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RESEARCH MEMORANDUM

THE RATE OF DECOMPOSITION OF LIQUID PENTABORANE FROM 85° TO 202° C

By Glen E. McDonald

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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RESEARCH MEMORANDUM

THE RATE OF DECOMPOSITION OF LIQUID PENTABORANE FROM 85° TO 202° C

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SUMMARY

The thermal stability of liquid pentaborane was investigated at seven temperatures from 85° to 202° C and over a ratio of reaction rates of 100,000 to 1. The products of decomposition are hydrogen, a nonvolatile boron hydride, and traces of decaborane. From dilution with n-heptane, it was determined that the reaction is second-order at 128° and at 187° C. Second-order reaction-rate constants were determined for the initial reaction at each temperature investigated. A linear correlation was found for the effect of temperature on the initial rate of decomposition. From the variation of the reaction rate with temperature, an over-all activation energy of 34.2 kilocalories per mole was calculated.

By use of the following two equations, the time required to decompose a given percentage of pentaborane at other temperatures may be calculated:

$$\log k = 14.45 - \frac{7.44\times10^{3}}{T}$$

$$\log c = 2.0 + k\rho t$$

where k is a reaction constant, T is temperature in $^{\circ}$K, c is the percent of pentaborane undecomposed, ρ is density in moles per milliliter, and t is time in seconds.

INTRODUCTION

The thermal decomposition of boron hydrides was first reported by Stock (ref. 1), who found that diborane slowly dissociated at room temperature to form, among other products, decaborane and hydrogen. More recently, the kinetics of the pyrolysis of gaseous diborane were more completely investigated by Bragg, McCarty, and Norton (ref. 2) and also by Clarke and Pease (ref. 3). It was concluded that, between temperatures of 85° and 165° C, the reaction had an activation energy of approximately 26 kilocalories per mole and a 1.5 order. The pyrolysis produced a solid, high-melting boron hydride.

Since pentaborane is of interest to aircraft propulsion because of its high energy and high reactivity, a need has existed for data on its thermal stability in the liquid phase. The data would permit estimates to be made of the degree of decomposition to be expected in fuel tanks and fuel lines.

In previous preliminary work at the NACA Lewis laboratory, the liquid-phase pyrolysis of pentaborane was measured at temperatures from 165° to 202° C by measuring the percentage of solid products formed. Bulk storage of pentaborane is normally as a liquid, and operation of aircraft fuel systems is normally with a liquid fuel. Therefore, in these experiments the decomposition was measured in the liquid phase.

In the present work the measurement of the liquid-phase thermal decomposition of pentaborane has been extended to a temperature of 85° C. The order of the reaction has been determined at two temperatures (by _n_-heptane dilution), and an activation energy for the over-all reaction has been calculated.

APPARATUS AND PROCEDURE

The pentaborane was stored in a steel cylinder, removed as a liquid, and distilled from trap to trap on a conventional vacuum system before use. The pentaborane was heated in a cylindrical stainless-steel bomb, 1.6 centimeters outside diameter, 0.9 centimeter inside diameter, and 7.0 centimeters inside length. The internal volume was approximately 4 milliliters. The bomb was closed with a 1/8-inch stainless-steel Hoke valve. The bomb was heated in an aluminum block furnace which fitted closely about the bomb. The furnace was insulated and electrically heated. The temperature was measured with a thermocouple placed in a well which extended through the block to the midpoint on the bomb wall. For the experiments at 85° and 100° C, a series of bombs was placed in heated and thermostated oil baths.

The decomposition was measured by adding 2 milliliters of pentaborane to the bomb on a vacuum line, weighing, and placing in the furnace for the desired time. After removal from the furnace, the bomb was quenched in liquid nitrogen and weighed, and the volatile material was removed on a vacuum system until constant weight was obtained. Errors due to inaccuracies in weighing were not more than 5 milligrams. In those experiments where it was desired to obtain the weight of undecomposed pentaborane, the bomb was cooled to -196° C and the hydrogen was removed. The bomb was then warmed to 25° C and weighed, and the undecomposed pentaborane was removed and the bomb was reweighed. The hydrogen and boron content of the residue could be calculated. The ratio of hydrogen to boron in the residue was constant for any temperature. The pentaborane required to form a given amount of residue could be calculated.

For those experiments with diluted pentaborane, *n*-heptane that had been dried and degassed was placed in the bomb and the desired quantity of pentaborane was added. Undecomposed pentaborane, together with *n*-heptane, was removed in the manner previously described. Decaborane was determined in the nonvolatile residue by vacuum sublimation of the decaborane from the nonvolatile residue and direct weighing of the decaborane. The identity of the decaborane as well as undecomposed pentaborane was established by melting-point determination.

RESULTS AND DISCUSSION

The rate of pyrolysis of pentaborane was first measured as a function of time at the temperatures of 85°, 100°, 128°, 165°, 177°, 187°, and 202° C. The results are shown in figure 1, where the fraction of pentaborane decomposed is plotted against the time. At each temperature the rate of decomposition decreases with increasing time.

At higher temperatures, where the times for decomposition are measured in minutes, a delay occurs in the start of the reaction. If this were a true induction period, a proportionately long delay might also occur at the lower temperatures. No induction period is observed at either 128° C or lower temperatures where the reaction is measured in hours or days. Since the liquid sample and the steel vial containing the sample are at room temperature when placed in the furnace, the delay may represent the time required to heat the sample to reaction temperature.

In order to determine the time required to heat the sample, mineral oil was heated in the vial to 187° C, and the temperature was measured as a function of time. The results are shown in figure 2, where the temperature is plotted against time. The intersection of the extrapolated straight lines has a value of 2 minutes, to the nearest minute. This is also approximately the time obtained when the curves of decomposition against time are extended to zero decomposition. It is concluded that the delay represents the time required to heat the sample. In all calculations a time of 2 minutes was subtracted from the elapsed time in order to determine the reaction time. From the correspondence between the location of the solid deposit and the position of the liquid in the vial, it was determined that the reaction was in the liquid phase.

In order to determine the effect of concentration on the rate of disappearance of pentaborane, the pentaborane was diluted with *n*-heptane. The effect of *n*-heptane dilution on the rate of decomposition of pentaborane at the temperature of 187° C is shown in figure 3(a). The concentration of pentaborane is approximately 15, 40, and 100 mole percent.

The log initial rate of change of concentration of pentaborane, as calculated from the initial slope measured in figure 3(a), is plotted against log initial concentration in figure 3(b). The slope of the straight line drawn through the data points indicates an order of 1.9 at the start of the reaction.

The effect of dilution with n-heptane was also measured at 128° C. The effect on the rate of disappearance of pentaborane is shown in figure 3(c). In figure 3(d), the slope of the line obtained by plotting the log initial rate of change of concentration of pentaborane, as calculated from the initial slope measured in figure 3(c), against the log of the initial concentration indicates that the reaction has an order of 2.1 at 128° C. Since there was no significant change in order of the reaction at 128° and 187° C, it may be concluded that the initial reaction is second-order over the temperature range investigated.

Next, the data were treated in the following manner in order to calculate second-order rate constants for the decomposition of pure pentaborane. For each temperature a plot was made of the reaction time against the log of the fraction of undecomposed pentaborane. The initial portions of these plots were straight lines, as shown in figure 4. The slopes of the straight lines were calculated in units of seconds. These were converted to second-order constants by dividing by the density of pentaborane, expressed in moles per milliliter, at the reaction temperature. The density of pentaborane was obtained from unpublished calculations of R. S. Brokaw. The values for the rate constants and densities are shown in table I. The effect of temperature on the rate constant was determined by a plot of 1/T (°K) against the log k, shown in figure 5(a). A straight line may be drawn through the points obtained; this indicates a uniform effect of temperature on the reaction. From the slope of the line, an activation energy of 34.2 kilocalories per mole was calculated.

From this value and the following expression, the reaction constant may be estimated at other temperatures:

$$\log k = 14.45 - \frac{7.44\times10^3}{T} \qquad (1)$$

where k is the reaction constant (ml/(mole)(sec)), and T is the temperature (°K).

Equation (1), together with the following expression, permits estimates to be made of the time required to decompose a given percentage of pentaborane at any temperature within the range covered:

$$\log c = 2.0 + k\rho t \qquad (2)$$

where c is the percent of pentaborane undecomposed, ρ is the density (moles/ml) obtained from a plot of density (table I) against temperature, and t is time (sec). The use of these equations is limited to percentages of decomposition less than 40 percent.

The effect of temperature was also determined by calculating the initial slope of the curves in figures 1 from measurements of the slope of the tangent at zero-percent decomposition. This was expressed as a second-order constant in terms of ml/(mole)(sec). Figure 5(b) is a plot of $1/T$ ($^{\circ}K$) against log of the k which was obtained from the initial slope. The activation energy calculated from the slope of the straight line drawn through the points is 33.9 kilocalories per mole.

At all temperatures, the decomposition of pentaborane produces a light-yellow solid as a principal product. The hydrogen content of the residue varies, being less at higher temperatures. The hydrogen content of the residue varies from about 8 percent (or a B-H ratio of 1-1) at 200° C to 11 percent (or a B-H ratio of 1-1.3) at 100° C. Hydrogen is the gaseous product of the reaction. Decaborane has been isolated in a small amount from the reaction products. The amount of decaborane present is less than 2 percent of the residue. The solid reaction product shows no evidence of melting up to 250° C and has only a very low vapor pressure at room temperature. In summary, pentaborane decomposes to form principally hydrogen and an insoluble, nonvolatile, high-molecular-weight boron hydride together with traces of decaborane. No evidence was found of any other boron hydride such as diborane or tetraborane.

In order to determine whether the residue was pyrolysing at the temperature of decomposition of pentaborane, a sample of residue was heated at 187° C for 45 minutes. The change in weight was less than 1.5 percent of the weight of the residue. The pentaborane was 50 percent decomposed at a corresponding time at this temperature. Therefore, the change in weight as the result of any one run represents the change in weight due to the pentaborane decomposition.

Finally, the possible effect of the solid product on the decomposition of the pentaborane was investigated. Pentaborane was added to the solid product from a previous run, and the amount of decomposition was determined. At 202° C and a corrected time of decomposition of 8 minutes, 3.5 percent less pentaborane was decomposed in the presence of the added solid product than with pure pentaborane. Therefore, it appears that, in the initial phases of the reaction, the presence of the solid boron hydride residue has only a slight effect on the decomposition of the pentaborane.

CONCLUSIONS

The results obtained indicate that the pentaborane liquid-phase pyrolysis proceeds as a second-order reaction that has an over-all activation energy of 34.2 kilocalories per mole. The over-all reaction may be formulated as follows:

$$B_5H_9 \text{ -- traces } B_{10}H_{14} + \text{higher hydrides} + m\ H_2$$

where the higher hydrides and hydrogen are the only products produced other than traces of decaborane and where m varies from slightly more than 2 at lower temperatures to 4 at higher temperatures. The results constitute a direct measurement of pentaborane stability over the very extended range of reaction rates between the temperatures of 85° and 202° C. The linearity of the plot from which the activation energy was calculated suggests that there is no significant change in the character of the initial reaction over this temperature range.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, June 22, 1955

REFERENCES

1. Stock, Alfred: Hydrides of Boron and Silicon. Cornell Univ. Press, Ithaca (New York), 1933.

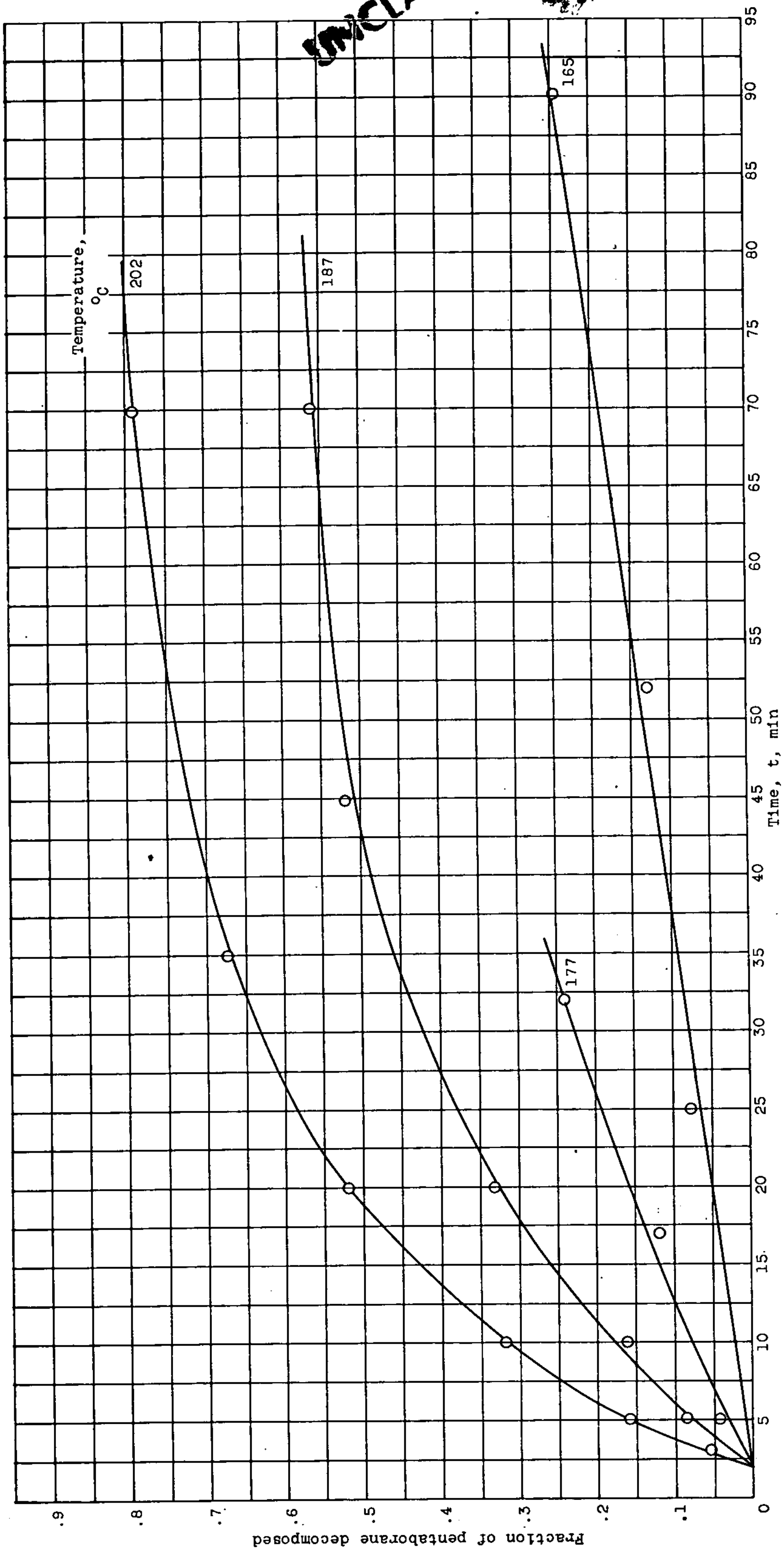
2. Bragg, John K., McCarty, Lewis V., and Norton, F. J.: Kinetics of Pyrolysis of Diborane. Jour. Am. Chem. Soc., vol. 73, no. 5, May 1951, pp. 2134-2140.

3. Clarke, Richard P., and Pease, Robert N.: A Preliminary Study of the Kinetics of the Pyrolysis of Diborane. Jour. Am. Chem. Soc., vol. 73, no. 5, May 1951, pp. 2132-2134.

TABLE I. - RATE CONSTANTS AT VARIOUS TEMPERATURES

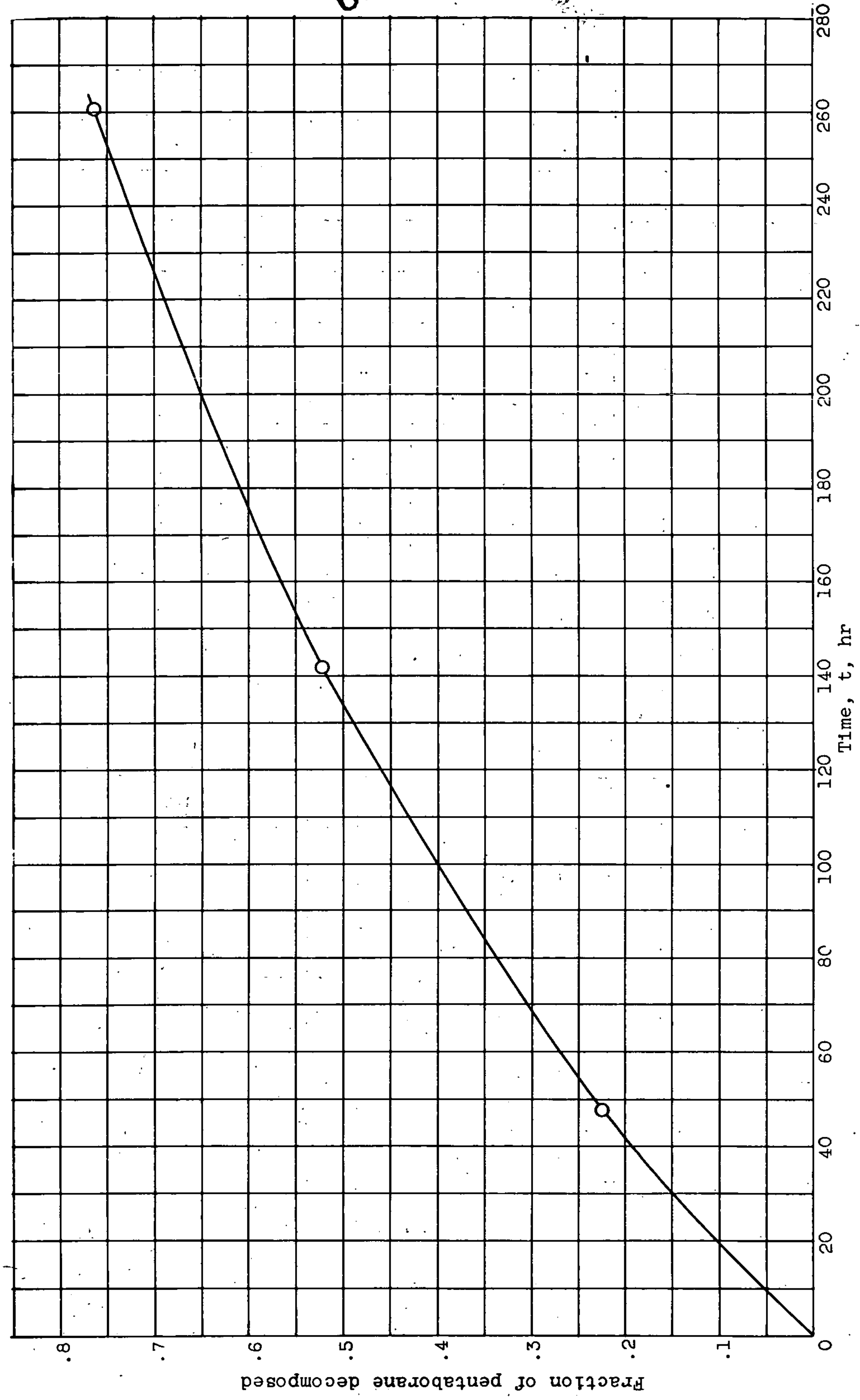
Temperature, °C	Temperature, °K	Density of pentaborane,[a] ρ, moles/ml	Reaction constant, k, ml/(mole)(sec)
85	358.2	0.00892	-5.06×10^{-7}
100	373.2	.00862	-4.09×10^{-6}
128	401.2	.00814	-7.69×10^{-5}
165	438.2	.00734	-2.775×10^{-3}
177	450.2	.00702	-8.82×10^{-3}
187	460.2	.00674	-2.402×10^{-2}
202	475.2	.00622	-6.33×10^{-2}
227	500	.00348	-----------

[a] Calculated.



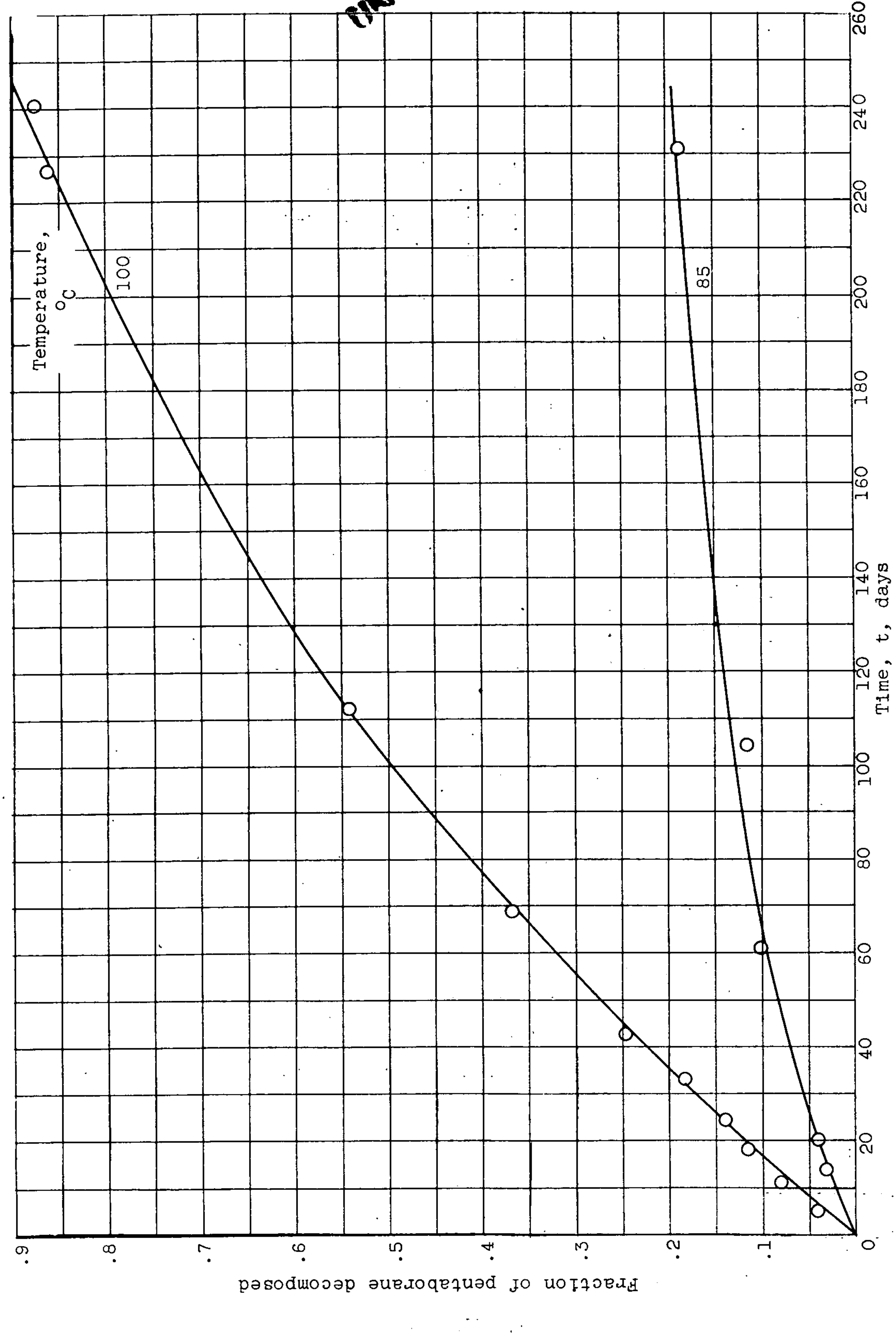
(a) Temperature, 165° to 202° C.

Figure 1. - Decomposition of pentaborane as function of time.



(b) Temperature, 128° C.

Figure 1. - Continued. Decomposition of pentaborane as function of time.



(c) Temperature, 85° and 100° C.

Figure 1. - Concluded. **Decomposition of pentaborane as function of time.**

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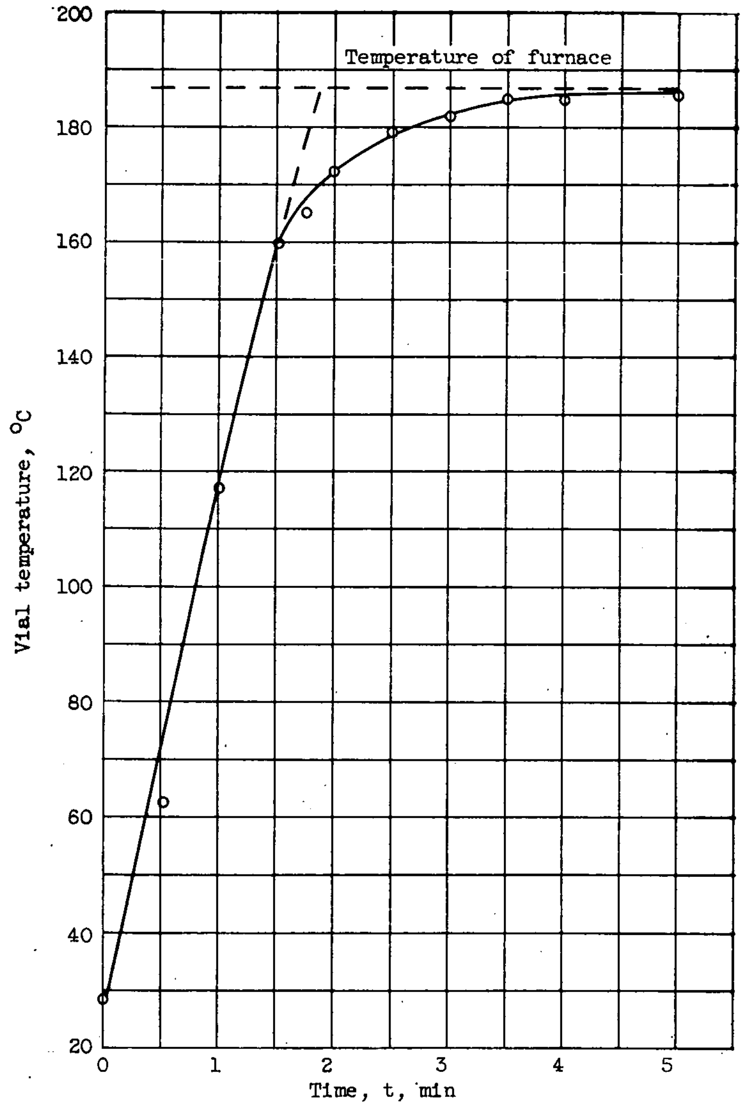
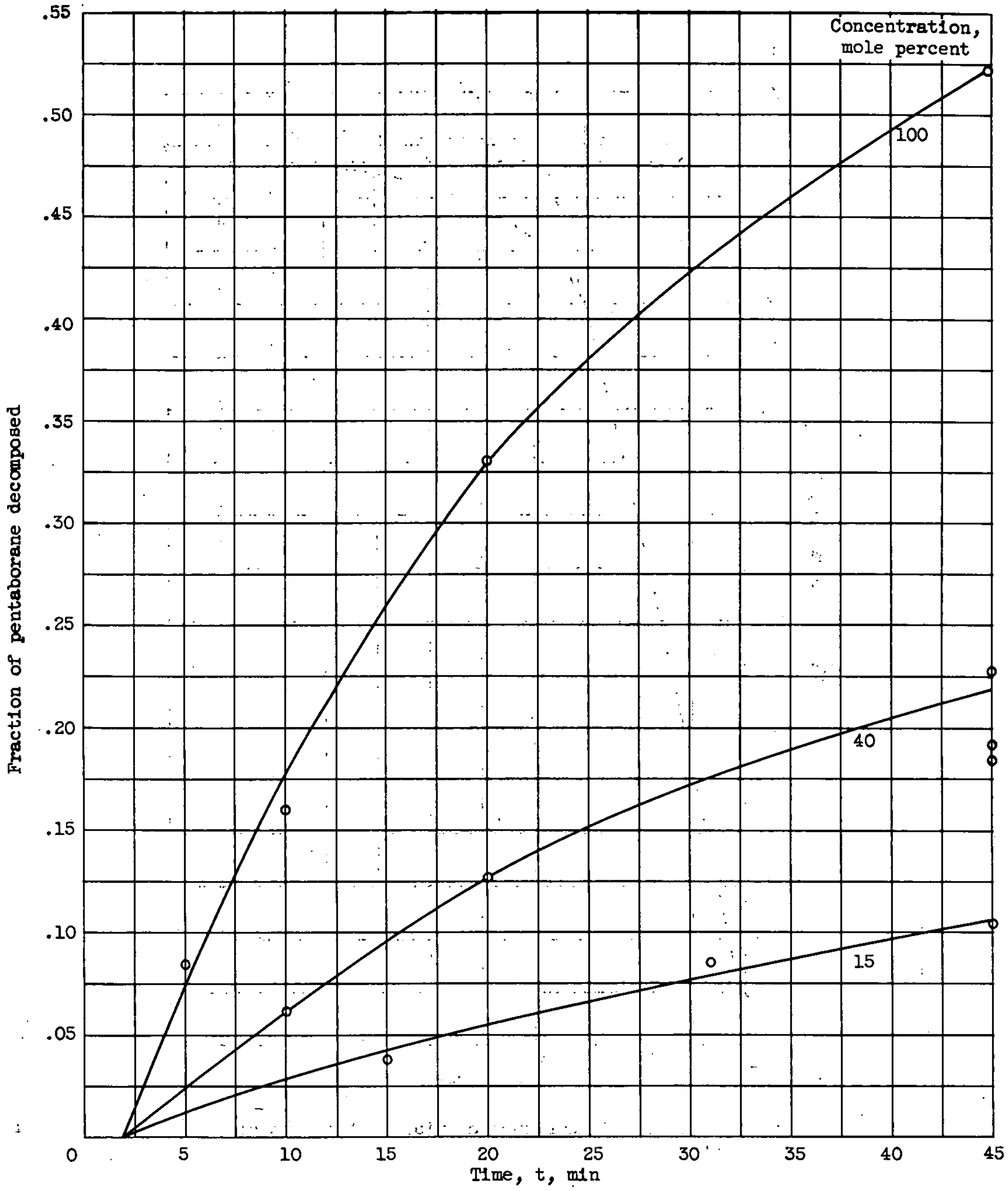
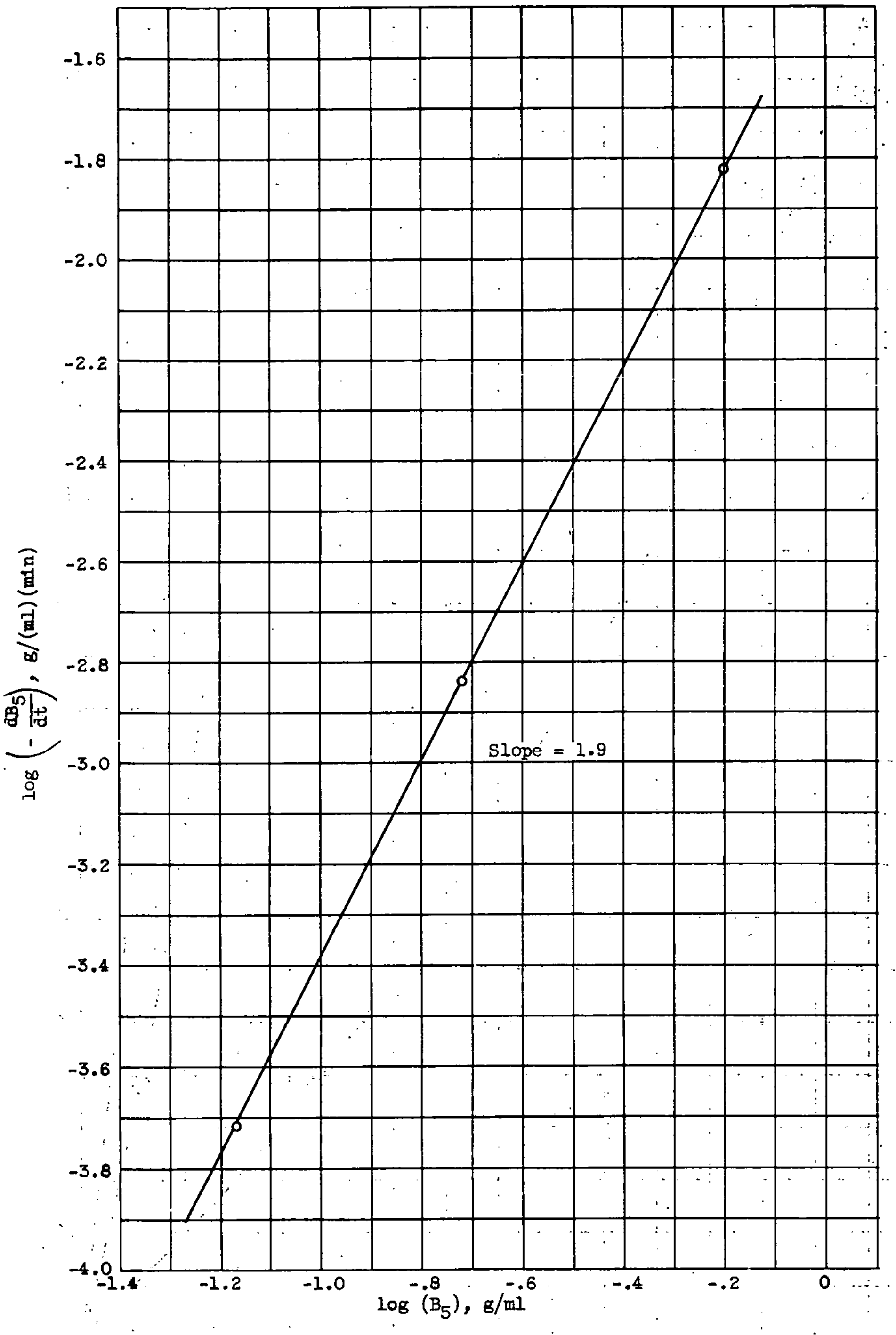


Figure 2. - Temperature of vial as function of time.



(a) Temperature, 187° C; pentaborane concentration, 15 to 100 mole percent.

Figure 3. - Effect of n-heptane dilution on pentaborane decomposition.



(b) Correlation at 187° C.

Figure 3. - Continued. Effect of n-heptane dilution on pentaborane decomposition.

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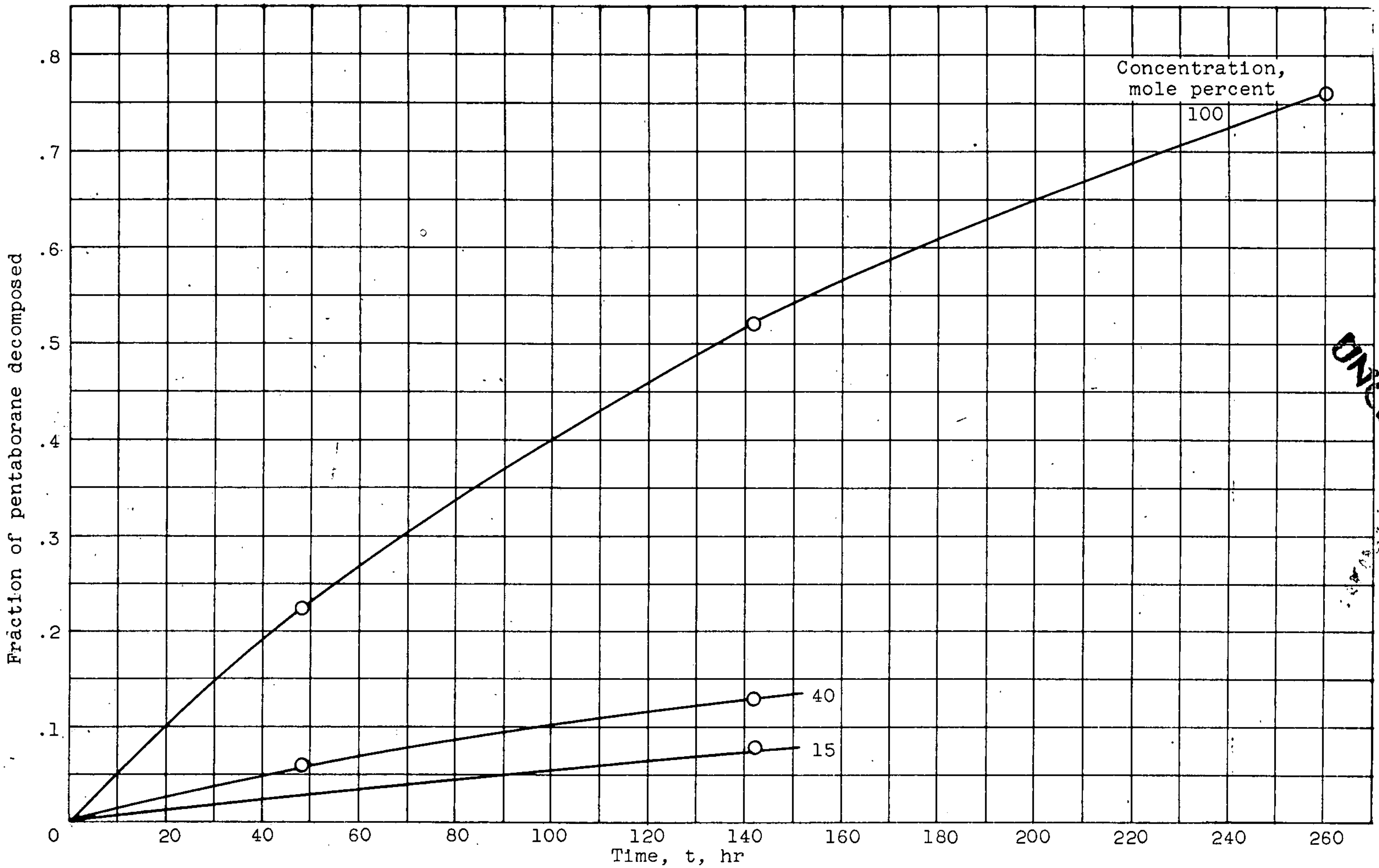
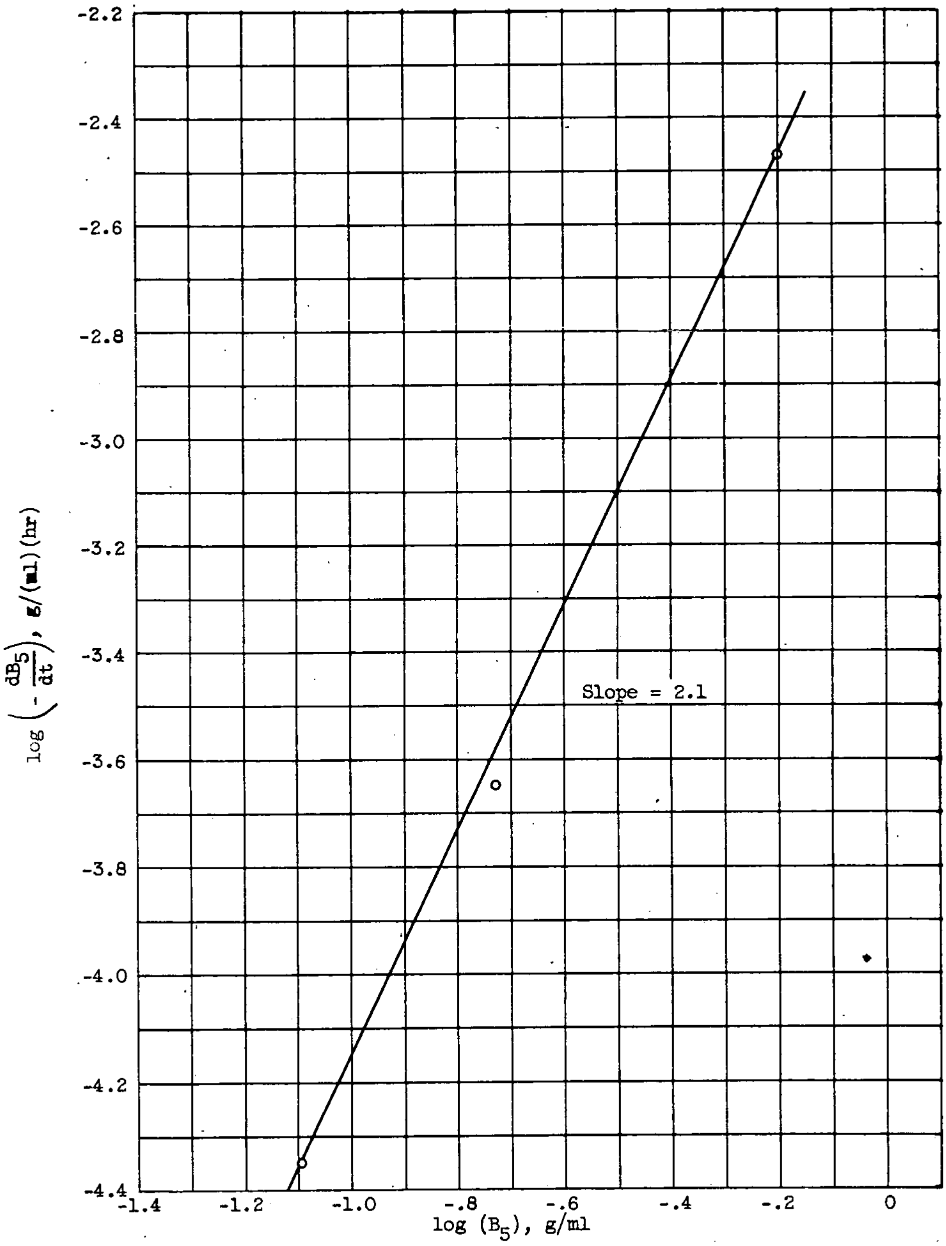


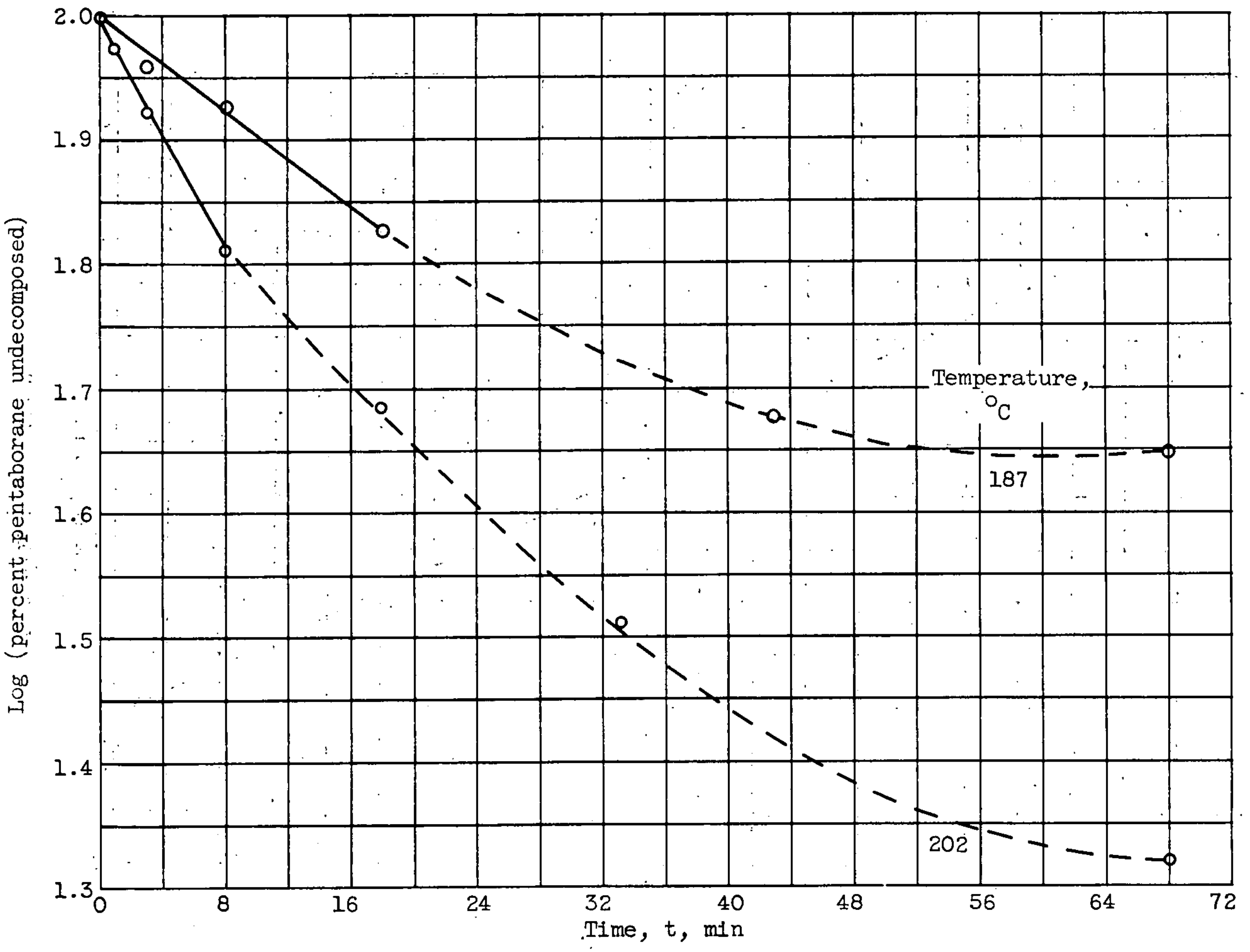
(c) Temperature, 128° C.

Figure 3. - Continued. Effect of n-heptane dilution on pentaborane decomposition.



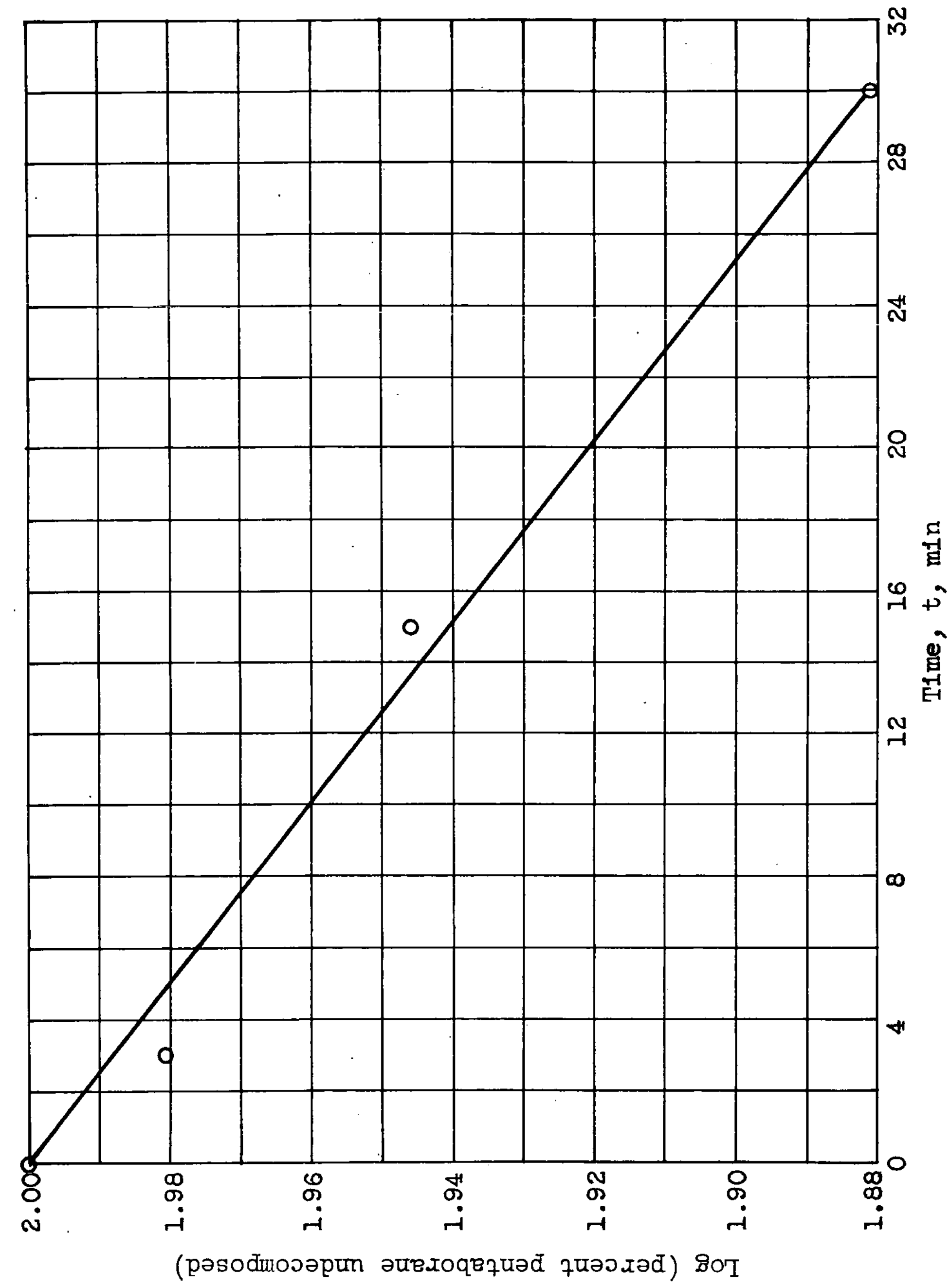
(d) Correlation at 128° C.

Figure 3. - Concluded. Effect of n-heptane dilution on pentaborane decomposition.



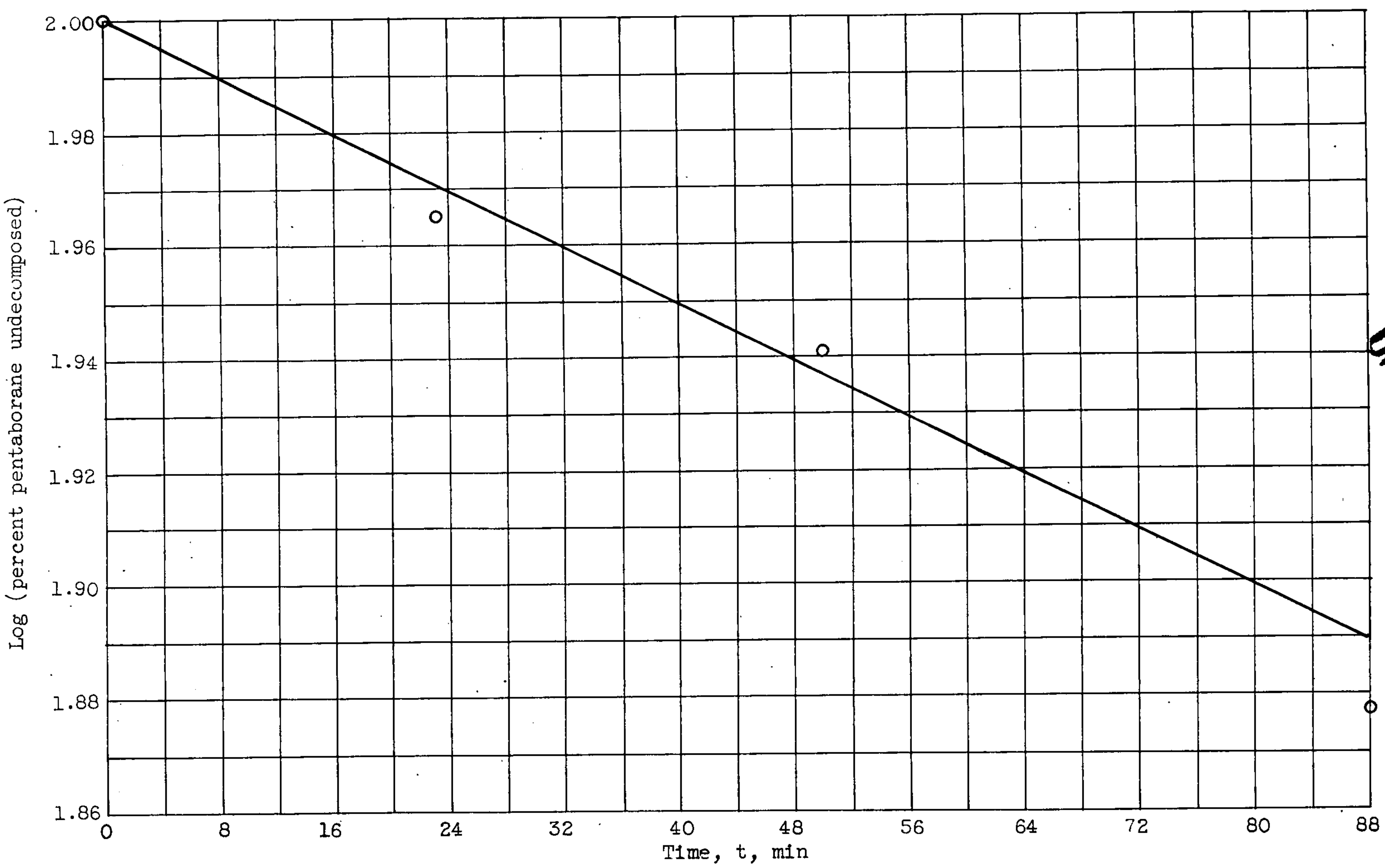
(a) Temperature, 187° and 202° C.

Figure 4. - Correlation of rate of reaction with time.



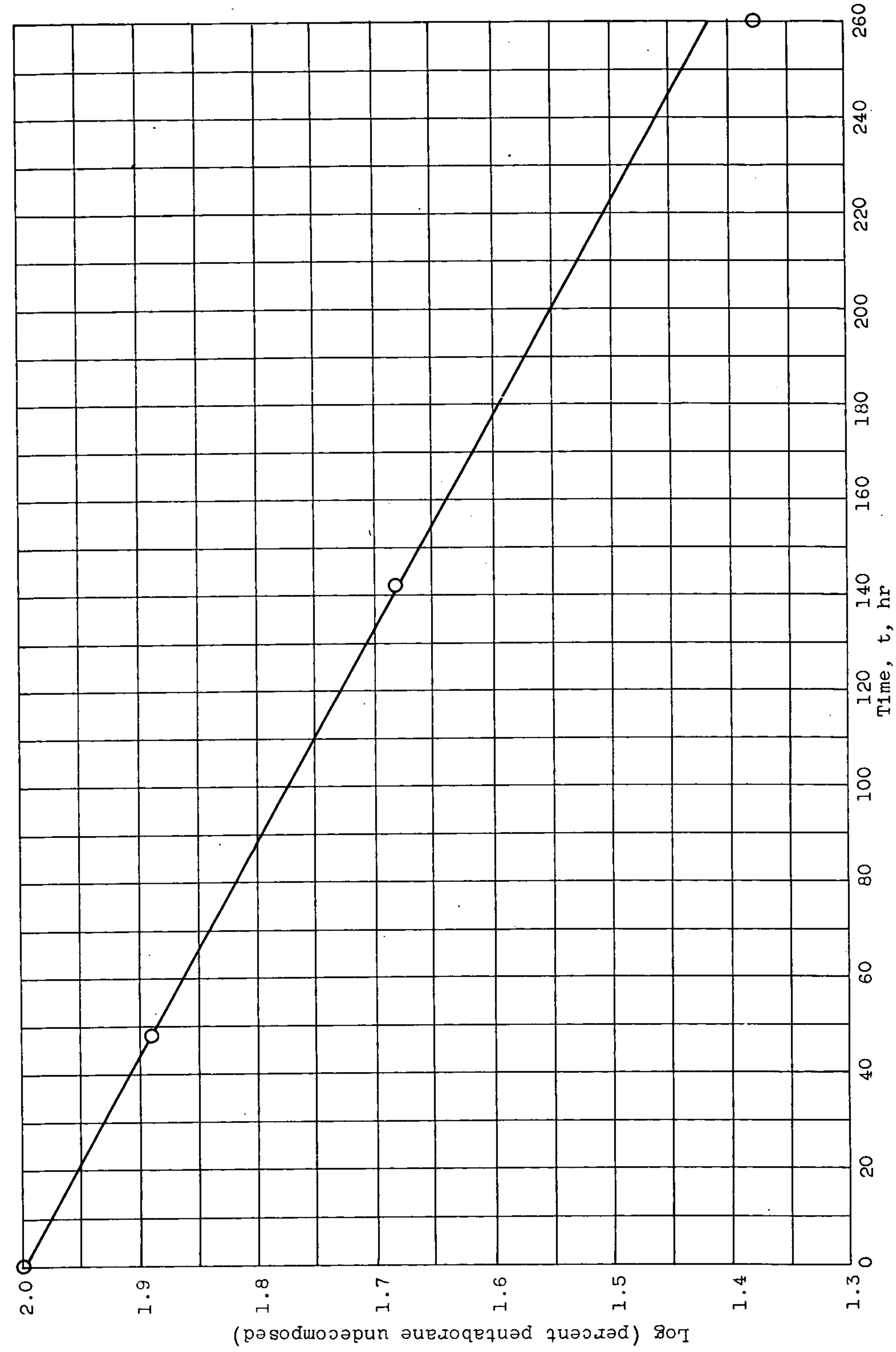
(b) Temperature, 177° C.

Figure 4. - Continued. Correlation of rate of reaction with time.



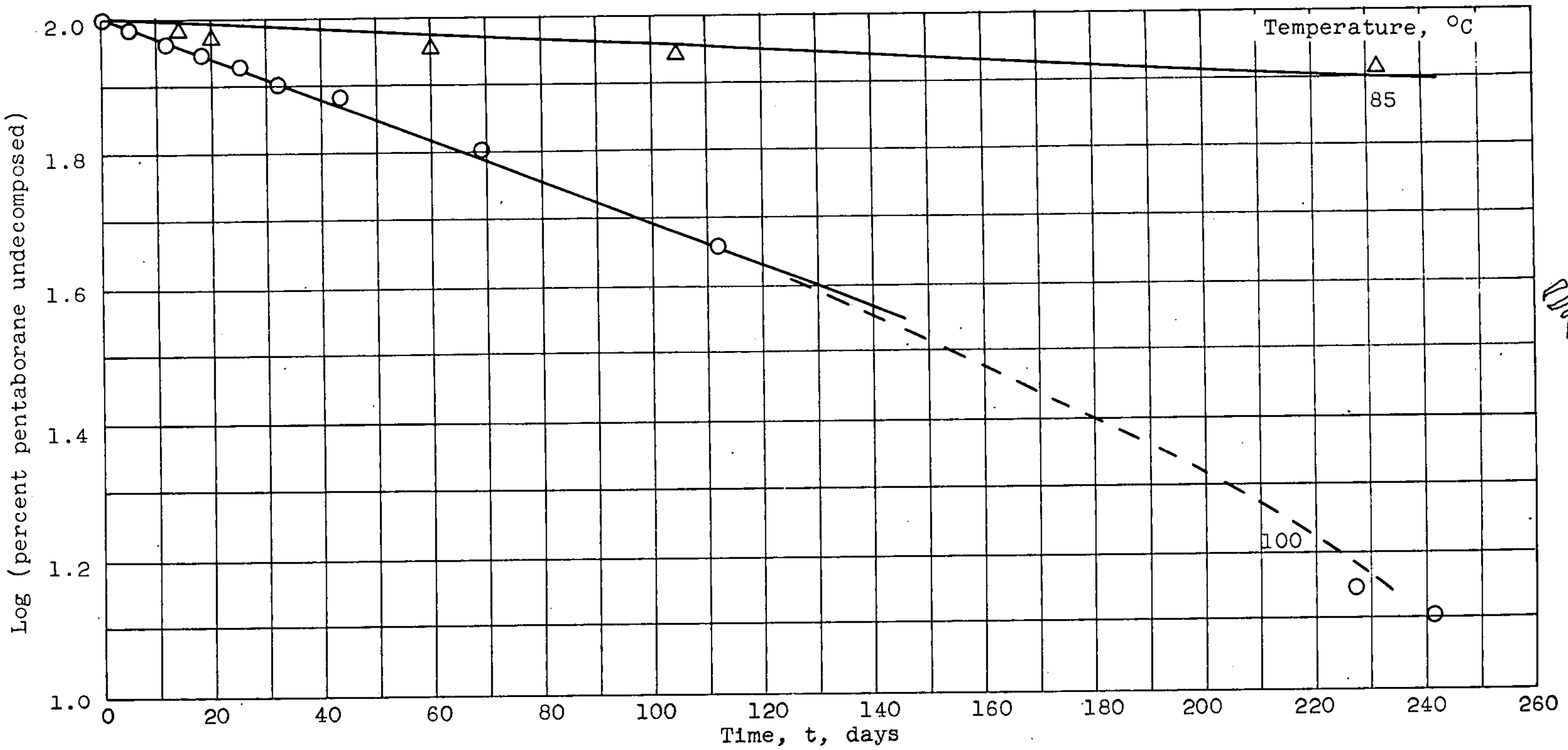
(c) Temperature, 165° C.

Figure 4. - Continued. Correlation of rate of reaction with time.



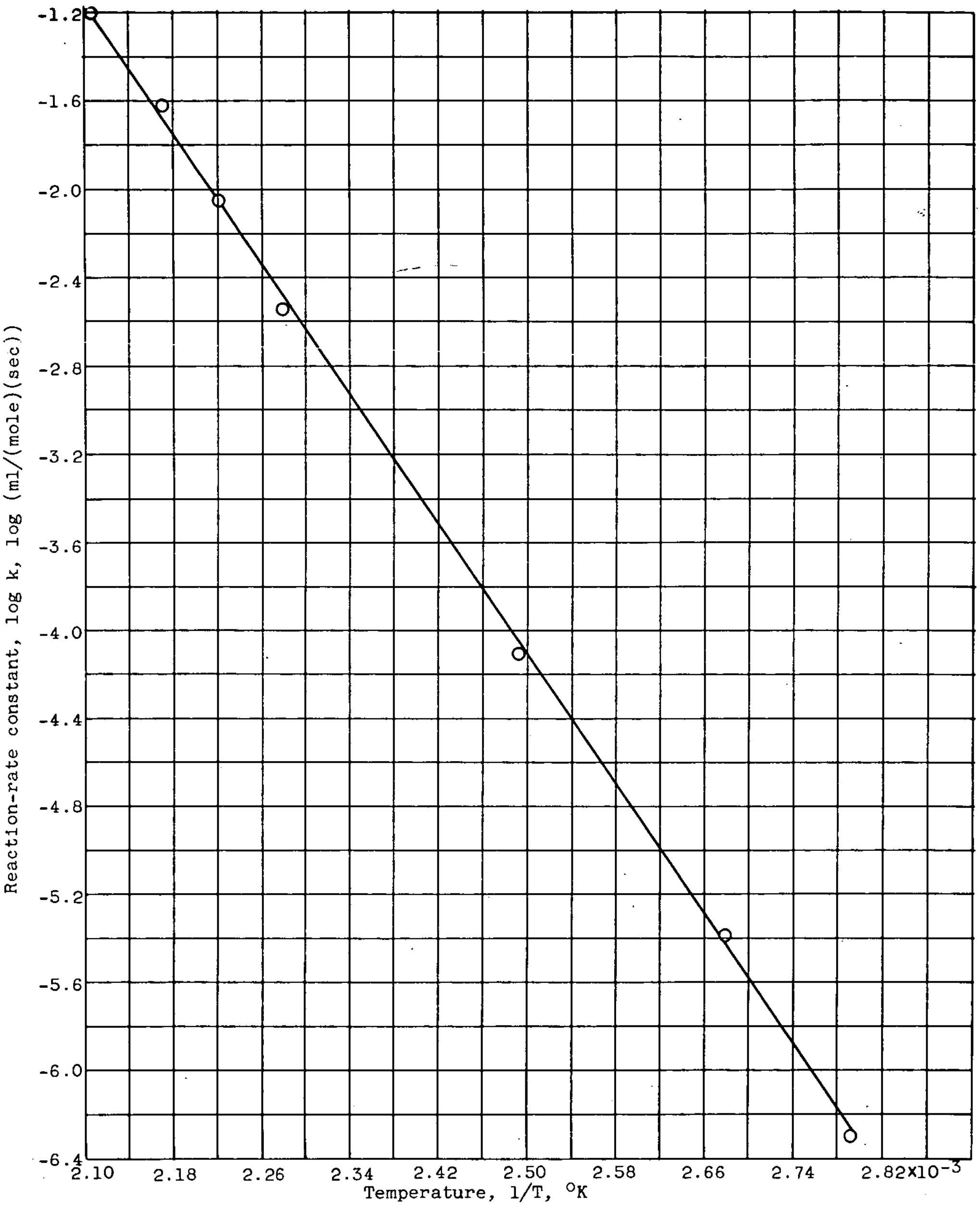
(d) Temperature, 128° C.

Figure 4. - Continued. Correlation of rate of reaction with time.



(e) Temperature, 85° and 100° C.

Figure 4. - Concluded. Correlation of rate of reaction with time.



(a) Constant obtained from slopes of figure 4.

Figure 5. - Correlation of reaction-rate constant with temperature.

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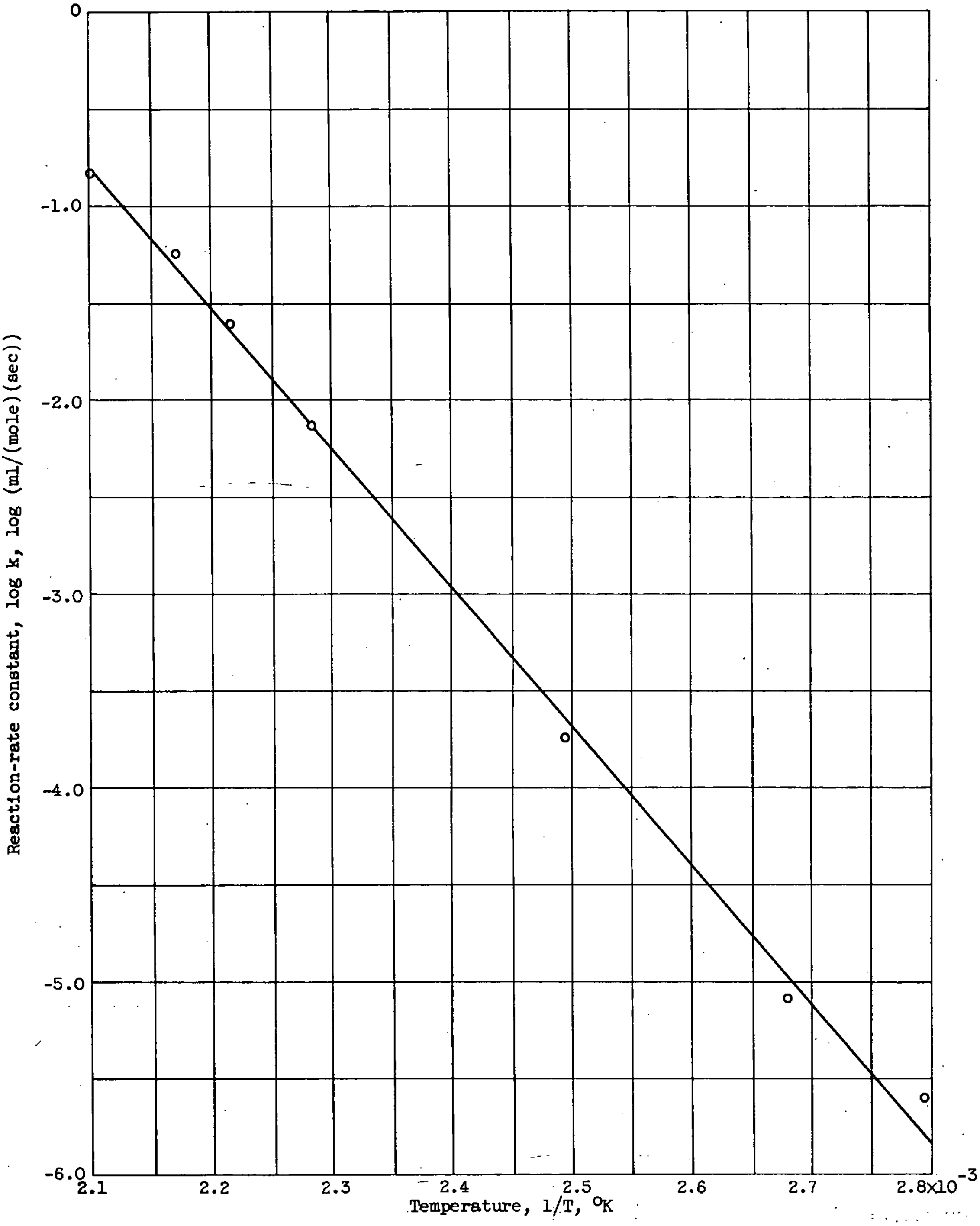

(b) Constant obtained from slopes of figure 1.

Figure 5. - Concluded. Correlation of reaction-rate constant with temperature.

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