

THEORY OF THE HEAT CONDUCTION CALORIMETER

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ABSTRACT

Boundary value problems are derived and analyzed, describing a model of a heat conduction calorimeter in which the calorimeter consists of three domains thermally connected, viz. the thermal reaction domain, the heat flow domain and the constant temperature surroundings domain. These solutions provide basic theorems for the measurements of the total quantity of heat and thermogenesis (calorific power) occurring in the thermal reaction domain. The proportionality relation between the total quantity of heat and the time integral of the temperature deviation from steady state is deduced under uniform temperature conditions in the thermal reaction domain or uniform temperature gradient over the surface of the domain. The relation provides a method for evaluating the total quantity of heat in heat conduction calorimeter experiments. The method is an alternative to that usually used in isoperibol calorimeter experiments. A formula for use in calculating thermogenesis from the measured thermogram (time–temperature data) is derived assuming uniform temperature in the thermal reaction domain and time-independent thermal physical properties of the domain.

The sensitivity of calorimeters is defined and the conditions of maximum sensitivity are derived for one-dimensional, spherical and cylindrical models of heat conduction calorimeters.

The conditions and assumptions under which the theory is derived suggest sources of error to be avoided in the design and operation of heat conduction calorimeters.

INTRODUCTION

There is no authorized rational system of classification of calorimeters. Designations such as “isothermal”, “combustion”, “glass-Dewer-vessel” or “ice” calorimeters are historical and not based on any comparable or essential characteristics of the calorimeters. However, Calvet and Prat gave a clear and fairly rational classification of calorimeters according to the magnitude of the heat flow, ϕ , inside the calorimeter [1].

They considered that a calorimeter consists of three parts, a container, a cavity and the surroundings. The container, in which the thermal effect to be studied occurs, is placed in the cavity, and heat exchanges between the container and the surroundings through the cavity. They referred to the walls

of the container as the “internal boundary” and to the walls of the surroundings as the “external boundary”. The temperature of the external boundary is kept at constant (the “constant temperature environment” calorimeter) or, alternatively, at a temperature which can be varied at will (the “adiabatic” calorimeter).

They classified calorimeters into three types according to the magnitude of the coefficient for the heat transfer, p , between the internal and the external boundary in the calorimeter. The heat flux, ϕ , and the coefficient for heat transfer, p , are connected by the equation (called Newton’s law of cooling)

$$\phi = p(T_i - T_e) \quad (1)$$

where T_i and T_e are the temperatures of the walls defining the internal and the external boundaries, respectively. Although eqn. (1) is only approximate, it can reasonably be used when the temperatures T_i and T_e are uniform over the boundaries and the temperature difference $T_i - T_e$ is small. The first type of calorimeter is adiabatic, i.e. $p = 0$ or is very small. The heat produced in the calorimeter container is accumulated in the container with little or no loss of heat. The second type is isothermal, i.e. p is very large and all the heat produced in the calorimeter container is rapidly transferred to the outer jacket. The third type, which does not belong to either of the two above types, is when the heat flow and the coefficient p are moderate. In this type, heat exchange between calorimeter container and surroundings is actively assisted by physical means [2] and, essentially, the heat flux between the internal and external boundaries is measured.

Several designations for the third type of calorimeter are used, e.g. “heat conduction”, “heat flow”, “non-isothermal–non-adiabatic” and “Tian–Calvet” calorimeter. The term “heat flow calorimeter” is also used for the labyrinth flow calorimeter [3] and for the calorimeter with a constant temperature difference between the container and the surroundings [4]. The term “non-isothermal–non-adiabatic calorimeter” is used both for the isoperibol calorimeter and calorimeters of the third type [6]. The isoperibol calorimeter, often called the “constant temperature environment calorimeter”, is designed to minimize heat transfer between the calorimeter container and the surroundings [5] and should be classified as adiabatic, although it is more accurately described as “very nearly” adiabatic in operation. As the second and third types of calorimeter are usually operated maintaining the temperature of the surroundings constant, the term “constant temperature environment calorimeter” cannot distinguish between the second and the third types of calorimeter. In this paper, the term “heat conduction calorimeter” is used for the third type, following Calvet and his school’s nomenclature.

In recent years, a considerable development of the theory of calorimetric systems has taken place [6]. The aim of the theory is to recognize the static-dynamic thermal properties of the calorimeter systems and to produce

methods for the accurate determination of the total amount of heat and thermogenesis (calorific power or rate of heat generation) developed in a calorimetric system. In this paper, the theory of the heat conduction calorimeter is discussed and some fundamental theorems on this type of calorimeter are derived. An important difference between the usual theory of the isoperibol calorimeter and that of the heat conduction calorimeter discussed here should be noted. In the usual operation of the isoperibol calorimeter, essentially a temperature difference between the beginning and the end of a main period, in which the principal temperature rise or fall takes place as a result of thermal reaction occurring, is observed. This observed temperature difference is corrected for thermal leakage and heat of stirring in order to obtain the corrected temperature rise resulting from the thermal reaction under investigation. The main aim of the theory of the isoperibol calorimeter is to obtain a method for the accurate determination of the temperature correction by considering the heat flow in the calorimeter. On the other hand, the theory of the heat conduction calorimeter in this paper is essentially intended to establish an alternative method for the determination of the amount of heat and thermogenesis, evolved or absorbed in the calorimeter container, in terms of heat flow.

MODEL OF CALORIMETER

The model of a heat conduction calorimeter is represented schematically in Fig. 1. The calorimeter consists of three domains, the thermal reaction domain, D_1 , the heat flow domain, D_2 , and the surroundings domain, D_3 . The thermal reaction domain, D_1 , in which the thermal phenomena under investigation are carried out and studied, is completely enclosed by the surroundings domain, D_3 . The surfaces S_1 and S_2 are D_1 - D_2 and D_2 - D_3 interfaces, respectively.

The following assumptions for this model are introduced.

(1) Calorific power $w(t)$ is developed in the confined domain D_1 at time t . $w(t)$ is also called thermogenesis (function) [1].

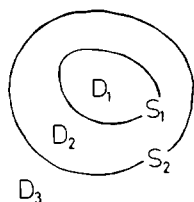


Fig. 1. Schematic diagram of model of a heat conduction calorimeter. D_1 , Thermal reaction domain; D_2 , heat flow domain; D_3 , surroundings; S_1 , the interface between D_1 and D_2 ; S_2 , the interface between D_2 and D_3 .

(2) The surroundings domain D_3 is kept at a uniform constant temperature T_s .

(3) Thermal properties such as the heat capacity, c , thermal diffusivity, κ , and thermal conductivity, λ , of the heat flow domain D_2 are independent of time and temperature. This assumption requires that, in the operation of the calorimeter, the temperature ranges of the domain D_2 are small and the variation of the thermal physical properties with temperature can be neglected.

(4) Temperature $T(\mathbf{r}, t)$ at a point represented by the position vector \mathbf{r} in the heat flow domain D_2 at time t is given by the equation

$$\theta(\mathbf{r}, t) = T(\mathbf{r}, t) - T_s \quad (2)$$

$$\frac{\partial \theta(\mathbf{r}, t)}{\partial t} = H\theta(\mathbf{r}, t) \quad (3)$$

where operator H is linear in temperature and commutable with Laplace transform operator $L\{\theta(t)\} = \int_0^\infty e^{-st}\theta(t)dt$.

$$LH\theta = HL\theta \quad (4)$$

If $H = \kappa \nabla^2$ ($\nabla^2 =$ the Laplacian), eqn. (3) becomes identical with Fourier's equation for the conduction of heat. If H is constant, eqn. (3) represents Newton's law of cooling, which is generally assumed in the analysis of calorimeters by many authors. Thus, eqn. (3) is a general expression for heat transfer which is linear in temperature. Heat transfer in the domain D_2 by convection and radiation is excluded because it is non-linear in temperature. From the standpoint of design and operation of a calorimeter, convection and radiation are not a problem if domain D_2 and temperature difference θ are kept small.

(5) The initial temperature of the calorimeter is equal to T_s at D_3 throughout D_1 , D_2 , and D_3 .

BOUNDARY VALUE PROBLEM FOR UNIFORM TEMPERATURE IN THE THERMAL REACTION DOMAIN

The following new assumptions are added.

(6) The temperature in the thermal reaction domain D_1 is uniform and the temperature gradient at a point on the surface S_1 is uniform everywhere over the surface S_1 .

(7) Thermal physical properties of the thermal reaction domain D_1 are independent of time and temperature.

The assumptions (3) and (7) require that the temperature ranges of the whole calorimeter and change of the matter in D_1 are small and that the variations of the thermal physical properties of D_1 and D_2 can be neglected.

Then, a boundary value problem for this case is described as follows.

The initial condition is

$$\theta(\mathbf{r}, 0) = 0 \quad (5)$$

In D_1 and on S_1

$$w(t) = c \frac{\partial \theta}{\partial t} - \lambda S_1 \left(\frac{\partial \theta}{\partial n} \right)_{s_1} \quad (6)$$

In D_2

$$\frac{\partial \theta}{\partial t} = H\theta \quad (7)$$

In D_3 and on S_2

$$\theta(\mathbf{r}, t) = 0 \quad (8)$$

In these equations, $\theta(\mathbf{r}, t) = T(\mathbf{r}, t) - T_s$ is the temperature measured relative to the temperature of D_3 , c is the heat capacity of the domain D_1 , S_1 is the surface area of the surface S_1 , $\partial/\partial n$ is differentiation in the direction of the outward normal to the surface S_1 .

By application of the Laplace transform to these equations, they become

$$\bar{w}(s) = cs\bar{\theta}(\mathbf{r}, s) - \lambda S_1 \frac{\partial}{\partial n} \bar{\theta}(\mathbf{r}, s) \quad (9)$$

$$s\bar{\theta}(\mathbf{r}, s) = H\bar{\theta}(\mathbf{r}, s) \quad (10)$$

$$\bar{\theta}(\mathbf{r}, s) = 0 \quad (11)$$

where $\bar{w}(s)$ and $\bar{\theta}(\mathbf{r}, s)$ are the Laplace transform of the function $w(t)$ and $\theta(\mathbf{r}, t)$.

Let $f(\mathbf{r}, t)$ be the temperature when $w(t) = w_0 =$ a constant independent of time. Then, the Laplace transform of the temperature, $\bar{f}(\mathbf{r}, s)$, satisfies the following equations. In D_1 and on S_1

$$\frac{w_0}{s} = cs\bar{f}(\mathbf{r}, s) - \lambda S_1 \frac{\partial}{\partial n} \bar{f}(\mathbf{r}, s) \quad (12)$$

In D_2

$$s\bar{f}(\mathbf{r}, s) = H\bar{f}(\mathbf{r}, s) \quad (13)$$

In D_3 and on S_2

$$\bar{f}(\mathbf{r}, s) = 0 \quad (14)$$

It follows that the product $s\bar{f}(\mathbf{r}, s)\bar{w}(s)/w_0$ satisfies eqns. (9)–(11), and therefore

$$\bar{\theta}(\mathbf{r}, s) = \frac{s\bar{f}(\mathbf{r}, s)\bar{w}(s)}{w_0} \quad (15)$$

Let $g(\mathbf{r}, t)$ be the temperature when $w(t) = \delta(t) =$ Dirac's delta function. Then the Laplace transform of the temperature, $\bar{g}(\mathbf{r}, s)$, satisfies the follow-

ing equations. In D_1 and on S_1

$$1 = cs\bar{g}(\mathbf{r}, s) - \lambda S_1 \frac{\partial}{\partial n} \bar{g}(\mathbf{r}, s) \quad (16)$$

In D_2

$$s\bar{g}(\mathbf{r}, s) = H\bar{g}(\mathbf{r}, s) \quad (17)$$

In D_3 and on S_2

$$\bar{g}(\mathbf{r}, s) = 0 \quad (18)$$

It follows that the product $\bar{g}(\mathbf{r}, s)\bar{w}(s)$ satisfies eqns. (9)–(11), and therefore

$$\bar{\theta}(\mathbf{r}, s) = \bar{g}(\mathbf{r}, s)\bar{w}(s) \quad (19)$$

From eqns. (15) and (19), the following theorem is obtained.

Theorem 1. If assumptions (1)–(7) are valid in a calorimeter, the relation between the Laplace transform of the temperature, $\bar{\theta}(\mathbf{r}, s)$, and the Laplace transform of the calorific power, $\bar{w}(s)$, in the calorimeter system is given by

$$\bar{\theta}(\mathbf{r}, s) = G(\mathbf{r}, s)\bar{w}(s) \quad (20)$$

where $G(\mathbf{r}, s)$ is the “transfer function” of the calorimeter system [7] and is given by

$$G(\mathbf{r}, s) = \frac{s\bar{f}(\mathbf{r}, s)}{w_0} \quad (21)$$

or

$$G(\mathbf{r}, s) = \bar{g}(\mathbf{r}, s) \quad (22)$$

In these equations, $\bar{f}(\mathbf{r}, s)$ is the Laplace transform of the temperature for constant calorific power, w_0 , and $\bar{g}(\mathbf{r}, s)$ is the Laplace transform of the temperature for impulse calorific power, $\delta(t)$.

In view of the convolution property of the Laplace transform, the following theorem is obtained from eqns. (20)–(22).

Theorem 2. If assumptions (1)–(7) are valid in a calorimeter, the equation of the thermogram (time–temperature variation) for the calorific power, $w(t)$, in the calorimeter is given by the equations

$$\theta(\mathbf{r}, t) = \int_0^t \frac{w(\tau)}{w_0} \frac{\partial}{\partial t} f(\mathbf{r}, t - \tau) d\tau \quad (23)$$

$$= \frac{\partial}{\partial t} \int_0^t \frac{w(\tau)}{w_0} f(\mathbf{r}, t - \tau) d\tau \quad (24)$$

or

$$\theta(\mathbf{r}, t) = \int_0^t w(\tau) g(\mathbf{r}, t - \tau) d\tau \quad (25)$$

where $f(\mathbf{r}, t)$ is the temperature for constant calorific power w_0 and $g(\mathbf{r}, t)$ is the temperature for impulse calorific power $\delta(t)$. The vector \mathbf{r} denotes the

position where the temperature is observed.

In order to derive a formula to obtain the total quantity of heat, Q , developed in thermal reaction domain D_1 , eqn. (23) is integrated with respect to t from $t = 0$ to $t = \infty$.

$$\int_0^\infty \theta(\mathbf{r}, t) dt = \int_0^\infty \int_0^t \frac{w(\tau)}{w_0} \frac{\partial}{\partial t} f(\mathbf{r}, t - \tau) d\tau dt \quad (26)$$

If changes of variables $u = \tau$ and $v = t - \tau$ are substituted in the integral in eqn. (26), then the double integral of the right-hand side of eqn. (26) can be changed to the repeated integral

$$\begin{aligned} \int_0^\infty \theta(\mathbf{r}, t) dt &= \int_0^\infty \int_0^\infty \frac{w(u)}{w_0} \frac{d}{dv} f(\mathbf{r}, v) du dv \\ &= \int_0^\infty \frac{w(u)}{w_0} du \int_0^\infty \frac{d}{dv} f(\mathbf{r}, v) dv \\ &= \frac{f(\mathbf{r}, \infty)}{w_0} \int_0^\infty w(u) du \end{aligned} \quad (27)$$

In this derivation, the initial condition (5) is used: $f(\mathbf{r}, \infty)$ denotes the convergence temperature of the calorimeter for the constant calorific power w_0 as $t \rightarrow \infty$ and the convergence of the integrals $\int_0^\infty \theta(\mathbf{r}, t) dt$ and $\int_0^\infty w(u) du$ are assumed.

The left-hand side of eqn. (27) is the time integral of the temperature deviation from the initial temperature or the area enclosed by the thermogram curve and the base line. The integral $\int_0^\infty w(u) du$ is the total quantity of heat developed, Q , and eqn. (27) can be written as follows.

Theorem 3. If assumptions (1)–(7) are valid in a calorimeter, the total quantity of heat developed in the calorimeter thermal reaction domain, Q , is given by

$$Q = \frac{w_0}{f(\mathbf{r}, \infty)} A \quad (28)$$

where $A = \int_0^\infty \theta(\mathbf{r}, t) dt$ and $f(\mathbf{r}, \infty)$ is the convergence temperature for constant calorific power w_0 as $t \rightarrow \infty$.

BOUNDARY VALUE PROBLEM FOR UNIFORM HEAT FLUX OVER THE SURFACE OF THE THERMAL REACTION DOMAIN

Let us drop the previous assumptions (6) and (7) and add the following new assumption.

(8) The heat flux (quantity of heat per unit area per unit time transferred across the surface), $q(t)$, at a point on the surface S_1 does not change from point to point and is uniform everywhere over the surface S_1 .

A boundary value problem under the assumptions (1)–(5) and (8) is described as follows. The initial condition

$$\theta(\mathbf{r}, 0) = 0 \quad (29)$$

On S_1

$$q(t) = -\lambda \left(\frac{\partial \theta}{\partial n} \right)_{S_1} \quad (30)$$

In D_2

$$\frac{\partial \theta}{\partial t} = H\theta \quad (31)$$

In D_3 and on S_2

$$\theta(\mathbf{r}, t) = 0 \quad (32)$$

Then, the Laplace transform $\bar{\theta}(\mathbf{r}, s)$ satisfies the conditions

$$\bar{q}(s) = -\lambda \left(\frac{\partial \bar{\theta}}{\partial n} \right)_{S_1} \quad \text{on } S_1 \quad (33)$$

$$s\bar{\theta}(s) = H\bar{\theta} \quad \text{in } D_2 \quad (34)$$

$$\bar{\theta}(\mathbf{r}, s) = 0 \quad \text{in } D_3 \text{ and on } S_2 \quad (35)$$

Let $h(\mathbf{r}, t)$ represent the temperature in the special case in which $q(t) = q_0 = \text{constant}$ independent of time. Then the Laplace transform $\bar{h}(\mathbf{r}, s)$ satisfies the boundary conditions

$$\frac{q_0}{s} = -\lambda \left(\frac{\partial \bar{h}}{\partial n} \right)_{S_1} \quad \text{on } S_1 \quad (36)$$

$$s\bar{h}(\mathbf{r}, s) = H\bar{h}(\mathbf{r}, s) \quad \text{in } D_2 \quad (37)$$

$$\bar{h}(\mathbf{r}, s) = 0 \quad \text{in } D_3 \text{ and on } S_2 \quad (38)$$

It follows that the product $s\bar{h}(\mathbf{r}, s)\bar{q}(s)/q_0$ satisfies the conditions (33)–(35) and, therefore equals $\bar{\theta}(\mathbf{r}, s)$. Using the convolution property of the Laplace transform, equations for $\theta(\mathbf{r}, t)$ are obtained and will be shown later in eqns. (40) and (41). If we assume that the calorific power generated in D_1 ceases within a finite interval of time, then the total quantity of heat, Q , is given by

$$\begin{aligned} Q &= \int_{S_1} \int_0^\infty q(t) dt dS \\ &= S_1 \int_0^\infty q(t) dt \end{aligned}$$

Proceeding as in the previous section, we can find the expression for Q . Then, the theorem for the cases of the uniform heat flux over the thermal reaction domain S_1 is obtained as follows.

Theorem 4. If assumptions (1)–(5) and (8) are valid in a calorimeter, the following equations for the cases of uniform heat flux over the surface of the

thermal reaction domain of the calorimeter are obtained.

$$\bar{\theta}(\mathbf{r}, s) = \frac{s\bar{h}(\mathbf{r}, s)}{q_0} \bar{q}(s) \quad (39)$$

$$\theta(\mathbf{r}, t) = \int_0^t \frac{q(\tau)}{q_0} \frac{\partial}{\partial t} h(\mathbf{r}, t - \tau) d\tau \quad (40)$$

$$= \frac{\partial}{\partial t} \int_0^t \frac{q(\tau)}{q_0} h(\mathbf{r}, t - \tau) d\tau \quad (41)$$

$$Q = \frac{S_1 q_0}{h(\mathbf{r}, \infty)} \int_0^\infty \theta dt \quad (42)$$

In these equations, $h(\mathbf{r}, t)$ is the temperature for the constant heat flux, q_0 , and the bar denotes the Laplace transform of the quantity represented by the notation under the bar.

It should be noticed that there is no restriction in theorem 4 on the uniformity of the temperature and on the constancy of the physical thermal properties in the thermal reaction domain during the occurrence of the thermal phenomena under investigation. This point is favorable for the measurement of heat Q and will be discussed in detail later. In actual experiment, it is very difficult to hold the heat flux, $q(t)$, constant during the full time interval of the calorimeter experiment and to observe the temperature $h(\mathbf{r}, t)$. Thus it seems that theorem 4 is not useful for actual experiments. However, eqn. (42) is useful to interpret the basis of the measurement of heat Q as shown later.

DETERMINATION OF THERMOGENESIS

Recently, heat conduction calorimeters have been increasingly utilized to determine not only the total heat effect associated with the thermal phenomena under study, but also the changes of thermal power with time, the thermogenesis [8–10]. Several methods have been proposed for the determination of thermogenesis from experimental data of a thermogram, i.e. temperature vs. time data. All the methods are started from an a priori assumption of a linear relation between input thermogenesis, $w(t)$, and output thermogram, $\theta(t)$, and are not based on a clear model of a calorimeter or an explicit theoretical basis. Macqueron et al. [11] try to treat the mathematical model of a calorimeter to arrive at an analytical form of the transfer function. But they start from a non-zero initial temperature condition and fail to obtain an explicit form of a relation between the input thermogenesis, output thermogram and transfer function. The theorems derived from the model in this paper can present a method for the determination of thermogenesis and suggest the conditions under which the

linear relation between thermogenesis and the thermogram is valid.

Theorems 1 and 2 present basic equations for the determination of thermogenesis from the analysis of thermogram data. The Fourier transform analysis method [12–15] is based on eqns. (20) with (21) or (22) if we set $s = j\omega$ ($j = \sqrt{-1}$ and $\omega =$ angular frequency). The analog electronics inverse filter method [16,21] is based on eqn. (20) assuming that the form of transfer function $G(s)$ is a rational fractional function of s . The dynamic optimization method [17,18] is based on eqn. (25).

It is important to judge whether a calorimeter satisfies the conditions under which these equations are valid. Theorems 1 and 2 with the assumptions (1)–(7) suggest the conditions that the temperature of the thermal reaction domain should be uniform and the thermal properties of the calorimeter remain unchanged. A calorimeter with stirring or heat distributing vanes, if possible, may insure the uniformity of the temperature.

Most authors have determined the transfer function $G(s)$ or $G(j\omega)$ from the thermogram for impulse joule heating by use of eqn. (22). Impulse heating requires the generation of a very intense heat for a short time in the calorimeter cell, and implies deviations from the assumption of uniform temperature distribution and possible systematic errors. Some authors have treated the problem in terms of “location of calibrating heater” which produces the impulse heating [19–20]. Determination of the transfer function from the thermogram for step heating by use of eqn. (21) [15] may reduce the errors caused by deviations from temperature uniformity.

A change in composition is an important consideration for thermochemical studies which may cause appreciable change of the content and the thermal properties of the calorimeter. It is difficult to estimate the extent of the errors caused by change in composition.

DETERMINATION OF TOTAL QUANTITY OF HEAT

Theorems 3 and 4 present a method for determining the quantity of heat, Q , from time–temperature data in heat conduction calorimeter experiments. As pointed out in the introduction, the method is an alternative to that usually used in isoperibol calorimeter experiments. Equations (28) and (42) and the assumptions made in the derivation of the equations give the basis of the method. Both the equations show that the heat, Q , evolved or absorbed in the thermal reaction domain is proportional to the temperature–time integral from $t = 0$ to $t = \infty$

$$Q = kA \quad (43)$$

where

$$A = \int_0^{\infty} \theta dt \quad (44)$$

is taken as the area under the time–temperature curve and k is a constant independent of the form of the time–temperature curve. The proportionality relationship between Q and A has also been derived for one-dimensional [22], ideal three-dimensional [23], spherical and cylindrical [24] models of heat conduction calorimeters. The same form of the relation (43) is also established in the study of differential thermal analysis (DTA) and is used for the determination of the heat of transition or reaction by DTA [25]. If DTA apparatus has a thermal barrier between the sample holder and the metal block, and if the thermocouple which measures the differential temperature is located on the surface of the sample holder, the DTA apparatus is strictly regarded as a dynamic heat conduction calorimeter which is operated in heating or cooling at a uniform rate [26].

According to theorem 4, the relation (43) is derived without using any assumptions about the temperature distribution and the form of heat flow inside the thermal reaction domain. The relation is derived, instead, assuming a uniform temperature gradient over the surface of the domain. The assumptions made in the derivation of the proportionality relation (43) are in accord with those in a previous paper [23] and are favorable for measuring relative enthalpies at high temperature. In high temperature enthalpy measurements, a hot body at a high temperature is dropped into the calorimeter where the heat given up on cooling is compared with a known energy. Because of the large temperature difference between the hot body and the calorimeter, we cannot assume uniform temperature distribution and linear heat transfer inside the thermal reaction domain. However, the assumption of a uniform temperature gradient on the surface of the thermal reaction domain requires design features of the calorimeter. Geometrically symmetrical construction of calorimeter or stirred-water type of calorimeter can satisfy the requirement of the assumption and the relation (43) can be used as a basic formula for the measurements.

MAXIMUM SENSITIVITY OF THE CALORIMETER

From the results obtained hitherto, we can discuss a best condition for maximum sensitivity of calorimeter. The problem is, what size of thermal reaction domain, D_1 , gives maximum calorimeter sensitivity at a confined volume of the domain $D_1 + D_2$ (see Fig. 1)?

The sensitivity, σ , of the calorimeter is defined by

$$\sigma = \frac{\int_0^{\infty} \theta(\mathbf{r}, t) dt}{\int_0^{\infty} j(\mathbf{r}, t) dt} \quad (45)$$

where $j(\mathbf{r}, t)$ is the density of thermogenesis, thermal power per unit volume

of D_1 , and relates with the thermogenesis, $w(t)$, of the domain D_1 by the equation

$$w(t) = \int_{V_{D_1}} j(\mathbf{r}, t) dV \quad (46)$$

We shall only consider the case of uniform density of thermogenesis, $j_0(t)$, and eqn. (46) becomes

$$w(t) = j_0(t) V_{D_1} \quad (47)$$

where V_{D_1} is the volume of D_1 . From eqns. (27) and (47), the sensitivity, σ , is represented by

$$\sigma = \frac{\int_0^\infty \theta dt}{\int_0^\infty j_0 dt} = \frac{f(\infty) V_{D_1}}{w_0} \quad (48)$$

We shall calculate the sensitivity, σ , for the particular models of heat conduction calorimeter and obtain the optimum conditions for maximum sensitivity. The results are shown as follows.

One-dimensional model [22]

$$\sigma = \frac{L(L_0 - L)}{\Lambda} \quad (49)$$

$$L_{\max} = \frac{L_0}{2} \quad (50)$$

$$\sigma_{\max} = \frac{L_0^2}{4\Lambda} \quad (51)$$

where L is the length of D_2 , L_0 the length of $D_1 + D_2$, and Λ the thermal conductivity of D_2 .

Spherical model [24]

$$\sigma = \frac{R^2(R_0 - R)}{3\Lambda R_0} \quad (52)$$

$$R_{\max} = \frac{2}{3} R_0 \quad (53)$$

$$\sigma_{\max} = \frac{4R_0^2}{81\Lambda} \quad (54)$$

where R is the radius of D_2 , and R_0 the radius of $D_1 + D_2$.

Cylindrical model [24]

$$\sigma = \frac{R^2}{2\Lambda} \ln\left(\frac{R_0}{R}\right) \quad (55)$$

$$R_{\max} = \frac{R_0}{\sqrt{e}} \quad (56)$$

$$\sigma_{\max} = \frac{R_0^2}{4e\Lambda} \quad (57)$$

where R is the radius of D_1 and R_0 the radius of $D_1 + D_2$. Ozawa [26] also obtained the same result for his quantitative DTA cylindrical sample holder.

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