

A NEW FURNACE CALORIMETER:
THE HEAT CAPACITY OF GRAPHITE

By

WILLIAM R. WILLIS

Bachelor of Science

West Virginia Wesleyan College

Buckhannon, West Virginia

1948

Master of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

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**A NEW FURNACE CALORIMETER:
THE HEAT CAPACITY OF GRAPHITE**

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Thesis Approved:

John Johnson

Thesis Adviser

W. D. Dyer

Robert Woodson

Dean of the Graduate School

321657

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FRATHEMORE PARCIMENT

100% RAG U.S.A.

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CHAPTER I

INTRODUCTION

K. K. Kelly¹ has divided the field of high-temperature calorimetry into three divisions on the basis of the method used for measurement. These are: (1) the method of mixtures, (2) methods utilizing heating and cooling rates, and (3) the method measuring the resultant temperature change from adding definite amount of heat. Methods (2) and (3) are known as furnace calorimetry, since the measurements are made at the particular elevated temperature.

Owing to the relatively great precision with which heat quantities may be measured at lower temperatures, the method of mixtures has been used most extensively for high-temperature specific heat measurements. There are two difficulties inherent in this method which limit its usefulness and precision. These are that (1) only mean specific heats are found from the difference of two large numbers, and (2) that slow transformations in the range between the furnace temperature and the calorimeter temperature are not adequately handled.

Furnace calorimetry, while it eliminates the two difficulties mentioned above, introduces several new problems. However, there is this essential difference: the main prob-

blems of furnace calorimetry are experimental in nature and not necessarily inherent in the method. There is hope that by extremely accurate control and measurement of temperature and by building into the calorimeter the proper characteristics, furnace calorimetry may be made as accurate as the method of mixtures and much more general.

While Kelly's division of furnace calorimetry is the most basic, for a complete description of a particular instrument the following characteristics should be given: (1) whether or not the instrument is operated adiabatically. If the instrument is non-adiabatic, then one must know whether or not there is internal heating of the sample, and whether an increment of temperature ΔT or a time rate of change of temperature \dot{T} is measured. Each of these methods emphasizes some of the errors in calorimetry while minimizing others. The particular method chosen then will be decided by which of the errors the worker feels he may most successfully eliminate.

As the temperature rises, the errors involved in calorimetry are accentuated and several new difficulties appear. The major errors are that (1) accurate measurement of temperature becomes more difficult, (2) suitable materials of construction become scarce, (3) electrical leaks develop, (4) lags and temperature gradients become more pronounced, (5) radiating surfaces become more important so that slight changes in the condition of these surfaces introduce large errors in calibration factors, and (6) radiation corrections become very large for non-adiabatic methods.

The temperature error may be divided into two parts, that of measuring accurately the temperature of the temperature-sensitive element and that of determining how closely this element temperature corresponds to the quantity desired.

The first of these problems is a familiar one which has been well worked out.² The absolute error in determining the temperature of the experiment is not particularly important since by most methods of furnace calorimetry these values are used only to label a particular value of C_p . Since this quantity varies rather slowly with temperature at elevated temperatures, the percentage error in the final result may be rather small. The particular quantity with the biggest effect on C_p is the error in reading a difference of temperature between two bodies both of which are at an elevated temperature and nearly equal in temperature. Here the precision of the instrument has more effect than its absolute accuracy.

The second possible error in temperature measurement, that of being sure that the temperature measured is the desired quantity, is much more difficult to overcome. It is here that the design of the particular instrument involved becomes of importance. In the case of measurement with thermocouples or by optical pyrometry, the temperature of only a relatively small portion of the system is actually measured. Then if the thermel is at the same temperature as this area, the problems of inhomogeneity and temperature lags still remain. The sampling problem is often overcome by the use of some integrating instrument which gives a mean value of the temperature.

Obviously, however, the best solution is the elimination of inhomogeneity of temperature. One may say then that the limiting factors in the accurate measurement of temperature are those connected with lags, electrical leaks, and undesired surface temperature gradients.

The fact that suitable materials for calorimetry become scarce as the temperature rises must be regarded as just another necessary evil. Most of the difficulties may be reduced again to the fact that excessive lags and gradients enter as a direct result of the use of inferior materials. Thus the availability of water as a fluid heat-transfer medium for low-temperature work is of great help. A comparable liquid has not yet been used at higher temperatures and in any case the difficulty of handling fluid heat-transfer is much greater. As the temperature goes up, insulating properties of all materials deteriorate. Or if one obtains the desired insulation then excessive gradients enter the picture.

Of the lags and gradients it may suffice to say that these lead one to measure the wrong quantity at the wrong time. With reference to lags, White³ has stated that if they remain constant, empirical calibration of the instrument tends to cancel the errors due to this source.

Electrical leaks are of two types: (1) those affecting the electrical measuring system itself and (2) those which occur between the thermocouple and the calorimeter. By rather well known methods³ the first may be reduced to very low values. The latter, however, are much more obstinate. • In one instance

reported in the literature⁴, these leaks would not allow accurate differential temperature readings because of potential developed between the two surfaces whose temperatures were measured. In this particular case, however, separate readings and consequent calculation of the difference was possible. This difficulty is seldom mentioned in the literature except as an unevaluated source of possible error. It seems to be assumed that if the results are not irregular the error may be ignored.

The extremely rapid rise in radiative transfer of heat is one of the distinctive features of high-temperature work. In the equation for this transfer there appears but one term which depends upon the nature of the radiating material, ϵ , the emissivity of the surface. If the heat transfer properties of any portion of the system help determine a calibration factor, then ϵ must obviously remain constant. It is possible for ϵ to vary by as much as 10^2 for the tarnishing of a metal surface. Elimination of the error depends mainly upon proper design of the calorimeter and, where design is of no help, upon careful control of the surfaces involved.

The work being reported here is an attempt to design and use a furnace calorimeter which is non-adiabatically operated and utilizes the value of \dot{T} in finding C_p .

CHAPTER II

HISTORICAL REVIEW

A very cursory survey of the history of calorimetry reveals that most of the methods in use today were devised early in the development of the science of thermodynamics. Thus, before 1800, Black⁴ had devised a form of ice calorimeter and, indeed, this instrument had undergone considerable modification at the hands of Lavoisier and Laplace⁵. Black is also credited with employing a method of mixtures in determining specific heats, although it was Regnault who brought the method to a high degree of accuracy in the mid-eighteenth century. Dulong and Petit⁶ devised the method of cooling, early in the nineteenth century.

These three methods are the principal methods of calorimetry, and the history of calorimetry is the story of their refinement.

Stephens⁷ credits the early development of calorimeters utilizing a phase change to the fact that such a fixed point helped alleviate errors due to inaccurate thermometry. In general, other forms of the method of mixtures are faster and more convenient.

With the advent of Bunsen's⁸ ice calorimeter, really good

accuracy was obtainable with these "phase-change" calorimeters, limited mainly by the fact that the density of ice appeared to be a function of the history of the calorimeter. This difficulty has been overcome in recent years⁹, to the extent that the most accurate high-temperature measurements of specific heat have been made with an ice calorimeter.

Of these methods only the method of cooling is strictly applicable to furnace calorimetry. A modified form of the method of mixtures, the Nernst¹⁰ method, is used in furnace calorimetry but it came only after other necessary advances in the field.

There were two major developments which allowed furnace calorimetry to develop and progress, the advent of electrical heating and the technique of adiabatic operation.

The first of these, electrical heating, depended upon an accurate determination of the electrical equivalent of heat. Previous to this, workers were tied to the specific heat of water as a standard for the measurement of heat quantities. Since this property varied with temperature, confusion reigned, with workers using various values of the calorie depending upon their experimental temperature and personal preference. Also, furnace calorimetry, independent of the ice calorimeter or the method of mixtures employing water, could not develop. With accurate values for the electrical equivalent of heat, it became possible to define the calorie as a unit of energy in standard unit systems, and to perform direct calibrations of calorimeters.

One of the earliest uses of electrical heating was that of Nernst¹⁰ and Eucken¹¹. The first paper seems to be that of Eucken and he is often given credit, but he states that the basic idea was due to Nernst.

This method, which may be considered a form of the method of mixtures, uses a heater which is imbedded in the material to be tested. The whole assembly is then suspended in a high vacuum to reduce heat transfer to the surroundings as much as possible. Then, a measured amount of heat is supplied the heater, and the resultant rise of temperature is measured. From this data, the specific heat may be calculated.

The method is widely used for low-temperature measurements and has been used at higher temperatures¹², although the difficulties are greatly increased.

The second of the two major developments mentioned above was the perfection of the technique of adiabatic calorimetry. The development of the adiabatic calorimeter is credited to T. W. Richards¹³. Richards states that the idea was suggested by S. N. Holman¹⁴.

Adiabatic calorimetry depends upon having the surroundings of the calorimeter at the same temperature as the calorimeter at all times. In Richards' instrument, a rapidly stirred bath of sodium hydroxide was titrated with sulfuric acid to keep the surroundings at the same temperature as the calorimeter.

It may be stated that the main requirement for this technique is a shield or bath with a very rapid response so that the fluctuation of the calorimeter may be accurately followed.

The addition of adiabatic operation to a Nernst-type calorimeter is particularly effective and has been used for some very accurate high-temperature measurements.

The methods mentioned thus far constitute the major portion of the techniques in furnace calorimetry. Some of the odd and special equipment will be mentioned at the end of this review, but the remainder will not be in chronological order. Rather, the discussion will follow the more natural order of the method being used.

There have been two first-class examples of adiabatic calorimeters, those of Sykes¹⁵ and Moser¹⁶.

Sykes developed an instrument which might best be described as a "dynamic" adiabatic calorimeter. The specimen was supplied with an internal heater and placed in a closed copper cylinder which could be externally heated. By preliminary experiments, the conditions necessary to give a constant rate of temperature increase to the copper block were determined. Then as this block was heated, the specimen was heated by the internal heater in such a manner as to be heating alternately more rapidly and then more slowly than the outer block. At any instant at which the two temperatures coincided, adiabatic conditions prevailed and

$$Q = MC_p [dT_s/dt] T_s = T_b$$

where

- Q = the heat input to the internal heater
- M = the mass of the sample
- C_p = the specific heat of the sample
- T_s = the temperature of the sample
- T_b = the temperature of the surroundings.

Sykes found that since T_b was very uniform with time it was better to use

$$dT_s/dt = dT_b/dt \neq d(\Delta T)/dt.$$

This equipment could also be operated non-adiabatically by experimentally determining a correction factor to be applied. The apparatus operated in vacuo so that the correction was essentially one due to radiative losses with a small conductive loss. To determine this factor, Sykes measured cooling curves at definite temperatures. From this the true zero of the differential thermocouple was determined, and also Q of the equation above which gave the heat loss for definite values of ΔT at experimental temperatures. Obviously C_p must be determined adiabatically to use this method of calibration.

Moser's apparatus, although more nearly a true adiabatic calorimeter, also involved a constantly changing temperature of the shield.

Very simply, his calorimeter was of the Nernst type with the difference that the whole unit was mounted in a furnace. The temperature of this furnace was varied at a constant rate and, by means of an internal heater in the calorimeter proper, adiabatic conditions were maintained. Then the rise in temperature of the calorimeter could be attributed only to the power input of the internal heater, and heat capacity could be calculated directly.

Since Moser's equipment was very elegant (accuracy of 0.5% was claimed by the author) a closer examination seems worthwhile.

The calorimeter, calorimeter shield, and two external shields used to distribute the power input of the furnace evenly were cylinders of silver. The calorimeter and first shield could be dismantled by a bayonet arrangement for easy access.

To each of the two inner cylinders, three constantan wires were attached with silver rivets. All six constantan wires were of the same length and were brought to a common binding post made of constantan. A single silver wire was attached to each of the two cylinders and brought to two silver binding posts. Then the e.m.f. between the two silver leads indicated the mean temperature difference between the two silver cylinders. The true temperature of each may be found from the e.m.f. between the constantan binding post and the proper silver post.

Moser found that the magnetic field of the furnace windings, when operated on alternating current, would produce a very evident heating effect in metallic samples. He, therefore, wound a "compensating" coil around his furnace which carried current out of phase with the current in the furnace windings. This destroyed the heating effect in the samples.

Since it was found difficult to obtain a good vacuum at elevated temperatures, Moser placed his calorimeter in argon gas at reduced pressure, thus stopping oxidation of the samples. It also kept the heat transfer coefficient between the two cylinders at a reasonably low value.

The thermocouples used were calibrated in place so that

no inhomogeneities were introduced into the constantan wire.

It was found that the heat transfer from the calorimeter to the surroundings was not zero even though the differential thermocouple indicated that there was no temperature difference. To correct for this Moser found that a two-constant form of Newton's cooling law was necessary, i. e.

$$q = K_1 \Delta T / K_2.$$

Since the internal heater was a cylinder which surrounded the test sample, it was also necessary to correct the temperature readings by an amount ΔT which indicated the thermal lag of the sample behind the calorimeter proper.

Carpenter and co-workers¹⁷ have developed an interesting non-adiabatic furnace calorimeter. Their purpose was to measure heat capacities of elements over large temperature ranges and especially in the regions near the melting points. This goal imposed some stringent conditions on the instrument, i. e., operation over a small temperature range and accurate knowledge of the heat capacity of the sample container.

The most novel feature of the instrument was the method of heating the sample. It was developed to overcome what is undoubtedly the most vexing problem of high-temperature calorimetry, that of obtaining a high order of electrical insulation for heaters without introducing undue thermal insulation and thus undesirable thermal lags. With the possible exception of the mineral periclase, the electrical insulators are also thermal insulators. While it is difficult to envisage as a constructional material, only a high vacuum really fulfills

the requirements of an electrical insulator at elevated temperatures.

Carpenter utilized this fact and insulated his heater from the calorimeter by a high vacuum. By blackening both the platinum heater coil and the nickel-plated calorimeter, good thermal contact was maintained.

The heater coil was used as a platinum resistance thermometer to measure the temperature of the calorimeter after heat input ceased. The coil was, of course, at a higher temperature than the calorimeter when the power input was turned off, but rapidly came into equilibrium with the calorimeter. A correction was necessary for the amount of heat lost during the time of heat input and the time required for the coil to cool to equilibrium with the calorimeter. Carpenter carefully analyzed the operation of the calorimeter and found that in order to minimize errors it was necessary for the heating period to be twice the cooling period. He further found that the general rule stated by White³ that the dimensions of the calorimeter should be as small as possible did not hold for this instrument. This was true since the heat capacity of the container should remain a small part of the total heat capacity and since the time of the experiment is governed not only by the time needed to dissipate thermal gradients in the calorimeter but also by the time needed for the coil to attain equilibrium.

Carpenter considered one other problem that is common to all furnace calorimeters with resistance heating. One must be very careful that the heat is developed at the heater itself

and not in the leads. To assure that this is so, the resistance of the leads should be a small part of the total resistance. It must not, however, be so small that there is excessive heat loss along the leads. As in the case of the problem of heater insulation, one is faced with two opposing factors, the result of which must be minimized.

Klinkhardt¹⁸ has attempted another solution of the heater problem which avoids the errors involved in insulating the heater and in supplying proper leads to the heater. His method is to heat the sample by bombarding with electrons from a hot filament.

In general, the apparatus consisted of a cylindrical sample which was suspended in a vacuum system by quartz hoops. The cathode was either supported below the sample, or led through a hole drilled along the axis of the cylinder. The heat supplied to the sample is given by

$$q = Eit$$

where i and t are the amperage and time respectively and E is the effective voltage between the glowing cathode and the sample. This effective voltage is made up of three parts: (1) the thermal energy of the electrons as they leave the filament, expressed in volts, (2) the applied potential difference, and (3) the work function of the sample.

The furnace used was unusual in that it had a very low heat capacity and thermal resistance. It consisted merely of two rings, placed above and below the sample, around which platinum ribbon was laced to form a non-inductive winding.

The lower ring was heavier than the top, and was free to move so that the ribbon was always kept taut. This furnace should have been rather unstable and, in fact, Klinkhardt mentions that the voltage needed to be very carefully regulated.

The greatest difficulty which occurred with the calorimeter was outgassing of the assembly. Since ionization of the gas by the electron stream occurs at fairly low pressures, rather small amounts of gas would seriously affect the measurements. Specifically, the ions and electrons formed by the ionization process would contribute to the current flow i , although they would not transfer the calibrated quantity of heat. This would tend to increase the measured value of C_p above the true quantity.

There is one further source of error which was not recognized as such by Klinkhardt; that was his method of forming thermocouples. In an attempt to obtain a mean surface temperature of the sample, he formed the thermocouple so that the sample was the hot junction. Due to the possible difference in $\partial E/\partial T$ for the two thermocouples thus formed, one can make serious errors if there is a difference in temperature between the two junctions of sample and thermocouple wire.² In the cases (below 700° C.) in which the cathode was supported outside the sample, such a difference in temperature could exist. Since the slopes of the fore and after periods were used to obtain ΔT , there is a very possible source of unevaluated error.

The last adiabatic instrument to be discussed is of interest chiefly because it is the only example in the literature

of a spherical calorimeter. Designed by J. R. Winckler¹⁹, it consists of a series of five spherical shells, each being in theory an isothermal surface. The inner sphere was a ball of Nichrome consisting of two threaded hollow hemispheres. A small platinum heater wound on mica was inserted thus forming a spherical heater. The heater was placed inside the next shell, the sample, which was contained in a platinum sphere. This assembly formed the calorimeter proper. A second larger platinum sphere was placed around the calorimeter to act as an adiabatic shield. All positioning and spacing of the assemblies was accomplished by means of tripods made of quartz tubes. The final sphere was the furnace itself made of Alundum cement with Nichrome windings. The entire apparatus was placed in several inches of Sil-O-Cel insulation.

In practice, three temperatures were measured: T_1 , the temperature at the surface of the heater, and T_2 and T_3 , the temperatures of the inner and outer platinum spheres respectively. The value of T_1 is not needed for specific heat calculations, but was used in determining the thermal conductivity of the samples.

To obtain specific heat, the instrument was brought to steady state with internal heating and the temperatures measured. Then $(T_3 - T_2)$ gives a measure of the heat transfer coefficient between the two spheres. Now, the internal heat input is stopped and a new steady state attained. Here, $(T_3 - T_2)$ is the zero point for maintaining adiabaticity. The internal heat supply is again turned on for a measured interval and the

temperatures T_2 and T_3 measured. The furnace is controlled so that $(T_3 - T_2)$ remains as close as possible to the determined zero point. After steady state is again attained, the value of Q , the total heat input, $(T_2' - T_2^0)$ and the determined correction factor of Q allow one to calculate C_p .

Winckler reports an error of about 5% for his measurements. Much of this can be attributed to inferior design. The furnace with a very low value of thermal conductivity and a high value of heat capacity should have been slow to respond to control. Thus, the corrections for non-adiabatic conditions would have been fairly large. His method of obtaining the thermal transfer also was not satisfactory since it involved but two measurements. Anticipating some later results, it has been found in this research that steady state measurements are difficult to obtain accurately so that there is a definite possibility of an appreciable error in this measurement. In spite of the poor accuracy, however, the experiment is noteworthy since it attempts to utilize a geometric form which calorimetrists agree is theoretically the most sound. Most also agree, however, that it is experimentally too difficult.

Dulong and Petit's method of cooling and its subsequent refinements will be the last major method to be considered in this brief review.

It follows from the definition of heat capacity that

$$1. \quad C = q/\dot{T}$$

where

C = heat capacity of the body
 q = rate of transfer of heat from the body
 \dot{T} = time rate of change of the sample temperature.

If a calorimeter is constructed such that q may be held constant for different experiments then it is possible to derive relative values of C by

$$2. \quad C_1/C_2 = \dot{T}_2/\dot{T}_1.$$

The above equations define the work of Dulong and Petit and of subsequent workers until 1933. It should be pointed out that this refers to measurements of specific heat. Steiner and Johnston²⁰, Plato²¹, and Wittig²² and others have utilized the analysis of cooling curves to measure heats of transformation.

The method of cooling was in disrepute for a number of years. Chiefly, this is due to the fact that the cooling of bodies depends not only upon their heat capacities but also upon their thermal conductivity. Or, for a more exact statement, transient heat flow depends upon geometric shape and thermal diffusivity as given by the Fourier equation for heat conduction²³

$$3. \quad \partial T/\partial t = K(\nabla^2 T)$$

where T is the temperature and t the time. K , the thermal diffusivity is given by

$$K = k/\rho C$$

where k is the thermal conductivity, ρ is the density and C is the specific heat.

The equation shown earlier (1) embodies the assumption that \dot{T} found experimentally is truly representative of the whole body. This may be stated more exactly as

$$4. \quad \partial(\text{grad } T)/\partial t = 0$$

a condition which is never exactly fulfilled. If the experimenter attempts to measure C_p by comparing the cooling rates of two substances, he must be certain that this condition is fulfilled. In the past, only work with well-stirred liquids has yielded even fair accuracy.

In 1933 and 1934, Marley²⁴ and Stephens⁷ devised techniques which departed from the traditional method of cooling.

Marley worked with a method for measuring C_p for insulating materials. His work could not be considered true furnace calorimetry since the measurements were made at rather low temperatures. The value of his results, for purposes of this review, lies in the fact that he clearly grasped the chief difficulty of the method of cooling, and was able to demonstrate the correct solution.

To obtain the conditions stated in equation 4, it is not necessary to use samples with high values of thermal conductivity. The important factor is the ratio of the thermal conductivity of the sample to the heat transfer coefficient from the sample to its surroundings. Applying this reasoning to furnace calorimetry, one must be sure that, for any particular material to be tested, the heat transfer per unit area of the sample is smaller than the thermal conductivity of the sample.

Since radiative transfer of heat is large at elevated temperatures one must eliminate or strongly limit all other forms of heat transfer. This will require that the calorimeter be simple with few leads and supports and that it be operated in a high vacuum.

With values of heat exchange of $0.003 \text{ cal. sec.}^{-1} \text{ deg.}^{-1}$, Marley found it necessary to allow cooling periods of three hours to elapse before equation 4 was satisfied.

Stephens developed another phase of the cooling method, that is, to try to obtain an absolute measurement of C_p . What he actually obtained were values of C_p/k where k was the thermal conductivity of the container material.

The apparatus consisted of a cylinder of insulating material which contained the liquid whose specific heat was to be determined. The apparatus was fitted with a stirrer and a thermometer which measured the temperature of the inside wall of the cylinder. A measurement of temperature was also made at the outside wall. Stephens derived an equation for the behavior of this system when cooling, and found that specific heat could be calculated if one knew the physical dimensions of the system, the value of k for the container, the two temperatures and their time rate of change. He was able to demonstrate that the quantity

$$\left[\frac{T_1 - T_2}{T_1} \right] dT_1/dt$$

varies linearly with C_p . Thus two independent values of C_p to fix the slope of the straight line obtained in this plot would allow one to find values of C_p and a value for k . Or an independent value of k would lead to values of C_p .

Knappworst²⁵ utilized a somewhat similar apparatus for measuring C_p for solids. The solid needed no container, of course, and the insulating cylinder of Stephens was replaced by a cylindrical gas mantle. To stop convection the gas was kept at a reduced pressure. This strongly limits the method

to temperatures below 200° C. where radiative transfer of heat is negligible compared to that transferred by gaseous conduction.

To find C_p , Knappworst utilized equation 1 where q was found from the known properties of the gas. This introduced a geometric factor and a temperature-dependent factor in q . This is true because k for the gas depended on the temperature which varied across the gas mantle.

Knappworst found that if the measured values of \dot{T} were used in equation 1, the value of C_p varied badly. He then plotted \dot{T} against ΔT , the temperature drop across the gas mantle, and smoothed the values of \dot{T} . The resulting values of C_p were in good agreement with other measured values.

It can be seen from the above discussion that while the groundwork has been laid for developing a cooling method which yields values of C_p independent of other thermal properties, it has not been done as yet. It may also be seen that no apparatus as yet developed will allow measurements to be made at higher temperatures.

There have been some relatively unimportant methods developed for finding C_p at higher temperatures. One of these (Davies and Thomas²⁶) depends on forming a coil with the material as a core. Then eddy currents are introduced in the material and an analysis of the power used with and without the core will yield C_p .

Several methods using an incandescent filament have been developed. Some of these²⁷ find values of C_p which depend on

the value of $\partial R/R\partial T$ where R is the electrical resistance of the filament. Another²⁸ used the transient behavior of the temperature when alternating current was passed through the filament.

None of these have been very accurate nor have they been developed to any great extent.

CHAPTER III

THEORY OF THE CALORIMETER

It was stated in the last chapter that high-temperature cooling methods for measuring C_p did not exist. The problem of this research was to design and construct a calorimeter utilizing this method.

From the previous discussion, some of the necessary characteristics of such an instrument may be enumerated: (1) the calorimeter must not be inaccurate when radiative heat transfer becomes a large part of the total transfer, (2) the loss of heat from the calorimeter to its surroundings must be small in comparison to the thermal conductivity of the sample so that slow, uniform cooling may occur, (3) there should be a direct electrical calibration of the instrument so that true values of specific heat may be measured, (4) since radiative transfer of heat is to be an important part of the total transfer, radiating surfaces must not change with operation, and (5) for maximum accuracy one should make full utilization of the precision of the thermels rather than their absolute accuracy. This last point is one of the strongest reasons for using a cooling method. Such a method will give results of C_p depending on $\partial E/\partial T$ for a thermocouple over a short range of temperature.

It was decided that the best solution to the problem of radiative heat transfer was to utilize it as an integral part of the instrument since it is impossible to eliminate. Thus heat transfer in this calorimeter is primarily by radiation with a minimum of conduction. Gaseous conductive and convective transfer were eliminated by the use of a high vacuum. Such a limitation of the heat transfer had the added advantage of keeping the rate of cooling small and also keeping radiating surfaces clean.

Very simply, the calorimeter consists of a sphere of graphite and is surrounded by a spherical shell wound with Nichrome which acts as a radiation shield or heat "sink". This shield was to be kept at a constant temperature.

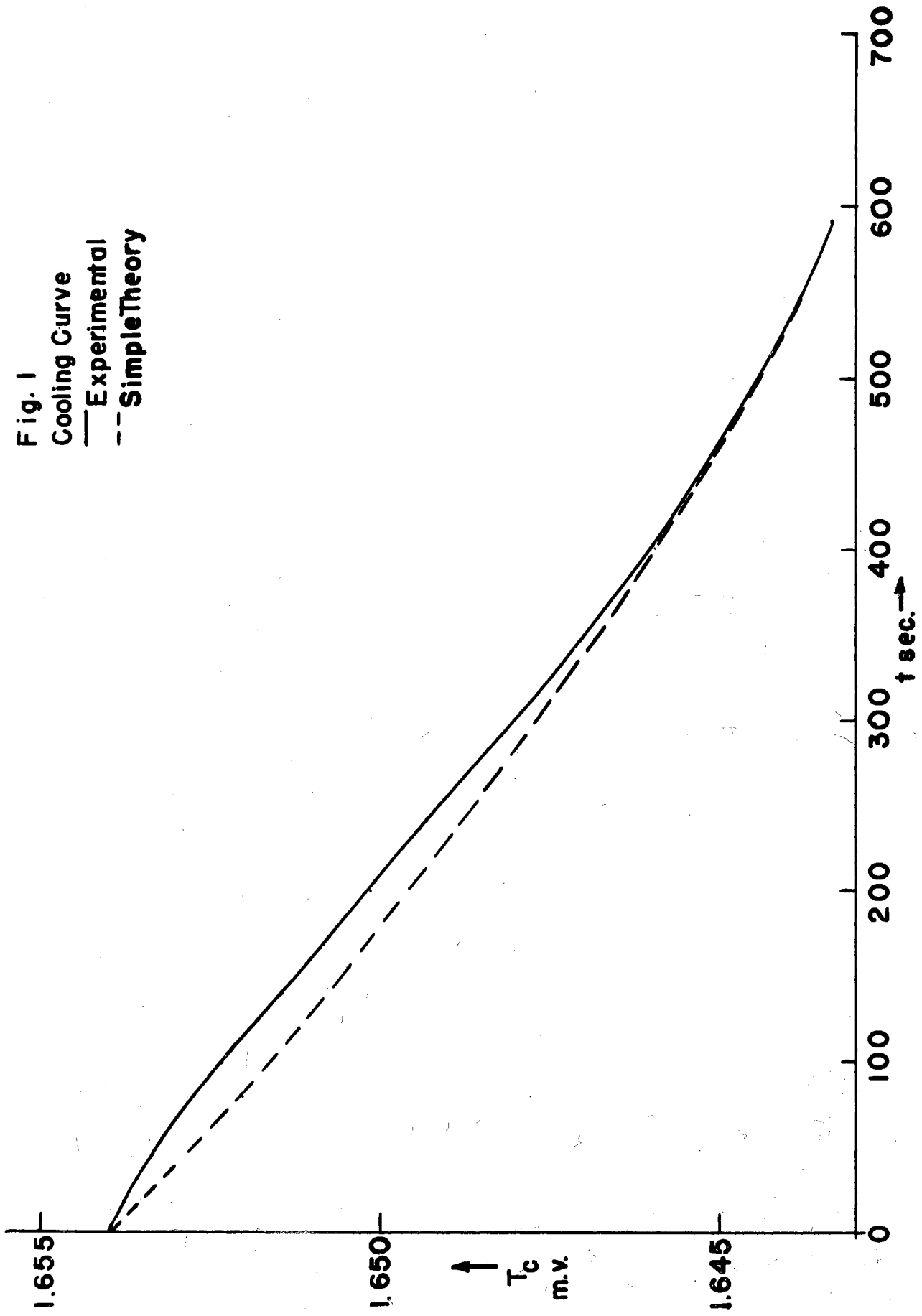
The inner sphere was to be supplied with an internal heater so that a direct electrical calibration of the amount of heat being transferred for a given difference in temperature between the calorimeter and the shield could be measured. It may be pointed out at this point that such a calibration would be independent of the true temperature difference between the two spheres. It would instead require that the same indicated temperature difference between the two spheres express the same conditions in a given experiment. The accuracy involved is limited, therefore, by the reproducibility of the thermels and not by their absolute accuracy. Further, one is not required to measure a surface temperature, but only a temperature which has a constant relationship to the surface temperature throughout the experiment.

Fig. 1

Cooling Curve

— Experimental

- - - Simple Theory



Now from equation 1 and if the shield temperature (T_s) remains constant, one may write

$$5. \quad b(T_c - T_s) = C\dot{T}_c.$$

This assumes that q is a linear function of ΔT , which was found experimentally, and arbitrarily assigns a negative value to q when heat is being lost by the body. Thus b is a negative quantity.

Now if T_s is constant,

$$\dot{T}_c = \Delta \dot{T}$$

and

$$6. \quad \Delta T = \Delta T_0 \exp.(bt/c).$$

Then one may write

$$7. \quad T_c = T_s / \Delta T_0 \exp.(bt/c).$$

From this T_c should be a simple exponential function of time. This is not found experimentally (Fig. 1). Instead one obtains a curve which shows a very slow drop in temperature for low values of time and then an inflection point followed by a distorted exponential curve which exhibits a larger value of \dot{T}_c than that predicted from equation 4.

The original slow drop of T_c is attributed to an internal temperature gradient which must collapse before the sphere may be said to be cooling uniformly. This does not mean that gradients may not exist, of course. Rather one should state that

$$4. \quad \partial(\text{grad } T)/\partial t = 0$$

is a necessary condition for equation 1 to be true.

For a sphere of graphite cooling slowly in surroundings of uniform temperature this condition is very quickly attained.

The experimental fact of distortion of the curve is obviously due to the effect of the internal heater. Very simply, since the heater has a finite, though small, heat capacity, and is running at a temperature higher than that of the graphite, one does not stop the heat generation within the sphere by opening a switch. Instead, a finite time is required to allow the heater to cool to the temperature of the graphite, or rather, to a state for which condition 4 is true.

The behavior described above places some stringent requirements on the construction of the internal heater. First, the heat capacity of the heater should be reduced as far as possible. Second, and probably more important, the thermal resistance

8.

$$R = l/k_T$$

l = geometric factor expressing path length of heat flow

k_T = thermal conductivity of heater material

should be reduced as far as possible so that the distorting gradient may disappear rapidly.

With the exception of periclase, almost all electrical insulators have low values of k_T so that the only control one has over R is in so constructing the heater that l is as small as possible. This would demand that any material used as an insulator be used in as thin sections as possible.

The heater used in this research may be considered as a sphere of graphite with a thin-walled hollow cylinder of Lava imbedded in it. The inside of this cylinder was also filled with graphite. The windings were insulated from the surrounding graphite by reduced pressure in a gap. This gives good insu-

lating properties, and at high temperatures, a very good value of k_T . The details of this heater will be given in the chapter describing the apparatus.

This heater was not truly a separate unit from the total graphite sphere, but its outer boundary was defined by the lowest value of the radius of the sphere for which an isothermal shell existed.

The second distortion of the cooling curve, that of the too large value of \dot{T}_c , is attributed to the fact that T_s is not a constant but a function of time.

Consider an idealized system of a sphere surrounded by a spherical shell which is smoothly heated on its outer surface. Now if one assumes there are no heat losses from the interior, simple consideration of the second law of thermodynamics will show there can be no temperature gradient through the spherical system. If now heat is generated at the center of the system, a slight temperature rise of the outer surface will occur so as to dissipate the heat generated and, at steady state conditions, a definite temperature gradient will be established. Now at steady state one may write

$$3. \quad \partial T_s / \partial t = K \nabla^2 T_s = 0.$$

For a sphere this becomes

$$\nabla^2 T_s = \partial^2 T_s / \partial r^2 + 2 \partial T_s / r \partial r = 0.$$

Now let

$$U = T_s r$$

Then since all factors of T_s but r are ignored,

$$d^2 U / dr^2 = 0$$

$$U = C_1 r + C_2$$

and

$$T_s = C_1 + C_2/r.$$

Now from Fourier's equation

$$\dot{q} = -k_s A dT_s/dr$$

where \dot{q} is the net heat loss in unit time of the shell, k_s is the thermal conductivity and A is the area of the spherical shell defined by r . From this and the equation for T_s ,

$$\begin{aligned} dT_s/dr \Big|_{r_1} &= -C_2/r_1^2 = -\dot{q}/k_s 4\pi r_1^2 \\ C_2 &= \dot{q}/4\pi k_s. \end{aligned}$$

Now if one states that $T_s = 0$ for $r = r_1$, the outer radius of the shell then

$$\begin{aligned} T_s = 0 &= C_1 + \dot{q}/4\pi k_s r_1 \\ C_1 &= -\dot{q}/4\pi k_s r_1 \end{aligned}$$

and

$$\begin{aligned} T_s &= \dot{q}/4\pi k_s r - \dot{q}/4\pi k_s r_1 \\ 9. \quad T_s &= [\dot{q}/4\pi k_s](1/r - 1/r_1). \end{aligned}$$

Equation 9 is independent of the specific heat of the shell, so that the total temperature drop of the shield during an experiment is determined not by the specific heat but by its thickness and thermal resistance.

When the internal heat generation is stopped the change in temperature of the inner surface of the spherical shell will express the collapse of the thermal gradient through the shell and will be expressed by

$$10. \quad dT_s/dt = f(q, k_s, r_1, r_2, \text{sp.ht.}).$$

Thus the rate at which the sphere returns to the steady

state of no heat generation will depend upon its specific heat. This problem has been recognized before ²⁵.

Since in the present calorimeter k_s is small, T_s will vary throughout the entire cooling period of the calorimeter.

It would appear that the best solution to the problem would be to reduce k_s to a very small value and then to control the temperature precisely so that T_s is constant. However, the above analysis does not give a complete picture. Since any reduction of k_s would likely involve a very small heat capacity also, the resulting system would be rather unstable. Also, precise control of temperatures at higher temperatures is a difficult and expensive task.

The alternate solution would be to maintain the exterior heat input constant, a less difficult job, and then to eliminate the dependence of the results on T_s by the manner of handling the data. This has been done in the present research.

To show how this may be accomplished, consider the following:

1. $\dot{T}_c = q/c$

11. $\Delta T = a + bq$ empirical equation

12. $T_s = T_\infty + \beta e^{-\delta t}$ empirical equation

13. $\Delta T = T_c - T_s$

Then define

$$\Delta T' = \Delta T - a$$

so that

14. $q = \Delta T'/b$

Now from 12 and 13

$$T_c = T_s + \Delta T = T_\infty + \beta e^{-\delta t} + \Delta T.$$

Differentiating one obtains

$$15. \quad \dot{T}_c = -\beta\delta e^{-\delta t} + \Delta\dot{T}.$$

So that from 1 and 14 and 15

$$16. \quad q/C = \Delta T' / bC = -\beta\delta e^{-\delta t} + \Delta\dot{T}'$$

or

$$17. \quad \Delta\dot{T}' - (1/bC)\Delta T' - \beta\delta e^{-\delta t} = 0.$$

Equation 17 being a linear differential equation the solution is:

$$18. \quad \Delta T' = \beta\delta / (1/bC + \delta) [e^{t/bC} - e^{-\delta t}] + \Delta T_0' e^{t/bC}.$$

From equation 18 it can be seen that the effect of the variation of T_s with time is to increase the value of $\Delta T'$ by the quantity

$$\beta\delta / (1/bC + \delta) [e^{t/bC} - e^{-\delta t}] = f(t).$$

If one could evaluate this term then a plot of $\log[\Delta T' - f(t)]$ vs. t should give a straight line with a slope

$$19. \quad m = 1/2.303bC.$$

From this expression one may evaluate C . It appears impossible to obtain a simple algebraic expression for C in terms of experimentally determined constants.

The factors of equation 18 have the following physical significance:

- a - the intercept of the plot of q vs. ΔT from the calibration. Expressed in μv .
- b - slope of the calibration plot in $\mu v/cal$.
- β - the total change of T_s when the instrument returns to steady state conditions if no change in the external heat source has occurred.
- δ - 2.303 times the slope of the plot of $\log(T_s - T_\infty)$ vs. t .

- q - rate of heat flow from the calorimeter at the given time. A function of ΔT .
 C - heat capacity of the calorimeter expressed in cal./ μv .

One may obtain β and γ by fitting the experimental data for T_s to equation 11. To find T_∞ for a trial solution, one may plot T_s vs. q from the calibration data and extrapolate to $q = 0$. In theory, these quantities may be calculated but they would involve k_s , the specific heat of the shield, and its dimensions so that an empirical evaluation would be better.

The constants a and b are easily evaluated from the calibration data. One would think that a should be zero, and if true surface temperatures were measured it would be. However, the thermels were imbedded in the walls of the calorimeter and shield so that in the case of the shield, the thermal gradient present causes ΔT to be larger than the actual ΔT of the surfaces by a small amount. Since k, the thermal conductance, is small, the gradient collapses very slowly. Then one could expect that for a given value of q the same gradient and, thus, the same ΔT would be present. Thus no error is introduced. The largest part of a is thought to be due to leakage of d. c. to the shield thermocouple.

Since all factors but C are known in the expression for $f(t)$, one may use a method of successive approximations to find C.

The computational procedure is as follows:

- (1) Assume a reasonable value of C. This does not have to be reasonable, but the labor involved is reduced if C is within 10% or 20% of the true value.

- (2) Calculate $\log [\Delta T' - f(t)]$ and plot versus t .
- (3) Find C from the plot in 2, then
- (4) Repeat the calculation using the new value of

$$C_2 = \frac{1}{2}(C_1 + C_r).$$

When the value of C no longer varies, the correct value has been obtained.

CHAPTER IV

DESCRIPTION OF THE APPARATUS

The instrument consisted of four main sections which will be discussed separately. These four sections were: (A) the calorimeter proper, (B) the shield heater, (C) the vacuum jacket and water bath, and (D) the control console with its measuring and heating circuits.

A. The Calorimeter

In its final form the calorimeter consisted of a two inch sphere of graphite in which the internal heater was imbedded.

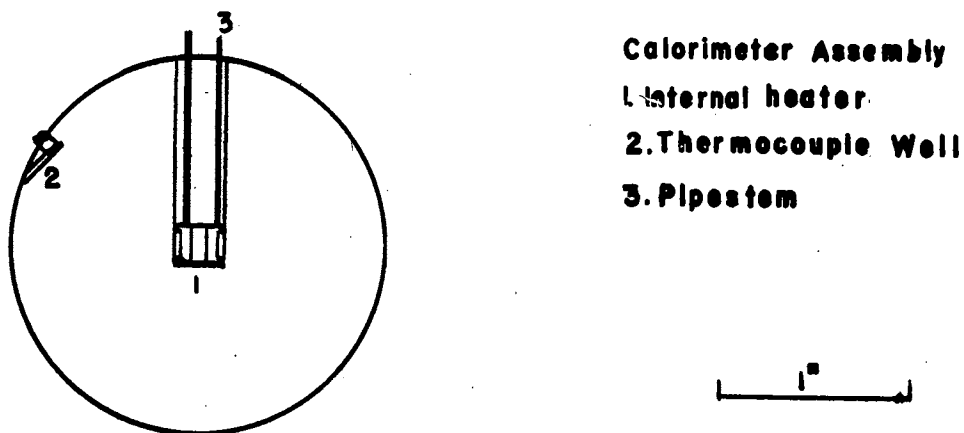


Fig. 2 Calorimeter Assembly

A Pt - Pt 13% Rh thermocouple was imbedded in the outer surface and was held in place by a graphite screw. This arrange-

ment insured good thermal contact between the graphite and the thermocouple.

The internal heater was at the center of the sphere, placed in a cylindrical heater well. This heater well was threaded and a graphite plug screwed in so that the heater was pressed firmly against graphite on both ends. Two fine holes were drilled into the plug and lined with pipestem. The heater leads were led to the outside through these pieces of pipestem.

The difficulties of machining and assembly limit one in how closely he may follow the theoretical requirements in constructing the internal heater. The form shown in Figure 3 was evolved after many attempts and was used in the instrument described here.

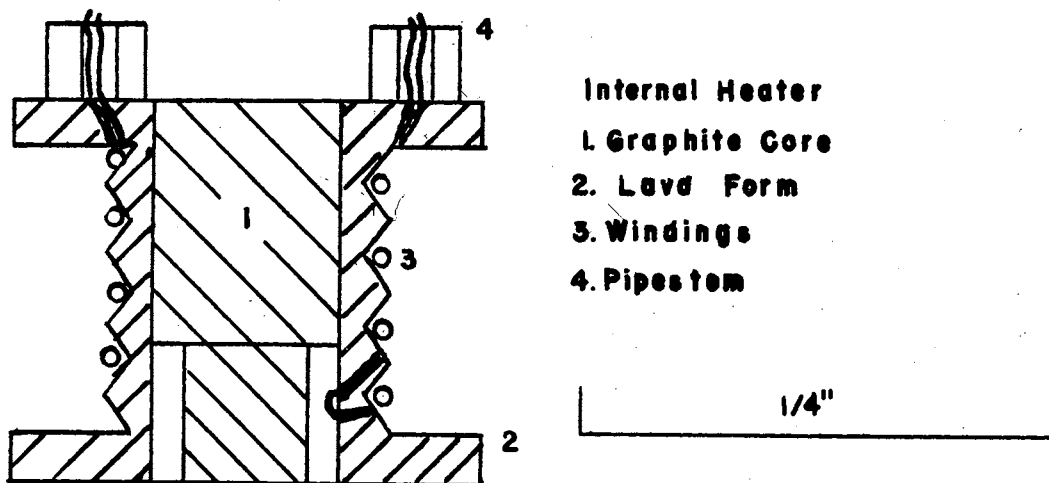


Fig. 3 Internal Heater

The heater consisted of a ceramic form machined from grade A Lava, a graphite core, and windings of B. & S. #40 gauge Nichrome wire. In general appearance it resembled a spool with threads cut into the recessed portion. The ceramic form was 250 mils in diameter with a length of 200 mils. The recessed

portion of the form was 190 mils in diameter and 100 mils long. Into this were cut two turns of a double thread giving four turns of wire on the heater. A hole was drilled through the body of the heater from each thread and two holes were drilled through the top shoulder of the heater. A continuous length of wire was threaded through the two bottom holes, wound into the threads, and then led through the holes in the top shoulder. Here they were silver-soldered to B. & S. #26 gauge copper wire, which led out of the shield heater.

The graphite core of the heater was made to fit snugly into the center hole, about 90 mils in diameter, over most of its length. There was a smaller diameter at the bottom end so that the wire of the heater did not make contact and thus short-circuit through the graphite.

B. The Shield Heater

The shield heater was rather difficult to construct, although simple in design. It consisted of two hemispheres of Missouri fire clay 5 inches in diameter, into the surface of which was cut a spiral groove which formed a loxodrome. These were wound with B. & S. #16 gauge Nichrome wire and then covered with Rutland brand black asbestos furnace cement.

The fire clay forms were produced in the Oklahoma A. and M. College pottery shop by jiggering the clay in a plaster mold. After these forms had thoroughly dried, the groove was cut into them using a special jig equipped with a flexible-shaft hand tool and a dentist's drill.

It was found necessary to tie the heater windings into

the fire clay form. Attempts were made to anneal the wire so as to attain an easily deformed wire but these met with indifferent success. To keep the windings in place, fine holes were drilled into the clay form from the lands to the bottom of the grooves. As the windings were being placed, B. & S. #40 gauge Nichrome wire was threaded through these holes and tied. The windings were thus held in position during the remainder of the construction process.

After the forms had been fired and the windings put on, a layer of cement was placed over them, air dried, and the finished form was again fired at 1000° C.

The bottom hemisphere was fitted with three holes which held Lava spears used to position and support the calorimeter. It also contained an entry hole and a pocket for the shield thermocouple. There were several grooves in the lip of the bottom hemisphere to allow the internal heater leads and the calorimeter thermocouple to be led out of the shield.

The top hemisphere contained several "breather holes" to expedite evacuation of the assembly.

All holes through the shield were drilled along chords of the sphere. This was done in such a manner that the calorimeter could never "see" the surroundings of the shield and thus a relatively low-temperature surface.

Electrical connections between the two hemispheres and from the power source were made by crimping bands of copper around pig-tails of wire which were allowed to protrude from the cement covering.

C. Vacuum Jacket

The calorimeter and shield heater assembly was placed in a vacuum chamber made of an eleven-inch length of oil casing pipe which was thirteen inches inside diameter. Two steel flanges were welded to the ends of this steel cylinder. Grooves were cut into the two flanges to hold rubber gaskets for vacuum seals. The ends of the cylindrical chamber were closed with plates of $\frac{1}{2}$ -inch-thick steel which were held in place with twelve $\frac{1}{4}$ -inch bolts at either end.

The top plate of the main chamber had a hole into which a length of six-inch pipe had been welded to lead to the vacuum pump. From this vertical length of pipe, a four-inch pipe led horizontally for about three feet and then a vertical length of four-inch pipe ended in a flange which was bolted to the top flange of the oil diffusion pump.

The top plate of the six-inch chamber contained one Stupakoff brand Kovar-to-glass eight-junction seal and two heavy duty Stupakoff seals. The first was used for the internal heater leads and the last two for the shield heater power leads.

Since the thermocouple wires used in this research were continuous to a constant-temperature-zone box outside the system, there were four seals to allow entry of the thermocouple wires to the vacuum system.

These were made in the following manner. Four brass male standard-taper joints were threaded into the top plate of the vacuum system and sealed with Glyptal. These were mated to glass female joints using Apiezon N high vacuum grease. The

ends of the glass joints were drawn into capillaries fitting the thermocouple wire loosely, with a small bowl blown above the capillary. After the thermocouples were installed and the joints in place, these bowls and capillaries were filled with picein wax. It was found that this method usually gave a tight seal without destroying the flexibility of the system.

Four lengths of steel rod were threaded into blind holes in the bottom of the main top plate. These rods supported a steel plate which carried the calorimeter and shield assembly. The latter assembly was mounted on a tripod arrangement made of heavy lengths of pipestem with conical Lava tips. Three steel blocks were placed in holes in the steel plate and the pipestems were set in holes drilled into the tops of these blocks. There were set screws in the blocks to hold the pipestems firmly in place.

Lengths of B. & S. #10 gauge copper wire were soldered to the heavy-duty Stupakoff seals. These led down two of the steel support rods, but were insulated from the rods by Lava blocks. Two Lava terminal strips were fastened to the lower portion of these rods to simplify assembly of the shield. A length of B. & S. #16 gauge Nichrome wire was doubled and twisted together. One end of this was connected to the terminal strip and the other to the end of the heater winding, by crimping copper bands around the wires.

Leads for the internal heater and the thermocouple wires were insulated in lengths of pyrex glass tubes while in the upper chamber. Lava spacer bars were placed at the bottom of this

chamber by bolting them to the main top plate and all wires were led through these bars. From this point, the wires were insulated with small-diameter pipestem. The thermocouple wires were bare after passing through the shield.

The four internal heater leads were silver-soldered into pairs, and made contact with the internal heater lead just outside the shield. This left but a small length of B. & S. #28 gauge copper wire leading into the calorimeter.

Pressure was measured with a Distillation Products Industries Phillips Gauge which was mounted in the top plate. A Hastings thermocouple-type vacuum gauge was mounted between the diffusion pump and the forepump to measure forepressure.

The two pumps used were a Distillation Products Industries "275" series oil diffusion pump backed by a Cenco Megavac mechanical pump.

The entire assembly was mounted on a low laboratory table, with the vacuum jacket and the diffusion pump on a rack constructed of two-inch pipe. Provisions were made for surrounding the vacuum jacket with a large sheet-metal water bath in which a continuous flow of water was maintained.

D. The Control Console and Circuits

To mount all the instruments and controls necessary for the operation of the calorimeter, a console-type instrument rack was constructed of wood and masonite. This rack contained two low desks for potentiometers, with vertical racks behind, flanked by three sloping racks. At each of the two stations, a Leeds and Northrup galvanometer type 243A, sensitivity

0.4 μ v/mm, was mounted at eye level in the vertical rack. At the station used for temperature measurements there was a Leeds and Northrup type K-2 potentiometer, equipped with a lock-down key of high sensitivity, and a one-one hundredth range. The other station, used for measuring and controlling the power input to the internal heater, was equipped with a Leeds and Northrup type K potentiometer.

The switches, indicator light, Variac, water valve, and a visual water flow indicator controlling the oil diffusion pump were mounted on the vertical rack of the internal heater station. The sloping panel to the right of this station contained the internal heater controls.

The controls for the shield heater were mounted in the sloping panel between the two stations. Each of the two vertical panels contained a double outlet which came from the 5KVA voltage regulator placed on the floor beneath the console. This regulator was Thyatron controlled and manufactured by the Superior Electric Company.

The standard resistor and dummy heater resistor of the internal heater power circuit were made by winding nylon covered Advance wire on an aluminum core. The value of the standard resistor was measured in situ by the following method.

Heavy copper leads were soldered to the B. & S. #10 gauge copper wire connected to the ends of the standard resistor and as close as possible to these points. The resistance of this circuit was then measured with a Leeds and Northrup Wheatstone Bridge #397978. After this measurement was completed, the

leads were removed and soldered together. The resistance of the resulting circuit was then measured and by the difference of the two readings R_{std} was found. Figure 4 shows the circuit for this measurement and Table 1 gives the results.

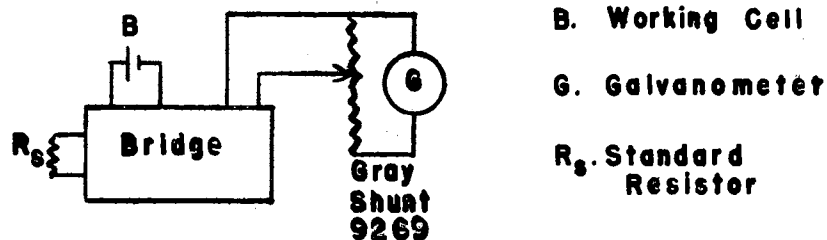


Fig. 4 Circuit for Measuring R_{std} .

Table 1. Data for Measurement of R_{std}

	1	2
$R_{std} \nearrow R_L \sim$	5.0002	4.9999
$R_L \sim$	0.0289	0.0289
$R_{std} \sim$	4.9713	4.9710
	Average = 4.9711	

Figure 5 shows the internal heater power circuit.

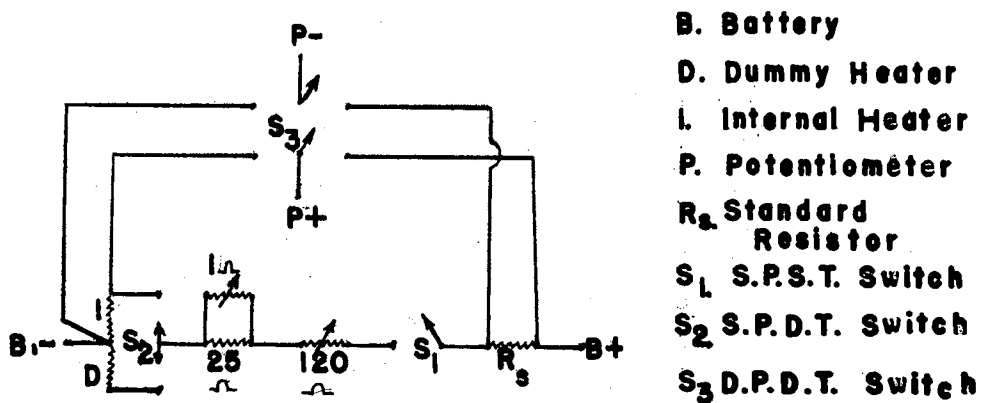


Fig. 5 Internal Heater Power Circuit

The controls for the shield heater consisted of (1) a 20-ampere-capacity Variac autotransformer which was powered by the voltage regulator, (2) a switch and (3) a voltmeter and ammeter as safety devices. The circuit diagram appears in Figure 6.

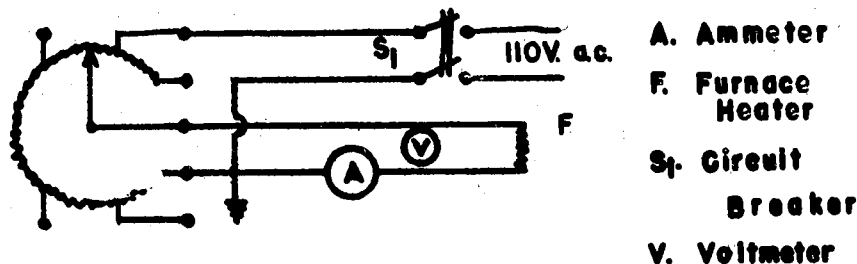


Fig..6 Shield Heater Power Circuit

The thermocouple circuit was as simple as possible to avoid dangers of contact potentials. Figure 7 gives this circuit.

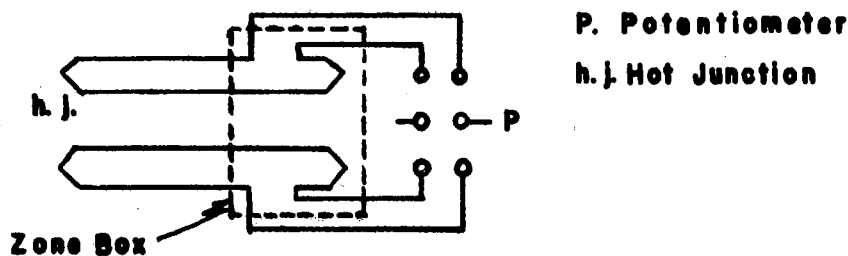


Fig. 7 Thermocouple Circuit

The cold junction assembly served as a zone box for the copper-to-platinum junctions. The thermocouples were broken near the cold junction to allow this to be done. A small copper box with four tubes leading into the top and two leading from the bottom was made. This had one face fitted on with a rubber gasket and screws. The leads were brought into the top of the box and the cold junctions led down through the two bottom tubes. All bare leads were carefully wrapped with cord and

covered with paraffin to insulate them from the copper. A small piece of bakelite was made to fit the box and tapped to take four screws. The copper-to-platinum connections were friction connections made at these screws. After all connections were made and checked the body of the box was filled with paraffin as were the top tubes so that no water could get in or water vapor condense inside. The resulting assembly was placed in a silvered Dewar flask, packed with crushed ice as tightly as possible and then filled with ice water. The packing was repeated periodically. The top of the Dewar was filled with a thick split cork which contained four holes for the top tubes of the zone box. These tubes were placed in the cork and the cork was then wedged into the Dewar so as to form a firm assembly.

After the copper leads were led from the zone box, each pair was twisted together to avoid capacitance effects and then connected to the thermocouple switch.

The above resulted in a system which was very stable and satisfactory in operation. At one time difficulty was experienced with 60-cycle a. c. leaking into the circuit and giving difficulty since the galvanometer tended to respond. This led to a very noticeable thickening of the hair line in the lamp and scale arrangement. The leak was traced to a contact between the vacuum jacket and the thermocouples, and was easily corrected.

The potentiometer circuits followed standard procedures in both cases. As working cells special heavy-duty one-cell lead

storage batteries were used. These cells were manufactured by the Willard Battery Company and were found highly satisfactory. They supplied a very constant voltage so that the calibration of the potentiometers remained constant for periods of several hundred seconds.

The standard cells used were saturated Weston cells prepared by Dr. H. M. Trimble of the Oklahoma A. and M. College Chemistry Department. The E.M.F. of these cells was taken to be 1.0183 volts.

CHAPTER V

THE HEAT CAPACITY OF GRAPHITE

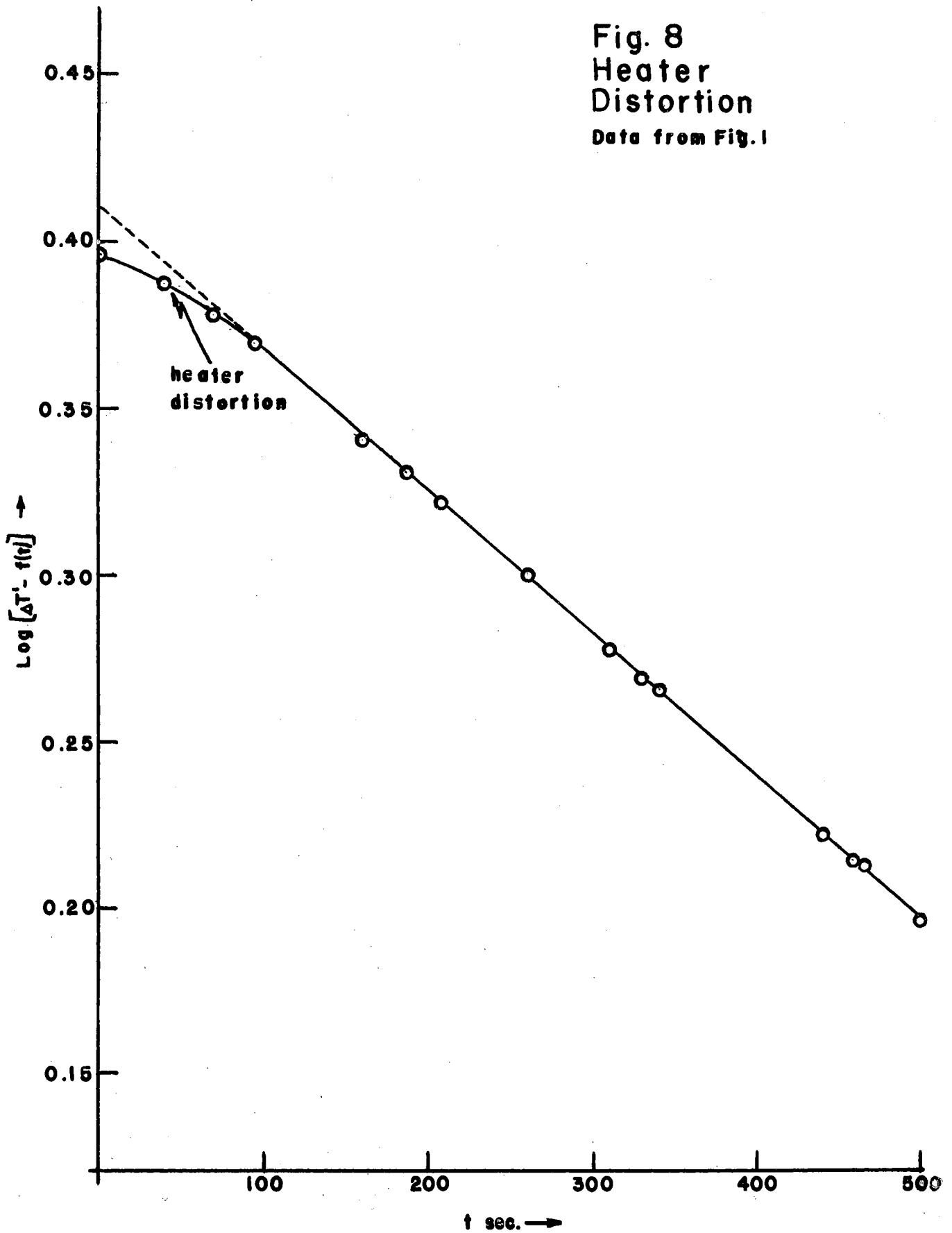
A. Method of Operation

To obtain a measurement, the following operations are necessary: (1) the shield heater is set to give the temperature desired for the measurement and the apparatus allowed to come to steady state, (2) measured amounts of heat are passed through the internal heater and, after about two hours, the temperatures of the shield and calorimeter are measured. This is done for about four or five different power settings. (3) The internal heater is turned full on until a steady state is approached and then turned off. When the difference in temperature between the calorimeter and the shield falls to a value in the calibration range, values of temperature and time are recorded.

It often requires several hours to attain a steady state of the system since the temperature tends to rise as a better and better vacuum is attained. It has been found possible on occasion to maintain a constant temperature for long periods of time after a steady state is attained.

Obtaining steady-state conditions during the calibration is found to be a difficult task and is perhaps the most unsat-

Fig. 8
Heater
Distortion
Data from Fig. 1



isfactory portion of the measurements. Data which will be presented in a later section show that perfect steady-state conditions for an entire calibration were attained only in about 60% of the calibrations reported in this thesis. The variation from a steady state was generally quite small, but definitely meaningful.

There is a definite time needed to allow the resistance of the internal heater to reach a steady value. This time is smaller than that necessary for the temperatures to stabilize so that it is not a factor in the calibrations.

In general, it is believed preferable to approach the steady state in calibration by cooling rather than heating. This seems to give more reproducible calibrations and is thought to give a better approximation of the conditions of the cooling curve.

After the calorimeter has been heated well above the range of calibration and the heater turned off, a period of fifteen to twenty minutes is required to cool to the range of the calibration. This is believed to be ample to allow any distorting gradients due to the internal heater to dissipate. In the data analyzed and in the example shown (Fig. 8), a period of 200 to 300 seconds sufficed to allow the heater distortion to disappear.

B. Calculations

The data which one obtains in a measurement consist of the following: (1) a series of measurements at a steady state giving

T_c - temperature of the calorimeter
 T_s - temperature of the shield
 E_h - voltage drop across the internal heater
 E_{std} - voltage drop across standard resistor.

(2) Measurements of T_c and T_s versus time from an arbitrary zero of time.

From the first series, one calculates the power dissipated in the internal heater from the relation

$$q = E_h E_s / (R_{st} \times 4.1840) \text{ cal. sec.}^{-1}$$

where

q = the rate of heat development in the internal heater
 R_{st} = the resistance of the standard resistor
 4.1840 = the conversion factor from absolute joules to the thermochemical calorie.

After one has obtained the values of q , one finds

$$\Delta T = a / bq.$$

Now for this calorimeter, heat is transferred only by radiation and by conduction, or

$$q = q_r / q_c.$$

Expressing these two modes of heat transfer by the Stefan-Boltzmann Law and by Newton's Law respectively, one obtains

$$q = A\sigma\epsilon(T_c^4 - T_s^4) / K_N\Delta T$$

where A is the area of the calorimeter, σ is the Stefan-Boltzmann constant, ϵ is the emissivity of the system and K_N is the Newton constant for the system. One may substitute the proper quantities for the area of the calorimeter so that

$$q = 4\pi r^2 \sigma \epsilon (T_c^4 - T_s^4) / K_N \Delta T.$$

This would be true if T_c and T_s were the true surface temperatures.

Now from the identity

$$T_c^4 - T_s^4 \equiv T(T_c / T_s)(T_c^2 / T_s^2)$$

and the definition of T_{av} as

$$T_{av} = (T_c + T_s)/2$$

one may write

$$T_c^4 - T_s^4 = \Delta T (2T_{av})(2T_{av}^2 + \Delta T^2/2)$$

$$T_c^4 - T_s^4 = 4T_{av}^3 \Delta T + T_{av} \Delta T^3.$$

The second quantity on the right hand side of this equation is only 0.01% of the total if

$$T_{av} = 500^\circ\text{K}$$

and

$$\Delta T = 2^\circ\text{K}.$$

Then one may say that

$$q = [(16\pi r^2 \sigma \epsilon T_{av}^3) / K_N] \Delta T.$$

Now if we assume that the true surface temperature should be

$$T_s' = T_c - \Delta T'$$

then

$$1/b = -(16\pi r^2 \sigma \epsilon T_{av}^3 / K_N).$$

If one assumes that ϵ and K_N are independent of T , then this is a linear equation and $1/b$ plotted versus T_{av}^3 should be a straight line. This would allow one to smooth the values for b . It has been found that a plot such as this is a straight line if one plots the values of b in $\mu\text{v}/\text{cal}$. rather than $\text{deg.}/\text{cal}$. Here the combination of the variation of $\partial E/\partial T$, ϵ , and K_N with temperature cancel within the experimental error of the calorimeter. Only values of b from calibrations giving unique linear plots of ΔT against q have been used in determining the line. Other poor calibrations have been corrected from these smoothed

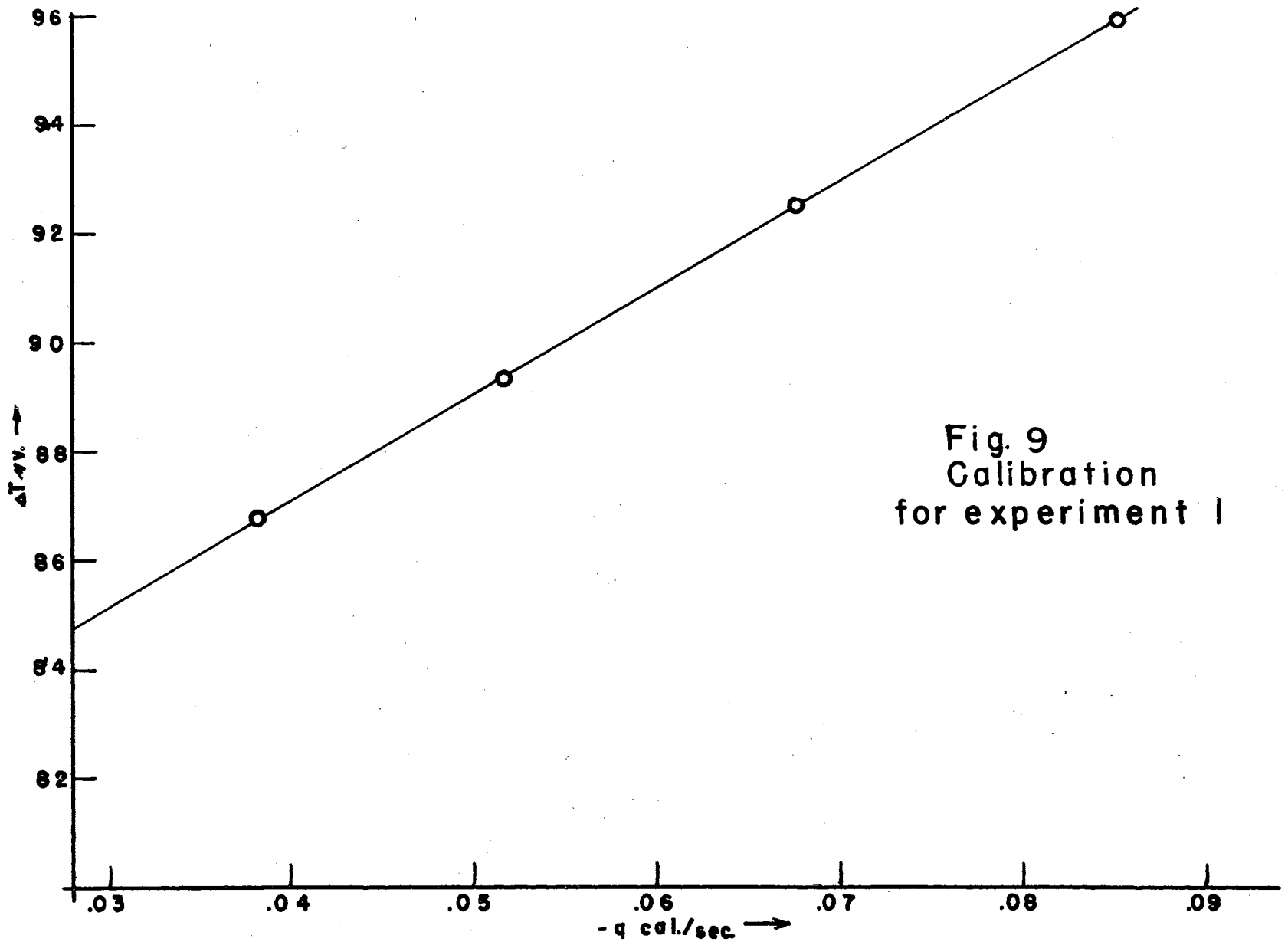


Fig. 9
Calibration
for experiment 1

Fig. 10
Calibration Plot

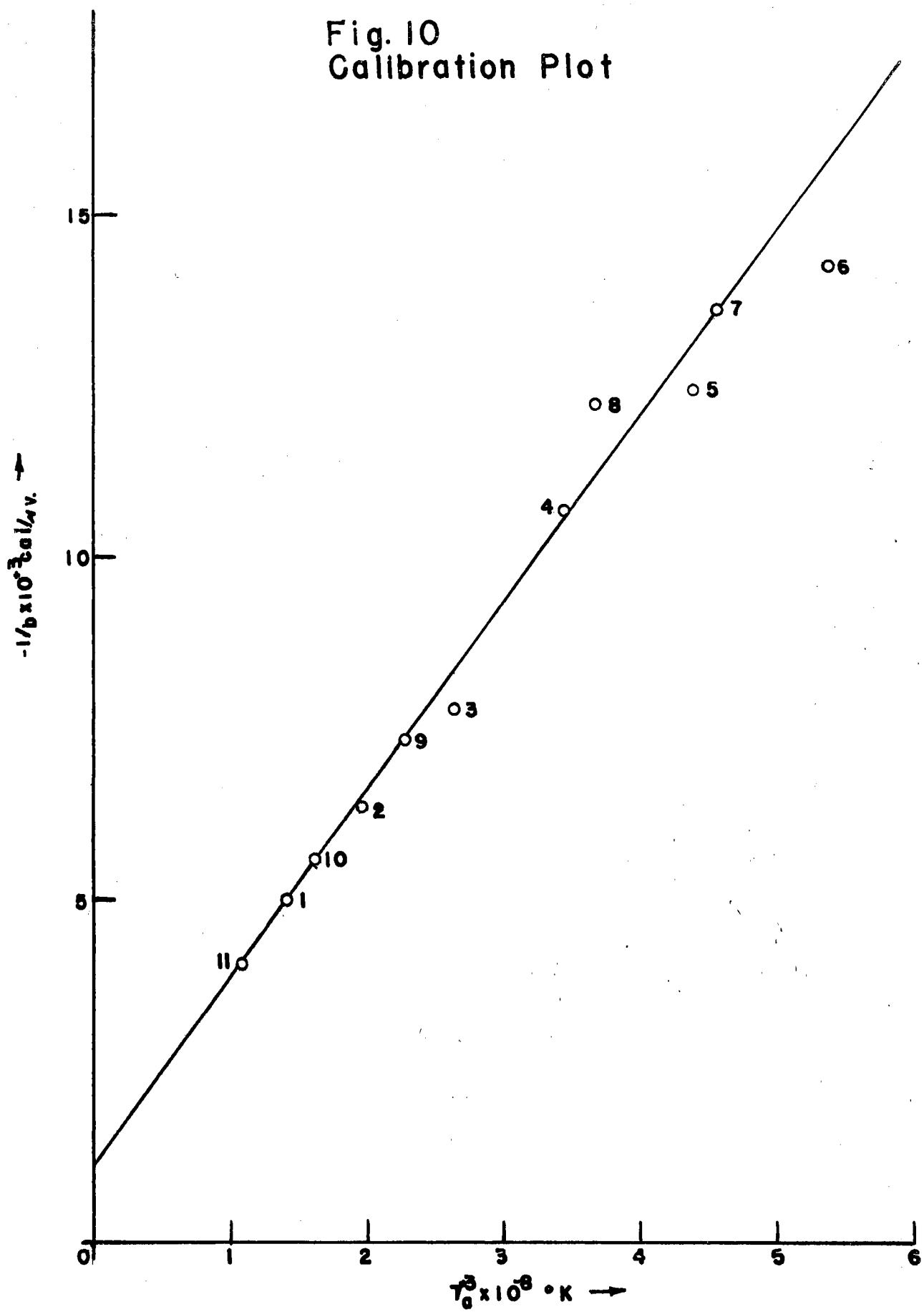
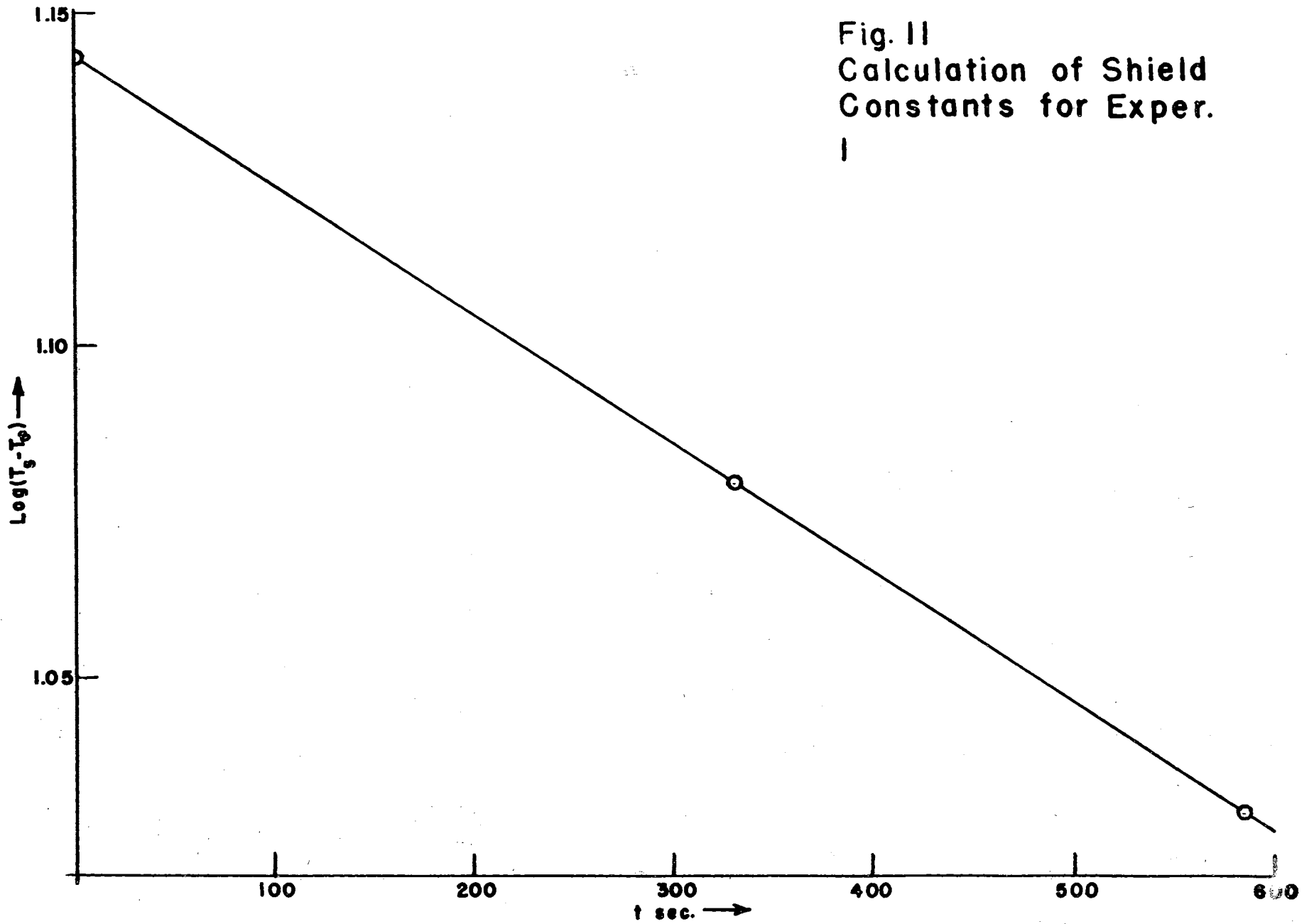


Fig. II
Calculation of Shield
Constants for Exper.
I



values. From these values of b , a straight line was fitted to the calibration data and a was determined.

For the series of measurements in (2), the values of T_s versus t were fitted to the empirical equation

$$T_s = T_\infty + \beta e^{-\gamma t}$$

by plotting $\log(T_s - T_\infty)$ versus t . From this β and γ were determined. With these constants it was possible to solve the equation 18

$$\Delta T' = \beta \gamma / (1/bC + \gamma) [(e^{t/bC} - e^{-\gamma t})] + \Delta T_0 e^{t/bC}$$

for C by the method of reiteration described in Chapter III.

The following tables and graphs give the solution for a typical experiment.

As an example, the calculation for experiment 1 will be given in detail. Data for this experiment appear in Tables 3 and 4 of the next section. The calibration gave data shown in Figure 9. From this plot it is found that

$$\begin{aligned} a &= 78.78 \\ b &= -200 \end{aligned}$$

as indicated on the figure. Comparison of the value of b found with that shown on the calibration plot, Figure 10, shows that this value is correct.

The next step in the calculation is to fit the $t - T_s$ data to equation 12 by using several trial values of T_∞ . Figure 11 shows the plot of $\log(T_s - T_\infty)$ against t . From this it is found that

$$\begin{aligned} T_\infty &= 1.8255 \text{ mv} \\ \beta &= 13.9 \mu\text{v} \\ \gamma &= 4.485 \times 10^{-4} \text{ sec.}^{-1}. \end{aligned}$$

From these constants, and the original $t - T_c$ data, a table

Table 2. Data for Calculation of C_p in Experiment 1

sec	T_{smv}	$\Delta T'_{\mu v}$	$f(t)_1_{\mu v}$	$\log[\Delta T' - f(t)_1]$	$f(t)_2_{\mu v}$
39	1.83916	13.06	0.23	1.1082	0.24
65	1.83900	12.72	0.38	1.0913	0.38
95	1.83883	12.39	0.54	1.0738	0.55
25	1.83869	12.08	0.69	1.0565	0.70
59	1.83845	11.77	0.85	1.0382	0.86
90	1.83826	11.46	0.99	1.0199	1.00
25	1.83806	11.16	1.14	1.0008	1.16
59	1.83798	10.84	1.27	0.9809	1.29
95	1.83768	10.54	1.40	0.9609	1.43
72	1.83726	9.96	1.65	0.9196	1.69
12	1.83705	9.67	1.76	0.8982	1.81
52	1.83685	9.37	1.86	0.8756	1.91
93	1.83664	9.08	1.96	0.8525	2.02
37	1.83656	8.66	2.05	0.8202	2.11

sec	$\log[\Delta T' - f(t)_2]$	$f(t)_3_{\mu v}$	$\log[\Delta T' - f(t)_3]$	$f(t)_4_{\mu v}$	$\log[\Delta T' - f(t)_4]$
39	1.1079	0.23	1.1082	0.24	1.1079
65	1.0913	0.38	1.0913	0.38	1.0913
95	1.0734	0.54	1.0738	0.55	1.0734
25	1.0561	0.70	1.0561	0.70	1.0561
59	1.0378	0.86	1.0378	0.87	1.0374
90	1.0195	1.00	1.0195	1.01	1.0191
25	1.0000	1.15	1.0004	1.16	1.0000
59	0.9800	1.28	0.9805	1.29	0.9800
95	0.9595	1.42	0.9600	1.43	0.9595
72	0.9175	1.67	0.9186	1.68	0.9180
12	0.8954	1.78	0.8971	1.80	0.8960
52	0.8727	1.90	0.8733	1.91	0.8727
93	0.8488	1.99	0.8506	2.00	0.8500
37	0.8162	2.09	0.8176	2.11	0.8162

Fig. 12

Graphical Calculation
of C_p for Experiment
1

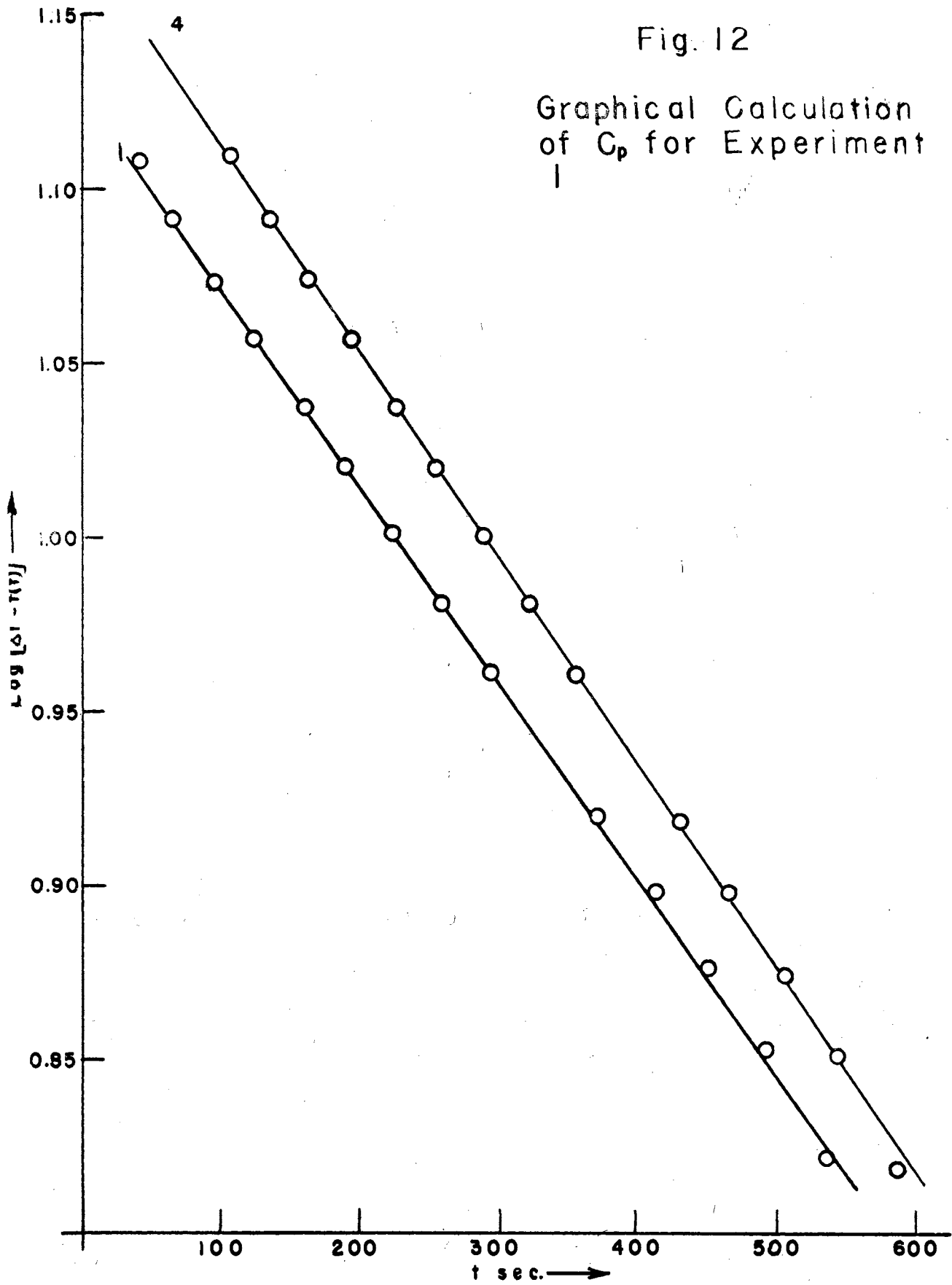
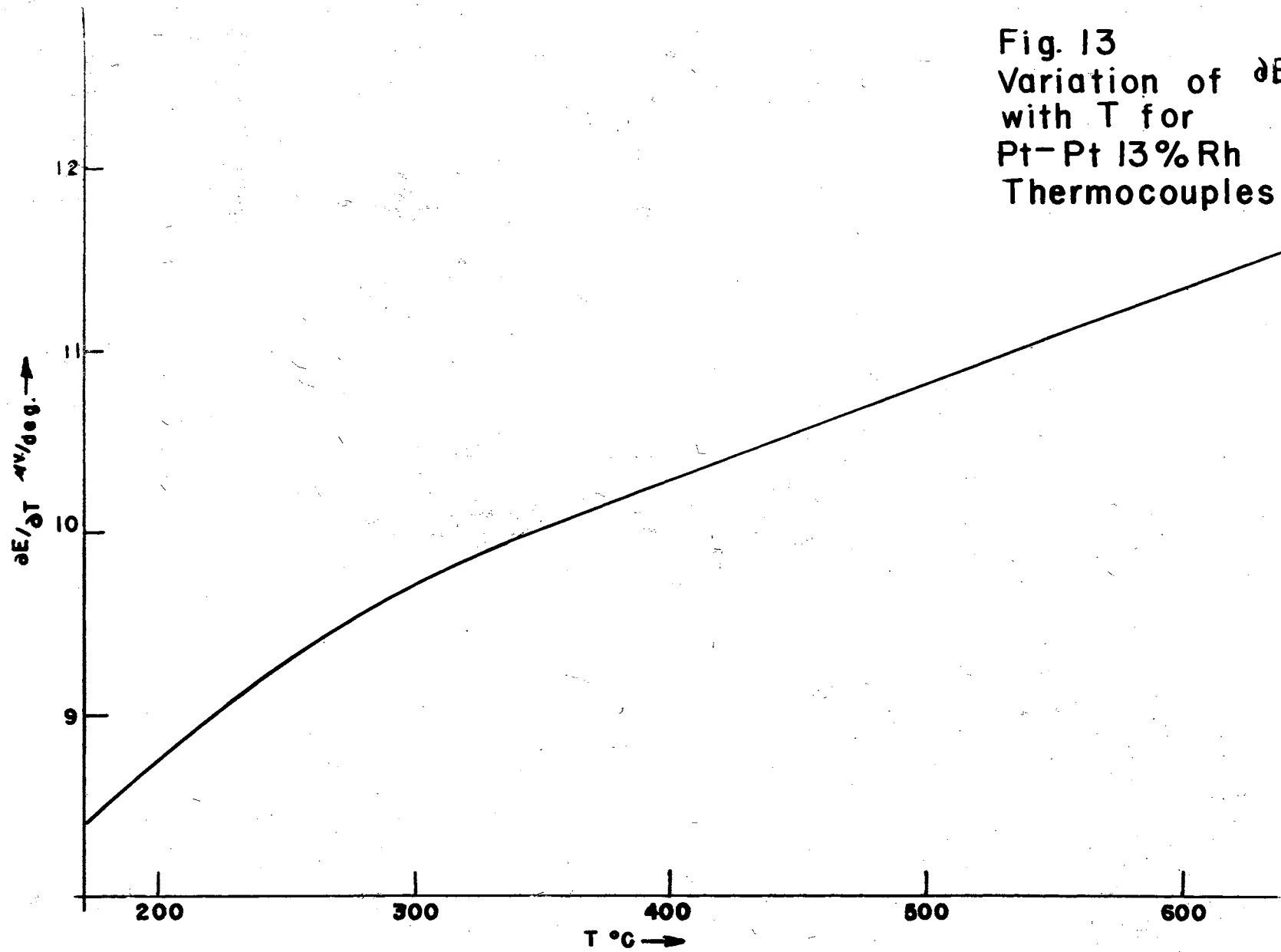


Fig. 13
Variation of $\frac{\partial E}{\partial T}$
with T for
Pt-Pt 13%Rh
Thermocouples



is constructed (Table 2) showing t , T_c , T_s , $\Delta T'$, $f(t)$, $(\Delta T' - f(t))$, and $\log[\Delta T' - f(t)]$ for a particular value of C in (cal./ μ v). $\log[\Delta T' - f(t)]$ is then plotted against t (Figure 12) and C determined from the slope of this plot. In experiment 1, $C_1 = 3.5$ was the initial trial value. A value of $C_p = 3.838$ was found from the slope of Figure 12. The next iteration was performed using a value of $C_2 = 3.66$ and so on until finally values of $C = 3.74$ and 3.80 both yielded 3.82 cal./ μ v from the slopes. This value was accepted. To obtain C_p from this value, the heat capacity of the internal heater, the number of moles of graphite in the calorimeter, and the value of $\partial E/\partial T$ for the thermocouples at this temperature must be known.

From the data presented in the next section it is seen that there were 9.56 moles of graphite in the calorimeter. Taking Lava as $MgSiO_4$ and pipestem as an aluminum silicate the heater was estimated to have a heat capacity¹ of $0.1 \pm 100\%$ cal./deg. The maximum error in using the value of 0.1 cal./deg. at all temperatures would amount to less than 0.3% . To find $\partial E/\partial T$, data taken from Leeds and Northrup table Std. 31031, for Pt - Pt 13% Rh thermocouples with reference junction at $0^\circ C.$, were plotted against temperature. This is shown in Figure 13. From this figure, $\partial E/\partial T$ was found to be 9.31μ v/deg. We may now find C_p to be

$$C_p = (3.82 \times 9.31 - 0.1)/9.56$$

$$C_p = 3.71 \text{ cal./deg. mole at } 524^\circ K.$$

C. Data

The following tables give the experimental data of this

Table 3. Calibration Data

T_s mv	T_C mv	ΔT μ v	E_s V	E_h V	q cal./deg.
Experiment 1					
1.8322	1.9280	95.8	0.9831	1.8023	0.08520
1.8301	1.9224	92.3	0.8159	1.6015	0.06746
1.8277	1.9168	89.1	0.7685	1.4008	0.05177
1.8267	1.9132	86.5	0.6605	1.2001	0.03812
Experiment 2					
2.3793	2.4790	99.7	1.0844	1.9977	0.10420
2.3759	2.4725	96.6	0.9775	1.8025	0.08472
2.3728	2.4663	93.5	0.8711	1.6034	0.06716
2.3718	2.4630	91.2	0.7624	1.4030	0.05143
Experiment 3					
2.9908	3.0923	101.5	0.9224	1.7030	0.07554
2.9889	3.0881	99.2	0.8140	1.5029	0.05883
2.9870	3.0843	97.3	0.7069	1.3045	0.04434
2.9873	3.0839	96.6	0.6502	1.1998	0.03751
Experiment 4					
3.5926	3.7071	114.5	0.9191	1.7020	0.07522
3.5901	3.7029	112.8	0.8119	1.5030	0.05868
3.5904	3.7019	111.5	0.7035	1.3018	0.04404
3.5892	3.6995	110.3	0.5956	1.1021	0.03156
Experiment 5					
4.1853	4.3178	132.5	0.9160	1.6995	0.07486
4.1839	4.3153	131.4	0.8085	1.4994	0.05830
4.1820	4.3121	130.1	0.7019	1.3009	0.04391
4.1820	4.3111	129.1	0.5912	1.1015	0.03147
Experiment 6					
4.7637	4.9199	156.2	0.9136	1.7002	0.07470
4.7541	4.9086	154.5	0.7536	1.4018	0.05080
4.7500	4.9031	153.1	0.5916	1.1004	0.03131
4.7494	4.9019	152.5	0.4312	0.8004	0.01660

Table 3. Calibration Data Contd.

T_s mv	T_C mv	ΔT μ v	E_s V	E_h V	q cal./deg.
Experiment 7					
4.2892	4.4283	138.1	0.91561	1.7000	0.07485
4.2880	4.4243	136.3	0.75392	1.3986	0.05071
4.2867	4.4216	134.9	0.59554	1.1057	0.03167
4.2844	4.4183	133.9	0.43690	0.80982	0.01701
Experiment 8					
3.7602	3.8811	120.9	0.97574	1.8131	0.08507
3.7565	3.8753	118.8	0.79818	1.4905	0.05721
3.7546	3.8707	116.1	0.59300	1.1018	0.03142
3.7480	3.8635	115.5	0.46760	0.86745	0.01951
Experiment 9					
2.6582	2.7564	98.2	0.94160	1.7478	0.07914
2.6561	2.7510	94.9	0.77947	1.7400	0.05457
2.6539	2.7461	92.2	0.63465	1.1925	0.03640
2.6527	2.7430	90.3	0.49274	0.90169	0.02137
Experiment 10					
2.0411	2.1361	95.0	0.91541	1.7464	0.07940
2.0370	2.1284	91.4	0.80094	1.4739	0.05677
2.0346	2.1223	87.7	0.64645	1.1887	0.03645
2.0330	2.1185	85.5	0.54049	0.98528	0.02561
Experiment 11					
1.4433	1.5384	95.1	0.93954	1.7311	0.0782
1.4399	1.5312	91.2	0.79800	1.4995	0.05755
1.4379	1.5258	87.9	0.70715	1.2900	0.04383
1.4356	1.5205	84.9	0.60175	1.0914	0.03156

Table 4. Time - Temperature Data

t sec	T _C mv	t sec	T _C mv	t sec	T _S mv
Experiment 1					
39	1.9310	259	1.9275	0	1.8394
65	1.9305	295	1.9270	330	1.8375
95	1.9300	372	1.9260	584	1.8362
125	1.9295	412	1.9255		
159	1.9290	452	1.9250		
190	1.9285	493	1.9245		
225	1.9280	537	1.9240		
Experiment 2					
52	2.4795	288	2.4745	0	2.3818
72	2.4790	346	2.4735	312	2.3798
92	2.4785	372	2.4730	617	2.3780
113	2.4780	400	2.4725		
137	2.4775	431	2.4720		
160	2.4770	462	2.4715		
185	2.4765	497	2.4710		
209	2.4760	533	2.4705		
234	2.4755	568	2.4700		
261	2.4750				
Experiment 3					
93	3.1000	497	3.0930	35	2.9981
111	3.0995	530	3.0925	384	2.9952
135	3.0990	568	3.0920	692	2.9215
159	3.0985	609	3.0915	1164	2.9905
185	3.0980	651	3.0910		
211	3.0975	741	3.0900		
238	3.0970	782	3.0895		
266	3.0965	832	3.0890		
296	3.0960	883	3.0885		
325	3.0955	940	3.0880		
358	3.0950	993	3.0875		
403	3.0945	1056	3.0870		
427	3.0940	1122	3.0865		
462	3.0935				
Experiment 4					
56	3.7160	364	3.7105	0	3.6011
79	3.7155	400	3.7100	428	3.5971

Table 4. Time - Temperature Data Contd.

sec	T _C mv	t sec	T _C mv	t sec	T _S mv
102	3.7150	476	3.7090	760	3.5946
127	3.7145	513	3.7085		
155	3.7140	553	3.7080		
180	3.7135	593	3.7075		
211	3.7130	637	3.7070		
238	3.7125	678	3.7065		
268	3.7120	727	3.7060		
298	3.7115	836	3.7050		
331	3.7110				

Experiment 5

39	4.3270	294	4.3225	0	4.1932
60	4.3265	324	4.3220	346	4.1904
84	4.3260	401	4.3210	696	4.1879
09	4.3255	433	4.3205		
39	4.3250	472	4.3200		
68	4.3245	512	4.3195		
01	4.3240	552	4.3190		
31	4.3235	596	4.3185		
63	4.3230	645	4.3180		

Experiment 6

42	4.9160	372	4.9115	0	4.7595
73	4.9155	408	4.9110	337	4.7573
03	4.9150	448	4.9105	756	4.7545
34	4.9145	498	4.9100		
66	4.9140	547	4.9095		
99	4.9135	602	4.9090		
37	4.9130	656	4.9085		
73	4.9125	724	4.9080		
13	4.9120				

Experiment 7

30	4.4395	347	4.4315	0	4.2975
45	4.4390	375	4.4310	227	4.2946
39	4.4385	404	4.4305	458	4.2925
55	4.4380	433	4.4300	886	4.2892
11	4.4375	501	4.4290		
19	4.4370	533	4.4285		
17	4.4365	572	4.4280		
07	4.4360	608	4.4275		
05	4.4355	659	4.4270		

Table 4. Time - Temperature Data Contd.

t sec	T _C mv	t sec	T _C mv	t sec	T _S mv
185	4.4350	705	4.4365		
253	4.4335	753	4.4360		
275	4.4330	802	4.4355		
297	4.4325	852	4.4350		
322	4.4320				
Experiment 8					
64	3.8775	393	3.8715	0	3.7563
84	3.8770	428	3.8710	297	3.7535
105	3.8765	469	3.8705	542	3.7518
129	3.8760	510	3.8700	945	3.7447
154	3.8755	600	3.8690		
178	3.8750	652	3.8685		
207	3.8745	693	3.8680		
238	3.8740	742	3.8675		
265	3.8735	799	3.8670		
331	3.8725	860	3.8665		
359	3.8720	922	3.8660		
Experiment 9					
34	2.7600	359	2.7545	0	2.6625
58	2.7595	395	2.7540	229	2.6609
82	2.7590	430	2.7535	501	2.6590
109	2.7585	471	2.7530	830	2.6571
139	2.7580	559	2.7520		
166	2.7575	596	2.7515		
196	2.7570	643	2.7510		
264	2.7560	689	2.7505		
292	2.7555	737	2.7500		
325	2.7550	787	2.7495		
Experiment 10					
47	2.1380	404	2.1325	0	2.0450
73	2.1375	442	2.1320	250	2.0435
100	2.1370	478	2.1315	551	2.0415
128	2.1365	518	2.1310	819	2.0404
159	2.1360	607	2.1300		
189	2.1355	653	2.1295		
223	2.1350	703	2.1290		
294	2.1340	752	2.1285		
327	2.1335	802	2.1280		
366	2.1330				

Table 4. Time - Temperature Data Contd.

t sec	T _C mv	t sec	T _C mv	t sec	T _S mv
Experiment 11					
74	1.5335	417	1.5285	0	1.4404
108	1.5330	461	1.5280	254	1.4398
134	1.5325	499	1.5275	531	1.4392
167	1.5320	582	1.5265	874	1.4384
199	1.5315	630	1.5260		
228	1.5310	682	1.5255		
305	1.5300	731	1.5250		
336	1.5295	774	1.5245		
380	1.5290	837	1.5240		

Table 5. Constants of the Calorimeter

D = 1.994 inches

Material	Wt. g.	Moles
Lava	0.2554	
Pipestem	0.234	
Nichrome	0.0015	
Graphite	114.9323	9.56

Table 6. Summary of Results

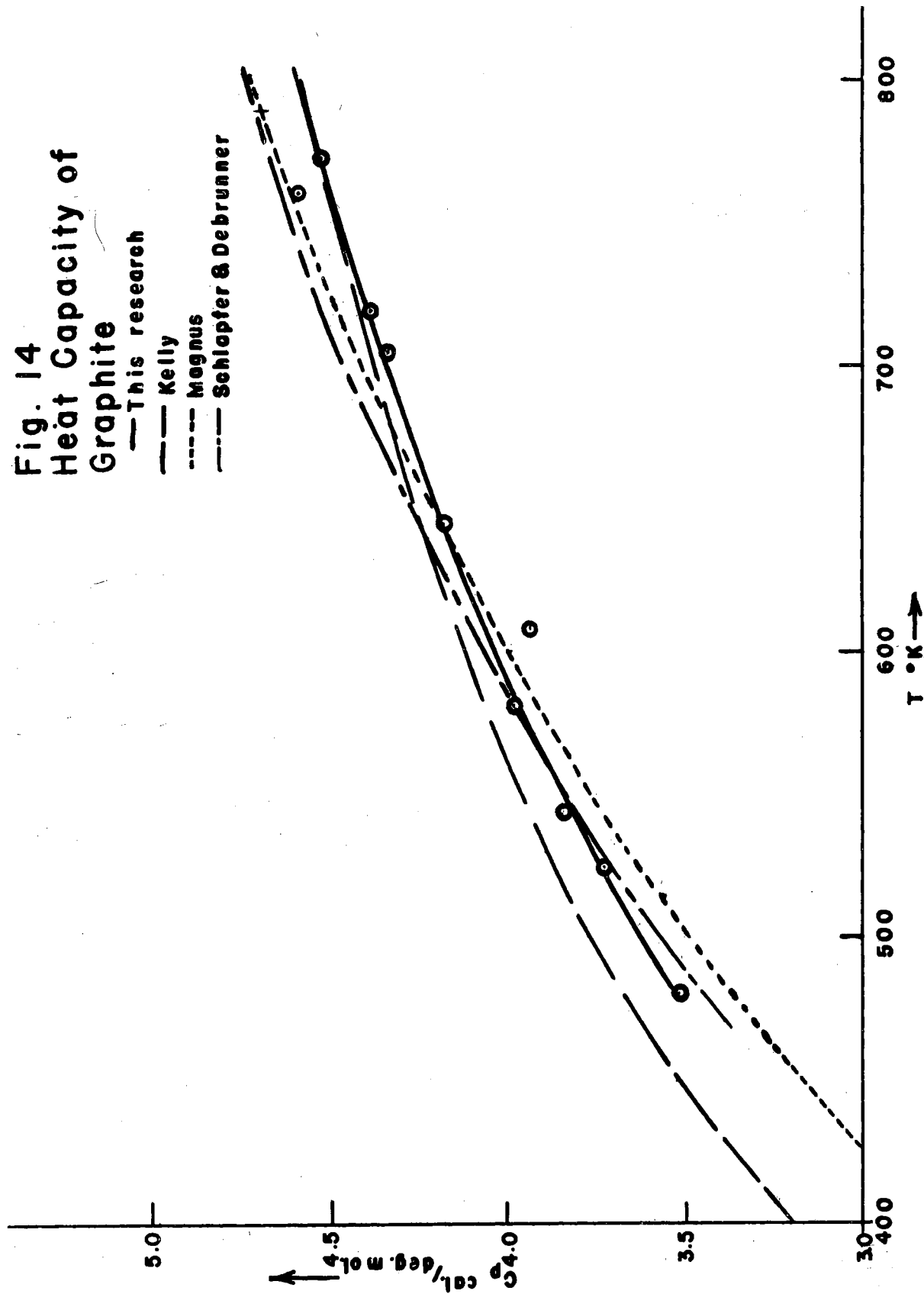
Exper.	T °K	T mv	β μ v	sec ⁻¹
1	524	1.8255	13.9	4.485x10 ⁻⁴
2	581.7	2.3576	24.2	2.770x10 ⁻⁴
3	643.6	2.9824	15.9	6.155x10 ⁻⁴
4	703.2	3.5815	19.6	5.305x10 ⁻⁴
5	760.7	4.1685	24.7	3.470x10 ⁻⁴
6	-----	-----	-----	-----
7	771.3	4.2835	14.0	1.015x10 ⁻⁴
8	718.6	3.7455	10.8	1.000x10 ⁻⁴
9	609.9	2.6400	22.5	3.312x10 ⁻⁴
10	546.1	2.0100	35.05	1.830x10 ⁻⁴
11	480.3	1.4000	40.4	5.560x10 ⁻⁵

Table 6. Summary of Results Contd.

Exper.	a μ v	b μ v/cal sec	C cal/deg mole
1	78.78	-200	3.71
2	83.35	-155	3.98
3	91.60	-130	4.18
4	107.2	- 96.5	4.33
5	126.8	- 76.3	4.58
6	-----	-----	-----
7	132.61	- 73.5	4.54
8	113.8	- 89.2	4.38
9	87.4	-136.5	3.93
10	80.9	-180.1	3.84
11	77.2	-245	3.52

Fig. 14
Heat Capacity of
Graphite

— This research
- - - Kelly
- · - · - · Magnus
- · - - · Schlopf & Debrunner



CHAPTER VI

DISCUSSION

A. Heat Capacity of Graphite

Eleven measurements have been made of the heat capacity of graphite in the temperature range from 480°K to 780°K . Of these, eight measurements are within 0.5% of the smoothed curve. Of the three points showing considerable variation, two were from experiments depending on very poor calibrations; thus the values of a were uncertain. There is no obvious explanation for the variation in the third experiment.

There have been three measurements of the heat capacity of graphite over this temperature range, made by Dewar²⁹, Magnus³⁰, and Schlapfer and Debrunner³¹. Unfortunately for purposes of comparison, there is considerable variation in the reported values in this range, although below 300°K and above 1000°K agreement is good. There have been two critical evaluations of the available data in recent years, by Kelly¹ and by Rossini³². Of these, the latter follows exactly the earlier data of Magnus, while Kelly's compilation appears to be a critical evaluation of all the data. The data of Magnus and Schlapfer and Debrunner and Kelly's compilation are shown in Figure 14 with the values from this research.

As can be seen, the values from this research fall about on the median of the reported values below 600°K and slightly below the median above this temperature. There seems to be no adequate explanation of the variation in the heat capacity of graphite. While many of the properties of this material are highly dependent on the history of the sample, Ephraim³³ states that the heat capacity should be constant. This was found experimentally by Schlapfer and Debrunner, who measured the heat capacity of natural Ceylon graphite and an artificial retort graphite.

It can be said only that agreement with the literature is satisfactory.

The absolute accuracy of the method will depend upon three measurements: (1) the accuracy of measurement of the temperature, (2) the accuracy of determination of b , and (3) the precision with which conditions of calibration are reproduced in the cooling curve.

The calibration of the thermocouples, which was done by Mr. Wynn Fife, is shown in Appendix 1. The variation from the standard tables exceeds 2 μv . in only one measurement out of eight. Thus the thermocouples indicated the junction temperature to 0.2°C . An error of 1°C in the experimental temperature would give an error of 0.2% in the value of C_p .

The heat input q was measured with an accuracy of about 0.1% or better. The resistance of the copper leads to the internal heater varied from about 0.019 to 0.024 Ω (calculated from length of wire and known properties of copper³⁴) which is

about 0.3% of the heater resistance.

It is difficult to assign any definite error to the reproducibility of the thermocouples. In general, variation from the smoothed cooling curves and from the linear plot used in analyzing the data was about 0.05%v. or less. Since the shield thermocouple exhibited a marked pickup phenomenon, there is the possibility of a systematic error. It is believed that for any given measurement this pickup remained constant since linear relationships were obtained for the calibration data.

The error, aside from systematic variations in reproducibility, is estimated to be about 1%. This could be reduced by means discussed in the next section to about 0.5%.

To find systematic variations, one should measure C_p for a substance whose specific heat is better known than that of graphite.

B. Suggested Modifications

The three main difficulties encountered in this research could be partially or completely eliminated by: (1) elimination of the pickup in the shield calorimeter, (2) measurement of the voltage drop of the internal heater at the surface of the calorimeter, and (3) more precise measurements of calibration data.

The first difficulty was very puzzling since no source of d. c. pickup was obvious in the system and the measuring system would not respond to a. c. in the manner found. It has been found by Stansbury³⁵ that many ceramics act as semiconductors at high temperatures. Thus the shield is rectifying a small amount of the current fed to the shield heater. It is known that some

forms of high-purity Alundum do not have this property, so that a shield constructed of this material would help considerably. Another possibility (believed to be more likely by Stansbury) is that the surface temperature of the shield is not homogeneous. An alternate solution would be to insert a second shield of metal which had a relatively low resistance to ground. This would serve the additional purpose of reducing the heat transfer between the calorimeter and the shield and thus permitting measurements at higher temperatures.

Since the work reported here was done, a new technique for attaching the heater leads to the internal heater has been found. Small-diameter precision-bored tubes are crimped instead of soldered to the wires. This gives a relatively simple and very satisfactory connection. It should then be possible to attach two B. & S. #40 gauge wires to the internal heater power leads at the point at which they emerge from the pipestem. Such an arrangement would not appreciably increase the conductance loss of the calorimeter and would eliminate most of the error in measuring q , the heat input.

It is believed that an analysis of the behavior of the system while approaching a steady state, rather than a passive waiting for steady state to be attained, would improve the calibration data. The most logical approach would seem to be to measure \dot{T}_C and \dot{T}_S during the calibration and to devise empirically a test for steady state using these values. This is probably the most serious problem found in this research.

CHAPTER VII

SUMMARY

A furnace calorimeter using a modified form of the Du-long and Petit cooling method has been built.

It has been shown that the general condition for the method of cooling to yield values of specific heat is that

$$\partial(\text{grad } T)/\partial t = 0.$$

This is a physical impossibility, but may be approached closely enough if the transfer of heat from the calorimeter to its surroundings is small compared with the thermal conductivity of the calorimeter. Thus the highest temperature at which the method of cooling may be used is determined by the thermal conductivity of the material being tested and the design features of the calorimeter which determine its heat transfer characteristics.

The present calorimeter has been designed as a vacuum calorimeter so that (1) the heat transfer from calorimeter-to-surroundings is minimized, (2) the sample is protected from oxidation, and (3) the radiative transfer of heat and, thus, the calibration of the calorimeter, is reproducible at a given temperature.

A direct electrical calibration of the calorimeter was

an important part of the design. This allowed one to obtain true specific heats which did not depend on any other physical property of the material. Further, since radiative transfer of heat was utilized as an important design feature, the calibration freed the instrument of the error usually found due to the rapid increase of radiative transfer with temperature.

The heat capacity of graphite has been measured over the temperature range from 480°K to 780°K . The values found are in satisfactory agreement with those found by previous workers.

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APPENDIX

The following calibration data for the calorimeter thermocouples were obtained by Mr. Wynn Fife. All samples were certified by the National Bureau of Standards. The reference junction was at 0°C.

Metal	T _c mv.	T _s mv.	T _{NBS} mv.
Sn	1.7490	1.7490	1.7504
Pb	2.6607	2.6596*	2.6624
Zn	3.5986	3.5987	3.6000
Al	6.2470	6.2488	6.2479

*Average of several. Not as accurate as others.

William Russell Willis
candidate for the degree of
Doctor of Philosophy

Thesis: A NEW FURNACE CALORIMETER: THE HEAT CAPACITY
OF GRAPHITE

Major: Physical Chemistry

Biographical and Other Items:

Born: February 14, 1926 at Moundsville, West Virginia

Undergraduate Study: West Virginia Wesleyan College,
Buckhannon, West Virginia, 1946-1948

Graduate Study: Oklahoma Agricultural and Mechanical
College, 1948-1953

Experience: Naval Air Corps, 1943-1946; Teaching Fellow
O.A.M.C., 1948-1951; Research Associate, 1951-1953.

Member of Phi Lambda Upsilon, The American Chemical Society,
and Associate Member of The Society of the Sigma Xi.

Date of Final Examination: August 24, 1953.

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AUTHOR: William R. Willis

THESIS ADVISER: Dr. Irving Johnson

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TYPIST: Jean E. Willis