NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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XXXII - MEASUREMENT OF THERMAL CONDUCTIVITY OF AIR AND OF EXHAUST GASES BETWEEN 50° AND 900° F

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SUMMARY

By means of a hot-wire method, the thermal conductivity of air was measured from air temperatures of 50° to 900° F and the thermal conductivity of gasoline-engine exhaust gases was measured from gas temperatures of 250° to 900° F. The values obtained for air are in good agreement with other data that are available. The values for exhaust gases from an engine operating on fuel-air ratios between 0.056 and 0.085 are practically the same as those for air at the same temperature, but the richer mixtures (fuel-air ratios of 0.10 to 0.15) show increasingly larger values of thermal conductivity, the largest being approximately 30 percent greater than that of air. The thermal-conductivity data obtained are shown in graphs at the end of this report.

INTRODUCTION

The object of the present work was to measure, over a limited temperature range, the thermal conductivity of gasoline-engine exhaust gases. Although thermal conductivity is one of the more important properties needed for the design of efficient heat exchangers of many types, very few data are available even for air, and apparently none are available for exhaust gases. Until recently, thermal-conductivity data were restricted almost entirely to a very narrow temperature range and the agreement between the results of various investigators was very poor. In the last 20 years considerable progress has been made so that there has been relatively good agreement between values recently measured in ice baths; also a few measurements have been made at higher temperatures. However even yet, for such an important gas as air, there are only a few measurements above 200° F and for most industrial gases there are less. No data were found for exhaust gases and therefore the attack on the problem was begun by a series of measurements on exhaust gases at convenient temperatures between 250° and 900° F. Measurements were also made on air over the same temperature range (and a few at lower temperatures) in order to check the performance of the equipment by comparison of the data with that previously obtained. It was also desired to extend the range of the data for air and to have a comparison of the relative conductivities of air and exhaust gases.

This research was carried out in the laboratories of the Division of Mechanical Engineering of the University of California under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

APPARATUS AND PROCEDURE

Necessary Measurements

The thermal conductivity of a material may be determined by simultaneous measurement of four quantities: (1) The rate of heat conduction; (2) the area, measured at right angles to the direction of heat flow, through which the heat is conducted; (3) the length of the path along which the heat flows; and (4) the temperatures at each end of the flow path. For a gas, heat transfer by convection must be eliminated and the heat transferred by radiation must be deducted from the total heat losses in order to obtain thermal-conductivity values experimentally. Several means of measurement have been devised to meet these conditions, but except for a few attempts by the cooling-thermometer method, all are variations of two methods. Both methods utilize electrical measurements.

Previous Methods

In one method, a measured quantity of electrical energy is liberated within a body so that the resulting heat is transferred across a narrow gap between the hot body and another adjoining metallic body of similar shape. The surface temperatures of the two bodies, usually flat plates or cylinders, are measured by means of thermocouples. This method undoubtedly offers the most positive means of eliminating heat transfer by convection because the surfaces may be made in the form of horizontal flat plates with the upper plate hotter than the lower plate. On the other hand, the apparatus is then not adapted for use over a large temperature range and the problems of temperature distribution over the plates and conduction losses through supports are serious. If cylinders are to be used, a second method is superior.

In a second method, the two bounding surfaces are concentric cylinders. The inner cylinder serves as both heat source and resistance thermometer, its resistance having been previously calibrated as a function of temperature. This method offers the advantages of adaptability to measurements over a great temperature range, greater ease in securing an isothermal hot body, greater precision of temperature measurement of the hot body, and better methods of preventing heat losses through spacers and leads.

Present Method

For the present work a modification of the second or hot-wire method used by Sherratt and Griffiths (reference 1) was selected. By this method, convection was eliminated by using a tube of very small diameter (I.D., 0.2 in.) and small temperature differences between the wire and tube wall. Previous work has indicated that, for the dimensions and temperature gradients employed, there should be no measurable heat transfer by convection. To check this premise, a series of conductivity measurements was made with conditions most favorable for convection, that is, at a low value of the wire temperature and a high value of the temperature gradient through the air. The wire temperature was held constant while the pressure was lowered after each set of equilibrium measurements over a range from 36.5 inches to 0.4 inch of mercury. Heat transfer by conduction and radiation is known to be unaffected by pressure changes in this range, but if heat were being transferred by convection, the apparent conductivity would decrease as the pressure was decreased. As shown by table I, the conductivity was not decreased by decreasing the pressure. In fact, in the second series of runs, which was the only series with enough data to be reasonably conclusive, the measured conductivity values are slightly higher at the low pressure.

Conduction losses from the test section (through the leads) were prevented by means of auxiliary heaters on each end of the test section (fig. 1). The hot wire was centered in a thin-walled platinum tube, which, because of its high thermal conductivity, insured that the thermocouples on the outside of the tube wall were at practically the same temperature (drop of approximately 0.03° F through the tube wall in the case of maximum heat transfer) as the inside wall and also prevented large temperature differences along the length of the tube.

The length of the hot wire was measured at room temperature with a steel rule and magnifying glass. The values of L at higher temperatures were calculated from the results of Holborn and Day (reference 2) on thermal expansion of platinum. The radius of the hot wire was measured to the nearest 0.0001 inch with a hand micrometer. From the weight of mercury that the platinum tube would contain, the internal radius was obtained. The average hot-wire temperature was obtained from consecutive potential measurements on the hot wire and standard resistor. These potential measurements gave the wire resistance, which was known to be a function of temperature from a previous calibration. The average tube-wall temperature was the arithmetic-average wall temperature of the platinum tube as indicated by three thermocouples.

The details of the apparatus and the calibration of the test section are described in appendixes A and B, respectively. The samples of gas used are described in appendix C.

Calculations

When heat is transferred between two concentric, isothermal cylinders under equilibrium conditions, the thermal conductivity of the enclosed gas may be calculated from the following equation:

$$q_{cond} = \frac{2\pi kL(t_1 - t_2)}{\log_e\left(\frac{r_2}{r_1}\right)} \tag{1a}$$

If the inner cylinder is heated electrically, as in the present case, equation (1b) also applies,

$$q_{cond} = 3.413EI - q_{rad} \tag{1b}$$

By combining the two equations,

$$k = \frac{1}{2\pi}\log_e\left(\frac{r_2}{r_1}\right)\left[\frac{3.413EI - q_{rad}}{L(t_1 - t_2)}\right] = 0.2950\left[\frac{3.413EI - q_{rad}}{L(t_1 - t_2)}\right] \tag{2}$$

where

A_1 surface area of hot wire, square feet

E potential drop along hot-wire length L, volts

I electric current through hot wire, amperes

k mean thermal conductivity of enclosed gas (for small temperature differences may be assumed to be $k\left(\frac{t_1+t_2}{2}\right)$ because k is practically a linear function of t), Btu/(hr)(sq ft)(°F/ft)

L length of hot wire measured between potential leads, feet

q_{cond} rate of heat transfer from wire to tube by conduction through enclosed gas, Btu/(hr)

q_{rad} net rate of heat transfer by radiation from hot wire to tube, Btu/(hr) $\left(\frac{\sigma(T_1^4 - T_2^4)A_1}{\frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1}\right)$

r_1 radius of hot wire, inches

r_2 internal radius of platinum tube, inches

T_1 temperature of hot wire, $^{\circ}R$

T_2 temperature of inside wall of platinum tube, $^{\circ}R$

t_1 average hot-wire temperature, $^{\circ}F$

t_2 average tube-wall temperature, $^{\circ}F$

α_1, α_2 absorptivity (fraction of total radiant energy incident upon hot wire and platinum tube, respectively, that is absorbed (fig. 2)). (At thermal equilibrium, the absorptivity of a surface is equal to its emissivity.)

σ Stefan-Boltzmann constant, 0.173×10^{-8}, Btu/(sq ft)(hr)($^{\circ}R^4$)

DISCUSSION OF RESULTS

Apparatus

The results obtained (see figs. 3 to 5 and tables I to X) with the present apparatus indicate that the method is suitable for determining the thermal conductivity of a gas to a temperature of at least 900° F.

If the apparatus were to be reconstructed, the only basic change necessary would be to make it more stable mechanically. This could be done by changing the construction detail to prevent the possibility of independent rotation of the hot wire, platinum tube, and soapstone spacers, by giving the auxiliary-heater leads enough freedom of movement to allow them to lengthen when heated without applying stresses to the ends of the hot wire, and by sealing the test section and leads in a glass tube so that the entire sealed unit could be slipped into various boiling-point tubes without injury.

It seems probable that the temperature range could be extended several hundred degrees by replacing the glass sample chamber with one

of quartz or glazed porcelain and by using a suitable electric furnace in place of vapor baths to attain higher temperatures. However, to attain higher temperatures, the conduction of heat from hot-wire leads by the spacers would have to be cut to a minimum and the auxiliary heaters placed as close as possible to the ends of the hot wire.

Data for Air

Evaluation.- The measurements on air show reasonably good precision as indicated by the data of figure 3 and tables I to VI. The maximum spread of the points amounts to a little over 3 percent. The only check on the accuracy of the data is a comparison of the measurements on air with previous results. As shown by figure 3, the curve obtained agrees almost exactly with that obtained by Sherratt and Griffiths, but is about 7 percent higher than the value at the highest temperature attained by Vargaftik and Parfenov (reference 3). The values agree well with those partly reported in reference 4.

Radiation correction.- At least part of the reason for the lower values given in reference 3 is the larger radiation correction which was applied to the total heat loss from the wire. Figure 6 shows emissivity values, calculated from data given by Timrot and Vargaftik (reference 5) and used by Vargaftik and Parfenov, compared with the curve used for calculating the present results. All three sets of emissivities were determined by total-heat-loss measurements on a platinum wire in an evacuated glass tube; therefore they should be identical.

For most of the previous measurements, the tube surrounding the hot wire was made of glass, which has a high absorptivity (and low reflectivity) for energy in the wavelengths concerned, and the return radiation from the tube to the wire was negligible. For the present case, in which a platinum tube of low absorptivity was used, an allowance must be made for the return radiation from the tube to the wire. Equation (2), which was used to calculate the radiation loss, is based on the postulate that platinum is a specular reflector. This postulate is not correct; the actual radiation losses are between the values given by the equations for specular and diffuse reflectors. For the present work, the maximum radiation correction based on the assumption of a specular reflector was 6 percent of the total heat loss; if the assumption of a diffuse reflector were made, the maximum correction would be 10 percent of the total heat loss.

Data for Exhaust Gases

Scattering of data.- The data obtained for exhaust gases (fig. 4) are less satisfactory than those obtained for air (fig. 3), as indicated by the scattering of the experimental points. This scatter of data is

perhaps partly due to inability to reproduce exhaust-gas samples taken from the engine. Further, most of the scattering occurred for the rich mixtures, at high temperatures, and often on runs made from consecutive samples from the same sample flask. Thus additional errors were probably introduced because of the necessity of taking data while the conductivity of the sample was apparently changing (appendix D). The magnitude of this apparent change in thermal conductivity appears to be too great (about 10 percent in a case followed to equilibrium in 18 hr) to be accounted for by a catalytic oxidation of the hydrogen by the oxygen originally in the samples (fig. 7). However, it does not appear probable that additional oxygen entered the sample chamber because all joints and seals were constantly checked for leaks and no data were taken when an appreciable leak existed. Part of the change was possibly due to catalytic action and part to some unexplained transient effect of hydrogen or carbon monoxide on the hot-wire surface. In figure 7, for rich fuel to air mixtures, calculations based on the analyses indicate that the values for the carbon to carbon and hydrogen ratio are lower than for normal mixtures and that the fuel-air ratios are lower than those measured.

Evaluation of data.- The cause for the necessity of decreasing the power input necessary to maintain thermal equilibrium was not definitely determined, but it appears, from the relative conductivity values for various fuel-air ratios at any given temperature, that the values obtained are not in doubt by more than a few percent.

Relation of thermal conductivity to fuel-air ratio.- The principal difference between the air which enters a gasoline engine and the exhaust gases which leave is the replacement of most of the entering oxygen by carbon dioxide, carbon monoxide, water, hydrogen, and unburned hydrocarbons. The conductivity measurements of this investigation indicate that under normal operating conditions, when the replacement gases are practically all carbon dioxide, carbon monoxide, and water, the thermal conductivity of the exhaust gases is approximately the same as that of air at the same temperature.

As the fuel-air ratio increases and combustion becomes less complete, the thermal conductivity increases rapidly. The only significant changes in exhaust-gas composition with increasing fuel-air ratio are the increase of hydrogen and carbon monoxide and the decrease of water and carbon dioxide; both of these changes tend to increase the conductivity of the mixture, but the magnitudes of the effects probably differ greatly. The thermal conductivity of hydrogen is roughly seven times greater than the conductivity of any of the other constituent gases (the conductivities of the other gases are all the same order of magnitude), therefore, it seems quite probable that hydrogen is the most important factor in determining the variation of the thermal conductivity of exhaust gases with fuel-air ratio.

Gaseous radiation to and from carbon monoxide, carbon dioxide, water, methane, and other hydrocarbons may slightly affect the values of thermal conductivity obtained on this apparatus.

SUMMARY OF RESULTS

From a measurement of the thermal conductivity of air and of exhaust gases between 50° and 900° F, the following results were obtained:

1. The results of the measurement of the conductivity of air were found to be in substantial agreement with other data which are available.

2. The thermal conductivity of exhaust gases from a single-cylinder gasoline engine operating on a range of fuel-air ratio from lean to normal (0.056 to 0.085) is approximately the same as the thermal conductivity of air at the same temperature.

3. The thermal conductivity of exhaust gases from an engine with rich fuel-air ratios (0.10 to 0.15) increases rapidly with increasing fuel-air ratio (as the hydrogen content increases) until at a fuel-air ratio of 0.15 the thermal conductivity is roughly 30 percent greater than for air at the same temperature.

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Berkeley, Calif., November 12, 1945

APPENDIX A

DETAILS OF APPARATUS

Test Section

The essential features of the test section are shown in figures 1 and 8. The length of the test section was bounded by two thermocouples of platinum to 90 percent platinum and 10 percent rhodium (10.50 in. apart) whose platinum leads also served as potential leads for the hot wire. Outside the thermocouples, enclosing the current leads on each end of the test section, were small helical Nichrome heaters (1 ohm, no. 24 wire) which prevented conduction losses through the ends of the hot wire (0.0309-in. diam.) during conductivity runs. Surrounding the vertical hot wire was a 0.197-inch-inside-diameter, 0.240-inch-outside-diameter platinum tube which had three thermocouples, of platinum to platinum and rhodium, welded to the outer surface. Soapstone spacers centered the hot wire in the platinum tube.

Leads

The current leads inside the sample chamber were nickel. All the thermocouple wires were led out to ice bottles (at each end of the apparatus), where each wire was connected to a copper lead which led to a potentiometer. The hot-wire leads were bare, but all other leads inside the sample chamber were encased in porcelain or glass tubing and those outside the sample chamber were covered with woven glass.

The 2-ounce platinum tube rested on a spacer supported by the lower hot-wire lead. In addition, a 3-ounce stainless-steel weight was hung on the lead to prevent the test section from being displaced. Below the weight was an expansion joint in the form of a flexible copper helix, which allowed the hot wire to move vertically without appreciably changing the tension on it. At each end of the sample chamber, the leads were taken out through rubber stoppers by means of De Khotinsky cement seals.

Current Circuits

The electric currents for the hot wire and auxiliary heaters were supplied by three independent groups of almost constant-voltage lead batteries. Each circuit was also equipped with an ammeter and rheostats to provide adequate current control, and in addition the main circuit had a 0.1-ohm standard resistor in series with the hot wire.

Potential Circuits

The calibration measurements for the hot wire and all thermocouple measurements were made on a new Leeds and Northrup White model potentiometer (left-hand side of fig. 9) using a Leeds and Northrup type H.S. galvanometer to measure the last increment of unbalanced electromotive force. The measurement of the voltages across the hot wire and standard resistor were made with a Leeds and Northrup type K_2 potentiometer with a Leeds and Northrup type R galvanometer as the null instrument. The K_2 potentiometer was checked at several points on the low range against the White model and the two instruments were found to be in good agreement. The standard cell, which was used in both potentiometer circuits, was kept in an insulated box to prevent sudden temperature changes and was periodically checked against a group of cells calibrated by the National Bureau of Standards. The 0.1-ohm standard resistor was calibrated by the manufacturers (Leeds and Northrup Co.) and was maintained in a well-stirred oil bath at approximately 77° F.

Temperature Control

The temperature of the apparatus was maintained by immersion in ice or vapor baths (fig. 2) both during the calibration and during the conductivity measurements. These baths were provided by a series of glass boiling-point tubes (adapted from a type developed by Mueller and Burgess, reference 6) with built-in sample chambers, which provided the uniform and constant temperatures necessary for both calibration and conductivity runs.

APPENDIX B

CALIBRATION OF TEST SECTION

Preparation for Calibration

The thermometer and thermocouple wires were annealed at about 2200° F for 20 minutes before the test section was assembled. All thermocouple and heater junctions were made by spot-welding the pure metals. After assembly of the test section an insulated stainless-steel weight was suspended from the lower hot-wire lead (by trial 5 oz was judged to be the minimum total weight necessary to return the wire after displacement) to provide the necessary tension. The test section was then ready for calibration at the standard temperatures provided by ice, steam, naphthalene, benzophenone, and sulphur baths.

General Procedure

Except for the steam-bath calibrations, for which a hypsometer of the type developed by Mueller and Sligh (reference 7) was used, the test section occupied the same position in the various baths during the calibration and conductivity measurements. In fact, often before starting the daily series of conductivity runs, checks were obtained on the calibrations by making the required potential measurements using hot-wire currents of 20 to 50 milliamperes instead of the 2- to 5-ampere currents used for the conductivity runs. No heating effect was observed in any of the baths from the use of hot-wire currents of less than 75 milliamperes; but for convenience the thermocouples on the hot wire were calibrated with no current flowing. When a current was flowing through the hot wire, the thermocouple electromotive force was the sum of the electromotive forces generated by the platinum to platinum and rhodium junction and an electromotive force due to the fact that the two thermocouple wires could not be welded at one point on the length of the hot wire. Consequently, the leads of each thermocouple acquired an added electromotive force whose magnitude was determined with the displacement of the leads and the total voltage drop along the hot wire. This additional electromotive force, which varied from a fraction of a microvolt to almost 300 microvolts, was eliminated by taking an average of the thermocouple potentials before and after a rapid reversal of the hot-wire current.

The original calibrations were obtained from measurements in the sulphur bath (832.3° F), then in the steam bath (212° F), and finally in an ice bath (32° F). These three baths, as well as the naphthalene (424.3° F) and benzophenone (582.6° F) baths, which later gave additional data points for the curves of thermocouple electromotive force plotted

against temperature, each provided isothermal and practically constant temperature conditions over an 18-inch section of the sample chamber.

Hot-Wire Calibration

Potential measurements on the hot wire and 0.1-ohm standard resistor, the former at the temperatures of melting ice, boiling water, and boiling sulphur (U.S.P.), allowed calculation of the constants necessary for use of the Callendar equation, which expresses temperature as a function of resistance over the entire range of the conductivity measurements. It will be noted that the temperatures in this equation, which is used to define the International Temperature Scale between 0° and 660° C, are given in degrees centigrade.

$$t - \left(\frac{R_t - R_0}{R_{100} - R_0}\right)100 + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \tag{4}$$

where R_0, R_{100}, R_t are the electrical resistances of the wire at 0°, 100°, and t° C, respectively, and δ is a constant obtained by substituting for R_t the resistance of the wire at the boiling temperature of sulphur. The constants for the original hot-wire calibration are:

$R_0 = 0.055473$ ohm

$R_{100} = 0.077205$ ohm

$R_{444.6} = 0.14717$ ohm

$\delta = 1.48$

$\frac{R_{100}}{R_0} = 1.392$

The values of δ and R_{100}/R_0 indicate that the hot-wire characteristics are within the narrow limits which are generally accepted as an indication of a satisfactory resistance thermometer.

Equation (4) was used to calculate enough points to make possible a series of large-scale plots of resistance against temperature. By use of these plots, the temperature corresponding to the measured resistance could be quickly read to the nearest 0.1° F. The accuracy of the temperature measurements made by the hot wire depends on several variables and is difficult to estimate, but measurement of the boiling points of naphthalene (Eastman's no. 168) and benzophenone (Eastman's no. 346) indicates that the accuracy was good. The measured boiling points, when corrected for barometric pressure, agreed in both cases with the accepted standard values within 0.2° F.

Recalibration of Hot Wire

During the measurements in the steam bath, frequent calibration checks between conductivity runs indicated that the resistance of the hot wire at a given temperature was unchanged. However, after transfer of the test section to the naphthalene bath, the hot wire was found to be touching the platinum tube wall (the maximum clearance was only 0.083 in.) so that it became necessary to increase the hot-wire tension to restore the wire to its original position. In an attempt to insure centering of the wire, the tension was increased to approximately 25 ounces. Repetition of earlier measurements indicated that the apparatus was restored to its original condition and the measurements were continued. As higher temperatures were reached, the resistance at a given temperature increased very slowly at first, then more rapidly.

The hot wire was then recalibrated at the ice, steam, and sulphur points. The constants had all increased somewhat ($\delta = 1.51$), but a recheck of the naphthalene and benzophenone boiling points indicated that the temperature measurements were as accurate as they were when the hot wire was calibrated originally. The measurements were then continued with a 5-ounce tension on the wire until the last few measurements were being made, when it became necessary to increase the total hot-wire tension to 15 ounces to overcome bending stresses which were evidently applied to the ends of the hot wire by the thermal expansion of the auxiliary-heater leads. This extra tension slowly increased the hot-wire resistance until on the last measurement (at 909° F) a correction of 2.3° F was necessary. This is by far the largest correction applied to any of the hot-wire measurements and was necessary only for the exhaust-gas data at 909° F.

Thermocouple Calibration

The five thermocouples (0.008-in.-diam., platinum to 90-percent platinum and 10-percent rhodium wire) were calibrated in each bath against the temperatures indicated by the hot wire. This method of calibration should prevent appreciable errors in measuring the temperature difference between the hot wire and tube wall because the conductivity measurements never involved temperatures that were more than 125° F from the closest calibration point at which the hot wire and thermocouples were compared. This fact is important because, from the nature of the measurements, most of the errors in the values of thermal conductivity are likely to be due to errors in measuring the temperature difference.

The curves of thermocouple electromotive force and temperature were all very close to the average curve determined by the National Bureau of Standards (reference 8). The greatest deviation from this curve by any of the thermocouples was 6 microvolts (1.2° F) at the sulphur boiling point. This close agreement permitted accurate temperatures to be obtained quickly from a series of large scale plots of the average

data of the National Bureau of Standards plus a small correction plot of the individual deviations from the curve.

Despite the rather rough treatment to which the delicate thermocouple wires were unavoidably subjected during the transfers of the test section, the original relation between the temperature and electromotive force was retained during the several months of use. The one exception to this otherwise excellent thermocouple performance occurred when the thermocouple 5 suddenly showed a decrease in electromotive force at the naphthalene point of 35 microvolts. An examination of the thermocouple revealed no definite cause for the change, but a calibration check showed that the former temperature – electromotive-force relation was restored.

APPENDIX C

GAS SAMPLES

Air

For most of the runs on air, the gas was dry and free of carbon dioxide but at times, for reasons of convenience, runs were made with the apparatus unsealed so that atmospheric air entered the sample chamber without passing through the water and carbon-dioxide absorption columns. No difference in thermal conductivity was observed between samples of dry carbon-dioxide-free air and atmospheric air.

Exhaust Gases

Source.- The exhaust-gas samples were obtained from a single-cylinder engine using first-structure gasoline. The compression ratio was approximately 6 and the normal spark setting was used. Because past work (references 9 and 10) has indicated that the fuel-air ratio is the only important variable in determining the exhaust-gas composition, other factors such as engine speed and load were varied, when necessary, to obtain extremely high or low fuel-air ratios.

Method of transferring samples from engine to sample chamber.- The exhaust-gas samples were obtained by means of a short sample pipe in the exhaust-gas line about 1 foot from the cylinder. The hot gases cooled immediately upon entering the evacuated glass sample flask, but were reheated in an oil bath to temperatures between 250° and 300° F before entering the sample chamber. This reheating retained the water vapor, but practically all carbon particles, which were present in the rich mixtures, remained in the sample flasks.

The temperature of the sample chamber was always well above the condensation temperature of water vapor except possibly at the end seals, which were cooled by air jets. The glass capillary tubing that connected the sample flasks to the sample chamber was not heated but was made as short as possible to reduce the water-vapor loss to a minimum. In order to fill the sample chamber for a conductivity determination, the gas pressure within the chamber was reduced to a few tenths of an inch of mercury by means of a mechanical vacuum pump; then the hot sample gases were allowed to enter the chamber. Unless the gases that were pumped out were similar in composition to the new sample, the chamber was filled at least twice to insure a pure sample. The system was periodically checked for leaks and a few runs were rejected because of increase of pressure during the runs.

APPENDIX D

METHOD OF MAKING OBSERVATIONS

General Procedure

The measurements required for the thermal-conductivity runs were similar to those for the calibrations except for two important differences. For conductivity runs, much larger currents were used (2 to 5 amperes as compared with 20 to 50 milliamperes), the magnitude being determined by the desired temperature difference between the hot wire and the tube wall. For conductivity runs, the use of the auxiliary heaters to prevent conduction losses through the hot-wire leads also became necessary.

In each bath, the base temperature was fixed by the melting point (for ice) or the atmospheric boiling point of the bath fluid, but the thermal conductivity of a gas sample could be measured at higher temperatures by increasing the hot-wire current. This simultaneously increased the values of t_1 and t_2, thus giving a higher average temperature as well as a higher temperature difference and allowing an almost continuous series of measurements over the entire temperature range.

Attainment of Thermal Equilibrium

It was found that the most satisfactory method of attaining thermal equilibrium was to select the desired hot-wire temperature, then from the calibration curves to note the hot-wire resistance and the electromotive force of thermocouples 1 and 2 (on the ends of the hot wire) that were equivalent to the selected temperature. Next, by means of rheostats in each of the three independent circuits, the currents in the hot wire and the two auxiliary heater circuits were continuously adjusted so that the equivalent resistance and electromotive-force values were attained. As the test section approached thermal equilibrium, the hot wire and auxiliary-heater currents also approached constant values. The time necessary for obtaining equilibrium depended largely on the magnitude of the hot-wire current.

To obtain the best possible operating conditions when the resistance thermometer and thermocouple readings indicated that the hot-wire temperature was uniform and constant within $\pm 0.2^{\circ}$ F sometimes required several hours of manipulation. Once established, equilibrium conditions could be maintained indefinitely with only slight rheostat adjustments if the sample were air or exhaust gases from low-fuel-air-ratio combustion. However, since other variables affecting the conductivity of the exhaust gases could not be controlled closely enough to warrant such laborious measurements, slightly larger deviations were allowed for exhaust-gas measurements than for measurements on air.

In the case of the richer mixtures it was discovered that above a temperature of about 450° F, the hot-wire-current value necessary to maintain a given equilibrium temperature had to be slowly decreased. The rate of current reduction necessary decreased with time of contact with the apparatus and increased with temperature of the sample. Cases of shifting equilibrium were followed for long periods and some still showed a very slight continuous change after as long as 30 hours.

The cause of the shifting equilibrium was never positively identified, but since the available experimental evidence tended to disprove such possibilities as increasing wire resistance, loss of water vapor from the samples, and continuous shifting of the hot wire, it seems most likely that small amounts of oxygen must have been causing the catalytic oxidation of the hydrogen and carbon dioxide at the platinum surfaces. This idea was supported by the slight decrease in pressure which accompanied the equilibrium shifts and the gas analyses of the original samples. The analyses showed that even rich mixtures contained small amounts of oxygen as well as hydrogen and carbon monoxide. Platinum is known to be a catalyst for the oxidation of hydrogen at temperatures as low as 400° F and carbon monoxide at slightly higher temperatures (reference 11), but it had been expected that the oxygen content would be too small to produce a noticeable effect. The oxidation of small amounts of carbon monoxide to carbon dioxide would tend to decrease the power necessary to maintain thermal equilibrium, because both carbon monoxide and oxygen have slightly higher thermal conductivities than carbon dioxide. However, the oxidation of hydrogen would be much more important because the conductivity of hydrogen is roughly seven times that of air, and the conductivity of the end product, water, is slightly lower that that of air. Because the decrease in the conductivity of the samples amounted to only a few percent over a period of several hours, the practical solution seemed to be to reach equilibrium as soon as possible and use the first data obtained for calculations. Results obtained using this procedure naturally showed more erratic variations because of the unavoidable inclusion of some data taken before true equilibrium temperatures were established and some after the conductivity had decreased.

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TABLE I.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, steam; temperatures, 302° and 367° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))	p (in. Hg)
335.8	273.6	305	3.509	0.3221	1.130	0.012	1.118	0.0207	43.2
332.6	271.4	302	3.469	.3170	1.100	.012	1.088	.0204	39.4
332.8	272.5	303	3.451	.3155	1.089	.012	1.077	.0205	21.6
415.6	319.5	367	4.293	.4337	1.862	.025	1.837	.0219	36.5
415.6	319.5	367	4.289	.4332	1.858	.025	1.833	.0219	29.9
415.4	319.8	367	4.285	.4328	1.855	.025	1.830	.0220	26.0
415.6	319.1	367	4.307	.4351	1.874	.025	1.849	.0220	22.0
415.4	319.6	367	4.292	.4335	1.861	.025	1.836	.0220	18.1
415.6	319.3	367	4.309	.4353	1.876	.025	1.851	.0221	18.1
415.6	319.1	367	4.356	.4312	1.878	.025	1.853	.0220	14.2
415.6	318.9	367	4.320	.4364	1.877	.025	1.852	.0220	9.8
415.6	318.6	367	4.336	.4380	1.899	.025	1.874	.0222	6.3
415.6	317.8	367	4.364	.4409	1.924	.025	1.899	.0223	2.0
415.6	318.4	367	4.142	.4184	1.733	.025	1.708	.0202	.4

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TABLE II.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, ice; pressure, 1 atmosphere; temperature range, 42° – 87° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watt)	q_{rad} (watt)	q_{cond} (watt)	k (Btu/(hr)(sq ft)(°F/ft))	p (in. Hg)
46.9	37.2	42	1.430	0.08194	0.1172	0.0003	0.1169	0.0139	29.9
66.6	44.2	55	2.1870	.1306	.2850	.0009	.2841	.0146	29.9
111.9	61.7	87	3.2242	.2102	.6777	.0024	.6753	.0155	29.9

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TABLE III.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, steam; pressure, 1 atmosphere; temperature range, 239° – 367° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
250.0	227.8	239	2.179	0.1780	0.3879	0.0029	0.3850	0.0199
278.2	242.6	260	2.701	.2297	.6204	.0055	.6149	.0199
332.8	272.5	303	3.451	.3155	1.089	.012	1.077	.0205
415.6	319.5	367	4.289	.43324	1.858	.025	1.833	.0219
266.0	235.6	251	2.531	.2116	.5353	.0041	.5312	.0201
266.0	237.4	252	2.409	.2026	.4881	.0041	.4840	.0195
338.0	275.0	306	3.525	.3264	1.151	.012	1.139	.0208
338.0	275.0	306	3.5180	.3258	1.146	.012	1.134	.0207

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TABLE IV.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, naphthalene; pressure, 1 atmosphere; temperature range, 466° – 570° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
482.0	449.1	466	2.557	0.2777	0.7101	0.0138	0.6963	0.0243
481.6	448.5	466	2.571	.2792	.7178	.0138	.7040	.0244
481.6	448.2	466	2.587	.2810	.7269	.0138	.7131	.0245
554.5	482.9	518	3.754	.4385	1.646	.037	1.609	.0258
481.6	448.0	465	2.587	.2809	.7267	.0138	.7129	.0244
625.3	514.6	570	4.597	.5734	2.638	.069	2.569	.0266

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TABLE V.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, benzophenone; pressure, 1 atmosphere; temperature range, 623° – 712° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
643.3	603.9	624	2.754	0.3490	0.9611	0.0314	0.9297	0.0271
642.7	603.3	623	2.742	.3476	.9535	.0314	.9221	.0269
768.6	653.9	711	4.661	.6547	3.052	.118	2.934	.0293
768.7	654.3	712	4.664	.6580	3.069	.118	2.951	.0296
644.0	603.3	624	2.815	.3590	1.011	.031	.980	.0276
770.0	645.1	712	4.715	.6663	3.127	.118	3.009	.0297
707.0	627.3	667	3.921	.5272	2.067	.071	1.996	.0287

TABLE VI.– THERMAL-CONDUCTIVITY DATA

[Sample gas, air; bath used, sulphur; pressure, 1 atmosphere; temperature range, 861° – 909° F]

t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
878.0	844.0	861	2.623	0.4010	1.052	0.053	0.997	0.0336
914.0	854.2	884	3.429	.5373	1.842	.108	1.734	.0332
877.1	844.5	861	2.531	.3869	.9792	.0530	.9262	.0325
948.2	869.5	909	3.958	.6352	2.514	.149	2.365	.0344

TABLE VII.- THERMAL-CONDUCTIVITY DATA

[Sample gas, exhaust gases; bath used, steam; pressure range, 0.5 - 1.0 atmosphere; temperature range, 233° - 370° F]

Fuel-air ratio	t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
0.056	327.9	262.2	295	3.548	0.3224	1.144	0.012	1.32	0.0198
.070	327.9	262.0	295	3.537	.3214	1.137	.012	1.125	.0196
.152	245.5	220.5	233	2.526	.2050	.5178	.0033	.5145	.0237
.152	415.6	323.6	370	4.728	.4775	2.258	.025	2.333	.0279
.152	327.9	264.4	296	3.972	.3609	1.433	.012	1.421	.0257
.070	266.0	230.2	248	2.612	.2183	.5702	.0051	.5651	.0182
.056	266.0	230.2	248	2.640	.2208	.5829	.0051	.5778	.0186
.073	266.2	235.0	251	2.421	.2024	.4900	.0051	.4849	.0179
.073	415.6	298.9	357	4.665	.4712	2.198	.028	2.170	.0213
.073	415.6	301.5	359	4.596	.4642	2.133	.028	2.105	.0212
.095	415.6	301.5	359	4.801	.4851	2.329	.028	2.301	.0229
.070	415.6	300.9	358	4.607	.4654	2.144	.028	2.116	.0212
.0152	266.0	236.1	251	2.822	.2360	.6660	.0041	.6619	.0254
.095	266.0	233.4	250	2.625	.2195	.5762	.0045	.5717	.0202
.095	266.0	233.4	250	2.620	.2191	.5740	.0045	.5695	.0201
.095	266.0	233.4	250	2.627	.2197	.5772	.0045	.5727	.0202

TABLE VIII.- THERMAL-CONDUCTIVITY DATA

[Sample gas, exhaust gases; bath used, naphthalene; pressure range, 0.66 – 1.0 atmosphere; temperature range, 465° – 572° F]

Fuel-air ratio	t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
0.152	482.0	449.6	466	2.798	0.3038	0.8500	0.0138	0.8362	0.0296
.152	554.9	486.1	520	4.106	.4797	1.970	.037	1.933	.0322
.064	482.0	449.2	466	2.521	.2738	.6902	.0138	.6764	.0237
.095	482.0	449.8	466	2.606	.2830	.7375	.0138	.7237	.0258
.064	481.6	448.0	465	2.563	.2784	.7135	.0138	.6997	.0239
.114	481.6	448.9	465	2.746	.2982	.8189	.0138	.8051	.0283
.064	481.6	447.6	465	2.560	.2780	.7117	.0138	.6979	.0236
.056	481.6	447.6	465	2.561	.2781	.7122	.0138	.6984	.0236
.070	481.6	447.8	465	2.562	.2783	.7130	.0138	.6992	.0237
.095	481.6	448.7	465	2.660	.2890	.7687	.0138	.7549	.0263
.114	481.6	448.9	465	2.980	.2744	.8177	.0138	.8039	.0282
.152	481.6	449.4	465	2.849	.3095	.8818	.0138	.8680	.0309
.073	481.6	449.4	465	2.590	.2813	.7286	.0138	.7148	.0255
.055	481.6	448.2	465	2.554	.2773	.7082	.0138	.6944	.0239
.055	481.6	448.0	465	2.555	.2775	.7090	.0138	.6952	.0238
.055	554.4	482.0	518	3.728	.4356	1.624	.037	1.587	.0252
.073	554.4	482.4	518	3.757	.4389	1.649	.037	1.612	.0257
.152	554.4	484.3	519	4.139	.4836	2.002	.037	1.965	.0322
.152	554.4	484.0	519	4.149	.4847	2.011	.037	1.974	.0322
.152	625.3	519.3	572	5.109	.6373	3.256	.069	3.187	.0345
.152	625.3	517.3	571	5.101	.6363	3.246	.069	3.177	.0338
.073	625.3	514.9	570	4.655	.5807	2.703	.069	2.634	.0274
.055	625.3	514.6	570	4.587	.5722	2.625	.069	2.556	.0265

TABLE IX.- THERMAL-CONDUCTIVITY DATA

[Sample gas, exhaust gases; bath used, benzophenone; pressure range, 0.45 - 1.0 atmosphere; temperature range, 623° - 713° F]

Fuel-air ratio	t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
0.055	643.3	604.0	624	2.730	0.3461	0.9449	0.0314	0.9135	0.0267
.073	643.3	603.1	623	2.770	.3512	.9728	.0314	.9414	.0269
.095	643.3	604.0	624	2.799	.3548	.9931	.0314	.9617	.0281
.114	643.3	603.9	624	2.933	.3716	1.090	.031	1.059	.0308
.152	643.3	604.6	624	3.037	.3850	1.169	.031	1.138	.0337
.114	643.1	604.0	624	2.941	.3729	1.097	.031	1.066	.0313
.122	642.7	604.0	623	2.977	.3774	1.115	.031	1.084	.0321
.098	642.7	604.0	623	2.913	.3693	1.076	.031	1.045	.0310
.098	642.6	603.7	623	2.890	.3663	1.059	.031	1.028	.0303
.098	642.6	603.1	623	2.813	.3572	1.005	.031	.974	.0283
.073	705.7	628.2	667	3.910	.5227	2.044	.071	1.973	.0292
.114	705.6	628.7	667	4.133	.5524	2.283	.071	2.212	.0330
.055	705.6	627.8	667	3.850	.5146	1.981	.071	1.910	.0282
.055	768.6	654.6	712	4.680	.6575	3.077	.118	2.959	.0298
.073	768.6	654.8	712	4.720	.6632	3.130	.118	3.012	.0304
.114	768.6	656.8	713	5.000	.7023	3.512	.118	3.394	.0348
.065	643.3	603.7	624	2.748	.3483	.9571	.0314	.9257	.0277

TABLE X.- THERMAL-CONDUCTIVITY DATA

[Sample gas, exhaust gases; bath used, sulphur; pressure range, 0.5 - 1.0 atmosphere; temperature range, 861° - 909° F]

Fuel-air ratio	t_1 (°F)	t_2 (°F)	t_{av} (°F)	I (amp)	E (volt)	q_{total} (watts)	q_{rad} (watt)	q_{cond} (watts)	k (Btu/(hr)(sq ft)(°F/ft))
0.055	877.3	844.5	861	2.596	0.3969	1.030	0.053	0.977	0.0341
.114	877.3	844.5	861	2.678	.4095	1.097	.053	1.044	.0365
.073	877.3	844.3	861	2.627	.4018	1.056	.053	1.003	.0348
.073	877.1	844.7	861	2.577	.3941	1.016	.053	.963	.0341
.073	877.1	844.7	861	2.587	.3956	1.023	.053	.970	.0343
.114	877.1	844.9	861	2.668	.4079	1.088	.053	1.035	.0368
.114	877.1	845.1	861	2.704	.4135	1.118	.053	1.065	.0381
.073	949.1	866.8	908	4.088	.6562	2.683	.149	2.534	.0353
.114	947.7	868.8	909	4.293	.6891	2.958	.149	2.809	.0408
.114	947.7	869.2	909	4.351	.6983	3.038	.149	2.889	.0422
.055	947.7	870.3	909	3.980	.6389	2.543	.149	2.394	.0355
.055	947.7	870.6	909	3.989	.6402	2.554	.149	2.405	.0357

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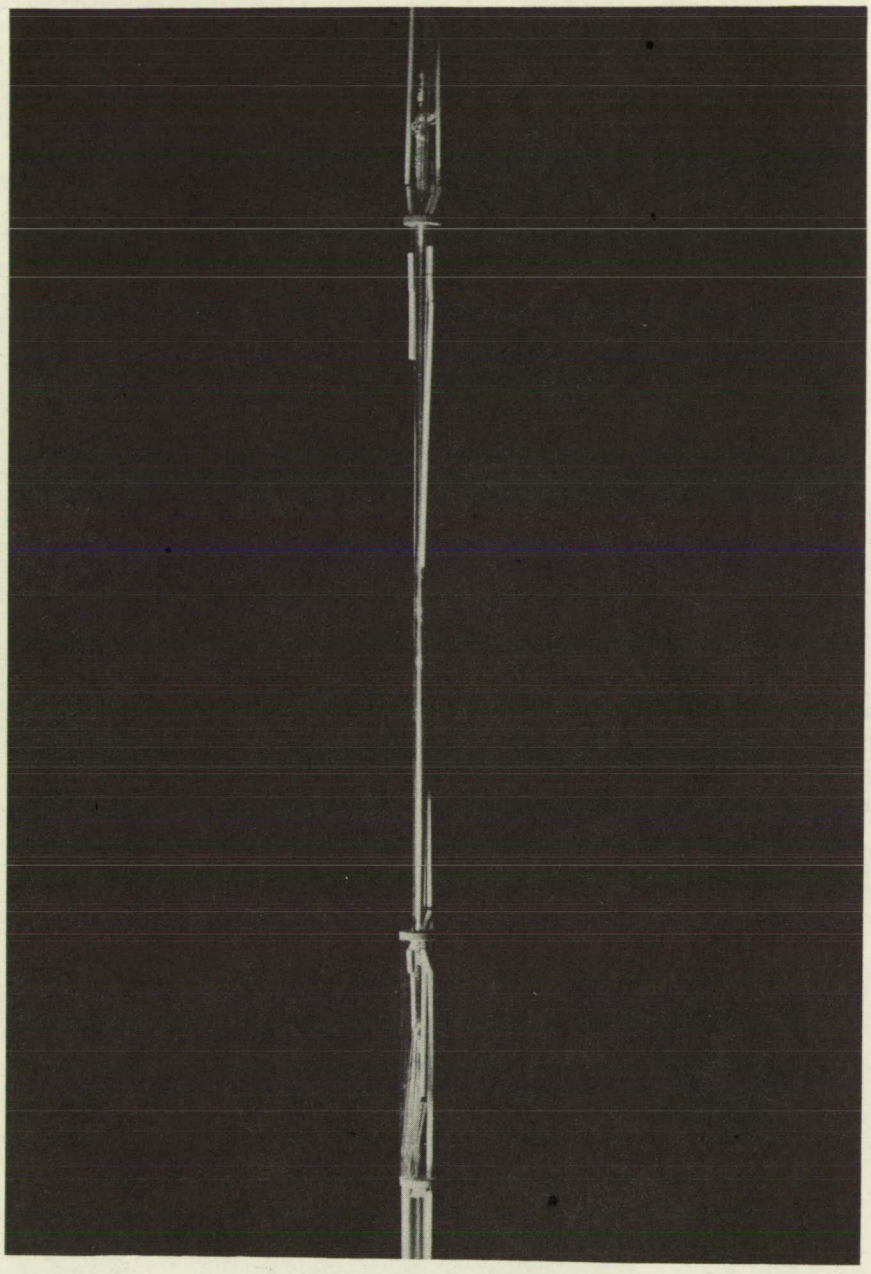

Figure 1.- Test section.

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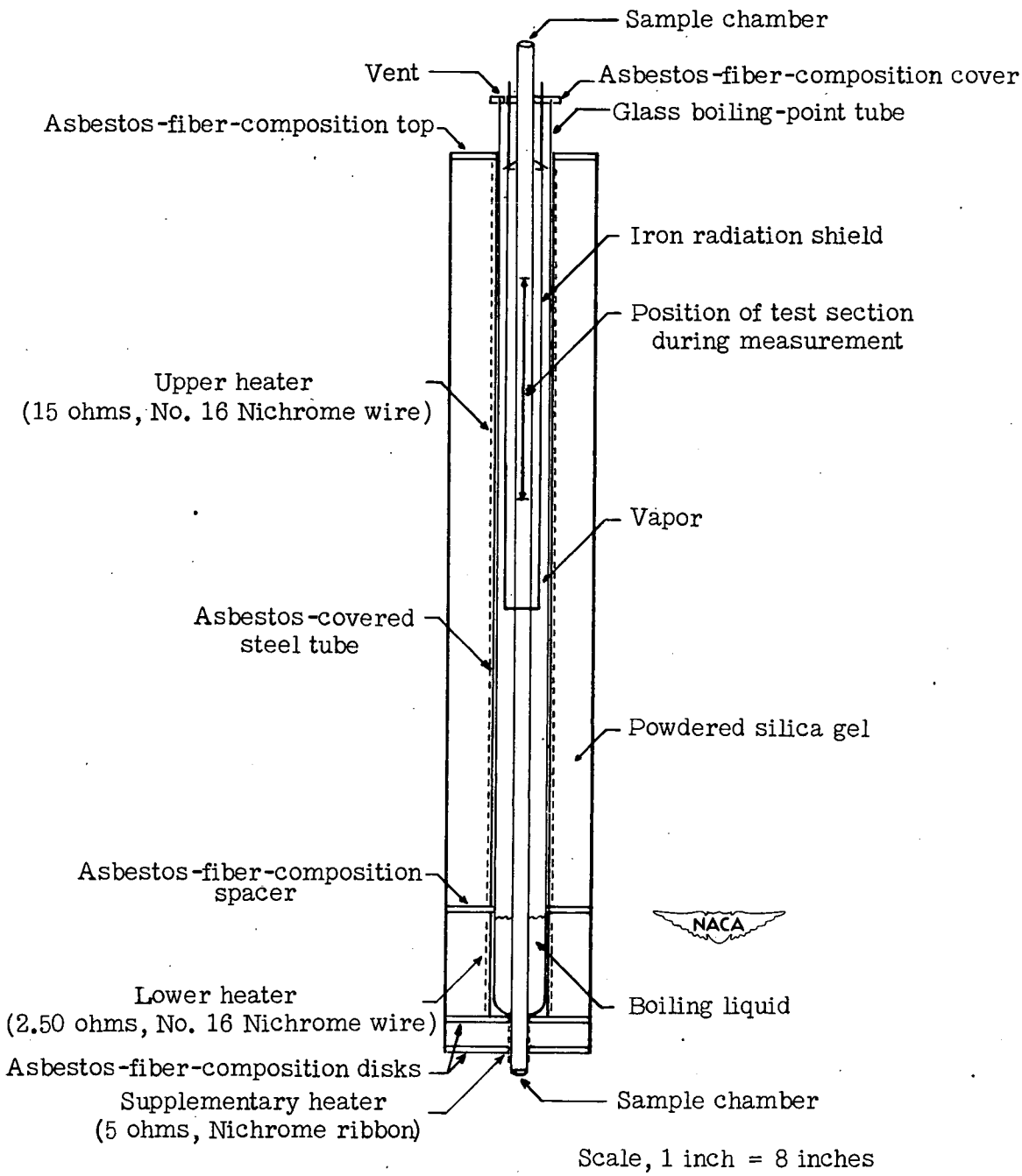


Figure 2.- Boiling-point tube in furnace.

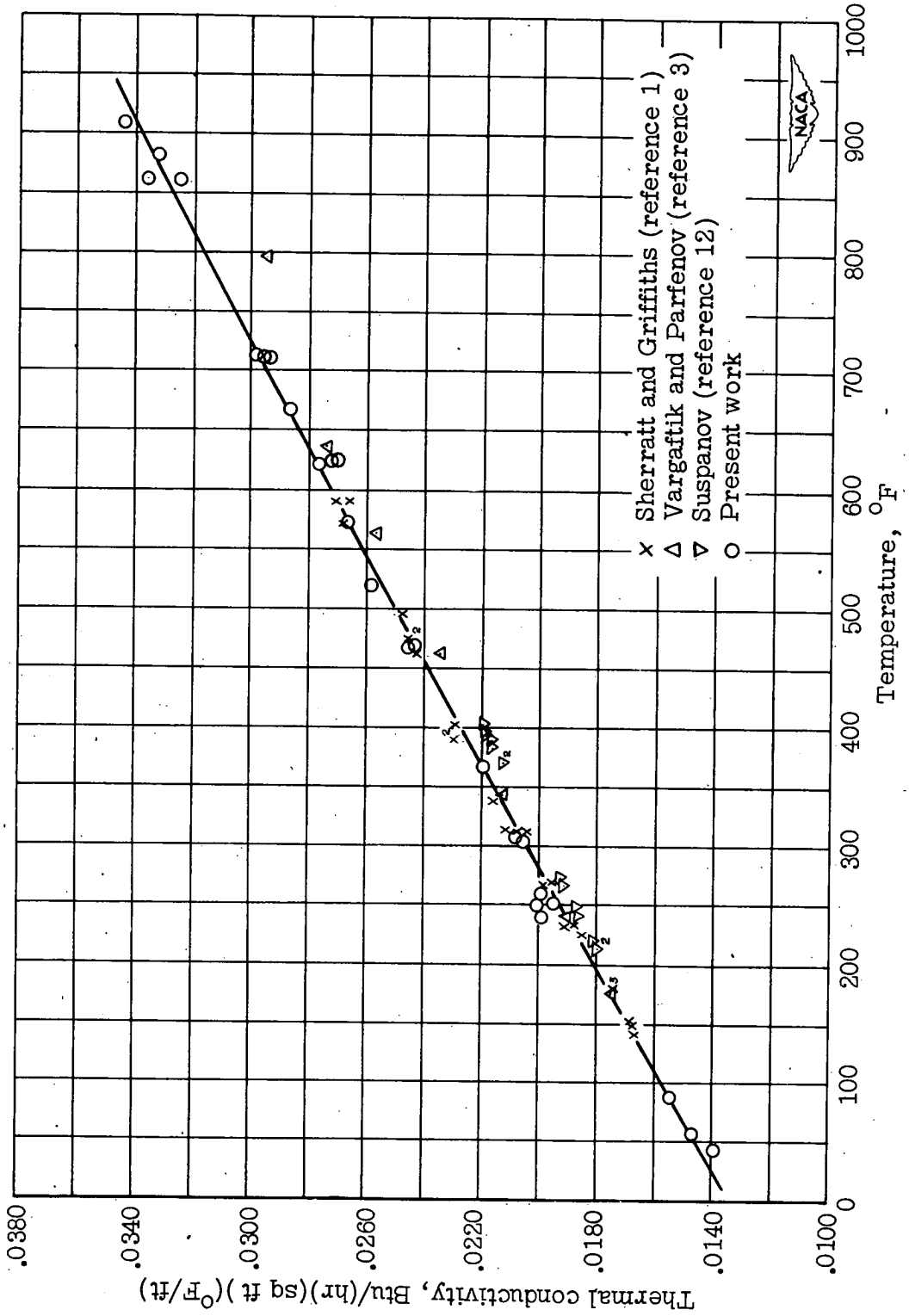


Figure 3.- Thermal conductivity of air plotted against temperature. (Numbers near data-point symbols represent number of measurements for which identical data were recorded.)

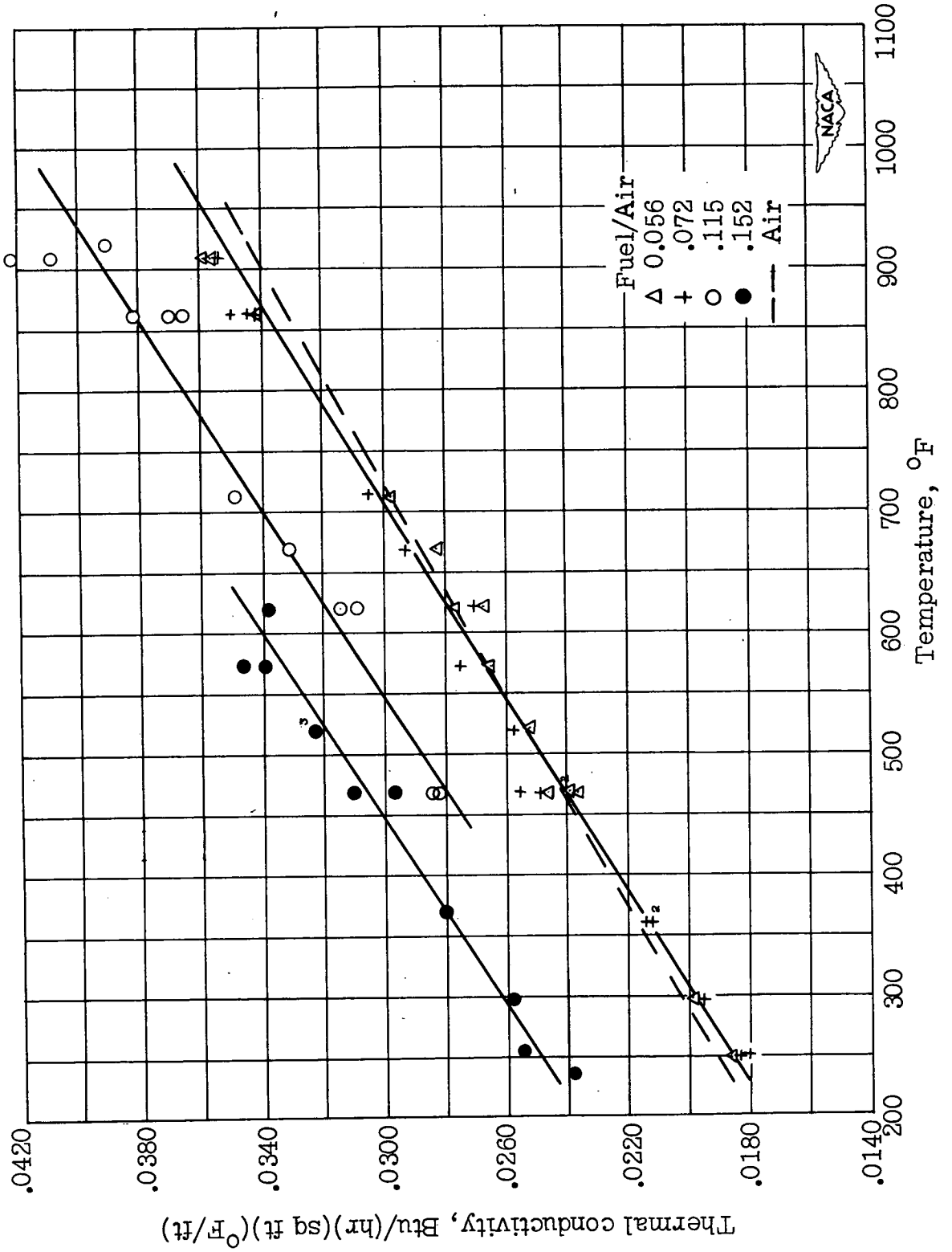


Figure 4.- Thermal conductivity of exhaust gases plotted against temperature. (Numbers near data-point symbols represent number of measurements for which identical data were recorded.)

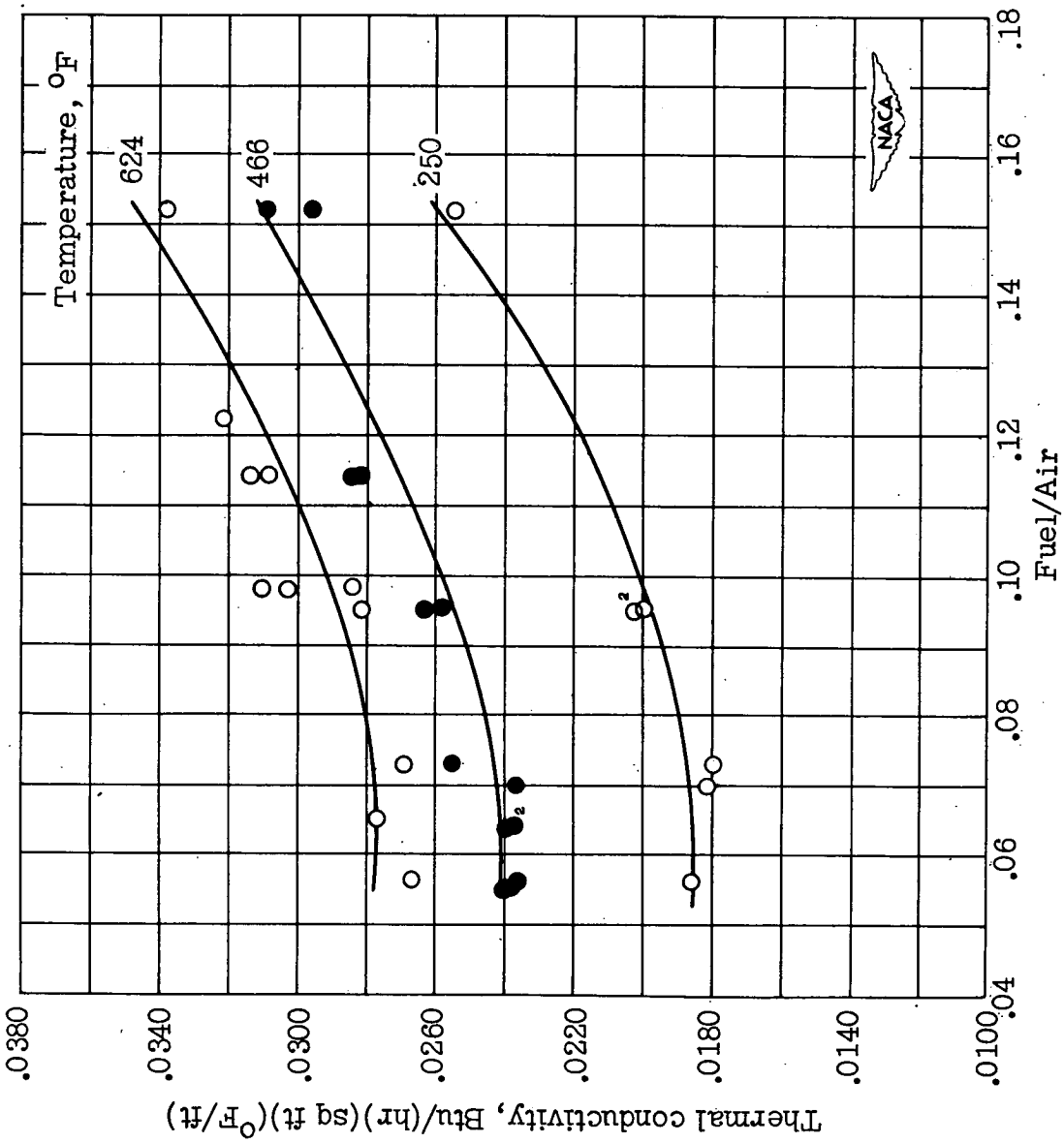


Figure 5.- Thermal conductivity of exhaust gases plotted against fuel-air ratio. (Numbers near data-point symbols are number of measurements for which identical data were recorded.)

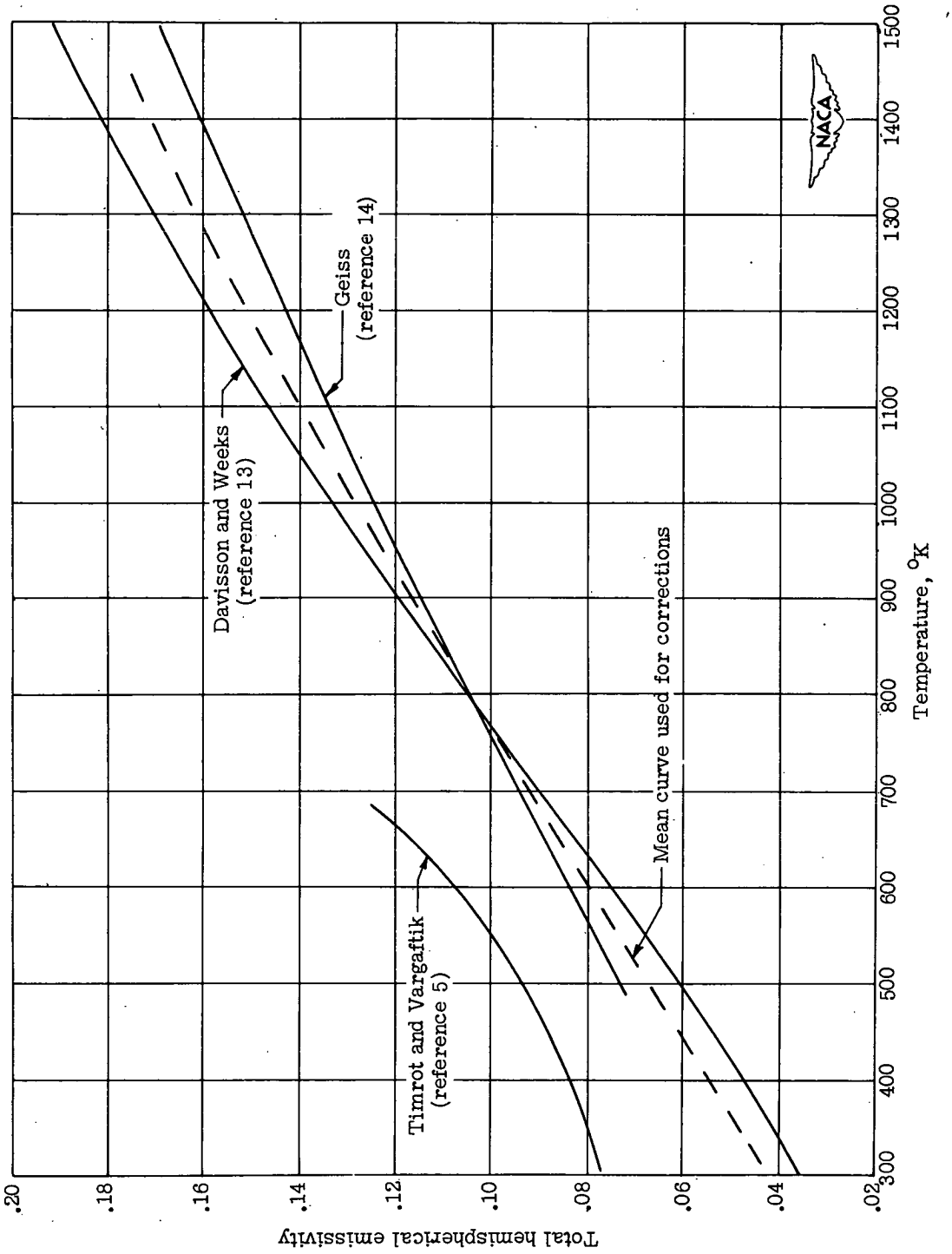
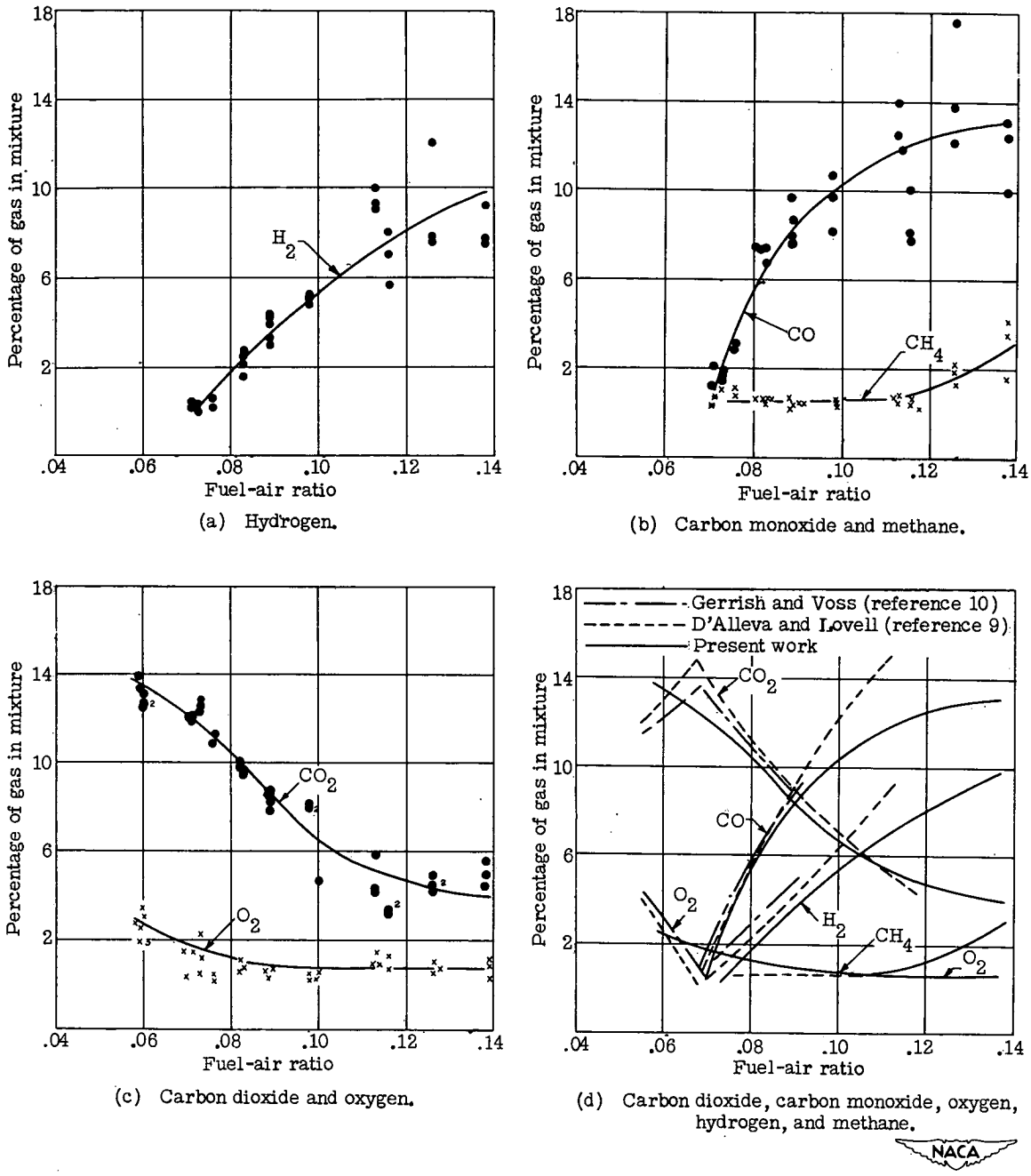


Figure 6.- Emissivity of platinum plotted against temperature.



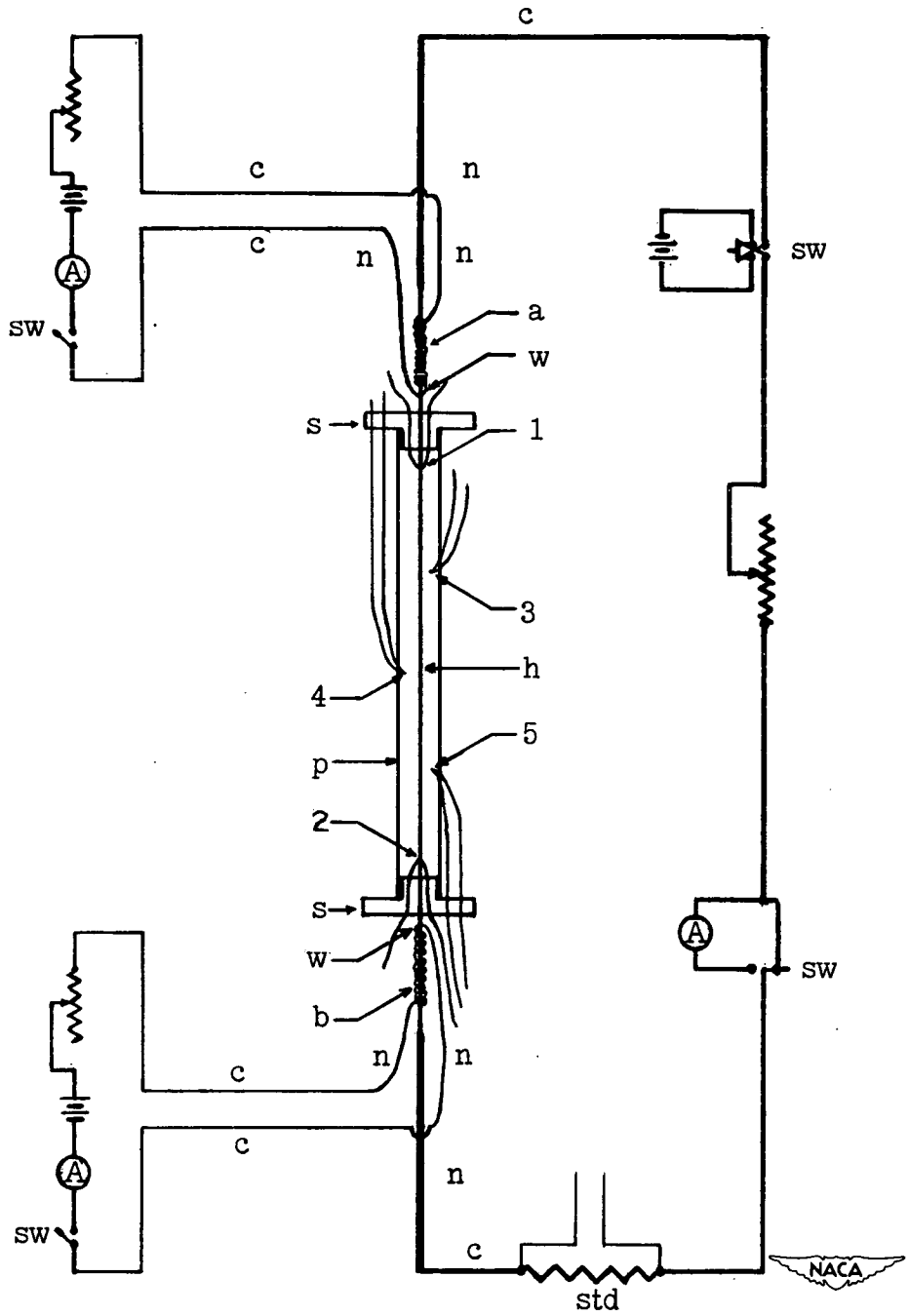
(a) Hydrogen.

(b) Carbon monoxide and methane.

(c) Carbon dioxide and oxygen.

(d) Carbon dioxide, carbon monoxide, oxygen, hydrogen, and methane.

Figure 7.- Exhaust-gas composition plotted against measured fuel-air ratio. (Small numbers near data-point symbols are number of determinations for which identical data were recorded.)



A ammeter
a,b auxiliary heaters, insulated from platinum wire except at w
c copper current leads
h hot wire
n nickel current leads
p platinum tube
s soapstone spacer
std 0.1-ohm standard resistor
sw switch
w Nichrome welded to platinum
1,2,3,4,5 platinum-rhodium thermocouple

Figure 8.- Diagrammatic sketch of test section and heater circuits.

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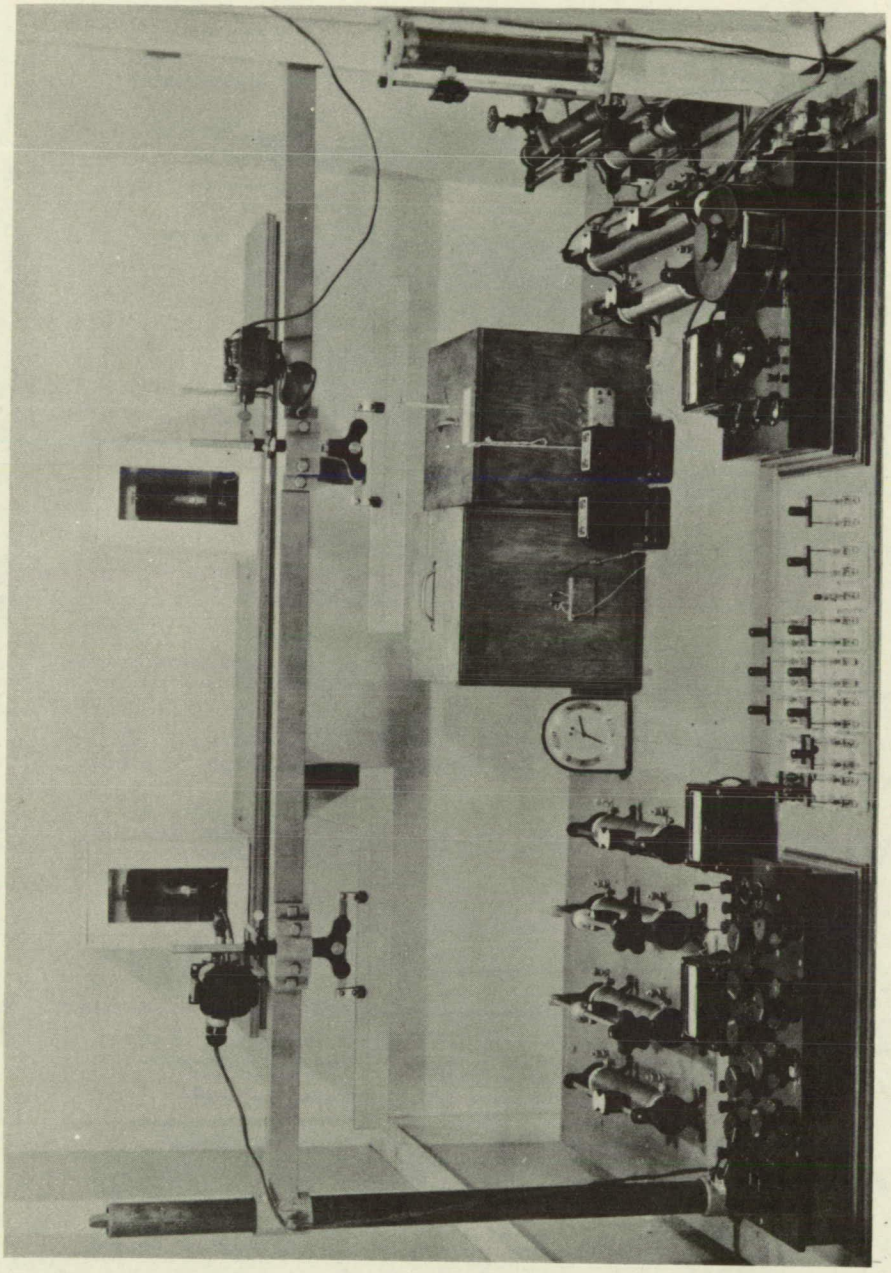

Figure 9.- Equipment used for electrical measurements.