WADC TECHNICAL REPORT 54-417

METHOD OF DETERMINING THERMAL STABILITY OF SYNTHETIC OILS

Oliver M. Ballentine

Materials Laboratory

March 1955

Project No. 3044

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the Lubricant Section, Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center. The work was accomplished under Project Number 3044 entitled "Aviation Lubricants", Task Number 73314 entitled "Lubricants", formerly RDO 613-15 entitled "Fuels, Lubricants, and Related Materials", with Oliver M. Ballentine as project engineer.

ABSTRACT

An apparatus has been developed for determining thermal stability of synthetic oils. Thermal decomposition temperatures were determined by plotting vapor pressures over a wide temperature range as $\log p$ vs. $\frac{1}{T}$. The point at which the curve deviates from a straight line relationship will be the point at which thermal decomposition occurs. The following advantages are gained through this method of determining thermal decomposition points; the utilization of small size samples (2.0 to 3.0 grams), a wide temperature of operation (up to 1500°F), a high degree of accuracy in the final results, simplicity of operation (requiring one operator), and increased rapidity of operation.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I INTRODUCTION

With the development of jet and rocket propelled aircraft and missiles, various components (including fluids and lubricants) of these high speed vehicles will be subjected to temperatures of 700°F or higher. These high temperatures stem from such aerodynamic heating as radiation from the engine, exhaust gases, high speed skin friction, etc. Since many of the aircraft components, especially the fluids and lubricants, are in close proximity to these hot areas and in many cases cannot be cycled to dissipate the heat absorbed it is necessary that fluid and lubricants be resistant to such heating. An apparatus and procedure have been developed for the determination of thermal decomposition temperatures whereby quantitative determinations can be made to measure the extent that a fluid or lubricant can be heated in the absence of oxygen before that material will break down in molecular structure thereby altering its original properties.

II GENERAL DISCUSSION ON THE METHOD OF DETERMINING THERMAL STABILITY OF SYNTHETIC OILS

A. Theoretical Determination of Thermal Decomposition Temperatures of Fluids

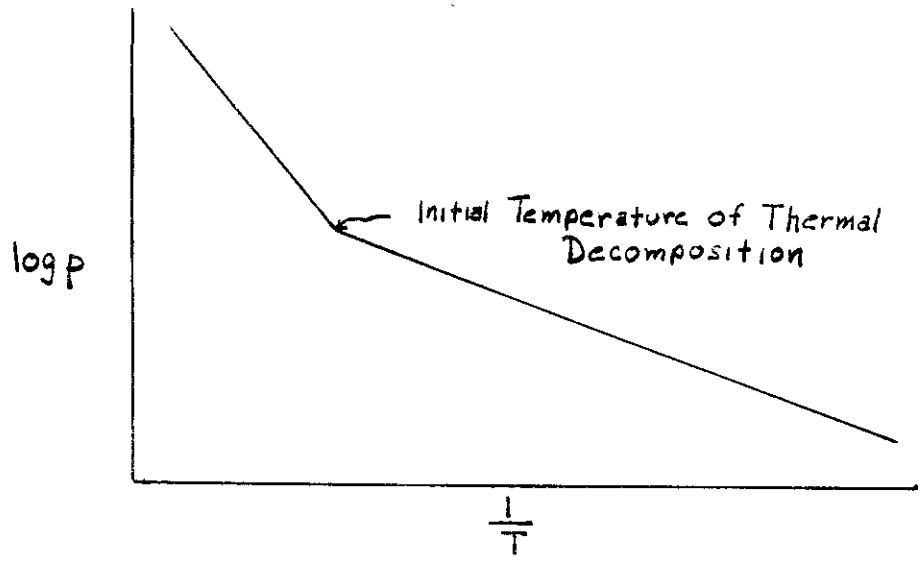
Thermal decomposition measurements are obtained by plotting vapor pressures vs temperatures as $\log p$ vs. $\frac{1}{T}$.

Vapor pressures of all fluids will increase proportionately with increasing temperatures. The Clapeyron–Clausius equation best shows the relationship between vapor pressure changes with temperature. By changing this equation to a more workable form and integrating, the Clapeyron–Clausius equation may be written as

$$\log p = \frac{a}{T} + c.$$

It is now readily seen that the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature should result in a straight line curve as shown in Figure 1.

When thermal decomposition occurs the long chain length and heavy molecular weight molecules are broken down to considerably greater numbers of molecules having a higher volatility. This decomposition will result in a sharp increase of vapor pressure, since pressure is directly related to the number of molecules present. Therefore, thermal decomposition occurs at a point in which the curve deviates from a straight line relationship. (See the figure below.) This initial temperature of decomposition is shown in Figure 1 as approximately 550°F for di–(2–ethylhexyl)sebacate.



B. Experimental Equipment

The equipment used to determine thermal stability of fluids consists essentially of a high temperature metal bath, various pressure measuring gages, a glass isoteniscope and a high vacuum system. A schematic diagram of the equipment is shown in Figure 5. A photograph of the same equipment is shown in Figure 6.

1. High Temperature Metal Furnace

A high temperature furnace replaced the silicone oil bath used in the earlier work so that higher temperature region studies could be employed. This furnace is shown isometrically in Figure 2.

This furnace, red brass composition, (aluminum, if available, would be more desirable) was fabricated to determine thermal decompositions of high boiling synthetic oils. The furnace was heated by four glow bars (carbon rods) 0.037 Ω each. Two of the glow bars were connected in series and the other two in parallel so that a 115V source would be sufficient in providing current to heat the metal block to 1500°F. To eliminate serious heat loss the metal block was insulated with aluminum foil and asbestos and finally covered with ceramic fire brick. The heating rate of the furnace, i.e. °C/min, was regulated by a 115V, 20 amp. variable transformer. It was necessary to nullify the temperature gradient loss by variac adjustment so that a constant rate of heating could be maintained. This permitted time to be a constant factor in the thermal decomposition determinations. A calibration curve to maintain a constant heating rate is given in Figure 3.

The glass apparatus (modified isoteniscope) in which vapor pressure changes are observed was lowered into the center of the furnace through a cavity slightly larger than the glass apparatus. The manometer portion of

the modified isoteniscope can be observed through a double plate of Vycar glass. A thermo-regulator was connected to the furnace so that a constant temperature if desired could be maintained.

2. Modified Isoteniscope

The glass **isoteniscope** shown schematically in Figure 4 is an apparatus used in the measurement of vapor pressure. This instrument differs from the accepted, standard isoteniscope in the following ways:

A low vacuum type stopcock was added to the isoteniscope as shown in Figure 4. This allowed the fluid filled instrument to be dismanteled from the vacuum system to be placed in the furnace without destroying the vacuum within the isoteniscope. In the earlier method the evacuated isoteniscope was rotated from the horizontal to the verical position and the bath furnace was raised to engulf the apparatus. Cleaning the isoteniscope and charging it with the fluid to be tested is more convenient and efficient with the stopcock arrangement. Cleaning the isoteniscope is conducted in the following manner:

a. Open stopcock and evacuate isoteniscope.

b. Close stopcock and pour in open end a suitable acid or solvent to satisfactorily clean the apparatus.

c. Open stopcock. The difference in pressure will force the cleaning fluid over into bulb C, Figure 4. With the earlier isoteniscope it was quite difficult to get fluid into this bulb.

d. The cleaning fluid is easily removed by again evacuating the isoteniscope.

Charging the modified isoteniscope with test fluid is conducted in a similar manner. Here the proper quantity of fluid (as indicated by marks on the tube between the stopcock and ball connector, Figure 4) is flushed over into bulb C. The charged isoteniscope is connected, external to the furnace, to the vacuum system by a ball connector and subjected to evacuation for a period sufficient to reduce the pressure to at least 0.05 mm of Hg. With the earlier isoteniscope, evacuation had to take place while the liquid was retained in bulb A thereby restricting somewhat the efficiency of evacuation. To remove any dissolve gases in the liquid, the liquid is heated with a bunsen burner for several minutes and allowed to reflux over into bulb A. The isoteniscope's stopcock is then closed and the evacuated isoteniscope is lowered into the furnace and connected again to the vacuum system. The liquid retained in bulb A can now be balanced in the legs of

the manometer F in accordance with the directions given in the Experimental Procedure Section (C). It may be noted in Figure 4 that the manometer leg connected to bulb C is shorter than the manometer leg connected to bulb A. This permits breaking of the fluid as it is slowly forced from bulb A to C so that a sufficient quantity will be left in manometer F for vapor pressure indications.

3. Vacuum System Employed

The vacuum system was divided into two separate sections to enable different pressures to be maintained at one time in the system. Thus it was possible to bleed into the manifold (Figure 5) a small amount of nitrogen gas through a slight pressure differential. This was imperative, especially at the start of a run, since it was difficult to keep the liquid, trapped in capillary F, Figure 4, from being forced over into bulb C, Figure 4, when pressure was introduced into a high vacuum system.

The vacuum system, shown in Figure 5, was fabricated out of 20 mm heavy wall glass tubing and was designed to have a minimum number of stopcocks and other probable sources of leaks. The two stopcocks, #1 and #2, separating the high and low pressure sections I and II are mercury seal high vacuum stopcocks. These stopcocks have a 15.0 mm bore to insure a good evacuation technique. Stopcock #2 governs the flow of nitrogen gas from the high I to the low II pressure side. Stopcock #3 was connected to the fore pump. Stopcock #4 was used as a nitrogen gas bleed to the system. A two liter surge tank was used to decrease the sensitivity of pressure changes and to minimize the effect of small leaks.

Due to the accuracy required for obtaining vapor pressure data, two types of pressure measuring gages were employed, i.e. a McLeod tipping gage for pressures up to 20 mm of Hg. and an open end manometer for pressure changes from 20 mm Hg. to atmospheric pressure.

C. Experimental Procedure for Determining Thermal Decomposition Temperatures

1. Filling and Cleaning the Isoteniscope

This procedure is given in section under B under 2. Modified Isoteniscope.

2. Method of Determination

a. Attach fluid filled isoteniscope to the vacuum system by ball connectors (C in Figure 5). The isoteniscope should be in a horizontal position at this point, external to the furnace, so that the manometer ends of F (Figure 4) at D and B are open to evacuation. (Use a high vacuum stopcock grease on the ball connectors and the stopcock in the modified isoteniscope that

is readily soluble in a suitable solvent since some of the grease may be swept into the isoteniscope during the cleaning process. All of the stopcocks in the vacuum system Figure 5 should be greased frequently to insure non leaking and freezing of these components.

b. Open stopcocks #1, 2, 3 and the isoteniscope's stopcock and evacuate the entire system to the lowest possible pressure (maximum 0.05 mm Hg.). Record this pressure obtained from the tipping McLeod Gage as the absolute system pressure (Pa) and the reading obtained from the open end manometer, A Figure 5, as the initial starting pressure (Pm).

c. Heat bulb C of the isoteniscope several minutes with a bunsen burner to remove any dissolved gases. Most of the fluid will be refluxed over into the manometer and bulb A of the isoteniscope.

d. Close the stopcock of the isoteniscope.

e. Close stopcock #3 to the vacuum fore pump and vent the system by opening stopcock #4.

f. Remove the evacuated isoteniscope from the vacuum system and replace it in the furnace.

g. Connect the isoteniscope again to the vacuum system making sure the thermocouple has been placed in the indentation of bulb C.

h. Evacuate the system again to a low pressure (i.e. 0.05 mm Hg.) by opening stopcocks #1, 2 and 3 and closing #4.

i. Heat the furnace until the liquid in the isoteniscope's manometer begins to reflux at the low system pressure. Allow the furnace to come to constant temperature by setting the thermo-regulator at this refluxing temperature.

j. Reflux for several minutes.

k. Close stopcocks #1, 2 and 3.

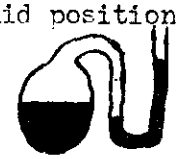
l. Open stopcock #4 to nitrogen and bleed in slowly so that a small amount of nitrogen gas (several millimeters) enters Pressure Side I, Figure 5. This is determined by observing the mercury levels of manometers A and B.

m. Close stopcock #4 and open stopcock #2 until refluxing ceases and the liquid in the manometer F legs is equal.

Record this pressure at the maintained constant temperature. When the pressures and temperature after two successive periods of refluxing agree, the gas has been expelled and the isoteniscope is ready for measurement of thermal stability.

n. Set the variac to control the rate at which the furnace is heated. (See Figure 3 for the correct setting of the variac to give a constant heating rate at different temperatures.) This is necessary to eliminate time as a variable in these studies.

o. As the temperature is increased at a constant rate the vapor pressure of the fluid will increase. This is noted by a change in the liquid position in manometer F, Figure 4.



p. Pass in nitrogen from Pressure #1 side through stopcock #2 until the levels are again made equal.

q. Continue to bleed in nitrogen (through reduced pressures) into the system to maintain equal liquid levels in the legs of the capillary manometer F.

r. At predetermined intervals, i.e. every 5°C, make the levels equal and record both the temperature and pressure.

s. Follow this procedure until atmospheric pressure is reached or until the pressure changes too rapidly to be accurately followed.

t. In the course of operation, nitrogen will have to be replenished in Pressure #1 side of the system. This can be done quite easily by replenishing nitrogen between temperature-pressure readings by opening stopcock #4 to the nitrogen bleed.

u. Plot the temperature and pressure obtained experimentally as the log of the pressure against the reciprocal of the absolute temperature.

i.e. $\log p$ vs. $\frac{1}{T}$

v. The point in which the curve deviates from a straight line curve will be the point at which thermal decomposition occurs.

III CONCLUSIONS

The thermal stability apparatus described in this report can be considered standard for determining within several degrees the temperature at which fluids decompose under the prime variable of temperature if time is held constant. This will aid in the screening and separation of those materials that cannot be used as high temperature fluids, thereby eliminating further costly studies.

The developed apparatus **incorporates such advantages as:**

1. Utilization of small size samples (2.0 to 3.0 grams).

2. Operation of the apparatus at a pressure as low as 200μ to remove all significant presence of air.

3. Accuracy in final results (approximately ±5°F reproducibility).

4. Simplicity of operation.

5. More rapid testing.

This equipment can also be employed in investigating the basic factors influencing thermal instability such as chemical bond strengths. This information would be of guidance to the organic research chemists in the synthesis of future high temperature fluids and lubricants.

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TABLE I

TEMPERATURE–VAPOR PRESSURE DATA OF
DI–(2–ETHYLHEXYL)SEBACATE

Temperature (°F)	Vapor Pressure (mm)
425	1.1
435	1.4
445	1.7
455	2.5
465	3.0
475	4.0
485	5.1
495	6.9
505	8.3
515	11.1
525	15.0
535	19.2
545	25.0
555	34.0
565	45.0
575	
585	87.0
595	117.0
605	164.0
615	227.0
625	311.0
635	429.0

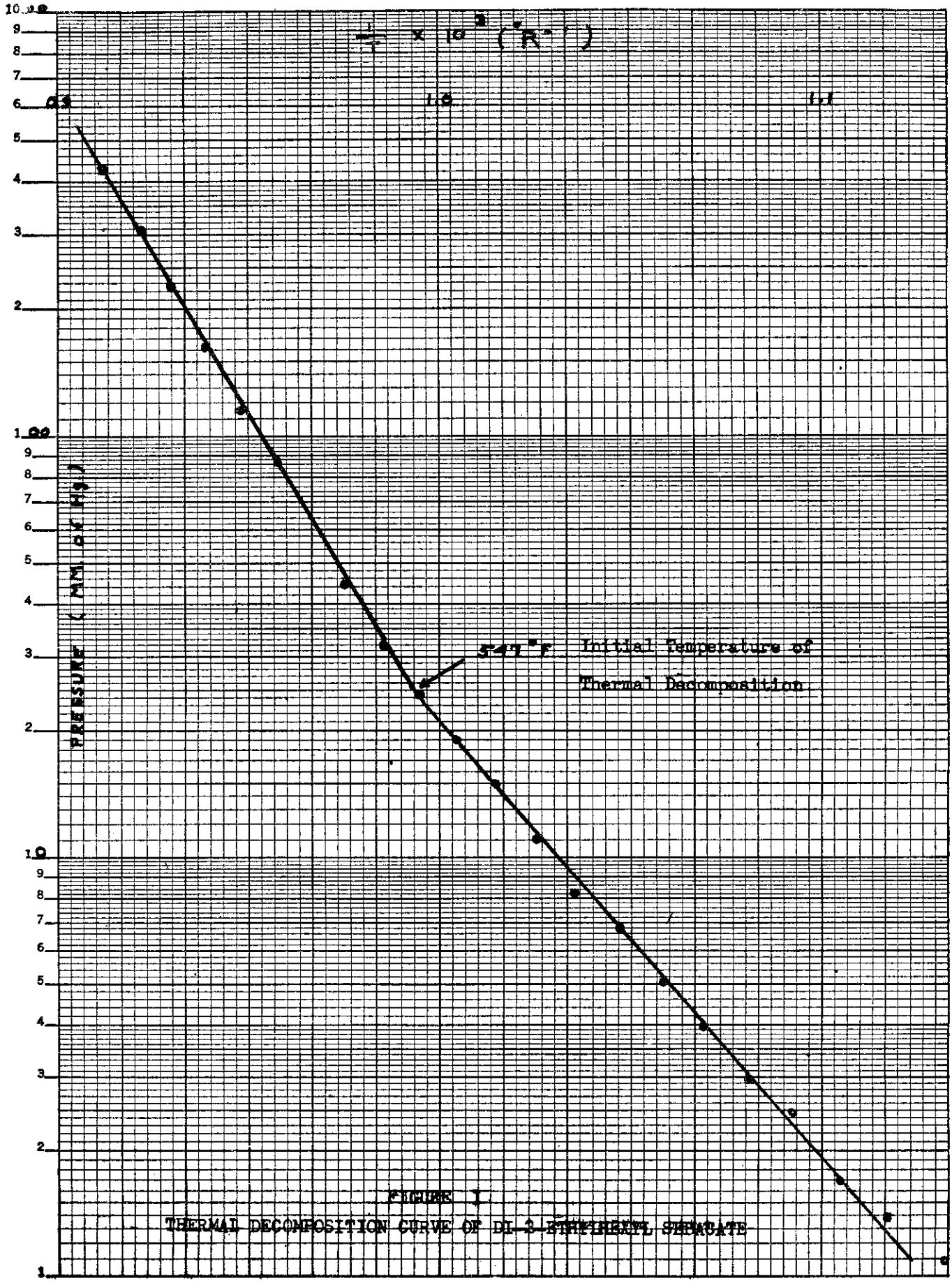

FIGURE 1

THERMAL DECOMPOSITION CURVE OF DI-2-ETHYLHEXYL SEBACATE

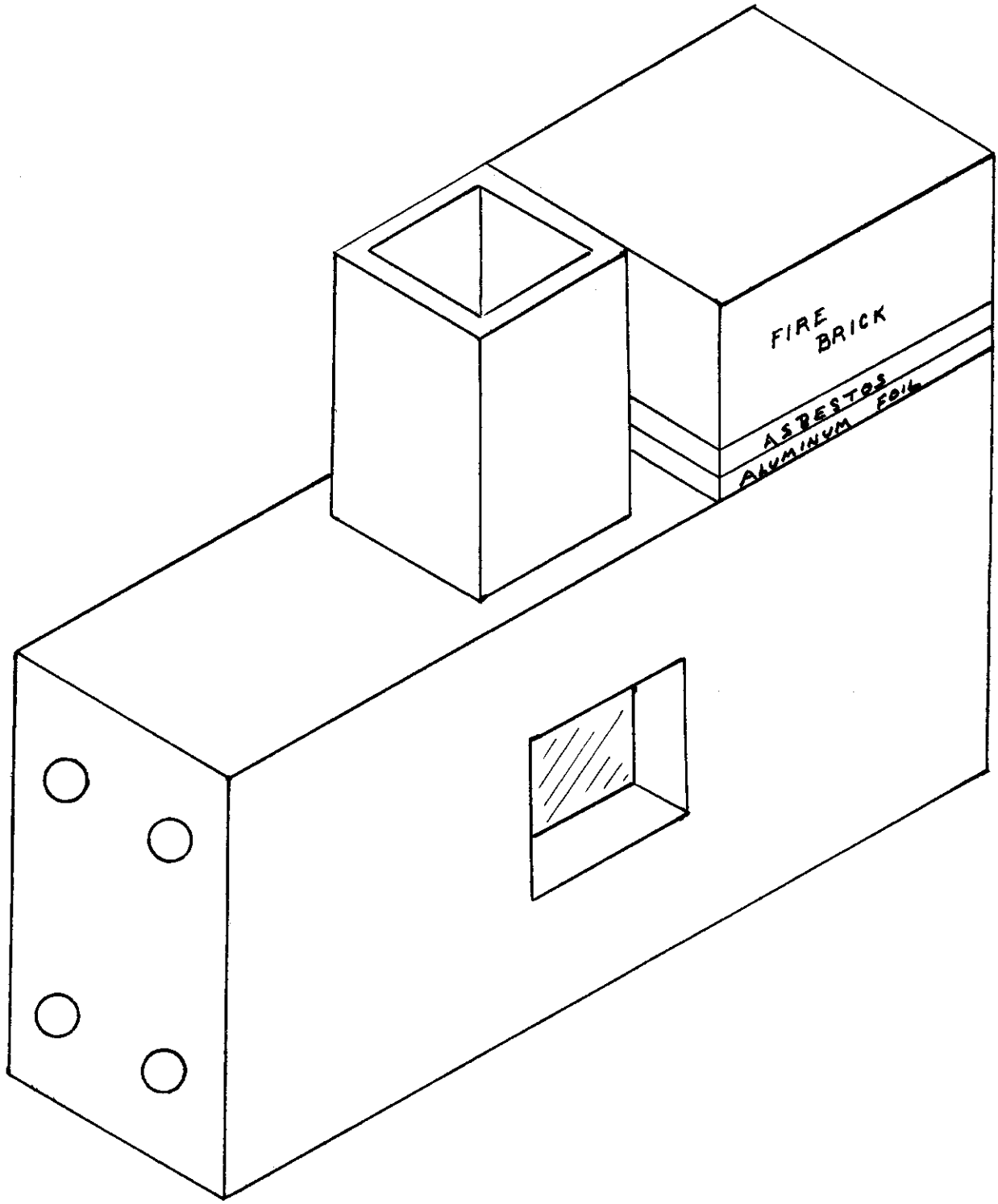

FIGURE 2

HIGH TEMPERATURE FURNACE

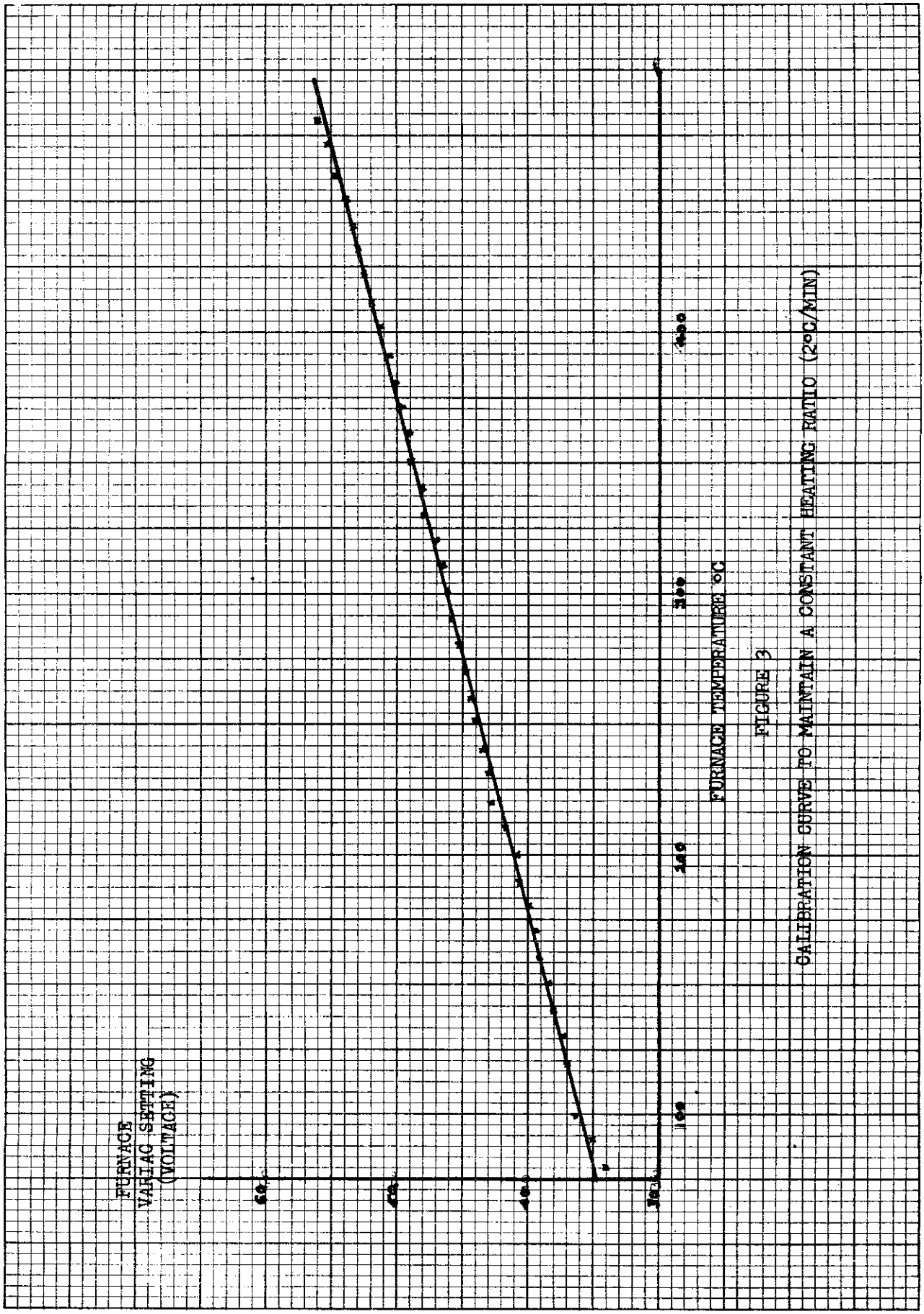

FIGURE 3

CALIBRATION CURVE TO MAINTAIN A CONSTANT HEATING RATIO (20C/MIN)

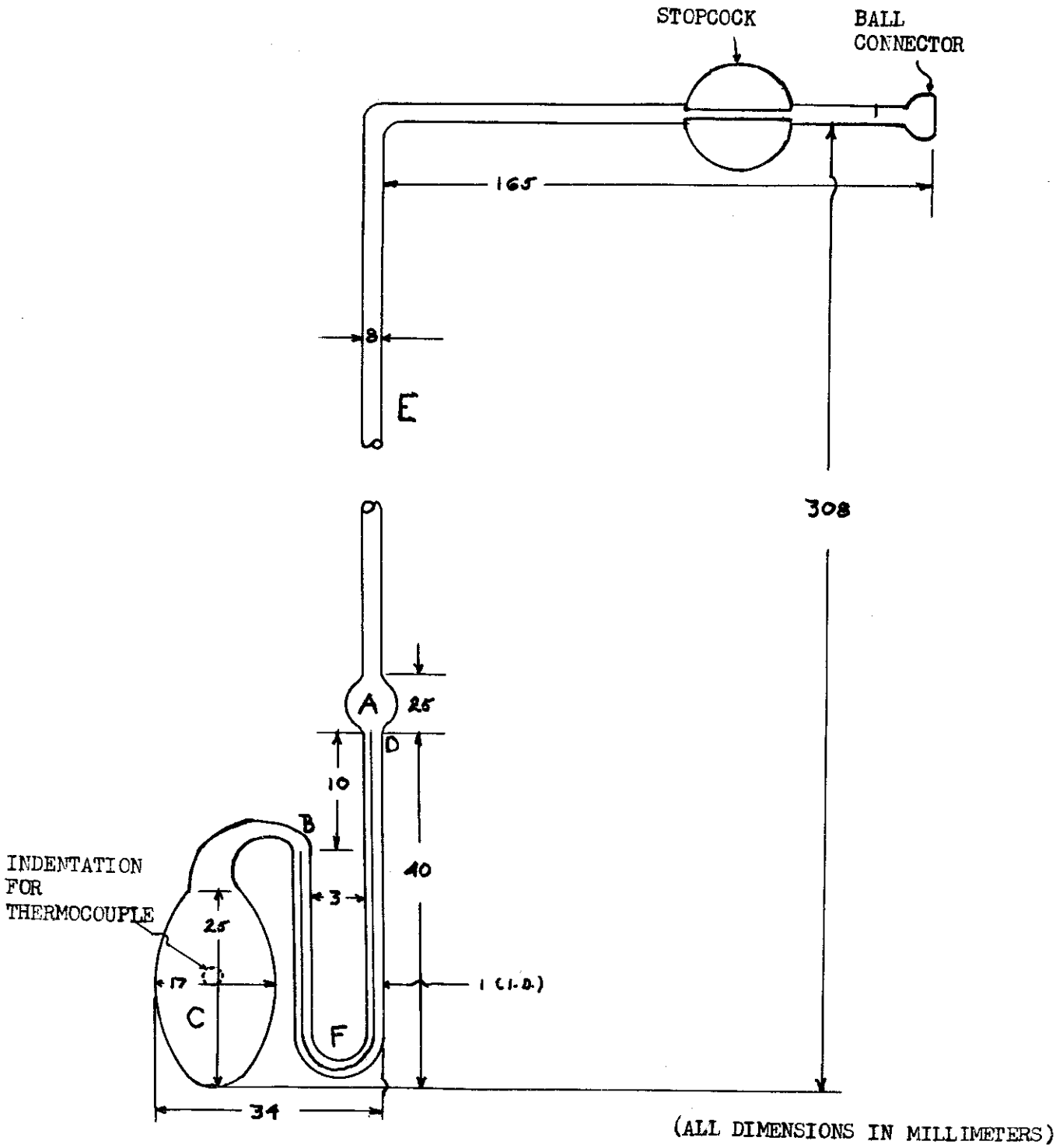

FIGURE 4

MODIFIED ISOTENISCOPE

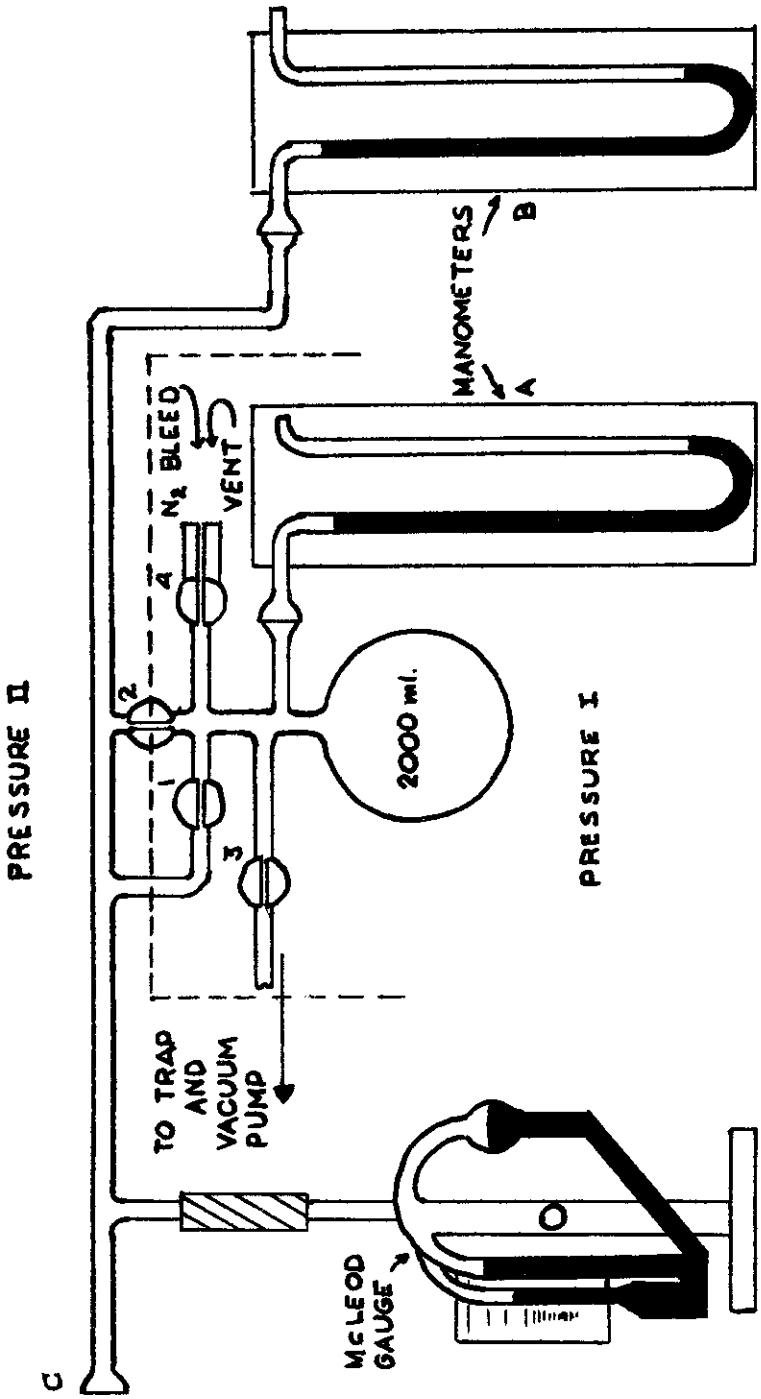

FIGURE 5
VACUUM SYSTEM

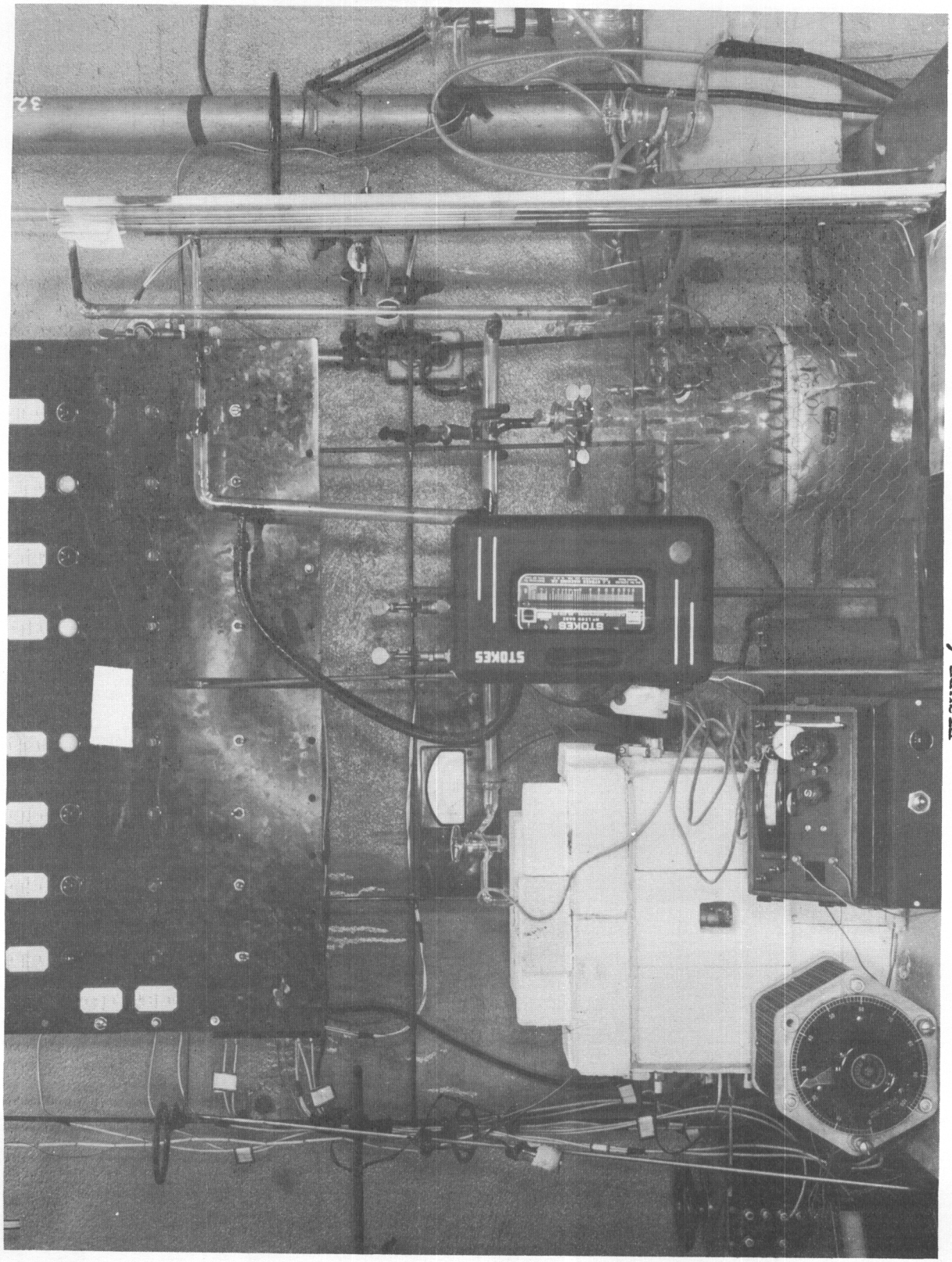

FIGURE 6

PHOTOGRAPH OF THE THERMAL DECOMPOSITION APPARATUS