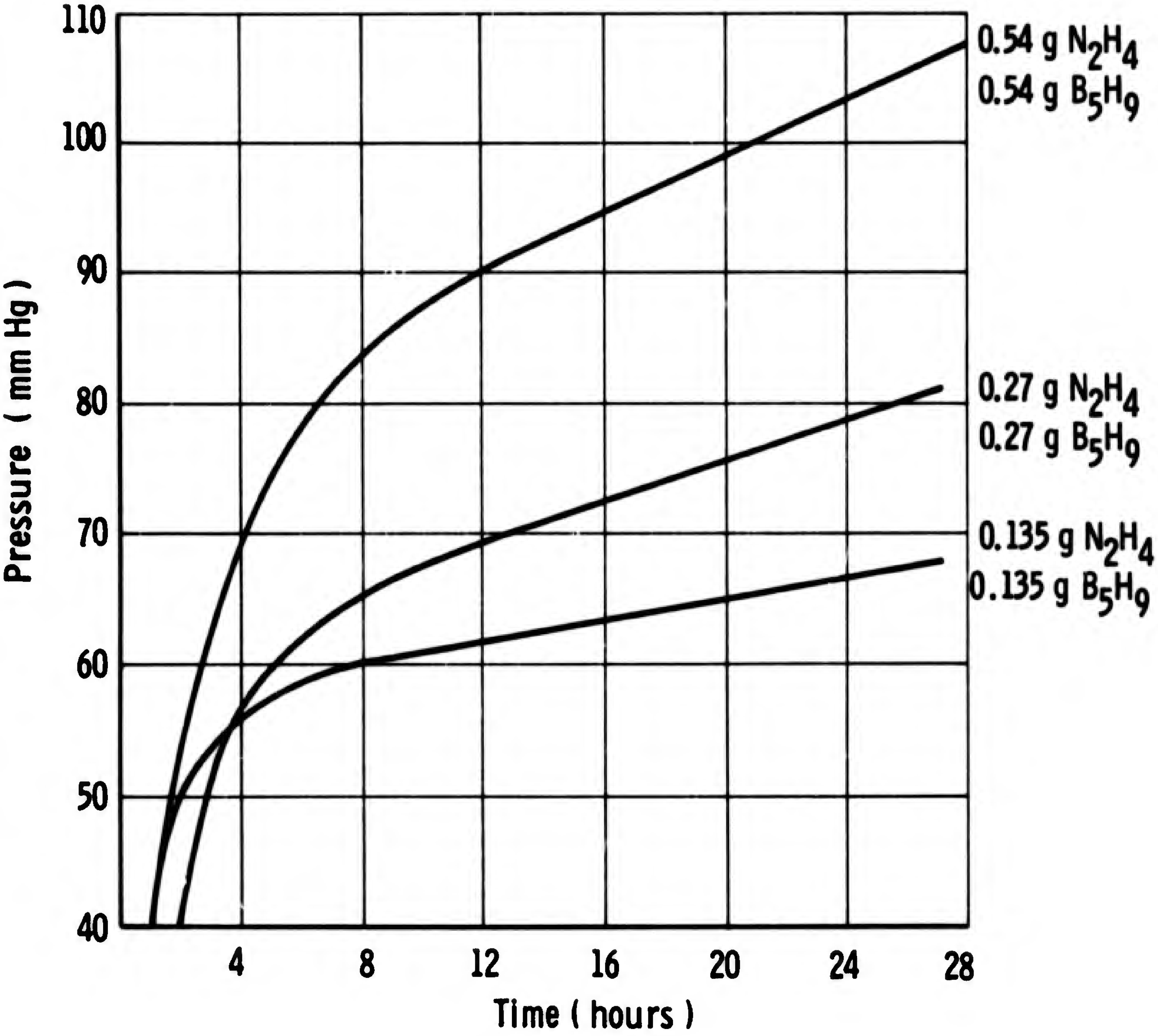
View of Apparatus Used in Manometric Determination of Kinetics

Figure 4



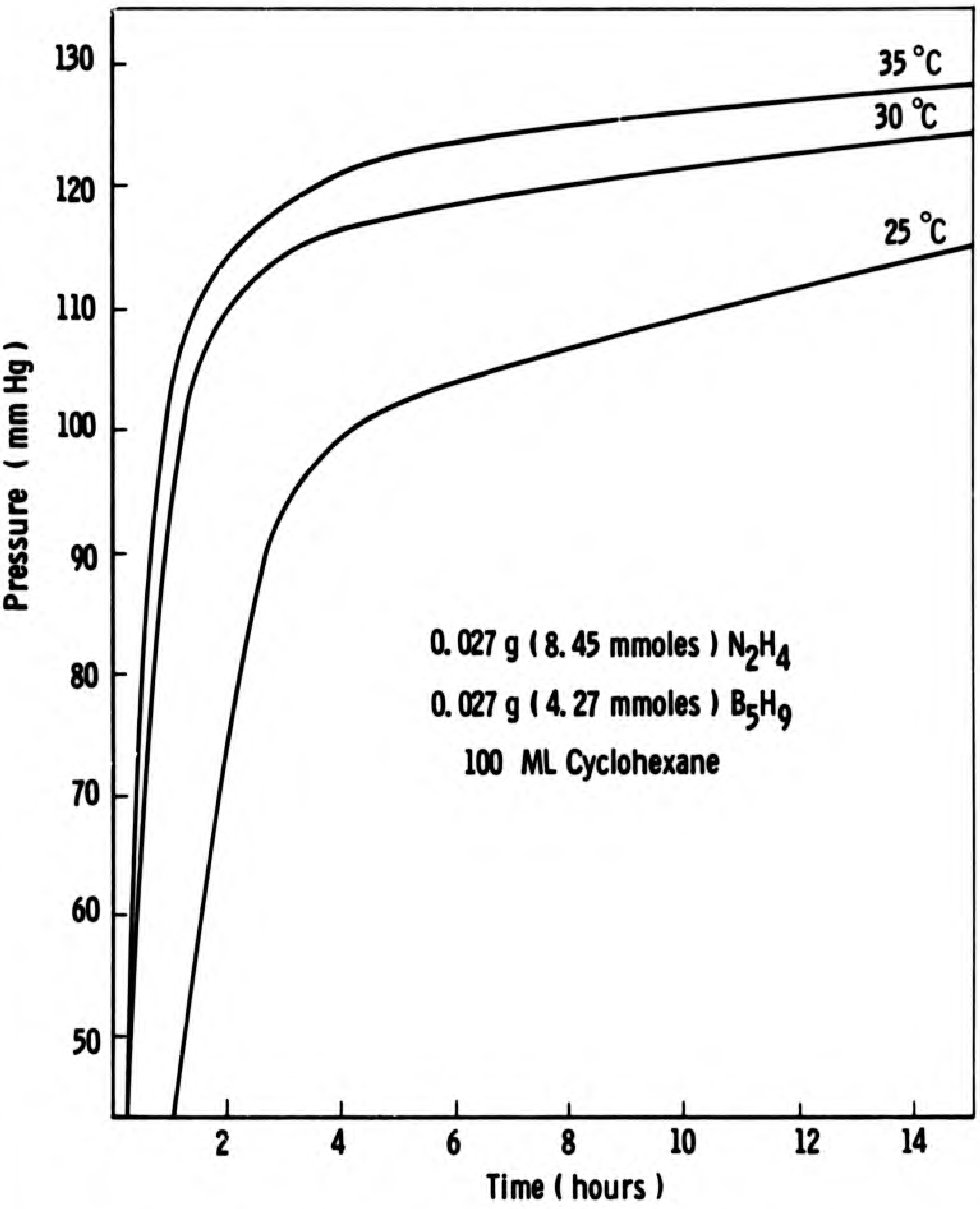
Apparatus Used in Manometric Determination of Kinetics (Schematic)

Figure 5

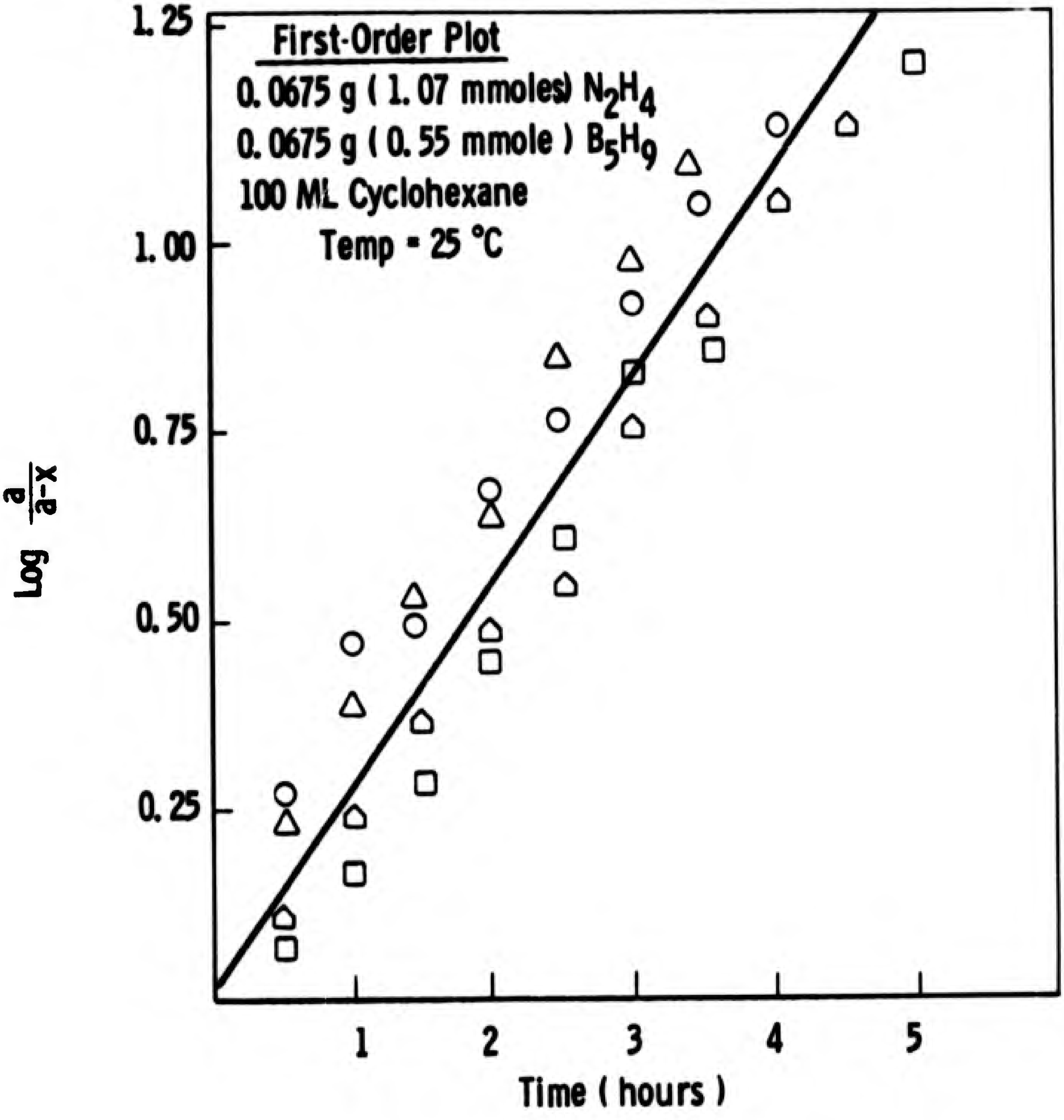


Effect of Concentration of Reaction Mixture on
Reaction of Pentaborane with Hydrazine

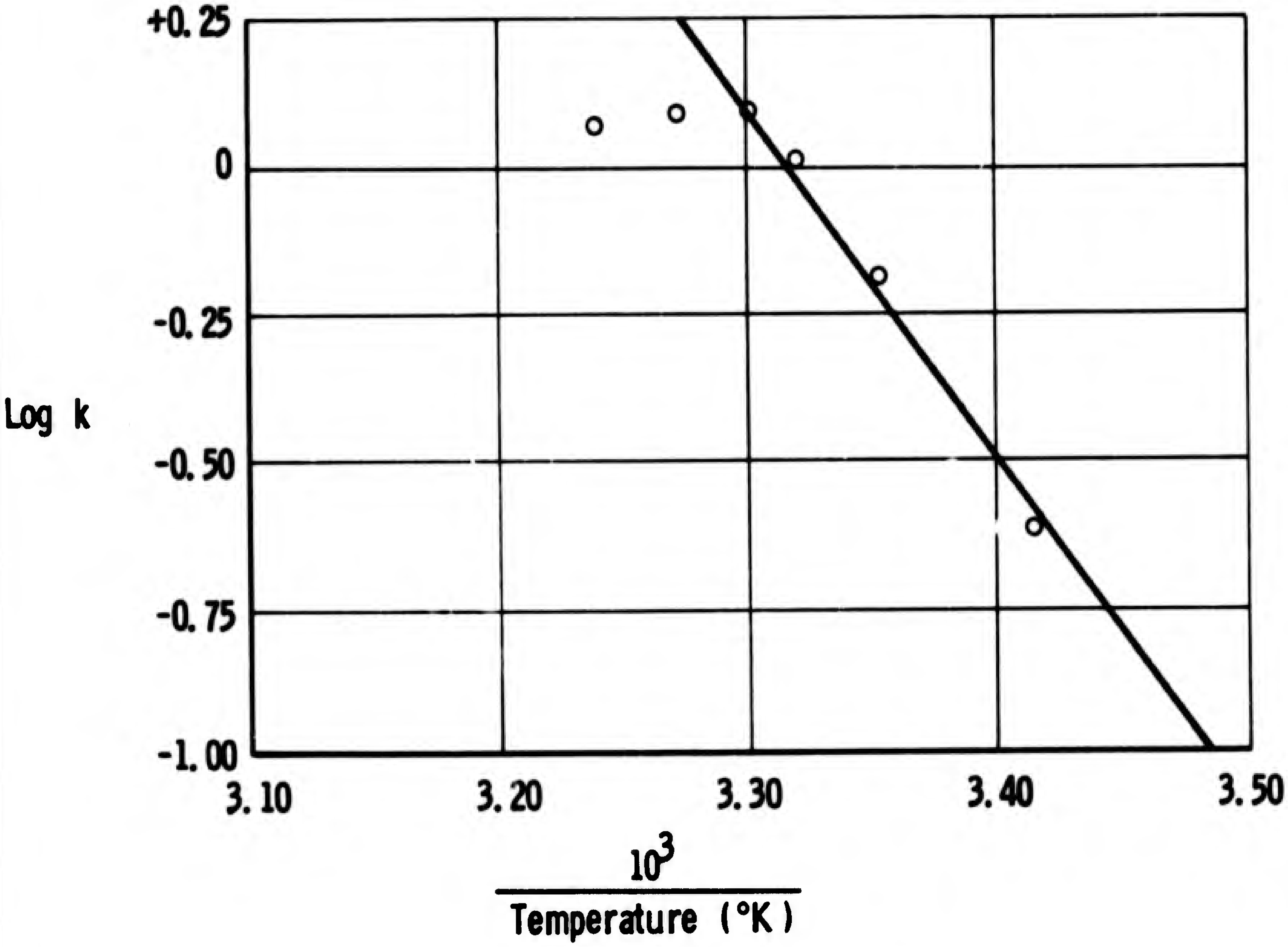
Figure 6



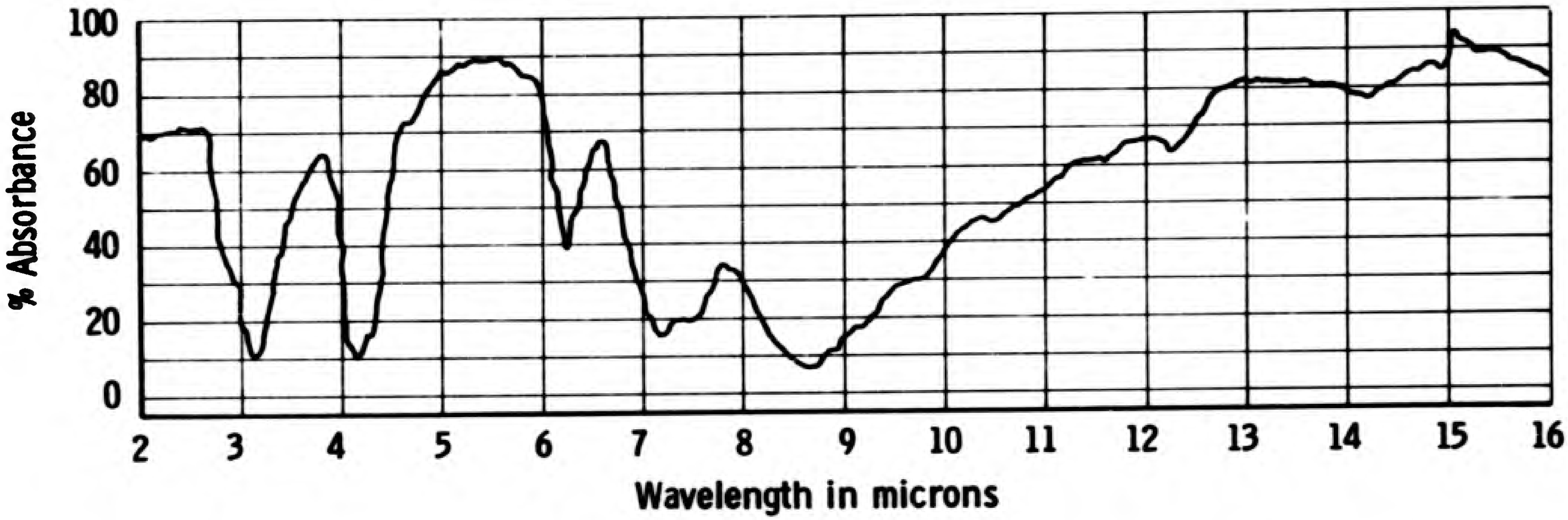
Effect of Temperature on Reaction of Pentaborane with Hydrazine



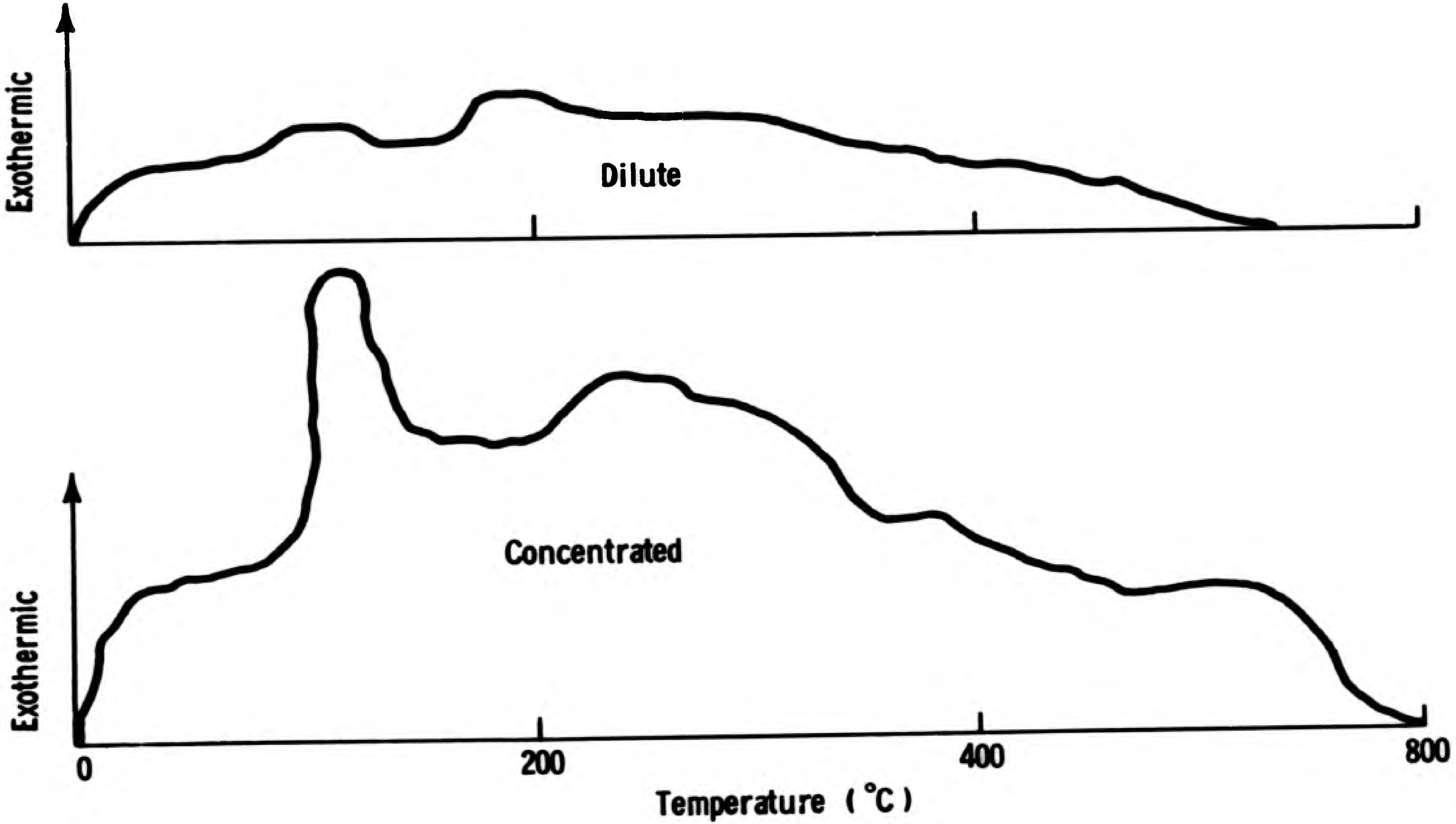
Degree of Precision of First-Order Rate Data for Pentaborane-Hydrazine Reaction



Temperature Dependence of Rate Constant for
Pentaborane-Hydrazine Reaction



Infrared Spectrum of Insoluble Product of
Pentaborane-Hydrazine Reaction



Differential Thermal Analyses of Representative Products of Pentaborane-Hydrazine Reaction

Figure 11