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Theory of a heat conduction calorimeter for scanning. Part 3. Stepwise change in the temperature of the surrounding thermal bath

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Abstract

When the temperature of the surrounding thermal bath of a heat conduction calorimeter is changed in a stepwise manner and the temperature distribution in the sample domain is not uniform, equations have been derived which are used for evaluation of the thermal properties of separate domains of the calorimeter. The surface average temperature over the outside surface of the sample domain is defined, and measurement of the surface average temperature as a function of time gives thermal properties such as enthalpy difference, heat capacity and thermal conductivity with use of the equations derived here. The validity of the equations does not depend on the method of stepwise change of the surrounding thermal bath temperature, but depends on the temperature difference before and after the stepwise change of the temperature.

INTRODUCTION

Instead of continuously changing the temperature of a sample or the surrounding thermal bath, a stepwise change in the temperature technique is used in DSC measurements. Staub and Perron applied the technique to purity determination by heat-flow DSC [1]. Flynn used the technique to determine the heat capacities, glass transition temperature and enthalpies of the transition between the two thermodynamic states of substances [2]. Mraw and Naas described the measurement of heat capacity of pyrite over the range 100–800 K by the technique [3].

Their method [1–3] for calculating the results obtained by the DSC technique is based on the assumptions that the temperature of a sample is uniform and that the heat exchange rate between the sample and the surroundings is proportional to the difference in temperature between them. In the usual DSC measurements, a sample amount in the order of milligrams is used, and their assumptions may be reasonable for such a small sample. However, in heat conduction calorimeter experiments, a

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sample of more than a milliliter is used and their assumptions should be replaced by those allowing for temperature distribution in the sample.

MODEL AND BOUNDARY-INITIAL VALUE PROBLEM

The model is similar to that shown in Part 1 of this series of papers (see Fig. 1 of ref. 4). It consists of three concentric domains: D_B, D_1 and D_2. Sample domain D_2 at the center is surrounded by heat conducting domain D_1, and D_1 is surrounded by a thermal bath D_B, of which the temperature T_B is changed to a predetermined extent in a stepwise manner with respect to the 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; $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are unit vectors on the surfaces S_1 and S_2 respectively, and they are directed toward the interior of D_1.

Assumptions similar to those in Part 2 of this series of papers [5] are introduced here as follows.

Thermal physical properties such as heat capacities C, specific heat capacities c, thermal conductivities λ, thermal diffusivities κ and densities ρ of the domains are assumed to be constant over the temperature range of the stepwise change in the temperature of the domains.

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

Uniformity of the temperature of the sample domain 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 the positional vector $\boldsymbol{r}$ at time t $(i = 1, 2)$.

Boundary-initial conditions of the model are as follows.

At D_B and S_1, we set

$$T_B = T_i + (T_f - T_i)a(t) \tag{1}$$

and

$$\begin{aligned} a(t) &= 0 && \text{for } t < t_i \\ &= \text{any function of } t && \text{for } t_i < t < t_f \\ &= 1 && \text{for } t > t_f \end{aligned} \tag{2}$$

At D_1 we have

$$\kappa_1 \nabla^2 T = \partial T/\partial t \tag{3}$$

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 [4] gives the rate of enthalpy change of D_2 as

$$\frac{dH_2}{dt} = \lambda_1 \iint_{S_2} \left(\frac{\partial T}{\partial n_2} \right)_{S_2} dS + p(t) \tag{4}$$

where $p(t)$ is the electrical power supplied to D_2 during the calibration period and is zero except during the calibration period. Similarly we have at D_1, D_2 and S_1

$$\frac{dH_1}{dt} + \frac{dH_2}{dt} = -\lambda_1 \iint_{S_1} \left(\frac{\partial T}{\partial n_1} \right)_{S_1} dS + p(t) \tag{5}$$

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

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

$$\begin{aligned} &T(\boldsymbol{r}, t) = T_B = T_i \\ &p(t) = 0 \\ &dH_1/dt = dH_2/dt = 0 \end{aligned} \tag{6}$$

When $t \gg t_f$, we set the approaching conditions as follows.

$$\begin{aligned} &T(\boldsymbol{r}, t) = T_B = T_f \\ &p(t) = 0 \\ &dH_1/dt = dH_2/dt = 0 \end{aligned} \tag{7}$$

PROPERTIES OF $\theta(r, t) = T(r, t) - T_B$

We set

$$\theta(\boldsymbol{r}, t) = T(\boldsymbol{r}, t) - T_B \tag{8}$$

Considering eqns. (1)–(7), we have boundary-initial conditions of $\theta(\boldsymbol{r}, t)$ as follows.

$$\theta(\boldsymbol{r}, t) = 0, \qquad \boldsymbol{r} \in D_B \cup S_1 \tag{9}$$

$$\kappa_1 \nabla^2 \theta = \frac{\partial \theta}{\partial t} + (T_f - T_i)\frac{da(t)}{dt}, \qquad \boldsymbol{r} \in D_1 \tag{10}$$

$$\frac{dH_2}{dt} = \lambda_1 \iint_{S_2} \left(\frac{\partial \theta}{\partial n_2} \right)_{S_2} dS + p(t) \tag{11}$$

$$\frac{dH_1}{dt} + \frac{dH_2}{dt} = -\lambda_1 \iint_{S_1} \left(\frac{\partial \theta}{\partial n_1} \right)_{S_1} dS + p(t) \tag{12}$$

When $t \leqq t_i$ and $t \gg t_f$, we have

$$\begin{aligned} &\theta(\boldsymbol{r}, t) = 0 \\ &p(t) = 0 \end{aligned} \tag{13}$$

We assume a finite value

$$J(\boldsymbol{r}) = \int_0^\infty \theta(\boldsymbol{r}, t)\, \mathrm{d}t \tag{14}$$

Integrating eqns. (9)–(12) with respect to t from 0 to ∞, we get the following boundary conditions of $J(\boldsymbol{r})$.

$$J(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in \mathrm{D_B} \cup \mathrm{S_1} \tag{15}$$

$$\kappa_1 \nabla^2 J(\boldsymbol{r}) = T_\mathrm{f} - T_\mathrm{i}, \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{16}$$

$$\Delta H_2 = \lambda_1 \iint_{\mathrm{S_2}} \frac{\partial J(\boldsymbol{r})}{\partial n_2}\, \mathrm{d}S, \qquad \boldsymbol{r} \in \mathrm{D_2} \cup \mathrm{S_2} \tag{17}$$

$$\Delta H_1 + \Delta H_2 = -\lambda_1 \iint_{\mathrm{S_2}} \frac{\partial J(\boldsymbol{r})}{\partial n_1}\, \mathrm{d}S, \qquad \boldsymbol{r} \in \mathrm{D_1} \cup \mathrm{D_2} \cup \mathrm{S_1} \tag{18}$$

Application of Green's theorem in symmetrical form [6] to $\mathrm{D_1}$ enclosed by surfaces $\mathrm{S_1}$ and $\mathrm{S_2}$ gives

$$\iiint_{\mathrm{D_1}} (\phi \nabla^2 J - J \nabla^2 \phi)\, \mathrm{d}\tau = \iint_{\mathrm{S_1+S_2}} \left(-\phi \frac{\partial J}{\partial n_i} + J \frac{\partial \phi}{\partial n_i} \right) \mathrm{d}S \tag{19}$$

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

$$\nabla^2 \phi(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in \mathrm{D_1} \tag{20}$$

$$\phi(\boldsymbol{r}),\ \partial\phi/\partial n_i\text{: uniformly equal on surface } \mathrm{S}_i, \qquad (i = 1, 2) \tag{21}$$

and $\mathrm{d}\tau$ is the volume element. For example, $\phi = 1/r$ for the spherical $\mathrm{D_B}$, $\mathrm{D_1}$, $\mathrm{D_2}$ model and $\phi = \ln r$ for the cylindrical model.

By (16) and (20), the left-hand side of eqn. (19) becomes

$$\iiint_{\mathrm{D_1}} = \iiint_{\mathrm{D_1}} \phi \nabla^2 J\, \mathrm{d}\tau = \frac{(T_\mathrm{f} - T_\mathrm{i})}{\kappa_1} \iiint_{\mathrm{D_1}} \phi\, \mathrm{d}\tau \tag{22}$$

The right-hand side of (19) becomes

$$\iint_{\mathrm{S_1+S_2}} = \iint_{\mathrm{S_1}} + \iint_{\mathrm{S_2}} \tag{23}$$

Considering eqns. (15), (18) and (21), we have

$$\begin{aligned} \iint_{\mathrm{S_1}} &= \iint_{\mathrm{S_1}} \left(-\phi \frac{\partial J}{\partial n_1} + J \frac{\partial \phi}{\partial n_1} \right) \mathrm{d}S \\ &= -\phi_1 \iint_{\mathrm{S_1}} \left(\frac{\partial J}{\partial n_1} \right)_{\mathrm{S_1}} \mathrm{d}S + \left(\frac{\partial \phi}{\partial n_1} \right)_{\mathrm{S_1}} \iint_{\mathrm{S_1}} J\, \mathrm{d}S \\ &= -\phi_1 \iint_{\mathrm{S_1}} \left(\frac{\partial J}{\partial n_1} \right) \mathrm{d}S \\ &= \frac{\phi_1}{\lambda_1} (\Delta H_1 + \Delta H_2) \end{aligned} \tag{24}$$

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

$$\iint_{S_2} = \iint_{S_2}\left(-\phi\frac{\partial J}{\partial n_2} + J\frac{\partial \phi}{\partial n_2}\right) dS$$
$$= -\phi_2\iint_{S_2}\left(\frac{\partial J}{\partial n_2}\right)_{S_2} dS + \left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}\iint_{S_2} J\, dS$$
$$= -\frac{\phi_2}{\lambda_1}\Delta H_2 + A_2\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}\int_0^{\infty}\bar{\theta}_2(t)\, dt \tag{25}$$

where ϕ_2 is the value of ϕ on S_2 and A_2 is the area of S_2; $\bar{\theta}_2(t)$ is the surface average value of $\theta(\boldsymbol{r}, t)$ over surface S_2 defined as follows.

$$\bar{\theta}_2(t) = \frac{1}{A_2}\iint_{S_2}\theta(\boldsymbol{r}, t)\, dS \tag{26}$$

Substituting eqns. (22)–(25) into (19), we get

$$\frac{(T_f - T_i)}{\kappa_1}\iiint_{D_1}\phi\, d\tau = \frac{1}{\lambda_1}[\phi_1 H_1 + (\phi_1 - \phi_2)\Delta H_2]$$
$$+ A_2\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}\int_0^{\infty}\bar{\theta}_2(t)\, dt \tag{27}$$

We assume no physical phase change or chemical reaction in D_1. Then, substituting

$$\Delta H_1 = (T_f - T_i)C_1 \tag{28}$$

into (27) and rearranging, we get

$$\int_0^{\infty}\bar{\theta}_2(t)\, dt = (T_f - T_i)k_1 + k_2\Delta H_2 \tag{29}$$

where

$$k_1 = \frac{C_1}{\lambda_1 A_2\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}}\left(\frac{1}{V_1}\iiint_{D_1}\phi\, d\tau - \phi_1\right) \tag{30}$$

where V_1 = volume of D_1 and

$$k_2 = \frac{(\phi_2 - \phi_1)}{\lambda_1 A_2\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}} \tag{31}$$

When no physical phase change or chemical reaction occurs in D_2

$$\Delta H_2 = (T_f - T_i)C_2 \tag{32}$$

Then eqn. (29) becomes

$$\frac{1}{(T_f - T_i)} \int_0^{\infty} \bar{\theta}_2(t)\, \mathrm{d}t = k_1 + k_2 C_2 \tag{33}$$

Constants k_1 and k_2 are determined by the geometry and thermal physical properties of D_1, and are independent of those of D_2.

TEMPERATURE CHANGE CAUSED BY CALIBRATING THE ELECTRICAL POWER

When the temperature of the surrounding thermal bath T_B is held constant and a finite extent of calibrating electrical power

$$\begin{aligned} p(t) &\neq 0, \qquad 0 < t_1 < t < t_2 \\ &= 0, \qquad t < t_1,\ t_2 < t \end{aligned} \tag{34}$$

is produced in D_2, a change in temperature in D_1 and D_2 is caused. Referring to previous boundary-initial conditions (9)–(13), we have the conditions of $\theta(\boldsymbol{r}, t) = T(\boldsymbol{r}, t) - T_B$ in the case of constant T_B as follows.

$$\theta(\boldsymbol{r}, t) = 0, \qquad \boldsymbol{r} \in D_B \cup S_1 \tag{35}$$

$$\kappa_1 \nabla^2 \theta = \partial\theta/\partial t, \qquad \boldsymbol{r} \in D_1 \tag{36}$$

$$\frac{\mathrm{d}H_2}{\mathrm{d}t} = \lambda_1 \iint_{S_2} \left(\frac{\partial\theta}{\partial n_2} \right)_{S_2} \mathrm{d}S + p(t) \tag{37}$$

$$\frac{\mathrm{d}H_1}{\mathrm{d}t} + \frac{\mathrm{d}H_2}{\mathrm{d}t} = -\lambda_1 \iint_{S_1} \left(\frac{\partial\theta}{\partial n_1} \right)_{S_1} \mathrm{d}S + p(t) \tag{38}$$

When $t < 0$, we set

$$\theta(\boldsymbol{r}, t) = 0, \qquad t < 0 \tag{39}$$

We assume a zero approaching value of $\theta(\boldsymbol{r}, t)$

$$\lim_{t \to \infty} \theta(\boldsymbol{r}, t) = 0 \tag{40}$$

We also assume a finite value (14) and

$$W_c = \int_0^{\infty} p(t)\, \mathrm{d}t \tag{41}$$

Integrating eqns. (35)–(38) with respect to t from 0 to ∞, we have

$$J(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in D_B \cup S_1 \tag{42}$$

$$\kappa_1 \nabla^2 J(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in D_1 \tag{43}$$

$$0=\lambda_1\iint_{S_2}\left(\frac{\partial J}{\partial n_2}\right)_{S_2}\mathrm{d}S+W_c \tag{44}$$

$$0=-\lambda_1\iint_{S_1}\left(\frac{\partial J}{\partial n_1}\right)_{S_1}\mathrm{d}S+W_c \tag{45}$$

Here we set

$$\Delta H_1=\int_0^{\infty}\frac{\mathrm{d}H_1}{\mathrm{d}t}\,\mathrm{d}t=0 \tag{46}$$

and

$$\Delta H_2=\int_0^{\infty}\frac{\mathrm{d}H_2}{\mathrm{d}t}\,\mathrm{d}t=0 \tag{47}$$

because we assume no changes in the physical and chemical properties of D_1 and D_2 before and after the input of electrical work.

Application of Green's theorem to D_1 enclosed by S_1 and S_2 gives the same form as that in eqn. (19), which is rearranged in this case as follows. From eqns. (20), (42) and (43), the left-hand side of (19) becomes

$$\iiint_{D_1}=0 \tag{48}$$

From eqns. (21), (42), (44) and (45), the right-hand side of (19) becomes

$$\begin{aligned}\iint_{S_1+S_2}&=\phi_1\iint_{S_1}\left(\frac{\partial J}{\partial n_1}\right)_{S_1}\mathrm{d}S+\phi_2\iint_{S_2}\left(\frac{\partial J}{\partial n_2}\right)_{S_2}\mathrm{d}S-\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}\iint_{S_2}J\,\mathrm{d}S\\&=-\frac{\phi_1}{\lambda_1}W_c+\frac{\phi_2}{\lambda_1}W_c-A_2\left(\frac{\partial \phi}{\partial n_2}\right)_{S_2}\int_0^{\infty}\bar{\theta}_2(t)\,\mathrm{d}t\end{aligned} \tag{49}$$

where $\bar{\theta}_2(t)$ is defined by eqn. (26).

From eqns. (19), (48) and (49), we get

$$\begin{aligned}\int_0^{\infty}\bar{\theta}_2(t)\,\mathrm{d}t&=\frac{(\phi_2-\phi_1)}{\lambda_1A_2\left(\dfrac{\partial \phi}{\partial n_2}\right)_{S_2}}W_c\\&=k_2W_c\end{aligned} \tag{50}$$

where k_2 is defined by eqn. (31).

EVALUATION OF THERMAL PROPERTIES

When the temperature of the surrounding thermal bath of a heat conduction calorimeter is changed in a stepwise manner, measurement of the surface average temperature over the outside surface of the sample as a function of time and the use of the equations previously derived give the thermal properties of domains D_1 and D_2.

Equation (29) gives the enthalpy difference ΔH_2 of D_2 between temperatures T_i and T_f, and (33) gives the heat capacity C_2 of D_2. The value of k_1 is determined by the measurement when D_2 is empty and the temperature T_B is changed in a stepwise manner; k_2 is determined by producing electrical work W_c of a known level of energy in D_2 and using eqn. (50). If k_2 is given by eqn. (31), the value of k_2 and the geometry of D_1 give the thermal conductivity λ_1 of D_1.

It is noteworthy that the validity of all the equations previously described does not depend on the mode of the stepwise temperature change of the surrounding thermal bath, $a(t)$.

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