AN ANALYSIS OF SELECTED TECHNIQUES IN MICROCALORIMETRY

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ABSTRACT

AN ANALYSIS OF SELECTED TECHNIQUES
IN MICROCALORIMETRY

By

David Russell Thompson

The objective of the research conducted was to analyze three aspects of microcalorimetry. Many processes with small heats of reaction are being studied with microcalorimeters. The magnitude and the variations with time of the reaction heats may be of considerable importance. As the scientific understanding of food processes increases, the measurement of the heat of immersion and other small thermal effects will become more important. Because the required accuracy of these measurements has increased, a more detailed analysis of microcalorimeters has become necessary.

The calibration of certain microcalorimeters was investigated by studying the sensitivity coefficients. It was shown that the unknown parameters of the instruments could be determined simultaneously if the calibration experiment was appropriately designed. The theory of sensitivity coefficients was extended to include the

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determination of unconstrained variables. The parameters of the microcalorimeter are expected to change slightly during the experiment. However, it was shown that unless the reaction heat is known to follow a given functional form, the changes cannot be measured during the experiment. The sensitivity coefficients also indicate that accurate compensation heating is impossible.

The effectiveness of metallic sinks for maintaining a uniform temperature environment around a set of twin reaction vessels was studied. A numerical technique was devised to model a cross section of a solid cylindrical thermal sink with separate cavities for the reaction and reference cells. The influence of eleven parameters related to metallic sinks on the relative error was investigated. The simulation indicated that the relative measurement error can be maintained below 0.1% if the metallic sink is properly designed.

A family of techniques for determining the reaction heat as a function of time is presented. These techniques are based on Duhamel's theorem with least squares smoothing. The new methods are shown to be more accurate than techniques reported earlier for some functional forms of the reaction heat.

Approved ______________
Major Professor

March 1970

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AN ANALYSIS OF SELECTED TECHNIQUES IN MICROCALORIMETRY

By

David Russell Thompson

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I. INTRODUCTION

1.1 General Remarks

Thermal effects accompany many chemical and biological phenomena. The magnitude of these effects may be of considerable theoretical and practical importance. The stability and structure of molecules, the conditions of chemical equilibria, and the heat exchange in industrial processes can all be calculated from a knowledge of these thermal effects.

Many processes have been studied by calorimetric methods. Heats of combustion and other processes that evolve large quantities of thermal energy have been extensively investigated. The advent of microcalorimetric measurements has extended the range of calorimetric studies. Various examples of these microthermal processes are reviewed by Swietoslawski (1946).

Microcalorimetric techniques have been used to measure the energy released by radioactive materials, the heat produced by growing plants, by bacteria, and by the germination of seeds. The gradual change in structure of metallic alloys have been studied using microcalorimetors. The thermal phenomena which take place when different kinds of cement react with water give a direct indication of how they can best be used in both cold and warm seasons. The evolution of heat by the adsorption or the absorption of gases and vapors has also been investigated.

1.2 Hygroscopic Bonds

Drying is one of the most widely used methods of food preservation. Drying or dehydration of agronomic products reduces the transportation and packaging costs and can increase shelf life. The importance of drying has provided the stimulus for a large body of scientific literature. Much of this work has been primarily experimental in nature. Consequently vast quantities of data exist but only a small portion of it relates to the fundamental aspects of the drying process.

Microorganisms, metabolic processes, oxidation, desiccation, abosrption of foreign odors, water damage, and faulty preparation can all reduce the storage life of biological materials. The moisture content of dried products must be low enough to retard the action of microorganisms and metabolic processes. Oxidation may cause rancid flavors if the moisture content is too low. Thus, the bond energy between the water molecule and the product must be sufficiently high to make the water unavailable to microorganisms although some water molecules should be left to reduce the number of sites available for oxidation. The optimum moisture content has been related to the

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monomolecular layer discussed by Brunauer, Emmett, and Teller (1938). Microcalorimetric measurements of this bond energy are expected to refine this concept.

Ngoddy (1969) explained the importance of the theoretical development of the isothermal curves for biological materials. Equations representing the adsorption isotherms are not only the most convenient form in which to plot experimental data, but also they represent an important step in the theoretical treatment of the drying process. Adamson (1967) pointed out that although a theoretically derived isotherm must be able to fit the experimental data, this is not a sufficient test. He noted that relationships derived from different models have been found to yield equations which are graphically and even algebraically identical. The distinguishing characteristic is the heats and possibly the entropies of adsorption. Jura and Hill (1951) showed that theoretically the entropies can be obtained from the combination of heats of emersion data and a single isotherm with considerably more accuracy than from calculations dependent on the isotherms at two temperatures.

The water in biological materials may exist as free, chemically bound, and adsorbed moisture (Kuprianoff, 1958). The hygroscopic point as defined by Lewis (1921) divides the free moisture in food from the moisture that is subject to surface sorption phenomena. The free water is subject to the forces of osmosis, liquid diffusion, capillary action, and gravity and is removed during the so called constant rate drying period. Lykov (1955) presents a unifying theory of transport for free water. Transport of moisture below the hygroscopic point is primarily related to the surface forces. For this reason this type of moisture is called adsorbed moisture. The falling rate drying period is related to the removal of this type of moisture. The transport of moisture below the hygroscopic point is still the object of many studies. It is generally agreed that this moisture is held by forces of the van der Waal's type. The variety of sites and energy levels available for water molecules on a particular surface is reflected in the adsorption isotherm.

Several problems prevent the direct measurement of the various site energy levels. Frequently the reactions at surfaces are very slow and the energies involved are very small. Water molecules released near a surface may not select the highest energy site for adsorption. Thus, the apparent energy release by a few molecules of water added to the product, is not representative of the maximum site energy available. Chessick and Zettlemoyer (1959) indicated that most of these problems are surmounted by the heat-of-immersion technique. The heat-of-immersion or heat-of-wetting (also called the "Pouillet effect") is usually a small exothermic quantity approximately equal to the heat of adsorption. In order to avoid carrying the negative sign, Boyd and Harkins (1942) introduced the term heat of emersion and defined it as the negative of the heat of immersion.

1.3 Thermodynamics of Immersional Wetting

Chessick and Zettlemoyer (1959) have reviewed the thermodynamics of adsorption and immersional wetting. All of their equations are on a per unit area basis; however, the porous nature of biological materials may necessitate utilizing a per unit of mass basis. Either way, the heat of immersion is approximately equal to the difference in the energies of the solid surface and the solid-liquid interface because volume changes during the immersion process are usually negligible.

The energy of adhesion of a liquid to a solid is defined to be the sum of the surface energies of the liquid and solid less the energy of the solid-liquid interface. Therefore, the adhesion energy is approximately equal to the heat of immersion plus the surface energy of the liquid.

The adsorption and immersional processes are also related through the heat effects. The integral heat of adsorption of a given number of moles of adsorbate in the vapor state at equilibrium pressure and temperature is equal to the difference in the heats of immersion before and after the moles are adsorbed plus the molar heat of liquefaction times the number of adsorbed moles. The net heat of adsorption is defined to be the difference in the heats of immersion. The net heat of adsorption is also equal to the difference in the molar energies of the adsorbed film and the liquid times the number of moles.

Isosteric heats of adsorption can be determined from heat of immersion data also. The integral of the isosteric heat of adsorption over the number of moles adsorbed is defined to be equal to the heat of adsorption. Therefore, the difference in the heats of immersions before and after the adsorption of N moles is equal to the integral of the isosteric heat from zero to N less N times the molar heat of liquefaction.

Entropy changes have also been related to heats of immersion and the isothermal curves. If the entire entropy change can be attributed to the adsorbate, Jura and Hill (1951) showed that the difference in entropy between the adsorbed film and the bulk liquid is equal to the difference in the heats of immersion per mole plus the film pressure per mole all divided by the absolute temperature less the Boltzman constant times the natural log of the relative equilibrium pressure.

II. REVIEW OF MICROCALORIMETRY

2.1 Introduction

In principle the design and operation of a microcalorimeter is simple. The basic parts of the calorimeter include the product under study, water, one or more thermometers, perhaps an electric heater, and devices for mixing and stirring. A calorimeter is surrounded by an insulative jacket in which thermometers may be located; it has a provision for controlling its temperature. Heat may be transferred between the calorimeter and the jacket by conduction, by convection, or by thermal radiation. Energy in the form of work may also be transferred to the calorimeter by a mechanical stirrer or by compression or expansion against an external pressure. Energy in the form of heat may be supplied by an electric current used to operate a heater or by the flow of electricity through a resistance thermometer.

At least two microcalorimeters are commercially available. Sunner and Walso (1966) reported on a microcalorimeter made in Sweden that is capable of measuring the heat of immersion. A French built microcalorimeter is being imported and marked by Imass Corporation. This instrument has su

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instrument has sufficient sensitivity to measure the heat of immersion but physically the instrument is not designed for this application.

Although two microcalorimeters are commercially available, Wilhoit (1967) reported that often it will still be necessary for the experimenter to modify existing instruments or construct them entirely to his own specification. This review is not intended to discuss all the instruments which have been used. However, an attempt will be made to discuss the variations in the parts of a typical calorimeter. A very large number of new calorimeters are being built each year, but most of these involve only slight modifications of the basic parts.

2.2 Microcalorimeter Jackets

Most microcalorimeters now in use can be classified according to the type of thermal relationship between the reaction vessel and the calorimeter jacket. The thermal relationship is indicated by the thermal time constant of the calorimeter--the rate of heat transfer between the reaction vessel and the calorimeter jacket divided by the heat capacity of the reaction vessel. The thermal time constant of an adiabatic microcalorimeter is infinite since no heat loss occurs. Microcalorimeters classified as nonadiabatic have time constants between 1,000 and 100,000 seconds. Most nonadiabatic microcalorimeters have time constants of about 20,000 seconds. The thermal time constant of conduction microcalorimeters is less than 1,000 seconds.

Swietoslawski (1946) reported that most calorimeters provide thermal insulation without regulating the jacket temperature. To make the heat exchange between a calorimeter and the jacket more uniform, the calorimeter was placed inside one or two empty cylindrical containers. Usually the calorimeter held a large amount of water so that its temperature change was very small. In this way reactions that produced a large amount of heat could be studied without considering heat loss to the surroundings. With the advent of microcalorimetry this approximation could no longer be made. Thus the type of jacket employed became a distinguishing characteristic of microcalorimeters.

2.2.1 Adiabatic Microcalorimeters

If the temperature of a calorimeter's jacket is maintained at the temperature of its reaction vessel, no heat loss will occur and the jacket becomes an adiabatic shield. Maintaining the temperature equality is an ideal situation that cannot be exactly obtained in actual practice. Sturtevant (1946) listed four advantages to be realized by using the adiabatic procedure. First, the overall heat transfer coefficient is more nearly constant if the temperature differences are minimized. As a temperature difference increases, the value of the convective and radiative transfer coefficients change. Thus, heat loss due to imperfect adiabatic control can be calculated more accurately than heat losses resulting from larger temperature variations. Secondly, the maintenance of very small temperature differences reduces the convective heat transfer coefficient. It is thus permissible to use wider air spaces for insulation. Third, errors due to evaporation from an incompletely sealed calorimeter are less serious if the adiabatic method is used. Fourth, the adiabatic procedure gives more reliable results in prolonged calorimetric experiments. In such cases the heat loss in other type calorimeters in contrast with the adiabatic type may be as large as the total quantity of heat to be measured. Morrison *et al*. (1951) employed an adiabatic microcalorimeter to investigate the relatively slow process of gas adsorption on solid surfaces.

To increase the accuracy of the adiabatic control, it is usually necessary to enclose the adiabatic shield in an isothermal or a second adiabatic shield. Stubblefield (1965) submerged his adiabatic calorimeter in a water bath controlled to within one hundredth of a degree centigrade. Other investigators have reported using the outer shield for advantages other than just thermal protection. Morrison and Los (1950) used liquid hydrogen to provide an isothermal shield around their adiabatic calorimeter and also to provide the low temperature necessary for their experiment. Howard and Culbertson (1950) used two concentric adiabatic shields or jackets. The outer shield was a heavy steel vacuum chamber so that convective heat transfer could be nearly eliminated if small temperature differences did occur. The inner and outer shields were carefully insulated. Rather than measuring the temperature rise of the reaction chamber, these authors determined the heat of the reaction by measuring the energy necessary to maintain the inner shield at equilibrium with the reaction chamber.

At least two variations of the adiabatic microcalorimeter have been reported. Belousov and Ponner (1968) utilized a kerosene bath to provide the jacket for their microcalorimeter. The temperature of the bath was maintained below the temperature of the calorimeter by an amount sufficient to exactly balance the heating effects of the resistence thermometers used in the calorimeter. In other words, the heat input from the electrical energy was balanced by the heat loss to the jacket. Abrosimov and Krestov (1967) used an isothermal steel chamber as a jacket for their microcalorimeter. They reduced the air pressure inside the steel jacket to 10^{-5} torr. The radiation heat transfer was reduced by chrome plating the reaction vessel and the steel chamber. The sensitivity of the calorimeter was reported to be plus or minus 0.1 millicalories. Corrections for heat loss were reported to change the experimental results by less than 2%. Although the calorimeter was nonadiabatic, the heat loss compared very well with many adiabatic calorimeters.

2.2.2 Nonadiabatic Microcalorimeters

Most nonadiabatic calorimeters employ constant temperature, isothermal, jackets. This type of calorimeter is distinguished from the conduction calorimeter by a relatively low heat flow between the reaction vessel and the calorimeter jacket. The equipment required to maintain an isothermal shield is substantially less expensive than that needed for an adiabatic shield or jacket. The primary disadvantage of the nonadiabatic microcalorimeter is the increased heat loss from the reaction vessel to the shield. Long term reactions cannot be studied in nonadiabatic microcalorimeters because of the inadequate knowledge of the heat loss. The accuracy of the heat transfer calculations is limited in nonadiabatic calorimeters because the overall heat transfer coefficient becomes increasingly dependent on the temperature difference as this difference increases. Reversely, the temperature difference can be known with greater accuracy when an isothermal jacket is used. It is difficult to prevent temperature gradients from existing within an adiabatic shield. However, an isothermal shield can be sufficiently massive or else consist of a well stirred fluid so that temperature gradients are minimized. In order to minimize temperature gradients within the isothermal jacket, Zverev and Krestov

(1968) used a heavy aluminum block inside a well stirred bath of water which in turn was inside an environmentally controlled chamber.

Twin calorimeter vessels can be utilized with any type of jacket. However, they are most frequently employed inside isothermal shields. Bartell and Suggitt (1954) studied the heat of wetting of several inorganic substances in twin calorimeter vessels in a nonadiabatic microcalorimeter. Both vessesl were treated identically except for the release of a small quantity of the inorganic solid in the reaction vessel. In this way, the electrical and mechanical heat inputs could be neglected. Ostrovskii et al. (1968) used four vessels in one isothermal enclosure. This instrument is capable of testing two reactions simultaneously. In order to reduce the inaccuracy of heat loss calculations, electrical energy was added to either the reaction vessel or the comparison vessel to maintain their temperatures as near equal as possible. The authors recognized that the temperature equality was not maintained and used heat loss calculations to correct for this. Berger et al. (1968) used twin vessels in an isothermal enclosure and employed a numerical technique to approximate the heat loss from the reaction vessel. The temperature difference between the twin vessels was measured rather than measuring the difference between each vessel and the sink.

2.2.3 Conduction Microcalorimeters

If heat is removed from the reaction vessel at approximately the same rate as it is produced by the reaction, the temperature of the reaction vessel remains constant. For this reason this type of calorimeter is sometimes labeled isothermal; however, more frequently it is called a conduction microcalorimeter. The heat of the reaction being studied is determined by measuring the heat loss rather than the temperature rise of the reaction vessel. Conduction calorimeters are frequently used to study reactions that require long periods of time to run to completion. Generally the only stirring used in a conduction calorimeter is that required to initiate the reaction.

The original conduction microcalorimeters were designed by Tian and modified by Calvet (Calvet and Prat, 1963). The Calvet conduction microcalorimeter resembles a twin vessel nonadiabatic calorimeter. It consists of a reaction vessel and a reference vessel, each inside a metal block which in turn is enclosed by an isothermal shield. The reaction and reference vessels are tall, slender containers. No mechanical stirring is provided; thus the temperature of the vessels is not uniform and the heat transfer to the heavy metal block is a function of location. A battery of thermocouples is judiciously placed between the vessel and the heat sink. It can be shown that the sum of the emf's produced by the thermocouples is directly proportional to the heat loss if one pair of thermocouples is located in each heat flux tube. This of course assumes that the temperature difference remains small. If the thermal effects of the reaction under study are larger than can be readily removed by conduction through the bank of thermocouples, Joule heating or Peltier cooling is supplied. In order to eliminate some of the methodical errors, the difference in potential between the bank of thermocouples surrounding the reaction cell and that surrounding the reference cell is recorded. The integral of the potential recorded over time is proportional to the heat of the reaction under study plus or minus the heating or cooling provided. For an analysis of the reaction kinetics, Tian and Calvet have devised techniques which reconstruct the heat input as a function of time. One of the principle difficulties with the Calvet microcalorimeter is the amount of work required to assemble and mount the banks of thermocouples.

The heat of reaction in a heat burst microcalorimeter is all conducted through thousands of thermocouple wires to the sink. Benzinger and Kitzinger (1963) explain the principal of heat burst microcalorimetry in the following way. In the classical calorimeter, that is a calorimeter with either an adiabatic or nonadiabatic jacket, the heat generated in the reaction vessel escapes very slowly. If an instantaneous reaction proceeds in the reaction vessel, the temperature of this vessel will rise slightly.

Since the heat escapes very slowly, the temperature would remain almost constant for a very long period of time. The temperature change could be measured with the thermometric device almost immediately. Thus the remaining "potential thermal energy" would be wasted.

Now instead of one thermometric device or perhaps a few thermocouples, imagine a reaction vessel connected to the sink with an almost infinite number of thermocouples. Each couple would measure the temperature of an almost infinitesimally small segment of the reaction vessel. A jump in potential would be registered in each of the individual couples in response to the instantaneous chemical reaction. Each of these potential jumps would be of the same magnitude as the single jump registered in the classical calorimeter. The heat produced by the reaction would be transferred very rapidly from the reaction vessel to the sink through the thermocouple wires. Thus the response of the thermocouples would decay very rapidly. However, all of the single electrical potentials could be made additive by wiring the thermocouples in series. The result would be one very high though rapidly decaying spike of potential. In effect the duration of the potential in the classical calorimeter has been traded for the height of the potential. It should be noted that many of the classical microcalorimeters have used banks of thermocouples for measuring the temperature change of the reaction vessel. Generally, these thermopiles included less than one hundred fifty pairs of junctions. The thermal response time of these instruments remained very long. In contrast, heat burst microcalorimeters employ thousands of thermocouples and the thermal response time is made as short as is practical.

In a phase change conduction microcalorimeter, the quantity of heat produced is measured by the amount of an isothermal phase change which it produces in the calorimeter material. The ice calorimeter is the most common and the most convenient type of phase change calorimeter. Basically an ice calorimeter consists of the reaction vessel sealed in an outer vessel which is filled with air free water--ice, and mercury. The bottom of the outer vessel is connected by means of a small glass tube to a device for measuring the change in volume of the water ice mixture. The concentric vessels are completely immersed in a mixture of ice and water in a Dewar flask. Thermal effects occurring in the reaction vessel transfer heat to the water ice mixture in the outer vessel and hence cause part of the ice or melt or water to freeze. The amount of heat transferred is determined by measuring the change in volume. Valee (1962) has reported a very simple design for an ice calorimeter. His instrument is constructed of concentric glass containers. Because of the isothermal characteristic of the ice calorimeter, it is possible to keep the heat exchange with the ambient very low. The apparatus is therefore particularly useful for determining small or very slow heat effects.

Some disadvantages of ice calorimeters have been reported. Swietoslawski (1946) reported that some secondary phenomena apparently occur inside the ice microcalorimeter. He used twin ice calorimeters of conventional size and equal volume to determine whether or not the rate of volume changes would be the same when both calorimeters were placed in the same large ice bath. The results of this experiment were negative. The same author theorized that the erratic behavior was caused by the hydraulic head within the calorimeter which prevented the existence of a thermodynamic equilibrium. He did succeed in building an ice calorimeter which could measure heating rates as low as 0.03 calories per hour. However, this required considerable skill on the part of the experimenter and still occasional erratic results were obtained.

A second disadvantage of the ice calorimeter is that it can be employed only at 0 degrees C. This disadvantage is partially removed by employing substances other than ice. Sturtevant (1945) reported that diphenylmethane, diphenyl ether, and acetic acid have all been used in place of ice. Phase changes other than the freezing-melting one can also be used. Chessick, Young, and Zettlemoyer (1954) reported using a phase change microcalorimeter with liquid nitrogen being vaporized.

Statistically the overall error for measuring heat of immersion in their calorimeter was less than 5 per cent.

If both of the reactants to be studied can be pumped through small tubes, a flow type microcalorimeter may be employed. Flow calorimeters represent a special type of conduction calorimeter. Stoesser and Gill (1967) described a precision flow microcalorimeter. The reactants are continuously pumped into the mixing chamber and the product is continuously removed. The thermal effect of the reaction is determined by measuring the equilibrium rate of heat removal. Obviously it is not possible to measure the heat of immersion of a solid using the flow calorimeter. However the stopped flow calorimeter such as was suggested by Berger and Stoddart (1965) suggests some possibilities.

2.3 Temperature Measurement

2.3.1 Background

Wilhoit (1967a) reported that the calorimetrist is likely to spend more of his time in measuring and controlling temperature than any other single activity. Progress in microcalorimetry is dependent on the availability of suitable thermometers, sufficient sensitivity, and stability in the temperature range of interest. To be suitable for use in a microcalorimeter, a thermometer must not introduce appreciable disturbing influences on the measurement. In other words, the sensor must be small in size and in heat capacity and not conduct excessive heat to or from the calorimeter. Usually remote recording and rapid response to changes of temperature are important characteristics.

The various calorimeter designs have differing requirements for the temperature measuring equipment. Frequently even one calorimeter will require several kinds of temperature measurement. Therefore it is not possible to generally recommend a particular thermometer for microcalorimeter applications. Comparison calorimeters use thermometric devices to measure the temperature difference between the reaction vessel and a reference vessel. Makrides and Hackerman (1959) reported using twin Dewar flasks in a constant temperature bath for reaction and reference vessels. They treated each of the flasks identically except for the absence of a reaction in the reference cell. Identical equipment was installed in the two flasks, similar sample holders were broken in each flask, and the stirrers were connected by a positive drive system, so that energy inputs to each flask was as near identical as possible.

Other authors, for example Young and Bogel (1932) have used references without any equipment in them in an effort to maintain a stable reference temperature. Some correction for the work input to the reaction vessel is then necessary unless this energy input can be kept sufficiently low (Privalov and Monaselidge, 1966).

The difference between the temperatures of two surfaces must be measured in a comparison calorimeter. A similar measurement is necessary also in a nonadiabatic calorimeter if the heat exchange between the calorimeter and the jacket is to be evaluated. Frequently these temperature sensors are placed directly on the surfaces. When this is done, it should be established that the thermometer does not introduce undesirable disturbances in the temperature distribution. The primary thermometer requirements for this type of measurement are a high sensitivity (since the differences may be small) and a short response time (because temperature changes may be rapid).

Compensation calorimeters are very similar to the comparison units except that the reference vessel is maintained at the temperature of the reaction vessel. Berghausen (1954) reported controlling the reference vessel temperature to within one micro-degree C of the temperature of the reaction vessel. If the two vessels are identical and are treated identically except for the reaction occurring in the reaction vessel and the energy added to the reference vessel, the heat of reaction can be determined by measuring the heat added to the reference vessel. A similar temperature sensor is required in calorimeters using adiabatic jackets. The requirements for these temperature sensors are very similar to the requirements for the sensors in the comparison

calorimeters. The primary difference is that the accuracy of the sensors in the compensation calorimeter is unimportant since it serves only as a component in the control circuit as opposed to the sensor in the comparison calorimeter which is being used to obtain a measurement.

A few microcalorimeters with one vessel have been designed. In this case the temperature sensor must be capable of measuring the absolute temperature instead of a relative temperature between two bodies. Frisch and Mackle (1965) reported using this type of calorimeter. The accuracy of this type of instrument is usually limited for rather obvious reasons. If a temperature sensor must measure a temperature change from 100 degrees to 101 degrees with an accuracy of 1%, the accuracy of the sensor must be 0.01%. On the other hand if a sensor must sense the difference between two bodies and the difference varies from zero to one degree, the measurement can be made with an accuracy of 1% with a sensor that is accurate to only plus or minus 1%. High accuracy temperature sensors usually either add thermal energy to the bodies which they are sensing or are thermal conductors to the ambient.

Kington and Smith (1964) have combined some of the advantages of the absolute temperature calorimeter with those of the comparison calorimeter. They use a single reaction vessel but compare its temperature to a metal block whose temperature in turn is followed by an absolute temperature measuring device. In this way they are able

to measure the absolute temperature changes of the reaction vessel but have isolated the undesirable characteristics of the absolute temperature measuring equipment.

Absolute temperature sensors are also necessary to measure the temperature at which the measurement is made. Accuracy for these measurements usually is much less important than for the measurement of the change in temperature in the reaction vessel. Usually accuracies of plus or minus 0.1 degree or even 1 degree C are sufficient.

2.3.2 Mercury-in-Glass Thermometers

Mercury-in-glass thermometers have played an important role in calorimeters designed for measuring the heats of combustion. Although they are not often used in microcalorimeters, they should not be entirely overlooked. These thermometers allow the measurement of temperatures with moderate precision in the range of -35 degrees to 360 degrees, or even higher if the mercury is under pressure. The short interval mercury thermometer is the most important in calorimetric work. The Beckmann type can be read with a lense to 0.001 degrees or with a microscope to 0.5 millidegrees C (Keffler, 1930). Barry (1920) has described a thermometer with a range of 15 to 21 degrees C which can be read to 0.1 millidegree. He considers this to be about the limit of precision obtainable with mercury thermometers.

Mercury thermometers have several disadvantages. Sensitive mercury thermometers necessarily have a relatively high lag and therefore are not suitable for the observation of rapidly changing temperatures. The volume of the bulb of a good mercury-in-glass thermometer will change when heated. It may not regain its original volume for several days. Errors of as much as 0.01 degrees for each 10 degrees the bulb has been heated above the normal temperature are common. The difficulty in adapting them to remote indicating, recording, and controlling is also a disadvantage. Busse (1941) had discussed the various errors associated with mercury-in-glass thermometers. These thermometers are too large, their lag times are too long, and the thermal conduction along their stems is too large for them to be employed inside the reaction vessel of microcalorimeters. However they are being used to measure the temperature of the jackets.

2.3.3 Resistance Thermometers

The measurement of temperature as a function of the electrical resistance of a sensitive element is a familiar method. Resistance thermometers may be produced from a coil of metallic wire such as copper, nickel, or platinum; a semi-conducting element such as carbon or germanium or from a semi-conducting metallic oxide. Because of the considerable versatility, reliability, and sensitivity, resistance thermometers have a wide application to calorimetry.

Daneman and Mergner (1967) indicated that platinum is the most popular resistance thermometer sensor because it can be obtained in a highly reproducible and pure condition, is relatively unaffected by aging or by gases and fumes over a wide temperature range, can be drawn into fine wires, and has a high melting point. Many other metals and alloys have temperature coefficients of resistivity somewhat larger than platinum's 0.4 per cent per degree. However, these other materials are not as widely employed as platinum for precise measurements because of their greater susceptibility to external physical and chemical effects.

Watson (1966a) indicated that because mechanical strain alters the electrical resistance of metals, platinum resistance thermometers must be wound of annealed wire on mica supports in such a way that the metal is subjected to as slight a strain as possible when the thermometer is heated or cooled. For most applications the coil is enclosed in a sealed glass or silica tube. However, to minimize the lag of the thermometer for calorimetric applications, the coil may be enclosed in a thin metal case. In this way it is possible to achieve a time response as short as one micro second.

The principal disadvantages of platinum resistance thermometers are their relatively high cost and the self heating caused by the energy dissapation in the sensors. The self heating disadvantage is of course a characteristic of all resistance thermometers. Other sources of errors with these thermometric devices include the resistance of the leads and thermoelectric emf's in the circuits.

Loeffler (1967) indicated that the cost of resistance thermometers can be decreased if nickel sensors are substituted for the platinum units. The thermal coefficient of resistivity of nickel is larger than that for platinum. However the nickel sensors are more non-linear. Rall and Hornbaker (1967a) reported that Balco, an iron nickel alloy has similar characteristics to those of nickel. Westrum and Eyring (1952) have utilized copper wire as a resistance thermometric sensor in an automatic control circuit in a compensation type calorimeter. The copper sensor is much less expensive than any of those previously mentioned. However, its thermal coefficient of resistivity is not as well defined nor as large as that of nickel or Balco. In spite of these problems, Quigg (1966) was able to measure small temperature differences with a copper sensor.

The resistance of certain semiconductors made from inpurity doped metallic oxides is strongly dependent on temperature. A thermistor is made by connecting two lead wires to a small bead of this material. Even when covered with glass, thermistors are usually one millimeter or less in diameter. The temperature coefficient of resistance for thermistors is large and negative. Richards (1967) reported a typical coefficient of minus 4.5 per cent per degree. The magnitude of this coefficient is about eleven times that of platinum. Usually thermistors are manufactured to have a high resistance in the temperature range in which they are to be employed so that the resistance of the leads can be ignored and the self heating will be minimized. The functional relationship between resistance and temperature for thermistors is highly nonlinear and is difficult to represent mathematically. However, for use over a limited temperature range, it is possible to use an exponential function to fit the relationship reasonably well.

The stability and reproducability of the resistance of thermistors is generally lower than for metallic resistance thermometers. Therefore, they are not generally practical for making accurate measurements of absolute temperature. Nevertheless, Hutchinson (1947) and Muira et al. (1956) both were able to use thermistors to measure the absolute temperature change of a reaction vessel employed for studying the heats of immersion. Over short time periods, sensitivities of plus or minus 10 micro degrees have been reported by Sharifov et al. (1966). Manufacturing tolerances for thermistors tend to be very large. However, matched thermistors are now available for comparison measurements in microcalorimetry (Nancollas and Hardy, 1967). These authors also indicate that the stability problem is reduced by using very low voltages. The heat capacity of most thermistors is very low. However, the surface area for heat exchange is also usually low; therefore, the time response may not be any better, if as good as, metallic resistance thermometers.

Some of the disadvantages of thermistors are being overcome by replacing them with germanium temperature sensors. Maker (1968) reported measuring temperatures with a germanium transitor with the base connector left open circuited. This sensor is shown to have a sensitivity at least as high as that of a thermistor, to have a linear resistance as a function of temperature, and to be stable over long time periods. The disadvantage of this temperature sensor is the relatively long time constant. Pure crystals of germanium have been shown to have a slightly lower sensitivity than the germanium transitor. However the crystals can be manufactured to have large surface areas and thus very small time constants. Rall and Hornbaker (1967) indicated that germanium crystals may have an accuracy and sensitivity as high as those of any resistance thermal sensor available.

2.3.4 Resistance Thermometry Circuits

Several methods are available for accurately determining the change in resistance of the resistive thermometers. Daneman and Mergner (1967) have discussed direct current methods in precision resistance thermometry. Each of the direct current bridges mentioned below is described by them in more detail. The Mueller bridge is the most commonly used method for accurately measuring the absolute temperature with platinum resistance thermometers in the Western Hemisphere. It utilizes elements of equal resistance in the ratio arms of the bridge circuit to provide the following characteristics. If the resistance of the leads to the temperature sensor is constant, this bridge can compensate for the lead resistance with very high accuracy. The circuit employed reduces the effect of switch contact resistances in the measuring arm. However, the contact resistance of the internal switches of the bridge is very critical. This bridge is available in several models with accuracies ranging from one part in one million to one part in one hundred million. The latter accuracy represents a temperature measurement of plus or minus 0.1 millidegree. With the present technology, errors in thermometric measurements prevent accuracies any greater than can be achieved with the Mueller bridge.

In the Eastern Hemisphere the Smith type III D.C. bridge is the most frequently used detector in precision resistance thermometry. The following characteristics of this bridge are a result of the ratio of the resistance of the calibrated variable arm and the thermometer resistance being about one hundred. This bridge is easier to use and the contact resistance of the internal switches is not as critical as with the Mueller bridge. The disadvantages of the Smith bridge include less accurate compensation for the resistance of the leads to the temperature sensor, and the effect of switch contact resistances in the measuring arm are greater than in the previously mentioned bridge.

Several automatic or direct reading bridges are available. However, their accuracy is less than that of the Mueller or the Smith type III bridges. The potentiometric method of measuring resistance offers some advantages in thermometry. A constant current is passed through the thermometer and an external standard resistance which is connected in series. The resistance of the thermometer may be calculated from the measured ratio of the potential drops across the thermometer and the standard resistance. If a potentiometer is used for this measurement, the procedure may be simplified by connecting the standard resistance in place of the standard cell. A potentiometer is somewhat more economical than a bridge of the same accuracy, although the potentiometric method requires a more sensitive null detector and a source of more accurately controlled current. It has a very definite advantage for the measurement of low resistances. Since no current flows in the potential leads, their resistance has very little effect on the measurement. Hall (1966) indicated that the most serious disadvantage of potentiometers is that their maximum accuracy does not equal that of the best bridges.

Alternating current methods of resistance thermometry are employed more frequently in microcalorimetry than are the D.C. methods. By using narrow band filters, it is possible to eliminate nearly all stray voltages in alternating current equipment. High gain alternating current amplifiers are less expensive than their D.C. counterparts. Inductors and capacitors can sometimes be used advantageously in alternating current equipment. There are also several disadvantages associated with A.C. equipment. The leads from the temperature sensor to the detector and from the detector to the amplifier or any other equipment must be kept short, and their positions relative to each other and to other equipment in the room must remain constant. Any relative motion of the leads will change the inductance and capacitance characteristics of the leads. The A.C. properties of the resistance temperature sensor must also be considered. Morrison and Hanlan (1957) reported using a Wheatstone bridge with thermistor type temperature sensors in their calorimetry work. This bridge or simple modifications of it has been frequently used in microcalorimetry. Daneman and Mergner (1957a) indicated that there are at least three bridges that are more accurate than the Wheatstone design. The Hill and Miller bridge is accurate to one micro degree. The Frisch and Mackle bridge is more frequently used in calorimetry even though its accuracy is somewhat less. For comparative temperature measurements the Foord, Langlind, and Binnie bridge is frequently used.

For microcalorimetric measurements, it is usually necessary to have continuous records of the temperatures measured. Over very small temperature ranges, the inbalance in any of the bridges discussed is approximately proportional to the change in a resistance thermometer. Very sensitive galvanometers or electronic null detectors can be connected across the terminals of these bridges to give a continuous read out of the temperature change. For continuous recording of the temperature change, a high gain, low noise amplifier can be connected across the bridge terminals. If an A.C. bridge is being used, a narrow band amplifier should be selected. Similar techniques are used for automatic recording when the potentiometric method is used. However, Wilhoit (1967) indicated that the instrumentation for automatic recording with potentiometers is somewhat less expensive than that for bridges.

2.3.5 Thermocouples

In microcalorimetry temperatures are frequently measured with thermocouples. The electric potential generated by a thermocouple is directly proportional to the temperature difference between the hot and cold junctions. The thermoelectric power and thus the electrical potential per degree of temperature difference is of the order of 50 microvolts per degree, depending on the metals and temperature. Thermocouples are well suited for measuring temperature differences. They may also be used for absolute measurements by keeping one junction, the reference junction, at a constant temperature. Holmes (1968), however, indicated that thermocouples generally cannot be relied upon to be better than about one part in one thousand. Therefore, to have an accuracy of 0.1 millidegree, the hot and cold junction must be within 0.1 degree C. Thermocouples can be made to have low heat capacities and small lags if constructed of fine wires, and thus are capable of following rapid temperature changes. Another important advantage of thermocouples is that many junctions may be connected in series and carefully mounted on a surface or throughout a volume to average out slight temperature irregularities in the body under observation. Kitzinger and Benzinger (1967) reported covering the reaction chamber with 10,000 thermocouple junctions.

A large variety of materials are being used in the manufacture of thermocouples for calorimetry. Pirro (1967) reported that generally platinum-platinum rhodium thermocouples are preferable for high precision measurements. However, Chromel-alumel is attractive particularly because of its very small diameter and relatively high thermoelectric power. King (1968) reported that gold-nickel thermocouples, if properly constructed, are desirable for measuring temperature differences and for sensing surface temperatures. Chromel-constantan junctions are also employed in microcalorimeters.

One difficulty of junctions in which neither lead is copper is that normally a junction between the thermocouples and the lead wires will be necessary. Evans and Richards (1952) indicated that chromel-constantan and copper-constantan junctions could be combined so as to avoid heterogeneous junctions between the thermocouples or thermopile and the leads.

The measurement of low D.C. voltages is required when thermocouples are employed. The reduction of noise and extraneous sources of potential below the level of a few microvolts requires the exercise of some care. Potentials of this magnitude are produced by electrostatic effects, changes in the magnetic field, insulation leakage, thermoelectric effects, inhomogeneities in the wires in the thermocouple, and instability in the ground. The junctions are usually pressed together or welded. An electroplating process for producing large numbers of thermocouples for microcalorimetry has also been reported by Evans et al. (1968).

The electric potential generated by a thermocouple is usually measured with a potentiometer. Since the potentials developed by thermocouples are small, potentiometers of high precision are required for calorimetric work. Interpolation between the steps of the last decade of the potentiometer is accomplished with galvanometers or ammeters (Lindeck method) rather than with slide wires. Frequently the White double potentiometer is combined with thermocouple sensors in microcalorimetry. If a relatively small number of thermocouples are used, a sensitive galvanometer or indicating electronic D.C. null meter may be required. Gucker _et al_. (1939) and others have reported also utilizing extremely sensitive recorders to monitor the potentiometer output. When very large numbers of thermocouples are connected in series, less sensitive detectors can be selected. The nanovoltmeter is an alternate way of measuring the thermocouple potential (Berger _et al_., 1968).

Some potential errors in thermocouple measurements are accented when surface temperatures are being measured. Heat conduction along the leads to the sensor will cause the sensor temperature to vary slightly from the temperature of the surface. Watson (1966b) indicated that this problem can be reduced by mounting the sensors below the surface or placing them into grooves cut into the surface. If this is not feasible, then the leads should parallel the wall for 50 to 100 lead diameters.

Maintaining good thermal contact between the sensor and the surface may be difficult. If a thermel is measuring the temperature of a metallic surface, good electrical insulation must be provided between the sensor and the surface. This further aggravates the thermal contact problem. Watson (1966) suggested flattening the tip of the sensor or using thermocouples that have been especially prepared for the measurement of surface temperatures to overcome the thermo-contact problem.

2.3.6 Quartz Crystal Thermometers

Gardner et al. (1967) discussed a microcalorimeter that replaced the usual thermister with a quartz crystal thermometer. They indicated increased stability and greater accuracy were obtained with the quartz sensor. This thermometer is based upon a principal which is relatively new to precision thermometry. It utilizes the temperature dependence of the resonant vibrational frequency of a quartz crystal. These crystals have served for some time as a standard of frequency. However, it is possible by cutting the crystal in a different way, to produce a sensor with a resonant frequency that is nearly a linear function of temperature. A commercial version with a digital readout is available with a resolution of 0.1 millidegree (Wilhoit, 1967a).

2.4 Temperature Control

The problem of temperature control arising in microcalorimetry generally belong to one of two types--the maintenance of constant temperature or the maintenance of a constant temperature difference. The temperature control apparatus consists of three essential parts. The thermoregulator which senses the temperature or temperature difference, the relay or amplifier, and the heater. The relay or amplifier may either be automatic or manual. The heater can be an electrical resistance element, a cooling coil, or it may be the addition of warm or cold water to a well stirred bath.

The most convenient means of constant temperature control is afforded by a mercury regulator in conjunction with a sensitive electromagnetic relay. Swietoslawski (1946) discussed some of the important design criteria for this type of temperature controller in order to achieve an accuracy of plus or minus one millidegree. In order to decrease the lag of the controller, the surface area of the container should be as large as possible in relationship to its volume. To increase the sensitivity of the regulator the volume should be fairly large, perhaps one or two liters, and filled with a liquid such as toluene which has a higher coefficient of expansion than mercury. Of course, mercury is used in the part of the regulator at which the circuit is made and broken.

The current carried by the mercury contact should be as low as possible. Currents of the order of magnitude of 1 milliamp may cause sparking when the relay current is broken. The result is a fouling of the mercury surface in the capillary with an accompanying excessive sticking of the meniscus. Zettlemoyer et al. (1953), used a thyratron relay in connection with a mercury thermoregulator so that the current at the mercury contact was of the order microamperes. Very low amplitude vibrations have also been shown to reduce the sticking of the mercury meniscus. Zverev and Crestov (1968) substituted visual observation and manual on-off control for the automatic control and electric current flow. This of course permits the use of a much smaller capillary as well as eliminating the arching of the electric current.

A mercury thermoregulator provides only on-off control. Therefore the bath temperature will necessarily oscillate about an equilibrium point. To minimize this oscillation, either the room in which the bath is located should be maintained at very nearly but slightly below the temperature of the bath, or a small steady heater should be provided that will supply most of the required heat energy. The control heater should be adjusted so that it is on approximately one-half of the time. The oscillation of the control temperature can be substantially reduced by giving very small but rather high frequency vertical oscillations to the contacting wire. As the wire passes through the lower part of its oscillation, electric contact will be made. The period of the contact will vary with the height of the mercury. If the period of the oscillation of the wire is short as compared with the regulator action, this has the effect of partially changing the control to proportional or continuous.

Resistance thermometers are frequently applied in precise isothermal temperature control. Makrides and Hackerman (1959) used a thermister in a bridge circuit, the output of which was amplified by a thyratron circuit for controlling the heater. For control purposes carefully made temperature sensors are not necessary. Therefore, homemade sensors such as the copper wire resistance sensor are frequently constructed (Westrum and Eyring, 1952). The Wheatstone bridge circuit is usually satisfactory for control circuits. If a direct current bridge is selected, the output is usually indicated by a galvanometer which either controls the heater by an on-off photocell or by means of a phase-shifting thyratron circuit in conjunction with a photocell so that proportional control is obtained. If the bridge input is A.C., the output is usually then amplified directly by a thyratron circuit as indicated above.

Although any of the thermometric devices discussed in the previous section are satisfactory for maintaining a constant temperature difference between two bodies, the differential characteristic of thermocouples makes them a more frequent choice. Thermocouple control is frequently selected in adiabatic calorimetry. Morrison and Hanlan (1957) observed the deflection of a sensitive galvanometer connected to a thermopile and manually maintained adiabatic conditions by adding hot or cold water to the bath as necessary. Sturtevant (1937) reported maintaining the jacket to calorimeter vessel temperature difference to less than 0.2 millidegrees by manually controlling the jacket heating current. He also used a sensitive galvanometer to observe the potential of a thermel. Sauer (1968) attempted to provide automatic control of adiabatic conditions with thermocouple sensors. However, the accuracy of his control was much less than that of the previously mentioned systems. The compensation type calorimeter also requires a means of maintaining a minimum temperature difference. Berghausen (1954) used a D.C. breaker amplifier with 124 pairs of thermocouple junctions to maintain a reference vessel to within one microdegree of the reaction vessel in his microcalorimeter. For very accurate control work, proportional controls are always used and sometimes some degree of automatic compensation for changes in the temperature in the surroundings is also provided (Sturtevant, 1938).

2.5 Calibration and Compensation

Prior to the twentieth century the heat capacity of a calorimeter was frequently estimated from a knowledge of masses and the specific heats of the materials used in its construction. This method is rarely used in any calorimeters today and never used in microcalorimeters. Experimental calibration is essential for several reasons. First a calorimeter is not a perfectly isolated body. Even in an adiabatic calorimeter there are connections between the jacket and the calorimetric vessel. Part of the heat required to raise the temperature of these connections comes from the calorimeter vessel and part of it comes from the jacket. The proportion that comes from each source depends on the control system used with the jacket.

The only way to determine this proportion is to experimentally calibrate the instrument under conditions as nearly as possible like those during the measurements. White (1928) has shown that even constant lags in the adiabatic control have a negligible effect if the experimental calibration heat exactly duplicates that of the measured reaction. The magnitude of the heat loss and heat inputs other than the reaction heat must also be determined through an experimental calibration.

Most compensation energy used in microcalorimeters is also some form of electrical energy. The accuracy, availability, and relatively low cost of instruments for measuring electrical energy make them very desirable for calibration and compensation.

The most frequent application of electrical energy in calibration or compensation is in the form of Joule heating. For this purpose resistive heating elements are built into most calorimeter vessels. Heating elements are usually homemade from any one of several materials. Small gage manganin wire of sufficient length to make 25 to 250 ohms is frequently noninductively wound onto a Lucite or mica frame. The entire assembly is then insulated by applying several thin layers of Glyptal varnish or Parylene C. Manganin is frequently selected because of its constant resistive properties. Gucker _et al_. (1939) found that the resistance of a manganin heater changed less than 0.01 per cent for a current change from 0.005 to 0.015 amperes.

However, other materials such as constantan are also used in the heater elements. The properties of constantan are nearly constant with changes in current and temperature and it has the additional advantage of being more readily available than manganin. Belousov and Ponner (1968) reported using a constantan heater that was mounted in grooves into the calorimeter vessel. Nichrome heaters have also been reported (Stubblefield, 1965).

Several different electrical circuits have been used with these resistive heaters. Until the last year or two most of the heater circuits have either been a parallel or series combination of the heater element and a standard resistor. Four leads were provided both from the heater element and the standard resistor so that the potential drops across these two resistive elements could be compared with a potentiometer. A more accurate method of determining the energy dissipated in the series type heater circuit has been proposed by Vorob'ev and Klyuchnikov (1967).

More recently Firth and VanMal (1968) suggested that heater circuits should be compared on their ability to meet four conditions. First, the power dissipated in the heater element should not be altered significantly by variations in the element's resistance. Second, it should be possible to vary the energy dissipation from the heater over a wide range without violating the first condition. Third, it should be possible to substitute other heater elements in the circuit without altering the characteristics of the circuit with respect to the first two requirements. Fourth, because mercury cells and other batteries are frequently used as energy sources, the current drain should be minimized. Firth and VanMal went on to show that a combination series and parallel network would be much more satisfactory than the more traditional series or parallel networks. Picker (1968) suggested employing Zener diodes as heating elements in a series circuit rather than using more elaborate circuitry with the traditional resistive elements. Since the potential drop across the diode is constant, the current is directly proportional to the energy dissipated in the diode. Therefore, the stability of the power supply is not as critical as with other resistive elements in similar circuits. For compensation purposes it is sometimes desirable to remove heat energy rather than adding it. Calvet and Prat (1963) have reported using Peltier cooling with apparently good success. Other authors have questioned the accuracy of this method.

Non-electrical means of calibration have also received some attention in the last few years. The heating value of some chemical reactions is well established. Vanderzee and Swanson (1963) and Hale _et al_. (1963) calculated independently the heat of neutralization of HCl with NaOH. Their values and the value published by Parker of the National Bureau of Standards in 1965 are considered to be accurate within one part in 500. One advantage of using a chemical reaction of this type is that the reaction proceeds (and the heat is liberated) instantaneously. A disadvantage of this method is that although it may calibrate the equipment, it does not calibrate the equipment with the experimental reaction materials in it. Therefore, an electrical calibration is still necessary. Calvet and Prat (1963) reported calibrating a microcalorimeter with radioactive materials. Radioactive materials are a very stable heating source. However, the walls of the calorimeter vessel must be sufficiently thick to absorb the radiation from the materials. Also it is a steady heating which can be easily supplied by the electric calibration heater.

2.6 The Sample Holder

Almost all reports of heat of immersion or heat of adsorption studies indicate the sample of material to be immersed is sealed in a glass or metallic bulb. The bulb is broken under the surface of the liquid in the reaction vessel to initiate the reaction. A bulb serves two functions: first, as a container for the sample to separate it from the solution used in the immersion study and secondly, as a container which can be evacuated or outgassed prior to the experiment. Typical outgassing conditions for heat of immersion samples of constant thermal conditions between 110 and 400 degrees until a residual pressure of one namo-meter of mercury was attained have been reported by Whalen (1961, 1962). This treatment has been demonstrated to be necessary in order to yield reproducible heat of immersion values. Unfortunately the bulb is the most important source of uncertainty in immersional calorimetry. When the bulb is broken, a small amount of heat is given off. Millard et al. (1955) reported that the heat of breaking a ten milliliter glass sample bulb is 0.15 plus or minus 0.02 calories. Other reports indicated higher or lower values; however, frequently very erratic results have been reported.

Guderjahn et al. (1958) were the first to systematically study the heat of bulb breaking. They evacuated and sealed three sets of bulbs. The first series of bulbs were small five cubic centimeter glass containers blown in their own lab. The volume was varied by partially filling some of the bulbs with glass beads or water. The results of the tests on these bulbs were somewhat erratic. The authors credited this to varying degrees of residual strain.

A second series of metal bulbs of various volumes having openings at the ends covered with thin brassfoil were tested. The foil withstood the vacuum but could easily be penetrated by a plunger to admit water with a very small expenditure of mechanical energy. The heat evolved when a bulb was broken was approximately equal to the product of the atmospheric pressure and the volume of the empty bulb. A rather small amount of scatter was observed with the metal bulbs.

The third series consisted of glass bulbs commercially produced with a volume of about ten cubic centimeters and then annealed. The heat of breaking these bulbs exhibited slightly more scatter than did the heat for the metal bulbs; however, all of the points fell close to the PV energy line. The authors concluded that the major contribution to the heat of breaking the bulbs is the work done by the pressure of the gas above the liquid. Heat is released in the turbulent flow as the liquid rushes into the bulb.

Since a tightly sealed reaction vessel was not used, some evaporation may have occurred from the surface of the water in their reaction vessel to raise the humidity of the air that entered from the ambient to replace the volume of the bulb. This could amount to as much as 0.1 calories for a 10 ml bulb. However, the air in the cabinet surrounding the calorimeter vessel was about five degrees below the temperature of the ambient. Thus, if the ambient humidity was 50 per cent or greater, the air that entered the reaction cell was probably nearly saturated. Guderjahn et al. concluded that under the conditions of the experiment, adsorption of heat due to evaporation of water was not significant. If these authors are correct in attributing the heat of bulb breaking to the PV energy, then it is not correct to adjust the heat of immersion data by the energy adsorbed when breaking an empty bulb.

Young and Bursh (1960) found that they could remove some of the erratic behavior of the bulb breaking by using a spring loaded breaking-rod coupled with a solenoid. They attempted to determine the heat of bulb breaking by varying the amount of sample material put into similar bulbs. The apparent change in heat of immersion of these samples was attributed to the heat of bulb breaking. They fitted a curve to the data and extrapolated it to zero sample weight and called the intercept the heat of breaking. The range of their data was not adequate and the scatter was too large to provide a further check on the PV work theory.

2.7 Stirring

Most microcalorimeters include some means of stirring or mixing the contents of the reaction vessel. In general, the temperature of a body can be observed only at one or at best at a finite number of points. Therefore, not only the jacket, but also the calorimeter vessel should be at uniform and measurable temperatures if the heat losses are to be accurately evaluated and corrected. This temperature uniformity can be obtained in two ways--by taking advantage of the high thermal conductivity of some metals or by thorough stirring of the liquid.

The second reason stirrers are frequently employed is to mix the reactants. If a powder is being mixed with a liquid, an upward or downward stirring motion is selected, depending on whether the powder is heavier or lighter than the liquid. In most cases the stirring of a liquid is accomplished by a propeller. Greater efficiency is achieved by mounting the propeller in a tube through which the liquid streams. The propeller type stirrer may serve other special purposes. Hutchinson (1947) blew sample holder glass bulbs on the ends of glass tubes and then slipped the stirrer propeller over the tube down to the bulb. In the vessel the sample holder was rotated to turn the propeller. Bartell and Suggitt (1954) used their stirring rods also as the breaking rods for their glass sample bulbs. Sturtevant (1937) used a reciprocating manually operated stirrer for mixing the reactants in his microcalorimeter. The stireer consisted of five thin platinum discs on a platinum wire. The stireer was operated for 30-45 seconds at the outset of each experiment to mix the reactants. Berger and Bowman (1964) reported good mixing action by using a single stroke of a ball mixer.

Several techniques have been devised to avoid the direct connection between the calorimeter and its surroundings by a stirring shaft and to permit tight sealing of the calorimeter. Callot and Fouvry (1966) used a magnetic arrangement to bring the reactants together efficiently. Winterhalter and VanNess (1966) used continuous magnetic stirring to mix their reactants and to maintain a uniform temperature. Evans et al. (1968) and others have rotated, tipped, or swung their reaction vessels to cause mixing of the reactants and in some cases limited temperature leveling. Several authors have reported using no stirring except for the action caused by breaking the sample bulb. Belousov and Ponner (1968) placed their reaction vessel in a bath of mercury. The heat conduction of the mercury was considered to be high enough to cause temperature uniformity at the surface of its container. Calvet and others have used long thin calorimeter vessels so that rapid temperature equalization is obtained even in the absence of stirring. The heat loss to the surroundings is increased because of the large surface to volume ratio. Calvet distributed a large number of thermocouples over the surface of the calorimeter in order to more accurately evaluate this heat loss. These thermocouples further increase the rate of heat loss to the surroundings and thus the uniformity of the temperature within the reaction vessel.

The efficiency of the stirring is important. If the reaction kinetics are being studied, the temperature uniformity and mixing of the reactants must be accomplished as rapidly as possible. This requires that all materials beyond the immediate range of the stirring, or other temperature-equalization mechanisms, should have as low a heat capacity and as high a thermal conductivity as is possible. In other words, the calorimeter vessel should probably be metallic and its supports should be as light as possible. Berger and Stoddart (1965) determined the mixing efficiency of their microcalorimeter with an instantaneous reaction, the neutralization of HCl with NaOH.

If a stirrer is used, the measured heat of the reaction must be corrected for the heat of stirring. Several authors indicated difficulty in obtaining an accurate correction factor for the energy due to the stirring process. Boyd and Harkins (1942) found that introducing more than 10 grams of powder in 650 cc of liquid caused a viscosity change that significantly changed the heating rate of the stirrer. Millard *et al*. (1955) reported that it was necessary to use a voltage controller on the stirring motor in order to obtain reproducible heats of stirring. Evans and Richards (1952) found that even matched stirrers driven at the same rate of speed in identical calorimeter vessels caused a drift in temperature between the vessels of ten to twenty-five microdegrees per minute.

Similar considerations to those above also apply in the design of the jacket or sink of most microcalorimeters. Either a well stirred bath or a heavy metallic shield is employed. In a well stirred bath a much higher rate of stirring is employed than in the reaction vessel since the heat of stirring is of little significance. The size and shape of the metallic solid shield or jacket is the subject of some debate among calorimeterists. However, no studies on this subject have been reported.

2.8 Sensitivities

The heat of immersion of dry powders in liquids varies with the surface area available for adsorption and the energy level of the sites available for adsorption. Energy levels from 0.1 to 27.0 calories per gram have been reported for the heat of immersion of various dried powders. The energy available per site decreases with increasing rehydration. Therefore, greater sensitivity is required for studying the differential heats of immersion than for determining the heat of immersion of a dry powder.

The sensitivities that have been reported for the various microcalorimeters vary considerably. The volume of the reaction vessels also varies over a wide range. However, most of the basic designs have been reported to have sensitivities approaching one millicalory per 100 ml of solution. The sensitivities of the calorimeters have been determined by either statistically analyzing the data gathered from them or by determining the minimum amount of calibration energy necessary to give a deflection on the indicating equipment. This provides no check against systematic or methodical errors. Very few authors have reported any analysis of design or any computations of expected sensitivities based on their design. A few calorimeterists have attempted to optimize the wire diameter and the number of thermocouples in thermopiles in order to minimize heat loss while maximizing the potential output of the thermel. A few authors have also looked at the degree of similarity and symmetry required when using twin calorimeter vessels. Berger et al (1968) used a computer model to evaluate the conductive heat loss from their reaction vessel. They reported using this computer program to assist in the design of the instrument.

Most of the calorimeters discussed provide an easy method for determining the integral heats of the reaction. However most calorimetric studies today are also interested in the reaction kinetics, or in otherwords the heat production as a function of time. Several schemes have been devised for reconstructing the heat input as a function of time for the various types of calorimeters. However for the most part these schemes have either been insensitive to rapid changes in the heat input or over sensitive to noise in the measured values.

2.9 Some Sources of Error

Errors in microcalorimetry can arise from many sources. No attempt will be made here to list all possible sources of error. However, it does seem worthwhile mentioning some of the more important sources that have been reported by other authors. Some of these have already been mentioned earlier in this paper.

McGlashan (1964) lists four errors and means of preventing them. The heat of evaporation is large compared with the heat of immersion. Therefore, this potential source of error must be eliminated. One way to prevent evaporation is to eliminate any contact between the liquid and any vapor spaces in or around the calorimeter. As was mentioned earlier, the mixing of the reactants must be complete. The complete process that takes place within the reaction vessel must be known. Particular care must be exercised to either prevent or account for any changes in pressure or volume. The fourth source of error indicated by this author is contamination of the reactants. The surface of the powder to be immersed must not be contaminated with adsorbed molecules. In otherwords once the sample has been prepared, it should not be brought into contact with air or particularly damp air.

Vendeborgh and Spall (1968) suggested that particular care be exercised with respect to the self heating of resistance thermometers. It may not be sufficient to merely maintain the energy of the self heating at a negligible level with respect to the heat of the reaction being studied. The self heating of the temperature sensor causes its temperature to be slightly above the temperature it is to measure. If the current flow through the resistive temperature sensor changes due to an unbalance of the measuring circuit, the temperature difference between the sensor and the temperature to be measured will change. This change may be significant even though the energy given off by the self heating is negligible.

White (1928) cautions against two additional sources of error. Convective heat losses are not necessarily directly proportional to temperature differences. In fact for small temperature differences the convective heat loss is not even a smooth function. Therefore unless the heat loss is through a vacuum, the magnitude of this loss must be determined when the temperature is similar to that that will occur during the actual experiment. White also cautions the calorimeterist about the lag of temperature sensors. Modern sensors have greatly reduced this lag; however, in some installations it is still important.

Calvet and Prat (1963) listed some other causes of errors. If heat loss is being evaluated between two surfaces, either the surfaces must both be at uniform temperatures or else thermocouples or other temperature measuring devices must be distributed over the surfaces properly. If the distribution of the thermocouples on the surfaces is irregular, the emf in the detector will not be proportional to the heat flow between the surfaces. Parasitic thermoelectric emf's are also a source of error. These can be suppressed by having all electrical circuits and equipment enclosed within the calorimeter jacket. The calorimeter should be isolated from any sources of vibration. The changes in mechanical strain caused by vibration or shock produce small quantities of heat. The ambient humidity must be low. Numerous thermal and electrical effects are caused by a humid atmosphere.

Numerous authors have indicated additional sources of errors. If comparison or compensation measurements are being used, the similarity of the two vessels is extremely important. Evans and Richards (1952) found that seemingly identical stirrers produced slightly different heats of stirring when driven at the same rate of speed. Picker (1968) found that changes in the dimensions of his twin chambers as small as three micrometers or differences in the mass of the vessels as low as one milligram caused measurable errors. Several authors have found that it is difficult to provide true adiabatic conditions or to provide accurate compensation. Howard and Culbertson (1950) found it necessary to use some corrections in their adiabatic calorimeter because their temperature tended to drift. Ostrovskii et al. (1968) found it was experimentally impossible to reduce the error due to imperfect compensation in their reference vessel to below 3 per cent.

III. OBJECTIVES

As a result of the review of literature in microcalorimetry, the following three objectives were selected for the research:

1. The sensitivity coefficients and the amount of information that can be obtained from microcalorimetry measurements.
2. A numerical technique to study the effects of several parameters associated with metallic sinks on the relative temperature measurement error.
3. A new method for determining the rate of heat production in a reaction as a function of time from the temperature data.

IV. SENSITIVITY COEFFICIENTS

The sensitivity coefficients for experiments designed to measure parameters or coefficients should be studied prior to the construction of equipment. Beck (1964) indicated some of the information that can be obtained from the sensitivity coefficients. If the effect of the measured characteristic with respect to a parameter of interest is zero, this parameter cannot be determined regardless of the accuracy of the measurement. If more than one parameter is to be determined simultaneously, the sensitivity coefficients with respect to these parameters must be linearly independent.

Unlike in previous sensitivity studies, one of the parameters to be determined in a microcalorimeter may be an unconstrained variable. In some instances the heat of the reaction being studied may be known to follow a particular functional form from the reaction kinetics. Then the problem of determining the reaction heat reduces to one of establishing the constant parameters in the function. This case is no different from other sensitivity studies. However, frequently the functional form of the reaction heat is unknown or in other words the reaction heat is an unconstrained variable. The experiment must then supply sufficient information to determine a constant reaction heat value for each time increment, Δt.

The value of an unconstrained variable can be determined as a function of the independent variables if the sensitivity coefficient is non-zero. Furthermore, if the sensitivity coefficient is not zero, the measured variable can be varied indefinitely by varying the variable of interest. Therefore, no more information is available from the measured variable than the values of the unconstrained variable if the sensitivity coefficient is not zero. In the microcalorimeter, if the sensitivity of temperature with respect to reaction heat is non-zero at time, t, a unique value for the reaction heat may be determined during the preceding time increment. But no information on any other parameter, regardless of the value of its sensitivity coefficient is available from the temperature measurement simultaneously. Conversely, if the sensitivity of temperature with respect to reaction heat is zero at time t, the value of the reaction heat during the previous time increment cannot be determined, but information is available for determining other parameters with non-zero independent sensitivity coefficients.

The required sensitivity of the measurement instruments can be predicted from the sensitivity coefficients. After the experimental work has been started, the sensitivity coefficients should be compared with a statistical accuracy. If the statistical accuracy does not compare closely with the accuracy predicted from the sensitivity coefficients, the system should be checked for systematic errors. The sensitivity coefficients also provide a means of determining the optimal experimental technique.

4.1 Background

There are two methods for determining the sensitivity coefficients from a mathematical model of the experimental system. The sensitivity coefficients should be determined analytically when this is possible. Generally an analytic solution provides a better understanding of the system. If it is not possible to determine the sensitivity coefficients analytically, numerical techniques must be employed. Beck (1966) suggested a method for determining the sensitivity of a measured variable, T, with respect to a constant parameter, c:

$$T_c = \left.\frac{\partial T}{\partial c}\right/ c_o = \frac{T[c(1+\varepsilon)] - T(c)}{c\varepsilon} \tag{1}$$

where ε is a small number.

If the sensitivity of the measured variable is to be determined with respect to a second variable, y, the method must be changed to the more traditional derivative formula:

$$T_y = \left.\frac{\partial T}{\partial y}\right/_{y_o} = \frac{T(y+\varepsilon) - T(y)}{\varepsilon} \tag{2}$$

Both analytical and numerical techniques have been employed to determine the sensitivity coefficients in this study. In order to determine the sensitivity coefficients numerically, the appropriate differential equation was solved using the modified Runge-Kutta technique presented by Gill (1951). Equation (1) or (2) was used depending on whether the parameter was a constant or another function. The sensitivity coefficients were nondimensionalized by multiplying them by either the value of the constant divided by the maximum temperature or the maximum value of the parameter divided by the temperature maximum if the parameter was a function. In order to more easily detect linear dependence, unitized sensitivity coefficients--the sensitivity coefficients divided by the maximum value which it assumes through the range of interest--were graphed on the Calcomp plotter.

The calorimeter to be studied can be described by the following equation:

$$C\,\frac{dT}{dt} = q_w(t,T) + q_r(t) + q_b(t) + q_e(t)$$

$$- H[T(t) - T_s(t)] \tag{3}$$

where

C is the heat capacity of the reaction vessel and its contents.

T is the temperature of the reaction vessel.

t is the time.

q_w is the energy input to the reaction vessel from resistance thermometric devices and/or stirring. It is called the heat input due to work.

q_r is the heat of reaction.

q_b is the heat generated by breaking the sample container.

q_e is the calibration heat input.

H is the overall heat transfer coefficient. It includes radiation, conduction and convection from the total surface area of the reaction vessel.

T_s is the temperature of the cavity surrounding the reaction vessel.

The values of each of the variables in (3) were estimated from values given in the literature and from basic heat transfer considerations. The heat capacity of the reaction vessel and its contents, C, was considered to be constant. The numerical value of the heat capacity was assumed to be 15 calories per degree C if no heat input due to work was included. If stirring or resistance thermometers are employed in the calorimeter vessel, the physical size of the vessel must be increased; therefore, the heat capacity was increased to 200 calories per degree C. The overall heat transfer coefficient, H, was assumed to have a numerical value of 0.05 calories per degree C-second, if a heat input due to work was included. If energy due to work was neglected, the value for H was 0.01 calories per degree C-second.

The heat input due to work, q_w, is a function of temperature because the self heating of resistance thermometers depends on the inbalance of the bridge or potentiometer. It is also a function of time because the viscosity of the solution may vary or the speed of the stirrer may change slightly. Either of these variations will cause a change in the mechanical input of energy. Because these variations can be limited to small values and the functional form is a function of the equipment and the experimental conditions, the mechanical heat input was assumed to be a constant. If this term was included in the equation, its numerical value was set at 0.01 calories per second.

It was assumed throughout this study that the calorimeter being considered should be capable of measuring the reaction heat, q_r, as a function of time. Since all microcalorimeters remain at essentially the same temperature throughout the experiment (even adiabatic ones), any dependence of the heat of reaction on temperature should be negligible. Several functional forms were assumed for the reaction heat during this study. The total amount of heat evolved due to the reaction was also varied.

The heat caused by breaking the sample bulb, q_b, was assumed negligible throughout all of the calculations. It can be shown that the heat of reaction and the heat due to bulb breaking cannot be simultaneously determined as a function of time. Therefore the heat due to sample bulb breaking must be determined in a separate experiment in which this term will be the heat of reaction. It was shown that neglecting this term does not change the remaining sensitivity coefficients significantly.

Several heating rates and functional forms were tried for the calibration heat, q_e. The sensitivity coefficients are expected to be functions of the calibration heat. Therefore, it is anticipated that the amount of information that can be obtained about the parameters also depends on the form and magnitude of the calibration heat. The overall heat transfer coefficient is a function of temperature; therefore the integral over time of the calibration heat must be similar to the anticipated integral heat of reaction.

The functional form was restricted to those that can be accurately generated without elaborate equipment. Constant value functions, sine waves, and square waves were all tried because they are easily generated electrically. Ramp (linear increasing or decreasing) functions may be slightly more difficult to generate electrically, but they were employed in this study also. If the sensitivity coefficients are known for the ramp and constant calibration heat functions, it should be possible to predict the approximate shape of the coefficients for any heating function. Impulse calibration heating functions were also simulated because these can be accurately generated by a chemical reaction.

The temperature of the surroundings, T_s, is usually independent of the other variables. Therefore if it does not remain constant or in a constant relationship to the temperature of the reaction vessel, it must be measured. The effect of small fluctuations in the ambient temperature on the sensitivity coefficients was tested numerically and found to be negligible. Therefore, for most of the calculations T_s was considered to be a constant, the zero of the temperature scale.

4.2 Results

4.2.1 Calibration of Instrument Parameters with Only a Known Heat Input

The experiment, which represents the calibration of the Calvet microcalorimeter, can be mathematically simulated by

$$\frac{dT}{dt} = c_1 q_e + c_2 T \tag{4}$$

where

$$c_1 = \frac{1}{C} \left[\frac{°C}{cal}\right] \quad \text{and} \quad c_2 = -H/C \; [sec^{-1}]$$

Although there are several possible initial conditions, only two are very likely. If a constant heat has been applied for a sufficient length of time so that the heat loss matches the heat input, the initial temperature is

$T_i = -c_1 q_e / c_2$. For this initial condition the dimensionless sensitivity coefficients with respect to c_1 and c_2 are positive and negative unity, respectively. Therefore, only one of the constants can be determined from this experiment.

If the no heat equilibrium condition, $T_i = 0$, is selected, the temperature of the reaction vessel is given by:

$$T = \frac{-c_1}{c_2} q_e \, (1 - e^{c_2 t}) \tag{5}$$

From this equation the maximum temperature, T_m, and the dimensionless sensitivity coefficients for a constant calibration heat input can be found directly:

$$T_m = - \frac{c_1}{c_2} q_e \tag{6}$$

$$\frac{c_1}{T_m} T_{c_1} = 1 - e^{c_2 t} \tag{7}$$

$$\frac{c_2}{T_m} T_{c_2} = (1 - c_2 t) e^{c_2 t} - 1 \tag{8}$$

The sensitivities have also been numerically computed and plotted in Figure 1. These two sensitivity coefficients are clearly linearly independent even for short calibration experiments; therefore, it is possible to determine c_1 and c_2 simultaneously in one calibration experiment.

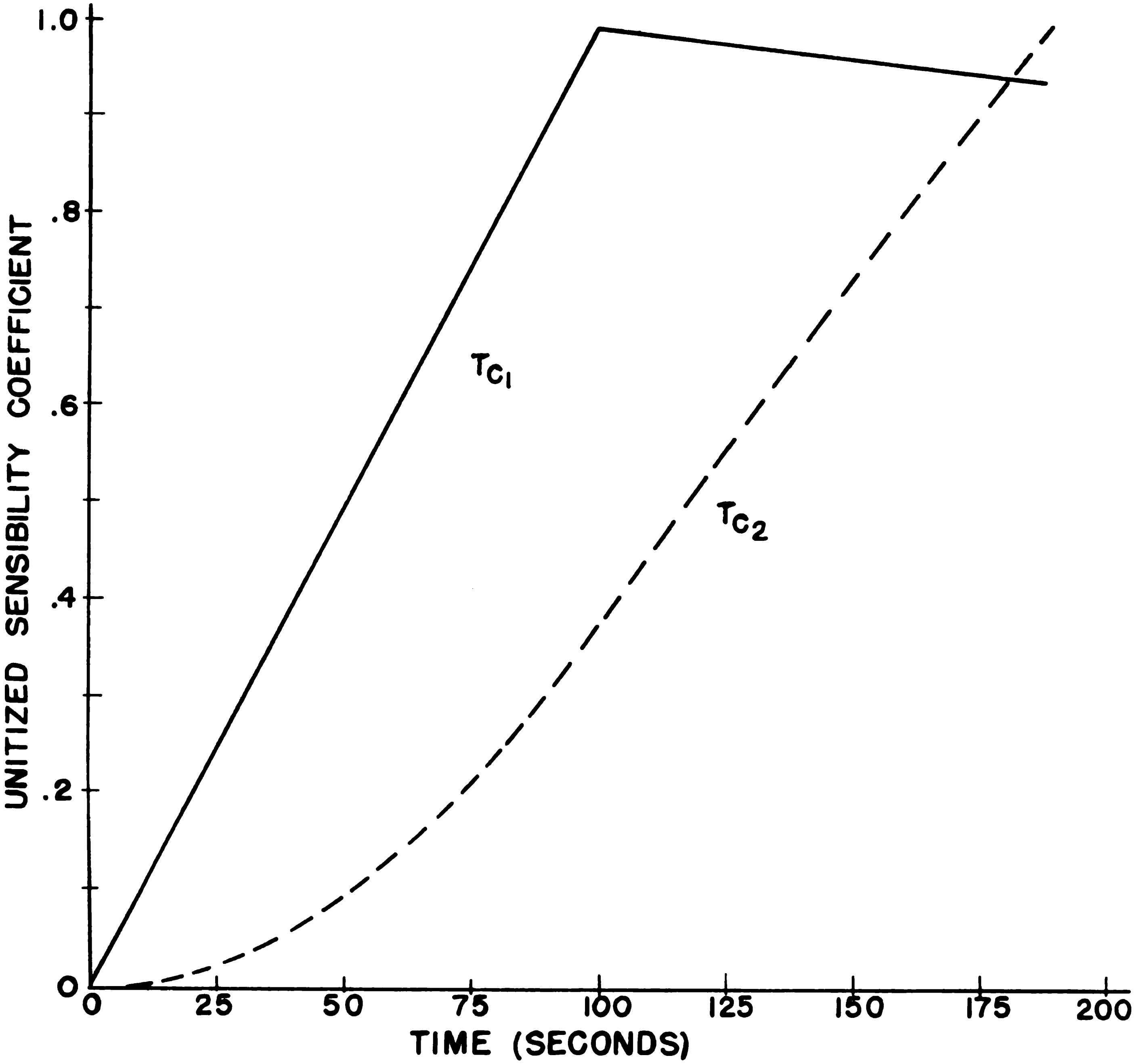

Figure 1. The sensitivities of temperature with respect to the constants c_1 and c_2 for the initial condition of $T_i = 0$ in a microcalorimeter without any heat input due to work. A constant calibration heat of 0.016 cal./sec. was added from t = 0 to t = 100 sec. The maximum values of the dimensionless sensitivity coefficients were 1.0 and 0.069 for c_1 and c_2, respectively. The maximum temperature was 0.129° C.

Sensitivities for non-constant forms of the calibration heat input were tested numerically. For heating functions that increase with time, the sensitivities tend to become more nearly linearly dependent, Figure 2. Decreasing heat functions emphasize the non-dependence and increase the sensitivity with respect to c_2, Figure 3.

4.2.2 Calibration of Instrument Parameters with Heat from Calibration and Work

This instrument is mathematically modeled by

$$\frac{dT}{dt} = c_1(q_w + q_e) + c_2 T \tag{9}$$

If the initial condition $T_i = 0$ is selected, the temperature of the reaction vessel is given by

$$T = -\frac{c_1}{c_2}(q_e + q_w)(1 - e^{c_2 t}) \tag{10}$$

and the sensitivity coefficients with respect to c_1 and q_w are clearly linearly dependent. The sensitivity coefficient with respect to c_2 and either c_1 or q_w can be determined simultaneously from this experiment.

A second initial condition that could be used with this instrument is that of an initial temperature such that the heat loss was matched by the heat input from the work energy and the calibration heater. However, this leads to a reaction vessel temperature and to sensitivity coefficients that are all constant with respect to time. This

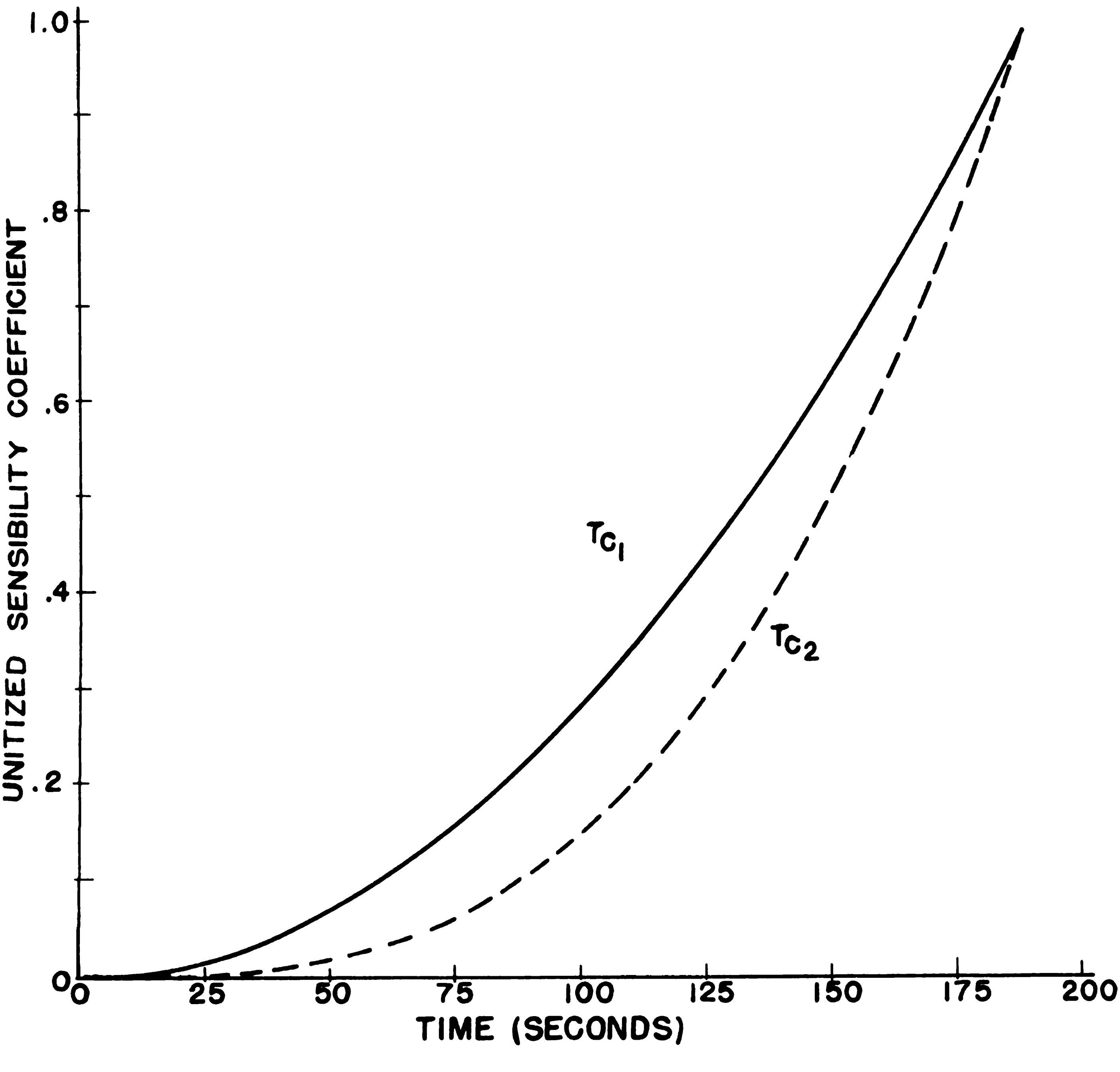

Figure 2. The sensitivities of temperature with respect to the constants c_1 and c_2 for the initial condition of $T_i = 0$ in a microcalorimeter without any heat input due to work. The calibration heat function was an increasing ramp from 0 at t = 0 to 0.04 cal./sec. at t = 200 sec. The maximum value of the dimensionless sensitivity coefficients were 1.0 and 0.041 for c_1 and c_2, respectively. The maximum temperature was .228° C.

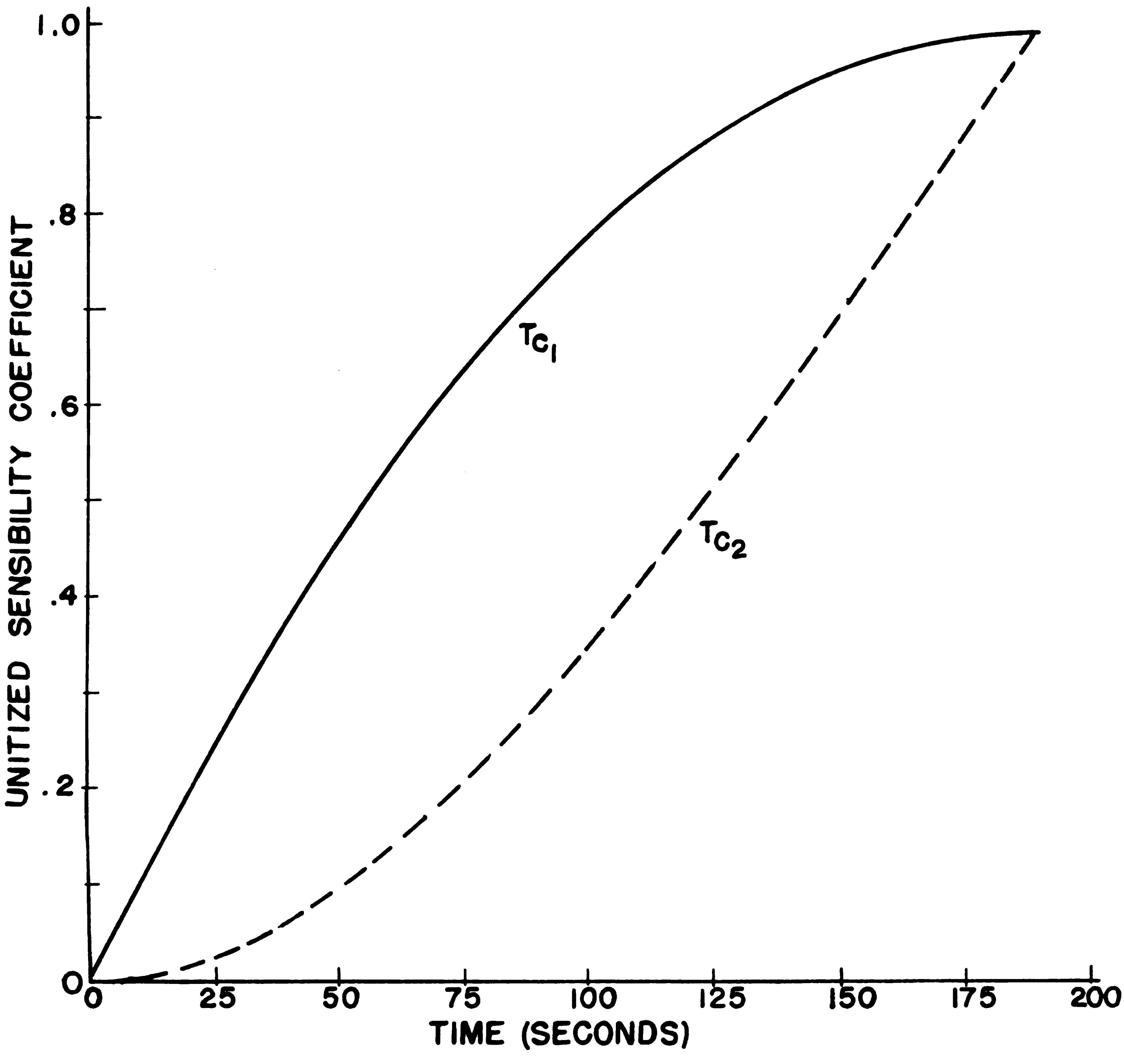

Figure 3. The sensitivities of temperature with respect to the constants c_1 and c_2 for the initial condition of $T_i = 0$ in a microcalorimeter without any heat input due to work. The calibration heat function was a decreasing ramp from 0.04 cal./sec. at t = 0 to 0 at t = 200 sec. The maximum value of the dimensionless sensitivity coefficients were 1.0 and 0.081 for c_1 and c_2, respectively. The maximum temperature was 0.245° C.

initial condition would only provide information for one of the unknowns.

A third initial condition is an initial temperature such that the heat loss is matched by the heat input due to work only. The resulting dimensionless sensitivity coefficients are:

$$\frac{c_1}{T_m} T_{c_1} = + \frac{1}{q_e + q_w} [q_w + q_e(1 - e^{c_2 t})] \tag{11}$$

$$\frac{c_2}{T_m} T_{c_2} = \frac{q_e}{q_e + q_w} (1 - c_2 t)e^{c_2 t} - 1 \tag{12}$$

$$\frac{q_w}{T_m} T_{q_w} = \frac{q_w}{q_w + q_e} \tag{13}$$

The linear independence of these coefficients can be seen in Figure 4. It is therefore possible to simultaneously determine all three unknown constants when a constant calibration heat is added and the initial temperature is $T_i = \frac{-c_1 q_w}{c_2}$.

The sensitivity coefficients for this experiment were also studied numerically. Other functional forms of the calibration heat, q_e, produce sensitivity curves similar to those in Figure 4. The important variable in the calibration experiment is time. For the first three minutes of the experiment the sensitivity coefficient with respect to c_2 varies less than 1 per cent from a constant value. Only in calibration experiments running ten to

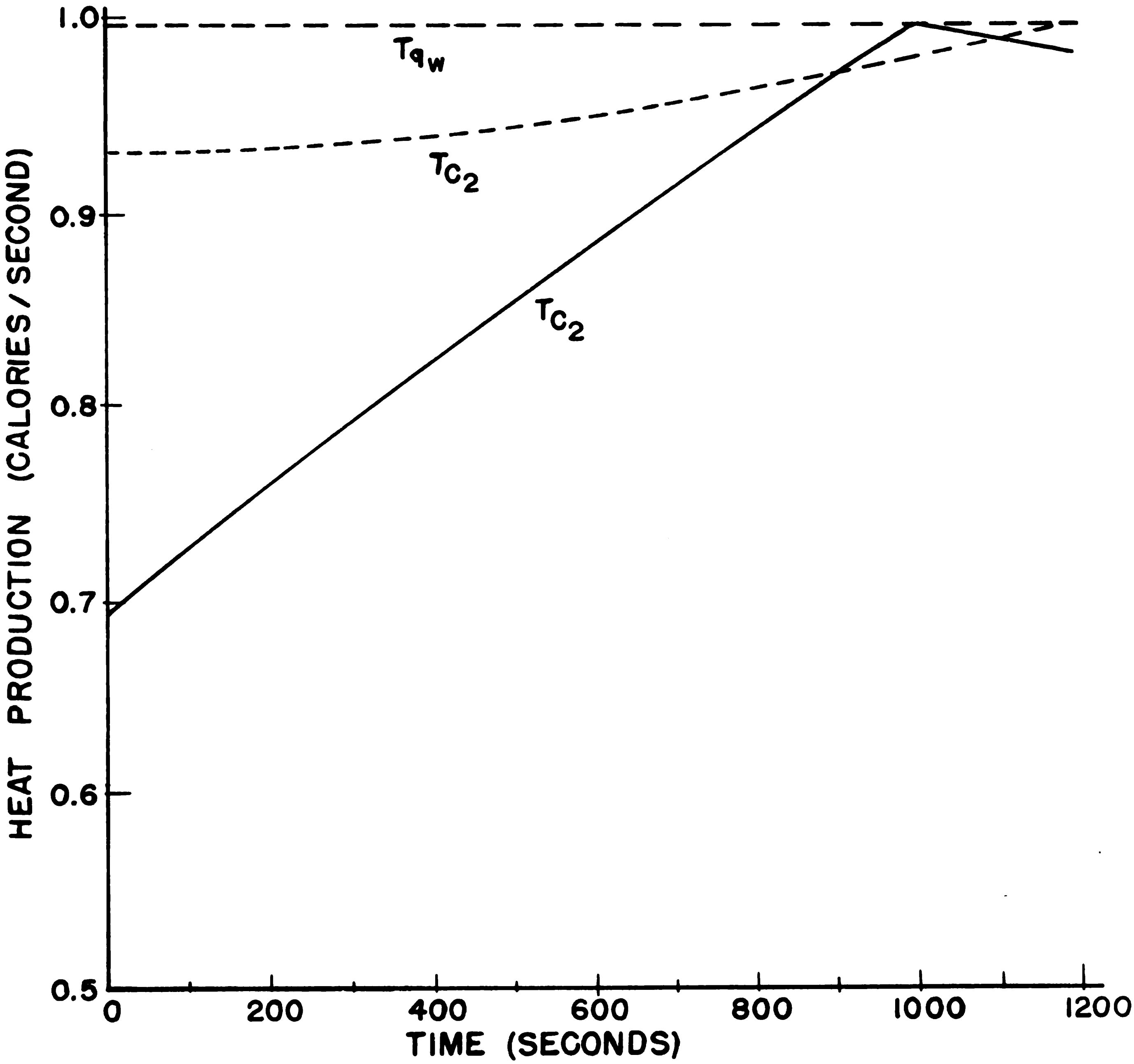

Figure 4. The sensitivity coefficients of temperature with respect to c_1, c_2, and q_w for the initial condition of $T_i = -c_1 q_w/c_2$ in a microcalorimeter with heat input due to work. A constant calibration heat of 0.016 cal./sec. was added from t = 0 to t = 1,000 sec. The maximum value of the dimensionless sensitivity coefficients was 1.0, 0.74, and 0.69 for c_1, c_2, and q_w, respectively. The maximum temperature was .288° C.

fifteen minutes can q_w and c_2 be determined simultaneously. Varying the calibration heat has the greatest impact on the sensitivity with respect to c_1.

4.2.3 Sensitivity of Temperature to Reaction Heat

The purpose of microcalorimetry studies is to determine the reaction heat. For this study the reaction heat was considered to be an unconstrained variable; therefore it is the only parameter than can be determined during the reaction if its sensitivity coefficient is not zero. The dimensional sensitivity coefficient of temperature with respect to reaction heat, given by equation (14), is derived directly from either equation (4) or equation (9) with any initial condition that is independent of the reaction heat. Thus equation (14) is correct either with or without heat due to work or bulb breaking:

$$T_{q_r} = - \frac{c_1}{c_2} (1 - e^{c_2 t}) \qquad (14)$$

Three important conclusions can be drawn from the general character of the sensitivity with respect to the heat of reaction. First, the sensitivity is non-zero for all time greater than zero. Therefore, a value for the heat of reaction can be determined uniquely for each time increment during the reaction. Thus, after the reaction is initiated, no other information on any other parameters is available from the temperature measurements. Second, several authors have reported difficulty achieving accurate adiabatic control or accurately providing compensation heat to the reference vessel. Since the sensitivity coefficient is zero at the start of the heating cycle, it is obvious that to maintain the equality of the two temperatures is not only experimentally difficult but theoretically impossible. For in effect every time increment begins a new reaction of an unknown heating rate, and until some time has elapsed the sensitivity of the temperature to the reaction heat is zero. Third, stirring and other inputs of heat due to work may decrease the accuracy of the microcalorimeter, but it does not influence the sensitivity of the temperature measurements to the reaction heat.

The necessary sensitivity of the temperature measurement apparatus for a microcalorimeter may also be determined from equation (14). If a constant rate of heat production is to be determined during a time increment, Δt, with an accuracy of $\pm\ \Delta q_r$, the temperature measurement equipment must be sensitive to temperature changes, ΔT, at least as small as:

$$\Delta T = -\frac{c_1 \Delta q_r}{c_2}\left(1 - e^{c_2 \Delta t}\right) \tag{15}$$

For example, to determine the reaction heat to within one millicalory for each one second interval in a calorimeter with a heat capacity of 15 calories per degree C and an overall heat transfer coefficient of 0.01 calories per degree C-second, it would be necessary to measure the temperature to within 6.3×10^{-5}° C. This assumes that there are no other errors to reduce the accuracy. In general the parameters of the calorimeter and the time increment will not be known exactly and may impose a more stringent requirement than is given by equation (15).

V. THE EFFECTIVENESS OF METALLIC SINKS

Several techniques have been used for providing uniform ambient conditions around the reaction vessel in microcalorimeters. When twin vessels are employed the uniformity requirement becomes more stringent than when a single vessel is employed. One of the principle advantages of twin vessels is that the temperature of the sink may be permitted to vary with time without introducing an error. Well stirred baths of water or other liquids have frequently been utilized to maintain the temperature uniformity condition. A number of the microcalorimeters reported in the last decade have substituted a large metallic block for the well stirred bath. A simpler design and a more stable ambient thermal condition are achieved by substituting the solid metallic sink for the well stirred bath.

Various designs of the metallic sinks have been reported. Berger (1968) reported using a cylindrical aluminum block. One oval shaped cavity contained both the reaction and comparison vessels. The aluminum block was set in styrofoam insulation. When operated in a closed room this sink was considered to provide a uniform thermal boundary for the two vessels. In contrast to this cylindrical block, the sinks reported by Calvet and Prat (1963) are much more complicated. Although Calvet also uses a cylindrical metallic heat sink, his calorimeter vessel is placed in an individual cavity cut into the block. The block is made of aluminum or sometimes silver. The block sets between the bases of two truncated solid metallic cones centrally placed within an outer thick metal cylinder. This cylinder is in turn enclosed in a series of concentric thermally controlled metal canisters. The temperature measurement technique is also a distinguishing characteristic between the Berger and Calvet microcalorimeters. Calvet measured the potential difference between two banks of thermocouples. One bank measured the temperature difference between the reaction vessel and its cavity in the sink and the second bank measured the temperature difference between the comparison cell and its cavity. Berger employed a single thermopile to directly measure the temperature difference between his twin vessels. The thermal sensitivities of these two instruments are similar in spite of the large variations in design.

It is very difficult to evaluate the effectiveness of the metallic sinks experimentally. Microcalorimeters require temperature measurement equipment with the highest sensitivities available for measuring the temperature difference between the reaction and comparison vessel. However, this temperature difference is much larger than the temperature variation in a good sink. Some indication of the effectiveness of the metallic sink can be obtained by increasing the reaction heat to a level that causes measurable thermal variation within the sink. However, it is not easy to relate the latter measurements to the effectiveness of the sink for reactions with small heat outputs. Both radiative and convective heat transfer characteristics are functions of the temperature differences, and therefore the sink's ability to maintain a uniform temperature with reactions of low heating value is not the same as its effectiveness with reactions of higher heating value. Furthermore because of the exacting requirements or similarity between the reaction and comparison vessels and their cavities, the cost of testing several physical models is extremely high.

This study attempted to model a cross section of a cylindrical metal sink. Individual cylindrical cavities for the reaction and comparison cells were included. The effectiveness of the sink was determined by computing the relative error in the temperature measurements. That is, the temperature measurements from the simulated real system were compared with the measurements from a reaction vessel enclosed in an absolutely constant environment.

5.1 The Computer Model

5.1.1 Selection of a Numerical Method

A number of numerical methods have been suggested for the solution of the transient heat conduction equation. These methods are classified into two broad categories, as explicit or implicit methods. The forward difference technique is the most commonly used explicit method. The second order spacial derivatives utilize the temperature values at the present time. The first order time derivatives are evaluated from the present and future temperatures. The stability of the forward difference technique is dependent on the size of the time and space increments. This technique could not be employed in the model of the heat sink because the space increments must be varied to account for the unusual configuration. This would cause instability for any reasonable time step.

The implicit method suggested by Crank and Nicolson (1947) is stable for all possible time and space increments. However, this method requires the solution of a large number of simultaneous, linear, algebraic equations at each time step. This means that the computer time required for this technique is very large. Furthermore it would be difficult to generalize this technique to three dimensions. This particular study was only concerned with the two dimensional model. However, it was desirable to

use techniques that could be easily generalized to three dimensions at some future time.

The backward difference implicit method contains fewer terms to be evaluated than the Crank-Nicolson method. This method still requires a large amount of computer time, particularly for large grid systems or in three dimensions.

A third implicit method known as the "alternating-direction-implicit-procedure," ADIP, has been suggested by Peaceman and Rachford (1955). The amount of calculations required by this method per time step is much less than other implicit methods, but the authors indicated that the necessary calculations are somewhat larger than that required by explicit methods.

In 1957 Saul'ev suggested a new explicit technique. Allada and Quon (1966) compared an extension of the technique suggested by Saul'ev and some of the other numerical methods. Their method, the alternating-direction-explicit-procedure, or ADEP, was much faster than any of the implicit techniques tested. They concluded that the ADEP appears to combine the computational ease of explicit with the stability of implicit methods.

Barakat and Clark (1966) compared another extension of the Saul'ev method with various numerical techniques. The extension reported by these authors utilizes the same molecule equation that was developed by Saul'ev but solves the equation twice at each node for each time step. First, the equation is solved for each node beginning at one corner of the object being thermally modeled and progressing to the opposite corner. Second, the equation is resolved proceeding through the array of nodes in the opposite direction. Barakat and Clark claimed that a more accurate model was obtained by averaging these two solutions for each time step period. Their technique required twice the computer time of the technique proposed by Allada and Quon. Barakat and Clark also employed the von Neumann method for stability analysis which is described in Richtmyer (1957) to show that either of the extensions of the Saul'ev method are unconditionally stable.

The Saul'ev technique was selected for the numerical model of the heat sink. The model was written so that either the Allada-Quon or the Barakat-Clark extensions could be applied.

5.1.2 The Grid System

The irregular boundary of the heat sink made the selection of a coordinate system difficult. Two considerations were paramount in the selection of the grid system. Since the primary interest is in the temperatures around the cavities, the system must accurately model the heat sink in these areas. Furthermore, if a number of different sizes and configurations were to be modeled, the boundary conditions must be determined at each node by the computer. Therefore, ease of programming the boundary conditions in a general way was also important.

A third consideration was also taken into account in the final selection of a grid system. It is very difficult to guarantee that a computer program actually performs the operations intended. The probability of errors existing in the program can be greatly reduced if the final program is developed from an initial crude but simple model. If the original model is sufficiently simple, the errors in it can be removed with reasonable certainty. If the modifications are of modest magnitude, it is possible to maintain a low probability of errors occurring in the program.

A Cartesian network was constructed on the cross section of a metallic sink for the first crude model, Figure 5. A cell, the smallest area enclosed by the lines in the network, was considered to either lie entirely in the sink or entirely outside of the sink, depending on whether more of its area lay inside or outside of the boundary of the sink. The resulting simulated boundary is illustrated by the dashed line in Figure 5. The temperature nodes used in the heat transfer calculations were considered to be located at the centroid of each cell. Since none of the nodes were located on the boundary, the following convective boundary equation was written:

$$\frac{q}{A} = h(T_\infty - T_w) = \frac{k}{d}\,(T_w - T_{i,j})\,[\text{cal./cm}^2] \qquad (16)$$

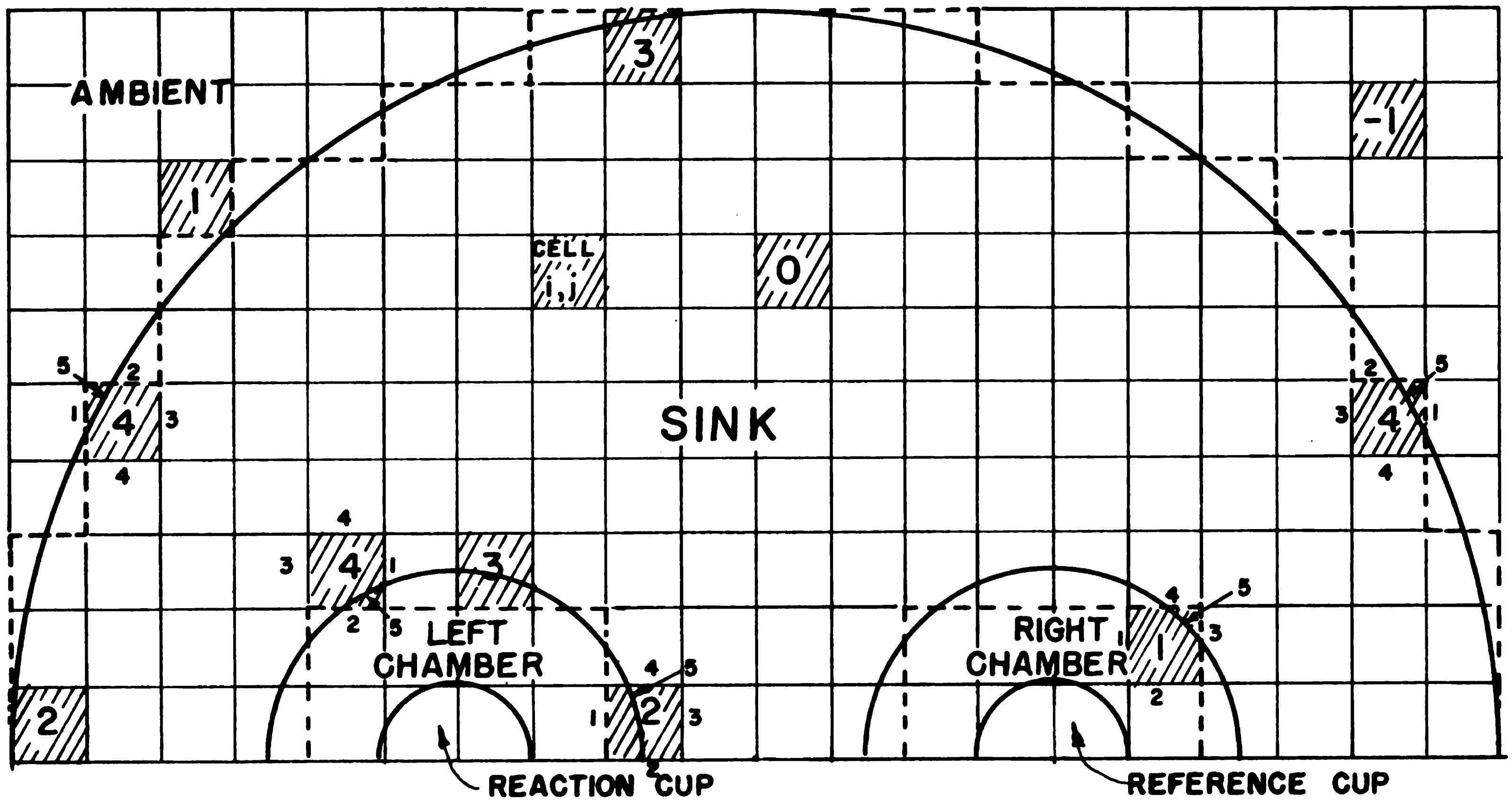

Figure 5. The grid system for the model of the sink.

where

q is the rate of heat transfer, cal./sec.

A is the boundary area, cm^2.

T is the ambient temperature, °C.

T_w is the wall temperature, °C.

$T_{i,j}$ is the temperature of the node in the cell of interest, °C.

h is the convective heat transfer coefficient, cal./°C-cm^2-sec.

k is the conductivity of the sink, cal./°C-cm-sec. and

d is the distance from the node to the surface, cm.

The wall temperature was eliminated in this equation leaving a multiplicative constant of heat transfer between the node and the ambient given by:

$$c_5 = \frac{hA}{hd + k} \text{ [cm]} \tag{17}$$

such that

$$q = kc_5(T_\infty - T_{i,j}) \text{ [cal.]} \tag{18}$$

This constant was appropriately employed in the Saul'ev model.

This model was modified to improve the approximation at the boundary. In the improved model the size and shape of each cell lying on the boundary of the sink was modified. For programming purposes each cell was recognized as having one of six possible relationships with the boundary of the sink. In order to visualize these relationships, only the second quandrant of the external boundary was considered. The sides of each cell were numbered one through four, proceeding clockwise from the 9:00 o'clock position, Figure 5. If the cell was cut by the boundary of the sink, the new surface was numbered five. Once the relationships for the cells in the second quadrant near the external boundary were found, the relationships for any other quadrant of the external boundary or any of the quadrants for the internal boundaries could be found by judiciously changing the numbering of the sides of the cell. If a cell laid entirely external to the mass of the sink, it was assigned a type of negative one. If the cell was located entirely within the sink, it was assigned a type of zero.

All cells that laid on the boundary of the sink were assigned a type of 1, 2, 3, or 4. If the boundary of the sink intersected sides three and four of a cell, that cell was assigned a type of one. If sides two and four were cut by the boundary, the cell was assigned a type two designation. In type three cells, the first and third sides were cut by the boundary of the sink. The first and second sides of a type four cell were cut by the sink's border.

For the mathematical model, the boundary of the sink was replaced in each cell by a straight line. The straight line intersected the border of the cell at the same locations as did the boundary of the sink. The numerical value for the cell's volume, the areas for heat transfer to other cells, and to the ambient, and the distance from the temperature node in this cell to the adjacent temperature nodes and to the boundary were all adjusted. The temperature node for each cell that was intersected by the boundary was assumed to lie at the centroid of the remainder of the cell. The necessary mathematical relationships for these adjustments are derived in Appendix A.

After the numerical values for the thermal coefficient of the cells intersected by the boundary of the sink had been adjusted, the necessary adjustments were made to the adjacent cells. Finally, adjustments were made to any cells that were directly influenced by the external and internal boundaries of the sink. In final form the program would accept information on the thermal characteristics, the heat transfer values, the radii of the sink and chambers, the location of the chambers, and the function describing the heat produced by the reaction. The computer model would then determine the necessary boundary conditions, compute the temperatures of the reaction and comparison cells, and find the temperature distribution in the sink for each time step. The model also computed the temperature of a reaction vessel in an ideal sink and printed out the relative error at given time intervals.

5.1.3 Tests on the Model

The accuracy of the model was tested with several techniques. The computation of boundary conditions by the model was checked by hand calculations on the various cell types. The application of the Saul'ev method and the stability of the technique was checked by printing out the entire array of temperatures for each time step. It was thus possible to see if the technique was being correctly applied to every node.

The Saul'ev technique has been shown by Barakat and Clark (1966) to be unconditionally stable. However, the coefficient in front of the temperature of the node of interest at the previous time may under some circumstances become negative. Physically, this is a violation of the second law of thermodynamics, and may cause the calculated values to oscillate about the true solution. The fact that the method is stable means that the oscillations should be damped. Because of their reduced volume, cells intersected by the boundary of the sink are more likely to cause the coefficient to become negative. In order to partially offset this condition, the heat transfer from the ambient was always employed at the future time. Even with this precaution, temperature oscillation was observed for very small boundary cells when large time steps were employed.

The ability of the model to accurately predict transient thermal behavior in the sink was also observed.

The size of the cavities and the reaction heat were both reduced to zero. The initial temperature of the sink was then set to a numerical value of 1 and the temperature of the ambient was established at 0. The transient temperature as predicted by the model at various locations agreed with the curves published by Boelter et al. (1942).

The maximum size of the time and space increments that could be employed without introducing significant errors was determined experimentally. The relative error predictions did not vary more than a few percentages for increments in length varying up to one-fourth of a chamber diameter. However, increasing the step size from 20 per cent to 40 per cent of the chamber diameter caused the predicted relative error to decrease 15 per cent. The maximum time step allowable depended on the thermal properties of the sink, the square of the space increment, and especially on the size and shape of the boundary cells. The maximum time step that would not produce oscillations was found experimentally to be:

$$\Delta t = \frac{(\Delta x)^2}{\alpha 10} \tag{19}$$

where

Δt is the time step, sec.

Δx is the space increment, cm.

α is the thermal diffusivity, cm^2/sec.

The Allada-Quon technique was compared with the Barakat-Clark method. The same results were obtained from each; therefore, the Allada-Quon procedure was adopted to reduce the necessary computer time.

5.2 Results

The numerical model of the sink was utilized to study the effect of eleven parameters on the relative error in the temperature measurement. The parameters investigated include: the kind of metal in the sink, the heat transfer coefficient from the ambient to the sink, the external temperature control, the diameter of the sink, the distance between the centers of the chambers and the center of the sink, the diameter of the chambers, the heat capacity of the twin cups, the amount of heat generated by the reaction, the length of the reaction, the overall heat transfer coefficient between the reaction vessel and the sink, and the Calvet measurement configuration as opposed to the Berger measurement configuration. The model was solved for all the parameters in an initial condition. Then the parameters were individually varied and the model was then resolved. Because of the large number of parameters, very few of the interrelationships were investigated. The study was restricted to the two dimensional model of the sink. In effect the model simulated a sink and twin vessels of infinite length. In a finite sink that totally encloses the twin vessels, the relative error should be slightly less than was predicted by the model. The magnitude of this error was not investigated.

The model was initially solved for an aluminum sink twenty centimeters in diameter. The cavities were five centimeters in diameter and located four centimeters off center, Figure 5. The heat transfer coefficients to the ambient and cups were 0.000136 and 0.000271 calories per degree centigrade-centimeter squared-second, respectively. Both represent heat transfer through still air, however the internal coefficient includes the conduction along the thermocouple wires. The heat capacity of each vessel was fifteen calories per degree centigrade. The ambient temperature was assumed to be a uniform zero degrees. The Calvet measurement technique was assumed. Five calories of reaction heat were added in the functional form shown in Figure 6.

The results of the investigation are summarized in Table 1. The significance of the relative errors depends on the measurements to be made with the instrument. For very precise measurements an error of 0.1 per cent could be significant. However, for heat of immersion studies and for any measurements on biological materials, the same error can usually be neglected. Therefore, for these measurements the standard aluminum sink is adequate.

Calvet reported employing a silver sink. The results in Table 1 show that a copper sink would provide approximately the same accuracy. The radiation heat transfer

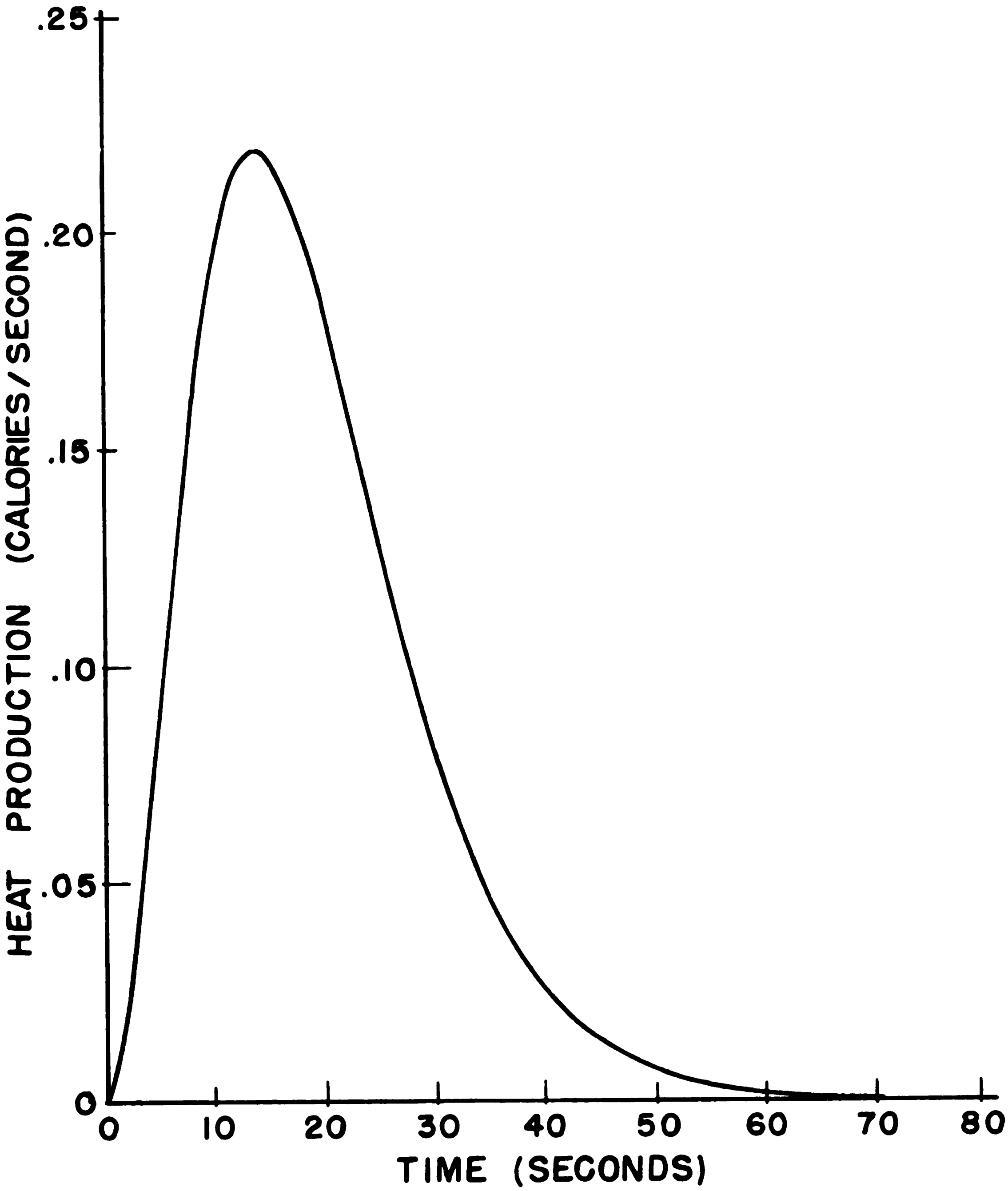

Figure 6. The functional form of the first assumed reaction heat.

TABLE 1. The maximum relative errors introduced by the non-ideal sink.

Parameter Varied	Predicted Maximum Per Cent Error
Standard conditions*	0.104
Silver heat sink	0.054
Copper heat sink	0.058
External heat transfer coefficient increased to 0.0136 cal./°C-cm^2-sec.	0.092
External heat transfer coefficient increased to 0.1 cal./°C-cm^2-sec.	0.067
Silver heat sink with external heat transfer coefficient of 0.0136 cal./°C-cm^2-sec.	0.050
Copper heat sink with external heat transfer coefficient of 0.0136 cal./°C-cm^2-sec.	0.054
Vary external temperature 0.1° C across the sink	0.126 or 0.082
Copper sink with external temperature varied 0.1° C and external heat transfer coefficient of 0.0136 cal./°C-cm^2-sec.	0.938
Copper sink with temperature variation and external heat transfer coefficient of 0.1 cal./°C-cm^2-sec.	3.56
Diameter of sink reduced to 16 cm.	0.131
Distance to cavity center reduced to 3 cm.	0.077
Diameter of cavity increased to 6 cm.	0.136
Size of reaction vessel reduced such that heat capacity is 6 cal./°C.	0.103
Heat of reaction reduced by a factor of 10	0.105
Reaction rate reduced by a factor of 10	0.099
Internal heat transfer coefficient increased to 0.001 cal./°C-cm^2-sec.	0.417
Berger Measurement technique	10

*The standard conditions were: an aluminum sink 20 cm in diameter with cavities 5 cm in diameter and located 4 cm off center. The heat transfer coefficients to the ambient and cups were 1.36×10^{-4} and 2.71×10^{-4} cal./°C-cm^2-sec., respectively. The heat capacity of each vessel was 15 cal./°C. Five cal. of heat was added during a period of 90 sec. The ambient was a uniform 0°. The Calvet measurement technique was simulated.

from the copper sink would be higher than from the silver, but if this was a serious disadvantage the copper could be plated with chrome or gold.

The heat transfer coefficients can have an important influence on the relative error. The effect of increasing the external heat transfer coefficient by a factor of 800 was only about one-tenth as large as the effect of increasing the internal heat transfer coefficient by a factor of four. However, if the external temperature was not uniform, then the magnitude of the external heat transfer coefficient was very important.

Changes in the physical size caused only small variations in the relative error. Increasing the diameters of the cavities by one centimeter, decreasing the distance between the cavities by two centimeters, or decreasing the diameter of the sink by four centimeters would change the relative error only 0.03 per cent.

Since variations in the physical size had only a small effect on the relative error in the two dimensional model, changes in the third dimension would not be expected to be important either. This provides some justification for studying only the two dimensional problem. Also, it indicates that the elaborate sinks reported by Calvet are very little better than a simple cylindrical block like Berger's.

Changes in the heat capacity of the reaction vessel, the amount of heat produced, or the length of the reaction did not alter the relative error significantly.

The large relative error shown in Table 1 for the Berger measurement technique does not reflect on the accuracy of his instrument. It does mean that the data collected from this instrument must be corrected for heat transfer. The thermocouple arrangement in the Berger instrument is easier to construct than the Calvet arrangement. In the balance, it is necessary to correct the data from the Berger instrument for heat transfer. The Calvet instrument can be designed so that no data correction is necessary.

VI. DETERMINING THE REACTION HEAT AS A FUNCTION OF TIME

6.1 Background

In order to study the reaction kinetics in a microcalorimeter, it is necessary to determine the heat of reaction as a function of time. The recent literature on microcalorimeters indicates an interest in reproducing the reaction heat curve from the temperature data. This problem represents the inverse of the usual problem. In the traditional heat transfer problem, the boundary and initial conditions along with the internal heat generations are known and the interior temperature distribution is sought. The problem studied here attempts to determine the heat generation from measurements of the temperature distribution within the body.

Several approximate procedures exist for solving such an inverse problem. If the general functional form of the reaction heat is known, the problem becomes one of determining the parameters in the function. A nonlinear least squares technique can be utilized to find the parameter values that minimize the sum of the square of the differences between the experimental and predicted temperature values. The same technique can be used for an unknown functional form by approximating the reaction heat by a polynominal or some other general function. However, this technique tends to be insensitive to erratic changes in the heating function.

Calvet and Prat (1963) have discussed two techniques for determining the reaction heat as a function of time. The first technique was developed by Tian (Calvet and Prat, 1963). He inverted the differential equation that describes the Calvet calorimeter so that the reaction heat was given as a function of temperature:

$$q = \frac{c_2}{c_1} T + \frac{1}{c_1} \frac{dT}{dt} \tag{20}$$

This procedure has several weaknesses. It implicitly assumes that the temperature indicated by the thermopile in the Calvet microcalorimeter is the same as the temperature of the reaction solution. Because of the size of the reaction vessel and the lack of stirring, this assumption may not be correct unless the reaction proceeds slowly. For fast reactions Calvet included two exponential lag terms to give adjusted temperatures, T_1, to be used in equation (20):

$$T_1 = \frac{\omega_2}{\omega_2 - \omega_1} \left(T + \frac{1}{\omega_2} \frac{dT}{dt}\right) \tag{21}$$

where

ω_1 and ω_2 are time constants in the expoential lag terms.

Calvet emphasizes that his calorimeter does not have any temperature uniformity requirements for the reaction vessel. However, the inverse technique without a lag factor, equation (20), assumes that the temperature of the vessel is uniform. Equation (21) relaxes this requirement, but it still requires the temperature distribution to be the same during the calibration and reaction experiments. The evaluation of the reaction heat with the Tian equation requires that the derivative of the temperature measurements be taken with respect to time. Derivatives of data inherently increase the magnitude of any noise in the measurements. Thus, if the Tian or Calvet equations are employed, small errors in the temperature measurements are expected to cause the predicted heat of reaction values to oscillate. Calvet reported compensating for 90 to 95 per cent of the reaction heat in his microcalorimeter in order to increase the measurement accuracy. It may be possible to eliminate the need for the compensation energy if the technique for determining the reaction heat as a function of time can be improved.

The inverse problem is not unique with calorimeters. Determining a surface heat flux from internal temperature measurements is also an inverse problem. Beck (1967) has proposed a family of methods for solving this inverse problem based on the numerical inversion of the Duhamel integral equation. He found that a simple inversion similar to that proposed by Stolz (1960) was unstable for small time steps but the stability could be increased by using future temperature measurements in a least squares approximation of the future heat fluxes. The technique proposed in the next section for determining the heat of reaction closely parallels the method developed by Beck.

6.2 Improved Techniques for Finding the Heat of Reaction

If the temperature of the reaction vessel is uniform, Duhamel's theorem in the form:

$$T(t) = T_i + \int_0^t q(\lambda)\frac{\partial\phi(t-\lambda)d\lambda}{\partial t} \tag{22}$$

may be used to calculate the heat of reaction. In this equation ϕ is the temperature response at t seconds after a unit step increase in the reaction heat. The function, ϕ, can be obtained from an exact or numerical solution if the thermal characteristics of the calorimeter are known. The exact solution was used throughout this study. The uniformity of the temperature in the reaction vessel depends on the dimensions of the vessel and the rate of the reaction. If there is no internal heat generation and if the reaction vessel is approximated by a solid cylinder, the error introduced by the assumption of uniform temperature will at no time exceed one-half the value of the Biot number (Kreith, 1965, p. 128). Thus, to maintain the error below 1 per cent, the following restriction should be observed:

$$B_i = \frac{hL}{k_s} < 0.02 \tag{23}$$

where

B_i is the Biot number.

h is the convective heat transfer coefficient, cal./°C-cm^2-sec.

k_s is the conductive heat transfer coefficient of the solid, cal./°C-cm-sec.

L is the characteristic length obtained by dividing the volume by the surface area, cm.

Approximating the reaction vessel and its contents by a solid is not expected to introduce a significant error because the extremely small temperature gradients will not establish convective currents in the solution.

For a reaction vessel with a height that is five times its radius, the restriction in equation (23) requires the radius of the reaction vessel to be less than 0.5 cm if it is filled with water ($k = 0.00149$ cal./°C-cm^2-sec.).

The restriction may not be sufficiently stringent if the heat from a rapid reaction is being measured. The temperature distribution in an infinite cylinder with uniform heat generation (Kreith, 1965, p. 46) can be compared with the convective heat loss from the same cylinder to show that equation (23) is valid for a constant heat generation. However, Calvet (1963) reported that rapid reactions caused temperature gradients to exist in a reaction vessel that maintained adequate uniformity of temperature for slower reactions. The uniformity requirement for rapid reactions was not investigated during this study.

A more general form of Duahmel's theorem would permit the temperature of the reaction vessel to be determined as a function of location as well as time. However, this was not considered for two reasons.

First, the only justification for applying Duhamel's theorem at several locations would be that the temperature uniformity requirement could be relaxed. However, if the uniformity of temperature is not maintained, natural convective currents will be established in the reaction vessel. The numerical solution of the differential equations describing natural convection in a finite cylinder represents a major study by itself. Forced convection is also present in the reaction vessel when the reactants are mixed. Finally, if ϕ were known as a function of location and time, the set of integral equations that results from applying Duhamel's equation at several locations in the vessel would have to be solved simultaneously.

The difficulty of measuring temperatures inside the reaction vessel was the second reason for not applying Duhamel's theorem as a function of location. The accuracy of the temperature sensors is reduced if they are subjected to mechanical strain. Therefore each sensor would have to be supported and protected from the currents in the reaction solution. These supports would increase the difficulty of determining ϕ.

If the integral in equation (22) is solved numerically by the trapezoidal rule, the heat generation, q_M, at time, $t = M\Delta t$, can be found directly:

$$q_M = \frac{2}{c_1} T_M - 2 \sum_{n=1}^{M-1} q_n \phi'_{M-n} \Delta t \qquad (q_o \equiv 0) \tag{24}$$

where

$c_1 = \Delta t/C$, sec.°C/cal.

$c_2 = -H\Delta t/C$.

$M = t/\Delta t$.

$n = \lambda/\Delta t$.

q_M = the heat generation at time, $M\Delta t$, cal.

q_n = the heat generation at time, $n\Delta t$, cal.

T_M = the measured temperature at time, $M\Delta t$, °C.

$\phi'_{M-n} = \frac{d\phi}{dt}(t-\lambda)$, °C/cal.-sec.

For the Calvet calorimeter described by equation (4), $\phi'_{M-n}\Delta t$ can be replaced by the derivative of the analytical solution, $e^{c_2(M-n)}$. It was assumed in the derivation of equation (24) that the temperature measurements were started before any heat was added and that the initial temperature was zero. As would be expected from the study of sensitivity coefficients, this equation tends to oscillate about the true solution and is unstable for small Δt's. The reason is that only temperature information at the present time when the sensitivities are at a minimum is employed.

6.2.1 An Improved Inverse Technique

The improved procedures given below are similar to the technique discussed by Beck (1968) for determining a surface heat flux. In order to improve the stability and to reduce the oscillation expected from equation (24), more temperature measurements and a least squares smoothing were utilized to find q_M. Temperatures at times less than $M\Delta t$ are independent of the heat generation at time $M\Delta t$; therefore, since the earlier heats are already established, the earlier temperature measurements cannot be employed. On the other hand, temperature measurements at a future time do contain information on the present rate of heat generation. In general Duhamel's theorem can be applied at future times to give:

$$T_{M+j} = c_1 \left[\sum_{n=1}^{M-1} q_n \phi'_{M-n+j} + \sum_{n=0}^{j-1} q_{M+n} \phi'_{j-n} + \frac{q_{n+j}}{2} \right] \qquad (q_o \equiv 0) \qquad (25)$$

where

$$\phi'_{a-b} = \exp[c_2(a-b)]$$

for the Calvet microcalorimeter. The heat generation term for future times may be expressed by

$$q_{M+j} = A_o + A_1 i + A_2 i^2 + \ . \ . \ . + A_\eta i^\eta \qquad (26)$$

in which the coefficient A_o is equal to q_M. Assuming that r, the number of future temperature measurements utilized is greater than η, the coefficients in this equation can be determined by minimizing the sum of the squares of the differences between the measured and predicted future temperatures.

The general temperature T_{M+j} in equation (25) can be combined with the polynominal for the future heat generation:

$$T_{M+j} = c_1 \left[\sum_{n=1}^{M-1} q_n \phi'_{M-n+j} + \sum_{p=0}^{\eta} A_p C_{pj} \right] \quad (q_o \equiv 0) \qquad (27)$$

where

$$C_{pj} = \sum_{\ell=0}^{j-1} \ell^p \phi'_{j-\ell} + \frac{j^p}{2} \qquad (28)$$

Differentiating the sum of squares with respect to the coefficients, A_p, gives the set of linear equations:

$$\sum_{j=0}^{r} \left(T_{M+j} - T_{e,M+j} \right) C_{pj} = 0 \qquad (29)$$

for

$$p=0,\ 1,\ 2,\ .\ .\ .\ \eta$$

where the subscript e denotes future measured temperatures as opposed to the future temperatures predicted by the polynominal expression for future heat generation terms. With some algebraic manipulation, this set of equations can be rewritten as:

$$\sum_{s=0}^{\eta} \beta_{r,sp} A_s = S_{rp} \qquad p=0,\ 1,\ 2,\ .\ .\ .\ \eta \tag{30}$$

where

$$\beta_{r,sp} = \beta_{r,ps} = \sum_{j=0}^{r} C_{sj} C_{pj} \qquad \begin{array}{l} 0 \leq s \leq \eta \\ 0 \leq p \leq \eta \end{array}$$

and

$$S_{rp} = \sum_{j=0}^{r} C_{pj}\ T_{e,M+j} \Big/ c_1 - \sum_{n=1}^{M-1} \sum_{j=0}^{r} C_{pj} q_n \phi'_{M-n+j}$$

or

$$S_{rp} = \sum_{j=0}^{r} \frac{C_{pj}}{c_1} T_{e,M+j} - \sum_{n=1}^{M-1} q_n \Phi_{rp,M-n}$$

where

$$\Phi_{rp,M-n} = \sum_{j=0}^{r} C_{pj} \phi_{M-n+j}$$

This system of equations can be readily solved for $A_o = q_M$ provided η is not too large.

6.3 Computer Simulation

The stability and accuracy of the Tian method, equation (20), the inverse Duhamel equation given in (24), and six of the low order members of the family of techniques suggested by (30) were compared in a computer simulation. Calvet and Prat (1963) did not report what method was employed to determine the derivative in equation (20). For this study the derivative at time $M\Delta t$ was evaluated by the following two techniques:

$$\left.\frac{dT}{dt}\right/_{M\Delta t} = \frac{T_M - T_{M-1}}{\Delta t} \tag{31}$$

and

$$\left.\frac{dT}{dt}\right/_{M\Delta t} = \frac{T_{M+1} - T_{M-1}}{2\Delta t} \tag{32}$$

The six techniques suggested by equation (30) included constant, linear, and quadratic ($\eta = 0,1,2$) polynomials for the future heats with one and two extra data points for each (for $\eta = 0$, $r = 1$ and 2; for $\eta = 1$, $r = 2$ and 3; and for $\eta = 2$, $r = 3$ and 4). Artificial temperature data was generated numerically for several heat generation functions. The inverse techniques were then employed to estimate the heat generation as a function of time. The root mean square, RMS, value of the differences between the heat generation function and the predicted values was then computed.

Three heat generation functions were selected. The first function, Figure 6, was intended to represent a moderately slow, smooth reaction heat. This function provided an opportunity to compare the accuracy of the various techniques under conditions that might be similar to an actual heat of immersion study. The effect of noise in the temperature data was also studied with this function by adding noise with a peak value of less than 1 per cent of the maximum temperature to the numerically computed temperature values. The random number function, RANF(-1), of the CDC 3600 computer was utilized to generate the noise, y, by the function:

$$y = 0.004[\mathrm{RANF}(-1) - 0.5] \tag{33}$$

The second function, Figure 7, was a step input of heat. The behavior of the various techniques near the abrupt change in heating rate provided some insight into the stability of the methods. Although it is not a rigorous definition, if the predicted heating values tended to oscillate with increasing magnitude after the step change, the technique was considered unstable for that size time step.

The third function, Figure 8, was selected to represent the reaction heat of a moderately fast reaction.

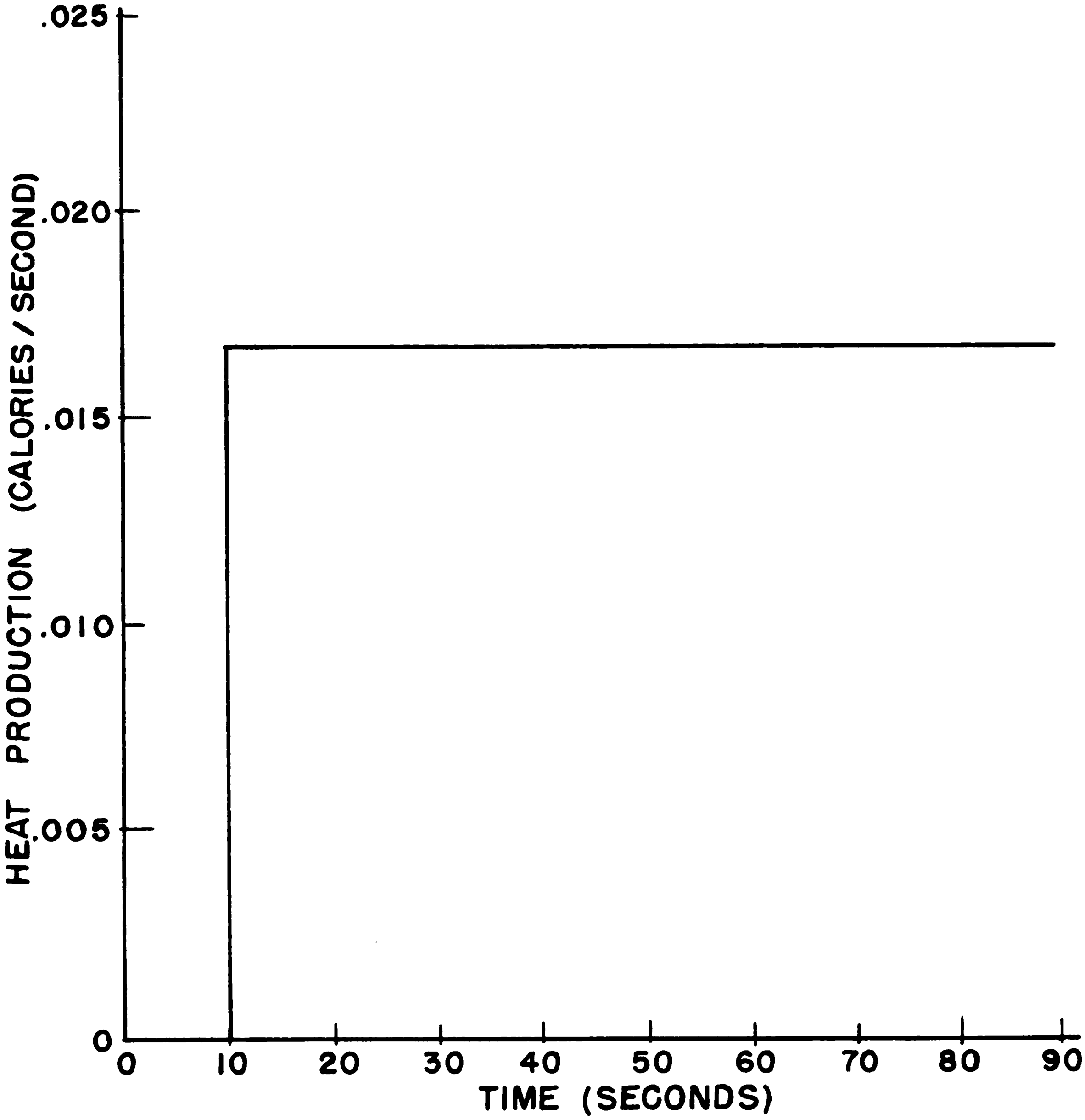

Figure 7. The second functional form selected to test the stability of the inverse techniques.

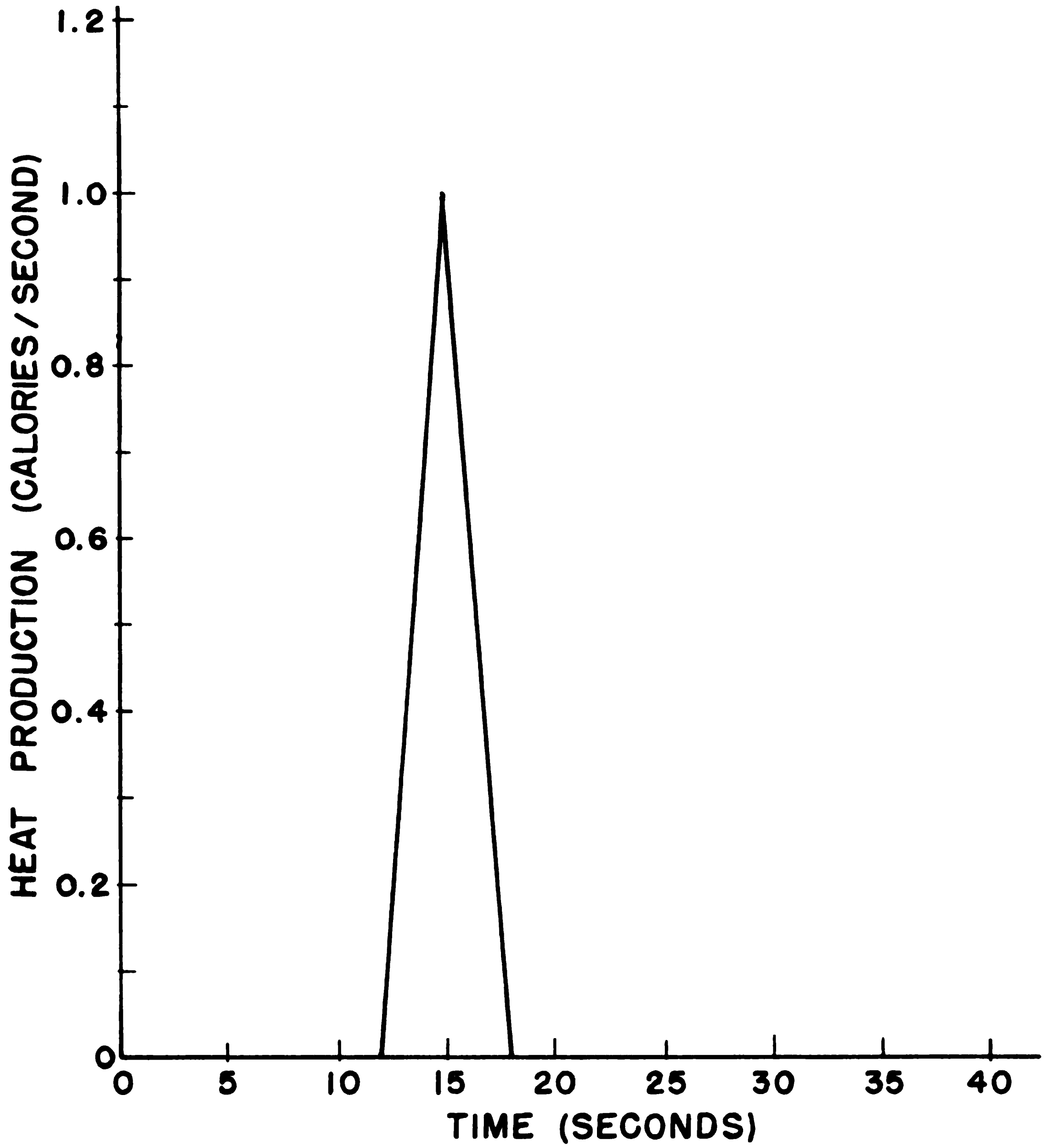

Figure 8. The third functional form selected to represent a rapid reaction.

6.4 Results

The results of the computer simulation are summarized in Table 2. The significance of the numbers in this table becomes more evident when they are compared with the average heating rate for each of the functions. The average heating rates were 0.056, 0.014, and 0.075 calories per second for functions one, two, and three, respectively. The RMS value of the error for all of the techniques using a 0.1 second time step on the first function was below 1 per cent of the average heating rate. The Tian equation with the derivative evaluated over $2\Delta t$ and several of the Duhamel methods with least squares smoothing maintained the RMS value of the errors below 1 per cent of the average heating rate with a time step of one second.

The accuracy of all of the methods was reduced when noise was added to the temperature data. Although the peak level of the noise was less than 1 per cent of the maximum temperature measured, the smallest RMS value for the errors was just below 10 per cent of the average heating rate. If the RMS value of the artificial noise is used for ΔT in equation (15), the minimum RMS value expected in the errors of the reconstructed heating rates can be predicted from the sensitivity coefficients. For the smallest through largest time steps employed, the approximate minimum expected error was 10^{-1}, 10^{-2}, and 10^{-3} calories per second, respectively. This means that the smallest RMS value of the errors to be expected with a 0.1 second time step is

TABLE 2. The RMS value of the errors of several inverse techniques.

Technique	Time Step (Sec)	Root-Mean-Square of the Errors: Heating Function No. 1	Heating Function No. 1 with Noise in the Data	Heating Function No. 2	Heating Function No. 3
Tian with derivative given by: $\frac{T_M - T_{M-1}}{\Delta t}$	0.1	4.08×10^{-4}	2.39×10^{-1}	4.63×10^{-4}	6.46×10^{-3}
	1	4.05×10^{-3}	2.53×10^{-2}	2.91×10^{-4}	6.38×10^{-2}
	10	3.71×10^{-2}	3.72×10^{-2}	8.62×10^{-4}	2.99×10^{-1}
Tian with derivative given by: $\frac{T_{M+1} - T_{M-1}}{2\Delta t}$	0.1	2.98×10^{-6}	1.19×10^{-1}	2.36×10^{-4}	1.02×10^{-3}
	1	2.64×10^{-4}	1.29×10^{-2}	7.42×10^{-4}	3.19×10^{-2}
	10	1.47×10^{-2}	1.49×10^{-2}	2.23×10^{-3}	2.11×10^{-3}
Duhamel with no least squares	0.1	1.00×10^{-5}	7.96	1.02×10^{-2}	2.04×10^{-7}
	1	9.83×10^{-4}	2.97×10^{-1}	1.01×10^{-2}	1.14×10^{-4}
	10	4.13×10^{-2}	5.57×10^{-2}	9.65×10^{-3}	1.02
Duhamel with least squares $\eta=0$, $r=1$	0.1	5.14×10^{-6}	1.20×10^{-1}	2.04×10^{-4}	1.25×10^{-3}
	1	4.02×10^{-4}	1.23×10^{-2}	9.05×10^{-4}	3.88×10^{-2}
	10	8.58×10^{-3}	8.05×10^{-3}	7.14×10^{-4}	9.74×10^{-2}
Duhamel with least squares $\eta=0$, $r=2$	0.1	2.11×10^{-5}	5.59×10^{-2}	3.02×10^{-4}	2.79×10^{-3}
	1	1.63×10^{-3}	5.69×10^{-3}	1.14×10^{-3}	7.80×10^{-2}
	10	1.81×10^{-2}	1.81×10^{-2}	1.03×10^{-3}	9.43×10^{-2}
Duhamel with least squares $\eta=1$, $r=2$	0.1	7.83×10^{-5}	1.75×10^{-1}	5.87×10^{-3}	4.34×10^{-4}
	1	7.34×10^{-4}	1.78×10^{-2}	5.87×10^{-3}	1.35×10^{-2}
	10	7.33×10^{-3}	6.69×10^{-3}	5.56×10^{-3}	5.89×10^{-1}
Duhamel with least squares $\eta=1$, $r=3$	0.1	1.35×10^{-6}	1.18×10^{-1}	2.21×10^{-4}	1.21×10^{-3}
	1	1.33×10^{-4}	1.17×10^{-2}	1.05×10^{-3}	3.86×10^{-2}
	10	8.62×10^{-3}	8.99×10^{-3}	5.77×10^{-4}	9.54×10^{-2}
Duhamel with least squares $\eta=2$, $r=3$	0.1	1.59×10^{-6}	3.03×10^{-1}	1.74×10^{-4}	5.33×10^{-4}
	1	1.88×10^{-4}	3.25×10^{-2}	1.03×10^{-3}	1.80×10^{-2}
	10	4.47×10^{-3}	5.03×10^{-3}	1.44×10^{-3}	2.53×10^{-1}
Duhamel with least squares $\eta=2$, $r=4$	0.1	1.57×10^{-6}	1.78×10^{-1}	2.05×10^{-4}	9.16×10^{-4}
	1	2.06×10^{-4}	1.87×10^{-2}	1.03×10^{-3}	2.54×10^{-2}
	10	8.51×10^{-3}	1.06×10^{-2}	1.75×10^{-3}	2.27×10^{-1}

twice the average rate of heating. The values in Table 2 indicate that all of the methods are near the limit in accuracy for the two shorter time steps. For the ten second time step the RMS values of the errors were not changed significantly by the noise.

The second heat function was selected to give some indication of the stability of the inverse methods. The Duhamel method without least squares smoothing was the only technique that exhibited large oscillations. The magnitude of the errors for the remaining methods was not considered significant because a heat of reaction is not expected to have a step change.

The third heating function was intended to approximate a rapid reaction. Because of the linear character of the function, the Duhamel technique without least squares smoothing could predict the heating function very accurately for small time steps. A real heating function would not be this linear and although it was not tested, the accuracy of the Duhamel technique would be expected to decrease sharply for a nonlinear function. The only other techniques that exhibited RMS errors below 1 per cent of the average heating rate were two of the Duhamel methods with least square smoothing. Each employed one extra data point in the least squares smoothing.

This study indicated that none of the techniques tested are unequivocally better than the remaining techniques. For the slow heating function without noise in the data, the Duhamel methods with least squares smoothing were almost always better than the other techniques. When noise was added to the data, the results were mixed for the smaller time steps. However, the error of the Duhamel method with least squares smoothing ($\eta = 0$, $r = 2$) was about one-half of the next smallest error for both time steps. The Duhamel methods with least squares smoothing were slightly better than the remaining techniques with the ten second time step. The Duhamel technique without least squares smoothing exhibited some instability. The results with the rapid reaction were mixed. The Tian equation with the derivative evaluated over $2\Delta t$ was consistently better than the Tian technique that utilized only adjacent data points. In general it can be concluded that the selection of an inverse technique should be based on the functional form of the heat of reaction and the errors in the temperature measurements.

VII. SUMMARY AND CONCLUSIONS

A survey of literature indicated three facets of microcalorimetry needed further study. The technique employed by a calorimeterist is as much art as science. The metallic heat sinks being employed vary considerably in size and shape. And the techniques for determining the reaction kinetics from temperature measurements are extremely sensitive to errors in the measured data.

A study of the sensitivity coefficients of calorimeters with and without mechanical energy being added revealed:

1. The parameters of the calorimeter cannot be determined during the experiment unless the functional form of the reaction heat is known.
2. The two parameters of a calorimeter without mechanical energy being added can be determined simultaneously by adding known heat provided the temperature measurements are started before the system reaches equilibrium.
3. If the rate of heat loss from the calorimeter vessel is equal to the mechanical energy input, the three parameters of the instrument may be

determined simultaneously by adding a known heat over a period of 15 minutes or more.

A numerical model of a solid heat sink was utilized to determine the effectiveness of metallic sinks. This model indicates that the sinks generally introduce less than 0.5 per cent error in the measurements.

A family of methods for determining the reaction heat as a function of time are introduced. The new methods are shown to be more accurate for some functional forms of the reaction heat than the technique employed by Tian and Calvet.

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APPENDICES

APPENDIX A

THE HEAT TRANSFER EQUATIONS FOR CELLS ON THE BOUNDARY OF THE SINK

THE HEAT TRANSFER EQUATIONS FOR CELLS
ON THE BOUNDARY OF THE SINK

Background

Although the following derivations are elementary, they are considered essential for understanding the computer model of the heat sink in Appendix B. Therefore, these equations are presented to aid the reader. Only two dimensional heat flow is considered, but the model is assumed to have a unit depth so that the phrases "area for heat transfer" and "cell volume" have meaning.

As was explained in Chapter V, a rectangular grid was drawn over the cross section of a sink forming small cells. A temperature node was assumed to be located at the centroid of each cell. The problem is to describe in general mathematical terms the necessary constants for a transient heat transfer equation compatible with the Saul'ev technique for cells intersected by the border of the sink.

Imagine a five sided cell with a temperature at time $n\Delta t$ of T^n. An equation is desired to give the temperature of this cell at time $(n+1)\Delta t$. In general the change in internal energy of the cell, ΔE, is equal to the net heat flow into the cell:

$$\Sigma q_i = \Delta E \tag{A-1}$$

where q_i is understood to be positive if the heat flow is inward, and negative if the heat flow is outward. The heat flow into the cell of interest from each of the adjacent cells can be approximated by:

$$q_i = \frac{k_i A_i}{d_i}(T_i - T) \tag{A-2}$$

where

k_i is the thermal conductivity, cal./°C-cm-sec.

A_i is the area for heat transfer, cm^2.

d_i is the distance between the temperature nodes, cm.

T_i is the temperature of node i, °C.

The change in internal energy of the cell of interest can be approximated by:

$$\Delta E = \frac{\rho C_p V}{\Delta t}(T^{n+1} - T^n) \tag{A-3}$$

where

ρ is the density of the material in the cell, gm/cm^3.

C_p is the specific heat of the material in the cell, cal./°C-gm.

V is the volume of the cell, cm^3.

Δt is a time increment, sec.

If the temperature of cells 1, 4, and 5 is known at time $(n+1)\Delta t$, and the temperature of cells 2 and 3 is known at time $n\Delta t$, equation (A-1) can be rewritten):

$$\frac{k_1A_1}{d_1}(T_1^{n+1} - T^{n+1}) + \frac{k_2A_2}{d_2}(T_2^{n} - T^{n}) + \frac{k_3A_3}{d_3}(T_3^{n} - T^{n})$$

$$+ \frac{k_4A_4}{d_4}(T_4^{n+1} - T^{n+1}) + \frac{k_5A_5}{d_5}(T_5^{n+1} - T^{n+1})$$

$$= \frac{\rho C_p V}{\Delta t}(T^{n+1} - T^{n}) \qquad \text{(A-4)}$$

Each parameter group, $\frac{k_iA_i}{d_i}$, can be replaced by kc_i and the constants $\frac{\rho C_p V}{k\Delta t}$ can be replaced by c_6. With these changes and some algebraic manipulation, equation (A-4) can be written in the following form:

$$T^{n+1} = [c_5T_5^{n+1} + c_4T_4^{n+1} + c_1T_1^{n+1} + c_3T_3^{n} + c_2T_2^{n}$$

$$+ (c_6 - c_3 - c_2)T^n]/(c_6 + c_1 + c_4 + c_5) \qquad \text{(A-5)}$$

If the cell of interest is located at (i,j), cells one through four may be renamed to indicate their position relative to the cell at (i,j). Cell one is located at $(i-1,j)$, cell two is at $(i,j+1)$, cell three is at $(i+1,j)$, and cell four is at $(i,j-1)$. Equation (A-5) can then be written:

$$T_{i,j}^{n+1} = [c_5T_5^{n+1} + c_4T_{i,j-1}^{n+1} + c_1T_{i-1,j}^{n+1}$$

$$+ c_2T_{i,j+1}^{n} + (c_6 - c_3 - c_2)T_{i,j}^{n}]/$$

$$(c_6 + c_1 + c_4 + c_5) \qquad \text{(A-6)}$$

If there are only four sides to cell (i,j), ($c_5 = 0$) and if $c_1 = c_2 = c_3 = c_4$, equation (A-6) reduces to the equation given by Allada and Quon (1966). Thus equation (A-6) is compatible with the Saul'ev technique. The additional cell, 5, has been included to account for heat transfer with the ambient. The problem is now reduced to one of finding the constants c_1, c_2, c_3, c_4, c_5, and c_6.

Each of the first four constants represent an area for heat transfer divided by a distance. More specifically, c_1 is equal to the area of contact between cell (i,j) and cell (i-1,j) divided by the distance between nodes (i,j) and (i-1,j) dotted into the normal of the area. It can be seen in Figure A-1 that the dot product of the distance and normal is equal to the sum of the absolute distances from each node to the plane of contact between the cells. Thus the values of c_1, c_2, c_3, and c_4 are given by:

$$c_1 = \frac{A_1}{d_{i,j,1} + d_{i-1,j,3}} \qquad \text{(A-7)}$$

$$c_2 = \frac{A_2}{d_{i,j,2} + d_{i,j+1,4}} \qquad \text{(A-8)}$$

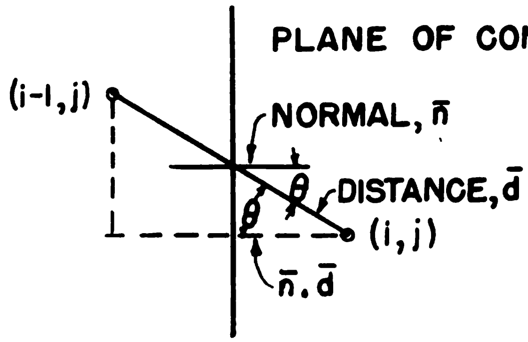

Figure A-1. Graphical computation of the dot product.

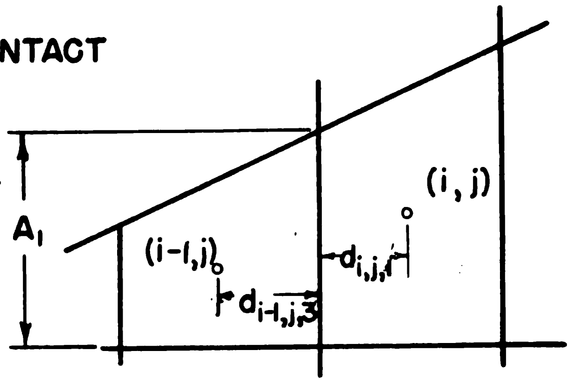

Figure A-2. The variables needed to compute c_1.

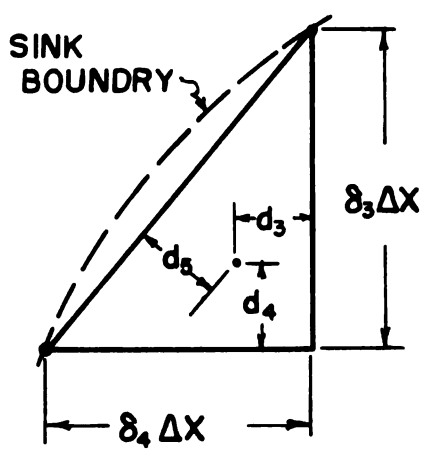

Figure A-3. A type one cell.

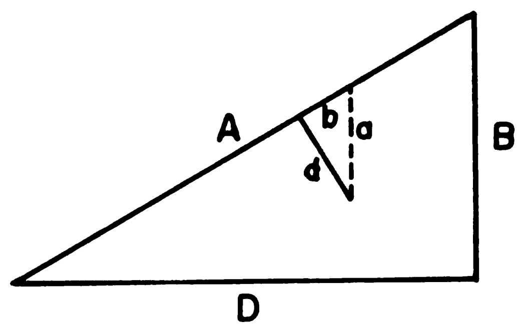

Figure A-4. The similar triangles used to find d_5 for a type one cell.

$$c_3 = \frac{A_3}{d_{i,j,3} + d_{i+1,j,1}} \qquad \text{(A-9)}$$

and

$$c_4 = \frac{A_4}{d_{i,j,4} + d_{i,j-1,2}} \qquad \text{(A-10)}$$

where $d_{i,j,k}$ is the shortest distance from node (i,j) to the k^{th} boundary of the same cell. Figure A-2 illustrates the variables in equation (A-7).

The value of c_5 was derived in Chapter V and is given by:

$$c_5 = \frac{hA_5}{hd_{i,j,5} + k} \qquad \text{(A-11)}$$

where

- h is the convective heat transfer coefficient, cal./°C-cm^2-sec.
- A_5 is the area of the cell exposed to the ambient, cm^2.
- $d_{i,j,5}$ is the shortest distance from the node (i,j) to the ambient, cm.
- k is the thermal conductivity of the material in the sink, cal./°C-cm-sec.

The constant c_6 is defined by:

$$c_6 = \frac{\rho C_p V_{i,j}}{k\Delta t} \qquad \text{(A-12)}$$

where

$V_{i,j}$ is the volume of cell (i,j).

As was shown in Chapter V, it is only necessary to consider the cells intersected by the boundary of the sink in the second quadrant. The four types of cells illustrated in Figure 5 are considered individually below. The equations for each type of cell assume that the points of intersection of the boundary of the sink and the cell walls is known. These points are easily found by assuming the radius of the sink is the hypotenuse of a right triangle whose sides are the coordinates of the point of intersection. All equations assume that the boundary of the sink is replaced in each cell by a straight line connecting the points of intersection. The node of the cell is then moved to the centroid of the polygon. The notation is also simplified from $d_{i,j,k}$ to d_k with the i,j understood.

A Type One Cell

Figure A-3 illustrates the triangular form of a type one cell. The distance from a side of a right triangle to its centroid is one-third of the length of the remaining side. Therefore,

$$d_3 = \frac{\delta_4 \Delta x}{3} \qquad \text{(A-13)}$$

$$d_4 = \frac{\delta_3 \Delta x}{3} \tag{A-14}$$

$$A_3 = \delta_3 \Delta x \tag{A-15}$$

$$A_4 = \delta_4 \Delta x \tag{A-16}$$

$$A_5 = (\delta_4{}^2 + \delta_3{}^2)^{\frac{1}{2}} \Delta x \tag{A-17}$$

and

$$V = \frac{\delta_3 \delta_4 (\Delta x)^2}{2} \tag{A-18}$$

The length of d_5 can be found from the similar triangles illustrated in Figure A-4. The length of side a is one-third the length of side B and the small and large triangles are equalangular. Therefore, the lengths:

$$\frac{d}{D} = \frac{a}{A} \tag{A-19}$$

or

$$d_5 = \frac{\delta_3 \delta_4 \Delta x}{3(\delta_3{}^2 + \delta_4{}^2)^{\frac{1}{2}}} \tag{A-20}$$

A type one cell has no sides one or two; therefore, $c_1 = c_2 = 0$.

A Type Two Cell

A cell of the second type is illustrated in Figure A-5. The location of the centroid can be easily found if

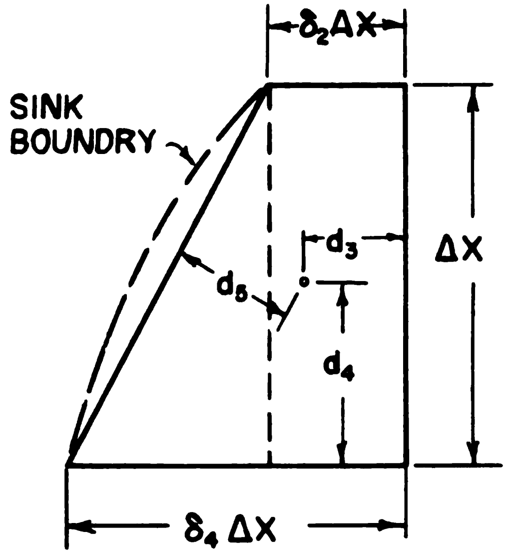

Figure A-5. A type two cell.

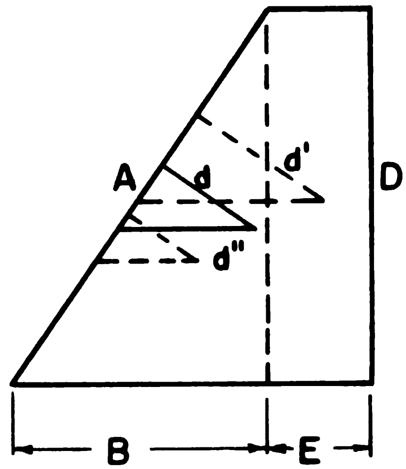

Figure A-6. The similar triangles utilized to find d_5 for a type two cell.

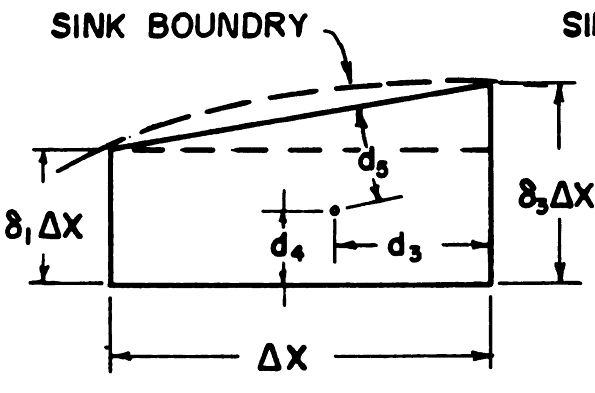

Figure A-7. A type three cell.

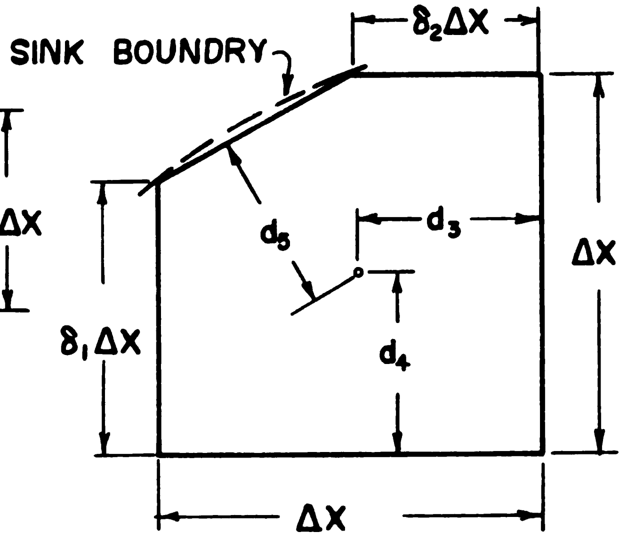

Figure A-8. A type four cell.

the cell is visualized as the combination of a rectangle and a triangle. The centroid of the cell is the average of the locations of the two centroids:

$$d_3 = \frac{\Delta x}{3}\left(\frac{\delta_2{}^2 + \delta_2\delta_4 + \delta_4{}^2}{\delta_2 + \delta_4}\right) \qquad \text{(A-21)}$$

$$d_4 = \frac{\Delta x}{3}\left(\frac{2\delta_2 + \delta_4}{\delta_2 + \delta_4}\right) \qquad \text{(A-22)}$$

$$A_2 = \delta_2\Delta x \qquad \text{(A-23)}$$

$$A_3 = \Delta x \qquad \text{(A-24)}$$

$$A_4 = \delta_4\Delta x \qquad \text{(A-25)}$$

$$A_5 = [1 + (\delta_4 - \delta_2)^2]^{\frac{1}{2}}\Delta x \qquad \text{(A-26)}$$

and

$$V = \frac{(\delta_4 + \delta_2)(\Delta x)^2}{2} \qquad \text{(A-27)}$$

Similar triangles can be employed to find d_5 (see Figure A-6). The three points correspond to the centroids of the rectangle, triangle, and cell. If the lengths of the sides are represented by the letters,

$$d'' = \frac{DB}{3A} \qquad \text{(A-28)}$$

$$d' = \frac{D(B+E)}{2A} \qquad \text{(A-29)}$$

and

$$d = \frac{DEd' + \frac{DBd''}{2}}{D(E + \frac{D}{2})} \qquad \text{(A-30)}$$

therefore

$$d_5 = \frac{\delta_4{}^2 + \delta_2\delta_4 + \delta_2{}^2}{3A_5(\delta_4 + \delta_2)}(\Delta x)^2 \qquad \text{(A-31)}$$

There is no heat transfer with cell (i-1,j); therefore $c_1 = 0$. Notice that expressions for d_1 and d_2 are not required since $d_1 = \Delta x - d_3$ and $d_2 = \Delta x - d_4$.

A Type Three Cell

The techniques employed to find the parameters of a type two cell can be used to find the following parameters of a type three cell (Figure A-7):

$$d_3 = \frac{\Delta x}{3}\left(\frac{2\delta_1 + \delta_3}{\delta_1 + \delta_3}\right) \qquad \text{(A-32)}$$

$$d_4 = \frac{\Delta x}{3}\left(\frac{\delta_1{}^2 + \delta_1\delta_3 + \delta_3{}^2}{\delta_1 + \delta_3}\right) \qquad \text{(A-33)}$$

$$d_5 = \frac{\delta_3{}^2 + \delta_3\delta_1 + \delta_1{}^2}{3A_5(\delta_3 + \delta_1)}(\Delta x)^2 \qquad \text{(A-34)}$$

$$A_1 = \delta_1\Delta x \qquad \text{(A-35)}$$

$$A_3 = \delta_3 \Delta x \tag{A-36}$$

$$A_4 = \Delta x \tag{A-37}$$

$$A_5 = [1 + (\delta_3 - \delta_1)^2]^{\frac{1}{2}} \Delta x \tag{A-38}$$

and

$$V = \frac{(\delta_3 + \delta_1)(\Delta x)^2}{2} \tag{A-39}$$

The constant c_2 is zero for a type three cell.

A Type Four Cell

A type four cell, Figure A-8, has heat exchange through five surfaces. The location of the centroid and the distances d_3, d_4, and d_5 are found by assuming that a square consists of the cell and the triangle that has been removed. The centroids of a square and a triangle are already known. The location of the centroid of the cell is such that the average of it and the triangle's centroid is the center of the square. The resulting parameters are:

$$d_3 = \frac{1 + 2\delta_1 + (\delta_2 + \delta_2^2)(1 - \delta_1)}{1 + \delta_1 + \delta_2 - \delta_1\delta_2} \frac{\Delta x}{3} \tag{A-40}$$

$$d_4 = \frac{1 + 2\delta_2 + (\delta_1 + \delta_1^2)(1 - \delta_2)}{1 + \delta_1 + \delta_2 - \delta_1\delta_2} \frac{\Delta x}{3} \tag{A-41}$$

$$d_5 = \left[1 - \delta_1\delta_2 + \frac{\delta_1^2(1 - \delta_2) + \delta_2^2(1 - \delta_1)}{1 + \delta_1 + \delta_2 - \delta_1\delta_2}\right] \frac{(\Delta x)^2}{3A_5} \tag{A-42}$$

$$A_1 = \delta_1 \Delta x \tag{A-43}$$

$$A_2 = \delta_2 \Delta x \tag{A-44}$$

$$A_3 = A_4 = \Delta x \tag{A-45}$$

$$A_5 = [(1 - \delta_1)^2 (1 - \delta_2)^2]^{\frac{1}{2}} \tag{A-46}$$

and

$$V = \frac{(1 + \delta_1 + \delta_2 - \delta_1 \delta_2)(\Delta x)^2}{2} \tag{A-47}$$

The computer program in Appendix B finds the δ_i values and stores them in an array called PRE(I,J,K). The distances, $d_{i,j,k}$ are computed in the function subroutine D. The c_i's are computed by the subprogram CØNST.

APPENDIX B

THE COMPUTER PROGRAM OF THE HEAT SINK

```
      PROGRAM TWOC (INPUT,OUTPUT)
C  THE ORGINAL DECK.
      COMMON PRE(10,3,3),DX,DT,Y(4),X(2),A(4,4),Q(3),BK(3),IX(2),
     1C(10,10,7),CH(12,12,7),T(20,11)
    1 FORMAT(11F7.0)
    2 FORMAT(1H1,* ALLADA-QUON MODEL OF A CALORIMETER SINK WITH A RADIUS
     1 OF*,F8.3,*UNITS WITH CHAMBERS*, F8.3,* UNITS OFF CENTER AND RADII
     2 OF*/F5.2, * UNITS.  EACH TIME STEP IS *       F10.6,* SECOND(S)
     3AND ONE UNIT OF DISTANCE IS *,F10.6,* CENTIMETER(S).*/* THE THERMA
     4L CHARACTERISTICS ARE--THERMAL CONDUCTIVITY = *F10.7,* CALS./CM.-D
     5EG. C.-SEC.*/ 33X,*AND HEAT CAPACITY PER UNIT VOLUME = *,F10.4* CA
     6LS./CC-DEG. C.*/* THUS THE PROGRAM CONSTANTS HAVE VALUES OF--BETA
     7= *E12.5* CALS./CM.-SEC.-DEG. C.*/42X,*C1 = *E12.5 / 42X *AND C2 =
     8 * E12.5 /* THE CONVECTIVE HEAT TRANSFER COEFFICIENTS ARE--*,
     9E12.5, * CALS./CM.-CM.-DEG. C.-SEC. BETWEEN THE SINK AND THE OUTSI
     1DE.* / 48X,E12.5, * CALS./CM.-CM.-DEG. C.-SEC. BETWEEN THE SINK AN
     2D THE CHAMBERS.* / 48X, * AND *, E12.5,* CALS./DEG. C.-SEC. IS THE
     3 AREA TIMES THE HEAT TRANSFER COEFFICIENT * / 60X, *BETWEEN THE SI
     4NK AND THE CHAMBERS. * / * THE HEAT CAPACITY OF EACH CHAMBER AND I
     5TS CONTENTS IS * F10.5,* CALORIES/DEG. C.*)
    3 FORMAT(1H0,* TIME      SINK TEMPERATURE AROUND CHAMBERS *18X,
     1*CHAMBER TEMPERATURES *29X*RELATIVE ERROR*/* SECONDS*10X*LEFT*
     210X*RIGHT*20X*LEFT*12X*RIGHT*12X*IDEAL*)
    4 FORMAT(1H0,F6.2,5X,2(E14.7,2X),10X,3(E14.7,2X),10X,E14.7)
  101 FORMAT(1H0,* ERROR AT *I5 * , *I5, * THE EXTERNAL AND INTERNAL BOU
     1NDARIES MUST NOT BOTH INTERSECT THE SAME CELL.*)
  500 FORMAT(1H0,//,60X,*RESULTS*)
  213 READ 1,R,DCH,RCH,AK,RC,DT,DX,HO,HI,HA,HC
C  R IS THE RADIUS OF THE SINK,
C  DCH IS THE DISTANCE FROM THE CENTER OF THE SINK TO THE CENTER OF THE
C     CHAMBERS IN UNITS OF DISTANCE.
C  RCH IS THE RADIUS OF THE CHAMBERS IN UNITS OF DISTANCE.
C  AK IS THE THERMAL CONDUCTIVITY OF THE METAL IN THE SINK.
C  RC IS THE HEAT CAPACITY OF THE METAL IN THE SINK PER UNIT VOLUME.
C  DT IS THE TIME STEP SIZE.
C  DX IS THE LENGTH OF THE SPACE STEP.
```

```
C  HO IS THE HEAT TRANSFER COEFFICIENT FROM THE SINK TO THE AMBIENT.
C  HI IS THE HEAT TRANSFER COEFFICIENT FROM THE SINK TO  THE CHAMBERS.
C  HA IS HI TIMES THE THE AREA OF THE CHAMBERS.
C  HC IS THE HEAT CAPACITY OF THE REACTION CUP.
      IF(R.EQ.0.) GO TO 214
C INITIALIZE SOME ARRAYS.
      DO 7 I=1,10
      DO 6 J=1,10
  6   C(I,J,7)=-1.
      DO 7 J=1,3
      DO 7 K=1,3
  7   PRE(I,J,K)=0.
      DO 10 I=1,3
 10   Q(I)=0.
      DO 5 I=1,12
      DO 5 J=1,12
  5   CH(I,J,7)=0.
      A(1,1)=A(1,3)=A(2,4)=A(4,4)=A(4,3)=0.5
      A(1,2)=A(4,2)=2.
      A(1,4)=A(3,4)=0.
      A(2,1)=A(2,3)=1.-SQRT(0.5)
      A(2,2)=A(3,2)=1.0
      A(3,1)=A(3,3)=1.+SQRT(0.5)
      A(4,1)=1./6.
      TICO=0.001
      IR=R+0.99      $I=II=1      $Y(1)=-1       $JJ=2
      ID=2*IR     $TI=0.0001    $TR=0.
      IRP=IR+1      $IDC=DCH       $BETA=RC*DX**2/DT
      C1=AK/(BETA+2.*AK)           $C2=(BETA-2.*AK)/AK
      PRINT 2,R,DCH,RCH,DT,DX,AK,RC,BETA,C1,C2,HO,HI,HA,HC
C FIND THE OUTSIDE BOUNDARY CONDITIONS.
      RS=R*R
C FIND DELTA THREE, FOUR, AND FIVE IN A NEW ROW.
C  PRE(I,J,1) IS THE TYPE OF CELL (I,J).
C  PRE(I,J,2) AND PRE(I,J,3) ARE THE INTERNAL LENGTHS OF THE CELL BORDERS
C    THAT ARE CUT BY THE SINK≠S BOUNDARY.
```

```
   11   J=Y(1)=Y(1)+1.
        IE=I     $IS=II
        IF(J.GE.IR) GO TO 18
        Y(2)=Y(1)+1.
        X(1)=SQRT(RS-Y(1)*Y(1))
        AX=IX(1)=X(1)-0.001
        IF(Y(2).GE.R) GO TO 8
        X(2)=SQRT(RS-Y(2)*Y(2))
        GO TO 9
    8   X(2)=0.
    9   IX(2)=X(2)+0.001
        II=I=IR-IX(1)
        IF(IX(1).GT.IX(2)) GO TO 12
C  THE CELL IS OF THE SECOND TYPE.
        PRE(I,JJ,1)=2.
        PRE(I,JJ,2)=X(2)-AX
        PRE(I,JJ,3)=X(1)-AX
        GO TO 16
C THE CELL IS OF THE FIRST TYPE.
   12   Y(3)=SQRT(RS-AX*AX)
        PRE(I,JJ,1)=1.
        PRE(I,JJ,2)=Y(3)-Y(1)
        PRE(I,JJ,3)=X(1)-AX
C DETERMINE THE TYPE OF THE NEXT CELL.
   13   AX=IX(1)=IX(1)-1
        I=I+1
        IF(IX(1).LE.IX(2)) GO TO 15
C A TYPE THREE CELL.
   14   Y(4)=SQRT(RS-AX*AX)
        PRE(I,JJ,1)=3.
        PRE(I,JJ,2)=Y(3)-Y(1)
        PRE(I,JJ,3)=Y(4)-Y(1)
        Y(3)=Y(4)
        IF(AX) 13,16
   15   IF(AX.EQ.0.) GO TO 14
C A TYPE FOUR CELL.
```

```
      PRE(I,JJ,1)=4.
      PRE(I,JJ,2)=Y(3)-Y(1)
      PRE(I,JJ,3)=X(2)-AX
C THIS IS THE END OF THE BOUNDARY CONDITIONS FOR THAT ROW.
  16  IF(J.GT.0.) GO TO 18
      JJ=3
C SET ROW 1 EQUAL TO ROW TWO FOR CENTERLINE.
      DO 17 IA=II,I
      PRE(IA,1,3)=PRE(IA,2,2)
      PRE(IA,1,2)=PRE(IA,2,3)
  17  PRE(IA,1,1)=PRE(IA,2,1)
      GO TO 11
C FIND THE C≠S AND V.
  18  DO 19 IA=IS,IE
      KA=PRE(IA,2,1)
      IM=IA-1
      IP=IA+1
      CALL CONST(C(IA,J,1),C(IA,J,2),C(IA,J,3),C(IA,J,4),C(IA,J,5),
     1C(IA,J,6),C(IA,J,7),KA,PRE(IA,2,2),PRE(IA,2,3),DX,DT,HO,AK,IA,IM,
     2IP,1,3,IR,RC)
  19  CONTINUE
C  FILL IN THE REMAINING C≠S.
      IA=IE   $JM=J-1   $IF(IE.GE.IR) GO TO 20
      IE=IE+1  $C(IE,J,2)=C(IE,J,3)=C(IE,J,4)=C(IE,J,7)=1.
      C(IE,J,5)=0.   $C(IE,J,1)=C(IA,J,3)   $C(IE,J,6)=BETA/AK
      IF(JM) 200,24,20
  20  IF(C(IA,JM,7).GT.0.) GO TO 21   $C(IA,JM,5)=0.
      C(IA,JM,1)=C(IA,JM,3)=C(IA,JM,4)=C(IA,JM,7)=1.
      C(IA,JM,2)=C(IA,J,4)   $C(IA,JM,6)=BETA/AK   $IA=IA-1   $GO TO 20
  21  IF(C(IA,JM,5).GT.0.) GO TO 24
      C(IA,JM,2)=C(IA,J,4)
C EXCHANGE PRE ROWS.
  24  DO 25 IA=IS,I
      DO 25 KA=1,3
      PRE(IA,1,KA)=PRE(IA,2,KA)
  25  PRE(IA,2,KA)=PRE(IA,3,KA)
```

```
      IF(J.GE.IR) GO TO 27
      IS=IE+1
      DO 26 IA=IS,IR
   26 C(IA,J,7)=0.
      GO TO 11
C THE OUTSIDE BOUNDARY CONDITIONS ARE FOUND.
   27 CONTINUE
C THE BOUNDARY CONDITIONS AROUND THE CHAMBERS.
   30 RCHS=RCH*RCH
      IRC=RCH+.99
      IRCP=IRC+1   $IDCP=IRCP+IRCP  $ISS=IR-IDC-IRCP+1
      Y(1)=-1.      $JJ=2       $I=II=1
C SET UP TO START A ROW.
   31 J=Y(1)=Y(1)+1.
      IE=I     $IS=II
      IF(IRC.LE.J) GO TO 38
      Y(2)=Y(1)+1.
      X(1)=SQRT(RCHS-Y(1)*Y(1))
      AX=IX(1)=X(1)-0.001
      IF(Y(2).GE.RCH) GO TO 310
      X(2)=SQRT(RCHS-Y(2)*Y(2))
      GO TO 311
  310 X(2)=0.
  311 IX(2)=X(2)+0.001
      II=I=IRC-IX(1)
      IF(IX(1).GT.IX(2).OR.AX.EQ.0.) GO TO 35
C THE CELL IS TYPE TWO.
      PRE(I,JJ,1)=2.
      PRE(I,JJ,2)=AX+1.-X(1)
      PRE(I,JJ,3)=AX+1.-X(2)
C END OF ROW J+1.
   32 IF(J)38,33
C SET ROW ONE EQUAL TO ROW TWO.
   33 JJ=3
      DO 34 IA=II,I
      PRE(IA,1,3)=PRE(IA,2,2)   $PRE(IA,1,2)=PRE(IA,2,3)
```

```
   34  PRE(IA,1,1)=PRE(IA,2,1)
       GO TO 31
C A TYPE FOUR CELL.
   35  Y(3)=SQRT(RCHS-AX*AX)
       PRE(I,JJ,1)=4.
       PRE(I,JJ,2)=Y(2)-Y(3)
       PRE(I,JJ,3)=AX+1.-X(1)
C DETERMINE THE TYPE OF THE NEXT CELL.
   36  AX=IX(1)=IX(1)-1
       IF(AX.LT.0.) GO TO 32
       I=I+1
       IF(IX(1).GT.IX(2).OR.Y(2).GT.RCH) GO TO 37
C A TYPE ONE CELL.
       PRE(I,JJ,1)=1.
       PRE(I,JJ,2)=Y(2)-Y(3)
       PRE(I,JJ,3)=AX+1.-X(2)
       GO TO 32
C A TYPE THREE CELL.
   37  Y(4)=SQRT(RCHS-AX*AX)
       PRE(I,JJ,1)=3.
       PRE(I,JJ,2)=Y(2)-Y(4)
       PRE(I,JJ,3)=Y(2)-Y(3)
       Y(3)=Y(4)
       IF(AX) 36,32
C FIND THE C=S AND V.
   38  DO 39 IA=IS,IE
       KA=PRE(IA,2,1)
       IM=IA+1
       IP=IA-1
       IB=IA+1
       CALL CONST(CH(IB,J,1),CH(IB,J,2),CH(IB,J,3),CH(IB,J,4),CH(IB,J,5),
      1CH(IB,J,6),CH(IB,J,7),KA,PRE(IA,2,2),PRE(IA,2,3),DX,DT,H1,AK,
      2IA,IM,IP,3,1,IRC,RC)
   39  CONTINUE
C MOVE PRE UP.
       DO 40 IA=IS,I
```

```
      DO 40 KA=1,3
      PRE(IA,1,KA) = PRE(IA,2,KA)
   40 PRE(IA,2,KA)=PRE(IA,3,KA)
C  FILL IN THE REMAINING CH≠S.
      IA=IS
   44 CH(IA,J,3)=CH(IA,J,4)=1.
      CH(IA,J,5)=CH(IA,J,7)=0.    $CH(IA,J,6)=BETA/AK
      CH(IA,J,1)=CH(IA+1,J,3)    $JM=J-1
      IF(JM.LT.1) JM=1    $CH(IA,J,2)=CH(IA,JM,4)
      IF(IA.LE.1) GO TO 45    $IA=IA-1    $GO TO 44
   45 IS=IDCP-IE
      DO 46 IA=IS,IDCP
      IB=IDCP-IA+1
      CH(IA,J,1)=CH(IB,J,3)   $CH(IA,J,2)=CH(IB,J,2)
      CH(IA,J,3)=CH(IB,J,1)
      DO 46 KA=4,7
   46 CH(IA,J,KA)=CH(IB,J,KA)
      IF(J-IRC)41,43,43
C SET UNUSED CELLS TO NEGATIVE ONE.
   41 IS=IE+2    $IE=IDCP-IS+1
      DO 42 IA=IS,IE
   42 CH(IA,J,7)=-1.
      GO TO 31
C  ADD THE TOP ROW.
   43 JM=J    $J=J+1
      DO 47 IA=1,IDCP
      CH(IA,J,1)=CH(IA,J,3)=CH(IA,J,4)=1.   $CH(IA,J,2)=CH(IA,JM,4)
      CH(IA,J,5)=CH(IA,J,7)=0.
   47 CH(IA,J,6)=BETA/AK
C  CORRECT ANY EDGE CH≠S.
      IF(IDC-IRCP) 48,205,203
   48 I=IDCP-1
      DO 49 J=1,IRC
   49 CH(I,J,1)=1./(2./CH(I,J,1)-1.0)
      GO TO 205
  203 IS=IDCP+1    $IE=IR-ISS+1
```

```
      DO 204 I=IS,IE
      DO 204 J=1,IRCP
      CH(I,J,5)=CH(I,J,7)=0.   $CH(I,J,6)=BETA/AK
      DO 204 K=1,4
 204  CH(I,J,K)=1.
 205  DO 212 J=1,IRCP
      I=ISS  $IB=1
 206  IF(C(I,J,7)) 207,212,208
 207  CH(IB,J,6)=0.  $IB=IB+1  $I=I+1  $GO TO 206
 208  IF(C(I,J,5)) 200,209,210
 209  C(I,J,7)=0.   $CH(IB,J,3)=1./(1./CH(IB,J,3)+1./C(I,J,1)-1.0)
      CH(IB,J,4)=1./(1./CH(IB,J,4)+1./C(I,J,2)-1.0)  $I=I+1   $IB=IB+1
      GO TO 206
 210  CH(IB,J,6)=0.
      IF(CH(IB,J,5)) 200,211,200
 211  C(I,J,3)=1./(1./C(I,J,3)+1./CH(IB,J,1)-1.0)
      C(I,J,4)=1./(1./C(I,J,4)+1./CH(IB,J,2)-1.0)
      I=I+1   $IB=IB+1   $GO TO 206
 212  CONTINUE
C  END OF PROGRAM TWOA.
C  INPUT TO THE ITERATIVE PART OF THE PROGRAM, TWOB.
      TAT=0.
      DO 50 I=1,IDCP
      DO 50 J=1,IRC
  50  IF(CH(I,J,7).GT.0.) TAT=TAT+CH(I,J,7)*2.
      DO 51 I=1,ID
      DO 51 J=1,IRP
  51  T(I,J)=0.
      DO 52 I=1,4
  52  Y(I)=0.
      X(1)=X(2)=0.
      PRINT 500
      PRINT 3
C  START THRU THE SINK AFTER FINDING THE CHAMBER TEMPERATURES.  BEGIN AT THE
C    LOWER RIGHT.
  53  CALL RKG(TI,HA,HC)
```

```
      X(1)=X(2)=0.
      DO 73 J=1,IR
      I=0    $LA=1    $JJ=J+1    $JP=JJ+1    $JM=J
      IF(JP.GT.IRP) JP=IRP
      M1=1   $M2=2   $M3=3   $M4=4
   54 I=I+1   $IP=I+1   $IM=I-1    $IC=I
      IF(I.GT.IR) GO TO 69
      IF(C(IC,J,7)) 54,56,55
   55 IF(IP.GT.ID ) IP=ID        $IF(IM.LT.1) IM=1
      T(I,JJ)=(C(IC,J,M1)*T(IM,JJ)+C(IC,J,M2)*T(I,JP)+C(IC,J,M3)*T(IP,
     1JJ)+C(IC,J,M4)*T(I,JM)+C(IC,J,5)*TR+(C(IC,J,6)-C(IC,J,M3)-
     2C(IC,J,M2))*T(I,JJ))/(C(IC,J,6)+C(IC,J,5)+C(IC,J,M4)+C(IC,J,M1))
      GO TO (54,70),LA
C THE BOUNDARY IS FINISHED.
   56 IA=I
      IF(J.GT.IRCP) GO TO 71
      IF(I-ISS) 57,59,60
   57 IE=ISS-1
C  THE CELLS BETWEEN THE OUTSIDE AND THE LEFT CHAMBER.
      DO 58 I=IA,IE
   58 T(I,JJ)=C1*(T(I-1,JJ)+T(I,JM)+T(I+1,JJ)+T(I,JP)+C2*T(I,JJ))
   59 IS=ISS  $IB=0  $IE=IR  $GO TO 61
   60 IS=I  $IB=I-ISS  $IE=IR
   61 M1=3  $M2=4  $M3=1  $M4=2  $IC=IB  $IG=1
C  THE CHAMBERS.
   62 DO 63 I=IS,IE
      IC=IC+IG
      IF(CH(IC,J,7).LT.0.) GO TO 63
      IM=I-1  $IP=I+1
      T(I,JJ)=(CH(IC,J,M1)*T(IM,JJ)+CH(IC,J,M2)*T(I,JP)+CH(IC,J,M3)*
     1T(IP,JJ)+CH(IC,J,M4)*T(I,JM)+CH(IC,J,5)*Y(LA)+(CH(IC,J,6)-
     2CH(IC,J,M3)-CH(IC,J,M2))*T(I,JJ))/(CH(IC,J,6)+CH(IC,J,5)+
     3CH(IC,J,M4)+CH(IC,J,M1))
      X(LA)=X(LA)+T(I,JJ)*CH(IC,J,7)/TAT
   63 CONTINUE
      GO TO (64,65),LA
```

```
 64  LA=2  $IE=ID-IS+1   $IS=IR+1   $IG=-1     $IC=IC+1
     M1=1   $M3=3   $GO TO 62
C  THE CHAMBERS ARE FINISHED.
 65  IF(IA-ISS) 66,68,68
 66  IS=IE+1  $IE=ID-IA+1
C  THE CELLS PROCEEDING THE RIGHT BOUNDARY.
 72  DO 67 I=IS,IE
 67  T(I,JJ)=C1*(T(I-1,JJ)+T(I,JM)+T(I+1,JJ)+T(I,JP)+C2*T(I,JJ))
 68  I=IE+1   $IC=IA
C  THE RIGHT BOUNDARY.
 69  I=I-1  $M1=3  $M2=2  $M3=1  $M4=4  $LA=2
 70  IM=I  $I=I+1  $IP=I+1  $IC=IC-1
     IF(IC.LT.1) GO TO 73
     IF(C(IC,J,7)) 73,200,55
 71  IS=I  $IE=ID-IA+1  $GO TO 72
 73  CONTINUE
C  EQUATE THE TEMPERATURES ACROSS THE ADIABATIC BOUNDARY.
     DO 78 I=1,ID
 78  T(I,1)=T(I,2)
     TICO=TICO+DT
C  BEGIN AT THE UPPER RIGHT AND GO TO LOWER LEFT.
     CALL RKG(TI,HA,HC)
     X(1)=X(2)=0.
     DO 99 JR=1,IR
     J=IR-JR+1   $I=ID+1           $LA=2   $JJ=J+1
     JP=JJ+1   $JM=J   $IC=0
     IF(JP.GT.IRP) JP=IRP
     M1=3   $M2=2   $M3=1   $M4=4
 79  IP=I   $I=I-1   $IM=I-1   $IC=IC+1
     IF(IC.GT.IR) GO TO 95
     IF(C(IC,J,7)) 79,81,80
 80  IF(IP.GT.ID) IP=ID     $IF(IM.LT.1) IM=1
     T(I,JJ)=(C(IC,J,M1)*T(IM,JJ)+C(IC,J,M2)*T(I,JP)+C(IC,J,M3)*T(IP,
    1JJ)+C(IC,J,M4)*T(I,JM)+C(IC,J,5)*TR+(C(IC,J,6)-C(IC,J,M3)-
    2C(IC,J,M2))*T(I,JJ))/(C(IC,J,6)+C(IC,J,5)+C(IC,J,M4)+C(IC,J,M1))
308  GO TO (96,79),LA
```

```
C  THE END OF THE RIGHT BOUNDARY.
 81  IA=ID-I+1
     IF(J.GT.IRCP) GO TO 97
     IF(IA-ISS) 82,84,85
C  THE FREE CELLS BETWEEN RIGHT CHAMBER AND BOUNDARY.
 82  IS=ID-ISS+2  $IE=I
     DO 83 IB=IS,IE
     I=IS+IE-IB
 83  T(I,JJ)=C1*(T(I-1,JJ)+T(I,JM)+T(I,JP)+T(I+1,JJ)+C2*T(I,JJ))
 84  IE=ID-ISS+1  $IS=IR+1  $IC=0  $GO TO 86
 85  IE=I  $IS=IR+1  $IC=IA-ISS
 86  M1=1  $M2=4  $M3=3  $M4=2  $IG=1
C  COMPUTE THRU THE CHAMBERS.
 87  DO 88 IB=IS,IE
     IC=IC+IG
     IF(CH(IC,J,7).LT.0.) GO TO 88
     I=IS+IE-IB  $IM=I-1  $IP=I+1
     T(I,JJ)=(CH(IC,J,M1)*T(IM,JJ)+CH(IC,J,M2)*T(I,JP)+CH(IC,J,M3)*
    1T(IP,JJ)+CH(IC,J,M4)*T(I,JM)+CH(IC,J,5)*Y(LA)+(CH(IC,J,6)-
    2CH(IC,J,M3)-CH(IC,J,M2))*T(I,JJ))/(CH(IC,J,6)+CH(IC,J,5)+
    3CH(IC,J,M4)+CH(IC,J,M1))
     X(LA)=X(LA)+T(I,JJ)*CH(IC,J,7)/TAT
 88  CONTINUE
     GO TO (90,89),LA
 89  LA=1   $IS=ID-IE+1   $IE=IR   $IG=-1    $IC=IC+1
     M1=3  $M3=1   $GO TO 87
C  THE CHAMBERS ARE FINISHED.
 90  IF(IA-ISS) 91,94,94
 91  IS=IA  $IE=IS-1
C  THE FREE CELLS PROCEEDING THE LEFT BOUNDARY.
 92  DO 93 IB=IS,IE
     I=IS+IE-IB
 93  T(I,JJ)=C1*(T(I-1,JJ)+T(I,JM)+T(I,JP)+T(I+1,JJ)+C2*T(I,JJ))
 94  I=IS-1  $IC=IA
C  THE LEFT BOUNDARY.
 95  I=I+1  $M1=1  $M2=2  $M3=3  $M4=4  $LA=1
```

```
 96   IP=I  $I=I-1  $IM=I-1  $IC=IC-1
      IF(IC.LT.1) GO TO  99
      IF(C(IC,J,7)) 99,200,80
 97   IS=IA  $IE=I  $GO TO 92
 99   CONTINUE
      DO 201 I=1,ID
201   T(I,1)=T(I,2)
      TICO=TICO+DT
      IF(TICO.LT.15.) GO TO 53
      TICO=0.001
      PRINT 4,TI,X,Y
      IF(TI.LT.300.) GO TO 53
      GO TO 213
200   PRINT 101,I,J
      GO TO 213
214   CONTINUE
      END
```

```
      FUNCTION D(I,J,K)
C  D(I,J,K) IS THE DISTANCE FROM THE CENTROID OF CELL (I,J) TO THE K TH
C    BORDER OF ITS CELL.
      COMMON PRE(10,3,3),DX
      IF(PRE(I,J,1).GT.0.) GO TO 12
      D=DX/2.      $RETURN
   PRE(I,J,1) IS THE CELL TYPE.
  12  KA=PRE(I,J,1)
      KA=3*KA+K-5
C  NOTE THAT THE DISTANCE IS ONLY COMPUTED IN DIRECTIONS 3,4,AND 5.
C  THE REMAINING DISTANCES ARE DX LESS ONE OF THESE DISTANCES.
      GO TO (1,2,3,4,5,6,5,4,6,7,7,7),KA
C  TYPE ONE CELL, DIRECTION THREE.
  1   D=DX*PRE(I,J,3)/3.
      RETURN
C  TYPE ONE CELL, DIRECTION FOUR.
  2   D=DX*PRE(I,J,2)/3.
      RETURN
   TYPE ONE CELL, DIRECTION FIVE.
  3   D=DX*PRE(I,J,2)*PRE(I,J,3)/(3.*SQRT(PRE(I,J,3)**2+PRE(I,J,2)**2))
      RETURN
C  TYPE TWO CELL, DIRECTION THREE OR TYPE THREE CELL, DIRECTION FOUR.
  4   D2=PRE(I,J,2)
      D4=PRE(I,J,3)
      D=DX*(D2*D2+D2*D4+D4*D4)/(3.*(D2+D4))
      RETURN
C  TYPE TWO CELL,DIRECTION FOUR OR TYPE THREE CELL ,DIRECTION THREE.
  5   D=DX*(2.*PRE(I,J,2)+PRE(I,J,3))/(3.*(PRE(I,J,2)+PRE(I,J,3)))
      RETURN
C  TYPE TWO OR THREE CELL, DIRECTION FIVE.
  6   D2=PRE(I,J,2)
      D4=PRE(I,J,3)
      D=DX*(D4*D4+D2*D4+D2*D2)/(3.*(D4+D2)*SQRT(1.+(D4-D2)**2))
      RETURN
C  TYPE FOUR CELL.
  7   D1=PRE(I,J,2)
```

```
      D2=PRE(I,J,3)     $KA=KA-9
      GO TO (8,9,10),KA
C  DIRECTION THREE.
  8   D=DX*(1.+2.*D1+D2*(1.+D2)*(1.-D1))/(3.*(1.+D1+D2-D1*D2))
      RETURN
C  DIRECTION FOUR.
  9   D=DX*(1.+2.*D2+D1*(1.+D1)*(1.-D2))/(3.*(1.+D1+D2-D1*D2))
      RETURN
C  PREVENT DIVISION BY ZERO.
 10   IF(D1+D2.LT.1.9) GO TO 11
      D=DX/1.414
      RETURN
C  DIRECTION FIVE.
 11   D=DX*(1.-D1*D2+(D1*D1*(1.-D2)+D2*D2*(1.-D1))/(1.+D1+D2-D1*D2))/
     1(3.*SQRT((1.-D1)**2+(1.-D2)**2))
      RETURN
      END
```

```
      SUBROUTINE CONST(C1,C2,C3,C4,C5,C6,C7,K,D1,D2,DX,DT,H,AK,I,IM,IP,
     1JM,JP,IR,RC)
C  THIS SUBTOUTINE COMPUTES THE *AREA / DISTANCE* CONSTANTS (C1,C2,C3,C4,
C    C5) IN EACH DIRECTION FROM CELL (I,J).  IT ALSO COMPUTES THE NEW
C    *VOLUME / THERMAL CONDUCTIVITY* (C6) AND THE *AREA FOR HEAT TRANSFER
C    ACROSS THE SINK BOUNDARY* (C7) FOR A TYPE K CELL.
      GO TO (1,2,3,7),K
    1 C1=C2=0.
      C3=D1*DX/(D(I,2,3)+DX-D(IP,2,3))
      C4=D2*DX/(D(I,2,4)+DX-D(I,JM,4))
      C5=H*DX*SQRT(D1*D1+D2*D2)/(H*D(I,2,5)+AK)
      C6=DX*DX*D1*D2*RC/(2.*DT*AK)
      C7=DX*SQRT(D2*D2+D1*D1)
      RETURN
    2 C1=0.
      C2=D1*DX/(DX-D(I,2,4)+D(I,JP,4))
      IF(D2.LT.0.001) C2=0.
      C3=DX/(D(I,2,3)+DX/2.)
      C4=D2*DX/(D(I,2,4)+DX-D(I,JM,4))
      C5=H*SQRT(1.+(D1-D2)**2)*DX/(H*D(I,2,5)+AK)
      C6=DX*DX*(D1+D2)*RC/(2.*DT*AK)
      C7=DX*SQRT(1.+(D2-D1)**2)
      RETURN
    3 IF(I-IR) 5,4
    4 IF(IM.LT.I) GO TO 8
      C1=D1*DX/(2.*(DX-D(I,2,3)))
      C3=D2*DX/(D(I,2,3)+DX-D(IP,2,3))
      GO TO 6
    8 C1=D1*DX/(DX-D(I,2,3)+D(IM,2,3))
      C3=D2*DX/(2.*D(I,2,3))
      GO TO 6
    5 C1=D1*DX/(DX-D(I,2,3)+D(IM,2,3))
      C3=D2*DX/(D(I,2,3)+DX-D(IP,2,3))
    6 C2=0.
      C4=DX/(D(I,2,4)+DX/2.)
      C5=H*DX*SQRT(1.+(D2-D1)**2)/(H*D(I,2,5)+AK)
```

```
      C6=DX*DX*(D1+D2)*RC/(2.*DT*AK)
      C7=DX*SQRT(1.+(D2-D1)**2)
      RETURN
    7 C1=D1*DX/(DX-D(I,2,3)+D(IM,2,3))
      C2=D2*DX/(DX-D(I,2,4)+D(I,JP,4))
      IF(D2.LT.0.001) C2=0.
      C3=DX/(D(I,2,3)+DX/2.)
      C4=DX/(D(I,2,4)+DX/2.)
      C5=H*DX*SQRT((1.-D1)**2+(1.-D2)**2)/(H*D(I,2,5)+AK)
      C6=DX*DX*RC*(1.+D1+D2-D1*D2)/(2.*DT*AK)
      C7=DX*SQRT((1.-D1)**2+(1.-D2)**2)
      RETURN
      END
```

```
      SUBROUTINE RKG(T,HA,HC)
C THIS SUBROUTINE COMPUTES THE TEMPERATURES OF THE REACTION,REFERENCE
C   AND IDEAL CHAMBERS.
C   THE GILL MODIFICATION OF THE RUNGE-KUTA TECHNIQUE IS EMPLOYED.
      COMMON PRE(10,3,3),DX,DT,Y(4),X(2),A(4,4),Q(3),BK(3)
      DO 1 J=1,4
      T=T+DT*A(J,4)
C   THE REACTION CUP.
      BK(1)=DT*(0.153989734*(T/5.)**3/(EXP(T/5.)-1.)+HA*(X(1)-Y(1)))/HC
C   THE REFERENCE CUP.
      BK(2)=DT*HA*(X(2)-Y(2))/HC
C   THE CUP IN THE IDEAL SINK.
      BK(3)=DT*(0.153989734*(T/5.)**3/(EXP(T/5.)-1.)-HA*Y(3))/HC
C   COMPUTE THE REMAINING CONSTANTS IN THE RKG METHOD FOR ALL THREE CASES.
      DO 1 K=1,3
      Y(K)=Y(K)+A(J,1)*(BK(K)-A(J,2)*Q(K))
    1 Q(K)=Q(K)+3.0*(A(J,1)*(BK(K)-A(J,2)*Q(K)))-A(J,3)*BK(K)
      Y(4)=(Y(1)-X(1)-Y(2)+X(2)-Y(3))/Y(3)
      RETURN
      END
```