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To the Graduate Council:

I am submitting herewith a thesis by James William Wright entitled "A New Adiabatic Calorimeter for Specific Heat Determinations from 100° to 800°C." I recommend that it be accepted for nine hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.

C R Brooks
Major Professor

We have read this thesis and recommend its acceptance:

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A NEW ADIABATIC CALORIMETER FOR SPECIFIC HEAT DETERMINATIONS FROM 100° TO 800°C.

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

James William Wright

December 1964

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ABSTRACT

Calorimeters of various types exist by which certain thermal energy of substances can be measured. A program of dynamic adiabatic calorimetry was initiated at The University of Tennessee in 1950 to further existing work on specific heat data. The calorimeters have continuously been improved in both construction and the operational methods.

This thesis constitutes a phase of the program in the use of dynamic adiabatic calorimeters. Modifications were made on previously existing calorimeters to an extent that specific heat data on various metal systems could be obtained to temperatures as high as 850°C. The calorimeter was then used to determine the specific heat of copper, nickel, and a nickel-20 weight per cent chromium alloy.

The calorimeter used in this investigation consists of an adiabatic surrounding into which a highly polished specimen is suspended. The specimen is heated with a direct current power. The temperature of the surroundings is forced to follow the temperature of the specimen. This is accomplished by use of platinum:platinum-13 weight per cent rhodium thermocouples welded on shields; the emf of these thermocouples activates a control circuit which supplies power to the heaters of the shields. The maintenance of adiabatic conditions causes all of the power fed to the

specimen to be consumed in heating it. The power supplied to the specimen is determined by measuring the voltage drop across the heater and the current through the heater. Temperatures are determined from emf readings taken on a potentiometer from thermocouples. The time necessary to raise the temperature of the specimen a preset amount is measured. From the voltage and current measurements and the time necessary to heat the specimen over a particular temperature interval, the average value of the specific heat can be obtained. The system is held at 10^{-4}-10^{-5} Torr to prevent oxidation and convectional heat transfer.

Following the design and construction of the new calorimeter, it was used to obtain specific heat data, from which the following results were obtained.

1. The specific heat data of copper and nickel were obtained from 100° to 800°C. Reproducibility of ±0.7 per cent was obtained on copper where the heating rate ranged from 1.5° to 6.0°C./min. and samples of 172.794 grams and 368.778 grams were used. A reproducibility of ±0.2 per cent was obtained for nickel where only the heating rate was varied (2.2° to 6.4°C./min.). The high degree of reproducibility allows the conclusion that accurate data can be obtained to 800°C. There are no apparent reasons why data could not be obtained to

higher temperatures on the same calorimeter.

2. The specific heat of nickel experienced a magnetic transformation at its Curie temperature of 355°C. Data were obtained to 800°C. such that predicted data without the magnetic transformation could be compared in a manner that allowed the determination of the energy and entropy of the transformation. These values were 954 joules/gm.-atom and 1.967 joules/gm.-atom °K., respectively. Comparison of the above values to theoretical predictions, based on magnetic models, indicate that 0.3 nickel atoms have two holes in the 3d level with an electron spin of one.
3. The specific heat data of the nickel-20 weight per cent chromium alloy experienced an anomaly at approximately 575°C. Analogies were drawn between the experimental data and work of other investigators to support the theory that short-range order was causing the anomaly.
4. The problems encountered in the operation of the calorimeter indicated that inconel should not be used in a vacuum system that is to operate at high temperatures.

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CHAPTER I

INTRODUCTION

The experimental determination of thermodynamic properties of solid state material is of interest for its use in engineering application and in aiding interpretation of phenomena occurring in solid state material. Theoretically, the thermodynamic properties are valuable because they can be used in various ways to aid in obtaining a theoretical model that explains certain behavior. A useful thermodynamic property for this purpose is the specific heat, which is determined by various calorimeter methods, one being the dynamic adiabatic calorimeter.

A program in calorimetry was initiated at The University of Tennessee by the Metallurgical Engineering division in 1950 through support of the Atomic Energy Commission. The dynamic adiabatic calorimeter has been incorporated because of several advantages such as: (1) data can be obtained over a wide range of temperatures, (2) the method of taking data is uncomplicated, (3) a high degree of reproducibility is obtained, (4) samples of various sizes can be used, (5) various heating rates can be used to allow study of the kinetics of various reactions, and (6) the corrections that must be applied are small.

The method employed is one of obtaining an average

value of the specific heat over a small temperature interval. A constant amount of direct-current power is fed to the sample. During the heating, adiabatic conditions are maintained to insure complete absorption by the sample of the power fed to it. The time necessary to heat the sample through a specified temperature interval is recorded. With these values it is possible to determine the specific heat at the mean of the temperature interval.

Since 1950 the calorimeter has continuously been improved both in construction and technique of operation. Prior to the work of this investigation, the calorimeter existed as reported by Stansbury *et al.* (45). With the design reported by them, it has been difficult to make specific heat determinations above 600°C. that were reproducible.

Improvements in the calorimetric technique made in this investigation have enabled the determination of specific heat with precision up to 800°C. The improvements made were: (1) the use of new methods of thermal insulation, (2) a decrease in the mass and improvements in the heat transfer properties of the immediate sample surroundings, (3) increases in available power that can be fed to the heaters of the adiabatic surroundings, and (4) concentric heating of the surroundings.

The new calorimeter was used to determine the specific

heat of copper, nickel, and an alloy of nickel-20 weight per cent chromium. Copper was the metal initially studied. It has been studied by many investigators, and it was felt that its study would serve as a check on the calorimeter, as well as provide more data on copper. During the study of copper, the calorimeter was operated under a wide range of conditions to notice the effect of variables such as sample size and dimensions, heating rate and method of data correction. Following the evaluation of the modifications made on the calorimeter, the determination of the specific heat was extended to the other metals.

Nickel experiences a ferromagnetic transformation. The effect of the transformation is manifested in the specific heat curve. This ferromagnetic behavior is associated with the electron spin system of the individual atoms. There are several models that attempt to explain the spin system and, as a result of these models, predictions of the energy and entropy associated with the transformation are reported. These values of energy and entropy can be compared to values obtained experimentally from the study of specific heats, as was done in this investigation. The experimental specific heat with the transformation is compared to a theoretical prediction of the specific heat without the transformation. By taking the difference in the areas under these curves of specific heat versus temperature, the energy associated with

the transformation is obtained. The entropy is obtained in a similar manner from plots of specific heat over temperature versus temperature. A comparison can then be made between experimental and theoretical values of energy and entropy of the transformation.

The final study was carried out on a nickel-20 weight per cent chromium alloy. An anomalous increase in the specific heat is manifested near 560°C. This anomalous behavior is associated with an order-disorder transformation. Arledge (2) has previously carried out specific heat studies of this alloy but found some inconsistencies. This alloy was restudied to determine whether these inconsistencies were real or only associated with the calorimeter. Further, the study allowed the prediction as to the type order-disorder reaction that occurs.

CHAPTER II

THE SPECIFIC HEAT OF METALS

I. THE SPECIFIC HEAT WITHOUT ANOMALIES

The term specific heat refers to the heat capacity of a unit mass of a substance under consideration. The heat capacity of a substance is the heat required to raise its temperature 1 degree and hence it is an extensive property. The specific heat is the heat capacity per unit of mass and is an intensive property.

The heat capacity term is defined from basic thermodynamic relationships. From the first law, for a closed system,

$$dE = \delta q - pdv, \tag{1}$$

when only the work against external pressure is considered. The quantities in the above equation are: energy (E), heat (q), pressure (p), and volume (v). The derivative of $E=f(v,T)$ can be taken to give

$$dE = \left(\frac{\partial E}{\partial v}\right)_T dv + \left(\frac{\partial E}{\partial T}\right)_v dT, \tag{2}$$

where T is the absolute temperature. Equation 2 can be substituted into the first law to give

$$\delta q = \left(\frac{\partial E}{\partial T}\right)_v dT + \left[\left(\frac{\partial E}{\partial v}\right)_T + p\right] dv \quad . \tag{3}$$

Theoretical considerations of the heat capacity usually consider constant volume, and from Equation 3,

$$C_v \equiv \left(\frac{\delta q}{dT}\right)_v = \left(\frac{\partial E}{\partial T}\right)_v \quad . \tag{4}$$

Experimentally, it is more convenient to determine the heat capacity at constant pressure (C_p). The two heat capacities can be related by

$$C_p \equiv \left(\frac{\delta q}{dT}\right)_p = C_v + \left[p + \left(\frac{\partial E}{\partial v}\right)_T\right] \left(\frac{\partial v}{\partial T}\right)_p \quad . \tag{5}$$

These equations indicate methods by which C_p or C_v may be determined experimentally throughout reversible paths.

The specific heat of a solid is composed of two parts, generally. These are the contributions of energy in increasing the amplitude and/or frequency of oscillation of the atoms about an equilibrium site and of the energy consumed by the outer valence electrons. They are called the lattice contribution and the electronic contribution, respectively. These contributions are assumed to be additive to give the expression

$$C_p = C_p(\text{lattice}) + C_p(\text{electronic}). \qquad (6)$$

Theoretical models exist to predict these respective contributions.

The theoretical lattice contribution for pure metals is best exemplified by the Debye (15) function

$$C_v(\text{lattice}) = 3\ R\ F\ (\frac{\Theta}{T})\ , \qquad (7)$$

where C_v is the lattice contribution to specific heat at a constant volume, R is the gas law constant, and $F(\frac{\Theta}{T})$ is the Debye function, with Θ being the Debye temperature and T the absolute temperature. Debye obtained this approximate expression by considering the crystal as a continuous elastic solid, vibrating in $3N$ (N=number of atoms) different vibrational modes. The Debye temperature can be evaluated from tables (44). The Debye temperature is a constant for a given metal and can be determined experimentally. Since the experimental determinations of specific heat are taken at constant pressure, it is necessary to use a relation similar to Equation 5 (15). This leads to

$$C_p(\text{lattice}) = C_v(\text{lattice}) + \frac{v\beta^2}{k} = C_v(\frac{v/k}{C_v/\beta}\beta T+1), \qquad (8)$$

where v is the molar volume, β is the coefficient of volume expansion, and k is the isothermal compressibility.

Due to a lack of these values as a function of temperature, it is necessary to make the substitution of Gruneisen's constant ($\Gamma = \frac{v/k}{C_v/\beta}$), which is found experimentally to be rather independent of temperature. Making this substitution the expression now is

$$C_p(\text{lattice}) = 3\,R\,(1+\Gamma\beta_{(T)}T)\,F\,(\Theta/T), \qquad (9)$$

where $\beta_{(T)}$ is the coefficient of volume expansion expressed as a function of temperature.

The electronic specific heat contribution has been given by Wilson (54) as

$$C_v(\text{electronic}) = \frac{\pi^2 nk}{2T_o}\left[1-\frac{3\pi^2}{10}\left(\frac{T}{T_o}\right)^2 - \ldots\right] \qquad (10)$$

and by eliminating terms above the second order the resulting expression is

$$C_v(\text{electronic}) = \frac{\pi^2 nk}{2T_o}\,T\left[1-\frac{3\pi^2}{10}\left(\frac{T}{T_o}\right)^2\right], \qquad (11)$$

where $\frac{\pi^2 nk}{T_o}$ is usually written as γ, the electronic specific heat constant. In this equation, T_o is called the degeneracy temperature, n is the number of effective electrons, and k is Boltzman's constant. The dilation correction is usually assumed to be negligible. Thus,

$C_v(\text{electronic}) \cong C_p(\text{electronic})$. The value of T_o can be determined from the value of γ at low temperatures and a particular value of n.

The total theoretical specific heat can now be obtained by adding the lattice and electronic contributions, which gives the expression

$$C_p = \gamma T \left[1-\frac{3\pi^2}{10}\left(\frac{T}{T_o}\right)^2\right] + 3\,RF\left(\frac{\Theta}{T}\right)\left[1+\Gamma\beta_{(T)}T\right]. \qquad (12)$$

At temperatures where $T \ll T_o$ the above expression reduces to

$$C_p = \gamma T + \beta T^3. \qquad (13)$$

The value of γ is obtained by making a plot of C_p/T versus T^2 and extrapolating to T equals zero, the C_p/T intercept giving the value of γ. Dilation measurements give the values of β.

II. THE EFFECT OF COOPERATIONAL PHENOMENA ON SPECIFIC HEAT AND KINETICS OF TRANSFORMATIONS

The process of cooperation is in general the ability of units to join forces in opposition to disruptive influences, like thermal agitation, and is greatly enhanced by any increase in the existing degree of cooperation. Thus when the disruptive forces are not large the units establish a

cooperational state (37).

Cooperational phenomena cause "abnormal" behavior in properties. For example, changes in the degree of cooperation with temperature lead to heat effects which cause "abnormal" specific heat behavior. That is, the specific heat has a contribution in addition to lattice and electronic contributions. This contribution can be due to ferromagnetism or order-disorder transformations in metal systems.

Ferromagnetism

Ferromagnetism is the alignment of electron spin in atoms having unfilled electron bands in a manner that causes the magnetic moments of the electrons to be additive. The effect of this electron spin alignment is to cause a magnetic behavior in the metal. The alignment is brought about by electrostatic interactions between adjacent atoms and is related to temperature. At low temperatures this alignment is favorable, where the probability of a thermal fluctuation sufficient to upset the state is low. However, as the temperature increases the disruptive forces become greater and tend to destroy the cooperation. At a characteristic temperature (Curie temperature) the disruptive forces completely destroy the electron alignment and the magnetic effect associated with it.

This ferromagnetic effect introduces an anomalous

behavior into the specific heats of metals. The electrostatic interaction energy, the electronic energy, and the lattice energy change with the spin system and thus on heating so does the specific heat. This ferromagnetic behavior can be studied by analyzing specific heat data.

The theories proposed to explain the ferromagnetic behavior depend on the proper description of the atoms and their interactions. This involves an analysis from solid state physics which is beyond the scope of this thesis and thus only the results of the proposed theories will be noted. The theories are based on a spin system and the atoms contained in that system.

Heisenberg (19) assumed that the molecular interactions were independent of distance indicating extremely long-range interactions. That is, the atoms close together have the same interactions as atoms far apart in magnetic materials. This simplified model resulted in the expression

$$H_m = \frac{3\ snk\ T_C}{2(s+1)}\ , \qquad (14)$$

where H_m is the energy of the magnetic ordering, n is the number of magnetic atoms, T_C is the Curie temperature, k is the Boltzman's constant, and s is the spin per atom.

The theoretical entropy of magnetic order is obtained from Boltzman's (29) definition of entropy applied to a spin

system of n atoms, each of spin s, giving

$$S_m = nk \ln (2s+1) . \qquad (15)$$

Now that approximate methods of the determination of the theoretical energy and entropy of the magnetic transformation exist, it is necessary to apply a model as to the spin per atom and the number of atoms contained in the spin system.

Order-Disorder Transformations

An order-disorder transformation is where the relationship between solvent and solute atoms pass from a preferred atom arrangement to a random arrangement. Plausible explanations for non-random behavior of atoms in alloys have been based on the interatomic forces between like and unlike atoms by Bragg and Williams (5), Bethe (4), Kirkwood (24), and Peierls (42). Recent reviews of order-disorder transformations have appeared in Solid State Physics, one in 1955 by Muto and Takagi (35) and the second in 1956 by Guttman (18).

Solid solution alloys are usually thought of as having atoms randomly located throughout the matrix. However, if the interaction energies of like atoms are compared to unlike atoms the energies are different and thus generate a tendency for some type non-random arrangement, or ordering. Due to

the thermal energy of the atoms, they have a tendency to move about. Since these energies are temperature dependent, a characteristic degree of order is expected at a specific temperature.

Bragg and Williams (5) have looked at the simplest case where the order is considered to be "long-range." If the lattice is composed of A and B atoms which are placed on α sites and β sites, respectively, Bragg and Williams give a parameter S which relates the degree of long-range order by

$$S = 1 - \frac{W_B}{F_A} \tag{16}$$

where W_B is the fraction of β sites wrongly occupied by A atoms and F_A is the fraction of A atoms. When the atoms are randomly located, S equals zero. However, when the alloy is perfectly ordered no A atoms are wrongly located and S equals 1. The effect of temperature was related by the Boltzman factor. Their detailed studies were for stoichiometric ratios such as AB and AB_3.

Bethe's (4) theory was to eliminate some of the weaknesses of the Bragg and Williams proposal, which were macroscopic in nature. Bethe made a more detailed study of the interaction of forces between pairs of atoms. He further assumed that the interaction energy between pairs of atoms

fell off rapidly with distance and thus he considered only nearest neighbors as interacting. This interaction is called "short-range" order. Chang (10) has extended Bethe's work to next nearest neighbors. Kirkwood (24) and Peierls' (42) contributions to the theory of order-disorder reactions have also been extensions of Bethe's work. Bethe defines a short-range order parameter σ by

$$\sigma = \frac{q - q_r}{q_m - q_r} \tag{17}$$

in order to have the same limits as the parameter, S, defined by Bragg and Williams. The parameter σ indicates how on the average each atom is surrounded by unlike atoms. The quantity q equals Q_{A-B}/Q, where Q is the number of pairs in the lattice and Q_{A-B} will be the number of pairs of A-B atoms. Thus, q_m is the maximum q possible and q_r is the value of q at random positioning of atoms on the lattice. The two theories predict that the parameters of ordering will vary with temperature as shown in Figure 1.

The Bragg and Williams treatment predicts that at a critical temperature complete disorder is obtained, whereas Bethe's treatment indicates some small amount of order will exist at higher temperatures. These parameters indicate the possible effect that may result in the specific heat at a particular temperature. Bragg and Williams' long-range order

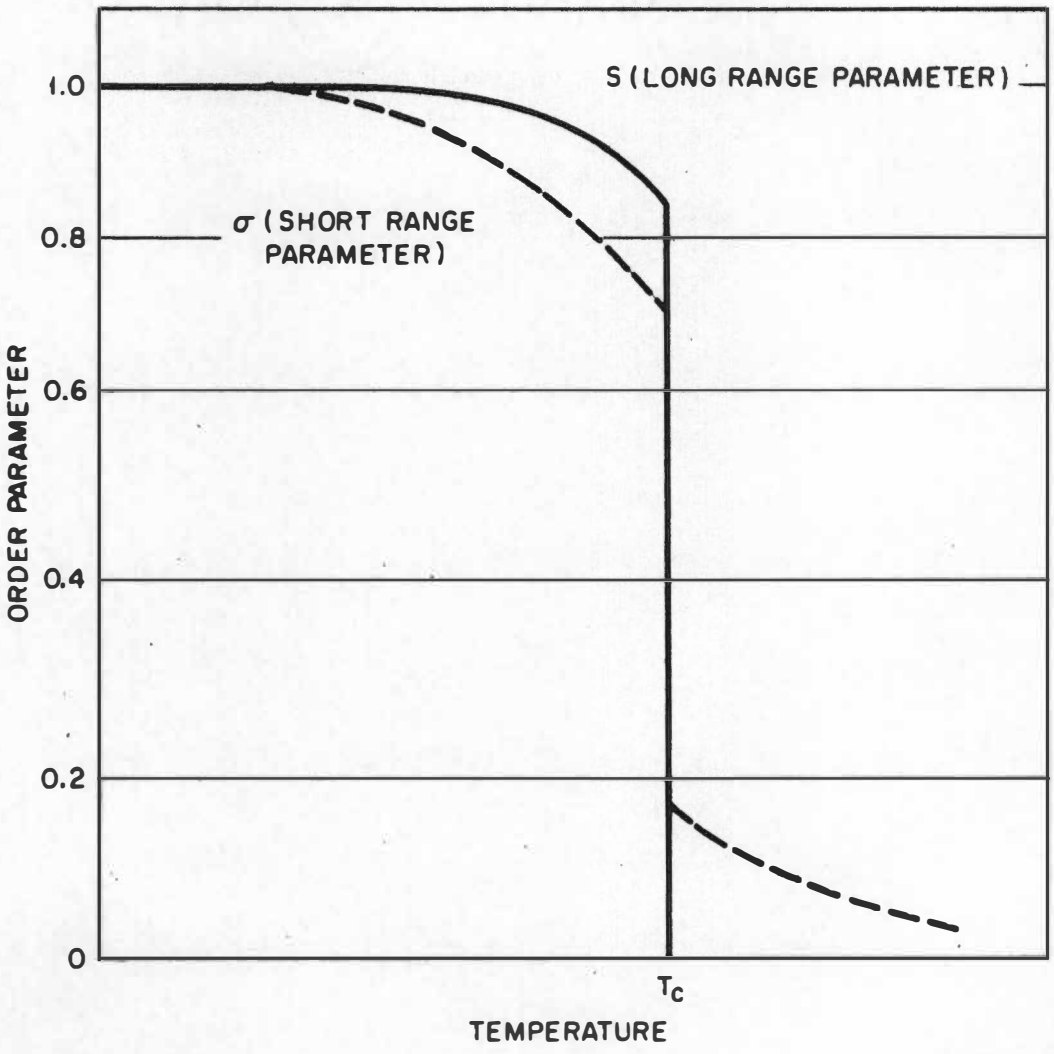


Figure 1. Order Parameters versus Temperature.

should have no effect on the specific heat above the critical temperature, but Bethe's short-range order would since it continues to exist to a slight degree above the critical temperature. The theory of long-range order indicates that at the critical temperature there should be no tendency for ordering and thus a random solid solution should exist. At low temperatures where the atomic arrangement is stable there should be no anomalous behavior. If these ideas are correct it should be possible to extrapolate low temperature specific heat data such that it will coincide with high temperature specific heat data. The short-range order theory indicates that there is some degree of order remaining above the critical temperature, which should prevent extrapolation of low temperature data to meet the high temperature data. Short-range ordering is usually favored for non-stoichiometric compounds.

The above treatments of order-disorder transitions have been for systems in an equilibrium state. The change from order to disorder has been accompanied by an energy absorption. However, in cases not under equilibrium conditions, the transition may manifest a varied effect on the specific heat curve. Such a condition would be the variation of specific heat with temperature for a previously quenched sample. Quenching from above the critical temperature would quench-in a disordered state as opposed to a stable, ordered

state. Thus, upon heating there would be a tendency for ordering to occur. Vacancies would also be available to contribute to the rate at which any ordering or disordering might occur. An evolution of energy would be expected as the quenched-in disorder takes on the equilibrium degree of order characteristic of a temperature. The specific heat curves for the quenched and non-quenched states will coincide only at temperatures where there is no atom exchange (at low temperatures) and above the temperature at which the equilibrium degree of order has been established.

III. THE SPECIFIC HEAT OF NICKEL

Nickel, a transition metal, experiences a ferromagnetic transformation which is manifested by heating to a temperature above its Curie temperature. Specific heat measurements show the character of such a transformation. The origin of the ferromagnetic effect is in the alignment of electron spin which is energetically favorable at temperatures below the Curie point as a result of partially filled "d" bands. This alignment becomes unfavorable at higher temperatures.

Models have been proposed to explain theoretically the phenomena associated with the ferromagnetic transformation. A test for these models is the comparison of experimentally determined magnetic energy to the theoretically predicted

values. The creation of electron band models has taken up the major portion of the theoretical study of ferromagnetic transitions.

Models have been advocated to designate the spin system that exists in the nickel atoms. Van Vleck (52) has proposed a model for nickel that applies a single or zero 3d hole per atom of $n=0.6N$, and a spin, s, of 1/2. Both Mott and Jones (33) and Mott and Stevens (34) have proposed that nickel should have two or zero holes per atom in the 3d level. A "cluster approach" by Brown and Lutlinger (8) considers that only short-range interactions are controlling. These models that explain the spin system can be used in conjunction with Equations 14 and 15 to predict the theoretical energy and entropy, respectively, for the magnetic transformation. Some values of the quantities from these theories are reported in Table I.

The specific heat of nickel is composed of three components: lattice, electronic, and magnetic contributions. By assuming that these contributions are additive, the total specific heat of nickel can be found by determining each of its component parts separately, and adding them. Presently, there are models to predict the contributions of the lattice and electronic nature which show reasonable agreement with experimental specific heats of metals experiencing no anomalous behavior. Equation 12, which gives the sum of these

TABLE I

THEORETICAL VALUES OF ENERGY AND ENTROPY
FOR THE MAGNETIC DISORDERING OF NICKEL

Source	Energy joules/gm-atom	Entropy joules/gm-atom°K
Calculated on Heisenberg theory, $n=0.6N_o$, $s=\frac{1}{2}$	1561	3.474
Calculated on Heisenberg theory, $n=0.3N_o$, $s=1$	1155	2.729
Calculated on cluster theory, $n=0.6N_o$, $s=\frac{1}{2}$	2252	3.474
Calculated on cluster theory, $n=0.3N_o$, $s=1$	1465	2.729

contributions, comes from such a model. In order to make these calculations, values of γ, T_o, $F(\Theta/T)$, Γ and $\beta_{(T)}$ for nickel are required. From the definition of γ a value of T_o is obtained. The Guneisen constant (Γ) has a value of 1.9 (25). The values of $\beta_{(T)}$ and Θ (390°K.) are determined from tables, references (21) and (44), respectively.

If the specific heat without the anomalous behavior is determined from these constants and compared to specific heat data determined experimentally, the energy and entropy of the magnetic transformation can be obtained. The difference in the area under these two specific heat curves is the energy of the magnetic transformation. The entropy is determined in a similar manner from plots of C_p/T versus T. The values obtained permit a comparison to values predicted according to particular models (Table I), which indicates the validity of the model.

IV. THE SPECIFIC HEAT OF NICKEL-20 WEIGHT PER CENT CHROMIUM ALLOY

The specific heat of a solid solution alloy can be determined approximately from the Kopp-Neumann rule of

$$C_p = x_A C_{pA} + x_B C_{pB} , \qquad (18)$$

where C_p is the specific heat, x is the weight per cent,

and A and B denote the respective components of the alloy. This rule only holds where the bonding energy of A-B can be neglected. When this is involved cooperational phenomena occur and an ordered state is more stable. This tendency to order at various temperatures causes an anomalous effect in the specific heat, which may be considered as the deviation of the specific heat from the Kopp-Neumann rule. The determination of the specific heats of solid solution alloys experiencing the anomalous behavior aids in specifying the type of order associated with the anomaly, long-range or short-range.

Anomalous behavior in the specific heat of solid solution has been reported for a number of alloys (12, 31, 7, 28, 30, 39), with limited data on nickel-chromium alloys (2, 51, 17). However, the explanation of the abnormality in the nickel-chromium alloys has been complicated by uncertainties in the phase diagram.

Work by Williams (53), Taylor and Floyd (50), and Stein and Grant (47), have obtained agreement as to the solubility of chromium in nickel at temperatures above 500°C., where the solubility is greater than 30 atomic per cent. Baer (3) reports a superstructure of Ni_2Cr between approximately 25 and 36 atomic per cent chromium at temperatures below 500°C. with chromium being soluble at lower compositions. The combination of these results insures that the anomaly

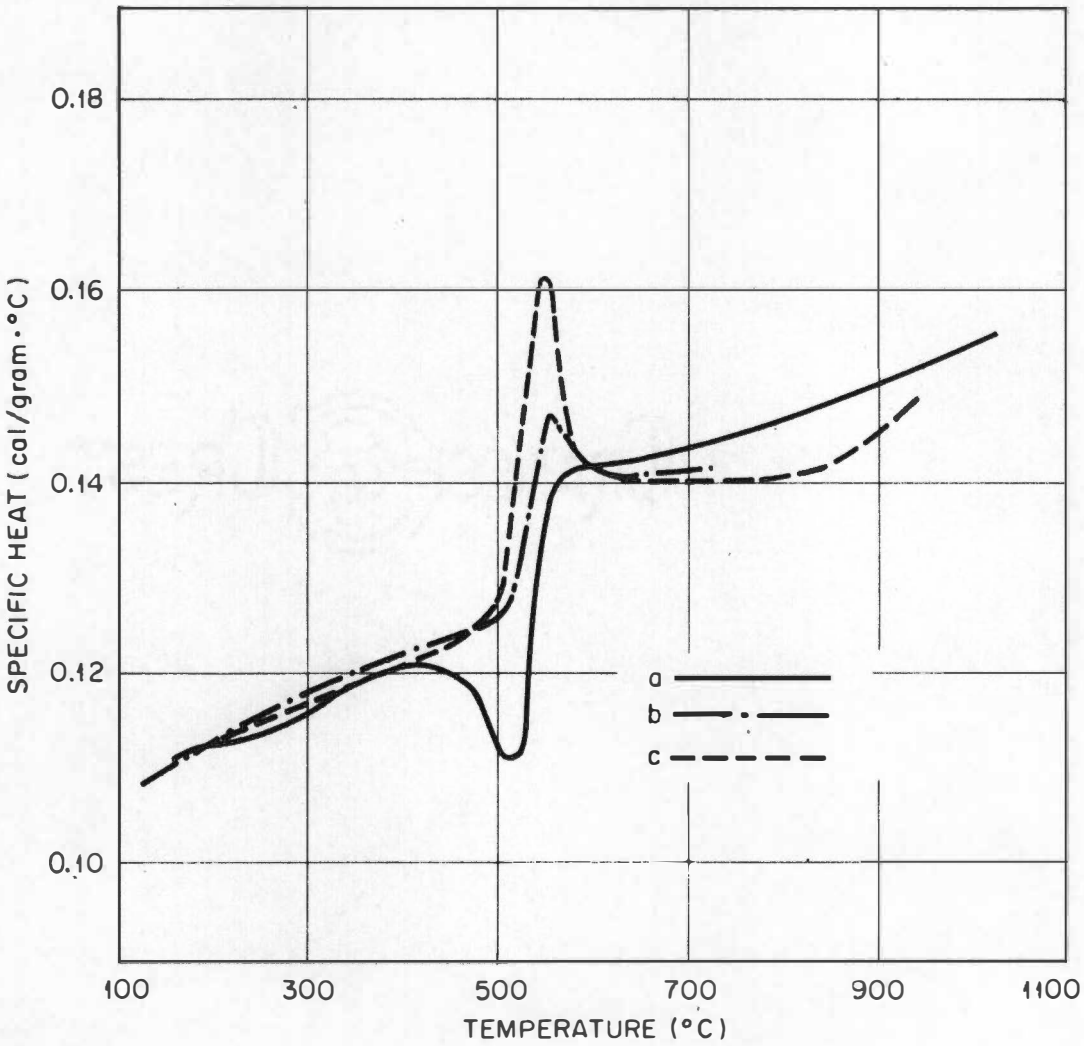
appearing in the nickel-20 weight per cent chromium is not attributed to precipitation or a phase transformation. Information of the lowering of the Curie temperature of nickel by the addition of chromium has been reported by Hultgren and Land (20). Their survey shows the complete disappearance of the ferromagnetic anomaly in alloys of 11 atomic per cent and above; Chevenard (11) places this limit at about 7 atomic per cent.

The anomaly observed in the nickel-20 weight per cent alloy has been attributed to short-range order. Recent work concerning this anomaly has been research by Taylor and Hinton (51) using electrical resistivity, specific heat, and x-ray measurement; by Nordheim and Grant (38) using electrical resistivity measurements; and by Koster and Rocholl (26) using electrical resistivity and Hall constant determinations. X-ray measurements are the only method of measuring short-range order directly, the other methods being indirect. However, due to the similarity of the atomic scattering of the nickel and chromium, it is difficult to measure the type and degree of order. Taylor and Hinton (51), making x-ray studies of the ternary alloy $Ni_{15}Cr_4Al$, detected long-range order. Because of the similarity of the behavior in properties of this alloy to the binary Ni_3Cr, they concluded that the anomalous behavior is due to long-range order. However, Nordheim and Grant (38) interpreted their results of

resistivity data to conclude that short-range order is responsible for the anomaly.

Taylor and Hinton (51), Arledge (2), Hultgren and Land (20), and Grover and Hutzenlaub (17) report the only known calorimeter data on nickel-chromium solid solutions. However, Taylor and Hinton and Arledge made the only reliable specific heat measurements for nickel-chromium alloys. Taylor and Hinton made determinations on the nickel-25 atomic per cent alloy. They report information on this alloy following three particular heat treatments. Figure 2 shows their specific heat data. Curve (a) is for a sample quenched from 1150°C. where disorder is trapped due to a lack of atomic mobility. Upon reheating, the atomic mobility increased to a point at which a part of the disorder quenched-in re-ordered, giving off energy and thus causing a decrease in the specific heat curve. An equilibrium degree of order was obtained and upon further heating disordering occurred. Curves (b) and (c) show the effect of slow cooling. The specimen that was more rapidly cooled showed less of an anomaly due to a less degree of order prior to reheating. Under all conditions the anomaly was observed to be at approximately 550°C. The curves also show a tendency to coincide at high temperatures where the same equilibrium degree of order may be obtained.

Arledge made more detailed studies of the alloys



(a) Water quenched after 8 hr. at 1150°C.
(b) Furnace cooled in 16½ hr. from 777°C.
(c) Water quenched after 8 hr. at 1150°C., and furnace cooled in 15 hr. from 670°-540°C., 20°C./hr., 20°C./day to 480°C., 10°C./day to 430°C., and 4°C./day to 370°C.

Figure 2. Specific Heats of Alloy of Composition Ni_3Cr.

5, 10, and 20 weight per cent chromium. The 5 weight per cent alloy did not show an anomaly while the 10 and 20 weight per cent alloys did. A decrease in magnitude of the anomaly is shown for the 10 per cent alloy. The appearance of the anomaly is at essentially the same temperature as that observed by Taylor and Hinton (51) in all cases. This supports the short-range order explanation. If long-range order were the case, the anomaly would appear at lower temperatures for lower compositions. A lack of extrapolation of the low temperature curve to meet the curve at temperatures above the anomaly also supports short-range order. Theory predicts that if long-range order is present then complete disorder is obtained at the critical temperature. In this case, extrapolation of low temperature specific heat data should coincide with data above the critical temperature.

Another argument indicating short-range order is the low magnitude of the energy of disordering. It is the difference in the bonding energies of short-range order as compared to long-range order that causes this. The energy of disordering is determined experimentally by the difference in area under the experimental specific heat curve and a curve representing only lattice and electronic contributions (i.e., Kopp-Neumann curve). In alloys showing long-range order and for which the energy has been determined (48, 49), the energy is about 5 times greater than that for the

nickel-chromium alloys.

CHAPTER III

THE NEW DYNAMIC ADIABATIC CALORIMETER AND ITS OPERATION

The operation of physical systems at elevated temperatures has always presented an experimental problem to the investigator. This project, likewise, experiences such difficulty. The construction and operation of a calorimeter from which thermodynamic quantities can be obtained suffers significantly from radiative heat transfer problems at high temperatures. The dynamic adiabatic calorimeter has been incorporated at The University of Tennessee due to the advantages in eliminating the radiative heat transfer problems to an extent that data can be obtained over a wide range of temperatures. There are other advantages associated with this type calorimeter such as the reproducibility of data, the small corrections that have to be applied and the wide range of conditions under which data can be obtained. This investigation was concerned with the measurement of specific heats from the calorimeter. The specific heat is usually the quantity obtained from a dynamic adiabatic calorimeter. This quantity can then be used to relate other thermodynamic quantities.

I. GENERAL CONSTRUCTIONAL AND OPERATIONAL SCHEME

The dynamic adiabatic calorimeters that have been used at The University of Tennessee have been continuously improved since the program was initiated in 1950. Prior to this investigation, the calorimeter was essentially that described by Stansbury *et al.* (45) and Nauman (36). The operational scheme has remained basically the same.

The calorimeter consists of an adiabatic surrounding into which a highly polished specimen is suspended. The specimen is heated with direct current power; the temperature of the surrounding shields is forced to follow the temperature of the specimen to within $\pm 0.05^{\circ}C$. by temperature monitoring at a point on the specimen and at a point on each shield with platinum:platinum-13 weight per cent rhodium thermocouples welded directly to these points. The thermal emfs are compared using a modified Dauphinee (14) circuit as described by Stansbury, Nauman, and Brooks (46). The differences in emfs are amplified and the resulting potentials are caused to activate control systems which supply power to the heaters on the various shields. The system approaches an adiabatic condition during the process of heating the sample. The system is evacuated to a pressure of 10^{-4}-10^{-5} Torr in order to eliminate convectional heat transfer and oxidation. The time necessary to

raise the temperature of the specimen a preset amount is measured. By measuring the power to the sample heater and the weight of the sample, the average specific heat is calculated. A correction for the weight of the heater is usually unnecessary if the heater weight is small in comparison to that of the sample. A technique devised by Pawel (40) is used for correcting for non-adiabatic conditions. A schematic diagram of the calorimeter prior to this investigation is shown in Figure 3. The new calorimeter was obtained from a similar system by employing numerous modifications as discussed later.

II. THE NEW CALORIMETER

The construction of a new calorimeter has been undertaken to make improvements primarily in connection with the adiabatic surroundings and in increasing the range of temperature within which specific heat data can be taken, while still maintaining a high degree of reproducibility. Previously, the problems encountered at elevated temperatures (700°-800°C.) have been the lack of sensitivity of response of the surroundings as conditions deviate from adiabatic behavior. This prevents the maintaining of adiabatic conditions and thus it is impossible to make applicable corrections. Low reproducibility is attained since the conditions change between runs. The problem has been attributed to the massive

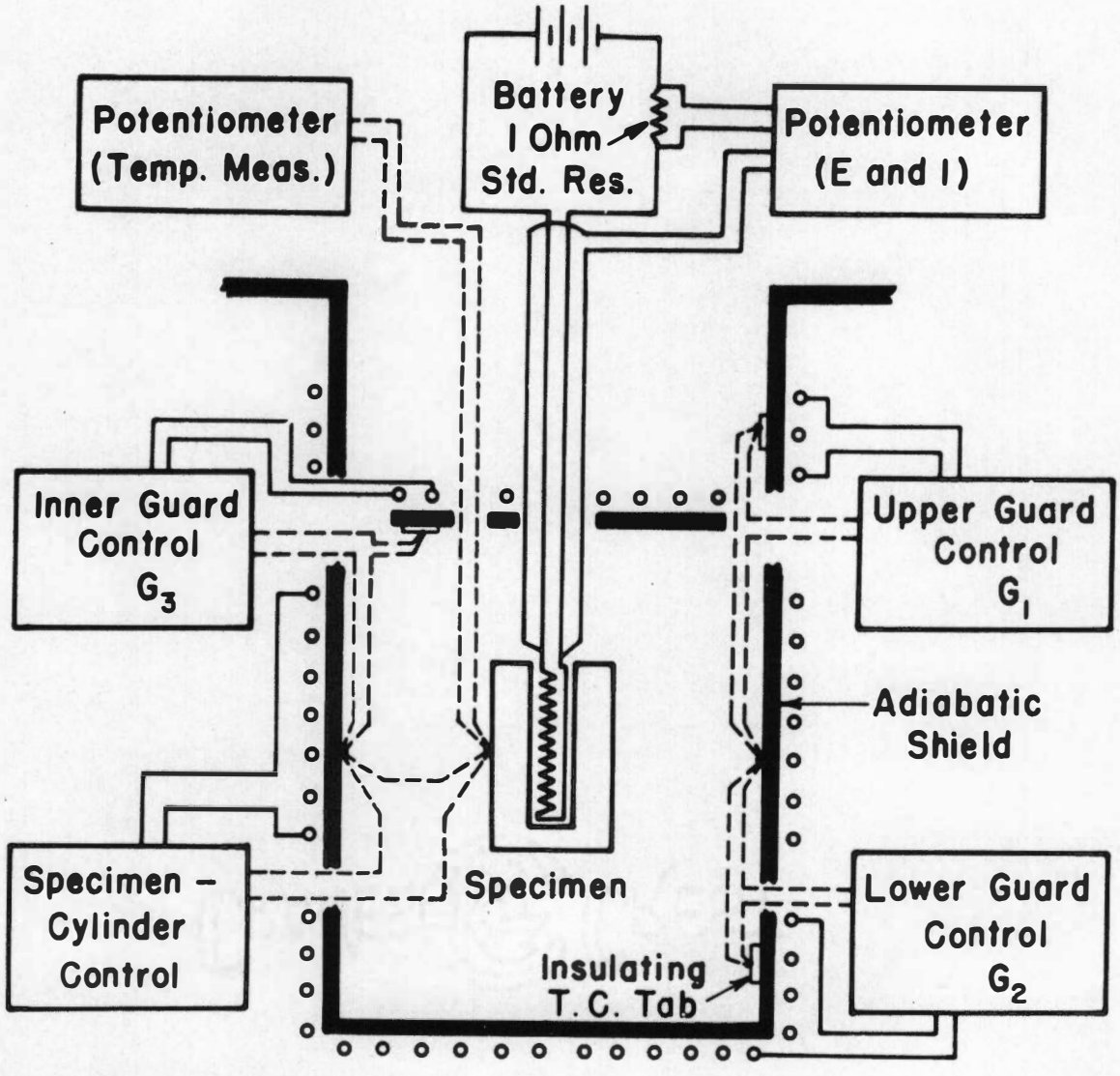


Figure 3. Schematic Diagram of Old Calorimeter System.

surroundings and the heat transfer characteristics of these surroundings. The major improvements have been concerned with this problem, even though other improvements have been made such as the use of new controlling equipment and changes in the thermocouple circuit.

The new calorimeter and its control panel are shown in Figure 4. The picture denotes the respective parts of the control panel. The actual calorimeter is shown in the lower left-hand corner.

Adiabatic Surroundings

The adiabatic system is composed as shown in Figure 5. A 39-inch long inconel cylinder is suspended from the top and makes up one of the insulating shields. The inconel tube has mounted on its outside perimeter a heater so as to maintain a temperature within a desired range of that of the specimen. This allows faster response of the immediate sample surroundings. The inconel cylinder is then surrounded by an insulating shield which aids in the prevention of heat losses from the calorimeter. The insulation is a fibrous potassium titanate material marketed by Dupont under the trade name "Tipersul." The new insulation was used because of its low thermal conductivity and its usefulness at high temperatures. A water-cooled jacket is mounted beyond this insulation to prevent heating of the room. Thus far, except for the

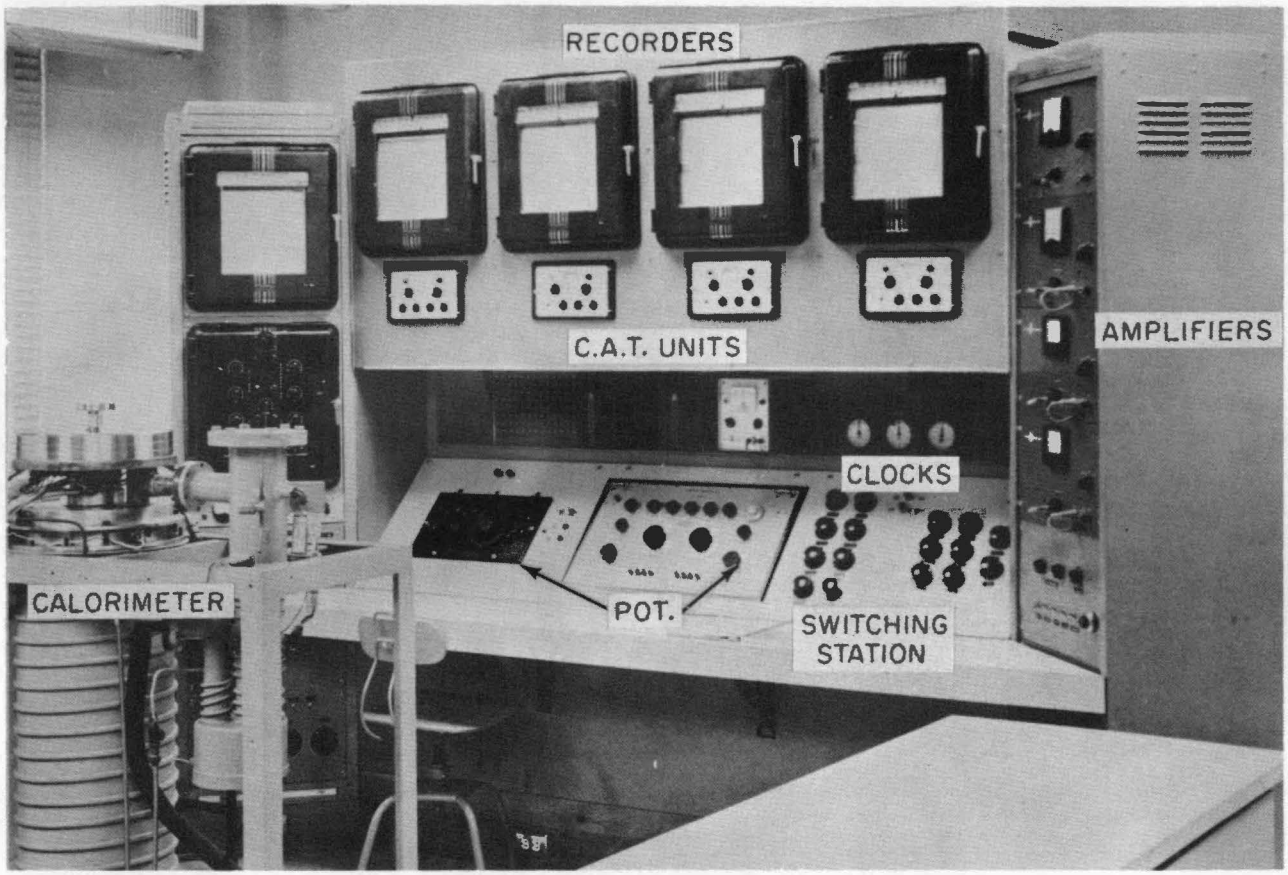


Figure 4. Photograph of New Calorimeter and Control Panel.

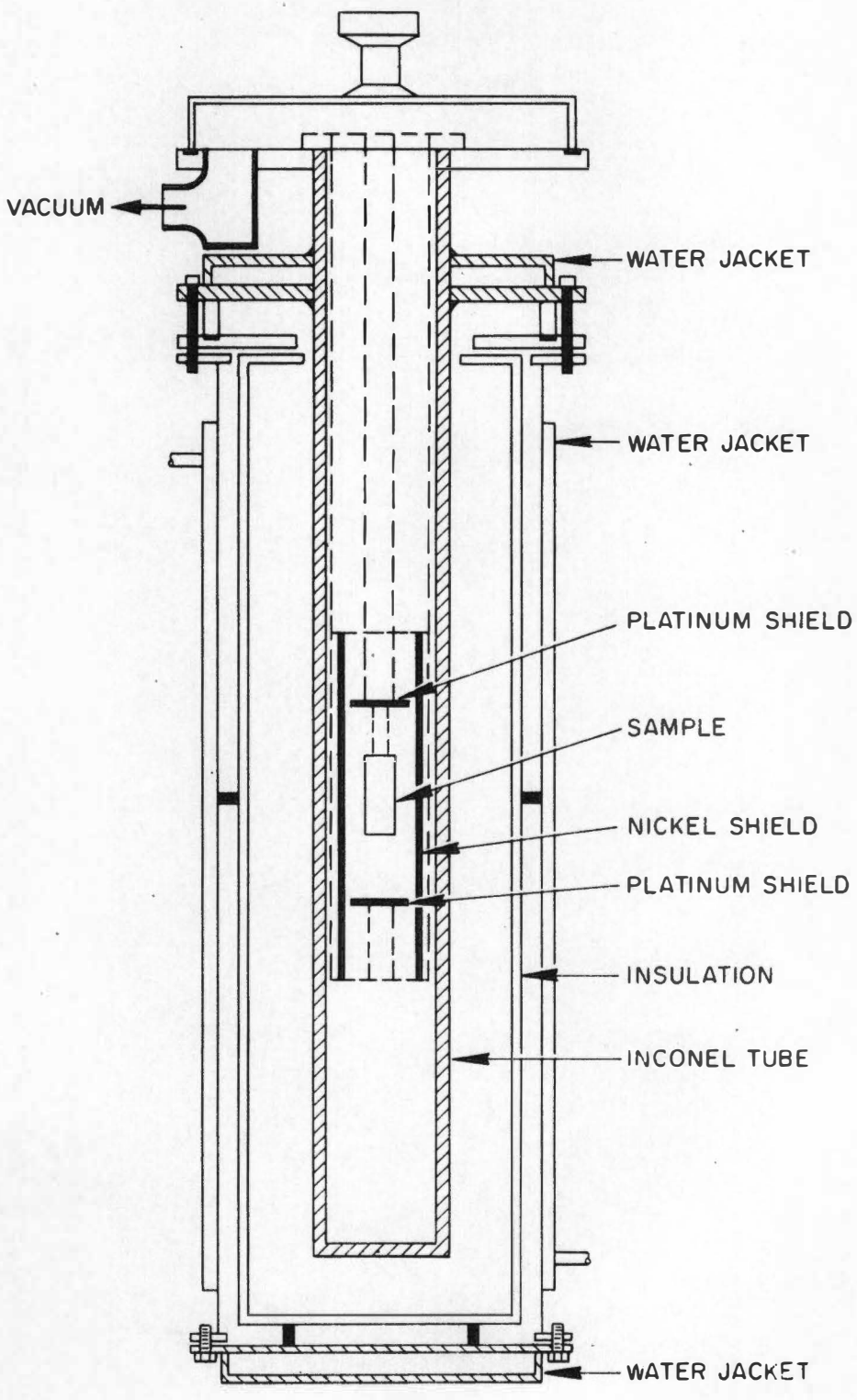
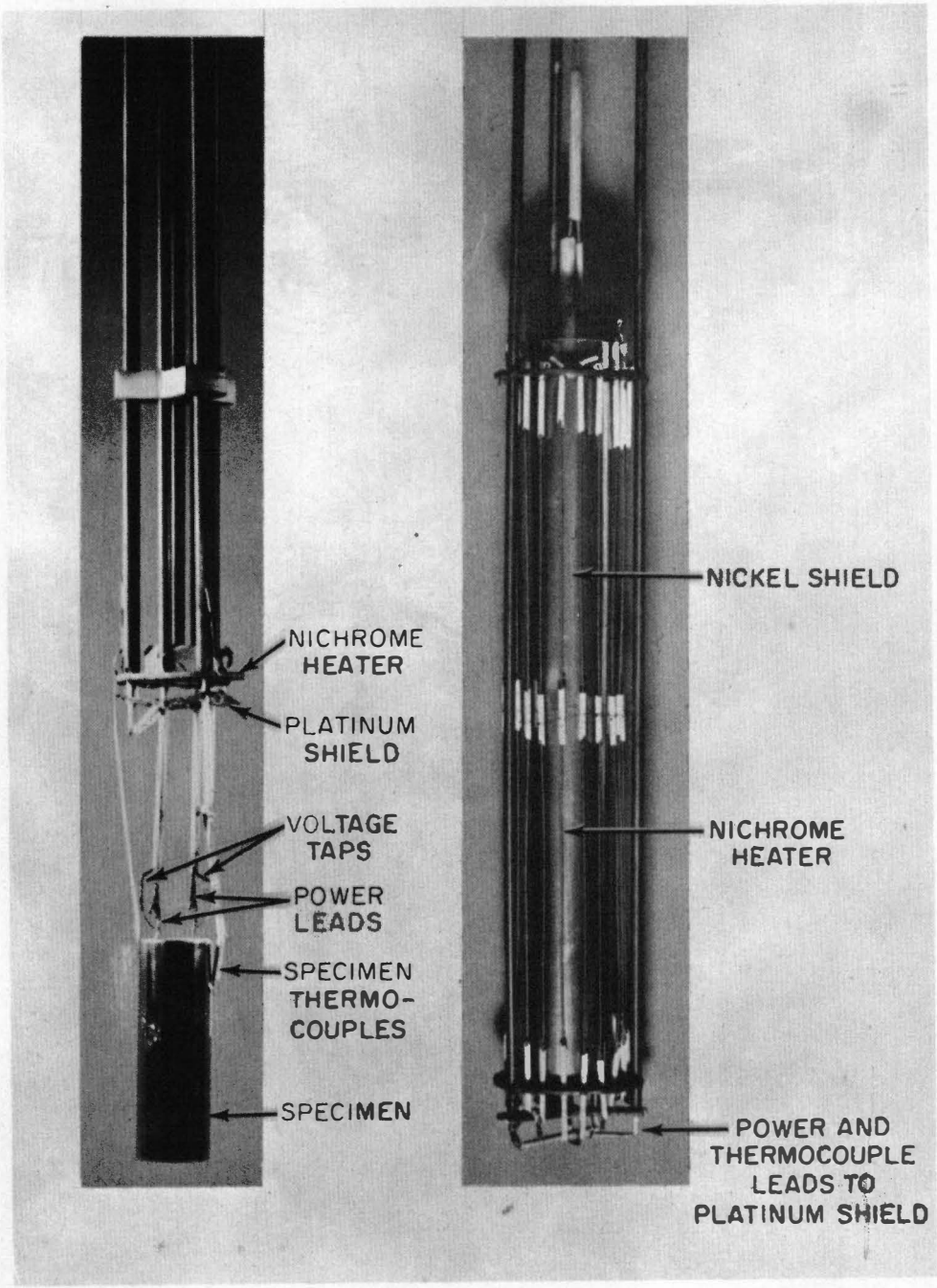


Figure 5. Schematic Diagram of New Calorimeter.

insulating shield, the calorimeter is as previously constructed and reported by Stansbury et al. (45).

The specimen and its immediate surroundings are lowered from the top into the 3.50-inch inside diameter inconel tube. Support is at the top, as are all electrical and thermocouple connections. A 2-inch diameter cylinder of 0.010-inch thick nickel sheet and two circular disks of platinum at each end of the nickel cylinder serve as the immediate surroundings. These nickel and platinum shields are of very low mass, which allows rapid response to heat impulses. The inconel tube beyond the immediate sample surroundings is of a large mass; thus its temperature is not affected rapidly by impulses of power. The combination of the low mass shields and the surrounding high mass shield operate together to give better adiabatic control than either shielding method would give separately. By this concentric shielding the advantages of both methods can be obtained.

Heaters of nichrome wire are mounted behind these shields to serve as their source of energy. The interior to the inconel tube is made up of two suspensions, one fitting within the other. Figure 6 shows these suspensions. Suspension A contains the specimen and top platinum shield, while Suspension B contains the nickel cylinder and bottom platinum shield. All power leads and thermocouples are carried to the top through high purity Al_2O_3 ceramic and inconel tubes;



A B

Figure 6. Suspension Units for Adiabatic Surroundings.

these latter tubes also serve as support. Figure 7 shows a top view of the calorimeter with the suspension unit in place; all electrical connections and the method of suspension can be noted.

Power Measuring Circuit

There have been no changes in the power measuring circuit. The specimen is continuously heated at approximately a constant heating rate. Power leads from a direct current source are carried down the internal calorimeter suspension where they are attached to the specimen heater. The specimen heater is completely enclosed so that the heater leads are allowed to achieve thermal equilibrium which prevents thermal leakage along the heater leads. A small nichrome heater is enclosed in a quartz tube and inserted from the bottom of the sample where power leads that pass through the specimen are attached. The leads are large with low resistance and by passing through the sample they reach thermal equilibrium which makes the heat losses along the leads very small. The design of this heater is discussed in more detail by Brooks (6). The current is measured by obtaining the voltage drop across a standard 1-ohm resistor located in series with the heater. The voltage drop across the specimen heater is obtained by use of voltage taps placed just above the surface of the sample. The values of voltage

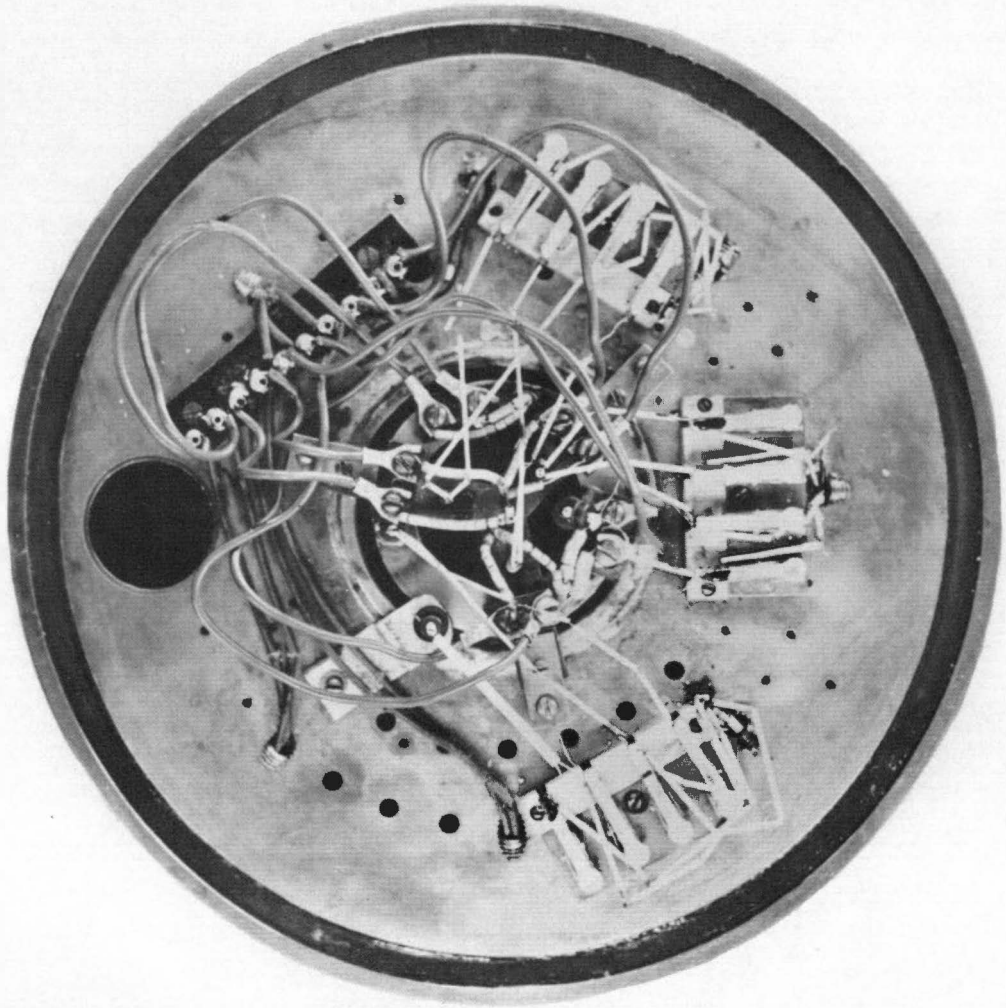


Figure 7. Top View of Calorimeter Showing All Electrical Connections.

and current can be read directly by use of a potentiometer. A suppressor and multiple point recorder are used to continuously monitor these values. Due to limitations of the range of the potentiometer, it is necessary to pass the voltage across a voltage divider that reduces the voltage to values that can be read by the potentiometer. A reduction of 10 per cent is normally used. From the potentiometer readings and by making use of the suppressor it is possible to record the voltage to the third decimal place and the current to the fourth decimal place. The product of the voltage and current gives the power fed to the calorimeter specimen. A small correction factor is applied due to the voltage divider reduction and standard resistor as described by Brooks (6).

Thermocouple Circuits

All thermocouple circuits, both those used in direct measurement and as differential thermocouples, are platinum: platinum-13 weight per cent rhodium. This type thermocouple is used due to the high accuracy which is retained even to temperatures as high as 1000°C. It is well known that such thermocouples generate only small emfs, thus requiring a sensitive method of measurement. A potentiometer designed by Dauphinee is used which enables the accurate measurement of emfs to $\pm$0.1 microvolt, corresponding to a temperature equivalent of $\pm$0.01°C. The accurate emf measurement is

needed to insure a specific temperature interval in taking data.

The calorimeter thermocouple system is composed of six thermocouples, placed as temperature sensing devices. Four of these thermocouples are attached to the four shields surrounding the specimen and the other two are attached to the specimen. Of the two specimen thermocouples, one is used as the temperature sensing device for the control circuit while the other is used for direct temperature measurement during operation. The thermocouples running from G_1, G_2, G_3, cylinder, and specimen (Figure 8) are contained in ceramic and quartz tubing while inside the calorimeter to prevent both contamination from vaporizing metals or other sources and the occurrence of short circuits. From the calorimeter, they pass to an ice-water reference junction where the platinum:platinum-13 weight per cent rhodium wires are joined to copper leads which pass to a thermal-free switching station. The switching station is constructed such that all temperatures can be read directly. Thermal emfs can be picked up by testing emf values between the specimen platinums and specimen rhodiums. Part of these thermocouple wires then pass out of the switching station to the control circuit, which is discussed in the following section.

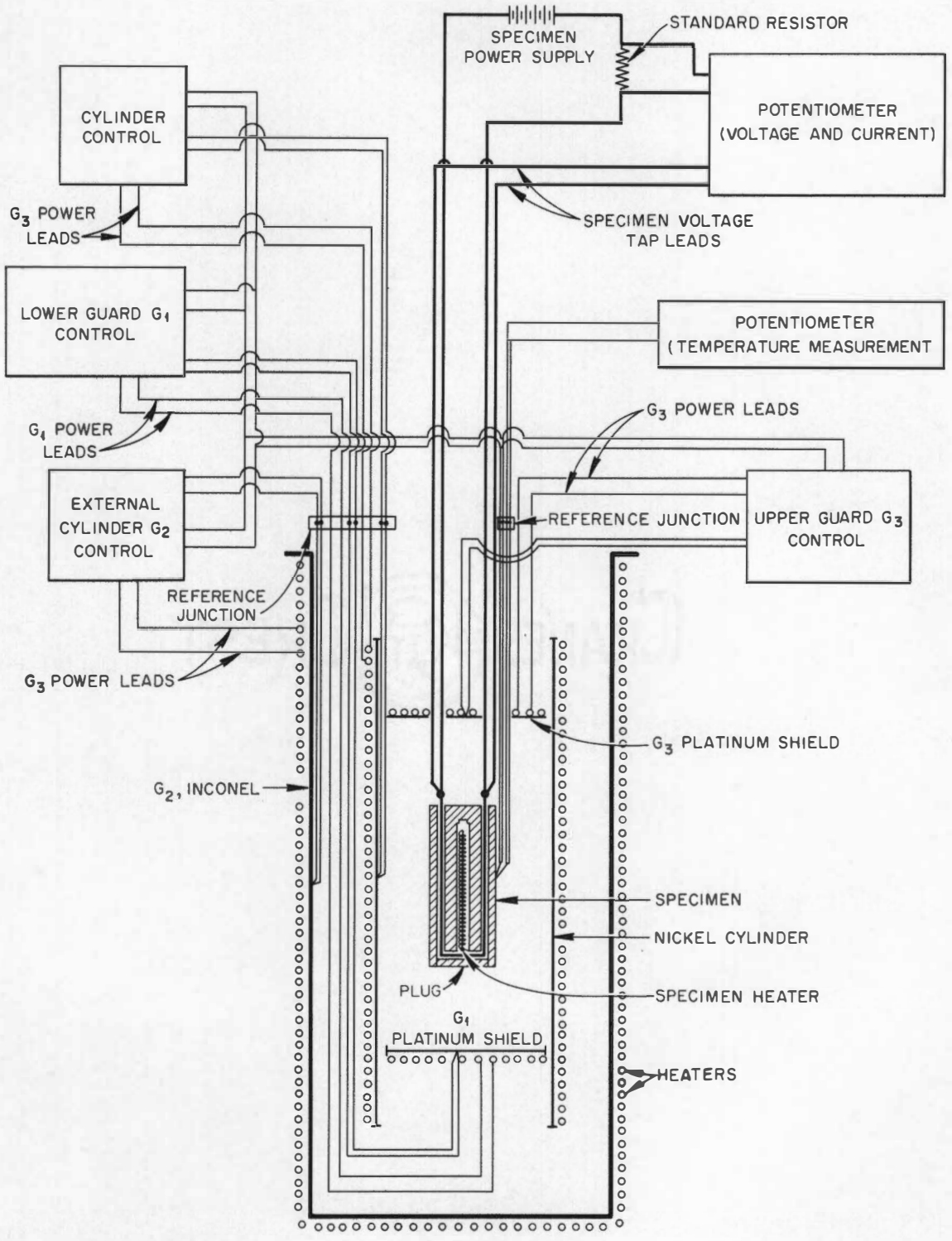


Figure 8. Schematic Diagram of the New Calorimeter and the Measuring Control System.

Control Circuit

It is the controlling method that makes possible the operation of a dynamic adiabatic calorimeter. As the name implies, the system must be so constructed that adiabatic conditions exist continuously as the temperature of the sample changes.

The thermocouples from each shield and from the specimen pass into a comparator circuit as designed and built by Nauman (36) and discussed by Stansbury, Nauman, and Brooks (46). The comparator is composed of low leakage capacitors which store thermocouple emfs. A chopper exists that allows two thermocouples' emfs to be alternately stored in such a manner that their difference can be compared. This allows comparison of the thermocouples without direct contact between the thermocouples. The comparator circuit made it possible to compare thermocouples at different ground potentials. Further it prevented current leakage from the specimen from creating false emfs in the thermocouples. There are four separate comparator units in the control system, one for each shield. The emf in the thermocouple from the respective shield is compared to the emf of the specimen thermocouple. This comparing system then acts as a differential thermocouple. The emf difference, if any exists, is fed to a direct current microvolt-amplifier, which sends the amplified difference to a Speedomax recorder. When

the respective shield is at some temperature other than the specimen temperature, the recorder sees this difference and operates a Leeds and Northrup three-action, continuous action type (C.A.T.) control unit. This latter instrument contains a control setting device which signals the heater power source as the measured variable temperature difference deviates from control point setting. The heater power source is a Labac which sends a continuous voltage across the respective heater ranging from zero to the maximum output available. The C.A.T. current output ranges from zero to 5 milliamperes. The Labac receives this current which activates two solid state diodes to control the relative voltage output to the respective heaters.

CHAPTER IV

OPERATIONAL DETAILS OF THIS INVESTIGATION

I. CALORIMETER TECHNIQUE

The experimental procedure of obtaining results is carried out as follows. The technique is to obtain an average of the specific heat over a small temperature interval, instead of an instantaneous value for a respective temperature. However, the actual procedure involves problems that can be appreciated only by one who has carried out work requiring the greatest degree of accuracy.

The specimen is fed a constant voltage, but due to variations in the heater resistance, the power that the specimen receives varies slightly. The average power and time necessary to raise the temperature some pre-specified interval is noted. This interval is usually either 10^{o} or $20^{o}C.$, depending on the expected variation of the specific heat within that temperature interval and the heating rate. Clocks are used to record the time to heat over the temperature interval. The emf corresponding to a temperature is set on the thermofree potentiometer and as the sample obtains the temperature, as noted by a null-point detector which is connected in conjunction with the potentiometer, the clocks are switched such that one stops and simultaneously another

begins. The next temperature is set on the potentiometer and the procedure repeated. Thus, the clocks report the time necessary to heat through the specific interval.

With the time necessary to heat through a specific temperature interval and the average values of the voltage and current, it is possible to obtain an average value of the specific heat as given by

$$\bar{C}_p = \frac{\bar{E}\,\bar{I}\,\Delta t\, f}{w\,\Delta T} \quad . \tag{19}$$

In the above equation for the average specific heat, $\bar{E}$ and $\bar{I}$ are the average voltage and current fed to the specimen over the temperature interval ΔT, Δt is time required to pass through this interval, w is the combined weight of the specimen and its heater, and f is a factor which corrects for errors in $\bar{E}$ and $\bar{I}$, as discussed later. The values are recorded in units such that the average or apparent specific heat has units of joules/gm.-^{o}C.

The value of the specific heat obtained by the above equation will be the true specific heat only provided that adiabatic conditions exist and that all power fed to the specimen is recorded by the voltage and current measurements. Extensive studies have been made by both Pawel (40) and Brooks (6) to characterize all sources of error and, in cases where these errors are significant, provide a means of

correction. This is discussed in more detail later.

II. SPECIFIC HEAT CORRECTIONS AND ERROR ANALYSIS

The value of the specific heat obtained by Equation 19 will be the true specific heat only if there are no corrections to be applied. However, there are three corrections that must be applied to obtain the true specific heat. One of these, the factor f, is already incorporated into Equation 19. The other two corrections are for lack of maintaining truly adiabatic conditions and the fact that not all the power fed to the sample is consumed in heating it. All other sources of error have been shown to be negligible by Pawel (40) and Brooks (6).

The previous discussion of the specimen power circuit should readily indicate corrections necessary there. The factor f corrects the recorded voltage and current due to errors inherent in the specimen power circuit and the way the voltage and current are measured. This factor includes the effect due to the standard resistor not having a resistance of exactly 1 ohm and the voltage divider not dividing exactly by 10.

It is necessary to apply a correction for the heat required to heat the specimen heater over the same temperature range that the specimen is heated. Pawel (20) has obtained a relation that expresses the heat necessary to heat the

heater and its components over any temperature range. From this a correction can be applied readily to correct for the heater as given by

$$\overline{C}_{p_s} = \overline{C}_p + \frac{w_H}{w_s} (\overline{C}_p - 0.4729), \qquad (20)$$

where $\overline{C}_{p_s}$ is the average specific heat of the specimen, $\overline{C}_p$ is the total average specific heat (from Equation 19), w_H is the weight of the heater and w_s is the weight of the specimen. This equation is derived from a heat balance during some time interval Δt. Pawel estimated a relationship between the change in temperature of the specimen as related to a change in the temperature of the heater, which was shown by Brooks (reported in Reference (36)) to be applicable. The small change in the specific heat of the heater and its components with temperature allowed the use of a constant value for its specific heat. This value was 0.858 joules/gm.-°C.

In cases where w_H/w_s is less than 0.01 the correction is usually less than 0.1 per cent and can be neglected. This criterion was used as the basis as to whether a correction for the heater was to be applied.

A correction, known as a "drift correction," was necessary for the deviation from adiabatic conditions. The name of the correction is derived from the method by which it is determined. The drift is measured by removing the power fed

to the sample and allowing the system to come to steady state conditions. The steady state drift in temperature of the sample is noted. This heat loss is then applied as a correction, when taking data at this same temperature.

The location of the various thermocouples is very critical as to what this correction is. Since these thermocouples are the controlling method for the adiabatic conditions, only the regions in the immediate vicinity of the thermocouples are at the same temperature as the specimen. It is expected that various temperature gradients will be set up along the various shields, depending on the heat transfer of the system. The use of the thin nickel shield was an attempt to decrease these gradients. The temperature gradients on the shields act to either add or remove heat from the sample by radiation. The system under use and study experienced a loss in heat from the sample at all times.

There is some concern as to whether the drift correction is valid under dynamic operation. The gradients under dynamic operation have been assumed to be the same as those under static operation. Pawel (40) has applied the drift correction to data taken under dynamic operations by the equation

$$C_p = \frac{\overline{C}_p}{1-\frac{\overline{C}_p\, R(T)}{k}} \quad , \tag{21}$$

where C_p is the "true" specific heat, $\overline{C}_p$ is the apparent or average specific heat (Equation 20), R(T) is the drift rate and k is the energy imput rate.

There is sufficient basis to allow the assumption that static drift and dynamic drift are the same for temperatures below 600°C. However, above 600°C. this correction has not always been found to be applicable. If specific heat data could be taken with an infinite heating rate there would be no drift correction, since under that condition there would be no time for drift to occur. An indirect method can be taken to obtain the specific heat under an infinite heating rate. Specific heat data are taken for at least three various energy imput rates. These runs must be taken under constant calorimeter variables, except for the heating rate. It is then possible to construct plots of C_p versus C_p/k for various temperatures, where k is the energy imput rate. A set of curves is obtained, one curve for each temperature. An extrapolation of each of these curves to where C_p/k equals zero gives the true specific heat at that temperature, as would have been obtained if the heating rate had been infinite. In this investigation above 600°C., Equation 21 was not applicable and the above method had to be applied. The specific heat data determined in this manner agree with the values obtained from Equation 21 for temperatures below 600°C. Appendix A contains a more detailed discussion of

this method.

Other sources of error existed but they were not significant enough to require a correction since their magnitude was well within the reproducibility of data. These possible errors include such things as accuracy of the potentiometer measurements of voltage, current, and temperature, measurement of the sample weight, and measurement of the time intervals. Brooks (6) has made an extensive study of these sources of error and has found them to be well within the reproducibility of the experimental data of ± 0.5 per cent.

III. SOURCES OF OPERATIONAL DIFFICULTY

Calorimeter operation did not cause any difficulty until the later stages of the investigation. A problem arose as a result of continued operation at high temperatures (700°-800°C.). The method of correction of data in this temperature range required constant calorimeter variables, i.e., the same drift conditions. This was found not to exist. The drift correction was changing between and during runs, which prevented the correction of data. The problem was related to changes in the thermocouples' emf characteristics, which resulted in continually changing temperature gradients in the surroundings. The cause of such changes in the emf characteristics had to be a result of thermocouple contamination,

either existing on or within their surface.

Communication with McElroy (32) of the Oak Ridge National Laboratory indicated that he had previously had similar thermocouple problems. He was concerned with thermal conductivity measurements of inconel at high temperatures (1000°C.). Platinum:platinum-13 weight per cent rhodium thermocouples, enclosed in high purity aluminum oxide ceramic, were used to record temperatures. He believed that the chromium was vaporizing from the inconel and depositing on the available aluminum oxide, causing a reaction that allowed aluminum to contaminate the thermocouples. This was based on chemical analysis of the thermocouples which showed as high as 0.4 per cent aluminum in thermocouples which had errors as high as 90°C. at 1000°C. in their calibration. The problem of thermocouple contamination encountered in the present investigation was attributed to the same phenomena. This was confirmed to some extent by comparing the various thermocouples to each other. They were found not to agree in emf readings.

A method which would eliminate or reduce the existing problem was considered. An attempt was made to completely enclose those thermocouples being contaminated by placing them in a protective tube and making electrical connections to the shields by the use of pure platinum which surrounded the thermocouples' effective junction. Improvements

resulted to allow the completion of this thesis. A project is being undertaken at the present to replace the inconel, which was initiating the problem, with nickel.

CHAPTER V

ANALYSIS OF SAMPLES USED IN THE PRESENT INVESTIGATION

This investigation was involved with the study of the specific heat of four calorimeter samples, which were samples used previously at The University of Tennessee. It might be of some value to give a brief history of the samples used.

As already mentioned, there were two copper samples employed having different weights and sizes. The smaller sample's weight (including heater) is 172.794 grams and it has outside dimensions of 2.125 inches long and 0.875 inch in diameter. This sample was cast by Pawel (40) but he makes no mention of the melting procedure. Its specific heat has been determined by Pawel (40) and Brooks (6). The larger copper sample was produced by Brooks. Its weight (including heater) is 368.778 grams and it has outside dimensions of 3.00 inches long and 1.125 inches in diameter. The sample was produced by melting high-purity electrolytic copper in a high purity graphite crucible. The size of the crucible was about 1-1/4 inches inside diameter and about 8 inches deep with a cap at its top. Molten copper was melted to a depth of about 5 inches leaving a gap between the metal and the top where a reducing carbon monoxide-carbon dioxide atmosphere was generated from the crucible and oxygen, which prevented

oxidation of the melt. The molten metal was chill cast into a round copper mold giving an ingot from which the sample was machined. Table II gives the chemical analysis of these copper samples. The table shows a purity of greater than 99.99 per cent for both samples. The two copper samples were studied to denote the effect of sample size on the data obtained.

The nickel sample employed was also that prepared and used by Pawel (40). This sample was machined from a commercial high-purity plating electrode. Its dimensions are rather small and similar to those of the small copper sample. Its weight (including heater) is 182.59 grams. It has dimensions of 2.625 inches long and 0.875 inch diameter. Its specific heat has been investigated by Pawel (40), Nauman (36), Alig (1), and Arledge (2). The chemical composition is not as high purity as that of the copper samples (Table II).

The nickel-chromium alloy studied was secured from the Hoskins Manufacturing Company and is marketed by them under the name of a Chromel A alloy. They indicated its composition to be 1.5 per cent silicon, 20 per cent chromium, and the balance nickel. However, a qualitative spectrographic analysis gave a somewhat different result as reported in Table II. This analysis shows the presence of a considerable amount of manganese. Microscopically, there existed a segregation-free matrix containing a very small amount of a

TABLE II

ANALYSIS OF SPECIMENS

Specimen	Cu	Ni	Cr	Fe	Ag	Mn	Co	Si	Al	Elements Checked But Not Found
Large Copper	Bal.	-	-	0.000X*	0.00X	-	-	-	-	Si, B, Ni, Cd, In, Bi, Sb, As, P, Pb, Sn, Th, Ga, Ge, Al, Ti, Mg, Zr, Mn, Ni, Cr, Co, Mo, V, W, Ca, Ba, Na, Sr, K, Li
Small Copper	Bal.	-	-	0.00X	0.00X	-	-	-	-	As, Sb, Cd, In, Ga, Th, Ge, P, Si, Mg, Al, Ni, Co, Cr, Mo, W, Ti, V, Mn, Na, Ca, K, Li, Ba, Sr, Pb, Sn, Zn, Bi
Nickel	0.00X	Bal.	-	0.00X	-	-	0.0X	0.00X	0.00X	Mn, Cr, Ti, Mg, W, V, Mg, Zn, Pb, Sn, Bi, As, Zr, Nb, Na, Ca, K, Li, Ba, Sr
Ni-20%Cr	0.X	79.32	18.94	0.X	-	1.5	0.X	0.X	0.X	Zn, Cd, In, Bi, Sb, As, Sn, Tl, Ga, Ge, Mo, V, W, Mg, Ti, Zr, Ag

*X means that the number here is from 1 to 9 weight per cent.

second phase (2), possibly due to the presence of other elements, since 20 per cent chromium is completely soluble in nickel. The weight (including heater) of the sample is 259.308 grains and it has dimensions of 3.00 inches long and 1.125 inches diameter.

All the samples had a similar heater mounted within the specimen to serve as its source of power. Brooks (6) reports the general design of such calorimeter specimens.

CHAPTER VI

PRESENTATION OF DATA AND RESULTS

I. THE SPECIFIC HEAT OF COPPER

The study of the specific heat of copper has been carried out by many investigators. Its specific heat has been investigated here as a means of insuring accuracy of the new calorimeter. Copper's specific heat, as for all normal pure metals where no transitions occur until the melting point, is composed of only lattice and electronic contributions. The lattice contribution comes from the energy added to atoms in increasing the amplitude and/or frequency of oscillation about an equilibrium site. The electronic contribution is the energy consumed by the outer valence electrons. It is the degree of lattice vibration and valence electron energy that give such a pure metal its respective temperature. Thus, its specific heat will be concerned with the energy absorbed in increasing the energy within each of these components.

The specific heat can thus be determined by the energy supplied in heating through some finite temperature range. This approach, as described earlier, was used to measure the specific heat within the temperature range from 100°C, to 800°C. The data obtained for this investigation were

determined under a wide range of operating conditions available within the limitations of the calorimeter and its corresponding control system. Figure 9 shows these data and those of other investigators at this University. The circles indicate all the data points taken. The black dots indicate the data points taken during one run. A variation of about ±0.2 per cent from a smooth curve was always obtained for a given run. Two samples were used with a large difference in size. One of the samples weighed 368 grams and the other weighed 173 grams. The G_2 heater (back-up heater) was held at 250 and 50 μv.'s behind that of the remaining adiabatic system. The lower the temperature of the G_2 heater was, as compared to the remainder of the adiabatic surrounding, the higher the drift rate. The increased drift rate caused the application of larger percentages of the specific heat as a correction. The variation of the G_2 thermocouple setting caused the greatest variation of data between runs. Various power imput rates ranging from 39 to 159 joules/gm.-hr. were used. These power imput rates correspond to heating rates of approximately 1.5° to 6.0°C./min. Under these variables, a variation of ±0.7 per cent was experienced in the specific heat data. Pawel (40) used the 173-gram sample and Brooks (6) used both the 173-gram and 368-gram samples to obtain the specific heat data also reported in Figure 9. Any difference that occurs between one of these investigators and the present

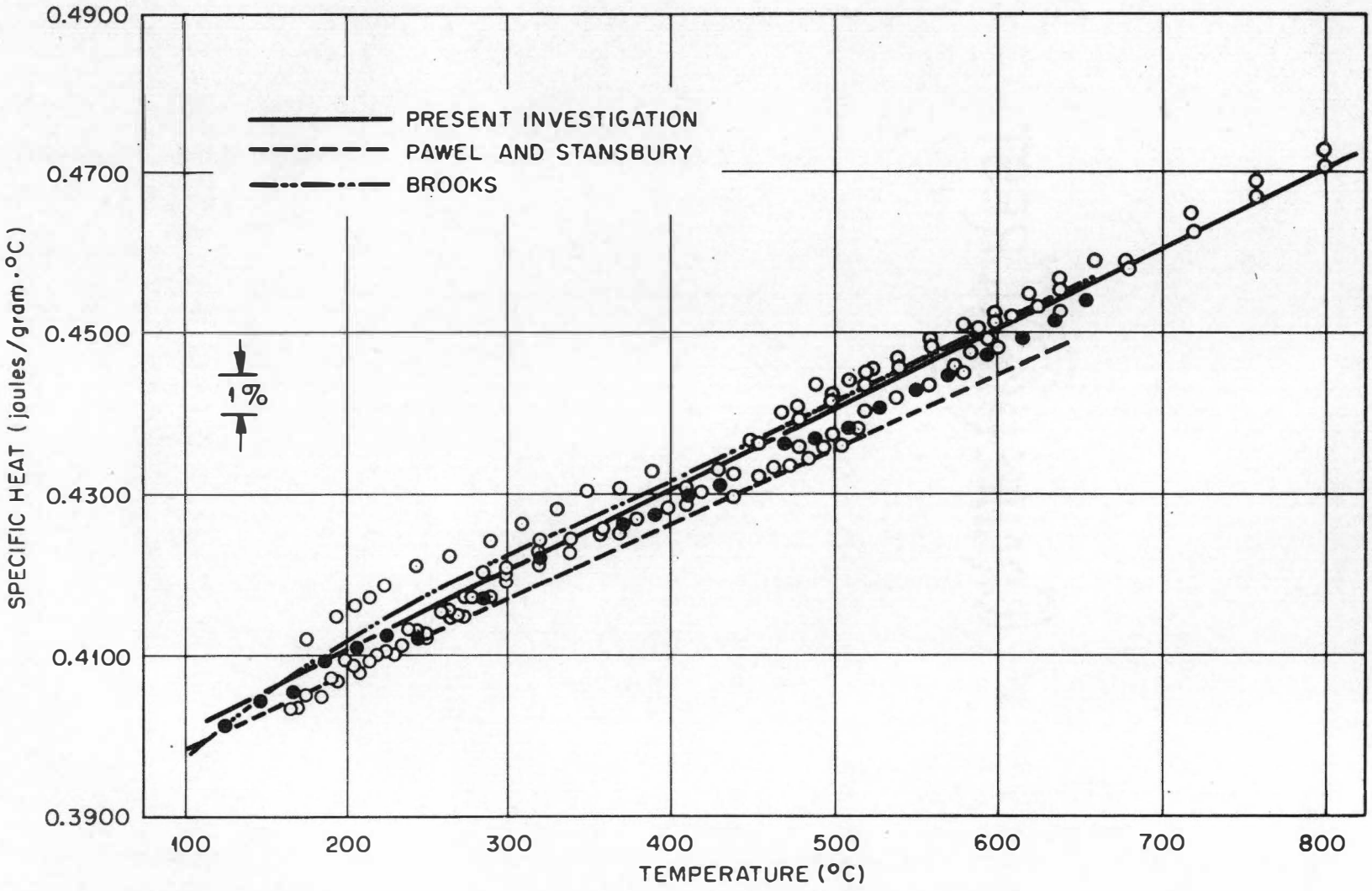


Figure 9. The Specific Heat of Copper from the Present Investigation.

investigation must be explained by the method or instruments used in making this investigation.

The data of the present investigation indicate the same results as obtained by Brooks (6); Pawel's (40) data are approximately 1 per cent below those of Brooks. An analysis of the difference in the calorimeters used by Brooks and Pawel showed that the difference in data can be attributed to the use of insulating tabs on particular thermocouples. Pawel, not utilizing the comparator circuit, had to use insulating tabs which cause a significant difference between the drift correction under dynamic and static operating conditions. The tab used consisted of a thermocouple junction mounted in ceramic which was attached in the thermocouple position. This had the effect of causing the effective thermocouple junction to be approximately 1/16 inch from the position desired. It was shown by Nauman (36) and Brooks (6) that such a tab did cause a temperature lag between the shield and the thermocouple under dynamic conditions which did not exist under static conditions. The effect of the lag was to manifest an error in the drift correction in a direction such that the data would appear lower.

The data above 600°C. for this investigation were corrected by the extrapolation method as discussed earlier and which appears in more detail in Appendix A.

The data obtained by Pawel agree well with those

obtained by other investigators such as the collation of data by Kelley (23) and the University of California (44) and experimental data from Sykes and Jones (48) and Seekamp (43). These data are compared in Figure 10.

Both the data obtained by Brooks and in this investigation are approximately 1 per cent above those of the other sources. Due to the reproducibility of the data obtained here and the explanation offered by Brooks concerning Pawel's data it is felt that the data obtained here are a true measure of the specific heat of copper. The discrepancy of other investigators with this work is probably a result of the type of system and method of investigation used.

Figure 11 shows a comparison of a theoretically predicted curve to that of the present investigation. This theoretical curve is based on recent values of γ (16) and $\beta_{(T)}$ (21) and Equation 12. Analysis shows that small errors in the values for γ and $\beta_{(T)}$ have an appreciable effect on the predicted curve. The experimental data obtained here agree within 1 per cent of the predicted curve based on the theoretical data. The above comparison indicates close agreement to the true value of the specific heat of copper.

The study of copper has been of tremendous importance in serving as a test for the newly designed calorimeter. As already reported, the reproducibility of the data was

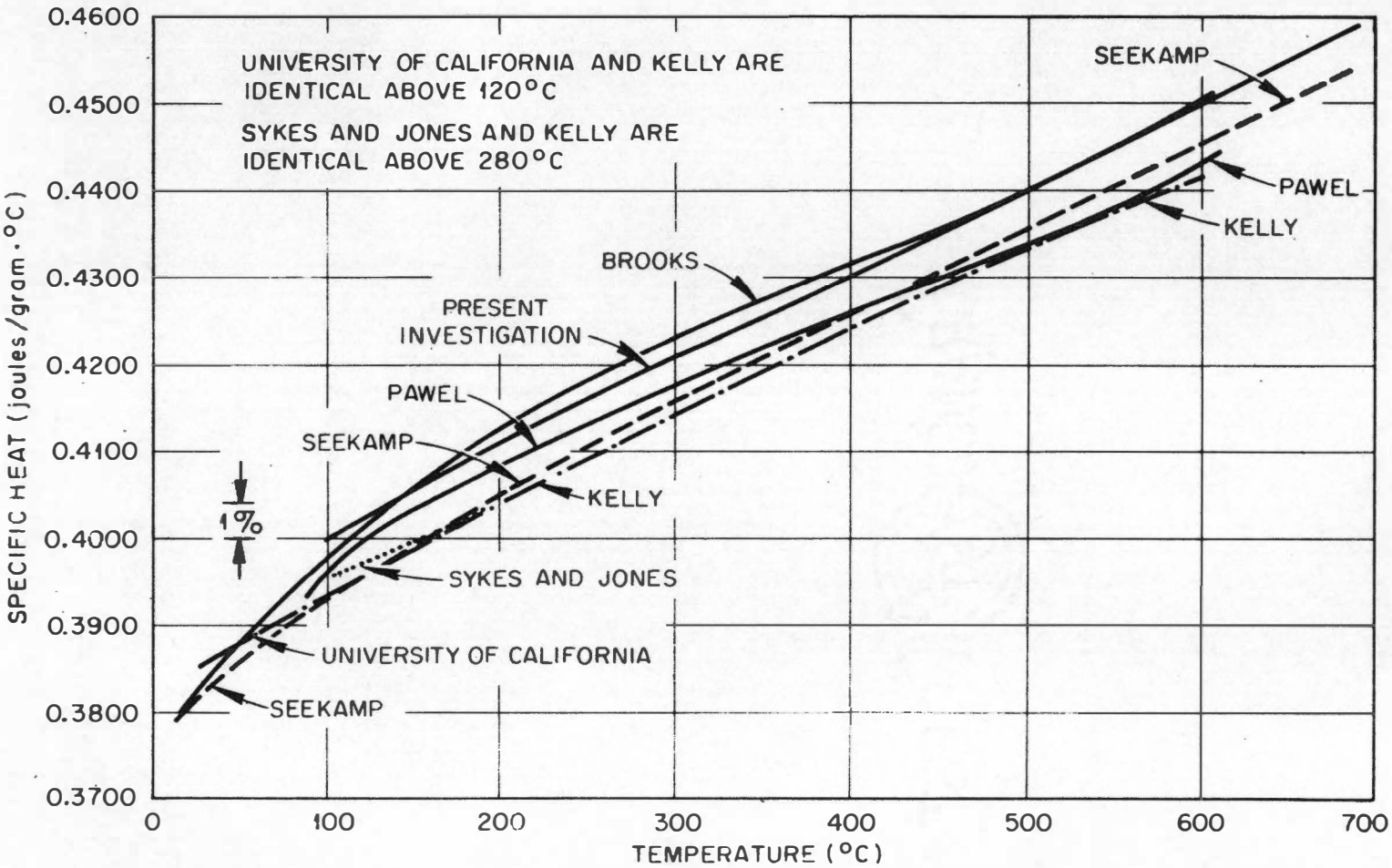


Figure 10. The Specific Heat of Copper as a Function of Temperature from Several Sources.

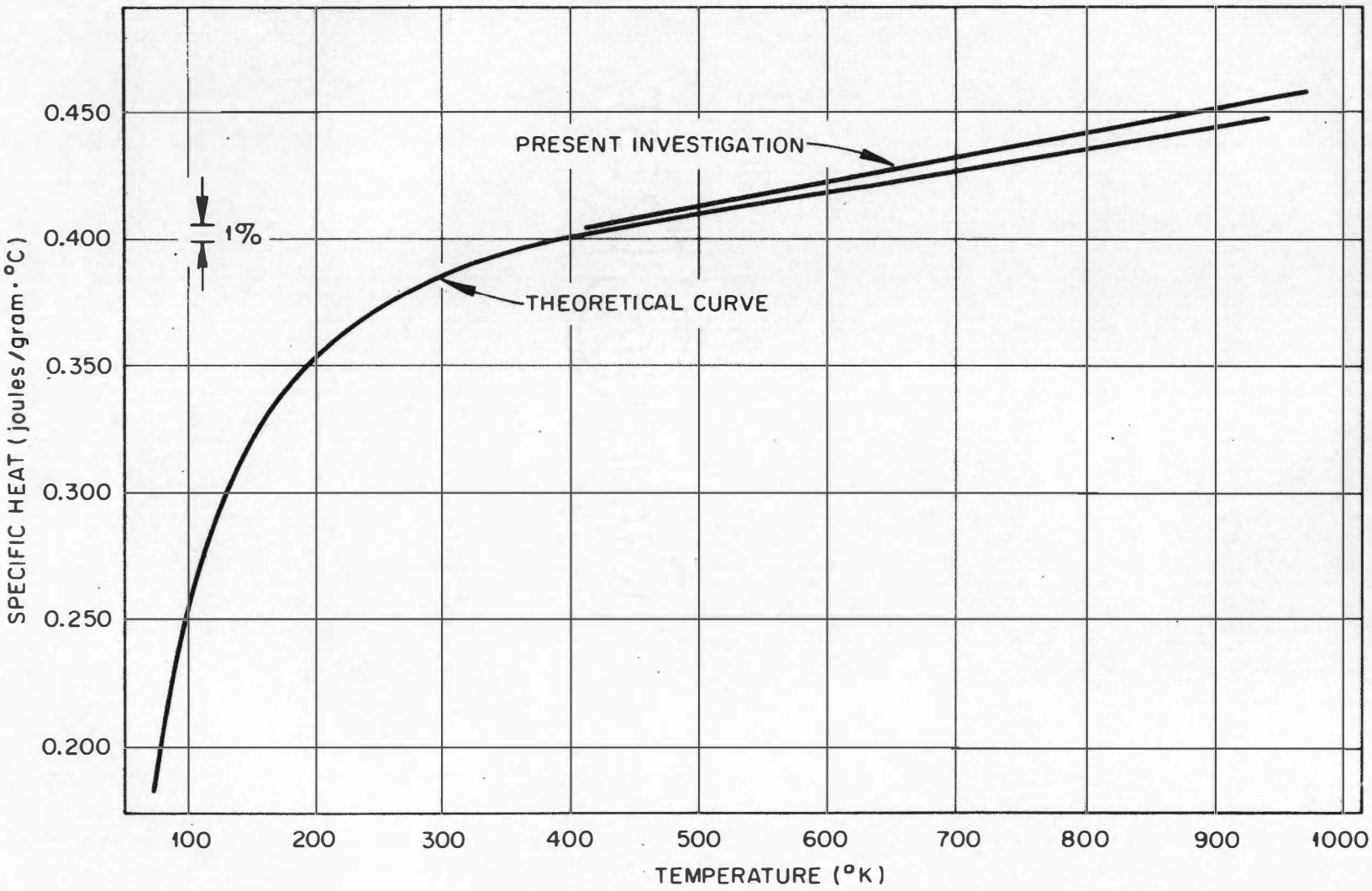


Figure 11. Comparison of Theoretical Specific Heat of Copper to That of the Present Investigation.

extremely good, considering the wide range of variables applied during operation. The appearance of the data being high as compared to Pawel has been attributed to other causes and not to the operation of this calorimeter.

The incorporation of the new adiabatic surroundings and the use of better operative controlling equipment has aided in the ability to operate at high temperatures while still maintaining good adiabatic conditions. As a result, the specific heat curve for copper has been extended to 800°C. with a reproducibility of ±0.7 per cent.

II. THE SPECIFIC HEAT OF NICKEL

Nickel experiences a magnetic transformation associated with a specific temperature. Experimental investigations of this effect, as manifested in the specific heat curve, are of considerable interest in proposing its explanation. The experimental data obtained here between 100° and 800°C. are shown in Figure 12. The data were obtained during three runs with a range of heating rates from about 2.2° to 6.4°C./min. There was no noticeable effect of the heating rate on the data as exemplified by the small variation of ±0.2 per cent from a smooth curve. The data from 600° to 800°C. were obtained from one run.

The data of Pawel (40) and Alig (1) are compared in the same figure. Their respective data were obtained on very

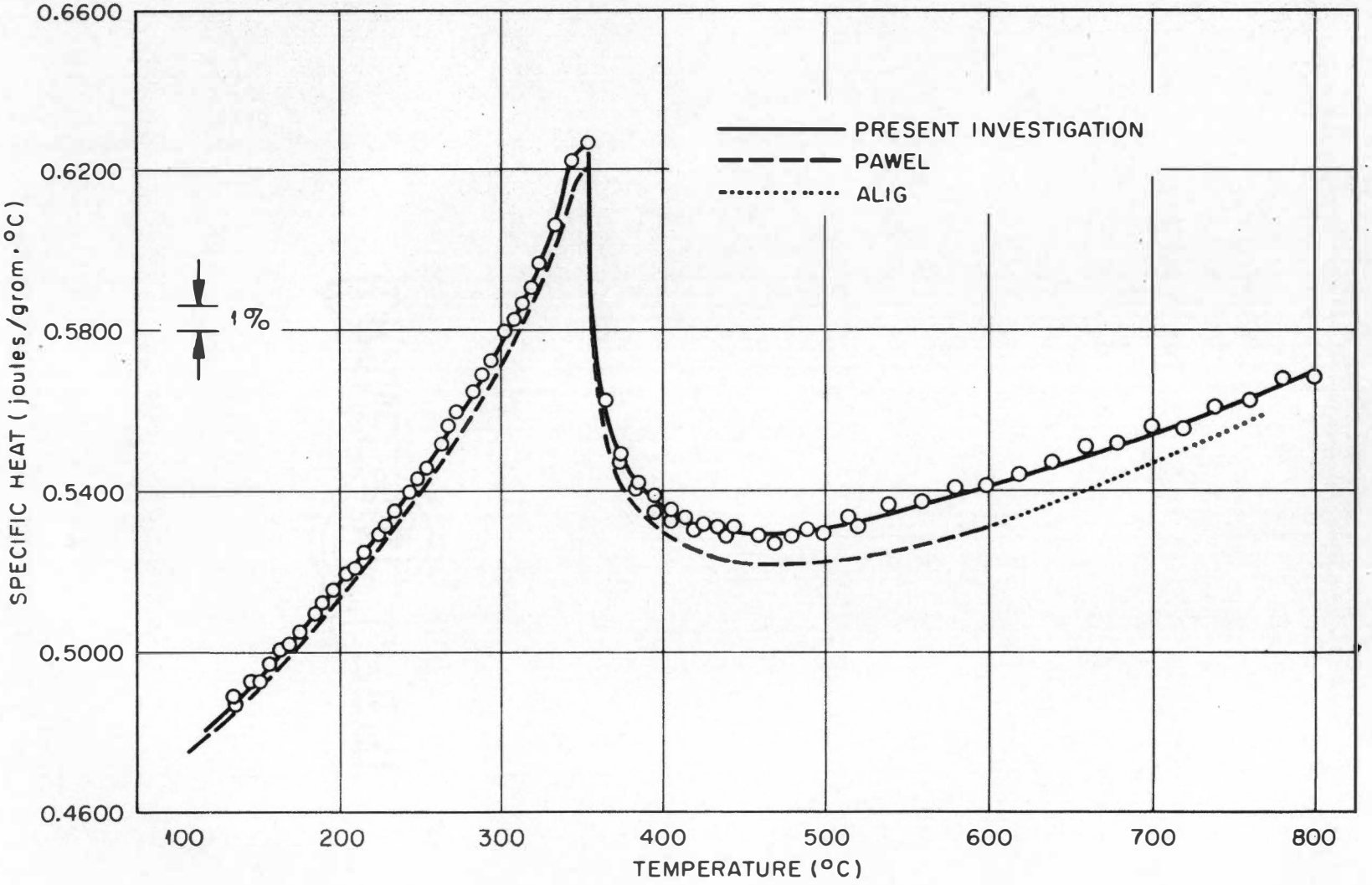


Figure 12. The Specific Heat of Nickel from the Present Investigation.

similar calorimeters under essentially the same conditions. The difference in the specific heat curves experienced here is of the same order as obtained for the copper data and the same explanation applies. Krauß and Warncke (27) have obtained specific heat data of nickel for high temperatures. Their data are within ±0.5 per cent at all temperatures studied to the data of this investigation. Previously there have been considerable discrepancies in the specific heat curve in that region just beyond the Curie temperature. Theoretically, there should not be any such tail after the Curie temperature as shown by the data, but the specific heat should drop straight down at the Curie temperature and then have a steady rise in the specific heat with temperature at higher temperatures. The tail is explained by the kinetics of the disordering. Heating at a constant rate prevents equilibrium conditions from existing at any temperature. Thus, at the Curie temperature and just beyond, the alignment of the election spin has not completely broken up and is still giving a slight contribution to the specific heat. It is necessary for time to pass before the disordering reaction comes to completion. Once it does, the specific heat of nickel behaves in a manner normal for that of pure metals. The severity of this inherent problem is associated with the calorimeter and the method of taking data. Since the wide variation in data in this range is a problem of the rate at

which the transformation takes place, the slowest possible heating rate would be the most appropriate. Rather slow heating rates were used here to reduce this effect. A small tail may exist if one looks at the Curie temperature as the temperature at which the atoms obtain enough energy to disrupt the electron alignment. Then there remains a statistical chance that a portion of the atoms will retain the electron alignment.

The specific heat data obtained in the high temperature range are critical since they are to be used in finding the constants of Equation 12 such that it best fits the high temperature curve. Equation 12 is the specific heat of a metal with only lattice and electronic contributions. The values of γ and $\beta_{(T)}$ for nickel are very critical in determining the theoretical prediction of the specific heat without the magnetic contribution. In determining the energy and entropy of the magnetic transformation, it is necessary that the experimental specific heat curve and the theoretical specific heat curve without the magnetic transformation coincide at temperatures below where the magnetic effect contributes to the specific heat and at temperatures above where the magnetic effect has subsided. This necessity re-emphasizes the importance of having accurate high temperature data, since the values of γ and $\beta_{(T)}$ are chosen to force the theoretical curve to coincide at these high

temperatures. There is little variation of the specific heat with γ and $\beta_{(T)}$ at low temperatures. The value of γ is the more critical of these two values due to its weight in Equation 12 and the possible error involved in its determination. Its determination requires the use of low temperature specific heat data, which are highly subject to error, and an extrapolation of a curve making use of these low temperature data. The values of $\beta_{(T)}$ (21) used are accepted due to the accuracy with which they are determined.

There are two values of γ that have been cited often. These values are 1.74×10^{-3} cal./gm.-atom$^{\circ}$K.^{2} (22) and 1.25×10^{-3} cal./gm.-atom$^{\circ}$K.^{2} (9). Their use in determining the theoretical specific heat causes at least a 3.0 per cent variation at 775°K. The value of 1.74×10^{-3} cal./gm.-atom$^{\circ}$K.^{2} was used here since it causes agreement of the specific heat curve with the present data at temperatures above 775°K. and with the data of Busey and Giauque (9) below 300°K. Figure 13 shows the comparison of this theoretical curve from Equation 12 with that of the experimental curve. In the range between the data of Busey and Giauque and the present investigation there has been an extrapolation to join the data. The difference in the area under the specific heat curves constitutes the energy associated with the magnetic transformation. Similar plots of C_p/T versus T were made to determine the entropy (See Appendix B).

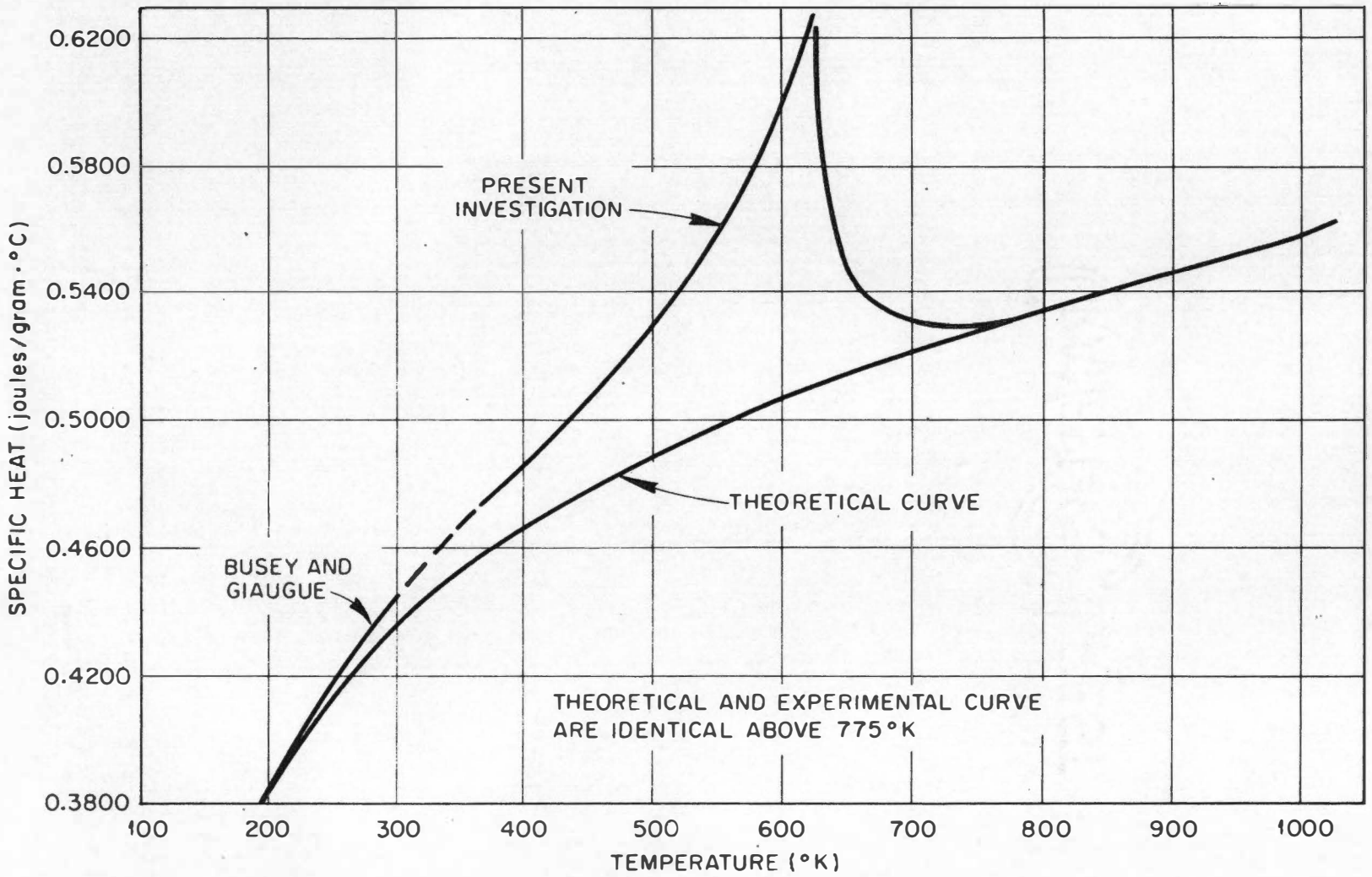


Figure 13. Comparison of Theoretical Specific Heat of Nickel to That of the Present Investigation.

The integration was carried out mechanically by the use of a planimeter. Table III reports the values of energy and entropy obtained here as well as those of other investigators and the proposed predictions of the theoretical models. It is noted that the values obtained in this investigation are less than that proposed by any of the theoretical models. However, due to the considerable degree of error that could possibly exist in the experimental values as a result of the use of an improper value of γ, the experimental values obtained here are within the experimental error associated with the values of γ available for use.

The experimental data tend to support the model based on Heisenberg's (19) theory where $n=0.3N_0$ and $s=1$. This case can arise only when it is assumed that the nickel atoms have either zero or two holes in the 3d band giving a 0.3 fraction of atoms having two holes. A difference of 17 per cent exists between these theoretical values and the experimental values. This degree of error could arise from a 3 per cent error in the theoretical specific heat curve due to the value of γ used. Pawel *et al.* (41) and Alig (1) used 1.38×10^{-3} cal./gm.-atom $^{o}K.^{2}$ for γ and their experimental values of the energy and entropy were within 0.3 per cent of the theoretical prediction. The same electronic model of $n=0.3N_0$ and $s=1$ has been proposed by Mott and Jones (33) and Mott and Stevens (34).

TABLE III

COMPARISON OF EXPERIMENTAL VALUES TO THEORETICAL VALUES OF ENERGY AND ENTROPY FOR MAGNETIC DISORDERING OF NICKEL

Source	Energy joules/gm-atom	Entropy joules/gm-atom-°K
Calculated on Heisenberg theory, $n=0.6N_o$, $s=\frac{1}{2}$	1561	3.474
Calculated on Heisenberg theory, $n=0.3N_o$, $s=1$	1155	2.729
Calculated on cluster theory $n=0.6N_o$, $s=\frac{1}{2}$	2252	3.474
Calculated on cluster theory $n=0.3N_o$, $s=1$	1465	2.729
Pawel *et al.* (41), experimental data	1193	2.512
Alig (1), experimental data	1206	2.421
Present investigation	954	1.967

III. THE SPECIFIC HEAT OF NICKEL-20 WEIGHT PER CENT CHROMIUM ALLOY

An alloy of nickel-20 weight per cent chromium was shown by Taylor and Floyd (50), Stein and Grant (47), and Baer (3) to be a solid solution alloy. Hultgren and Land (20) have shown that such a nickel-chromium alloy does not show the existence of any magnetic transformations above room temperature. The addition of the chromium to the nickel has the effect of suppressing the Curie temperature of this alloy, if one exists. If the alloy is a solid solution alloy and there is no magnetic effect to be concerned with, the specific heat of the alloy will not show any abnormal behavior, unless there is some type ordering of the component atoms to cause an anomalous behavior. When the difference in atom sizes of the solvent and solute metal and the difference in bonding energies are considered, it is recognizable that some preferred type of ordering may be stable at various temperatures. Such an ordering would affect the specific heat to show some type anomalous behavior.

The specific heat of nickel-20 weight per cent chromium was determined and such an anomaly was found to exist. The data are reported in Figure 14. There exists a variation of ± 0.75 per cent in the data, based on the three curves obtained while using various energy imput rates. There was no

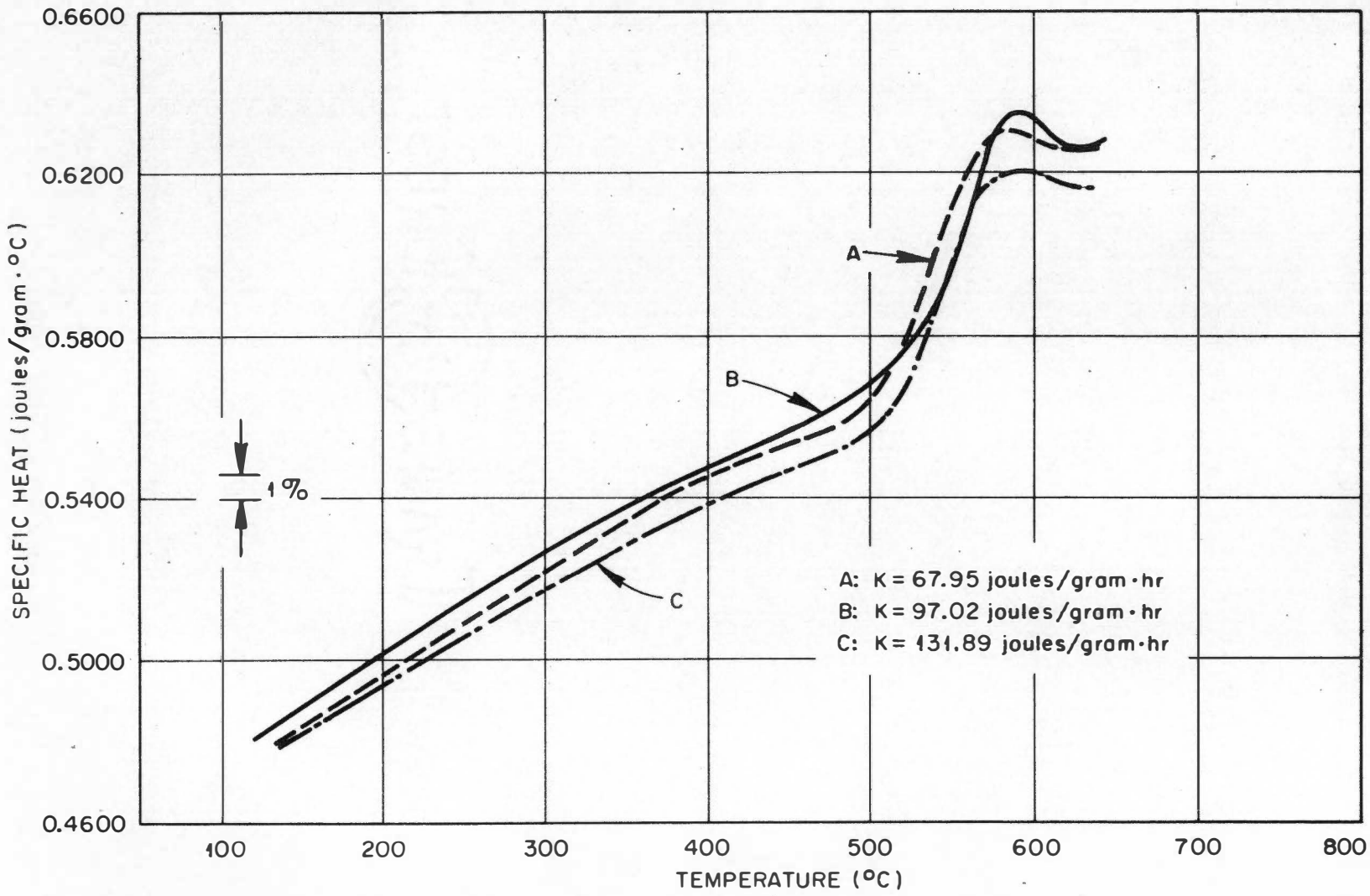


Figure 14. The Specific Heat of Nickel-20 Weight Per Cent Chromium from the Present Investigation.

consistent effect of heating rate, which leads one to believe that the variation in data is due to other causes, such as differences in prior thermal history. However, the sample was slowly cooled from 650°C. prior to each run. The chemical analysis shown in Table II indicates that the sample is somewhat contaminated by small amounts of copper, iron, cobalt, silicon, aluminum, and approximately 1.5 per cent manganese. When a portion of the specimen was analyzed microscopically (2), a segregation-free matrix containing a very small amount of a second phase was found. A slight difference in the thermal history of a sample containing a second phase could cause variations in specific heat between runs. Heat effects can result from precipitation or absorption of the second phase on heating. However, such a heat effect would probably not appreciably affect the magnitude of the specific heat.

Arledge (2) determined the specific heat of this same alloy. He obtained a similar variation in data, with his data being 0.5 per cent lower than that of the present investigation. It was thought that the variation might have been a result of the calorimeter, but it is now felt that the effect was due to the specimen used.

The specific heat data can still be used to aid in the understanding of the ordering mechanism taking place within the alloy. Long-range and short-range order are the types of

order usually associated with anomalies in the specific heat of binary solid solution alloys where there is no magnetic contribution to the specific heat. The nickel-chromium system has been studied only slightly in respect to ordering phenomena.

Taylor and Hinton (51) have studied the alloy system using electrical resistivity, specific heat, and x-ray measurements. Nordheim and Grant (38) have studied the system using electrical resistivity measurements. The x-ray measurements by Taylor and Hinton on a terniary alloy indicated to them that the ordering in Ni_3Cr was of the long-range type. Nordheim and Grant interpreted their resistivity data to conclude that short-range order is responsible for the anomaly. The specific heat data obtained by Taylor and Hinton are similar to those of this investigation.

Various analogies can be drawn from the specific heat data to give support to a particular type of ordering. The analogies are drawn by comparing previous experimental determinations of the effect of long-range and short-range order on the specific heat. If short-range order is present the critical temperature of the anomaly should remain almost constant with variations in the solute content. The critical temperature should decrease proportionally to decreases in the solute content. Arledge (2) has found only small variations in the critical temperature with chromium content in

the nickel-chromium system. The critical temperatures obtained by Taylor and Hinton (51) for a 25 atomic per cent sample, by Arledge (2) for 5, 10, and 20 weight per cent alloys, and that of the present investigation for a 20 weight per cent sample are very close to 575°C. This supports short-range order.

There are other analogies that can also be drawn to obtain similar conclusions. Short-range ordering is found to contribute to the specific heat above the critical temperature as well as below it. This contribution appears to exist in the present data. Experimental determinations of the energies associated with long-range ordering have shown them to be four or five times that for short-range ordering. A long-range ordering energy of 23.02 joules/gm. has been obtained for Cu_3Au (48) and a value of 3.60 joules/gm. has been obtained for the short-range ordering energy of α-brass (13). An approximate value of the ordering energy for the nickel-20 weight per cent chromium can be obtained by comparing the experimental specific heat data to a curve without the anomaly. Such a curve can be obtained by use of the Kopp-Neumann rule. This rule requires the use of specific heat values of the pure nickel and chromium without the presence of any transformation. The specific heat values for nickel were obtained from the theoretical curve in Figure 13. The values of chromium were obtained from tables (44). The

Kopp-Neumann curve obtained from these data is shown in Figure 15, where it is compared to the experimental data of the alloy. Since these curves do not coincide at any temperature, it is necessary to extrapolate the lower portion of the experimental curve, parallel to the Kopp-Neumann curve, to obtain a measure of the energy. The energy for the anomaly was obtained by taking the area between the experimental curve and the extrapolated curve between 500° and 650°C. A value of 4.71 joules/gm. was obtained. This compares to a value of 6.3 joules/gm. as obtained by Arledge (2) and a value of 7.33 joules/gm. as obtained by Taylor and Hinton (51). These energies are small as compared to those usually obtained for long-range order.

There still exist wide discrepancies in the explanation as to the type ordering phenomena occurring in the alloy. However, the specific heat data obtained here favor that of short-range ordering.

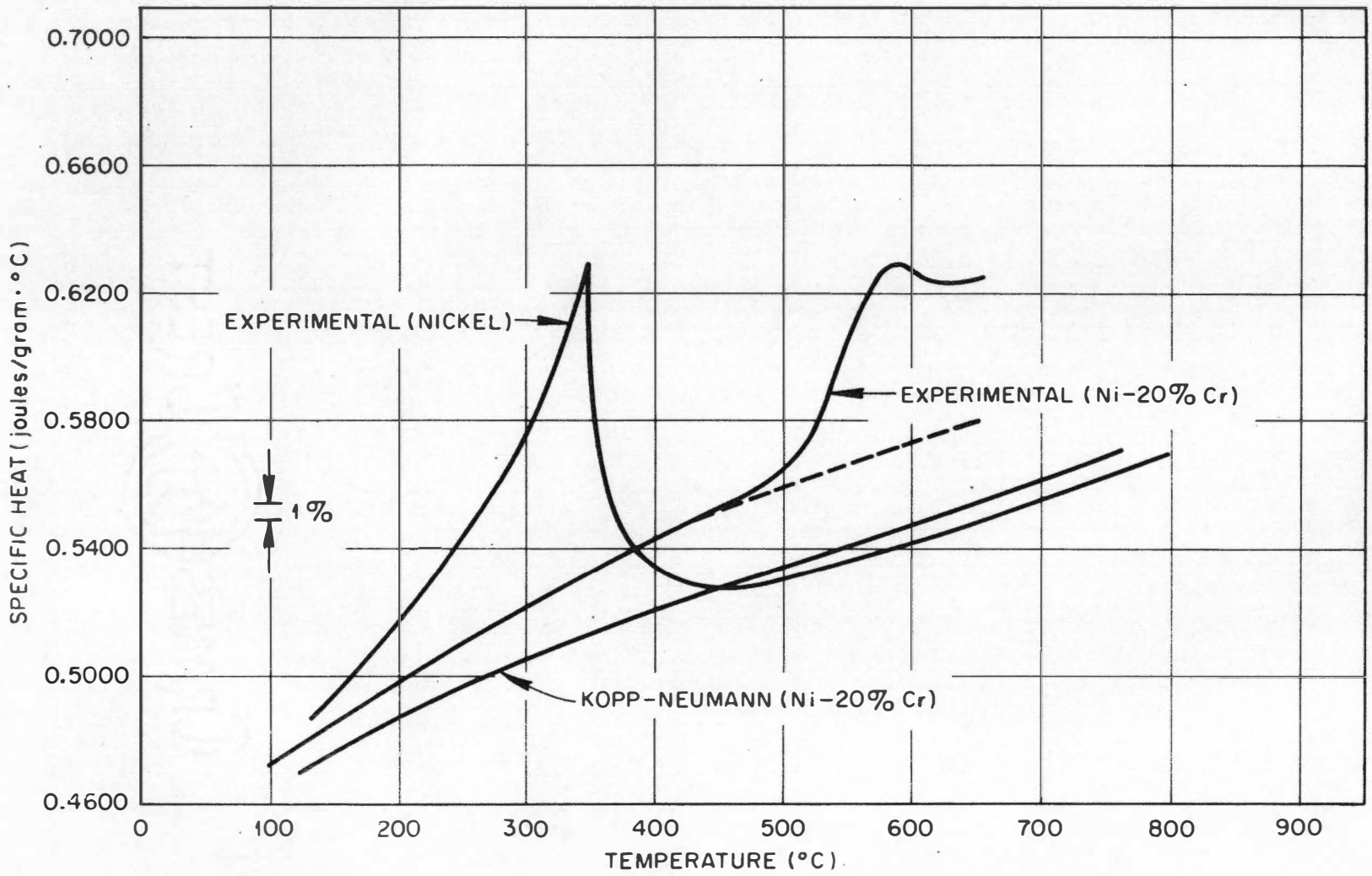


Figure 15. Comparison of Experimental and Kopp-Neumann Specific Heat Curves for Nickel-20 Weight Per Cent Chromium.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

A new and improved adiabatic calorimeter has been achieved through various modifications such that data can be obtained from 100° to 850°C. with a reproducibility of ±0.7 per cent. The previous calorimeters were limited to around 650°C. A new adiabatic surrounding and changes in the controlling instruments have made this calorimeter beneficial for specific heat investigations to high temperatures.

From the modifications on the calorimeter and the controlling equipment, the following conclusions are made.

1. Operating on the principle that radiative heat losses are less than conductive heat losses through opaque substances, an insulating shield was used in making improvements in decreasing the heat losses from the adiabatic system.
2. The use of concentric heating enabled the holding of adiabatic conditions at high temperatures. The outer shield was maintained at some 5° to 25°C. colder than the internal shield. This caused the need for less power to the internal shield and allowed better control of the surroundings.
3. The use of low mass in the immediate sample surroundings allowed more rapid response, once

deviations from adiabatic conditions occurred.

4. The comparing of all thermocouples to the specimen allowed the operator to bring the equipment into control with less difficulty due to the independent operation of each shield.
5. The use of new controlling equipment made it possible to feed continuous power to the shields. This prevented impulses of power at various intervals to heaters. With only minor changes occurring in the power imput to the various heaters, it was found that each heater acted more independently of the others, i.e., an increase in the power to one heater did not have an effect on the other parts of the system.

The new calorimeter was used to study the specific heat of copper, nickel, and a nickel-20 weight per cent chromium alloy. The copper was studied as a test for the new calorimeter since copper is a metal whose specific heat has been reported by many investigators. The specific heat of nickel was studied to obtain accurate high temperature (600°-800°C.) data so that the energy and entropy of the magnetic disorder could be obtained and these values used to explain the spin system that exists in nickel. Similar specific heat data were taken on nickel-20 weight per cent

chromium to aid in clarifying the discrepancies as to the type of ordering transformation that occurs upon heating.

The phase of this work concerning the specific heat of the above mentioned metal systems led to the following results.

1. The specific heat of copper was obtained from 100° to 800°C. with a reproducibility of ±0.7 per cent. These data were very close to those of Brooks (6) but were approximately 1 per cent above those of Pawel (40) and other investigators, as noted in Figure 9.
2. The static drift correction applied by Pawel (40) was found not to be applicable above 600°C. At these temperatures it was necessary to use the extrapolation method as described in Appendix A.
3. The degree of reproducibility obtained under the extreme conditions for which data were taken indicates that the new calorimeter is a significant improvement over the previous calorimeters.
4. The specific heat data of nickel were determined to 800°C. These data were used to determine experimentally the energy and entropy of the magnetic order for pure nickel to be 945 joules/gm.-atom and 1.967 joules/gm.-atom °K., respectively. Comparison of these values to the theoretical values

based on specific spin models for the spin system in nickel indicates that nickel should have 0.3 nickel atoms with two holes in the 3d level with a spin of 1. This arrangement has been proposed by Mott and Jones (33) and later by Mott and Stevens (34).

5. An anomaly was observed in the specific heat curve of the nickel-20 weight per cent chromium alloy at approximately 575°C. The energy of the anomaly was approximately 4.71 joules/gm. The low energy of the anomaly and the behavior of the specific heat curve support the existence of short-range order as compared to long-range order.

It was found that the new calorimeter would operate to obtain reproducible data to 800°C. However, toward the conclusion of this investigation a problem arose due to the contamination of thermocouples, apparently by the inconel tube, which was one of the adiabatic shields. As a result of this and the experience gained from operation of the calorimeter, the following recommendations are suggested to further improve the calorimeter and control system.

1. The removal of all inconel from the internal parts of the calorimeter and the incorporation of a pure metal such as nickel that will not cause

contamination of the thermocouples.

2. The installation of a double set of thermocouples such that when one became inoperable the other could be used without ceasing operation. At the present when any one of the six thermocouples breaks loose from its position, the calorimeter must be cooled and the vacuum system broken to repair the trouble.
3. A provision that would allow the sample to be rapidly cooled following a heating cycle would be advisable. Presently it takes the sample about 8 hours to cool from 700°C. to room temperature in vacuum. The passing of an inert gas through the system would allow this cooling.
4. A provision by which the potentiometer could be connected to an electrical circuit with the clocks in a manner to cause one clock to stop and another to start simultaneously at the time the specimen reaches a temperature equivalent to the setting on the potentiometer. Brooks (6) has shown that the manual operation of the clocks by the operator introduces one of the largest errors associated with taking data, although the error involved is probably only of the order of $\pm$0.1 per cent.

LIST OF REFERENCES

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1. Alig, R. L., "An Adiabatic Calorimetric Investigation of the Specific Heat of Nickel from 250° to 750°C," The University of Tennessee Thesis, M.S. (1960).

2. Arledge, T. A., "An Adiabatic Calorimetric Investigation of the Specific Heat of Nickel-Chromium Alloys from 80° to 700°C," The University of Tennessee Thesis, M.S. (1963).

3. Baer, H. G., "Uberstrukutr und K-Zustand im System Nickel-Chrom," Z. Metallkunde 49, 614 (1958).

4. Bethe, H. A., "Statistical Theory of Superlattices," Proc. Royal Soc. 150A, 552 (1935).

5. Bragg, W. L. and Williams, E. J., "The Effect of Thermal Agitation on Atomic Arrangement in Alloys," Roy. Soc. of London 145, 699 (1934).

6. Brooks, C. R., "A Calorimetric Investigation of the Anomalies in the Specific Heat of Binary Solid Solutions of Copper Containing Aluminum and Gallium," The University of Tennessee Thesis, Ph.D. (1960).

7. _____, and Stansbury, E. E., "The Effect of Heating Rate and Neutron Irradiation on the Specific Heat Behavior of a Cu-16.8 at.% Al and a Cu-17.2 at.% Ga Solid Solution," Acta Metallurgica 11, 1303 (1963).

8. Brown, H. A., and Luttinger, J. M., "Ferromagnetic and Antiferromagnetic Curie Temperature," Physical Review 100, 685 (1955).

9. Busey, R. H. and Giauque, W. F., "The Heat Capacity of Nickel from 15 to 300°K. Entropy and Free Energy Functions," J. Am. Chem. Soc. 74, 3157 (1952).

10. Chang, Y. S., "An Extension of Bethe's Theory of Order-Disorder Transitions in Metallic Alloys," Proc. Roy. Soc. 161A, 546 (1937).

11. Chevenard, P., "Thermal Anomalies of Certain Solid Solutions," J. Inst. Metals 36, 39 (1926).

12. Clarebrough, L. M., Hargraves, M. E., and Loretto, M. H., "Order-Disorder Phenomena in α-Brass. IV. Nature

of Order and the Role of Atomic Mobility," Proc. Roy. Soc. A257, 500 (1960).

13. _____, and Loretto, M. H., "Order-Disorder Phenomena in α -Brass. I. Development of Order," Proc. Roy. Soc. A257, 326 (1960).

14. Dauphinee, T. M., "An Apparatus for Comparison of Thermocouples," Can. J. Physics 33, 275 (1955).

15. Denbigh, K. G., "Principles of Chemical Equilibrium," London, Cambridge University Press (1961).

16. Giauque, W. F., and Meads, P. F., "The Heat Capacities and Entropies of Aluminum and Copper from 15 to 300°K," J. Am. Chem. Soc. 63, 1897 (1941).

17. Grover, H. and Hutzenlaub, J., "The Specific Heat of Nickel-Chromium Alloys," Physical Review 56, 212 (1939).

18. Guttman, L., "Order-Disorder Phenomena in Metals," Solid State Physics 3, 145 (1956).

19. Heisenberg, W. Z., "Theory of Ferromagnetism," Z. Physik 49, 619 (1928).

20. Hultgren, R. and Land, C., "The Heat Capacity of Dilute Solutions of Chromium in Nickel," AIME 215, 169 (1959).

21. Jordan, L. and Swanger, W. H., Journal of Research, National Bureau of Standards 5, 129 (1930).

22. Keesom, W. H. and Clark, C. W., "The Atomic Heat of Nickel From 1.1 to 19.0°K," Physica 2, 513 (1935).

23. Kelley, K. K., "Contribution to the Data on Theoretical Metallurgy," U.S. Bureau of Mines Bull., 476 (1949).

24. Kirkwood, J. G., "Order-Disorder in Binary Solid Solutions," Journal of Chem. Phys. 6, 70 (1938).

25. Kittel, C., "Elementary Solid State Physics," New York, John Wiley and Sons (1962).

26. Koster, W. and Rocholl, P., "Leitfahigkeit und Hallkonstante I. Nickel-Chrom-Legierungen," Z. Metallkunde 48, 485 (1957).

27. Krauß, V. F. and Warncke, H., "Die speczifische Warme von Nickel zwischen 180 and 1160°," Z. Metallkunde 46, 61 (1955).

28. Kussman, A. and Wollenberger, H., "Kaloremetric Untersuchung der Ordnungsvorgange in α-Messung-und Neusilver-Legierungen," Z. Metallkunde 50, 94 (1959).

29. Lewis, G. N. and Randall, M., revised by Pitzer, K. S. and Brewer, L., "Thermodynamics," New York, McGraw-Hill Book Company (1961).

30. Masumoto, H., Saito, H. and Takahashi, M., "Anomaly of Specific Heat in α-Phase Alloys of Copper and Aluminum," Sci. Rep. of Res. Inst. of Tohoku Univ. 47, 465 (1955).

31. Matsuo, S. and Clarebrough, L. M., "Short Range Order in Copper-Aluminum Alloys," Acta Met. 11, 1195 (1963).

32. McElroy, D. L., Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A., private communication (1964).

33. Mott, N. F. and Jones, H., "The Theory of the Properties of Metals and Alloys," London, Oxford University Press (1936).

34. _____, and Stevens, K. W. H., "Band Structure of the Transition Metals," Phil. Mag. Series 8, 2, 1364 (1957).

35. Muto, T. and Takagi, Y., "The Theory of Order-Disorder Transformation in Alloys," Solid State Physics 1, 193 (1955).

36. Nauman, E. B., "Analysis of a High Temperature Adiabatic Calorimeter," The University of Tennessee Thesis, M.S. (1961).

37. Nix, F. C. and Shockley, W., "Order-Disorder Transformations in Alloys," Rev. Modren Physics 10, 1 (1938).

38. Nordheim, R. and Grant, N. J., "Resistivity Anomalies in the Nickel-Chromium System as Evidence of Ordering Reactions," J. Inst. Metals 82, 440 (1953).

39. Panin, V. E. and Zenkova, E. K., "On the Question of

Super-Structure in Aluminum Bronze," Akad. Nauk, Doklady, SSST, 129, 1024 (1959).

40. Pawel, R. E., "The Application of Dynamic Adiabatic Calorimetry to the Copper-Nickel System from 50 to 620°C," The University of Tennessee Thesis, Ph.D. (1956).

41. _____, and Stansbury, E. E., "Specific Heat Effects of the Ferromagnetic Transition in Nickel and Ni-Cu Alloys," unpublished (1964).

42. Peierls, R., "Statistical Theory of Superlattices with Unequal Concentrations of the Components," Proc. Roy. Soc. 154A, 207 (1936).

43. Seekamp, H., "Uber die Messung wahrer specifischer warmen fester und flussinger Metalle bei hohen Temperaturen," Z. Anorg. im Allgemeine Chem. 195, 345 (1931).

44. "Selected Values for the Thermodynamic Properties of Metals and Alloys," Minerals Research Laboratory, Institute of Engineering Research, University of California (1960).

45. Stansbury, E. E., McElroy, D. L., Picklesimer, M. L., Elder, G. E., and Pawel, R. E., "Adiabatic Calorimeter for Metals in the Range 50 to 1000°C," Review of Scientific Instruments 30, 121 (1959).

46. _____, Nauman, E. B., and Brooks, C. R., "A Modified Dauphinee Thermocouple Comparator Circuit For Adiabatic Calorimeter," unpublished (1964).

47. Stein, G. and Grant, N. J., "Chromium-Rich Portion of the Chromium-Nickel Phase Diagram," AIME 203, 127 (1955).

48. Sykes, C. and Jones, F. W., "The Atomic Rearrangement Process in the Copper-Gold Alloy, Cu_3Au," Proc. Roy. Soc. 60, 78 (1936).

49. _____, "Formation Energy of Superlattice for Ni_3Fe. I. Cooperative Formation of Superlattice at Critical Temperature," J. Phys. Soc. Japan 7, 373 (1952).

50. Taylor, A. and Floyd, R. W., "The Constitution of Nickel-Rich Alloys of the Nickel-Chromium-Titanium System,"

J. Inst. Metals 80, 577 (1951).

51. _____, and Hinton, K. G., "A Study of Order-Disorder and Precipitation Phenomena in Nickel-Chromium Alloys," J. Inst. Metals 81, 169 (1952).

52. Van Vleck, J. H., "Present Status of the Theory of Ferromagnetism," Physica 15, 197 (1949).

53. Williams, R. D., "Nature of the Ni-Cr System," AIME 209, 1257 (1957).

54. Wilson, A. H., "The Theory of Metals," Cambridge, Cambridge University Press (1953).

APPENDICES

APPENDIX A

CORRECTION OF DATA ABOVE 600°C.

The data obtained from the present calorimeter above 600°C. showed an inability to be corrected by the application of static drift. The slower the heating rate, the less applicable is the drift correction. At these high temperatures (600°-800°C.) extremely large temperature gradients are set up causing high drift rates. The drift was found to be nearly linear with T^3, indicating how rapid the drift correction increases; for copper the drift was about -1.0°C. per hour at 300°C. and about -4.5°C. per hour at 600°C.

To circumvent the difficulty of correcting data, a new method was introduced that would correct the data on the basis of obtaining a value for the specific heat with an infinite heating rate. Under an infinite heating rate one would be insured that all the power fed to the sample would be consumed in heating the specimen.

A method by which data, corresponding to an infinite heating rate, could be obtained was undertaken by arriving at the method indirectly. Data can be obtained for three or more heating rates while holding all other variables constant. Figure 16 shows a plot of three runs of data between 600° and 800°C. obtained under the same conditions within the calorimeter. The data in Figure 16 are on a copper sample

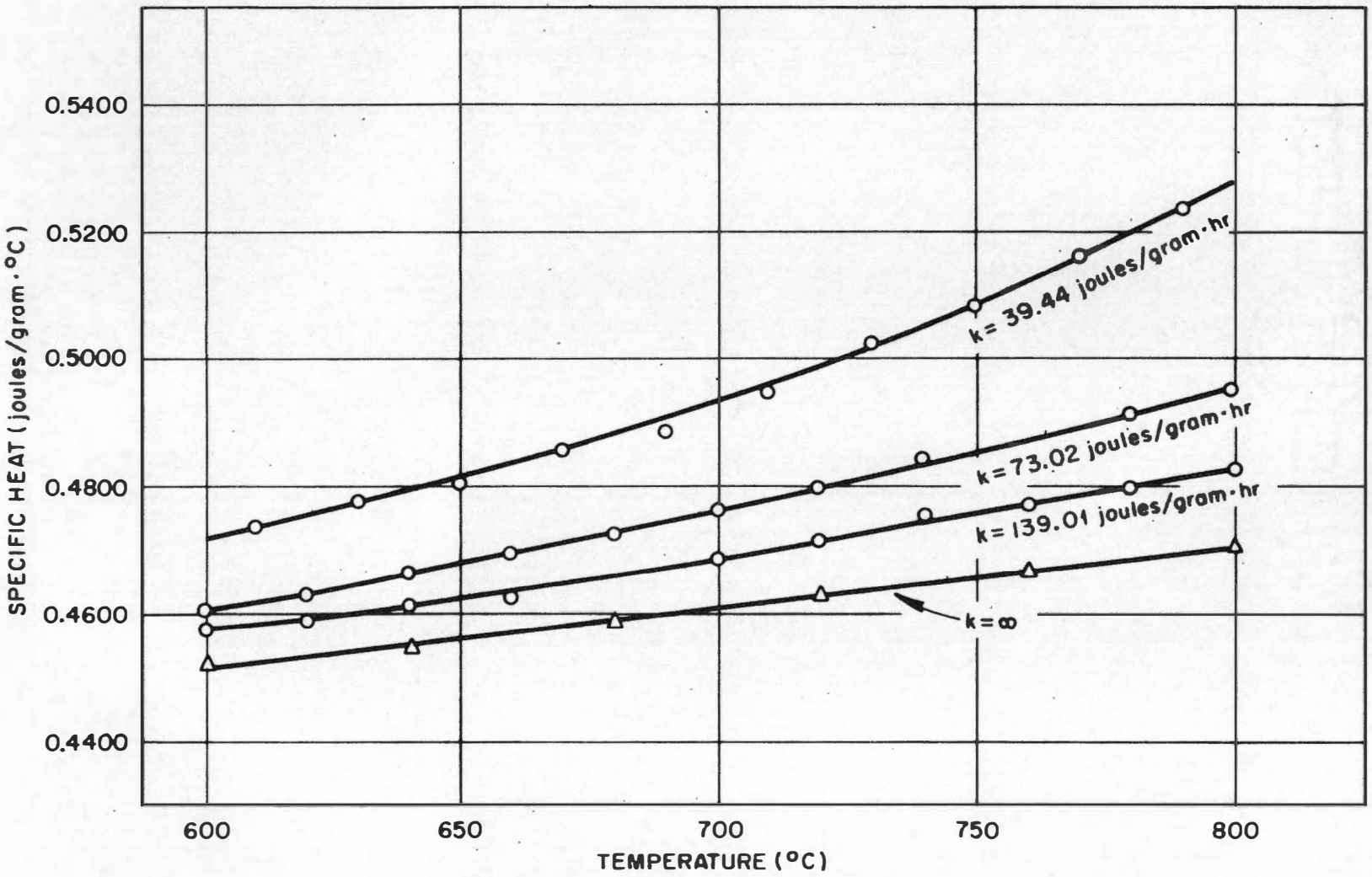

Figure 16. Data Showing the Correction Method for Specific Heat Values Above 600°C.

and are representative of data that can be obtained for any similar sample. By the use of these three curves, a plot of C_p versus C_p/K can be obtained for all temperatures within the given range. The new curve of C_p versus C_p/K for a constant temperature gave approximately a straight line which could be extrapolated to C_p/K equals zero and intercepts the C_p coordinate. When C_p/K equals zero, this indicates that K is equal to ∞ and thus the C_p intercept will correspond to the true specific heat value for the corresponding temperature. If C_p versus C_p/K plots are made for several temperatures, a specific heat curve versus temperature can be obtained which is equivalent to data being taken at an infinite heating rate. Such a curve is shown in Figure 16.

Due to limitations of the calorimeter, heating rates were never greater than 175 joules/gm.-hr. Heating rates of this order leave a large area which is to be extrapolated through on the C_p versus C_p/K plot. It was shown by Brooks (6) that the scatter in the specific heat obtained by this extrapolation method was ± 0.5 per cent, a scatter similar to that obtained in data below these high temperatures.

APPENDIX B

DETERMINATION OF ENERGY AND ENTROPY OF ANOMALOUS SPECIFIC HEAT BEHAVIOR

The determination of energies and entropies associated with anomalous specific heat behavior is beneficial in allowing explanations of the phenomena causing the anomalous behavior.

These thermodynamic quantities can be obtained by making comparisons of experimental specific heat data to similar data without the anomaly. Two such specific heat curves can be used to determine the heat of the transition by

$$\Delta H_T = \Delta H_{T_C} + \int_{T_C}^{T} (C_{p_2} - C_{p_1})\, dT, \qquad (22)$$

where ΔH_T is the heat of the transition, ΔH_{T_C} is the heat of the transition at a reference temperature, T_C, and C_{p_1} and C_{p_2} are the specific heats along the various specific heat curves. Specific heat curves of this type usually coincide both at low temperatures where the specific heat is not affected and at high temperatures where random positioning of the atoms has destroyed the tendency for anomalous behavior. If these conditions are met, Equation 22

could be reduced to

$$\Delta H_T = \int_{T_C}^{T} (C_{p_2} - C_{p_1})\, dT, \tag{23}$$

where the integral is taken over the temperature range where the specific heat curves do not coincide. This was done for nickel by use of Figure 13.

The entropy of such an anomalous behavior in the specific heat can be obtained by use of the relation

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(\text{exp})}{T}\, dT - \int_{T_1}^{T_2} \frac{C_p(\text{theor})}{T}\, dT, \tag{24}$$

or

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(\text{exp}) - C_p(\text{theor})}{T}\, dT\ . \tag{25}$$

Plots of C_p/T versus T for the experimental data and theoretical values without the anomalous behavior allow the determination of entropy. Figure 17 shows such plots for nickel data. The integration as noted in Equation 25 was carried out mechanically to determine the entropy.

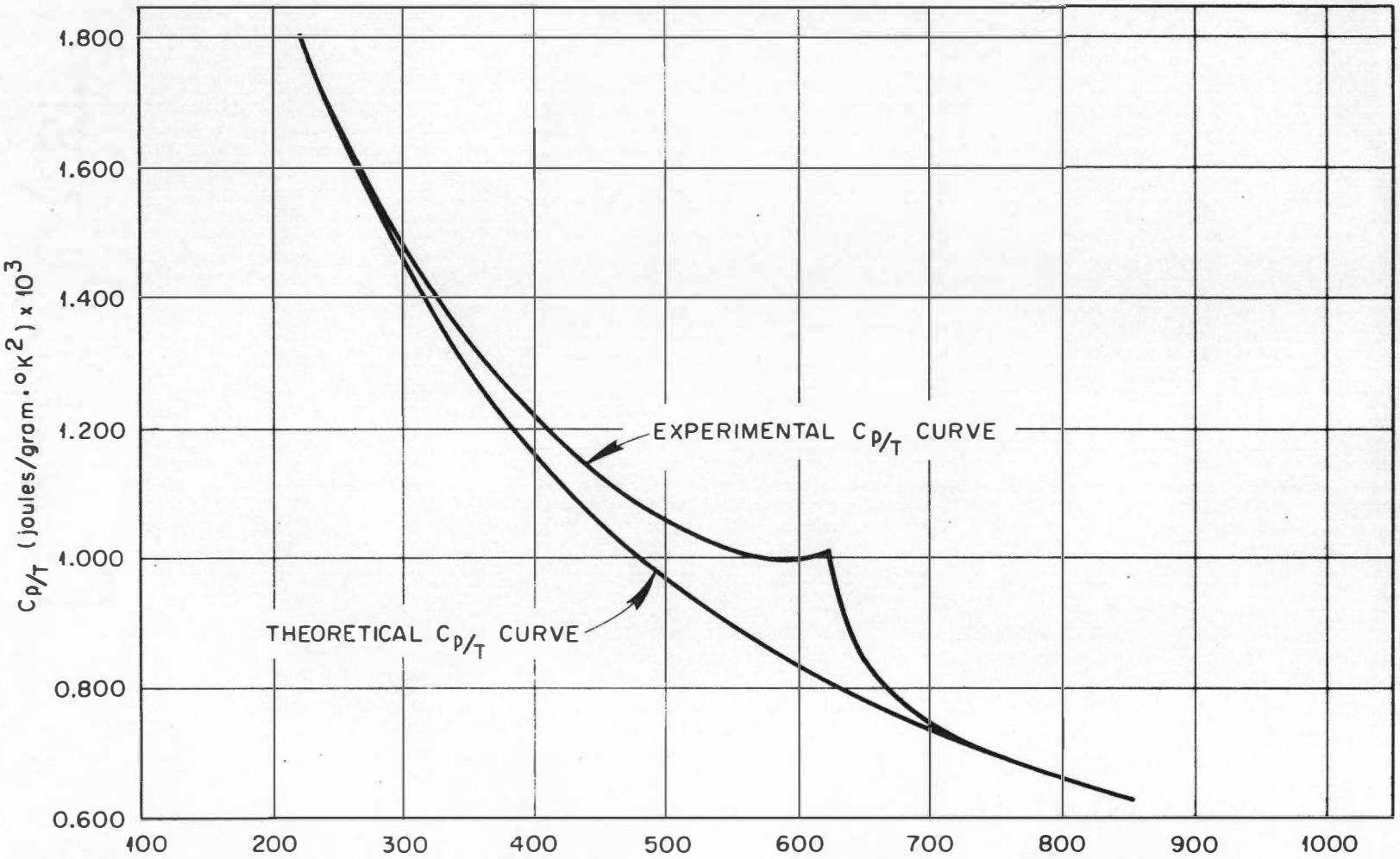

Figure 17. Plots of C_p/T versus T for Nickel.

APPENDIX C

TABLE IV

SPECIFIC HEAT OF PURE COPPER[a,b,c]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
K=73.12 joules/gm-hr		K=72.37 joules/gm-hr	
300	0.4210	290	0.4244
320	0.4240	310	0.4265
340	0.4245	330	0.4280
360	0.4259	350	0.4303
410	0.4306	370	0.4309
430	0.4332	390	0.4330
450	0.4372	480	0.4411
470	0.4403	500	0.4426
490	0.4438	520	0.4454
510	0.4444	540	0.4462
530	0.4456	560	0.4488
565	0.4473	580	0.4510
590	0.4505	600	0.4528
610	0.4522	620	0.4548
630	0.4536	640	0.4569
650	0.4550	660	0.4591

[a] Large copper sample, weight is 368.778 grams.
[b] G_2 heater was maintained at -50μv.
[c] C_p is the true specific heat as corrected.

TABLE V

SPECIFIC HEAT OF PURE COPPER[a,b,c]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
K=98.17 joules/gm-hr		K=44.96 joules/gm-hr	
125	0.4016	165	0.4034
145	0.4042	175	0.4052
165	0.4059	185	0.4052
185	0.4094	195	0.4071
205	0.4112	205	0.4089
225	0.4127	215	0.4094
245	0.4127	225	0.4109
265	0.4150	235	0.4118
285	0.4205	245	0.4126
320	0.4236	265	0.4151
370	0.4262	275	0.4173
390	0.4277	285	0.4171
410	0.4300	300	0.4195
430	0.4313	320	0.4217
470	0.4366	340	0.4229
490	0.4369	370	0.4256
510	0.4385	390	0.4276
530	0.4110	410	0.4289
550	0.4431	440	0.4299
570	0.4449	455	0.4326
595	0.4477	465	0.4335
615	0.4492	475	0.4337
635	0.4517	485	0.4344
655	0.4539	495	0.4362
		505	0.4361
		515	0.4382
		575	0.4460
		585	0.4478
		595	0.4495

[a] Large copper sample, weight is 368.778 grams.
[b] G_2 heater was maintained at -250μv.
[c] C_p is the true specific heat as corrected.

TABLE VI

SPECIFIC HEAT OF PURE COPPER[a,b,c]

T, °C	$\bar{C}_p$, joules/gm-°C	T, °C	$\bar{C}_p$, joules/gm-°C
K=39.44 joules/gm-hr		K=73.06 joules/gm-hr	
590	0.4700	600	0.4606
610	0.4738	620	0.4632
630	0.4776	640	0.4661
650	0.4805	660	0.4691
670	0.4858	680	0.4726
690	0.4881	700	0.4760
710	0.4945	720	0.4795
730	0.5025	740	0.4842
750	0.5084	760	0.4851
770	0.5161	780	0.4912
790	0.5237	800	0.4952

[a] Large copper sample, weight is 368.778 grams.
[b] G_2 heater was maintained at -50 μv.
[c] $\bar{C}_p$ is the average specific heat, no correction.

TABLE VII

SPECIFIC HEAT OF PURE COPPER[a,b,c]

T, °C	$\overline{C}_p$, joules/gm-°C
K=139.01 joules/gm-hr	
600	0.4574
620	0.4588
640	0.4615
660	0.4628
680	0.4689
700	0.4684
720	0.4712
740	0.4756
760	0.4763
780	0.4796
800	0.4825

[a]Large copper sample, weight is 368.778 grams.
[b]G_2 heater was maintained at - 50 μv.
[c]$\overline{C}_p$ is the average specific heat, no correction.

TABLE VIII

SPECIFIC HEAT OF PURE COPPER[a,b]

T, °C	C_p, joules/gm-°C
	$K=\infty$
600	0.4527
640	0.4557
680	0.4588
720	0.4630
760	0.4670
800	0.4710

[a]Large copper sample, weight is 368.778 grams.

[b]C_p is the true specific heat as corrected by the extrapolation method; the data used are reported in Tables VI and VII.

TABLE IX

SPECIFIC HEAT OF COPPER[a,b,c]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
K=111.23 joules/gm-hr		K=65.60 joules gm-hr	
200	0.4093	170	0.4037
220	0.4102	190	0.4077
240	0.4136	210	0.4081
260	0.4156	230	0.4104
280	0.4174	250	0.4129
300	0.4195	270	0.4152
320	0.4224	290	0.4174
360	0.4260	310	0.4205
380	0.4270	330	0.4224
400	0.4285	370	0.4241
420	0.4303	390	0.4269
440	0.4327	410	0.4283
480	0.4361	430	0.4309
500	0.4375	450	0.4325
520	0.4403	470	0.4347
540	0.4420	490	0.4375
560	0.4435	510	0.4402
580	0.4454	550	0.4443
		570	0.4463
		590	0.4487
		610	0.4510
		630	0.4535

[a]Small copper sample, weight is 172.794 grams.
[b]G_2 heater was maintained at -50 μv.
[c]C_p is the true specific heat as corrected.

TABLE X

SPECIFIC HEAT OF COPPER[a,b,c]

T, °C	$\bar{C}_p$, joules/gm-°C	T, °C	$\bar{C}_p$, joules/gm-°C
K=111.23 joules/gm-hr		K=65.60 joules/gm-hr	
580	0.4535	590	0.4632
610	0.4572	610	0.4668
630	0.4603	630	0.4708
650	0.4635	670	0.4784
670	0.4667	690	0.4822
690	0.4684	710	0.4881
710	0.4721	730	0.4955
730	0.4760	750	0.5025
750	0.4810	770	0.5095
770	0.4837	790	0.5162
790	0.4865		

[a] Small copper sample, weight is 172.794 grams.
[b] G_2 heater was maintained at -50 μv.
[c] $\bar{C}_p$ is the average specific heat, no correction.

TABLE XI

SPECIFIC HEAT OF COPPER[a,b,c]

T, °C	$\overline{C}_p$, joules/gm-°C
K=158.90 joules/gm-hr	
580	0.4480
630	0.4557
650	0.4595
670	0.4619
690	0.4654
710	0.4671
730	0.4726
750	0.4752
770	0.4794
790	0.4822

[a] Small copper sample, weight is 172.794 grams.
[b] G_2 heater was maintained at -50 μv.
[c] $\overline{C}_p$ is the average specific heat, no correction.

TABLE XII

SPECIFIC HEAT OF COPPER[a,b]

T, °C	C_p, joules/gm-°C
K= ∞	
600	0.4480
640	0.4530
680	0.4590
720	0.4650
760	0.4690
800	0.4730

[a]Small copper sample, weight is 172.794 grams.

[b]C_p is the true specific heat as corrected by the extrapolation method; the data used are reported in Tables X and XI.

APPENDIX D

TABLE XIII

THEORETICAL SPECIFIC HEAT OF COPPER[a]

T, °K	$\overline{C}_p$, joules/gm-°C	T, °K	$\overline{C}_p$, joules/gm-°C
8	0.0006	315	0.3889
16	0.0042	373	0.3972
24	0.0130	423	0.4035
32	0.0301	473	0.4086
47	0.0841	523	0.4131
63	0.1457	573	0.4178
79	0.1993	623	0.4219
95	0.2407	673	0.4261
126	0.2964	723	0.4303
158	0.3299	773	0.4345
189	0.3499	823	0.4387
221	0.3646	873	0.4429
252	0.3751	923	0.4466
284	0.3826		

[a] C_p values were calculated from

$$C_p = (0.178 \times 10^{-3} T) + \left[1 + 1.96\ \beta_{(T)} T\right](T/\Theta)\ \frac{\text{cal}}{\text{gm-}^\circ\text{C}}\ .$$

APPENDIX E

TABLE XIV

SPECIFIC HEAT OF PURE NICKEL[a,b,c,d]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
135	0.4873	425	0.5316
150	0.4930	435	0.5317
170	0.5023	445	0.5313
190	0.5126	470	0.5269
210	0.5211	490	0.5307
230	0.5314	515	0.5336
250	0.5430	540	0.5367
270	0.5562	560	0.5375
290	0.5689	580	0.5412
310	0.5831	600	0.5414
325	0.5969	620	0.5443
335	0.6076	640	0.5473
345	0.6215	660	0.5513
355	0.6273	680	0.5520
365	0.5625	700	0.5561
375	0.5494	720	0.5560
385	0.5412	740	0.5615
395	0.5389	760	0.5622
405	0.5355	780	0.5682
415	0.5334	800	0.5682

[a]Sample weight is 182.59 grams.
[b]G_2 was maintained at $-50\ \mu v$.
[c]K=74.50 joules/gm-hr.
[d]C_p is the true specific heat as corrected.

TABLE XV

SPECIFIC HEAT OF PURE NICKEL[a,b,c]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
K=146.90 joules/gm-hr		K=58.15 joules/gm-hr	
320	0.5910	135	0.4892
335	0.6057	145	0.4928
345	0.6224	155	0.4975
355	0.6259	165	0.5016
365	0.5616	175	0.5056
375	0.5479	185	0.5097
385	0.5407	195	0.5154
395	0.5346	205	0.5199
405	0.5327	215	0.5248
420	0.5310	225	0.5294
440	0.5288	235	0.5350
460	0.5286	245	0.5406
480	0.5287	255	0.5466
500	0.5299	265	0.5517
520	0.5320	275	0.5600
		285	0.5642
		295	0.5726
		305	0.5806
		315	0.5870

[a] Sample weight is 182.59 grams.
[b] G_2 was maintained at -50μv.
[c] C_p is the true specific heat as corrected.

APPENDIX F

TABLE XVI

THEORETICAL SPECIFIC HEAT OF NICKEL[a]

T, °K	C_p, joules/gm-°C	T, °K	C_p, joules/gm-°C
9.75	0.00167	390	0.46340
19.50	0.00670	423	0.47180
29.25	0.01758	473	0.48220
39.00	0.03726	523	0.49270
58.50	0.09795	573	0.50230
78.0	0.16700	623	0.5115
97.50	0.22690	673	0.5174
117.00	0.27420	723	0.5241
156	0.33910	773	0.5308
195	0.37930	823	0.5371
234	0.40520	873	0.5433
273	0.42490	923	0.5488
312	0.44040	973	0.5534
351	0.45250		

[a] C_p values were calculated from

$$C_p = 1.74 \times 10^{-3} T \left[1 - 2.96 \left(\frac{T}{337}\right)^2\right] + \left[1 + 1.9\, \beta_{(T)} T\right] F\left(\frac{\Theta}{390}\right) \frac{cal}{gm\text{-}^\circ C} .$$

APPENDIX G

TABLE XVII

SPECIFIC HEAT OF NICKEL-20 WEIGHT PER CENT CHROMIUM[a,b,c,d]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
130	0.4801	470	0.5571
150	0.4841	490	0.5624
195	0.4951	505	0.5685
220	0.5012	520	0.5813
240	0.5078	535	0.5989
260	0.5115	545	0.6104
280	0.5190	555	0.6225
300	0.5234	565	0.6280
320	0.5286	575	0.6334
340	0.5346	585	0.6324
365	0.5400	595	0.6323
390	0.5443	615	0.6287
410	0.5498	625	0.6215
430	0.5520	635	0.6282
450	0.5551	645	0.6212

[a] Sample weight is 259.308 grams.
[b] G_2 was maintained at -50μv.
[c] K=67.95 joules/gm-hr.
[d] C_p is the true specific heat as corrected.

TABLE XVIII

SPECIFIC HEAT OF NICKEL-20 WEIGHT PER CENT CHROMIUM[a,b,c,d]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
120	0.4817	420	0.5535
180	0.4971	440	0.5580
200	0.5010	460	0.5610
220	0.5071	480	0.5642
240	0.5155	500	0.5700
260	0.5162	555	0.6093
280	0.5240	565	0.6259
300	0.5289	575	0.6312
320	0.5300	585	0.6375
340	0.5357	605	0.6329
360	0.5405	615	0.6281
380	0.5450	635	0.6280
400	0.5491	645	0.6312

[a]Sample weight is 259.308 grams.

[b]G_2 was maintained at -50μv.

[c]K=97.02 joules/gm-hr.

[d]C_p is the true specific heat as corrected.

TABLE XIX

SPECIFIC HEAT OF NICKEL-20 WEIGHT PER CENT CHROMIUM[a,b,c,d]

T, °C	C_p, joules/gm-°C	T, °C	C_p, joules/gm-°C
140	0.4805	480	0.5530
160	0.4854	495	0.5566
180	0.4946	505	0.5587
200	0.4952	515	0.5659
220	0.4983	525	0.5741
240	0.5020	535	0.5811
260	0.5091	545	0.5936
280	0.5134	555	0.6043
320	0.5290	565	0.6178
340	0.5342	580	0.6219
380	0.5362	595	0.6235
400	0.5403	605	0.6205
420	0.5438	615	0.6190
440	0.5473	625	0.6193
460	0.5498	635	0.6182
		645	0.6190

[a] Sample weight is 259.308 grams.

[b] G_2 was maintained at -50 μv.

[c] K=131.89 joules/gm-hr.

[d] C_p is the true specific heat as corrected.

APPENDIX H

TABLE XX

KOPP-NEUMANN CALCULATIONS FOR NICKEL-20 WEIGHT PER CENT CHROMIUM[a,b,c]

T, °C	C_{p_A} (Ni) joules/gm-°C	C_{p_B} (Cr) joules/gm-°C	C_p of Ni-20 wt.% Cr joules/gm-°C
127	0.4650	0.4893	0.4696
227	0.4870	0.5151	0.4924
327	0.5060	0.5296	0.5105
427	0.5210	0.5376	0.5241
527	0.5340	0.5489	0.5368
627	0.5450	0.5771	0.5511
727	0.5580	0.6077	0.5675

[a] Specific heat values for C_{p_A}(Ni) are from the theoretical nickel data without the magnetic transformation (Table XIII).

[b] Specific heat values for C_{p_B}(Cr) were obtained from references (44).

[c] Specific heat values for C_p of Ni-20 wt.% Cr were obtained from the relation

$$C_p = X_A C_{p_A} + X_B C_{p_B} \quad .$$

VITA

The author was born in Mt. Juliet, Tennessee, on September 9, 1940. He received both his primary and secondary education in the Wilson County school system, graduating from Mt. Juliet High School in May of 1958. The following September he enrolled at The University of Tennessee, Martin Branch. He transferred to the main campus of the University in September of 1959. While working on his undergraduate degree, he participated in the University's cooperative engineering program, spending his work periods in Aiken, South Carolina, working for E. I. Dupont de Nemours Company. He received his B.S. in Metallurgical Engineering in June of 1963. Since then the author has been serving as a research assistant in the Department of Chemical and Metallurgical Engineering at The University of Tennessee while pursuing his graduate studies.