ANL-4938

Argonne National Laboratory

APPARATUS FOR THE MEASUREMENT OF THE THERMAL CONDUCTIVITY OF SOLIDS

JAMES L. WEEKS and RALPH L. SEIFERT

DISCLAIMER

ANL-4938
Chemistry

30977

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

APPARATUS FOR THE MEASUREMENT OF THE THERMAL CONDUCTIVITY OF SOLIDS

James L. Weeks and Ralph L. Seifert

Chemistry Division

December 8, 1952

Operated by The University of Chicago
under
Contract W-31-109-eng-38

APPARATUS FOR THE MEASUREMENT OF THE THERMAL CONDUCTIVITY OF SOLIDS

by

James L. Weeks and Ralph L. Seifert

ABSTRACT

An apparatus has been developed with which thermal conductivities can be measured in the temperature range from 40°C to 100°C with a probable error of ± 0.003 cal sec^{-1} cm^{-1} deg^{-1} or ± 3 per cent, whichever is the larger. It requires only a small sample (0.1875 x 0.1875 x 1.75 inches), does not require the attaching of thermocouples to the sample, and permits introduction and removal of the sample by remote control, if this is necessary. The apparatus is therefore especially useful to measure the thermal conductivity of large single crystals and also to observe the effect upon thermal conductivity of heat treatment, irradiation, or any other treatment which will not deform the sample yet which cannot be carried out readily with thermocouples attached to the sample.

INTRODUCTION

Various forms of apparatus have been used to measure the thermal conductivity of solids by the longitudinal heat flow method. In this method a thermal gradient is established longitudinally in a sample while zero gradient is maintained laterally by use of a properly heated guard ring. The longitudinal temperature gradient in the sample is usually measured by imbedded thermocouples. The rate of heat flow at a given temperature gradient has been measured by use of a calorimeter heat sink at the cool end of the sample[1] or by the temperature gradient established in a known sample placed in series with the unknown.[2] The accurate methods that have been used require rather large samples in which must be imbedded thermocouples at known distances from each other, and the assembly of the required

---

[1]A.S.T.M. tests C182-47, C201-47, C202-47; 1949 Book of A.S.T.M. Standards, Part 3 (American Society for Testing Materials, Philadelphia, Pa., 1950), pp. 454-456, 467-473, and 427-430.

[2]M. S. Van Dusen and S. M. Shelton, J. Research Natl. Bur. Standards 12, 429-440 (1934).

apparatus is not readily adapted to remote control operations. The following apparatus is free of these disadvantages.

APPARATUS

This apparatus is based on the same principle as that of Van Dusen and Shelton.[2] Armco iron of known thermal conductivity is used as a reference standard. A small electric heater at the end of an Armco iron rod supplies heat that flows through the iron rod, through the sample, and then through another Armco iron rod to a heat sink. The iron rods and sample are surrounded <u>in vacuo</u> by a radiation shield which is maintained approximately at the temperature and temperature gradient corresponding to that of the iron rods and sample. Under these conditions very little heat is lost from the sides of the rods and sample, and the thermal conductivities of the sample and of the Armco iron rods are inversely proportional to their temperature gradients and their cross-sectional areas. The conductivity of the iron being known, that of the sample is readily calculated. The temperature gradient in each of the Armco iron rods is measured by imbedded thermocouples. The temperature gradient in the sample is determined from the measurement of its surface temperature at two points. Boyer and Buss[3] have discussed the difficulties involved in the measurement of surface temperatures and have designed a thermocouple compensated for heat losses so that it could be used to measure surface temperatures accurately. Their design is based on the principle that there will be no heat loss from a thermocouple junction that is present in isothermal surroundings. The thermocouples used in this apparatus to measure the surface temperature of the sample operate on the same principle. Tests made with such thermocouples indicated that surface temperatures can be measured within ± 0.1°C.

A sketch of the apparatus is shown in Figure 1. The sample is in the form of a rectangular parallelepiped, 0.1875 x 0.1875 x 1.75 inches, or of a cylinder, 1.75 inches long and 0.22 inch in diameter. It is placed inside the radiation shield assembly at the center of the apparatus. Note that the sample itself is not shown in Figure 1. Actually, the upper radiation shield should be shown in the "up" or retracted position to be consistent with the retracted bellows of the heat source and sink as shown. The radiation shield assembly is shown in greater detail in Figure 2. Near each end of the radiation shield, four thermocouples are placed at exactly the same distance from the end of the shield and are therefore in the same plane, which is perpendicular to the axis of the sample. Of each group of four thermocouples, two are mounted on small quartz blocks. The junctions of these two thermocouples are covered with a ball of silver solder about 0.03 to 0.04 inch in diameter.

---

[3]M. W. Boyer and J. Buss, Ind. Eng. Chem. <u>18</u>, 728-9 (1926).

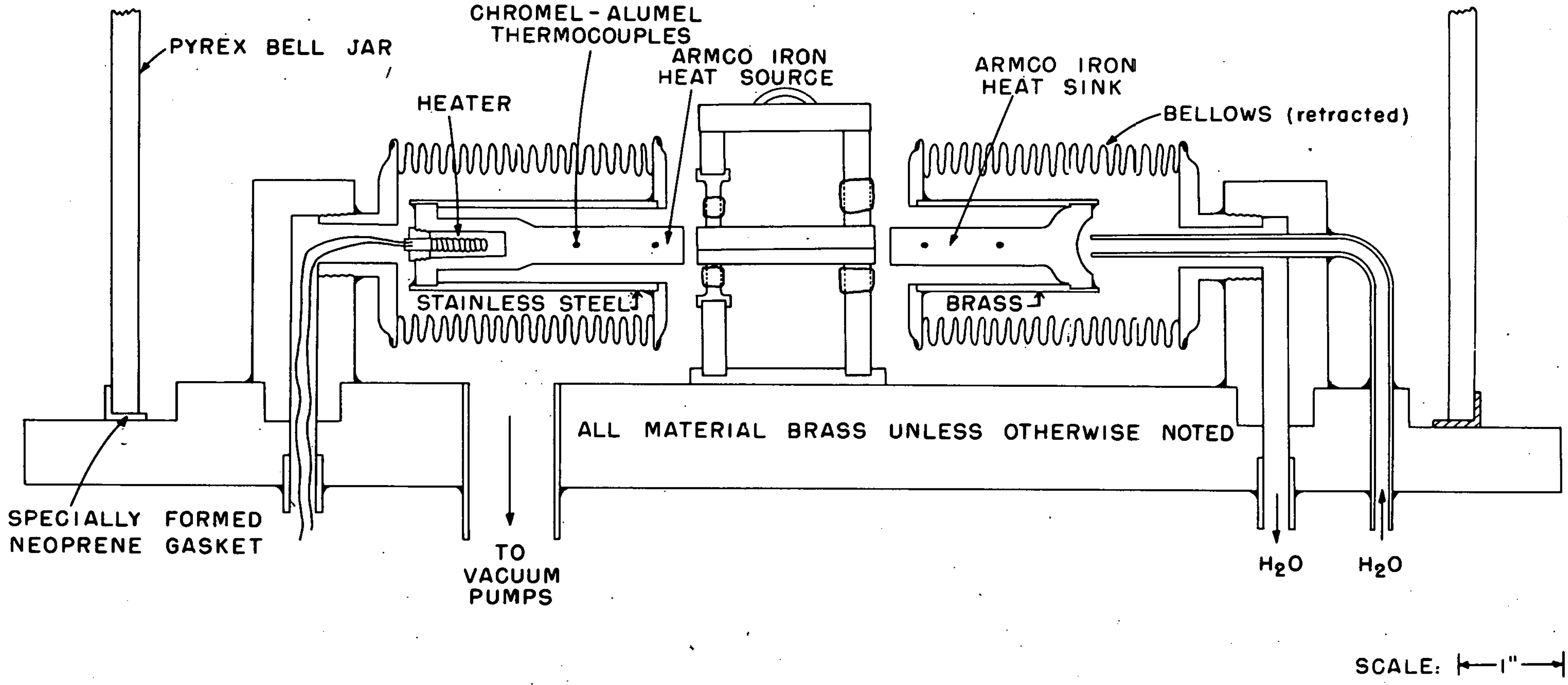

FIGURE I.

THERMAL CONDUCTIVITY APPARATUS.

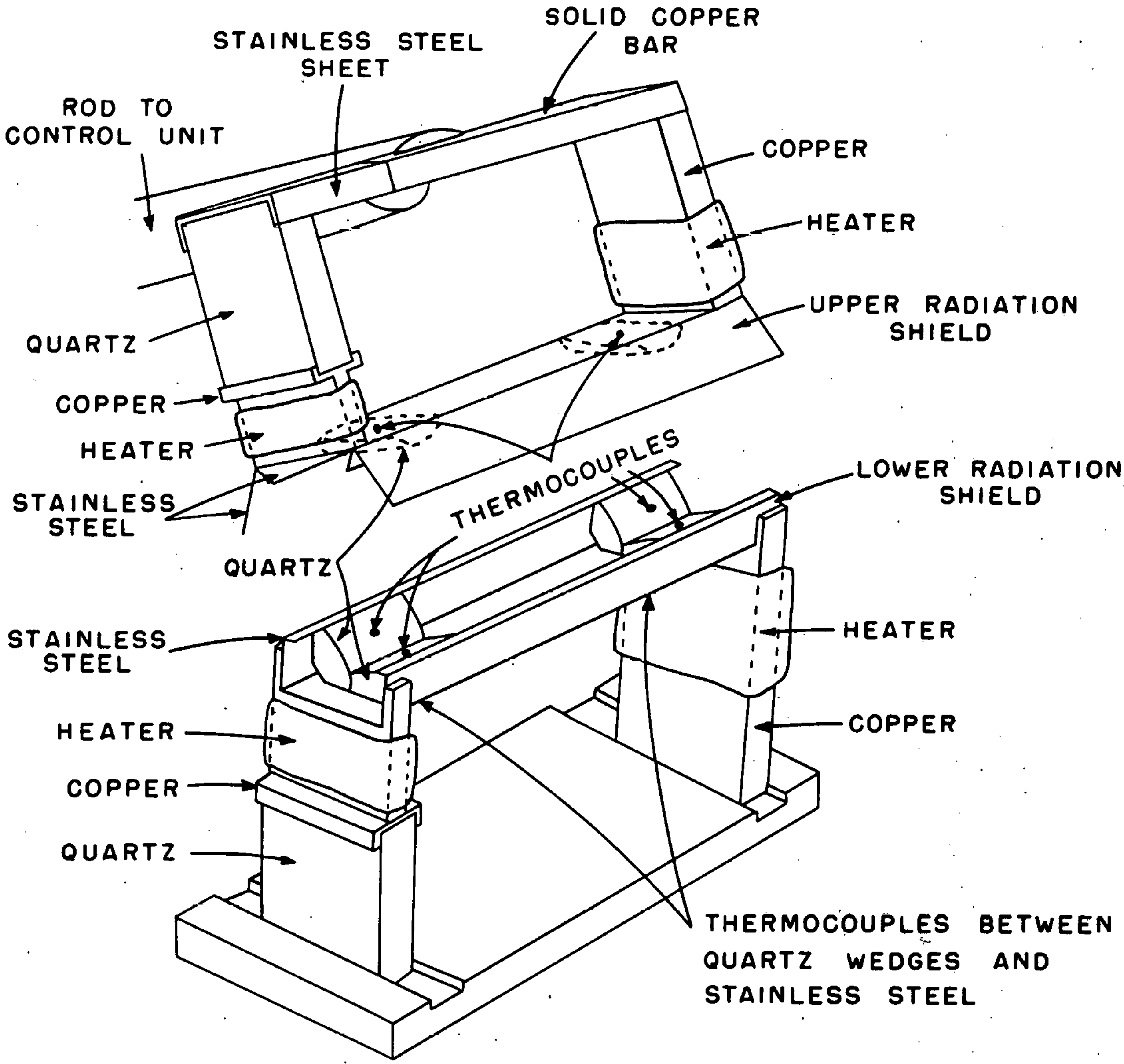

FIGURE 2.

RADIATION SHIELD ASSEMBLY.

The sample is supported at each end by these junctions. At each end, the junction of a third thermocouple is sealed between the quartz wedges and the lower stainless steel radiation shield. The fourth thermocouple is sealed between the upper stainless steel radiation shield and a semi-cylindrical piece of quartz, which presses down on the sample when the upper shield is in place. The leads from the thermocouples (not shown in Figure 2) are sealed to the radiation shield but insulated from it by refractory cement. To avoid heat loss from the junctions all thermocouples in the apparatus are constructed from 3-mil chromel-P and 3-mil alumel, and about a 2-cm length of each lead from the couples in the radiation shield assembly is sealed to the shield approximately in the plane of the junctions. Heaters are provided on the supporting posts at each end of the shields to permit adjustment of the temperature and temperature gradient of the shield to correspond to that of the sample at all points.

To insert or remove a sample the upper radiation shield can be lifted and pushed back. This is made possible by the control unit shown in Figure 3. The shield is pulled forward by hand and is lowered and pressed against the sample by the expanding bellows when the apparatus chamber is evacuated.

Evacuation of the apparatus chamber also causes the end bellows, shown in Figure 1, to expand until the Armco iron heat source and heat sink each touch an end of the sample and are pressed against the sample by the atmospheric pressure in the bellows. If additional space is required to insert a sample, the bellows may be evacuated, thus retracting the iron rods. This means of clamping the sample in position permits using samples of slightly different dimensions and facilitates handling the samples by remote control devices. The temperature drop at the interface between iron rod and sample may be minimized by inserting a thin disc of lead. The ends of the sample must in all cases be ground flat, and if possible, the two ends should be parallel to each other and perpendicular to the axis of the sample, though there may be slight deviation from the latter requirement without interference with the operation of the sample holder. In some cases the four thermocouples on the quartz wedges do not all touch the sample, but at least one at each end will touch the sample. The radiation shield is heated so that its temperature approaches that of the sample from below. If a thermocouple is not touching the sample, its temperature is then less than that of the other junction at that end of the sample. Thus it is readily determined which junction is in contact with the surface of the sample.

Stainless steel and quartz are used wherever it is desirable to reduce the heat leak. Brass or copper is used for all other parts except the Pyrex bell jar and the iron heat source and heat sink. These two rods were fabricated from a piece of Armco iron furnished by the Battelle Memorial Institute together with values of the thermal conductivity of the iron measured at different temperatures by the method of Van Dusen and Shelton.[2] The thermocouple and heater leads are brought through the brass base by Steatite

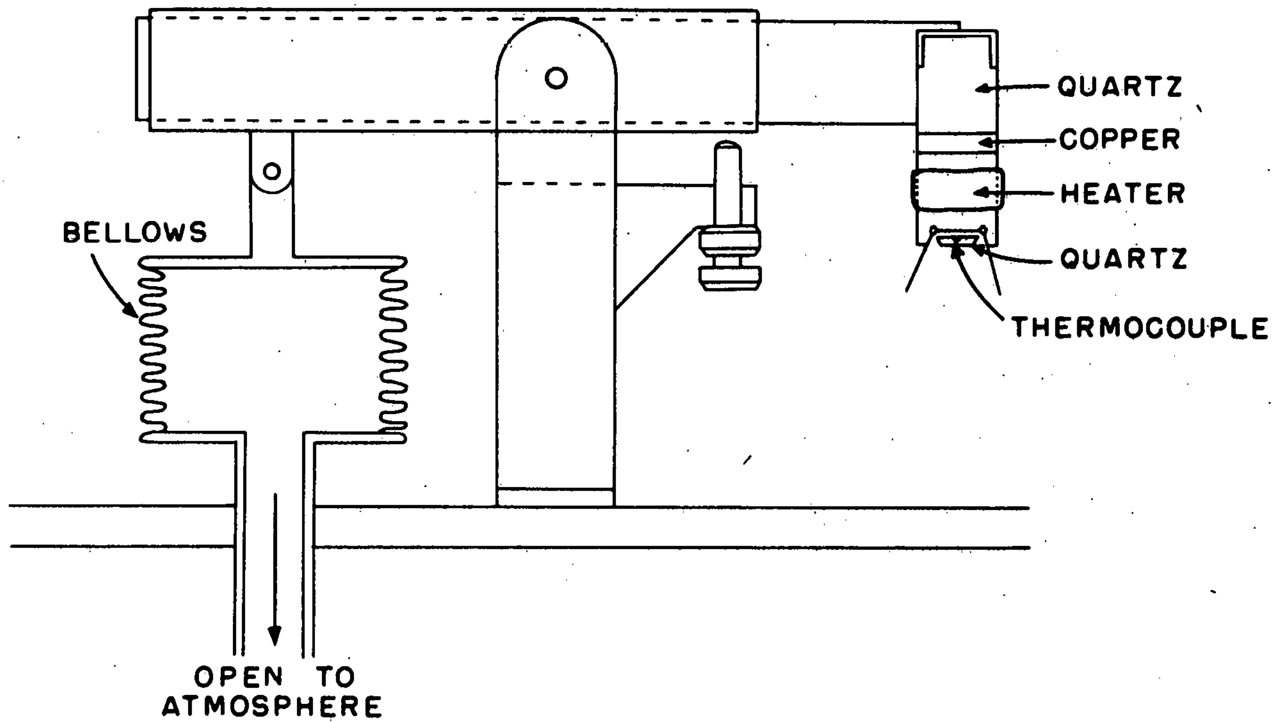

FIGURE 3.

CONTROL UNIT FOR UPPER
RADIATION SHIELD.

hermetically sealed bushings. The electric current for the various heaters is furnished by a constant-voltage transformer supplying four step-down transformers. The heaters are individually controlled by variable resistors. Constant-temperature water is circulated over the end of the iron rod heat sink and also through a coil soldered to the brass base plate. When adjustments are made with proper care, it is possible to heat the top and bottom radiation shields so that each of the four thermocouples at either end of the shield assembly records the same temperature within $\pm$ 0.1°C, for any constant power input to the iron rod heat source.

The stainless steel tube surrounding the heat source and the brass tube surrounding the heat sink do not form perfect radiation shields in that their temperature at every point is not identical with that of the iron rod at the same point. Also, short sections at the end of each iron rod and at each end of the sample are not surrounded by a radiation shield. Even in high vacuum there is some loss of heat at these points, about one per cent with samples of high thermal conductivity and more with samples of low conductivity. Measurement of the temperature of each of the four thermocouples in the iron rods permits a calculation of heat input to the sample and also heat output. If there is a significant difference, the output should be used as the heat flow through the sample. Better yet, a weighted average may be calculated by considering the areas of the exposed surfaces and their temperatures.

CALIBRATION

All wire used to construct thermocouples was tested for homogeneity by the method described by Roeser and Wensel.[4] If the thermal e.m.f. produced in any section of wire by a temperature gradient of about 200°C per cm exceeded that corresponding to 0.1°C in the completed thermocouple, that section was discarded. The thermocouple junctions were welded, and the completed thermocouples were each calibrated against a platinum resistance thermometer that had been calibrated by the National Bureau of Standards. The thermocouples that were used did not differ significantly from each other in their calibration values.

The Armco iron heat source and heat sink were originally fabricated as part of a single rod of such length that a standard-sized sample (1.75 inches long) could later be cut out of the middle section, leaving the two rods that were used in the apparatus. Two small holes, each large enough to contain a three-mil thermocouple junction without touching the walls, were drilled at the desired points at each end of the 0.375-inch portion of the Armco rod. The distances between these holes, 0.75 inch, were measured with a traveling

[4]W. F. Roeser and H. T. Wensel, J. Research Natl. Bur. Standards 14, 247-282 (1935).

microscope. Each hole was enlarged somewhat at its two ends so that a short section of alundum tubing could be inserted to insulate the thermocouple leads from the iron rod. The leads were wrapped around the outside of the rod twice, sealed to it but insulated from it by ceramic cement.

The values of the thermal conductivity of the Armco iron, as furnished by the Battelle Memorial Institute, were checked for this rod by the following method. The single iron rod, with four thermocouples attached, was supported at the cold end only in the bell jar assembly to be later used for the apparatus. Constant-temperature water could be circulated over the cold end of the rod. An Armco iron radiation shield was placed around the rod and also soldered to the support at the water-cooled end. Thermocouples were fastened to the inside surface of the radiation shield opposite the two end thermocouples in the iron rod. A heating coil was fastened to the free end of the shield, a heater was inserted in the free end of the iron rod, and a radiation cap was placed on the end of the shield so as to enclose the rod without touching it at any point except its cold end. The apparatus was evacuated. At various different heat inputs to the iron rod heater, calculated from heater current and potential drop across the heater, the temperature of the radiation shield was adjusted to correspond to that of the iron rod. The temperature gradient in the iron rod was determined for each heat input by measurement of the temperature of the four thermocouples in the rod. The resulting values for the thermal conductivity of the Armco iron agreed with the values given by Battelle Memorial Institute within experimental error.

The final apparatus was checked by using it to measure the thermal conductivity of the Armco iron sample cut from the center of the above rod. The value obtained agreed with that determined in the above calibration. By following this procedure to calibrate the heat source and heat sink, these parts may be constructed from other materials of initially unknown thermal conductivity. The final apparatus will give most accurate results for thermal conductivities that are the same order of magnitude as that of the reference material from which the heat source and sink are constructed.

COMPENSATED THERMOCOUPLES

The thermocouples used in this conductivity apparatus function on the same principle as those of Boyer and Buss;[3] namely, that there is no net transfer of heat away from a thermocouple if it is in isothermal surroundings. The accuracy of such compensated thermocouples for measuring surface temperatures has been discussed by Adams and Kean[5] and was checked in this laboratory by an experiment that was carried out in an earlier form of the apparatus described above. The compensated thermocouple units were constructed as shown in Figure 4. The thermocouples were made from

---

[5] F. W. Adams and R. H. Kean, Ind. Eng. Chem. 18, 856-7 (1926).

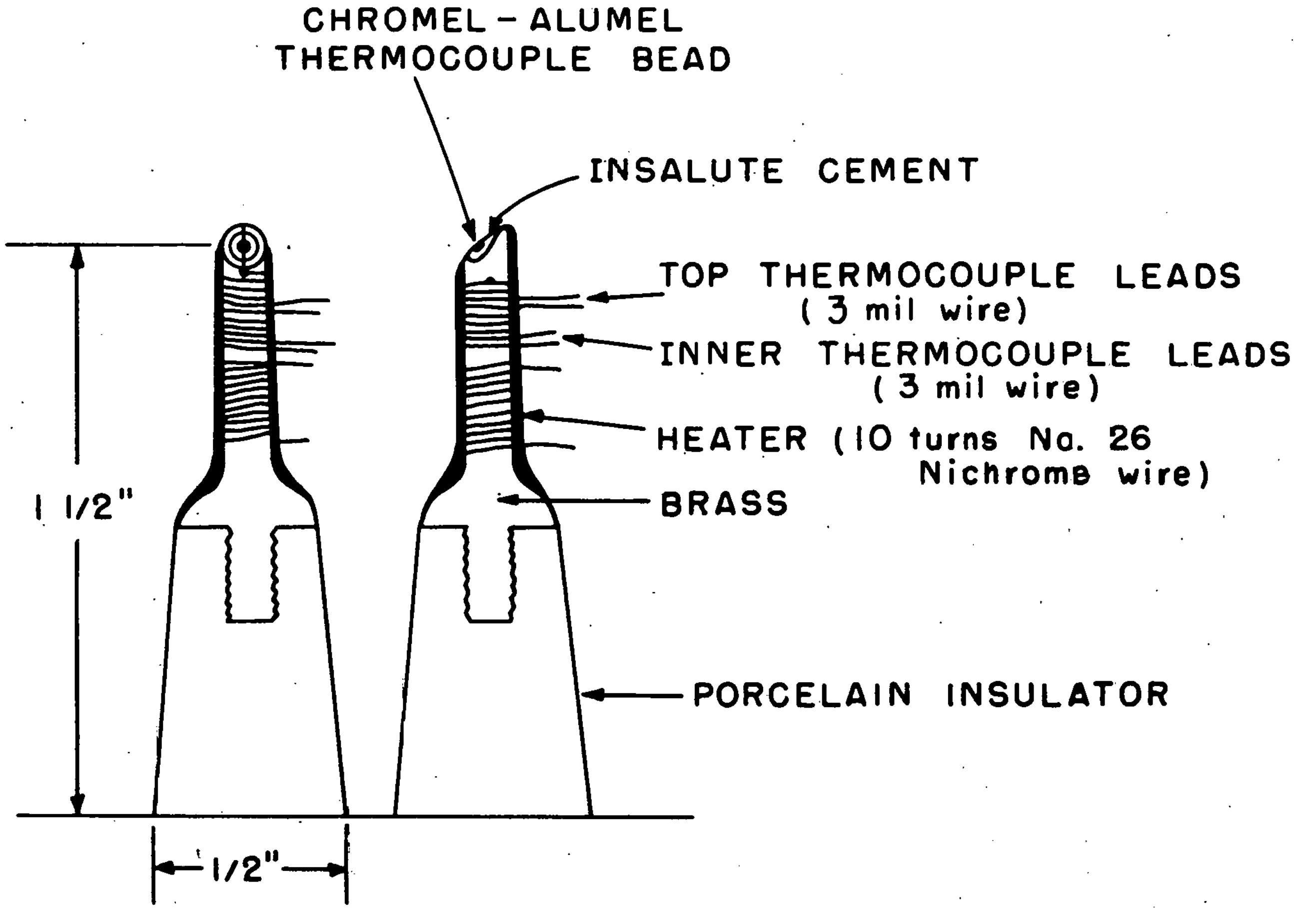

FIGURE 4.

COMPENSATED THERMOCOUPLE POSTS.

3-mil chromel-P and 3-mil alumel. The junctions were welded. A small ball of silver solder was melted onto the junction of each measuring thermocouple, shown at the top of the brass post in Figure 4. This thermocouple junction lay on a layer of refractory cement of low thermal conductivity. A second thermocouple was sealed into the interior of the brass post near the top. The leads to both thermocouples were wrapped around the brass post several times, sealed in place, and insulated from the post by refractory cement. Several turns of resistance wire around the base of the post served as a heater for regulating the temperature of the post to coincide with the temperature registered by the measuring thermocouple. The temperature of the post was always made to approach the temperature of the measuring thermocouple from below. When the temperatures of the two thermocouples were identical, no temperature gradient existed across the refractory cement at the top of the post, and there was no heat loss from the measuring thermocouple.

The accuracy of this type of compensated thermocouple for measuring surface temperatures was determined as follows. Three compensated thermocouple posts were mounted at the center of an apparatus similar to that shown in Figure 1, in place of the radiation shield assembly. A sample could be placed on the three measuring thermocouples so that one side was in contact with the two end thermocouples and a second side was in contact with the center thermocouple. A quartz knife edge could be pressed against the top of the sample at the position of the central thermocouple by a bellows assembly similar to that shown in Figure 3. The quartz knife edge could be heated to the temperature of the central thermocouple. A nickel sample was prepared in which two small holes were drilled near the positions of the end compensated thermocouples. A thermocouple was mounted in each of these holes midway through the sample with a short piece of alundum tubing on each side of the junction insulating the leads from the nickel. The thermocouple leads were wrapped around the sample several times at the position of the interior thermocouple. The leads were insulated from the nickel but sealed to it with refractory cement. When the nickel sample was in place, the positions of the interior thermocouples were near those of the end compensated thermocouples. These positions could not be made to coincide because of the presence of the thermocouple leads on the surface of the nickel sample. The positions of all five thermocouples were measured relative to the hot end of the nickel sample. With the sample in place between the heat source and sink and in contact with the compensated thermocouples, the apparatus was evacuated. A constant temperature gradient was established in the nickel sample, and the heater currents to the compensated thermocouple posts were adjusted so that the temperature of each internal thermocouple coincided with that of the corresponding measuring thermocouple in contact with the nickel. The interior temperature of the nickel sample was then measured at three points by the compensated thermocouples. In order to compare the two sets of temperatures it was assumed that the surface temperature measurements were exactly right. On the basis of these temperatures the constants were calculated for a binomial equation giving the temperature of the nickel sample as a function of distance from the hot end. The temperature of the nickel at the position of each of the two interior thermocouples was calculated and compared to the temperature as measured by the imbedded thermocouples. The results of two representative measurements are given in Table I where ℓ is the distance of each thermocouple from the hot end of the nickel sample and Δt is equal to the observed temperature of the internal thermocouple minus the calculated temperature at that point. $\Delta \ell$ is the increment of length along the bar corresponding to a temperature change of Δt.

Table I

DETERMINATION OF THE ACCURACY OF COMPENSATED THERMOCOUPLES

Thermocouple	ℓ (cm)	Run A			Run B		
		t_{obs} (°C)	Δt	$\Delta \ell$ (cm)	t_{obs} (°C)	Δt	$\Delta \ell$ (cm)
Internal No. 1	0.633	120.99	-0.17	0.010	55.14	+0.04	-0.005
Compensated No. 1	0.65	120.86			54.97		
Compensated No. 2	2.16	93.87			44.14		
Compensated No. 3	3.665	65.76			34.95		
Internal No. 2	3.801	62.96	-0.20	0.010	34.29	+0.09	-0.016

Since in each run both increments of length are in the same direction, part of the discrepancy in temperature may be the result of error in properly determining the position of the compensated thermocouples relative to the end of the sample in the final assembly. The position of the sample may have shifted slightly with change in power input to the main heater.

In view of the manner in which these data were obtained and the fact that all experimental error is attributed to two of the five thermocouples in the calculation of Δt in Table I, it seems reasonable to conclude that surface temperatures can be measured to better than $\pm$ 0.1°C by use of a compensated thermocouple of this type.

RESULTS

The thermal conductivity of a sample as measured by this apparatus is an average conductivity for the temperature range indicated by the measuring thermocouples in contact with the sample. The thermal conductivity is assumed to be approximately linear with temperature throughout short temperature ranges, and the measured conductivity is taken to be that of the material at the mean temperature. If it is desired to obtain the thermal conductivity at a specified temperature, it is easier to obtain a value at a neighboring temperature on either side of the desired temperature and interpolate the desired value than it is to adjust the heat input so as to obtain the desired temperature in a single measurement. This procedure has been followed to obtain the representative results given in Table II.

Table II

THERMAL CONDUCTIVITIES AT 70°C

Substance	Density ($g\ cm^{-3}$)	Conductivity at 70°C ($cal\ sec^{-1}\ cm^{-1}\ deg^{-1}$)
Quartz (⊥ optical axis)	2.6	0.014
Spinel (single crystal)*	3.6	0.028
Uranium	18.8	0.035
Sapphire (axis 60 deg from c axis)*	4.0	0.071
Nickel ("A")	8.8	0.152
Iron (Armco)	7.8	0.164
Graphite (⊥ axis of extrusion)**	1.7	0.367
Beryllium oxide (hot pressed)	3.0	0.435
Silicon carbide (polycrystalline)***	2.8	0.489
Aluminum (2S)	2.7	0.543
Graphite (‖ axis of extrusion)**	1.7	0.605

*Obtained from Linde Air Products Co.

**The graphite used was Acheson graphite similar in properties to National Carbon Co. spectroscopic electrodes, except that it showed a high anisotropy.

***Obtained from The Carborundum Co., courtesy of Dr. G. M. Butler.

The probable error to be associated with the results given in Table II and other values obtained by this apparatus is $\pm$ 0.003 cal sec^{-1} cm^{-1} deg^{-1} or $\pm$ 3 per cent, whichever is the larger. In order to obtain conductivities at lower temperatures the heat input must be less. This decreases the temperature drop down the Armco iron rods and increases the probable error of the results. If lead foil is used at the interface between the iron rods and the sample, the temperature drop at these points is usually decreased. This decreases the probable error in the final result since it causes a larger temperature difference between the thermocouples in the iron rods.

ACKNOWLEDGMENT

The authors wish to thank O. C. Simpson and J. R. Gilbreath for the many helpful discussions during the course of this work. We would also like to acknowledge the very able assistance of the personnel of the Chemistry machine shop under the supervision of F. Hartford.

1-14

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK