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# LINEAR THEORY APPLIED TO A CALORIMETER DURING QUASI-ISOTHERMAL OPERATION

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## ABSTRACT

The first law of thermodynamics is applied to a calorimeter model in which the reaction domain is surrounded by a heat-conducting domain through which heat is exchanged linearly with constant-temperature surroundings. Equations describing the quasi-isothermal operation of the calorimeter are derived.

It proves possible to represent the temperature change of the reaction domain or the wall of the reaction domain for any thermal reaction in terms of the rate of enthalpy change and temperature response caused by impulse or step power input. The proportionality relation between the change in the enthalpy and the time integral of the deviation of the temperature from the convergence temperature is obtained. The proportionality constant is shown to depend only on the geometrical structure and the physical nature of the heat-conducting domain and to be independent of those of the reaction domain.

It is also shown that when the temperature and the concentrations of the reactants in the reaction domain are uniform, the thermodynamic state of the reaction domain can be represented by two variables, the extent of reaction and the temperature, thus providing theoretical bases for the deconvolution methods used in thermokinetics.

Equations describing a twin calorimeter system are also derived and shown to have the same forms as those for the single calorimeter system.

Some problems in the recent treatment of a time-varying calorimeter system are discussed, and the advantages of an isothermal calorimeter with regulation of power are illustrated.

## INTRODUCTION

Both the isoperibol calorimeter and heat conduction calorimeter consist of essentially common parts, a reaction vessel, a heat-conducting interspace and a surrounding thermostat, which allow heat transfer to occur between the reaction vessel and the thermostat. However, there is an important difference between the two calorimeters. In the operation of the isoperibol calorimeter, the heat transfer between the reaction vessel and the surrounding thermostat is kept as small as possible, and essentially the temperature difference between the beginning and the end of the thermal reaction period is measured. On the other hand, the heat transfer between the reaction vessel and the thermostat of the heat conduction calorimeter is made large so that

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heat developed in the vessel dissipates rapidly into the thermostat. In the operation of the heat conduction calorimeter, the temperature difference between the vessel and the thermostat is continuously observed. The calorimeter is usually operated under conditions in which the temperature difference remains small, and is widely used for the study of slow reactions.

The isoperibol calorimeter is almost adiabatic and can be called a quasi-adiabatic calorimeter. The heat conduction calorimeter is operated under almost isothermal conditions and can be called a quasi-isothermal calorimeter. This paper deals with a simple basic model of a calorimeter with linear heat flow over the surface of the reaction vessel and presents fundamental formulae for the use of such a calorimeter during quasi-isothermal operation.

## APPLICATION OF THE LAWS OF THERMODYNAMICS TO CALORIMETRY THEORY

Only a few authors have paid attention to the application of the laws of thermodynamics to calorimetry theory. Wilhoit applies the first law of thermodynamics to a calorimetric system and discusses the treatment of the experimental data [1]. West and Churney propose a theory of isoperibol calorimetry in terms of the first law of thermodynamics [2,3]. Equations which are not based on the laws of thermodynamics have difficulty in distinguishing heat from internal energy or enthalpy. For example, the equation for adiabatic calorimetry

$$Q = C\,\Delta T \tag{1}$$

is usually described in many text-books, where $C$ is the heat capacity, $\Delta T$ is the measured temperature change and $Q$ is usually referred to as the total quantity of "heat" evolved in the process. Equation (1) is not a result of the application of the laws of thermodynamics to calorimetry. In fact, eqn. (1) appears to be in conflict with the adiabatic condition which requires $Q = 0$ in the calorimeter, and gives a positive temperature change for an endothermic process and a negative one for an exothermic process, contrary to thermodynamic terms.

In this paper, the theory of heat conduction calorimetry presented in the previous paper [4] is reconstructed in terms of the first law of thermodynamics, assuming a linear heat flow between the wall of the sample vessel and that of its constant-temperature surroundings.

## CALORIMETER MODEL

The calorimeter model used is represented schematically in Fig. 1. It consists of four domains, $D_0$–$D_3$. $D_0$ is the surrounding area at constant

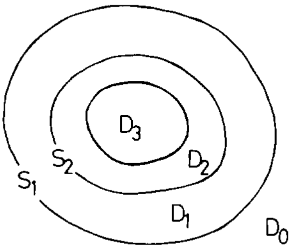

Fig. 1. Calorimeter model. $D_0$, $S_1$, surrounding area of constant temperature and its surface; $D_1$, heat-conducting domain; $D_2$, $S_2$, wall of reaction domain and its external surface; $D_3$, reaction domain.

temperature and $S_1$ is its internal surface. $D_3$ is the reaction domain in which the thermal reaction under investigation occurs and $D_2$ is the wall of the reaction domain which has a uniform but time-dependent temperature. $S_2$ is the external surface of the wall. $D_1$ is the heat-conducting domain in which heat flow occurs between the surfaces $S_1$ and $S_2$. In this model, the following assumptions are introduced:

(a) Thermal physical properties such as heat capacity, thermal conductivity and thermal diffusivity of the domains $D_1$ and $D_2$ outside the reaction domain are constant and independent of time during the thermal reaction process under investigation.

This assumption requires that the ranges of the temperature changes of the calorimeter system remain small during operation and that the variation of the physical properties with temperature can be neglected.

(b) Linear heat flow over the external surface $S_2$ takes place.

(c) The temperature of $D_2$ is uniform.

(d) The temperature gradient $\partial T(\mathbf{r}, t)/\partial n$ in the direction of the outward-drawn normal to the surface $S_2$ is uniform over $S_2$ where $T(\mathbf{r}, t)$ denotes the temperature at a point represented by position vector $\mathbf{r}$ at time $t$.

(e) The initial temperatures of the system are equal to the convergence temperature (steady-state temperature) $T_c(\mathbf{r})$ independent of time.

## CASE 1. UNIFORM TEMPERATURE AND CONCENTRATIONS OF REACTANTS INSIDE THE REACTION DOMAIN

We add the following new assumptions to the previous assumptions:

(f) The temperature of the reaction domain $D_3$ is uniform and equal to that of $D_2$, and the concentrations of reactants in $D_3$ are also uniform.

(g) The thermal physical properties of $D_3$ are independent of time during the thermal reaction process under investigation.

Application of the first law of thermodynamics to $D_2 + D_3$ inside the surface $S_2$ for an infinitesimal time interval $\mathrm{d}t$ gives

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \tag{2}$$

where $\mathrm{d}Q$ and $\mathrm{d}W$ represent the heat and the work received by $D_2 + D_3$, and $\mathrm{d}U$ is the increment of the internal energy of $D_2 + D_3$. If the thermal reaction takes place in $D_3$ at constant pressure, we may write

$$\mathrm{d}H = \mathrm{d}Q + \mathrm{d}W \tag{3}$$

where $\mathrm{d}H$ is the increment of the enthalpy of $D_2 + D_3$. As experiments using heat conduction calorimetry are usually carried out at atmospheric pressure, we prefer to start our discussion from eqn. (3). Similar results can also be obtained when we start from eqn. (2). Dividing both sides of eqn. (3) by $\mathrm{d}t$ gives

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} + \frac{\mathrm{d}W}{\mathrm{d}t} \tag{4}$$

Considering assumption (f) and the constant pressure under which the thermal reaction occurs in $D_3$, we can determine the thermodynamic state of $D_2 + D_3$ by two variables, the temperature $T$ and the extent of reaction $\xi$. Then we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial \xi}\frac{\mathrm{d}\xi}{\mathrm{d}t} + \frac{\partial H}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}t} = v(t) + C\frac{\mathrm{d}T}{\mathrm{d}t} \tag{5}$$

where

$$v(t) = \frac{\partial H}{\partial \xi}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{6}$$

is the rate of enthalpy change caused by a reaction or a transformation and

$$C = \frac{\partial H}{\partial T} \tag{7}$$

is the heat capacity of $D_2 + D_3$.

$$\phi = \frac{\mathrm{d}Q}{\mathrm{d}t} = \lambda A \frac{\partial T}{\partial n} \tag{8}$$

is the heat flow through the surface $S_2$, where $\lambda$ is the thermal conductivity of $D_1$ and $A$ is the surface area of $S_2$.

$$\frac{\mathrm{d}W}{\mathrm{d}t} = P_0 + P(t) \tag{9}$$

is the power produced at $D_2 + D_3$, where $P_0$ is the time-independent part caused by electric currents in the resistance thermometer and mechanical stirring, and $P(t)$ is the transient time-dependent part due to calibration or compensation. Equation (4) can be written as follows:

$$v(t) + C\frac{\mathrm{d}T}{\mathrm{d}t} = \lambda A \frac{\partial T}{\partial n} + P_0 + P(t) \tag{10}$$

When $v(t) = 0$ and $P(t) = 0$, the calorimetric system reaches steady state and eqn. (10) becomes

$$0 = \lambda A \frac{\partial T_c}{\partial n} + P_0 \tag{11}$$

where $T_c(\mathbf{r})$ is the convergence temperature of the system. Subtracting eqn. (11) from eqn. (10), we obtain

$$v(t) + C\frac{d\theta}{dt} = \lambda A \frac{\partial \theta}{\partial n} + P(t) \tag{12}$$

where

$$\theta(\mathbf{r}, t) = T(\mathbf{r}, t) - T_c(\mathbf{r}) \tag{13}$$

If $\mathbf{r} \in D_2 + D_3$, $T(\mathbf{r}, t)$ and $\theta(\mathbf{r}, t)$ are independent of $\mathbf{r}$ (assumption (f)). If $\mathbf{r} \in D_0$, $\theta(\mathbf{r}, t) = 0$.

We can now write eqn. (12) for three special cases. When the reaction takes place in $D_3$ and no transient work is done, eqn. (12) becomes

$$v(t) + C\frac{d\theta}{dt} = \lambda A \frac{\partial \theta}{\partial n} \tag{14}$$

When no reaction occurs and impulse work is done, $P(t) = \delta(t)$, eqn. (12) becomes

$$C\frac{dg}{dt} = \lambda A \frac{\partial g}{\partial n} + \delta(t) \tag{15}$$

where $g = g(\mathbf{r}, t)$ is the temperature response for the impulse power $P(t) = \delta(t)$ and $\delta(t)$ is the delta function of $t$. When no reaction occurs and step work is done, $P(t) = W_0 u(t)$, eqn. (12) becomes

$$C\frac{df}{dt} = \lambda A \frac{\partial f}{\partial n} + W_0 u(t) \tag{16}$$

where $f = f(\mathbf{r}, t)$ is the temperature response for step power input $W_0 u(t)$ and $u(t)$ is the unit step function

$u(t) = 0$ for $t < 0$

$u(t) = 1$ for $t > 0$

Taking the Laplace transform of eqns. (14), (15) and (16) with respect to $t$, we get

$$\bar{v}(s) + Cs\bar{\theta}(\mathbf{r}, s) = \lambda A \frac{\partial \bar{\theta}(\mathbf{r}, s)}{\partial n} \tag{14'}$$

$$Cs\bar{g}(\mathbf{r}, s) = \lambda A \frac{\partial \bar{g}(\mathbf{r}, s)}{\partial n} + 1 \tag{15'}$$

and

$$Cs\bar{f}(\mathbf{r}, s) = \lambda A \frac{\partial \bar{f}(\mathbf{r}, s)}{\partial n} + \frac{W_0}{s} \tag{16'}$$

where $\bar{v}(s)$, $\bar{\theta}(\mathbf{r}, s)$, $\bar{g}(\mathbf{r}, s)$ and $\bar{f}(\mathbf{r}, s)$ are the Laplace transforms of $v(t)$, $\theta(\mathbf{r}, t)$, $g(\mathbf{r}, t)$ and $f(\mathbf{r}, t)$, respectively and $s$ is the parameter. From eqns. (14′)–(16′) we obtain the following relations

$$\bar{\theta}(\mathbf{r}, s) = -\bar{v}(s)\bar{g}(\mathbf{r}, s) \tag{17a}$$

$$\bar{\theta}(\mathbf{r}, s) = -s\bar{v}(s)\bar{f}(\mathbf{r}, s)/w_0 \tag{17b}$$

$$\bar{g}(\mathbf{r}, s) = s\bar{f}(\mathbf{r}, s)/w_0 \tag{17c}$$

Taking the inverse Laplace transforms of eqns. (17a–c), we obtain

$$\theta(\mathbf{r}, t) = -\int_0^t v(\tau)g(\mathbf{r}, t-\tau)\,\mathrm{d}\tau \tag{18a}$$

$$\theta(\mathbf{r}, t) = -\frac{1}{w_0}\int_0^t v(\tau)\frac{\partial f(rt-\tau)}{\partial t}\,\mathrm{d}\tau \tag{18b}$$

and

$$g(\mathbf{r}, t) = \frac{1}{w_0}\frac{\mathrm{d}f(r, t)}{\mathrm{d}t} \tag{18c}$$

Equations (17a–c) and (18a–c) are the fundamental equations for the deconvolution methods in thermokinetics [5–7].

Next, we try to derive a formula for the enthalpy change $\Delta H_\xi$ caused by the reaction or the transform. Integrating both sides of eqn. (18b), we obtain

$$\int_0^\infty \theta(t)\,\mathrm{d}t = -\frac{1}{w_0}\int_0^\infty\int_0^t v(\tau)\frac{\partial f(t-\tau)}{\partial t}\,\mathrm{d}\tau\,\mathrm{d}t \tag{19}$$

Using a step function

$u(t-\tau) = 0 \quad$ for $\tau > t$

$u(t-\tau) = 1 \quad$ for $\tau < t$

we obtain

$$\int_0^t v(\tau)\frac{\partial f(t-\tau)}{\partial t}\,\mathrm{d}\tau = \int_0^\infty v(\tau)\frac{\partial f(t-\tau)}{\partial t}u(t-\tau)\,\mathrm{d}\tau \tag{20}$$

Substituting eqn. (20) into eqn. (19) and interchanging the order of the integrals on the right hand side of eqn. (19), we have

$$\int_0^\infty\int_0^t v(\tau)\frac{\partial f(t-\tau)}{\partial t}\,\mathrm{d}\tau\,\mathrm{d}t = \int_0^\infty v(\tau)\left\{\int_0^\infty\frac{\partial f(t-\tau)}{\partial t}u(t-\tau)\,\mathrm{d}t\right\}\mathrm{d}\tau \tag{21}$$

If we then put $\eta = t - \tau$, the integral in the brace in eqn. (21) becomes

$$\int_0^\infty\frac{\partial f(t-\tau)}{\partial t}u(t-\tau)\,\mathrm{d}t = \int_{-\tau}^\infty\frac{\partial f(\eta)}{\partial\eta}u(\eta)\,\mathrm{d}\eta = \int_0^\infty\frac{\partial f(\eta)}{\partial\eta}\,\mathrm{d}\eta = f(\infty) \tag{22}$$

From eqns. (19), (21) and (22), we obtain

$$\int_0^\infty\theta(t)\,\mathrm{d}t = -\frac{f(\infty)}{w_0}\int_0^\infty v(\tau)\,\mathrm{d}\tau = -\frac{f(\infty)}{w_0}\Delta H_\xi \tag{23}$$

where

$$\Delta H_\xi = \int_0^\infty v(t)\,\mathrm{d}t$$

is the enthalpy change caused by the thermal reaction.

Under constant power $P(t) = w_0$, the calorimetric system reaches a steady state and eqn. (16) becomes

$$0 = \lambda A \frac{\mathrm{d}f(r, \infty)}{\mathrm{d}n} + w_0 \tag{24}$$

We can then add the new assumption (h) as follows.

(h) Linear heat flow takes place in the whole space of the domain $D_1$ and the surface area $A$ is a function of a variable $\mathbf{r}$.
We then have a solution for eqn. (24), thus:

$$f(\mathbf{r}_2, \infty) = \frac{w_0}{\lambda} \int_{S_2}^{S_1} \frac{\mathrm{d}n}{A} = \frac{w_0}{\lambda\sigma} \tag{25}$$

where

$$\frac{1}{\sigma} = \int_{S_2}^{S_1} \frac{\mathrm{d}n}{A} \tag{26}$$

and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors on $S_1$ and $S_2$, respectively. When the surface is spherical, eqn. (26) becomes [8]

$$\frac{1}{\sigma} = \int_{r_2}^{r_1} \frac{\mathrm{d}r}{4\pi r^2} = \frac{(r_1 - r_2)}{4\pi r_1 r_2}$$

From eqns. (23) and (25), we get

$$\Delta H_\xi = -\frac{w_0}{f(\infty)} \int_0^\infty \theta(t)\,\mathrm{d}t \tag{27}$$

$$= -\lambda\sigma \int_0^\infty \theta(t)\,\mathrm{d}t \tag{28}$$

## CASE 2. NON-UNIFORM TEMPERATURE INSIDE THE REACTION VESSEL

In this case, we drop assumptions (f) and (g) made in CASE 1. Applying the first law of thermodynamics to $D_2 + D_3$, we can write

$$\frac{\mathrm{d}H_3}{\mathrm{d}t} + C_2 \frac{\mathrm{d}T}{\mathrm{d}t} = \lambda A \frac{\partial T}{\partial n} + P_0 + P(t) \tag{29}$$

where $H_3 = H_3(t)$ is the enthalpy of $D_3$ and $C_2$ is the heat capacity of $D_2$. Hereafter we can proceed in a manner analogous to that in CASE 1. Rearranging eqn. (29), we obtain

$$h(t) + C_2 \frac{\mathrm{d}\theta}{\mathrm{d}t} = \lambda A \frac{\partial\theta}{\partial n} + P(t) \tag{30}$$

where

$$h(t) = \frac{\mathrm{d}H_3}{\mathrm{d}t} \tag{31}$$

is the rate of change in the enthalpy of $D_3$ and $\theta$ is defined in eqn. (13). Equation (30) is similar to eqn. (12) in form and we can derive the following formulae similar to those in CASE 1 using the same process.

$$\bar{\theta}(\mathbf{r}, s) = -\bar{h}(s)\bar{g}(\mathbf{r}, s) \tag{32a}$$

$$\bar{\theta}(\mathbf{r}, s) = -s\bar{h}(s)\bar{f}(\mathbf{r}, s)/w_0 \tag{32b}$$

$$\bar{g}(\mathbf{r}, s) = s\bar{f}(\mathbf{r}, s)/w_0 \tag{32c}$$

$$\theta(\mathbf{r}, t) = -\int_0^t h(\tau)g(\mathbf{r}, t-\tau)\,\mathrm{d}\tau \tag{33a}$$

$$\theta(\mathbf{r}, t) = -\frac{1}{w_0}\int_0^t h(\tau)\frac{\partial f(rt-\tau)}{\partial t}\,\mathrm{d}\tau \tag{33b}$$

$$g(\mathbf{r}, t) = \frac{1}{w_0}\frac{\mathrm{d}f(r, t)}{\mathrm{d}t} \tag{33c}$$

$$\Delta H_3 = -\frac{w_0}{f(r, \infty)}\int_0^\infty \theta(\mathbf{r}, t)\,\mathrm{d}t \tag{34}$$

$$= -\lambda\sigma\int_0^\infty \theta(\mathbf{r}, t)\,\mathrm{d}t \tag{35}$$

$\Delta H_3$ is the change in the enthalpy of $D_3$.

## TWIN CALORIMETER SYSTEM

The twin calorimeter system is widely used and is practically essential when high precision is sought with a heat conduction calorimeter. The system consists of two physically identical calorimeters symmetrically disposed within a thermostated environment. The thermal reaction under investigation is carried out in one of the calorimeters (the "laboratory" element), the other serving as the "reference" element. In the system, we do not measure the temperature of the laboratory element, $T_L$, nor the difference between the temperature of the element and that of its surroundings, $T_L - T_s$, but measure the difference $T_L - T_R$, where $T_R$ is the temperature of the reference element. Therefore, it is desirable to represent the equation in terms of the quantity to be measured, $T_L - T_R$. The equation can be derived in a manner analogous to the treatment of differential thermal analysis [9].

Equation (10) can be written for the laboratory element as

$$v(t) + C_L\frac{\mathrm{d}T_L}{\mathrm{d}t} = \lambda_L A_L\frac{\partial T_L}{\partial n} + P_{OL} + P(t) \tag{36}$$

In the reference element, $v(t)=0$ and $P(t)=0$, so we can write

$$C_R\frac{dT_R}{dt}=\lambda_R A_R\frac{\partial T_R}{\partial n}+P_{OR} \tag{37}$$

The subscripts L and R refer to the laboratory and the reference element, respectively. Subtracting eqn. (37) from eqn. (36) and rearranging, we obtain

$$\begin{aligned} &v(t)+C_L\frac{dy}{dt}+(C_L-C_R)\frac{dT_R}{dt} \\ &\quad=\lambda_L A_L\frac{\partial y}{\partial n}+(\lambda_L A_L-\lambda_R A_R)\frac{\partial T_R}{\partial n}+(P_{OL}-P_{OR})+P(t) \end{aligned} \tag{38}$$

where

$$y=T_L-T_R \tag{39}$$

is a measured quantity in the twin calorimeter system. In the steady state, $y$ and $T_R$ become their convergence values, $y_c$ and $T_{cR}$, respectively. Then we have

$$\begin{aligned} &C_L\frac{dy_c}{dt}+(C_L-C_R)\frac{dT_{cR}}{dt} \\ &\quad=\lambda_L A_L\frac{\partial y_c}{\partial n}+(\lambda_L A_L-\lambda_R A_R)\frac{\partial T_{cR}}{\partial n}+(P_{OL}-P_{OR}) \end{aligned} \tag{40}$$

It can be assumed that thermal effects in the laboratory element do not have any effects on the reference element, so that
$T_R=T_{cR}$
constantly applies throughout the whole course of the twin calorimeter experiment. Subtracting eqn. (40) from eqn. (38), we get

$$v(t)+C_L\frac{dz}{dt}=\lambda_L A_L\frac{\partial z}{\partial n}+P(t) \tag{41}$$

where

$$z=y-y_c \tag{42}$$

is the deviation of the observed thermogram curve from the baseline.

Similarly, we obtain an equation

$$h(t)+C_{2L}\frac{dz}{dt}=\lambda_L A_L\frac{\partial z}{\partial n}+P(t) \tag{43}$$

for the twin system in CASE 2.

Equations (41) and (43) are similar in form to eqns. (12) and (30), and the previous results obtained in CASE 1 and CASE 2 are also valid for the twin calorimeter system.

## MEASUREMENTS OF ENTHALPY CHANGE

Equations (27), (28), (34) and (35) show that enthalpy change is proportional to the time integral of the temperature deviation from the convergence temperature, and that the proportionality constant depends only on the physical structures of the calorimeter outside the reaction domain and does not depend on the nature and the state of the reactants. The equations provide a method for evaluating the enthalpy change in heat conduction calorimeter experiments. The method can be considered to be quasi-isothermal and is an alternative to the quasi-adiabatic method usually used in isoperibol calorimetry.

The theory of CASE 2 is preferred for measurements of high-temperature enthalpy in drop calorimetry and of enthalpy change in vigorous chemical reactions such as combustion. In these measurements, we cannot assume a uniform distribution of temperature and concentrations of reactants nor linear heat transfer inside the reaction vessel. The theory of CASE 2 does not require any assumptions regarding the reaction domain $D_3$ but assumptions (a)–(e) are required for the domains outside the reaction domain.

Equations (27) and (28) in CASE 1 can be used for estimating the enthalpy change for a reaction or a transformation, $\Delta H_\xi$, separately from the total enthalpy change, $\Delta H$. However, $\Delta H$ becomes equal to $\Delta H_\xi$ when the initial and final temperatures of the sample before and after the reaction are equal.

## THERMOKINETICS

Recently, thermokinetic methods for obtaining the rate of enthalpy change for a chemical reaction from analysis of data on temperature changes in a calorimeter, often called deconvolution methods, have been developed [5–7]. The theory of CASE 1 provides the theoretical basis and the fundamental equations, (17a–c) and (18a–c), for these deconvolution methods.

One of the important conditions in the theory of CASE 1 is that the temperature and the concentration of the reactants inside the reaction domain are uniform (assumption (f)). Zielenkiewicz and Tabaka present a multi-domain theory which allows non-uniform distribution of temperature inside the calorimeter reaction vessel [10], and they construct a calorimeter which has two thermometers and two calibrating heaters in the reaction vessel [11]. They assume linear heat transfer between the domains and a constant heat capacity for each domain. Therefore, their theory cannot be applied to vigorous reactions accompanied by non-linear heat transfer and large changes in physical properties of the reaction system. Moreover, their theory does not show any clear principle as to how to divide a real calorimeter reaction vessel into separate domains. A calorimeter equipped with two or more thermometers and heaters inside the reaction vessel seems to be rather complicated for use in "laboratory" calorimeter experiments. In such a "laboratory" calorimeter, it may be better to use heat distribution vanes or a stirring device inside the reaction vessel to produce uniform distributions of temperature and concentration of reactants inside the vessel. Their theory and method may be useful for analysis of "industrial"-scale calorimetry involving a moderate reaction.

Assumptions (a) and (g) state that the thermal physical properties of the whole calorimeter system should be constant during the thermal change in the calorimeter, and they are further important necessary conditions for application in deconvolution methods. However, studies on time-varying calorimetric systems in which some thermal physical properties vary linearly with time have been developed recently [12–15]. Cesari et al. state that changes in sensitivity occur if the heat capacity of a calorimeter reaction vessel changes with time, $C = C(t)$ [12]. They start from the simple Tian–Calvet's equation for impulse heating, $\delta(t)$

$$C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + PT = \delta(t) \tag{44}$$

where $P$ is the "heat transfer coupling constant" (their term in ref. 12) between the calorimeter reaction vessel and the thermostat. Integration of eqn. (44) gives

$$\int_0^\infty C(t)\frac{\mathrm{d}T}{\mathrm{d}t}\mathrm{d}t + P\int_0^\infty T(t)\,\mathrm{d}t = 1 \tag{45}$$

They define the sensitivity $S$ as the time integral of the temperature response for impulse heating

$$S = \int_0^\infty T(t)\,\mathrm{d}t \tag{46}$$

Equations (45) and (46) give

$$S = \frac{1}{P} - \frac{1}{P}\int_0^\infty C(t)\,\mathrm{d}T \tag{47}$$

and they conclude that the sensitivity $S$ cannot be constant if the heat capacity of the reaction vessel $C(t)$ changes with time. However, when the heat capacity $C(t)$ changes within a limited range, it can be shown (as follows) that integration of the second term on the right-hand side of eqn. (47) becomes zero and that the sensitivity $S$ is a constant equal to $1/P$. From the first mean value theorem of integration [16], we get

$$L\{T(\infty) - T(0)\} \leqslant \int_0^\infty C(t)\,\mathrm{d}T \leqslant U\{T(\infty) - T(0)\} \tag{48}$$

where $L$ and $U$ are the lower and upper bounds of $C(t)$ in the range $0 < t < \infty$. In usual heat conduction calorimeter experiments, we make

$$T(0) = T(\infty) \tag{49}$$

and then from eqn. (48) we get

$$\int_0^{\infty} C(t)\,\mathrm{d}T = 0 \tag{50}$$

and

$$S = 1/P \tag{51}$$

Ortin et al. have presented a model for a heat conduction calorimeter in which the heat capacity of the reaction vessel and the heat transfer coupling constant change with time, together with a method for analyzing experimental data with a time-varying calorimeter system [14]. However, their model (ref. 14, Fig. 1) is not suitable for precise calorimetry. Their model has two thermal paths in parallel between the reaction vessel $A_1$ and the thermostat $A_0$ (notations $A_0$–$A_3$ are introduced in the present paper for the sake of clarity). One path is a straight connection of $A_1$ and $A_0$, and has a time-independent heat transfer coupling constant $P_{10}$ between $A_1$ and $A_0$. The other path is a series consisting of the vessel $A_1$, two domains $A_2$ and $A_3$, and the thermostat $A_0$. The heat transfer coupling constant between $A_1$ and $A_2$ is assumed to be time-varying, $P(t)$. In their model, the temperature response for any thermal effect in the reaction vessel is measured at the domain $A_2$. They try to obtain the thermal power generated in the vessel $A_1$ from analysis of temperature changes in the domain $A_2$. If the heat transfer coupling constant $P_{12}(t)$ changes with time, the ratio of the two heat flows from the vessel through the two paths changes with time. Let us now examine the most extreme case in which $P_{12}(t) = 0$. The temperature of $A_2$ becomes equal to that of $A_0$ and we cannot observe any temperature response in $A_2$, irrespective of the heat evolution in the reaction vessel $A_0$.

## ADVANTAGES OF ISOTHERMAL CALORIMETRY WITH POWER REGULATION

Let us consider an isothermal calorimeter the temperature of which is controlled to a constant $T_c$ by regulation of power $P(t)$. Putting $T = T_c =$ constant in eqn. (10), we obtain an equation

$$v(t) = \lambda A \frac{\partial T_c}{\partial n} + P_0 + P(t) \tag{52}$$

for the isothermal calorimeter. When no reaction occurs, eqn. (52) becomes

$$0 = \lambda A \frac{\partial T_c}{\partial n} + P_0 + P_s \tag{53}$$

From eqns. (52) and (53), we get

$$v(t) = P(t) - P_s \tag{54}$$

$P_s$ is regarded as the "baseline" power.

Equation (54) tells us that we can obtain the rate of enthalpy change $v(t)$ directly by measuring the power needed to regulate a constant calorimeter temperature. The total enthalpy change $\Delta H_\xi$ can be obtained by the time integration of eqn. (54) as follows

$$\Delta H_\xi = \int_0^{t_f} \{P(t) - P_s\}\,\mathrm{d}t \tag{55}$$

where $t_f$ is the time to the end of the reaction period.

The advantages of the isothermal calorimeter in thermokinetics are as follows: it does not need any complex treatment of time–temperature data such as the deconvolution methods used in heat conduction calorimetry; the necessary conditions for isothermal calorimetry are uniform temperature and concentrations of the reactants in the reaction vessel; no constant physical properties of the reaction system during thermokinetic measurement are necessary.

The isothermal calorimeter also has an advantage in measuring the total enthalpy change, $\Delta H$. In heat conduction calorimetry, the time required to complete the measurement of the enthalpy change is from time zero to a time when the temperature reaches the "baseline", the convergence temperature. The temperature deviation from the baseline, $\theta$, does not become zero when the reaction stops and continues to decay to the baseline within the time required by the time constant of the calorimeter. On the other hand, in isothermal calorimetry, the measuring power $P(t)$ reaches a baseline $P_s$ simultaneously with the cessation of the reaction under investigation, so that the time required for a complete measurement is shorter than that required in heat conduction calorimetry.

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