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Note

Rate of change of reference temperature in DSC and DTA

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INTRODUCTION

In the analysis of DSC (or DTA) curves it is usually assumed, either implicitly or explicitly, that the rate of change of the reference temperature is equal to the programmed temperature rate[1,2]. This does not seem to be immediately obvious. The following is an attempt at a rigorous treatment of this question, and the analysis is applicable to both DSC and DTA.

MATHEMATICAL MODEL

Since at any instant of time energy must be conserved, we may write the law of conservation of energy for the inert reference cell, assuming that losses from the cell are negligible:

$$\left\{ \begin{matrix} \text{net rate of} \\ \text{thermal energy} \\ \text{to the reference} \end{matrix} \right\} = \left\{ \begin{matrix} \text{rate of} \\ \text{accumulation} \\ \text{of thermal energy} \end{matrix} \right\}, \tag{1}$$

or

$$\frac{dq_R}{dt} = C_R \frac{dT_R}{dt} \tag{2}$$

where C_R is the total heat capacity of reference and container, and T_R is the temperature of reference and container (assumed to be identical).
The rate of heat flow from the thermal energy source to the reference is controlled by the temperature difference and the thermal resistance between these two positions according to Newton's law

$$\frac{dq_R}{dt} = \frac{T_P - T_R}{R} \tag{3}$$

where T_P is the programmed temperature and R is the thermal resistance between thermal energy source and reference.

The time derivative of Eqn. (3), for constant R, is

$$\frac{d^2 q_R}{dt^2} = \frac{1}{R}\frac{dT_P}{dt} - \frac{1}{R}\frac{dT_R}{dt}. \tag{4}$$

Substituting dT_R/dt from Eqn. (2) into Eqn. (4) and rearranging

$$\frac{d^2 q_R}{dt^2} + \frac{1}{RC_R}\frac{dq_R}{dt} = \frac{1}{R}\frac{dT_P}{dt}. \tag{5}$$

Eqn. (5) is of the form (sometimes called Leibentz' equation)

$$\frac{dy}{dt} + Py = Q \tag{6}$$

where

$$\frac{dy}{dt} = \frac{d^2 q_R}{dt^2},\ y = \frac{dq_R}{dt},\ P = \frac{1}{RC_R},\ \text{and}\ Q = \frac{1}{R}\frac{dT_P}{dt}. \tag{7}$$

The solution to Eqn. (6) is given by

$$y = e^{-\int P dt}\int e^{\int P dt} Q dt + Ke^{-\int P dt}. \tag{8}$$

Substituting the terms of Eqn. (7) into Eqn. (8) and solving, with C_R, R, and dT_P/dt assumed to be constant

$$\frac{dq_R}{dt} = C_R\frac{dT_P}{dt} + Ke^{-t/RC_R}. \tag{9}$$

The integration constant, K, is found from the initial condition,

$$\text{I. C. at t} = 0,\ \frac{dq_R}{dt} = 0 \tag{10}$$

to be

$$K = -C_R\frac{dT_P}{dt}. \tag{11}$$

Substituting Eqn. (11) into Eqn. (9)

$$\frac{dq_R}{dt} = C_R\frac{dT_P}{dt}(1-e^{-t/RC_R}). \tag{12}$$

The heating rate of the reference is then found by combining Eqn. (2) and Eqn. (12)

$$\frac{dT_R}{dt} = \frac{dT_P}{dt}(1-e^{-t/RC_R}). \tag{13}$$

As $t \to \infty$ Eqn. (13) becomes

$$\frac{dT_R}{dt} = \frac{dT_P}{dt}. \tag{14}$$

The transition from Eqn. (13) to Eqn. (14) is, of course, the major practical question and is controlled by the value of the time constant RC_R. For many situations, $RC_R \sim 1$ sec, and Eqn. (14) will be valid after a few seconds. For example, at $t = 5$ sec,

$$\frac{dT_R}{dt} > 0.99 \frac{dT_P}{dt}. \tag{15}$$

However, there can be occasions (*e.g.*, where the reference includes "inert" material as a blank) when the time constant can be much larger[3]. In this case, the time to reach the simpler condition of Eqn. (14) can be appreciably longer.

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