AN ABSTRACT OF THE THESIS OF

Lee Wolochuk for the degree of __Master of Science__ in Mechanical Engineering presented on August 4, 1993.
Title: Small Sample, Low-Temperature Calorimetry

Redacted for privacy

Abstract approved:
William H. Warnes

A calorimeter capable of measuring the heat capacity of 1 mg size samples from 4.2 to greater than 100 K has been designed, constructed, and tested. The sample is bonded to the end of a 0.002 inch diameter, 0.5 cm long chromel-constantan thermocouple (type E) and heated optically with a laser and fiber optic. An advantage of this calorimeter is the low addenda heat capacity of the thermocouple. The thermocouple, which serves not only as the temperature sensor of the sample but also as the thermal link between the sample and a constant temperature reservoir, is anchored to a copper block, which acts as the constant temperature reservoir. Heat capacity is determined from the temperature rate of decay of the sample using a sweep method.

The sample is heated to an initial temperature above the block temperature by the laser. The laser is then turned off and the sample temperature is allowed to decay to the block temperature. By measuring the temperature of the sample as a function of time and relating it to the thermal conductivity of the thermocouple in a separate experiment, the sample's heat capacity can be determined. The thermal conductivity of the thermocouple is determined by performing an experiment with a sample of known heat capacity.

A design model created with a spreadsheet helped to determine what size thermocouple should be used as well as the best materials and dimensions of the components that make up the calorimeter. The model was also useful in determining the nature of a calorimetry experiment and helped determine how high above the block temperature the sample should be heated, how low the pressure inside the calorimeter should be, and how much time a calorimetry experiment would require.

Experiments using copper samples have confirmed the validity of the design. The results of an experiment using a 1.1 mg copper sample agree (within expected uncertainty) with the accepted heat capacity of copper from 7 to 100 K. One factor in the uncertainty is the large heat capacity of the grease (Apiezon N) used to bond the sample to the tip of the thermocouple, especially below 15 K.

Small Sample,
Low-Temperature Calorimetry

by

Lee Wolochuk

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed August 4, 1993
Commencement June 1994

APPROVED:

Redacted for privacy

_____
Associate Professor of Mechanical Engineering & Material Science in charge of major

Redacted for privacy

_____
Chairman of the Department of Mechanical Engineering

Redacted for privacy

_____
Dean of Graduate School

Date thesis is presented _____August 4, 1993_____

Typed by Lee Wolochuk for _____Lee Wolochuk_____

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SMALL SAMPLE, LOW-TEMPERATURE CALORIMETRY

<u>Chapter 1   INTRODUCTION</u>

In general, calorimetry reveals information about the chemical, electronic, and structural properties of materials and as such is an important tool in materials science research. Due to their temperature dependence characteristics, the various contributions to specific heat can only be separated out at low temperatures (T<50 K) [1]. This can be seen when a material's constant pressure heat capacity, Cp, is given theoretically at low temperatures [2] as

$$C_p = \gamma T + \beta T^3, \tag{1}$$

where γ and β are defined by

$$N(0) \cdot (1+\lambda) = 0.4244\gamma, \tag{2}$$

$$\theta_D = 10 \cdot (1944/\beta)^{1/3}, \tag{3}$$

where N(0) = electron density of states at the Fermi energy;

θ_D = Debye temperature, which is proportional to interatomic forces;

λ = coupling strength of electrons to phonons and other electrons.

A typical plot of specific heat vs. temperature is shown in Figure 1 for niobium from 1.5 to 100 K [3].

The first term of equation (1) represents the electronic contribution to specific heat, while the second term represents the lattice contribution. As shown, the lattice contribution is proportional to T^3, while the electronic component is proportional to T; at higher temperatures, therefore, the lattice contribution dominates Cp, and it is difficult to obtain an accurate value of the electronic contribution when the lattice contribution is subtracted from Cp. Also, at high temperatures, Cp becomes approximately constant and independent of temperature. Measurement of the specific heat at low temperatures is the most common way to determine N(0) and θ_D. One material system in which the density of states and Debye temperature are important parameters is in superconducting materials.
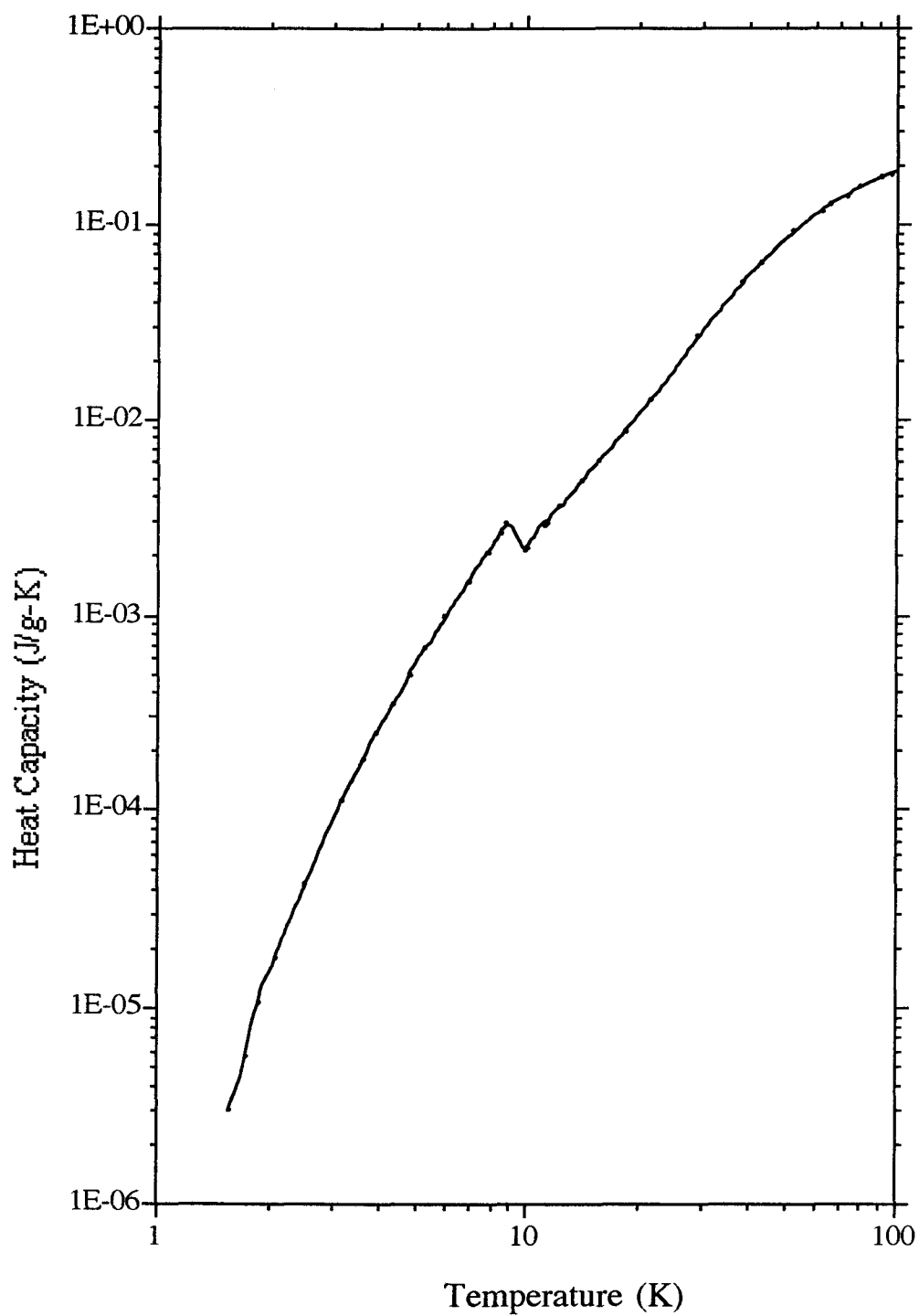
Knowledge of θ_D and N(0) are useful in determining the superconducting transition temperature of a material, T_c. Theoretically, the superconducting transition temperature is given as

$$T_c \approx \theta_D \cdot \exp[-1/V \cdot N(0)], \tag{4}$$

where V is a measure of electron-phonon coupling strength [2].

Figure 1: Heat Capacity vs. Temperature, Niobium

When a material experiences a superconducting ordering transition, a discontinuity in its specific heat occurs at T_c. The size of the discontinuity, ΔC, is given by

$$\Delta C / (\gamma T_c) \approx 1.43, \tag{5}$$

where the value of 1.43 is valid for materials with a weak electron-phonon coupling strength and is greater for materials with a stronger coupling force, possibly as high as 3.0 [2]. Inderhees *et al.* [4] found that plots of γ vs. T_c for high T_c ceramic materials lie above the range of other superconducting materials. The value of the expression in equation (5) for $YBa_2Cu_3O_{7-\delta}$ ($T_c=90$ K) was found to be 1.23, suggesting a weak electron-phonon coupling strength. Niobium has a superconducting transition temperature of 9.25 K, as is shown in Figure 1 by the discontinuity in specific heat at this temperature.

Low temperature specific heat measurements also are useful in studying magnetic ordering transitions. Salamon [5] used specific heat measurements at low temperatures to study anisotropy effects in crystals of CoO, a magnetic material. Also, by knowing a material's specific heat at the temperature of a magnetic ordering transition, T_{mag}, the amount of entropy, S, produced during the transition can be determined [2]:

$$S = \int_{T_{mag}-\Delta T}^{T_{mag}+\Delta T} (C_p / T) dT, \tag{6}$$

where $2\Delta T$ is the length of the transition. This is useful for designing techniques for magnetic refrigeration.

There are two primary reasons for using small samples to investigate calorimetric properties of materials. First, small samples of a given material are likely to be more homogeneous than a larger sample, and the properties of a more homogeneous sample can be measured more precisely. Second, samples of many materials of interest, such as Nb_3Ge, $YBa_2Cu_3O_{7-x}$, and $La_{1.85}Sr_{0.15}Cu_3O_{4-x}$, are normally prepared by thin-film techniques, which can only produce small-sized samples [2, 4, 6]. To measure any property of such materials requires an apparatus that will accept small samples.

A technique known as adiabatic calorimetry is the most common method for measuring the heat capacity of large samples. With this method, a small heater and thermometer are bonded to the sample; the sample is heated and the heat capacity is determined by dividing the heat input by the sample's temperature rise. This assumes that any heat transferred out of the sample (including heat transfer down lead wires, gas conduction, and radiation) is negligible [7]. The problem with using this technique for

small samples is that the heat input into the sample to achieve a slight temperature rise can be extremely small, and the amount of heat transferred from the sample through the lead wires would not be negligible.

Small sample measurements are typically accomplished using non-adiabatic techniques, which involve some type of thermal link from the sample to a constant temperature reservoir. When the sample is heated to some temperature above the temperature of the reservoir and then allowed to cool, heat flows from the sample to the reservoir. By determining the thermal conductance of this thermal link, the amount of heat leaving the sample can be determined; with knowledge of the heat leaving the sample as a function of time, heat capacity can be calculated.

Due to the small sample sizes used with non-adiabatic calorimetry, the heat capacity of the thermometer and heater and the thermal link are not negligible and must be subtracted out from the final heat capacity measured. This extra heat capacity is known as the addenda heat capacity, or simply as the addenda. A major goal in designing any small sample calorimeter is to keep the addenda as small as possible so it does not dominate the measurement.

At low temperatures, the specific heat of any material is very small compared to the value at higher temperatures. It is therefore necessary to keep stray heat leaks into the system, known as parasitic heat leaks, as small as possible. A seemingly negligible heat leak through lead wires, for example, could cause a sample's temperature to increase as much as a few degrees K, making the measurement inaccurate.

The goal of this work is to design, construct, and test a calorimeter capable of measuring the specific heats of 1 mg size samples of as wide a variety of materials as possible over the temperature range from 4.2 to 100 K. Most calorimeters are used either to measure heat capacity at higher temperatures (T>75 K) or lower temperatures (T<35 K). A more versatile design that has no limitations as far as temperature is ideal. Also, the calorimeter must be designed so that it could easily be built using the facilities available at Oregon State University .

1.1 CALORIMETER DESIGNS: LITERATURE SURVEY

The current literature indicates five major types of non-adiabatic calorimeters. The first and most common design mounts the sample on a platform onto which a heater and temperature sensor are bonded, forming a bolometer. The second type of calorimeter is similar to the first but uses a strain gauge as the sample heater and two unencapsulated thermometer elements to monitor the temperature of the sample; the calorimeter design is

simple and allows for quick and easy construction. A third design uses an optical source to heat the sample instead of a resistive heater. The fourth type of calorimeter mounts the sample to the tip of a thermocouple, thus eliminating the thermal mass of the sample holder, and the temperature of the bath (i.e. thermal reservoir) is modulated rather than that of the sample. The final type of calorimeter combines an optical heating method with a thermocouple-mounted sample.

Bachmann *et al.* [8] describe a calorimeter used to measure the specific heat of small samples (1-500 mg) from 1 to 35 K. The sample is attached to a silicon platform, on which a thin layer of silicon has been doped and cut into two sections, one that acts as the sample heater and the other that acts as the sample thermometer. The bolometer is suspended from a ring by four gold-copper wires, which serve as a thermal link between the bolometer and a constant temperature reservoir. The addenda contribution of the thermal link is shown theoretically to be one third of the total heat capacity of the thermal link, which is confirmed by experimental results. Heat capacity is measured by relating heater power input, temperature change of bolometer plus sample, and thermal conductance of the thermal link. A measurement technique known as the relaxation method is introduced. Most low-temperature, small sample calorimetry research to date has used calorimeters that are either variations of this design [4-6, 9-11] or duplicates of it [1, 12, 13].

Bolometers are normally used in the temperature range between 1 and 35 K, and sample masses typically range from 1 mg to 100 mg. Different bolometer designs include the original silicon one used by Bachmann *et al.*, one that uses a thin sapphire disk with a chromium heater and a thin-film germanium resistor evaporated onto one side [14], and one that uses a silicon heater and temperature sensor on a sapphire platform and is known as an SOS bolometer [15]. Sample masses as low as 0.1 mg have been measured with an SOS bolometer. A bolometer has a low thermal mass at low temperatures (<30 K), but above 30 K, its thermal mass dominates the measurement. This is one of the most severe limitations to the bolometer, as will be discussed later in more detail, and is the reason that it is only used between 1 and 35 K. One final disadvantage of bolometers is that they are difficult to fabricate; thin-film deposition technology is normally required to create a bolometer.

Four calorimeter designs differ from the one used by Bachmann *et al.* The first [9] describes an easily constructed calorimeter that simply uses a strain gauge as the sample heater and a slab of copper as the sample support. A 34-gauge copper wire is used as the thermal link. Heat capacity is measured from 0.4 to 10 K using a relaxation technique while heating and cooling the sample by increasing or decreasing the heater

output in a stepwise manner. The major factor separating this calorimeter from the others is that it is easy to use and can supposedly be constructed in one day.

The second original design [6] uses an LED to heat the sample, which helps to keep the addenda down by removing the heater mass from the sample holder. The sample is mounted on a platform that is suspended by four Kevlar threads; a Au-Ge thermometer is mounted on back of the platform. Measurements are made between 0.06 and 4 K.

The third design [10, 11] uses a 0.002 inch diameter, 1mm long chromel-constantan thermocouple both as a thermal link between the sample and temperature bath and as the sample thermometer. The sample is bonded to the end of the thermocouple with GE 7031 varnish and is not heated; instead, the temperature of the bath is modulated sinusoidally. Measurements are made from 6 to 60 K, but measurements at temperatures as low as 10 mK can be achieved by using a more sensitive thermocouple, such as a chromel-Au(Fe) thermocouple. Extremely small samples were measured with this apparatus (2.9 μg) at an estimated accuracy of 10%.

The final design [4, 5] bonds a sample (about 18 mg) to the end of a 0.001 inch diameter chromel-constantan thermocouple and uses a quartz-iodide lamp to heat the sample. An ac heat input is maintained using a mechanical chopper, and an estimate of the amount of heat input into the sample by the lamp is made by performing the experiment with a strain gauge as the sample heater and comparing the data at a given temperature with the data obtained when the lamp was used as the heater.

1.2 MEASUREMENT TECHNIQUES

Two main measurement techniques, the relaxation method and the ac method (or variations of either method), are used by all of the research groups covered in this literature review, irrespective of the calorimeter design adopted. All measurement techniques basically involve recording the time it takes for a heated sample to decay from an initial temperature to some final temperature. Figure 2 illustrates the two techniques. With the relaxation method, the sample is heated to a constant temperature above the bath (i.e. constant temperature reservoir) temperature and then allowed to cool. The governing equation for the relaxation technique is

$$\Delta T(t) = (T_1 - T_0)exp\left[\frac{t}{\tau}\right], \qquad (7)$$

Figure 2: Measurement Techniques

(a) relaxation method
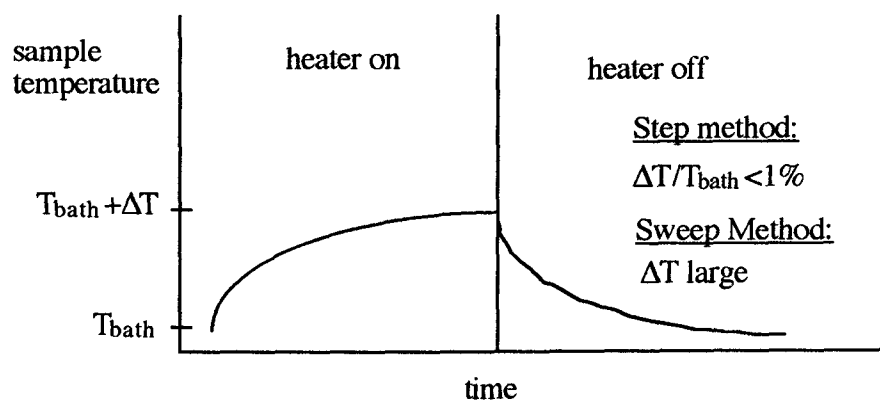
(b) ac method
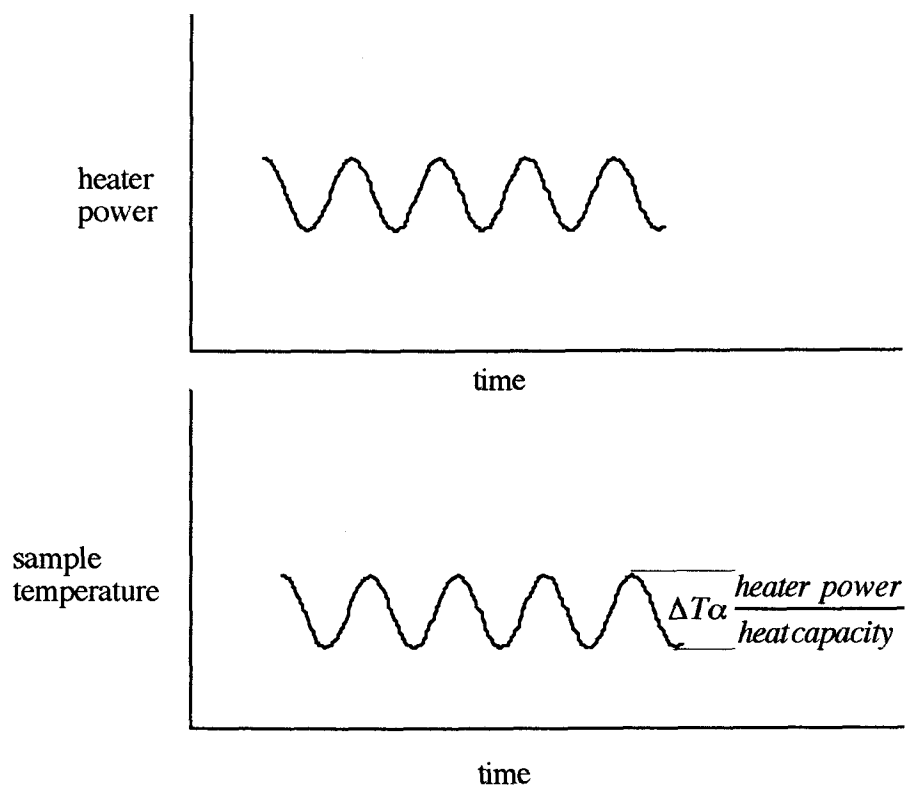
where t = time;

$\Delta T(t) = T_{sample} - T_{bath}$;

$T_0 = T_{bath}$;

$T_1 = T_{sample}$ at t=0;

τ = time constant = $\dfrac{C}{k}$;

C = heat capacity of sample plus heat capacity of addenda;

k = thermal conductance of thermal link.

This equation is valid as long as the temperature within the sample is assumed to be uniform and ΔT is small enough so that the sample's heat capacity and the thermal conductance of the thermal link can be assumed to be constant throughout the decay. If the temperature within the sample varies, the sample will have its own internal time constant, τ_2, and the analysis becomes more complicated. Usually, $\dfrac{\Delta T}{T_0}$ is around 1%.

Two methods using the relaxation technique are the step and the sweep (or scanning) methods. With the step method, the sample is heated until its temperature is slightly above the bath temperature. The sample heater is then turned off, and the sample temperature decays to the bath temperature. The bath temperature is then increased and the sample temperature is again raised slightly above the bath temperature and allowed to decay. This stepwise procedure is repeated throughout the desired temperature interval. Temperature can be recorded either while heating or cooling the sample.

With the sweep method, heat capacity is measured continuously over a small or large temperature interval. The governing equation with the sweep method [8] is

$$C(T) = \left(\frac{dT}{dt}\right)^{-1} \int_{T_0}^{T} k \, dT', \qquad (8)$$

where C(T) = heat capacity of sample plus heat capacity of addenda at a given temperature;

$\dfrac{dT}{dt}$ = rate of change of sample temperature with respect to time;

k = thermal conductance of thermal link;

$\int_{T_0}^{T} k \, dT'$ = conduction heat transfer through thermal link from sample to bath.

By measuring the slope of the sample's temperature decay curve and measuring the thermal conductance of the thermal link and the addenda heat capacity in a separate experiment, the sample's heat capacity can be calculated continuously between T_0 and T.

The accuracy in determining the sample's heat capacity depends on how accurately the slope to the temperature decay curve can be determined. The highest uncertainty occurs at the ends of the curve, and the uncertainty decreases as the total decay time increases [16]. The slope of the sample's heating curve can be measured as well as that of the cooling curve to give a more accurate value of heat capacity [16-18]. Forgan and Nedjat use a sweep method to measure heat capacity continuously from 1.5 to 10 K [18].

With the ac method, introduced by Sullivan and Seidel [19], the heater power is varied sinusoidally with a frequency much greater than $\frac{1}{\tau}$, and the temperature response of the sample is recorded. The change in temperature of the sample is proportional to the heater power divided by the heat capacity of the sample plus addenda.

A variation of the ac method is the square wave excitation method, where a square wave is used instead of a sine wave for the heater power output. The ripple method [20] is a further variation; with the ripple method, the pulse width is very small so that the sample's temperature response can be approximated with a triangular wave.

Xu, Watson, and Goodrich [16] present a measurement technique that is a combination of the ac and relaxation methods. The power level of the sample heater is increased and decreased alternately, allowing enough time at the end of each pulse for the sample to heat or cool for a few seconds; the sample's temperature is recorded throughout each heating and cooling phase.

Table 1 summarizes some of the advantages and disadvantages of the major measurement techniques. The relaxation method is good for point-by-point measurements, and if the conductance of the thermal link connecting the sample to the constant temperature reservoir is known, then the amount of power entering the sample need not be known. It is time consuming with this technique to cover a wide temperature range, however, and difficult to analyze the data [2]. Also, measurements must be repeated several times for accurate data. The ac method works well for continuous measurement of heat capacity over narrow temperature ranges and can detect small changes in heat capacity, but the amount of heat entering the sample must be known accurately. Because it is difficult to determine absolute values of heat capacity with the ac method, another method is usually used to calibrate the experiment.

Table 1: Summary of Measurement Techniques

	Advantages	Disadvantages
Step Method	Accurate point-by-point measurement. Do not need to know sample heater power input if thermal conductance of thermal link is known.	Time consuming to cover a wide temperature range. Difficult to analyze data.
Sweep Method	Wide temperature range covered continuously. Do not need to know sample heater power. Sample temperature can be close to bath temperature or much higher than bath temperature.	Must repeat measurement several times to improve signal-to-noise ratio. Sample temperature decay rate is much higher at lower temperatures than at higher temperatures.
ac Method	Continuous measurement over entire temperature range. Best technique if addenda is high. Detects very small changes in heat capacity.	Must know power input to sample. Works well only with narrow temperature range. Must calibrate with another method.

Chapter 2   CALORIMETER DESIGN

2.1 MATHEMATICAL MODELS

After reviewing the literature on small sample, low-temperature calorimetry, a calorimeter design that mounts the sample to the tip of a thermocouple and uses an optical method to heat the sample was chosen. This design was chosen over others because it could best meet the goals of this project, which include easy fabrication with available facilities and no limit on the temperature range over which measurements can be made. One major advantage of this type of calorimeter over a bolometer-based calorimeter is the fact that the heat input into the sample is spread uniformly over the entire sample area, whereas a bolometer depends on good thermal contact between the sample and heater, which can be difficult to achieve. Other advantages include low addenda heat capacity, easy sample mounting and dismounting, ability to use a variety of measurement methods, and easy thermocouple replacement.

Two mathematical models were set up on spreadsheets to help in the design of the calorimeter apparatus. The first model was used in the early stages of the design to help understand the nature of a small sample, low-temperature calorimetry experiment. Its primary goal was to determine the thermocouple type and size that would work best, and it helped give insight into the behavior of the addenda heat capacity with respect to temperature and the range of time constants that could be expected in a given experiment. The model assumes that a step method of measurement would be used; this means that the sample temperature must be within 1% of the reservoir temperature, so that the sample's temperature decay range is narrow. With this narrow temperature range, the heat capacity of sample plus addenda and thermal conductance of the thermal link can be considered constant.

The second model was used later in the design process when a sweep method of measurement was considered more feasible with the proposed calorimeter design. With a sweep method, the temperature of the sample is increased anywhere from 1 to 100 K above the reservoir temperature and then allowed to decay. This model was helpful in determining the possible temperature ranges that a given sweep could cover, the amount of radiation heat transfer from the sample to its surroundings, the amount of convection heat transfer from the sample to its surroundings, and the amount of time it would take for a sample to decay from a given initial temperature to the reservoir temperature.

2.1.1 Thermal Link Dimensions

The nature of a calorimetry experiment is largely determined by the thermal link connecting the sample to the constant temperature reservoir. The dimensions and thermal properties of this thermal link determine the total time the experiment will take, the rate that the sample temperature decays from an initial temperature to the reservoir temperature, and part of the addenda heat capacity. The size and type of thermocouple was chosen so that the time that the sample takes to decay from some initial temperature higher than that of the reservoir to the reservoir temperature is neither too long nor too short. A good indication of this decay time is the time constant, τ (defined earlier). The addenda contribution of the thermocouple was also considered.

The thermocouple dimensions and material were chosen so that τ remains between 0.001 sec and 1000 sec over the entire temperature range from 4 to 100 K for a wide variety of materials. Using a spread sheet, a model was created to help determine the dimensions and type of thermocouple that would work best as the thermal link. Figure 3 shows a schematic flow chart of the model. The basic idea is as follows:

1. The sample's mass, an estimate of the sample's heat capacity, an estimate of the thermal conductivity of the thermocouple/thermal link, and an estimate of the heat capacity of the thermocouple are entered at various temperatures between 4 and 100 K; because ΔT is small, these properties are assumed to be constant.

2. A target time constant is chosen, which then determines the thermal link conductance, k.

3. A thermocouple diameter is chosen, which, in combination with k and κ, determines the required thermocouple wire length.

4. The thermocouple dimensions are used to find the addenda heat capacity.

5. The actual time constant is determined from k and the total heat capacity.

This single-iteration procedure outputs the following results for a given thermocouple length: thermocouple diameter, addenda fraction of total heat capacity, and time constant.

Two thermocouples commonly used at low temperatures were considered: type T, copper-constantan, and type E, chromel-constantan. (The thermal conductivity of a chromel-constantan thermocouple was measured by Graebner [10].) Because the heat capacity of chromel at low temperatures could not be found, it was assumed to be the same as constantan at all temperatures; it will later be shown that an accurate value of the heat capacity of chromel is not necessary for useful model results.

Figure 3: Schematic of Model Calculations
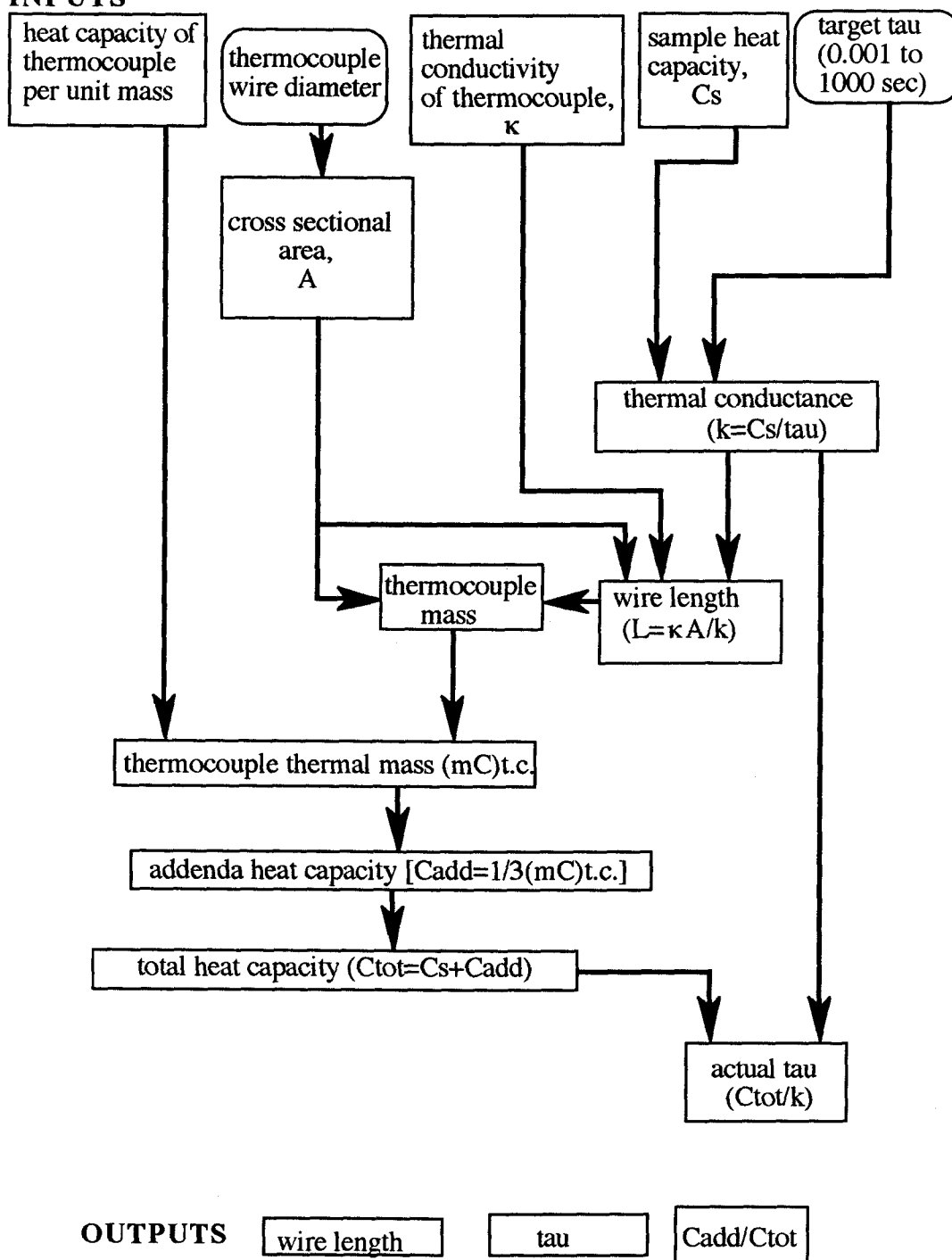
To determine possible limitations to the calorimeter design, the heat capacities [3] of 1 mg samples of copper, beryllium, aluminum, niobium, and silicon at 4, 10, 30, 70, and 100 K were input into the model. As shown in Figure 4, these materials exhibit a wide range of heat capacities. Calculations showed that the thermal conductivity of the copper-constantan thermocouple was too high, leading to time constants of less than 1 msec at lower temperatures, but the chromel-constantan thermocouple gave better results.

Figure 5 shows a typical plot of wire diameter vs. τ for a 1 mg copper sample. An important feature of this plot is that the time constants at higher wire diameters remain the same with increasing diameter. This can be explained by taking a close look at the equation used to determine τ:

$$\tau = \frac{C_{tot}}{k} = \frac{C_{sample} + 1/3 C_{t.c.}}{k}, \qquad (9)$$

where τ = time constant;

C_{sample} = sample heat capacity, which is the same for all wire diameters;
$C_{t.c.}$ = thermocouple heat capacity, which decreases with decreasing wire diameter;
k = thermal conductance of thermal link, which decreases with decreasing wire diameter.

The total heat capacity is determined by the sample heat capacity plus the addenda heat capacity, which consists of the grease bonding the sample to the thermocouple and the thermocouple itself. As explained earlier, Bachman et al. [8] showed that the addenda contribution of the thermal link connecting the sample to the constant temperature reservoir is approximately one third of the heat capacity of the thermal link. The addenda contribution of the grease used to bond the sample to the thermocouple was assumed to be negligible and not considered in either equation (9) or the model; as will be discussed later, the contribution of the grease to the total measured heat capacity can actually be quite large, possibly twice that of the sample at lower temperatures (less than 15 K) to one quarter that of the sample at higher temperatures.

At 4 K, the constant τ trend begins when the wire diameter is about 0.03 cm, which, according to Figure 6, corresponds to an addenda fraction of total heat capacity of about 80%. At 70 K, the constant τ trend begins when the wire diameter is about 0.06 cm, which also corresponds to an addenda fraction of total heat capacity of about 80%. This trend of the addenda dominating the measurement when it is about 80% of the total heat capacity was found to be true at all temperatures for all materials used in the model.

Figure 4: Heat Capacity vs. Temperature [3]
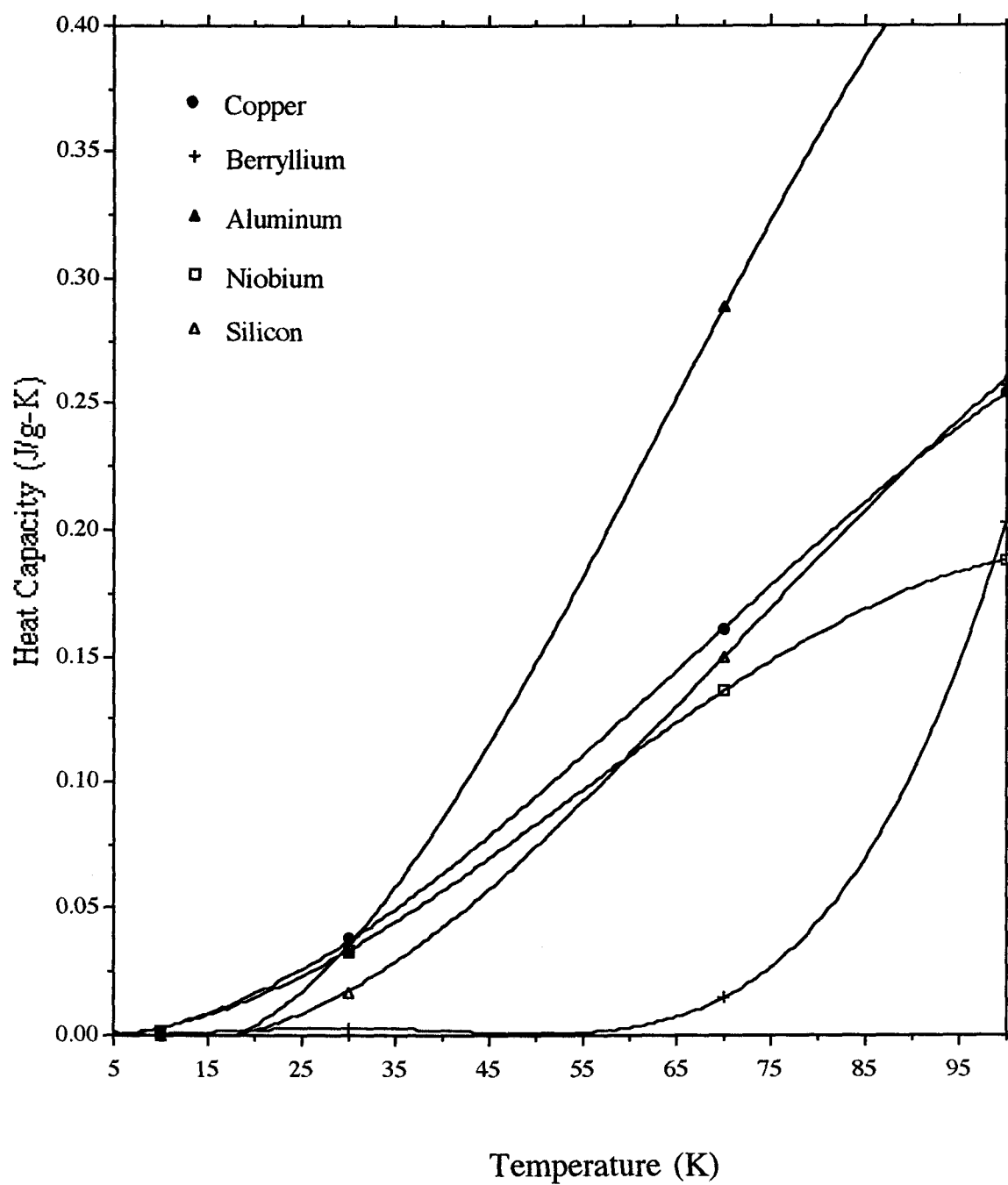
Figure 5: Wire Diameter vs. Tau (L=0.5 cm)

Chromel-Constantan Thermocouple
1 mg Copper Sample

Tau (seconds)
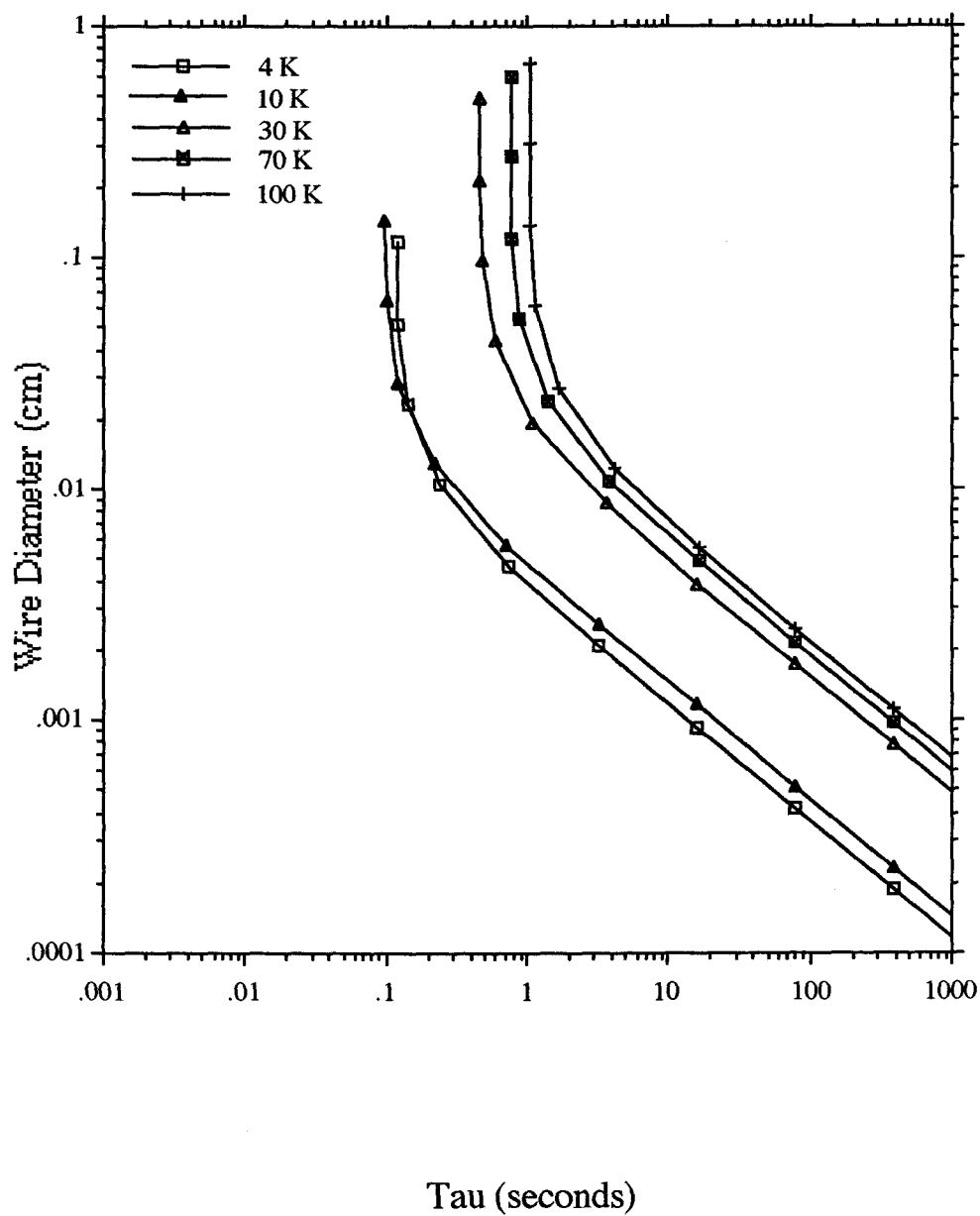
Figure 6: Fraction of Addenda Heat Capacity vs. Wire Diameter

(L=0.5 cm)
Chromel-Constantan Thermocouple
1 mg Copper Sample

When the addenda fraction of the total heat capacity is higher than 80%, the addenda dominates the total heat capacity, the numerator of equation (9). As wire diameter decreases, both the numerator and denominator of equation (9) decrease at similar rates, causing τ to remain constant. At smaller diameters, the addenda heat capacity becomes less important compared to the sample's heat capacity, thus the total heat capacity is dominated by the sample. As wire diameter decreases, the numerator in equation (9) remains relatively constant while the denominator decreases, causing τ to increase as diam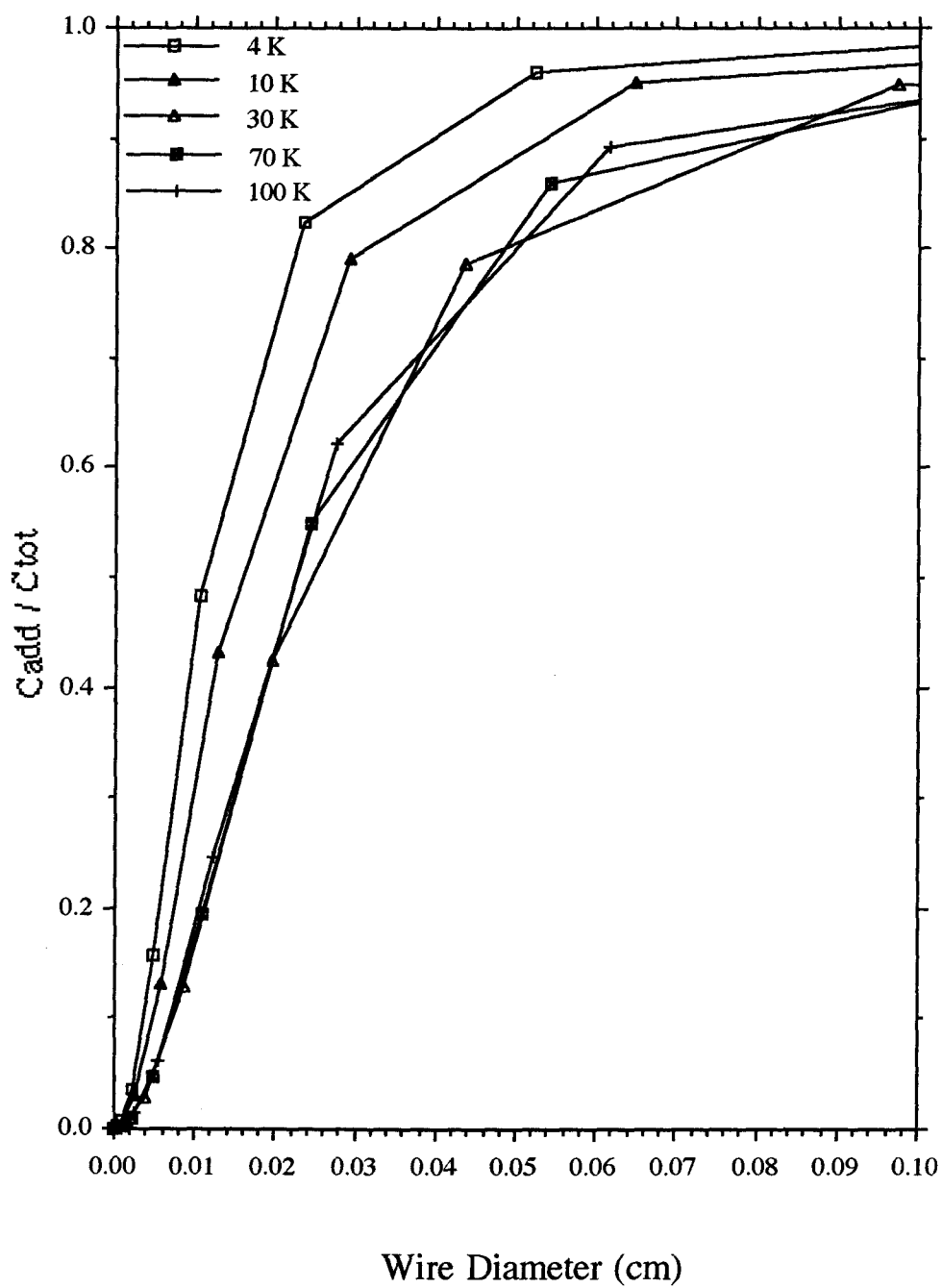eter decreases. The preceding analysis leads conveniently to the following design criterion: the addenda heat capacity should be kept below 80% of the total heat capacity.

Figure 6 also shows that the maximum addenda occurs at 4 K and decreases with increasing temperature. This was found to be true for most of the materials used in the model and means that if the addenda fraction of the total heat capacity can be kept below 80% at 4 K for most materials, then it will be below 80% for the entire temperature range from 4 to 100 K.

Figure 7 shows the addenda fraction plotted against τ for various wire diameters and lengths using a 1 mg aluminum sample. The dotted lines represent different wire lengths, ranging from 0.5 cm to 4 cm (left to right), while the dashed lines represent different wire diameters, ranging from 0.0005 inch to 0.005 inch (right to left). By choosing a thermocouple length and diameter, the addenda fraction at 4 K and the time constant can be determined from Figure 7. The shaded area represents the "design window," and a successful design would be one where all design parameters lie somewhere within this window. The following criteria were used in determining the boundaries of the window:

1. Addenda heat capacity must be below 80% of the total heat capacity;
2. Wire diameter > 0.0005 inch, (AWG #56); this is a very optimistic minimum diameter - such small wires are very difficult to work with;
3. Wire length ≥ 0.5 cm (shorter wire is difficult to work with);
4. Time constant between 0.001 sec and 1000 sec.

These design criteria help give a general idea of the factors that must be considered in determining the final dimensions of the thermal link. The design window expands, shrinks, or shifts when the heat capacities of different materials are entered into the model, but the most suitable dimensions of the thermocouple would lie within the design window of as wide a variety of materials as possible at all temperatures.

Figure 7: Fraction of Addenda vs. Tau (T=4 K)

Chromel-Constantan Thermocouple
1 mg Aluminum Sample

Tau (seconds)
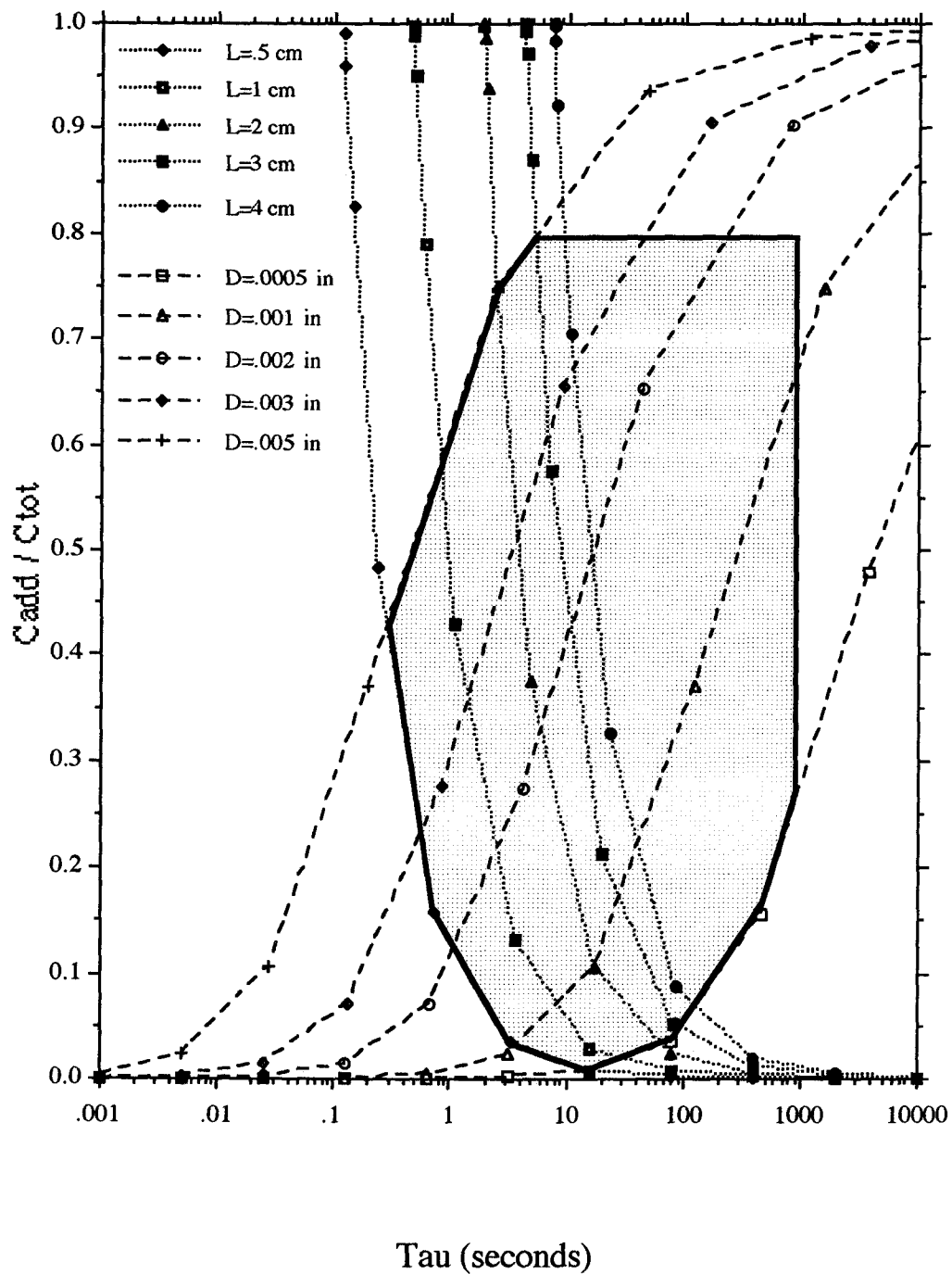
After inputting the heat capacities of 1 mg of many of materials, it was found that a 0.5 cm long, 0.002 inch diameter chromel-constantan thermocouple would give the most reasonable time constants for the widest variety of materials. With this thermocouple, the addenda fraction of the total heat capacity would be less than 20% for 1 mg samples of most materials at all temperatures between 4 and 100 K, and still less than about 60% for low heat capacity materials, such as beryllium, at low temperatures.

Unlike a bolometer system, the highest addenda fraction of the total heat capacity with the proposed calorimeter design would normally occur at 4 K and decrease as temperature increases; for most materials, the addenda drops below 5% by 10 K. With a bolometer system, on the other hand, the addenda increases with temperature and begins to dominate the measurement around 30 K. The bolometer used by Bachmann *et al.* [8] was made from a 25 mg piece of silicon; germanium has also been used as a bolometer material [14]. Figure 8 compares the thermal masses of 1 mg of copper, 10 mg of copper, 10 mg of silicon, 25 mg silicon, 25 mg germanium, and a 0.5 cm long, 0.002 inch diameter chromel-constantan thermocouple; once again, the heat capacity of chromel was estimated to be the same as that of constantan. The mass of the thermocouple is only 0.18 mg.

The bolometer's large mass (typically greater than 10 mg) has less effect on the total thermal mass at temperatures below 30 K due to the very low heat capacity of the bolometer at these temperatures. Around 30 K, however, the thermal mass of the bolometer increases rapidly with temperature, and it is obvious why it dominates the heat capacity measurement. A 10 mg copper sample would have roughly the same thermal mass as a 25 mg silicon bolometer at 30 K, but the bolometer heat capacity would begin to take over as the temperature is raised above 30 K.

The addenda fraction of the total heat capacity depends on the difference between the sample thermal mass curve and the bolometer thermal mass curve. With a 25 mg silicon bolometer, the thermal mass of the bolometer stays above that of the sample, and the difference between the two curves increases with temperature. The results are the same for germanium, which is also a common bolometer material. This explains why the addenda fraction of the total heat capacity increases with temperature with a bolometric calorimeter.

The thermal mass of a 0.5 cm long, 0.002 inch diameter chromel-constantan thermocouple stays well below that of a 1 mg copper sample, and it seems safe to say that this would be true with a 1 mg sample of any material. Not only does the thermocouple's thermal mass stay below that of the sample, but the difference between the two actually increases with temperature, which explains why the addenda fraction of the total heat

Figure 8: Thermal Mass vs. Temperature
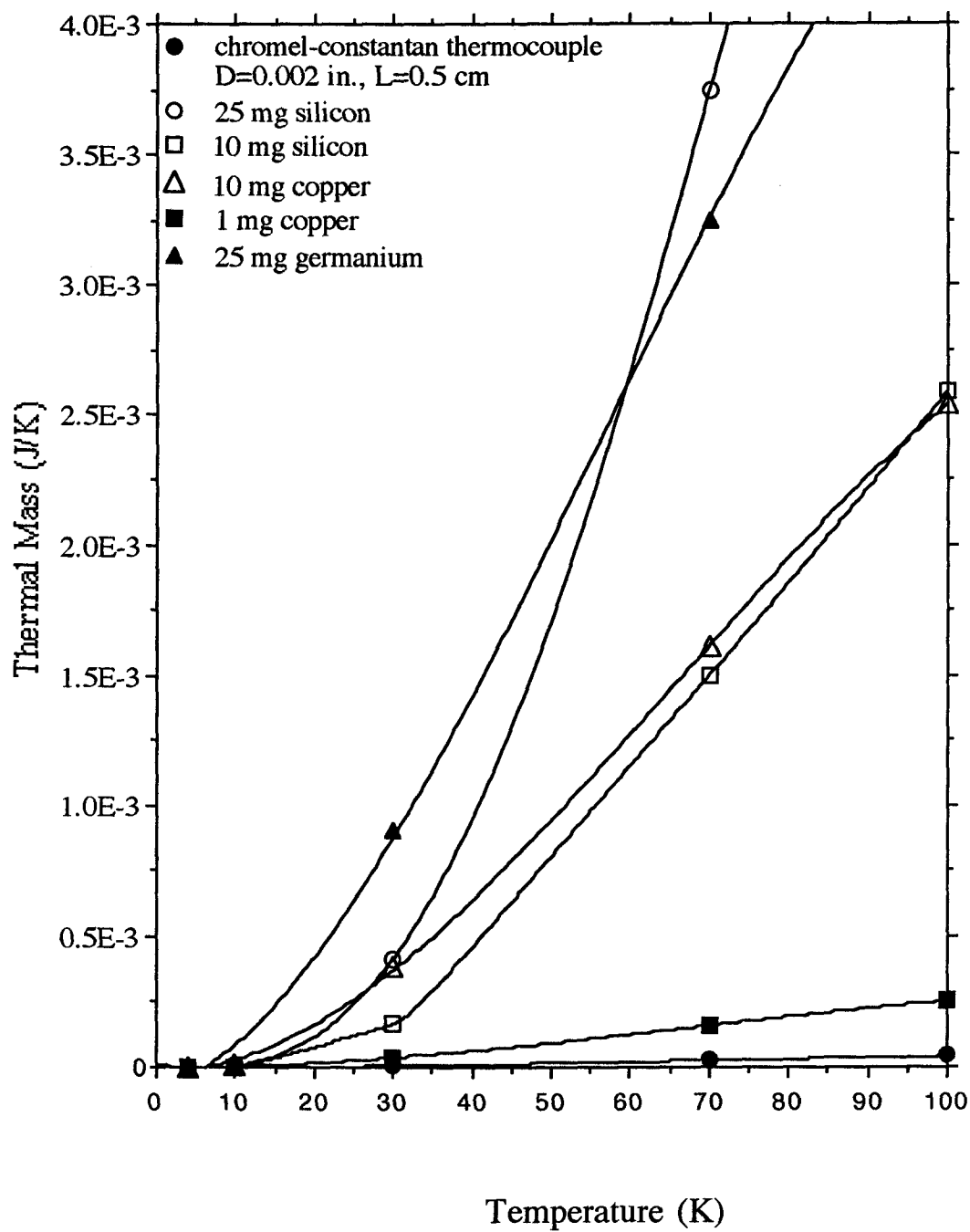
capacity normally decreases as temperature increases with a thermocouple type of calorimeter. The major advantage of this type of calorimeter, therefore, is not so much the thermal properties of a chromel-constantan thermocouple versus a silicon bolometer, but the enormous difference in the masses.

One final point regarding the thermal mass of the thermocouple is that it is inconsequential that the heat capacity of chromel has only been estimated in all calculations up until now. Even if it is much higher or lower than estimated, the extremely small mass of the thermocouple would keep the thermal mass of the thermocouple well below that of the sample, and all conclusions drawn thus far would remain unchanged.

2.1.2 Second Model

As explained earlier, the second design model was used to help determine the possible temperature ranges that a given sweep could cover, the amount of radiation heat transfer from the sample to its surroundings, the amount of convection heat transfer from the sample to its surroundings, and the amount of time it would take for a sample to decay from a given initial temperature to the reservoir temperature. This model assumes that instead of raising the sample temperature slightly above the reservoir temperature (step method), the sample's temperature is raised many degrees above the reservoir temperature (sweep method). Calculations are done using the properties of a 0.5 cm long, 0.002 inch diameter chromel-constantan thermocouple.

All of the conclusions drawn from the first model are still valid, except that the time constant with a sweep method is different from that of the step method; with the step method, the heat capacity of the sample and the thermal conductance of the thermal link are assumed to be constant because of the narrow temperature interval, but with a sweep method, both of these parameters vary greatly over a given temperature interval. For a given sweep, the sample's heat capacity and the thermocouple's thermal conductance would be different at every temperature, thus there is really no characteristic "time constant" for the sweep. The parameter that would control a given sweep is the time rate of change of the sample's temperature, and a successful sweep would be one where this parameter's order of magnitude does not change significantly from an initial temperature to the reservoir temperature.

Temperature was incremented by 1 K starting from the reservoir temperature and ending at 100 K, and the following results at each temperature were output: the amount of heat energy transferred via conduction through the thermocouple from the sample to the

constant temperature reservoir, the amount of heat energy transferred via radiation from the sample to its surroundings, the amount of heat energy transferred from the sample to its surroundings via gas conduction (i.e. convection), and the time rate of change of the sample's temperature. These results helped to determine the most reasonable temperature range a sweep should cover for a given reservoir temperature.

Radiation Heat Transfer: One of the major assumptions made when performing non-adiabatic calorimetry is that all of the heat leaving the sample escapes through the thermal link to the constant temperature reservoir. If the sample's temperature is much higher than the temperature of the surroundings, heat will be radiated from the sample to its surroundings. It is important that this amount of heat leak due to radiation must be negligible compared to the heat leak due to conduction through the thermal link.

The amount of radiation heat transfer from the sample to its surroundings can be estimated using an equation for a general two surface enclosure [21]:

$$Q_{radiation} = \sigma(T_s^4 - T_\infty^4) \div \left[\left(\frac{1-\varepsilon_s}{\varepsilon_s A_s} \right) + \left(\frac{1}{A_s F_{s\infty}} \right) + \left(\frac{1-\varepsilon_\infty}{\varepsilon_\infty A_\infty} \right) \right], \qquad (10)$$

where $\sigma = 5.67 \times 10^{-8}$ W/m^{2}K^4;

T_S = sample temperature;

T_∞ = surroundings temperature;

A_s = sample area;

A_∞ = surroundings area;

ε_s = sample emissivity;

ε_∞ = surroundings emissivity;

$F_{s\infty}$ = view factor between sample and surroundings. For small sample-to-surroundings area, $F_{s\infty} \approx 1$.

The model outputs the amount of radiation heat transfer from the sample as a fraction of the conduction heat transfer through the thermocouple. As long as this fraction remains low (less than 5%), the radiation to the surroundings can be considered negligible compared to the conduction through the thermocouple. This is one of the disadvantages of using a low thermal conductivity thermocouple; with a thermal link with a high thermal conductance, the conduction heat transfer would be so high that any stray heat leaks from the sample, such as radiation or gas conduction, would always be negligible.

The area of the sample was assumed to be around 1.5 mm^2 while the area of the

surroundings was estimated to be 70 cm^2. Results show that the emissivity and area of the surroundings would have negligible effect on the radiation heat transfer from the sample, primarily because the sample is so small compared to the surroundings. The radiation heat transfer is controlled mostly by the sample's emissivity and slightly by the sample's area. Most metals have emissivities lower than 0.2 at temperatures below 100 K; with a reservoir and surroundings temperature of 4.2 K, the radiation heat transfer from a 1 mg copper sample with $\varepsilon=0.1$ would be 0.06% of the conduction heat transfer at 5 K and 0.13% at 100 K. Radiation heat transfer from metallic samples is therefore negligible over the entire temperature interval.

Oxides can have emissivities of 0.6 or higher at low temperatures, so a worst case condition of high sample area and an emissivity of 1 was input into the spreadsheet. Reservoir and surroundings temperatures of 4.2 K were entered, and the results showed that the radiation heat transfer reaches 1% of the conduction heat transfer around 50 K and 5% at 100 K.

Ideally, the temperature of the surroundings would be kept at exactly the same temperature as the sample; this would assure that no radiation heat transfer takes place between the sample and its surroundings. Because the sample's temperature is constantly decreasing, this is not practical. Results show that the minimum radiation to conduction ratio would occur at all temperatures when the reservoir and surroundings are kept at the same temperature. In this case, the driving force for conduction is high enough at all temperatures to make radiation negligible. When the reservoir and surroundings are set to a higher temperature, the ratio of radiation to conduction heat transfer is in general slightly higher at all temperatures, but the amount of radiation is still negligible compared to conduction.

The conclusion drawn from these modeling exercises is that as long as the surroundings are kept at a temperature near the reservoir temperature and the area of the sample is kept small (less than about 15 mm^2), the amount of radiation heat transferred from the sample to its surroundings will be negligible compared to the amount of heat conducted through the thermocouple from the sample to the constant temperature reservoir. A calorimeter that will be using a sweep method should be designed so that the temperature of the surroundings is kept near the reservoir temperature.

Gas Conduction Heat Transfer: Another way heat could leak from the sample to its surroundings is through gas conduction. If the sample's temperature is much higher than the temperature of the surroundings and there any are gas molecules inside the calorimeter chamber, gas conduction heat transfer might be a problem. Ideally, a perfect

vacuum would exist inside the calorimeter, thus there could be no gas conduction; however, a "perfect" vacuum is not possible, and the limiting pressure that would assure that gas conduction would be negligible compared to the conduction heat transferred through the thermocouple must be determined.

The governing equation for this process [22] is

$$Q = A \cdot K \cdot a_0 \cdot P \cdot (T_{surroundings} - T_{sample}), \qquad (11)$$

where A = area of sample;

K = a constant that depends on the gas (2.1 for helium, 1.2 for air);

a_0 = a constant ranging from 0 to 1 depending on the material of the sample and surroundings; typically $a_0 \cong 0.5$;

P = pressure of gas inside vessel;

$T_{surroundings}$ = surroundings temperature;

T_{sample} = sample temperature.

Calculations show that when the reservoir and surroundings temperatures are at 4.2 K and the pressure inside the chamber is 10^{-4} torr, gas conduction would be less than 1% of the conduction heat transfer through the thermocouple when the sample temperature is between 45 to 100 K, less than 5% when the sample temperature is between 10 and 45 K, and less than 10% when the sample temperature is between 5 and 10 K. Below 5 K, the heat transferred by gas conduction could be as high as 15% of the heat transferred by conduction through the thermocouple. When the reservoir and surroundings temperature are raised to any value above 10 K, the heat transferred by gas conduction is less than 2% of the heat transferred by conduction over the entire temperature decay.

This analysis has shown that when the sample is within about 0.5 K of the reservoir temperature, the heat transferred from the sample by conduction through the thermocouple is so small that gas conduction could be a problem, and thus any data taken near the end of a temperature decay should be discarded.

As long as the vacuum is very low, therefore, heat transferred by gas conduction would be negligible compared to the amount of heat transferred by conduction through the thermocouple. Two possible ways of achieving an extremely low vacuum are the use of a diffusion pump and cryopumping; cryopumping occurs when gas molecules collide with the walls of a chamber that is at cryogenic temperatures and condense onto the walls. Because the system must be flushed with helium gas to cool it down quickly (this is explained in more detail later), the use of a diffusion pump is necessary to initially evacuate the system (a mechanical pump alone is ineffective in pumping out helium).

Given that the outer can is immersed in the 4.2 K helium bath, cryopumping will always occur, thus assuring an extremely low vacuum inside the calorimeter chamber. Assuming the system can be pumped down to a pressure of 10^{-4} torr at room temperature, cryopumping should produce a vacuum on the order of 10^{-5} torr.

Decay Time: An estimate of the time it would take for a sample to decay from an initial temperature to the reservoir temperature was determined from the average decay rate over the entire temperature range. According to the model's calculations, it would take around 85 seconds for a 1 mg copper sample to decay from 100 to 4 K. This does not include the addenda heat capacity, which would tend to increase the decay time .

The model predicts that for any given sweep, the temperature of the sample would decay very rapidly at first and then slow down as the sample temperature approaches the reservoir temperature. The decay rate for a 1 mg copper sample would range from 3 K/s at higher temperatures to around 0.5 K/s at temperatures near the reservoir temperature; the maximum decay rate depends mostly on the upper temperature limit of the sweep.

2.2 APPARATUS DESIGN

Figure 9 shows the design of the apparatus. For the most part, Figure 9 is drawn to scale. The basic idea of the design is as follows: the sample is bonded with grease to the tip of a thermocouple that is attached to the top of a copper block, which acts as the constant temperature reservoir. A single strand fiber optic wire is used to transport light energy from a laser (outside the cryostat) to the sample, while the thermocouple is used both to measure the sample's temperature and conduct heat from the sample to the copper block. The most important design criterion is that all heat transfer from the sample must be through the thermocouple to the copper block. Another important consideration is to keep the mass as small as possible, as will be discussed later.

The 3/8 inch thick, 1 inch diameter copper block is supported by a 3/8 inch diameter, hollow copper support. A copper can, modeled as a box around the block in Figure 9, encloses the block and is easy to mount and dismount. This can acts as a radiation shield between the sample and its surroundings and is in good thermal contact with the copper block so that its temperature is always close to that of the block; this assures that the amount of heat radiated from the sample to its surroundings remains much smaller than the heat conducted through the thermocouple.

The copper post screws into a G-10 plastic rod which in turn screws into an upper

Figure 9: Calorimeter Design

Key:

● stainless steel

● copper

G-10 plastic

heater wire

fiber optic

thermometer
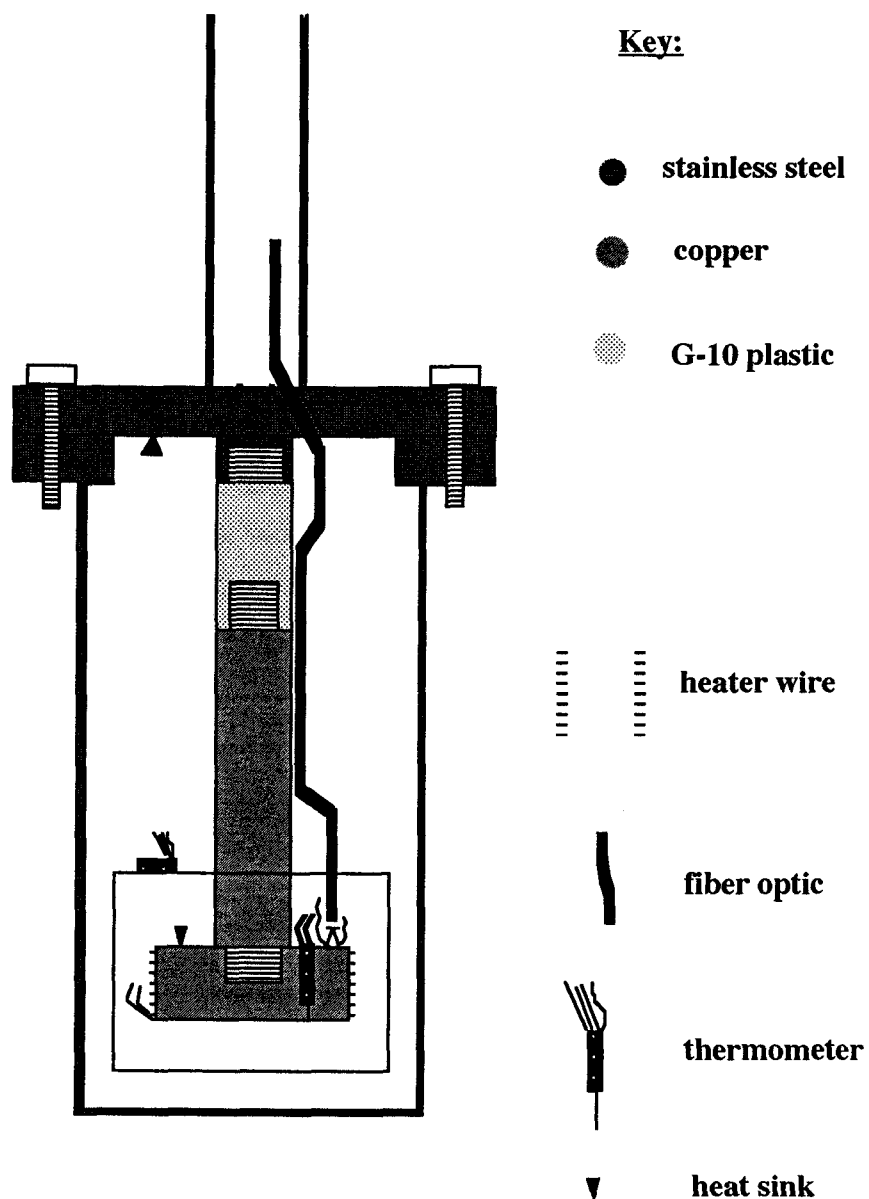
▼ heat sink

stainless steel flange. On the top of the copper block are three heat sinks that thermally anchor the thermometer and thermocouple leads to the copper block. The heat sinks consist of small copper posts around which lead wires are wrapped; a small amount of epoxy is applied to assure good thermal contact. Along with a heater wrapped around the circumference of the copper block, a silicon diode temperature sensor on top of the block regulates the temperature of the block.

The fiber optic is heat sunk to the copper support by clamping it snugly to the support as it enters this inner chamber. A small copper piece clamped around the copper support rod holds the bottom of the fiber optic so that it is centered on the sample. These intricate pieces are not shown in Figure 9.

A stainless steel outer can holds a vacuum and serves as the boundary between the experiment and the liquid helium. The top of the can consists of a stainless steel flange, and once everything inside is set up, vacuum grease is spread evenly over the top surface of the flange and it is bolted to an upper stainless steel flange. This vacuum seal is easy to use and has been found to be effective. The upper flange has passageways for all lead wires and the fiber optic. Seven copper heat sinks are attached to the bottom side of the upper flange to thermally anchor all lead wires to the stainless steel can, which is immersed in liquid helium. The fiber optic also is thermally anchored here with a support that screws into the upper flange and clamps the fiber optic as it enters the chamber.

A 0.5 inch outer diameter stainless steel tube is welded to the upper flange. This tube serves three purposes: it supports the entire experiment, it acts as a passageway for all lead wires and the fiber optic to exit the cryostat, and it connects the vacuum pump to the apparatus. At the top end of this tube is a lead wire vacuum-tight feed-through, fiber optic vacuum-tight feed-through, a pressure relief valve, an ionization pressure gauge, and a valve and tube connecting the apparatus to a vacuum pumping station.

2.3 THERMAL ANALYSIS

A thermal analysis was performed on the system to determine how much power would be required by the block heater, the rate of liquid helium boil-off during a calorimetry experiment, how long it would take to cool the entire apparatus down to 4.2 K from room temperature, and the amount of liquid helium that would evaporate when the apparatus is cooled down to 4.2 K. A successful calorimeter design would include a combination of a low helium boil-off rate, a fast cool down time, and a low thermal mass. Using a spreadsheet, the dimensions and material properties of the inner components of the calorimeter were varied to determine the best design.

The magnitude of the power required by the heater and the rate of liquid helium boil-off are directly related to the size of the thermal link connecting the inner components of the calorimeter to the stainless steel can, which is immersed in liquid helium. This thermal link consists of conduction heat transfer through all of the electrical lead wires (0.005 inch diameter, formvar insulated copper) running from the inner components to the bottom of the upper flange, and conduction through the rod connecting the inner components to the upper flange; also, radiation from the radiation shield to the stainless steel outer can serves as a small heat flow path. The amount of helium boil-off also depends on the thermal link connecting the upper flange to room temperature, which consists primarily of conduction through the lead wires and stainless steel support tube.

The rate of liquid helium boil-off is determined from the equation

$$\dot{V} = \frac{\dot{Q}}{L},\qquad(12)$$

where $\dot{V}$ = rate of boil-off;

$\dot{Q}$ = heat transfer rate to the helium;

L = latent heat of vaporization of helium.

The maximum rate of helium boil-off would occur when the inner components are near the upper end of the temperature interval, around 100 K. To minimize the amount of helium boiled off during an experiment, a weak thermal link between the inner components and the liquid helium is desired. Three materials were considered for this part: G-10 plastic, stainless steel, and brass. If brass were used, over 15 W of heat would be transferred to the helium when the inner components are at the higher temperatures, corresponding to a rate of helium boil-off of around 18 L/hour. With a stainless steel rod, the heat transferred to the helium would be around 3 W, corresponding to a boil off of 3 L/hr. The best material for the rod is G-10 plastic, which has a very low thermal conductivity. With a G-10 rod, most of the heat would have to escape from the inner components through the lead wires; at most, 0.4 W would be transferred to the helium, corresponding to about 0.4 L/hr.

The outer stainless steel can is immersed directly in the cryogen bath and would cool down fairly quickly; however the inner components of the calorimeter are connected to the cryogen by a weak thermal link and therefore would take longer to cool down. To determine how fast the inner components cool down to 4.2 K, the mass of the inner components was lumped together and an average value of heat capacity between room temperature and 4.2 K was estimated. The amount of time it would take to cool down the

inner components of the apparatus is derived from equation (8) and is approximated by the following equation:

$$t = \frac{C_p}{k}\ln\left(\frac{T_f - T_b}{T_i - T_b}\right) \tag{13}$$

where t = time required to cool down inner components to 4.2 K;

C_p = average heat capacity of inner components;

k = average thermal conductance of thermal link connecting inner components to cryogen;

T_f = final temperature, 4.2 K;

T_i = initial temperature, 300 K;

T_b = cryogen temperature, either 77 K for liquid nitrogen or 4.2 K for liquid helium.

Calculations show that if the system is evacuated before cooling, the inner components would take over 30 hours to cool down to 4.2 K. Changing the support rod material from G-10 to brass or stainless steel would cut this time down to less than 30 minutes, but as discussed earlier, a strong thermal link between the inner components and the liquid helium would cause a high helium boil-off rate and is therefore undesirable.

A common method for cooling down an apparatus quickly is to use an exchange gas, such as helium. By flushing the system with a small amount of helium, the thermal link between the inner components and the stainless steel can is greatly increased due to convection heat transfer between the inner walls of the stainless steel can and the inner components. Once the system is cooled to 4.2 K, the helium can be pumped out fairly quickly with a diffusion pump.

An important consideration to the design of any apparatus that will be used in liquid helium is the total thermal mass of apparatus; helium has a very low latent heat of vaporization, and a large thermal mass would tend to evaporate a large amount of helium. It is therefore desirable to keep the total mass of the apparatus as low as possible.

To determine the initial amount of helium boil off, the average heat capacity of the calorimeter components between 77 and 4.2 K (the apparatus is precooled to 77 K in liquid nitrogen, which has a high latent heat of vaporization) was estimated to determine how much energy must be removed from the apparatus. This value was then divided by the latent heat of vaporization for helium to determine the amount of helium required to cool down the apparatus. Calculations show that only about 0.83 L of helium would be required to cool the apparatus down to 4.2 K, assuming the apparatus is immediately submerged in the liquid helium. A common technique used to lower any apparatus into

liquid helium is to lower it slowly so that the system is first cooled by the helium vapors rising from the boiling helium, thus allowing the cool vapors to absorb as much heat as possible from the system before it is submerged in the liquid. This would tend to decrease the initial helium boil-off.

2.4 MEASUREMENT TECHNIQUE

A sweep method is used to measure heat capacity between 4.2 and 100 K; the sample can ideally be heated to 100 K (or any desired upper temperature limit) while the constant temperature block remains at 4.2 K. When the heater power is turned off, the sample's temperature decays from 100 to 4.2 K as heat flows from the sample to the constant temperature reservoir through the thermal link (the thermocouple). Because the decay rate would be much higher at lower block temperatures, the interval can be broken up into smaller increments, which would allow for more reasonable sampling rates over the entire temperature range from 4.2 to 100 K. The governing equation for this process is

$$Q_{in} - Q_{out} = Q_{stored}. \tag{14}$$

Once the laser is turned off and the temperature decay of the sample begins, Q_{in} is zero and Q_{out} is the heat conduction from the sample to the copper block through the thermocouple. Equation (14) becomes:

$$-Q_{conduction} = C\frac{dT_s}{dt}, \tag{15}$$

$$\frac{A}{L}\int_{T_s}^{T_b}\kappa dT = C\frac{dT_s}{dt}, \tag{16}$$

where C = heat capacity of sample and addenda;

T_s = sample temperature;

A = cross sectional area of thermocouple;

L = length of thermocouple;

$\frac{A}{L}\kappa$ = thermal conductance of thermocouple;

κ = thermal conductivity of thermocouple;

t = time;

T_b = block temperature.

By measuring the thermal conductance of the thermocouple and addenda contribution in a separate experiment, the sample's heat capacity can be determined from the slope of the sample's temperature decay curve. The decay can be measured several times to improve the signal to noise ratio.

The thermal conductance between the sample and the constant temperature bath must be determined before performing a calorimetry experiment. The most common method [8] of determining this thermal conductance is to put a known amount of heat into the sample thermometer, measure the temperature rise, and calculate the conductance using the equation

$$k = \kappa \frac{A}{L} = \frac{P}{\Delta T} , \tag{17}$$

where k = thermal conductance between thermometer and bath (W/K);

P = heat input into sample (W);

ΔT = temperature difference between thermometer and bath (K); it is assumed that ΔT is small enough (less than 0.1 K) so that k is constant within ΔT.

With a bolometer type of calorimeter, this is an easy measurement to make. The bolometer has a resistive heater built into it, and it is easy to determine the exact amount of heat entering the sample. Problems arise if this method is used with a thermocouple type of calorimeter, however. The major problem is that the tip of the thermocouple is so much smaller than the heater bonded to it that most of the heat produced by the heater is either radiated to the surroundings or escapes through the heater lead wires instead of entering the thermocouple. It is also difficult to bond a heater to the end of a thermocouple. Because knowledge of the exact amount of heat entering the thermocouple is essential to determine the thermal conductance, this method for calibration may not work with the present design.

An alternative way of determining the thermal conductance between the sample and constant temperature bath is to use a calibrated sample, for example a high purity copper sample, of known heat capacity. The copper is bonded to the end of the thermocouple with grease, just like any other sample, and the calorimetry is done with this sample. In a normal calorimetry experiment, the sample's heat capacity is unknown while the thermal conductance, and thus $Q_{conduction}$, is known. Now, however, the sample's heat capacity is known and it is the thermal conductance that must be calculated from equation (16). Once $Q_{conduction}$ is determined, it can be differentiated with respect to temperature and divided by A/L to determine the thermal conductivity of the thermocouple at any desired temperature.

For this method to work, the heat capacity of the calibration sample must be known accurately at all temperatures throughout the desired temperature range. Copper is a common reference material for low-temperature calorimetry experiments, and its heat capacity is known to within 1% from 0.3 to 100 K [23].

One advantage of using this method is that all temperature dependent parasitic heat leaks, defined as Q_p and including any heat leak from the sample besides conduction through the thermocouple (such as gas conduction), will cancel out of the final results:

$$\text{calibration:} \qquad -Q_{conduction} + Q_p = C_{Cu}\frac{dT_{Cu}}{dt}, \qquad (18)$$

$$\text{actual experiment:} \qquad -Q_{conduction} + Q_p = C_s\frac{dT_s}{dt}. \qquad (19)$$

Subtracting equation (19) from equation (18),

$$0 = C_{Cu}\frac{dT_{Cu}}{dt} - C_s\frac{dT_s}{dt}, \qquad (20)$$

$$C_s = C_{Cu}\left[\frac{dT_{Cu}}{dt}\right] \div \left[\frac{dT_s}{dt}\right]. \qquad (21)$$

Equation (21) assumes that the parasitic heat loss is the same during a calibration experiment as during an actual calorimetry experiment. Parasitic heat leaks that depend on sample dimensions or properties such as emissivity would not be subtracted out unless the sample has the same dimensions and/or properties as the copper sample used in the calibration experiment.

The addenda heat capacity can be determined along with the thermal conductance of the thermocouple by heating the thermocouple with a small amount of grease on the tip to 100 K and performing the calorimetry experiment. The equation for this process is

$$-Q_{conduction} = C_{addenda}\left[\frac{dT_{addenda}}{dt}\right]. \qquad (22)$$

By using equation (22) along with equation (18) and ignoring Q_p, both the addenda heat capacity and the conductance of the thermal link can be determined.

Due to the small area of the tip of the thermocouple, it may not be possible to heat a bare thermocouple with an optical heating method. If this is the case, the addenda heat capacity and thermal conductance of the thermal link can be determined by performing the calorimetry using two masses of the high purity copper sample. For example, if two

experiments are done, one with a 1.0 mg sample and one with a 1.5 mg sample, the addenda could be determined as follows:

1 mg sample:
$$(1C_{Cu} + C_{add})\frac{dT_1}{dt} = -Q_{conduction}, \tag{23}$$

$$C_{add} = \frac{-Q_{conduction}}{\dfrac{dT_1}{dt}} - 1C_{Cu}, \tag{24}$$

1.5 mg sample:
$$C_{add} = \frac{-Q_{conduction}}{\dfrac{dT_{1.5}}{dt}} - 1.5C_{Cu}. \tag{25}$$

Combining equations (24) and (25),

$$Q_{conduction} = 0.5C_{Cu} \div \left(1 \Big/ \frac{dT_1}{dt} - 1 \Big/ \frac{dT_{1.5}}{dt} \right). \tag{26}$$

The addenda heat capacity can now be solved by plugging $Q_{conduction}$ into equation (24):

$$C_{add} = C_{Cu} \left[0.5 \div \left(1 - \frac{dT_1/dt}{dT_{1.5}/dt} \right) + 1 \right]. \tag{27}$$

Chapter 3   CALORIMETER PERFORMANCE

3.1 THERMOCOUPLE CALIBRATION

The temperature of the sample is assumed to be the same as the tip of the thermocouple, and the temperature of the copper block is assumed to be the same as the base of the thermocouple. The sample temperature, therefore, can be determined by measuring the block temperature and the voltage difference between the two legs of the thermocouple at the base, where they are thermally anchored to the copper block.

For a given thermocouple, this voltage depends only on the difference between the thermocouple's base and tip temperature. If the temperature of the base is 0 K and the tip is at a temperature T_1, a voltage V_1 would be produced across the thermocouple; if the temperature of the base is 0 K and the tip was at a temperature T_2, a voltage V_2 would be produced across the thermocouple. Now, if the base is at T_1 and the tip is at T_2, the voltage across the thermocouple would be V_2-V_1.

The voltage vs. temperature (V vs. T) characteristics of the thermocouple must be known if the raw voltage is to be converted to temperature. Standard tables of voltage as a function of temperature (V vs. T) and sensitivity as a function of temperature (dV/dT vs. T) were produced by Sparks and Powell at cryogenic temperatures for various thermocouple materials [24]. Figures 10 and 11 show the standard V vs. T and dV/dT vs. T curves for a type E thermocouple.

Although the V vs. T curve should be the same for all thermocouples of the same type, it can actually vary slightly from one thermocouple to the next. This would normally occur only if the thermocouple was made using different spools of wire for a given leg; for example, if one chromel-constantan thermocouple was made using chromel wire from one spool and another chromel-constantan thermocouple was made using chromel wire from a different spool, the V vs. T curves of the two thermocouples may be slightly different, especially if the two spools of chromel were purchased from different companies. This is due to very small differences in the alloying content of the metals that make up the legs of the thermocouples.

Ideally, the materials would have the exact same chemical composition, regardless of where they are produced; in reality, though, the composition of two samples of supposedly the exact same material may be slightly different. This difference affects the V vs. T characteristics of the material [25]. The difference between the actual V vs. T curve of a type E thermocouple and the standard data can range from 0 to 40 μV, which corresponds to temperatures ranging from anywhere between 0 to 3 K. The difference is

Figure 10: Voltage vs. Temperature

Standard data for a type E thermocouple [24]

(Base Temperature = 0 K)
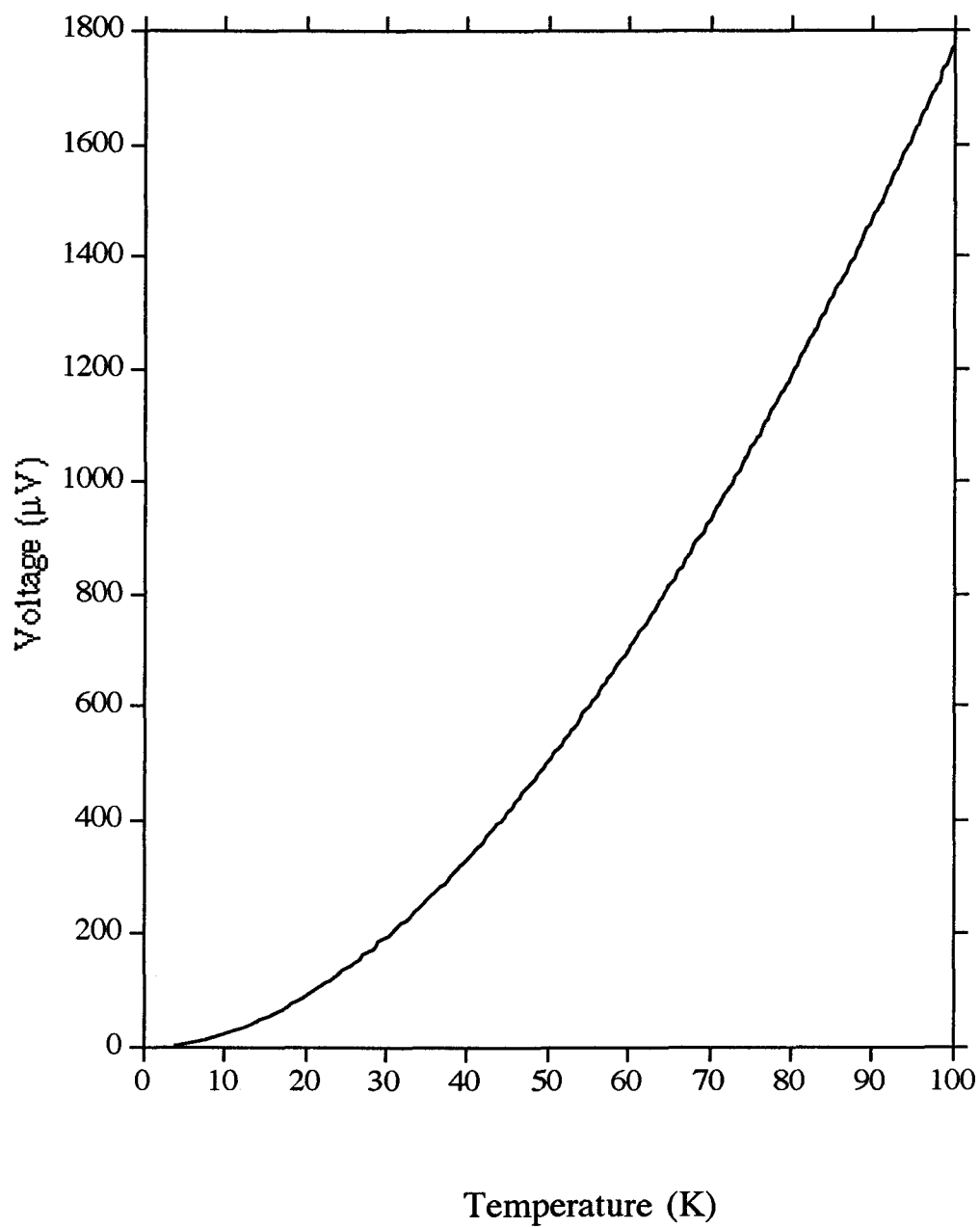
Temperature (K)

Figure 11: Sensitivity vs. Temperature

Standard data for a type E thermocouple [24]
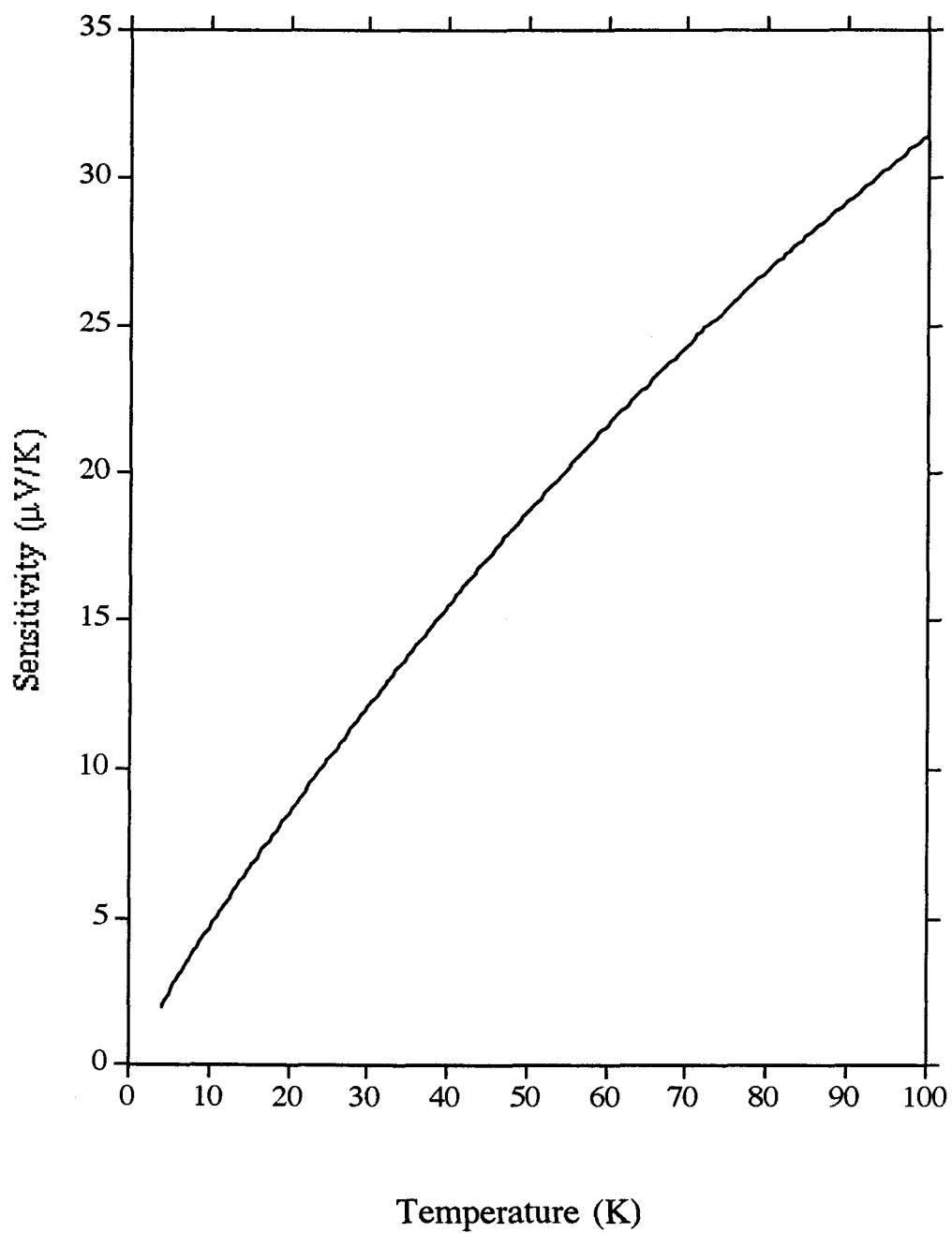
typically small at lower temperatures and a function of temperature, usually linear; both chromel and constantan contain about average inhomogeinities, making the type E thermocouple voltage-temperature characteristics very reproducible [25].

The voltage output at only a few base-tip temperature combinations, therefore, is usually sufficient to determine the thermocouple's actual V vs. T characteristics. Once the relationship between a thermocouple's actual voltage output at a certain temperature and the voltage output predicted by the standard data are determined, it can be applied to the entire standard data curve. The standard data can therefore be adjusted to represent the actual characteristics of a certain thermocouple. The new V vs. T curve would be good for all thermocouples made from the wire spools used to make the calibrated thermocouple.

An easy way to determine if the standard data accurately represent the thermocouple used for the calorimeter is to heat sink the tip of the thermocouple to the upper flange, which is in contact with the cryogen and thus held at either 4.2 K or 77 K, depending on the cryogen. The block temperature can then be adjusted, thus creating a known temperature difference across the thermocouple, and the voltage output by the thermocouple can be measured. The thermocouple voltage can be compared to the voltage predicted by the standard data for a type E thermocouple and the standard data can be adjusted accordingly to represent the actual V vs. T characteristics of a given thermocouple.

A simple experiment was performed to determine if a correction to the standard V vs. T data for a type E thermocouple would be necessary. A long thermocouple (about 6 cm) was made and the end was epoxied to a copper heat sink. The heat sink was then screwed into the upper flange and the two legs of the thermocouple were soldered onto a soldering terminal on the copper block. A thermometer was placed near the heat sink that the thermocouple tip was bonded to and held in place with Apiezon N grease.

The calorimeter was then placed in liquid nitrogen and the inner components were allowed to cool to 77 K. The block temperature was raised to various temperatures between 80 and 130 K and the voltage produced at each base-tip combination was measured.

Figure 12 shows a plot of the voltage produced by the thermocouple as a function of the temperature at the base of the thermocouple. Both the actual base temperature and the base temperature that would be predicted from measured voltage using the standard data are shown. The temperature of the tip was kept constant at about 78 K. The difference between the actual base temperature and the predicted value is negligible when the base of the thermocouple is within a few degrees of the tip and still extremely small

Figure 12: Thermocouple Voltage vs. Temperature

(Tip Temperature = 80 K)
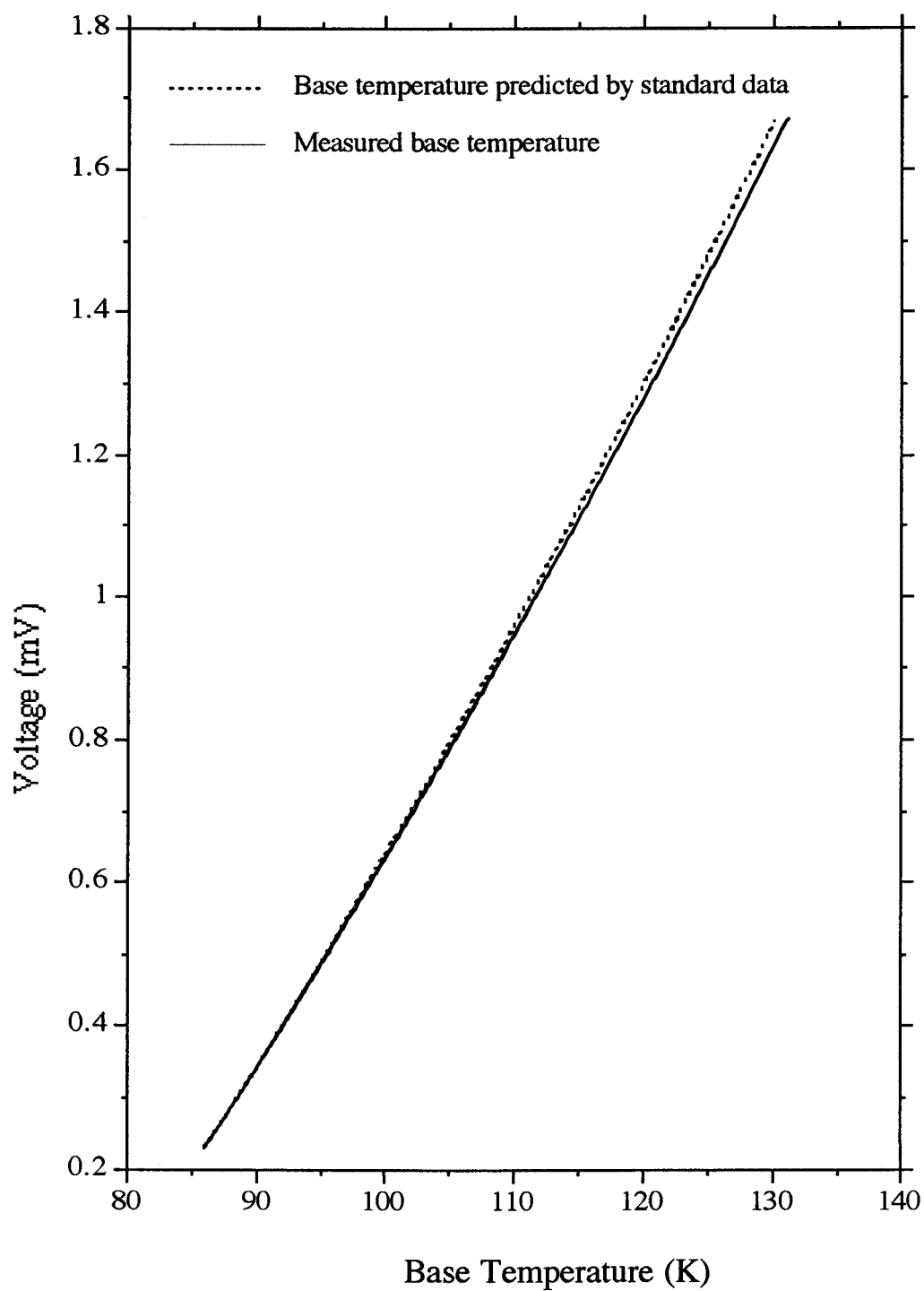
when the base is within 20 K of the tip. Only when the difference between the base and the tip of the thermocouple is large (greater than 30 K) does the measured temperature vary noticeably from the predicted temperature.

The variation between the measured base temperature and the predicted temperature is less than 0.1 mK when the base is within 30 K of the tip temperature and as high as 1 K when the base is 52 K above the tip temperature. As long as the difference between the base and tip temperature is within about 20 K, any variation between the thermocouple's actual V vs. T characteristics and the standard V vs. T characteristics of a type E thermocouple can be neglected.

As explained earlier, the variation between a thermocouple's actual V vs. T characteristics and the standard data increases with temperature; thus, even though this experiment was performed at high temperatures (above 70 K), the results should be valid for all temperatures below 70 K, where the variation between actual and predicted results should decrease.

This analysis leads to the conclusion that temperature sweeps should be limited to starting sample temperatures within about 20 K of the reservoir temperature if the standard data are to be used to convert the thermocouple voltage to a temperature. This is not a severely limiting factor; as will be discussed later, this is about the maximum temperature rise possible with the laser and fiber optic system used in the calorimeter.

3.2 DATA ACQUISITION AND MANIPULATION

Three parameters must be measured during a calorimetry experiment: sample mass, block temperature, and the voltage output by the thermocouple as a function of time. It is also useful to measure the temperature of the radiation shield enclosing the sample and copper block, as well as the pressure inside the calorimeter.

The mass of the sample is determined with a Mettler H30 mass balance, which has a resolution of 0.1 mg. The temperature of the block is measured by a LakeShore DT-470-SD-11 silicon diode temperature sensor, while the temperature of the radiation shield is measured by a Scientific Instruments Si410B silicon diode temperature sensor; both thermometers are read by a LakeShore DRC-93CA temperature controller. The pressure is measured by a Varian model 843 vacuum ionization gauge. The thermocouple voltage is read by a Keithley model 182 Sensitive Digital Voltmeter, which has a resolution of 1 nV, amplified with a gain of 10,000, and read as a function of time by a Tektronix TestLab 2505 data acquisition and analysis instrument, where it is stored on the instrument's hard drive for later analysis.

After the experiment is over, the collected data are sent to a Macintosh Quadra 700 personal computer and analyzed with LabVIEW software. Figure 13 shows a flow chart of the data reduction process. Once the desired base temperature is chosen, the sample is heated to some initial temperature and then allowed to cool. The raw thermocouple voltage is read by the Sensitive Digital Voltmeter and amplified. The amplified signal is sent to the TestLab 2505, which records the voltage as a function of time, smoothes the curve using a simple method of averaging nine data points at a time, and stores the curve. Once the desired number of decays have been recorded, the entire experiment is saved on the hard drive of the TestLab 2505.

The data are sent to LabVIEW, which uses the following subroutines to convert the Voltage vs. Time (V vs. t) data to Heat Capacity vs. Temperature (C_p vs. T) data:

Thermocouple Reader: This routine converts the V vs. t array to a Temperature vs. Time (T vs. t) array, taking into account any amplification and offset of the original signal. The standard data [24] are represented by a 13th order polynomial:

$$V(T) = \sum_{i=1}^{13} a_i T^i, \tag{28}$$

where V = voltage across the two legs of the thermocouple, μV;

T = temperature at the tip of the thermocouple, K;

a = polynomial coefficient.

Equation (28) is only valid if the base temperature is 0 K, so the actual voltage across a given thermocouple is described by

$$V_{actual} = V(T_{tip}) - V(T_b), \tag{29}$$

where V_{actual} = the actual voltage across the thermocouple;

T_{tip} = temperature of the tip of the thermocouple;

T_b = temperature at the base of the thermocouple.

T_b is measured, and $V(T_b)$ can be determined from equation (28) and added to V_{actual} to determine $V(T_{tip})$:

$$V(T_{tip}) = V_{actual} + V(T_b). \tag{30}$$

Because few data on temperature as a function of voltage are available, a Newton-Raphson iteration technique is used to solve for T_{tip} when $V(T_{tip})$ is input. By

Figure 13: Data Reduction Process

thermocouple voltage

182 Sensitive Digital Voltmeter

amplified thermocouple signal

TestLab 2505

1. Acquire data	2. Smooth Curve	3. store curve	4. Repeat 1-3 until desired number of curves have been acquired
V ... t	V ... t	curve #: 1 | 2 | 3...	5. Send curves to LabVIEW

DRC-93CA Temperature Controller

T_b

Voltage vs. Time data

LabVIEW

1. Place data into a 2-d array	2.Convert from V vs. t to T vs. t array	3. Calculate dT/dt	4.Call up thermal conductance and $C_{p\text{-addenda}}$ data
index | V | t \\ 1 \\ 2 \\ 3 \\ ⋮	index | T | t \\ 1 \\ 2 \\ 3 \\ ⋮	smooth/ derivative	

5. Calculate thermal conductance	6.Calculate sample heat capacity and plot against temperature (√=known, o=unknown)
T— determine \\ Tb— conductance —Qcond	$\sqrt{}\quad\sqrt{}\ o \qquad \sqrt{}\ \sqrt{} \qquad \sqrt{}\ \sqrt{} \qquad \sqrt{}$ \\ dT/dt[(mCp)sample+(mCp)grease+(mCp)t.c.]=Qcond

inputting the voltage read across the thermocouple and the base temperature into the subroutine, the tip temperature of the thermocouple, and thus the sample temperature, is determined. This routine does not consider any special calibration correction factor for a specific type E thermocouple, but this can easily be added to the routine if necessary.

Smooth/Derivative: This subroutine inputs a T vs. t array and smoothes out any random noise before differentiating the curve represented by the data. It takes a few points from the array at a time (the number of points specified by the user) and curve fits them with a polynomial whose order also is specified by the user. The derivative of the polynomial is then computed and a new array of T vs. dT/dt is created.

After this new array is created, the main program is ready to compute the sample's heat capacity as a function of temperature. The program loops from the base temperature to the initial sample temperature in steps specified by the user (for instance every 0.5 K), and calculates the sample's heat capacity, $C_{p-sample}$, at each step. The next subroutines are accessed at each temperature step.

Determine Conductance: This subroutine inputs the sample temperature and block temperature and calls up a two dimensional array containing the thermal conductivity of the thermocouple as a function of temperature, an array representing a smooth curve that was obtained during a calibration experiment. The amount of heat conducted from the sample to the copper block, Q_{cond}, is given by

$$Q_{cond} = \frac{A}{L} \int_{T_b}^{T_s} \kappa dT, \tag{31}$$

where T_s = sample temperature;

T_b = block temperature;

κ = thermal conductivity of thermocouple.

Because the κ vs. T array contains data from 0 to 100 K, the portion from T_b to T_s is removed and placed into a subarray. A simple trapezoid rule numerical integration method is then used to determine Q_{cond}. As long as the κ vs. T array contains many closely spaced data points (every 0.1 K), this simple integration method is accurate.

Addenda Heat Capacity The addenda heat capacity, which consists of the heat capacity of the thermocouple and a small amount of Apiezon N grease on the tip of the thermocouple, is measured in a separate experiment and the data are stored in a two

dimensional array of addenda heat capacity vs. temperature. The mass of the sample, measured at the beginning of the experiment, is input by the user. Now all of the necessary parameters in step 6 of Figure 13 are known, and $C_{p\text{-sample}}$ can be determined.

The procedure outlined in Figure 13 has many advantages. The major advantage is that all raw data are stored in a file on the hard drive of the TestLab 2505; each experiment takes up roughly 0.6 Mbytes of memory, and the hard drive can store up to 80 Mbytes, or about 130 experiments. Old files can be copied onto floppy disks, and erased from the hard drive if so desired.

Not only are the raw data stored, but the entire configuration of the instrument is stored as well, including input voltage range, offset, trigger level, etc. Also, the user can enter notes under each curve recorded. This is a convenient place to enter parameters such as the pressure inside the calorimeter, copper block temperature, temperature of the surroundings, amplifier gain, sample dimensions, and any other information about the conditions present when the curve was recorded. Some of this information may not seem relevant at the time of the experiment, but it may help if unexplainable results are obtained in future experiments.

It is also useful to store all raw data so that different data reduction schemes can be tried. For example, it may be that using the TestLab 2505's smoothing function and then smoothing the data further with LabVIEW would cause the true shape of the decay curve to become distorted, and only one smoothing technique is required. Future refinements in the data reduction procedure can easily be implemented on any data that were collected and stored on the hard drive of the TestLab 2505. This will be extremely useful for early calorimetry experiments, where different data manipulation techniques must be compared to see which leads to the best results.

3.3 CALORIMETRY PROCEDURE

A standard procedure has been devised for a typical calorimetry experiment and is outlined here. A video tape of the procedure has been made and can be obtained from Oregon State University. The sample is first weighed and then mounted to the tip of the thermocouple with Apiezon N grease. The radiation shield is mounted and a thermometer is secured to this shield with Teflon tape; after cleaning both the top and bottom flange of the stainless steel vacuum barrier with acetone, a thin layer of vacuum grease is spread over the top surface of the lower flange and the can is bolted tightly to the upper flange. Because acetone leaves a thin film behind, it may be wise to follow

with methanol in future experiments.

The apparatus is next pumped down to about 1 mtorr, flushed with helium gas, and then pumped out again. This is to assure any impurities are removed from the inside of the calorimeter before cooling it down to 4.2 K; because almost all gas molecules at room temperature, except for helium, would either freeze or condense out at 4.2 K, any molecule besides helium must be removed from the calorimeter. If, for instance, water vapor was present inside the calorimeter at room temperature and the apparatus was cooled down to 4.2 K, some water could possibly freeze onto the sample, thus altering the heat capacity measurement and ruining the experiment.

Once the inside of the calorimeter has been cleansed of any impurities, the calorimeter is placed in liquid nitrogen and again flushed with helium gas. The helium exchange gas helps to cool down the inner components quickly, as explained earlier; only about 30 minutes are required to cool down the inner components to 77 K.

The apparatus is next placed in liquid helium, where it is lowered slowly into the dewar to make use of the cooling power of the helium vapor. Once the temperature of the copper block reaches 4.2 K, the helium gas is pumped out so that the final pressure inside the calorimeter is below 10^{-4} torr.

The procedure used for the rest of the experiment consists of repeating the following steps: the temperature of the copper block is raised to a desired temperature and allowed to stabilize. The shutter on the laser is opened, allowing the sample to heat up to a starting temperature above the copper block. After the sample temperature has stabilized, the shutter is closed, allowing the sample to cool. As soon as the sample temperature begins to decrease, the TestLab 2505 data acquisition and analysis instrument is triggered and records the entire sample decay from its starting value to the block temperature.

The initial sample temperature is dependent on the power output by the laser, the emissivity of the sample, and the orientation in which the sample is mounted. The laser used is an Oriel model 79426 diode laser with a maximum output of 45 mW. Because of the simple way that the fiber optic is coupled to the laser (it is simply centered in a plug that screws into the housing at the front of the laser), most of the energy emitted from the laser never reaches the sample. This simple laser-fiber coupling scheme was chosen primarily for its simplicity; lenses would be needed to couple the laser energy into the fiber more effectively. The simple coupling method allows for easy fiber replacement as well as quick assembly.

For a 1 mg copper sample, the highest initial temperatures attainable are as follows: with a block temperature around 4.2 K, the sample could be heated to 25 K; with

a block temperature of 25 K and above, the sample could be heated roughly 10 to 15 K above the block temperature. The entire temperature interval from 4.2 to 100 K can ideally be covered with about six temperature sweeps. These initial sample temperatures are only attainable if the sample is mounted properly on the end of the thermocouple (i.e. the sample is mounted so that it intercepts as much optical power as possible from the fiber optic). In reality, however, it is sometimes difficult to mount the sample so that it is horizontally oriented and directly under the center of the fiber optic, and a temperature rise of only about 5 K is attainable at low temperatures and 2 K at higher temperatures.

One advantage to temperature sweeps limited to initial sample temperatures that are not too far above the block temperature is the fact that any deviation of the thermocouple V vs. T characteristics from the standard data can be neglected, as explained earlier.

3.4 DESIGN PERFORMANCE

The design of the calorimeter took into consideration three major factors. First, the temperature of the surroundings should be close to that of the constant temperature copper block in order to minimize the radiation heat transferred from the sample. Second, the pressure inside the calorimeter should be less than 10^{-4} torr to minimize the amount of heat transferred by gas conduction from the sample. Third, the thermal link between the copper block and the liquid helium should be small to minimize the rate of helium boil-off.

The temperature of the radiation shield has been found to follow that of the constant temperature block fairly well, especially if a small amount of grease is applied at the position the shield contacts the copper post (see Figure 9). The temperature of the shield is typically within 5 K of the block temperature, thus keeping to a minimum the heat transferred via radiation from the sample to its surroundings.

The pressure inside the calorimeter during an experiment is always less than 1×10^{-4} torr and normally is on the order of 5×10^{-5} torr. These pressures assure that the amount of heat transferred from the sample to its surroundings by gas conduction is small compared to the heat transferred by conduction through the thermocouple. The lowest pressure attainable with the diffusion pump and cryopumping is about 3×10^{-5} torr. Ideally, the pressure would be on the order of 10^{-6} torr, but any pressure below 10^{-4} torr is acceptable.

Finally, the rate of helium boil-off is exactly as predicted in section 2.3. When the block temperature is close to 100 K, the boil-off rate is about 0.5 L/hr. At lower

block temperatures, the boil-off rate is much smaller; during an entire experiment, which takes about three hours, the average boil-off rate is about 0.3 L/hr.

Originally, data were only attainable down to 7 K, because below 7 K, the block temperature was difficult to control. The block was heated slightly by the laser; for example, when the block started out at 4.2 K, the laser would heat it to 5 K. This occurred because the thermal link between the copper block and the liquid helium was so small, and it was difficult for the copper block to dump off any excess heat to the liquid helium if the temperature gradient between the block and the helium was too small.

The thermal link between the copper block and the liquid helium was therefore increased by attaching four 1 mm diameter copper wires to the copper block and one of the heat sinks on the upper flange. With a larger heat leak from the copper block, the radiation heat from the fiber optic to the copper block could be transported away from the block faster, thus allowing data to be taken at lower block temperatures. With the stronger thermal link, data can be obtained to about 5.5 K.

Another reason that data cannot be obtained down to 4.2 K is that during the data analysis procedure, the end of the temperature decay curve must be cut off, as explained in section 2.1.2. Typically, when the temperature of the sample reaches from 0.5 to 1 K above the block temperature, the data are no longer valid. This is possibly due to the fact that when the sample temperature is close to that of the block, the decay rate becomes extremely small, and the slope of the decay curve is too small to measure accurately.

If data are desired below 5.5 K, the boiling point of the liquid helium can easily be lowered from 4.2 K to about 2 K by lowering the pressure inside the helium dewar. The driving force for conduction through the lead wires on the block to the helium would be reasonable probably down to a block temperature of 4 K, thus allowing usable data down to about 4.5 or 5 K.

3.5 RESULTS

Early calorimetry experiments were carried out according to the following procedure: the mass of the sample was measured, a small amount of grease was placed on the sample, then the mass of the sample plus grease was measured. The heat capacity of Apiezon N grease is well documented [26, 27]; therefore by measuring the mass of the grease, the contribution of the grease to the total heat capacity can be determined. Because the mass of the thermocouple is only 0.35 mg, it contributes a negligible amount to the total measured heat capacity, and the total addenda heat capacity could be assumed to come from the grease alone.

The problem with this procedure was that the Mettler H30 mass balance has a resolution of 0.1 mg, and the amount of grease typically used is between 0.1 and 0.6 mg. If the mass of grease was determined to be 0.2 mg, for instance, its true mass could really lie anywhere between 0.1 and 0.3 mg. If the heat capacity of the grease is to be known accurately, its mass must be measured accurately (to within at least 1%), which is not possible with the Mettler H30 mass balance.

Figure 14 is a plot of the thermal mass of Apiezon N grease vs. temperature for various masses of grease between 0.1 and 0.7 mg. Also shown is the thermal mass of a 1 mg copper sample [23]. Because the heat capacity of Apiezon-N grease is fairly high and comparable to that of any sample with a mass on the order of 1 mg, an inaccurate determination of the mass of the grease would lead directly to an inaccurate determination of the sample's heat capacity; this will be discussed in more detail in the next section. If the grease had a heat capacity on the order of one tenth that of the sample, the sample heat capacity could possibly be determined with only a good approximation of the grease's heat capacity, but this is not the case.

Another way to determine the addenda heat capacity is to place a small amount of grease on the tip of the thermocouple, perform a calorimetry experiment, and then place the sample on the grease and repeat the experiment. The first experiment would output the addenda heat capacity, which can be subtracted from the total heat capacity (addenda plus sample) determined in the second experiment to determine the sample's heat capacity. This procedure has been found to work well. The only drawback is that two full experiments must be performed, rather than one, to determine a sample's heat capacity.

The next problem encountered involved the addenda contribution of the grease to the total heat capacity. As Figure 14 shows, Apiezon N grease has a fairly high heat capacity compared to that of copper (and in fact most metals), especially at low temperatures. The easiest way to mount a sample to the end of the thermocouple so that it is guaranteed to remain in place and intercept as much laser power as possible is to use a large amount of grease; roughly 0.5 mg of grease was found to hold 1mg copper sample in place well, but as Figure 14 shows, the thermal mass of 0.5 mg of grease is much higher than that of a 1 mg copper, sample especially below 40 K. The thermal mass (and therefore the heat capacity) of the grease would dominate the measurement, causing inaccurate measurements.

Two possible solutions to this problem are to use a larger sample or to use less grease. The problem with using a large sample is that more grease is required to hold it to the thermocouple, thus defeating the purpose of the larger size. Samples smaller than

Figure 14: Thermal Mass of Apiezon N Grease vs. Temperature
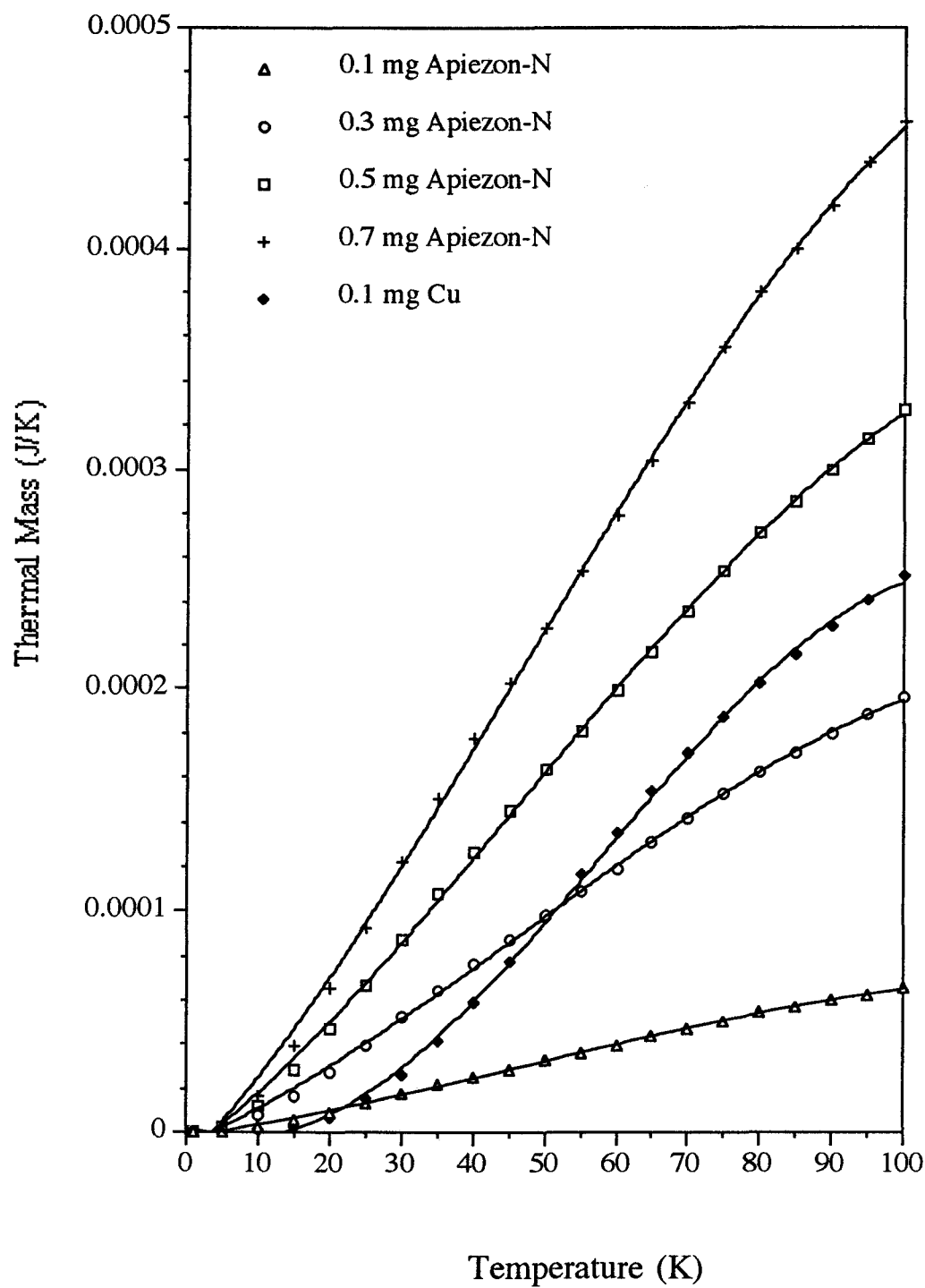
3 mg have been found to stay on the tip of the thermocouple with less than 0.5 mg of grease.

A problem with using less grease is that it is difficult to keep the sample in position if too little grease is used. Also, the thermal contact between the sample and the tip of the thermocouple can become poor if too little grease is used. This effect, explained earlier as a τ_2 effect, causes the temperature decay to be choppy and inaccurate; Figure 15 shows a typical decay curve, while Figure 16 shows one where there was probably poor thermal contact between the sample and the tip of the thermocouple. Experience shows that at least 0.1 mg of grease is required to hold a 1 mg size sample to the end of the thermocouple.
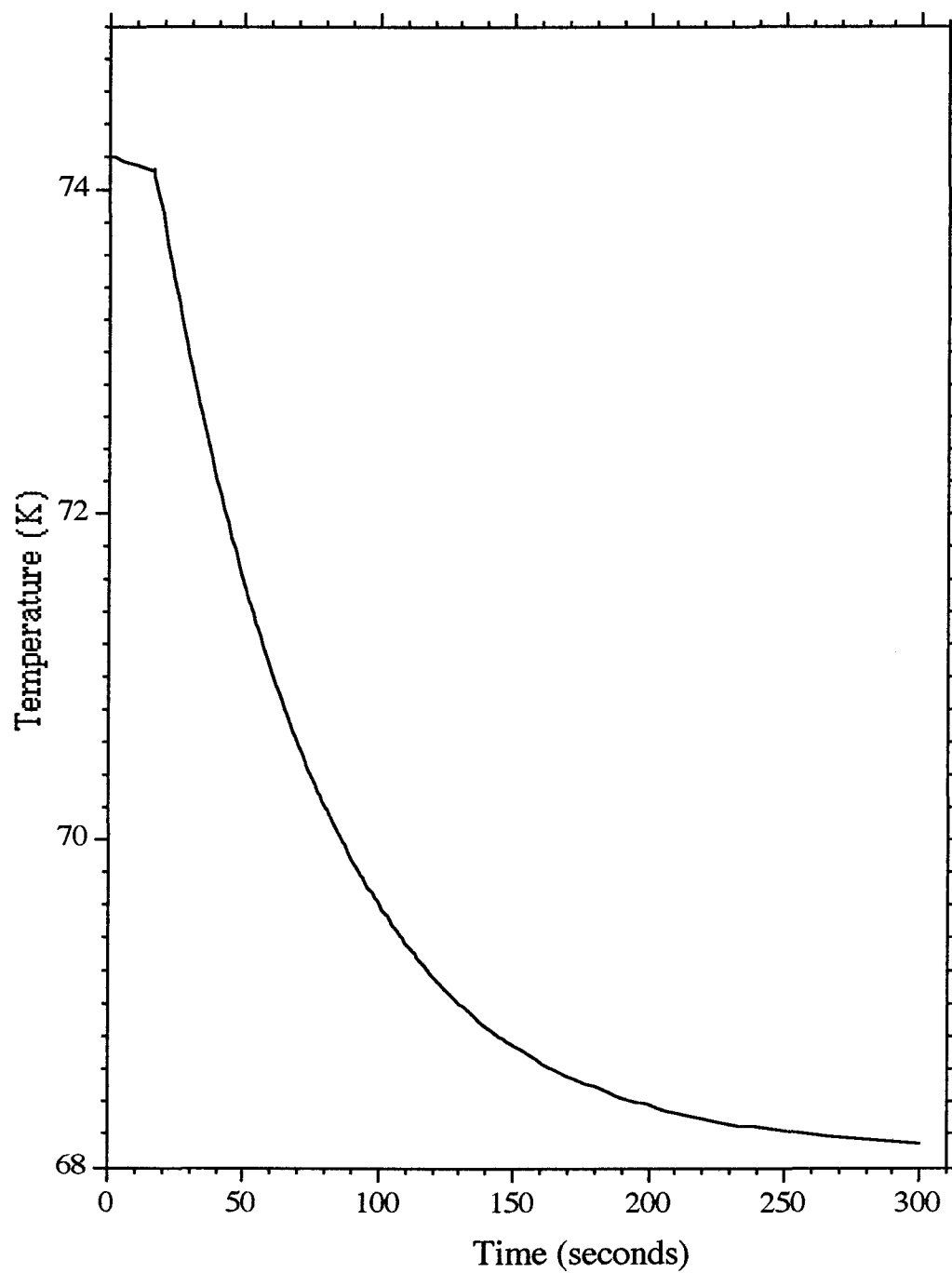
The thermal conductivity of the thermocouple was originally going to be determined with a copper sample, as explained in section 2.4. The reason for using copper was that it's heat capacity is known to within 1% below 100 K. Because the grease contribution to total heat capacity is comparable to that of a copper sample with a mass on the order of 1 mg, the uncertainty in the heat capacity of the grease becomes significant. This heat capacity is measured and can at best be determined to within a few percent. If the addenda can only be determined to within a few percent, then the thermal conductivity could at best be determined to within a few percent, even if the heat capacity of the copper was known to a few tenths of a percent. The addenda would in fact dictate the final accuracy of the thermal conductivity.

The best way to calibrate the thermal conductivity of the thermocouple would be to use a sample with as high of a heat capacity as possible; this would assure that the calibration is controlled by the sample's heat capacity and not the addenda heat capacity. The drawback to using a sample other than copper is that the sample's heat capacity will almost certainly not be known as accurately as that of copper.

A material with a heat capacity much higher than copper is indium; heat capacity data for indium are available from Touloukian [3]. A thermal conductivity calibration experiment was performed using a 2.4 mg indium sample. Figure 17 shows the thermal mass of the 2.4 mg indium sample as well as the addenda thermal mass. Also shown is the thermal mass of 0.5 mg of Apiezon N grease, which is only shown to get an idea of how much grease was being used. Because the addenda curve follows the curve of 0.5 mg of grease closely, it is a good guess that about 0.5 mg of grease was used.

As Figure 17 shows, the thermal mass of the indium far outweighs that of the addenda within the entire temperature interval between 6 and 100 K, which means that the accuracy of the thermal conductivity would be determined by that of the indium instead of the addenda. Figure 18 shows a plot of the thermal conductivity of the

Figure 15: Sample Temperature vs. Time
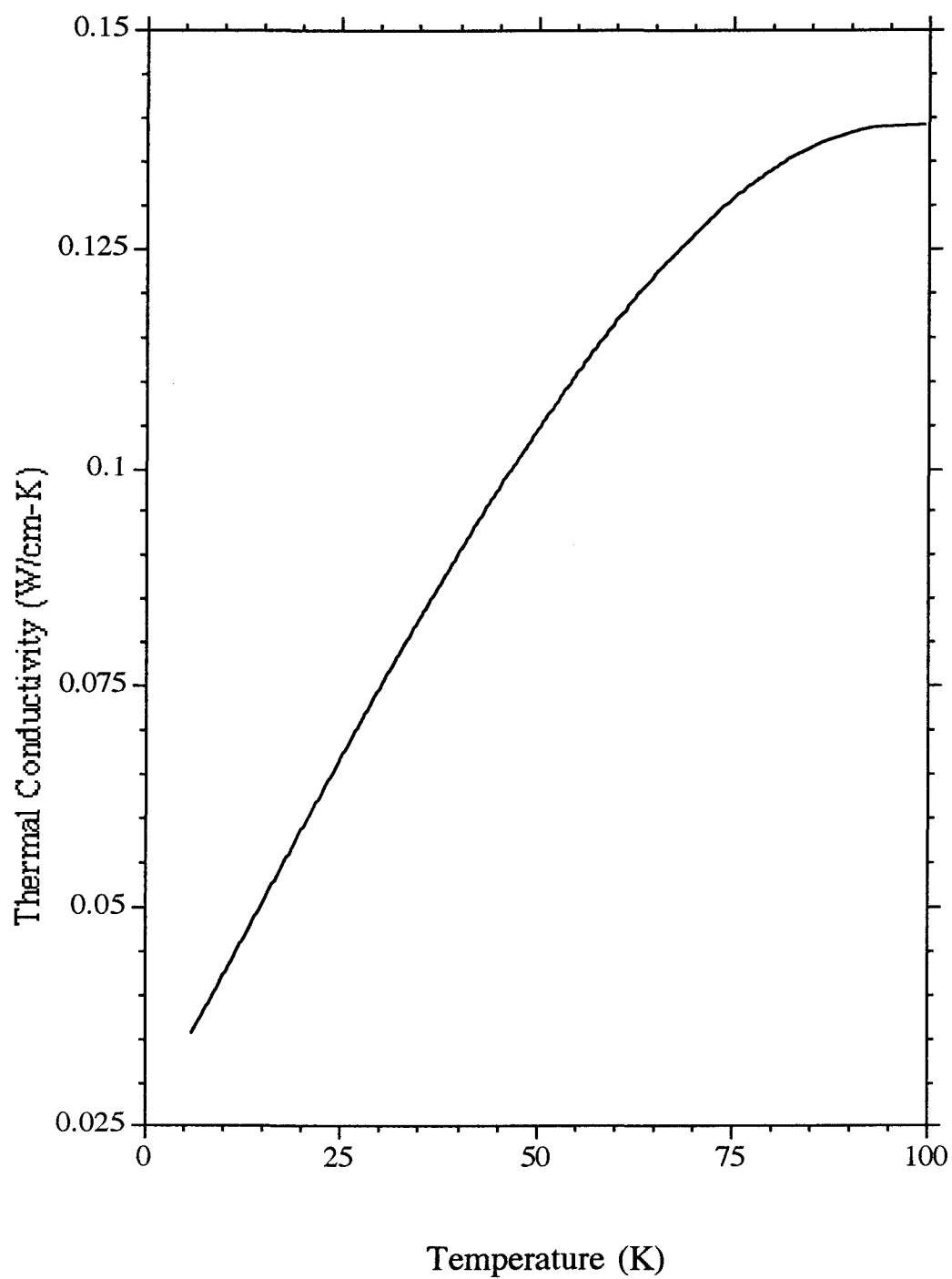
(2.4 mg Indium, 0.5 mg Apiezon N Grease)

Figure 16: Sample Temperature vs. Time

(2.6 mg Coper, 0.5 mg Apiezon N Grease)

Figure 17: Thermal Mass of Indium vs. Temperature
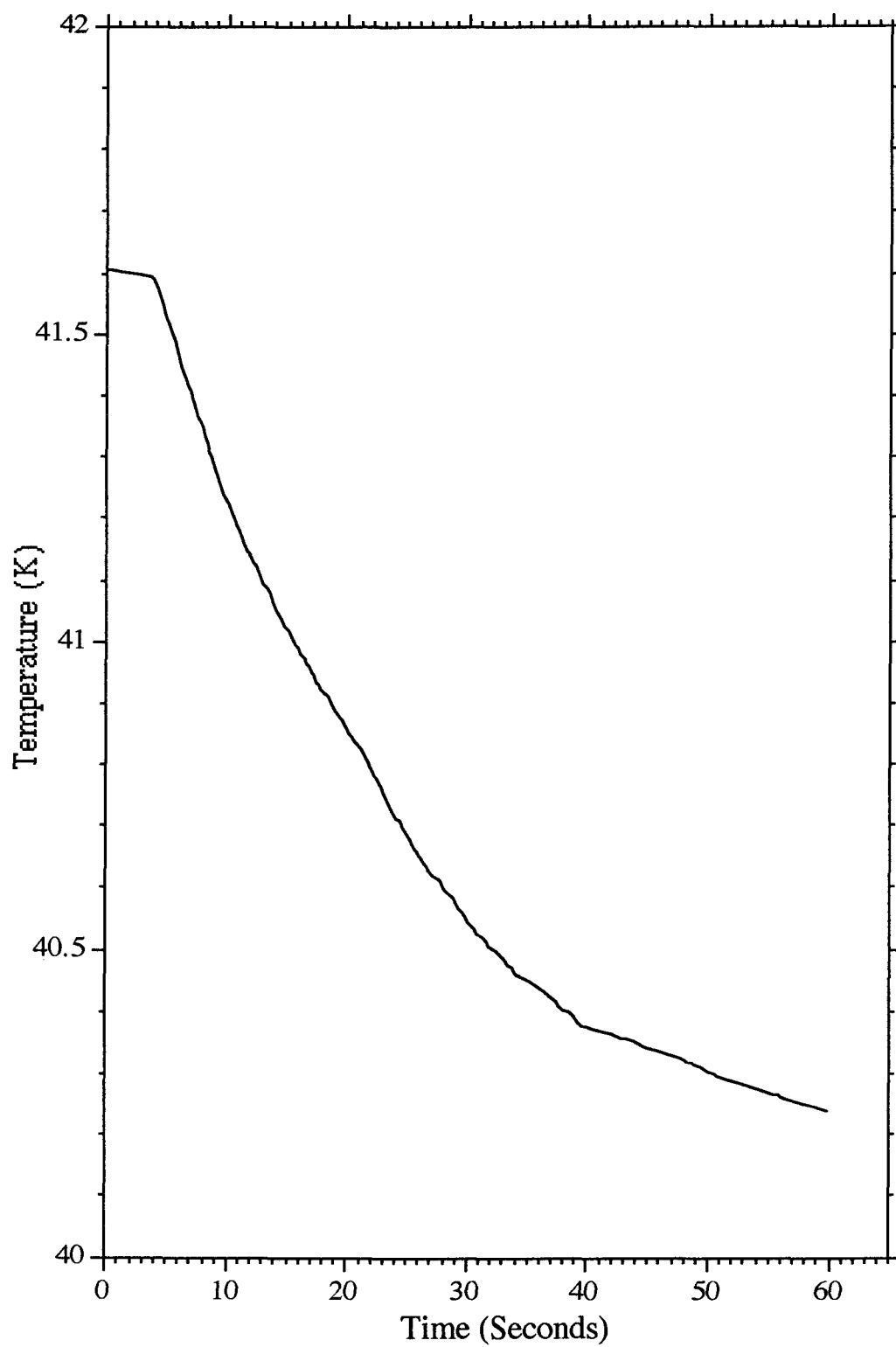
Figure 17: Thermal Mass of Indium vs. Temperature
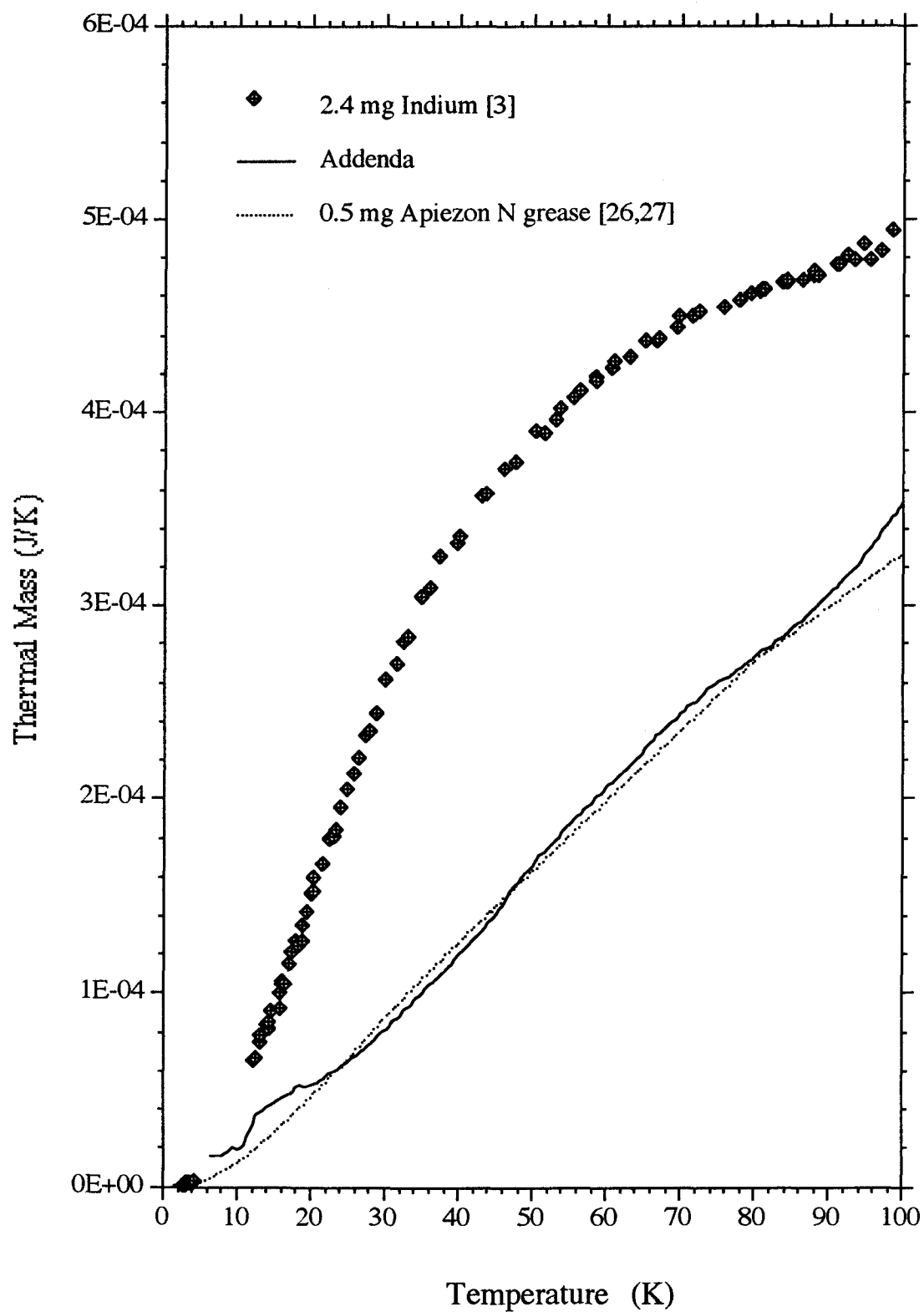
Figure 18: Thermal Conductivity vs. Temperature

(Chromel Constantan Thermocouple)

Temperature (K)

thermocouple as a function of temperature; the data agree fairly well with the literature [10] above 30 K but differ from the literature values quite a bit at lower temperatures.

Two copper samples were tested to determine how close the heat capacity measured by the calorimeter is to the actual heat capacity of copper. Figure 19 is a plot of the measured heat capacity of a 2.6 mg copper sample vs. temperature. Also shown is the actual heat capacity of copper and the addenda heat capacity. Figure 20 is a similar plot, but this time the sample was 1.1 mg of copper.

The results are close to the accepted heat capacity of copper, especially at the higher temperatures. Above 50 K, the results are within about 15% of the actual values. Below 50 K difference grows from 40% at 40 K to over 100% at 10 K. In this experiment, the thermal contact between the sample and the tip of the thermocouple was poor, causing choppy temperature decay curves (see Figure 16).

The poor thermal contact may explain why the shape of the curve follows that of the actual heat capacity curve for copper but is slightly higher. A poor thermal contact would slow down the heat leak rate from the sample, causing the decay to take longer than it should have. The longer decay time would indicate that the heat capacity measured is higher than it actually is, because a sample with large heat capacity would take longer to decay than one with a smaller heat capacity.

The experiment done with the 1.1 mg copper sample had results that are within 15% of the actual values all the way down to 10 K. Below 10 K the curve of the measured heat capacity is much higher than the curve of the actual heat capacity. This is possibly due to the fact that the addenda heat capacity is much larger than that of the sample below 20 K and especially so below 10 K.

These results prove that the basic design and calorimetry procedure described throughout this paper is valid. The calorimeter can indeed measure heat capacity of materials over most of the range from 4 to 100 K.

3.6 ERROR ANALYSIS

Two types of uncertainty can be responsible for experimental error. The first type of uncertainty, known as systematic error, involves the validity of the equations used to describe the experiment. Data are analyzed assuming the experiment follows exactly the equations used to model the actual physical phenomenon that is occurring. For example, this calorimetry experiment assumes that the governing equation for a decay process, equation (15), is strictly obeyed. This equation is only a model for the actual situation, and systematic errors would arise if the physical phenomenon strays from this equation.
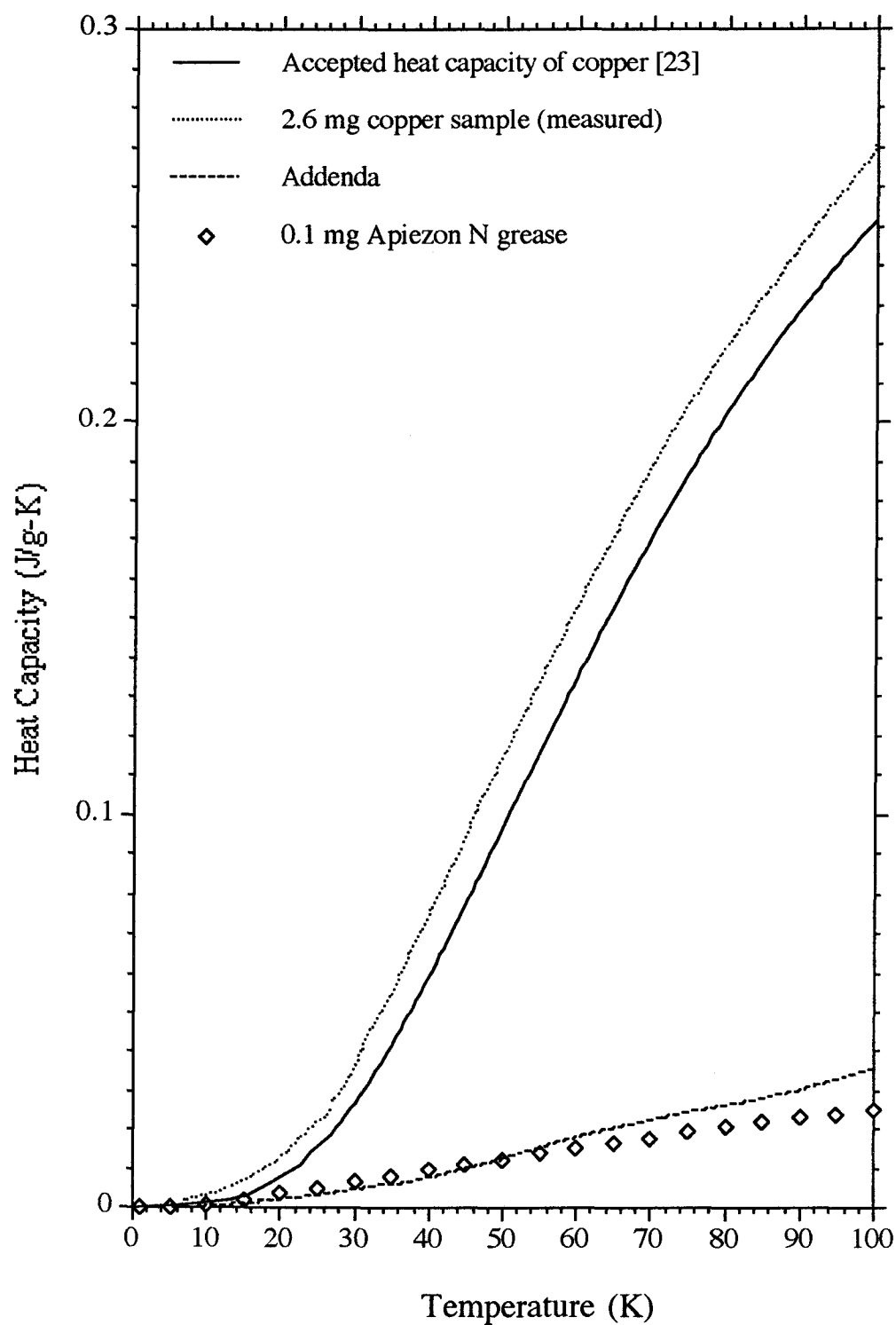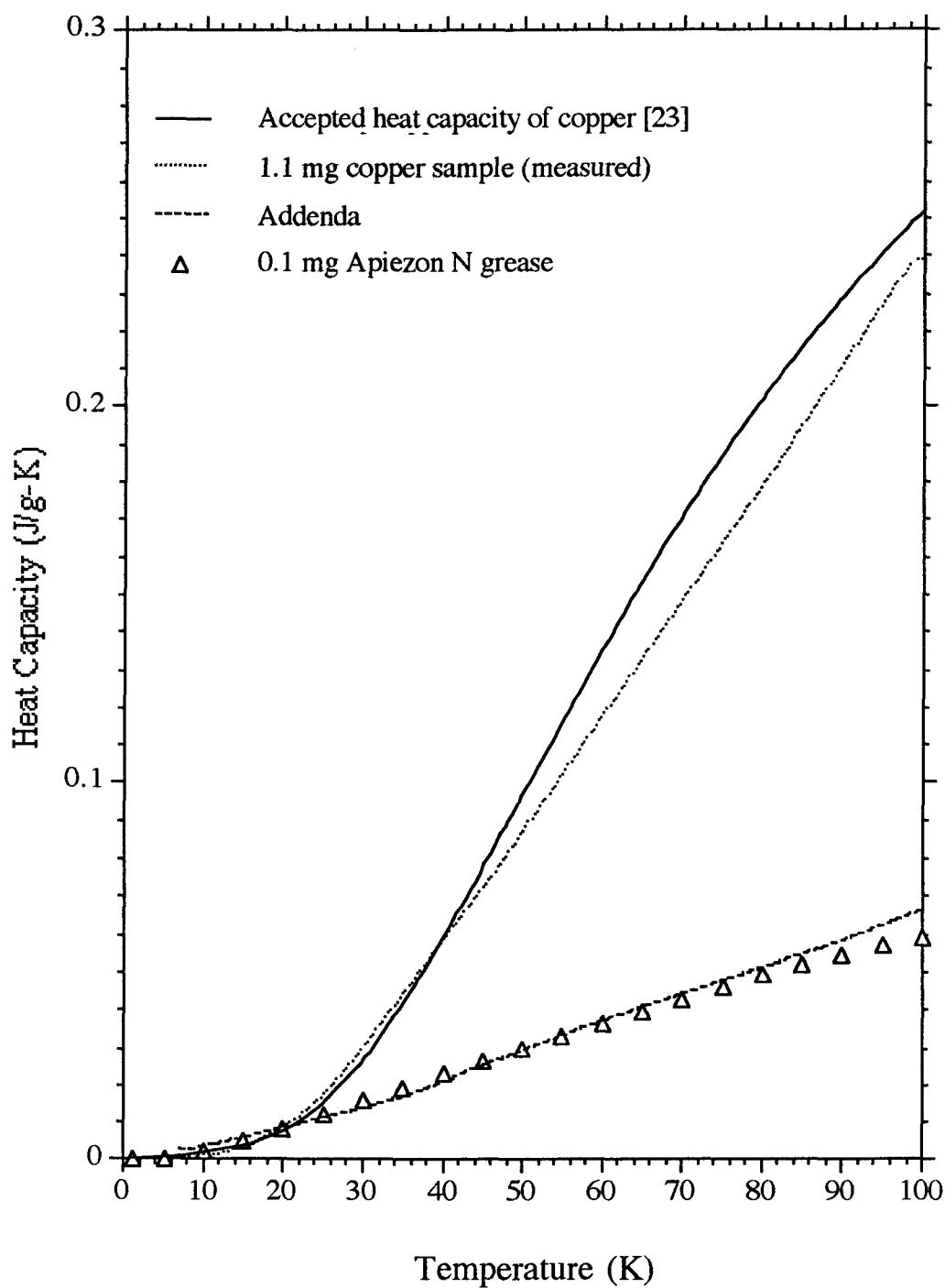
Figure 19: Heat Capacity of a 2.6 mg Copper Sample vs. Temperature

Figure 20: Heat Capacity of a 1.1 mg Copper Sample vs. Temperature

Any effect such as radiation or gas conduction heat transfer from the sample to its surroundings would cause the physical occurrence to deviate from this ideal situation, causing errors in the final data. The temperature of the sample is assumed to be the same as that of the tip of the thermocouple, and the temperature of the copper block is assumed to be the same as the temperature of the silicon diode temperature sensor placed in it. If any of these assumptions are incorrect, the actual temperature decay would be much more complicated than the process described by equation (15).

The design process of the calorimeter was such that these systematic errors are minimized. Effects such as radiation should contribute a negligible amount of error to the final results. Gas conduction effects are more difficult to quantify; the design model predicted that gas conduction would contribute no more than about 5% error, but this is only a rough estimate and the true error contribution could be anywhere from 1% to 10%.

The second type of uncertainty involves the uncertainty in the raw data and is known as random error. Every measurement instrument has a maximum attainable accuracy, and the accuracy of any final data are dependent on these instrumental uncertainties. When reducing, analyzing, and manipulating these data, the errors propagate through the analysis until the final results are obtained. An uncertainty that starts out small can grow considerably as it propogates through to the final data. Random errors also include fluctuations in a measurement due to random noise picked up by the signal, such as 60 Hz frequency electrical noise picked up by a small voltage signal.

Ideally, the magnitude of uncertainty due to random errors can be estimated with a strict statistical analysis. A simplified error analysis will be performed to get a general idea of the magnitude of this type of uncertainty in a calorimetry experiment. This analysis will attempt to answer the following questions:

·How does the uncertainty behave as the temperature decreases?
·Is it reasonable to expect more accurate data at higher temperatures?
·How small must the addenda heat capacity be compared to that of the sample so as not to dominate the measurement?
·How does the uncertainty in the calibration of the thermal conductivity of the thermocouple affect the final accuracy of heat capacity measurements?

Answers to these questions should indicate the general behavior of the system and help to predict the accuracy of results one can expect in future calorimetry experiments. Table 2 summarizes the results of the following error analysis.

Table 2: Summary of Error Analysis

Parameter, i	Approximate Relationship error(i) $\propto$
$\dfrac{dT}{dt}$	error(T) $(1/N)^{1/2}$ $1/t_{fit}$
Cp_{add}	error($Q_{conduction}$) error$\left(\dfrac{dT}{dt}\right)$
Cp_s	error($Q_{conduction}$) error$\left(\dfrac{dT}{dt}\right)$ error(Cp_{add}) x $\left[\dfrac{Cpadd}{mCps}\right]$ error(m)
$Q_{conduction}$	error$\left(\dfrac{dT}{dt}\right)$ error(Cp_{add}) x $\left(\dfrac{1}{1 + \dfrac{mCps}{Cpadd}}\right)$ error(mCp_s) x $\left[\dfrac{1}{1 + \dfrac{Cpadd}{mCps}}\right]$

KEY:

T = Temperature	Cp = Heat capacity
t = Time	m = Sample mass
N = Number of data points	add = Addenda
t_{fit} = Time length of curve fit	s = Sample
Qconduction = Conduction heat transfer from sample	

3.6.1 Random Errors

A first order approximation of the final error in a certain parameter [28] is given by

$$\sigma_f^2 = \left[\frac{\partial f}{\partial x}\right]^2 \sigma_x^2 + \left[\frac{\partial f}{\partial y}\right]^2 \sigma_y^2 + \ldots, \tag{32}$$

where f = desired parameter;

x,y, . . . = parameters that must be measured directly to compute f;

σ_i = uncertainty of parameter i.

This equation is used to determine how an uncertainty is propagated from raw data measurements to the final results.

Only two parameters must be measured directly during a calorimetry experiment: the voltage output by the thermocouple and the temperature of the copper block. Experimental uncertainty begins with the raw thermocouple voltage measurement, read by the Keithley 182 Voltmeter. There is next a small uncertainty associated with the amplification of the signal. Next, the signal is read by the TestLab 2505 as a function of time, and yet another uncertainty is introduced to the voltage signal. The voltage-time data are sent to LabVIEW , where it is converted to temperature-time data; an uncertainty in the conversion must be considered.

The temperature time data are next fit to a smooth curve, where two types of uncertainty must be considered. First, there is the uncertainty of the fit itself; when a curve is drawn through a set of data points, every point is not going to lie exactly on the curve. The goodness of the fit is judged by how close all of the data points are to the fitted curve. The scatter in the data points is mostly due to random noise the signal picks up when traveling from the thermocouple to the Keithley 182 Voltmeter.

The second uncertainty involves the error in the temperature data being fit. Even if the scatter among data points is extremely small, the actual data being fit may be poor, so that although the fitted curve is an accurate representation of the given data, the curve itself may in fact be a poor representation of the physical system due to a high uncertainty in temperature.

The next uncertainty arises from taking the derivative of the temperature-time curve. The temperature-time data are fit using batches of a 400 data points at a time (out of 5000, typically) with a quadratic curve. The error in taking the derivative of this curve depends on the error in the fit coefficients.

The final set of uncertainties are due to the errors in the parameters needed in the final step of the data reduction process, and include the sample's mass, the addenda heat capacity, and the thermal conductance of the thermocouple. These uncertainties, combined with that of the temperature-time derivative, dictate the final uncertainty in a heat capacity measurement.

The instruments, according to their respective manufacturers, have the following uncertainties:

-LakeShore DRC-93CA: ±0.01 K;

-Keithley 182 Voltmeter: ±11 nV;

-TestLab 2505: ≈0.5% error for signals on the order of 1 V,

≈1% error for signals on the order of 10 mV.

The error due to the amplification is negligible; the uncertainty in converting the thermocouple voltage to temperature is difficult to know for certain. Based on the voltage-temperature calibration experiment, described in section 3.1, this error should be extremely small when the thermocouple base temperature is within 20 K of the tip temperature, which was the case for all of the experiments done so far. According to those results, the uncertainty in converting the voltage to temperature would be negligible compared to the error in reading the voltage and random noise picked up by the signal; it therefore will be neglected.

A rough estimate shows that the final uncertainty in the measurement of the sample temperature is about 0.06 K at higher temperatures and as high as 0.4 K at the very low temperatures (below 8 K). This is due to the fact that the sensitivity of the thermocouple decreases from about 30 μV/K at 100 K to 2 μV/K at 4 K.

The next step in the error analysis is to determine the errors associated with the curve fit and differentiation of the temperature-time data. The data are fit with a quadratic of the form

$$T = at^2 + bt + c, \tag{33}$$

where T = temperature;

t = time;

a, b, c = curve fit coefficients.

The derivative of this curve is given by

$$\frac{dT}{dt} = 2at + b. \tag{34}$$

The uncertainty in $\frac{dT}{dt}$ is determined directly by the uncertainty in the fit coefficients a and b, and is given by equation (32):

$$\sigma^2_{dT/dt} = \left[\frac{\partial\, dT/dt}{\partial a}\right]^2 \sigma^2_a + \left[\frac{\partial\, dT/dt}{\partial b}\right]^2 \sigma^2_b + \left[\frac{\partial\, dT/dt}{dt}\right]^2 \sigma^2_t, \qquad (35)$$

Assuming the uncertainty in the time is negligible, equation (35) simplifies to

$$\sigma^2_{dT/dt} = 4t^2\sigma^2_a + \sigma^2_b. \qquad (36)$$

Xu, Watson, and Goodrich [16] give a detailed derivation of the uncertainty in the derivative of data which are curve fit with a quadratic curve and differentiated analytically. By assuming that the sample rate of a given temperature decay curve is constant, the uncertainty in time is negligible, and the uncertainty in temperature is constant over an entire decay curve, they derive the following expressions for the uncertainties in the fit parameters:

$$\sigma^2_a \approx \frac{180\,\sigma^2_T}{N(N\delta)^4}, \qquad (37)$$

$$\sigma^2_b \approx \frac{192\,\sigma^2_T}{N(N\delta)^2}, \qquad (38)$$

where N = number of data points fit;

δ = time spacing between data points.

Using equations (37) and (38), the uncertainty in the slope of the decay curve (taken at the midpoint of the decay, $t=t_{fit}/2$) is approximated by

$$\sigma_{dT/dt} \approx \frac{19.3\,\sigma_T}{N^{1/2}t_{fit}}, \qquad (39)$$

where $t_{fit} = N\delta$ = total time of fit.

Equation (39) is only an approximation, but as the number of points increases, it becomes more accurate. For example, if only ten data points are used, the approximation of the error as expressed in equation (39) is off by about 7%, but if fifty data points are used, the approximation is good to about 1.1% [16].

Equation (39) describes some important concepts regarding the accuracy to which

the slope of the temperature decay curve can be determined. The uncertainty in $\frac{dT}{dt}$ is directly proportional to the uncertainty in temperature, inversely proportional to the total time of the fit, and inversely proportional to the square root of the number of data points fit. Decreasing the uncertainty in $\frac{dT}{dt}$ is more dependent on decreasing of the uncertainty in the temperature than increasing the sample rate, because the uncertainty of the slope is directly proportional to the uncertainty in temperature, whereas the sample rate has only a square root affect.

In general, the temperature-time data have been extremely well-behaved, leading to excellent curve fits. A parameter that describes the goodness of the fit is the square root of the mean squared error, which is basically a measure of how close the actual data points lie to the curve used to describe them. At higher temperatures, this parameter is on the order of 10^{-6} K, while at lower temperatures it is on the order of 10^{-5} K. It is therefore safe to assume that practically no error is introduced into the data reduction process due to curve fitting the data, and any error in the temperature-time curve is totally due to the error in the temperature. The higher scatter at lower temperatures is due to the fact that the signal is on the order of a few μV, and random electrical noise picked up by the signal becomes more significant.

Typically, temperature decay curves are fit using 400 data points at a time; at low temperatures the sample rate is 10 msec, while at higher temperatures the sample rate is increased to 20 msec. As explained earlier, the uncertainty in temperature is about 0.06 K at higher temperatures and 0.4 K at lower temperatures. Plugging these values into equation (39), the uncertainty in $\frac{dT}{dt}$ becomes 0.0073 at higher temperatures and 0.024 at lower temperatures. The decay rate typically ranges from 0.1 to 0.3 K/s, so the uncertainties translate to roughly a 5% error in $\frac{dT}{dt}$ at higher temperatures and a 16% error at lower temperatures. The higher uncertainty at lower temperatures is due to the thermocouple's low sensitivity at low temperatures.

From equation (15), the heat capacity of the sample is given by

$$Cps = \left[\frac{-Qcond}{dT/dt} - Cpadd \right] + m.$$ (40)

The uncertainty in the heat capacity can now be estimated using equation (32):

$$\sigma^2_{Cps} = \left[\frac{\partial Cps}{\partial Qcond}\right]^2 \sigma^2_{Qcond} + \left[\frac{\partial Cps}{\partial \frac{dT}{dt}}\right]^2 \sigma^2_{\frac{dT}{dt}}$$
$$+ \left[\frac{\partial Cps}{\partial Cpadd}\right]^2 \sigma^2_{Cpadd} + \left[\frac{\partial Cps}{\partial m}\right]^2 \sigma^2_{m} . \tag{41}$$

This simplifies to

$$\sigma^2_{Cps} = \left[\frac{1}{m\frac{dT}{dt}}\right]^2 \sigma^2_{Qcond} + \left[\frac{Qcond}{m\frac{dT}{dt}}\right]^2 \sigma^2_{\frac{dT}{dt}} + \left[\frac{1}{m}\right]^2 \sigma^2_{Cpadd}$$
$$+ \left[\left(\frac{Qcond}{\frac{dT}{dt}} - Cpadd\right) + m^2\right]^2 \sigma^2_{m} . \tag{42}$$

The easiest way to determine the uncertainty in heat capacity due to the uncertainty of a certain parameter, such as addenda heat capacity, is to isolate the desired term in equation (42) and assume all other uncertainties are zero. The uncertainty in the heat capacity due to the addenda heat capacity term is approximated by

$$\sigma_{Cps} = \frac{\sigma_{Cpadd}}{m} . \tag{43}$$

Multiplying each side of equation (43) by $\frac{Cpadd}{Cps}$ leads to a more informative form of the equation:

$$e(Cps) = e(Cpadd)\left(\frac{Cpadd}{mCps}\right) , \tag{44}$$

where $e(Cp_s) = \dfrac{\sigma_{Cps}}{Cps} = $ error in sample heat capacity. Equation (44) shows that the error in the sample's heat capacity is equal to that of the addenda, weighted by the ratio of the thermal masses. For example, if the addenda thermal mass is known to 5% and the sample's thermal mass (i.e. mCp_s) is equal to that of the addenda, the error in the

sample's heat capcacity would also be about 5%. If the addenda heat capacity outweighed that of the sample by a factor of two, the error in the sample's heat capacity increases to 10%. If the addenda heat capacity outweighed that of the sample by a factor of five, which is quite possible below 15 K, the error in measuring the sample's heat capacity would increase to 25%.

Accurate measurements, therefore, depend either on knowing the addenda heat capacity accurately or using a sample that has a heat capacity much larger than that of the addenda. If the sample's heat capacity was ten times that of the addenda, for instance, any error in measuring the addenda heat capacity would likely be negligible, thus greatly decreasing the total error in measuring a sample's heat capacity. Equation (44) helps explain why the data collected so far appear much less accurate at lower temperatures; with a 1 mg copper sample and 0.1 mg of Apiezon N grease, the addenda begins to dominate the measurement below 15 K.

Similarly, the error in heat capacity is directly proportional to the error in the mass of the sample. Ideally, the error in the sample mass would be extremely small, possibly as low as a few tenths of a percent. Unfortunately, the mass balance used for calorimetry experiments so far is accurate only to 0.1 mg, and if a 1 mg sample is used, the error is 10%. This source of error can easily be avoided by using a mass balance that can measure to at least one more decimal place.

Finally, the uncertainty in heat capacity due to the uncertainty in $\frac{dT}{dt}$ is also directly proportional to the error in $\frac{dT}{dt}$, so a 5% error in $\frac{dT}{dt}$ would lead to a 5% error in heat capacity. Because the uncertainty of $\frac{dT}{dt}$ increases with decreasing temperature, the contribution of this term to the uncertainty in heat capacity also increases as temperature decreases.

A similar analysis can be done with the conduction heat transfer through the thermocouple. Assuming all uncertainties except that for the heat conduction through the thermocouple are zero, the weighing function turns out to be unity, and equation (42) simplifies to

$$e(Cps) = e(Qcond). \tag{45}$$

If the thermal conductivity is known to 5%, then the error contibuted to the measured heat capacity would also be 5%.

The thermal conductance of the thermocouple is determined by the equation

$$Qcond = (mCps + Cpadd)\frac{dT}{dt},\qquad(46)$$

and the uncertainty in thermal conductance is given by

$$\sigma^2_{Qcond} = \left[\frac{\partial Qcond}{\partial mCps}\right]^2 \sigma^2_{mCps} + \left[\frac{\partial Qcond}{\partial dT/dt}\right]^2 \sigma^2_{dT/dt} + \left[\frac{\partial Qcond}{\partial Cpadd}\right]^2 \sigma^2_{Cpadd},\qquad(47)$$

where mCp$_s$ represents the thermal mass of the calibration sample. This thermal mass is known and used as a thermal conductivity calibration specimen. Equation (46) reduces to

$$\sigma^2_{Qcond} = \left[\frac{dT}{dt}\right]^2 \sigma^2_{mCps} + \left[\frac{dT}{dt}\right]^2 \sigma^2_{Cpadd} + (mCps + Cpadd)^2 \sigma^2_{dT/dt}.\qquad(48)$$

Using the same reasoning as before, equation (48) shows that the error in thermal conductance is directly proportional to the error in $\frac{dT}{dt}$. If the heat capacity of the sample is known accurately, it's uncertainty contribution to the uncertainty in thermal conductance could be neglected. Also ignoring the uncertainty in $\frac{dT}{dt}$ (so that the addenda term can be isolated and examined), equation (48) simplifies to

$$e(Qcond) = e(Cpadd)\frac{1}{1 + \frac{mCps}{Cpadd}}\qquad(49)$$

The important point suggested by equation (49) is the fact that even if the sample's heat capacity is known accurately, thus adding little uncertainty to the determination of thermal conductance directly, it could still contribute a large amount of uncertainty through the addenda heat capacity term. If the sample's heat capacity is much smaller than that of the addenda, the second term in equation (49) approaches unity and the uncertainty in thermal conductance is dictated by the uncertainty of the addenda heat capacity.

If the sample's heat capacity outweighed that of the addenda, however, the contribution of the addenda uncertainty to the error in thermal conductance diminishes. For example, if the sample's heat capacity outweighed the addenda's by a factor of ten, and the addenda was only known to 10%, the uncertainty in thermal conductance due to

the addenda's uncertainty would only be 1%.

This analysis suggests that the thermal conductance calibration should be done with a sample that has a heat capacity greater than that of the addenda's if the accuracy in thermal conductance is to be dictated by that of the sample and not the addenda. Ideally, the heat capacity of the sample would be known accurately.

As explained earlier, the heat capacity of copper is known to 1%, but unfortunately it has a fairly low heat capacity that is swamped out by the addenda at low temperatures. The accuracy of the thermal conducivity calibration, therefore, is controlled by the addenda and not the copper.

The indium sample used for the calibration has a high heat capacity compared to that of the addenda, but unfortunately the data used were taken from a single source and the accuracy of the data is unknown. It is probably within 5%, but no information regarding its accuracy is given [3].

One source of error in the thermal conductivity measurements not yet mentioned comes from differentiating Q_{cond} (heat transferred by conduction through thermocouple) to determine k, the thermal conductance of the thermocouple. The data are differentiated and stored in a temperature-conductance array, which is called up by certain subroutines and reintegrated. This manipulation of the data, if not done carefully, could easily lead to large errors in determining the heat leak from the sample.

According to this error analysis, heat capacity could be determined to within 10% at higher temperatures and about 30% at lower temperatures, assuming the sample's thermal mass is larger than that of the addenda. These uncertainties are probably very conservative; the results of the experiments done using copper samples are well within these values.

Chapter 4   CONCLUSION

The calorimeter described in this paper has been shown to work well. The mathematical models were useful tools in designing the calorimeter. Unlike most calorimeters described in the literature, this apparatus can measure heat capacity continuously from 7 to 100 K, as demonstrated with a 1.1 mg copper sample, and this temperature range can likely be expanded. The calorimeter was designed so that future use in a magnetic field is possible, and a chromel-constantan thermocouple is one of the least field-dependent, low-temperature thermocouples available.

The thermal conductivity of the thermocouple can likely be determined more accurately by performing more calibration experiments, possibly using different materials as calibration specimen. Hopefully, the data would converge into a single curve, thus defining the thermal conductivity of the thermocouple as accurately as possible with the current setup.

The calorimeter is limited to samples smaller than about 4 mg, but the basic idea of the design can easily be extended to larger samples, possibly by using larger thermocouple wire. If accurate data are needed at temperatures below 10 K, a more sensitive thermocouple, such as a gold-iron one, can be used, but the thermal conductivity of such a thermocouple would be much higher than that of the chromel-constantan one.

As the error analysis suggests, the accuracy to which the calorimeter can measure heat capacity depends quite a bit on the magnitude of the heat capacity being measured, especially at temperatures below 20 K. Obviously, it is easier to measure something large than something small. Materials that have heat capacities larger than the small amount of Apiezon N grease used to bond a sample to the tip of the thermocouple would be ideal for these types of measurements.

REFERENCES

1. Regelsberger-M., Wernhardt-R., Rosenberg-M. *Fully automated calorimeter for small samples with improved sensitivity.* **Journal of Physics E-Scientific instruments.** Vol. 19, pp. 525-32. July, 1986.

2. Stewart-G.R. *Measurement of low-temperature specific heat.* **Review of Scientific Instruments.** Vol. 54, Iss. 1, pp. 1-11. January, 1983.

3. Touloukian-Y.S., Buyco-E.H. **Specific Heat of Metallic Elements and Alloys-Thermophysical Properties of Matter, Vol.4.** Plenum Press, New York, 1970.

4. Inderhees-S.E.Salamon-M.B., Friedmann-T.A., Ginsberg-D.M. *Measurement of the specific-heat anamoly at the superconducting transition of $YBa_2Cu_3O_7$- ∂.* **Physical Review B.** Vol. 36, Iss. 4, pp. 2401-3. August, 1987.

5. Salamon-M.B. *Specific heat of CoO near T_N: anisotropy effects.* **Physical Review B.** Vol. 2, Iss. 1, pp. 214-20. July, 1970.

6. Gutsmiedl-P., Probst-C., Andres-K. *Low-temperature calorimetry using an optical heating method.* **Cryogenics.** Vol. 31, Iss. 1, pp. 54-7. January, 1991.

7. White, Guy K. **Experimental Techniques in Low-Temperature Physics,** 3rd ed., Oxford University Press, New York, 1987, p. 174.

8. Bachmann-R., DiSalvo-F.J., Geballe-T.H., Greene-R.L., Howard-R.E., King-C.N., Kirsch-H.C., Lee-K.N., Schwall-R.E., Thomas-H.U., Zubeck-R.B. *Heat capacity measurements on small samples at low temperatures.* **Review of Scientific Instruments.** Vol. 43, Iss. 2, pp. 205-14. February, 1972.

9. Depuydt-J.M., Dahlberg-E.D. *Low-temperature calorimetry for small samples.* **Review of Scientific Instruments.** Vol. 57, Iss. 3, pp. 483-486. March, 1986.

10. Graebner-J.E. *Modulated-bath calorimetry.* **Review of Scientific Instruments.** Vol. 60, Iss. 6, pp.1123-28. June, 1989.

11. Graebner-J.E., Haddon-R.C., Chichester-S.V., Glarum-S.H. *Specific heat of superconducting k-$(BEDT$-$TTF)_2Cu(NCS)_2$ near T_c.* **Physical Review B.** Vol. 41, Iss. 7, pp. 4808-10. March, 1990.

12. Schwall-R.E., Howard-R.E., Stewart-G.R. *Automated small sample calorimeter.* **Review of Scientific Instruments.** Vol. 46, Iss. 8, pp. 1054-9. August, 1975.

13. Dutzi-J., Dixit-R.N., Shete-S.Y., Pattalwar-S.M. *Specific-heat measurements in small samples at low temperatures.* **Pramana..** Vol. 31, Iss. 4, pp. 253-62. October, 1988.

14. Regelsberger-M., Wernhardt-R., Rosenberg-M. *Thin-film bolometer with fast response.* **Review of Scientific Instruments.** Vol. 58, pp. 276-8. February, 1987.

15. Early-S.R., Hellman-F., Marshall-J., Geballe-T.H. *A silicon on sapphire thermometer for small sample low temperature calorimetry.* **Physica 107B**. Vol. 107, pp. 327-28. 1981.

16. Xu-Jing-chun, Watson-C.H.,Goodrich-R.G. *A method for measuring the specific heat of small samples.* **Review of Scientific Instruments**. Vol. 61, Iss. 2, pp. 814-821. February, 1990.

17. Riegel-S., Weber-G. *A dual slope method for specific-heat measurements.* **Journal of Physics E-Scientific Instruments**. Vol. 19, Iss. 10, pp. 790-1. 1986.

18. Forgan-E.M., Nedjat-S. *Heat capacity cryostat and novel methods of analysis for small specimens in the 1.5-10 K range.* **Review of Scientific Instruments**. Vol. 51, Iss. 4, pp. 411-17. April, 1980.

19. Sullivan-Paul F., Seidel-G. *Steady-State, ac-Temperature Calorimetry.* **Physical Review**. Vol. 173, Iss. 3, pp. 679-85. September, 1968.

20. Machado-F.L.A., Clark-W.G. *Ripple method - An application of the square wave excitation method for heat-capacity measurements.* **Review of Scientific Instruments**. Vol. 59, pp. 1176-81. July, 1988.

21. Incropera-Frank P., DeWitt-David P. **Fundamentals of Heat and Mass Transfer.** 2nd ed. John Wiley and sons, Inc. New York, 1985. p. 646.

22. White, p. 128.

23. White-G.K., Collocott-J. *Heat capacity of reference materials: Cu and W.* **J. Phys. Chem. Ref. Data.** Vol. 13, No. 4, pp. 1251-7. 1984.

24. Sparks-Larry L., Powell-Robert L. *Reference data for thermocouplem materials below ice point.* **Temperature- Its Measurement and Control in Science and Industry.** Vol. 4, Part 3, pp. 1569-77. 1972.

25. Hust-J.G., Powell-Robert L., Sparks-L.L. *Methods for cryogenic thermocouple thermometry.* **Temperature- Its Measurement and Control in Science and Industry.** Vol. 4, Part 3, pp. 1525-35. 1972.

26. Bevolo-A.J. *Heat capacity of Apiezon N grease from 1 to 50 K.* **Cryogenics**. pp. 661-2. December 1974.

27. Bunting-J.G., Ahworth-T., Steeple-H. *The specific heat of Apiezon N grease.* **Cryogenics**. pp. 385-86. October 1969.

28. Bevington-Philip R. **Data Reduction and Error Analysis for the Physical Sciences,** McGraw-Hill Book Company, New York, 1969, p. 60.