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A One-dimensional Model of a Conduction Calorimeter*[1]

Masaru HATTORI

Department of Machine Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

and Satohiro TANAKA and Kazuo AMAYA

Government Chemical Industrial Research Institute, Tokyo, Shibuya-ku, Tokyo

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An idealized one-dimensional model of a conduction calorimeter, composed of a container in which thermal change occurs, a thermal bath, and a solid thermal conductor connecting the container with the thermal bath, is presented. The boundary-value problem of heat conduction in the model calorimeter is solved by the Laplace transformation method. A proportionality relation between the quantity of heat evolved in the calorimeter container and the area enclosed by the recorded temperature curve and the time axis is establised.

The quantity of heat given off in a reaction or process can be determined by various types of calorimeters.[1-3] One of these types consists of

*[1] Any communications concerning this work should be sent to Mr. Tanaka.

1) "Experimental Thermochemistry," Vol. 1, ed. by F. D. Rossini, Interscience Publishers, New York, N. Y. (1956).

conduction or heat-flow calorimeters which have already found successful application in measurements of the quantity of heat and in studies of thermokinetics.[4-14]

A calorimeter consists essentially of a container in which the thermal phenomena under investigation are carried out and studied. In general, this container is placed in a cavity the walls of which are kept at a constant temperature (a "constant temperature environment" calorimeter) or, alternatively, at a temperature which can be varied at will (an "adiabatic" calorimeter). Calvet and Prat refer to the walls of the calorimeter container as the "internal boundary," and to the walls of the surrounding cavity as the "external boundary.[7]"

In the conduction calorimeter, all or nearly all of the heat evolved or absorbed in the calorimeter container is conducted to or from the surrounding "external boundary," which is kept at a constant temperature. The measurement of the quantity of heat or the study of thermokinetics depends entirely on the calculation of the heat exchange. This, in turn, depends on a knowledge of the temperatures of the calorimeter container and the surrounding external boundary at all times during the measurement and on a knowledge of the rate of heat transfer as a function of these temperatures.

In the case of processes which cause only slow variations in the temperature of the container, the simplified theory of Tian is very useful.[4,5,7] In the theory of Tian, the rate of the heat transfer, ϕ, between the calorimeter container and the surrounding external boundary is assumed to be given by Newton's cooling law; thus:

$$\phi = p(\theta_i - \theta_e) = p\theta, \qquad (1)$$

where θ_i=container temperature, θ_e=external boundary temperature, $\theta=\theta_i-\theta_e$, and p=leakage modulus of the system. Let W be the calorific power developed in the container at time t. During the dt time, the quantity of heat given off is $W\mathrm{d}t$. This heat, $W\mathrm{d}t$, is in part lost from the container as a flow of heat, represented by $\phi\mathrm{d}t=p(\theta_i-\theta_e)\mathrm{d}t$; the remaining part of the $W\mathrm{d}t$ causes an increase, $\mathrm{d}\theta$, in the container temperature (assuming that the temperature, θ_e, is basically constant). If the thermal capacity of the container is μ, the container heating consumes power by $\mu\mathrm{d}\theta$. Hence, it follows that:

$$\begin{aligned} W\mathrm{d}t &= p(\theta_i-\theta_e)\mathrm{d}t + \mu\mathrm{d}\theta \\ &= p\theta\mathrm{d}t + \mu\mathrm{d}\theta \end{aligned} \qquad (2)$$

or that:

$$W = p\theta + \mu\frac{\mathrm{d}\theta}{\mathrm{d}t}\ , \qquad (3)$$

(the later is called "Tian's equation").

The finite quantity of heat, $Q=\int W(t)\mathrm{d}t$, produced in the time interval, [0,∞), is obtained from Eq. (2) by integration:

$$Q = \int_0^\infty W\mathrm{d}t = p\int_0^\infty \theta\mathrm{d}t + \mu(\theta_\infty - \theta_0), \qquad (4)$$

where $\theta=\theta_0$ at $t=0$ and $\theta=\theta_\infty$ at $t=\infty$. In an experiment, it is possible to make $\theta_0=\theta_\infty$. Therefore, a very simple relation

$$Q = p\int_0^\infty \theta dt = pA \qquad (5)$$

can be obtained. The integral, $\int_0^\infty \theta\mathrm{d}t$, is equal to the area, A, under the recorded curve and the time-axis over the interval [0,∞). The expression (5) relates the heat of the reaction of the sample to the area of the recorded curve through the use of the proportionality constant, p, which is independent of the heat capacity of the sample. This expression is perhaps one of the most simple, useful and, fundamental theorems in calorimetry by means of the conduction method.

The above expressions by Tian are, however, only approximate relationships. One of the inherent limitations of Tian's theory is the assumption that the rate of heat transfer between the container and the external boundary is given by Newton's cooling law (1). Newton's law of cooling has been proposed for the transfer of heat from the surface of a solid to a fluid flowing past; in fact, the expression is a rather approximate one, and the coefficient, p, in (1) depends not only on the fluid but on the temperature differences $(\theta_i-\theta_e)$.[15,16] This limitation is considered to be very important

2) "Experimental Thermochemistry," Vol. 2, ed. by H. A. Skinner, Interscience Publishers, New York, N. Y. (1962).
3) R. C. Wilhoit, *J. Chem. Educ.*, **44**, A571 (1967).
4) E. Calvet, "Experimental Thermochemistry," Vol. 1, Chap. 12, ed. by F. D. Rossini, Interscience Publishers, New York, N. Y. (1956).
5) E. Calvet, *ibid.*, Vol. 2, Chap. 17, ed. by H. A. Skinner, Interscience Publishers, New York, N. Y. (1962).
6) H. Prat, *ibid.*, Chap. 18.
7) E. Calvet and H. Prat, "Recent Progress in Microcalorimetry," ed. and translated by H. A. Skinner, Pergamon Press, London (1963).
8) K. Amaya and S. Hagiwara, Preprints for the 1st Japanese Calorimetry Conference, 2 (1965), Osaka.
9) K. Amaya, S. Hagiwara and S. Takagi, Preprint for the 2nd Japanese Calorimetry Conference, 1—8 (1966), Tokyo.
10) K. Amaya and S. Hagiwara, *ibid.*, 1—9 (1966).
11) K. Amaya, S. Hagiwara and M. Uetake, Preprint of the 3rd Japanese Calorimetry Conference, B210 (1967), Osaka.
12) K. Amaya, S. Hagiwara and J. Suzuki, Preprint of the 4th Japanese Calorimetry Conference, 14Ba5 (1968), Tokyo.
13) K. Amaya, *Kogyo Kagaku Zasshi*, **69**, 1571 (1966).
14) K. Amaya, *Bunseki Kiki*, **5**, No. 5, Sangyo Kaihatsu Co. (1967), p. 6.

15) W. H. McAdams, "Heat Transmission," McGraw-Hill, New York (1942), p. 3.
16) U. Grigull, "Die Grundgesetze der Warmeubertragung," Springer-Verlag, Berlin (1961), §8.5.1.

when the heat flow from or to the container is conducted by a solid thermal conductor and when the thermal process is rapid one. In actuality, nearly all of the heat flux is conducted away by the thermocouple wires (Tian-Calvet calorimeter)[4,7] or by the thermoelement (Amaya-Hagiwara calorimeter).[8-12]

Calvet has developed a theory of a more general form applicable to the study of a rapid process.[5,7] He has proposed the expression:

$$\theta = a_1\int_0^t W(u)e^{-\omega_1(t-u)}du + a_2\int_0^t W(u)e^{-\omega_2(t-u)}du + \cdots \tag{6}$$

for the temperature of the calorimeter container, θ, where $W(t)$ is the calorific power produced in the container as a function of the time t and where the heating time extends from $u=0$ to $u=t$. The coefficients, a_1, a_2, $\cdots$ and ω_1, ω_2, $\cdots$, are constants of the calorimeter for a given arrangement. However, the model on which his theory is based and the mechanism of the heat transfer are both obscure; therefore, the parameters, a_1, a_2, $\cdots$ and ω_1, ω_2, $\cdots$, must be determined from a calibration experiment and cannot be evaluated *a priori* before the construction of the calorimeter.

It is, then, necessary to develop a definite model of the calorimeter considering a distinct mechanism of heat transfer.

An Idealized One-dimensional Model of a Conduction Calorimeter

In the actual case of a conduction calorimeter, a heat flux from or to the container is conducted in part by conduction and in part by convection and radiation through the space formed by the internal and external boundaries of the calorimeter. To obtain a precise theory, it is necessary to consider all these processes. However, it is so difficult to take into account all the mechanism of the heat transfer and the complex shape of the boundaries of a calorimeter that the calculation must start from a simplified model. As a first step, an idealized one-dimensional model, in which heat transfer by only conduction is considered, can be adopted; it may be a fairly good approximation for a calorimeter in which a considerable amount of the heat flux is conducted by such solid thermal conductors, as thermocouple wires (Tian-Calvet's calorimeter) or a thermoelement (Amaya-Hagiwara's calorimeter).

Figure 1 illustrates a one-dimensional model

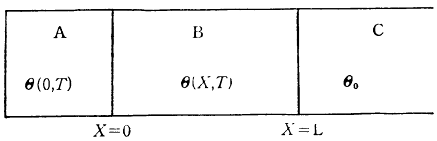

Fig. 1. A one-dimensional model of conduction calorimeter.

of a conduction calorimeter with a container, A, a solid thermal conductor, B, and a thermal bath, C, kept at a constant temperature. The following assumptions are adopted:

1) Calorific power, $W(T)$, is developed in the container at time T, and the temperature of the container is uniform. Let C_0 be the thermal capacity of the container.

2) The solid thermal conductor is a bar with its lateral surface insulated against the flow of heat; the area of its cross section is S, and its ends are $X=0$ and $X=L$. Let $\Theta(X,T)$ denote the temperature at any point in the thermal conductor, and K, the thermal diffusivity of the material.

3) The container is in perfect thermal contact with the $X=0$ side face of the thermal conductor. Heat transfer from or to the container takes place only through the $X=0$ side face of the conductor according to the basic postulate for the conduction of heat in solids, so the quantity of heat per unit of time transferred across the $X=0$ face is given by:

$$-\Lambda S\left(\frac{\delta\Theta}{\delta X}\right)_{X=0},$$

where Λ is the thermal conductivity of the conductor.

4) The thermal bath kept at a constant temperature,Θ_0, is in perfect thermal contact with the $X=L$ side face of the thermal conductor, so that:

$$\Theta_{X=L} = \Theta_0.$$

5) The initial temperature of the calorimeter, $\theta_{T=0}$, is Θ_0 throughout the container, the conductor, and the thermal bath.

6) The C_0, K, and Λ quantities are always constant while the thermal change in the container is taking place. The boundary-value problem for this calorimeter is then:

$$\frac{\partial\Theta}{\partial T} = K\frac{\partial^2\Theta}{\partial X^2} \qquad (0<X<L,\ T>0), \tag{7}$$

$$W(T) = C_0\left(\frac{\partial\Theta}{\partial T}\right)_{X=0} - \Lambda S\left(\frac{\partial\Theta}{\partial X}\right)_{X=0} \tag{8}$$

$$\Theta_{X=L}=\Theta_0, \tag{9}$$

$$\Theta = \Theta_0 \qquad (T\leqq 0). \tag{10}$$

It is convenient to introduce the following dimensionless reduced variables and quantities for the universal forms of the solution of the problem:

$$\left.\begin{aligned} x &= \frac{X}{L} \\ t &= \frac{K}{L^2}T \\ \theta(x,t) &= \frac{\Theta(X,T)-\Theta_0}{\Theta_0} \\ w(t) &= \frac{L^2}{KC_0\Theta_0}W(T) \\ h &= \frac{L\Lambda S}{KC_0}\ . \end{aligned}\right\} \tag{11}$$

The boundary-value preblem can, then, be written;

$$\frac{\partial\theta}{\partial t}=\frac{\partial^2\theta}{\partial x^2} \qquad (0<x<1,\ t>0) \tag{12}$$

$$w(t)=\left(\frac{\partial\theta}{\partial t}\right)_{x=0}-h\left(\frac{\partial\theta}{\partial x}\right)_{x=0} \tag{13}$$

$$\theta=0,\ x=1 \tag{14}$$

$$\theta=0,\ t=0. \tag{15}$$

Solution of the Boundary-value Problem by the Laplace Transformation Method[17,18]

Let $\bar{\theta}(x,s)$ be the Laplace transform of $\theta(x,t)$;

$$\bar{\theta}(x,s)=\int_0^\infty e^{-st}\theta(x,t)dt,\ \mathrm{Re}\{s\}>0.$$

If the Laplace transformation is applied to (12), the transformed equation is:

$$\int_0^\infty e^{-st}\frac{\partial\theta}{\partial t}dt=\int_0^\infty e^{-st}\frac{\partial^2\theta}{\partial x^2}dt. \tag{16}$$

This becomes, in view of the initial condition (15), and by a formal integration by parts:[19]

$$s\bar{\theta}(x,s)=\frac{d^2}{dx^2}\bar{\theta}(x,s). \tag{17}$$

The boundary conditions, (13) and (14), treated in the same way, give:

$$\bar{w}(s)=s\bar{\theta}(0,s)-h\frac{d}{dx}\bar{\theta}(0,s), \tag{18}$$

$$\bar{\theta}(1,s)=0, \tag{19}$$

where $\bar{w}(s)$ is the Laplace transform of $w(t)$.

A convenient form of the general solution of Equation (17) is:

$$\bar{\theta}(x,s)=Ae^{\sqrt{s}x}+Be^{-\sqrt{s}x}, \tag{20}$$

where A and B may be functions of s. When this equation is substituted into Eqs. (18) and (19), these equations become:

$$\bar{w}(s)=A(s-\sqrt{s})+B(s+\sqrt{s}), \tag{21}$$

$$Ae^{\sqrt{s}}+Be^{-\sqrt{s}}=0. \tag{22}$$

From (21) and (22), the values of A and B are found to be:

$$A=\bar{w}(s)\frac{e^{\sqrt{s}}}{(s-h\sqrt{s})e^{-\sqrt{s}}-(s+h\sqrt{s})e^{\sqrt{s}}}, \tag{23}$$

$$B=-\bar{w}(s)\frac{e^{\sqrt{s}}}{(s-h\sqrt{s})e^{-\sqrt{s}}-(s+h\sqrt{s})e^{\sqrt{s}}}. \tag{24}$$

When these values are substituted into (20), Eq. (20) can be written as:

$$\bar{\theta}(x,s)=\bar{w}(s)\frac{\sinh\sqrt{s}(1-x)}{\sqrt{s}(\sqrt{s}\sinh\sqrt{s}+h\cosh\sqrt{s})}$$
$$=\bar{w}(s)\bar{f}(s), \tag{25}$$

where:

$$\bar{f}(s)=\frac{\sinh\sqrt{s}(1-x)}{\sqrt{s}(\sqrt{s}\sinh\sqrt{s}+h\cosh\sqrt{s})}. \tag{26}$$

Now the inverse transform of the $\bar{\theta}(x,s)=\bar{w}(s)\bar{f}(s)$ gives $\theta(x,t)$ as the convolution[20] of the $w(t)$ and $f(t)$ functions:

$$\theta(x,t)=\int_0^t w(\tau)f(t-\tau)d\tau. \tag{27}$$

The $f(t)$ function is the inverse transform of $\bar{f}(s)$ and is given by the use of the Inverse Theorem for the Laplace transformation.[21]
This states that:

$$f(t)=\frac{1}{2\pi i}\lim_{\beta\to 0}\int_{\gamma-i\beta}^{\gamma+i\beta}e^{zt}\bar{f}(z)dz=\sum_{n=1}^{\infty}\rho_n(t), \tag{28}$$

where:

$\rho_n(t)=$ the residue of $e^{zt}\bar{f}(z)$ at $z=s_n$

and where:

$z=s_n=$ the singular point of $\bar{f}(z)$.

The singular points $\bar{f}(z)$are:

$$z=0 \tag{29}$$

and the roots of the equation are:

$$\sqrt{s}\sinh\sqrt{s}+h\cosh\sqrt{s}=0. \tag{30}$$

The roots of Eq. (30) are given by[22]:

$$s=-\alpha_n^2, \tag{31}$$

where α_n are the positive roots of the equation:

$$\alpha\sin\alpha-h\cos\alpha=0. \tag{32}$$

The residue for the singular point, $z=0$, is given by:

$$\lim_{s\to 0}s\bar{f}(x,s)e^{st}=0, \tag{33}$$

while the residues, ρ_n, for the singular points, $z=-\alpha_n$ are given by:[21]

$$\rho_n(t)=\lim_{s\to-\alpha_n^2}(s+\alpha_n^2)\bar{f}(x,s)e^{st}$$
$$=\left[\frac{\sinh\sqrt{s}(1-x)}{\frac{d}{ds}\sqrt{s}(\sqrt{s}\sinh\sqrt{s}+h\cosh\sqrt{s})}e^{st}\right]_{s=-\alpha_n^2}$$
$$=\frac{2\sin\alpha_n(1-x)}{(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}e^{-\alpha_n^2 t}. \tag{34}$$

Thus, from (27), (28), (33) and (34), the expression for $\theta(x,t)$ can be obtained as:

17) H. S. Carlslaw and J. C. Jager, "Conduction of Heat in Solids," 2nd Ed., Oxford (1959), Chap. XII.
18) R. V. Churchill, "Operational Mathematics," 2nd Ed., McGraw-Hill, New York, N. Y. (1958).
19) R. V. Churchill, *ibid.*, p. 112.
20) R. V. Churchill, *ibid.*, p. 37.
21) R. V. Churchill, *ibid.*, Chap. 6.
22) H. S. Carlslaw and J. C. Jager, *ibid.*, p. 119.

$$\theta(x,t)=\sum_{n=1}^{\infty}\frac{2\sin\alpha_n(1-x)}{(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}\int_0^t w(\tau)e^{-\alpha_n^2(t-\tau)}\,d\tau, \tag{35}$$

where α_n are the positive roots of the equation:

$$\alpha\sin\alpha-h\cos\alpha=0.$$

The final result (35) thus obtained is in a form similar to that of Calvet's general expression (6). The coefficients, a_n and ω_n, in Calvet's expression correspond to those in (35) as follows:

$$a_n\sim\frac{2\sin\alpha_n(1-x)}{(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}$$

$$\omega_n\sim\alpha_n^2.$$

The coefficients in (35) are physically clear and can be evaluated a priori from the materials and the dimensions of the calorimeter, while a_n and ω_n in Calvet's expression are experimental and physically obscure.

Let us now deduce a property of the series on the right hand of (35), which can be useful in proving the proportionality relation (5). When the quantity $w(t)$ is constant and equals w_0, the series (35) becomes:

$$\theta(x,t)=\sum_{n=1}^{\infty}\frac{2\sin\alpha_n(1-x)}{(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}\int_0^t w_0e^{-\alpha_n^2(t-\tau)}d\tau$$

$$=\sum_{n=1}^{\infty}\frac{2w_0\sin\alpha_n(1-x)}{\alpha_n^2(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}(1-e^{-\alpha_n^2t}).$$

The steady temperature, $\theta(x,\infty)$, is obtained as:

$$\theta(x,\infty)=\lim_{t\to\infty}\theta(x,t)$$

$$=\sum_{n=1}^{\infty}\frac{2w_0\sin\alpha_n(1-x)}{\alpha_n^2(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}. \tag{36}$$

On the other hand, the steady temperature, $\theta(x,\infty)$, can be easily obtained from the steady-state solution of the boundary-value problem, (12), (13), (14), and (15), as:

$$\theta(x,\infty)=w_0\frac{(1-x)}{h}. \tag{37}$$

From (36) and (37), the relation:

$$\sum_{n=1}^{\infty}\frac{2\sin\alpha_n(1-x)}{\alpha_n^2(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}=\frac{1-x}{h} \tag{38}$$

is obtained.

Proof of Proportionality Relation between the Quantity of Heat and the Integral, $\int_0^\infty\theta dt$

When the rate of heat transfer between the calorimeter container and the thermal bath is given by Newton's cooling law (1), it has easily been shown that the proportionality relation (5) between the quantity of heat, Q, and the "area", $\int_0^\infty\theta dt$, holds. On the other hand, when the container is connected with the thermal bath by a solid thermal conductor, as has been discussed above, and when the rate of heat transfer given by Fourier's Eq. (12), we cannot expect a clear answer to the question of whether the proportionality relation (5) holds or not. However, it will be proved below that the relation is also valid in this case.

The area enclosed by the recorded curve and the time axis is:

$$\int_0^\infty\theta dt=\sum_{n=1}^{\infty}\frac{2\sin\alpha_n(1-x)}{(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}\int_0^\infty\int_0^t w(\tau)e^{-\alpha_n^2(t-\tau)}d\tau dt. \tag{39}$$

By a formal integration by parts, the integral part on the right hand of (39) becomes:

$$\int_0^\infty\int_0^t w(\tau)e^{-\alpha_n^2(t-\tau)}d\tau dt$$

$$=\frac{1}{\alpha_n^2}\left\{-\lim_{t\to\infty}e^{-\alpha_n^2t}\int_0^t w(\tau)e^{-\alpha_n^2\tau}d\tau+\int_0^\infty w(t)dt\right\}. \tag{40}$$

Now, it can be shown that the first term on the right-hand side of Eq. (40) becomes zero if the total quantity of heat, either evolved or absorbed in the container, has a limited value:

$$Q=\int_0^\infty w(t)dt. \tag{41}$$

A necessary and sufficient condition[23] for the convergence of $\int_0^\infty w(\tau)d\tau$ is that, corresponding to any one positive number, ε, another positive number T should exist so that:

$$\left|\int_T^t w(\tau)d\tau\right|<\varepsilon \tag{42}$$

wherever $t>T$. Therefore,

$$\left|e^{-\alpha_n^2t}\int_0^t w(\tau)e^{\alpha_n^2\tau}d\tau\right|$$

$$=\left|e^{-\alpha_n^2t}\left\{\int_0^T w(\tau)e^{\alpha_n^2\tau}d\tau+\int_T^t w(\tau)e^{\alpha_n^2\tau}d\tau\right\}\right|$$

$$\leqq\left|e^{-\alpha_n^2t}\int_0^T w(\tau)e^{\alpha_n^2\tau}d\tau\right|+\left|e^{-\alpha_n^2t}\int_T^t w(\tau)e^{\alpha_n^2\tau}d\tau\right| \tag{43}$$

The function $e^{\alpha^2_n\tau}$ is a positive increasing function and has an upper boundary., $e^{\alpha^2_nt}$, in the $[T,t]$ range:

$$e^{-\alpha_n^2t}\left|\int_T^t w(\tau)e^{\alpha_n^2\tau}d\tau\right|\leqq e^{-\alpha_n^2t}\left|\int_T^t w(\tau)e^{\alpha_n^2t}d\tau\right|$$

$$=e^{-\alpha_n^2t}\left|e^{\alpha_n^2t}\int_T^t w(\tau)d\tau\right|$$

$$=\left|\int_T^t w(\tau)d\tau\right|<\varepsilon.$$

23) E. T. Whittaker and G. N. Watson, "A Course of Modern Analysis," 4th Ed., Cambridge University Press (1965), p. 70.

Therefore, (43) becomes:

$$\left|e^{-\alpha_n^2 t}\int_0^t w(\tau)e^{\alpha_n^2\tau}d\tau\right| < e^{-\alpha_n^2 t}\left|\int_0^T w(\tau)e^{\alpha_n^2\tau}d\tau\right| + \varepsilon. \qquad (44)$$

As $t\to\infty$, (44) becomes:

$$\lim_{t\to\infty}\left|e^{-\alpha_n^2 t}\int_0^t w(\tau)e^{\alpha_n^2\tau}d\tau\right| < \varepsilon,$$

or, by the definition of the limit,

$$\lim_{t\to\infty} e^{-\alpha_n^2 t}\int_0^t w(\tau)e^{\alpha_n^2\tau}d\tau = 0. \qquad (45)$$

From (38), (39), (40), and (45), it can be shown that:

$$\int_0^\infty \theta(x,t)dt = \sum_{n=1} \frac{2\sin\alpha_n(1-x)}{\alpha_n^2(1+h+\frac{\alpha_n^2}{h})\sin\alpha_n}\int_0^\infty w(t)dt$$

$$= \frac{(1-x)}{h}\int_0^\infty w(t)dt$$

$$= \frac{(1-x)}{h}\, Q. \qquad (46)$$

This is what we desired to prove. It can thus be concluded that the simple method of evaluating the total quantity of heat generated in a thermal process by the simple proportionality relation (5) can well be used when using a conduction calorimeter in which the heat transfer between the container and the surrounding external boundary is effected by conduction.

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