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PRELIMINARY RESULTS OF NOBLE METAL THERMOCOUPLE RESEARCH PROGRAM - 1000 -2000 C

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SUMMARY REPORT

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FOREWORD

The research described herein, conducted at the National Bureau of Standards, Washington, D. C., is performed under NASA Contract C-19068-B, dated January 31, 1968, as NBS Project 4253439. The work is controlled by NASA Project Manager, I. Warshawsky, Chief of Instrument Research Branch, NASA Lewis Research Center and Technical Advisor, G. E. Glawe.

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ABSTRACT

This report describes the work performed to date on the Noble Metal Thermocouple Research program. The study involved the effects of combustion gases on three characteristics of noble metal thermocouples.

The areas reported here are: 1. An investigation to determine the effect of catalysis on platinum disclosed significant effects over the temperature range of 1000 to 1500 C at very low velocities. A facility was designed to extend these studies to higher flow rates. 2. Development, design, construction, and test of a facility for thermoelectric stability studies of the thermocouple combination 60% iridium 40% rhodium versus iridium at temperatures up to 2000 C in oxidizing media. 3. Development, design and initiation of construction of a facility for generating controlled temperature gradients so that their effects on thermocouple calibration may be determined.

SUMMARY

The research program sponsored by NASA involves three particular characteristics of temperature sensors, particularly noble metal thermocouples in combustion gas environments. Preliminary experimental studies have been made on Characteristic I. This is a study of the effects of catalysis on the temperature indication of noble metal thermoelements particularly platinum. Investigations were conducted over the temperature range 1000 to 1500 C and at very low velocities, 2×10^{-3} to approximately 9×10^{-3} meters per second. In these studies, the influence on catalysis error of such parameters as temperature and flow rate were evaluated for the following mixtures of gases:

(a) air +2% hydrogen

(b) air +2% carbon monoxide

The results of these preliminary investigations at very low flow rates indicates that catalytic effects can affect significantly the accuracy of noble metal thermocouple measurements up to 1500 C.

Since the flow rate of the combustible medium is one of the important parameters, a new facility is being planned to provide higher velocities over the thermoelements.

Characteristic II is concerned with the thermoelectric stability of a high temperature thermocouple system, namely 60% iridium 40% rhodium versus iridium, for measuring temperatures up to 2000 C in flowing gas oxidizing media such as air. A new facility has been designed and constructed suitable to investigate this and other performance characteristics. The principal unit of the facility is a furnace capable of

subjecting sample wires to an accurately known uniform temperature zone, in controlled atmospheres, including oxidizing mixtures, at temperatures up to 2000 C, and testing the samples without removing the operative portions from the uniform hot zone.

Characteristic III is an investigation of the effects of temperature gradients on the accuracy and stability of thermocouple measurements. After exploratory experiments were conducted, a Nd:YAG laser was chosen as the heat source to raise the thermocouple junction to a temperature of 2000 C. This concentration of heat at the junction would allow for both small and steep gradients along the lead wires of the thermocouple.

1. INTRODUCTION

The measurement of temperature can involve studies whose base can be as broad as the many fields in which temperature transducers are used. In most applications involving measurement and control of prime movers, temperature is of fundamental importance as a guide to successful operation of the equipment. At present, the thermocouple is one of the most important sensors for temperature measurement. The vast majority of thermocouples now in use as high temperature sensors in the temperature range of 1100 to 2000 C are made from noble metals, such as platinum, rhodium, iridium and their various alloys. These metals provide thermocouples whose characteristics include high melting point, stable temperature-emf relations in oxidizing atmospheres and low emissivity to reduce radiation effects. Because of these features, noble metal thermocouples are used in aerospace-power research.

A research program on noble metal thermocouple performance, sponsored by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio under NASA Contract C-19068-B dated January 31, 1968, NBS Project 4253439 involves three areas in which temperature sensors, particularly noble metal thermocouples, are affected in gaseous mixtures which contain combustibles.

Characteristic I is a study of the effects of catalysis on the temperature indication of noble metal thermoelements, particularly platinum 13% rhodium and platinum wires. Earlier investigators Dahl and Fiock (ref. 1), Stanforth (ref. 2), Olsen (ref. 3) and Alverman and Stottman (ref. 4) observed that in air breathing systems, working with hydrocarbons as fuel, gas mixtures are present whose reactions can be initiated or accelerated under the influence of catalysts. Thus, in measuring the temperature of gases by means of noble metal thermocouples there is danger that, because of catalytic effects, certain reactions are initiated or accelerated in which thermal energy is liberated. This will result in an increase in the temperature of the thermocouple, so that the indicated temperature is higher than the temperature of the medium.

The investigations conducted at the National Bureau of Standards and elsewhere by the earlier experimenters indicated that catalysis by thermocouple wires significantly affected the accuracy of temperature measurement below 650 C, and to a lesser degree up to 1000 C. The significance of catalysis on the higher temperature ranges was not clear. Investigation of catalytic effects above 650 C was complicated by the fact that 650 C is close to the autoignition point of the fuel or gas mixture used. Consequently, it was difficult to separate the temperature rise resulting from normal combustion from the temperature increase caused by catalytic activity. However, the preliminary results of the Characteristic I investigations conducted at NBS under this contract, give evidence that with improved instrumentation, catalytic effects can be evaluated over the planned temperature range of 1000 to 1500 C with the chosen gaseous combustible mixtures.

Characteristic II is concerned with the determination of the thermoelectric stability of a thermocouple system considered for measuring temperatures up to 2000 C in a flowing oxidizing medium such as air. At the present time only iridium and alloys of iridium appear suitable for use at these temperatures and conditions. Much work has been done to provide comprehensive reference tables for thermocouples of iridium-rhodium alloys versus iridium. The work done by Blackburn and Caldwell (ref. 5) covered the alloys from the standpoint of most usefulness such as 40, 50 and 60 percent rhodium. The study did not yield results on which a definite preference could be based or indicate the thermoelectric stability of the various combinations.

Very little information is available on the thermoelectric stability of iridium and alloys of iridium-rhodium in oxidizing atmospheres. Lapp and Maksimova (ref. 6) studied the thermoelectric stability of iridium wire in vacuum and argon at 1800-2000 C. Rudnitskii and Tyurin (ref. 7) observed changes of thermal emf of the iridium 60% rhodium versus iridium system after 10 hours at 1800 C. The total change did not exceed 0.8% of the measured temperature.

Walker, Ewing, and Miller (ref. 8) studied iridium thermoelements in air at 1380 C and checked periodically at 860 C against a reference element of like material and observed changes of 36 μV after 120 hours. This change is equivalent to about 6 C for an iridium-50% rhodium versus iridium thermocouple. The change in the alloy leg was about 3 times as great. Aleksaklin, Lepin, Lapp and Bragin (ref. 9) observed at 2000 C that iridium-60% rhodium versus iridium thermocouples allow sufficient accuracy to measure the temperature for a period of 10 to 20 hours.

Much work has been done with an alloy of 60 percent rhodium. Carter (ref. 10) proposed to replace this alloy with either 40 or 50 percent rhodium. Carter assumed that at high temperature the iridium will volatilize from the iridium-rhodium alloy preferentially and the alloy will change in composition, becoming enriched with rhodium. Since the emf output is a maximum for the 50% rhodium alloy, the thermal output of the original 40% rhodium alloy will then increase slightly to a composition of 50% rhodium then decrease slightly to a composition of 60% rhodium. Thus, as all these major compositions provide almost the same output, the thermoelectric response will remain satisfactory for a longer time.

It is the 60% iridium 40% rhodium versus iridium thermocouple combination that the second phase of this study is concerned with. Its thermoelectric stability is being investigated at temperatures up to 2000 C in oxidizing media.

The third characteristic of this program is development of a method to determine the effects of temperature gradients typical of those that are encountered in practical applications of interest. Thermocouples will be exposed to these gradients in gaseous environments of interest at temperatures up to 2000 C and the effects on performance will be analyzed and evaluated.

2. APPARATUS AND TEST PROCEDURE

I. The investigation to determine catalytic effects on noble metals received first priority. However, the velocities used were only about one-thousandth of those that are encountered in aircraft propulsion research. The effect of catalysis on the temperature indication to be expected of thermocouple-wire pairs was initially evaluated by using single wires of the positive and negative elements that are resistance heated to achieve exposure temperature. The thermoelements specified for this study were 87% platinum-13% rhodium and platinum. Procurement of these thermoelements was accomplished and the wires were tested to assure that they are of thermocouple grade reproducible in composition and thermoelectric force. The wires are homogeneous and the thermal output when made into thermocouples conforms to the table values given in NBS Circular 561, Reference Tables for Thermocouples, to within ± 0.25 percent of the values tabulated. The thermoelements are smooth and of uniform cross-section.

Preliminary studies were made with platinum wire test samples located in the low-velocity catalysis chamber. Figure 1 shows the test facility as it is used and Figure 2 is a general schematic diagram with the test element in position. In the course of putting the test facility into operation, exploratory measurements were made on a 0.8 mm platinum wire of NBS storeroom grade and on a gold wire which was expected to be free of catalytic effects. After the operation of test facility and instrumentation was debugged, preliminary measurements on the newly acquired thermocouple grade wire was begun.

The test element was formed into a hair-pin configuration as shown in Figure 3. The wire was 200 mm in length and 0.8 mm diameter. Platinum wires of 0.3 mm diameter serving as voltage leads were welded to the test element. The sample was electrically heated to various temperatures between 900 and 1500 C by use of a current-regulated dc power supply. Three parameters were measured after the temperature of the test element had reached temperature stability, i.e., a change of less than 1.0°C/10 minutes.

The parameters are as follows:

1. The dc current flowing through the sample.
2. The voltage drop (IR) across the 150 mm test length of the sample.
3. The brightness temperature of the test element as determined with a calibrated optical pyrometer.

The above parameters were first measured at each temperature with air only flowing through the test chamber. Then with the mixture of air plus a known amount of a combustible gas. The mixtures used were first air plus 2% hydrogen (2% H_2-air) and later air plus 2% carbon monoxide (2% CO-air).

Measurements were made on a 0.8 mm diameter platinum test sample with air and then a combustible mixture of 2% H_2-air at velocities of 2.2×10^{-3}, 4.4×10^{-3}, 6.6×10^{-3} and 8.8×10^{-3} meters per second.

Additional data were obtained with a second 0.8 mm diameter platinum wire sample and a 0.5 mm diameter platinum wire in the catalysis chamber. The former of the two samples was exposed first to an air environment and then to 2% CO-air flowing at 2.2×10^{-3}, 4.4×10^{-3}, 6.6×10^{-3} and 8.8×10^{-3} meters per second. The latter sample was exposed to the same environmental conditions except at a velocity of 2.2×10^{-3} meters per second.

II. The major portion of the work on Characteristic II consisted of development, design and procurement of a test facility and procurement of the necessary thermocouple materials. The furnace facility was designed to maintain an oxidizing atmosphere at 2000 C for extended periods with four zirconium oxide test cells located inside a tantalum heating element. During operation of the furnace at temperatures between 1500 and 2000 C, a hot zone uniform in temperature to within ± 1% is maintained inside the heating element over approximately 460 mm of its length.

This approach allows a sufficient length of thermocouple wire to be in a zone of constant temperature. When periodic checks are made, all segments of the thermocouple--the segment remaining in the constant temperature zone, the section located in a region of gradients, and the portion now at room temperature--will have been aged at the test temperature for the test period. In this way the segment of thermocouple that had been exposed to the temperature gradient will not contribute to the thermoelectric output, so that it is assured that observed changes in thermal output are due to aging at the test temperature.

The furnace is provided with a tantalum tube temperature well within which a calibrated thermocouple is located so that a good indication of the true temperature of the four zirconium tube test cells can be obtained. Also attached normal to the well is a small tantalum tube serving as a blackbody or target so that optical measurements of temperature can be made simultaneously.

III. Characteristic III is an investigation of the effects of temperature gradient on the accuracy and stability of thermocouple measurements at temperatures up to 2000 C. The materials involved are the same as for Characteristic II. The work performed has consisted of experiment and study to develop a means of heating the thermocouple wires, and forming the required gradients without affecting the flow of gas over the thermocouple. A laser was the ultimate choice to provide the necessary temperature and gradient. Experiments were performed with argon ion, CO_2, and Nd:YAG lasers. Only the Nd:YAG provided sufficient intensity to raise the temperature to the specified 2000 C.

The exploratory laser experiments provided an unexpected benefit in facilitating fabrication of thermocouples. Initial difficulties in shaping and welding iridium and iridium-rhodium alloy wires were overcome in this way. Photograph 4 shows the parts of a thermocouple made of 0.8 mm wire of these materials and Photograph 5 shows them assembled. Achievement of the straight butt weld no larger than the diameter of the wire requires exceptional skill and patience when done by torch welding. The laser was found to provide much better control in welding and shaping these difficult materials.

3. DISCUSSION OF RESULTS

The results of the experiments on catalysis by noble metal thermocouple materials at very low gas velocities are from preliminary measurements. The work in its initial phase consisted of studying catalysis by thermocouple wires of the same composition, namely pure platinum, as it is affected by such parameters as:

1. Gas composition having stoichiometric fuel-oxygen compositions.
2. Flow rate and temperature, separately or synergistically.
3. Wire properties such as size (diameter).

The preliminary measurements show a temperature increase which appears to be due to catalysis over the entire temperature range of 1000 to 1500 C, for the gas mixtures studied. Figure 6 is a plot showing a comparison of the catalytic error observed in two platinum test samples with one exposed to a 2% H_2-air mixture and the other to a

2% CO-air mixture. The error resulting from catalysis of the 2% H_2-air on the platinum element was observed to be greater at 1000 C than that obtained from the mixture of 2% CO-air. It appears to decrease as the temperature increases to 1500 C, so that effects appear to be nearly alike at the higher temperature. The velocity in both cases was 6.6 x 10^{-3} meters per second, at a pressure level of approximately 1 atmosphere.

Figure 7 shows the effect of flow rate on catalysis error. The temperature rise caused by catalysis appears to be nearly proportional to flow rate in the range .002 to .01 meter per second. The greater flow of combustible gases over the resistance element produces more combustion, transferring more heat to the wire while thermal loss by radiation is increased only slightly by the higher temperature of the wire. The magnitude of the effect at the lowest temperature in on the order of what might be expected from a heat balance between rate of combustion and the rate of convective heat transfer. It should be understood that extrapolation of these conclusions to higher velocities is not warranted by these experiments. On the contrary, one would expect the heating effect to fall off when the time that a gas molecule is in contact with the wire surface becomes short compared to the reaction-rate time constant of the combustion reaction. Measurements obtained with increasing wire temperature agree with measurements obtained with decreasing wire temperature within ± 1.0 C.

Figure 8 shows the catalytic temperature rise becomes greater with a decrease in wire diameters. Since the surface to mass ratio for a given length increases with decreasing diameter, the results are as expected.

4. CONCLUSIONS

The preliminary results indicate temperature sensing instruments made from platinum materials are subject to errors from catalysis in the temperature range of 1000 to 1500 C, when used to measure the temperatures of the two gaseous mixtures studied in these experiments at very low gas velocities. The plots show the magnitude of the error to be dependent upon the type of combustible in the air mixture, flow rate of the medium and the wire size. Additional expanded studies of these parameters and other influencing factors on the magnitude of the catalytic temperature rise will follow these preliminary experiments.

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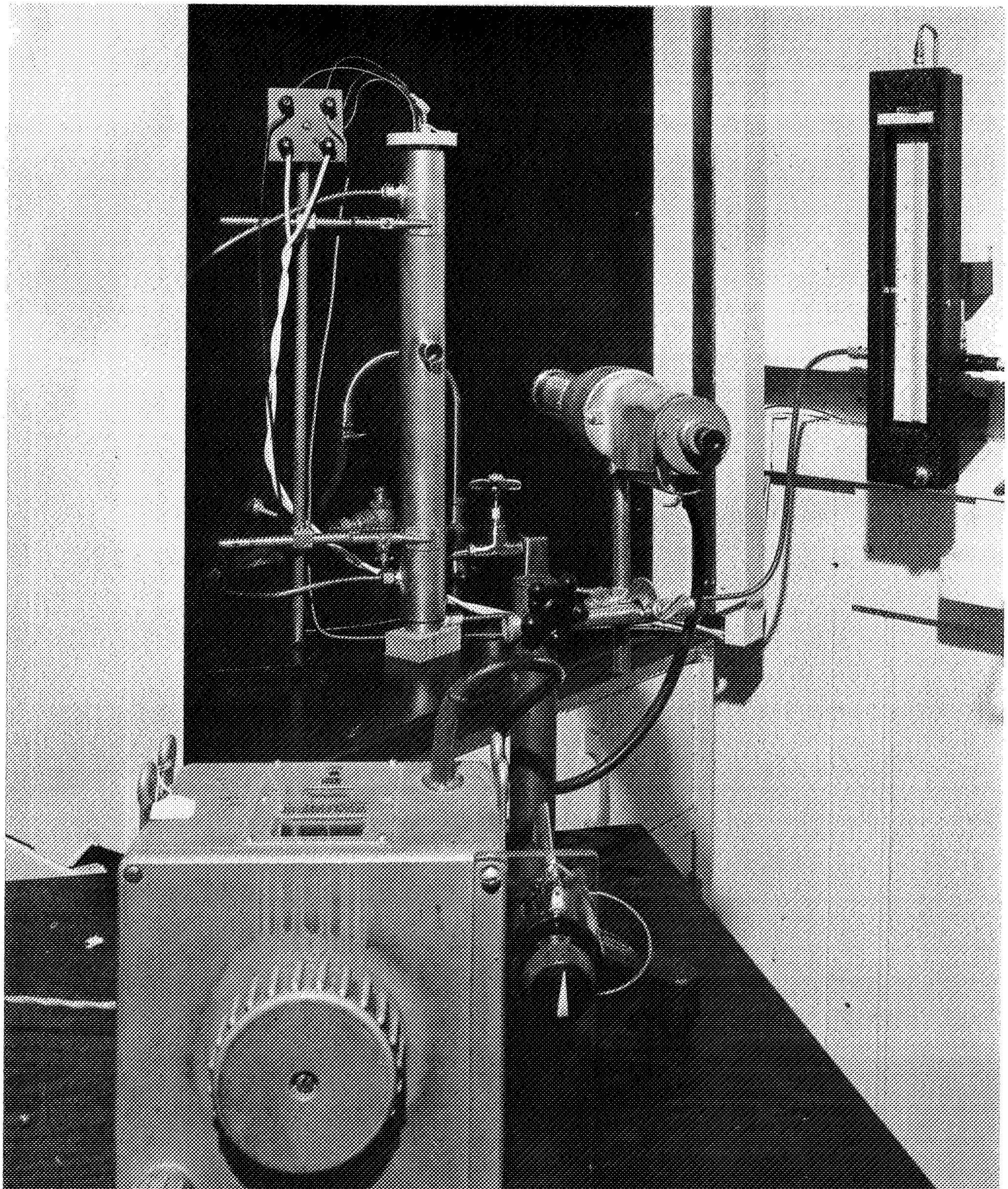

FIGURE 1. - CATALYSIS TEST FACILITY

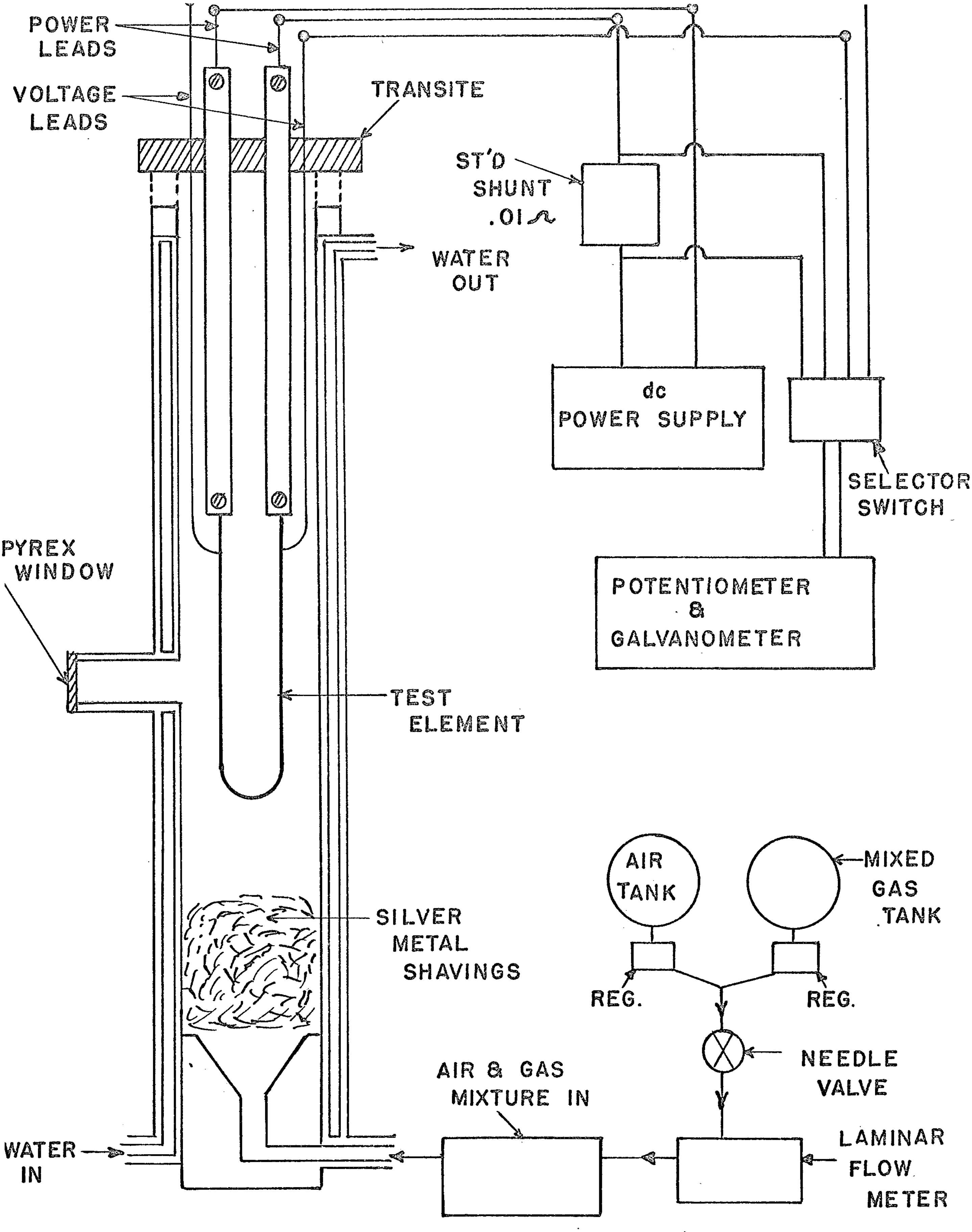

FIGURE 2.–SCHEMATIC DIAGRAM OF FACILITY WITH THE TEST ELEMENT IN POSITION

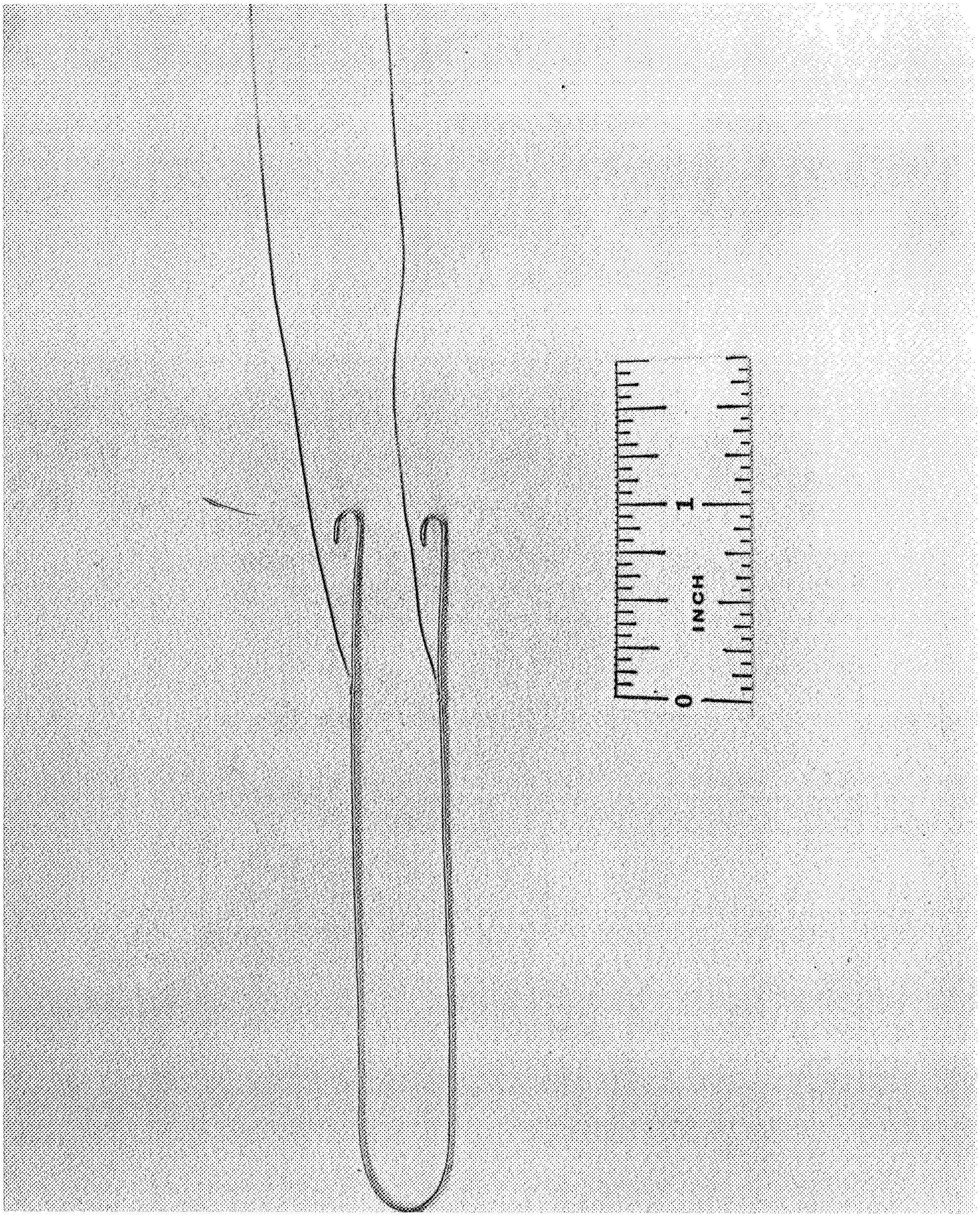

FIGURE 3. - SAMPLE TEST ELEMENT

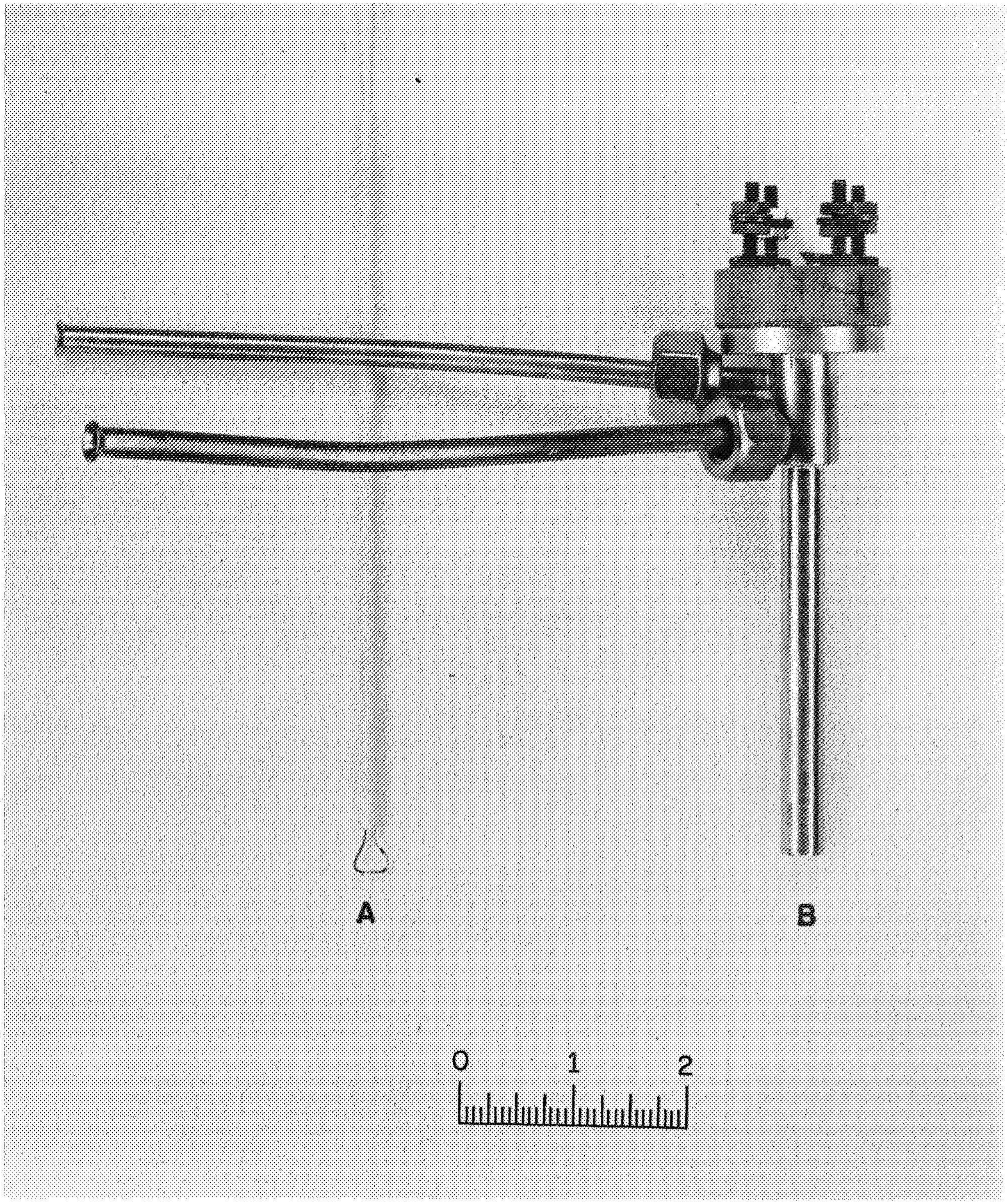

FIGURE 4. - COMPONENT PARTS OF WATER-COOLED THERMOCOUPLE

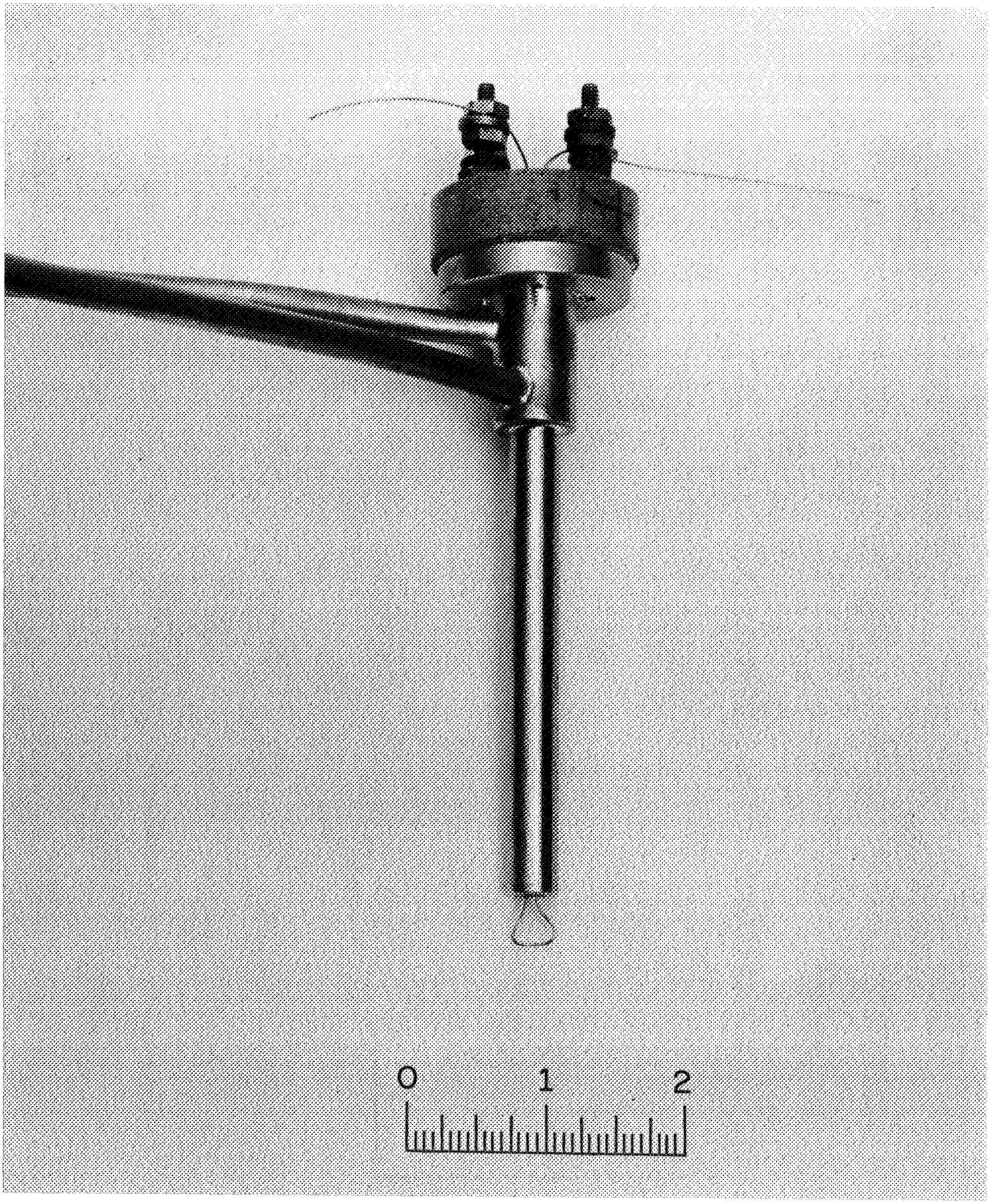

FIGURE 5. - ASSEMBLED WATER-COOLED THERMOCOUPLE

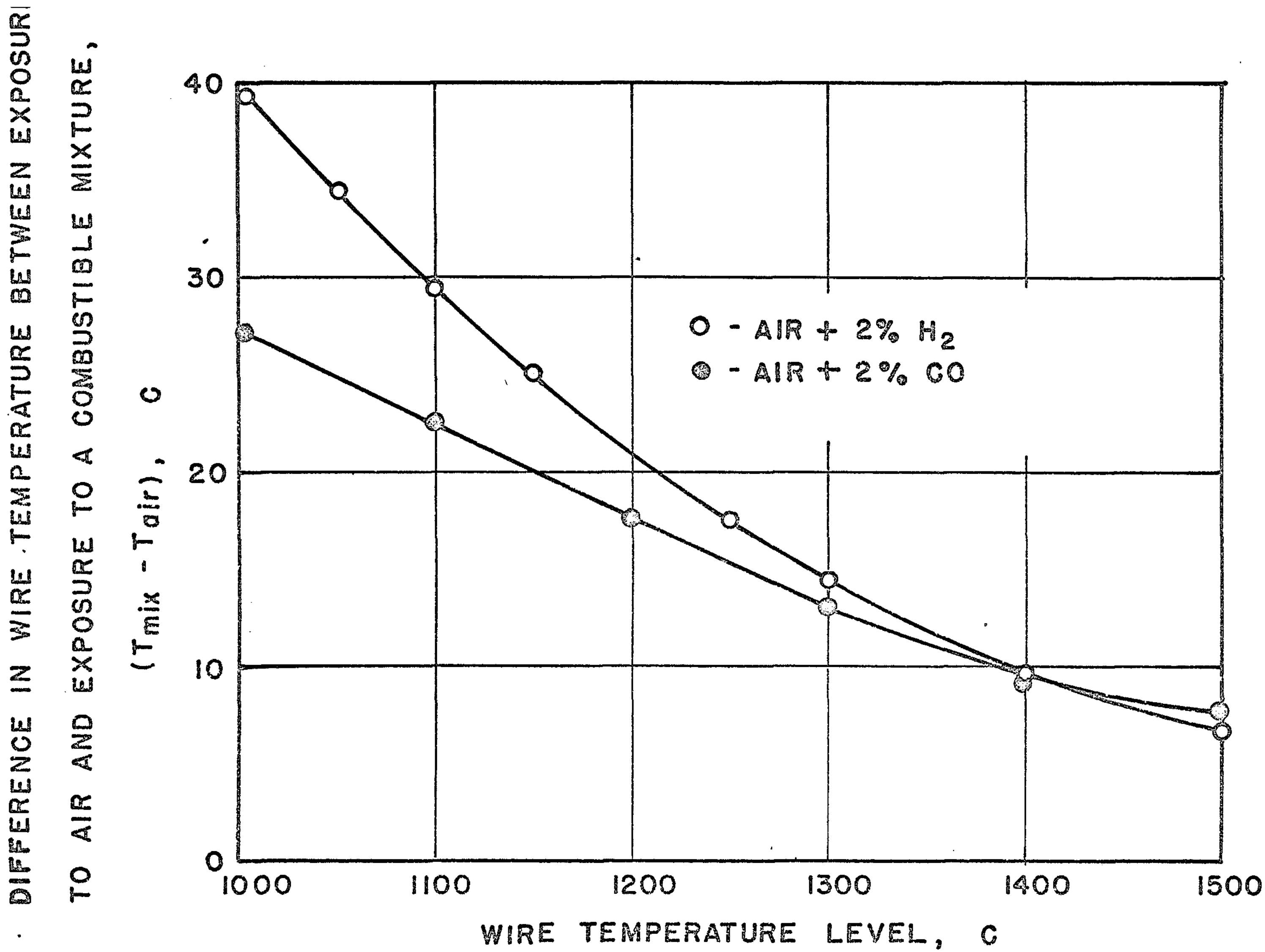

FIGURE 6.–CATALYTIC ERROR FOR 0.8 mm DIAMETER PLATINUM WIRES FOR TWO COMBUSTIBLE MIXTURES FLOWING AT 6.6×10^{-3} METERS PER SECOND

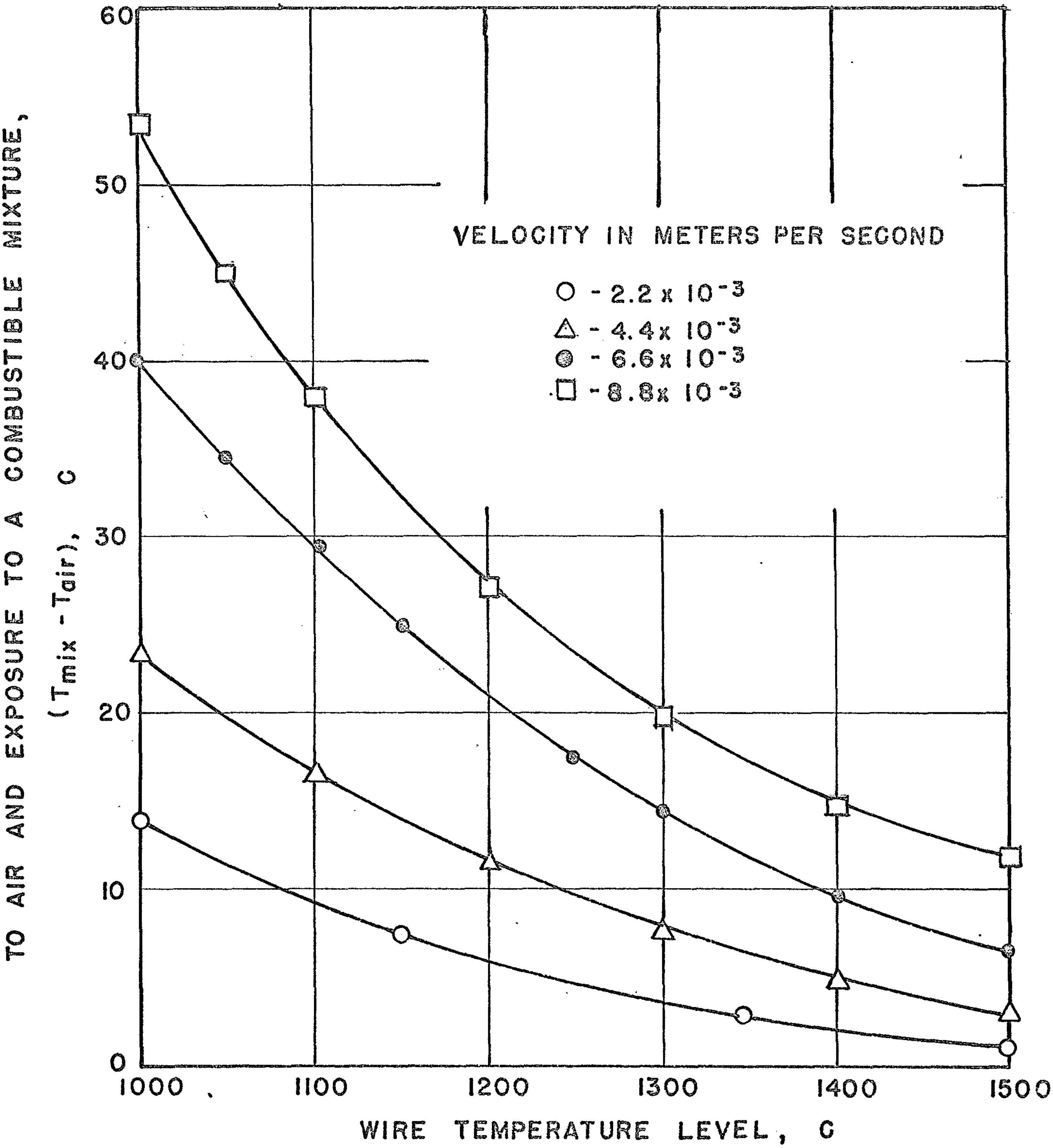

FIGURE 7.–VARIATION IN CATALYTIC ERROR FOR 0.8 mm DIAMETER PLATINUM WIRE EXPOSED TO AIR + 2 % H_2 MIXTURE FOR VARIOUS FLOW VELOCITIES

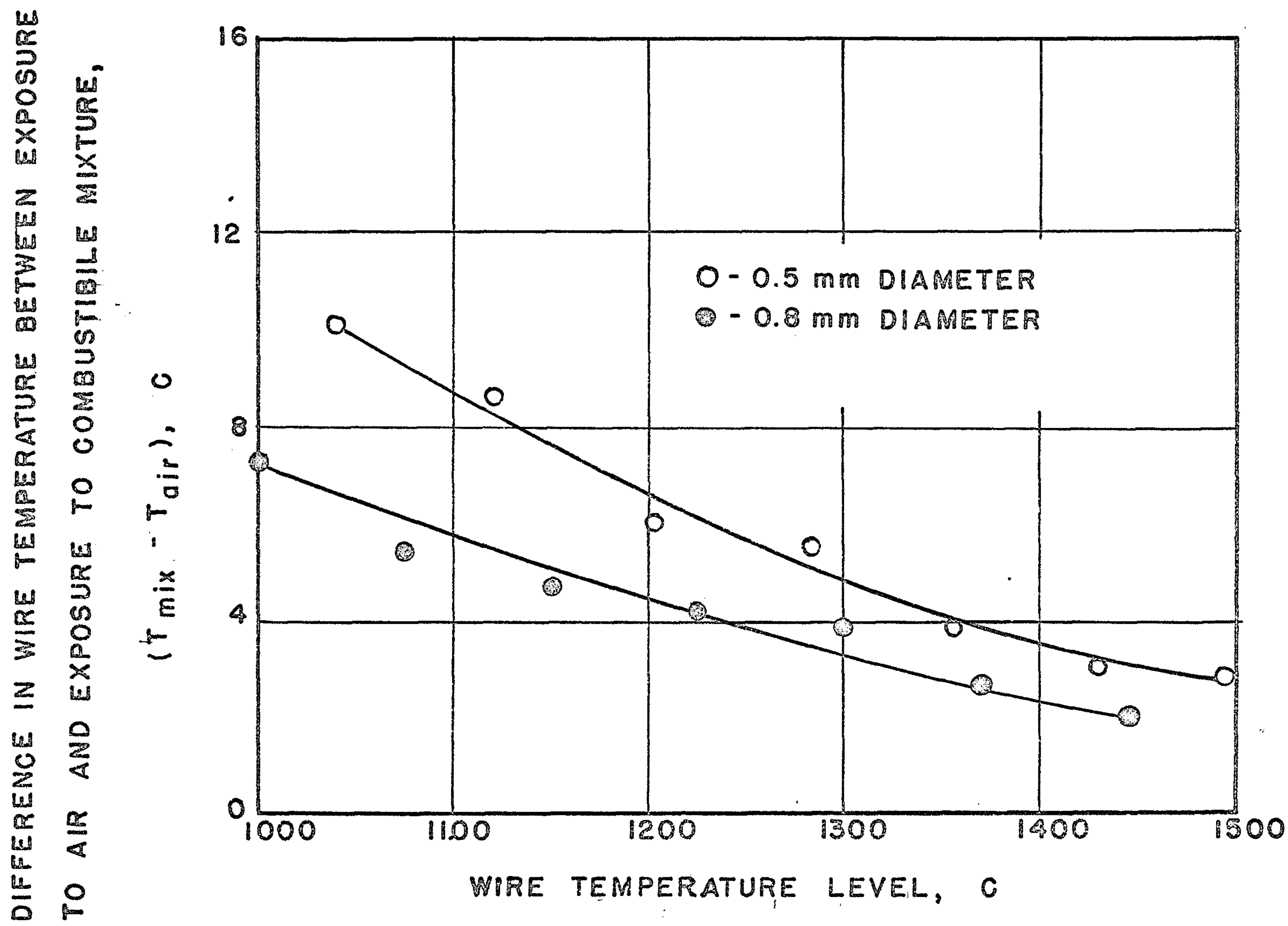

FIGURE 8.-FOR TWO SIZES OF PLATINUM WIRE AT A FLOW RATE VELOCITY OF 2.2×10^{-3} METERS PER SECOND IN AN (AIR PLUS 2% CO) MIXTURE