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Verification of the Conduction Method in Calorimetry

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An ideal three-dimensional model of a conduction calorimeter is presented. In the model, the heat transfer takes place only by conduction. The proportionality relation between the quantity of heat and the area enclosed by the recorded temperature curve and the time axis is proved under several sets of ideal conditions under which the proportionality relation is valid are examined, and thermal compensation is recommended for more precise measurements of heat and for convenience in obtaining thermogenesis curves.

Calorimetric studies are now made of various systems under a wide range of conditions. The wide range of systems and conditions studied in calorimetry requires a large variety of specific calorimeters and techniques. One of these calorimeters is the conduction or heat-flow calorimeter, which has been used for a long time by many investigators. The technique which the calorimeter requires may be called the "conduction method"; it has also been widely not only for static but also for dynamic calorimeters. Some popular calorimeters of this type are the Tian-Calvet calorimeter,[1] the Benzinger-Kitzinger microcalorimeter,[2] the Amaya-Hagiwara calorimeter,[3] and Ozawa's quantitative differential thermal analyzer.[4] Of these calorimeters, Ozawa's is of the dynamic type.

In the conduction method, all or nearly all of the heat evolved or absorbed in the calorimeter container is conducted to or from the jacket through the space formed by the walls of the container and the jacket. The space between the walls of the container and the jacket is sometimes called the cavity[1] or the thermal barrier.[4] The measurement of the heat depends on the calculation of the heat exchange between the container and the jacket. This depends on a knowledge of the temperatures of the jacket and the container at all times during the measurement and on a knowledge of the rate of heat transfer as a function of these temperatures. The rate of the transfer of heat from the jacket to

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[1] E. Calvet and H. Prat, "Recent Progress in Microcalorimetry," ed. and translated by H. A. Skinner, Pergamon Press, London (1963).

[2] T. H. Benzinger and C. Kitzinger, "Microcalorimetry, New Methods and Objectives," in C. M. Herzfeld (ed.), "Temperature; Its Measurement and Control in Science and Industry," Vol. 3, Part 3, Reinhold, New York (1963).

[3] K. Amaya and S. Hagiwara, Preprint for the 1st Japanese Calorimetry Conference, Vol. 2 (1965), Osaka.

[4] T. Ozawa, This Bulletin, **38**, 1881 (1965).

the container, ϕ, is nearly always represented by Newton's cooling law:

$$\phi = p_c(\theta_c - \theta_j) = p\theta, \tag{1}$$

where θ_c = the temperature at a point on the outside surface of the container, θ_j = the temperature at a point on the inside surface of the jacket, $\theta = \theta_c - \theta_j$, and p = the leakage modulus of the system. If once Newton's law (1) is adopted as the expression for the rate of the heat transfer, it is easy to show that the total quantity of heat evolved or absorbed in the container, Q, is proportional to the area under the curve of the temperature difference, θ, and the time axis;[1-3)]

$$Q = p\int_0^\infty \theta \mathrm{d}t, \tag{2}$$

where t = time and p = the leakage modulus of the calorimeter, independent of the heat capacity of the calorimeter container.

In the dynamic experiment of DTA, the proportionality relation (2) also holds approximately; in this case, θ denotes the temperature difference between the sample and the thermally inert reference substance rather than the difference between the container and the jacket.[5)]

Although Newton's law (1) is widely used as an expression for the rate of heat transfer in a calorimeter, it is only an approximate one, since the value of the coefficient, p, depends on the temperature difference, θ, the nature of the fluids, and other factors.[6,7)] In particular, when the heat flow between the container and the jacket is conducted mainly by conduction in solids, as in the case of the Amaya-Hagiwara calorimeter and Ozawa's quantitative differential thermal analyzer, we must use Fourier's law for the conduction of heat rather than Newton's law.

Hattori *et al.*[8)] have presented a one-dimensional model of a conduction calorimeter, solved the boundary-value problem of the heat conduction in the model, and verified that the proportionality relation (2) is also valid in the case of heat flow conducted by conduction in solids. Ozawa[4)] also solved the boundary-value problem of a cyrindrical model of the differential thermal analyzer and also concluded that the proportionality relation holds in good approximation if some devices are used to decrease the temperature gradient in the sample cell. The present work to be descrived in this paper was undertaken to see if the proportionality relation hold in a three-dimensional model of a conduction calorimeter and to investigate the foundation of the conduction method in calorimetry.

An Idealized Three-dimensional Model of a Conduction Calorimeter

Figure 1 illustrates an idealized three-dimensional model of a conduction calorimeter composed of three solid domains, D_1, D_2, and D_3. The D_1 domain, in which heat is evolved or absorbed, is surrounded by the D_2 domain. The D_2 domain is surrounded by the D_3 domain, the temperature of which is kept constant. The three domains, D_1, D_2, and D_3 correspond, respectively, to the calorimeter container, the space of the solid thermal conductor between the surfaces of the container and the jacket, and the jacket.

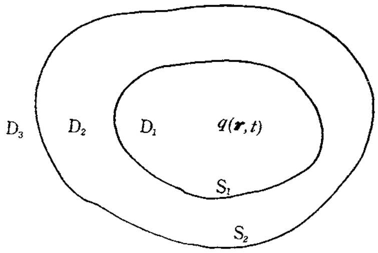

Fig. 1. Three-dimensional model of conduction calorimeter.

The boundary value problem may then, in this case, be written as follows:

1. the D_1 domain:

$$c_1\rho_1\frac{\partial\theta_1}{\partial t} = \lambda_1\Delta\theta_1 + q \tag{3}$$

2. the D_2 domain:

$$c_2\rho_2\frac{\partial\theta_2}{\partial t} = \lambda_2\Delta\theta_2 \tag{4}$$

3. the D_3 domain:

$$\theta_3 = 0 \tag{5}$$

4. the S_1 boundary surface:

$$\theta_1 = \theta_2 \tag{6}$$

$$\lambda_1\frac{\partial\theta_1}{\partial n_1} = \lambda_2\frac{\partial\theta_2}{\partial n_1} \tag{7}$$

5. the S_2 boundary surface:

$$\theta_2 = \theta_3 = 0 \tag{8}$$

6. the initial conditions:

$$\theta_1 = \theta_2 = \theta_3 = 0 \qquad t \leqq 0,\ t = \infty \tag{9}$$

$$q(\boldsymbol{r}, t) = 0 \qquad t \leqq 0,\ t > t_0 \tag{10}$$

$$q(\boldsymbol{r}, t) \neq 0 \qquad 0 < t < t_0, \tag{11}$$

where:

[5)] W. W. Wendlandt, "Thermal Methods of Analysis," Interscience Publishers, New York (1964), p. 136.

[6)] U. Grigull, "Die Grundgesetze der Wärmeübertragung," Springer-Verlag, Berlin (1961), §8.5.1.

[7)] H. A. Skinner, "Experimental Thermochemistry," Vol. 2, Interscience Publishers, New York, (1962), p. 159.

[8)] M. Hattori, S. Tanaka and K. Amaya, This Bulletin, **43**, 1027 (1970).

θ = temperature measured from the temperature of D_3,
t = time,
r = coordinate vector,
q = the heat evolved or absorbed per unit of time and unit of volume in D_1.
c = the specific heat capacity,
ρ = the density,
λ = the thermal conductivity,
$\partial/\partial n_1$ = differentiation in the direction of the out-ward normal to the surface,
Δ = the Laplacian,

The subscripts, 1, 2, and 3, denote the quantity in the D_1, D_2, and D_3 domains respectively.

Treatments of the Boundary-value Problem and the Proportionality Relation

Let the volume integral extended throughout D_1 apply to (3). Equation (3) then becomes:

$$c_1\rho_1\int_{D_1}\frac{\partial\theta_1}{\partial t}\mathrm{d}v=\lambda_1\int_{D_1}\Delta\theta_1\mathrm{d}v_1+\int_{D_1}q(r,t)\mathrm{d}v,$$

where it is assumed that the values of c, ρ, and λ are constant throughout the process of the thermal change. By Green's theorem,

$$\int_{D_1}\Delta\theta_1\mathrm{d}v=\int_{S_1}\frac{\partial\theta_1}{\partial n_1}\mathrm{d}s.$$

The quantity

$$w(t)=\int_{D_1}q(r,t)\mathrm{d}v$$

denotes the quantity of heat evolved or absorbed per unit of time in the D_1 domain. Therefore,

$$c_1\rho_1\int_{D_1}\frac{\partial\theta_1}{\partial t}\mathrm{d}v=\lambda_1\int_{S_1}\frac{\partial\theta_1}{\partial n_1}\mathrm{d}s+w(t). \tag{12}$$

The integration of (12) with respect to t from zero to infinity gives:

$$c_1\rho_1\int_0^\infty\int_{D_1}\frac{\partial\theta_1}{\partial t}\mathrm{d}v\mathrm{d}t=\lambda_1\int_0^\infty\int_{S_1}\frac{\partial\theta_1}{\partial n_1}\mathrm{d}s\mathrm{d}t+\int_0^\infty w(t)\mathrm{d}t.$$

When the order of integration can be interchanged, the left-hand side of the above equation becomes:

$$\begin{aligned}c_1\rho_1\int_0^\infty\int_{D_1}\frac{\partial\theta_1}{\partial t}\mathrm{d}v\mathrm{d}t&=c_1\rho_1\int_{D_1}\mathrm{d}v\int_0^\infty\frac{\partial\theta_1}{\partial t}\mathrm{d}t\\&=c_1\rho_1\int_{D_1}\{\theta_{1,t=\infty}-\theta_{1,t=0}\}\mathrm{d}v\\&=0,\end{aligned}$$

considering the initial condition (9). The quantity

$$Q=\int_0^\infty w(t)\mathrm{d}t=\int_0^\infty\int_{D_1}q(r,t)\mathrm{d}v\mathrm{d}t$$

is the total quantity of heat evolved or absorbed in D_1. Therefore, the integration of (12) becomes:

$$0=\lambda_1\int_0^\infty\int_{S_1}\frac{\partial\theta_1}{\partial n_1}\mathrm{d}s\mathrm{d}t+Q. \tag{13}$$

By applying the same calculation to (4) in D_2 we obtain:

$$\begin{aligned}0&=\lambda_2\int_0^\infty\int_{S_1+S_2}\frac{\partial\theta_2}{\partial n}\mathrm{d}S\mathrm{d}t\\&=-\lambda_2\int_0^\infty\int_{S_1}\frac{\partial\theta_2}{\partial n_1}\mathrm{d}S\mathrm{d}t+\lambda_2\int_0^\infty\int_{S_2}\frac{\partial\theta_2}{\partial n_2}\mathrm{d}S\mathrm{d}t.\end{aligned} \tag{14}$$

From (7), (13) and (14),

$$\begin{aligned}Q&=-\lambda_1\int_0^\infty\int_{S_1}\frac{\partial\theta_1}{\partial n_1}\mathrm{d}S\mathrm{d}t\\&=-\lambda_2\int_0^\infty\int_{S_1}\frac{\partial\theta_2}{\partial n_1}\mathrm{d}S\mathrm{d}t\\&=-\lambda_2\int_0^\infty\int_{S_2}\frac{\partial\theta_2}{\partial n_2}\mathrm{d}S\mathrm{d}t.\end{aligned} \tag{15}$$

The main purpose of calorimetry is to obtain the Q quantity; Equation (13) shows that the measurement of the $\partial\theta/\partial n$ quantity over the boundary surface enables us to obtain the Q quantity. However, it is not easy to measure the $\partial\theta/\partial n$ quantity.

On the other hand, from Green's formula the temperature at a point, P, inside D_2, $\theta_2(\mathrm{P})$, is given by:

$$4\pi\theta_2(\mathrm{P})=-\int_{D_2}\frac{\Delta\theta_2}{r}\mathrm{d}v+\int_{S_1+S_2}\left\{\frac{1}{r}\frac{\partial\theta_2}{\partial n}-\theta_2\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\right\}\mathrm{d}S, \tag{16}$$

where r is the distance from P to points on the boundary surfaces, S_1 and S_2. The integration of $\theta_2(\mathrm{P})$ with respect to t from zero to infinity then gives:

$$\begin{aligned}4\pi\int_0^\infty\theta_2(\mathrm{P})\mathrm{d}t=&-\int_0^\infty\int_{D_2}\frac{1}{r}\Delta\theta_2\mathrm{d}v\mathrm{d}t\\&+\int_0^\infty\int_{S_1+S_2}\left\{\frac{1}{r}\frac{\partial\theta_2}{\partial n}-\theta_2\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\right\}\mathrm{d}S\mathrm{d}t.\end{aligned} \tag{17}$$

The first term on the right-hand side of Eq. (17) becomes zero, because, from (4) and (9);

$$\begin{aligned}\int_0^\infty\int_{D_2}\frac{1}{r}\Delta\theta_2\mathrm{d}v\mathrm{d}t&=\int_{D_2}\frac{\mathrm{d}v}{r}\int_0^\infty\Delta\theta_2\mathrm{d}t\\&=\int_{D_3}\frac{\mathrm{d}v}{r}\int_0^\infty\frac{c_2\rho_2}{\lambda_2}\frac{\partial\theta_2}{\partial t}\mathrm{d}t\\&=\frac{c_2\rho_2}{\lambda_2}\int_{D_2}\frac{\mathrm{d}v}{r}\{\theta_{2,t=\infty}-\theta_{2,t=0}\}\\&=0.\end{aligned}$$

Therefore, (17) becomes:

$$\begin{aligned}4\pi\int_0^\infty\theta_2(\mathrm{P})\mathrm{d}t&=\int_0^\infty\int_{S_1+S_2}\left\{\frac{1}{r}\frac{\partial\theta_2}{\partial n}-\theta_2\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\right\}\mathrm{d}S\mathrm{d}t\\&=\int_0^\infty\int_{S_1}\left\{\frac{1}{r}\frac{\partial\theta_2}{\partial n}-\theta_2\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\right\}\mathrm{d}S\mathrm{d}t\\&\quad+\int_0^\infty\int_{S_2}\left\{\frac{1}{r}\frac{\partial\theta_2}{\partial n}-\theta_2\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\right\}\mathrm{d}S\mathrm{d}t\\&=\int_0^\infty\int_{S_1}\left\{-\frac{1}{r}\frac{\partial\theta_2}{\partial n_1}+\theta_2\frac{\partial}{\partial n_1}\left(\frac{1}{r}\right)\right\}\mathrm{d}S\mathrm{d}t\\&\quad+\int_0^\infty\int_{S_2}\frac{1}{r}\frac{\partial\theta_2}{\partial n_2}\mathrm{d}S\mathrm{d}t,\end{aligned} \tag{18}$$

considering $\theta_2=0$ on the S_2 surface, as (8) shows.

Now, if we assume that:

(1) $\partial\theta_2/\partial n_1$ and θ_2 are equal everywhere over the S_1 boundary surface and are functions of the time, t, only, and that

(2) $\partial\theta_2/\partial n_2$ is equal everywhere over the S_2 boundary surface and is a function of t, (19)

Equation (15) becomes:

$$\begin{aligned} Q &= -\lambda_1 S_1\int_0^\infty \frac{\partial\theta_1}{\partial n_1}\mathrm{d}t \\ &= -\lambda_2 S_1\int_0^\infty \frac{\partial\theta_2}{\partial n_1}\mathrm{d}t \\ &= -\lambda_2 S_2\int_0^\infty \frac{\partial\theta_2}{\partial n_2}\mathrm{d}t, \end{aligned} \tag{20}$$

where S_1 and S_2 are the areas of the S_1 and S_2 surfaces respectively. Also (18) becomes, considering (20):

$$\begin{aligned} 4\pi\int_0^\infty \theta_2(\mathrm{P})\mathrm{d}t &= -\int_{S_1}\frac{\mathrm{d}S}{r}\int_0^\infty \frac{\partial\theta_2}{\partial n_1}\mathrm{d}t - \int_{S_1}\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S\int_0^\infty \theta_2\mathrm{d}t \\ &\quad + \int_{S_2}\frac{\mathrm{d}S}{r}\int_0^\infty \frac{\partial\theta_2}{\partial n_1}\mathrm{d}t \\ &= \frac{Q}{\lambda_2 S_1}\int_{S_1}\frac{\mathrm{d}S}{r} - \int_{S_1}\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S\int_0^\infty \theta_2\mathrm{d}t \\ &\quad - \frac{Q}{\lambda_2 S_2}\int_{S_1}\frac{\mathrm{d}S}{r} \\ &= \frac{Q}{\lambda_2}\left\{\frac{1}{S_1}\int_{S_1}\frac{\mathrm{d}S}{r} - \frac{1}{S_2}\int_{S_2}\frac{\mathrm{d}S}{r}\right\} \\ &\quad - \int_{S_1}\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S\int_0^\infty \theta_2\mathrm{d}t, \end{aligned} \tag{21}$$

where the integrals, $\int_S \frac{\mathrm{d}s}{r}$ and $\int_S \frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S$, are not functions of t but are determined by the geometric shapes of the boundary surfaces. The boundary surfaces, which fulfill the assumptions (19), are symmetrical surfaces, for example, the surface of a sphere, a circular cylinder, or a plane.

If the P point is taken on the S_1 surface, $\theta_2(\mathrm{P})=\theta_2$, and if the S_1 and S_2 surfaces do not coincide, the rearrangement of (21) gives:

$$\begin{aligned} Q &= \frac{\lambda_2\left\{4\pi + \int_{S_1}\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S\right\}}{\frac{1}{S_1}\int_{S_1}\frac{\mathrm{d}S}{r} - \frac{1}{S_2}\int_{S_2}\frac{\mathrm{d}S}{r}}\int_0^\infty \theta_2\mathrm{d}t \\ &= p\int_0^\infty \theta_2\mathrm{d}t, \end{aligned} \tag{22}$$

where the coefficient:

$$p = \frac{\lambda_2\left\{4\pi + \int_{S_1}\frac{\partial}{\partial n}\left(\frac{1}{r}\right)\mathrm{d}S\right\}}{\frac{1}{S_1}\int_{S_1}\frac{\mathrm{d}S}{r} - \frac{1}{S_2}\int_{S_2}\frac{\mathrm{d}S}{r}} \tag{22'}$$

is a constant determined only by the shape of the boundary surface of the calorimeter.

Conditions for the Reliability of the Proportionality Relation

Let us summarize the main conditions under which the proportionality relation (22) is valid and the conduction method in calorimetry is possible:

(1) The heat transfer in the calorimeter takes place by conduction.

(2) The boundary surfaces of the calorimeter should be symmetrical.

(3) The c, ρ, and λ values of the materials of which the calorimeter is constructed are constant throughout the process of the thermal change in the container.

In the case of an actual conduction calorimeter, none of these conditions are fulfilled. The heat is conducted not only by conduction but by convection and radiation. The surface of the calorimeter container and the inner surface of the jacket are not perfectly symmetrical. Moreover, the values of c, ρ, and λ sometimes change considerably during the process of a thermal change, *e. g.*, phase-change or chemical reactions.

Therefore, the proportionality relation fundamental in conduction calorimetry is only an approximate one in any actual experiment; this is thought to be one of the main causes of the accuracy being less than with an isothermal or adiabatic jacket calorimeter.

For precise heat measurement, it is necessary to compensate the heat of the process being studied.[9] Although it is difficult to achieve a precise thermal compensation, recent progress in servo mechanism and electronic devices favors a precise compensation. When the calorimeter is compensated, it then behaves essentially as an isothermal calorimeter. Since the heat compensated is equal to the rate of heat production or absorption, $w(t)$, it is not necessary to use Calvet's complex method[10] of transforming the recorded curve $\theta=\theta(t)$ into a thermogenesis curve $w=w(t)$.

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9) E. Calvet and H. Prat, "Recent Progress in Microcalorimetry," ed. and translated by H. A. Skinner, Pergamon Press, London (1963), p. 10.

10) E. Calvet, "Experimental Thermochemistry," Vol. 2, Interscience Publishers, New York, N. Y. (1962), p. 388.