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ANALYSIS OF HEAT-FLUX CALORIMETER SIGNALS

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ABSTRACT

General results on the operation of heat-flux calorimeters are obtained from a hereditary integral formulation of the calorimeter response. The behaviors of heat-flux calorimeters at long time intervals after a thermal event are examined using final value theorems of Laplace transforms. Experimental confirmation of the resulting predictions suggests an analytic procedure for desmearing or inverting calorimeter signals without the need for specific models or computer numerical techniques. Particular solutions are obtained for instantaneous heat and heat flow corresponding to an apparatus function of interest in the practice of heat-flux calorimetry.

INTRODUCTION

Heat-flux calorimeters are non-adiabatic, non-isothermal devices that are used to determine the total heat or rate of heating for a process. A time-dependent change in temperature or pressure in the calorimeter cell is typically measured, the area under which is found to be proportional to the total heat liberated or absorbed during the thermal event. However, at present there is no mathematical basis for this empirical observation, except in the case of the simplest type of heat-flux calorimeter, i.e. the Tian–Calvet type [1].

As well as obtaining the total heat of a process, it is normally desirable to invert or 'desmear' the temperature–time or pressure–time response curve in order to reconstruct the actual heat flow occurring at the sample during the process. In calorimetry, this desmearing operation is known as thermogenesis. The actual heat flow of the process in the cell, $\dot{Q}$, is often estimated by formulating a heat-transfer model for the calorimeter and solving the resulting differential equation relating the heat flow at the sample surface to

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the transient temperature or pressure response curve [2]. Desmearing of the response curve to reconstruct the true heating function is then performed analytically after the experiment, or electronically using analog computer circuitry to operate on the response signal in real time [3]. In the absence of a heat-transfer model for the calorimeter, it is thought that desmearing can only be accomplished through the use of numerical techniques involving Fourier transform or recursion methods (4).

In this paper some general analytical results obtainable from a hereditary integral formulation of heat-flux calorimeter operation [4,5] are briefly considered. In particular, we use final-value theorems for Laplace transforms to examine the behavior of heat-flux calorimeters at long times, i.e. as $t \to \infty$, following a thermal event such as a heat pulse or a step change in heating rate. Experimental confirmation of the results of these analyses suggests a general mathematical procedure for desmearing or inverting calorimeter signals without the need for specific models or computer numerical techniques.

BACKGROUND

The excellent review of the fundamentals and practice of heat-flux calorimetry by Hemminger and Hohne [4] should be consulted for details of apparatus construction and operation. Recommended mathematical references include any text on Laplace transforms, in particular Wylie and Barrett [6] or Thomson [7]. As calorimeter signals are typically slowly varying functions of time having a finite number of maxima and minima, they will normally satisfy the necessary conditions for the existence of a Laplace transform, i.e. they are piecewise continuous over the time interval [0, ∞] and of exponential order. The Laplace transform is defined

$$\bar{f}(s) \equiv \int_0^\infty f(t)\, e^{-st}\, dt \tag{1}$$

where $\bar{f}(s)$ denotes the Laplace transform of a time-dependent function $f(t)$ in terms of the transform variable, s. Differentiating both sides of eqn. (1) by s

$$\frac{d\bar{f}(s)}{ds} = -\int_0^\infty tf(t)\, e^{-st}\, dt \tag{2}$$

shows that the derivative of the transformed function, $d\bar{f}(s)/ds$ is the Laplace transform of $-tf(t)$. In addition

$$s\bar{f}(s) \equiv \int_0^\infty f'(t)\, e^{-st}\, dt \tag{3}$$

is the Laplace transform of the derivative, $f'(t) \equiv df(t)/dt$ for a time-dependent function where $f(0) = 0$.

It will also be necessary to introduce the convolution (or Faltung) integral, denoted $f(t) * g(t)$

$$f(t) * g(t) \equiv \int_0^t f(t-\xi) g(\xi) \, \mathrm{d}\xi = \int_0^t f(\xi) g(t-\xi) \, \mathrm{d}\xi \tag{4}$$

In eqn. (4), ξ is the time variable of integration and $(t-\xi)$ the elapsed time.

The Laplace transform of the convolution integral denoted, $\overline{f(t) * g(t)}$, can be expressed as the product of the two Laplace-transformed functions, $\bar{f}(s)$ and $\bar{g}(s)$, according to

$$\bar{f}(s)\bar{g}(s) = \int_0^\infty \mathrm{e}^{-st} \left[\int_0^t f(t-\xi) g(\xi) \, \mathrm{d}\xi \right] \mathrm{d}t = \overline{f(t) * g(t)} \tag{5}$$

The following final-value properties will also be useful in the analysis of calorimeter signals

$$\lim_{s \to 0} \bar{f}(s) = \int_0^\infty f(t) \left[\lim_{s \to 0} \mathrm{e}^{-st} \right] \mathrm{d}t = \int_0^\infty f(t) \, \mathrm{d}t \tag{6}$$

$$\lim_{s \to 0} s\bar{f}(s) = \lim_{t \to \infty} f(t) = f(\infty) \tag{7}$$

$$\lim_{s \to 0} \frac{\mathrm{d}}{\mathrm{d}s} \bar{f}(s) = -\lim_{s \to 0} \int_0^\infty t f(t) \, \mathrm{e}^{-st} \, \mathrm{d}t = -\int_0^\infty t f(t) \, \mathrm{d}t \tag{8}$$

GENERAL RESULTS

We are now in a position to obtain some general results for heat-flux calorimeters. It is assumed that the measured, time-varying calorimeter signal, $\theta(t)$, the actual heat flow in the calorimeter cell, $\dot{Q} = \mathrm{d}Q(t)/\mathrm{d}t$, and the 'apparatus function' or kernel function, $K(t)$, are related by the linear hereditary integral, or convolution integral [4,5]

$$\theta(t) = \int_0^t K(t-\xi) \frac{\partial Q}{\partial \xi} \, \mathrm{d}\xi \tag{9}$$

where the kernel function depends only on the apparatus and is not dependent on sample properties or on any particular thermal history.

We postulate that eqn. (9) is a sufficiently general governing equation to adequately represent all heat-flux calorimeters and proceed to demonstrate that, regardless of the form of the kernel function, the heat of a process is proportional to the total area under a calorimeter response curve. Taking the Laplace transform of eqn. (9)

$$\bar{\theta} = s\overline{Q}\overline{K} \tag{10}$$

where, as usual, superscripted bars denote the Laplace-transformed function

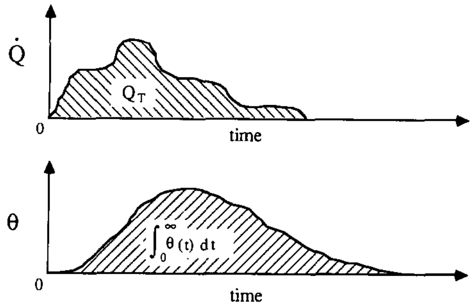

Fig. 1. Calorimeter response to arbitrary heat pulse.

and s is the transform variable, and applying the appropriate limit theorems (eqns. (6) and (7)) to eqn. (10)

$$\lim_{s\to 0} \bar{\theta}(s) = \left[\lim_{s\to 0} s\bar{Q}(s)\right]\left[\lim_{s\to 0} \bar{K}(s)\right] \tag{11}$$

the final result is

$$\int_0^{\infty} \theta(t)\ \mathrm{d}t = \frac{Q(\infty)}{C} \tag{12}$$

where $Q(\infty) = Q_{\mathrm{T}}$, is the total heat of the process, with

$$C = \left[\int_0^{\infty} K(t)\ \mathrm{d}t\right]^{-1} \tag{13}$$

the thermal capacitance of the calorimeter. Equation (12) states mathematically that for a heat-flux calorimeter obeying eqn. (9), the total area under the measured response curve, after the baseline is re-established following a thermal pulse, is proportional to the total heat of the process, regardless of the form of the kernel function. The shaded portions of Fig. 1 demonstrate the areal quantities required to determine the numerical value of the thermal capacitance C via a pulsed heating experiment for arbitrary $\dot{Q}(t)$ and $\theta(t)$ histories.

Alternatively, the value of the kernel-function integral at infinite time can be determined from the steady-state calorimeter response to a constant heating rate. For a system initially at rest. experiencing a heating history, $\mathrm{d}Q/\mathrm{d}t = \dot{Q}_{\mathrm{o}}u(t)$ where $\dot{Q}_{\mathrm{o}}$ is a constant heat flow and $u(t)$ is the unit step function

$$u(t) = \begin{pmatrix} 0 & t < 0 \\ 1 & t > 0 \end{pmatrix}$$

Equation (9) gives

$$\theta(t) = \dot{Q}_{\mathrm{o}} \int_0^{t} u(\xi) K(t-\xi)\ \mathrm{d}\xi \tag{14}$$

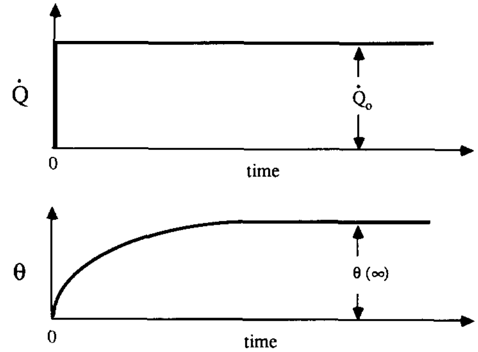

Fig. 2. Calorimeter response to constant heat flux.

The Laplace transform of eqn. (14) is

$$\bar{\theta} = \dot{Q}_o \frac{1}{s} \bar{K} \tag{15}$$

Applying the appropriate limit theorems to both sides of eqn. (15) as previously, the result is

$$\theta(\infty) = \frac{\dot{Q}_o}{C} \tag{16}$$

with C defined as in eqn. (13). Equation (16) shows that the steady-state calorimeter response at infinite time $\theta(\infty)$ is proportional to the constant heat-flow rate in the calorimeter cell. Figure 2 demonstrates a typical heat-flux calorimeter response to step-function, constant heating with the associated relevant quantities.

An average time constant or response time for the calorimeter $\bar{\tau}$ can be defined as the mathematical expectation (or mean value) of the continuous time variable if the apparatus or kernel function $K(t)$ is considered as a density function such that the usual definition of the mean applies

$$\bar{\tau} \equiv \frac{\int_0^\infty tK(t)\,\mathrm{d}t}{\int_0^\infty K(t)\,\mathrm{d}t} \tag{17}$$

General results for arbitrary kernel functions are obtained by differentiating the Laplace transform of eqn. (9) by s

$$\frac{\mathrm{d}\bar{\theta}}{\mathrm{d}s} = \bar{K}\frac{\mathrm{d}\bar{\dot{Q}}}{\mathrm{d}s} + \bar{\dot{Q}}\frac{\mathrm{d}\bar{K}}{\mathrm{d}s} \tag{18}$$

Using eqn. (2) and the final-value theorems, eqn. (18) becomes

$$\int_0^\infty t\theta(t)\,\mathrm{d}t = \int_0^\infty K(t)\,\mathrm{d}t \int_0^\infty t\dot{Q}(t)\,\mathrm{d}t + \int_0^\infty tK(t)\,\mathrm{d}t \int_0^\infty \dot{Q}(t)\,\mathrm{d}t \tag{19}$$

which, together with eqn. (12), allows the mean response time to be written as

$$\bar{\tau} = \frac{\int_0^\infty t\theta(t)\,\mathrm{d}t}{\int_0^\infty \theta(t)\,\mathrm{d}t} - \frac{\int_0^\infty t\dot{Q}(t)\,\mathrm{d}t}{\int_0^\infty \dot{Q}(t)\,\mathrm{d}t} \tag{20}$$

Expressions for higher moments of the response-time distribution can be obtained using the same limit theorems applied to successively higher derivatives of eqn. (8).

For a single square-wave heat pulse beginning at $t = 0$, having amplitude $\dot{Q}_o$ and duration t_o, the last term on the right-hand-side of eqn. (20) can be solved analytically by making the substitution $\dot{Q}(t) = \dot{Q}_o[u(t) - u(t - t_o)]$, with the result that

$$\bar{\tau} = \frac{\int_0^\infty t\theta(t)\,\mathrm{d}t}{\int_0^\infty \theta(t)\,\mathrm{d}t} - \frac{t_o}{2} \tag{21}$$

which is an expression for the mean time constant of a calorimeter having an arbitrary apparatus (or kernel) function in terms of integrals of the response curve and its time product.

A means for testing the validity of a linear hereditary integral formulation of heat-flux calorimeter operation is provided by the above results. According to eqns. (12) and (16), a calorimeter in which the response to heat flow is linear should yield the same value for the thermal capacitance, C, in both pulsed and constant rate heating experiments.

EXPERIMENTAL VERIFICATION

Experiments were performed at 25 °C using a new version of a heat-flux calorimeter originally designed to measure the heat of solid deformation [5]. The instrument senses heat flow between a deforming sample and the isothermal cell wall as a pressure change in the surrounding gas at constant (differential) volume. Heat generation within the cylindrical cell (25 cm long × 2.2 cm diameter) was accomplished using electrical heating of 5, 10, and 15 cm-long Stableohm 650 resistance wires (California Fine Wire) having a diameter of 0.320 mm and a resistivity of 13.517 Ω m^{-1}. A Keithley 220 Programmable Current Source provided a constant electrical current I from which the heat flow in the calorimeter cell is calculated as $\dot{Q}_o = I^2R$ from the measured wire resistance R.

Pulsed-heating calibration experiments were conducted using programmed square-wave current pulses of various duration t_o to produce heat

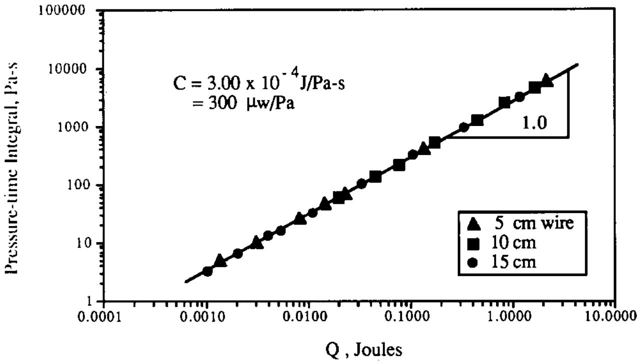

Fig. 3. Pressure–time integral versus total heat for pulsed heating experiments.

pulses $Q_T = \dot{Q}_o t_o$ ranging from 1 to 3200 mJ within the calorimeter cell. The gas-pressure signal output from the differential pressure transducer $\Delta P(t)$ was integrated electronically using a digital recorder over a time period sufficiently long to allow reestablishment of the baseline following the pulse, as indicated schematically in Fig. 1. The thermal capacitance C was calculated according to eqn. (12), with $\theta(t) = \Delta P(t)$ for this particular calorimeter, i.e.

$$C = \frac{Q_T}{\int_0^\infty \Delta P(t)\, dt} \tag{22}$$

Results of the pulsed-heating experiments are shown in Fig. 3 for the three lengths of resistance wire. An average thermal capacitance of $C = 300 \pm 11$ μw Pa^{-1} was calculated from all of the data. Linear behavior is demonstrated by the strict proportionality between the pressure–time integral and the total heat delivered during the pulse, as indicated by the unit log–log slope over the entire 3+ decade range covered in these experiments.

Experiments were also conducted in which the steady-state pressure $\Delta P(\infty)$ in the calorimeter cell was measured after equilibration at various constant heating rates $\dot{Q}_o$ ranging from 0.1 to 20 mw. Data for the steady-state pressure at constant heating rate for the three wire lengths are shown in Fig. 4. Again, strict proportionality implies linear response over three decades of heating rate. The thermal capacitance was found to be $C = 299 \pm 6$ μw Pa^{-1} by averaging the data over the range of heating rates investigated in these experiments, using eqn. (16) with the appropriate substitution, $\theta(t) = \Delta P(t)$

$$C = \frac{\dot{Q}_o}{\Delta P(\infty)} \tag{23}$$

The predicted agreement between thermal capacitance values obtained by pulsed heating and steady-state heating is confirmed in these experiments.

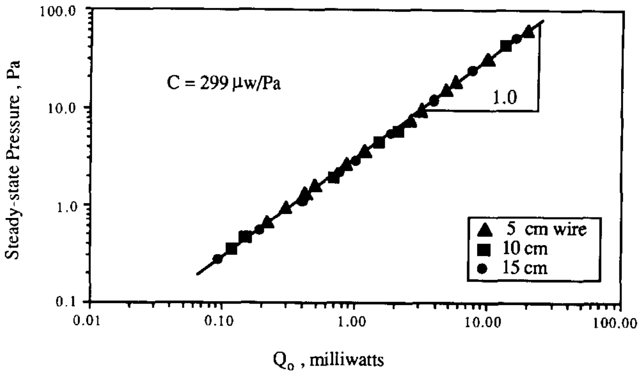

Fig. 4. Steady-state pressure versus heating rate for constant heat flux.

Moreover, eqn. (21) has been shown to yield mean response-time values in excellent agreement with those obtained by least-squares fitting of the response curve for step-function heating to a single exponential [8]. These results suggest that a linear hereditary integral provides a general representation of heat-flux calorimeters independent of any assumptions about the path by which heat is transferred into or out of the calorimetric cell. A mathematical framework for inverting or 'desmearing' heat-flux calorimeter signals, without reliance on specific models, is thus established.

THERMOGENESIS

It follows from the convolution theorem that it is possible to determine the response of a system to a general excitation if the response to a unit step function is known. Reconstruction of the actual heat flow in the calorimeter cell from the smeared response curve is therefore possible if the calorimeter response to a step-change in heat flow is measured. Typically, a transient temperature–time or pressure–time response to an instantaneously imposed constant heat-flow is obtained experimentally, as depicted in the θ–t curve in Fig. 2. The rising (or falling) transient is then fitted with as many exponentials, or functions of exponential order, as is necessary to obtain the desired level of accuracy. This constitutes an empirical evaluation of the kernel function. Based on experimental evidence it is found that a finite sum of exponentials will provide a sufficiently accurate description of the transient behavior, so that a useful kernel function is of the form

$$K(t) = \sum_{i=1}^{n} \frac{1}{c_i \tau_i} e^{-t/\tau_i} \tag{24}$$

where c_i and τ_i are the thermal capacitance and time constant of the ith transfer element, respectively. It then follows from eqn. (13) that

$$\frac{1}{C} = \int_0^\infty \sum_{i=1}^{n} \frac{1}{c_i \tau_i} \,\mathrm{e}^{-t/\tau_i}\,\mathrm{d}t = \sum_{i=1}^{n} \frac{1}{c_i} \tag{25}$$

A familiar result is obtained if it is found that the transient calorimeter-response can be described by a single exponential. In this case, $n = 1$ in eqn. (24) and the kernel function or apparatus function is simply

$$K(t) = \frac{1}{C\tau}\,\mathrm{e}^{-t/\tau} \tag{26}$$

Substituting eqn. (26) into eqn. (9)

$$\theta(t) = \int_0^t \frac{1}{C\tau}\,\mathrm{e}^{-(t-\xi)/\tau}\left(\frac{\partial Q}{\partial \xi}\right)\mathrm{d}\xi \tag{27}$$

and taking Laplace transforms

$$\bar{\theta} = \frac{1}{C\tau}\left[\frac{1}{s + 1/\tau}\right][s\bar{Q}] \tag{28}$$

or

$$\bar{\theta} = C\frac{\bar{\theta}}{s} + C\tau\bar{\theta} \tag{29}$$

which is inverse-transformed to give an equation for the instantaneous heat of the calorimetric process up to time t

$$Q(t) = C\int_0^t \theta(\xi)\,\mathrm{d}\xi + C\tau\theta(t) \tag{30}$$

Differentiation of eqn. (30) results in an expression for the instantaneous heat flow in the cell in terms of the measured $\theta(t)$

$$\dot{Q}(t) = C\theta(t) + C\tau\frac{\mathrm{d}\theta(t)}{\mathrm{d}t} \tag{31}$$

which is familiar as the Tian equation [1]. Consequently, we find that the Tian equation is simply a particular solution of the more general hereditary integral formulation.

If it has been determined that the Tian equation provides a sufficiently accurate means of desmearing the response curve, eqn. (21) can be used to obtain the average time constant of the apparatus for use in eqns. (30) and (31). It is easily shown that for a single exponential kernel function (eqn. (26)), eqn. (17) yields the expected result that $\tau = \bar{\tau}$.

CONCLUSIONS

A linear hereditary integral formulation of heat-flux calorimeter response provides a mathematical framework for obtaining general results on long-time behavior. Agreement between experimental data and predictions for pulsed and constant heating-rate thermal histories confirm the general validity of the convolution integral or linear hereditary integral approach to the analysis of heat-flux calorimeter signals.

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