THE CONSTRUCTION OF A FURNACE CALORIMETER AND THE EVALUATION OF A METHOD OF THERMAL ANALYSIS FOR OBTAINING THE SPECIFIC HEAT OF SOLIDS AT HIGH TEMPERATURES

By

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Special thanks also goes to Dr. James H. Boggs who has been most helpful and encouraging at all times and who supplied the trigger circuit used in the control.

Lastly, credit is given to George C. Beakley without whose assistance this thesis would not have been possible. He will be continuing this work toward a much more critical evaluation of the comparative method. To him I wish "good luck."

LIST OF ILLUSTRATIONS

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SENSITIVE EQUIPMENT DATA

Galvanometer

Leeds and Northrup, Ballastic, Type P.
Sensitivity_____0.01 C/mm
Critical Damping, External_____56 Ohms

Potentiometer

Leeds and Northrup, Portable, No. 8662
Serial No. 1031773
Standard Cell Voltage_____1.0191 abs. volts
Date measured_____Jan. 25, 1952

Recorder

Leeds and Northrup, Micromax, Model S, 40.000 Series
Serial No. 393905
Coil Resistance-----20 Ohms
R-7-PP Pointer
R-7-K-35 Suspension

CHAPTER I

INTRODUCTION

The present day trend toward obtaining the utmost of strength and endurance from materials in design, manifests itself nowhere more strongly than in the field of heat transfer. It is here that the requirement of specific heat data as a function of temperature is becoming more and more important. Problems in transient heat flow demand the use of the term "thermal diffusivity." This term is a function of specific heat and since temperature may vary widely, need for such data arises.

According to White (1,2), there are at present two general methods whereby specific heat data can be obtained. The first is the "drop method" or "method of mixtures" where the body is heated in a furnace to some predetermined temperature and then dropped into a calorimeter as quickly as possible to determine the heat capacity by measuring the temperature rise of a metal block, the amount of ice melted or the temperature rise of a given amount of water. Of this type, for solids at high temperatures, the "block calorimeter" (3) and the "ice calorimeter" (4) seem to be the most satisfactory of modern calorimeters.

By the second method the heat capacity is determined by measuring the duration of time required for a given electromotive force to raise the body a certain number of degrees and comparing results to those of a similar run made with a body of known temperature-specific heat characteristics. This method (which will be referred to as the comparative method) while not being utilized to the extent of the others, has some very interesting possibilities as suggested by Sykes (5, 6) and Smith (7).

Kelly (8) speaks of a third method, the "direct method." It is similar to the method of mixtures in that it involves the measurement of the heat required to raise the temperature of the substance by a relatively small amount, ranging from a fraction of a degree to a few degrees, depending on the method and equipment. Most attempts to use this method have failed to give accurate results beyond moderately high temperatures because it has been impossible to evaluate satisfactorily the corrections for heat interchange with the surroundings. One of the more successful attempts on record is that of Seekamp (9). His apparatus makes use of the Nernst idea (10) of internal heating in a vacuum.

There are two main disadvantages of the drop method or method of mixtures (1):

1. It is not effective for obtaining the heat effects at transition points, especially if the effect is small.

2. The apparatus for this process is especially elaborate, expensive, intricate and difficult to construct. Also, the calibration of such a device can become quite time consuming.

Some advantages are:

1. It is a direct method, i.e. not dependent on the properties of any other substance.

2. The results are precise within the limits of reproducibility in behavior of the substance.

Advantages of the comparative method are:

1. An apparatus is relatively simple to construct.

2. The data can be obtained much more quickly and at just as many points as desired with only one run. This enables the observer to detect quickly the presence and amount of any latent heat of transition.

Disadvantages of the comparative method are:

1. A slight change of position of the sample can throw the rate of heat conductance off to an extent that the information will be useless.

2. The temperature gradient within the container is not constant because the temperature is changing and the electromotive force in the thermocouples, due to the "Seebeck effect" (11), changes. This electromotive force, in turn, does not vary as a linear function of temperature.

These and other effects, however, are small and largely eliminated if the standard sample has a size and heat capacity of the same order of magnitude as the material to be tested. Another and perhaps far greater disadvantage, expecially at higher temperatures, is the following:

3. According to Weber (12), "There is a rapid increase of radient energy with temperature. As the temperature increases from 275^{o} to 400^{o} C. the radient energy (for wave length = 0.85 microns) increases from 3.23×10^{-6} to 933×10^{-6}." This error manifests itself in the empty heating curve (see Chap. II). At this time the temperature measuring thermocouple is suspended in the center of the crucible and is subjected to radiation from all sides. The resulting error could, perhaps, be partially corrected by use of a radiation shield for the thermocouple made from a foil with a high melting temperature (for example, gold leaf). Another possible method of correction might be to use a second known substance in place of the empty run. By this means an empty calibration curve could be calculated from the basic equation. A substance, which could be used for this purpose and which can be obtained, is aluminum oxide, Al_2O_3 (synthetic sapphire or corundum) (13).

Others in the field have traced the history and development of the various types of calorimeters (14, 15). One of the high lights of

this history is the first use of electrical heating (16). The delay in doing so was caused by the late determination of the electrical equivalent of heat. Previous to this, workers depended upon the specific heat of water as a standard for measurement of heat quantities. Since this value varies with temperature, confusion reigned. In using electrical power for heating, Nernst used a heater which was embedded in the material to be tested. The whole assembly was then suspended in a high vacuum in order to reduce heat transfer to the surroundings as much as possible. Then, a measured amount of heat was added and the temperature rise noted. From this data the specific heat could be calculated. This is a direct method and as indicated before has not been used above moderately high temperatures.

The history of the subject shows that the accurate determination of the specific heat data of a substance is a very formidable problem. However, the great demand for information on properties of materials has served to re-evaluate a few of the afore-mentioned methods of research. Even though some researchers are most discouraging in their remarks concerning the possibilities of the comparative method (1, 8), it may yet prove to be very fruitful. This is true in view of the comparative simplicity, time involved, and the fact that information within ten percent accuracy would be very much in demand on new materials.

CHAPTER II

THEORY AND DESCRIPTION OF THE METHOD EMPLOYED FOR OBTAINING SPECIFIC HEATS

The apparatus utilized in this experiment incorporates features which constitute departure from previous designs (see Fig. 1). This was due principally to difficulty in obtaining material for a heating wire holder which would withstand the design requirements.

A brief description of the process is as follows:

The specimen, which is a cylinder 3/4" in diameter and 1½" long, is contained in a refractory crucible cut on a lathe from Armstrong, A-20, insulating brick (17). This crucible is made with as close a fit as possible to eliminate radiation effects which exist because of differences in emissivity of the standard and of the unknown sample. The crucible was then covered with Sauereisen No. 6 cement (18) to protect it from crumbling during handling and to hold the differential thermocouples in place.

To control a temperature differential a Schmidt "trigger" circuit (see Fig. 7) was used in combination with an ordinary ballistic, mirror galvanometer. This circuit was designed so that when the heating rate was too great and the differential across the container (approximately 30° F. optimum) increased to the point where the mirror of the galvanometer would reflect light onto a photoelectric cell (see Fig. 16), the heating circuit would be de-energized thereby letting the differential decrease. In addition to this control circuit there was a continuous heating circuit which supplied power less than that required for the

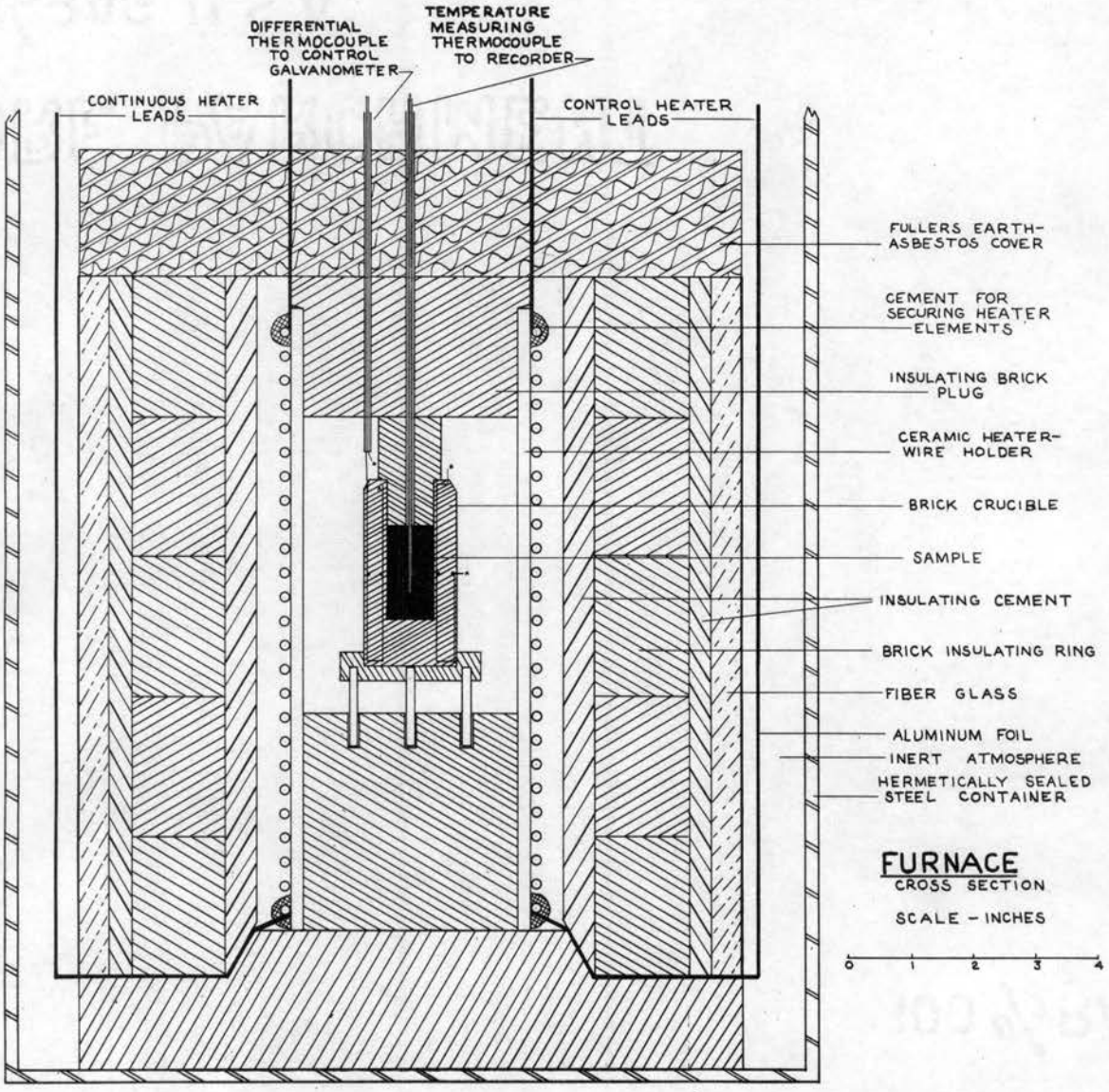


Figure 1.
Furnace cross section

proper heating rate. The purpose of the second circuit was to obtain closer control of the temperature differential. The objective in control was to maintain the "off" time equal to the "on" time. With the apparatus here described, the cycling time was 1.5 to 2.0 minutes for best control.

A Variac autotransformer was used in each circuit to control the proper input.

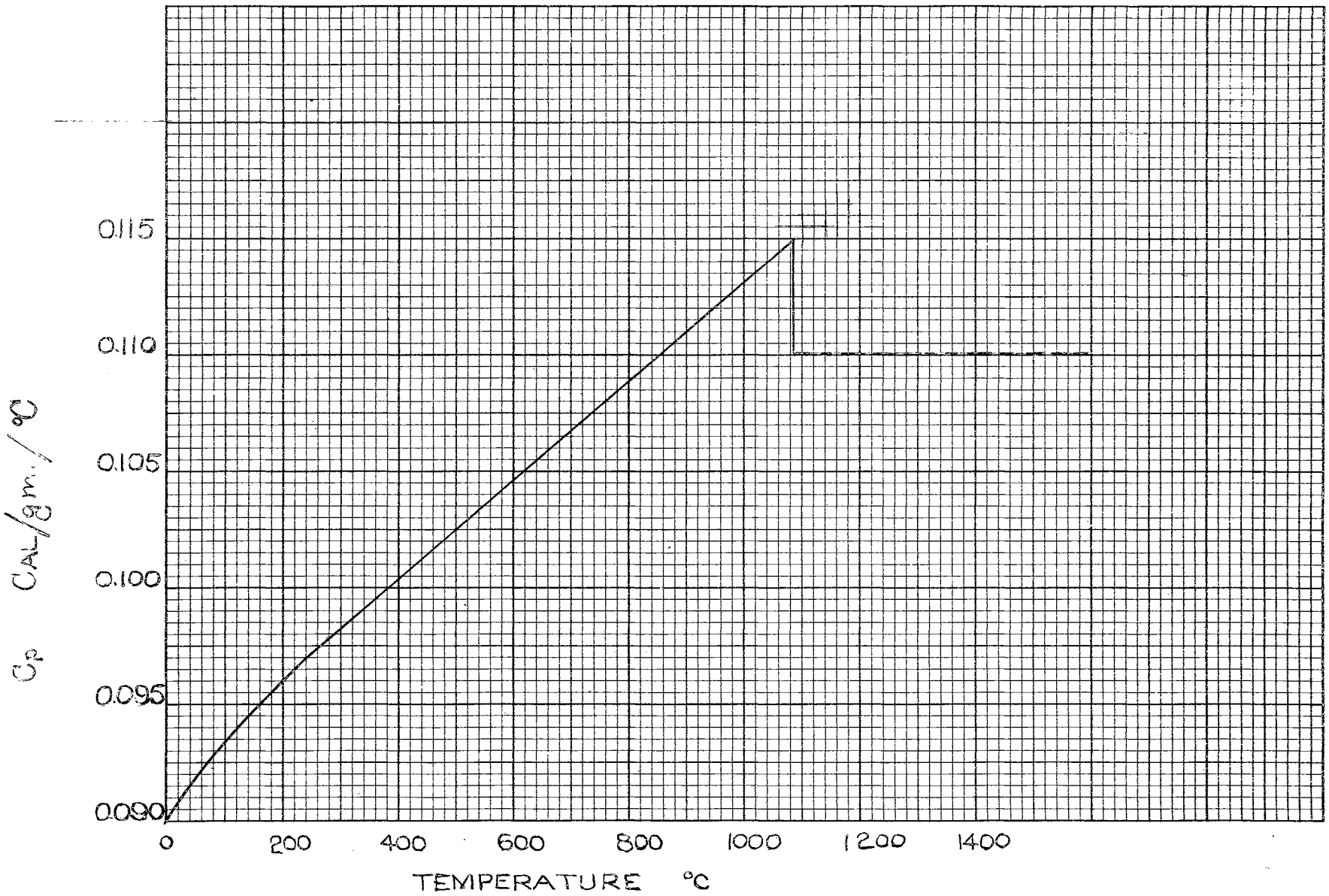
A temperature measuring thermocouple constructed of chromel-alumel was inserted in a 1/16" hole drilled axially in the specimen. Leads from this junction are connected to a Leeds and Northrup, Micormax recorder. This provided a time-temperature curve during the heating process.

Finally, the furnace and insulation were submerged in an inert atmosphere (helium for this experiment) contained in a hermetically sealed container. (Fig. 10). This provided against contamination of samples due to oxidation or reduction.

To obtain the specific heat of a material it is first necessary to calibrate the apparatus for heat input at various temperatures. This was accomplished by getting the time temperature curve for an empty crucible and for a substance of known specific heat as a function of temperature. Copper is a suitable standard (19) since it undergoes no allotropic transformation and its specific heat is known fairly accurately over a wide range of temperature (see Fig. 2). The rate of heat flow through the container is equal to the product of its conductivity, a constant (which is dependent on its size and shape) and the temperature differential. The resulting constant heat flow serves to supply the sensible heat of the sample, its heat of transformation, if any, and the

FIG. 2

SPECIFIC HEAT OF COPPER (19)



sensible heat of an indeterminate part of the container itself, i.e.

$$H \times \triangle t_s = \triangle T_s \times C_s W_s + L_s W_s + \triangle T_s \times C_e W_e$$

where

H = heat flow per unit time

C_e = specific heat of effective part of container

C_s = specific heat of a standard specimen

W_e = mass of effective part of container

W_s = mass of standard specimen

$\triangle T$ is the change of temperature in time $\triangle t$

L_s is the latent heat of any transformation that may occur in the temperature range of $\triangle T$.

If a third time-temperature curve is taken on a sample of heat capacity $C_u W_u$, then (if no transformation occurs in either sample so that latent heat may be ignored), by use of the equation for the empty container,

$$H \times \triangle t_e = \triangle T_e \times C_e W_e \quad \text{or} \quad C_e W_e = \left(\frac{H \times \triangle t_e}{\triangle T_e}\right)$$

for the standard sample,

$$H \times \triangle t_s = \triangle T_s \times C_s W_s + \triangle T_s \times \left(\frac{H \times \triangle t_e}{\triangle T_e}\right) \tag{1}$$

for the unknown sample,

$$H \times \triangle t_u = \triangle T_u \times C_u W_u + \triangle T_u \times \left(\frac{H \times \triangle t_e}{\triangle T_e}\right) \tag{2}$$

where subscript u refers to the unknown specimen.

Rearranging:

$$C_s W_s = H \left(\frac{\triangle t_s}{\triangle T_s} - \frac{\triangle t_e}{\triangle T_e}\right) \tag{3}$$

$$C_u W_u = H \left(\frac{\triangle t_u}{\triangle T_u} - \frac{\triangle t_e}{\triangle T_e}\right) \tag{4}$$

Dividing (4) by (3):

$$\frac{C_u W_u}{C_s W_s} = \frac{\frac{\Delta t_u}{\Delta T_u} - \frac{\Delta t_e}{\Delta T_e}}{\frac{\Delta t_s}{\Delta T_s} - \frac{\Delta t_e}{\Delta T_e}} \qquad (5)$$

The symbol $\frac{\Delta t}{\Delta T}$ represents the slope of a time-temperature curve. In the Equation (5), the subscripts e, s and u denote respectively the empty container and container with standard and unknown specimens. The heat capacities of the samples are thus directly proportional to the values of $\frac{\Delta t}{\Delta T}$ after they have been corrected by subtracting a reading obtained from a heating curve of the container alone.

The value of $\frac{\Delta t}{\Delta T}$ in this experiment was obtained by measurements from the recorded time-temperature curve directly. As is seen from the last equation, the only unknown is the specific heat of the unknown specimen.

It was by this means that a curve for the specific heat of commercially pure titanium was obtained.

CHAPTER III

THE DESIGN OF AN ELECTRIC FURNACE

Depending on the desired results, there are many methods of heating by means of an electric furnace. In the temperature range of this experiment (room temperature to 2000° F.) the apparently logical means was to utilize a resistance wire muffle furnace. Information on heaters of this type is presently very sketchy. Individual requirements require special design and for this reason information on muffle type heaters is limited and of a general nature.

The requirements assigned to this furnace for the first design were primarily 2000 watts of power to be applied in a limited space by means of two separate circuits and without inductive effects in the temperature measuring thermocouple. There are various alundum, porcelain or ceramic holders on the market suitable for single circuit heating. A number of these are cylindrical in shape with a helical groove cut on the outside for the winding of heating elements. A double helix thread arrangement seemed necessary in order that another circuit might be added and finally two more threads in order that each circuit could be wound back parallel to itself, thereby eliminating inductive effects in the temperature measuring thermocouple.

A method was decided upon whereby a piece suitable for the purpose could be slip cast and fired in the same manner as ceramic ware. (See Fig. 4). This requires a mold of plaster of paris. (See Fig. 3). Using the largest pitch lathe available, a piece of steel pipe of the approximate diameter was turned with a set of 1 inch pitch, quadruple threads.

The mold was made by casting this threaded pipe, one side at a time, in plaster of paris. (Machine oil is used to keep the plaster of paris from sticking to the steel pattern. Unless a vibrator is used it is difficult to obtain a casting without voids due to air bubbles. These can be touched up by hand when the plaster sets up). The materials and processing facilities of the Tamac Pottery plant of Perry, Oklahoma were used in the production of this piece. The firing temperature of their ware is approximately 2300° F. and it has good mechanical qualities. The material can be brought back up to firing temperature for an indefinite number of times but it begins to soften around 1900° F.

Since the shrinkage factor was unknown, it was difficult to determine design dimensions for the holder. It was later determined that shrinkage amounted to approximately 25%. This reduced the spacing of the threads to 0.75/4" (approximately 3/16"). This was a source of trouble later in the construction of the furnace in that it was difficult to keep the elements separated when heated and in an expanded state.

The first pieces produced were cylinders open on both ends. Since the material is very difficult to work after firing (It can be machined well with a diamond edged tool also, holes can be lapped in by using valve grinding compound or carborundum paste) the bottoms were cut out prior to firing. This led to an elongation of one end due to the weight of the piece during the firing process. It was decided, in working with later pieces, to leave a bottom in, since a refractory plug was to be used as both an insulator and a holder for the sample container. This resulted in a very smooth and uniform holder approximately ten inches in length with an inside diameter of 3½". The threads were without shoulders and approximately 1/16" from crest to root. The thickness of

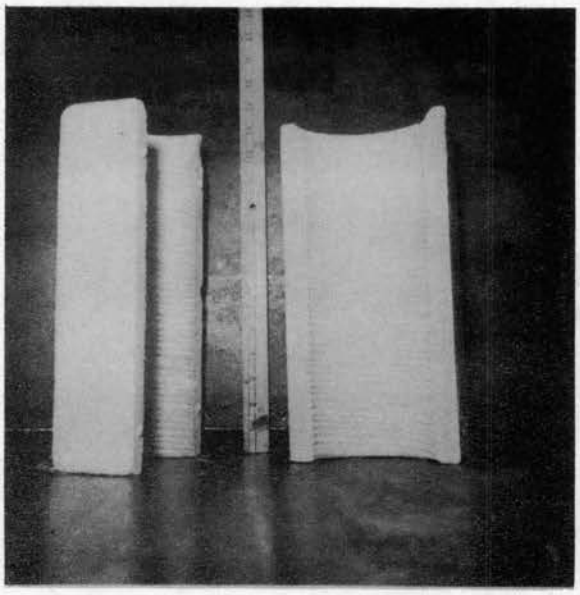


Figure 3.
Plaster of Paris mold for holder casting

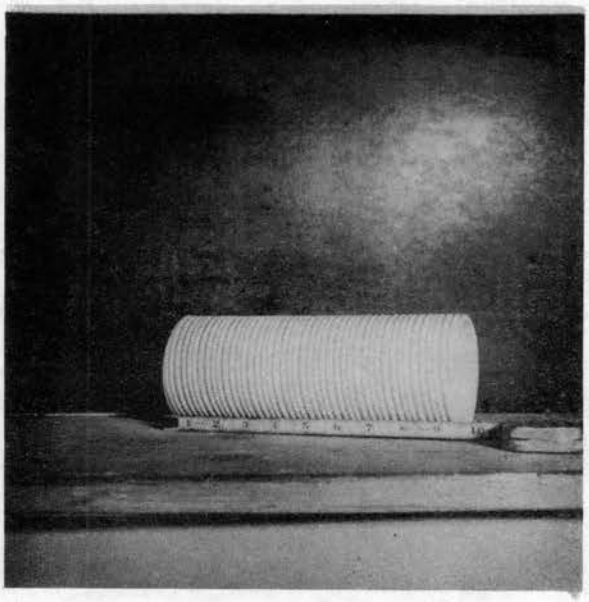


Figure 4.
Heater-wire holder

Figure 5.
Insulating materials used in construction of furnace

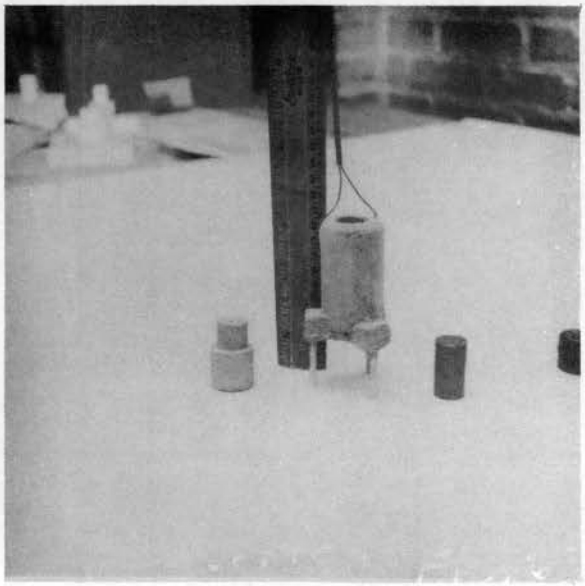


Figure 6.
Refractory crucible with lid and specimen

the cylinder was approximately 3/16". This dimension will vary according to the amount of time the slip is left in the mold. With this size piece, 3/16" is about the minimum however.

Since very little was known about the thermal shock characteristics of the ceramic material, it was decided to make tests with a "pilot model." In this, the furnace was wound with two pieces of utility heater resistance wire and connected in series to a 220v. circuit. It was found that the material stood up well when heated with bright red wire temperatures in open air and in further tests with the heating elements buried in A. P. Green refractory cement (Seraset) (see Fig. 5) and additional lagging of fiber glass and aluminum foil showed that with a 110 volt parallel hookup, the inside temperature of the cylinder would reach over 1000° F. in open air with the top open. These heatings were never of long duration however. The thermal shock characteristics proved to be very good. The current could be shut off at the temperature of a dull-red glow of the ceramic material with no apparent ill effects. It was noted that the material became more brittle and cracked very easily if handled roughly before complete cooling.

The slip used in making the ceramic piece has the following composition:

Ball Clay	similar to modeling clay and gives plastic qualities before firing.	25.5%
Kaolin or China Clay	used as a fluxing agent and is light in weight	24.0%
Silicate or Flint	used for hardness	0.5%
Nephylene Syenite		50.0%

Nephylene has the following structural formula:

$K_2O{-}3Na_2O{-}4Al_2O_3{-}9SiO_2$

Nephylene Syenite is a hard, grey, granite like rock and has the following analysis: (21)

Si	59.3%	CaO	0.3%	
Al_2O_3	24.7%	MgO	Trace	
FeO_3	0.1%	K_2O	5.1%	Ignition loss 0.4%
TiO_2	Trace	Na_2O	9.9%	

It has long sintering qualities and permits lower maturing temperatures and a longer firing range.

Having decided that the ceramic was of high enough quality to withstand at least 1500^0 F., the next problem was to decide upon a wire size and helix diameter to place 2000 watts on the holder. Since inductive and capacitative effects are neglected in resistance heater design, the basic formulas used were:

$$\text{Volts} = \text{Amperes} \times \text{Ohms}$$

$$\text{Watts} = \text{Volts} \times \text{Amperes} = (\text{Amperes})^2 \times \text{Ohms}.$$

It is observed that any temperature can be attained with only one watt of power, provided there is perfect insulation and enough time. There were many unknowns in this problem, such as the degree of insulation obtainable, thermal conductivities of the ceramic ware and of the cement on the refractory container. These unknowns plus the heating rate requirements created an almost impossible situation as far as estimating power requirements. The only information found in this regard was obtained from the Driver-Harris Company, resistance wire manufacturers. They suggest from one to three thousand watts per square foot of surface for small muffle furnaces. Here again the requirements vary according to the materials used in the muffle, type of insulation, method of application, etc.

Having obtained this information, a design figure of 2000 watts was selected. The groove to hold the heater was designed to be 10½' long. Because of the limited space (closeness of the grooves) the wire size was limited. A small diameter was required but in turn created a resistance problem which would not permit high enough power input.

It was found that the largest wire which could be wound in a helix to fit the purpose was a B&S Gauge No. 18 (0.040 inches). This could be wound to any desired length on a 1/16" mandrell by using a collet and allowing the portion already wound to project through the head stock of the lathe. The resistance of No. 18 Nichrome is 0.4219 ohms per foot.

The power calculations for one circuit follow:

In calculating the length of wire, assume the pitch diameter of the helix to be $1/16 + 1/25 = 0.102$ in.

The length of wire to make one circuit, assuming the helix stretched to two times its close wound or compressed length, is,

$$\text{Length} = \frac{(\pi \times 0.102 \times 25) \times 12 \times 10.5}{12}$$

$$= 84.2 \text{ ft.}$$

$$\text{Resistance} = 84.2 \times 0.4219 = 35.5 \text{ ohms}$$

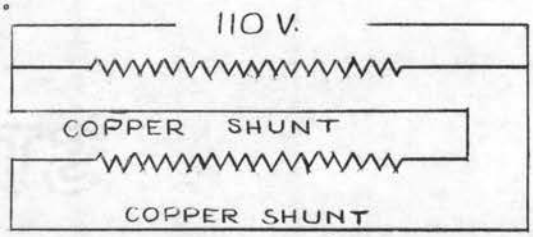
$$\text{Power} = \frac{110}{35.5} \times 110 = 341 \text{ watts}$$

It is seen that even with two circuits this will not begin to approach the intended input. If the circuit could be connected in parallel, the power input would be increased due to a decrease in resistance and an increase in amperage. Here again, however, one is faced with the induction problem in the thermocouple.

Finally the following circuit was worked out. Instead of making the winding down and back on the cylinder in series it was decided to

put the two windings in parallel and shunt them with copper straps so the current flow would be in opposite directions in adjacent windings for the same circuit.

Thus:



This cuts the resistance in four or $35.4/4 = 8.875$ ohms, which in turn gives an amperage of $110/8.875 = 12.4$ Amps. and a power of $I^2 R = (12.4)^2 \times 8.875 = 1370$ watts.

This design will give some difficulty in controlling, due to the high amperage but it is about the only way to achieve the design criteria.

A heater was made up in this fashion with the elements buried in Sauereisen No. 6 Cement. This was done to keep the overall apparatus as compact as possible. It was believed that in doing so the temperature could be reduced to a point where hard fiber glass could be utilized to an advantage (maximum temperature rating——1200^{o} F.) as it had been on the pilot model. The reason for compactness was that eventual submersion in an inert atmosphere was anticipated. The Sauereisen Cement has the published specifications of being electrically non-conductive up to 3000^{o} F.

This furnace failed on the first test run due to melting of the heating elements near the bottom of the cylinder. It was believed at the time that this was caused by an electrical break down in the cement which caused increased resistance and hot spots.

Another furnace was constructed with the same design, using four utility resistance elements which had been used on the pilot model.

These elements had a resistance of 16 ohms each; therefore the power input very closely approximated the first design. This furnace was covered with the A. P. Green refractory cement as had been the pilot model. The elements again melted near the point where the leads take off.

Upon further research it was found that most resistance furnaces of this nature burn out near where the leads take off. This is presumably caused by an increase in resistance of the wire due to mechanical working in bending or tying on. To remedy this, 1/18 in. O.D. copper tubing was used to crimp the leads to the heating elements and these were buried in Seraset for a distance, as was the heater wire. On testing, this furnace burned out near the center.

Most of the tests during this period were much more severe than actual requirements. The voltage, which was regulated by a Variac, was turned on near maximum from the beginning and the muffle was heated rapidly to a high temperature. There was no thermocouple available so it is not known what temperatures were attained before the burn-outs occurred. In some cases the ceramic glowed red over most of its area and in all cases there were bright red spots which later turned out to be the points of melting of the heating element. A pyrotechnic cone No. 018, which has a rating of 1328° F. for a heating rate of 150° F./hr., was melted in approximately 25 min. from a cold start in the pilot model. Since these cones are very sensitive to the rate of heating, it is believed that a temperature of at least 1500° F was achieved. It was still believed that the burn-outs were due to the cement actually breaking down or its inability to dissipate heat fast enough to keep the wire from melting. The melting point of Nichrome wire is approximately 2460° F. and it was attained only in localized spots indicating something more than poor heat conductivity.

At this point a different idea in design was attempted. It was decided to place the heating wire and holder in the center of a cylindrical container which was filled with a loose insulating material. There are two possibilities for the insulating material: expanded mica (trade name Vermiculite) and diatomacious earth (trade name, Fullers Earth or Sil-O-Cel). Both are excellent insulators and quite inert at high temperatures. Vermiculite was chosen because of its availability. (Most plant nurseries use the product for mulching the roots of small bushes). This new idea led to the difficulty in excessive size or bulkiness. When enough insulating material was used, the outside diameter would be quite large and unwieldy. This problem was solved by constructing a holder from the light weight insulating brick. Each 2¼ x 4½ x 9" brick was cut to supply a half circle with a 9" outside diameter. The A. P. Green refractory cement, Seraset, was used to bond the brick together and the inside and out was plastered with Armstrong Airtemp No. 116 insulating cement. This cement has a dry consistency of rock wool insulation and has a temperature rating of 1800^{0} F. It is mixed with water to the desired consistency and daubed in place by hand. This arrangement worked very well with the exception of expansion cracks which formed the entire length on diametrically opposite sides of the cylinder. This difficulty was overcome by using three bands of heavy wire which had to be tightened after the cement had fully dried. With the cement there was approximately one inch circumferential clearance for the heater coils. A base was formed from two of the insulating brick and vermiculite was poured in to fill the clearance space. Since the heating elements were not to be covered with cement, there was a problem of securing them to the holder. Instead of lapping the holes in for a mechanical fastener as previously

suggested, the Seraset cement was again used to secure the copper leads to the ends, care being taken not to cover any of the heater wire proper. This method proved to be satisfactory and after a brief firing period gave ample strength. On testing, the furnace increased in temperature to a dull-red glow but again the hot spots were observed and upon cooling it was again found that the element had fused with an accompanying large spot of molten ceramic with a glassy appearance. It was believed that the fusion could have been brought about by impurities in the vermiculite. With this in mind another heater was wound and set to heat in the brick enclosure with no insulating material.

After the furnace had attained an overall dull-red color and had been so for approximately a half hour, a bright red or hot spot was seen to form near the top on the inside of the ceramic cylinder. Since the outside was open, the heater wires could be observed directly and it was seen that what appeared to be a large bubble was forming on the ceramic threads. This burn-out occurred near the top because of the chimney or strong convective effect due to openings near the bottom of the insulating ring. This was remedied in later models by upsetting the brick base so it would fit into the insulating ring (see Fig. 1).

It was thus determined that the "weak link" in the chain was the ceramic holder itself. Upon cooling, it was observed that many small black specks had formed in the thread grooves each threatening a similar break down. It is believed that interaction of the metal and ceramic created a compound with a lower melting temperature, which in turn made the wire hotter creating more resistance thereby causing a localized hot spot. This condition would possibly be avoided in an inert atmosphere or the ceramic body could be dipped in the high temperature

Sauereisen cement to avoid interaction of wire and ceramic.

Due to the limited time and the added information that the inductive effect in the thermocouple was of no real consequence (see Appendix I), it was decided to limit the experiment to 1300° F. and to make only single windings on the heater, thereby creating an empty groove on the ceramic between each turn of heater wire. It was found that, with the insulation as described and an additional wrapping of pyrex fiber glass plus an outside covering of aluminum foil, this temperature could easily be attained with the previously designed input. That is, with 15 ohms resistance in each circuit, the power input would be $(\frac{115}{15})^2 \times 15 = 884$ watts for each circuit.

The Refractory Crucible

A previous investigation (7) specified Armstrong LW-20 brick with a thermal conductivity of 0.0006 Cal. $Cm^{-1}sec^{-1}{}^{o}C^{-1}$ at 540°C. Since this brick is no longer produced, the A-20 with a thermal conductivity of 1.536 Btu in. $ft^{-2}hr^{-1}{}^{o}F^{-1}$ at a temperature of 1200° F. was substituted. The thermal conductivity of A-20 is equivalent to 0.000527 Cal $cm^{-1}sec^{-1}{}^{o}C^{-1}$ (24). This number compares very favorably with 0.0006. There should be no appreciable difference in heat flow characteristics due to the brick.

No difficulty was experienced in machining the crucible to the proper dimensions. The material is quite soft and works easily both in a lathe and with a saw.

Since the object of the experiment was to obtain specific heat data, the differential thermocouple hook-up was used on the crucible as was suggested in the literature. Here, as with the temperature measuring thermocouple, chromel-alumel junctions were used. This

combination is recommended for accuracy up to 2000° F. A rather heavy gauge (B&S No. 22) was selected for the differential thermocouples, as it was believed that the crucible would place a great deal of twisting and bending strain on the wire during loading and unloading with subsequent breakage of a small gauge.

A series of two pair of junctions were arranged and placed on opposite sides of the crucible. This was rather difficult and took a great deal of time but it is believed that the time was well spent, both by obtaining a gain in electromotive force for control purposes and by the averaging effect of the two pairs over that of a single pair. (For both multiplying and averaging effect it must be kept in mind that the four junctions were placed alternately inside and outside the container. If the two center junctions are placed both inside and the end junctions placed outside, there will be an averaging but no multiplying effect.)

The junctions and wire were pressed well into the refractory brick and held in place until a coating of Sauereisen cement No. 6 could be baked on. The mechanical and temperature qualities of this cement were amply good for this purpose. The only adverse effect seemed to be an increase in thermal conductivity which made it almost impossible to maintain the recommended 60° C. or 108° F. The increase in thermal conductivity of helium over air added to this problem when the experiment was actually in progress. (See Chap. II).

Here, as in the temperature measuring thermocouples, the leads were made of the same material as the thermocouples. In this case the alumel wire was extended approximately 15 feet. This was done in both cases to eliminate an unknown junction effect and the consequent calibration problem. With a good lead connection the differential thermocouple leads

could have been made separate from the crucible since the actual temperature differential requirements are not exacting. This would eliminate the long cumbersome leads which were very awkward to handle while cementing and drying the crucible.

The problem of supporting the crucible inside the furnace was solved by making extensions of the refractory brick, cementing them with Sauereisen No. 6 and using thermocouple insulators for a tripod leg arrangement (see Fig. 6). Wire or sheet metal supports were first considered for this purpose but the idea was discarded in favor of the insulators because of the high heat conductivity of the metal. The entire process is dependent upon as nearly an isothermal body as possible and the use of metal legs would have led to hot spots near the supports. As even heating of a cylindrical body is most easily accomplished by input to the lateral surface only (perfect insulation on both ends would be ideal), the insulating properties of the added brick were considered to be helpful.

Trigger Circuit

The trigger circuit (see Fig. 7) was constructed and put into operation with a minimum of difficulty. The cost of all parts amounted to approximately $25.00. The circuit as described and built proved most effective for this setup.

The photoelectric cell shown in the circuit was connected to the chassis with a 6' length of shielded cable and affixed to a piece of 6" channel stock (see Fig. 13) in order to provide enough weight so it could be used in connection with a table top experiment. It was deemed best to have the galvanometer control on as solid a footing as possible to eliminate vibration. For this reason the galvanometer, trigger

circuit chassis and photoelectric cell were placed on a concrete floor (see Fig. 12). This necessitated the mounting of the photo cell to an adjustable ring stand (see Fig. 13). The hood, which was necessary for proper operation, was soldered together from two tin cans and grounded to the shield on the cable. The size of the opening for light passage was determined by trial and error.

Temperature Thermocouple

A special type of temperature measuring thermocouple (25) was made up by using approximately 2 feet of inconel sheathed material. This material has a 1/16" O.D. and contains two No. 30 B.&S. chromel and alumel wires. A junction was made by using an electric arc welding technique.* The leads of alumel were welded on using the same size wire. Since these latter junctions were so close together (less than 1" separation) and in the same atmosphere, reasonable accuracy could be expected without calibration. This couple proved very effective. The metal sheath is a great aid where durability and accessibility are factors.

Galvanometer

The galvanometer used for the control portion of this furnace calorimeter was a Leeds & Northrup, ballistic, wall type (see Fig. 8). This galvanometer differs from the ordinary current galvanometer mainly in that it is designed to measure a transient rather than a constant current (26). For this reason it is calibrated in coulombs rather than amperes. The

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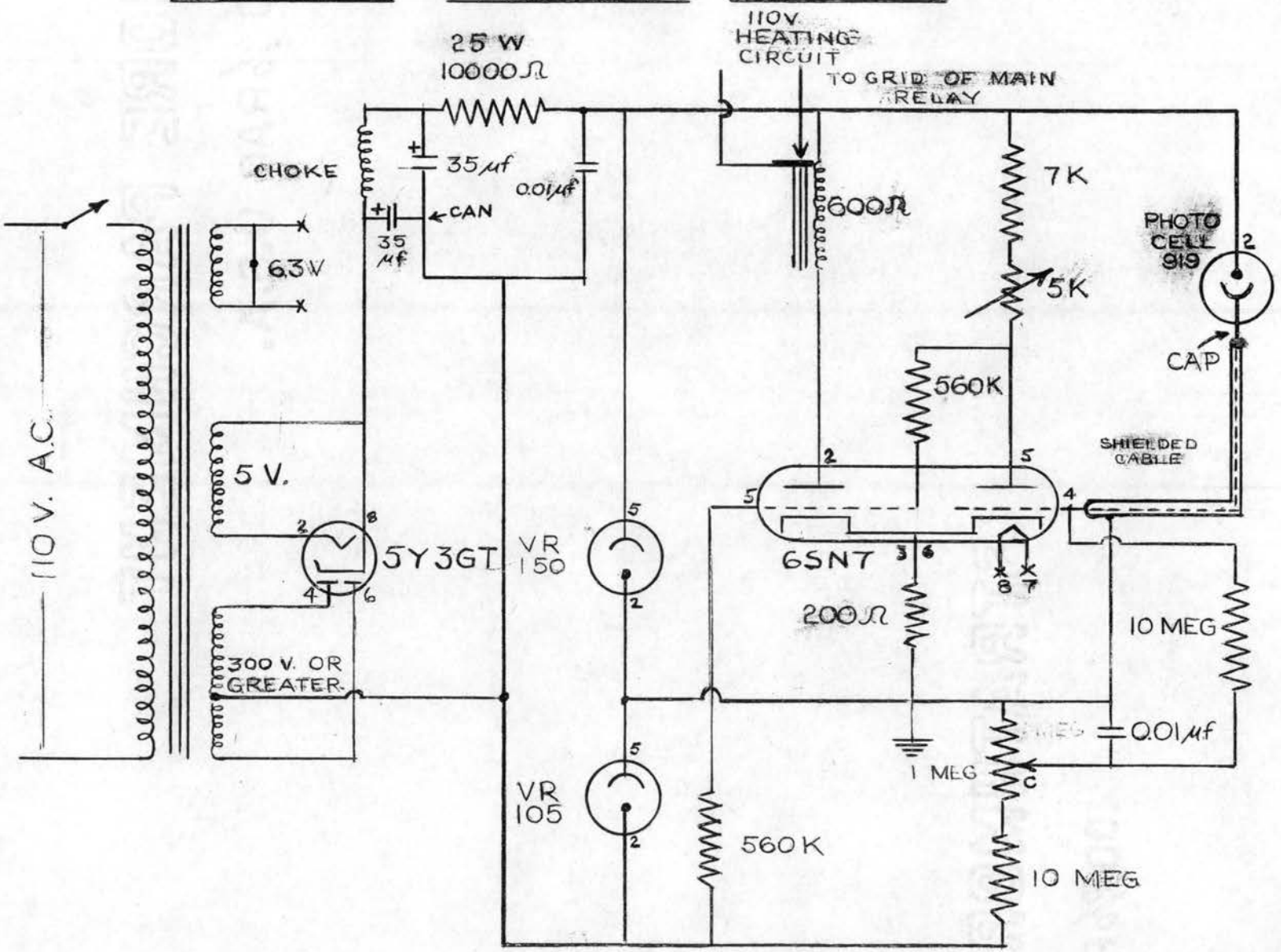
* This method utilizes a mercury terminal submerged in oil and 110 V power supply. The junction is twisted and trimmed as for a torch weld then the leads are connected to the second terminal and the twisted portion is lowered slowly through the oil until a flash is observed. The technique is highly recommended for junctions of approximately this size wire.

FIG. 7

SCHMIDT TRIGGER CIRCUIT



coil has a relatively high inertia as compared to those of other types of galvanometers; i.e. the coil is much larger in diameter and the period is longer (24 seconds in this case). These characteristics were deemed desirable for this experiment since the inherent lag in the furnace did not permit fast off-on type of control and a short period galvanometer would contribute to the "over control" problem. Since the control characteristics were changed with each different atmosphere, a series resistance was included in the circuit giving a suitably controlled time and heating rate. With the resistance in the circuit, the galvanometer was calibrated in the following manner.

1. A potentiometer (see Fig. 11) was connected across the terminals of the wall galvanometer to include the resistance.

2. The mirror of the wall galvanometer was then balanced in the neutral position using the reference junction slide wire with the main slide wire on zero.

3. The potentiometer galvanometer was then shunted and a measured electromotive force from the potentiometer fed into the wall galvanometer until the reflected light from a lamp was on the photoelectric cell (see Fig. 12).

This input was read directly from the main slide wire dial and divided by two times the average per degree increase of thermocouple voltage between 0^{o} and 1500^{o} F. (0.0225 M. V./^{o}F.) because of the two pair, series hookup of the differential thermocouple. This gave the temperature difference across the wall of the refractory crucible.

The Recorder

The Micromax recorder (see Fig. 9) was a galvanometer, mechanical balancing type recording potentiometer. The graph was made with time

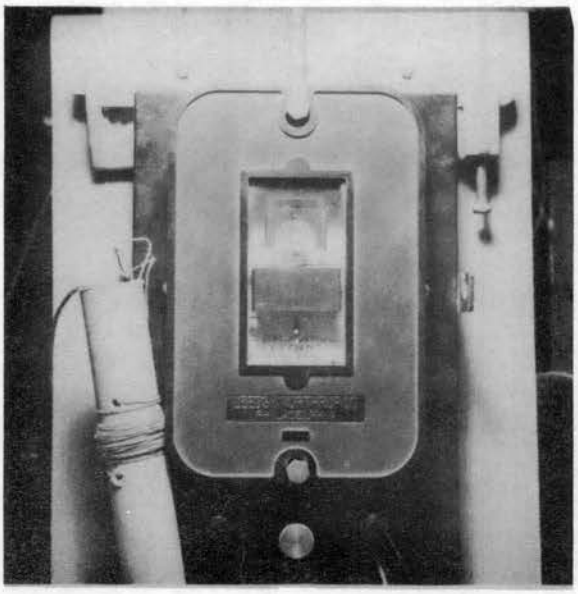


Figure 8.
Galvanometer with resistance coil

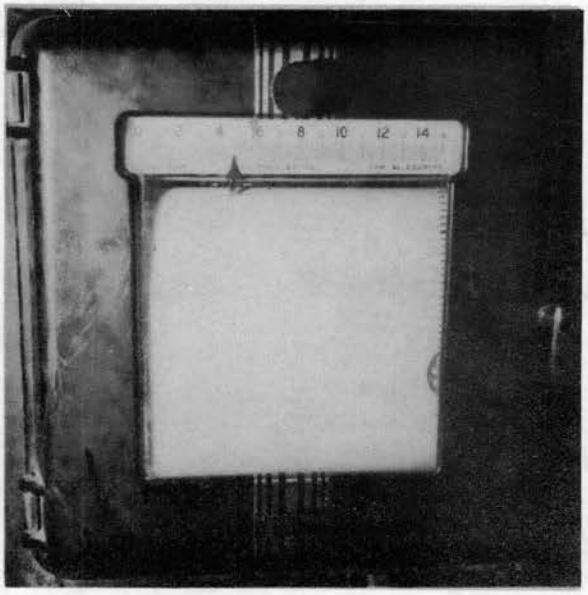


Figure 9.
Temperature recorder

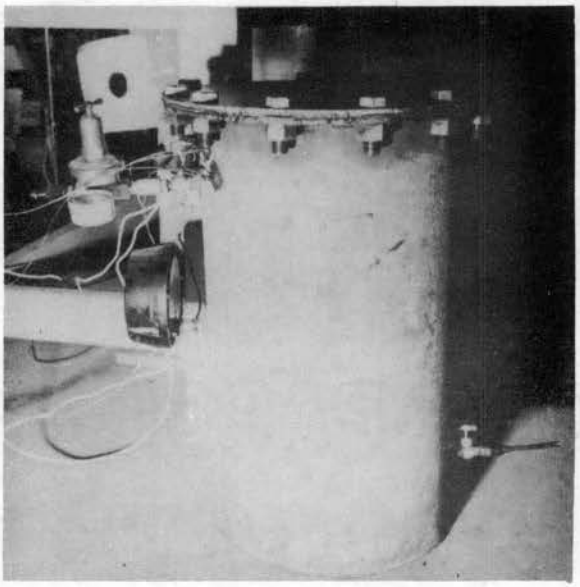


Figure 10.
Hermetically sealed container

Figure 11.
Potentiometer

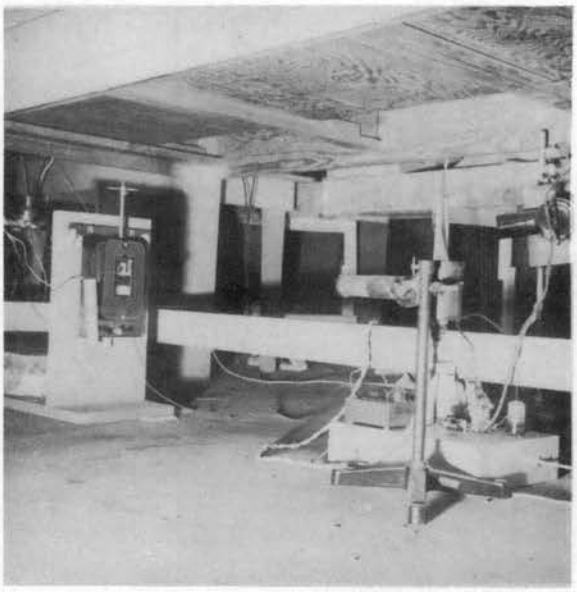


Figure 12.
Galvanometer, relay circuit and Photo Cell

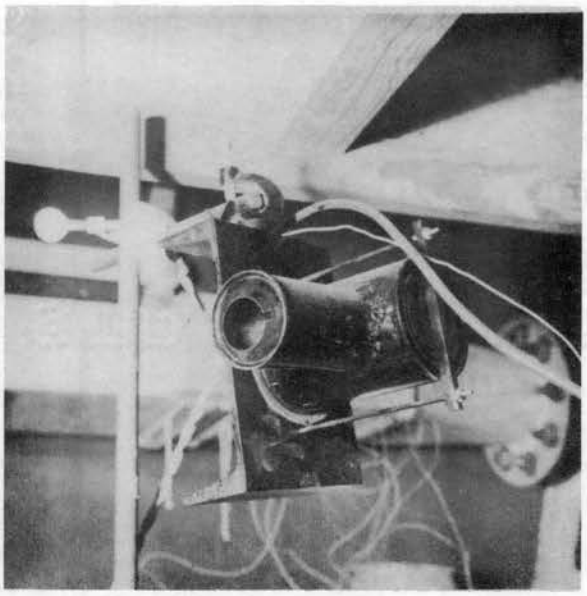


Figure 13.
Photoelectric Cell with hood

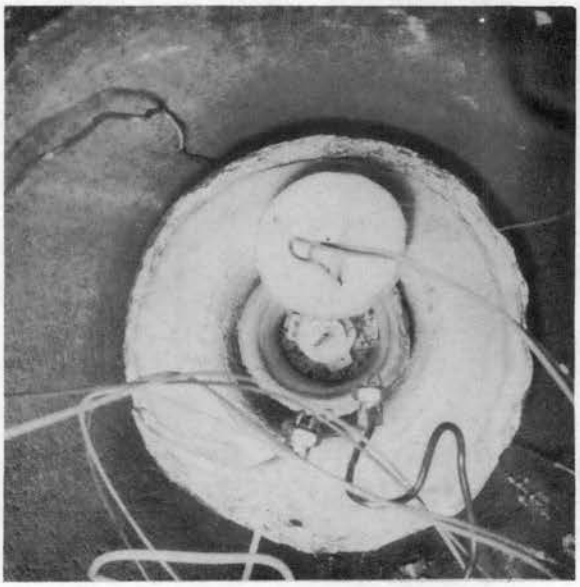


Figure 14.
Top view of furnace as placed in Hermetically sealed container

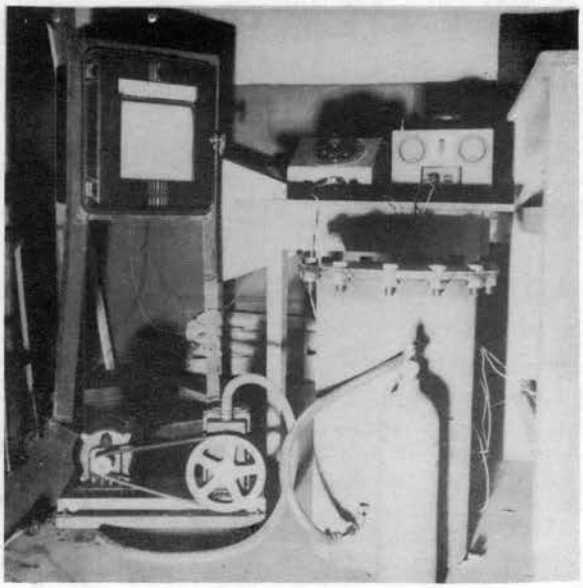


Figure 15.
General view in area of recorder showing Variac controls and vacuum pump

as the ordinate and temperature as the abcissa. Balance was made approximately once every second and the circuit automatically checked against a standard once every 48 minutes. The range of temperatures on the chart was 0^{o} to 1500^{o} F. and the rate of chart movement approximately 3"/hr.

The Hermetically Sealed Container

The entire furnace including insulation was housed in a hermetically sealed container (see Fig. 10). This consisted of a piece of 13" pipe approximately 25" long with a cap on one end. A flange welded to the other end provided a base to which a lid was bolted. An asbestos gasket was used in conjunction with Permatex (soft) cement to make an air tight seal. To get the thermocouple and power leads to the outside of the container, 1/8" ceramic insulator beads were inserted in drilled holes. After the wire leads had been inserted these insulators were covered with Sauereisen cement No. 1. This is a hard porcelain type of cement used for maintaining electrical insulation at high temperatures. This container did not prove to be entirely air tight. It would not hold a vacuum or any amount of pressure for more than a few minutes. Pressures of approximately 1 psig of helium were maintained throughout the run. This low pressure was maintained by adding more helium when the need arose (see Fig. 15).

CHAPTER IV

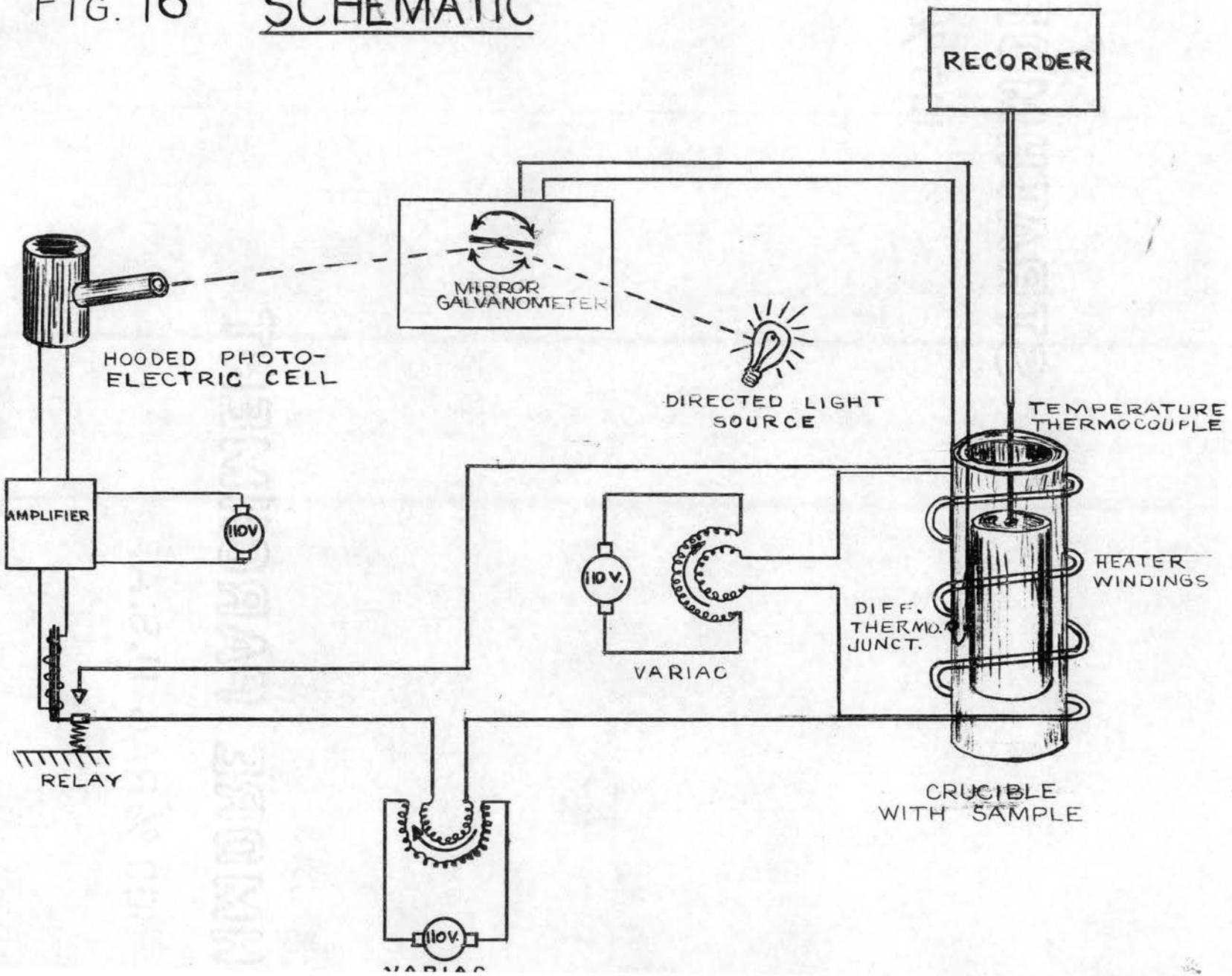
EXPERIMENTAL PROCEDURES AND RESULTS

Since very little was known concerning the power requirements of the described apparatus, the first part of the experiment was concerned with testing and calibration.

The Micromax recorder (see page vi) was adjusted and calibrated by means of a potentiometer (see page vi). The calibration was accomplished by beginning with the indicator of the recorder on the left or zero side of the chart. With a known input (taken from the Leeds and Northrup "Standard Conversion Tables" for chromel-alumel thermocouples) to the potentiometer, the indicator reading was checked at each 50^{o} F. rise in temperature against the temperature equivalent. There was never more than a maximum of one degree discrepancy in the lower ranges and never more than three degrees in the upper ranges. This is approximately as close as the chart can be read without the aid of a magnifying glass.

The first test runs were made with an empty crucible in free air. In this test it was observed that it was possible to attain a controlled rate of heating of approximately 240^{o} F/hr. with no additional resistance in the galvanometer circuit. The apparatus was then submerged in an atmosphere of helium (a pressure of approximately 1 psig. was maintained on this and all succeeding runs). The controlled heating rate in this atmosphere was more than twice that in free air or approximately 480^{o} F./hr. This was attributed to the high thermal conductivity of helium (24) as compared to that of air (0.0180 B hr^{-1} ft^{-1} F^{-1} for air

FIG. 16 SCHEMATIC



and 0.097 B hr^{-1} ft^{-1} F^{-1} for helium.

A sample of commercially pure titanium was chosen for the first test run using the galvanometer with no additional resistance. When the copper run was made, the controlled rate of heating dropped to 130° F./hr. This was a much lower rate than was expected but it was decided to proceed, as the lower rate might give information concerning transition points which would be helpful in a later analysis. The titanium heated at a slightly greater rate of 150° F./hr. All data was plotted and the curves obtained were fairly smooth and slightly convex upward. There were no sharp breaks in the titanium curve which indicated that no transition points had been crossed.

A line was drawn through this time-temperature graph to smooth out control variations, standardization blips and any other rough spots due to normal operation of the recorder. The slope of the resulting curve was then taken at 100° F. intervals by use of a magnifying glass. Because of the steepness of the curve plotted from data obtained during the low heating rate, a time increment of 20 minutes was used for the copper and titanium. Applying the formula given in Chap. II and the method outlined in the tables (see Table 1), the specific heat of titanium for a range of temperatures was calculated and plotted (see fig. 17 and 17A).

During these initial runs the control (or "off-on") circuit was kept at a voltage higher than the heating (or continuous) circuit. The initial settings were approximately 20 v. and 40 v. while the final settings in the upper temperature ranges were 45 v. and 85 v. By having the control circuit at a higher voltage a "stairstep effect" was produced in the time temperature curve. While giving a direct

indication of the reliability of control this was not considered good as measuring the slope would become quite difficult. The stair-step effect was eliminated in later runs by keeping the heating circuit at a voltage higher than the control circuit.

Since these heating rates were far below the one intended (4° C./min. or 430° F./hr (7)), more resistance was placed in the galvanometer circuit (see Chap. III). This amounted to a total of 233 ohms and gave a temperature differential of approximately 33.2° F. With this new value of differential a heating rate of around 380° F/hr was obtained for copper and 470° F/hr for titanium.

A new "empty" curve was taken for the new temperature differential and a new specific heat curve was plotted as before (see Table 2 and Fig. 17A).

During the first few runs a heavy accumulation of moisture was observed to form on the interior and near the top of the hermetically sealed container. This was at first believed to be due to incomplete evacuation of the air.* On later runs the moisture did not appear and it was decided that it was due to incomplete drying and hygroscopic effect of the insulation around the furnace.

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* A vacuum pump was connected to the helium container (see Fig. 15) and the pressure inside was reduced to approximately ½ atmosphere. Helium was then introduced under pressure to about 10 psig. Evacuation was again carried out to ½ atmosphere and helium again introduced and maintained to approximately 1 psig. throughout the run.

LONG RUNS

(Temp. Diff. on Differential Thermocouples = 9.55° F)

TABLE 1 A

EMPTY

Column Temp °F	Temp °C	1 Δt Min	2 From Graph °F T max	3 From Graph °F T min	4 ΔT 2 - 3	5 Slope $\frac{1}{4} = \frac{\Delta t_e}{\Delta T_e}$
300	148.9	10	330.5	269	61.5	0.1625
400	204.4	↓	431	369.5	61.5	0.1625
500	260.		531	470	61.0	0.164
600	315.6		630	570	60	0.1667
700	371.1		730	669	61	0.1612
800	426.7		830.5	769.5	61	0.1638
900	482.2		933	867.5	65.5	0.1526
1000	537.8		1032	966	66	0.1514
1100	593.3		1170	1032	70	0.1429
1200	648.9		1239.5	1165	74.5	0.1342
1300	704.4	↓	1340	1260	80	0.125

TABLE 1 B

COPPER

Column Temp °C	6 Δt Min	7 From Graph °F T max	8 From Graph °F T min	9 ΔT 7 - 8	10 Slope $\frac{6}{9} = \frac{\Delta t_s}{\Delta T_s}$
148.9	20	318	282	36	0.555
204.4	↓	419	382	37.5	0.533
260.		519	483	36	0.555
315.6		617.5	581.5	36	0.555
371.6		718	682	36	0.555
426.7		819	781.5	37.5	0.533
482.2		919	880.5	38.5	0.519
537.8		1020	980.5	39.5	0.507
593.3		1122	1080	42	0.482
648.9		1223	1179	44	0.454
704.4	↓	1325	1276	49	0.408

TABLE 1 C

Column Temp °C	11 Δt Min	12 From Graph °F T max	13 From Graph °F T min	14 ΔT 12 - 13	15 Slope $\frac{11}{14} = \frac{\Delta t_u}{\Delta T_u}$
148.9	20	324	274	50	0.4
204.4		424	375	49	0.408
260		523	477	46	0.434
315.6		623	578	45	0.444
371.1		720.5	677	43.5	0.46
426.7		820	778.5	41.5	0.482
482.2		923	877	46	0.434
537.8		1026	957	51	0.392
593.3		1125	1076	49	0.407
648.9		1225.5	1175	50.5	0.396
704.4		1327	1274	53	0.377

TABLE 1 D

Calculations of Specific Heat

Column Temp °C	16 $\frac{\Delta t_u - \Delta t_e}{\Delta T_u \ \Delta T_e}$ 15-5	17 $\frac{\Delta t_s - \Delta t_e}{\Delta T_s \ \Delta T_e}$ 10-5	18 $\frac{16}{17}$	19 C_p Copper Fig. 2	20 18x19	21 $\frac{W_s = 96.595}{W_t \ 47.26}$	22 C_p=20x21 (Titanium)
148.90	0.2375	0.3925	0.605	0.0946	0.0573	2.0415	0.117
204.4	0.2455	0.3705	0.663	0.096	0.0637		0.130
260	0.270	0.3910	0.691	0.0973	0.0673		0.137
315.6	0.2773	0.3883	0.7515	0.0985	0.0741		0.151
371.1	0.2988	0.3938	0.758	0.0994	0.0754		0.154
426.7	0.3182	0.3692	0.862	0.1008	0.0870		0.178
482.2	0.2814	0.3664	0.768	0.1022	0.0785		0.1613
537.8	0.2406	0.3556	0.677	0.10325	0.0700		0.143
593.3	0.2641	0.3391	0.779	0.1045	0.0814		0.166
648.9	0.2618	0.3198	0.818	0.1056	0.0864		0.176
704.4	0.252	0.2730	0.916	0.1069	0.0978		0.200

SHORT RUNS

(Temp. Diff. on Differential Thermocouples = 33.2° F)

TABLE 2 A

EMPTY

Column Temp °F	Temp °C	1 Δt Min	2 From Graph T max	3 T min	4 ΔT 2 - 3	5 Slope $\frac{1}{4} = \frac{\Delta t_e}{\Delta T_e}$
300	148.89	20	520	107	413	0.0484
400	204.44		634	194	440	0.0454
500	260		731	283	448	0.0446
600	315.56		827	372	455	0.0439
700	371.11		933	471	462	0.0433
800	426.67		1046	567	479	0.0417
900	482.22		1155	670	485	0.0413
1000	537.78		1260	761	499	0.0401
1100	593.33		1372	856	516	0.0395
1200	648.89	20	1487	952	535	0.0374
1300	704.44	10	1441	1167	274	0.0365

TABLE 2 B

COPPER

Column Temp °C	6 Δt Min	7 From Graph °F T max	8 T min	9 ΔT 7 - 8	10 Slope $\frac{6}{9} = \frac{\Delta t_s}{\Delta T_s}$
148.89	20	358	246	112	0.1785
204.44		457	343	114	0.1755
260		560	441	119	0.168
315.56		661	538	123	0.1626
371.11		761	640	121	0.1652
426.67		863	737	126	0.1587
482.22		965	836	129	0.155
537.78		1067	935	132	0.1515
593.33		1170	1033	137	0.146
648.89		1275	1128	147	0.136
704.44		1382	1224	158	0.1265

TABLE 2 C

TITANIUM

Column Temp °C	11 Δt Min	12 From Graph °F T max	13 From Graph °F T min	14 ΔT 12 - 13	15 Slope $\frac{11}{14} = \frac{\Delta t_u}{\Delta T_u}$
148.9	20	381	221	160	0.125
204.4	↓	480	322	158	0.1265
260		577	421	156	0.1282
315.6		677	524	153	0.1307
371.1		775	623	152	0.1315
426.7		873	727	146	0.1369
482.2		974	827	147	0.136
537.8		1078	926	152	0.1315
593.3		1179	1024	155	0.129
648.9		1282	1121	161	0.1242
704.4		1397	1219	178	0.1123

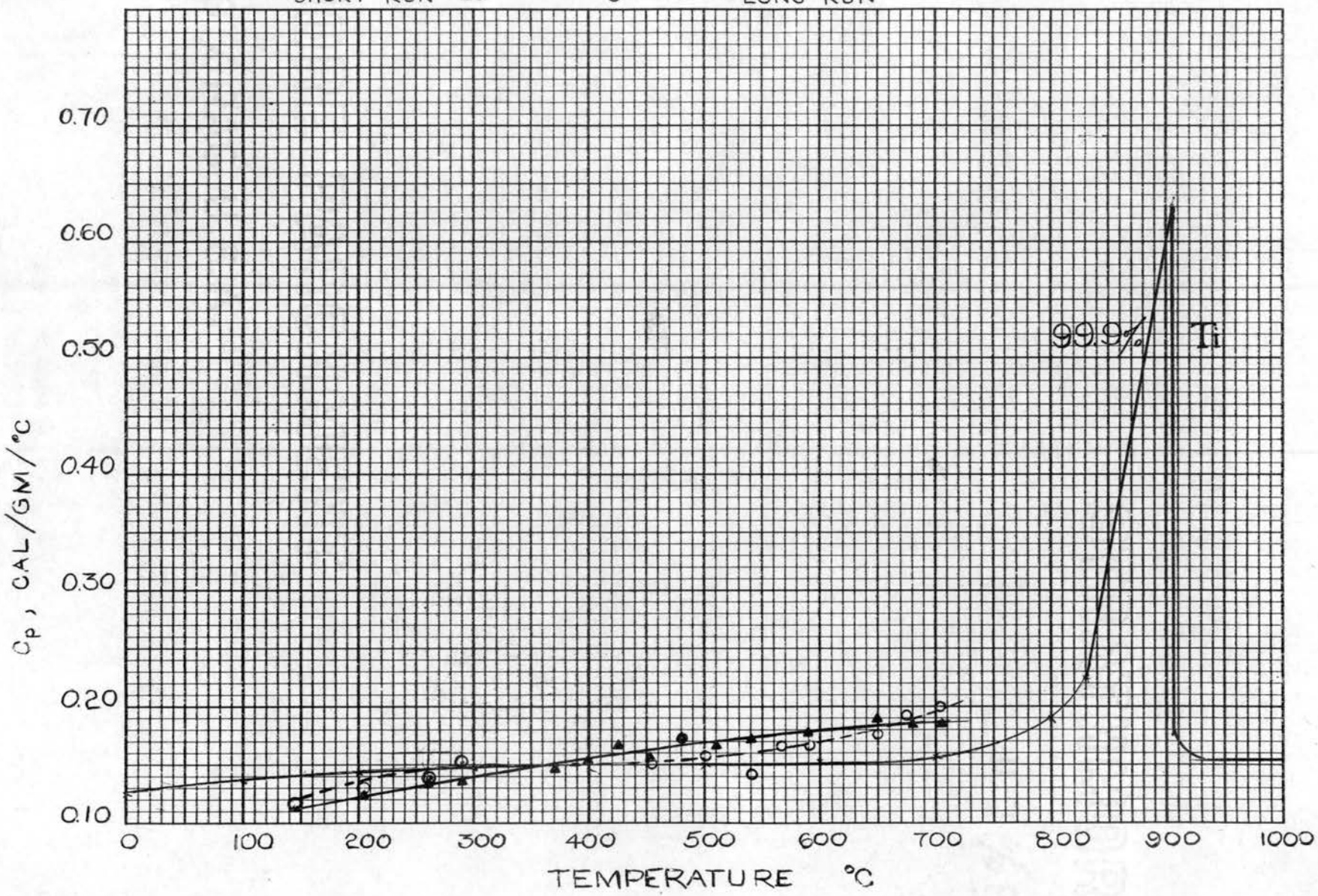
TABLE 2 D

Calculations of Specific Heat

Column Temp °C	16 $\frac{\Delta t_u}{\Delta T_u} - \frac{\Delta t_e}{\Delta T_e}$ 15-5	17 $\frac{\Delta t_s}{\Delta T_s} - \frac{\Delta t_e}{\Delta T_e}$ 10-5	18 $\frac{16}{17}$	19 C_p Copper Fig. 2	20 18x19	21 $\frac{W_s}{W_t} = \frac{96.281}{47.257}$	22 C_p=20x21 (Titanium)
148.9	0.0766	0.1301	0.587	0.0946	0.0556	2.04	0.1132
204.4	0.0811	0.1300	0.624	0.0960	0.0599	↓	0.1221
260.	0.0836	0.1234	0.677	0.0973	0.0658		0.1341
315.6	0.0868	0.1187	0.732	0.0985	0.0721		0.1469
371.1	0.0882	0.1226	0.724	0.0994	0.0720		0.1468
426.7	0.0952	0.1170	0.814	0.1008	0.0821		0.1672
482.2	0.0947	0.1137	0.834	0.1022	0.0854		0.1740
537.8	0.0914	0.1114	0.819	0.1033	0.0847		0.1725
593.3	0.0895	0.1065	0.840	0.1045	0.0873		0.1778
648.9	0.0868	0.0986	0.880	0.1056	0.0928		0.1892
704.4	0.0758	0.0900	0.843	0.1069	0.0902		0.1838

FIG. 17 SPECIFIC HEAT OF TITANIUM

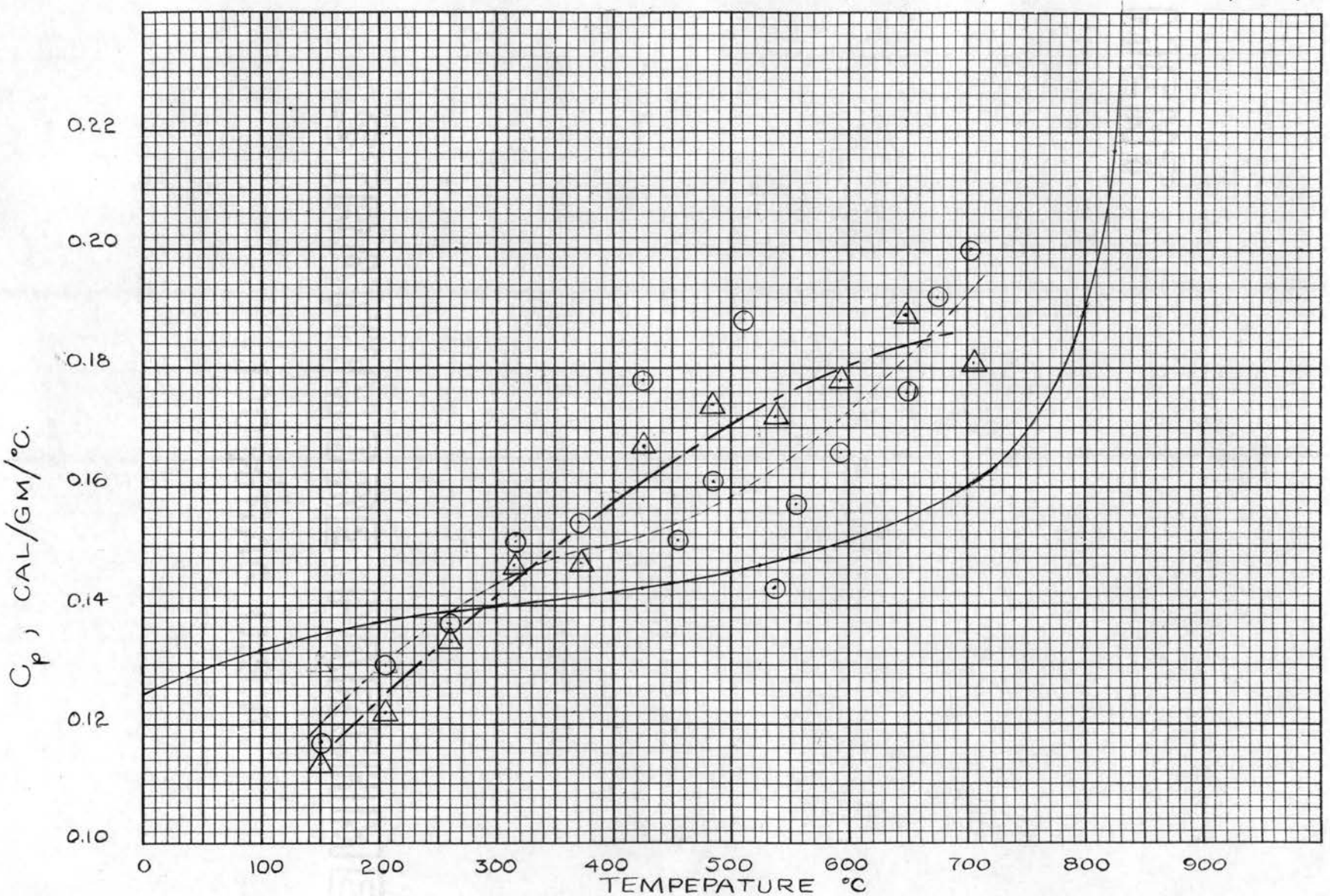
▲——— SHORT RUN O- - - - - - LONG RUN



TITANIUM

FIG. 17A SPECIFIC HEAT VS. TEMPERATURE (EXPANDED SCALE)

△——--——SHORT RUN ○--------LONG RUN ———— 99.9% Ti (28)



CHAPTER V

DISCUSSION OF ERROR AND ACCURACY

As in all work of this nature, consideration must be given to the experimental error.

The errors considered at this time are:

(1) Thermocouple error which is $\pm 4^{o}$ F for temperatures below 530^{o} F and $\pm$ 3/4% for temperatures between 530^{o} and 2300^{o} F (see Leeds and Northrup thermocouple wire catalog).

(2) Recorder error which was -1^{o} F in the low ranges and $+3^{o}$ F in the high ranges.

(3) An estimated error in reading the recorded time-temperature curve of $\pm 1^{o}$ F in temperature and 0.25 min. in time.

The first two errors can be considered as systematic. For purposes of this calculation, it is assumed that they amount to displacing the time-temperature curve (and consequently the specific heat-temperature curve) parallel to itself and that the slope of the curve is not affected. The percentage error in specific heat at a point due to these two errors can thus be considered and added to the third or haphazard error.

The experimental error is thus figured at 400^{o} and 1200^{o} F. The percent experimental error at 400^{o} F due to systematic error is calculated by the following procedure.

The slope of the specific heat curve, as plotted (Fig. 17a), at 400^{o} F is approximately $\frac{0.132 - 0.113}{100} = \frac{0.019}{100} = 0.00019$. A difference of 5^{o} F would make a difference of $5 \times 0.00019 = 0.00095$ in the specific heat at 400^{o} F. This is equal to a percentage error of $\frac{0.00095}{0.13} = .0073 = 0.73\%$.

The percent of experimental error at 400° F due to haphazard error can be calculated as follows:

Consider the specific heat formula (Chap. II).

$$C_u = \left(\frac{\frac{\Delta t_u}{\Delta T_u} - \frac{\Delta t_e}{\Delta T_e}}{\frac{\Delta t_s}{\Delta T_s} - \frac{\Delta t_e}{\Delta T_e}} \right) \frac{W_s C_s}{W_u} \qquad (1)$$

where the subscript u stands for titanium, subscript s stands for copper and all other symbols are the same as for the derivation in Chap. II.

For purposes of error calculation, the right bracket can be ignored since the weights, W_s and W_u, can be measured as accurately as desired and in this case were measured to four significant figures. Likewise, the error in accuracy of the specific heat of copper, C_s, would not add significantly to the total error.

Since there are errors in reading both temperature and time at each end of the increment, the numerical errors at 400° F are:

for the empty curve; $\Delta t = 10 \text{ min} \pm 0.50 = 10 \pm 5\%$
$\Delta T = 62 \text{ deg} \pm 2 = 62 \pm 3.2\%$

for the copper curve: $\Delta t = 20 \text{ min} \pm 0.5 = 20 \pm 2.5\%$
$\Delta T = 36 \text{ deg} \pm 2 = 36 \pm 5.5\%$

for titanium curve; $\Delta t = 20 \text{ min} \pm 0.5 = 20 \pm 2.5\%$
$\Delta T = 50 \text{ deg} \pm 2 = 50 \pm 4\%$

This gives a percentage error of,

8.2% for the slope of the empty curve,

8% for the slope of the copper curve,

and 6.5% for the slope of the titanium curve.

For the calculation indicated in the numerator in Equation (1) the percentage error for the difference of two numbers is calculated in this manner (30):

$$\% \text{ error} = \frac{nX \pm mY}{X - Y}$$

where

X = true value of the number having the highest % of error
n = the fraction of error in X
Y = the true value of the other number
m = the fraction of error in Y.

% error in the numerator =

$$\frac{\left(\frac{10}{62} \times 0.082\right) - \left(\frac{20}{50} \times 0.065\right)}{\frac{10}{62} - \frac{20}{50}} = 5.35\%$$

% error in the denominator =

$$\frac{\left(\frac{10}{62} \times 0.082\right) - \left(\frac{20}{36} \times 0.08\right)}{\frac{10}{62} - \frac{20}{36}} = 7.9\%$$

Therefore, the total percentage due to haphazard error in reading the time-temperature chart is $5.35 + 7.9 = 13.25\%$. This added to the percentage due to systematic error gives a total of $13.25 + 0.73 = 13.98\%$ possible experimental error in the specific heat determination at 400^{o} F.

In figuring the experimental error at 1200^{o} F by the same procedure a figure of approximately 13% is obtained.

It is observed that the systematic error is negligible. With such a large haphazard error it would seem that a different method of taking data would be in order. The potentiometer stop watch method might yield better results (7).

It is noted that no account has been taken of an emissivity error due to difference of the surfaces of the standard and unknown sample. It is believed at this time that there is no such error. This conclusion is based on the following reasoning:

When varying amounts of heat energy are reflected back to the

inner wall of the crucible, the differential thermocouple senses this energy by the increase in temperature and, to keep the temperature differential constant, transmits to the controller the signal for more power input. This automatically maintains a constant heat energy input. Except for the fact that there is a slight change of the thermal conductivity of the brick with temperature and that the previously mentioned Seebeck effect is nonlinear with temperature, there will be no error caused by emissivity.

Another important error which has been neglected thus far is the radiation effect while heating the empty crucible. This can be a sizeable error, especially at higher temperatures as has been noted in Chapter I. Due to the lack of time for further experimentation with a second standard and the fact that the data from this experiment varies considerably, no attempt has been made to evaluate this error.

The evaluation of the apparatus as a device for obtaining specific heat data was hampered by the selection of titanium as the trial material. It is known that this metal changes its physical properties radically with slight amounts of impurities in its composition and very little is known concerning its specific heat (27, 28). The best information available is shown in Fig. 17 for 99.9% titanium and the sample was stated to be commercially pure titanium.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Most of the laboratory hours on this problem were spent in obtaining a suitable heater-wire holder. It is felt that much more time need be spent in test runs with samples of known specific heat data.

A much higher temperature could probably be attained with the present furnace in the inert atmosphere. If the present ceramic material is used at higher temperatures, it is recommended that it be washed with the Sauereisen No. 6 cement to prevent chemical action with the heater wire.

On one occasion the power to the furnace was cut off at a temperature of 1400° F. The temperature continued to increase more than 50° F. This indicates a great deal of "thermal inertia" which is always a problem in electrically controlled heating. This could be partially overcome by decreasing the amount of mass in the immediate vicinity of the heating element. To do this would mean using a heater wire holder of much lighter construction. (One could be obtained commercially since the inductive effect in the thermocouple leads is negligible. This eliminates the complicated winding problem.)

Even with the thermal inertia present, it is believed that the apparatus maintained fairly close control of the thermal energy input. Justification of this statement comes from observing the smoothness of the recorded time-temperature curve. In addition, during one of the empty runs, the asbestos top was left off inadvertently. When the accident was noticed and another run made with the cover on, the data

obtained gave the resulting curve which when superimposed coincided perfectly with the curve made from data obtained by a run without the cover. Just how important thermal inertia is in the control would have to be determined by further testing.

Results of the different heating rates with different atmospheres indicates that a much closer control of the atmosphere is needed. Another inert gas such as argon, which has a thermal conductivity more nearly equal to that of air, and an automatic pressure regulator would be desirable. The inert atmosphere should be maintained during complete cooling as well as during heating to avoid oxidation or otherwise contaminating the specimen.

The variation of the experimental data from mean values (see Fig. 17A) could possibly be accounted for by experimental error as calculated in Chapter V. The variation of the mean below the values for 99.9% titanium could be caused by the fact that there was poor control of the heating circuit up to approximately 400° F. (Further experimentation with insulation in the immediate vicinity of the heater elements might indicate an improvement for the control in this region.) The displacement of the experimental mean from that of the 99.9% titanium curve in the upper temperature ranges could be due to impurities in the specimen tested.

The brief trial runs with the apparatus were most encouraging performance-wise. It is believed, however, that much could be gained toward evaluating the comparative method by further tests with the present setup.

A SELECTED BIBLIOGRAPHY

1. White, William P., Calorimetry in Furnaces, J. Phys. Chem., Pt. I v. 34 (1930), p. 1121.

2. White, William P., Calorimetry in Furnaces, J. Am. Chem. Soc., v. 40 (1918), p. 1858-98.

3. Southard, J. C., A Modified Calorimeter for High Temperatures, J. Am. Chem. Soc., v. 63 (1941), p. 3142.

4. Ginnings, D. C. and J. Corruccini, An Improved Ice Calorimeter, Nat. Bu. Sta. J. of Res., v. 38 (1947), p. 583.

5. Sykes, C. and H. Wilkinson, The Transformation in the B Brasses, J. of Inst. of Metals (London) v. LXI No. 2 (1937), p. 223.

6. Sykes, C. and F. W. Jones, Methods for the Examination of Thermal Effects Due to Order-Disorder Transformations, J. of Inst. of Metals (London) v. LIX (1936), p. 257.

7. Smith, Cyril S., A Simple Method of Thermal Analysis Permitting Quantitative Measurement of Specific and Latent Heat, Am. Inst. of Mining and Metallurgy Engrs. v. 137 (1940), p. 236-244.

8. Kelly, K. K., Contributions to the Data on Theoretical Metallurgy, Bureau of Mines Bul. 476 (1949), p. 2-3.

9. Seekamp, H., Ueber die Messung wahrer spezifischer Waermen fester und fluessiger Metalle bei hohen Temperaturen, Zeitschr. anorg. Chem., v. 195 (1931), p. 345.

10. Giaugue, W. F. and Wiebe R., Nernst Vacuum Calorimeter, J. Am. Chem. Soc., v. 50 (1928), p. 101.

11. Sweeney, R. J., Measurement Techniques in Mechanical Engineering, New York: John Wiley and Sons, Inc., (1953), p. 150-153.

12. Weber, Robert L., Heat and Temperature Measurement, New York: Prentice Hall, Inc., (1950), p. 254.

13. Ginnings, Defoe C., and George T. Furukawa, Heat Capacity Standards for the Range 14° to 1200° K, J. Am. Chem. Soc., v. 75 (1952), p. 522.

14. Willis, William R., A New Furnace Calorimeter: The Heat Capacity of Graphite, Oklahoma A. and M. College (1954).

15. Fife, Wynn B., A Study of Factors Affecting Operation of a Radiation Calorimeter, Oklahoma A. and M. College (1953).

16. Sucksmith, W. and H. N. Potter, Practical Applications of the Nernst Calorimeter at High Temperatures, Proc. Royal Soc. (London), v. 112 (1926), p. 157.

17. Armstrong's Industrial Insulations, Armstrong Cork Co., Lancaster, Pa. (1951).

18. Sauereisen Engineer's Production Manuel, Sauereisen Cements Co. Pittsburg 14, Pa. (1951).

19. Physical Properties of Copper, Metals Handbook, (1939), p. 1382.

20. Strong, John, Procedures in Experimental Physics, New York: Prentice Hall, Inc. (1938).

21. Ceramic Data Handbook with Buyer's Guide, Chicago: Industrial Publications, Inc. (1946-47), p. 318.

22. Driver - Harris Catalog No. R-54, Design of Small Furnaces, Driver - Harris Co., Harrison, N. J. (1954), p. 13.

23. Armstrong Armatemp Cements, Armstrong Cork Co., Lancaster, Pa. AlA File No. 37-D-3.

24. Jacob, M. and G. A. Hawkins, Elements of Heat Transfer, New York: John Wiley and Sons, Inc. (1950).

25. Ceramo Thermocouple Wires and Thermocouple Extension Wires, Catalog, Rochelle Park, N. J., Thermo Electric Co., Inc., Wire Section 31-300 (1955).

26. Smith, Arthur Whitmore, Electrical Measurements in Theory and Application, New York: McGraw-Hill Book Co., Inc. (1924).

27. Jaeger, F. M. and E. Rosenbohm, The Specific Heat of Titanium, Recueil Des Travaux Chimiques Des Pays Bas. v. 55 (1936), p. 615.

28. Specific Heat of Titanium (99.9 Ti), Metals Progress, v. 66 No. 1-A, Jul. 54, p. 87.

29. Smith, Arthur Whitmore, Electrical Measurements in Theory and Application, New York: McGraw-Hill Book Co., Inc. (1924), p. 39, 66.

30. Marshall, Roland B., Measurements in Electrical Engineering, Pt. I, Cincinnati; John B. Swift Co., Inc. (1948), p. 1-10.

OTHER REFERENCES

American Institute of Physics, Temperature, Its Measurement and Control in Science and Industry, New York: Reinhold Publ Corp. (1941).

Barksdale, Jelks, Titanium, Its Occurrence, Chemistry, and Technology, New York: Ronald Press Co. (1949).

Douglas, T. B. and J. L. Dever, Thermal Condictivity and Heat Capacity of Molten Materials, Part I, Wright Air Development Center Tech, Rpt. 53-201, (1953).

Ginnings, Defoe C. and Robert J. Corruccini, Enthalpy, Specific Heat & Entropy of Al_2O_3 from 0^o - 900^o C. National Bureau of Standards J. of Res., v. 38 (1947) p. 593.

Ginnings, Defce and Robert J. Corruccini, An Improved Calorimeter, Especially for Determination of Density of Ice, Nat. Bu. of Sta. J. of Res. v. 38, p. 583.

Harris, Forest K., Electrical Measurements, New York: John Wiley & Sons, Inc., (1952).

Jaeger, F. M. and E. Rosenbohm, On the Determination of the Specific Heat of Solid Substances between 0^o and 1625^o C. I Method and Apparatus, Proc. Acad. Sci. Amsterdam, v. 30, (1927) p. 905.

Swietoslawski, Wojciech, Micro-Calorimetry, New York: Reinhold Pub. Corp. (1946).

Sykes, C., Methods for Investigating Thermal Changes Occurring during Transformation in a solid Solution. Proceedings of the Royal Soc. of London, v. 148 (1935) p. 422.

Smithells, Colin J., Metals Reference Book, New York: Interscience Pub. (1949).

White, Marsh William, Experimental College Physics, New York: McGraw-Hill Co., Inc. (1940).

White, William P., Specific Heats at High Temperatures, Physical Review, v. 28 (1908) p. 461.

White, William P., Some Calorimetric Methods, Physical Review, v. 31 (1910).

White, William P., Easy Calorimetric Methods of High Precision, J. Am. Chem. Soc., v. 36 (1949) p. 2325.

White, William P., The Modern Calorimeter, New York: Book Dept. Chemical Catalog Co., Inc. (1928).

Wilcox, Edgar A., Electrical Heating, New York: McGraw-Hill Book Co., Inc. (1928).

APPENDIX I

A check of the inductive effect of the heating elements on the temperature measuring thermocouple was made in the following manner:

A thermocouple junction was made up and the leads attached to the Micromax recorder. The bead was submerged in ice water and the recorder pointer allowed to come to a stabilized position. A loop of one lead was then threaded in one hole and out the other of a two hole thermocouple lead insulator which was 1/16" in diameter. (This loop was approximately the same size as the one formed by the temperature measuring thermocouple.) The loop was then inserted in the hole in the top of the refractory crucible to the same position as the temperature thermocouple. The power to the heating coils was then turned off and on and movement of the recorder pointer observed. There was none. The resulting graph was a straight vertical line.

This indicated that the induced current in the temperature measuring thermocouple was negligible in this experiment.

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