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To the Graduate Council:

I am submitting herewith a thesis written by Richard E. Pawel entitled "The Application of Dynamic Adiabatic Calorimetry to the Copper-Nickel System From 50 to 620 °C." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgy.

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**THE APPLICATION OF DYNAMIC ADIABATIC CALORIMETRY
TO THE COPPER-NICKEL SYSTEM FROM 50 TO 620 °C**

A THESIS

**Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the degree of
Doctor of Philosophy**

**by
Richard E. Pawel
December 1956**

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CHAPTER I

SUMMARY

During the past several years, contributions of thermodynamic information by experimental research have been numerous, and have served to stimulate theoretical work leading to a more basic understanding of many complex problems. Data useful for this purpose have been obtained using calorimeters of various types and flexibility. This dissertation represents a contribution from a calorimetry research program which has been in progress during the past several years at The University of Tennessee. Initial phases of this program were concerned with the design and construction of dynamic adiabatic calorimeters. Two calorimeters are now being used to determine metallic specific heats, heats of transformation and other measurable heat effects. These data are useful and necessary in the complete analysis of metallic systems.

The phase of research reported in this dissertation is primarily concerned with the methods of extracting self consistent and reproducible true specific heat values from the data obtained in one of the above calorimeters. Since the long range objective of this program was the determination of the very small increases in the internal energy of plastically deformed specimens, a very high degree of accuracy and reproducibility was necessary. In order to obtain this accuracy, several problems inherent in high temperature operation were reconciled.

The calorimeter used in this investigation was a modified version of the calorimeter used by Picklesimer ²¹, and reported by Stansbury, Elder, and

Picklesimer ³² in 1953. Although the present design is considerably different, the basic method and fundamental aims are the same. The calorimeter is a dynamic (continuous) adiabatic type in which a specimen is heated by a known power under essentially adiabatic conditions. In this manner, any phenomenon which is reflected by energy input-temperature relations can be investigated. In specific heat determinations, the true specific heats are calculated from the apparent specific heat data by applying corrections for the specimen heater assembly and the deviation from true adiabatic conditions.

The calorimeter consists of a long monel tube with one main and two auxiliary nichrome windings. The inside of the tube, which houses the specimen, is kept under high vacuum, about 5×10^{-5} mmHg., to keep convection losses low; the outside of the tube is flooded with helium to increase the heat response from the windings. The specimen is maintained under adiabatic conditions by a series of controllers actuated by the amplified outputs of platinum-platinum 13 per cent rhodium differential thermocouples. The thermocouple system allows measurements of absolute temperatures, temperature differences, and spurious emf's in all components of the apparatus. The repression of these spurious potentials was an important step in the improvement of the data.

The specimens used in specific heat measurements were polished cylinders weighing approximately 250 grams. Each specimen was drilled to accommodate a 15 ohm winding of 30 gage nichrome wire which served as the specimen heater. The specimens used in this investigation were machined from ingots melted under argon in an induction furnace. Specific heat determinations from 60° to 620° C were made on specimens of pure copper, pure nickel, and three alloys containing approximately 90, 75, and 50 weight per cent nickel. In addition, several techniques were investigated with regard to the determination of stored energy in plastically deformed specimens of these

materials. Although the stored energy data were meager, the experience with several experimental methods may prove valuable in future work.

The conclusions reached in this phase of the program may be summarized as follows:

1. Through the use of careful techniques, and the solution of some of the experimental difficulties associated with high temperature operation, the design and operation of the calorimeter used in this research has reached a stage where extremely reproducible and self consistent specific heat data on metallic systems can be obtained.

2. The validity of the treatment of the apparent specific heat data has been proven by the manner in which the corrections rectify data taken under different conditions of operation.

3. The specific heat of copper has been determined from room temperature to 620 °C, and may be represented by a linear function of the temperature with an error of less than ± 0.5 per cent. A least squares treatment of the data resulted in $C_p = 0.0931 + 2.175 \times 10^{-5} T$ cal/gram °C.

4. The specific heat of nickel has been determined from room temperature to 620 °C with an accuracy better than ± 0.5 per cent. The specific heat values reported for nickel above the Curie point are significantly lower than those of most previous investigators, but agree well with the data of Moser ¹⁴. Because of the Curie behavior, the specific heat data are presented graphically rather than analytically.

5. The specific heats of the copper-nickel alloys have been determined to 620 °C with similar accuracies. It appears that above the Curie range, the data can be represented reasonably by a straight line, but not as well as that for pure copper. Kopp-Neumann behavior was illustrated in these data.

6. The stored energy values reported for cold-worked copper in this research, 0.23 to 0.37 cal/gram, appear high compared with the data of Gordon ⁴ and Clarebrough ^{5,6} , and low compared with those of Suzuki ³ , Quinney and Taylor ¹¹ , and other early investigators.

7. The techniques used with this calorimeter on the determination of stored energy will have to be improved considerably before reliable values can be obtained.

CHAPTER II

INTRODUCTION

The accurate measurement of changes in thermal energy in the solid state has long been the subject of investigators in many fields. Knowledge of thermal effects can contribute greatly to fundamental studies and the general understanding of many phenomena, as well as being the basis of thermodynamic and theoretical work leading to a better comprehension of the behavior of metals and alloys. High temperature calorimetric methods for the solid state may be naively considered to be identical, at least in principle, with the familiar adiabatic or isothermal type calorimeters used extensively in the vicinity of room temperature. A wealth of thermodynamic data for metals lies well above room temperature, and direct measurements of specific heats, heats of transformation, heats of solution, and non-equilibrium state effects necessitate operation at elevated temperatures. The problems and experimental difficulties encountered in high temperature calorimetry are numerous and have resulted in a great lack of precise data and agreement between investigators, the degree increasing as the temperature increases.

The Metallurgy Division of the Chemical Engineering Department at The University of Tennessee initiated an active program in calorimetry in 1950. Since this time, the majority of effort has been in the continuous improvement of the equipment and in the technique of operation. The motivating objective of this program was to measure quantitatively the amount of energy stored in a metallic lattice during deformation, and to relate this to the various deformation variables. Since, in principle, the release of stored energy can be associated with an extraneous heat effect superimposed on the specific heat, it becomes of

vital importance for an adiabatic calorimeter to show a very high degree of reproducibility of specific heat measurements. This dissertation is primarily concerned with this phase of the program: the obtainment of self consistent and reproducible apparent specific heat data, their correction to true specific heat values, and the determination of the stored energy in plastically deformed specimens.

The interest in stored energy measurements on metals has increased considerably with the improvement of the procedures used in its determination. Accurate data pertaining to the release of energy in a cold-worked metal, both during and prior to recrystallization, are necessary to furnish a thorough understanding of annealing and to serve as a basis for theoretical work relating to the behavior of vacancies, interstitials, and dislocations during the process.

The work of Stroh ¹ and Nicholas ², among others, is illustrative of the need for data of this type. Stroh, using the assumption that the bulk of the energy stored in metals during plastic deformation is due to "piled-up groups of dislocations", was able to arrive at a direct relationship between the stored energy and the strain. Since these groups presumably will be annihilated before bulk recrystallization takes place, this mechanism is compatible with the data of Suzuki ³, who found that the bulk of the energy in pure copper was liberated prior to recrystallization. Although the data of Gordon ⁴ and Clarebrough ⁵ show that the largest heat effect is due to recrystallization, their results do show a proportional relationship between the stored energy and the strain.

Nicholas theoretically treated the pre-recrystallization heat effects in deformed nickel using the data of Clarebrough. The deformed nickel was assumed to consist of an assembly of "grains" containing a uniform distribution of point defects. These defects were assumed to move independently by a diffusion controlled process with the "grain boundaries" acting as infinite sinks

for their removal. The heat effect would then be governed by the rate at which these defects reach a boundary. The end result of this treatment predicted, for a given heating rate, the temperature at which this rate would be a maximum, and this agreed well with the first energy release peak obtained by Clarebrough on pure nickel.

The interpretation of the available experimental data has resolved to a general explanation of the two stages of energy release which have been observed. The first stage, recovery, is associated with the annihilation of vacancies and dislocations in the bulk of the structure. The apparent success of Nicholas' treatment, as well as resistivity and density measurements support this mechanism. The effect of impurities upon the first stage heat release has been attributed to a "Cottrell" locking of the defects by foreign atoms. The second stage is attributed to recrystallization. The kinetics of this process have been shown by Gordon to be typical of that illustrated by a nucleation and growth mechanism. There is still disagreement on both the absolute and relative magnitudes of these heat effects.

The success of theoretical treatments will depend greatly upon reliable data. It appears that considerable additional research will be necessary, especially with regard to the pre-recrystallization phenomena, before experimental and theoretical correlation can be fully justified.

A survey of the literature indicated that several methods have been used to determine the heat effects in metals such as specific heats, phase changes, precipitation, or cold-working. These are:

1. The total heat at any stage is measured at a number of temperatures by means of a calorimeter.
2. The rate of cooling of the specimen is measured and the latent heat deduced on the assumption of Newton's law of cooling.

3. The rate of heating is measured when the specimen is placed in a furnace, the temperature of which rises at a uniform rate, Newton's law being used to deduce the increase of thermal energy.

4. The specimen can be heated electrically in such a way that all the energy is used in heating the specimen.

5. Differential methods may be used in which comparative measurements of temperature, heat of solution or power input are referred to a suitable base to obtain the desired heat effect. ^{4 5, 6, 7, 8, 9.}

Methods 1, 4, and 5 usually involve direct measurements which relate to latent energy, whereas 2 and 3 require a more indirect approach. The latter, however, are very sensitive and can be used very well, at least qualitatively, to measure small energies.

Pertinent to this research, Sato ¹⁰, in 1931, devised a differential method for determining the stored energy in cold-worked metals. Two specimens of the same material, one cold-worked, one annealed, were placed in two holes in a block of silver heated at a uniform rate. The difference in temperature between the two specimens during the heating was measured. After the initial run the apparatus was cooled, and the procedure repeated. If ΔT and ΔT_0 are recorded temperature differences for the initial and second runs, respectively, then the latent heat becomes proportional to $\int (\Delta T - \Delta T_0) dt$. To determine the heat effect quantitatively, knowledge of the thermal conductivities between the specimens and the silver block must be known, or gross assumptions must be made regarding the thermal contact behavior of calibrating specimens.

Quinney and Taylor's first calorimeter¹¹ was developed from Sato's experience and necessitated the much more reasonable assumption that the thermal contact resistance of a specimen remains unchanged during two successive heatings. This calorimeter, employing the differential method, was only

a mild improvement, and required very close control of the furnace power and heating rate. It became obvious that for the best results, a system involving the fewest possible assumptions about the nature of the thermal interchanges taking place should be developed.

With this in mind, Quinney and Taylor designed an adiabatic-type calorimeter in which a specimen was heated by an internal heater. Conduction losses were reduced by operating in vacuum, and radiation losses were avoided by maintaining a guard ring furnace around the specimen at the specimen temperature. Stored energy values were determined by calculations based on the temperature-energy input differences observed between the first run on cold-worked and subsequent runs on the annealed specimen. They report stored energies of the order: copper, 0.5 cal/gram; iron, 1.2 cal/gram; nickel, 0.8 cal/gram; and brass, 0.5 cal/gram. Specific heat data were also reported in this paper. The self consistency of the specific heat values was only mediocre at best, and poses some question as to the accuracy of their stored energy measurements. Quinney and Taylor's data for the specific heat of copper are given in Figure 1.

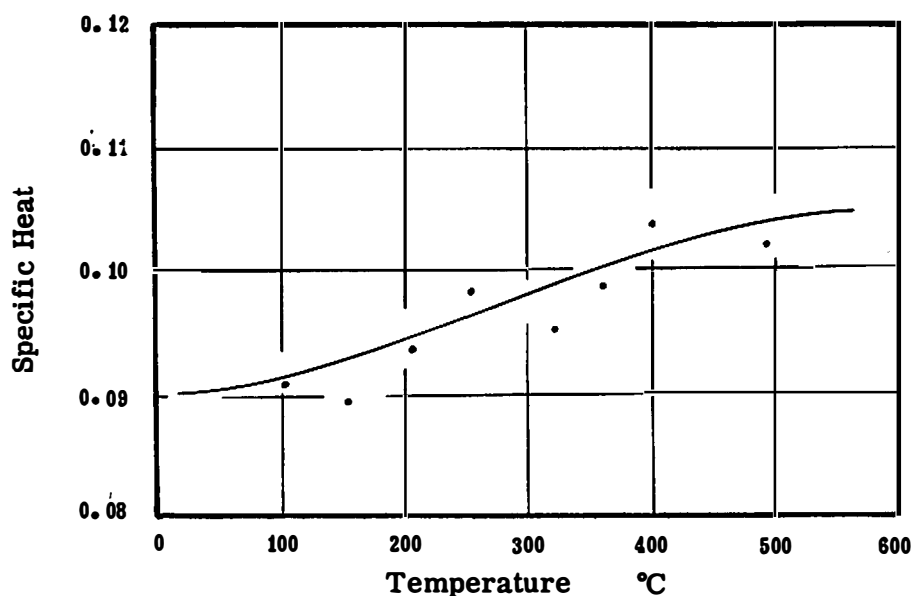


Figure 1. Specific heat of copper ¹¹.

Sykes and Jones ¹² used an adiabatic calorimeter of similar style, employing a specimen with a self-contained heater enclosed in a cylindrical copper block. Ceramic pegs insulated the specimen from the block, and the block from the main furnace assembly. The calorimeter was designed so that the copper cylinder could be heated at a uniform rate, and the specimen made to cycle about the rising cylinder temperature by careful regulation of the power input to the internal heater. Care was taken to insure a minimum of heat loss by using highly polished specimens, and radiation shields and tags on the power input wires. Specific heat data could be acquired by two methods: continuously, during the heating period at points where the specimen and block temperatures coincide, (at this point there are no heat losses, and the specific heat may be calculated if the power input and heating rate are accurately known), and at "constant temperature", where after steady state has been attained, the rate of increase in temperature is measured for a given power input.

Sykes and Jones investigated the specific heat of copper and the order-disorder transformation in copper-gold alloys by this method. The latter heat effects were measured by their effect on the specific heat curve. The specific heat of copper was reported reproducible to about ± 0.75 per cent, and the accuracy was estimated at ± 1.0 per cent. The method proved satisfactory for the measurements of order-disorder effects; however, these heat effects are quite large, at least an order of magnitude larger than stored energy values.

Awberry and Snow ¹³ realized the importance of quick control response of the shield in adiabatic calorimetry and designed their calorimeter with this in mind. Their specimen was a cylindrical slug with an internal heater held in place by an asbestos plug. Surrounding the specimen was a thin steel radiation shield enclosed in a box type furnace wound with wide resistance tape. The shield was thus subjected to radiation on all sides, and the low heat capacity of the components

made the temperature response to energy supplied very fast. Heat losses were reduced by outer radiation shields between the windings and the main body of the calorimeter; a vacuum of about 0.2 mmHg. was maintained. The specimen heater was supplied with alternating current and the dissipated energy measured with a wattmeter. In operation, the specimen was heated at a given rate, and the furnace power adjusted to keep the temperature difference between the specimen and the radiation shield at a minimum.

Moser ¹⁴ designed an adiabatic calorimeter from which very reproducible specific heat data were obtained. The specimen was encased in a tight fitting silver sleeve which contained a platinum resistance heater wound in an annular space surrounding the specimen. The specific heat was determined by power-time-temperature measurements which were corrected for the heat capacity of the specimen container, heat losses, and temperature differences. An interesting innovation of Moser was the placing of a copper winding outside of the specimen (and heater) container, having the same number of turns as the platinum and carrying the same current in the opposite direction. In this way, eddy current effects on the differential thermocouples were minimized. Moser's data for nickel will be reviewed in a later chapter.

Armstrong ^{15, 16} designed a high temperature adiabatic calorimeter for work on the transition metals. Solid or powdered materials could be used as specimen material, the specimen container and internal heater requiring calibration in order to obtain true specific heat values. The specimen container was supported in a heated guard furnace, in turn surrounded by the main shield windings. The calorimeter was either evacuated or filled with inert gas during a run. Temperature measurements were made with platinum-platinum 10 per cent rhodium thermocouples, and differential couples connected directly to galvanometers indicated important temperatures differences in the calorimeter.

Armstrong corrected for stray thermal emf's by introducing a compensating emf in the measuring circuit. All the power to the various heaters was controlled manually by a series of rheostats, necessitating at least two persons for operation. Specific heat measurements were made by two methods, continuously or intermittently applying power, and noting the associated temperature changes.

Using data obtained in this manner, Armstrong reported specific heat data for chromium, manganese, and cobalt to 800°C with an estimated accuracy of less than ± 1.0 per cent from the smoothed curve.

Other types of calorimeters used to obtain thermal data on the metallic state include the drop and solution calorimeters such as recently employed by Oriani ¹⁷ and Bever ⁷, among others. The principle of the Bunsen drop calorimeter is simple. A specimen at a known temperature is dropped into a water-ice mixture at 0°C, and the enthalpy change related to the amount of ice which is melted as a result. The method has serious limitations when non-equilibrium states result on rapid cooling, or when a non-equilibrium state is destroyed. Ticknor and Bever ⁷ have applied a solution calorimeter using liquid metal solvents to determine stored energy in plastically deformed metals. ^{8, 9} The method consists primarily of comparing the heats of solution of a cold-worked and an annealed metal. A rather unique feature permitting realization of the required precision consisted of using a system in which the overall heat effect, (i.e., specific heat plus heat of solution), was very small. In this way, the difference of the heat effects was of the same order of magnitude as the largest noticed, eliminating the necessity of determining stored energy as the difference of comparatively large numbers.

It appears from these investigations, then, that the experimental methods for determining high temperature thermal data may be grouped into three classes: (1) the method of mixtures, (2) methods depending upon heating or cooling rates,

and (3) methods of direct measurement. The trend in modern research has been significantly to the direct methods of measurement, although heating and cooling rate methods have been quite widely used. These later methods usually involve comparison with the rate of cooling or heating of a substance with the corresponding rate of a standard material, under conditions presumed to be the same. Differences in thermal conductivities and poor reproducibility of experimental conditions, especially at the higher temperatures, have precluded precise results. Direct measurements of specific heats at elevated temperatures have met with limited success only recently, the deterrent in this field being the difficulties inherent with precise high temperature operation. In 1930, White ¹⁸, summed up an account of furnace calorimetry by stating:

...our investigation shows many points which could be made clearer by further experiment. The very number of these is reason for not proceeding further. For even after a good deal more had been done still more would seem desirable. One reason for the present work was to test the probable value of the furnace calorimeter for certain very delicate determinations of specific heat. The conclusion reached was that the dropping method is more promising.

These words, perhaps discouraging, have nevertheless served as a challenge to the many who have entered this field since. Kubaschewski ¹⁹ claims that adiabatic methods are more reliable at elevated temperatures. Ideally, an adiabatic type of calorimeter offers the means for obtaining precise specific heat data. It also is applicable to measurements of heat of transformation and solution directly and non-equilibrium heat effects may be determined indirectly, usually by anomalies in specific heat data. However, the experimental realization of completely adiabatic conditions is essentially impossible, especially at elevated temperatures in apparatus where large temperature gradients exist. Small temperature differences, which can arise from innumerable causes, can create radiation losses (or gains) of considerable magnitude

and can ruin the reproducibility and accuracy of experimental data. This is true because of the extreme temperature dependence for losses of this type. This is perhaps the most important source of divergence of data of investigators in high temperature calorimetry.

This dissertation describes the design, development and operation of a high temperature adiabatic calorimeter, the majority of the experimental effort being directed toward the obtainment of highly reproducible true specific heat values. The requirement of reproducibility of data necessitated reproducibility of operating procedure and control; the obtainment of true specific heat data necessitated knowledge of the characteristics of the calorimeter operation, plus appropriate correction factors. The details of this calorimeter will be considered in another chapter. Copper and nickel were chosen as the materials of investigation because they exhibit no specific heat anomalies, with the exception of the Curie region in nickel. However, there is a divergence in the specific heat data for copper and nickel, especially at the higher temperatures, and a contribution could be made by supplying data for this important thermodynamic property for these two materials. In addition, the alloys of copper and nickel, being single phase, offer the opportunity for simple specific heat studies. Finally, another important reason for this choice was to attempt to rationalize the great range of reported data for the stored energy of cold-worked copper. The calorimeter offered opportunity to reproduce the experimental conditions of several previous investigators in this respect.

The specific heat of copper has been given by Kelly ²⁰, to be a linear function of the temperature, $C_p = 0.0917 + 2.36 \times 10^{-5} T$ cal/gram °C, to ± 1 per cent. The data of Sykes and Jones ¹² to 400 °C yield $C_p = 0.0923 + 2.2 \times 10^{-5} T$ cal/gram °C. These are perhaps the best available data for copper. The data of Quinney and Taylor ¹¹ among others, show a poor degree of self

consistency. Picklesimer's data ²¹ depend largely upon the accuracy of a heater correction of large proportion and admittedly appear doubtful. This lack of precise data on pure copper in the literature is surprising, considering the fact that it is often used as the "standard" specimen in differential measurements.²² Copper has also been used more than any other metal in investigations of stored energy.

A more fruitful although perhaps no more accurate literature exists for specific heat values of nickel. The interest here lies mainly with the Curie point behavior and the theoretical aspects of the various contributions to the specific heat as the temperature increases. Lapp ²³ used a non-adiabatic method employing a wire specimen to measure the specific heat of nickel. The nickel wire was placed in a furnace at a uniform temperature, a measured amount of energy momentarily passed through the wire, and the rise and fall of the temperature noted. The specific heat was computed from these measurements to an estimated accuracy of ± 2 per cent. Lapp's data showed a very sharp discontinuity at the Curie point, recorded at 353°C . This sharp drop (See Table I) has not been recorded in other investigations.

The data of Moser ¹⁴, whose method has been discussed, appear to be very self consistent. The specific heat rises to its maximum at the Curie point, about 353°C , then drops over a fifty degree interval to a gently increasing function of temperature. The values obtained by Moser differ from Lapp's data in two important respects: (1) The abrupt decrease in specific heat above the Curie point was not observed, and (2) the specific heat above the Curie point was much lower.

Sykes and Wilkinson ²⁴ carried out specific heat determinations on pure nickel in the manner of Sykes and Jones. The accuracy, except in the Curie point region was estimated not to exceed ± 1 per cent. The reported Curie point was a

little high, perhaps due to traces of cobalt present. These authors present a comparison of some of the better specific heat data on nickel. These data are compiled in Table I. The data were obtained from quite an array of experimental apparatus. Lapp, Grew and Ahrens used wire specimens which were heated by the passage of electric current. Klinkhardt ²⁵ heated a large specimen by means of electron bombardment. In both of these methods, the temperature of the enclosure surrounding the specimen was held constant, requiring a radiation correction to obtain true specific heats. Moser and Sykes reduced the radiation correction considerably by employing strictly adiabatic conditions.

The data of the several investigations in Table I agree reasonably well up to the Curie region. Above the Curie point, however, considerable spread exists. Apart from the sharp drop in specific heat described by Lapp, all the curves tail to a minimum and then increase. The manner in which they do this varies greatly, as seen in the plotted data of Figure 2.

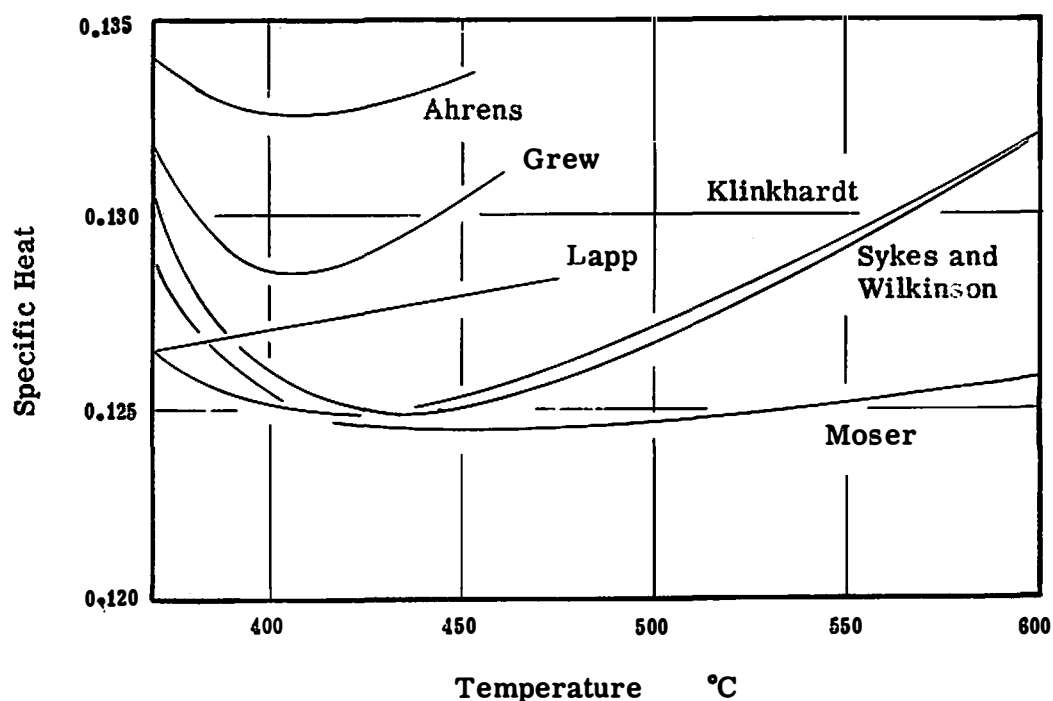


Figure 2. Specific heat of nickel ²⁴.

TABLE I

ATOMIC HEAT OF NICKEL (cal/gram-atom °C)

Temp. °K	Lapp	Grew	Ahrens	Moser	Klinkhardt	Sykes and Wilkinson	Sykes and Wilkinson "adj."	Most Probable Values
350	6.51	6.60	6.52	6.46	-	-	-	6.51
400	6.75	6.86	6.84	6.69	-	6.78	-	6.76
450	7.05	7.14	7.14	7.04	-	7.07	-	7.07
500	7.42	7.49	7.52	7.48	-	7.48	-	7.47
550	7.88	7.90	8.01	7.78	-	7.82	-	7.83
600	8.45	8.55	8.72	8.28	-	8.34	8.36	8.37
610	8.67	8.79	8.95	8.43	-	8.49	8.55	8.49
620	8.95	9.05	9.18	8.62	-	8.69	8.78	8.69
622	9.04	9.12	9.22	8.66	-	8.74	8.89	8.74
624	9.13	9.18	9.28	8.80	-	8.80	9.02	8.80
626	9.23	9.25	9.36	8.87	-	8.89	9.28	8.89
628	-	-	-	-	-	-	-	9.02 int.
630	7.80	8.70	8.25	8.22	-	9.28	8.12	9.28
635	7.42	8.25	8.18	7.93	-	8.04	7.87	8.04
640	7.43	7.98	8.06	7.72	-	7.87	7.74	7.87
650	7.44	7.70	8.00	7.48	7.31	7.62	-	7.50
700	7.51	-	-	7.32	7.35	7.37	-	7.35
750	-	-	-	7.31	7.42	7.37	-	7.37
800	-	-	-	7.33	7.51	7.48	-	7.44
850	-	-	-	7.36	7.68	7.66	-	7.50
Estimated Error, per cent	2	2	2	0.5	3	1 to 2		

The difference in the specific heats in this temperature region varies appreciably more than would be expected for the undoubtedly small composition differences which existed. The data of Ahrens, Grew, and Lapp, who used wire specimens, seem to be above that of the investigators using massive specimens. It is possible that this is a result of the greater losses associated with the wire method. Considering only the data by Klinkhardt, Sykes and Wilkinson, and Moser, the question still remains as to which is the more correct; in other words, what is the true specific heat of nickel above the Curie range? Sykes and Wilkinson determined the "best values" based upon a weighted average of the data, but this is a poor method when the differences are so great.

Grew²⁸ studied the specific heat behavior of a series of copper-nickel alloys in a manner similar to that of Lapp. His data on the nickel rich alloys show the trends of the Curie region as the alloy content increases. Thus he was able to obtain the effect of copper upon the Curie temperature and the heat effect. These data are summarized graphically in Figure 3.

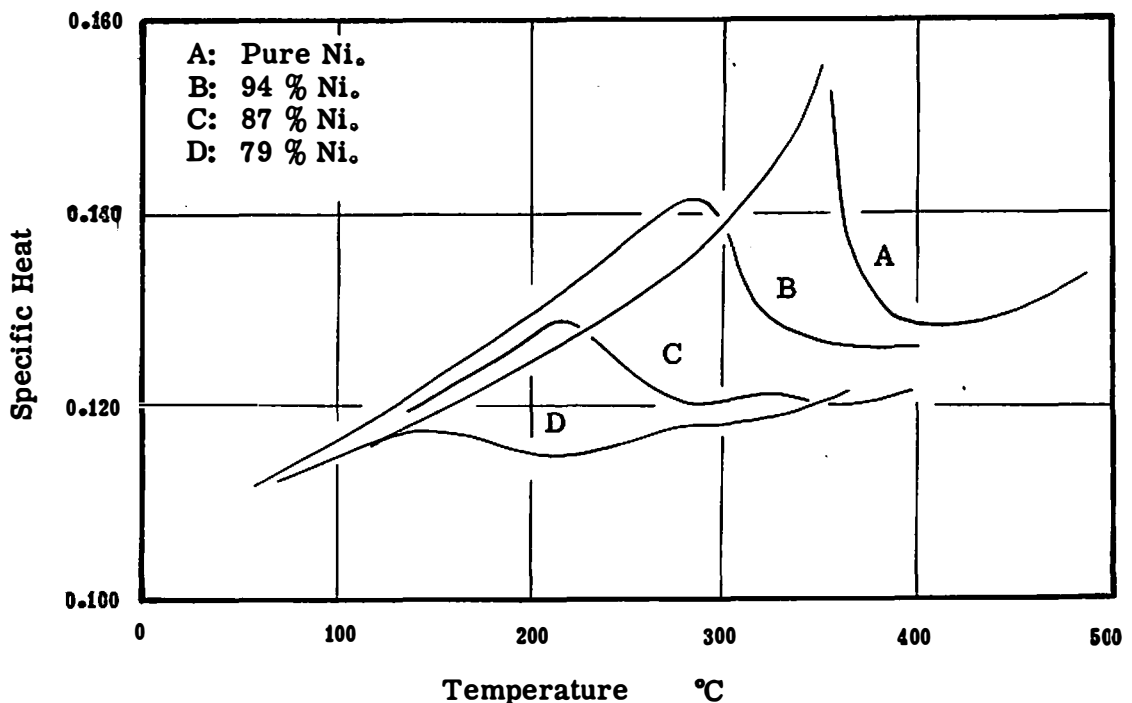


Figure 3. Specific heat of copper-nickel alloys²⁸.

The data on the alloys were not taken at high enough temperature to evaluate the applicability of Kopp-Neumann rule ¹⁹ which estimates the specific heat of alloys by proportionate additivity of the specific heats of the pure components. No comments on reproducibility other than an estimated ± 2 per cent accuracy were made.

There has been a great deal of work done in the determination of the energy stored in copper during plastic deformation. The comparatively low recrystallization temperature of copper permits more accurate calorimetric measurements, and is undoubtedly the reason for its popularity. Several of the earlier calorimetric efforts to determine this quantity have been reviewed. A discussion of some of the later explorations in this field is in order.

A controversial investigation of stored energy was made by Suzuki ³, who used an adiabatic method similar to that of Sykes and Jones. The method consisted of obtaining the specific heat curve for a cold-worked specimen, and obtaining the heat effect of recrystallization by integration between curves of the cold-worked and annealed specimens. The specific heat of the cold-worked specimens, determined at a heating rate of $2^{\circ}\text{C}/\text{min.}$, clearly showed two minima which were attributed to the recovery and recrystallization heats respectively. Suzuki's specific heat data for a series of strains are given in Figure 4.

Three controversial points have arisen pertaining to this investigation as a result of subsequent work by other investigators: (1) The magnitude of the total stored energy, in the range of 0.8 cal/gram for the higher deformations was high compared to those obtained by other authors. (2) The relative magnitudes of the recovery and recrystallization heat effects differed considerably from others who found a much smaller recovery effect. (3) Perhaps the most important point for disagreement was the fact that Suzuki claimed most of the

energy was released prior to actual recrystallization. The set of data obtained by Suzuki was published with very little of the experimental details. The curves, per se, appear to be self consistent, but it is difficult to comment effectively without further knowledge of experimental conditions. Since the energy released during the annealing is so very small, reproducibility becomes of prime importance to quantitative data.

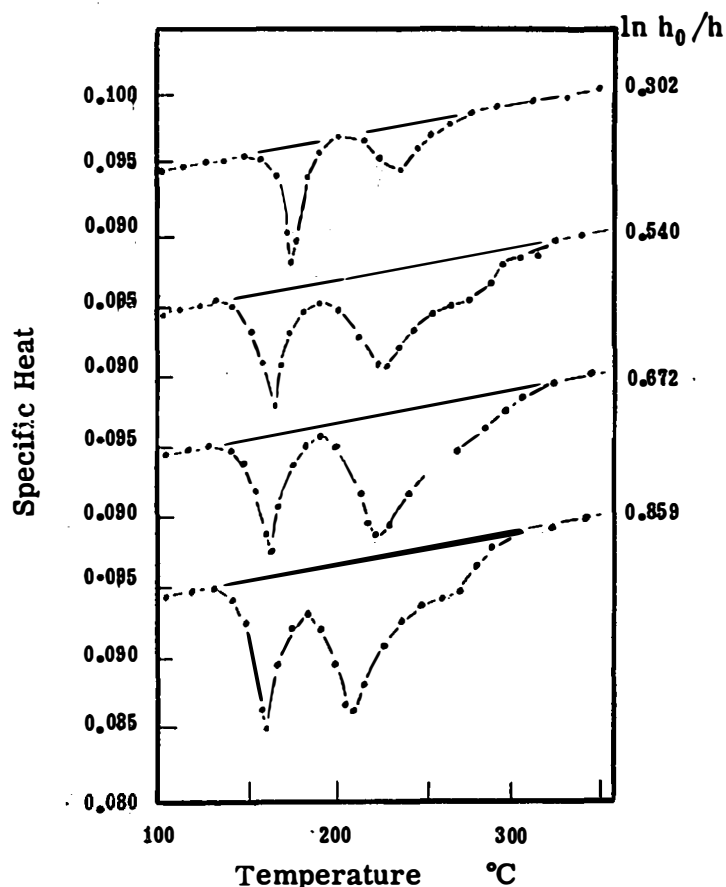


Figure 4. Specific heat of cold-worked copper ³.

Gordon ⁴ has effectively applied a very sensitive isothermal calorimeter to the determination of stored energy. Briefly, the cold-worked specimen was placed in an isothermal environment of infinite heat capacity accomplished by a vapor thermostat. A differential thermopile measured the temperature differences between the specimen and its surroundings. The procedure was as

follows: the specimen was brought to temperature in the calorimeter as quickly as possible, and the temperature difference between the specimen and its surroundings followed as a function of time. A calibration permitted conversion of the temperature difference-time curves to energy emitted by the specimen.

The data for pure copper indicate that the stored energy was released in two stages. The first, associated with recovery, accounted for only a small portion of the total energy release, in contrast to Suzuki. The second stage, associated with recrystallization, accounted for the major portion of the heat effect, and showed a rate of release typical of nucleation and growth processes. Again in contrast to Suzuki, Gordon showed that the second stage heat effect was synonymous with recrystallization. The total stored energy for copper was determined to vary from 0.04 to 0.10 cal/gram as the deformation varied from 10 to 40 per cent elongation. The reproducibility varied slightly with the total measured heat, averaging about ± 5 per cent. A tendency for stored energy "saturation" as a function of the degree of elongation was also noticed in these studies. No such tendency is apparent from Suzuki's results, even at higher deformation values. This investigation represents a real contribution to the field of research, especially in the manner of its presentation.

A method of determining stored energies using dual specimens has been used by Clarebrough, et. al.^{5,6}. The method involved the heating, in vacuum, of an annealed and a deformed specimen of equal weight, by small heating elements inside each specimen. The specimens were maintained at the same temperature by adjusting the power input to the two specimen heaters, and adiabatic conditions were provided by controlling the temperature of a strip wound box furnace and radiation shields surrounding the specimen. The stored energy was computed from measurements of the power difference necessary to maintain the specimens at equal temperature, a specially constructed differential wattmeter being used for this purpose.

Stored energy measurements were made on copper deformed in torsion, tension, and compression. Typical curves of the power difference are illustrated in Figure 5 for pure copper in compression.

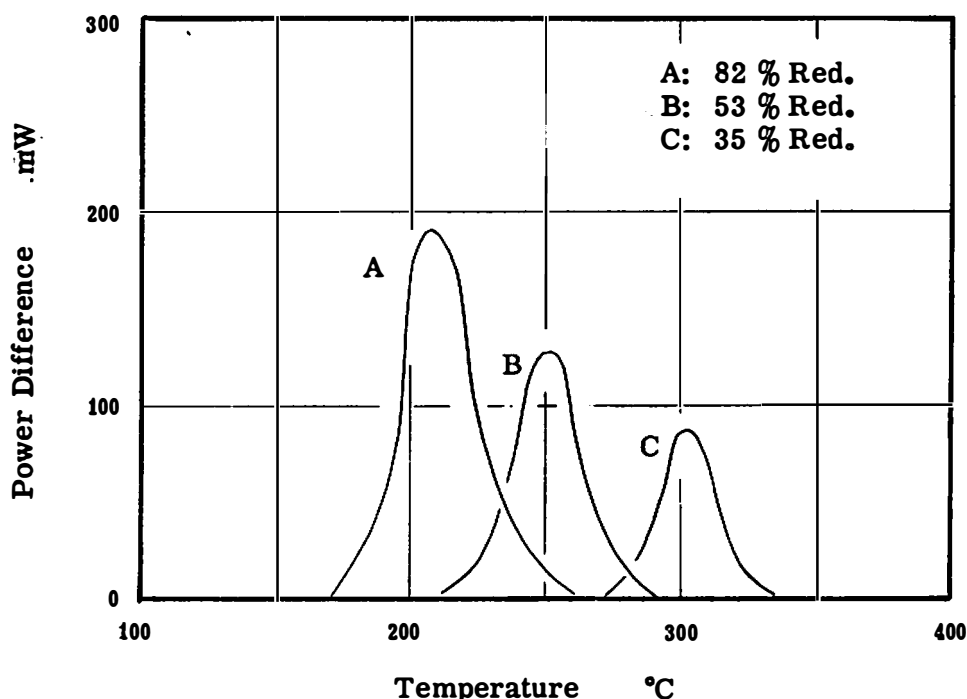


Figure 5. Heat evolution in compressed copper ⁶.

Apparently the reproducibility of the power difference curves was good for specimens taken from the same ingot. However, two batches of copper, 99.98 and 99.96 per cent by analysis, showed greatly different characteristics in both the shape of the power difference curves, and the recrystallization temperature. This emphasized the importance of purity in the analysis of such data, a fact also pointed out by Gordon. Accordingly, Clarebrough studied the stored energy characteristics of two batches of copper, one containing less than 0.02 per cent impurity, the other containing 0.35 per cent arsenic. A comparison of the behaviors is interesting. The power difference curves for the high purity copper showed only one distinct peak, indicating the release of energy in a single stage, without a heat effect associated with recovery. In the case

of the arsenical copper, a constant power difference occurred over quite a large temperature range prior to the large peak associated with recrystallization. This first stage was associated with the recovery effect. The stored energy is also noticeably increased by the presence of impurities.

The effect of type of deformation on the power difference curves was not as great as that of composition. Tensile and compressive deformation showed relatively sharp, single stage releases of energy. Those deformed in torsion tended to show a tailing effect, probably due to the deformation spectrum inherent with this type of deformation. A series of these curves are reproduced in Figure 6.

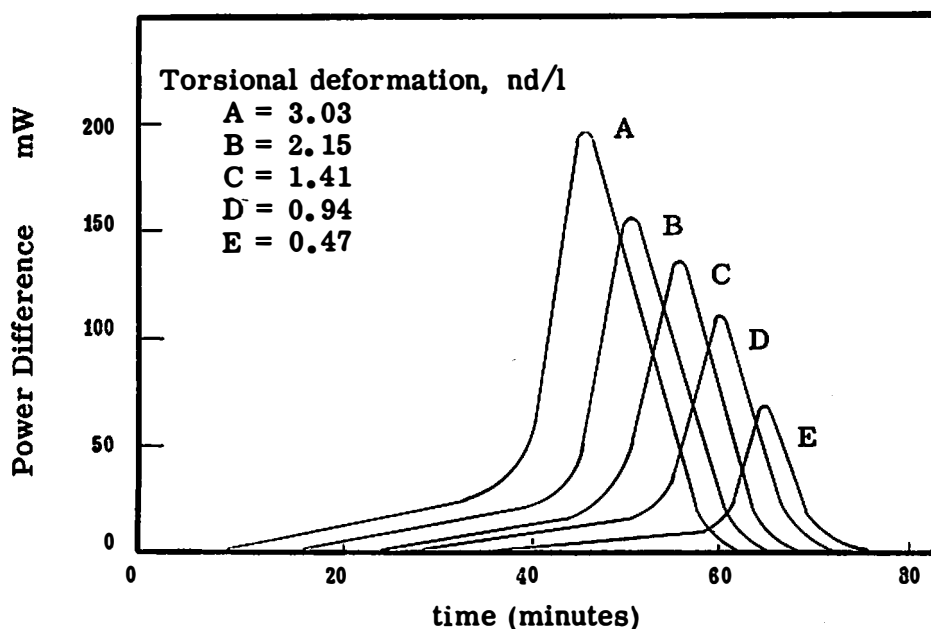


Figure 6. Heat effect of copper deformed in torsion ⁶.

In order to correlate macroscopic recrystallization with the measured heat effect, Clarebrough used hardness measurements and back reflection X-ray patterns taken on specimens quenched from a series of temperatures during a mock run. In contrast to Suzuki, the decrease in hardness associated with recrystallization corresponded to the large stored energy peak in all of the runs.

The results of Clarebrough on copper show that a linear relationship existed between the energy of recrystallization and the degree of deformation for specimens deformed in both torsion and compression. No tendency for saturation was noticed. The nature of the energy release corresponding to recovery differed from that observed by both Suzuki and Gordon in that an almost constant heat evolution was observed throughout this range. The comparative values of the recovery and recrystallization heats for Clarebrough's arsenical copper compare favorably with Suzuki's, but the recovery effect is considerably higher than that observed by Gordon. In light of the differences in the stored energy behavior reported by these investigators, there still appears to be considerable work to be done.

Clarebrough also studied the recrystallization of nickel by this method. Nickel specimens deformed in torsion showed three stages of energy release, the last and largest corresponding to bulk recrystallization. The energy associated with the second and third stages was a linear function of the strain and that associated with the first stage seemed independent of the strain.

It is difficult to comment upon the consistency of Clarebrough's results. The experimental apparatus was claimed "capable of measuring, with an accuracy of ± 5 per cent, a difference of 0.1 cal/gram in the energy supplied to the specimens in heating them through a temperature range of 240°C in a period of forty minutes". No indication is made as to whether the nearly ideal power difference curves which they report have been smoothed, corrected, or if they actually represent the data as such.

It is unfortunate that so few investigators describe the experimental details, reproducibility, and accuracy of their methods. This information is extremely useful to those following in similar research, and in evaluation of experimental data.

Modern instrumentation techniques have enhanced the trend toward adiabatic calorimetry not only for work in the microcalorimetry region, but for precision specific heats and related thermodynamic data. Proper use of these modern control components can appreciably reduce the human error in calorimetric measurements; however, the investigator must still interpret the results with a knowledge of the limitations of his instruments. It was realized in the early stages of this project that in order to achieve accurate thermal data many problems associated with operation at high temperatures would have to be repressed. Means for improvement of high-temperature control, temperature measurement, and heat interchange were studied in the first models of the calorimeter. Several troublesome phenomena directed considerable effort towards their study and possible solution.

The result of several years of experimental study at The University of Tennessee has been the construction and operation of two dynamic adiabatic type calorimeters capable of operation at high temperatures. The use of either of these calorimeters permits determination of metallic specific heats, heats of transformation, and other measurable heat effects, such as the heat associated with the recrystallization of a plastically deformed material. The only significant difference in the two calorimeters is the use of a lead gasket in the upper joints of the calorimeter described in this dissertation, resulting in a limitation of the safe operating temperatures to somewhat less than 700°C. The temperature control, specimen mounting, and power systems are equivalent; thus, general statements made in this report concern both calorimeters.

CHAPTER III

THE DEVELOPMENT OF THE CALORIMETER

Previous Work

The calorimeter used in this investigation was designed similar to one developed by McElroy ²⁷ and was first placed in operation by Elder ^{28, 29}.

The design attempts to meet the following requirements:

1. To be continuously operating from room temperature.
2. To provide as nearly adiabatic conditions as possible, so that corrections would be a minimum.
3. To permit high accuracy and reproducibility of specific heat data.
4. To permit sensitivity sufficient for stored energy measurements.
5. To permit ease of assembly, with a maximum degree of reproducibility of the experimental conditions.

Progress in calorimetry at The University of Tennessee has been reported in a series of reports by Stansbury ^{28, 30, 31, 32}, Picklesimer ²¹, and Elder ³³. The first calorimeter consisted of a specimen mounted in an upright position inside a polished heated spherical shield. The calorimeter was located in an evacuated chamber, surrounded by polished radiation shields. An internal heater supplied energy to the specimen. Temperature measurements were made with thermocouples, and the shield-specimen temperature difference controlled by using the output of a differential couple with a pulse-duration type controller. This design proved cumbersome, mainly with regards to ease of assembly. A cylindrical shield seemed more adaptable to ease of specimen interchange, and a new type shield and mount were made. This calorimeter is shown in Figure 7, the inset showing the spherical furnace. The calorimeter

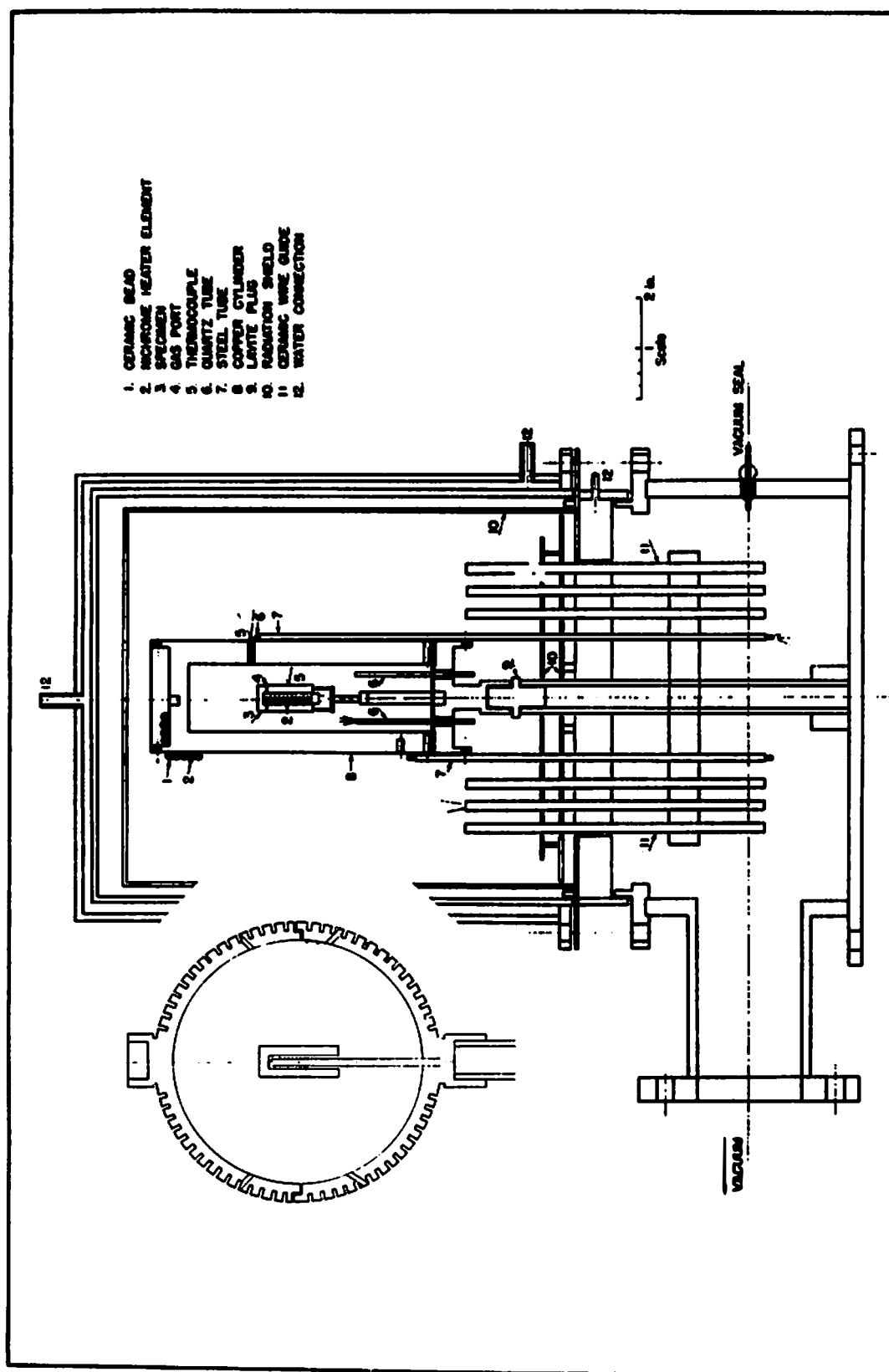


Figure 7. Early model of adiabatic calorimeter

was redesigned so that all thermocouple and power connections could be made and inspected quickly and easily. The cylinder length was increased to about 9 inches to decrease the amount of base "seen" by the specimen. The specimen, and specimen heater designs were changed to decrease losses from the heater and leads by entirely enclosing the heater in the specimen. The cylinder control system consisted of a D. C. amplifier feeding a zero-center Speedomax recorder and proportioning controller. The amplifier was activated by the output of the specimen-cylinder differential thermocouple. The base temperature was controlled similarly. The temperatures, heater currents and voltages were read with a potentiometer.

This calorimeter was essentially that used by Picklesimer ¹⁷ in investigating the specific heats and heats of transformation of high purity irons and steels. When compared to some of the older calorimeter designs, this calorimeter had the following advantages:

1. Only one operator was required.
2. Heating rates from 0 to 5°C per minute could be set by adjustment of variable resistances in the specimen heater circuit.
3. Specific rates of heating and cooling by radiation between the specimen and shield could be established by offsetting the control to the desired temperature difference. Corrections for heat losses could be made in this manner during the run. The offset required could be determined by opening the specimen heater circuit and allowing the control system to stabilize, the required offset being that necessary to prevent drift in the specimen temperature.
4. Specimen machining and installation were simple.
5. Mean specific heats, computed over temperature intervals of five degrees or more, could be measured from about 60°C to 950°C.

6. Specimen sizes could be varied from 7/16 inches in diameter and 1 inch long to 3/4 inches in diameter and 3 inches long with no change in the calorimeter with the exception of the specimen heater.

Full particulars are available in the original report ²¹. The majority of the presented results was given in the form of apparent specific heats. The correction to true specific heat, probably several per cent, was not reported in detail. The reproducibility of the apparent specific data was around ± 0.5 per cent, but the accuracy of the conversion to true values was complicated by the accuracy of the calibration of the specimen heater and of the calorimeter for specimen heat losses. The problem of calibration was a difficult one. No metallic specific heats have been determined with sufficient accuracy to use as a standard for calibration; non-metallics may not be used since the operating conditions would be different. If specimens of different weights are used to calibrate by the method of differences, the effect of different heating rates for the same power level, or vice-versa, must be taken into consideration. A more reliable method would be to essentially eliminate the heater correction by using massive specimens.

The Thermocouple Problem in High Temperature Calorimetry

Research up to this point has indicated that the accuracy of calorimetric measurements is greatly dependent upon the accuracy of the thermocouples used for temperature measurements. This is especially true at higher temperatures. Erroneous emf readings result from instability, and parasitic voltages arise from a number of sources. A great deal of time has been spent on this problem, the end result being the choice of a platinum-platinum 13 per cent rhodium thermocouple system.

A prime requisite of a good thermocouple is stability. Previous investigators on this program studied several possible combinations of

materials as thermocouples with special emphasis on stability and susceptibility to spurious thermal emf's. All of the base metal combinations investigated proved to be too inhomogeneous, to change composition by preferential vaporization of alloy components when operated in vacuum, or to be over-sensitive to temperature gradients. Pure metal combinations were tried in order to circumvent these difficulties, but in most cases these couples were too sensitive to contamination, and the stability was poor.

The problem of spurious thermal emf's arises from the necessity of having thermocouple wires pass through sharp temperature gradients as they lead out of the calorimeter. Theoretically and experimentally, a homogeneous material will not develop a thermal emf due to this gradient. On the other hand, any physical or chemical inhomogeneity lying in the gradient will result in a spurious thermal emf. To study the magnitude of such thermal emf's, and to check thermocouple materials for the calorimeter, a temperature gradient was passed along the wires and the resulting effects observed on a sensitive recorder.

A possible pure metal combination which showed promise was the palladium-molybdenum thermocouple. The choice of these materials was based upon the high thermal potential which they generate, and the stability at high temperatures in vacuum. These wires, as were specimens of all thermocouple materials used in this project, were passed through a small furnace or severe temperature gradient, and the parasitic thermals were measured. Spurious emf's of the order of six to ten microvolts were common for these materials, even in the pre-annealed condition. These thermals, roughly the same as those noticed for platinum-platinum 13 per cent rhodium temperature-wise, plus the difficulty encountered with the annealing and handling of molybdenum, led to the adoption of the platinum-platinum 13 per cent rhodium thermocouple.

The Pt-Pt 13 % Rh thermocouple showed very little effect to small amounts of cold-work when placed in the thermal gradient, and no apparent composition change due to preferential vaporization at operating temperatures. Although the thermal emf generated is undesirably low, being only about ten microvolts per degree, the reliability is sufficiently great to overcome this limitation.

The thermocouple table for Pt-Pt 13 % Rh used in this investigation was derived by Picklesimer ²¹. From his specific heat measurements on pure copper using this thermocouple system, systematic irregularities in the data of the order of 1 to 2 per cent were observed. These irregularities were reproducible although no cause due to calorimeter operation was evident. A further analysis of the errors involved in the calculation of specific heat pointed to the possibility of irregularities in the published thermocouple tables (NBS Bulletin No. 508) for Pt-Pt 13 % Rh. The error develops as a consequence of irregularities in the slope of the published temperature-emf curve beyond that accumulated by rounding the emf values to the nearest microvolt. Therefore, these tables were analyzed in terms of the slope as a function of the temperature, and an attempt made to "smooth" the experimental curve by fitting the values to a polynomial. However, no second, third or even fourth degree polynomial was satisfactory for more than a 50 degree interval above 300°C. Therefore, the values were "smoothed" by a method of successive differences, yielding a smooth emf-temperature plot which did not vary by more than two microvolts at the melting points of reference standards in the range to 1000°C. The details of this method and the emf-temperature results are given by Picklesimer ²¹. The specific heat values obtained using this new table yielded more acceptable data in that the irregularities were essentially eliminated.

The Pt-Pt 13 % Rh thermocouple has proved satisfactory in the present investigation with one exception--the relatively small thermal emf necessitates high sensitivity, expensive measuring instruments. For example, temperatures and temperature differences may be set on a Rubicon Thermofree Potentiometer to about ± 0.1 microvolt; this results in an error in the mean specific heat calculated over a 20° interval of 0.1 per cent, depending upon the calibration of the instrument. It would be desirable to reduce this error by one order of magnitude. A six-dial potentiometer would be helpful, but a different thermocouple system of high stability and sensitivity would be a real advance.

The Ceramic Problem

Another problem closely associated with the accuracy and reproducibility of calorimetric data at high temperatures are the characteristics of the ceramic parts of the assembly. Metal specimens with completely internal heating elements must be in intimate contact with the refractory components which electrically insulate them from the heater circuit. Also, other parts of the calorimeter must depend on a variety of refractory tubes and beads for insulation. A problem arises from the fact that at intermediate temperatures, around 500°C , the ceramics are observed to become slightly conductive. Two phenomena are perhaps operative here: the characteristic decrease of the resistance of the ceramic with increasing temperature, and the condensation of metal atoms on the ceramic to form a conducting film. In any case, a finite resistance could be measured between the specimen heater circuit and ground (specimen) both during and after operation at high temperatures. For example, a new specimen and heater when first installed may show a resistance of about 50 million ohms or more between the heater circuit and ground; as the temperature rises, the resistance decreases more or less uniformly and resistances as low as 100,000 ohms have been measured at 600°C . Upon cooling, the resistance usually does

not return completely to its initial high value; ten million ohms has been common "background" value for specimens having been run a number of times. High purity alundum refractories were found to be superior to magnesia in this respect, and were used almost exclusively.

This relatively low resistance of the ceramics at high temperatures may be very detrimental to precise measurements and control. As illustrated in the following section, the thermocouples were attached to the various components either directly, or by means of ceramic electrical insulating tabs designed to give good thermal but poor electrical contact. Any electrical conductivity of the refractory joins the specimen power and thermocouple measuring circuits if the power circuit is grounded. This coupling can give rise to large spurious IR potentials in the differential control thermocouple circuit unless care is taken. A simplified sketch illustrating this effect is given in Figure 8.

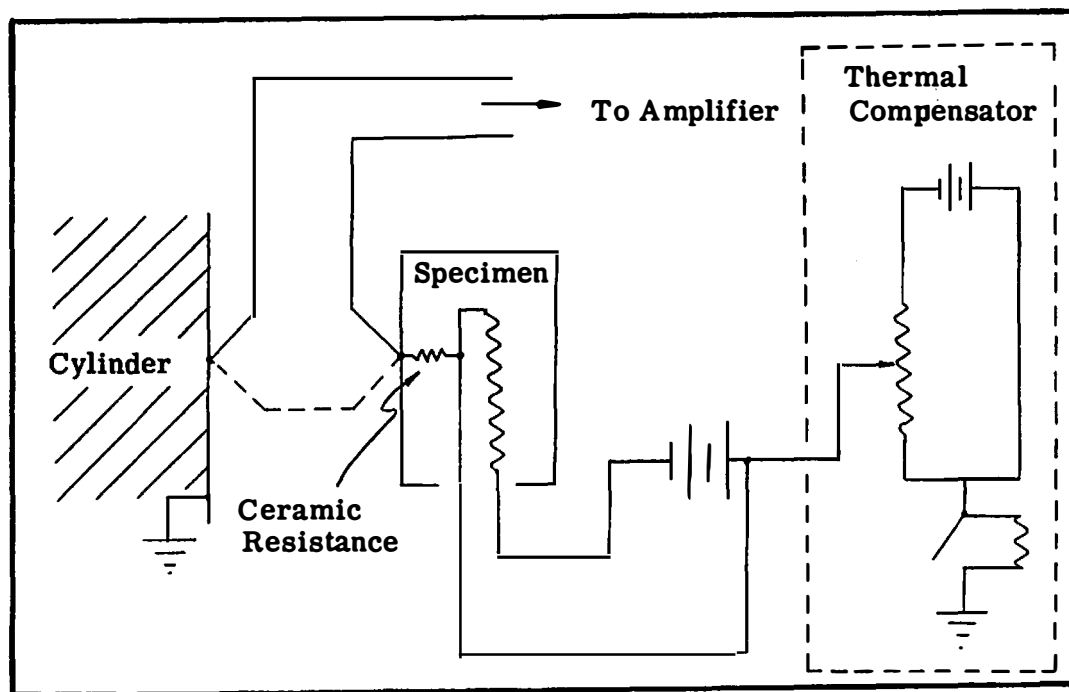


Figure 8. Thermal compensator circuit.

It is readily seen that any conduction due to faulty ceramic in the specimen may cause a current in the jumper of the differential thermocouple. This current produces a voltage drop, IR , which is added to the thermal emf.

The reason for grounding the specimen power circuit through the thermal compensator section is not immediately obvious. However, it was not until the latter was added that the experimental specific heat curves ceased to show high temperature anomalies. Without the thermal compensator, the system developed increasing error signals due to a combination of the increasing temperature gradients and electrons emitted from the heater. Ceramic conduction between the specimen heater and the control circuit also affected the behavior of the error in an unpredictable and hap-hazard manner, being especially sensitive to slight vibration of the calorimeter. These increasing apparent thermals as the temperature increased caused irregularities in the specific heat, and a pronounced increase in the specific heat values obtained.

The thermal compensator was able to counteract these error voltages by imposing a similar voltage drop of opposite sign into the circuit. This was accomplished by placing a variable D. C. bias between the specimen heater battery and ground. In effect, this regulated the potential with respect to ground, of the components of the specimen heater and leads, controlling the amount of current flowing in the jumper branch of the differential thermocouple. This depended upon the presence of a finite resistance between the specimen and heater circuits. When the observed error voltages became great enough to warrant correction, about 0.3 to 0.5 microvolts, the amount of conduction was almost always sufficient to permit operation of the thermal compensator. The bias was applied manually through a variable resistor. Control of the thermals by this method was very effective, but greatly dependent upon the smooth increase of the conduction between the heater components and the specimen. This

conduction seemed very dependent upon the degree of physical contact and, in some cases, vibration of the calorimeter caused fluctuations in the error and thus the control. Careful construction and installation of the specimen heater proved to be a necessity in elimination of this effect. Handling of the specimen, heater, and ceramic parts with surgeon's rubber gloves was also effective in reducing large thermal fluctuations.

Thus it was found possible to tolerate a small amount of conduction between the measuring and power circuits. The real difficulty was in controlling the fluctuation in the conductance, presumably caused by changes in the degree of physical contact of the specimen-ceramic-heater wire, by vibration. These fluctuations were much more serious at relatively high conduction, (at higher temperatures), than when the conduction was small.

The Calorimeter

The main differences in the physical appearance of the calorimeter used in this research, and those previously used on this project, are the size of the adiabatic chamber and the method of specimen mounting. The physical components of this calorimeter have been described in an earlier publication²⁸; however, the temperature measurement and control systems have been changed considerably, and a new control component added.

The main section of the calorimeter consists of a long monel tube with one main and two auxiliary nichrome windings. The main winding on the 1 1/2 inch I.D. tube consists of a 22 inch section wound with 18 gage nichrome wire insulated with refractory beads. The lower winding was constructed similarly, overlapping the main winding at the base for a length of about four inches. The upper winding extends eight inches above the main winding to the top of the adiabatic chamber. With the specimen in place, a small nichrome-wound, stainless, heated shield is positioned about six inches above the specimen

inside the tube. These four controlled heat sources completely encase the specimen and comprise the adiabatic chamber. These four components will be referred to respectively as the Cylinder, Base or G_2 , Guard or G_1 , and Heater or G_3 .

The tube, complete with windings is inserted into a nichrome sheath constructed such that helium gas may be passed into the 1/2 inch annular space between it and the windings. The helium provides a protective atmosphere as well as serving as a good heat transfer medium increasing the response between the windings and the tube. Surrounding the sheath is a four inch refractory lining which is water jacketed on the outside. The tube passes through a water cooled plate above the guard winding, and terminates on a flat plate which serves as a terminal board for the thermocouple and power leads. This plate is machined to seat a gasket and top plate for the vacuum seal, and also contains the channel through which the vacuum is pulled in the adiabatic chamber. The cross-section of this calorimeter is shown in Figure 9.

The vacuum necessary in the adiabatic chamber is maintained by a mechanical pump and an oil diffusion pump connected in series with the vacuum port in the top plate of the calorimeter. The vacuum is read with both thermocouple and ion gages inserted in the vacuum port. With dry ice-alcohol mixtures in the cold-trap above the diffusion pump, vacuums of 1×10^{-4} mmHg. or less are maintained.

The safe operating temperature for this calorimeter has been limited to about 700°C by the use of a lead gasket in the connection of the gas jacket and plate to the main body of the calorimeter. The thin-walled monel tube is also subject to failure at higher temperatures due to the high vacuum inside.

The Thermocouple System

All temperature and temperature difference measurements were made with Pt-Pt 13 % Rh, (Platinum-“Rhodium”), thermocouples attached to the component parts of the calorimeter. The thermocouple leads, after passing through the cold junction, went to a switching station consisting of three interconnected 11 pole thermal-free switches. These switches made possible the measurement of temperatures, temperature differences, and spurious emf's in all parts of the system in a minimum of time. The schematic thermocouple wiring diagram is shown in Figure 10. A list of measurements made available by the switching arrangement is given in Table II.

The guard heaters at either end of the cylinder were controlled by response from differential couples between points inside the cylinder opposite the junction of the windings and the main control point at the center of the main cylinder winding. Since thermocouples were attached directly to the metal wall at the latter point, it was necessary to electrically insulate the junctions from the wall at the end windings. Otherwise the Pt 13 % Rh jumper used in the differential couple would be in parallel with the monel tube. However, it is also essential that good thermal contact be maintained. This connection was made by means of a small tab designed specifically for this purpose. These tabs were constructed by melting platinum into both holes of a two-hole thin wall ceramic tube for a distance of about one quarter of an inch. The ceramic was ground away from one side for metal to metal contact, while the thermocouple junction was made in the other. The tab was spot welded to the wall of the adiabatic chamber. In this manner, the required electrical insulation was maintained by the ceramic separating the platinum in the two holes, and good thermal contact was assured by the close proximity of the platinum elements.

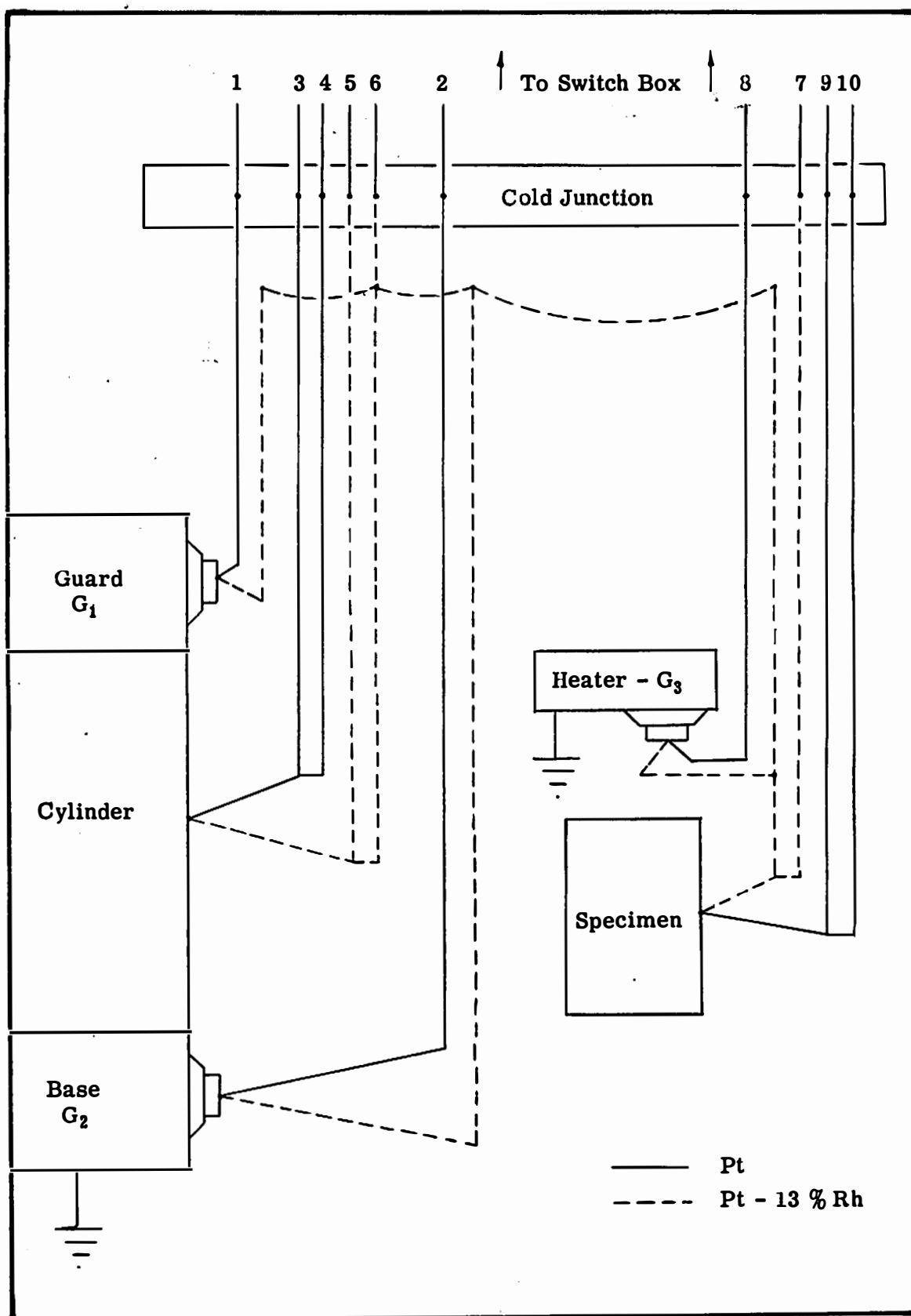


Figure 10. Schematic thermocouple wiring diagram.

TABLE II
THERMOCOUPLE SWITCHING SYSTEM

Switch Pos.	Thermocouples		Measurement	Comment
A 1	7*	9	Specimen Temperature	> Diff. due to Spec. Rhodiums.
A 2	6*	9	Specimen Temperature	
A 3	6*	4	Cylinder Temperature	> Diff. due to Cyl. Rhodiums.
A 4	5*	4	Cylinder Temperature	
A 5	6*	2	Base G ₂ Temperature	
A 7	6*	8	Heater G ₃ Temperature	
A 9	5*	1	Guard G ₁ Temperature	
B 1	10	3	Spec-Cyl Differential	> Diff. due to Spec. Platinums.
B 2	9	3	Spec-Cyl Differential	
B 3	1	3	Guard-Cyl Differential	> Diff. due to Cyl. Platinums.
B 4	1	4	Guard-Cyl Differential	
B 5	2	3	Base-Cyl Differential	
B 7	8	10	Heater-Spec Differential	> Diff. due to Spec. Platinums.
B 9	8	9	Heater-Spec Differential	
B 8	8	3	Heater-Cyl Differential	> Diff. due to Cyl. Platinums.
B 10	8	4	Heater-Cyl Differential	
C 1	9	10	Spec. Platinum Thermals	
C 3	4	3	Cyl. Platinum Thermals	
C 5	5*	6*	Cyl. Rhodium Thermals	
C 7	7*	6*	Spec. Rhodium Thermals	

(* - Pt 13%Rh)

Since the thermocouple connections were made on the inside of the adiabatic shield, this necessitated making welds deep inside the 1 1/2 inch monel tube. These welds were made using a condenser discharge spot welder, one terminal being the tube wall, and the other a long copper tube with welding tip, dentist's mirror and light source. The copper welding tip was positioned with the aid of the mirror so as to press the thermocouple to the wall. As the welds showed a tendency to fail during fast heating or cooling of the calorimeter, the tabs and cylinder thermocouple were first welded to a small strip of platinum foil, and this foil then welded to the wall. This permitted a large number of separate welds to be made and resulted in a more secure connection.

The base, cylinder, and guard thermocouple wires were brought up the side of the cylinder shield doubly encased in high purity alundum and quartz tubes. This double protection aided in the prevention of contamination due to vaporization of the metal components in the system. The leads were brought out of the tube and connections made to permanent exit leads by pressure junctions on the top plate. The exit leads passed through vacuum seals to the exterior of the calorimeter and the cold junction. The cold junctions were made inside oil-filled thin walled pyrex tubes immersed in a distilled water-ice mixture.

A Rubicon Thermofree Potentiometer, Serial 55515, was used to measure the outputs of all the desired thermocouple combinations. The scale on this potentiometer was such that measurements to ± 0.1 microvolts could be made.

The thermocouple system was arranged such that spurious thermals or voltages on the specimen and cylinder couples could be measured. This was accomplished by reading the potential between platinum and between "rhodiums" on both the cylinder and specimen, as two thermocouples were placed on each of these important control points. These values could also be determined by noting the difference in other absolute readings, as listed in Table II. The values of

these thermal emf's are not indicative of the true error in a given reading, as thermals in pairs of leads only may be measured. However, the values are significant in that they suggest the thermal behavior of the leads, and, if these values may be kept constant, the system characteristics will be more uniform from run to run. During this investigation the recorded thermals were controlled by means of the "thermal compensator", as described in a preceeding section. This device made possible runs of much greater reproducibility at the higher temperatures.

The Specimen

The specimens used in the determination of specific heats in this investigation consisted of cylindrical solid samples ranging in size from 3/4 to 1 inch in diameter and from 1 1/2 to 3 inches long. The specimens were machined to completely enclose a small wound resistance heater, plus a portion of the power leads as shown in Figure 11. The heater, about 30 inches of 30 gage Nichrome V wire, was wound on a piece of 0.075 inch single hole alundum tubing. The power leads, 22 gage nichrome wire, encased in thin walled alundum tubing, were introduced through the wall of the specimen longitudinally before connecting to the 30 gage heater element. The heater fitted into a quarter inch hole drilled in the center of the specimen, and was held in place, insulated from the specimen, by fitting the base end of the heater ceramic into a small hole centered in the blind end of the heater cavity. A threaded cap fitted over the open end of the specimen assembly.

The reason for constructing the heater in this fashion was to minimize the heat losses by the heater and power leads. By completely enclosing the heater, no direct radiation losses were possible. Enclosing the power leads in the specimen wall prevented large temperature gradients in the leads entering the specimen, thus decreasing the conduction losses along these wires. The

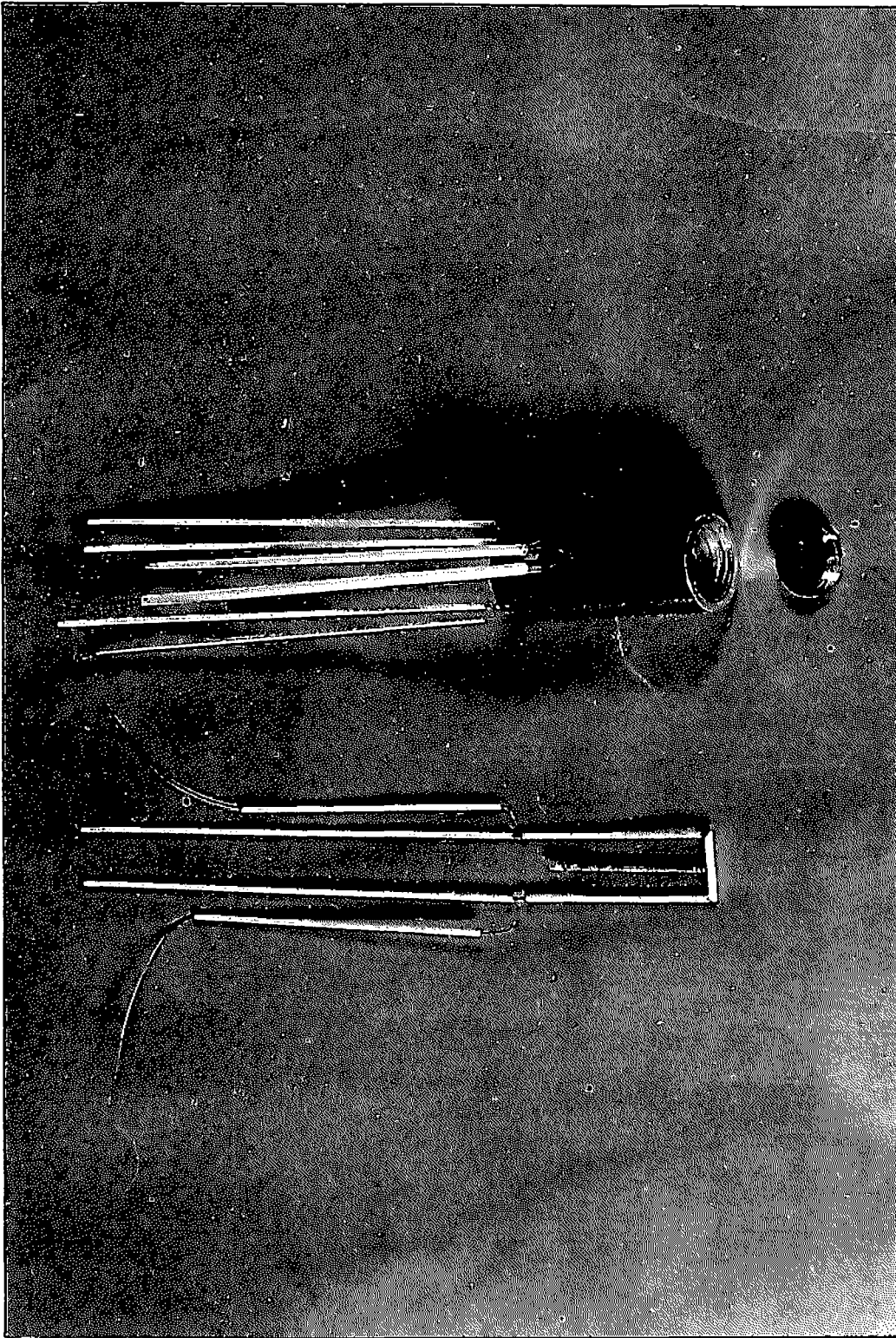


Figure 11. Specimen and specimen heater construction.

heater was oxidized slightly in air prior to its insertion into the specimen to increase the radiant heat transfer. The specimen was metallographically polished in order to decrease further the magnitude of any heat interchanges of the specimen with its surroundings.

The specimen was suspended in the calorimeter by means of its two power leads which in turn were attached to the main suspension consisting of one 1/4 inch I.D. quartz rod fastened to a supporting tee at the upper end. The lower end of this rod passes through and supports the small G_3 heater. This tube houses five ceramic encased thermocouple leads which go to the specimen and to the tab on the body of G_3 . Three additional refractory tubes are fastened to the supporting tee: one shields the power leads to the G_3 heater; the second grounds the metallic body of G_3 , and the last houses the specimen power leads and voltage taps. The lower end of this suspension is shown in Figure 12. The specimen power and voltage tap leads are brought down through two holes in the flange of G_3 directly to the specimen. The four specimen thermocouple leads are also brought down and fastened directly to the specimen. Initially, all four leads were beaded and welded to the specimen. However, it was found satisfactory to bead the platinum and the rhodiums separately immediately above the specimen and to continue with one of each, thus decreasing the effective area for any heat conduction along these wires. The voltage tap leads were welded to the specimen power leads just outside the specimen. Thus the measured voltage drop is the total drop inside the specimen. The power lead junction is secured by welding the overlapping 22 gage wires, plus a twisted platinum jumper welded on both sides of this connection. A close-up of these connections is given in Figure 13.

When the specimen is removed from the calorimeter, the entire suspension arrangement must be removed also. This requires the breaking of all the thermocouple, power, and voltage tap leads which are associated with

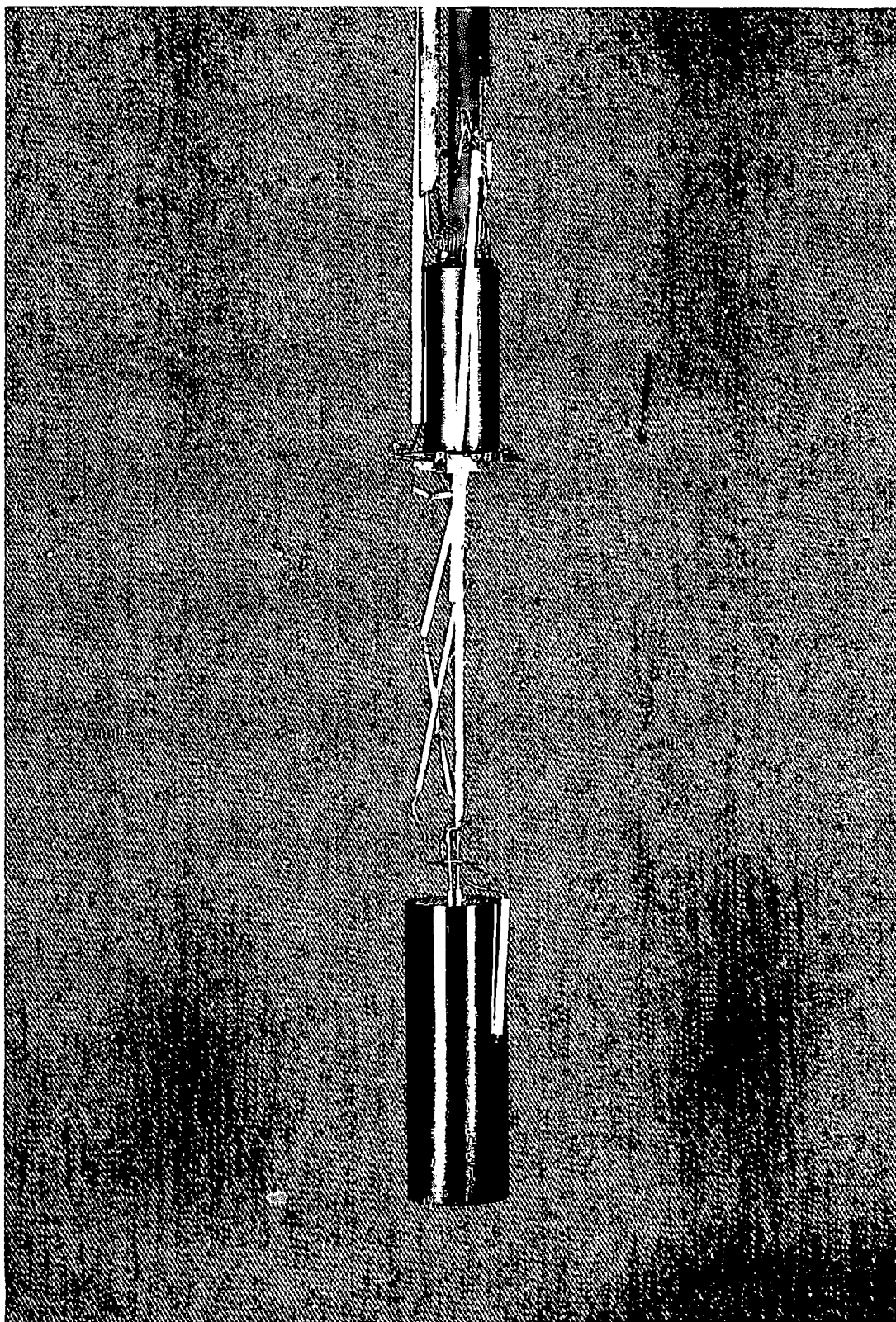


Figure 12. Lower end of specimen suspension.

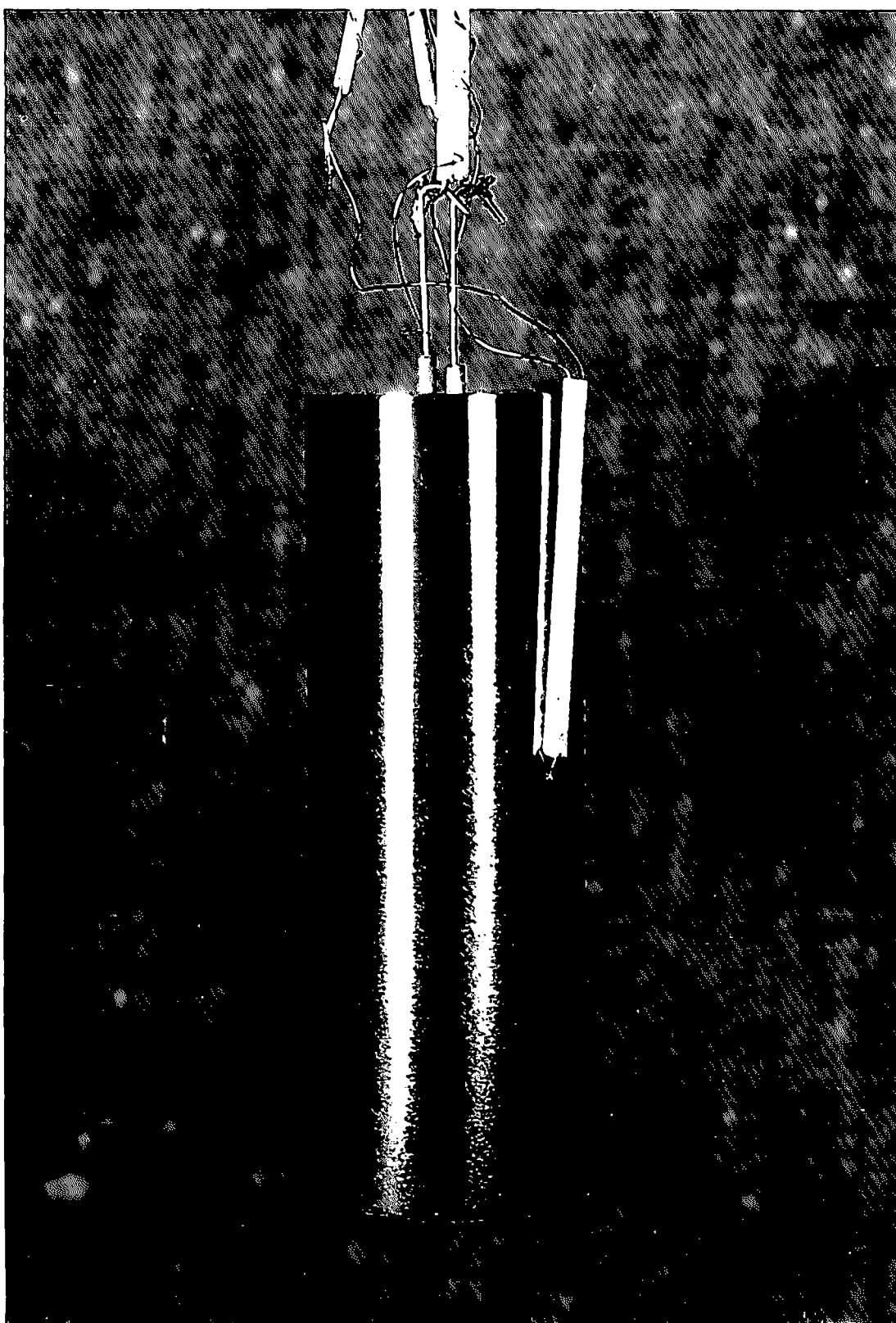


Figure 13. Photograph of specimen.

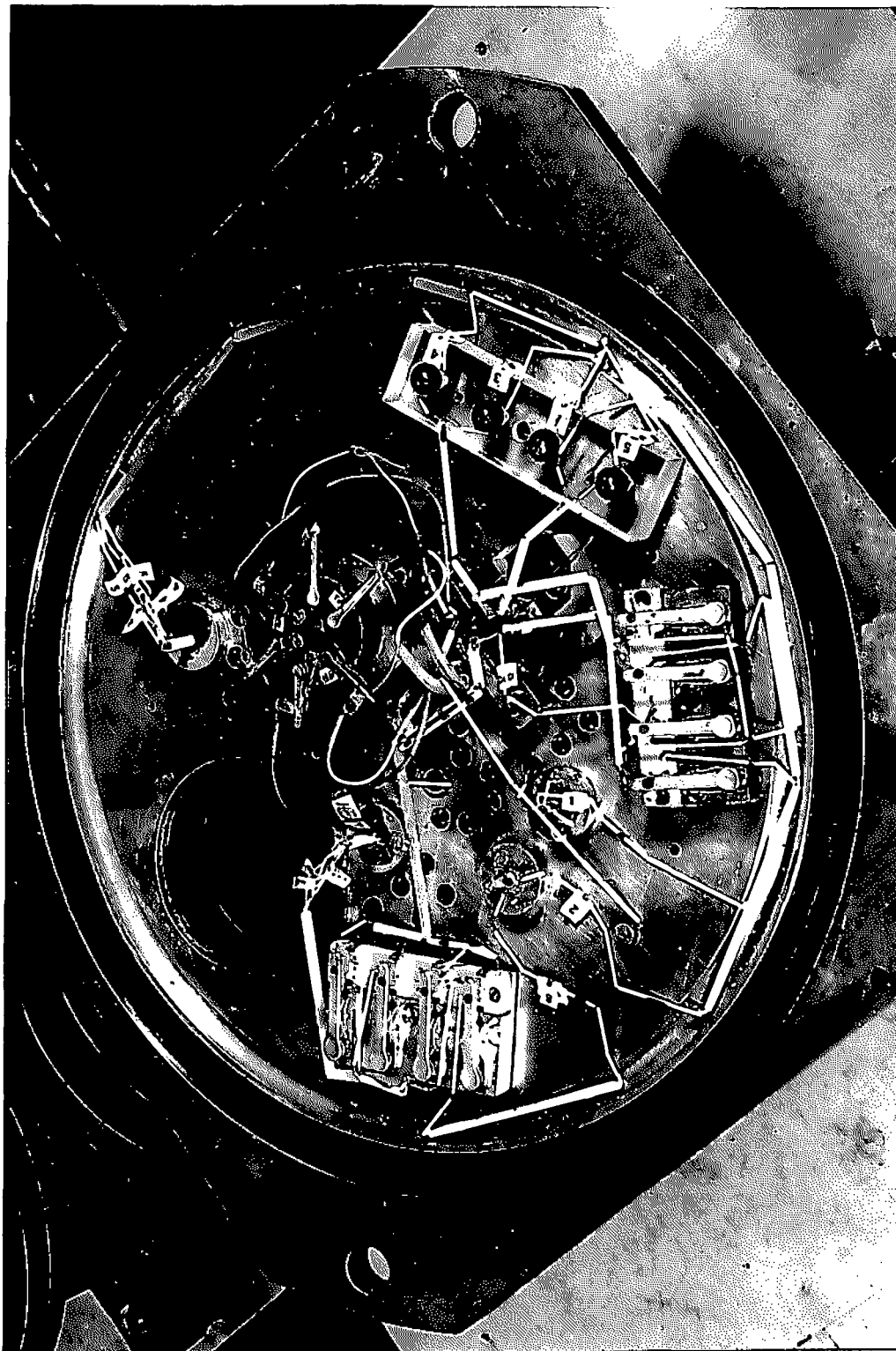


Figure 14. Top plate of calorimeter.

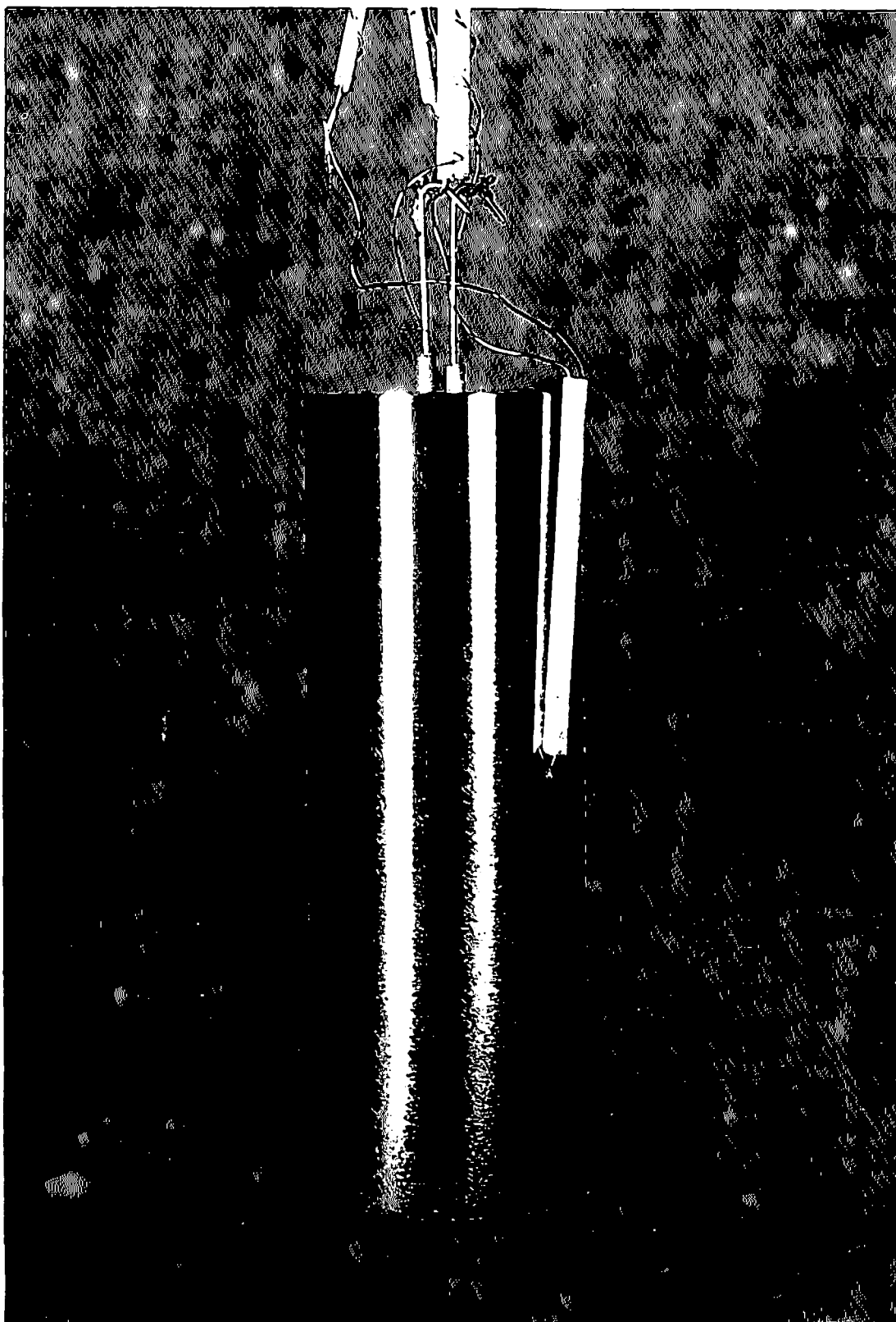


Figure 13. Photograph of specimen.

the applied voltage, determined by the setting on the high resistance voltage divider. The voltage divider was in the circuit only when the switch was thrown for measurement, therefore the correction for the current flowing in this circuit momentarily was negligible.

The Control System

The most important component of an adiabatic calorimeter is the control system. The method of control, its preciseness, sensitivity, and response, determine to a large extent the accuracy and reproducibility of the results. Modern methods of control have aided in the solution on many problems which proved serious deterrents in previous investigations.

The control problem in this investigation was to maintain adiabatic conditions about a metal specimen under essentially constant heating rates in the range of one to eight °C per minute. This required the precise temperature control of the adiabatic chamber. Strictly speaking, it is impossible to control every point of surface which is seen by the specimen. Therefore, four control points were chosen, in relation to the four separate windings composing the adiabatic chamber, and the control system designed to yield stable operation under the aforementioned conditions.

The control of the cylinder, comprising the bulk of the adiabatic chamber, was naturally of primary consideration. The G_1 , G_2 , and G_3 components were controlled principally to prevent large temperature gradients in any section of the tube near the specimen, and to aid in the control of the cylinder by decreasing the power load. The cylinder was therefore controlled directly to the specimen temperature, and the auxiliary components controlled to the cylinder temperature. Any temperature difference which existed between any of the control points appeared as a voltage on the corresponding differential thermocouple. These differential couples were not made with the jumper inside

the calorimeter, but rather on the terminal plate as indicated in a previous section and in Figure 10. These differential voltages were amplified in high gain D. C. amplifiers, (three Leeds and Northrup stabilized D. C. microvolt amplifiers and one Liston Becker D. C. microvolt amplifier were used), recorded on Leeds and Northrup Speedomax recorders, and sent to pulse type proportioning control instruments. Leeds and Northrup D. A. T., (Duration Adjustment Type), controllers were used for this purpose very satisfactorily. The ability of these controllers to hold a zero temperature difference between the components of the system depended greatly upon the ability of the operator to adjust the D. A. T. control settings to fit the conditions of operation. These settings varied with the heating rate and temperature, and choice of the proper settings was largely a matter of experience. Under normal operating conditions, the specimen-cylinder temperature difference was controlled to about ± 0.2 microvolts or less corresponding to $\pm 0.02^\circ\text{C}$. The auxiliary systems controlled only to one or two microvolts due to the positions of the thermocouples, and the slight lag induced by the insulating tabs. However, offset experiments on these components showed that differences of this order of magnitude are not serious, and reproducibility was not impaired. A schematic of the control system is shown in Figure 16.

Precise control of the specimen-cylinder temperature is more important from a reproducibility standpoint than absolute accuracy of the data. The degree of adiabaticity of the system is indicated by other means, (drift), and it is only coincidental if it is indicated quantitatively by the temperature differences of single points on the specimen and cylinder. However, in order to reproduce the operating conditions in the calorimeter, this criterion must be observed.

The Power Supply System

The main power supply to the calorimeter substations is a 230 volt A. C. source fused at 60 amperes. The substations function as four separate

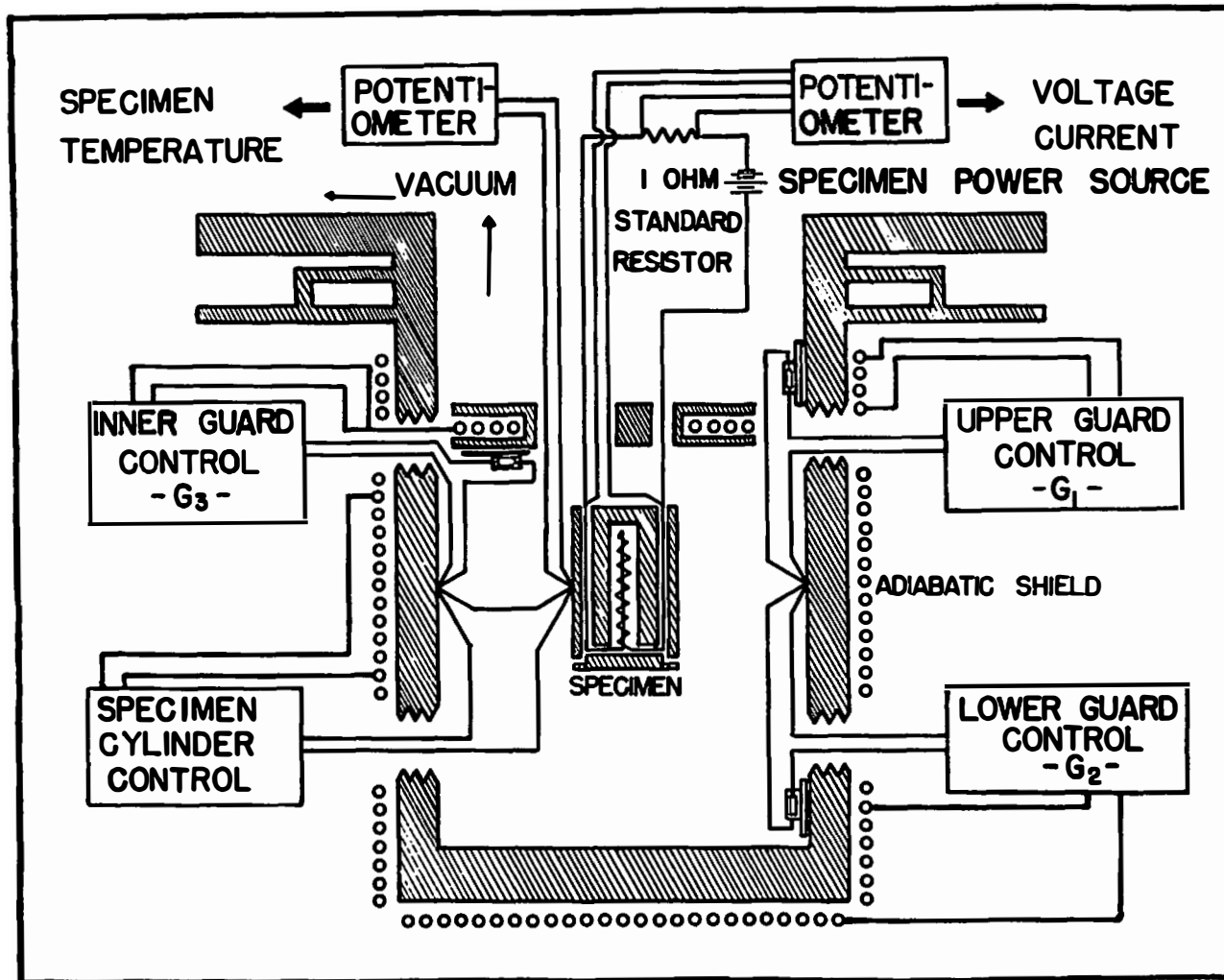


Figure 16. Schematic diagram of control system.

units, each delivering power to one of the four windings in the adiabatic shield. Each substation, separately housed in an angle-iron framework for accessibility, consists of a high-current variable power-transformer, a drive mechanism, and a high-current mercury relay actuated by the respective control system. The drive system consists of a thyatron-motor combination geared to the variac. The speed is controlled manually, and continuously adjusted during a run to keep the on-off times approximately equal as indicated by the D. A. T. Thus, the voltage to each component is smoothly increased as the temperature and demand for power in the calorimeter increases. The rate of voltage change does not affect the control system, unless very abrupt changes are necessary.

Operational Procedure

The method of obtaining apparent specific heat data was quite simple and could be performed by a single operator. After the calorimeter had reached stable operation, the measurements were made in the following way:

1. A temperature equivalent in microvolts was set into the Thermofree potentiometer to the nearest 0.1 microvolt.
2. A precision electric chronograph was started the instant the specimen temperature reached the set temperature, as indicated on a sensitive galvanometer. Voltage and current measurements, as well as other measurements relating to the control stability were made at this time.
3. For measurements made at a given temperature interval, the second temperature was set into the potentiometer.
4. As the specimen temperature passed this set temperature, the chronograph was stopped, and voltage and current readings again taken. These measurements could be made continuously, as dual chronographs, operated by a single switch, were used.

The mean specific heat over the set temperature interval was determined from these measurements, using the following equation:

$$C_{pa} = \frac{E_{avg} \times I_{avg} \times f \times \Delta t}{W_{s+H} \times \Delta T} \quad (1)$$

where: C_{pa} = mean apparent specific heat in the temperature interval, cal/gram °C.

E_{avg} = arithmetic average of voltage measurements.

I_{avg} = arithmetic average of current measurements.

f = 0.23895 cal/watt-sec, (accepted absolute std.)

W_{s+H} = total weight of specimen and heater.

Δt = time interval, seconds.

ΔT = temperature interval, °C.

This procedure for obtaining specific heat values became routine, and permitted the operator to pay strict attention to the various adjustments necessary to maintain control during the run. An experienced operator could "hear" if the control was satisfactory by the rhythm of the clicking of the power relays.

Before data were collected for any given run, a checkout procedure was followed. The complete inventory prior to a run involved the following:

1. The specimen was properly mounted and placed in the calorimeter.
2. All power and thermocouple connections were examined, and all thermocouple combinations read on the potentiometer to check for continuity and faulty readings. Special attention was paid to any spurious thermals occurring in the thermocouple leads.
3. The vacuum was pulled, and the ice-water mixture replenished in the cold junction.
4. The control system and power to the adiabatic chamber windings were turned on and the system allowed to stabilize. Helium gas was admitted to the sheath chamber.

5. The proper settings were made on the D.A.T.'s and power drive motors, and the specimen power was connected across the desired voltage.

6. A sufficient time, from 20 to 40°C, depending upon the heating rate, was allowed for the controllers to reach stable operation. Readings were then started at the desired temperature intervals.

During the run, it was necessary for the operator to keep a close check on the control as indicated on the Speedomax recorders. Corrections of the D.A.T. settings were necessary from time to time as the temperature increased. Any sudden parasitic emf's could be noticed on the control charts, and usually corrected by the thermal compensator. A photograph of the calorimeter and allied apparatus is presented in Figure 17.

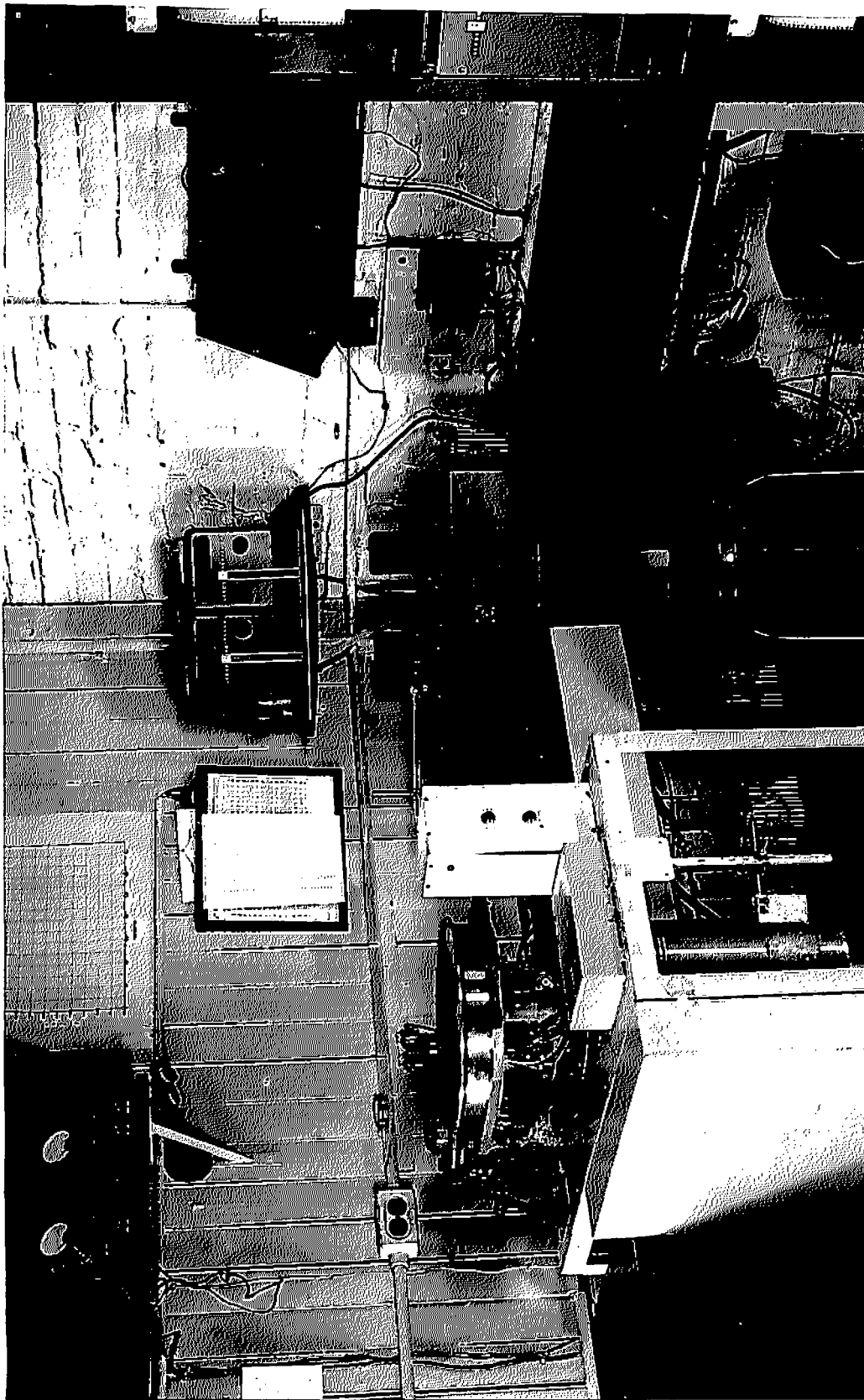


Figure 17. The calorimeter and allied equipment.

CHAPTER IV

OPERATIONAL CHARACTERISTICS OF THE CALORIMETER

In the ideal case, if perfectly adiabatic conditions were maintained for the specimen during operation, if the control were flawless, and if time, temperature, and power measurements could be made absolutely, the apparent specific heat values would be entirely reproducible and then conversion to true values would depend only upon a heater correction. Obviously, any real system cannot meet these requirements exactly, and a natural spread in the experimental data is observed. Some of these sources of error have already been discussed.

If the temperature control of the adiabatic chamber were accurate and reproducible, the measurements of temperature, power, and time will control the reproducibility of the apparent specific heat data. In the experimental method followed in this investigation, the errors in time and temperature were interrelated. The chronographs could be read to at least the nearest 0.05 second, making the error in time almost negligible at normal heating rates. The types of errors inherent in the temperature measurements have been discussed. Simply, the stability of the thermocouples, parasitic emf's, and the type of potentiometer used for the measurement controlled the accuracy of this reading. These errors were important, not for the measurement of a single temperature, but for accurate resolution of the temperature interval over which a specific heat determination was made. The smaller this interval, the larger the error associated with the temperature measurement. Thus a total error of only 0.2 microvolts in the set temperatures over an interval of ten degrees would lead to an error of roughly 0.2 per cent in the apparent specific heat. Extreme care was taken to make this type of

error as small as possible. Most of the specific heat determinations were made over 20°C intervals, except where the shape of the specific heat-temperature curve was changing rapidly.

Power measurements were recorded as the average of the voltage-current product taken at each end of the temperature interval. Since a simple wet cell was used as a power source, a certain amount of drift was prone to occur. The resistance of the heater also increased with increased temperature. For extreme accuracy in this measurement, a more elaborate system of averaging could have been used; but for the small, uniform power shifts which were observed, the error in using the arithmetic average is very small and negligible in a specific heat determination.

It was found early in the investigation that the most important factor concerning the reproducibility of the apparent specific heat data at a given heating rate was the ability to maintain good control as indicated by both the recorder traces and the absence of spurious emf's in the circuit. The various components were brought into control by changing the amplification scale on the D. C. amplifier from coarse to a more sensitive scale as the control responded to the D. A. T. The specimen-cylinder control recorder was run on a scale such that one microvolt corresponded to about 1/4 inch. Therefore, control difficulties in the microvolt region could be followed visually. The other controllers were run on a slightly less sensitive scale to minimize the "hunting" effect. In any case, small irregularities could be detected by pipping or undue drift from the normal straight line as indicated on the recorders. The recorder readings were checked against the differential couple readings on the potentiometer at regular intervals during a run.

The greatest difficulty in maintaining good adiabatic conditions, especially at high temperatures, was the apparent indication of a zero

temperature difference on the recorders and differential couples when error voltages were present in the circuit. The presence of this error, largely due to electrical leakage between the specimen heater and thermocouple circuits, could be detected by observing the emf's between the rhodium leads on the specimen and on the cylinder. This measurement was only a qualitative indication of the absolute magnitude of the error on the control couples as there was no way of determining the magnitude of the parasitic emf in each lead. However, since the greater part of the error could be attributed to the leakage current in the jumper of the differential circuit, (as in Figure 8), a condition of zero observed potential on a rhodium pair was used as the criterion that the control system was getting the proper thermocouple signal. Thus, when natural or "induced" thermals appeared in the circuit, they were controlled by the thermal compensator to give a zero reading on the respective thermal measuring couples. This procedure not only reduced the spread of the data, but decreased the very sharp increase of the specific heat values of both copper and nickel above 450°C.

The degree to which adiabatic conditions were maintained in the calorimeter was determined by drift rate measurements made at different temperatures for each specimen. Drift rate data were obtained by two methods: (1) the specimen power was turned off, the control allowed to stabilize, and the specimen temperature followed as a function of time; and (2) the adiabatic shield was made to control at a set temperature, and power was pulsed to the specimen to bring it above this temperature. Then, with specimen power off, the specimen temperature was followed until it dropped below that of the calorimeter. In either case, the drift rate was taken as the slope of the temperature-time curve at the set temperature. Drift rate data obtained by these methods agreed very well and, for a given specimen, were unusually reproducible. Since the first method was considerably less time consuming, most of the drift rate data were obtained in this manner.

The fact that there are drifts of this type indicate the necessity of applying appropriate corrections to the measured specific heat in order to obtain the true values. There are two main methods of applying a correction of this type. The first is by applying a controlled temperature offset during a run, which compensates for the predetermined losses. The second is by applying no offset, and correcting the final apparent specific heat data. The second method was chosen for this investigation, as better control can be maintained without manual offset adjustment during a run. Construction of a mechanical linkage to continuously apply the desired offset would be difficult, and small system changes would confuse the data obtained. The manner in which these drift rate corrections were applied to the data will be discussed in detail in the following chapter. In general, the necessary correction due to drift was less than one per cent up to about 400°C, depending upon the heating rate. Above 400°, the correction increased rapidly and corrections of two to three per cent at 600° were not unusual.

The versatility of the operation of this calorimeter made it very amenable to a range of experimental techniques and investigations. Many equilibrium and non-equilibrium heat effects could be investigated with little change in the system. For example, transformations could be followed with either adiabatic or isothermal control and the heat effect and kinetics derived. The isothermal method was used successfully by Elder ²⁹ in a study of the isothermal transformation kinetics of the epsilon phase in the copper-antimony system. In studies of this type, the adiabatic chamber of the calorimeter was made to control to a set temperature, regardless of the temperature of the specimen. This was accomplished by feeding the cylinder amplifier-control system with a voltage indicative of the difference in the cylinder temperature and the desired temperature. A constant emf, corresponding to the desired isothermal control temperature, was placed in opposition to the cylinder measuring

couple, and the difference used as this source. The system was arranged so that the only change necessary to operate in this manner was to plug in the desired emf against the cylinder couple. This was done as shown in Figure 18.

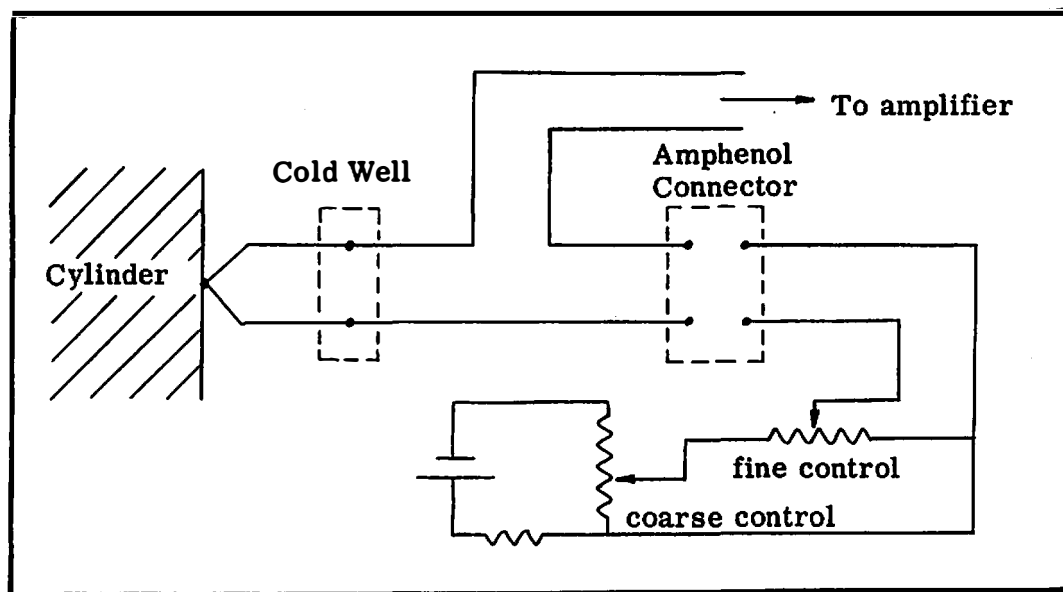


Figure 18. Arrangement for isothermal operation.

In isothermal operation, the calorimeter was capable of holding a steady temperature for long periods of time. For example a specimen was once held at about 400°C for over seven hours with no detectable drift, after the control stabilized.

This flexibility of operation was useful in the investigation of stored energy, as the experimental methods of several investigators, (Suzuki, Gordon, and Clarebrough), were tried. The results of these experiments will be discussed.

CHAPTER V

EXPERIMENTAL DATA AND RESULTS

Soon after the initial experiments with the calorimeter, it was realized that accurate and reproducible measurements of specific heat were difficult to obtain, and many experimental problems would have to be solved. As a consequence, a great portion of the time associated with this dissertation was devoted to the improvement of the data through modification of the existing equipment, and the standardization of the experimental procedure.

Operation of a physical system at elevated temperatures has always presented special problems to the investigator. This project was no exception. The frequent result of these difficulties was simply lack of control of the calorimeter components, leading to data in which little confidence could be placed. In the present case, the major problems were specifically: (1) instability and inhomogeneity of the thermocouples; (2) the presence of spurious emf's caused by temperature gradients and leakage from the specimen heater circuit due to electrical break-down of the refractory parts; (3) non-uniform temperature distributions leading to heat interchange between the specimen and surroundings; and (4) the inherent perversity of some of the electronic and mechanical components of the system. The first three of these problems were reconciled experimentally by methods previously described. The last was a problem for its nuisance value only. Broken thermocouples, stuck relays, loose connections, and similar failures which necessitated a shut-down constitute this category. Careful assembly and maintenance were essential to limit these occurrences.

Initial Specific Heat Data

The first series of specific heat determinations in this investigation was made on a specimen of low-cobalt nickel. At this time the calorimeter did not have a G_3 component, and the thermocouple system was wired without the use of insulating tabs, the monel tube being used as the jumper of the differential thermocouples controlling G_1 and G_2 . This series was initiated as a test of the operating condition and reproducibility of the data. In general, the data up to about the Curie point were reproducible to about ± 1 per cent; above the Curie point a definite spread existed which could be correlated to the presence of error voltages in the thermocouple circuit. The specific heat values were undoubtedly high, as excessive losses were indicated at the higher temperatures.

As a result of this initial work, the thermocouple system was changed to essentially the one presently in use, and the G_3 auxiliary heater and control system installed. The high temperature losses were decreased greatly by G_3 , and the apparent specific heat data at the higher temperatures were considerably lower. However, thermals were still a plague to reproducible data, varying from day to day for no apparent reason, other than contamination in the circuit. A resumé of the data obtained in this period is shown in Figure 19. This plot shows the behavior of the data with and without G_3 , and the range of the data above the Curie point. The trend of the data illustrated the need for a correction, either during operation or on the subsequent data, due to the non-adiabaticity of the calorimeter. This nickel specimen was run about 15 times, the self consistency of each run depending upon the control and, of course, the degree to which the parasitic voltages appeared. After experimenting with re-annealing the thermocouple leads, and several heater designs, a definite factor in inhibiting the thermals was revealed. It appeared that if the specimen heater assembly and installation were conducted by handling only with rubber gloves, a definite

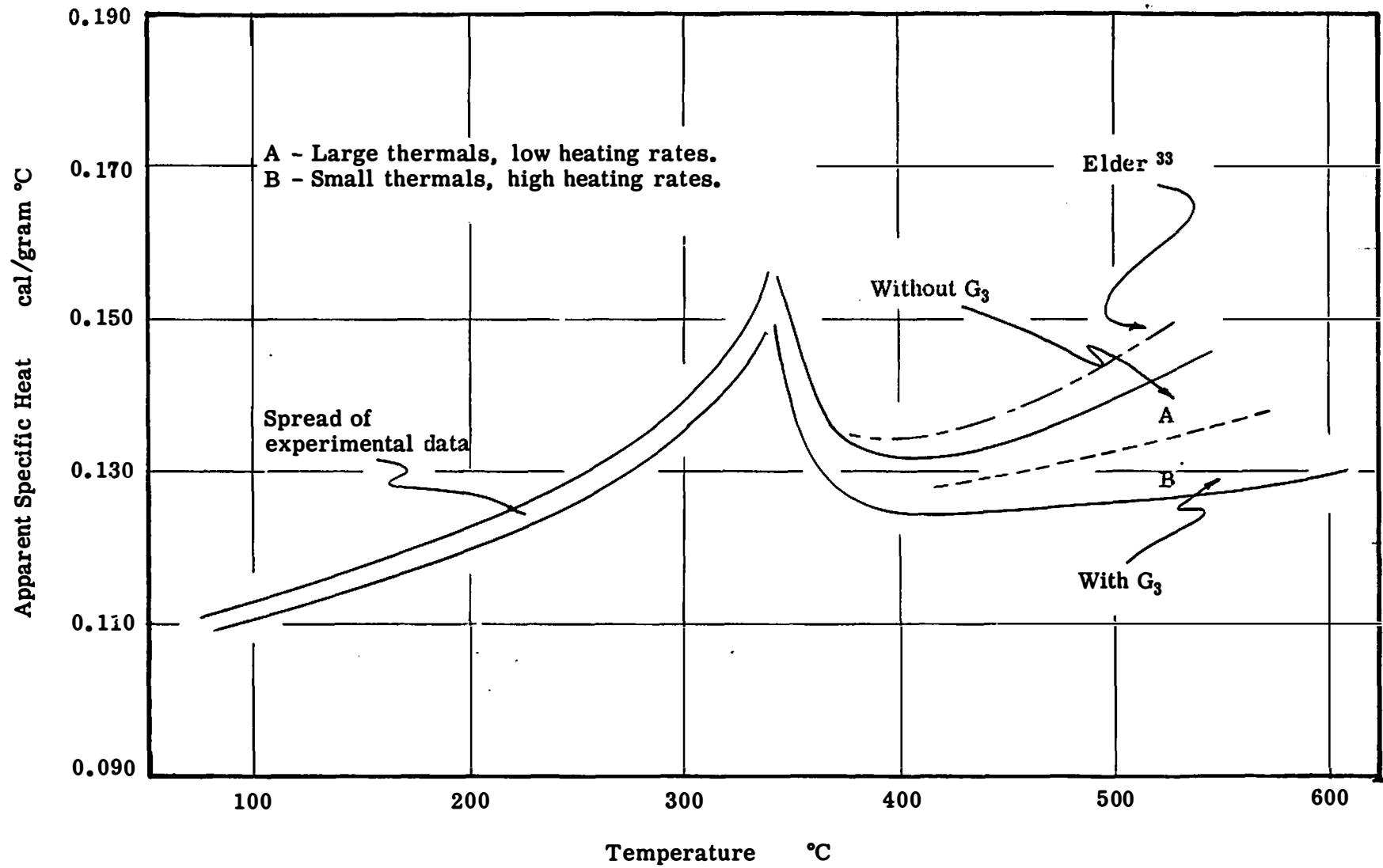


Figure 19. Initial specific heat determinations on nickel.

improvement in the thermocouple error behavior was observed. Hence, all ceramic parts in the hot zone of the calorimeter were installed with the use of surgeon's gloves.

Apparent Specific Heat of Pure Copper

The study of reproducibility in the calorimeter continued on a specimen of high purity copper*. The specimen was machined from a bicrystal and weighed slightly over 225 grams. The heater assembly weighed 1.3 grams. This in itself was a great improvement over the earlier models of the calorimeter where the relative heater-specimen weight ratio was considerably greater, necessitating large corrections.

Shortly after the installation of this specimen, experiments on the specimen heater circuit led to the installation of the thermal compensator. With a means at hand to control the thermals in the circuit, the reproducibility of the high temperature data became exceptionally good. It was also found that better control was possible by grounding the metallic body of G_3 . The apparent specific heat data from six runs made at heating rates of approximately 2.5 °C/min. are illustrated in Figure 20. The spread of the data is indicated where the individual points cannot be plotted separately. The high temperature data for a run made on this copper specimen without the use of the thermal compensator are also shown. This "tailing" of the data above 450°C is due to the appearance of thermals in the circuit, and a false indication of control.

A sufficient number of runs from room temperature to 620°C were made on this specimen to illustrate the characteristics of the calorimeter and to adopt techniques of operation conducive to improved reproducibility. Of the seventeen runs, eleven were made with G_3 grounded, and these runs showed the better reproducibility. These runs showed a very systematic trend as a function

*Specimen analyses, etc. are listed in the Appendix.

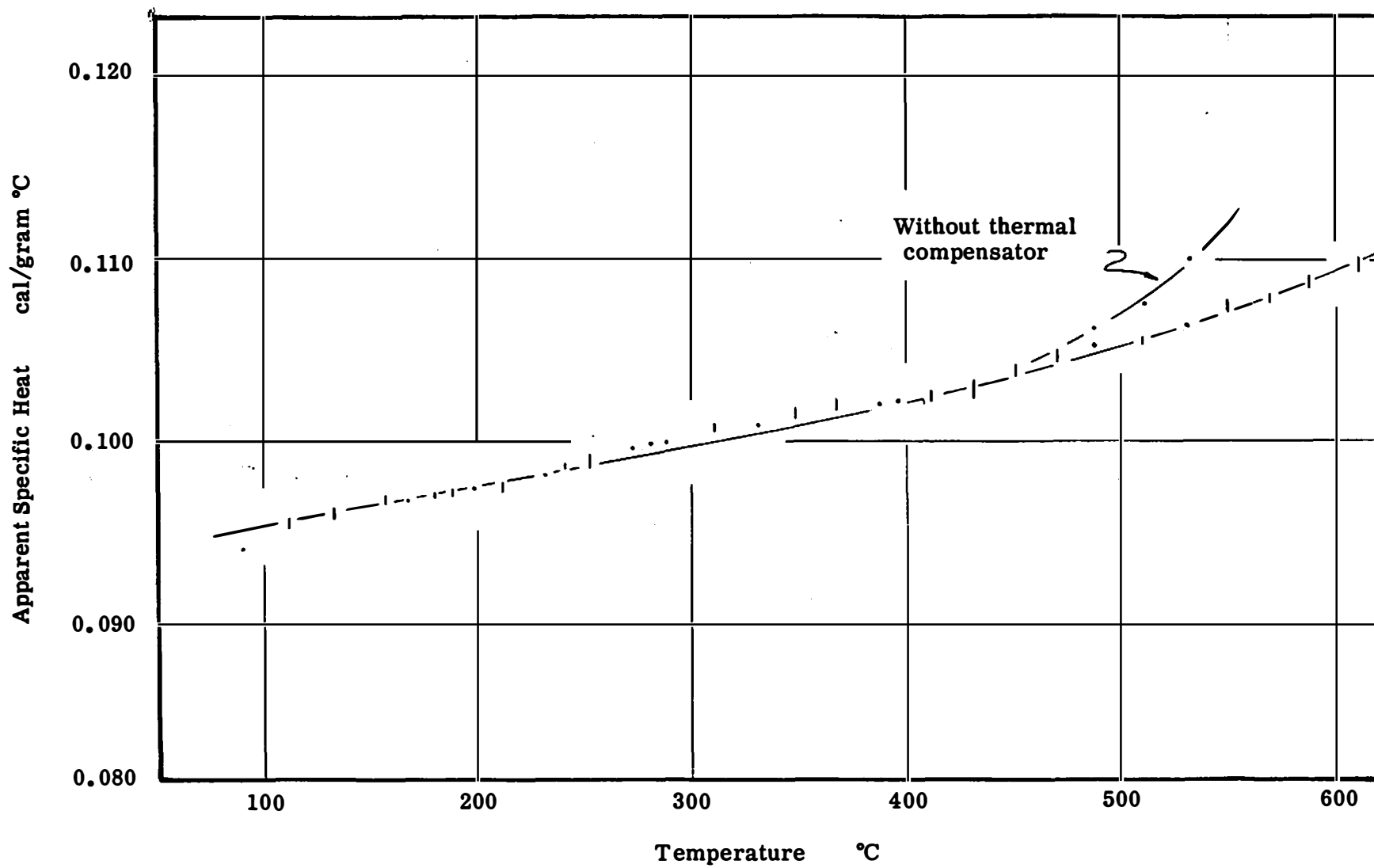


Figure 20. Apparent specific heat data for copper.

of the power level or heating rate. Since the ultimate objective was to achieve reproducibility of true specific heat values, appropriate correction terms would have to be applied. With this in view, a systematic treatment of the possible errors was made, with special emphasis on heat losses due to non-adiabatic conditions.

Correction of the Apparent Specific Heat Data

The apparent specific heat values computed from the experimental data through the equation given in Chapter III are subject to error from a number of sources. The measurements of time and temperature are subject to mechanical or calibration errors, as well as the human error in settings and readings. It is well that these errors are partly compensating for data taken in a continuous fashion. For data taken at 20°C intervals, the human error in temperature settings and chronograph readings are comparatively small. However, calibration errors in the measuring potentiometer and emf-temperature scale can cause small, reproducible deviations in the data. Some of the small reproducible irregularities in the data were investigated by heating and cooling curve techniques after a recalibration of the Thermofree Potentiometer failed to eliminate them.

The main sources of error which must be considered in correcting the apparent specific heat data are: (1) radiant heat losses, (or gains), due to temperature gradients in the adiabatic chamber; (2) heat leakage along the power and thermocouple leads attached to the specimen; and (3) the error involved in including the weight of the specimen heater in the calculations. The importance of reliable correction terms to compensate for these effects is obvious.

The general procedure for correcting the data for heat losses has been reviewed in Chapter IV. This method consisted of correlating the observed temperature drift rate of the specimen to the losses through an appropriate

equation. Thus, if accurate drift rate data were available for each specimen as a function of temperature, the data could be corrected for heat losses without changing the control of the calorimeter during the run. Several methods of applying the correction were tried. The method of drift rates was deemed the most applicable, primarily because it was the easiest to use and the correction was insensitive to small deviations in the apparent specific heat data. The alternative methods, which will be reviewed, occasionally required smoothing of the data before the correction was applied. In these methods, any irregularities in the data were magnified by the correction leading to very irregular corrected specific heat-temperature curves. If the data were smoothed before the correction, the corrected values were also smooth and agreed well with the drift correction.

Losses calculated from drift rate data do not include losses due to conduction along the specimen leads during operation. The temperature difference necessary for this sort of loss is present only when the specimen is heating at a finite rate, and becomes hotter than its leads. If a satisfactory estimation of these losses were not available, there would be some doubt as to the effective mass of the specimen. The heater leads were assumed not to contribute to losses of this type because of the construction of the heater and suspension. The leads are in thermal equilibrium with the specimen both at the specimen and at a point about four inches above, (G_3); the power dissipated in these leads compensates in part for the otherwise small loss. Losses due to conduction along the measuring thermocouple leads, as the sole remaining source, have been appraised. The temperature of a point on these leads was estimated from ideal radiant heating conditions assuming a constant heating rate, and the resulting conduction loss calculated. For a heating rate of $3^{\circ}\text{C}/\text{min.}$, these losses were $0.019 \text{ cal}/\text{min.}$; this value is believed high due to the

assumptions made in the calculation. In any case, this amounts to less than 0.05 per cent of the total measured power to the specimen. Therefore, within the limits of experimental accuracy, the total loss correction can be obtained from the drift correction.

A simple consideration of the apparent and true specific heats in the presence of losses, either by conduction or radiation, leads to the correction equation:

$$C_{p_T} = \frac{C_{p_a}}{1 - \frac{C_{p_a} R_{(T)}}{3600 f' \Delta T EI}} \quad (2)$$

where: C_{p_T} = specific heat corrected for losses, cal/gram-°C.
 C_{p_a} = apparent specific heat, cal/gram-°C.
 $R_{(T)}$ = drift rate, °C/hour.
 f' = C_p factor, $\frac{0.23895}{wt. \Delta T}$, cal/watt sec. gram °C.
 ΔT = temperature interval associated with f' .
 EI = average power to specimen, watts.

The derivation of this equation is given in the Appendix. For any given run, the power dissipated in the specimen was held essentially constant, and the equation above becomes:

$$C_{p_T} = \frac{C_{p_a}}{1 - \frac{C_{p_a} R_{(T)}}{K}} \quad (3)$$

where: K = cal/gram-hour.

The constant K is the calories per hour dissipated per gram of specimen, and is related to the heating rate through the specific heat. The degree to which K remained constant during a run was very good, and permitted a single evaluation, rather than separate solutions at every temperature interval. For example, a power input of $K = 25$ cal/gram-hour drifted less than ± 0.15 , and the error in

C_{p_T} resulting from considering this a constant was much less than 0.05 per cent. The presentation of the apparent specific heat data will be classified in terms of K values, rather than heating rates, as the heating rate may vary considerably during a run.

Methods of correction which do not require the determination of drift rate data may also be used. However, these methods require apparent specific heat data from a series of runs made at different power levels. From equation (2), it is seen that the corrected specific heat approaches the apparent value as the EI product, the power input, grows large. The values are equal for infinite heating rates, as the loss time becomes zero. Therefore, extrapolation of the apparent specific heat data to $K = \infty$ would yield the corrected value. These extrapolations must be made for each temperature, and the true specific heat curve formulated from the intercepts. The procedure was simplified somewhat in that a plot of C_{p_a} vs. C_{p_a}/EI was found to be approximately linear, and not as many points were necessary for a reasonable extrapolation. This graphical method was not used in this investigation except to show its applicability. An example of this correction is given in Figure 21 for apparent specific heat data at 470°C taken on two specimens of nickel showing different drift behavior. The corrected value obtained here differs by less than 0.1 per cent from that obtained by drift measurements.

As further proof of the accuracy of the drift correction, another method of correction was devised. If the drift rate term, $R_{(T)}$ is eliminated from the equation (3), assuming apparent specific heat data from at least two runs of different K are available, the following equation results:

$$C_{p_T} = \frac{C_{p_1} C_{p_2} (K_2 - K_1)}{C_{p_1} K_2 - C_{p_2} K_1}, \quad K_1 \neq K_2 \quad (4)$$

where C_{p_1} , C_{p_2} = apparent specific heat from runs of K_1 , K_2 respectively.

This equation proved very useful as a check on the drift rate method of correction. In fact, an error in the drift rate data for one specimen was detected and corrected after failing to obtain a check between the two methods. This method may be shown to be essentially identical with the graphical technique of Figure 21. The corrections obtained by this procedure agreed to within 0.2 per cent of those obtained by the drift method.

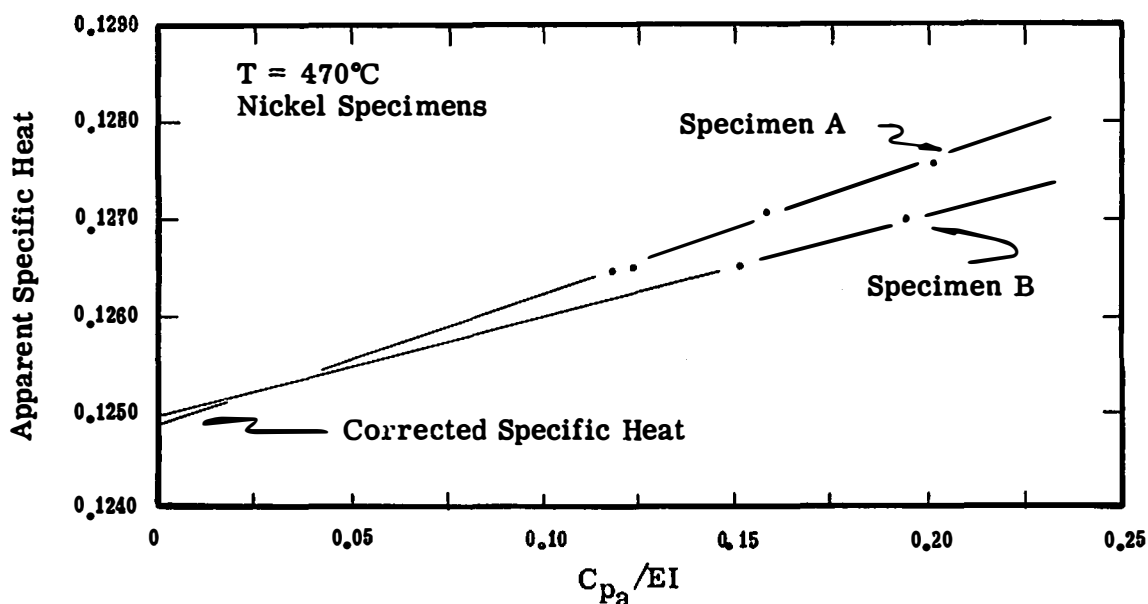


Figure 21. Extrapolation method of correction.

The correction which is necessary to compensate for the presence of the internal specimen heater depends upon the assumptions concerning its temperature behavior relative to the specimen. The magnitude of this correction is determined primarily by the relative weight of the heater components, whereas its precise value also depends upon the specific heat of the components, as well the temperature behavior. A common procedure is to assume that the specimen and heater temperatures are the same, and correct only for the difference in specific heat of the specimen and heater. However, the heater temperature must obviously be higher than that of the specimen, and its temperature must vary in a

different manner. However, if it is assumed that all the energy dissipated by the specimen heater is by radiation, then, the relative temperature characteristics can be estimated and an appropriate correction obtained. It is felt that the latter assumption, while admittedly not precise, offers a more accurate description of the system. Therefore, the heater correction equation was derived (see Appendix) on this basis, resulting in:

$$C_{p_S} = C_{p_T} + \frac{W_H}{W_S} (C_{p_T} - 0.55 C_{p_H}) \quad (5)$$

where C_{p_S} = specific heat corrected for specimen heater, cal/gram °C.

C_{p_T} = specific heat, computed on a basis of the total weight of specimen and heater, cal/gram-°C.

W_H = weight of heater, grams.

W_S = weight of specimens, grams.

C_{p_H} = specific heat of heater components, cal/gram °C.

Very little error is introduced by assigning a constant value to C_{p_H} , since the specific heats of nichrome and Al_2O_3 vary only slightly with temperature in this range. If this is done, the equation becomes:

$$C_{p_S} = C_{p_T} + \frac{W_H}{W_S} (C_{p_T} - 0.113) \quad (6)$$

It is seen that the magnitude of this heater correction depends upon the weight ratio, and the difference of the measured specific heat from 0.113. By the use of massive specimens, the weight ratio was always kept less than 0.01. For the copper-nickel system, the range of specific heat values are such that the differences from 0.113 cal/gram °C are also quite small. Therefore, a very small heater correction would be expected. For copper, this correction varied from -0.0001 to -0.00004 cal/gram °C from room temperature to 620°C. For the nickel specimen, the correction varied from -0.00003 to +0.00015 cal/gram °C, except in the extremities of the Curie region. The alloy specimens required

similar corrections. These corrections were deemed sufficiently small to be negligible in the final result. If the heater is large, or the specific heats vary greatly from 0.113 cal/gram °C, the heater correction must be included.

The corrections thus resolved to a single term, and the true specific heat was determined from the experimental data simply by applying the drift correction. The method successfully rectified data taken from a series of runs at different K values to a common curve.

True Specific Heat of Copper

The specific heat of copper was determined in this calorimeter by the described methods. Apparent specific heat data was obtained for a series of power levels, K varying from 9.56 to 20.89 cal/gram hour. The reproducibility of the apparent specific heat data was very seldom poorer than ± 0.2 per cent for runs made at the same power level; the average variation was considerably less than this. Several small irregularities in the specific heat-temperature curve, of the order of 0.25 per cent, were reproduced consistently. This was, of course, bordering on the limit of accuracy of the experiment, but the nature of its reproducibility implied an inherent error. A recalibration of the Thermofree potentiometer failed to have a significant effect, indicating a possible error in the smoothed thermocouple emf table in these regions.

The true specific heat of copper was determined by choosing representative data from four runs made at different power levels, correcting for losses. The reproducibility of the apparent specific heat data for the two higher power levels was checked several times in addition to the runs used in the final analysis. The reproducibility of the corrected data compared favorably with the reproducibility of apparent values taken at similar power levels. To illustrate the consistency of the drift correction, the apparent specific heat and the correction from three of these runs are shown in Figure 22. The circles surrounding the

data points were usually of sufficient size to enclose the spread in the corrected data. The average values of the true specific heats obtained in this manner are given in Table III.

Since it has been general practice to report the specific heat of copper in this range as a linear function of the temperature, a least squares line was taken on the final corrected curve. The maximum deviation of the data points from this line was about 0.4 per cent. The reproducibility, being less than this value, indicated that the specific heat is not exactly linear, or that the available emf data are not sufficiently smooth. In any case, a linear representation is reasonably accurate. The least squares line obtained for pure copper was:

$$C_p = 0.0931 + 2.175 \times 10^{-5} T \text{ (}^\circ\text{C)} \quad (7)$$

These data, along with the comparative values of Kelly, and Sykes and Jones, are plotted in Figure 23. Additional tabulated data, drift rates, and corrections are appended.

Specific Heat of Nickel

Exclusive of the initial investigation, twelve runs were made on specimens of nickel varying the power level from $K=17.83$ to 30.82 cal/gram hour. Several runs were made at very slow heating rates to determine the specific heat behavior in the region of the Curie point. The reproducibility of the apparent specific heat data for runs of similar power levels was again of the order of ± 0.2 per cent, although the K values were not exactly the same for any two runs. The reproducibility of the corrected data was of the same order as this, and the deviation from a smooth curve was rarely more than 0.1 per cent.

Specific heat values were obtained on two specimens of nickel weighing 305 and 234 grams. These specimens were machined from an ingot obtained by melting 99.95 per cent cobalt free nickel in a stabilized zirconia crucible under argon. The two specimens were used to check the effect of specimen size upon

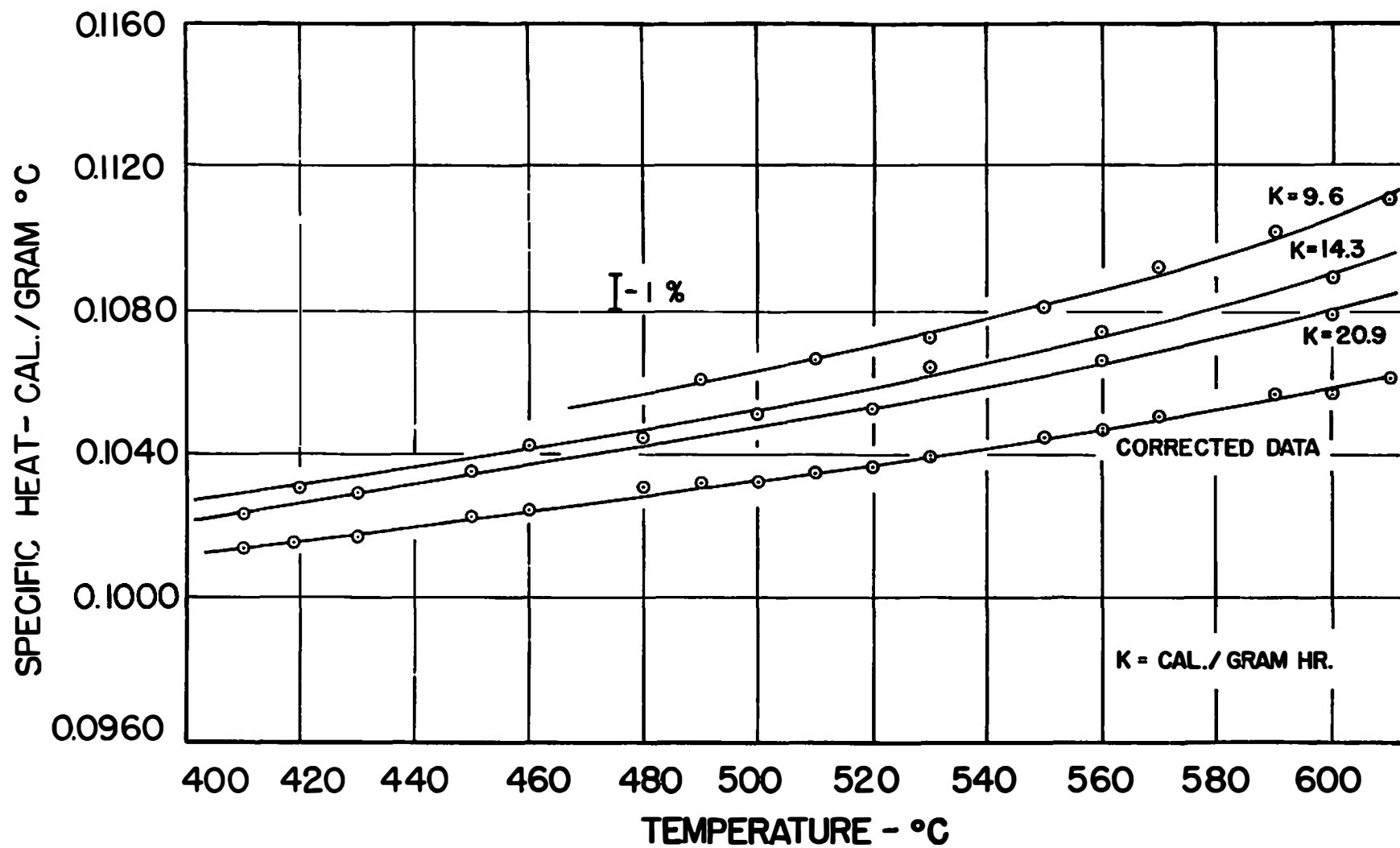


Figure 22. Apparent and true specific heat of copper.

TABLE III
TRUE SPECIFIC HEAT OF COPPER

(cal/gram °C)			
T °C	C _{pT}	T °C	C _{pT}
90	0.0942	320	0.1004
110	0.0953	330	0.1006
120	0.0957	350	0.1008
130	0.0961	360	0.1011
150	0.0965	370	0.1015
160	0.0968	390	0.1018
180	0.0972	400	0.1017
200	0.0976	410	0.1019
210	0.0977	430	0.1022
230	0.0984	440	0.1025
240	0.0987	450	0.1027
250	0.0990	480	0.1035
270	0.0994	520	0.1041
280	0.0996	560	0.1051
290	0.0999	600	0.1061
310	0.1003	610	0.1067

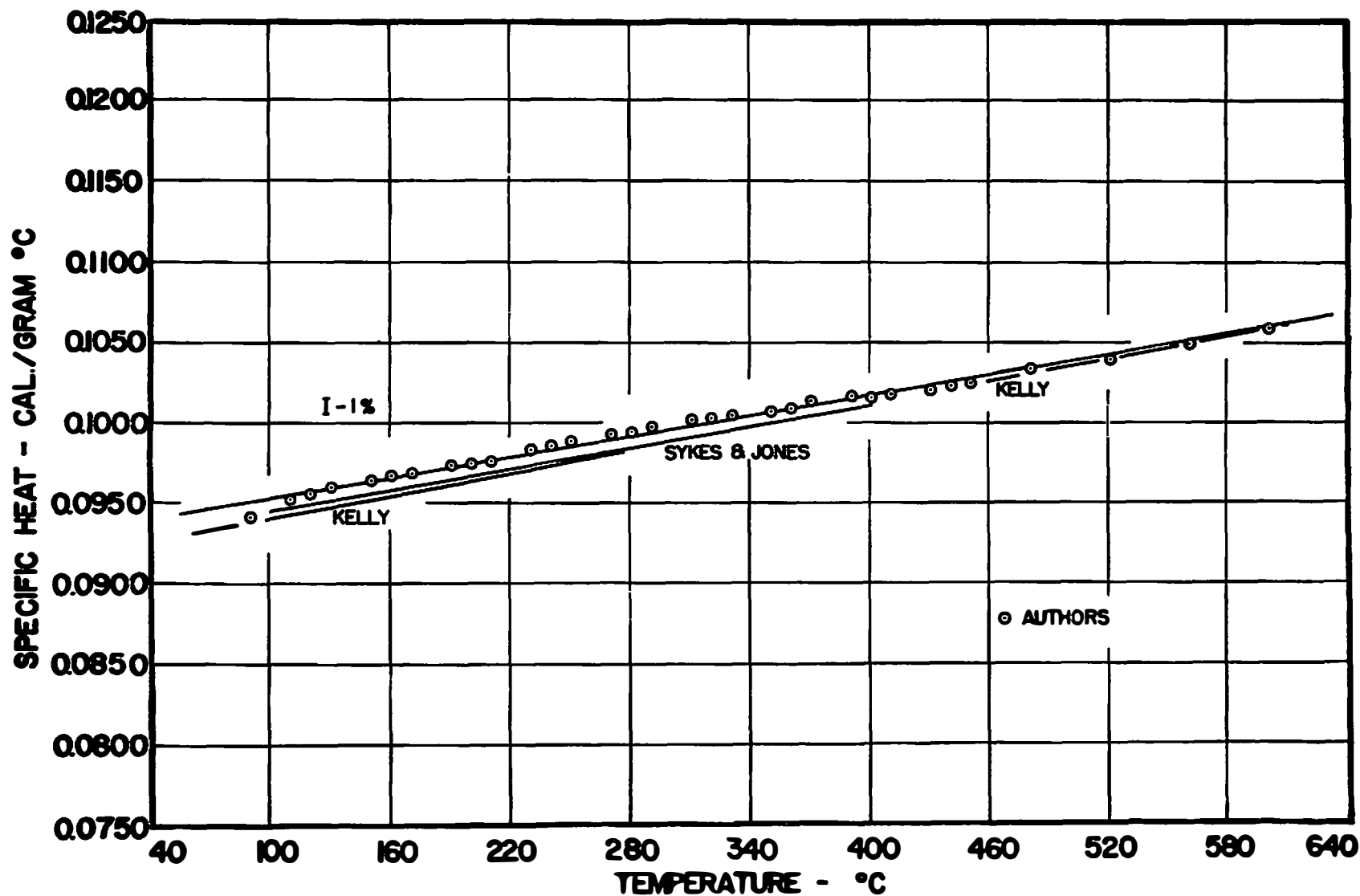


Figure 23. Specific heat of copper.

the data. This was also an indirect check of the heater correction and losses in the leads as these components remained equivalent. The corrected specific heat results from the two specimens were essentially identical, and data from both specimens were used in the final averaging. This fact supported the assumptions concerning the heater and lead corrections.

The true specific heat of nickel was determined by averaging the corrected values from six runs on the two specimens, K varying from 17.83 to 30.82. The reproducibility of this correction is shown in Figure 24, the spread of the corrected data for three of the runs being illustrated by the size of the "I" corresponding to the corrected values. A plot of the final averaged data given in Table IV is presented in Figure 25, the inset showing the specific heat behavior at the Curie point in more detail.

The Curie temperature for nickel was determined by very slow heating through the Curie region, with specific heat data being taken at two degree intervals. The Curie temperature was found to be about 354.5°C . The specific heat values obtained here were probably not as accurate as the rest of the data, as the low heating rates required a comparatively large correction.

A reproducible inflection in the specific heat curve for nickel was found on the high temperature side of the Curie region. This anomaly, although small, prompted cooling and heating rate experiments in order to determine if it were real, or the result of an error associated with the measuring procedure. Although cooling methods proved inadequate, heating rate data, (in terms of time required for a galvanometer sweep), for slow heating rates yielded curves that were somewhat smoother than the allied specific heat data. Although there is still some doubt, it is thought that the thermocouple calibration is responsible for small irregularities of this type.

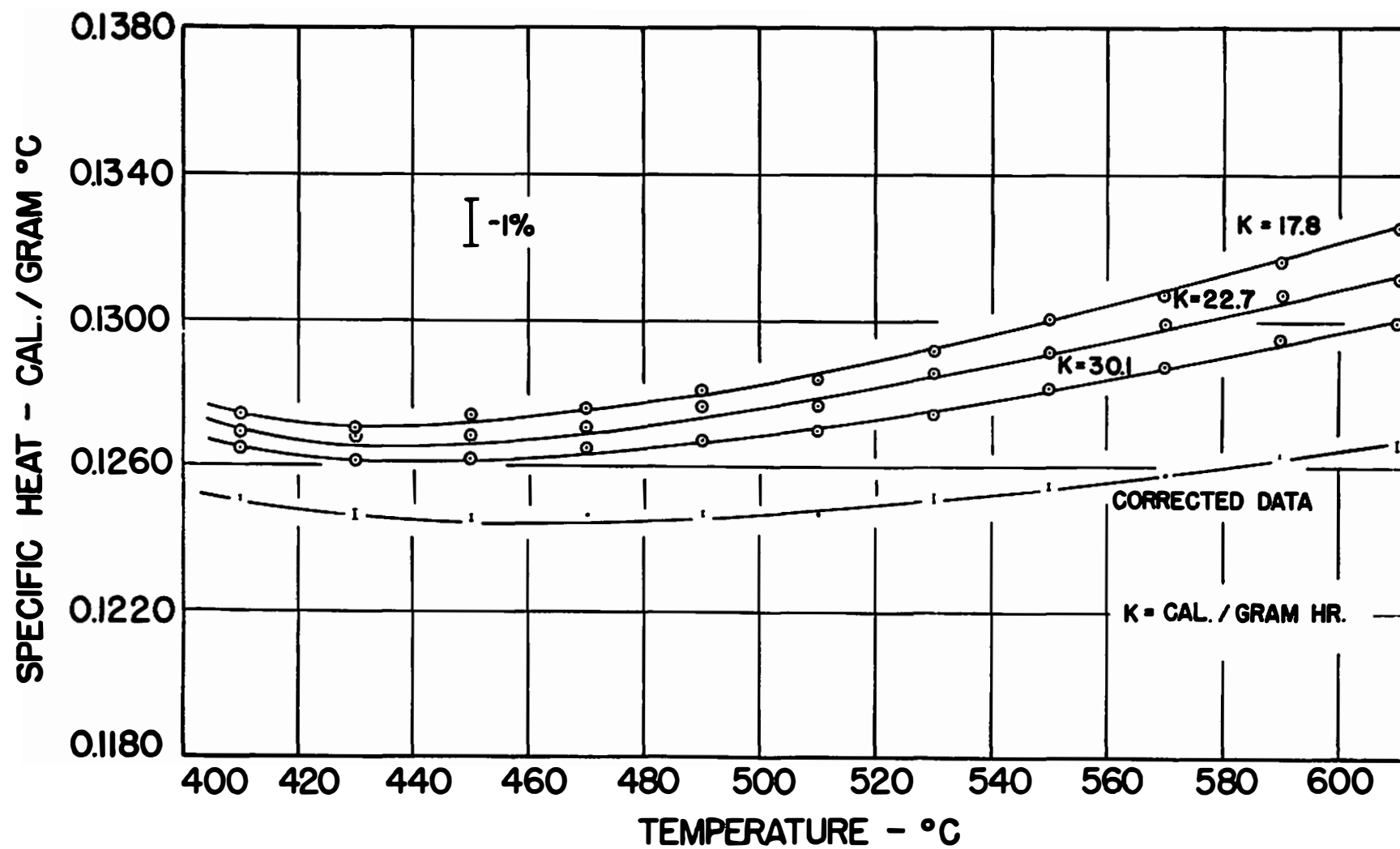


Figure 24. Apparent and true specific heat of nickel.

TABLE IV
TRUE SPECIFIC HEAT OF NICKEL

(cal/gram °C)			
T °C	C _{pT}	T °C	C _{pT}
50	0.1083	345	0.1470
70		355	0.1469
90	0.1113	365	0.1332
110	0.1139	375	0.1290
130	0.1161	385	0.1275
150	0.1181	395	0.1270
170	0.1198	410	0.1255
190	0.1218	430	0.1249
210	0.1238	450	0.1250
230	0.1265	470	0.1250
250	0.1292	490	0.1251
270	0.1318	510	0.1251
290	0.1249	530	0.1255
305	0.1272	550	0.1259
315	0.1392	570	0.1263
325	0.1411	590	0.1267
335	0.1437	610	0.1271

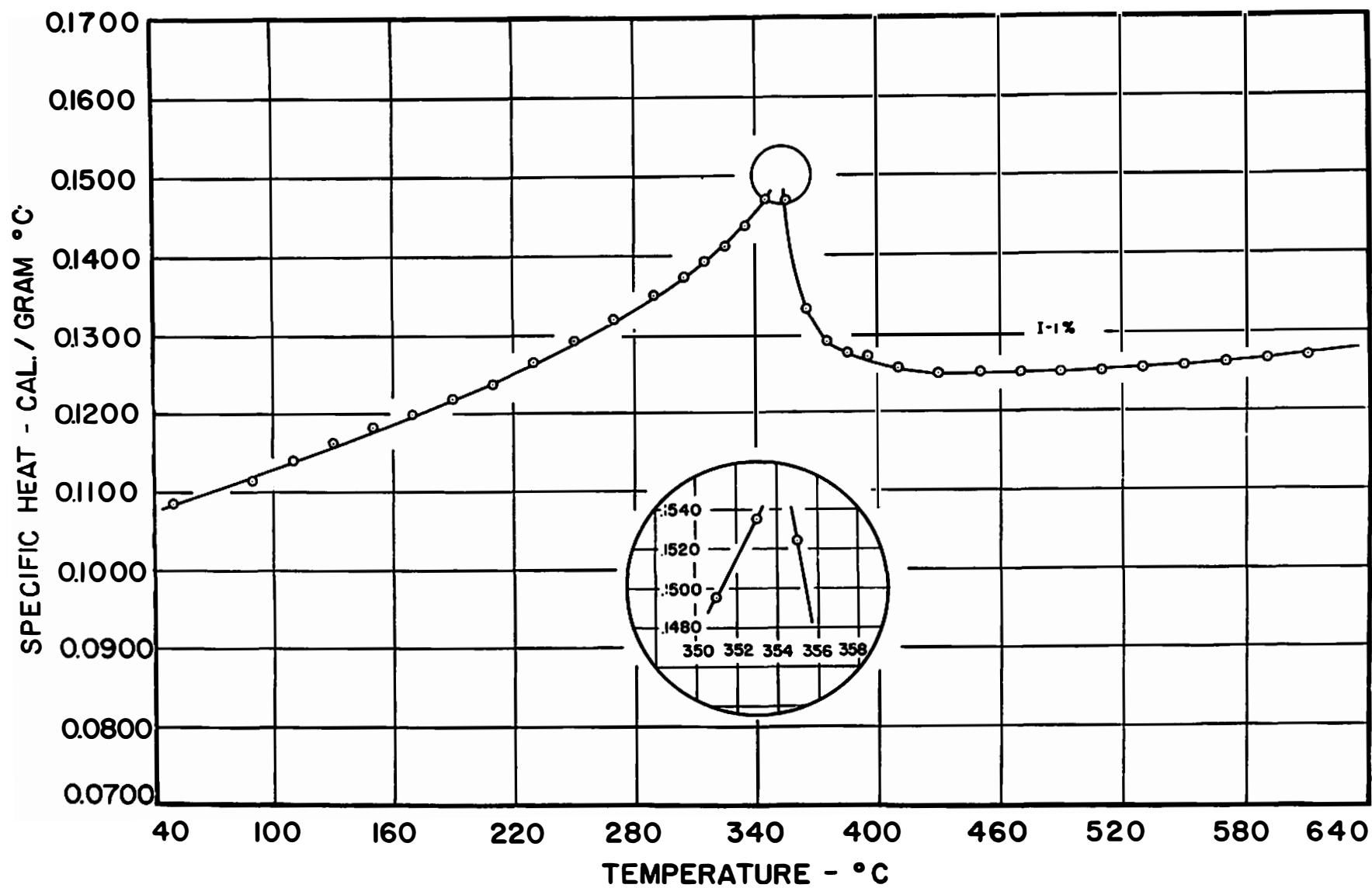


Figure 25. Specific heat of nickel.

Specific Heat Data on Copper-Nickel Alloys

Several copper-nickel alloys were prepared by melting under argon in an induction furnace. The ingots were homogenized at 900°C for 160 hours in a nitrogen atmosphere. The homogeneity of the ingots was checked by X-ray and metallographic techniques before machining the specimens. Three alloy specimens were investigated: 90.05, 75.07, and 50.04 weight per cent nickel.

The procedure used in the determination of the specific heats of these alloys was identical to the previous methods with one exception: the low temperature (below 200°C) data on the 50 and 75 per cent nickel specimens were obtained from runs made at low power levels. The reproducibility of the low temperature data was found to be improved by this procedure. Except for this low temperature data, the corrected data were obtained by averaging the specific heats from five of nine total runs for the 90 per cent alloy, six of ten total runs for the 75 per cent alloy, and four of nine total runs for the 50 per cent alloy. These final values are presented in Tables V, VI, and VII, and plotted in Figure 26 along with the data for the pure components. It is noticed that the specific heat of the alloys above the Curie region is not exactly a linear function of the temperature, but the error in assuming this would be very small.

Analysis of the Specific Heat Data

The reproducibility and self consistency of the specific heat data obtained in this investigation were most encouraging. It appears that the present design of the calorimeter is acceptable, and that specific heat data could be obtained for metals at high temperatures with an accuracy of better than ± 0.5 per cent.

Specifically, the data obtained for copper agree well with that reported by Kelly and Sykes and Jones over the whole range from room temperature to 620°C. The specific heat data obtained for nickel, especially above the Curie

TABLE V
SPECIFIC HEAT OF 90 WT. PER CENT NICKEL ALLOY

(cal/gram °C)			
T °C	C _{p_T}	T °C	C _{p_T}
50	0.1100	305	0.1219
70	0.1112	315	0.1217
90	0.1128	325	0.1213
110	0.1154	335	0.1214
130	0.1181	350	0.1212
150	0.1210	370	0.1217
170	0.1224	390	0.1218
190	0.1250	410	0.1219
205	0.1270	430	0.1224
215	0.1276	450	0.1230
225	0.1298	470	0.1234
235	0.1311	490	0.1239
245	0.1317	510	0.1242
255	0.1316	530	0.1251
265	0.1284	550	0.1251
275	0.1245	570	0.1255
285	0.1229	590	0.1258
295	0.1225	610	0.1261

TABLE VI
SPECIFIC HEAT OF 75 WT. PER CENT NICKEL ALLOY

(cal/gram °C)			
T °C	C _{p_T}	T °C	C _{p_T}
50	0.1045	205	0.1124
65	0.1061	210	0.1124
70	0.1065	230	0.1133
75	0.1075	250	0.1139
85	0.1088	270	0.1141
90	0.1089	290	0.1145
95	0.1091	310	0.1150
105	0.1105	330	0.1153
110	0.1113	350	0.1155
115	0.1115	370	0.1166
125	0.1130	390	0.1173
130	0.1124	410	0.1176
135	0.1126	430	0.1187
145	0.1129	450	0.1195
150	0.1126	470	0.1203
155	0.1126	490	0.1211
165	0.1122	510	0.1217
170	0.1122	530	0.1223
175	0.1119	550	0.1226
185	0.1122	570	0.1231
190	0.1123	590	0.1237
195	0.1122	610	0.1243

TABLE VII
SPECIFIC HEAT OF 50 WT. PER CENT NICKEL ALLOY

(cal/gram °C)			
T °C	C _{p_T}	T °C	C _{p_T}
35	0.0959	330	0.1096
50	0.0970	350	0.1103
70	0.0993	370	0.1113
90	0.1008	390	0.1122
110	0.1022	410	0.1128
130	0.1036	430	0.1136
150	0.1042	450	0.1143
170	0.1048	470	0.1149
190	0.1054	490	0.1153
210	0.1059	510	0.1156
230	0.1068	530	0.1160
250	0.1076	550	0.1163
270	0.1081	570	0.1167
290	0.1086	590	0.1170
310	0.1091	610	0.1173

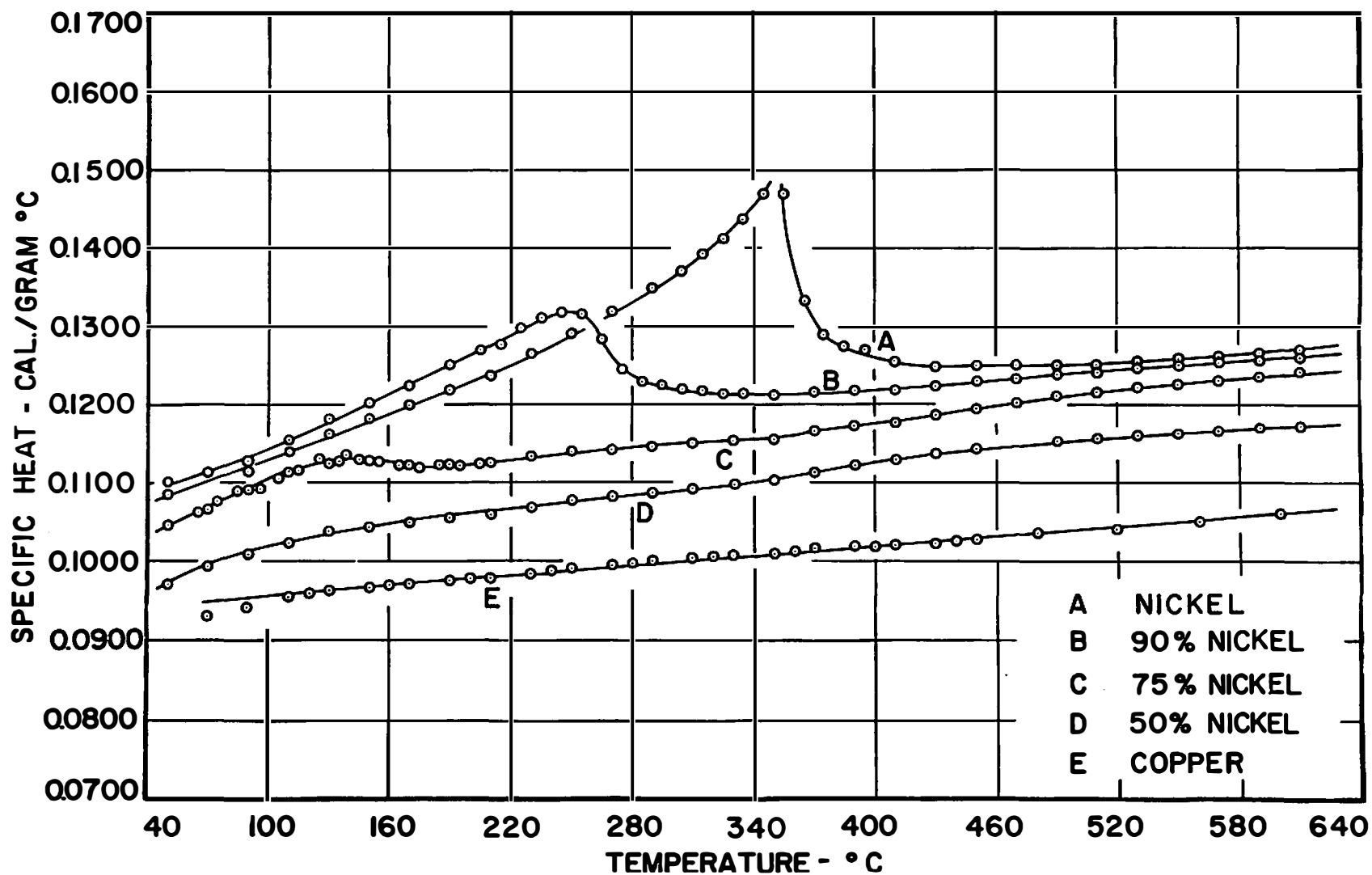


Figure 26. Specific heat of copper-nickel alloys.

point, represent a definite contribution to existing data, and should serve to clarify the true shape of the specific heat-temperature curve in this region. The majority of the data of previous investigators, (see Table I), appear to be high at temperatures above the Curie point; the slope of these curves also appears excessive. The spread of the data is considerably more than could be attributed to impurity levels of the specimens. The conditions under which data were obtained in this investigation make it very improbable that the specific heat values could be in error by as much as one per cent. Therefore, we are forced to conclude that the majority of the previous data was taken under conditions of excessive or uncorrected losses and are thus high. Comparative data are plotted in Figure 27. The data agree remarkably well with that of Moser, and the trend above the Curie region is evident.

Since the specific heat data for copper-nickel alloys above the Curie region by Grew are not conclusive, this investigation presents the first means of study of Kopp-Neumann behavior for the copper-nickel system from experimental high temperature specific heat data. Without the presence of magnetic effects on the specific heat, the curves are almost linear, and the applicability of the Kopp-Neumann rule to this system can be readily determined. The departure from this empirical rule was expressed as the difference in the observed and predicted specific heat values. The results are presented in Table VIII. The deviations are seen to vary slightly with temperature, and are different for the three alloys. However, as very small errors in the specific heat are accumulative in the calculation, only the general range of the data is important. The predicted specific heat values for the alloys vary from the experimental data up to about 1.5 per cent in this range of alloy contents. Positive values of ΔC_p , (in the nickel-gold system), have been published previously³⁴.

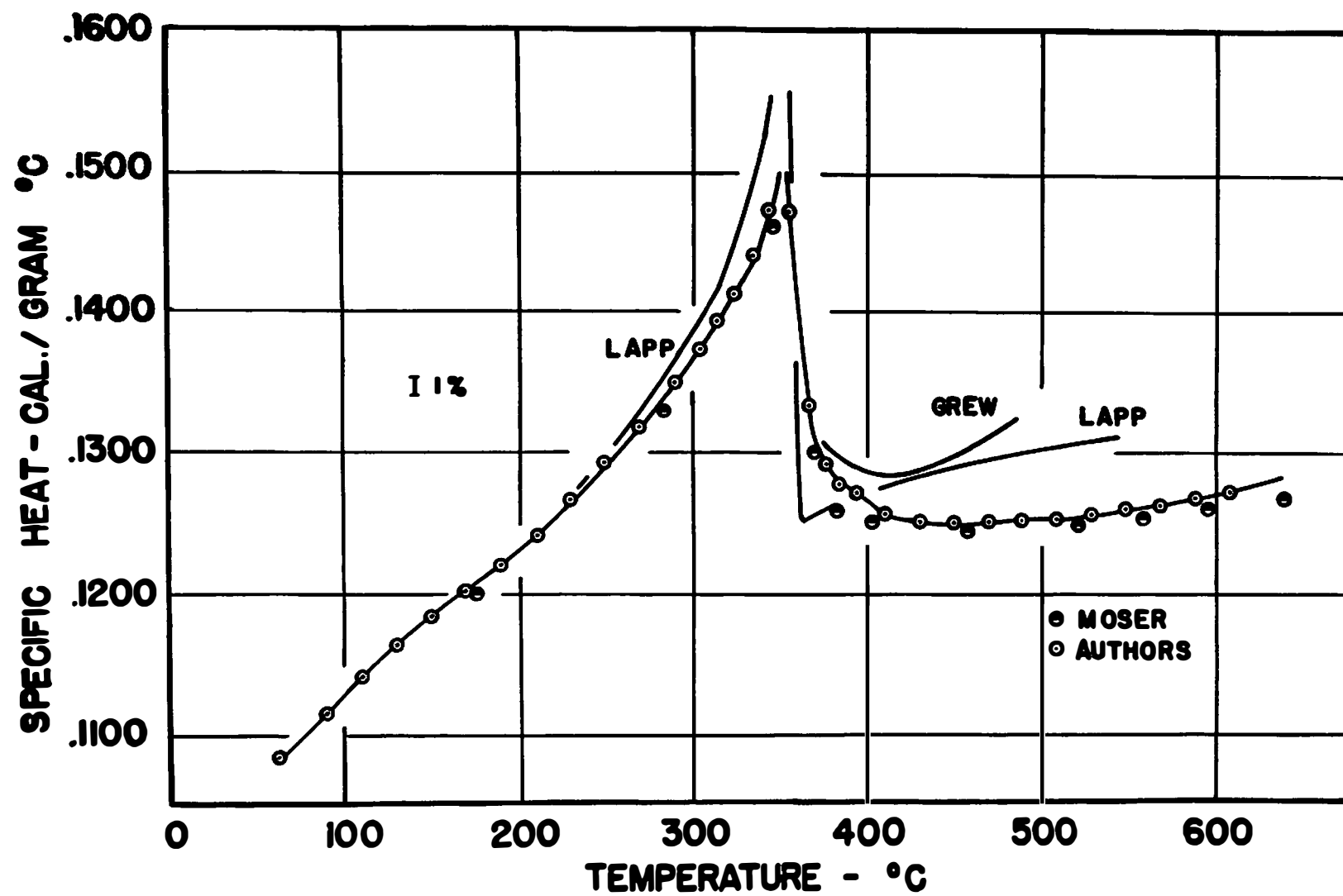


Figure 27. Comparative specific heat values for nickel.

TABLE VIII

KOPP-NEUMANN BEHAVIOR FOR Cu - Ni ALLOYS FROM 500 TO 640 °C

T °C	(C _p in cal/gram °C)								
	90.7 Mole % Nickel C _p (exp.)	76.5 Mole % Nickel C _p (exp.)	52.0 Mole % Nickel C _p (exp.)	90.7 Mole % Nickel C _p (K-N)	76.5 Mole % Nickel C _p (K-N)	52.0 Mole % Nickel C _p (K-N)	90.7 Mole % Nickel ΔC _p	76.5 Mole % Nickel ΔC _p	52.0 Mole % Nickel ΔC _p
500	0.1240	0.1216	0.1155	0.12295	0.11997	0.11482	0.0011	0.0016	0.0007
520	0.1243	0.1221	0.1158	0.12337	0.12039	0.11527	0.0009	0.0017	0.0005
540	0.1247	0.1225	0.1161	0.12377	0.12082	0.11572	0.0009	0.0017	0.0004
560	0.1251	0.1230	0.1164	0.12417	0.12121	0.11612	0.0009	0.0018	0.0003
580	0.1255	0.1235	0.1168	0.12459	0.12164	0.11657	0.0009	0.0019	0.0002
600	0.1259	0.1240	0.1171	0.12508	0.12214	0.11707	0.0008	0.0019	0.0000
620	0.1263	0.1245	0.1175	0.12549	0.12257	0.11751	0.0008	0.0019	0.0000
640	0.1267	0.1250	0.1178	0.12591	0.12298	0.11796	0.0008	0.0020	-0.0002

Stored Energy Measurements

With the accomplishment of considerably improved reproducibility of specific heat measurements, a series of experiments relating to stored energy determinations on cold-worked samples was undertaken. It was realized that a method would have to be obtained that would show the sensitivity and reproducibility necessary to extract reliable values of stored energy from the data. It was hoped that this could be done without modification of the calorimeter.

The problem was essentially one of measuring the small amount of energy liberated during the annealing process. The magnitude of this energy release has been experimentally determined for copper by a number of investigators, resulting in a considerable spread of values. The more recent publications show that the magnitude of the stored energy is smaller than at first proposed, perhaps due to the higher purity of the copper. Some of these data have been reviewed.

The first attempts to measure the stored energy in this investigation were patterned after the work of Gordon ⁴. The specimens were prepared by enclosing pieces of cold-worked copper sheet, 0.011 inches thick, in a thin steel container equipped with an internal heater similar to the type used in the solid specimens. The specimen was placed in the calorimeter, and heated quickly to the desired "reaction" temperature. The specimen power was turned off, the cylinder control offset slightly, if necessary, to prevent excessive drift, and the specimen temperature followed as a function of time under apparently adiabatic conditions. Theoretically, the energy release under these conditions should be accompanied by an associated temperature increase of the specimen, and the stored energy computed directly. However, three runs made in this manner, using approximately 75 per cent cold-rolled copper, failed to detect any temperature rise, even though the runs were continued from four to six hours.

Another similar method, involving the use of small rolled copper specimens without heaters, was also tried. Here, the specimen was suspended in the calorimeter and heated quickly to the reaction temperature by offsetting the cylinder control. When the specimen approached the desired temperature, the offset was removed and the isothermal cylinder control installed. The specimen temperature and cylinder-specimen temperature difference were then followed as a function of time. Except for the apparent lack of sensitivity, this was essentially the same experimental procedure as used by Gordon. The only temperature effect noted in these studies occurred when a specimen was inadvertently heated past the desired temperature range, and a definite inflection in its cooling curve was observed before it returned to the reaction temperature. The range of recrystallization temperatures used in these experiments were taken from Gordon's data, and were in all cases less than 180°C. It was later found that the recrystallization range for this copper was probably above that used by Gordon, and possibly not enough time at temperature was allowed for recrystallization to take place.

The first definite indications of stored energy release were obtained using the method of superimposed specific heats. In this case, the experimental method of Suzuki ³ was almost exactly duplicated. The specimen materials, cast rectangular blocks, were deformed in compression by a press of 200,000 pound capacity. The specimens were machined from these pressed blocks using a dry ice-acetone mixture as a coolant, and stored in the refrigerator until use. The stored energy was calculated from the difference of apparent specific heat values taken on two successive runs at the same power level.

An anomaly in the recrystallization behavior was observed for the four copper specimens used in these determinations. Copper specimens A and D (See Table X) recrystallized at about 275°C, as indicated by the largest heat

effect, while specimens B and C showed the largest heat effect at about 425°C. Neither specimen A nor specimen D showed any tendency for this high temperature heat release, while specimen B showed a secondary heat effect at 270°C. The apparent specific heat values and heat effects for the double runs on specimens A and B are given in Figures 28 and 29. The reproducibility was quite sufficient, and the reason for this unexpected behavior is not known. The results are contrary to those of Suzuki in both general appearance of the curves and magnitude of the stored energy. A single determination was made on a cold-worked 10.5 per cent nickel alloy specimen. An energy release comparable in magnitude to that observed in pure copper was found at 350°C. The data for this run are plotted in Figure 30.

The apparent failure of the specific heat method to yield more reproducible data was thought to be due to the small size of the observed heat effect, since the largest observed was approximately 0.05 cal/gram. In this case; errors in the apparent specific heat of ± 0.2 per cent for both runs over the temperature range of recrystallization could cause an error of 50 per cent or more in the calculated energy. For this reason, another method was attempted.

It was thought that the dual specimen method, essentially that used successfully by Clarebrough, et.al.^{5, 8}, could be adapted to the present calorimeter with a minimum of renovation of the main components of the system. In this method, two specimens, one annealed and one cold-worked, are heated under adiabatic conditions by internal heaters in each specimen. The temperature difference between the specimens, as indicated by a sensitive differential thermocouple, is kept negligible by continuous adjustment of the relative power inputs to the heaters. The release of stored energy is associated with the difference in the relative power-time curves for two consecutive runs. The advantage of this method is that the energy effect is measured directly, not as a temperature or

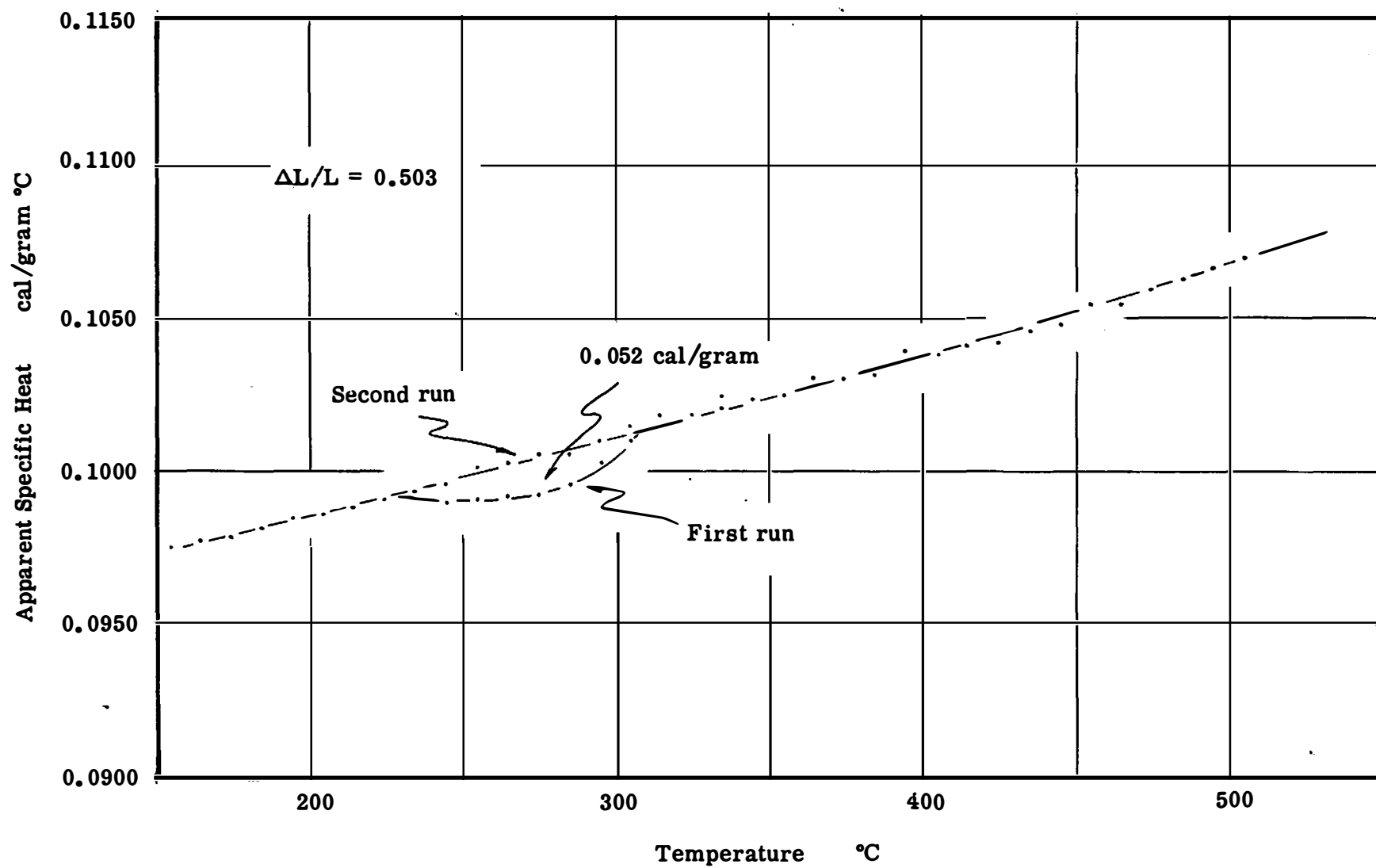


Figure 28. Apparent specific heat of cold-worked copper specimen A.

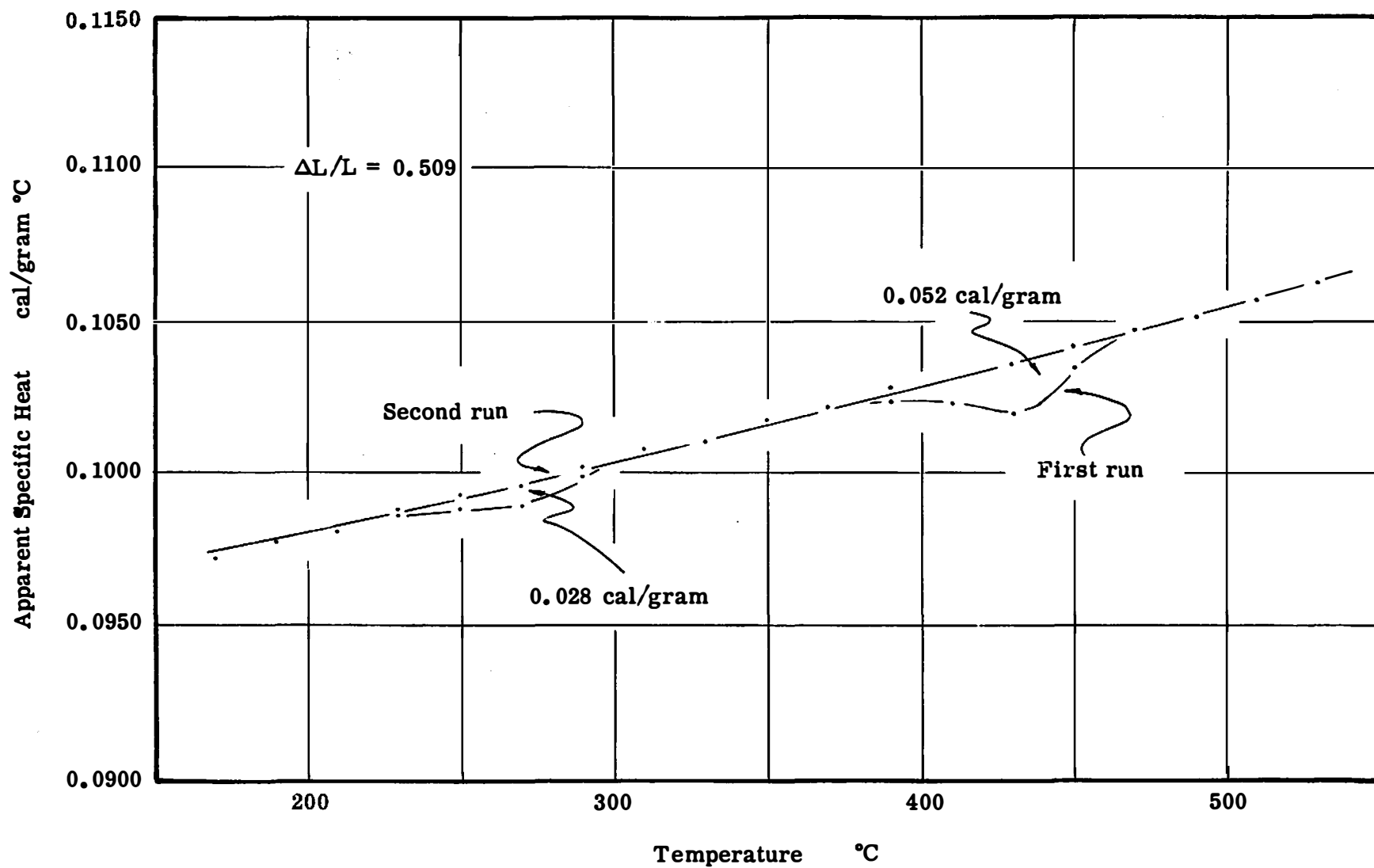


Figure 29. Apparent specific heat of cold-worked copper specimen B.

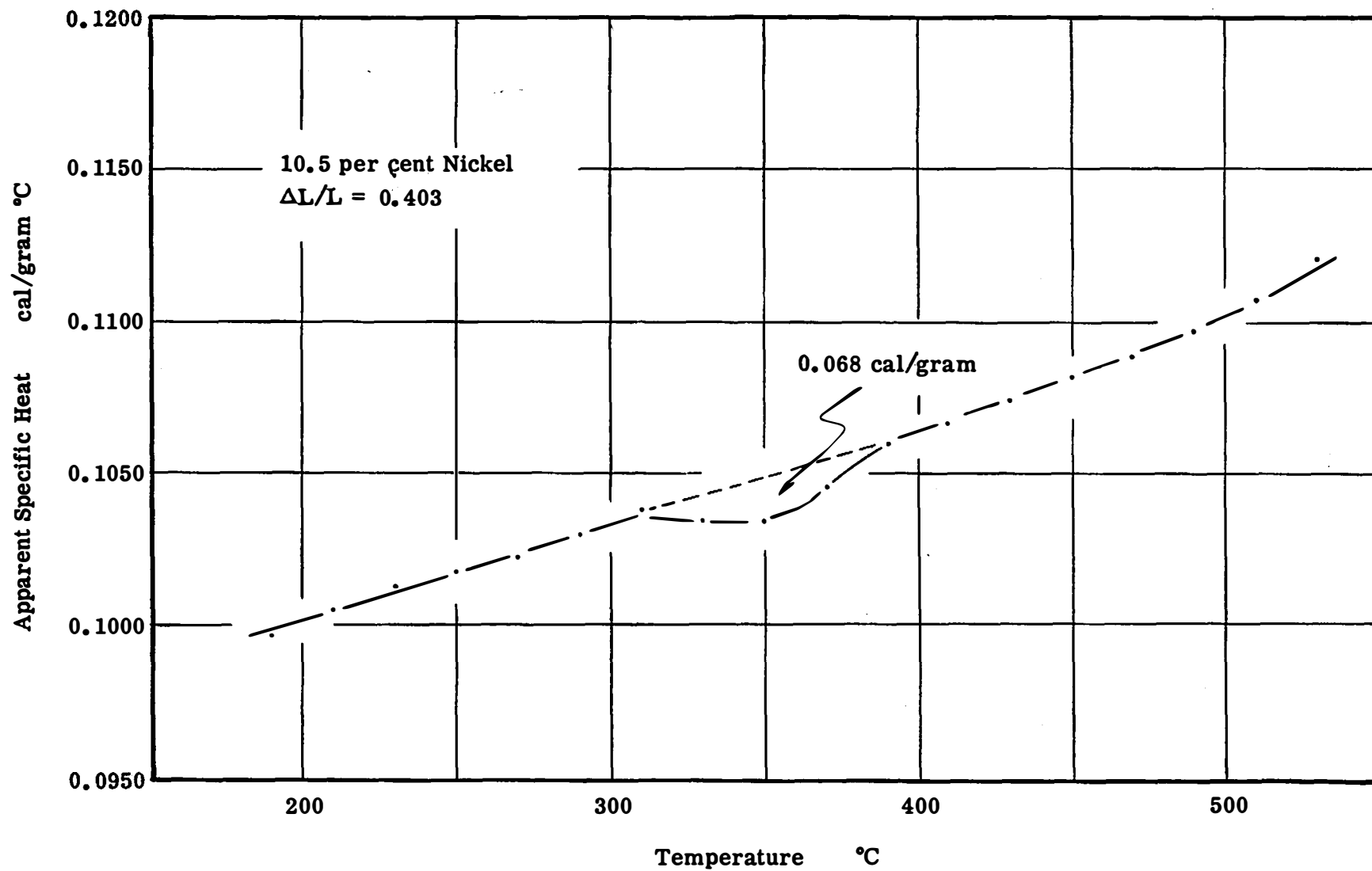


Figure 30. Apparent specific heat of cold-worked alloy J.

specific heat change. Also, the size of the specimens determines the maximum power difference for a given amount of deformation, so that large specimens offer greater accuracies of measurements.

The specimen power system, shown in Figure 31, was designed in such a way as to allow the necessary sensitivity in controlling the power difference between the specimens. This was accomplished by installing a precision 10 turn 1000 ohm helipot across the power source, with the variable tap connected to the common power lead. In this way very small changes in the relative power could be effected. Voltage and current measurements were made on both specimens in the usual manner.

The specimens were machined in the shape of half-cylinders, $7/8$ of an inch in diameter and about $2\frac{1}{4}$ inches long. The heater assembly was installed in the specimens in counter-bored $3/16$ inch holes, in a manner somewhat similar to that used in the larger specimens. Since the working diameter of the calorimeter tube is only $1\frac{1}{4}$ inches, space considerations were very important, and extreme care was necessary in mounting the specimens, especially since it was decided to suspend the specimens side by side. The complete specimen assembly consisted of the twin specimens, heaters, power leads, voltage taps, and the measuring and differential thermocouples and leads. A platinum-constantan differential thermocouple developing $46\text{ }\mu\text{v}$ per degree was used to measure temperature differences between the specimens. The specimens were separated by three small ceramic spacers. Heat interchange between the two specimens, although perhaps not as good as desirable, was kept as small as possible by the high polish of the specimen and the high vacuum. Photographs of the specimen and its suspension are given in Figures 32 and 33.

Two operators were required to make the necessary measurements and adjustments during a run. The first recorded the absolute temperatures and

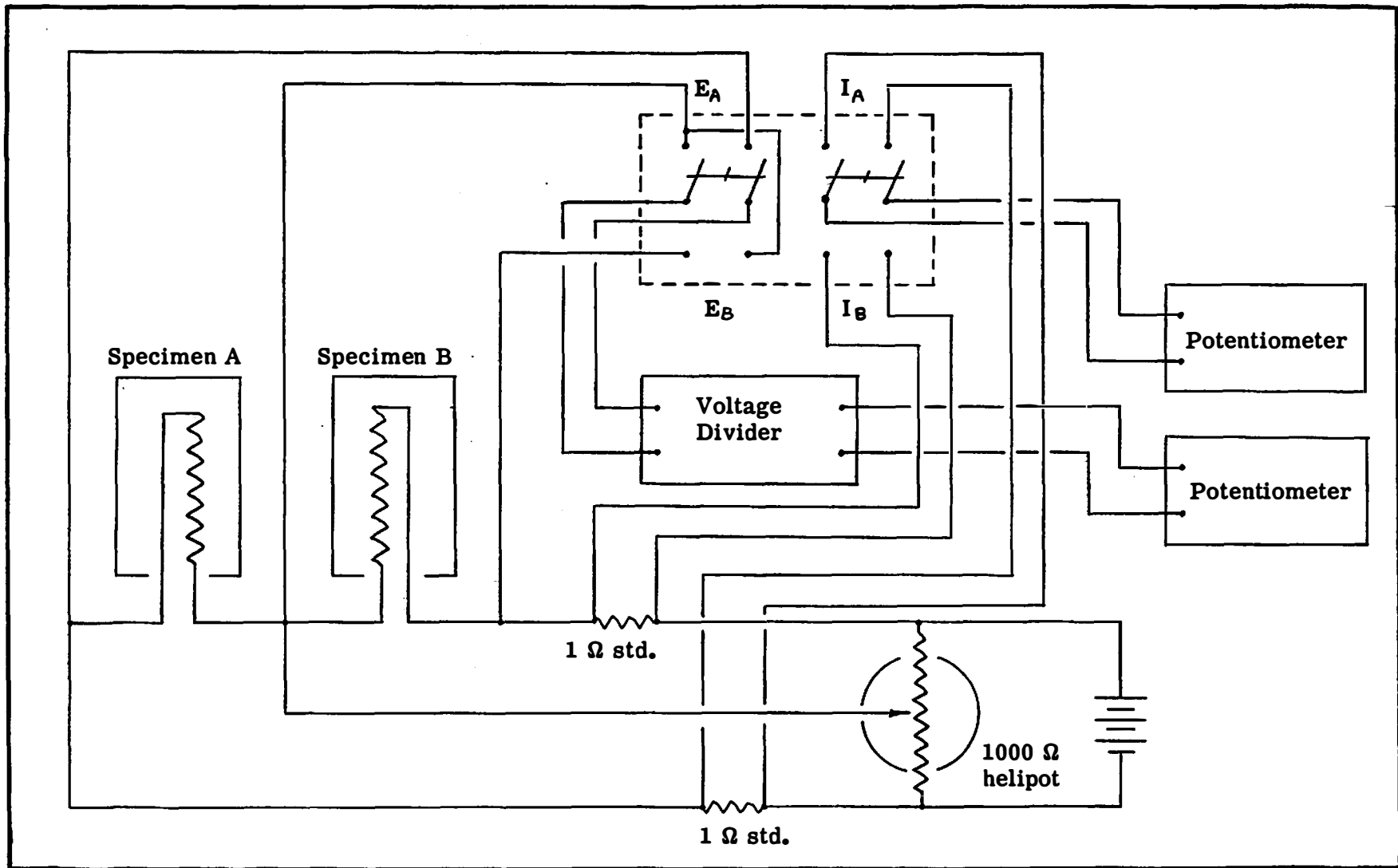


Figure 31. Schematic power and measuring circuit for dual specimens.

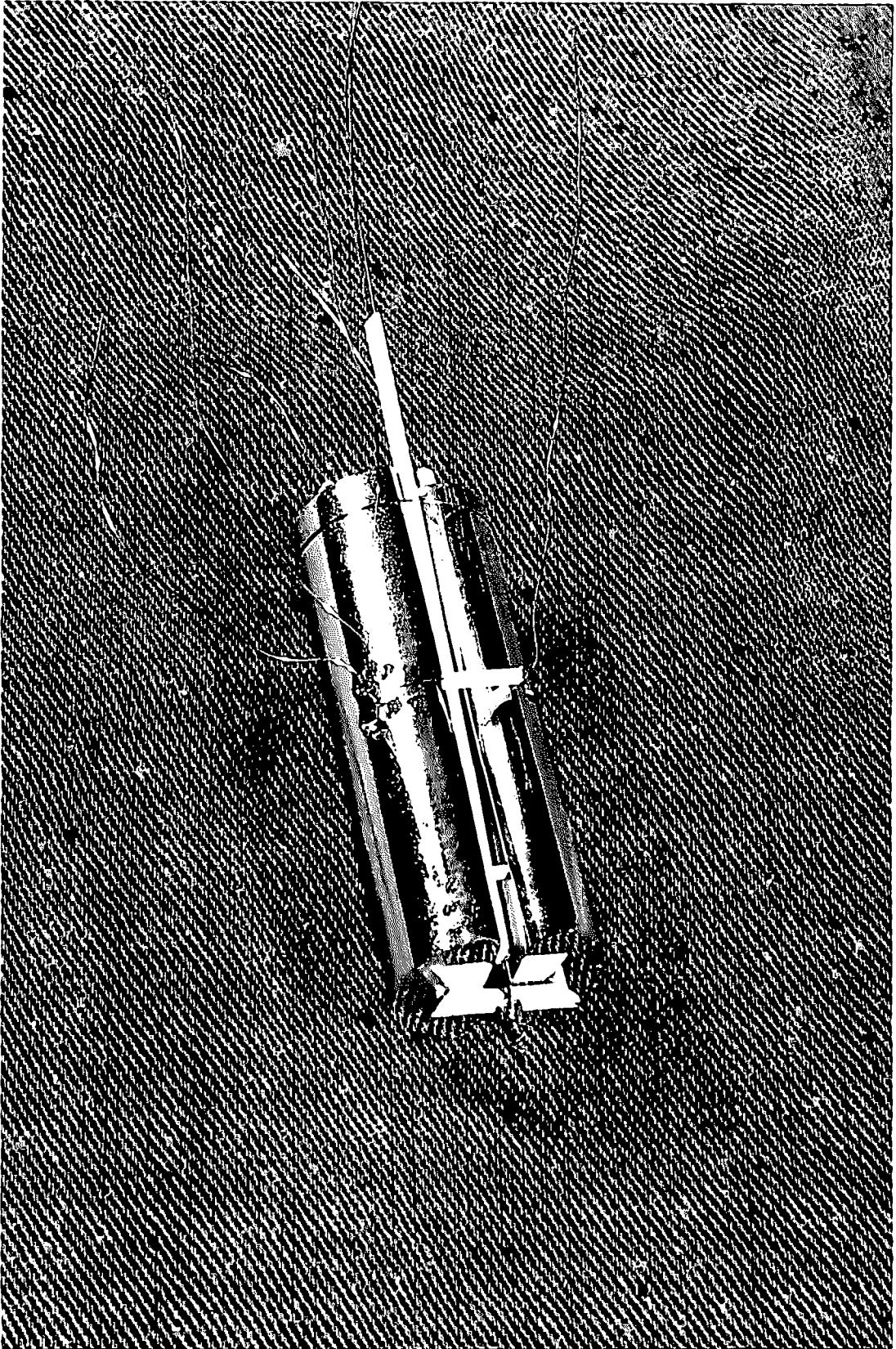


Figure 32. Photograph of dual specimen.

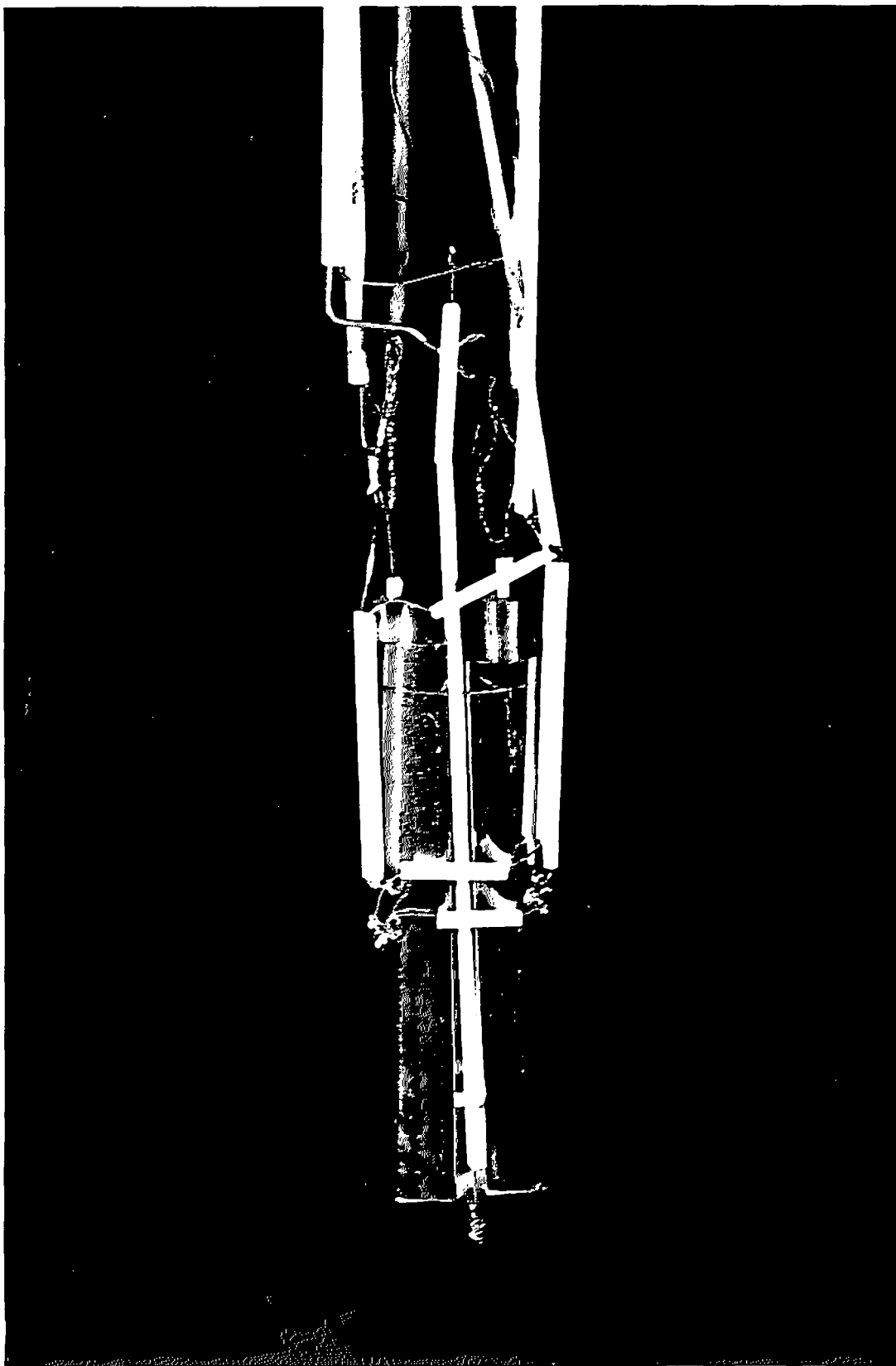


Figure 33. Photograph of suspended dual specimen.

temperature differences, adjusted the specimen power control, and inspected the control components of the calorimeter. The second observer recorded the voltage and current readings at definite time intervals. In this way a curve of differential power as a function of time was obtained, with corresponding temperature checks.

The method proved reasonably satisfactory as three of the first five determinations on pure copper gave plausible and consistent results. One of these five runs was lost due to a faulty specimen suspension; no apparent reason was evident for the other, except that no heat effect was observed. The heat effect was computed by graphically integrating the area between the cold-worked and annealed runs on the differential power-time curves. A more or less uniform background power difference was observed due to the slight difference in specimen weights and loss characteristics. The experimental data are tabulated in the Appendix.

The experimental power difference curves, both for the cold-worked and annealed runs, did not show sufficient consistency to accurately evaluate any heat effect prior to recrystallization. However, the irregularities in the curves became less as the temperature increased, and a reasonably accurate integration of the recrystallization heat effect could be made using Simpson's rule. If the background power is subtracted out by judicious use of the data obtained during the annealed run, the three runs may be plotted on a single graph for comparison. This is done in Figure 34. Some detail has been lost in this plot by using a temperature rather than a time basis, but since the heating rates were not identical the temperature comparison is more significant. The shape of the curves is interesting. The recrystallization curves for specimens D' and E', 67.5 and 46.7 per cent reduction in length respectively, heated at 3 °C/minute, are both very sharp and occur over a relatively small temperature interval. The curve for specimen A', 57.1 per cent reduction, heated at 2 °C/minute shows a peak

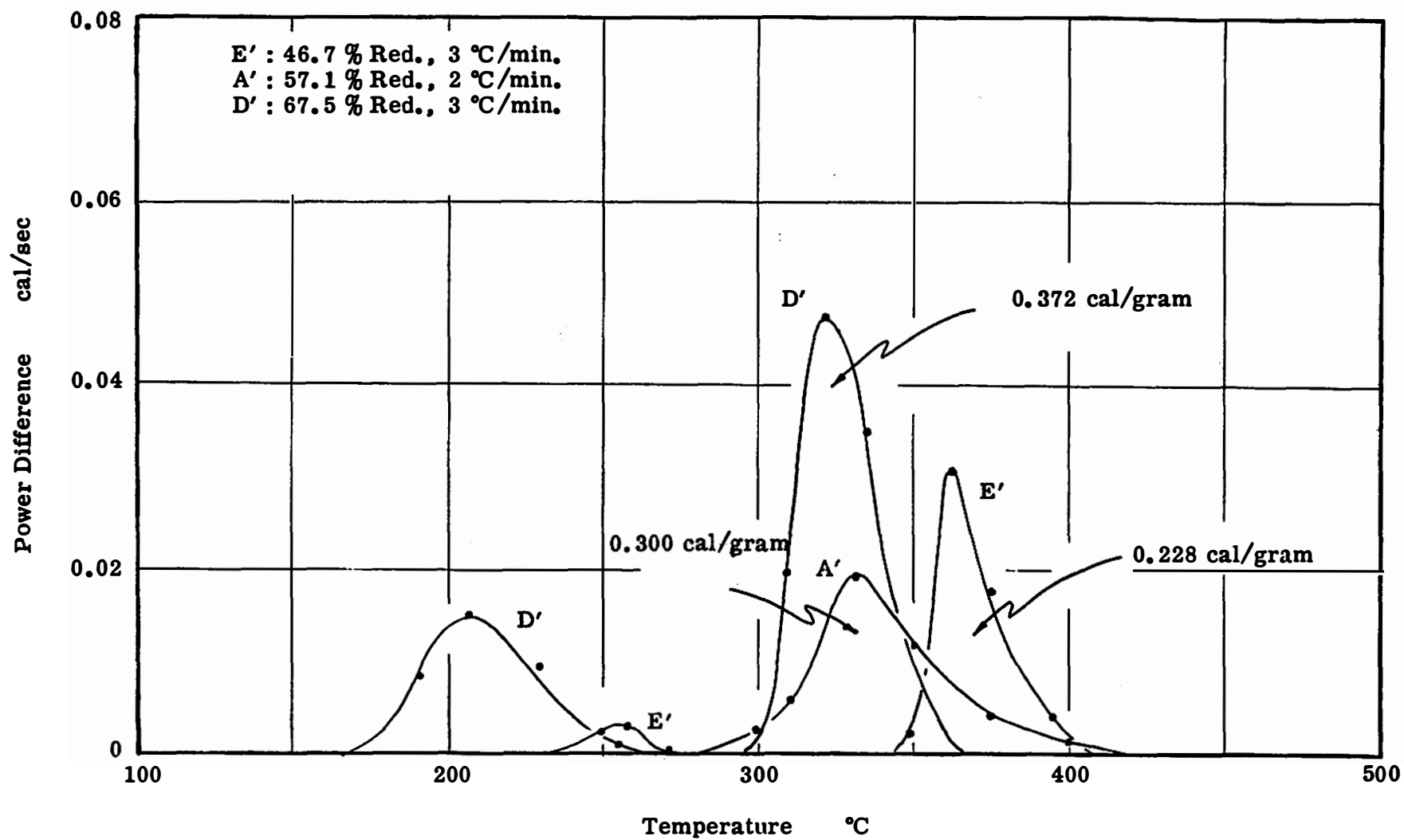


Figure 34. Power difference curves for cold-worked copper specimens.

at an intermediate temperature as expected, but the heat was released over a much wider temperature range. Since this was the first run of this type, and the sensitivity to power changes had not yet been determined, some of this lag in A' could have been due to experimental difficulty in eliminating the observed temperature difference by power adjustment. In any case, the error in the total integrated heat effect would be small, subject only to differential losses between the specimen due to the small temperature difference.

It is unfortunate that the data were not such that definite statements could be made about the nature of the possible heat effect of pre-crystallization or recovery phenomena. However, in two of the three runs there appeared to be a real heat effect prior to the onset of recrystallization. The magnitude of this energy was quite large in the case of sample D', amounting to approximately one third of the recrystallization heat. The shape of this recovery curve, if it may be termed such, is similar to the one obtained during recrystallization, in contrast to the type of recovery obtained by Clarebrough in arsenical copper. Gordon, using the isothermal procedure, found that recovery accounted for only a very small portion of the total heat effect.

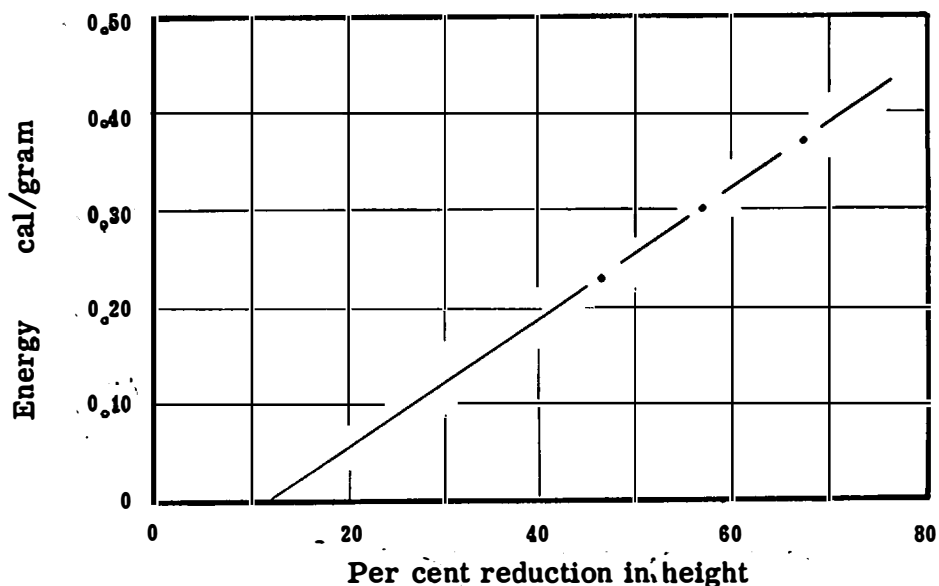


Figure 35. Heat of recrystallization for copper deformed in compression.

Graphical integration using Simpson's rule was used to determine the heat effect associated with recrystallization. The values obtained were 0.228, 0.300, and 0.372 cal/gram for specimens deformed in compression by 0.467, 0.571 and 0.675 reduction in height respectively. If the values of stored energy are plotted as a function of the per cent reduction, (Figure 35), a straight line may be drawn which intercepts the zero recrystallization energy at about 10 per cent reduction. Whether the data justify a linear extrapolation is problematical, but the results correspond to the general behavior observed by both Gordon and Clarebrough. The recrystallization energies of these investigators, although lower in magnitude by a factor of 2, extrapolate linearly to slightly positive values of the deformation.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

During the course of this investigation, the goal of obtaining highly reproducible true specific heat values over a wide range of temperature has been achieved. The equipment and techniques of operation used in attaining this degree of precision have been discussed. In general, the ability, the limitations, and the problems involved in the operation of a high temperature dynamic adiabatic calorimeter have been described. It is hoped that the solution to some of these problems found during this research will help in promoting the adiabatic calorimeter as a more common laboratory tool.

Considering the operating characteristics of this calorimeter, and the data obtained during this investigation, the following conclusions can be made:

1. The design and method of operation of this calorimeter have reached a stage where extremely reproducible and self consistent specific heat data on metallic systems can be obtained. This has become possible through the use of careful techniques, and solution to some of the experimental problems associated with high-temperature operation.
2. The validity of the treatment of the apparent specific heat data has been proven by the manner in which the correction terms rectify data taken under different conditions of operation. The consistency of the corrected data correspond almost exactly to the smoothness of the apparent specific heat data.
3. The specific heat of copper from room temperature to 620°C may be represented as a linear function of the temperature with an error of less than ± 0.5 per cent. The data compare well with that of Sykes and Jones ¹², and that reported by Kelly ²⁰.

4. The specific heat of nickel has been determined from room temperature to 620°C with an accuracy better than ± 0.5 per cent. The data compare favorably with the data of other investigators below the Curie point. However, the data above the Curie point are not as high as those obtained by Sykes ²⁴, Grew ²⁸, and others, but agree very well with the data of Moser ¹⁴. In fact, the agreement with Moser over the whole range is better than one per cent. The divergence of values above the Curie range cannot be reconciled by composition differences or experimental spread of the data. Therefore, it must be concluded that inherent experimental error has made the data of these previous investigators considerably high.

5. The specific heat of copper-nickel alloys, containing 90.05, 75.07, and 50.04 weight per cent nickel, has been determined to ± 0.5 per cent in the temperature range 70 to 620°C. Above the Curie range, the data can be reasonably represented by a straight line, but not as well as that for pure copper. The effect of copper additions to the Curie temperature as obtained in this investigation agree well with those obtained by Grew ²⁸, Krupkowski ³⁵, and Marian ³⁶. It appears that the Kopp-Neumann rule of additive heat capacities can be applied to this system above 450°C with only limited accuracy, -1.5 per cent of the absolute value. Naturally, the rule does not directly apply in the Curie region.

6. The calorimeter used in this investigation will not be easily adaptable for use in the precision determination of stored energy in metals. The failure to show sufficient sensitivity, especially by the method of superimposed specific heats, was surprising considering the reproducibility of the specific heat measurements. The dual specimen technique showed promise, but a considerable improvement will be necessary if more reliable data is to be obtained.

7. The stored energy values reported for cold-worked copper in this research, 0.2 to 0.37 cal/gram, appear high compared with the data of Gordon ⁴ and Clarebrough ⁶, and low compared with those of Suzuki ³, Quinney and Taylor ¹¹, and other early investigators. The reproducibility of these data has not been established, but the values from the three runs for different deformation were self consistent and compatible with the expected trends.

Although the calorimeter is now capable of permitting the computation of accurate specific heat data, heats of transformation, and other large thermal effects, further refinement of the data may be attained by appropriate changes of the system. The feasibility of these revisions would depend upon the type of measurements to be made and the specific system under observation. Some items which might prove beneficial to the overall operation of the calorimeter are listed below:

1. Replacement of the lead helium seal gasket, and installation of a monel tube with greater wall thickness would raise the safe operating temperature to 1000°C.

2. Improvement of the adiabatic conditions in the calorimeter by reducing the temperature gradients and possibility of hot spots would reduce the magnitude of the corrections to the apparent specific heat data. This could be done several ways, (rewiring, radiant heating, etc.), all of which would seemingly reduce the rate of response and control. A reasonable compromise would have to be made.

3. By placing the control thermocouples in appropriate positions on the outside of the adiabatic chamber, the necessity of running the leads, encased in ceramic and quartz tubes, inside the chamber would be eliminated. Not only do these tubes occupy precious space inside the calorimeter, but they can serve

as a heat sink for losses from the specimen. If this were done, the tedious task of making thermocouple welds inside the tube would also be eliminated.

4. Further improvements in the methods for eliminating thermals and pickup on the control system should continually be sought.

5. The possibility of using another thermocouple system in the calorimeter should not be eliminated. Materials of sufficient stability, generating higher thermal potentials, would enhance the reproducibility of the data, especially for those taken at small temperature intervals. If specific heat data over small temperature ranges are desired, a six dial potentiometer would be beneficial for use with the Pt-Pt 13 % Rh thermocouples.

6. If the study of stored energy is to be continued by dual specimen calorimetry, different methods of specimen suspension should be studied. Since the working space in the present calorimeter is small, this research might warrant the construction of another calorimeter with a larger adiabatic chamber.

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APPENDIX

TABLE IX
ANALYSIS OF SPECIMENS

Specimen or Material	Chemical		Spectrographic					Elements Checked But Not Found
	Cu	Ni	Co	Fe	Si	Al	Ag	
Copper Bicrystal Used in Specific Heat Determinations	Major	-	-	0.00X	-	-	-	Pb, Sn, Zn, Bi, As, Sb, Cd, In, Ga, Tl, Ge, P, Mg, Cr, Mo, W, Ti, V, Mn, Na, Ca, K, Li, Ba, Sr.
Electrolytic Copper Used in Alloy Prep.	Major	-	-	0.00X	-	-	0.000X	
Nickel Specimen and Alloy Material	0.00X	Major	0.0X	0.00X	0.00X	0.00X	-	Mn, Cr, Ti, Mg, W, V, Mo, Zn, Pb, Sn, Sb, Bi, As, Zr, Nb, Na, Ca, K, Li, Ba, Sr.
90 % Ni Specimen	9.85	Bal.	-	-	-	-	-	
75 % Ni Specimen	24.77	Bal.	-	-	-	-	-	
50 % Ni Specimen	50.65	Bal.	-	-	-	-	-	
Alloy J	Bal.	10.51	-	-	-	-	-	

TABLE X
CALORIMETER SPECIMENS

Specimen	Approximate Analysis	Treatment	Specimen Weight (grams)	Heater Weight (grams)	Total Weight (grams)
Copper	Pure Copper	As-grown bicrystal	225.874	1.318	227.192
Nickel A	Pure Nickel	Cast and annealed	303.084	2.183	305.267
Nickel B	Pure Nickel	Cast and annealed	231.854	2.183	234.037
90 % Nickel	90.05 wt. % Nickel	Cast and homogenized	167.994	1.730	169.724
75 % Nickel	75.07 wt. % Nickel	Cast and homogenized	231.166	1.778	232.844
50 % Nickel	50.04 wt. % Nickel	Cast and homogenized	226.485	1.748	228.233
C. W. Copper A	Pure Copper	$\Delta L/L = 0.503$	223.215	2.648	225.863
C. W. Copper B	Pure Copper	$\Delta L/L = 0.509$	218.209	1.899	220.108
C. W. Copper C	Pure Copper	$\Delta L/L = 0.618$	153.660	2.454	156.114
C. W. Copper D	Pure Copper	$\Delta L/L = 0.597$	172.513	2.228	174.741
Alloy J	10.55 wt. % Nickel	$\Delta L/L = 0.472$	138.130	2.613	140.743

TABLE XI**CALORIMETER DUAL SPECIMENS**

Specimen Pair	Cold-Worked Section Weight (grams)	Rate of Deformation (in/min.)	Deformation	Annealed Section Weight (grams)
Copper A'	85.784	0.05	0.571	85.880
Copper B'	85.361	0.05	0.737	85.880
Copper C'	85.653	0.10	0.428	85.880
Copper D'	84.880	0.10	0.675	85.784
Copper E'	85.482	0.10	0.467	85.784
8.9 wt. % Nickel	85.360	0.10	0.601	84.980

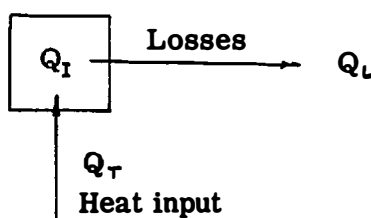
DERIVATION OF THE CORRECTION EQUATIONS

The two main errors in the apparent specific heat were compensated for by applying appropriate corrections terms to the experimental data. These errors arise from: (1) heat losses due to non-adiabatic conditions, and (2) finite weight and specific heat of the specimen heater.

The correction term for heat losses (or gains) is based on a simple heat balance, and can be derived as follows:

A. Drift Correction.

Consider the specimen, receiving energy Q_T from the specimen heater, and emitting, either by radiation or conduction, Q_L , during the time and temperature interval Δt and ΔT , respectively.



Therefore $Q_I = Q_T - Q_L$, the effective energy to the specimen.

now:

$$C_{p_T} = \frac{Q_I}{g\Delta T} = \frac{Q_T}{g\Delta T} - \frac{Q_L}{g\Delta T}, \text{ where } g = \text{specimen wt.}$$

Define the drift rate as $R_{(T)} = \frac{\Delta T}{\Delta t}$ when $Q_T = 0$ or $Q_I = -Q_L$

therefore:

$$R_{(T)} = \left. \frac{\Delta T}{\Delta t} \right]_{Q_T=0} = \frac{-Q_L}{C_{p_T} g \Delta t}$$

$$\text{or } Q_L = -R_{(T)} C_{p_T} g \Delta t$$

using the definition of C_{pa} , the apparent specific heat,

$$C_{p_{\tau}} = C_{pa} + \frac{R_{(\tau)} C_{p_{\tau}} g \Delta t}{g \Delta T}$$

Rearranging:

$$C_{p_{\tau}} = \frac{C_{pa}}{1 - \frac{R_{(\tau)} \Delta t}{\Delta T}}$$

The experimental apparent specific heat values are computed from the data by the equation:

$$C_{pa} = EI \Delta t \times f' \quad \text{where } f' = C_p \text{ factor} = f/g \Delta T$$

$$= \frac{\text{Conversion factor}}{\text{spec. wt.} \times \text{temp. interval}}$$

rearranging

$$\frac{\Delta t}{\Delta T} = \frac{C_{pa}}{f' \Delta T EI}$$

Substituting:

$$C_{p_{\tau}} = \frac{C_{pa}}{1 - \frac{C_{pa} R_{(\tau)}}{f' \Delta T EI}}$$

For a given specimen, data taken at a set temperature increment, and for a uniform power level, $f' \Delta T EI$ is very nearly constant, and the equation can be simplified to its final form.

$$C_{p_{\tau}} = \frac{C_{pa}}{1 - \frac{C_{pa} R_{(\tau)}}{K}}$$

If $R_{(\tau)}$ is measured in °C per hour, the exact value of K becomes equal to $3600 f' \Delta T EI$ cal/gram hour. This equation was used with experimental drift rate measurements to correct the apparent specific heat values for losses of this nature. Assuming that two or more runs at different power levels are available, a correction can be derived which does not depend upon

the drift rate. If the drift rate term is eliminated from the correction equation under these conditions; it can be shown that:

$$C_{p_T} = \frac{C_{p_1} C_{p_2} (K_2 - K_1)}{(C_{p_1} K_1) - (C_{p_2} K_1)}$$

This equation was used to check the corrected values obtained by the drift method. Normally, at least three runs were used to provide a sufficient number of combinations for a reliable test.

B. Heater Correction.

The specific heat values were computed on the basis of the total specimen weight, and the temperature rise of the specimen. An energy balance yields:

$$C_{p_T} (W_S + W_H) \Delta T_S = W_S C_{p_S} \Delta T_S + W_H C_{p_H} \Delta T_H$$

where the subscripts s and H refer to the specimen and heater, respectively.

If all the energy supplied to the specimen is assumed to be transmitted from the heater by radiation, the temperature dependence of the specimen heater can be estimated. For a common range of power levels, this results in the dependence shown in Figure 36. This is only an approximation, but should serve adequately in the correction, especially since the curve would shift only slightly over the range of power used.

From Figure 36,

$$\Delta T \cong 0.55 \Delta T_S \quad \text{in the range } 0-700^\circ\text{C}$$

then,

$$C_{p_T} (W_H + W_S) \Delta T_S = W_S C_{p_S} \Delta T_S + 0.55 W_H C_{p_H} \Delta T_S.$$

and,

$$C_{p_s} = \frac{W_H + W_S}{W_S} C_{p_r} - 0.55 \frac{W_H}{W_S} C_{p_H}$$

rearranging,

$$C_{p_s} - C_{p_r} = \frac{W_H}{W_S} (C_{p_r} - 0.55 C_{p_H})$$

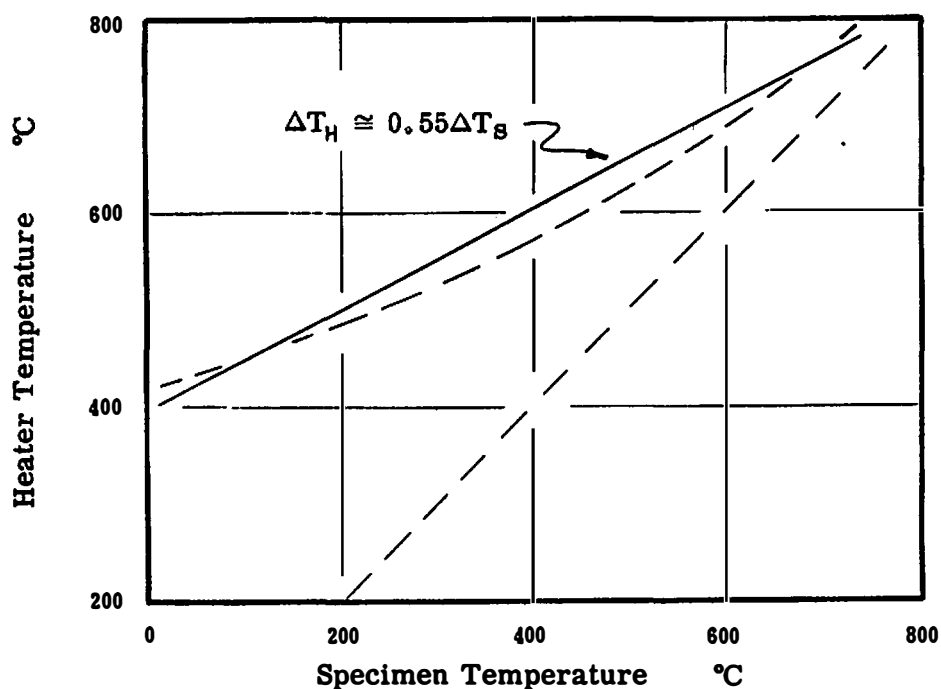


Figure 36. Specimen-heater temperature variation.

Thus, the difference in the calculated and true specific heats, with regard to the heater correction, depends upon the relative heater-specimen weights, and a proportional difference of their specific heats. The specific heats values of the heater components, refractory and nichrome, vary less than five per cent over this temperature range, and assuming a one to one

weight correspondence,

$$C_{p_H \text{ (avg)}} = 0.205 \text{ cal/gram } ^\circ\text{C}$$

substituting:

$$C_{p_s} - C_{p_T} = \frac{W_H}{W_S} (C_{p_T} - 0.113)$$

Since the heater-specimen weight ratios were less than 0.01 for the specimens used in this investigation, and since the specific heat values for copper, nickel and its alloys are in the range of 0.113 cal/gram $^\circ\text{C}$, the heater correction was observed to be very small. A consideration of the maximum values led to the conclusion that the heater correction could be neglected with an error of less than 0.1 per cent, except in the extremities of the Curie region for pure nickel. For systems in which the specific heat values vary considerably from 0.113 cal/gram $^\circ\text{C}$, the heater correction will have to be included.

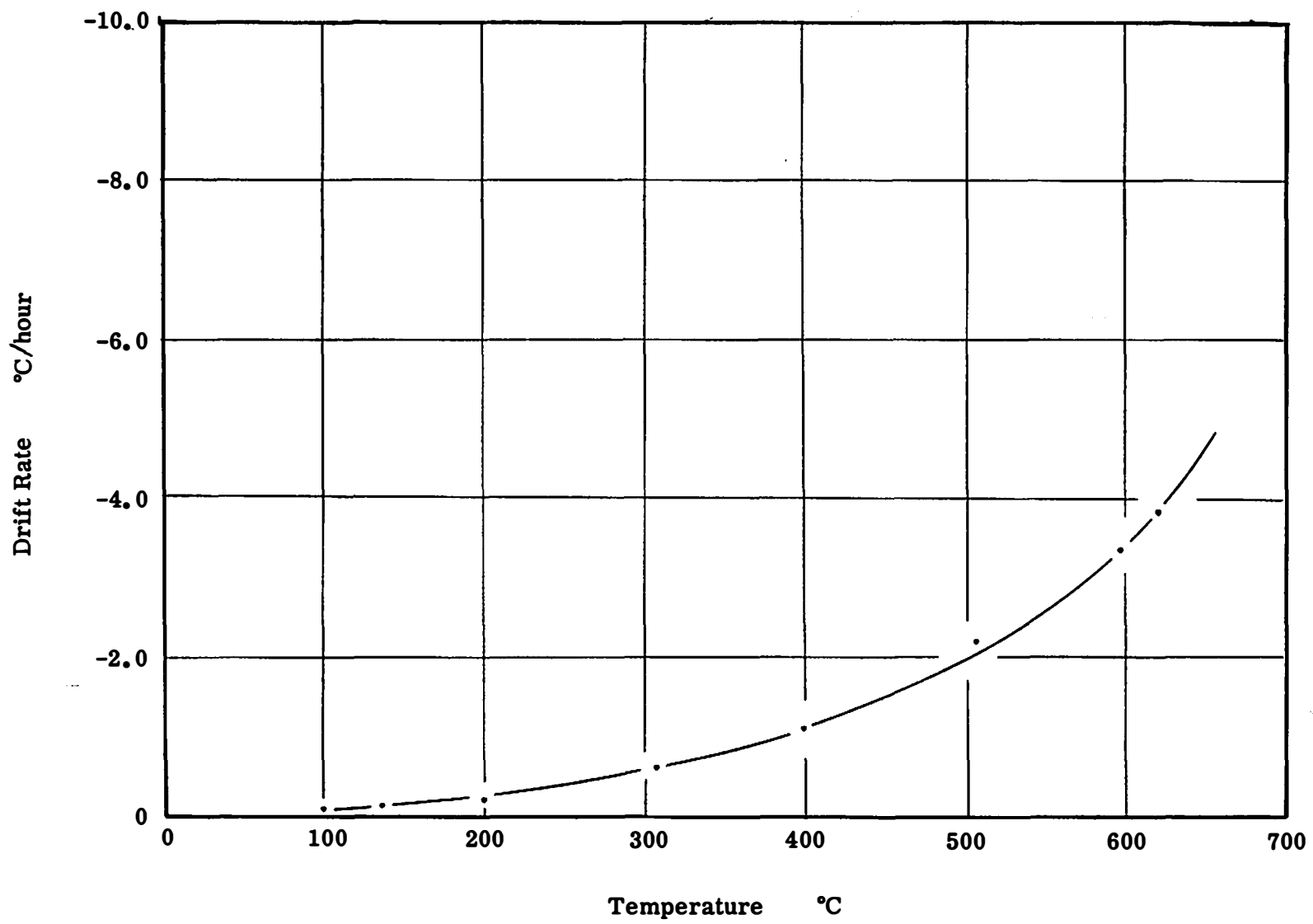


Figure 37. Drift rate data for copper specimen.

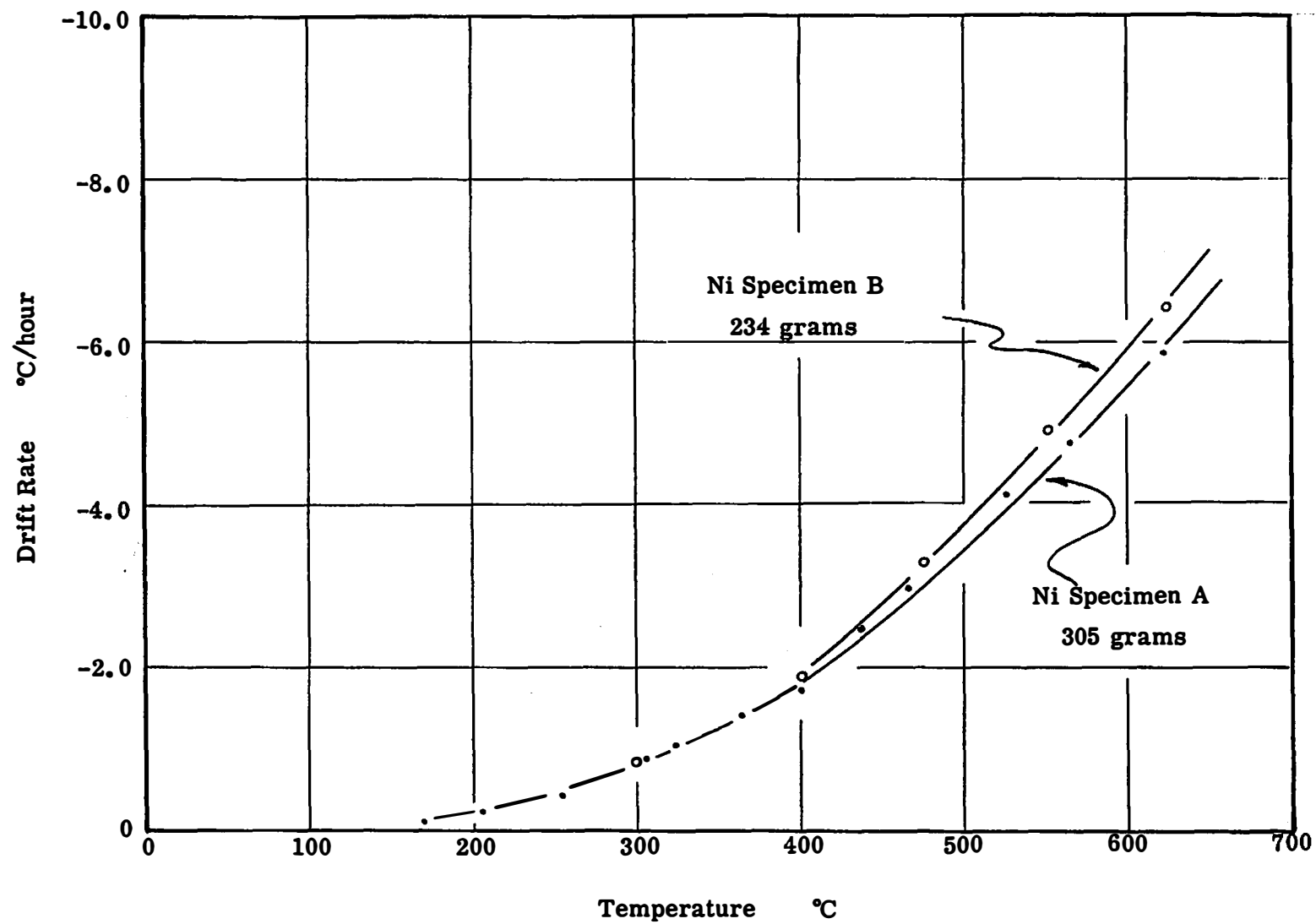


Figure 38. Drift rate data for nickel specimens.

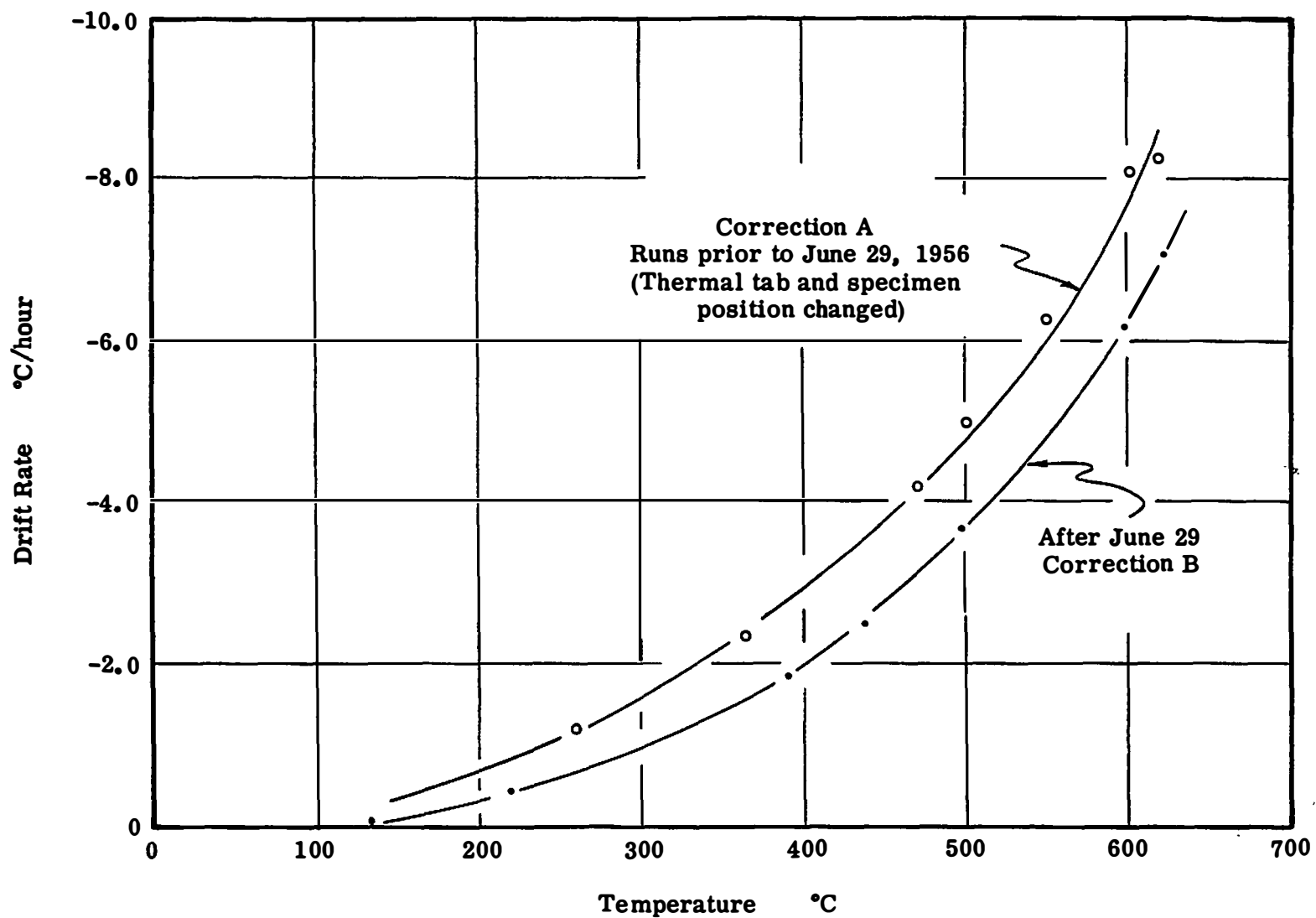


Figure 39. Drift rate data for 50 Ni - 50 Cu specimen.

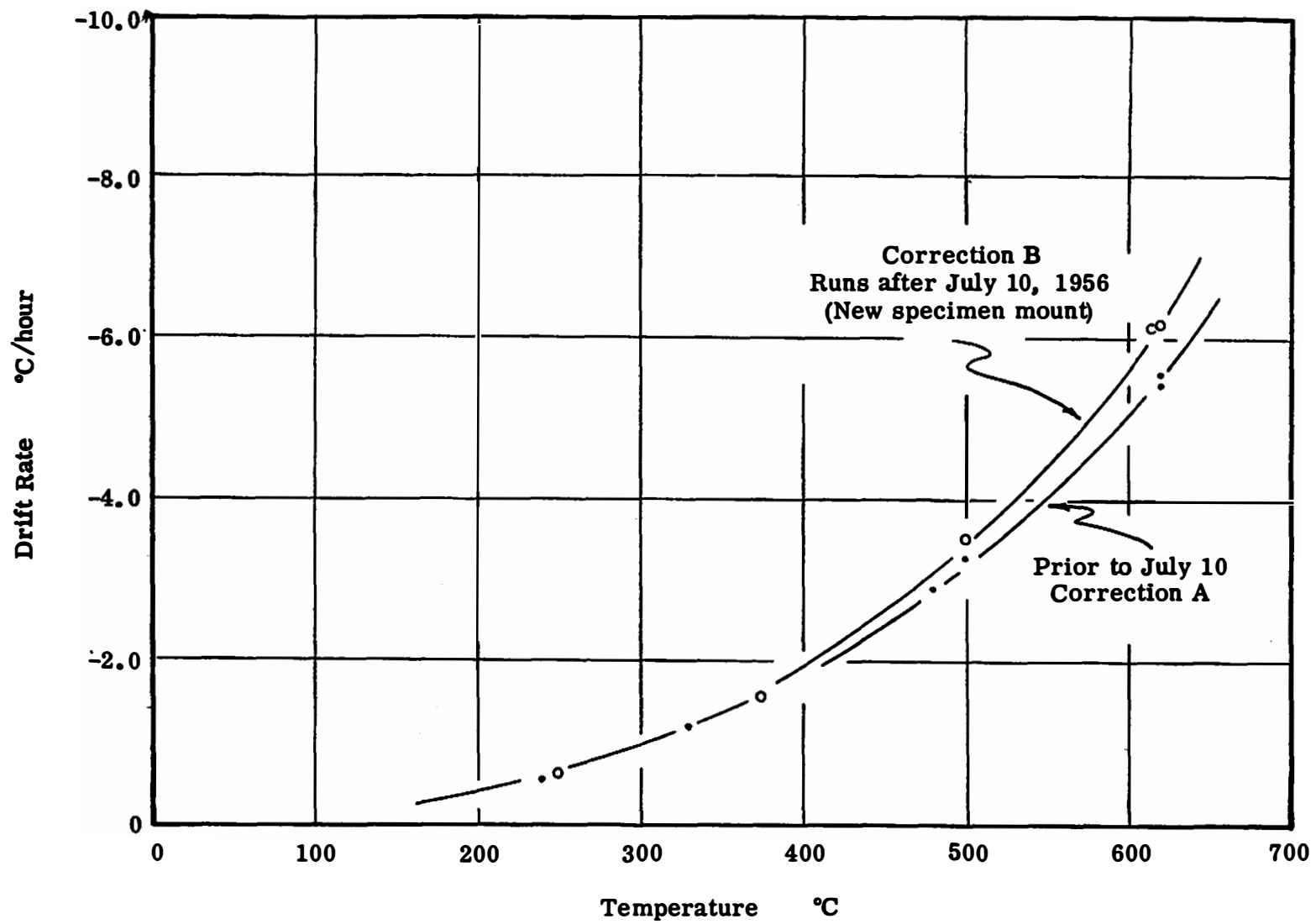


Figure 40. Drift rate data for 75 Ni - 25 Cu specimen.

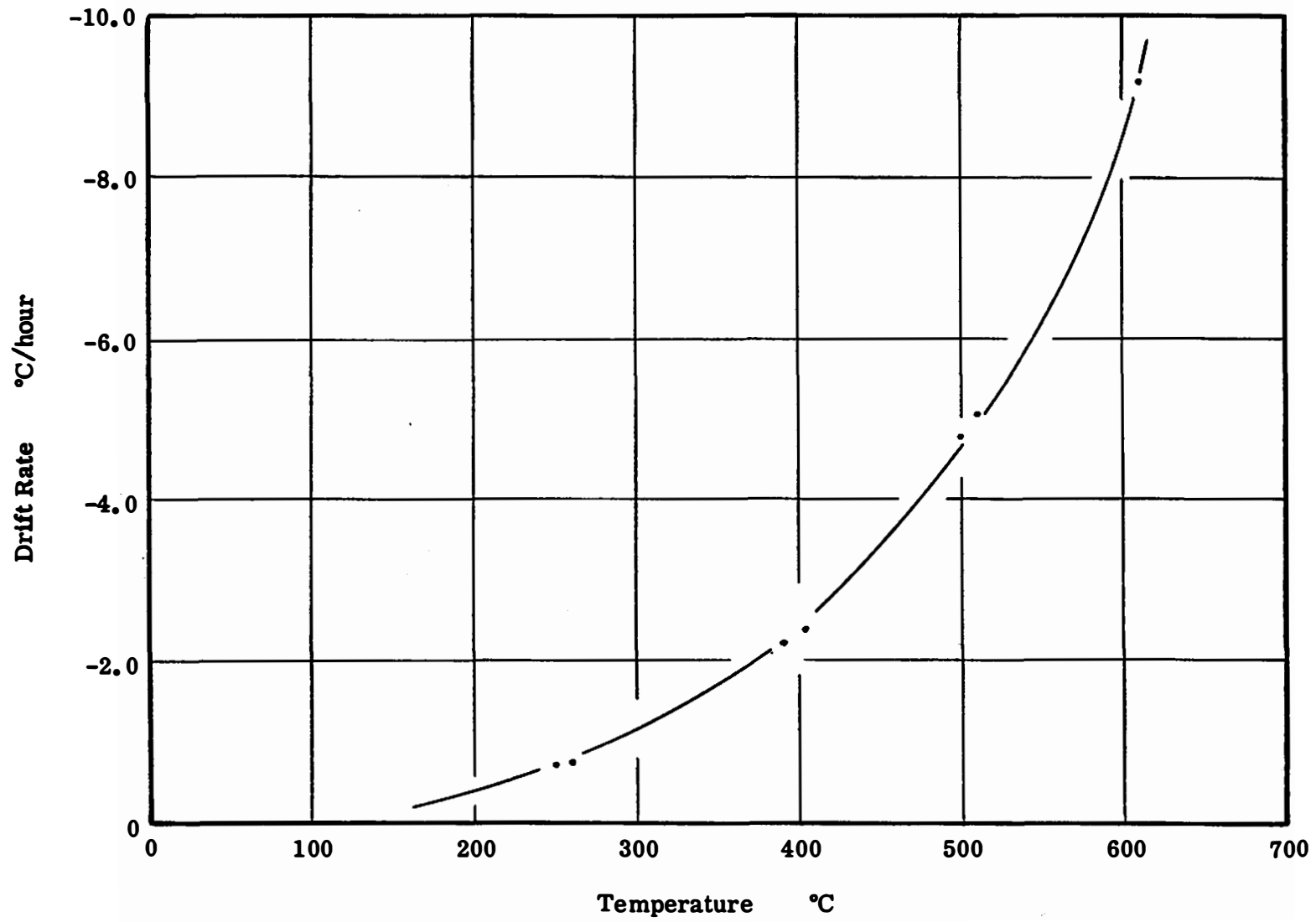


Figure 41. Drift rate data for 90 ni - 10 Cu alloy.

TABLE XII

SAMPLE CALCULATIONS

Nickel Specimen B, 234.037 grams, K=24.057

T (°C)	Δt sec.	T (μv)	Spec-Cyl Control (μv)	Rhodium Thermals (μv)	Thermal Comp.	V/10 (volts)	I (amps)	V _{avg.} (volts)	I _{avg.} (amps)	EIΔt (watt-sec.)	C _{pa} cal/gram °C	$-\frac{C_{pa} R_w}{K}$	C _{pr} cal/gram °C	T _{avg.} (°C)
80		501.1	ok	-	gd.	1.20136	0.55740							
100	326.30	846.6	0	-0.3	gd.	1.20004	0.55576	12.0070	0.55658	2180.62	0.11132	-	0.1113	90
120	335.00	798.8	ok	-	gd.	1.19952	0.55486	11.9978	0.55531	2231.94	0.11394	-	0.1139	110
140	342.95	958.5	ok	-	gd.	1.19878	0.55410	11.9915	0.55448	2280.29	0.11641	-	0.1164	130
160	348.90	1121.5	ok	-	gd.	1.19824	0.55310	11.9851	0.55360	2314.93	0.11818	-	0.1182	150
180	355.60	1291.4	ok	-	gd.	1.19742	0.55286	11.9783	0.55298	2355.41	0.12024	-	0.1201	170
200	362.35	1466.3	+0.2	-0.2	gd.	1.19684	0.55262	11.9713	0.55274	2397.68	0.12240	0.0007	0.1223	190
220	368.20	1644.6	ok	-	gd.	1.19616	0.55240	11.9650	0.55251	2434.09	0.12426	0.0012	0.1241	210
240	376.35	1827.1	ok	-0.2	gd.	1.19548	0.55216	11.9582	0.55228	2485.62	0.12688	0.0014	0.1267	230
260	385.50	2012.5	+0.2	-	gd.	1.19476	0.55196	11.9512	0.55206	2543.44	0.12984	0.0023	0.1295	250
280	393.85	2202.7	0	-0.2	gd.	1.19430	0.55172	11.9453	0.55184	2596.22	0.13254	0.0038	0.1320	270
300	402.90	2396.0	ok	-	gd.	1.19358	0.55156	11.9394	0.55164	2653.60	0.13547	0.0045	0.1349	290
310	205.60	2493.9	ok	-	gd.	1.19326	0.55146	11.9342	0.55149	1353.17	0.13816	0.0051	0.1375	305
320	208.60	2592.4	ok	-	gd.	1.19292	0.55140	11.9309	0.55143	1372.39	0.14012	0.0057	0.1393	315
330	211.55	2691.5	ok	-	gd.	1.19262	0.55128	11.9277	0.55134	1391.20	0.14204	0.0064	0.1411	325
340	215.90	2791.3	ok	-	gd.	1.19228	0.55122	11.9245	0.55125	1419.19	0.14490	0.0070	0.1439	335
350	221.05	2891.7	ok	-	gd.	1.19206	0.55116	11.9217	0.55119	1452.54	0.14830	0.0082	0.1471	345
360	221.10	2992.6	ok	+0.1	gd.	1.19174	0.55106	11.9190	0.55111	1462.34	0.14828	0.0088	0.1470	355
370	200.30	3093.2	ok	-	gd.	1.19144	0.55096	11.9159	0.55101	1315.13	0.13427	0.0083	0.1332	365
380	194.35	3195.2	ok	-	gd.	1.19116	0.55088	11.9130	0.55092	1275.54	0.13023	0.0085	0.1291	375
390	192.10	3297.9	ok	-	gd.	1.19094	0.55080	11.9105	0.55084	1280.33	0.12868	0.0094	0.1275	385
400	191.70	3401.3	ok	-	gd.	1.19068	0.55074	11.9081	0.55077	1257.29	0.12837	0.0102	0.1271	395
420	missed	3609.0	-0.1	+0.3	gd.	-	-	-	-	-	-	-	-	-
440	758.45	3819.0	ok	-	gd.	1.19002	0.55020	11.9035	0.55047	4969.76	0.12685	0.0120	0.1254	420
460	379.45	4029.9	+0.1	+0.4	gd.	1.18928	0.55014	11.8997	0.55017	2483.54	0.12678	0.0144	0.1250	450
480	380.40	4244.1	ok	-	gd.	1.18872	0.55002	11.8900	0.55008	2487.98	0.12701	0.0168	0.1249	470
500	381.95	4460.5	ok	+0.2	gd.	1.18822	0.55000	11.8847	0.55001	2496.69	0.12746	0.0192	0.1251	490
520	382.55	4678.0	ok	-	gd.	1.18814	0.54988	11.8818	0.54994	2499.89	0.12761	0.0208	0.1250	510
540	384.70	4897.5	ok	-	gd.	1.18816	0.54980	11.8815	0.54984	2513.22	0.12830	0.0231	0.1254	530
560	388.90	5117.9	+0.2	±0.2	V	1.18820	0.54960	11.8818	0.54970	2527.01	0.12900	0.0254	0.1258	550
580	389.40	5341.8	±0.2	±0.2	V	1.18848	0.54938	11.8834	0.54949	2542.71	0.12980	0.0277	0.1283	570
600	391.90	5567.8	±0.2	±0.2	V	1.18830	0.54924	11.8839	0.54931	2558.30	0.13060	0.0308	0.1287	590
820	395.00	5794.7	±0.2	±0.2	V	1.18834	0.54908	11.8832	0.54916	2577.68	0.13159	0.0338	0.1273	610

TABLE XIII

APPARENT AND TRUE SPECIFIC HEAT VALUES OF COPPER

K=20.89			K=20.18			K=14.30			K=9.56		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
90	0.0942	0.0942	70	0.0940	0.0940	90	0.0943	0.0943			
110	0.0954	0.0953	90	0.0943	0.0943	110	0.0953	0.0953			
130	0.0962	0.0961	120	0.0957	0.0957	130	0.0961	0.0961			
150	0.0966	0.0965	160	0.0968	0.0968	150	0.0969	0.0968			
170	0.0970	0.0969	200	0.0977	0.0976	170	0.0972	0.0971			
190	0.0976	0.0975	240	0.0988	0.0987	190	0.0979	0.0977			
210	0.0978	0.0977	280	0.0998	0.0995	220	0.0983	0.0981			
230	0.0985	0.0984	320	0.1008	0.1004	260	0.0995	0.0992			
250	0.0992	0.0990	360	0.1016	0.1011	300	0.1005	0.1001			
270	0.0996	0.0994	400	0.1023	0.1017	340	0.1013	0.1007			
290	0.1002	0.0999	440	0.1033	0.1025	380	0.1024	0.1016			
310	0.1006	0.1003	480	0.1045	0.1035	420	0.1030	0.1021			
330	0.1010	0.1006	520	0.1054	0.1041	460	0.1042	0.1029	490	0.1061	0.1038
350	0.1012	0.1008	560	0.1068	0.1052	500	0.1052	0.1036	510	0.1066	0.1040
370	0.1020	0.1015	600	0.1081	0.1061	530	0.1064	0.1045	530	0.1072	0.1048
390	0.1023	0.1018				560	0.1075	0.1052	550	0.1082	0.1049
410	0.1024	0.1019				600	0.1089	0.1062	570	0.1092	0.1050
430	0.1029	0.1022							590	0.1102	0.1063
450	0.1035	0.1027							610	0.1111	0.1067
480	0.1046	0.1036									
520	0.1053	0.1041									
560	0.1066	0.1051									
600	0.1080	0.1061									

TABLE XIV

APPARENT AND TRUE SPECIFIC HEAT VALUES OF NICKEL

Ni Specimen A, K=17.83			Ni Specimen A, K=22.72		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
			150	0.1169	0.1169
			170	0.1192	0.1191
			190	0.1216	0.1215
			210	0.1238	0.1236
			230	0.1264	0.1262
			250	0.1294	0.1291
			270	0.1320	0.1315
			290	0.1354	0.1348
			305	0.1379	0.1372
			315	0.1400	0.1392
			325	0.1420	0.1411
			345	0.1482	0.1470
			355	0.1482	0.1469
			365	0.1343	0.1331
			375	0.1304	0.1292
			385	0.1287	0.1274
390	0.1288	0.1271	395	0.1283	0.1270
410	0.1274	0.1255	410	0.1269	0.1255
430	0.1270	0.1249	430	0.1268	0.1252
450	0.1274	0.1250	450	0.1268	0.1250
470	0.1276	0.1250	470	0.1271	0.1250
490	0.1281	0.1251	490	0.1277	0.1254
510	0.1284	0.1251	510	0.1277	0.1251
530	0.1292	0.1255	530	0.1286	0.1257
550	0.1301	0.1260	550	0.1292	0.1260
570	0.1308	0.1263	570	0.1300	0.1265
590	0.1317	0.1268	590	0.1308	0.1270
610	0.1326	0.1272	610	0.1312	0.1270

TABLE XIV (Continued)

APPARENT AND TRUE SPECIFIC HEAT VALUES OF NICKEL

Ni Specimen A, K=29.06			Ni Specimen A, K=30.14		
T °C	C _{pa}	C _{p_T}	T °C	C _{pa}	C _{p_T}
50	0.1083	0.1083			
70	0.1086	0.1086			
90	0.1097	0.1097			
110	0.1133	0.1133			
130	0.1158	0.1158			
150	0.1180	0.1180			
170	0.1195	0.1195			
190	0.1219	0.1218			
210	0.1239	0.1238			
230	0.1269	0.1265			
250	0.1293	0.1290	250	0.1292	0.1289
270	0.1320	0.1316	270	0.1319	0.1316
290	0.1355	0.1350	290	0.1351	0.1346
305	0.1378	0.1372	305	0.1376	0.1370
315	0.1399	0.1392	315	0.1398	0.1392
325	0.1419	0.1412	325	0.1415	0.1408
335	0.1445	0.1437	335		
345	0.1477	0.1467	345	0.1479	0.1470
355	0.1482	0.1471	355	0.1478	0.1468
365	0.1341	0.1332	365	0.1342	0.1333
375	0.1299	0.1290	375	0.1299	0.1290
385	0.1285	0.1275	385	0.1285	0.1275
395	0.1280	0.1270	395	0.1280	0.1270
410	0.1267	0.1256	410	0.1265	0.1254
			430	0.1261	0.1249
440	0.1262	0.1249			
			450	0.1262	0.1248
470	0.1265	0.1249	470	0.1265	0.1250
490	0.1269	0.1251	490	0.1267	0.1250
510	0.1271	0.1251	510	0.1270	0.1251
530	0.1277	0.1255	530	0.1275	0.1254
550	0.1283	0.1258	550	0.1282	0.1258
570	0.1289	0.1262	570	0.1288	0.1262
590	0.1297	0.1267	590	0.1296	0.1267
610	0.1301	0.1269	610	0.1300	0.1269

TABLE XIV (Continued)

APPARENT AND TRUE SPECIFIC HEAT VALUES OF NICKEL

Ni Specimen B, K=24.06			Ni Specimen B, K=30.82		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
90	0.1113	0.1113			
110	0.1139	0.1139			
130	0.1164	0.1164			
150	0.1182	0.1182			
170	0.1202	0.1201			
190	0.1224	0.1223	190	0.1221	0.1220
210	0.1243	0.1241	210	0.1240	0.1239
230	0.1269	0.1267	230	0.1268	0.1266
250	0.1298	0.1295	250	0.1295	0.1292
270	0.1325	0.1320	270	0.1322	0.1319
290	0.1355	0.1349	290	0.1353	0.1349
305	0.1382	0.1375	305	0.1376	0.1371
315	0.1401	0.1395	315	0.1399	0.1393
325	0.1420	0.1411	325	0.1416	0.1409
335	0.1449	0.1439	335	0.1445	0.1437
345	0.1483	0.1471	345	0.1478	0.1469
355	0.1483	0.1470	355	0.1479	0.1469
365	0.1343	0.1332	365	0.1338	0.1330
375	0.1302	0.1291	375	0.1299	0.1290
385	0.1287	0.1275	385	0.1285	0.1276
395	0.1284	0.1271	395	0.1279	0.1269
			410	0.1264	0.1253
420	0.1269	0.1254			
			430	0.1260	0.1248
450	0.1268	0.1250	450	0.1263	0.1249
470	0.1270	0.1249	470	0.1266	0.1250
490	0.1275	0.1251			
			500	0.1270	0.1251
510	0.1276	0.1250			
530	0.1283	0.1254	530	0.1279	0.1256
550	0.1290	0.1258	550	0.1284	0.1259
570	0.1298	0.1263	570	0.1292	0.1264
590	0.1306	0.1267	590	0.1297	0.1267
610	0.1316	0.1273	610	0.1305	0.1272

TABLE XV
APPARENT AND TRUE SPECIFIC HEAT VALUES
OF 50 Ni - 50 Cu ALLOY*

K=19.11 (Corr. B)			K=19.35 (Corr. A)		
T °C	C _{pa}	C _{p_T}	T °C	C _{pa}	C _{p_T}
70	0.0982	0.0982	70	0.0980	0.0979
90	0.1000	0.1000			
110	0.1020	0.1019	100	0.1011	0.1009
140	0.1040	0.1039	130	0.1036	0.1034
170	0.1051	0.1050	150	0.1045	0.1042
190	0.1059	0.1057	170	0.1054	0.1050
210	0.1063	0.1061	190	0.1060	0.1056
230	0.1071	0.1068	210	0.1065	0.1060
250	0.1079	0.1075	230	0.1075	0.1069
270	0.1085	0.1081	250	0.1083	0.1076
290	0.1091	0.1086	270	0.1090	0.1082
310	0.1098	0.1092	290	0.1095	0.1086
330	0.1105	0.1097	310	0.1102	0.1091
350	0.1113	0.1104	330	0.1108	0.1096
370	0.1123	0.1113	350	0.1115	0.1101
390	0.1133	0.1121	370	0.1130	0.1114
410	0.1140	0.1126	390	0.1142	0.1123
430	0.1152	0.1136	410	0.1149	0.1129
450	0.1162	0.1143	430	0.1161	0.1138
470	0.1171	0.1150	450	0.1171	0.1145
490	0.1182	0.1157	470	0.1180	0.1150
510	0.1187	0.1159	490	0.1189	0.1155
530	0.1194	0.1162	510	0.1194	0.1157
550	0.1203	0.1167	530	0.1203	0.1161
570	0.1210	0.1170	550	0.1211	0.1164
590	0.1222	0.1177	570	0.1219	0.1168
			590	0.1128	0.1170
			610	0.1235	0.1174

*Data to 150°C checked by low power level runs.

TABLE XV (Continued)
 APPARENT AND TRUE SPECIFIC HEAT VALUES
 OF 50 Ni - 50 Cu ALLOY

K=26.86 (Corr. B)			K=34.26 (Corr. A)		
T °C	C _{pa}	C _{p_T}	T °C	C _{pa}	C _{p_T}
170	0.1040	0.1039	170	0.1045	0.1043
190	0.1053	0.1052	190	0.1053	0.1051
210	0.1058	0.1056	210	0.1060	0.1057
230	0.1069	0.1067	230	0.1072	0.1068
250	0.1078	0.1076	250	0.1080	0.1076
270	0.1083	0.1080	270	0.1086	0.1081
290	0.1089	0.1086	290	0.1091	0.1086
310	0.1096	0.1091	310	0.1099	0.1093
330	0.1100	0.1095	330	0.1104	0.1097
350	0.1105	0.1099	350	0.1111	0.1104
370	0.1120	0.1112	370	0.1126	0.1117
390	0.1131	0.1122	390	0.1133	0.1123
410	0.1138	0.1128	410	0.1140	0.1128
430	0.1147	0.1136	430	0.1149	0.1136
450	0.1155	0.1142	450	0.1157	0.1142
470	0.1163	0.1147	470	0.1163	0.1146
490	0.1170	0.1152	490	0.1171	0.1152
510	0.1174	0.1154	510	0.1176	0.1155
530	0.1182	0.1159	530	0.1183	0.1160
550	0.1187	0.1162	550	0.1187	0.1161
570	0.1194	0.1166	570	0.1193	0.1165
590	0.1201	0.1170	590	0.1201	0.1170
610	0.1206	0.1171	610	0.1206	0.1172

TABLE XVI

APPARENT AND TRUE SPECIFIC HEAT VALUES OF 75 Ni - 25 Cu ALLOY*

K=20.15 (Corr. B)			K=20.48 (Corr. B)			K=26.70 (Corr. B)		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
			190	0.1125	0.1123	190	0.1123	0.1121
			210	0.1127	0.1124	210	0.1125	0.1123
			230	0.1135	0.1132	230	0.1134	0.1132
			250	0.1143	0.1139	250	0.1141	0.1138
			270	0.1145	0.1140	270	0.1145	0.1141
			290	0.1149	0.1144	290	0.1151	0.1146
310	0.1153	0.1146	310	0.1156	0.1149	310	0.1157	0.1152
330	0.1158	0.1151	330	0.1161	0.1152	330	0.1161	0.1154
350	0.1162	0.1154	350	0.1162	0.1153	350	0.1164	0.1153
370	0.1173	0.1163	370	0.1174	0.1164	370	0.1177	0.1169
390	0.1181	0.1169	390	0.1182	0.1171	390	0.1185	0.1176
410	0.1189	0.1169	410	0.1189	0.1175	410	0.1189	0.1179
430	0.1200	0.1185	430	0.1200	0.1184	430	0.1198	0.1186
450	0.1211	0.1194	450	0.1211	0.1193	450	0.1209	0.1196
470	0.1224	0.1203	470	0.1224	0.1203	470	0.1220	0.1205
490	0.1235	0.1211	490	0.1236	0.1212	490	0.1232	0.1214
510	0.1244	0.1217	510	0.1244	0.1217	510	0.1239	0.1219
530	0.1253	0.1222	530	0.1253	0.1223	530	0.1248	0.1226
550	0.1258	0.1225	550	0.1259	0.1226	550	0.1250	0.1226
570	0.1268	0.1231	570	0.1268	0.1231	570	0.1257	0.1231
590	0.1279	0.1237	590	0.1278	0.1237	590	0.1265	0.1237
610	0.1290	0.1244	610	0.1288	0.1243	610	0.1274	0.1242

* Low temperature values given in Table XVII.

TABLE XVI (Continued)

APPARENT AND TRUE SPECIFIC HEAT VALUES OF 75 Ni - 25 Cu ALLOY

K=27.96 (Corr. B)			K=26.33 (Corr. A)			K=27.87 (Corr. A)		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
			210	0.1127	0.1125			
			230	0.1139	0.1136			
			250	0.1144	0.1141			
			270	0.1148	0.1144	270	0.1141	0.1138
			290	0.1153	0.1149	290	0.1147	0.1143
			310	0.1158	0.1153	310	0.1154	0.1149
			330			330	0.1158	0.1152
350	0.1161	0.1153	350			350	0.1161	0.1155
370	0.1171	0.1164	370	0.1175	0.1167	370	0.1175	0.1167
390	0.1181	0.1172	390	0.1181	0.1172	390	0.1187	0.1179
410	0.1181	0.1172	410	0.1186	0.1176	410	0.1193	0.1183
430	0.1196	0.1185	430	0.1200	0.1187	430	0.1201	0.1189
450	0.1207	0.1194	450	0.1210	0.1196	450	0.1208	0.1195
470	0.1217	0.1202	470			470	0.1218	0.1203
490	0.1228	0.1210	490			490	0.1229	0.1212
510	0.1236	0.1216	510	0.1236	0.1217	510	0.1236	0.1217
530	0.1244	0.1222	530	0.1247	0.1225	530	0.1245	0.1224
550	0.1250	0.1226	550	0.1250	0.1226	550	0.1248	0.1225
570	0.1255	0.1229	570	0.1256	0.1229	570	0.1258	0.1232
590	0.1267	0.1237	590	0.1265	0.1236	590	0.1265	0.1238
610	0.1275	0.1242	610	0.1276	0.1244	610	0.1275	0.1245

TABLE XVII

LOW TEMPERATURE SPECIFIC HEAT OF
75 Ni - 25 Cu ALLOY

K= 9.04		K=14.13		K= 14.3, 20.48	
T °C	C _{pT}	T °C	C _{pT}	T °C	C _{pT}
~~55~~	0.1048	55	0.1050		
65	0.1065	65	0.1057		
~~75~~	0.1081	75	0.1070	70	0.1065
85	0.1092	85	0.1087		
				90	0.1089
95	0.1096	95	0.1086		
105		105	0.1105	110	0.1113
115		115	0.1115		
125	0.1132	125	0.1129	130	0.1124
135	0.1127	135	0.1124		
		145	0.1129	150	0.1126
150	0.1127	155	0.1126		
165	0.1121	165	0.1123	170	0.1122
175	0.1119	175	0.1119		
185	0.1121	185	0.1124	190	0.1123
195	0.1121	195	0.1122		
205	0.1123	205	0.1126	210	0.1124
				230	0.1131

TABLE XVIII
APPARENT AND TRUE SPECIFIC HEAT VALUES
OF 90 Ni - 10 Cu ALLOY

K= 26.65			K= 26.78 to 370°C 27.07 above 450°C		
T °C	C _{pa}	C _{p_T}	T °C	C _{pa}	C _{p_T}
50	0.1102	0.1102	50	0.1100	0.1100
70	0.1112	0.1112	70		
90	0.1129	0.1129	90	0.1129	0.1129
110	0.1153	0.1153	110	0.1156	0.1156
130	0.1177	0.1177	130	0.1183	0.1183
150	0.1202	0.1201	150	0.1204	0.1204
170	0.1223	0.1223	170	0.1224	0.1223
190	0.1250	0.1249	190	0.1251	0.1250
205	0.1272	0.1270	205	0.1273	0.1271
215	0.1279	0.1277	215	0.1278	0.1275
225	0.1299	0.1296	225	0.1299	0.1296
235	0.1312	0.1309	235	0.1317	0.1314
245	0.1319	0.1315	245	0.1316	0.1312
255	0.1321	0.1317	255	0.1317	0.1312
265	0.1293	0.1288	265	0.1283	0.1278
275	0.1254	0.1249	275	0.1246	0.1241
285	0.1232	0.1227	285	0.1232	0.1227
295	0.1228	0.1222	295	0.1230	0.1224
305			305	0.1224	0.1217
315	0.1219	0.1212	315	0.1226	0.1219
325	0.1219	0.1212	325	0.1222	0.1214
335	0.1221	0.1213	335	0.1226	0.1217
350	0.1221	0.1212	350	0.1222	0.1212
370	0.1228	0.1216	370	0.1227	0.1216
390	0.1233	0.1219			
410	0.1234	0.1219			
430	0.1242	0.1225			
450	0.1249	0.1230	450	0.1250	0.1231
470	0.1257	0.1235	470	0.1257	0.1235
490	0.1265	0.1239	490	0.1265	0.1239
510	0.1271	0.1241	510	0.1271	0.1242
530	0.1283	0.1249	530	0.1282	0.1249
550	0.1291	0.1252	550	0.1290	0.1252
570	0.1298	0.1254	570	0.1299	0.1256
590	0.1309	0.1259	590	0.1307	0.1258
610	0.1317	0.1261	610	0.1317	0.1262

TABLE XVIII (Continued)

APPARENT AND TRUE SPECIFIC HEAT VALUES
OF 90 Ni - 10 Cu ALLOY

K=35.23			K=35.77		
T °C	C _{pa}	C _{pT}	T °C	C _{pa}	C _{pT}
130	0.1183	0.1183	110	0.1153	0.1153
150	0.1197	0.1197	130	0.1196	0.1196
170	0.1223	0.1223	160	0.1223	0.1222
190	0.1250	0.1249	190	0.1246	0.1245
205	0.1269	0.1267	210	0.1273	0.1271
225	0.1299	0.1297	230	0.1305	0.1302
235	0.1311	0.1308	250	0.1318	0.1315
245	0.1319	0.1316	270	0.1270	0.1267
255	0.1320	0.1317	290	0.1232	0.1228
265	0.1292	0.1288	310	0.1224	0.1219
275	0.1252	0.1248	330	0.1218	0.1212
285	0.1234	0.1230	350	0.1216	0.1209
295			370	0.1223	0.1215
305	0.1206	0.1201	390	0.1227	0.1217
315	0.1218	0.1213	410	0.1228	0.1217
325	0.1218	0.1212	430	0.1235	0.1222
335	0.1221	0.1213	450	0.1242	0.1228
350	0.1218	0.1211	470	0.1250	0.1234
370	0.1226	0.1218	490	0.1257	0.1238
390	0.1228	0.1219	510	0.1263	0.1241
410	0.1231	0.1220	530	0.1272	0.1247
430	0.1238	0.1225	550	0.1279	0.1250
450	0.1246	0.1231	570	0.1286	0.1253
470	0.1251	0.1234	590	0.1296	0.1259
490	0.1259	0.1230	610	0.1302	0.1261
510	0.1265	0.1242			
530	0.1273	0.1248			
550	0.1278	0.1250			
570	0.1288	0.1255			
590	0.1296	0.1258			
610	0.1313	0.1261			

TABLE XIX

SAMPLE HEATING RATE DATA FOR NICKEL FROM 330 TO 420 °C

Run No. 1, 23 μ v/sweep			Run No. 2, 23 μ v/sweep		
T °C	μ v/°C	sec./°C	T °C	μ v/°C	sec./°C
336.0	9.974	121.4	326.1	9.911	121.5
338.5	9.989	121.8	328.7	9.928	121.7
340.3	10.006	122.9	331.4	9.944	122.9
344.0	10.022	123.9	334.1	9.962	123.3
346.5	10.037	124.9	336.8	9.978	124.9
349.2	10.053	126.7	339.4	9.995	124.7
351.8	10.069	128.3	342.1	10.011	126.3
354.5	10.084	130.9	344.6	10.025	127.7
357.0	10.099	119.2	347.3	10.042	128.7
359.7	10.114	115.7	350.0	10.058	130.1
362.1	10.129	114.0	352.6	10.074	132.6
364.6	10.143	112.9	355.2	10.088	132.3
367.2	10.158	112.0	357.8	10.103	120.8
370.0	10.173	111.5	360.4	10.118	118.2
372.5	10.187	111.2	362.9	10.132	116.7
375.0	10.201	110.8	365.5	10.148	115.8
377.6	10.214	110.6	368.1	10.163	115.1
380.3	10.229	110.1	370.7	10.177	114.6
383.0	10.243	110.3	373.3	10.192	113.7
385.5	10.256	109.6	376.0	10.206	113.6
388.0	10.269	109.5	378.5	10.220	113.1
390.8	10.282	109.4	381.1	10.234	112.8
393.4	10.297	109.1	383.6	10.246	112.8
396.0	10.310	109.0	386.3	10.260	112.8
398.5	10.323	108.9	388.8	10.273	112.5
401.0	10.336	108.9	391.5	10.287	112.4
403.7	10.349	109.0	394.0	10.300	112.2
406.3	10.363	109.5	396.7	10.313	112.2
408.9	10.376	109.4	399.3	10.327	112.3
411.5	10.388	109.3	401.9	10.340	112.3
414.0	10.402	109.3	404.5	10.354	111.9
416.5	10.416	109.3	407.1	10.367	112.2
419.0	10.428	109.8	409.7	10.380	112.3
421.7	10.441	109.8	412.3	10.394	112.4
			415.0	10.417	112.2
			417.4	10.420	110.5
			420.0	10.433	111.1

TABLE XX
APPARENT SPECIFIC HEAT VALUES
FOR COLD-WORKED COPPER SPECIMEN A

50.28 Per Cent Reduction in Thickness					
T °C	C_p (C.W.)	C_p (Ann.)	T °C	C_p (C.W.)	C_p (Ann.)
65	0.0938	0.0938	295	0.1005	0.1011
75	0.0943	0.0942	305	0.1010	0.1013
85	0.0949	0.0946	315	0.1020	0.1019
95	0.0946	0.0947	325	0.1017	0.1017
105	0.0956	0.0954	335	0.1025	0.1021
115	0.0962	0.0960	345	0.1024	0.1022
125	0.0971	0.0968	355	0.1025	0.1025
135	0.0969	0.0968	365	0.1033	0.1033
145	0.0972	0.0970	375	0.1030	0.1030
155	0.0976	0.0974	385	0.1031	0.1032
165	0.0978	0.0975	395	0.1041	0.1040
175	0.0978	0.0977	405	0.1036	0.1036
185	0.0983	0.0982	415	0.1042	0.1041
195	0.0986	0.0983	425	0.1042	0.1044
205	0.0986	0.0986	435	0.1046	0.1048
215	0.0983	0.0983	445	0.1047	0.1048
225	0.0992	0.0991	455	0.1052	0.1056
235	0.0991	0.0992	465	0.1056	0.1056
245	0.0989	0.0994	475	0.1058	0.1061
255	0.0997	0.1002	485	0.1062	0.1064
265	0.0994	0.1004	495	0.1066	0.1068
275	0.0993	0.1005	510	0.1071	0.1071
285	0.0996	0.1005			

TABLE XXI
APPARENT SPECIFIC HEAT VALUES
FOR COLD-WORKED SPECIMENS

Copper Spec. B, 50.88 per cent Red.			10.5 per cent Ni, 40 per cent Red.		
T °C	C _p (C.W.)	C _p (Ann.)	T °C	C _p (C.W.)	C _p (Ann.) (From Curve)
			70	0.0963	
			90	0.0967	
			110	0.0979	
			130	0.0980	
150	0.0969	0.0972	150	0.0994	
170	0.0973	0.0972	170	0.0990	0.0998
190	0.0979	0.0975	190	0.0996	0.1002
210	0.0982	0.0981	210	0.1005	0.1007
230	0.0987	0.0989	230	0.1012	
250	0.0988	0.0994	250	0.1016	
270	0.0991	0.0997	270	0.1022	
290	0.1000	0.1002	290	0.1031	
310	0.1007	0.1010	310	0.1039	0.1037
330	0.1010		330	0.1036	0.1043
350	0.1018	0.1013	350	0.1036	0.1050
370		0.1022	370	0.1047	0.1054
390	0.1023	0.1028	390	0.1059	0.1060
410	0.1023		410	0.1067	
430	0.1022	0.1034	430	0.1074	
450	0.1035	0.1041	450	0.1083	
470	0.1046	0.1048	470	0.1089	
490	0.1051	0.1053	490	0.1097	
510	0.1055	0.1059	510	0.1108	
530		0.1065	530	0.1122	
			550	0.1140	
			570	0.1152	

TABLE XXII

POWER DIFFERENCE DATA FROM TWIN SPECIMEN CALORIMETER

Cold-Worked Copper Specimen A', 57.1% Red, ; 0.62 cal/sec. Power Level

t _{avg.} (min.)	ΔP _{avg.} (cal/sec)	t _{avg.} (min.)	ΔP _{avg.} (cal/sec)	t _{avg.} (min.)	ΔP _{avg.} (cal/sec)
1.5	0.0728	73.5	0.0071	145.5	0.0221
4.5	0.0463	76.5	0.0082	148.5	0.0203
7.5	0.0086	79.5 (190°)	0.0081	151.5	0.0185
10.5 (50°)	0.0061	82.5	0.0079	154.5	0.0175
13.5	0.0051	85.5	0.0077	158.0	0.0150
16.5	0.0068	88.5	0.0074	161.5	0.0134
19.5 (70°)	0.0072	91.5	0.0065	164.5	0.0122
22.5	0.0070	94.5	0.0051	167.5	0.0108
25.5	0.0058	97.5 (230°)	0.0040	170.5 (370°)	0.0096
28.5	0.0032	100.5	0.0035	173.5	0.0077
31.5	-0.0015	103.5	0.0028	176.5	0.0059
34.5	-0.0013	106.5	0.0040	179.5	0.0050
37.5	-0.0007	109.5	0.0062	182.5	0.0050
40.5	-0.0013	112.5	0.0066	185.5 (400°)	0.0050
43.5 (120°)	-0.0020	115.5	0.0066	188.5	0.0050
46.5	-0.0019	118.5 (270°)	0.0059	191.5	0.0046
49.5	-0.0011	121.5	0.0051	194.5	0.0037
52.5	-0.0002	124.5	0.0051	197.5	0.0029
55.5	0.0007	127.5	0.0055	200.5	0.0018
58.5	0.0030	130.5	0.0064	203.5	0.0009
61.5	0.0047	133.5	0.0071	206.5 (440°)	0.0013
64.5 (160°)	0.0046	136.5	0.0082	209.5	0.0018
67.5	0.0045	139.5	0.0119	212.5	0.0008
70.5	0.0053	142.5	0.0185	215.5	-0.0001

TABLE XXIII

POWER DIFFERENCE DATA FROM TWIN SPECIMEN CALORIMETER

Annealed Copper Specimen A', 0.62 cal/sec Power Level

$t_{\text{avg.}}$ (min.)	$\Delta P_{\text{avg.}}$ (cal/sec)	$t_{\text{avg.}}$ (min.)	$\Delta P_{\text{avg.}}$ (cal/sec)
2.5	0.0033	112.5 (280°)	0.0027
7.5	0.0032	117.5	0.0016
12.5	0.0053	122.5	0.0012
17.5	0.0080	127.5	0.0010
22.5	0.0089	132.5 (319°)	0.0010
27.5	0.0086	137.5	0.0010
32.5	0.0070	142.5	0.0008
37.5 (140°)	0.0057	147.5	0.0007
42.5	0.0057	152.5	0.0005
47.5	0.0060	157.5 (365°)	0.0005
52.5	0.0064	162.5	0.0005
57.5	0.0061	167.5	0.0003
62.5	0.0047	172.5	0.0001
67.5	0.0032	177.5 (400°)	0.0001
72.5 (210°)	0.0026	182.5	0.0002
77.5	0.0023	187.5	0.0002
82.5	0.0027	192.5	0.0004
87.5	0.0028	197.5 (440°)	0.0008
92.5	0.0023	202.5	0.0010
97.5	0.0024	207.5	0.0013
102.5	0.0035	212.5 (475°)	0.0016
107.5	0.0038		

TABLE XXIV

POWER DIFFERENCE DATA FROM TWIN SPECIMEN CALORIMETER

Copper Specimen D', 67.5% Red.: 0.87 cal/sec. Power Level

t (min.)	1st Run ΔP (cal/sec.)	2nd Run ΔP (cal/sec.)	t (min.)	1st Run ΔP (cal/sec.)	2nd Run ΔP (cal/sec.)
0	-0.0034	-0.0208	75	-0.0270	-0.0272
5	-0.0125	-0.0229	80	-0.0260	-0.0274
10 (85°)	-0.0179	-0.0249	85	-0.0294	-0.0275
15	-0.0129	-0.0263	93	+0.0194	-0.0275
20	-0.0156	-0.0265	96 (330°)	+0.0070	-0.0275
25	-0.0172	-0.0267	99	-0.0051	-0.0250
30 (145°)	-0.0189	-0.0301	102	-0.0197	-0.0245
35	-0.0191	-0.0302	105	-0.0254	-0.0238
40	-0.0154	-0.0303	108	-0.0318	-0.0238
45	-0.0103	-0.0322	111	-0.0253	-0.0238
48 (200°)	-0.0042	-0.0323	115 (385°)	-0.0201	-0.0221
51	-0.0044	-0.0323	120	-0.0163	-0.0223
54	-0.0106	-0.0342	125	-0.0164	-0.0200
57	-0.0066	-0.0321	130	-0.0165	-0.0177
60	-0.0109	-0.0309	135	-0.0167	-0.0183
65	-0.0158	-0.0308	140 (455°)	-0.0146	-0.0185
70 (260°)	-0.0210	-0.0278	145		-0.0192

TABLE XXV

POWER DIFFERENCE DATA FROM TWIN SPECIMEN CALORIMETER

Copper Specimen E', 46.7% Red.; 0.88 cal/sec. Power Level

t (min.)	1st Run ΔP (cal/sec.)	2nd Run ΔP (cal/sec.)	t (min.)	1st Run ΔP (cal/sec.)	2nd Run ΔP (cal/sec.)
0	-0.0538	-0.0429	80	-0.0342	-0.0327
5 (65°)	-0.0430	-0.0386	85	-0.0340	-0.0335
10	-0.0487	-0.0352	90	-0.0330	-0.0320
15	-0.0434	-0.0349	95	-0.0332	-0.0325
20	-0.0435	-0.0351	100	-0.0331	-0.0322
25 (120°)	-0.0496	-0.0397	105 (350°)	-0.0277	-0.0322
30	-0.0563	-0.0423	108	-0.0084	-0.0308
35	-0.0450	-0.0399	111	+0.0019	-0.0300
40	-0.0459	-0.0402	114	-0.0047	-0.0298
45 (180°)	-0.0410	-0.0401	117	-0.0125	-0.0287
50	-0.0435	-0.0378	120	-0.0220	-0.0275
55	-0.0397	-0.0379	125 (405°)	-0.0281	-0.0274
60	-0.0353	-0.0380	130	-0.0249	-0.0272
65 (235°)	-0.0353	-0.0352	135	-0.0298	-0.0264
70	-0.0302	-0.0335	140	-0.0280	-0.0252
75	-0.0269	-0.0328			