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Theory of a heat conduction calorimeter for scanning
Part 1. Uniform temperature and reactant concentration

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Abstract

The theory of a heat conduction calorimeter for quasi-isothermal operation is extended to that for scanning operation. The deconvolution method developed, based on heat conduction calorimetry during quasi-isothermal operation and used to determine the rate of energy change due to chemical or physical change of a sample, can be applied to the kinetic analysis of thermal data by calorimetry during scanning operation. It also serves to interpret thermal data from DTA and heat-flow DSC experiments

INTRODUCTION

Conventional heat conduction calorimeters are used at the constant temperature of the surroundings. Recently many types of calorimeters have been designed to operate with scanning operation and are used with the surroundings temperature being changed in a programmed manner with respect to time [1]. It is therefore desirable to extend the theory of the heat conduction calorimeter [2,3] to that for scanning. The heat conduction calorimeter and heat-flow DSC measure the temperature differences between the outside surface of a sample holder and the inner surface of the surroundings. Both are based on the same principle [4], but their theories are developed independently [3,5]. Thus, whether the extended theory of the heat conduction calorimeter is applicable to the data obtained by heat-flow DSC experiments is a point of some interest.

MODEL AND BOUNDARY INITIAL VALUE PROBLEM

A model of the heat conduction calorimeter is shown schematically in Fig. 1. It consists of three concentric and symmetrical domains. D_B is the surroundings, having a temperature T_B that is programmed controlled; D_1

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is the heat conducting domain and D_2 is the reaction domain. S_1 is the internal surface of D_B and S_2 is the external surface of D_2. The heat energy flows to or from reaction domain D_2 through heat conducting domain D_1. $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are unit vectors on surfaces S_1 and S_2 respectively, and they are directed toward the interior of D_1.

The assumptions of the model are as follows.

(a) Thermal physical properties such as heat capacity C, specific heat capacity c, thermal conductivity λ, thermal diffusivity κ and density ρ of the domains are constant over the temperature range of scanning and during the thermal reactions.

(b) Heat transfer takes place by solid conduction, and other mechanisms such as convection and radiation can be neglected.

(c) The temperature and concentration of the reactant in D_2 are uniform.

(d) Temperature gradients $(\partial T/\partial n_1)_{S_1}$ and $(\partial T/\partial n_2)_{S_2}$ are uniform over surfaces S_1 and S_2 respectively, where $\partial/\partial n$ denotes differentiation in the direction normal to the surface and toward the interior of D_1, and $T = T(\boldsymbol{r}, t)$ the temperature at a point represented by position vector $\boldsymbol{r}$ at time t.

Application of the first law of thermodynamics to D_2 under constant pressure gives

$$\frac{\mathrm{d}H_2}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} + \frac{\mathrm{d}W}{\mathrm{d}t} \tag{1}$$

where H_2 is the enthalpy of D_2, and Q and W are the heat energy and work received by D_2, respectively. Based on assumption (c) and the constant pressure under which the thermal reaction occurs in D_2, the thermodynamic state of D_2 can be determined by two variables, the temperature T and the extent of reaction ξ. We thus have $H_2 = H_2(\xi, T)$. It then follows that

$$\begin{aligned} \frac{\mathrm{d}H_2}{\mathrm{d}t} &= \frac{\partial H_2}{\partial \xi}\frac{\mathrm{d}\xi}{\mathrm{d}t} + \frac{\partial H_2}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}t} \\ &= v(t) + C_2\frac{\mathrm{d}T}{\mathrm{d}t} \end{aligned} \tag{2}$$

where

$$v(t) = \frac{\partial H_2}{\partial \xi}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{3}$$

is the rate of reaction in J s^{-1} and

$$C_2 = \frac{\partial H_2}{\partial T} \tag{4}$$

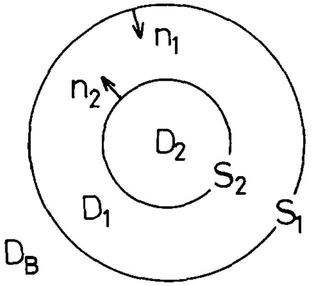

Fig. 1. Model of the heat conduction calorimeter. D_B, surroundings; D_1, heat conducting domain; D_2, reaction domain; S_1 and S_2, boundary surfaces between the domains; $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$, unit vectors on surfaces S_1 and S_2, respectively, directed towards the interior of D_1.

is the heat capacity of D_2 in J K^{-1}.

$$\phi = \frac{dQ}{dt} = \lambda_1 A_2 \left(\frac{\partial T}{\partial n_2} \right)_{S_2} \tag{5}$$

is the rate of heat flow from or to D_2 through surface S_2 in J s^{-1} and A_2 is the surface area of S_2.

$$\frac{dW}{dt} = p_0 + p(t) \tag{6}$$

is the power produced at D_2, where p_0 is the time-independent part caused by electrical current in the resistance thermometer and by mechanical stirring, and $p(t)$ is the transient time-dependent part due to calibration or compensation. Therefore we obtain the following equation at D_2 and S_2 considering eqns. (2), (5) and (6)

$$v(t) + C_2 \frac{dT}{dt} = \lambda_1 A_2 \left(\frac{\partial T}{\partial n_2} \right)_{S_2} + p_0 + p(t) \tag{7}$$

At D_1, D_2 and S_1, we have similarly

$$\frac{dH_1}{dt} + \frac{dH_2}{dt} = -\lambda_1 A_1 \left(\frac{\partial T}{\partial n_1} \right)_{S_1} + p_0 + p(t) \tag{8}$$

and

$$\frac{dH_1}{dt} = \iiint_{D_1} \rho_1 c_1 \frac{\partial T}{\partial t} d\tau \tag{9}$$

where H_1 is the enthalpy of D_1, A_1 is the surface area of S_1, ρ_1 is the density of D_1, c_1 is the specific heat capacity of D_1 and $d\tau$ is the volume element. From eqns. (2), (8) and (9) it follows that

$$v(t) + C_2 \left(\frac{dT}{dt} \right)_{D_2} + \iiint_{D_1} \rho_1 c_1 \frac{\partial T}{\partial t} d\tau = -\lambda_1 A_1 \left(\frac{\partial T}{\partial n_1} \right)_{S_1} + p_0 + p(t) \tag{10}$$

From assumption (b), we have at D_1

$$\kappa_1 \nabla^2 T = \frac{\partial T}{\partial t} \tag{11}$$

At D_B and S_1 we set

$$T_B = T_0 + \alpha t \tag{12}$$

where α is the rate of scanning.

When $t \leqq 0$, we set the initial conditions

$$\begin{aligned} &T(\boldsymbol{r}, t) = T_B = T_0 \\ &p(t) = p_0 = 0 \\ &\mathrm{d}H_1/\mathrm{d}t = \mathrm{d}H_2/\mathrm{d}t = 0 \end{aligned} \tag{13}$$

In the following, solution will be obtained for the boundary initial value problems (7) and (10)–(13).

DIVISION OF VARIABLE $T(\boldsymbol{r}, t)$

The following division of $T(\boldsymbol{r}, t)$ reduces the above boundary initial value problem to one that is simpler [6].

$$T(\boldsymbol{r}, t) = T_B + x(\boldsymbol{r}) + y(\boldsymbol{r}, t) + z(\boldsymbol{r}, t) \tag{14}$$

The divided variables are defined so as to satisfy the conditions

$x(\boldsymbol{r})$ satisfies

$$C_2 \alpha = \lambda_1 A_2 \left(\frac{\partial x}{\partial n_2} \right)_{S_2} + p_0 \tag{15}$$

$$(C_1 + C_2)\alpha = -\lambda_1 A_1 \left(\frac{\partial x}{\partial n_1} \right)_{S_1} + p_0 \tag{16}$$

$$\kappa_1 \nabla^2 x(\boldsymbol{r}) = \alpha \qquad \boldsymbol{r} \in D_1 \tag{17}$$

and

$$x(\boldsymbol{r}) = 0 \qquad \boldsymbol{r} \in D_B, S_1 \tag{18}$$

$y(\boldsymbol{r}, t)$ satisfies

$$C_2 \left(\frac{\partial y}{\partial t} \right)_{D_2} = \lambda_1 A_2 \left(\frac{\partial y}{\partial n_2} \right)_{S_2} \tag{19}$$

$$C_2 \left(\frac{\partial y}{\partial t} \right)_{D_2} + \iiint_{D_1} \rho_1 c_1 \left(\frac{\partial y}{\partial t} \right) \mathrm{d}\tau = -\lambda_1 A_1 \left(\frac{\partial y}{\partial n_1} \right)_{S_1} \tag{20}$$

$$\kappa_1 \nabla^2 y(\boldsymbol{r}, t) = \partial y(\boldsymbol{r}, t)/\partial t, \qquad \boldsymbol{r} \in D_1 \tag{21}$$

$$y(\boldsymbol{r}, t) = 0 \qquad \boldsymbol{r} \in \mathrm{D_B}, \mathrm{S_1} \tag{22}$$

and

$$y(\boldsymbol{r}, t) = -x(\boldsymbol{r}) \qquad t \leqq 0 \tag{23}$$

$z(\boldsymbol{r}, t)$ satisfies

$$v(t) + C_2\left(\frac{\partial z}{\partial t}\right)_{\mathrm{D_2}} = \lambda_1 A_2\left(\frac{\partial z}{\partial n_2}\right)_{\mathrm{S_2}} + p(t) \tag{24}$$

$$v(t) + C_2\left(\frac{\partial z}{\partial t}\right)_{\mathrm{D_2}} + \iiint_{\mathrm{D_1}} \rho_1 c_1\left(\frac{\partial z}{\partial t}\right) \mathrm{d}\tau = -\lambda_1 A_1\left(\frac{\partial z}{\partial n_1}\right)_{\mathrm{S_1}} + p(t) \tag{25}$$

$$\kappa_1 \nabla^2 z(\boldsymbol{r}, t) = \partial z(\boldsymbol{r}, t)/\partial t \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{26}$$

$$z(\boldsymbol{r}, t) = 0, \qquad \boldsymbol{r} \in \mathrm{D_B}, \mathrm{S_1} \tag{27}$$

and

$$z(\boldsymbol{r}, t) = v(t) = p(t) = 0 \qquad t \leqq 0 \tag{28}$$

PROPERTIES OF $x(\boldsymbol{r})$, $y(\boldsymbol{r}, t)$ AND $z(\boldsymbol{r}, t)$

From conditions (15)–(28), the following properties of $x(\boldsymbol{r})$, $y(\boldsymbol{r}, t)$ and $z(\boldsymbol{r}, t)$ are derived.

Application of Green's theorem in symmetrical form [7] to $\mathrm{D_1}$ enclosed by surfaces $\mathrm{S_1}$ and $\mathrm{S_2}$ gives

$$\iiint_{\mathrm{D_1}} (\phi \nabla^2 x - x \nabla^2 \phi)\, \mathrm{d}\tau = \iint_{\mathrm{S_1+S_2}} \left(-\phi \frac{\partial x}{\partial n} + x \frac{\partial \phi}{\partial n}\right) \mathrm{d}S \tag{29}$$

In the above equation, $\phi = \phi(\boldsymbol{r})$ is defined as

$$\nabla^2 \phi(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{30}$$

and is equal at each of surfaces $\mathrm{S_1}$ and $\mathrm{S_2}$ respectively. For example, $\phi = 1/r$ is for a spherical concentric model of $\mathrm{D_B}$, $\mathrm{D_1}$ and $\mathrm{D_2}$, and $\phi = \ln r$ for a cylindrical model. Considering expressions (17) and (30), the left hand side of eqn. (29) becomes

$$\iiint_{\mathrm{D_1}} = \frac{\alpha}{\kappa_1} \iiint_{\mathrm{D_1}} \phi \, \mathrm{d}\tau \tag{31}$$

From (15) and (16), we have

$$\left(\frac{\partial x}{\partial n_2}\right)_{\mathrm{S_2}} = \frac{1}{\lambda_1 A_2}(C_2 \alpha - p_0) \tag{32}$$

$$\left(\frac{\partial x}{\partial n_1}\right)_{\mathrm{S_1}} = -\frac{1}{\lambda_1 A_1}\{(C_1 + C_2)\alpha - \rho_0\} \tag{33}$$

From (18), (32) and (33), the right-hand side of eqn. (29) becomes

$$\iint_{S_1+S_2} = \iint_{S_1} + \iint_{S_2}$$

$$= -\phi_1 A_1 \left(\frac{\partial x}{\partial n_1} \right)_{S_1} - \phi_2 A_2 \left(\frac{\partial x}{\partial n_2} \right)_{S_2} + x_2 A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2}$$

$$= \frac{\phi_1}{\lambda_1} [(C_1 + C_2)\alpha - p_0] - \frac{\phi_2}{\lambda_1}(C_2 \alpha - p_0) + x_2 A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \qquad (34)$$

where the subscripts 1 and 2 denote the values of x and A at surfaces S_1 and S_2, respectively. Thus

$$\kappa_1 = \lambda_1 / \rho_1 c_1 = V_1 \lambda_1 / C_1 \qquad (35)$$

where V_1 is the volume of D_1. From eqns. (29), (31), (34) and (35) we get

$$x_2 = \left\{ \left[\left(\frac{1}{V_1} \iiint_{D_1} \phi \, \mathrm{d}\tau - \phi_1 \right) C_1 + (\phi_2 - \phi_1) C_2 \right] \alpha - (\phi_2 - \phi_1) p_0 \right\} /$$

$$A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \lambda_1 \qquad (36)$$

where x_2 is the baseline displacement from the zero line on a $(T - T_B)$ vs. t curve. Expression (36) shows the displacement to be linear with respect to the rate of scanning α and heat capacity C_2. Based on the above, the heat capacity of the reaction domain can be determined.

The boundary initial conditions of $y(\boldsymbol{r}, t)$, expressions (19)–(23), show that $y(\boldsymbol{r}, t)$ is the transient temperature of $D_1 + D_2$ surrounded by a thermal bath of zero temperature. The second law of thermodynamics thus indicates temperature $y(\boldsymbol{r}, t)$ to approach zero as t increases

$$\lim_{t \to \infty} y(\boldsymbol{r}, t) = 0 \qquad (37)$$

The boundary initial conditions of $z(\boldsymbol{r}, t)$, (24)–(28), indicate changes in temperature of the heat conduction calorimeter for quasi-isothermal operation [2]. The results of the theory of the calorimeter also hold. Accordingly

$$z(\boldsymbol{r}, t) = -\int_0^t v(\eta) g(\boldsymbol{r}, t - \eta) \, \mathrm{d}\eta$$

$$= -\frac{1}{p_c} \int_0^t v(\eta) \frac{\partial}{\partial t} f(\boldsymbol{r}, t - \eta) \, \mathrm{d}\eta \qquad (38)$$

$$\Delta H_R = \int_0^\infty v(t) \, \mathrm{d}t = -\frac{p_c}{f(\boldsymbol{r}, \infty)} \int_0^\infty z(\boldsymbol{r}, t) \, \mathrm{d}t \qquad (39)$$

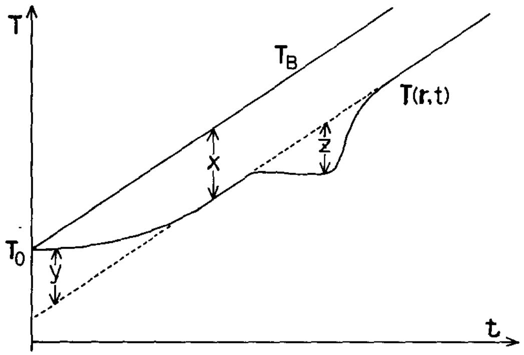

Fig. 2. The behavior of temperature of the reaction domain, $T(\boldsymbol{r}, t) = T_B + x(\boldsymbol{r}) + y(\boldsymbol{r}, t) + z(\boldsymbol{r}, t)$. T_B is the temperature of the surroundings which changes linearly with time. $x(\boldsymbol{r})$ represents baseline height from the zero line. $y(\boldsymbol{r}, t)$ is the transient part of temperature in the initial stage of scanning. $z(\boldsymbol{r}, t)$ is the part due to chemical or physical change of the reaction domain.

and

$$g(\boldsymbol{r}, t) = \frac{1}{p_c} \frac{\mathrm{d}f(\boldsymbol{r}, t)}{\mathrm{d}t} \tag{40}$$

where $g(\boldsymbol{r}, t)$ is $z(\boldsymbol{r}, t)$ for impulse power $p(t) = \delta(t)$ and $f(\boldsymbol{r}, t)$ is that for step power.

$$\begin{aligned} p(t) &= p_c \quad \text{for } t > 0 \\ &= 0 \quad \text{for } t < 0 \end{aligned} \tag{41}$$

ΔH_R is the enthalpy change due to chemical or physical change in the reaction domain.

The behavior of $T(\boldsymbol{r}, t)$ and its components $T_B(t)$, $x(\boldsymbol{r})$, $y(\boldsymbol{r}, t)$ and $z(\boldsymbol{r}, t)$ are shown schematically in Figs. 2 and 3.

Equations (38) and (40) show that the rate of enthalpy change $v(t)$ during scanning at a uniform rate is obtainable by the deconvolution

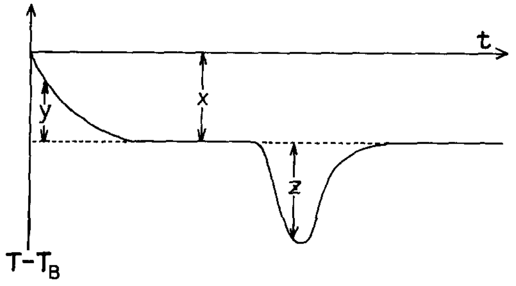

Fig. 3. Behavior of $T(\boldsymbol{r}, t) - T_B$. The curve represents a thermogram as usually observed during scanning for the heat conduction calorimeter.

method developed in the quasi-isothermal operation of the heat conduction calorimeter [2,3].

Nearly all methods for kinetic study by DTA or DSC are based on the assumption that the rate of reaction follows the single equation

$$v(t)=\frac{\partial H}{\partial \xi}\frac{\mathrm{d}\xi}{\mathrm{d}t}=\frac{\partial H}{\partial \xi}A\ \mathrm{e}^{-E/RT}(1-\xi)^{n} \tag{42}$$

throughout the scanning period, where A is the frequency factor, E is the activation energy and n is the order of the reaction [8]. Although this equation is considered inadequate by many authors for not being applicable to solid-state reactions [9,10], E and n by this equation are determined in many cases by DTA and DSC. The following two-step analysis of thermal data is better than the above methods used in kinetic studies by DTA and DSC. The first step is to obtain the rate of enthalpy change $v(t)$ by the deconvolution analysis of thermal data [11]. The second step is determination of the most reasonable reaction mechanism which fits the $v(t)$ data.

Equation (39) relates peak area $\int_0^\infty z(r,\ t)\ \mathrm{d}t$ in the (T_B-T) vs. t curve to enthalpy change ΔH_R through a proportionality constant $-p_c/f(r,\ \infty)$ and is the same as that generally used for determining the heat of reaction.

However, eqns. (38) and (39) are basically approximate relationships, since they assume constant thermal physical properties, uniform temperature, uniform concentration of the reactant and so on. The application of these equations is thus confined to a short range of scanning temperature and to small changes in the thermal properties of the reactant.

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