Thermochimica Acta, 204 (1992) 261–270
Elsevier Science Publishers B.V., Amsterdam

Theory of a heat conduction calorimeter for scanning. Part 2. Non-uniform temperature and reactant concentration

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(Received 27 September 1991)

Abstract

The theory of the heat conduction calorimeter for scanning in the case of non-uniform distribution of temperature in the reaction domain is presented. The surface average temperature over the outside surface of the reaction domain provides significant information on the thermal behavior of the reaction domain. If the surface average temperature is recorded against time, a thermogram curve is obtained and gives a peak due to the thermal reaction under investigation. The proportionality relationship between the time integral of the peak and the enthalpy change of the thermal reaction is proven, and a proportionality constant is derived.

INTRODUCTION

When the distribution of temperature and concentration of a reactant is uniform, the thermodynamic state of the reactant under constant pressure is determined by two variables, the temperature T and the extent of reaction ξ. The energy change rate due to chemical or physical change in the reactant can be determined by the deconvolution method developed based on heat conduction calorimetry during quasi-isothermal operation [1].

When the distribution of temperature and concentration of a reactant is non-uniform, the thermodynamic state of the reactant cannot be found from a simple set of thermodynamic variables (ξ, T), nor is it possible to determine the rate of energy change by the deconvolution method as shown previously [1]. However, if the surface average temperature over the outside surface of the reactant is defined, significant thermal information such as the enthalpy change due to the thermal reaction of the reactant can be obtained from measurement of the surface average temperature.

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MODEL AND BOUNDARY-INITIAL VALUE PROBLEM

The model is the same as that shown in the previous paper (see fig. 1 in ref. 1). It consists of three concentric domains D_B, D_1 and D_2. Reaction domain D_2 at the center is surrounded by a heat conducting domain D_1, and D_1 is surrounded by a thermal bath D_B, the temperature T_B of which is linearly changed with time t. S_1 is the surface between D_B and D_1 and S_2 is the surface between D_1 and D_2. The terms $\boldsymbol{n}_1$ 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.

Some of the assumptions in the previous paper [1] are introduced here, as follows.

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 assumed to be constant over the temperature range of scanning and during the thermal reaction.

Heat transfer takes place by solid conduction, and other mechanism such as convection and radiation can be neglected.

Uniformity of the temperature and concentration of the reactant is not assumed. Uniformity of temperature gradients $(\partial T/\partial n_1)_{S_1}$ and $(\partial T/\partial n_2)_{S_2}$ is not assumed, where $\partial/\partial n_i$ denotes differentiation in the direction of vector $\boldsymbol{n}_i$ and $T = T(\boldsymbol{r}, t)$ is the temperature at a point represented by positional vector $\boldsymbol{r}$ at time t.

Boundary-initial conditions of the model are as follows. At D_B and S_1, we set

$$T_B = T_0 + \alpha t \tag{1}$$

where α is the rate of scanning. At D_1, we have

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

where κ_1 is the thermal diffusivity of D_1. Hereafter, the subscripts 1 and 2 denote the quantities of D_1 and D_2, respectively.

Application of the first law of thermodynamics to D_2 and S_2 [1] gives the rate of enthalpy of D_2 as

$$\frac{\mathrm{d}H_2}{\mathrm{d}t} = \lambda_1 \int\!\!\int_{S_2} \left(\frac{\partial T}{\partial n_2}\right)_{S_2} \mathrm{d}S + p_0 + p(t) \tag{3}$$

where p_0 and $p(t)$ are the time-independent and time-dependent parts, respectively, of electrical or mechanical power in D_2. Similarly, we have at D_1, D_2 and S_1

$$\frac{\mathrm{d}H_1}{\mathrm{d}t} + \frac{\mathrm{d}H_2}{\mathrm{d}t} = -\lambda_1 \int\!\!\int_{S_1} \left(\frac{\partial T}{\partial n_1}\right)_{S_1} \mathrm{d}S + p_0 + p(t) \tag{4}$$

Here, H_1 and H_2 are the enthalpies of D_1 and D_2, respectively, and are represented by

$$\frac{dH_1}{dt} = \iiint_{D_1} \rho_1 c_1 \frac{\partial T}{\partial t} d\tau \tag{5}$$

$$\begin{aligned}\frac{dH_2}{dt} &= \frac{d}{dt}\iiint_{D_2} \rho_2 h_2 \, d\tau = \iiint_{D_2} \rho_2 \left(\frac{\partial h_2}{\partial \xi}\frac{\partial \xi}{\partial t} + \frac{\partial h_2}{\partial T}\frac{\partial T}{\partial t} \right) d\tau \\ &= v(t) + \iiint_{D_2} \rho_2 c_2 \frac{\partial T}{\partial t} d\tau \end{aligned} \tag{6}$$

where $h_2 = h_2\ (\xi, T)$ is the enthalpy of D_2 per unit volume and $d\tau$ is the volume element.

$$v(t) = \iiint_{D_2} \rho_2 \frac{\partial h_2}{\partial \xi}\frac{\partial \xi}{\partial t} d\tau \tag{7}$$

is the rate of enthalpy change of D_2 due to chemical or physical change and $\xi = \xi(\boldsymbol{r})$ is the extent of the reaction of D_2.

When $t \leq 0$, we set the initial conditions as follows

$$\begin{aligned} &T(\boldsymbol{r}, t) = T_B = T_0 \\ &p(t) = p_0 = 0 \\ &dH_1/dt = dH_2/dt = 0 \end{aligned} \tag{8}$$

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 [1,2].

$$T(\boldsymbol{r}, t) = T_B + x(\boldsymbol{r}) + y(\boldsymbol{r}, t) + z(\boldsymbol{r}, t) \tag{9}$$

The divided variables are so defined as to satisfy the conditions
$x(\boldsymbol{r})$ satisfies

$$x(\boldsymbol{r}) = 0 \qquad \boldsymbol{r} \in D_B \cup S_1 \tag{10}$$

$$\kappa_1 \nabla^2 x = \alpha \qquad \boldsymbol{r} \in D_1 \tag{11}$$

$$(C_1 + C_2)\alpha = -\lambda_1 \iint_{S_1} \left(\frac{\partial x}{\partial n_1} \right)_{S_1} dS + p_0 \qquad \boldsymbol{r} \in D_1 \cup D_2 \tag{12}$$

and

$$C_2 \alpha = \lambda_1 \iint_{S_2} \left(\frac{\partial x}{\partial n_2} \right)_{S_2} dS + p_0 \tag{13}$$

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

$$y(\boldsymbol{r}, t) = 0 \qquad \boldsymbol{r} \in \mathrm{D_B} \cup \mathrm{S_1} \tag{14}$$

$$\kappa_i \nabla^2 y = \partial y / \partial t \qquad i = 1, 2 \qquad \boldsymbol{r} \in \mathrm{D}_i \tag{15}$$

$$\iiint_{\mathrm{D_1 + D_2}} \rho_i c_i \frac{\partial y}{\partial t} \mathrm{d}\tau = -\lambda_1 \iint_{\mathrm{S_1}} \left(\frac{\partial y}{\partial n_1} \right)_{\mathrm{S_1}} \mathrm{d}S \tag{16}$$

$$\iiint_{\mathrm{D_2}} \rho_2 c_2 \frac{\partial y}{\partial \tau} \mathrm{d}\tau = \lambda_1 \iint_{\mathrm{S_2}} \left(\frac{\partial y}{\partial n_2} \right)_{\mathrm{S_2}} \mathrm{d}S \tag{17}$$

and

$$t \leq 0 \qquad y(\boldsymbol{r}, t) = -x(\boldsymbol{r}) \tag{18}$$

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

$$z(\boldsymbol{r}, t) = 0 \qquad \boldsymbol{r} \in \mathrm{D_B} \cup \mathrm{S_1} \tag{19}$$

$$\kappa_1 \nabla^2 z = \partial z / \partial t \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{20}$$

$$v(t) + \iiint_{\mathrm{D_1 + D_2}} \rho_i c_i \frac{\partial z}{\partial t} \mathrm{d}\tau = -\lambda_1 \iint_{\mathrm{S_1}} \left(\frac{\partial z}{\partial n_1} \right)_{\mathrm{S_1}} \mathrm{d}S + p(t) \tag{21}$$

$$v(t) + \iiint_{\mathrm{D_2}} \rho_2 c_2 \frac{\partial z}{\partial t} \mathrm{d}\tau = \lambda_1 \iint_{\mathrm{S_2}} \left(\frac{\partial z}{\partial n_2} \right)_{\mathrm{S_2}} \mathrm{d}S + p(t) \tag{22}$$

and

$$t \leq 0 \qquad v(t) = p(t) = z(\boldsymbol{r}, t) = 0 \tag{23}$$

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

The following properties of $x(\boldsymbol{r})$ and $y(\boldsymbol{r}, t)$ are derived from previous boundary-initial conditions (10)–(18).

Application of Green's theorem in symmetrical form [3] to $\mathrm{D_1}$ enclosed by surfaces $\mathrm{S_1}$ and $\mathrm{S_2}$ gives

$$\iiint_{\mathrm{D_1}} (\phi \nabla^2 x - x \nabla^2 \phi) \, \mathrm{d}\tau = \iint_{\mathrm{S_1 + S_2}} \left(-\phi \frac{\partial x}{\partial n_i} + x \frac{\partial \phi}{\partial n_i} \right) \mathrm{d}S, \tag{24}$$

where $\phi = \phi(\boldsymbol{r})$ is defined as

$$\nabla^2 \phi(\boldsymbol{r}) = 0 \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{25}$$

and

$$\phi(\boldsymbol{r}),\ \partial\phi/\partial n_i\text{: uniformly equal on surfaces } \mathrm{S}_i, \qquad i = 1, 2 \tag{26}$$

From eqns. (11) and (25), the left-hand side of eqn. (24) becomes

$$\iiint_{D_1} = \iiint_{D_1} \phi \nabla^2 x \, d\tau = \frac{\alpha}{\kappa_1} \iiint_{D_1} \phi \, d\tau \tag{27}$$

The right-hand side of eqn. (25) becomes

$$\iint_{S_1+S_2} = \iint_{S_1} + \iint_{S_2} \tag{28}$$

Considering eqns. (10), (12) and (13), we have

$$\begin{aligned}\iint_{S_1} &= \iint_{S_1} \left(-\phi \frac{\partial x}{\partial n_1} + x \frac{\partial \phi}{\partial n_1} \right) dS \\ &= -\phi_1 \iint_{S_1} \left(\frac{\partial x}{\partial n_1} \right)_{S_1} dS + \left(\frac{\partial \phi}{\partial n_1} \right)_{S_1} \iint_{S_1} x \, dS \\ &= -\phi_1 \iint_{S_1} \left(\frac{\partial x}{\partial n_1} \right) dS \\ &= \phi_1 [(C_1 + C_2)\alpha - p_0]/\lambda_1 \end{aligned} \tag{29}$$

where ϕ_1 is the value of ϕ on S_1. Similarly, we have

$$\begin{aligned}\iint_{S_2} &= \iint_{S_2} \left(-\phi \frac{\partial x}{\partial n_2} + x \frac{\partial \phi}{\partial n_2} \right) dS \\ &= -\phi_2 \iint_{S_2} \left(\frac{\partial x}{\partial n_2} \right)_{S_2} dS + \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \iint_{S_2} x \, dS \end{aligned} \tag{30}$$

where ϕ_2 is the value of ϕ on S_2. Using eqn. (13), (30) becomes

$$\iint_{S_2} = -\phi_2 (C_2 \alpha - p_0)/\lambda_1 + A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \bar{x}_2 \tag{31}$$

where $\bar{x}_2$ is the surface average value of x over surface S_2 and is defined as follows

$$\bar{x}_2 = \frac{1}{A_2} \iint_{S_2} x(\boldsymbol{r}) \, dS \tag{32}$$

From eqns. (24), (27), (29) and (31), we have

$$\begin{aligned}\bar{x}_2 = \Bigg\{ &\left[\left(\frac{1}{V_1} \iiint_{D_1} \phi \, d\tau - \phi_1 \right) C_1 - (\phi_1 - \phi_2) C_2 \right] \alpha \\ &+ (\phi_1 - \phi_2) p_0 \Bigg\} \Big/ \lambda_1 A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \end{aligned} \tag{33}$$

where V_1 is the volume of D_1.

The boundary-initial conditions of $y(\boldsymbol{r}, t)$, eqns. (14)–(18), 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 that the temperature $y(\boldsymbol{r}, t)$ approaches zero as t increases

$$\lim_{t \to \infty} y(\boldsymbol{r}, t) = 0 \tag{34}$$

The surface average value of $y(\boldsymbol{r}, t)$ on S_2 is defined as

$$\bar{y}_2(t) = \frac{1}{A_2} \iint_{S_2} y(\boldsymbol{r}, t) \, \mathrm{d}S \tag{35}$$

and the behavior of (35) is

$$\lim_{t \to \infty} \bar{y}_2(t) = 0 \tag{36}$$

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

When a finite extension of a reaction takes place, and

$$p(t) = 0$$

and

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

we assume finite values

$$J(\boldsymbol{r}) = \int_0^{\infty} z(\boldsymbol{r}, t) \, \mathrm{d}t \tag{38}$$

and

$$\Delta H_{\xi} = \int_0^{\infty} v(t) \, \mathrm{d}t \tag{39}$$

where ΔH_{ξ} is the enthalpy change due to a chemical or physical change in D_2. Integrating eqns. (19)–(22) with respect to t from 0 to ∞, we get the following $J(\boldsymbol{r})$ boundary conditions

$$J(\boldsymbol{r}) = 0 \qquad \boldsymbol{r} \in D_B \cup S_1 \tag{40}$$

$$\kappa_1 \nabla^2 J(\boldsymbol{r}) = 0 \qquad \boldsymbol{r} \in D_1 \tag{41}$$

$$\Delta H_{\xi} = -\lambda_1 \iint_{S_1} \left(\frac{\partial J}{\partial n_1} \right)_{S_1} \mathrm{d}S \tag{42}$$

$$\Delta H_{\xi} = \lambda_1 \iint_{S_2} \left(\frac{\partial J}{\partial n_2} \right)_{S_2} \mathrm{d}S \tag{43}$$

Applying Green's theorem [3] to D_1 enclosed by S_1 and S_2, we have

$$\iiint_{D_1} (\phi \nabla^2 J - J \nabla^2 \phi)\, d\tau = \iint_{S_1+S_2} \left(-\phi \frac{\partial J}{\partial n} + J \frac{\partial \phi}{\partial n} \right) dS \tag{44}$$

where ϕ is defined as before. From eqns. (25) and (41), the left-hand side of eqn. (44) becomes

$$\iiint_{D_1} = 0 \tag{45}$$

The right-hand side of eqn. (44) becomes

$$\iint_{S_1+S_2} = \iint_{S_1} + \iint_{S_2} \tag{46}$$

From eqns. (40) and (42), we have

$$\begin{aligned} \iint_{S_1} &= \iint_{S_1} \left(-\phi \frac{\partial J}{\partial n} + J \frac{\partial \phi}{\partial n} \right) dS = -\phi_1 \iint_{S_1} \left(\frac{\partial J}{\partial n_1} \right)_{S_1} dS \\ &= \phi_1 \Delta H_\xi / \lambda_1 \end{aligned} \tag{47}$$

We have also

$$\begin{aligned} \iint_{S_2} &= \iint_{S_2} \left(-\phi \frac{\partial J}{\partial n} + J \frac{\partial \phi}{\partial n} \right) dS \\ &= -\phi_2 \iint_{S_2} \left(\frac{\partial J}{\partial n_2} \right)_{S_2} dS + \left(\frac{\partial \phi}{\partial n_2} \right)_{S2} \iint_{S_2} J\, dS \end{aligned} \tag{48}$$

Here we notice that

$$\begin{aligned} \iint_{S_2} J\, dS &= \iint_{S_2} \left[\int_0^\infty z(\boldsymbol{r}, t)\, dt \right] dS = \int_0^\infty \left[\iint_{S_2} z(\boldsymbol{r}, t)\, dS \right] dt \\ &= A_2 \int_0^\infty \left[\frac{1}{A_2} \iint_{S_2} z(\boldsymbol{r}, t)\, dS \right] dt = A_2 \int_0^\infty \bar{z}(t)\, dt \end{aligned} \tag{49}$$

where we define the surface average of z over S_2 as

$$\bar{z}_2(t) = \frac{1}{A_2} \iint_{S_2} z(\boldsymbol{r}, t)\, dS \tag{50}$$

From eqns. (43) and (49), eqn. (48) becomes

$$\iint_{S_2} = -\phi_2 \Delta H_\xi / \lambda_1 + A_2 \left(\frac{\partial \phi}{\partial n_2} \right)_{S_2} \int_0^\infty \bar{z}_2(t)\, dt \tag{51}$$

From eqns. (44)–(51), we get

$$\int_0^{\infty} \bar{z}_2(t)\,\mathrm{d}t = -\frac{(\phi_1 - \phi_2)}{\lambda_1 A_2 \left(\dfrac{\partial \phi}{\partial n_2}\right)_{S_2}} \Delta H_{\xi} \tag{52}$$

When $v(t) = 0$ and $p(t) = p_c$, we set $z(\boldsymbol{r}, t) = f(\boldsymbol{r}, t)$ and assume a convergence value.

$$\lim_{t \to \infty} f(\boldsymbol{r}, t) = f(\boldsymbol{r}, \infty). \tag{53}$$

Boundary conditions of $f(\boldsymbol{r}, \infty)$ are derived from eqns. (19)–(22)

$$f(\boldsymbol{r}, \infty) = 0, \quad \boldsymbol{r} \in \mathrm{D_B} \cup \mathrm{S_1} \tag{54}$$

$$\kappa_1 \nabla^2 f(\boldsymbol{r}, \infty) = 0, \quad \boldsymbol{r} \in D_1 \tag{55}$$

$$0 = -\lambda_1 \iint_{S_1} \left\{ \frac{\partial f(\boldsymbol{r}, \infty)}{\partial n_1} \right\}_{S_1} \mathrm{d}S + p_c \tag{56}$$

$$0 = \lambda_1 \iint_{S_2} \left\{ \frac{\partial f(\boldsymbol{r}, \infty)}{\partial n_2} \right\}_{S_2} \mathrm{d}S + p_c \tag{57}$$

Applying Green's theorem to $\mathrm{D_1}$ enclosed by $\mathrm{S_1}$ and $\mathrm{S_2}$, and considering eqns. (54)–(57), we have

$$\begin{aligned} 0 &= \iint_{S_1 + S_2} \left\{ -\phi \frac{\partial f(\boldsymbol{r}, \infty)}{\partial n} + f(\boldsymbol{r}, \infty) \frac{\partial \phi}{\partial n} \right\} \mathrm{d}S \\ &= -\frac{\phi_1 p_c}{\lambda_1} + \frac{\phi_2 p_c}{\lambda_1} + A_2 \left(\frac{\partial \phi}{\partial n_2} \right) \bar{f}_2(\infty) \end{aligned} \tag{58}$$

where we define

$$\bar{f}_2(\infty) = \frac{1}{A_2} \iint_{S_2} f(\boldsymbol{r}, \infty)\,\mathrm{d}S \tag{59}$$

Rearrangement of eqn. (58) gives

$$\frac{\bar{f}_2(\infty)}{p_c} = -\frac{(\phi_1 - \phi_2)}{\lambda_1 A_2 \left(\dfrac{\partial \phi}{\partial n_2} \right)_{S_2}} \tag{60}$$

From eqns. (52) and (60), we get

$$\int_0^{\infty} \bar{z}_2(t)\,\mathrm{d}t = \frac{\bar{f}_2(\infty)}{p_c} \Delta H_{\xi} \tag{61}$$

INFORMATION FROM THE SURFACE AVERAGE TEMPERATURE

We define the surface average temperature $\bar{T}_2(t)$ over the outside surface of the reaction domain as

$$\bar{T}_2(t) = \frac{1}{A_2} \int\int_{S_2} T(r, t)\, \mathrm{d}S \tag{62}$$

Then, we have from eqn. (9)

$$\bar{T}_2(t) = T_B + \bar{x}_2 + \bar{y}_2(t) + \bar{z}_2(t) \tag{63}$$

The graphical behavior of $\bar{T}_2(t) - T_B$ as a function of t presents a thermogram of the reaction domain in scanning mode. $\bar{T}_2(t) - T_B$ is composed of three parts $\bar{x}_2$, $\bar{y}_2(t)$ and $\bar{z}_2(t)$. Time-independent part $\bar{x}_2$ is the baseline displacement from the zero line on a $\bar{T}_2(t) - T_B$ vs. t curve. Equation (33) shows that $\bar{x}_2$ is linear with the rate of scanning α and the heat capacity of the reaction domain C_2. Thus, measurement of $\bar{x}_2$ gives an estimate of the heat capacity of the reaction domain. Expression (33) also shows that the ratio of heat capacity C_1 and thermal conductivity λ_1 of the heat conducting domain can be estimated by the measurement. The term $\bar{y}_2(t)$ is the transient part which is observed at the beginning of scanning and approaches zero with the passage of time. Term $\bar{z}_2(t)$ is a part due to thermal reaction. The graphical behavior of $\bar{T}_2(t)$ and of $\bar{T}_2(t) - T_B$ is similar to that shown in the previous part (see figs. 2 and 3 in ref. 1). The thermogram shows a peak when a thermal reaction takes place in the reaction domain.

When the temperature distribution over the outside surface of the reaction domain is uniform, Boersma showed that the peak area, time integral of the peak, is proportional to the enthalpy change due to thermal reaction [4]. When the temperature distribution is non-uniform, surface average temperature (eqn. (62)) should be measured and recorded. Equations (52) and (61) show that the peak area is also proportional to the enthalpy change due to thermal reaction. The proportionality constant is given by eqn. (60). Thus, we can obtain the enthalpy change under investigation from a measurement of the surface average temperature in the case of non-uniform distribution of temperature in the reaction domain.

ACKNOWLEDGMENT

The author expresses his gratitude to Dr. I. Takeda of this laboratory for his valuable comments and advice.

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