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A Cell Model for Isoperibol Calorimeters

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Abstract

A calorimeter can be modeled as a large number of volume elements or cells in each of which the temperature may be considered uniform, and each of which can store heat and exchange heat with other cells. Application of the first law of thermodynamics to this set of cells leads to representations of the usual calorimetric equations for the energy change expressed in terms of measurable or estimatable heat capacities, heat transfer coefficients, temperatures, and work terms for the individual cells. Analysis of the results yields a framework within which most of the design and measurement problems of isoperibol calorimeters can be treated.

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1. Introduction and summary

A calorimeter is an instrument for measuring the energy of a phenomenon evidencing itself as an observable thermal effect. In current practice, this energy is considered to have been measured when it has been related to the metre, kilogram, and second; i.e. the International System of Units (S.I.).

In each of the experiments required for the measurement, the process of interest which may be an internal energy change, a heat transfer, or an amount of work done causes a thermal effect in the calorimeter which is evidenced by a change in temperature or, for example, a phase change in the calorimeter or some part of the calorimeter. Typical experiments consist of observing the thermal effects caused by a measured amount of electrical work in an "empty" or "full" calorimeter or of comparing the thermal effects of a chemical reaction and a measured amount of electrical work.

In each case, the observed thermal effect is related to the internal energy change, heat transfer, or work done by applying the first law of thermodynamics to the system identified as the calorimeter. This is done by equating the increase in internal energy of the system to the work done on the calorimeter plus the heat transferred to the calorimeter from its surroundings.

Isoperibol calorimeters[1], calorimeters having a constant temperature environment, are in common use for measuring many classes of thermo-

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[1] To be distinguished from phase change calorimeters as the Bunsen ice calorimeter.

chemical and thermodynamic properties (i.e. enthalpies of solution and combustion, enthalpies of reaction, and enthalpy changes between high temperatures and standard temperatures), energies of biological processes, the energy of laser or nuclear radiation, and the energies of other processes.

The accuracy of results calculated using accepted procedures [1][2] for this type of calorimeter has been subject to question [2]. The details of this particular controversy were resolved [3,4]. The question of the accuracy of the results obtained with this type of calorimeter[3], however, remained unanswered [5] because the theory of operation of isoperibol calorimeters was inadequate. At that time, the theory could be said to be based on either the analysis of an unrealistically simple model such as the two body model [4] or else on White's [6] apparently more comprehensive but ambiguous treatment. White does not describe clearly the model to which his theory applies so that it is hard or impossible to judge whether a calorimeter satisfies the conditions required for his conclusions to be valid. This point has been discussed earlier ([4], p. 4206). For this reason, the limitations of accepted practices and concepts that have been adopted to reduce systematic error in the measurements using isoperibol calorimeters, as well as other types of calorimeters, were still ambiguous.

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[2] Numbers in brackets refer to references at the end of the paper.

[3] To be fair, the same can be said to apply to a greater or lesser extent to other types of calorimeters.

It should be emphasized that without any theory of operation of a calorimeter there can be no independent means of judging experimental practice. A useful measurement theory must be based on the analysis of a model of a calorimeter for it is in only this way, for example, that general principles used in experimental practice acquire any useful meaning. For a measurement theory, based on an appropriate model, to be useful it must be stated in sufficiently precise terms that all of its assumptions and consequences can be subjected to the tests of experiment. The degree of precision of the theory in this respect determines to what extent a consideration of systematic error in a calorimetric measurement can be carried out in a rational way.

If the theory fails to meet all the tests of experiment and experience, it must be discarded and a better theory developed. For example, the simplest derivation of the method for calculating results obtained with an isoperibol calorimeter is based on the assumption that the temperature of the calorimeter is uniform. This assumption leads to the consequence that an experiment can be ended immediately after a power input to the calorimeter is completed. Since this is not confirmed by experiment, this model of an isoperibol calorimeter must be rejected.

By the same token, interpretation of an experimental test in a way not justified by theory is tantamount to making a systematic error. An example of this kind of situation is summarized later in this section in connection with the interpretation of calorimetric results obtained for different levels of power input to a calorimeter. Thus, analyses of more realistic models of an isoperibol calorimeter are of decisive importance not only in devising a measurement procedure for the real instrument but also in establishing the validity of the measurements made with it. To the extent that the sophistication of the model is not commensurate with the accuracy desired for the measurements, the results of experimental tests will have less significance.

A quantitative judgment of the adequacy of a theory for a given accuracy requirement is not a simple matter. Perhaps an unambiguous decision can never be made. Suffice it to say, however, that if the experimentalist ignores the consequences of measurement theory, he precludes the possibility of making any rational independent judgment as to the nature or magnitude of the systematic error inherent in his calorimetric measurements.

The presentation of the analysis of the model in this paper has been divided into two parts--the main text in sections 2. and 3. and the details in section 4. In the main text, we have selected and presented those results that we consider to be of central importance. In the details, the supporting mathematical development for the main text is given as well as some further conclusions and insight into the behavior of an isoperibol calorimeter predicted by the model. The presentation of results in the main text proceeds from the less to the more complex measurement problems, in terms of the analysis of this model. We believe that analysis of this model offers a general framework within which most of the problems of isoperibol calorimeters can be examined. The analysis is far from complete; this will require, for example, numerical calculations. A feature of the model which should prove extremely fruitful is that it is amenable to such numerical calculations. A brief introduction to the model and a summary of the main conclusions are presented in the remaining part of this section.

This paper represents the second in a series of analyses [7,8] of more sophisticated models of an isoperibol calorimeter based on the application of the first law of thermodynamics to the calorimeter or some part of the calorimeter as a thermodynamic system. The first law is applied with symbolism and meanings as follows: ΔU, the increase in internal energy of a system, is equal to the sum of Q, the heat transferred to the system from the surroundings, and W, the work done on the system. Heat is the energy transfer caused by a temperature difference between the system and its surroundings and work is the change in energy of the system caused by processes that are ultimately reducible to raising or lowering a weight in the surroundings. Thus, the common expressions, "electrical heat" and "heat of stirring" represent quantities which are treated as work in this paper.

The expression "storage of or conversion to heat", as used in this paper, means an increase in the internal energy of a system that can be completely described as a sum of terms each of which is the product of the heat capacity of some part of the calorimeter and an actual increase in temperature for this part of the calorimeter. Thus, in order to produce an observable thermal effect in an isoperibol calorimeter, energy or work is converted to heat inside the calorimeter. The positions in space inside the calorimeter where this occurs are referred to as the "location of or geometric distribution of the sources of heat or energy".

The model for an isoperibol calorimeter analyzed in this paper is a natural extension of the "two body" model [8]. In the "two body" model, the calorimeter is considered to consist of two cells enclosed by the surroundings, and having the following characteristics. The temperature of the surroundings is constant and uniform. The temperatures of the two cells are uniform but generally different from each other and the temperature of the surroundings. The heat capacities of the cells are constant--independent of temperature and time--but are not the same in general. The two cells exchange heat with each other at a rate equal to the product of a heat transfer coefficient and the difference in temperature of the cells. Each cell exchanges heat with the surroundings at a rate equal to the product of a heat-transfer coefficient and the difference in temperature of the cell and its surroundings. The heat transfer coefficients are constant but may be different. When heat transfer coefficients are constant, this type of heat transfer is referred to as "linear".

In this paper, we consider the calorimeter to consist of an arbitrarily large number of cells which again exchange heat in proportion to their temperature differences; an approach that parallels the work of Margas, Tabaka, and Zielenkiewicz [9a] and Davids and Berger [9b]. Temperature of the surroundings is now generalized to be non-uniform but constant. In section 4.2, we give the connection between this model and the linear partial differential equations and boundary conditions for heat flow in the continuum model for an aneroid isoperibol calorimeter [7]. In the following summary of results, we give the main conclusions; specific conditions for the validity of these conclusions are to be found in the main text.

In section 2, 4.2, and 4.3, we consider the case in which no chemical reaction or phase transition takes place in the calorimeter, the heat capacities of the cells are constant, and heat transfer is linear. Also, we consider only those processes of interest where work is done on the cells which is, in general, different for each cell.

During the time intervals in an experiment when the process of interest is not taking place, we establish the existence of rating periods (sections 2.1 and 4.2). In a rating period, the rate of change of temperature in each cell is proportional to the difference between the convergence temperature (i.e. steady state) and the actual temperature at any particular time. The constant of proportionality, the cooling constant which we designate as $-\lambda_1$, is the same for all cells. These results have been derived previously for the continuum and two body models [7,8]. These results are extended to include stirred fluid calorimeters (section 2.2) to the extent that our equations for heat flow by convection (section 4.1) are valid.

During the time interval in which the process of interest is taking place, the main period, we again establish (section 2.1, 2.2 and 4.3) that the results may be expressed in the usual [7] form: work done on the calorimeter equals an energy equivalent times a corrected temperature rise.

These results are a complete analogue of those derived for a continuum model [7] and the details show that the energy equivalent depends on the location of the sources of energy in the calorimeter. We call this the problem of equivalent sources. (We show that the energy equivalent depends upon the geometrical distribution of the work input to the calorimeter. This is a less restrictive assumption than that made previously [7], which was that the power input to the cells of the calorimeter during the main period is a product of a function of time and a function of cell location.)

It should be pointed out that this form of expressing the results again verifies (see [10]) that experiments carried out with different heating rates reveal nothing about the problem of equivalent sources. Also, the problem of equivalent sources is not necessarily eliminated by making the temperature-time curves the same in "calibration" and "unknown" experiments. This is due to the fact that a difference in the locations of the sources can cause a difference in the heat exchange with the surroundings even if the temperature time curves are the same (section 4.3). The difference in heat exchange shows up purely as a difference in the energy equivalents for the two experiments. The heat exchange is properly accounted for regardless of the shape of the temperature-time curve provided the sources are in the same location in a practical sense. It may be desirable to reproduce the temperature-time curves in calorimeters having non-linear thermal properties. However, Swietoslawski's [11] principle of substitution with its emphasis on the temperature-time curve should be modified to emphasize the geometrical equivalence of sources.

As in the continuum model [7] and two body model [4,8] we show (section 4.3) that energy equivalent is not simply the sum of heat capacities of the cells of the calorimeter. New results are that, by inspection of the relative temperature distribution in a rating period and at the convergence temperature (see section 4.2, eq. (4-29) and section 4.5) one can infer what these weighting factors are, and that the heat capacity of each cell makes a positive contribution to the energy equivalent (section 4.3). All these results apply to stirred fluid calorimeters within the limitations mentioned previously.

In the second part of the paper, section 3, we show what general constraints must be placed on the design of the calorimeter in order that heat transfer can be non-linear (i.e. no assumptions of linearity are made) during the main period in the region of the calorimeter where the process of interest is taking place. These constraints are in accord with those inferred from analysis of the two body model [4,8].

In addition, we derive a general[4] design criterion for the energy equivalent of the calorimeter to be independent of source location with which one may classify (section 3.1), as well as analyze (section 4.4), designs. This criterion formalizes and generalizes the concept given previously [7]. It also emphasizes the importance of another aspect of the problem of equivalent sources connected with, for example, the heater current lead problem of an electrical heater (section 3.2 and 4.3). It is our belief that this design criterion and the experimental test for equivalence of sources given here and previously [7] should now be incorporated in the principle of substitution.

In the final section of the main text (section 3.2), we analyze what general constraints must be placed on the design and operation of the calorimeter in order that we can properly electrically calibrate a calorimeter in which a chemical reaction or transition from one phase to another takes place. These contraints are in accord with those given previously [8]. Indications of how the analysis can be extended to drop calorimetry and flow calorimetry are outlined. Some comments on heat capacity measurements are given in section 4.5.

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[4] These constraints or criteria are general in the sense that they require a minimum of assumptions. They are not meant to imply that specific different arrangement could not solve, for example, the problem of equivalent sources.

2. Description of the cell model.

In this section and in section 3.1, we shall consider a calorimeter in which no chemical reaction or physical change in state (i.e. phase transition) occurs.

The basic problem is to describe the temperature distribution which changes with time in a calorimeter which is surrounded by some opaque (to radiation) constant-temperature region (the surroundings) in which the temperature does not change with time but may vary from point to point. The change in energy stored in the calorimeter and the heat exchanged with the surroundings during an experiment can then be deduced from the temperature distribution in the calorimeter.

An experiment is divided into three parts in time. In the first part, the initial rating period, the observed calorimeter temperature is either constant or varies exponentially with time. In the second part, the main period, the temperature is raised by some means such as supplying electrical power for a limited time interval to a resistance heater. In the third part, the final rating period, the observed calorimeter temperature is again a constant or varies exponentially with time.

In order to describe the temperature distribution in the calorimeter we treat the region inside the constant-temperature surroundings as an aggregate of an arbitrary but sufficiently large number $\underline{n}$ of volume elements or cells such that each is small enough that its temperature can be considered uniform. The location of the cells will be regarded as fixed in space but the boundaries shall be considered to be flexible to the extent that the mass in each volume element is the same at all temperatures it assumes during an experiment. Each cell may store heat and exchange heat with other cells. Heat exchange may be by conduction, by thermal radiation, or by steady forced convection[5] (in fluids) although some problems associated with convection have not been solved, as will become clear later. Heat exchange by free convection is excluded.

The first step in the analysis is to apply the first law of thermodynamics to a single cell inside the surroundings. We equate the rate of increase in the internal energy of a cell to the sum of the rates of absorption of heat by the cell and of doing work on the cell. For the *i*th cell, the rate of increase in energy is the product of its heat capacity, C_i, and the rate of change of its temperature, $dT_i(t)/dt$. The rate at which heat is transferred to the *i*th cell from the *j*th cell is proportional to the difference in temperature between the two cells. The constant of proportionality is a heat transfer coefficient, h_{ij}, which applies to conduction, radiation, or forced convection or to combinations of these. Thus the rate of heat transfer is $h_{ij}[T_j(t) - T_i(t)]$. In the case of conduction h_{ij} represents the thermal conductivity multiplied by the cross sectional area between cells and divided by a characteristic distance between them. In the case of radiation, h_{ij} represents the coefficient found for the approximation derived from the Stefan-Boltzmann law and valid only for small temperature differences--that the radiant energy transfer at a given average temperature of two bodies is proportional to the temperature difference between them. In the case of forced convection, h_{ij} is proportional to the rate of increase of internal energy caused by flow of liquid from cell *j* to cell *i*. More precise definitions of h_{ij} are given in section 4.1.

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[5] We use the term heat as well as energy exchange by steady forced convection because we assume a constant velocity distribution in the fluid. Thus, energy transfer occurs only when the temperatures of the cells are different.

In addition to heat exchange among the n cells inside the constant-temperature surroundings heat exchange may occur between the ith cell and the surroundings. To include this, we consider the surrounding also to be divided into cells, again small enough so that the temperature in each cell is uniform. Then some closed surface, S, that completely encloses the n cells of the calorimeter is drawn such that the contiguous cells, whose inner boundary constitute this surface, are in the surroundings. That is, the temperatures, T_s, of each of these contiguous cells, though different, is independent of time throughout an experiment. Where the boundary suface S is located is not so important as that it exist. (Some consequences of this assumption are given at the end of section 4.3). Then, the rate of heat transfer from the sth cell in the surface S to the ith cell in the calorimeter is $h_{is}[T_s - T_i(t)]$. This term is significant because it yields the total rate of heat transfer to the calorimeter from the surroundings when summed over all cells $i(1 \leq i \leq n)$ and cells s.

The rate of doing work on the ith cell is represented by the sum of a constant power, $P_i°$, due for example, to the rate of doing work against the internal stresses of the ith cell by its immediate neighbors, to electrical power supplied to a resistance thermometer, or to power due to stirring, and a time-varying power $P_i(t)$, for example, electrical power supplied to a resistance heater during the main period. $P_i(t)$ is zero except during the main period.

Summing over all cells s in the surroundings and the other interior cells j inside the surroundings that exchange heat with a particular cell i, we can write, for the application of the first law to the ith cell,

$$C_i \frac{dT_i(t)}{dt} = \Sigma_s h_{is}[T_s - T_i(t)] + \underset{j \neq i}{\Sigma_j} h_{ij}[T_j(t) - T_i(t)] + P_i^\circ + P_i(t) \qquad (1 \leq i \leq n) \qquad (1)$$

Many of the h_{ij} and h_{is} are zero, because the ith cell cannot exchange heat with all other cells. Except for radiant heat exchange (see section 4.1), h_{ij} or h_{is} will be zero except for direct heat exchange between cell i and cells s and j.

Eq. (1) can be written for each of the n cells inside the constant-temperature boundary, S, giving a set of n equations interrelating the temperature of the cells. Accordingly, we have appended the notation $1 \leq i \leq n$ to eq. (1). Details of the physical basis for eq. (1) in possibly more familiar terms, the corresponding linear partial differential equations and boundary conditions for heat transfer assumed for the model, are given in section 4.1.

In sections 4.2 and 4.3, eqs. (1) are put into matrix form, for ease of manipulation, and details of their solution to yield the results discussed in sections 2.1 and 2.2 are summarized.

2.1 Aneroid calorimeters

For calorimeters in which there is no stirred fluid, h_{ij} and h_{is} are positive and h_{ij} is symmetric (i.e. $h_{ij} = h_{ji}$).

In rating periods, all $P_i(t)$ are zero. Assuming all C_i, h_{is}, h_{ij}, and $P_i°$ to be independent of temperature and time, solution of eqs. (1) gives the following form of the temperature as a function of time in the *i*th cell:

$$T_i(t) = T_{\infty i} + \sum_{1}^{n}{}_k a_i(\lambda_k) d_i(\lambda_k) \exp[\lambda_k t], \quad 1 \leq i \leq n \qquad (2)$$

The terms in eq. (2) are as follows: (1) $T_{\infty i}$ is the temperature of the *i*th cell in the steady state due to all the constant power inputs, $P_i°$ for $1 \leq i \leq n$, and the constant temperatures, T_s for all s. (2) The λ_k are all real, negative numbers and are the eigenvalues of a matrix that is generated by writing eqs. (1) in matrix notation (see section 4.2). The sum over k is over all n eigenvalues λ_k, $1 \leq k \leq n$, of this matrix (i.e. some of the λ_k may be identical). (3) The $d_i(\lambda_k)$[6] are constants which depend on the thermal properties of the materials of the calorimeter and their placement in the calorimeter. The $a_i(\lambda_k)$ also depend upon the temperature distribution at time t = 0 ($T_i(0)$ for $1 \leq i \leq n$) as well as in the steady state ($T_{i\infty}$ for $1 \leq i \leq n$). Details are given in section 4.2.

Some cells of which temperatures are given by equation (2) belong to the thermometer and in particular to the sensing element. If more than one cell is involved, the observed temperature, that is, the

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[6] The $d_i(\lambda_k)$, $1 \leq i \leq n$, are proportional to the entries of the eigenvector for the eigenvalue λ_k of the matrix mentioned above.

instantaneous temperature sensed by the thermometer, T*(t), can be represented by a weighted average[7]

$$T^*(t) = \sum_1^n \omega_i T_i(t); \quad \sum_1^n \omega_i = 1 \tag{3}$$

The weighing factors ω_i are defined to be zero for cells outside the sensitive part of the thermometer so the sum in eq. (6) may be taken over all n cells of the calorimeter.

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[7] Eq. (6) implies a linear relationship between the observed temperature and the temperatures of cells making up the sensitive part of the thermometer. The value of T*(t) must be obtained by use of any calibration information, such as the temperature-resistance relationship of a resistance thermometer. In a simple case of a uniform resistance wire considered to be made up to 20 cells, the ω_i are all equal to 1/20.

When the exponential terms for λ_k for $k > 1$ in eq. (2) have become negligible at some time t_o, the calorimeter is in a rating period and the equation reduces to one term

$$T_i(t) - T_{\infty i} = a_i(\lambda_1)d_i(\lambda_1)\exp[\lambda_1(t - t_o)], \quad 1 \leq i \leq n \tag{4}$$

since it can be shown that the eigenvalue of smallest magnitude is distinct (i.e. unrepeated, see section 4.2). The general conditions for the absolute value of λ_2 being much larger than the absolute value of λ_1 have not been derived but some indication that this may be true in general is given by consideration of simple models of calorimeters (see the last part of section 4.5).

Equation (4) can easily be put in the customary form [1] for determining the cooling constant, $-\lambda_1$: multiply eq. (4) by ω_i and sum over all i; substitute from equation (3) to obtain

$$T^*(t) - T_\infty^* = \exp[\lambda_1(t - t_o)] \; \Sigma\omega_i a_i(\lambda_1)d_i(\lambda_1).$$

Differentiation of this equation and substitution of $T^*(t) - T_\infty^*$ gives

$$dT^*/dt = \lambda_1[T^*(t) - T_\infty^*] \tag{5}$$

As can be seen from eq. (4) or eq. (5), the cooling constant is the same for any location of the thermometer inside the surroundings. Other important properties of rating periods associated with the fact that the $d_i(\lambda_1)$ of eq. (4) all positive are derived and summarized in the last paragraph of section 4.2.

During the main period, not all the $P_i(t)$ are zero. Assuming as in the rating periods that all C_i, h_{is}, h_{ij} are constant, the solution of eq. (1) yields a more complex equation for the temperature of the ith cell containing the terms in eq. (2) plus terms involving integrals of the form $\int_0^t P_i(\tau)e^{\lambda_k(t - \tau)}d\tau$ where τ is the variable of integration. (See section 4.3.) Using this equation and eq. (2), which, respectively, describe the temperature distribution in the calorimeter as functions of time in the main period and in the rating periods, one can deduce the increase in internal energy and the total heat (transferred to or absorbed by) the calorimeter from the surroundings during the main period to derive the results to be summarized below. This procedure is the same as was used in the continuum model presented previously [7]. An equivalent but simpler procedure, summarized in section 4.3, is to integrate, directly, the matrix form of eqs. (1) from a time t_1 in the initial rating period to a time t_2 in the final rating period to obtain

$$W = E_i\{T_i(t_2) - T_i(t_1) + \lambda_1 \int_{t_1}^{t_2}[T_{\infty i} - T_i(t)]dt\} \qquad (6)$$

$$(1 \leq i \leq n)$$

In eq. (6) W is equal to $\Sigma_{1}^{n}{}_{i}\int_{t_1}^{t_2} P_i(t)dt$ or the total work done on the calorimeter by sources of energy in the process of interest.[8]

The total work rather than just the work on ith cell appears in eq. (6) because the temperature of the ith cell is altered by all the time varying power inputs $P_i(t)$, $1 \leq i \leq n$ to the calorimeter. E_i is an energy equivalent of the calorimeter that will be obtained if the temperature is measured at the ith cell. E_i is proportional to but is not exactly equal to the total increase in the internal energy of the entire calorimeter from the beginning to the end of the main period (see section 4.3, eq. (4-42)). In particular, E_i is proportional to a weighted rather than a direct sum of the heat capacities of all the

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[8] Strictly, W includes the net work done on the calorimeter that produces a change in strain at the boundary surface S. We assume this part of W is proportional to $T_i(t_2) - T_i(t_1)$ (see section 4.1) which requires, for example, that the pressure external to the surface S be constant throughout the duration of an experiment. In any event, this part of W will be relatively small and tend to cancel between "calibration" and "unknown" experiments.

cells of the calorimeter (see last paragraph of section 4.3). The weighting factors are all positive but are not equal, in general, unless λ_1 is identically zero (see section 4.5) which is not possible for an isoperibol calorimeter. In general, E_i will be different for each cell and, for a given cell, will be different, in general, for different relative magnitudes of the set of values of $\int_{t_1}^{t_2} P_i(t)dt$, $1 \leq i \leq n$ unless λ_1 is identically zero (see section 4.3 and 4.5). Eq. (6) states that work associated with the process under study, W, is equal to an energy equivalent nultiplied by the corrected temperature rise of convential isoperibol calorimetry [1] as measured in the ith cell.

If it is desirable to represent the thermometer as consisting of more than one cell, division of both sides of eq. (5) by E_i, multiplication by ω_i, summation over all n cells, and use of equation (3) gives

$$W = E^* \{T^*(t_2) - T^*(t_1) + \lambda_1 \int_{t_1}^{t_2} [T_\infty^* - T^*(t)]\}, \tag{7}$$

the energy equivalent E* is now a weighted average of the E_i related to the various cells making up the thermometer and is determined by a known work input W. Formally, E* is the reciprocal of $\sum_{i=1}^{n} \frac{\omega_i}{E_i}$.

The energy equivalent E*, as E_i, also depends in general on the geometric distribution of the work associated with the process under study. It can be shown (see eq. 4-45, section 4.3), as was shown previously [7], that this is due to the fact that in any real isoperibol calorimeter, the heat transferred to the calorimeter from the surroundings during the main period is proportional to both $\int_{t_1}^{t_2} [T_{\infty i} - T_i(t)]dt$ and to W of eq. (6). The proportionality constant for W is a function of the geometric distribution of the work input to the calorimeter and the heat transfer coefficients associated with the various cells of the calorimeter. (This proportionality constant is zero, in general, only if λ_1 is zero). Thus even if $\int_{t_1}^{t_2}[T_{\infty i} - T_i(t)]dt$ is the same for two experiments having different geometric distribution of the work input to the cells, the heat transferred to the calorimeter during the main period will be different and this shows up as a difference in energy equivalents for the two experiments.

Eqs. (2) and (7), for example, are analogous to the equations (6) and (2) developed previously for the continuum model of an aneroid calorimeter [7] and therefore this analysis reproduces the results given in that paper which may be summarized as follows: (I) The observed change in temperature is proportional to the change in internal energy of the calorimeter. (II) Conventional methods of determining the corrected temperature rise are valid for these more sophisticated models. The corrected temperature rise completely accounts for the heat transfer to the calorimeter from its surroundings only if the calorimeter is designed so that this heat exchange is the same for the different source locations of a "calibration" and "unknown" experiment. (III) The energy equivalent of the calorimeter depends on the location of the thermometer and the relative locations of energy sources to be compared.

The dependence of the energy equivalent on the location of sources constitutes a major obstacle to accurate calorimetry and its elimination, in so far as possible, is a major if not the paramount design problem of calorimetry. This problem, called the equivalence of sources, is examined further in section 3.1.

2.2 Calorimeters with stirred liquids

Because of the large number of calorimeters which contain stirred water, it is desirable to extend the analysis as far as we can to include forced convection. That part of h_{ij} that is due to forced convection is proportional to the component of the velocity in the direction of cell $\underline{j}$ to cell $\underline{i}$ and the sign of this velocity may be either positive or negative. From this, one can see that if heat is transferred entirely by convection, $h_{ij} = -h_{ji}$ and the sign of h_{ij} may be either positive or negative.

The case of steady laminar fluid flow, in which fluid velocities are constant in speed and direction, can be treated as given in section 4.1. If the cells are small enough, it can be shown that the net h_{ij} (i.e. due to conduction, radiation, and convection) is always positive but h_{ij} is asymmetric ($h_{ij} \neq h_{ji}$). Also, λ_1 is still real, negative, and distinct and the real part of λ_k for $k > 1$ are also negative and have a magnitude greater than λ_1. We have not shown that the λ_k for $k > 1$ cannot be complex and, in general, for an asymmetric h_{ij} they will be complex and occur in complex conjugate pairs. Consequently eq. (2) will be modified to the extent that for any distinct pair of complex conjugate roots $\exp(\lambda_k t)$ must be replaced by $\exp(b_k t)\cos(w_k t + v_k)$ where w_k, v_k, and b_k are real and b_k is negative[9]. However, all the other conclusions given for aneroid calorimeters still apply since the remainder of the analysis (see section 4.3) holds for the case when h_{ij} is asymmetric, but is positive.

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[9] In eq. (2), $d_i(\lambda_k)$ and $a_i(\lambda_k)$ are complex if λ_k is complex and $d_i^*(\lambda_k)a_i^*(\lambda_k) = d_i(\lambda_k^*)a_i(\lambda_k^*)$, where * = complex conjugate.

Turbulent flow, which is undoubtedly the most common condition in stirred-fluid calorimetry is very difficult to handle with confidence because heat transfer in turbulent convection has not been worked out as well as for heat transfer by radiation, conduction, and steady laminar convection. For the simplest empirical formula given by mixing length theory for heat transfer by turbulence for liquids stirred at a constant rate, h_{ij} is asymmetric and positive (see section 4.1). In this restricted case the results of section 2.1 again apply.

3. Non-linear heat transfer during the main period

3.1 Development of the problem

The analysis and, hence, the results of sections 2.1 and 2.2 are based on essentially three constraints which we summarize as follows. We assumed (1) that eq. (1) is valid everywhere in the calorimeter and all C_i, h_{ij}, and h_{is} are constant (independent of temperature and time) during the main period and (2) that these conditions apply during rating periods. We assumed that (3a) the temperatures of surface S of the surroundings are constant and, also, that (3b) there is no transfer of radiation across this surface and (3c) the total net transfer of mass across the surface is zero. Thus, the results of those sections strictly apply to adequately constrained experiments for example an experiment when electric power is supplied to a resistance heater during the main period (see the end of section 4.3 for further comments).

All of these constraints may be relaxed to a considerable extent within the framework of a linear theory of heat transfer provided certain restrictions on either the design or operation of the calorimeter (or both) are made. For example, to permit analysis of devices used in absolute radiometric measurements, the assumption that the constant-temperature surroundings surface is opaque to radiation (3b) must be removed. As has been discussed in detail previously [7] (see section 4.1), this can be done provided two conditions are met. First, the total rate of transfer of radiant energy to the calorimeter during rating periods is constant (so its effect can be included in the P_i° terms of eq. (1)). Second, radiant energy transfer occurs only between solid surfaces; that is, absorption of radiant energy in the gases inside the surface S can be neglected.

There is a significant number of types of experiments in which non-linear heat transfer inside the calorimeter occurs. In addition, some of the C_i, h_{ij} and h_{is} permanently change during the experiment; they are different in the initial and final rating periods. An important class of experiments of this type are those in which a chemical reaction or phase transition takes place in the calorimeter. The conditions for removing constraint (1), so that the case of non-linear heat transfer during the main period is permitted but all the C_i, h_{ij} and h_{is} are the same in both rating periods are given in this section. This affords some further insight into the problem of equivalence of sources. Using the results of this analysis, we consider the case of a chemical reaction occurring in the main period in section 3.3.

In order to treat the case of non-linear heat transfer during the main period, we restrict the calorimeter to one in which there is some closed surface A that is inside the constant-temperature surrounding surface S and that meets assumptions (3b) and (3c) of the previous section. In the region between A and S there are m cells, and to each cell eq. (1), with all C_i, h_{is} and h_{ij} constant, applies throughout the duration of an experiment. In addition, we require that the heat transfer coefficients of the ath cell of the envelope of contiguous cells whose outer boundaries constitute the surface A be constant, first, with respect to the cells between A and S, and second, with respect to the cells s making up surface S. These heat transfer coefficients are, respectively, h_{ia} for $1 \leq i \leq m$ and h_{as} for all s. The number of cells enclosed by the surface A will be ℓ, chosen so that $\ell + m = n$, and they will be numbered from 1 to ℓ. No confusion results with the numbering from 1 to m of the cells between A and S.

We may apply conservation of energy at each moment in time to either the entire calorimeter or just the cells inside the surface A. Leaving to section 4.4 a summary of the proof that the final equations will be the same in either case, we choose here to apply it to the cells inside the surface A. This gives

$$\sum_{1}^{\ell}{}_i C_i \frac{dT_i(t)}{dt} = \frac{dQ(A)}{dt} + \sum_{1}^{\ell}{}_i P_i{}^{\circ} + \sum_{1}^{\ell} P_i(t) \tag{8}$$

In eq. (8), $\sum_{1}^{\ell}{}_i C_i dT_i(t)/dt$ is the total rate of increase of the internal energy of the cells in A. The work terms, $\sum_{1}^{\ell}{}_i P_i{}^{\circ}$ and $\sum_{1}^{\ell} P_i(t)$, have the same meaning as before (ie. $P_i(t) = 0$ except during the main period). $dQ(A)/dt$ is the rate of heat transfer to the cells inside A from the constant-temperature surroundings surface S and the cells between the surfaces S and A in the inward direction as shown in fig. 1.

dQ(A)/dt, see section 4.4, is given by

$$\begin{aligned} \frac{dQ(A)}{dt} &= \Sigma_s \Sigma_a h'_{as}[T_s - T_a(t)] - \Sigma_a h'_a T_a(t) \\ & \sum_1^m \beta_i(A)[P_i{}^\circ + P_i(t) - C_i \frac{dT_i(t)}{dt}] \end{aligned} \qquad (9)$$

In eq. (9), h'_{as} is the <u>total</u> heat transfer coefficient by all paths, direct and indirect, between the <u>a</u>th cell of A, whose temperature is $T_a(t)$, and the sth cell of the surface S, whose temperature is T_s. h'_a is zero for aneroid calorimeters and, in general, $\Sigma_a h'_a = 0$. $\beta_i(A)$ is a dimensionless positive constant that has a value bounded by one and zero, is a function of only the various heat transfer coefficients of the cells between A and S, and depends upon the location of surface A. Physically, eq. (9) states that dQ(A)/dt is the sum of three parts. The first and second part, $\Sigma_a \Sigma_s h'_{as}[T_s - T_a(t)]$ and $-\Sigma_a h'_a T_a(t)$, respectively, are the rate of heat transfer across the surface A assuming the power input to the cells between A and S and the rate of change of internal energy of the cells between A and S is zero. The first part is caused by non-zero values of $T_s - T_a(t)$ and the second part is due to heat transfer across the surface A by convection caused by deviations of $T_a(t)$ from strict uniformity at each moment in time. (In eq. (9) each $T_a(t)$ is considered to be independent). The third part may be regarded as the sum of the fractions of the total power input, $P_i{}^\circ + P_i(t)$, to each <u>i</u>th cell between the surfaces A and S which is not stored as internal energy and appears as heat transferred across the surface A in the inward direction. Simple descriptions (for example, see [12]) neglect this second term. This is neither necessary nor is it desirable since the (imprecise) locations of both surfaces A and S preclude the assumption of zero mass between these two surfaces.

Eqs. (8) and (9) apply at all times during an experiment. During the main period each of the C_i for the cells inside A may depend upon temperature and/or time but during rating periods we assume they each have the same value. Combining eqs. (8) and (9) and integrating from time t_1 in an initial rating period to time t_2 in the final rating period gives, without any approximations, (see section 4.4),

$$\sum_{1}^{\ell}\int_{t_1}^{t_2} P_i(t)dt + \sum_{1}^{m}{}_i\,\beta_i(A)\int_{t_1}^{t_2} P_i(t)dt = E_A[T_A(t_2) - T_A(t_1) + \lambda\int_{t_1}^{t_2}[T_{\infty A} - T_A(t)]dt \qquad (10)$$

The left hand side of eq. (10) is of the general form of the work associated with the process under study. This equals an energy equivalent, E_A, times a corrected temperature rise as measured by a temperature $T_A(t)$ defined by eq. (11) where $\Sigma_s h''_{as} = \Sigma_s h'_{as} + h'_a$.

$$T_A(t) = \frac{\Sigma_a(\Sigma_s h''_{as})T_a(t)}{\Sigma_a(\Sigma_s h''_{as})} \qquad (11)$$

Eq. (10) differs from the analogous equations in section 2, eqs. (6) and (7), in three important respects. First, no assumption about the nature of the heat transfer inside the surface A during the main period is made so eq. (10) is valid for heat transfer of any type inside A during the main period. Second, the work terms in eq. (10) are in two parts. The first part is the total work done on the cells inside the surface A, $\sum_{1}^{\ell}{}_i\int_{t_1}^{t_2} P_i(t)dt$. The second part, from our previous discussion in connection with eq. (9), is equal to that fraction of the work done on the cells between surfaces A and S during the main period that appears as heat crossing the surface A and cannot be accounted for by the measurement of $T_A(t)$

throughout the time-course of the experiment. For an electrical calibration, it can be shown (see section 4.4) that this second work term is exactly analagous to the heater lead correction described by Ginnings and West [13]. Third, the energy equivalent, E_A, is independent of the location of the sources inside the surface A.

The invariance of E_A with the location of a source inside the surface A really requires that two conditions be fulfilled. First, we must be able to "correct" the work associated with the process under study for any associated work effects in the region between A and S. This requires either certain design restrictions or else auxiliary measurements, since these effects are not accounted for by the usual temperature measurements (ie. $T_A(t)$ in this case).

To the extent that the locations of the surfaces A and S are uncertain, these work effects should be made as small as possible. In particular, for an electrical calibration experiment, this requires that the total work supplied to the resistance heater current leads be small, by both design and choice of operating conditions (see section 4.4), as well as meeting other design criteria [13]. A sufficient test for the particular design and operating conditions would be to determine if the energy equivalent varies with different heater element resistances [14]. The same pair of current leads must be used in all experiments. Since the heater elements are the sources, their location must be the same unless the second or following condition is fulfilled.

The second condition is that we must be able to measure $T_A(t)$. In terms of eq. (3), the sensitive element of the thermometer must measure the temperature of all the cells forming the surface A with weighting factors $\omega_i = (\Sigma_s h''_{as})/\Sigma_a(\Sigma_s h''_{as})$ for i = all a, and $\omega_i = 0$ for i elsewhere. As White has pointed out [15], direct measurement of the required ω_i is not possible with any accuracy and the ω_i are not proportional to the areas of the various parts of the surface A. Thus, a surface thermometer cannot, in general, be constructed to exactly meet the second condition for equivalence of sources although it may well prove superior to a thermometer placed in a single location on the surface A.

Since we cannot measure $T_A(t)$ directly for any calorimeter as specified up to this point, we must constrain the design of the calorimeter so that the measurement of the temperature in a single location is equivalent to determining $T_A(t)$ of eq. (11). One such design choice is to attempt to make the temperature of some closed surface in the calorimeter isothermal. This condition is met to a greater or lesser extent in all calorimeters which contain a well-stirred fluid and also, for example, by the laminated wall design developed for an aneroid calorimeter by Prosen and Johnson [16].

A second design choice is to construct the calorimeter so $\Sigma_s h''_{as}$ is zero except for a small region on A. This condition is very nearly met by the attachment of radiation shields to the calorimeter "vessel" with a good thermal shunt (see [17], [18]).

It can be shown (see section 4.4) that for this type of design the temperature measured anywhere on the surface of the outermost (i.e. closest to the surface S) radiation shield, as well as at the thermal shunt, is equivalent to measuring $T_A(t)$. Because of this fact, the design of the stirred-water calorimeter developed by Coops (see [19] for details) is analogous to this type of calorimeter (the centrifugal stirrer, because of its mixing action, is the thermal shunt).

A third design choice is to place a thermometer in the region between A and S that measures $\Sigma_a \Sigma_s h''_{as}[T_s - T_a(t)]$ directly, essentially the design used in some conduction calorimeters (i.e. when the thermometer is a thermopile placed between the surface A and the constant temperature "block"). Ideally, the approach should be to attempt to force all the heat transferred to the surroundings to pass via the thermometer [20] since otherwise the ambiguity associated with the surface temperature measurements mentioned previously may arise. This means the heat transfer coefficients between the calorimeter and surroundings are necessarily large and the magnitude of λ_1 is large. We have inferred in section 2.1 that as λ_1 (or these heat transfer coefficients) increases, the variation in energy equivalent with different locations of sources may increase. The possible competition between these factors suggests that in cases where there are no other limitations, other designs may be preferrable. (For other comments on conduction calorimeters, see sections 4.4 and 4.5).

A suitable experimental test for designs intended to meet the second test for equivalence of sources has been described previously [7,8]. This test is the determination of the variation in the energy equivalent for different locations of an electric heater inside the surface A. Both the planning, execution, and interpretation of such tests must be done with care (i.e. see [21] or [22,23] for earlier work).

3.2 Changes in state of substances in the calorimeter

In this section, we shall restrict the calorimeter to be one which by design and experimental test is such that the energy equivalent is independent of the location of the sources for a fixed thermometer location. This means the measured thermometer temperature $T^*(t)$ will be treated as equivalent to a measurement of $T_A(t)$ of eq. (11). We will again assume as in section 3.1 the C_i, h_{ij}, h_{is}, h_{ia}, and $P_i°$ for all the cells between A and S are constant throughout the duration of an experiment. Maintaining the above limitations, we shall now consider the case where the heat capacities of at least some of the cells inside the surface A and their associated heat transfer coefficients,are different in the initial and final rating periods. (All the $P_i°$ for the cells in A are assumed to be the same for both rating periods.)

For purposes of illustration, it will be useful to consider the case where a chemical reaction occurs in a combustion bomb located inside the surface A, though the results will be applicable to other types of changes in state. In order to handle the experiment where a chemical reaction occurs inside this bomb, we must first reformulate the left hand side of eq. (8). Reformulation is necessary because eq. (8) implies the rate of change of the internal energy of the cells bounded by A is expressible in the form $\sum_1^{\ell} C_i dT_i(t)/dt$ throughout an experiment. This is not true during the main period of an experiment when the chemical reaction occurs. This can be seen by noting that while the integral of the above expression over the main period may be large, the total change in the internal energy of the cells bounded by A may be very small. For example, if the cells bounded by A were "completely isolated", (i.e. the region bounded by A has no interaction with its surroundings in terms of bath heat or mass transfer and work).

the change in their internal energy would be zero. Another reason the left hand side of eq. (8) must be reformulated is to separate the reactants and products of the chemical reaction from the inert calorimeter parts, so that the internal energy change associated with the chemical reaction can be expressed in terms of measurable quantities.

For our purposes it will suffice to return to the basic concept that the left hand side of eq. (8) is the rate of increase of the internal energy of the cells inside A, which we denote by $dU_A(t)/dt$. During the rating periods, $dU_A(t)/dt$ is expressible as $\sum_1^{\ell} C_i dT_i(t)/dt$, as was done previously. During the main period, however, $dU_A(t)/dt$ is due to both a rate of temperature change and the rate of change in internal energy caused by the chemical reaction. If no heat exchange occurs with either the cells between the surfaces A and S or the constant temperature surface S and no time varying power is supplied to the cells bounded by the surface A, these two contributions to $dU_A(t)/dt$ will be equal and opposite in sign, ie. $dU_A(t)/dt = 0$.

In order to express the energy of the chemical process in terms of measurable quantities, we divide the cells inside A into two groups. The first group will be called the reaction zone and are those cells whose chemical form and associated heat capacities have changed by virtue of a chemical reaction. The internal energy of these cells will be called $U_r(t_1)$ at the time t_1, the subscript r denoting reactants, and $U_p(t_2)$ at the time t_2, the subscript p denoting products. The second group, the remainder of the cells inside the surface A, will be called the empty system, referring to the fact that by design and construction the products or reactants can be removed from the calorimeter. The internal energy of the empty system at times t_1 and t_2 will be denoted by $U_c(t_1)$ and $U_c(t_2)$ respectively. Then we may write for the change in internal energy of the cells bounded by A

$$U_A(t_2) - U_A(t_1) = U_c(t_2) - U_c(t_1) + U_p(t_2) - U_r(t_1) \qquad (12)$$

Now suppose no reaction occurred in the reaction zone (ie. the reactant are present in the experiment in the final rating period) but the relative temperature distribution in the final rating period is identical to that which would have prevailed as if the reaction had occurred. We will call the internal energy in the reaction zone in this hypothetical state $U_{\underline{r}}(t_2)$, the subscript being underlined to emphasize it is a hypothetical state, in general.

Adding and subtracting $U_{\underline{r}}(t_2)$ in the right hand side of eq. (12) gives

$$U_A(t_2) - U_A(t_1) = [U_c(t_2) - U_c(t_1) + U_{\underline{r}}(t_2) - U_r(t_1)] \qquad (13)$$

$$+ [U_p(t_2) - U_{\underline{r}}(t_2)]$$

Up to this point, neither of the quantities in brackets are interpretable in terms of measurable quantities. Suppose now that the final rating period is the convergence rating period when the products are present. Since the convergence temperature is a steady state, the temperature distribution is independent of the heat capacities of any of the cells in the calorimeter, but will certainly depend in general on heat transfer coefficients.

It is shown, see section 4.2, that if the constant temperature of the surroundings surface S is uniform and the constant power inputs to the calorimeter approach zero, the convergence temperature distribution also tends to become independent of the heat transfer coefficients of the cells in the calorimeter. That is, it becomes uniform and equal to the temperature of the surroundings.

In this case, $U_r(t_2)$ can be associated with a real state. If the final rating period is taken as a convergence rating period and the above constraints are met, it can be shown that in place of eq. (10) we may write

$$-[U_p(T_A(t_2)-U_r(T_A(t_2)]+\sum_{1}^{\ell}{}_{i}\int_{t_1}^{t_2}P_i(t)dt+\sum_{1}^{m}{}_{i}\beta_i(A)\int_{t_1}^{t_2}P_i(t)dt \qquad (14)$$

$$=E_{Ar}\{T_A(t_2)-T_A(t_1)+\lambda_1\int_{t_1}^{t_2}[T_{\infty A}-T_A(t)]\}dt$$

In eq. (14) the first bracketed term on the left is the negative of the internal energy change of the reaction as if it had occurred at the convergence temperature, $T_{\infty A}$. The next two terms on the left hand side are the work terms that were discussed in the previous section. On the right hand side of the equation, E_{Ar} is the energy equivalent of the calorimeter with the reactants present, $T_A(t_2)$ is equal to $T_{A\infty}$ and λ_1 is a cooling constant determined in the initial rating period.

By a minor change in the analysis, it can be shown that if the initial rating period is at the convergence temperature and if the same constraints on the calorimeter design are met, then eq. (14) again holds except that in this case E_A is replaced by the energy equivalent when the products are present, $T_A(t_1)$, rather than $T_A(t_2)$, is equal to $T_{\infty A}$, and λ_1 is the cooling constant of the calorimeter determined during the final rating period.

It is to be noted that the temperature to which the chemical reaction or change in state is to be referred is completely unambiguous We believe that the possible uncertainty on this point as evidenced by differences in accepted procedures used in calorimetry (ie. compare [24] and [25]) is now resolved.

The constraints on the calorimeter operation and design are the most general ones that fulfill the condition that either the final or initial rating period temperature distribution be independent of changes in heat capacities and heat transfer coefficients of the cells of the reaction zone. Other conditions may serve to achieve the same aim.

For example, as λ_1 decreases in magnitude it can be shown (see section 4.5), that because the effect of a gradient on the constant temperature surroundings on the convergence temperature distribution is reduced, the effect of a change of a heat transfer coefficient inside the surface A will be correspondingly reduced. Also it is more important to make the constant power inputs negligible to the cells inside A and in particular those near the reaction zone. In cases, where this is not possible as, for example, in solution calorimeters, it suffices to note that if ratio of the power input divided by the heat transfer coefficients are small, the effect of small changes in heat transfer coefficients is correspondingly reduced (see section 4.5).

It should be pointed out that an additional constraint is required when the energy equivalent is determined by measuring the corrected temperature rise caused by a known ΔU for a standard chemical reaction. This is because it is assumed that energy equivalent of the calorimeter for the conditions applicable to the reaction under study, whose ΔU is unknown, can be calculated by adding or subtracting, as required, the appropriate heat capacities from the energy equivalent measured in the standard chemical reaction. It is shown (see section 4.5) that as λ_1 approaches zero, the energy equivalent, E_A, becomes more nearly an exact sum of the heat capacities of the cells inside the surface A or conversely, if λ_1 is not zero, it is never, in general, an exact sum although the weighting factors in the sum are always positive. Thus, for this situation it is desirable to design the calorimeter so λ_1 is small. If the energy equivalent is determined by electrical heating, it is not necessary to make these corrections. However, in this case the problem of equivalence of sources is more important.

To conclude this discussion of using a calorimeter for determining an energy of reaction, a few words about initiation and termination of the reaction are in order. To start the reaction, some work, though it may negligible in many cases, must be done on the calorimeter, (ie. in our example, it might be by doing electrical work on a fuse which ignites a sample). The measured amount of work constitutes the work terms on the left hand side of eq. (14).

Practically, the reaction will always stop of its own accord in a finite time: when either one of the reactants is exhausted or the net rate of formation of products is zero for either chemical equilibrium or kinetic considerations. Whether or not it has stopped within the time scale we have selected for our experiment can be established by whether or not a final rating period is reached [4] (ie. eq. (5) applies with $T^*(t)$ replaced by $T_A(t)$, and λ_1 and $T_{\infty A}$ are independent of the time selected for t_2, the beginning of the final rating period).

The above analysis applies equally well for a measurement of a physical change in state (ie. heat of fusion or transition). For example, in this type of experiment electrical work is necessary to heat a substance from a temperature below a transition point to a point above the transition point. Since part of the change in energy will not in general be associated with the actual heat of transition, appropriate heat capacity corrections as well as a separate determination of the transition temperature itself will be required. The analysis is quite specific about how these corrections should be made.

If, for example, we assume that the energy equivalent of the calorimeter has been determined when the reactants are present and we measure an energy of fusion in which the final temperature is above the melting point (and near the convergence temperature), then

$$U_p(t_2) - U_r(t_2) = C_p[T_A(t_2) - T_f] + \Delta U_f(T_f) + C_r[T_f - T_A(t_2)] \qquad (15)$$

In eq. (15) C_p is the heat capacity of the products and C_r is the heat capacity of the reactants at or near the fusion temperature, T_f and $\Delta U(T_f)$ is the required energy of fusion.

Equation (14) can be applied equally well to drop calorimetry provided we make the following assumption:

(1) The cells of the calorimeter and constant temperature surfaces are arranged so that all heat radiated in the direction of the calorimeter is absorbed by elements inside the calorimeter and none by cells between the surface A and surface S. (2) The temperature of the surroundings before and after the sample has been dropped are the same and independent of time.

That is, eq. (14) is equally valid if the closed surface S is allowed to be open for part of the main period provided we are able to properly account for the increase in internal energy, the work term, and the heat transfer term by measurements of a temperature, $T_A(t)$, associated with the surface A. (Otherwise additional measurements would be required.) It is clear that the boundary S can similarly open during rating periods provided the preceding statement is true and the rate of increase of internal energy, of doing work, and absorbing heat, are constant. Hence the analysis can be generalized to flow systems.

The other restrictions concerning the validity of eq. (14) still apply. The remainder of the analysis will not be presented since it closely follows the arguments presented in detail for the "two body" model of a drop calorimetric experiment given previously [4].

The problem of measuring heat capacities with isoperibol calorimeters due to the fact that the energy equivalent is not, for example, an exact sum of the heat capacities of the cells inside A has been mentioned before [7]. Some comments on this problem are given in section 4.5.

4. Details

4.1. Evaluation of the parameters in equation (1)

The physical interpretation of the parameters C_i, h_{is}, h_{ij}, and P_i° of eq. (1) or determination of numerical values for a specific model is based on the connection between eq. (1) and the description of the calorimeter heat flow problem in terms of partial differential equations and boundary conditions. We consider a calorimetric system for which heat transfer inside the surface S can be described by equations that are linear with respect to temperature and time. This excludes free convection which from a design standpoint poses no special problem [26]. For aneroid calorimeters, heat transfer occurs by conduction in solids and by both radiation and conduction in gases. When the absorption of radiant energy by the gas is negligible, the heat transfer problem can be formulated [7] in terms of the equation for heat conduction in solids and gases, eq. (4-1), the flux and temperature boundary conditions at gas-solid interfaces, eqs. (4-2) and (4-3), respectively, and the boundary condition at the surface S of the calorimetric system eq. (4-4).

$$c\frac{\partial T}{\partial t} = \nabla\cdot(k\nabla T) + p^\circ + p(t) \qquad (4\text{-}1)$$

$$k_a\left(\frac{\partial T}{\partial n}\right)_a = -k_g\left(\frac{\partial T}{\partial n}\right)_g - \oint_{A'} h(A,A')[T(A)-T(A')]\,dA', \quad \text{at } A \qquad (4\text{-}2)$$

$$T_a = T_g, \quad \text{at } A \qquad (4\text{-}3)$$

$$T = T(S), \quad \text{on } S \qquad (4\text{-}4)$$

In eq. (4-1), c is the heat capacity per unit volume. It is defined by $\frac{cdT}{dt} = (\frac{de}{dt})\frac{dT}{dt}$ where e is the internal energy per unit volume. (de/dT) is to be evaluated along the actual sequence of states occurring as a function of time at each position. For solids which are required to be elastic, c is approximately that at constant volume [27], while, for gases, it will usually be that at constant pressure or volume depending on the specific circumstances. T is the temperature as a function of time at a particular position. k is the thermal conductivity. p° and $p(t)$, are, respectively, the constant and time varying components of the power generated per unit volume by sources both internal and external to the unit volume under consideration. P° and $P(t)$ will include the rate of doing work against the internal stresses at a particular position.

In eqs. (4-2) and (4-3), the subscripts a and g denote the solid and the gas phases, respectively. $(\frac{\partial T}{\partial n})_a$ and $(\frac{\partial T}{\partial n})_g$ are the derivatives of the temperature with respect to position in the solid and gas, respectively, at the boundary A in the direction of the outward normal to A viewed from solid and gas, respectively. h(A',A) is the radiant heat transfer coefficient by all paths, direct and indirect, between a unit area on surface A and solid surfaces A' enclosing A [7]. The range of temperatures to which eqs. (4-1) - (4-4) apply is assumed to be small enough that c, k, p°, and h(A',A) are independent of temperature (and time) though they will vary with position.

Consider now the interior of S to be subdivided into cells fixed in space and of such size such that the temperature of each cell can be assumed to a first approximation as uniform. In addition, we shall assume that the boundaries of each shall be flexible to the extent that the mass in each cell is constant (so that the increase in internal energy due to a change in strain or volume is not caused by a change in mass). We will, for example, use the procedure described by MacNeal [29], see [30] Chp. 6) in which the cells can be constructed as polygons such that the interfaces are normal to a single interior point of each cell to which we assign values of temperature T_i to cell $\underline{i}$ and T_j to each of the cells $\underline{j}$ contiguous with cell $\underline{i}$.

Consider first the case where the cell i is located in the interior of a homogenious solid (or gas). Integrating eq. (4-1), using Green's Theorem, over the volume, V_i, enclosed by cell i, that has a total surface A_i, and calling $\bar{n}$ the outward normal to the surface of cell i

$$\oint_{V_i} c \frac{\partial T}{dt} dV = \oint_{A_i} k \bar{n} \cdot \nabla T \, dA + \oint_{V_i} p^\circ dV + \oint_{V_i} p(t) dV \qquad (4\text{-}5)$$

Assume c, k, p°, and p(t) are independent of position inside the cell, and are equal to c_i, k_i, p_i°, and $p_i(t)$, respectively. Define A_{ij} to be the area of the surface between cell i and j, l_{ij} to be the distance between the interior points of cells i and j, k_{ij} to be the thermal conductivity at the interface A_{ij}, and V_i to be the volume of cell i. Then using central differences to approximate grad T, eq. (4-5) can be approximated by

$$c_i V_i \frac{dT_i(t)}{dt} = \sum_j \frac{k_{ij} A_{ij}}{l_{ij}} [T_j(t) - T_i(t)] + p_i^\circ V_i + p_i(t) V_i \qquad (4\text{-}6)$$

To illustrate how the boundary conditions of eq. (4-2) and eq. (4-3) are treated, consider a simple two dimensional case where a solid-gas boundary, approximated as a plane, passes through the interior point of cell 1 constructed as shown in fig. (2). Assume that in the volume, V_{1a}, of cell 1 in the solid phase c, k, p°, and p(t) are independent of position and have the values c_a, k_a, $p_1{}^\circ{}_a$, and $p_{1a}(t)$ and in the volume of cell 1 in the gas, V_g, are again independent of position but have the values C_g, k_g, $p\,{}^\circ{}_g$, and $p_{1g}(t)$. Integrating eq. (4-1) first over the volume of cell 1 in the solid and then over the volume in the gas, and using eq. (4-2) (and the procedure used to derive eq. (4-6) one obtains the two equations

$$c_a V_{1a} \frac{dT_1(t)}{dt} = \overset{5}{\underset{4}{\sum}}{}_j\, k_a \frac{A_{ij}}{\ell_{ij}} [T_j(t)-T_i(t)] + k_a A_{1b}\left(\frac{\partial T}{\partial n}\right)_a + (p^\circ_{1a}+p_{1a}(t))V_{1a}$$

$$C_g V_{1g} \frac{dT_1(t)}{dt} = \overset{3}{\underset{2}{\sum}}{}_j\, k_g \frac{A_{1j}}{\ell_{1j}} [T_j(t)-T_i(t)] + k_g A_{1b}\left(\frac{\partial T}{\partial n}\right)_g + (p^\circ_{1g}+p_{1g}(t))V_{1g}$$

A_{1b} is the area of the boundary enclosed in cell 1. Integrating eq. (4-3) over the area A_{1b} one obtains

$$k_a A_{1b}\left(\frac{\partial T}{\partial n}\right)_a = -k_g A_{1b}\left(\frac{\partial T}{\partial n}\right)_g - \sum_j h(A_{1b},A_{jb})\,[T_j(t)-T_i(t)]\,A_{1b}A_{1j}$$

where A_{jb} is the area of the jth cell exchanging radiant energy with area A_{1b} of cell 1. Adding the preceding three equations gives

$$c_1 V_1 \frac{dT_1(t)}{dt} = \overset{5}{\underset{2}{\sum}}{}_j \frac{k_{ij}A_{ij}}{\ell_{ij}}[T_j(t)-T_i(t)] + \sum_j h(A_{1b},A_{1j})A_{1b}A_{jb}[T_j(t)-T_i(t)]$$

$$+ p_1^\circ V_1 + p_1(t)V_1 \qquad (4\text{-}7)$$

where $c_1V_1 = c_aV_{1a} + c_gV_{1g}$ and similarly for $p_1{}^\circ V_1$ and $p_1(t)V_1$. Comparing eqs. (4-6) and (4-7) with eq. (4-1), one obtains the following set of relations for the case of aneroid calorimeters.

$$C_i = c_iV_i \tag{4-8a}$$

$$h_{ij} = k_{ij}A_{ij}/\ell_{ij} + h(A_{ib},A_{jb})A_{ib}A_{jb} \tag{4-8b}$$

$$P_i^\circ = p_i^\circ V_i \tag{4-8c}$$

$$P_i(t) = p_i(t)V_i \tag{4-8d}$$

The values of C_i and h_{ij} are necessarily positive. h_{ij} is symmetric (see [28]) and can be interpreted as a direct heat transfer coefficient between nearest neighbors for conduction plus (or) a net heat transfer coefficient (ie. via all paths) for surfaces exchanging radiant energy. If ℓ is the size of a linear dimension of a cell h_{ij}/C_i varies as $1/\ell^2$ for conduction and as ℓ for the radiation contribution.

For calorimeters containing unstirred liquids we again exclude free convection which imposes more severe design constraints (see [26]). For liquids stirred at a constant rate or solids moving with a velocity u, the equation governing heat transfer [31] is

$$c\frac{dT}{dt} + c\,u\cdot\nabla T = \nabla\cdot(k\nabla T) + p^\circ + p(t) \tag{4-9a}$$

In eq. (4-9a) c, k, p(t) haves the same meaning as eq. (4-1), u is the velocity vector at a fixed position, and p° now includes the rate of dissipation of kinetic energy into heat per unit volume due to viscous effects. Taking the liquid to be essentially incompressible c is the heat capacity at constant volume (we exclude free convection, see [31] p. 188). Conservation of mass requires

$$\mathrm{div}\ u = 0 \tag{4-9b}$$

At solid-liquid boundaries, the tangential and normal components of the velocities must be equal and zero, respectively. Thus if the solid is stationary the flux and temperature boundary conditions will have the same form as eq. (4-2) and eq. (4-3) with $h_a(A,A') = 0$. For interior points of a stirrer shaft rotated at constant angular velocity, eq. (4-1) will apply since $u \cdot \mathrm{grad}\ T = 0$ as well as eq. (4-2) and (4-3).

For forced, steady laminar flow in the interior of a liquid, eqs. (4-9) apply with u independent of time though varying with position as for example in the laminar sublayer of the liquid. Transposing and integrating the convective term of eq. (4-9a) over the volume of cell *i* using eq. (4-9b) gives

$$-\oint_{V_i} c u\cdot\nabla T\, dV = -\oint_{A_i} c\bar{n}\cdot(uT)\, dA = c\sum_j A_{ij} u_{ij} \frac{[T_i(t)+T_j(t)]}{2}$$

Integrating eq. (4-9b) over the volume of cell i, one obtains

$$+\oint_{A_i} u\cdot\bar{n}\, dA = -\sum_j A_{ij} u_{ij} = 0 \tag{4-10}$$

In both equations u_{ij} is the velocity normal to the surface A_{ij} in the direction from the interior point of cell j to cell i. Combining the preceding two equations yields

$$-\oint_{V_i} c u\cdot\nabla T\, dV = c\sum_j A_{ij} \frac{u_{ij}}{2} [T_j(t)-T_i(t)]$$

so that the term to be added to the r.h.s. of eq. (4-8b) to account for convection is of the form + $c_iA_{ij}u_{ij}/2$ and is antisymmetric ($u_{ij} = -u_{ij}$). Because of eq. (4-10), the sum $\Sigma_j h_{ij}$ where j is over all cells exchanging heat with cell i will contain no convective contributions. If the linear dimentions of a cell are of size ℓ, then the part of h_{ij}/C_i due to convection will vary as $1/\ell$ and h_{ij} will be positive only when ℓ is sufficiently small. For water, this requires that ℓ be less than $0.029/|u|$, where $|u|$ is the magnitude of the velocity u.

When the flow is turbulent in a fluid stirred at a constant rate, the velocity u is no longer independent of time. Both u and T can be approximated [32,33] as the sums of fluctuating components, u' and T', due to turbulence and mean components, $\overline{u}$ and $\overline{T}$, (ie. u or T averaged over times long with respect to the flucuations). It can be shown [32,33] that eqs. (9) still formally apply with u and T replaced by $\overline{u}$ and $\overline{T}$ provided we add the term $-c\Sigma_{1}^{3}{}_{i}\frac{\partial}{\partial X_i}(u_i'T')$ to the r.h.s. of eq. (4-9a), The u_i' are the components of u' with respect to the bases X_i of an orthogonal coordinate system. Since no entirely adequate method for evaluating this term, the flux due to transport of heat by turbulence, exists, we appeal to empirical mixing length theory [33] and assume that

$$\overline{-u_i'T'} \sim e_i\frac{\partial\overline{T}}{\partial X_i} \quad, i=1,2,3 \tag{4-11}$$

where e_i is positive and a function of position. (In general, e_i could be an asymmetric tensor of the second order [33]. However the theory is at best approximate and the above assumption is essential to later developments). Integrating, eq. (4-11), the heat flux due to turbulence over a cell i in cartesian coordinates using eq. (4-10) and the notation that $e_{ij} = e_1$, e_2, or e_3 over the area of the interface, A_{ij} of cell i with cell j, one obtains

$$-c\oint_{V_i}\sum_{i=1}^{3}\frac{d}{dx_i}(\overline{u_i'T'})dx_i = c\sum_j e_{ij}\frac{A_{ij}}{\ell_{ij}}[T_j(t)-T_i(t)]$$

Thus, this term has the same form as the heat transfer coefficient for conduction and is to be added to the r.h.s. of eq. (4-8b) for turbulent convective flow.

Thus, eq. (4-8b) will in general be given by

$$h_{ij} = h_{ij}^{+} + h_{ij}^{-}$$

where

$$h_{ij}^{+} = \frac{k_{ij}A_{ij}}{\ell_{ij}} + h(A_{ib},A_{jb})A_{ib}A_{jb} + c_i\frac{e_{ij}A_{ij}}{\ell_{ij}}$$

$$h_{ij}^{-} = \frac{c_i A_{ij} u_{ij}}{2}$$

h_{ij}^{+} is associated with heat transfer by conduction and thermal radiation and by the component of turbulent convection caused by the correlated fluctuations in u_{ij}, T_i, and T_j. h_{ij}^{-} is associated with the heat transfer caused by convection calculated assuming u_{ij}, T_i, and T_j are uncorrelated and can be replaced by their values averaged over a time long in comparison with their fluctuations (but short in comparison to the time scale of a calorimetric experiment).

The method used to derive eqs. (1) and (4-8) from eqs. (4-1) through (4-4) and eqs. (4-9a) and (4-9b) is the so called "integration method) (see [30], chp. 6). Whatever method is used, we have adopted the point of view that it be equivalent to breaking up the regions into cells or regions in space having a uniform temperature and that heat transfer between each of these cells retain the physical meaning of the differential equations and boundary conditions previously cited. The latter necessarily requires that h^+_{ij} be positive and symmetric, and h^-_{ij} be of no fixed sign (but consistent with eq. (4-10)) and antisymmetric, and $\Sigma_j h^-_{ij} = \Sigma_j h^-_{ji} = 0$ where the sum over j is over all cells contiuous to cell i. The assumption that h_{ij} is constant requires differences in $T_i(t) - T_j(t)$ be small and the assumption that h_{ij} is positive requires that the cells be sufficiently small (beyond the initial assumption about the existence of cells) that $h'_{ij} > |h''_{ij}|$. Thus, eq. (1) and (4-8) are regarded as our basic assmuptions.

Though convergence of eqs. (1) and (4-8) to eqs. (4-1) through (4-4) and eq. (4-9) seems plausible on physical grounds, we are unaware of a suitable mathematical proof at this time. Because the time variable is not broken into discrete intervals, the problem of stability does not arise.

4.2 Solution of equation (1) for rating periods

Eq. (1) for rating periods ($P_i(t) = 0$, $1 \leq i \leq n$) may be written in matrix form as

$$(CD+H)T(t) = Y \tag{4-12}$$

In. eq. (4-12), D is the ordinary differential operator with respect to time, d/dt. C is the diagonal matrix diag ($C_1, C_2 ---, C_n$).[10] H is an nxn real asymmetric matrix having elements $H_{ii} = \Sigma_s h_{is} + \Sigma_j h_{ij}$, $j \neq i$, and $H_{ij} = -h_{ij}$ for $1 \leq i, j \leq n$.[10] T(t) and Y are the column matrices $[T_1(t), T_2(t) ---, T_n(t)]'$ and $[\Sigma_s h_{is} T_s + P_1°, ---, \Sigma_s h_{ns} T_s + P_n°]'$, respectively. The superscript prime, used in the latter, denotes the tranpose. By inspection eq. (4-12) can be rearranged to

$$(CD+H)X(t) = 0 \tag{4-13}$$

where

$$X(t) = T(t) - T_\infty \tag{4-14}$$

$$T_\infty = H^{-1}Y \tag{4-15}$$

and H^{-1} is the reciprocal of H.

Premultiplying both sides of eq. (4-13) by C^{-1} gives

$$(ID-A)X(t) = 0 \tag{4-16}$$

where I is the identity matrix of order n and A is defined by

$$A = -C^{-1}H \tag{4-17}$$

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[10] H and C can be assumed to have the same dimensions, with out loss in generality, see end of section 4.3.

Taking the Laplace transform [34] of both sides of eq. (4-16), one obtains

$$(\lambda I-A)X(\lambda)=X(0) \tag{4-18}$$

It can be shown (see [35], p. 176) that for a general matrix A that

$$(\lambda I-A)^{-1}=\sum_{\substack{k\\1}}\sum_{\substack{j\\1}}^{m_k}K_j(\lambda_k)/(\lambda-\lambda_k)^j \tag{4-19}$$

where

$$K_j(\lambda_k)=\frac{1}{(m_k-j)!}\left[\frac{d^{(m_k-j)}}{d\lambda^{(m_k-j)}}\frac{F(\lambda)}{\phi_k(\lambda)}\right]_{\lambda=\lambda_k},\ 1\le j\le m_k \tag{4-20}$$

and

$$\phi_k(\lambda)=\phi(\lambda)/(\lambda-\lambda_k)^{m_k} \tag{4-21}$$

In eq. (4-21), $\phi(\lambda)$ is the characteristic polynomial ([36], ch. 19) and, in eq. (4-19)-(4-21), λ_k are the distinct roots, each having a multiplicity m_k $(m_k \geq 1)$, of the characteristic equation of the matrix A (i.e. eigenvalues of A):

$$\phi(\lambda)=|\lambda I-A|=0 \tag{4-22}$$

where $|\ \ |$ indicates the determinant of the enclosed matrix. In eq. (4-20), $F(\lambda)$ is the adjoint ([36], ch. 6) of $\lambda I-A$. Substituting eq. (4-19) into eq. (4-18) and inverting the transform ([34], p. 72) gives the formal solution to eq. (1) in matrix form

$$x(t) = \sum_k \sum_{1j}^{m_k} K_j(\lambda_k) x(0)\, t^{(j-1)} (\exp(\lambda_k t))/(j-1)! \tag{4-23}$$

Based only on the symmetry properties of H, the $K_j(\lambda_k)$ and λ_k have the following properties. For aneroid calorimeters, H is symmetric and, hence, A is similar to a symmetric matrix since C is positive definite ([37], p. 67, prob. 27) (ie. $A = -L^{-1}(L^{-1}HL^{-1})L$ where $L = \text{diag}\,(C_1^{\frac{1}{2}}, C_2^{\frac{1}{2}}---, C_n^{\frac{1}{2}})$ and $L^{-1}HL^{-1}$ is symmetric, see [38], p. 34). It follows ([36], ch. 21) that all the λ_k are real and A is similar to a diagonal matrix. Thus, if λ_k has a multiplicity m_k = r, the rank of $\lambda_k I - A$ is n-r. The latter has two consequences. First, it requires that all $K_j(\lambda_k)$, $j > 1$, are all null (see [35], p. 61-62, or [36], p. 170, prob. 26). Hence for aneroid calorimeters, no terms in the r.h.s. of eq. (4-23) involving the product of $\exp(\lambda_k t)$ and t appear. Second, since $K_1(\lambda_k)$ is not null while $K_j(\lambda_k)$, $j > 1$, are null ([35], p. 17), $K_1(\lambda_k)$ has a rank r, satisfies the equation ([35], p. 61)

$$K_1(\lambda_k)(\lambda_k I - A) = (\lambda_k I - A) K_1(\lambda_k) = 0 \tag{4-24}$$

and may be factored ([35], p. 65) as

$$K_1(\lambda_k) = D_1(\lambda_k) B_1(\lambda_k) \tag{4-25}$$

In. eq. (4-25), $D_1(\lambda_k)$[11] and $B_1(\lambda_k)$ are (rxn) and (nxr) matrices, respectively, and $D_1(\lambda_k)$ and $B_1(\lambda_k)$ are proportional to the set of right and left

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[11] D with a subscript is a matrix, and without one is the differential operator d/dt.

handed (use [35], p. 64-67 and see [38], p. 4) eigenvectors, respectively, for a λ_k with a multiplicity r. (For the other properties of $K_1(\lambda_k)$, see [35], chp. 3 or [36], p. 160, prob. 26).

For calorimeters containing stirred liquids, H is asymmetric and we are able to say less about the $K_j(\lambda_k)$ and λ_k from symmetry alone. Since A is real, some of the λ_k may be complex and, if so, will occur in complex conjugate pairs. Further, from the form of $K_j(\lambda_k)$ (see [35], p. 75), it can be seen, for example, that sum of terms for an unrepeated pair of complex conjugate λ_k will involve terms that vary with time as $\exp(b_k t) \cos (w_k t + v_k)$ where b_k, w_k, and v_k are real. Further, since we have not proven that A is similar to a diagonal matrix in this case, it follows that $K_j(\lambda_k)$ for $1 < j \leq m_k$ may not all be null. Thus, for repeated roots, we cannot exclude the possibility of T(t) varying in an even more complicated fashion. It will be seen in subsequent analysis, however, that proving whether or not A is similar to diagonal matrix is not essential to our analysis.

The specific form of H determines the sign of the real parts of λ_k and a number of properties of the eigenvalue and eigenvector of smallest magnitude, λ_1. For arbitrary cell size for aneroid calorimeters and for sufficiently small cell size for stirred-water calorimeters, h_{ij} is positive. In either case, at least one $\Sigma_s h_{is}$ is non-zero. Hence the matrices H and A are irreducibly ([30], p. 20) diagonally dominant ([30], p. 23). Since all the diagonal entries of A are negative, the real parts of the λ_k are negative ([30], p. 23 or apply Th. 1.5 and 1.6). Since for some positive, real number s, the matrix $sI + A \geq 0$,[12] λ_1 the eigenvalue of smallest magnitude is real and

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[12] 0 is the nxn null matrix.

distinct, and the corresponding eigenvector is positive ([30], pp. 30, 258), that is, $-D_1(\lambda_1)$ is a column vector and every entry, $d_i(\lambda_1)$, is positive.

Thus, after sufficient time has elapsed, the ith entry of eq. (4-23) is given by eq. (4) with $a_i(\lambda_1)$ equal to

$$a_i(\lambda_1) = \sum_{1}^{n}{}_j\, b_j(\lambda_1)[T_j(0) - T_{\infty j}], \quad 1 \le i \le n$$

where $b_j(\lambda_1)$ is the jth entry of the row vector $B_1(\lambda_1)$. While we are assured of the separation of the eigenvalue, λ_1 and the eigenvalue whose real part is closest to that of λ_1, because λ_1 is distinct, a discussion of the probable magnitude of this separation is given in section 4.5.

Certain specific properties of the rating periods are necessary for all subsequent analyses. The first is that eq. (4) may be written in the form used to derive eq. (5):

$$\frac{dT_i(t)}{dt} = \lambda_1[T_i(t) - T_{\infty i}], \quad 1 \le i \le n \qquad (4\text{-}25)$$

The set of temperatures, $T_{\infty i}$, $1 \le i \le n$, represent the temperature in the convergence rating period (when all $dT_i(t)/dt = 0$) and is identical to the steady state temperature distribution when the time t goes to infinity. From eq. (4-15), one may write

$$T_{\infty i} = \sum_{1}^{n}{}_j\, \frac{\alpha_{ij}}{|H|}\left(\sum_{\ell} h_{j\ell}T_{\ell} + P_j^0\right), \quad 1 \le i \le n$$

where $\alpha_{ij}/|H|$ is the i, jth entry of H^{-1}, α_{ij} is the i, jth entry of the adjoint of H, (adj H) and $|H|$ is the determinant of H. Since H is irreducibily, diagonally dominant (see previous discussion) and by definition $H_{ii} > 0$ and $H_{ij} \le 0$ for all $i \ne j$, it can be shown (see

[30], p. 85) that $\alpha_{ij}/|H| > 0$, all i, j. Since $|H|$ is positive (H is positive definite, see [30], p. 23) the α_{ij} are also positive. The α_{ij} of the cells of some region within surface S are equal, in general, if and only if this region is isolated (see section 4.5).

By inspection of the form of H, one can see that

$$|H| = \sum_{1}^{n}{}_{j} \left(\sum_{s} {}'h_{js} \right) \alpha_{ji} = \sum_{1}^{n}{}_{j} \left(\sum_{s} h_{js} \right) \alpha_{ij} \qquad (4\text{-}26)$$

In eq. (4-26), $'h_{js} = h_{js}$ or h_{sj} for a cell j not in contact with the surface S and in contact with the surface S, respectively.

Thus, if we define the average temperature of the cells of surface S as $\overline{T}_s$, eq. (4-15) may be written as

$$T_{\infty i} = \overline{T}_s + \sum_{1}^{n}{}_{j} \frac{\alpha_{ij}}{|H|} \left[\left(\sum_{s} h_{js} \right) (T_s - \overline{T}_s) + P_j^{\circ} \right], \quad 1 \leq i \leq n \qquad (4\text{-}27)$$

Thus, eq. (4-27) says the convergence temperature of the ith cell is equal to the sum of three terms: the average temperature of the surroundings, a term which may be positive, zero, or negative caused by the deviation of the temperature of the surroundings from strict uniformity, and a positive term due to the constant power input to the calorimeter. From this, we conclude the convergence temperature distribution, in general, will be more nearly uniform, and hence, independent of all h_{ij}, h_{is}, as well as all C_i as the temperature of the surroundings becomes uniform and all P_i° approach zero.

The second important property of rating periods is that by differentiating eq. (4) one obtains eq. (4-28) and by comparing eq. (4-28) with eq. (4-25) one obtains eq. (4-29).

$$\frac{dT_i(t)}{dt} = \frac{d_i(\lambda_1)}{d_j(\lambda_1)} \frac{dT_j(t)}{dt}, \quad 1 \le i, j \le n \qquad (4\text{-}28)$$

$$T_i(t) - T_{\infty i} = \frac{d_i(\lambda_1)}{d_j(\lambda_1)} \left(T_j(t) - T_{\infty j}\right), \quad 1 \le i, j \le n \qquad (4\text{-}29)$$

Since the $d_i(\lambda_1)$ for all i have the same sign, eq. (4-28) indicates that if the rate of change of temperature is positive (or negative) anywhere in the calorimeter, it is positive (or negative) everywhere in the calorimeter. The $d_i(\lambda_i)$ of the cells of some region inside the surface S are equal, in general, if and only if this region is isolated (see section 4.5). Since all $d_i(\lambda_1)$ are dependent only on the thermal properties of the calorimeter eq. (4-29) indicates, first, that the set of temperatures $T_{i\infty}$, $1 \le i \le n$, and the temperature of any _i_th cell is sufficient to specify the temperatures of the remaining cells in the calorimeter during any rating period. Second, if all the C_i, h_{ij}, h_{is} of the calorimeter and the convergence temperature distirbution for two rating periods are the same, it follows that the difference in temperature of an arbitrary _i_th cell is sufficient to specify the difference in temperatures of the remaining cells between the two rating periods.

4.3 Solution of eq. (1) for the main period; linear heat transfer

Defining P(t) to be the column matrix $[P_1(t),---P_n(t)]'$; eqs. (1) during the main period may be written in matrix form (see eq. (4-12) as

$$(ID-A)X(t) = C^{-1}P(t) \tag{4-30}$$

To determine the form of T(t) during the main period, we consider the case for aneroid calorimeters where A is similar to a diagonal matrix. Applying the analysis given in section 4.2, one obtains

$$X(t) = T(t)-T_{\infty} = \sum_k K_1(\lambda_k)\left[X(0)+C^{-1}\int_{t_1}^{t} P(\tau)e^{-\lambda_k \tau}d\tau\right]e^{\lambda_k t} \tag{4-31}$$

As mentioned in section 2.1, eq. (4-31) may be used to obtain eq. (6) of that section. However a simpler method can be used that does not require that A be similar to a diagonal matrix and is as follows.

Premultiplying both sides of eq. (4-30) by the adjoint, F(D), of the matrix operator, ID-A, yields

$$\phi(D)X(t) = F(D)C^{-1}P(t) \tag{4-32}$$

where $\phi(D)$ is the determinant operator

$$\phi(D) = |DI-A| = a_0D^n+a_1D^{n-1}+\ldots+a_{n-1}D+a_n \tag{4-33}$$

The coefficients a_i, $0 \leq i \leq n$, are the corresponding coefficients of λ in the characteristic equation of A, eq. (4-22). Using eq. (4-33), we now integrate eq. (4-32) from an initial rating period ending at time t_1 to a final rating period beginning at time t_2. Assuming that $D^kP(t) = 0$, $1 \leq k \leq n-2$, in both rating periods, one obtains

$$a_0\Delta[D^{n-1}X(t)] + a_1\Delta[D^{n-2}X(t)] + \ldots + a_{n-1}\Delta X(t) + a_n\int_{t_1}^{t_2} X(t)dt =$$
$$= F(0)C^{-1}\int_{t_1}^{t_2} P(t)dt \tag{4-34}$$

where F(0) is the adjoint of -A and

$$\Delta[D^k X(t)] = [D^k X(t)]_{t=t_2} - [D^k X(t)]_{t=t_1}, \; 0 \leq k \leq n-1 \tag{4-35a}$$

From eq. (4-25) written in matrix form, $DX(t) = \lambda_1 X(t)$, one concludes that during rating periods

$$D^k X(t) = \lambda_1^k X(t), \; 1 \leq k \leq n-1 \tag{4-35b}$$

Substituting eqs. (4-35 into equation (4-34) one obtains

$$[a_0\lambda_1^{n-1} + a_1\lambda_1^{n-2} + \cdots + a_{n-1}]\Delta X(t) + a_n\int_{t_1}^{t_2} X(t)dt = \tag{4-36}$$
$$= F(0)C^{-1}\int_{t_1}^{t_2} P(t)dt$$

Using the fact that λ_1 substituted in place of D in eq. (4-33) yields $\phi(\lambda_1) = 0$ and that (see [36], p. 151)

$$\frac{F(0)}{a_n} = \frac{adj(-A)}{(-1)^n |-A|} = -\frac{adj\,A}{|A|} = -A^{-1} = H^{-1}C$$

One obtains from eq. (4-36)

$$-\frac{1}{\lambda_1}[X(t_2) - X(t_1) - \lambda_1\int_{t_1}^{t_2} X(t)dt] = H^{-1}\int_{t_1}^{t_2} P(t)dt \tag{4-37}$$

or the set of equations

$$W = E_i \left[T_i(t_2) - T_i(t_1) + \lambda_1 \int_{t_1}^{t_2} [T_{\infty i} - T_i(t)]dt, \quad 1 \leq i \leq n \right. \tag{4-38a}$$

where

$$W = \sum_{1}^{n}{}_{j} \int_{t_1}^{t_2} P_j(t)dt \tag{4-38b}$$

$$1/E_i = -\lambda_1 \sum_{1}^{n}{}_{j} d_{ij} q_j / |H| \quad , \quad 1 \leq i \leq n \tag{4-38c}$$

$$q_j = \left(\int_{t_1}^{t_2} P_j(t)dt \right) / W \quad , \quad 1 \leq j \leq n \tag{4-38d}$$

The expression for E_i can be put into a form better suited for physical interpretation by noting that from section 4.2, $D_1(\lambda_1)$ satisfies the equation

$$(\lambda_1 I - A) D_1(\lambda_1) = 0 \tag{4-40}$$

Premultiplying both sides of eq. (4-40) by C^{-1}, and looking at the $\underline{i}$th entry of the resulting equations gives

$$\lambda_1 C_i d_i(\lambda_1) = -\sum_{1}^{n}{}_{j} H_{ij} d_j(\lambda_1), \quad 1 \leq i \leq n$$

Summing both sides over i from 1 to n and using the definition of H_{ij}, and using eq. (4-26) gives:

$$\lambda_1 = -\frac{\sum_{1}^{n}{}_{j} \left(\Sigma_{\Delta}{}' h_{j\Delta} \right) d_j(\lambda_1)}{\sum_{1}^{n}{}_{j} C_j d_j(\lambda_1)} \tag{4-41}$$

Dividing the numerator and denominator of eq. (4-41) by $d_i(\lambda_1)$ and inserting into eq. (4-38c) gives

$$E_i = \frac{\left[\sum_{1}^{n}{}_j C_j d_j(\lambda_1)/d_i(\lambda_1)\right]}{\left[\sum_{1}^{n}{}_j \left(\Sigma'_\Delta h_{j\Delta}\right) d_j(\lambda_1)/d_i(\lambda_1)\right]\left[\sum_{1}^{n}{}_j \alpha_{ij} q_j/|H|\right]}, \quad 1 \leq i \leq n \tag{4-38e}$$

Eq. (4-38a) can be expressed in terms of the instantaneous temperature of the thermometer, eq. (3) of section 2.0, if $T_i(t)$ is replaced by $T^*(t)$, $T_{\infty i}$ by T^*_∞, and E_i is replaced by E^* where in place of eqs. (4-38c) or (4-38e) we have

$$1/E^* = -\lambda_1 \sum_{1}^{n}{}_i \sum_{1}^{n}{}_j w_j \alpha_{ij} q_j/|H|$$

$$E^* = \frac{\left[\sum_{1}^{n}{}_j C_j d_j(\lambda_1)/\sum_{1}^{n}{}_j w_j d_j(\lambda_1)\right]}{\left[\sum_{1}^{n}{}_j \left(\Sigma'_\Delta h_{j\Delta}\right) d_j(\lambda_1)/\sum_{1}^{n}{}_j w_j d_j(\lambda_1)\right]\left[\sum_{1}^{n}{}_i \sum_{1}^{n}{}_j w_i \alpha_{ij} q_j/|H|\right]}$$

The interpretation of the quantities in eqs. (4-38a), (4-38b), and (4-38d) are given in the text. In eq. (4-38c), λ_1 is the cooling constant. $|H|/\Sigma_j\, \alpha_{ij} q_j$ is the steady-state heat transfer coefficient, between the calorimeter and surroundings as measured at the ith cell if constant power is supplied from the source of time-varying power with a geometrical distribution that is identical to the set of q_j's of eq. (4-38d). (That is suppose $P_j(t) = P_j'$ and $P_j'/P' = q_j$ where $P' = \Sigma_{1}^{n}{}_j P_j'$. From eq. (4-27), the difference in the convergence temperature measured at the ith cell when $P(t) = 0$, $T_{\infty i}$, and $P(t) = P'$, $T'_{\infty i}$, is given by

$$\frac{|H|}{\sum_{1}^{n}{}_j \alpha_{ij} q_j}\left(T'_{\infty i} - T_{\infty i}\right) = P'$$

In eq. (4-38e) the numerator is equal to the increase in internal energy of the calorimeter, ΔU, divided by the change in the temperature as measured at the ith cell, $T_i(t_2) - T_i(t_1)$, in the final and initial rating periods. This follows from eq. (4-29) since

$$\Delta U = \sum_1^n {}_j C_j [T_j(t_2) - T_j(t_1)] = \left[\sum_1^n {}_j C_j d_j(\lambda_1)\right] [T_i(t_2) - T_i(t_1)]/d_i(\lambda_1) \tag{4-42}$$

The term $\sum_1^n {}_j (\Sigma_s' h_{js}) d_j(\lambda_1)/d_i(\lambda) = h_i'$ in the denominator of eq. (4-38e) is $-\lambda \Delta U/[T_i(t_2 - T_i(t_1))]$ from eq. (4-41). It can be shown to be equal to the heat transfer coefficient between the calorimeter and surroundings, as measured at the ith cell, if the denominator of eq. (4-38e) is one. This follows from eq. (4-37), the ith entry of which is

$$-\int_{t_1}^{t_2} [T_{\infty i} - T_i(t)]\,dt = [T_i(t_2) - T_i(t_1)]/\lambda_1 + \sum_1^n {}_j \alpha_{ij} q_j W/|H| \tag{4-43}$$

Premultiplying by $\Sigma_s h_{is}$, summing over all i, and using eqs. (4-26) and (4-29) gives, after interchanging i with j

$$-\sum_1^n {}_j (\Sigma_s' h_{js}) \int_{t_1}^{t_2} [T_{\infty j} - T_j(t)]\,dt = \frac{h_i'}{\lambda_1} [T_i(t_2) - T_i(t_1)] + W \tag{4-44}$$

Premultiplying eq. (4-43) by h_i', and subtracting from eq. (4-44)

$$\sum_1^n {}_j (\Sigma_s' h_{js}) \int_{t_1}^{t_2} [T_{\infty j} - T_j(t)]\,dt = h_i' \int_{t_1}^{t_2} [T_{\infty i} - T_i(t)]\,dt + W\left[h_i' \sum_1^n {}_j \frac{\alpha_{ij} q_j}{|H|} - 1\right] \tag{4-45a}$$

The left hand side of eq. (4-45a) is the heat absorbed by the calorimeter plus the work done by constant power sources during the main period

This may be established as follows. Summing eq. (1) overall i, $1 \leq i \leq n$, we have:

$$\sum_{1}^{n}{}_{i} C_i \frac{dT_i(t)}{dt} = \sum_{1}^{n}{}_{i} \sum_{s} h_{is}[T_s - T_i(t)] + \sum_{1}^{n}{}_{i} \sum_{\substack{1 \\ i \neq j}}^{n}{}_{j} h_{ij}[T_j(t) - T_i(t)] + \sum_{1}^{n}{}_{i} P_i^{\circ} + \sum_{1}^{n}{}_{i} P_i(t) \quad (4\text{-}45\text{b})$$

The second double sum on the r.h.s. of eq. (4-45b) can be broken into a sum over the set of i and j corresponding to interior cells (cells not adjacent to the surface S) and the set of i or j corresponding to boundary cells (cells contiguous to surface S). The first sum involving the exchange of heat between interior cells vanishes because $\sum_{\substack{j \\ j \neq i}} \bar{h}_{ij} = \sum_{\substack{j \\ j \neq i}} \bar{h}_{ji} = 0$ but the second sum will not vanish, in general, because for the ith boundary cell $\sum_j \bar{h}_{ij} = -\sum_s h_{is}$ if the surface S is located in a stirred fluid. In can be shown that (4-45b) reduces to

$$\sum_{1}^{n}{}_{i} C_i \frac{dT_i(t)}{dt} = \sum_{1}^{n}{}_{i} \sum_{s} h_{is} T_s - \sum_{1}^{n}{}_{i} \sum_{s} {}'h_{is} T_i + \sum_{1}^{n}{}_{i} P_i^{\circ} + \sum_{1}^{n}{}_{i} P_i(t) \quad (4\text{-}45\text{c})$$

where $'h_{is}$ has been defined in connection with eq. (4-26). It should be noted that, so long as the exchange of heat between the cells forming surface S and the cells enclosed by S is linear, eq. (4-45c) is valic whether or not the heat exchange between interior cells is linear or not.[13] The terms involving T_s and P_i° may be eliminated by noting that in a convergence rating period $dT_i(t)/dt = 0$ when $T_i(t) = T_{\infty i}$, $1 \leq i \leq n$. Substituting these conditions into eq. (4-54c), subtracting the resulting equation from eq. (4-54c), and integrating from time t_1 to t_2 completes the proof.

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[13] the l.h.s. of eq. (4-45c) is the rate of increase of internal energy of the system bounded by the surface S; the r.h.s. is the total rate of doing work on the system and the rate of absorption of heat by the system. Heat exchange between interior cells cannot contribute to the latter.

If the denominator of eq. (4-38e) is one, the term involving W vanishes. It can be shown (see section 4.5) that this occurs, in general, if and only if the region in which the various $q_j > 0$ is isolated (i.e. $\lambda_1 = 0$, see section 4.5).

From the previous discussion in section 4.2 and the α_{ij}'s and $d_i(\lambda_1)$'s, we can make the following statements:

(1) The energy equivalent, E_i, as measured by the corrected temperature rise of the ith cell, will, in general, be different for each ith cell and will also be different for different geometrical distributions of the work input, a different set of q_j, (since $\alpha_{ij}/|H|$ are not equal for all i, j inside the region where $q_j > 0$ unless the region is isolated).

(2) The energy equivalent is always positive, if W is positive (all $\alpha_{ij}/|H| > 0$, $d_i(\lambda_1)d_j(\lambda_1) > 0$).

(3) The energy equivalent is not equal to the sum of the heat capacities of cells of the calorimeter (since all $d_i(\lambda_1)$ are not equal) but the contribution of the heat capacity of every cell to the energy equivalent is positive ($d_i(\lambda_1)/d_j(\lambda_1) > 0$).

In sections 4.2 and 4.3 we assume that C and H are non-singular matrices having the same dimensions or, equivalently, that the temperature of every cell inside the surface S changes with time (even if only infinitesimally) while every cell forming the surface S is constant. This assumption involves no loss in generality provided the temperature of the surroundings is constant since eq. (1) for the sth cell making up the surface S is

$$0 = \Sigma_i h_{si}[T_i(t) - T_s] + \Sigma'_s h_{ss'}(T_s - T'_s) + P^\circ_s + P_s(t)$$

The sum over s' involves all cells in the region comprising the surroundings (including those making up the surface S) and the sum over i involves all cells inside the surface S that exchange heat with the sth cell. In order for T_s and all T_s' to be constant, $\Sigma_i h_{si} T_i(t) = -P_s(t)$. From the properties of the matrix form of the resulting equations for all the cells in the region comprising surroundings, it can be seen that the temperatures of another envelope of cells that completely encloses the surface S are uniquely related to the set of temperatures T_s (and vice versa). Thus, all locations of the surface S may be reduced to a single boundary surface S such that all temperature inside this surface change with time.

It should be noted that since, by definition, $d_i(\lambda_1)/d_j(\lambda_1)$ is zero outside the surface S and greater than zero inside this surface, and since $d_i(\lambda_1)/d_j(\lambda_1)$ is conceptually measurable from the temperature distribution in the convergence rating period and any other rating period (see eq. (4-29)), the location of the boundary surface, S, is in principle (i.e. not practically) determinable from experiment.

The implication of the assumption that each of the temperatures, T_s, is constant necessarily requires that the regulator of the constant-temperature jacket (see [1]) have "reset" as well as "proportional" control [39], and that all leads, stirrer shafts, etc. be well-tempered (thermally) [17] in their passage through the jacket. Also, the resistance of the current leads of an electrical heater must be sufficiently small that the change in temperature due to passage of current through the leads is negligible (see section 4.4). The importance of good temperature regulation of the jacket and thermal tempering is further emphasized by the requirement that the location of the boundary surface S must be the same in both "calibration" and "unknown" experiments.

4.4 Non linear heat transfer during the main period

Eq. (9) is derived as follows. By analogy with eq. (4-45c), dQ(A)/dt is given by

$$\frac{dQ(A)}{dt} = \sum_{i=1}^{m}\sum_a h_{ia} T_i(t) - \sum_{i=1}^{m}\sum_a h_{ia} T_a(t) + \sum_s\sum_a h_{as}[T_s - T_a(t)]$$

The terms involving $T_i(t)$ are eliminated by writing eq. (1) for all the m cells between A and S in the matrix forms

$$H_M T_M = Y_M \qquad (4\text{-}47)$$

H_M is a (mxm) matrix whose entries are defined by

$(H_M)_{ii} = \sum_s h_{is} + \sum_a h_{ia} + \sum_{j \neq i} h_{ij}$ and $(H_M)_{ij} = -h_{ij}$. T_M and Y_M are column vectors having, respectively, the entries

$T_i(t)$, $1 \leq i \leq m$, and $\left(\sum_s h_{is} T_s + \sum_a h_{ia} T_a + P_i^\circ + P_i(t) - C_i \frac{dT_i}{dt}(t)\right)$,

$1 \leq i \leq m$. Letting $G = H_M^{-1}$ (G exists since H_M is irreducibily diagonally dominant) we have

$$T_M = G Y_M \qquad (4\text{-}48)$$

Substituting the ith entry of T of eq. (4-48) into eq. (4-46) and rearranging gives

$$\frac{dQ(A)}{dt} = \sum_s\sum_a h_{as}[T_s - T_a(t)] + R + \sum_{j=1}^{m}\beta_j(A)\left[P_j^\circ + P_j(t) - C_j \frac{dT_j}{dt}(t)\right]$$

where

$$R = \sum_{i=1}^{m} \sum_{a} \left[{}^{\backprime}h_{ia} \sum_{j=1}^{m} G_{ij} \left(\sum_{s} h_{js} T_{s} + \sum_{a'} h_{ja'} T_{a'}(t) \right) - h_{ai} T_{a}(t) \right]$$

$$\beta_j(A) = \sum_{i=1}^{m} \sum_{a} {}^{\backprime}h_{ia} G_{ij} \qquad (4\text{-}49)$$

By adding all the rows or columns of H_M to the $\underline{i}$th row or column and expanding H_M by cofactors of this row or column, one obtains

$$1 = \sum_{j=1}^{m} \left(\sum_{s} {}^{\backprime}h_{js} + \sum_{a'} {}^{\backprime}h_{ja'} \right) G_{ji} = \sum_{j=1}^{m} \left(\sum_{s} h_{js} + \sum_{a} h_{ja} \right) G_{ij} \qquad (4\text{-}50)$$

Inserting eq. (4-50) into the expression for R gives eq. (9) with

$$h'_{as} = h_{as} + \sum_{i=1}^{m} \sum_{j=1}^{m} {}^{\backprime}h_{ai} h_{js} G_{ij} \; ; \; h'_{a} = \sum_{i=1}^{m} \sum_{j=1}^{m} \left[h_{ja} \sum_{s} {}^{\backprime}h_{is} - {}^{\backprime}h_{ia} \sum_{s} h_{js} \right] G_{ij} \qquad (4\text{-}51)$$

The terms involving T_s and T_a in eq. (9) can also be written in the form $\Sigma_s \Sigma_a h'_{as} T_s - \Sigma_s \Sigma_a h''_{as} T_a$ where

$$\sum_{s} h''_{as} = \sum_{s} h'_{as} + h'_{a} = \sum_{s} \sum_{i=1}^{m} \sum_{j=1}^{m} h_{js} {}^{\backprime}h_{is} G_{ij} \qquad (4\text{-}52)$$

By inspection, if H_M is symmetric then $h'_a = 0$ for each a and if $T_a(t)$ is uniform at each moment in time $\Sigma_a h'_a T_a = T_a \Sigma_a h'_a = 0$. If H_M is asymmetric, then G is asymmetric and vice versa so that for stirred fluids $G_{ij} \neq G_{ji}$, $1 \leq i \leq m$.

Since every entry of G is greater than 0 (see section 4.2), $\beta_i(A)$ is greater than zero and from eq. (4-50) is less than one.

Eqs. (10) and (14) may derived as follows. Substituting eq. (9) into eq. (8) and rearranging using $T_A(t)$ as defined in eq. (11), gives

$$\frac{dU_A(t)}{dt} + \sum_1^m{}_i \beta_i(A) C_i \frac{dT_i(t)}{dt} = h_A [T_S - T_A(t)] + P_M^\circ + P_M(t) + P_A^\circ + P_A(t) \tag{4-53}$$

where $h_A = \Sigma_s \Sigma_a h''_{as}$, $T_s = \Sigma_s \Sigma_a h'_{as} T_s / h_A$, $P_M^\circ = \Sigma_1^m{}_i \beta_i(A) P_i{}^\circ$, $P_M(t) = \Sigma_1^m{}_i \beta_i(A) P_i(t)$, $P_A^\circ = \Sigma_1^\ell{}_i P_i^\circ$, and $P_A(t) = \Sigma_1^\ell{}_i P_i(t)$. The terms involving T_S, P_M°, P_A° may be eliminated by noting that in a convergence rating period, $dU_A(t)/dt = 0$ and $dT_i(t)/dt = 0$, $1 \leq i \leq m$, $P_M(t) = P_A(t) = 0$, and $T_A(t) = T_{A\infty}$. Substituting these conditions into eq. (4-53) and substracting the resulting equation from eq. (4-53) gives

$$\frac{dU_A(t)}{dt} + \sum_1^m{}_i \beta_i(A) C_i \frac{dT_i(t)}{dt} = h_A [T_{\infty A} - T_A(t)] + P_M(t) + P_A(t) \tag{4-54}$$

h_A can be expressed in terms of λ_1 by noting that eq. (4-45) holds for rating periods when it can be shown that eq. (4-25), eq. (4-28), and eq. (4-29) are valid with $T_A(t)$ replacing $T_i(t)$, with $d_A(\lambda_1) = (\Sigma_a \Sigma_s h''_{as} d_a(\lambda_1))/h_A$ replacing $d_i(\lambda_1)$, and $T_{\infty A}$ replacing $T_{\infty i}$. Substituting the equations analogous to eqs. (4-45) and (4-48) into eq. (4-54) after replacing dU(A) dt with $\Sigma_1^\ell{}_i C_i dT_i(t)/dt$ gives

$$\lambda_1 = -\frac{h_A d_A}{\sum_1^\ell{}_i C_i d_i(\lambda_1) + \sum_1^m{}_i \beta_i(A) C_i d_i(\lambda_1)} \tag{4-55}$$

Integrating eq. (4-54) between the times t_1 and t_2 gives

$$U_A(t_2) - U_A(t_1) + \sum_1^m{}_j \beta_j(A) C_j [T_j(t_2) - T_j(t_1)] = h_A \int_{t_1}^{t_2} [T_{\infty A} - T_A(t)] dt + \int_{t_1}^{t_2} [P_M(t) + P_A(t)] dt \tag{4-56}$$

To derive eq. (10), we replace $U_A(t_2) - U(t_1)$ with $\sum_{1}^{\ell}{}_i C_i[T_i(t_2) - T_i(t_1)]$ in eq. (4-56), use the equation analogous to eq. (4-29) and eq. (4-55), and rearrange. E_A is then given by

$$E_A = -\frac{h_A}{\lambda_1} \tag{4-57a}$$

$$E_A = \frac{\sum_{1}^{\ell}{}_i C_i d_i(\lambda_1) + \sum_{1}^{m}{}_i \beta_i(A) C_i d_i(\lambda_1)}{\sum_a \sum_a h''_{aa} d_a(\lambda_1) / \sum_a \sum_a h'_{aa}} \tag{4-57b}$$

To derive eq. (14) one must reinterpret the steps in the previous procedure. In deriving eq. (4-54) we assume the convergence rating period and, in particular $T_{\infty A}$, is that appropriate to the initial rating period and also assume that the parameters in eq. (4-55) apply to the initial rating period only. Then, substituting eq. (13) for $U_A(t_2) - U_A(t_1)$ and following the same procedure as before eq. (14) where E_{Ar} replaces E_A in eq. (4-57) and the parameters on the r.h.s. of eq. (4-57) are those for the initial rating period only.

Identical results are obtained if instead of eq. (8), one applied conservation of energy at each moment in time to the entire calorimeter. Calling $dU_S(t)/dt$ the rate of increase in internal energy of the calorimeter and $dQ(S)/dt$ the rate of transfer of heat to the calorimeter in the direction from S to A one may write

$$\frac{dU_S(t)}{dt} = \frac{dQ(S)}{dt} + \sum_{1}^{n} P_i^\circ + \sum_{1}^{n}{}_i P_i(t) \tag{4-58}$$

Applying conservation of energy to the m cells between the surfaces A and S

$$\sum_{1}^{m}{}_i C_i \frac{dT_i(t)}{dt} = \frac{dQ(S)}{dt} - \frac{dQ(A)}{dt} + \sum_{1}^{m}{}_i \left[P_i^\circ + P_i(t)\right] \tag{4-59}$$

Solving the eq. (4-59) for $dQ(S)/dt$ and substituting into the eq. (4-58) along with the definition of $dU_S(t)/dt$,

$$\frac{dU_S(t)}{dt} = \frac{dU_A(t)}{dt} + \sum_1^m C_i \frac{dT_i(t)}{dt} \tag{4-60}$$

gives, upon rearrangement, eq. (4-53).

By inspection, E_A of eq. (4-55) is independent of the location of the sources. The numerator of the r.h.s. of eq. (4-57) is <u>not</u> proportional to the increase in the internal energy of the cells inside A (since some $\beta_i(A) > 0$), the denominator is not equal to one (since all $d_a(\lambda_1)$ are not equal), and E_A is not exactly additive with respect to the heat capacities of the cells inside the surface A (since the $d_i(\lambda_1)$ are not equal for $1 \leq i \leq \ell$). These statements are, however true (section 4.5) if and only if the surface A is located in some region that is isolated (from either the remainder of the cells inside surface S or surface S itself).

If the initial and final rating periods are the convergence temperature, as is frequently the case in conduction calorimeters, in section of eq. (4-57b) into eq. (14) yields

$$-U_p(T_A(t_2)) + U_r(T_A(t_2)) + \int_{t_1}^{t_2} \dot{P}_A(t)\,dt + \int_{t_1}^{t_2} \dot{P}_M(t)\,dt = h_A \int_{t_1}^{t_2} [T_A(t) - T_{\infty A}]\,dt$$

Thus, h_A is the steady state heat transfer coefficient between all the cells inside the surface A and its surroundings and the method of analyzing the data in this form is analogous to the method used in other types of isoperibol calorimeters where the magnitude of λ_1 is not large. The same deductions concerning equivalence of sources apply in either case since these are associated with an analysis of the terms $\Sigma_1^m{}_j \int_{t_1}^{t_2} \beta_j(A) P_j(t) dt$ and $T_A(t)$ of eq. (10).

The evaluation of the terms $\Sigma_1^m{}_j \beta_j(A) P_j(t) = P_M(t)$ for the case of an experiment where electrical power is supplied to a resistance heater can be performed as follows. We consider only the case given by West and Ginnings [13] which is illustrated by fig. 3. This involves the assumption that the heat transfer coefficients of each of the m' cells of the current lead between surfaces A and S with the other cells between A and S is negligible in comparison to the heat transfer coefficients between the cells of the lead. Following the analysis given by West and Ginnings, we assume that the pth cell of the current lead is located in the surface S and changes with time.[14] This is permissible since it can be seen from its derivation that eq. (9) is also valid when T_s is a function of time. It is assumed that none of the other cells forming the surface S change with time. The temperature of the elements of the surface A including the ($\underline{p} + \underline{m}' + \underline{1}$)th element are all assumed to change with time and are different. The number of elements of the heater inside S, p, and inside, A, ℓ'-m', are assumed to be sufficiently large that the heater lead can be assumed to be in contact with the surfaces A and S for an infinite distance, thermally speaking.

Consider those terms, $[(dQ(A)/dt]_h$, in eq. (9) which apply to the heater. They may be written in the form (note $P_i{}^\circ = 0$, $1 \leq i \leq \ell' + p$)

$$\left[\frac{dQ(A)}{dt}\right]_h = h'_{p,p+m'+1}\left[T_p(t) - T_{p+m'+1}(t)\right] + P(t)\sum_{p+1}^{p+m'}{}_j \beta_j(A) - \sum_{p+1}^{p+m'}{}_j C_j \frac{dT_j(t)}{dt}\beta_j(A) \quad (4\text{-}61)$$

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[14] If some of the T_s change with time these T_s and the associated $\Sigma_a h'_{as}$ must be known (or measured). In this case, neither T_p or $T_{p+m'+1}$ need be known provided we know all other T_s and T_a (see [13] or eq. (4-62)).

In eq. (4-61) we assume the power input per unit length is uniform and equal to P(t). The variation in time of $[T_p(t) - T_{p+m'+1}(t)]$ can be expressed in terms of the temperatures of the elements in S and A adjacent to the heater using eq. (4-48).

$$T_p(t) - T_{p+m'+1}(t) = h_s \Sigma_s T_s \sum_{j=1}^{p} \gamma_j + h_a \Sigma_a T_a(t) \sum_{j=p+m'+1}^{p+\ell'} \gamma_j + P(t) \sum_{j=1}^{p+\ell'} \gamma_j - \\ - \sum_{j=1}^{p+\ell'} \gamma_j C_j dT_j(t)/dt \qquad (4\text{-}62)$$

In eq. (4-62), h_s and h_a are assumed to be the uniform heat transfer coefficients per unit length with the surfaces S and A respectively. The sums over s and a are over only those elements of S and A, respectively, just adjacent to the heater lead.

γ_j, $1 \leq j \leq p + \ell'$, is the difference between the entries lying in the pth and (p + m' + 1)th rows but in the same jth column of the reciprocal of the $(p + \ell')$ square triadiagonal matrix $[q_{ij}]$ which is defined by:

$$\begin{aligned} q_{ii} &= h_s + 2h, && 1 \leq i \leq p \\ &= 2h, && p+1 \leq i \leq p+m' \\ &= h_a + 2h, && p+m'+1 \leq i \leq p+\ell' \\ q_{ij} &= -h, && j = i+1, i-1;\ 1 \leq i \leq p+\ell' \\ &= 0, && j > i+1, j < i-1;\ 1 \leq i \leq p+\ell' \end{aligned}$$

In this matrix, h is the heat transfer coefficient between adjacents cells of the current lead.

By symmetry it can be shown that if $h_a = h_s$, then $\sum_{j=1}^{p+\ell'} \gamma_j = 0$.. Thus, the power term will vanish in eq. (4-62) under these circumstances.

The third term on the r.h.s. of eq. (4-61) can be evaluated from eq. (4-49) to be

$$P(t)\sum_{p+1}^{p+m'}{}_{j}\,\beta_j(A) = P(t)h\sum_{1}^{m'}{}_{j}\,G_{m',j} = \frac{m'}{2}P(t) \tag{4-63}$$

where $G_{m',j}$ is the entry lying in the m'th row and jth column of the reciprocal of the m'-square tridiagonal matrix $[q'_{ij}]$ whose entries are defined by

$$\begin{aligned} q_{ii} &= 2h\,, \quad 1 \le i \le m' \\ q_{ij} &= -h\,, \quad j = i+1, i-1;\ 1 \le i \le m' \\ &= 0\,, \quad j > i+1, j < i-1;\ 1 \le i \le m' \end{aligned}$$

In this matrix, h is again the uniform heat transfer coefficient between adjacent elements of the heater lead. If one substitutes eqs. (4-63) and (4-62) into eq. (4-61) the net power term corresponding to $P_m(t)$ of eq. (4-54) when $h_a \neq h_s$ is

$$\frac{m'}{2}P(t) + h'_{p+1,p+m'+1}\,P(t)\sum_{1}^{p+l'}{}_{j}\,\gamma_j$$

The reason for the initial boundary selection was simplicity of calculation.

This net power term is exactly analagous that derived before [13], but has been shown to be equally valid when the temperatures of the elements of the surfaces S are different and the temperatures of the elements of A are not only different but change with time.

From an examination of the manner in which this new power term is derived here or as before [13], it can be seen the original assumptions amount to the condition that the matrices $[q_{ij}]$ and $[q'_{ij}]$ approximate the heat exchange problem for the increment in temperature in the lead due to passage of current. (The heat exchange when $P(t) = 0$ is completely accounted for by the measurement of $T_A(t)$ or its equivalent.) The operating condition mention in section 3.1 is that the current in the lead must be sufficiently small that heat transfer by thermal radiation can be neglected.

Since it has been assumed that the locations of the surfaces A and S are known and $h'_{p+1,\ p+m'+1}\Sigma_j \gamma_j$ is an unknown parameter, one may regard the location of potential taps on the leads as tantamount to specifying where the surfaces A and S are located in the vicinity of the current leads assuming this unknown parameter is zero. The experimental test cited in section 3.1 is a method for verifying this location of potential taps.

The comment made in section 3.1 concerning the type of radiation shield calorimeter described by Ginnings and West [17] or West and Westrum [18] is established as follows. Consider, as a practical example, a radiation shield calorimeter as sketched in figure 4 with two radiation shields, I and II. If these shields are designed properly, the overall heat transfer coefficient h'_{ba} between arbitrary elements a on surface A and b on surface B is effectively zero unless $A_b = T'_b$, that so called "lip" or "shunt". If follows that the temperatures, T_a, on the shield I should depend only upon the temperature T'_b.

Now apply eq. (4-48) to each of the elements of making up surface A.

$$T_a(t) = \sum_s \gamma_{as} T_s(t) + \sum_b \gamma_{ab} T_b(t) + \sum_{1\,j}^{m'} G_{aj} \left[P_j^0 + P_j(t) - C_j \frac{dT_j}{dt}(t)\right] \tag{4-64}$$

where

$$\gamma_{as} = \sum_{1\,j}^{m'} h_{aj} G_{aj}$$

$$\gamma_{ab} = \sum_{1\,j}^{m'} h_{bj} G_{aj}$$

In eq. (4-64), m' is the number of elements between B and S and each G_{aj} is derived from a matrix involving the various heat transfer coefficients of all these m' elements. Our assumption requires

$$\gamma_{ab} = 0 \;,\; b \neq b',\ \text{arbitrary } a$$

Selecting some arbitrary cell, a = k, of the surface A, one obtains from eq. (4-64) (ie. replace a by k in eq. (4-64) and subtract from eq. (4-64).

$$T_a(t) = \sum_s \left(\gamma_{as} - \gamma_{ks} \frac{\gamma_{ab'}}{\gamma_{kb'}} \right) T_s(t) + \frac{\gamma_{ab'}}{\gamma_{kb'}} T_k(t) + \sum_{j=1}^{m'} \left(G_{aj} - G_{kj} \frac{\gamma_{ab'}}{\gamma_{kb'}} \right) \left[P_j^\circ + P_j(t) - C_j \frac{dT_j(t)}{dt} \right] \tag{4-65}$$

The last sum of eq. (4-65) cannot vanish because otherwise the surface A would behave as if it had zero heat capacity.

Because S and A are closed surfaces, eq. (9) applies. Substituting eq. (4-65) into eq. (9) gives

$$\begin{aligned} \frac{dQ(A)}{dt} = {} & \sum_s \sum_a \left[h'_{as} - \sum_{s'} \left(\gamma_{as'} - \gamma_{ks'} \frac{\gamma_{ab'}}{\gamma_{kb'}} \right) \right] T_s(t) \\ & - \left[\sum_s \sum_a h'_{as} \frac{\gamma_{ab'}}{\gamma_{kb'}} \right] T_k(t) \\ & + \sum_{j=1}^{m} \beta_j(A) \left[P_j^\circ + P_j(t) - C_j \frac{dT_j(t)}{dt} \right] \\ & - \sum_{j=1}^{m'} \sum_s \sum_a h'_{as} \left[G_{aj} - G_{kj} \frac{\gamma_{ab'}}{\gamma_{kb'}} \right] \left[P_j^\circ + P_j(t) - C_j \frac{dT_j(t)}{dt} \right] \end{aligned} \tag{4-66}$$

In eq. (4-66), m is the total number of elements between A and S and h'_{as} and $\beta_j(A)$ are to be derived from a matrix containing the various heat transfer coefficients of only these elements. Carrying out an analysis analagous to that given previously in this section will show that the energy equivalent derived from a measurement of $T_k(t)$ will be independent of the spatial distribution of the power input to cells inside the surface B but not to elements between the surfaces B and S since the last two terms in eq. (4-66) are not zero.

4.5 Some consequences of the theory concerning the energy equivalent.

In this section, we establish the validity and examine some of the consequences of the statements made in both the main text and details that, in general, the energy equivalent is an exact sum of heat capacities and is independent of the location of the sources when $\lambda_1 = 0$. The case when $\lambda_1 = 0$ is called the "limiting case".

To start with, if $\lambda_1 = 0$, then some region inside the surface S is isolated (i.e. exchanges no heat or mass with its environment) and vice versa. For convenience, we shall call this region that bounded by the surface A and allow the position of this surface to be arbitrary to the extent it may be either inside or coincide with the surface S. Suppose first that the region bounded by the surface A is isolated. (We shall always use the expression "surface A" to denote the surface A and A alone shall denote the matrix A defined in section 4.2.)

Then the matrices H and A are factorable:

$$H = \mathrm{diag}(H_M, H_A) \qquad A = \mathrm{diag}(A_M, A_A)$$

where we have ordered the matrices H and A so H_M, A_M and H_A, A_A are to be associated with the cells between surfaces A and S and those inside surface A, respectively. Both H and A are singular since H_A and A_A are singular; $\lambda_1 = 0$ since A is singular. If the surface A coincides with the surface S, the row sums of the entries of the rows of matrices A and H are zero (see section 4.2 for definition of entries of A and H) and again A is singular. The converse case is required because $\lambda_1 = 0$ means A is singular (see [36], p. 151) and, since C is non singular, H is singular. In general, this implies the property that both A and H are factorable or the row sum of their entries are zero. (Thus, $\lambda_1 = 0$ is not possible for real isoperibol calorimeters.)

Using this result, we show that the α_{ij} of eq. (4-38e) (or eq. (4-45) (or eq. (4-45) and eq. (4-26)) which are the entries of the adjoint of H, adj H, are, in general, equal and differ from zero inside the surface A and are zero outside the surface A only when $\lambda_1 = 0$ and vice versa. We also show the same result for the entries of $D_1(\lambda_1)$ of eq. (4-25). Suppose first the region bounded by the surface A is isolated.

Partitioning the adjoint of H, adj H, and $D_1(\lambda_1)$ to be conformable with H and A, respectively, we have the result

$$\begin{aligned} H_M(\mathrm{adj}\,H)_M &= 0 \qquad & A_M(\mathrm{adj}\,A)_M &= 0 \\ H_A(\mathrm{adj}\,H)_A &= 0 \qquad & A_A(\mathrm{adj}\,A)_A &= 0 \end{aligned} \tag{4-67}$$

Since H_M and A_M are non singular, adj $H_M = 0$ and $[D_1(\lambda_1)]_M = 0$ (see [36], p. 76). Since H_A and A_A are of rank n - 1 (i.e. the first principal minors are irreducibly diagonally dominant), (adj $H)_A$ and $[D_1(\lambda_1)]_A$ have a rank of one and are not null (see [31], p. 50). Since the sums of the entries of the rows of H_A, A_A are zero, all the entries of (adj $H)_A$ or $[D_1(\lambda_1)]_A$ or $[B_1(\lambda_1)]_A$ are equal and positive. Suppose, on the ot hand, that the entries of (adj $H)_A$ or $[D_1(\lambda_1)]_A$ are equal. From the definition of the entries of H and A this requires $\lambda_1 = 0$ and $h_{ia'} = 0$ for all cells a' making up a surface A' that encloses A that is inside surface S and i refers to all cells between the surfaces S and A', the region M'. Also adj $H_{M'} = 0$, and $[D_1(\lambda_1)_{M'} = 0$. For later purposes, the surfaces A and A' can be taken as identical.

As indicated in sections 4.3 and 3.2 the important consequence of the results for $D_1(\lambda_1)$ is that, in general, the energy equivalent is not an exact sum of the heat capacities of cells inside A since $\lambda_1 = 0$ is not possible for a real isoperibol calorimeter. (i.e. from eq. (4-57) one can see that if the cells inside A are isolated, $\lambda_1 = 0$ and $E_A = \sum_{1}^{\ell} {}_i C_i$). To obtain an estimate of the deviation of $d_i(\lambda_1)/d_a(\lambda_1)$ from unity, where i is a cell bounded by surface A, assume all T_s are equal, all $P_i°$ are zero, let a' be a cell in those forming the surface A, and define $\epsilon_{ia'}$ by

$$\epsilon_{ia'} = \frac{d_i(\lambda_1)}{d_{a'}(\lambda_1)} - 1$$

Then from eq. (4-29) one can see that during a rating period

$$\frac{T_{a'}(t) - T_i(t)}{T_s \quad - T_{a'}(t)} = \epsilon_{ia'}$$

Thus, if the calorimeter is spherical (ie. if the surfaces A and S are concentrically located spheres, and the thermal properties of the cells between A and S are spherically symmetric), $\epsilon_{ia'} >$ 1 for a cell, $1 \leq i \leq \ell'$, inside the envelope of cells forming surface A; $\epsilon_{aa'} = 1$ for a cell a forming surface A; and $\epsilon_{ia'} < 1$ for a cell $1 \leq i \leq m$ between A and S.

The expression for E_A, eq. (4-55) can be written in terms of $\epsilon_{ia'}$ as

$$E_A = \frac{\sum_{1}^{\ell}{}_i C_i + \sum_{1}^{\ell'} C_i \epsilon_{ia'} + \sum_a C_a \epsilon_{aa'} + \sum_{1}^{m}{}_i \beta_i(A) C_i \, d_i(\lambda_1)/d_{a'}(\lambda_1)}{1 + \dfrac{\sum_a \sum_s h'_{as} \epsilon_{aa'}}{\sum_a \sum_s h'_{as}}}$$

where ℓ' is the number of cells inside but not including those making up the surface A. For a spherical calorimeter, the difference E_A(full) - E_A(empty) will be larger than the true heat capacity of a sample. From this expression for E_A, it can be seen that for the region inside the surface A containing cells i, $1 \leq i \leq \ell'$, where one locates a sample whose heat capacity is to be measured, $\epsilon_{ia'}$ and $\epsilon_{aa'}$ must be as close to one and zero, respectively, as possible. Calorimeter vessels containing vanes welded to the walls of the vessel are an example of a design to make $\epsilon_{ia'}$ close to one.

A sufficient experimental test to determine whether or not $\epsilon_{ia'}$ for the cells in the sample region deviate appreciably from one is not, as proposed previously [8], to determine whether or not E_A increases linearly as sample as added to the calorimeter (ie. suppose $\epsilon_{ia'}$ is constant for each cell i that contains the sample). Rather the procedure should be to extrapolate E_A to $\lambda_1 = 0$ constant for both full and empty calorimeter, which is the usual practice (see [40]). (As λ_1 -- 0, $B_i(A)$ -- 0 and $h_{as'}$ -- 0). Just how this extrapolation should be carried out has not been worked out and will depend upon the construction of the calorimeter. For example, it is evident from eq. (4-57) that in the event that h_A can be approximated as a power series in λ_1 and terms higher than λ_1^2 can be neglected, then a plot of E_A versus λ_1 would be the proper method of extrapolation. This assumption for h_A has not been verified, however, except for the case where λ_1 is extremely small (see [38], p. 67).

The consequence of the result for α_{ij} when the cells bounded by A are isolated is that the energy equivalent is also independent of the source location regardless of whether or not the thermometer measures a temperature equivalent to $T_A(t)$ so long as the thermometer is located inside the surface A. (The denominator of eq. (4-38e) becomes one as h_{ia}, $1 \leq i \leq m$ and all a, go to zero because $\sum_1^n \alpha_{ij} q_j / H \longrightarrow 1 \sum_1^m{}_i \sum_a h_{ia}$ and from eq. (4-67) $\sum_1^n{}_j \sum_s h_{js} d_j(\lambda_1)/d_i(\lambda_1) \longrightarrow \sum_1^m{}_i \sum_a h_{ia}$. In the case of the equations of section 4.3, this follows since then dQ(A)dt = 0 at all times).

A third less important consequence of the limiting case is that the non uniformity of the convergence temperature distribution produced by a non uniform temperature distribution on the surface S is reduced as the cells inside A become more isolated. This is perhaps best illustrated by a simple model in which the matrix H is given by

$$\begin{bmatrix} h_{10}+h_{13} & 0 & -h_{13} \\ 0 & h_{20}+h_{23} & -h_{23} \\ -h_{13} & -h_{23} & h_{13}+h_{23} \end{bmatrix}$$

where $h_{10} = h_{1s} + h_{1s'}$ and $h_{20} = h_{2s} + h_{2s'}$ and s and s' refer to the two cells of the surroundings surface S that have different constant temperatures, T_s and $T_{s'}$. If h_{10} and h_{20} are small, and one expands $|H|$ to the first order of small quantities, one obtains for the difference in the convergence temperature distribution if $T_s \neq T_{s'}$

$$T_{1\infty} - T_{2\infty} = \left[\frac{1}{h_{23}} + \frac{1}{h_{13}}\right] \frac{[h_{2s'}h_{1s} - h_{1s'}h_{2s}]}{[h_{10}+h_{20}]} [T_s - T_{s'}]$$

$$T_{1\infty} - T_{3\infty} = \frac{1}{h_{13}} \frac{[h_{2s'}h_{1s} - h_{1s'}h_{2s}]}{[h_{10}+h_{20}]} [T_s - T_{s'}]$$

The effect of constant power input $P_i°$, $1 \leq i \leq 3$, on these differences in convergence temperatures is

$$T_{1\infty} - T_{2\infty} = \left[\frac{X_2}{h_{23}} - \frac{X_1}{h_{13}}\right] \sum_{1}^{3}{}_{i} P_i^{\circ} + \left[\frac{P_1^{\circ}}{h_{13}} - \frac{P_2^{\circ}}{h_{23}}\right]$$

$$T_{1\infty} - T_{3\infty} = -\frac{X_1}{h_{13}} \sum_{1}^{3}{}_{i} P_i^{\circ} + \frac{P_1^{\circ}}{h_{13}}$$

where $X_1 = h_{10}/(h_{10} + h_{20})$ and $X_2 = h_{20}/(h_{10} + h_{20})$. Thus the effect of increasing the isolation of the calorimeter reduces the already small gradient in the convergence temperature distribution due to a non uniform temperature distribution in the surroundings. However, this does not reduce the gradient in the convergence temperature distribution due to the constant power inputs. The effect of constant power input is reduced if either h_{ij} $1 \leq i, j \leq 3$ are large relative to the values of $P_i°$ (thus producing a small change in the distribution for a given percent change in a h_{ij}), all $P_i°$'s are zero, or if the power input to the region where the process of interest takes place is reduced (ie. let this region be cells 1 and 2, let $h_{20} = 0$, and look at $T_{2\infty} - T_{3\infty}$).

As indicated in section 4.2, we have not established the general conditions under which λ_1 and the real part of λ_2 are well separated. Some suggestion that this is plausible, however, comes from simple numerical calculations. For example consider a three cell model where A is given by

$$\begin{bmatrix} -(1+e) & +e & 0 \\ +e & -(1+e) & +1 \\ 0 & +1 & -1 \end{bmatrix}$$

Letting the cell number equal the number of the diagonal entry of this matrix, this corresponds to the situations where cell 3 exchanges heat with only cell 2, cell 2 exchanges heat with cells 3 and 1, and cell 1 exchanges heat with only cell 2 and the surroundings which has a uniform temperature. ($h_{1s} = 1$, $h_{21} = h_{12} = e$, $h_{23} = h_{23} = 1$.) The calculated results for various values of e are as follows

e	$(-\lambda_1)$	$(-\lambda_2)$	$(-\lambda_3)$	$d_1(\lambda_1)$	$d_2(\lambda_1)$	$d_3(\lambda_1)$
1	.198	1.55	3.25	.328	.591	.737
.5	.145	1.40	2.45	.233	.632	.739
.1	.044	1.10	2.06	.065	.689	.721
.01	.005	1.01	2.01	.007	.705	.709
0	0	1	2	0	.707	.707

It can be seen that as e goes to zero cells one and two become isolated from cell 1 and have equal $d_i(\lambda_1)$ for cells two and three. As e increases $d_1(\lambda_1)$ and $d_2(\lambda_1)$ become progressively different but the separation of roots λ_1 and λ_2 is maintained; $d_3(\lambda_1) > d_2(\lambda_1) > d_1(\lambda_1)$ as we have shown on an apriori basis using physical arguments. These results suggest that the separation of λ_1 and λ_2 apply not only in the case where the magnitude of λ_1 is small, conventional isoperibol calorimeters, but also when it is relatively large, as in the case of conduction calorimeters.

Table 1. Summary of symbols

Symbol	Definition
	Matrix operations for a matrix H:
adj H	adjoint of H (transpose of a matrix formed from H by replacing its entries with the co-factors of the entries)
$\|H\|$	determinant of H
H^{-1}	reciprocal of H
diag( )	diagonal matrix
	Notation (location: equation number--section)
A	nxn matrix, eq. (4-17)-4.2
$a_i(\lambda_k)$	eq. (4), text before eq. (4-25)-4.2
C	nxn matrix, text after eq. (4-12)-4.2
C_i	*i*th entry of C, heat capacity of *i*th cell, text before eq. (1)-2., eq. (4-8a)-4.1
C_p	text after eq. (15)-3.3
C_r	text after eq. (15)-3.3
D	ordinary differential operator with respect to time, d/dt
$D_1(\lambda_k)$	eq. (4-25)-4.2
$d_i(\lambda_k)$	*i*th entry of eigenvector of A for the eigenvalue λ_k $(1 \leq h \leq n)$
$d_i(\lambda_1)$	*i*th entry of eigenvector of A for the eigenvector λ_1 (corresponds to the *i*th cell inside the surface S)
$d_a(\lambda_1)$	entry of eigenvector of A for the eigenvector λ_1 corresponding to a cell *a* forming the surface A

Symbol	Definition
E_i	energy equivalent measured at ith cell, text after eq. (6)-2.1, eq. (4-38e)-4.3
E^*	energy equivalent determined with a thermometer, eq. (7)-2.1, text after eq. (4-38e)-4.3
E_A	energy equivalent determined with a thermometer that measures $T_A(t)$, eqs. (10), (11)-3.1
E_{Ar}	energy equivalent determined with a thermometer that measures $T_A(t)$ with the reactants present in the calorimeter, text after eq. (14)-3.2
$F(\lambda)$	adj(λI-A), text after eq. (4-22)-4.2
$F(0)$	adj(-A), text after eq. (4-34)-4.3
H	nxn matrix, text after eq. (4-12)-4.2
H_M	mxm submatrix of H whose diagonal entries are for the m cells in the region between the surfaces A and S, text after eq. (4-47)-4.4
H_{ii}	ith diagonal entry of matrix H, text after eq. (4-12)-4.2
H_{ij}	i, jth entry of matrix H, text after eq. (4-12)-4.2
h_{is}	heat transfer coefficient between ith cell inside surface S and the sth cell forming surface S, text before eq. (1)-2., (eq. (4-8b)-4.1, text after eq. (4-10)-4.1)
h_{ij}	heat transfer coefficient between ith cell and jth cell; both cells inside the surface S, text before eq. (1)-2., eq. (4-8b)-4.1, text after eq. (4-10)-4.1
h'_{as}	total (i.e. all paths) heat transfer coefficient between the ath cell of surface A and sth cell of surface S, text after eq. (9)-3.1, eq. (4-51)-4.4
i	subscript, any cell inside surface S
I	nxn matrix, diag(1,---,1)
j	subscript, any cell inside surface S

Symbol	Definition
$K_1(\lambda_k)$	nxn matrix, eq. (4-20)-4.2
ℓ	number of cells enclosed by surface A
m	number of cells between surfaces A and S
n	number of cells enclosed by surface S
P_i°	constant power input to ith cell, text before eq. (1)-2., eq. (4-8c)-4.1
$P_i(t)$	time varying power input to ith cell, text before eq. (1)-2., eq. (4-8d)-4.1
s	subscript, any cell forming the surface S, text before eq. (1)-2.
t	time
t_o	a time after which $\exp(\lambda_k t)$, $k > 1$, can be neglected, text before eq. (4)-2.1
t_1	beginning of main period or end of initial rating period
t_2	end of main period or beginning of final rating period
$T(t)$	nx1 column matrix, text before eq. (4-12)-4.2
T_∞	nx1 column matrix, eq. (4-15)-4.2
$T(0)$	$T(t)$ when $t = 0$
$T_i(t)$	ith entry of $T(t)$, temperature of ith cell at time t
$T_{\infty i}$	ith entry of T_∞, convergence temperature of ith cell
$T_i(0)$	ith entry of $T(0)$, temperature of ith cell at $t = 0$
T_s	constant temperature of sth cell forming surface S, see text before eq. (1)-2.1, text at end of 4.3
$T_a(t)$	temperature of ath cell forming surface A, see text before eq. (8), (9)-3.1
$T^*(t)$	temperature of thermometer at time t, see eq. (3)-2.1

Symbol	Definition
T^*_∞	$T^*(t)$ at $t = \infty$
$T_A(t)$	eq. (11)-3.1
T_f	text after eq. (15)-3.2
$\Delta U(T_f)$	text after eq. (15)-3.2
$U_A(t)$	internal energy of region enclosed by surface A at time t, text before eq. (12)-3.2
$U_c(t)$	text before eq. (12)-3.2
$U_p(t)$	text before eq. (12)-3.2
$\bar{U}_r(t)$	text before eq. (12)-3.2
$U_{\underline{r}}(t)$	text before eq. (13)-3.2
W	total work done on all cells enclosed by the surface S, text after eq. (6)-2.1
X(t)	nx1 column matrix, $T(t) - T_\infty$, eq. (4-16)-4.2
X(0)	X(t) when t = 0
α_{ij}	$\underline{i}$, $\underline{j}$th entry of adj H, text after eq. (4-25)-4.2, eq. (4-27)-4.2, eq. (4-38c)-4.2, text 4.5
$\beta_i(A)$	text after eq. (9)-3.1, eq. (4-49)-4.4
λ_k	$\underline{k}$th eigenvalue of the matrix A
λ_1	eigenvalue of matrix A having the smallest magnitude
ω_i	weighting factors for thermometer, eq. (3)-2.1

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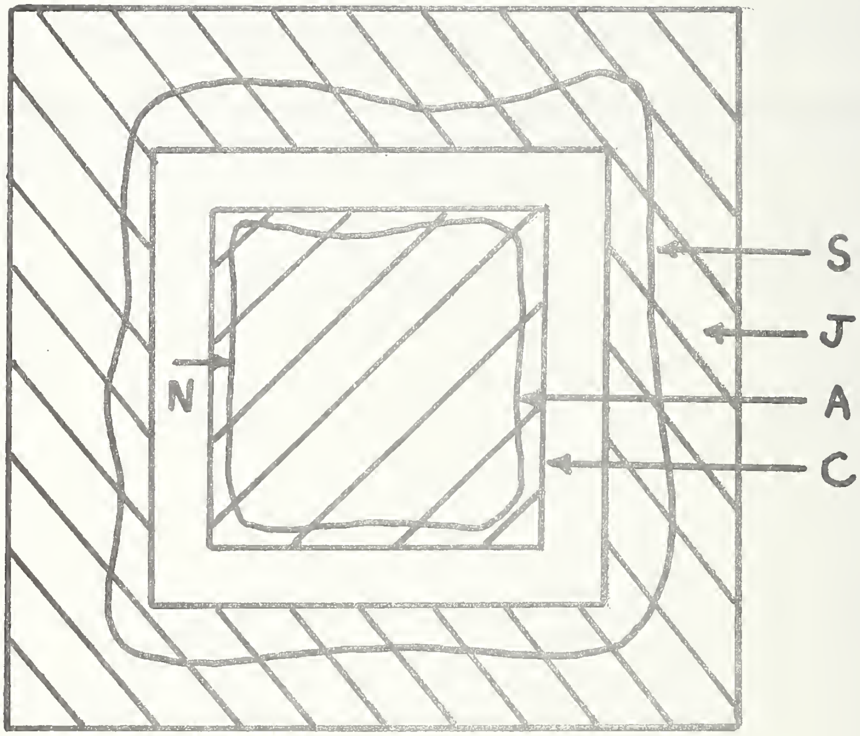

Fig. 1. Sketch of surfaces A and S for a calorimeter J, constant-temperature jacket; C, calorimeter, proper; S, surface S; A, surface A; N, direction of dQ(A)/dt.

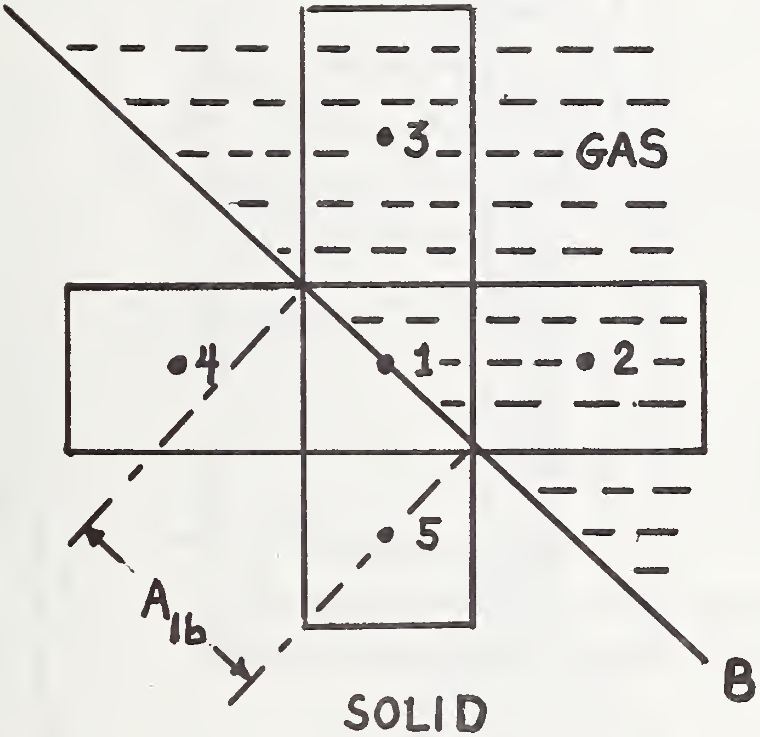

Fig. 2. Sketch of a cell located in a gas-solid boundary (·), interior point of a cell; B, gas-solid boundary; A_{1b}, area of gas solid boundary in cell 1.

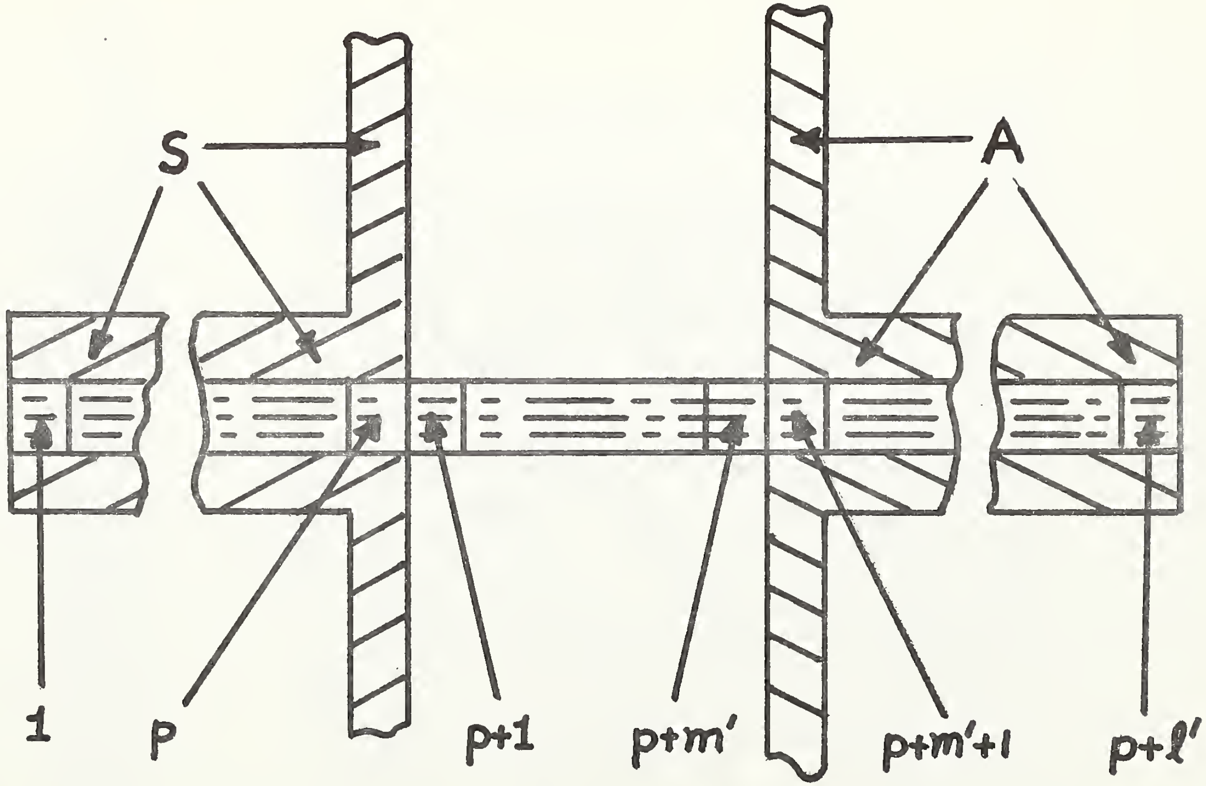

Figure 3. Sketch of a heater current lead
S, surface S; A, surface A; 1, p, p + 1, p + m', p + m' + 1, p + ℓ' are six cells of the p + ℓ' cells of a current lead.

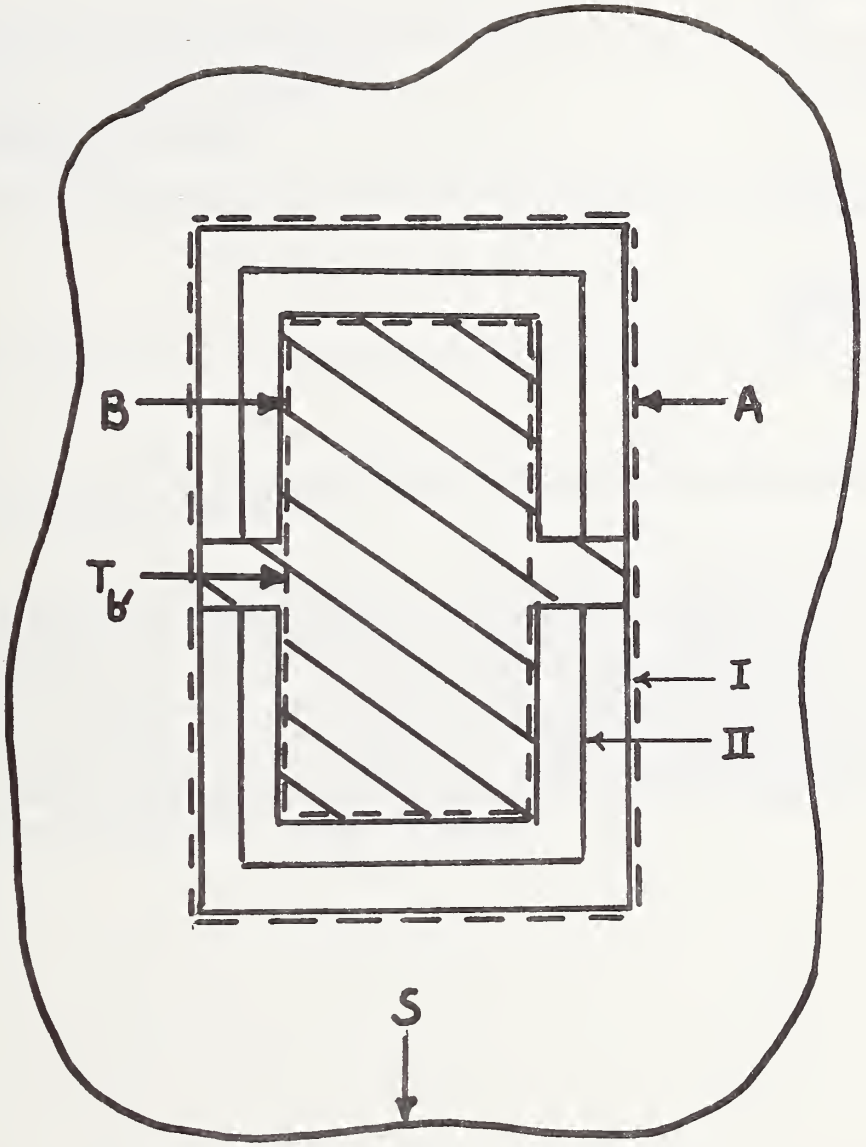

Fig. 4. Sketch of a radiation shield calorimeter
S, surface S; A, surface A; B, surface B; $T_{b'}$, temperature of "shunt" at surface B, I, shield I; II, shield II.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

A calorimeter can be modeled as a large number of volume elements or cells in each of which the temperature may be considered uniform, and each of which can store heat and exchange heat with other cells. Application of the first law of thermodynamics to this set of cells leads to representations of the usual calorimetric equations for internal energy change expressed in terms of measurable or estimatable heat capacities, heat transfer coefficients, temperatures, and work terms for the individual cells. Analysis of the results yields a framework within which most of the design and measurement problems of isoperibol calorimeters can be treated.

17. KEY WORDS (Alphabetical order, separated by semicolons) calorimetry; energy equivalents; energy measurement; heat transfer; internal energy measurement; isoperibol calorimeters; measurement theory.

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