

SCANNING CALORIMETERS CONTROLLED BY AN INDEPENDENT THERMODYNAMIC VARIABLE: DEFINITIONS AND SOME METROLOGICAL PROBLEMS

STANISŁAW L. RANDZIO

*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa,
ul. Kasprzaka 44/52 (Poland)*

(Received 7 January 1985)

ABSTRACT

A novel definition of scanning calorimetry is introduced. Thermodynamic formulae are derived to prove the accuracy of the new definition which is based on the calorimetric measurement of the power of the process of linear variation of an independent thermodynamic variable. A detailed analysis is given of the dynamic precision of the diathermic and compensation methods of power determination. To achieve this, dynamic errors in the time domain and dynamic errors in the parameter space are used. The main problems arising in obtaining the linear variation of independent thermodynamic variables are discussed. Problems of dynamic precision related to the organisation of a scanning calorimeter experiment controlled by an independent thermodynamic variable are discussed for the case of first-order phase transitions.

INTRODUCTION

It is well known that the best thermodynamic description of a system is made with the use of potential functions. Unfortunately, their direct experimental determination is very difficult. More often, they are determined through direct measurements of their derivatives against an independent thermodynamic variable. Scanning calorimetry is one of the techniques adapted to the determination of thermodynamic function derivatives. The scanning calorimeter is an instrument which enables the measurement of the power of a thermodynamic change induced by a known variation of an independent thermodynamic variable under given thermodynamic conditions. Linear variations of such variables are advantageous, because their time derivatives are constant. The objectives of this paper are to prove the accuracy of such a definition, to assemble the thermodynamic foundations for scanning calorimeters controlled by different independent thermodynamic variables, to perform a quantitative analysis of the respective metrological techniques, and to illustrate the advantages of using them in the

thermodynamic investigation of a system. For simplicity, only samples of pure substances will be considered as homogeneous systems and as two-phase systems with first-order phase transitions.

BASIC THERMODYNAMIC DEFINITIONS

The thermodynamic formulae given in this paragraph are written for one mole of a pure substance. The enthalpy differential is described by the following equations

$$dH(T, p) = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp \quad (1)$$

$$dH(T, p) = dQ + Vdp \quad (2)$$

When the pressure is kept constant and the temperature is varied as a linear function of time

$$p = \text{const}, dp = 0, T = T_0 \pm bt, dT = \pm bt \quad (3)$$

eqns. (1) and (2) reduce to

$$\left. \frac{dQ}{dt} \right|_p = q_p(T) = \left(\frac{\partial H}{\partial T} \right)_p b \quad (4)$$

where $q_p(T)$ is the power generated or absorbed under isobaric conditions and b is the rate of linear temperature variation. This is the fundamental thermodynamic principle for temperature-controlled scanning calorimetry at constant pressure [1].

When the temperature and kept constant is the pressure is varied as a linear function of time

$$T = \text{const}, dT = 0, p = p_0 \pm at, dp = \pm a dt \quad (5)$$

eqns. (1) and (2) reduce to the following form

$$\left. \frac{dQ}{dt} \right|_T = q_T(p) = \pm \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right] a = \pm \left(\frac{\partial S}{\partial p} \right)_T Ta = - \left[\pm \left(\frac{\partial V}{\partial T} \right)_p Ta \right] \quad (6)$$

where $q_T(p)$ is the power generated or absorbed under isothermal conditions and a is the rate of pressure variation. As it has been shown elsewhere [2,3], this is the fundamental thermodynamic principle for pressure-controlled scanning calorimetry at constant temperature.

In order to introduce volume as an independent variable it is advantageous to write thermodynamic equations for the change of internal energy

$$dU(T, V) = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (7)$$

$$dU(T, V) = dQ - p dV \quad (8)$$

When the volume is kept constant and the temperature is varied as a linear function of time

$$V = \text{const}, dV = 0, T = T_0 \pm bt, dT = \pm bdt \quad (9)$$

eqns. (7) and (8) reduce to

$$\left. \frac{dQ}{dt} \right|_V = q_V(T) = \pm \left(\frac{\partial U}{\partial T} \right)_V b \quad (10)$$

where $q_V(T)$ is the power generated or absorbed under isochoric conditions. This is the fundamental principle for temperature-controlled scanning calorimetry at constant volume.

When the temperature is kept constant and the volume is varied as a linear function of time

$$T = \text{const}, dT = 0, V = V_0 \pm ct, dV = \pm cdt \quad (11)$$

eqns. (7) and (8) reduce to the following form

$$\left. \frac{dQ}{dt} \right|_T = q_T(V) = \pm \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] c = \pm \left(\frac{\partial S}{\partial V} \right)_T cT = - \left[\pm \left(\frac{dp}{dT} \right)_V cT \right] \quad (12)$$

where $q_T(V)$ is the power generated or absorbed under isothermal conditions and c is the rate of linear volume variation. Equations (12) form the fundamental principle for a technique which, similarly, can be called volume-controlled scanning calorimetry at constant temperature.

To facilitate the formulation of a synthetic view of scanning calorimetry, all the equations derived above are presented together in Fig. 1. The term "temperature-controlled scanning calorimetry" was introduced by O'Neill [1]. Introduction of the other terms is a logical extension and a direct consequence of the thermodynamic description of a pure substance. In all the cases presented above of two independent thermodynamic variables, one is always kept constant and the other is controlled in a well-defined manner

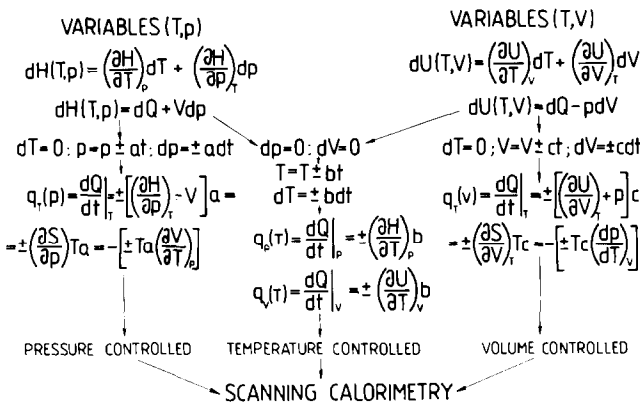


Fig. 1. A scheme of thermodynamic foundations for scanning calorimetry.

(linear variation). The resulting changes of the third, dependent variable are measured as heat power. For example, when the substance under investigation is an ideal gas, the derived equations reduce to:

(a) pressure-controlled scanning calorimetry at constant temperature

$$T = \text{const}, p = at, q_T(p) = -Ta \left(\frac{\partial V}{\partial T} \right)_p = -Va \quad (13)$$

(b) volume-controlled scanning calorimetry at constant temperature

$$T = \text{const}, V = ct, q_T(V) = -Tc \left(\frac{\partial p}{\partial T} \right)_V = -pc \quad (14)$$

(c) temperature-controlled scanning calorimetry at constant pressure

$$p = \text{const}, T = bt, q_p(T) = \left(\frac{\partial H}{\partial T} \right)_p b = bT \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_s = Vb \left(\frac{\partial p}{\partial T} \right)_s \quad (15)$$

(d) temperature-controlled scanning calorimetry at constant volume

$$V = \text{const}, T = bt, q_V(T) = \left(\frac{\partial U}{\partial T} \right)_V b = bT \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_s = pb \left(\frac{\partial V}{\partial T} \right)_s \quad (16)$$

Relations (13) and (14) not only directly confirm the possibilities of scanning calorimetry and prove the accuracy of the definitions proposed, but can also be used for calibration and/or verification procedures of given calorimetric systems. One can also see that scanning calorimetry is a powerful technique which enables the full thermodynamic description of a substance to be elucidated by dynamic calorimetric measurements of appropriate derivatives only.

From the metrological point of view, it is much easier to use intensive variables as controlled variables. This is one of the reasons why, of the three main thermodynamic variables: temperature, pressure and volume, the last was almost never used in dynamic calorimetry. The calorimeter of Johnson et al. [4] uses volume variations, but its output signals are temperature and pressure. Thus, at least in the sense of the equations presented and definitions proposed here, it is not a scanning calorimeter controlled by a thermodynamic variable. In the range of rapid variations of volume when the adiabacity of the system is easily maintained, the calorimeter gives information on $(\partial p/\partial T)_s$ values of the substance. One can see from eqns. (13) and (15) that the same information can be elucidated by scanning calorimeters controlled by pressure and temperature

$$\left(\frac{\partial p}{\partial T} \right)_s = - \frac{aq_p(T)}{bq_T(p)} \quad (17)$$

The subsequent analysis presented in this paper will be devoted mainly to pressure- and temperature-controlled scanning calorimeters. As stated above, all equations have been derived for one mole of a pure substance. In a real calorimeter these equations must be applied to all materials and substances

submitted to the action of pressure or temperature. Thus, the power output signal of a scanning calorimeter and its thermodynamic significance must be analysed for a given calorimetric construction. There are two basic and general conditions which must be fulfilled to make scanning calorimetry an accurate method. First, the calorimetric unit must be able to measure the power, and second, the independent variable must be changed strictly linearly, independently of internal and external disturbances. The independent variable must change uniformly over the whole of the sample investigated. Any disturbance of the homogeneity and/or of the linearity of the variations will cause perturbations of the calorimetric signal and the relations derived will not be valid. Of course, other continuous functions of the independent parameters could be used, but the constants a , b and c would then have to be replaced by the time derivatives of these functions. Below, an analysis is given of problems arising from calorimetric measurements of power and from the realisation of programs of linear variation of thermodynamic parameters, such as pressure and temperature.

CALORIMETRIC MEASUREMENTS OF POWER

Among different techniques of determination of power the most important are two calorimetric methods: diathermic and compensated. In this paper some problems will be discussed which arise from applications of these techniques to scanning calorimetry and which were insufficiently analysed in the calorimetric literature published so far.

The diathermic method

The diathermic method, also called heat-flux [5] or non-isothermal–non-adiabatic [6], belongs to the group of passive thermal systems [7,8]. Many papers have been devoted to the analysis of the dynamic properties of this method from the point of view of both the calorimetric transfer functions and correction techniques used for the elimination of thermal inertia. Reviews of correction techniques have been given by Randzio and Suurkuusk [9] and by Zielenkiewicz [10]. A comparison of digital correction techniques has been presented by Cesari et al. [11] as a result of a multi-national program. A comparison of harmonic and differentiation techniques has been made by Cesari et al. [12]. It is worth noting that the authors of that paper [12] have reduced the output signals of both techniques to the same level of noise and noticed that both techniques give comparable dynamic responses to the same input signal. From a visual appreciation of the results obtained in different laboratories, one could have previously thought that the harmonic technique was much more powerful than differentiation. This result shows the importance of the quantitative treatment of dynamic calorimetric mea-

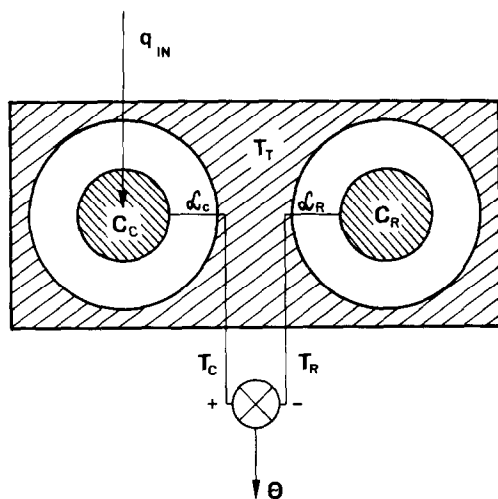


Fig. 2. A simplified model of a diathermic calorimeter.

measurements. Unfortunately, there is a lack of such treatments in dynamic calorimetry. In 1980, Randzio and Suurkuusk [9] proposed that some standard methods should be accepted by all laboratories when presenting dynamic calorimetric data for publication. The authors claimed that the dynamic parameters of the calorimeter used should always be given, together with the thermogram or with any other result of the dynamic calorimetric measurements. In this paper, the problem of dynamic accuracy will be analysed quantitatively with the use of the concept of dynamic errors of two types: dynamic errors in the time domain and dynamic errors in the parameter space. To achieve this, a very simple model of a differential calorimeter will be considered. A schematic diagram of this calorimeter is presented in Fig. 2. The differential equation of the measuring vessel can be presented as

$$\tau_C \frac{dT_C}{dt} + T_C = \frac{1}{\alpha_C} q_{IN} + T_T \quad (18)$$

A similar equation can be written for the reference cell

$$\tau_R \frac{dT_R}{dt} + T_R = T_T \quad (19)$$

where $\tau_C = C_C/\alpha_C$ and $\tau_R = C_R/\alpha_R$ are time constants of the measuring and reference vessels, respectively, and q_{IN} is the input power developed in the measuring vessel. By subtraction of eqns. (18) and (19), and assuming that the time constants of both vessels are equal, one can obtain the following equation in the time domain

$$\theta(t) + \tau_C \frac{d\theta(t)}{dt} = \frac{1}{\alpha_C} q_{IN}(t) \quad (20)$$

where $\theta = T_C - T_R$, and its homologue in the frequency domain

$$\theta(s) = \frac{1}{\alpha_C} \frac{1}{1 + \tau_C s} q_{IN}(s) = k_s G_d(s) q_{IN}(s) = G_C(s) q_{IN}(s) \quad (21)$$

where k_s is the static gain of the calorimeter, $G_d(s)$ is its complex dynamic gain and $G_C(s)$ its transfer function. Equations (20) and (21) show that the calorimetric output signal, θ , for rapid changes will not follow the input power, q_{IN} , and a certain dynamic error will appear. This dynamic error can be defined as follows [13]

$$\Delta_{dyn,t} = \theta(t) - \theta_0(t) \quad (22)$$

or in a quadratic form

$$\partial_{dyn,t}^2 = \int_0^\infty [\Delta_{dyn,t}]^2 dt \quad (23)$$

Similarly, a relative error can also be defined

$$\delta_{dyn,t} = \left[\frac{\int_0^\infty [\Delta_{dyn,t}]^2 dt}{\int_0^\infty [\theta_0(t)]^2 dt} \right]^{1/2} \quad (24)$$

where $\theta_0(t)$ is the output signal of a hypothetical calorimeter with the same static properties as the real calorimeter (the same static gain, k_s) and without any inertia ($G_d = 1$). The dynamic error $\Delta_{dyn,t}$ is a function of time while its quadratic forms, absolute and relative, are numbers.

As an example of application, an input signal of the following form will be considered

$$q_{IN}(t) = rt[f(t) - f(t-d)] \quad (25)$$

where

$$f(t) = \begin{cases} 1 & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{cases} \quad f(t-d) = \begin{cases} 0 & \text{for } t < d \\ 1 & \text{for } t \geq d \end{cases} \quad (26)$$

d is the time interval of the input signal and r is the rate of power variation. As will be discussed later, such a form of the input signal is very common in scanning calorimetry investigations of first-order phase transitions. The solution of eqn. (20) with the input signal defined by eqn. (25) gives the output signal of the model calorimeter

$$\theta(t) = \begin{cases} k_s r \tau_C \left(e^{-t/\tau_C} + \frac{t}{\tau_C} - 1 \right) & \text{for } 0 < t < d \\ k_s r \tau_C \left[1 + \left(\frac{d}{\tau_C} - 1 \right) e^{d/\tau_C} \right] e^{-t/\tau_C} & \text{for } t \geq d \end{cases} \quad (27)$$

Thus, according to definition (22) the dynamic error in this case is

$$\Delta_{\text{dyn},t} = \begin{cases} r\tau_c (e^{-t/\tau_c} - 1) & \text{for } 0 < t < d \\ r\tau_c \left[1 + \left(\frac{d}{\tau_c} - 1 \right) e^{d/\tau_c} \right] e^{-t/\tau_c} & \text{for } t \geq d \end{cases} \quad (28)$$

It was assumed for this example that the static gain of the calorimeter is equal to one ($k_s = 1$), so that the output signal of the hypothetical calorimeter is directly equal to the input signal defined by eqn. (25). It is worth noting that the integrals of the two parts of dynamic error (eqn. 28) in the respective time intervals are equal to each other with opposite signs. Thus, it is clear in this case that the dynamic error has no influence on the static precision of the calorimeter. The quadratic form of the dynamic error for the input signal (eqn. 25) is

$$\hat{\delta}_{\text{dyn},t}^2 = \begin{cases} \frac{r^2\tau_c^3}{2} \left(4e^{-d/\tau_c} - e^{-2d/\tau_c} + 2\frac{d}{\tau_c} - 3 \right) & \text{for } 0 < t < d \\ \frac{r^2\tau_c^3}{2} \left[2\left(\frac{d}{\tau_c} - 1 \right) e^{-d/\tau_c} + e^{-2d/\tau_c} + \left(\frac{d}{\tau_c} - 1 \right)^2 \right] & \text{for } t \geq d \end{cases} \quad (29)$$

and according to the definition given in eqn. (24), the relative dynamic error is

$$\delta_{\text{dyn},t} = \frac{\tau_c}{d} \left\{ 3\frac{\tau_c}{d} \left[e^{-d/\tau_c} \left(\frac{d}{\tau_c} + 1 \right) + 0.5 \left(\frac{d}{\tau_c} \right)^2 - 1 \right] \right\}^{1/2} \quad (30)$$

Graphic representations of the input and output signals and of the respective dynamic errors are given in Fig. 3a–c for the particular case when $r = 0.1$ W per one calorimetric time constant and the ratio d/τ_c is equal to 10. A graphic representation of the dependence of the relative dynamic error on the ratio d/τ_c is given in Fig. 3d. It is worth noting that eqn. (30) and the graphic presentation in Fig. 3d show how much the relative dynamic error for a given d value will decrease when the time constant, τ_c , is reduced by a proper correction technique [8], or how much, for the same case, the time of measurement can be shortened without increasing the relative dynamic error. From eqn. (28) one can see how a reduction of the calorimetric time constant also reduces the stationary dynamic error in the time interval $0 < t < d$, which is so important in phase transition investigations. For example, a reduction of the time constant by a factor of 10 reduces the stationary dynamic error by the same factor for the same rate of power evolution, r . The dependence of d and r on sample size and on the rates of pressure or temperature scans with relation to dynamic errors will be discussed later.

Equations (28)–(30) are only valid for the input signal defined by eqn. (25) and for the calorimeter with one time constant (eqns. 20 and 21). It is

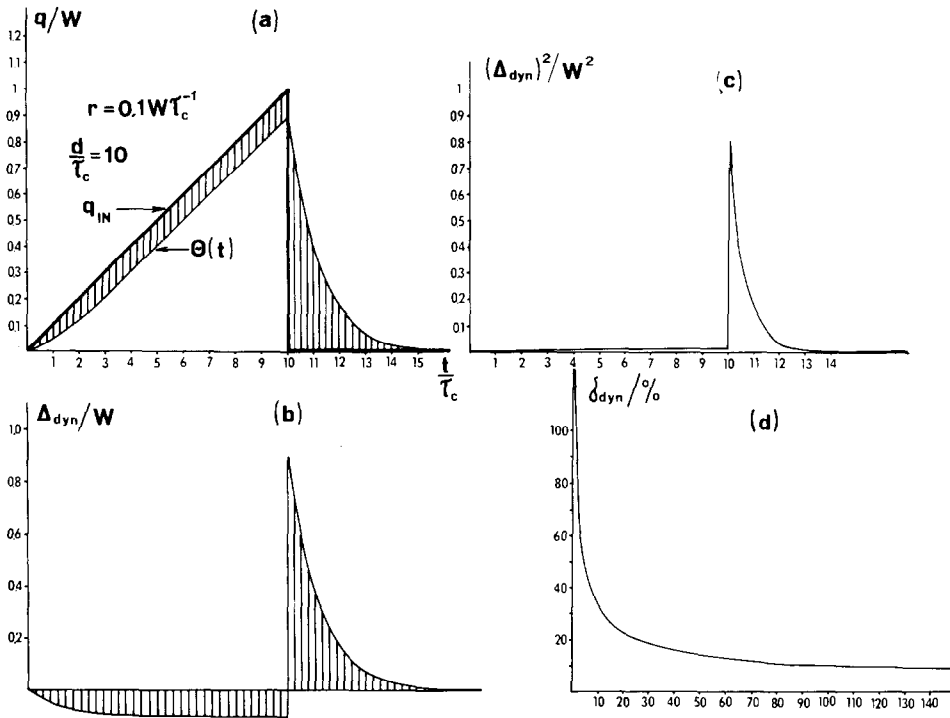


Fig. 3. A graphic presentation of dynamic errors in the time domain.

possible to derive similar equations for other particular input signals and for other calorimeters, but use of frequency analysis enables general relationships to be derived without assuming any particular form of the input signal or any particular form of the calorimetric transfer function. With the use of the Parseval equation

$$\int_0^{\infty} |f(t)|^2 dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |f(j\omega)|^2 d\omega \quad (31)$$

one can write

$$\int_0^{\infty} |\Delta_{\text{dyn},t}|^2 dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |\Delta_{\text{dyn}}(j\omega)|^2 d\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |\theta(j\omega) - \theta_0(j\omega)|^2 d\omega \quad (32)$$

By introducing eqn. (21) into eqn. (32) one obtains

$$\int_0^{\infty} |\Delta_{\text{dyn},t}|^2 dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |G_C(j\omega) - k_s|^2 |q_{\text{IN}}(j\omega)|^2 d\omega \quad (33)$$

where $|q_{\text{IN}}(j\omega)|^2$ is, by definition, the spectral density of the input signal, $S_{q_{\text{IN}}}(\omega)$, and eqn. (33) can be written as

$$\partial_{\text{dyn}}^2 = \int_0^{\infty} |\Delta_{\text{dyn},t}|^2 dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |G_C(j\omega) - k_s|^2 S_{q_{\text{IN}}}(\omega) d\omega \quad (34)$$

A similar equation for the relative dynamic error can be written

$$\delta_{\text{dyn}} = \left(\frac{\int_0^{\infty} |\Delta_{\text{dyn},t}|^2 dt}{\int_0^{\infty} |\theta_0(t)|^2 dt} \right)^{1/2} = \left(\frac{\int_{-\infty}^{+\infty} |G_C(j\omega) - k_s| S_{q_{\text{IN}}}(\omega) d\omega}{k_s^2 \int_{-\infty}^{+\infty} S_{q_{\text{IN}}}(\omega) d\omega} \right)^{1/2} \quad (35)$$

Equations (34) and (35) give a quantitative description of the relationship between the dynamic error, calorimeter properties represented by its transfer function and dynamic properties of the input signal represented by its spectral density. The main limitation of the equations presented is the fact that the spectral density of the input signal is not usually known a priori, often being the variable searched for in dynamic measurements. However, use of eqns. (34) or (35) allow the a priori determination of which signals can be measured in a given calorimeter at a desired dynamic precision.

The above discussion of the dynamic errors in diathermic measurements of thermal power was limited to the case where the metrological parameters of the calorimetric system remain constant and, consequently, the coefficients of the differential equation and the equation itself remain unchanged. For any change in these parameters during the course of the measurement, the calorimetric output signal evolves with time, without any obvious relationship with the input signal. This evolution causes errors in the dynamic measurement. To differentiate these errors from those in the time domain they are called dynamic errors in the parameter space and are related to the change of the structure of the system. The description of dynamic errors in the parameter space can most easily be accomplished with the use of sensitivity functions [14], defined in the time domain or in the frequency domain. In order to introduce the definition of the sensitivity function into the time domain for the diathermic calorimeter, a general form of the ordinary differential equation describing its properties is written as

$$f[\theta^{(n)}, \theta^{(n-1)}, \dots, \theta, t, \alpha_0] = 0 \quad (36)$$

where α_0 denotes the nominal value of the parameter. For simplicity, only a homogeneous equation has been written without any input signal. It can be assumed that the above nominal differential equation has a unique solution: $\theta_0 = \theta(t, \alpha_0)$. If it is now assumed that the parameter changes its value, $\alpha = \alpha_0 + \Delta\alpha$, then the corresponding actual differential equation can be written as

$$f[\theta^n, \theta^{(n-1)}, \dots, \theta, t, \alpha] = 0 \quad (37)$$

where α is called the actual parameter value. The solution of eqn. (37), $\theta = \theta(t, \alpha)$, is called the actual (or perturbed) solution. If it is assumed that $\theta(t, \alpha)$ is of the same type as $\theta(t, \alpha_0)$ and that $\theta(t, \alpha)$ deviates infinitesimally from $\theta(t, \alpha_0)$ if α deviates infinitesimally from α_0 , then $\theta(t, \alpha)$ is a continuous function of α . With these assumptions the actual solution $\theta(t, \alpha)$

can be expanded into Taylor series around α_0 and if $\Delta\alpha \ll \alpha_0$ it can be written as

$$\theta(t, \alpha) = \theta(t, \alpha_0) + \left. \frac{\partial \theta}{\partial \alpha} \right|_{\alpha_0} \Delta\alpha \quad (38)$$

The definition of the output sensitivity function in the time domain $\sigma(t, \alpha_0)$ can now be introduced for the diathermic calorimeter

$$\sigma(t, \alpha_0) = \left. \frac{\partial \theta(t, \alpha)}{\partial \alpha} \right|_{\alpha_0} \quad (39)$$

On introduction of this definition into eqn. (38) the actual output signal can be written as

$$\theta(t, \alpha) = \theta(t, \alpha_0) + \sigma(t, \alpha_0) \Delta\alpha \quad (40)$$

The second term in eqn. (40) is called the parameter-induced output error. The output sensitivity function defined in the time domain is a time function whose shape is dependent on the shape of the actual input signal. This is one of the shortcomings of sensitivity functions in the time domain. Sensitivity functions defined in the frequency domain have found more use. They are based on the transfer function or on the transfer matrix of the system. One of the sensitivity functions defined in the frequency domain is the Bode sensitivity function [15], $S_{\alpha_j}^{G_C}(s)$, related to a Bode plot of dynamic properties of a calorimeter [16] and defined as follows

$$S_{\alpha_j}^{G_C}(s) = \left. \frac{\partial \ln G_C}{\partial \ln \alpha_j} \right|_{\alpha_0} = \left. \frac{\partial G_C / G_C}{\partial \alpha_j / \alpha_j} \right|_{\alpha_0} = \left. \frac{\partial G_C}{\partial \alpha_j} \right|_{\alpha_0} \frac{\alpha_{j,0}}{G_{C,0}} \quad (41)$$

where $G_C = G_C(s, \alpha)$ is the actual transfer function of the system, $G_{C,0} = G_C(s, \alpha_0)$ is the nominal transfer function, α_0 is the nominal parameter vector and α is the actual parameter vector. The relationship between the output sensitivity function, $\sigma(t, \alpha_0)$, and the Bode sensitivity function, $S_{\alpha_j}^{G_C}(s)$, can be found by applying the Laplace transform to eqn. (39), then using relation (21) and definition (41)

$$\mathcal{L}\{\sigma(t, \alpha_0)\} = \frac{\partial \theta(s, \alpha)}{\partial \alpha_j} = \frac{\partial G_C(s, \alpha) q_{IN}(s)}{\partial \alpha_j} = S_{\alpha_j}^{G_C}(s) \frac{G_C(s, \alpha_0)}{\alpha_{j,0}} q_{IN}(s) \quad (42)$$

Integration of eqn. (42) gives the actual value of the output signal in terms of the complex frequency

$$\theta(s, \alpha) = \theta(s, \alpha_0) + \sum_{j=1}^l S_{\alpha_j}^{G_C}(s) \theta(s, \alpha_0) \frac{\Delta\alpha_j}{\alpha_{j,0}} \quad (43)$$

From this equation one can derive an equation defining the relative parameter-induced error, $\delta_{\text{dyn},p}$

$$\delta_{\text{dyn},p} = \frac{\theta(s, \alpha) - \theta(s, \alpha_0)}{\theta(s, \alpha_0)} = \sum_{j=1}^l S_{\alpha_j}^{G_C}(s) \frac{\Delta\alpha_j}{\alpha_{j,0}} \quad (44)$$

It can be seen that the relative parameter induced error, $\delta_{\text{dyn},p}$, is only related to the structure of the calorimeter. For the diathermic calorimeter analysed in this paper the transfer function is described by eqn. (21), $\alpha_1 \pm \alpha_C$, $\alpha_2 = \tau_C$, and the Bode sensitivity functions are as follows

$$S_{\alpha_1}^{G_C}(s) = S_{\alpha_C}^{G_C}(s) = -\frac{1 + 2\tau_{C,0}s}{1 + \tau_{C,0}s} \quad (45)$$

$$S_{\alpha_2}^{G_C}(s) = S_{\tau_C}^{G_C}(s) = -\frac{\tau_{C,0}s}{1 + \tau_{C,0}s} \quad (46)$$

Thus, the relative parameter-induced error of the calorimeter is equal to

$$\delta_{\text{dyn},p} = -\frac{\Delta\tau_C s}{1 + \tau_{C,0}s} - \frac{\Delta\alpha_C}{\alpha_{C,0}} \frac{1 + 2\tau_{C,0}s}{1 + \tau_{C,0}s} \quad (47)$$

It was assumed that the time constant of the calorimeter depends on the heat exchange coefficient, but the heat exchange coefficient does not depend on the time constant. Thus, the change in the time constant, for example by changing the heat capacity, does not alter the heat exchange coefficient. In some cases the change in the heat exchange coefficient, α_C , is a reproducible variable and can be introduced into the calculation procedure. Unfortunately, the change in α_C is often not reproducible, or not known a priori, when this procedure cannot be applied. The change in the calorimetric time constant depends not only on the heat exchange coefficient but also on the heat capacity, which frequently changes during the course of measurements. These are the limitations of the diathermic method, unless the real output data are corrected a posteriori with the use of eqns. (44) or (47), if the changes and nominal values of α_C and τ_C can be determined.

The compensation method

The compensation method belongs to the group of active thermal systems [7,8]. As it is known [17] the transfer function, $H(s)$, of the active system (closed feedback loop) is related to the transfer function of the passive system (the same system with open feedback loop) by the following equation

$$H(s) = \frac{k_{el}G(s)}{1 + k_{el}G(s)} \quad (48)$$

where k_{el} is a gain of the variable component. In the case of the calorimeter analysed in this paper with one time constant, eqn. (48) takes the following approximative form

$$H_C(s) = \frac{1}{1 + \frac{\tau_C}{K}s} \quad (49)$$

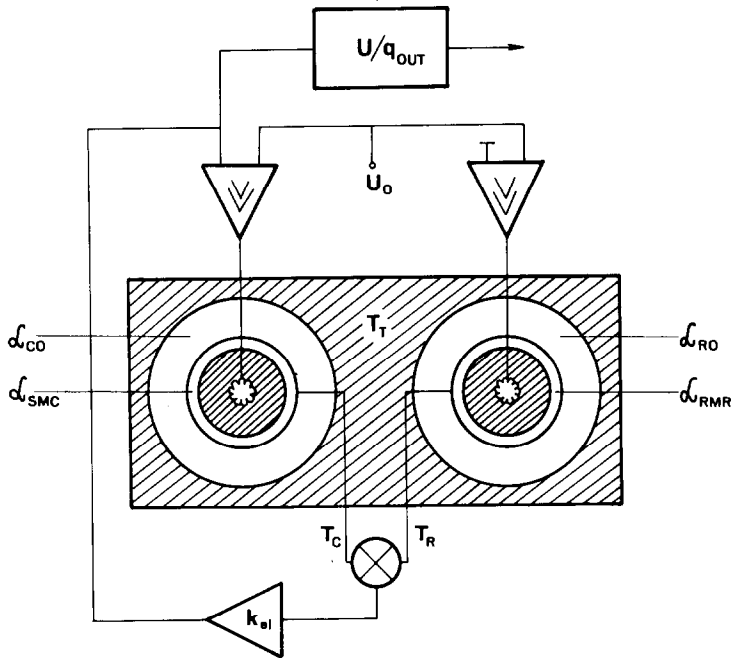


Fig. 4. A diagram of a differential power compensated calorimeter where the sample is inside the feedback loop.

where K is the total gain of the compensation feedback loop ($K = k_e k_s$). It can be seen that when K is large the influence of the time constant on calorimetric response is seriously reduced. As it was shown by Randzio and Sunner [18] this is true only under the condition that the substance investigated is located inside the feedback loop. If the construction of the calorimeter is such that the substance investigated is placed outside the feedback loop, the model description contains an extra term in which the time constant is not reduced by gain of the feedback loop. The analysis of Randzio and Sunner has been made for the simple calorimeter. It can be claimed that the situation is improved by a differential mounting of the calorimetric vessels. To verify this suggestion, a similar analysis is performed below of the influence of the sample position in differential compensated calorimeters. A schematic diagram of the differential compensated calorimeter, where the sample is placed inside the feedback loop, is presented in Fig. 4. The model is based on calorimetric vessels described elsewhere [2,8,19]. On the basis of this model the following equations can be written

$$C_{SM} \frac{dT_{SM}}{dt} + \alpha_{SMC}(T_{SM} - T_C) = q_{IN} + q_{OUT} \quad (50)$$

$$C_C \frac{dT_C}{dt} + \alpha_C(T_C - T_0) - \alpha_{SMC}(T_{SM} - T_C) = 0 \quad (51)$$

$$C_{RM} \frac{dT_{RM}}{dt} + \alpha_{RMR}(T_{RM} - T_R) = 0 \quad (52)$$

$$C_R \frac{dT_R}{dt} + \alpha_R(T_R - T_0) - \alpha_{RMR}(T_{RM} - T_R) = 0 \quad (53)$$

$$q_{OUT} = k_{el}(T_R - T_C) \quad (54)$$

where C_{SM} , C_{RM} , C_C and C_R are heat capacities of the sample material under investigation, reference material, calorimetric measuring cell and calorimetric cell, respectively; α_{SMC} , α_{RMR} , α_C and α_R are heat exchange coefficients between the sample material and the calorimetric measuring cell, between the reference material and the calorimetric reference cell, between the calorimetric measuring cell and outside environment, and between the calorimetric reference cell and outside environment, respectively; T_{SM} , T_{RM} , T_C , T_R and T_0 are the temperatures of the sample material, reference material, calorimetric measuring cell, calorimetric reference cell and environment, respectively; and q_{OUT} is the measured power (compensating power). For simplicity, it was assumed that there is no thermal effect in the reference material. On the basis of eqns. (50)–(53), and using procedures from a previous paper [18], the following equations are obtained for the measuring and reference cells, respectively

$$\begin{aligned} C_{SM}C_C \frac{d^2T_C}{dt^2} + [C_{SM}(\alpha_{SMC} + \alpha_C) + C_C\alpha_{SMC}] \frac{dT_C}{dt} + \alpha_{SMC}\alpha_C T_C \\ = \alpha_C C_{SM} \frac{dT_0}{dt} + \alpha_C \alpha_{SMC} T_0 + (q_{OUT} + q_{IN})\alpha_{SMC} \end{aligned} \quad (55)$$

$$\begin{aligned} C_{RM}C_R \frac{d^2T_R}{dt^2} + [C_{RM}(\alpha_{RMR} + \alpha_R) + C_R\alpha_{RMR}] \frac{dT_R}{dt} + \alpha_{RMR}\alpha_R T_R \\ = \alpha_R C_{RM} \frac{dT_0}{dt} + \alpha_R \alpha_{RMC} T_0 \end{aligned} \quad (56)$$

By subtracting eqns. (55) and (56) by sides, then eliminating $T_R - T_C$ and their time derivatives with the help of eqn. (54), and assuming, for simplicity, that the time constants and the heat exchange coefficients are the same for the measuring and reference cells, one obtains the following equation

$$\begin{aligned} q_{OUT} = -q_{IN} - \frac{\alpha_{SMC} + \alpha_C}{k_{el}} \\ \times \left[\tau_{SM}\tau_C \frac{d^2q_{OUT}}{dt^2} + (\tau_{SM} + \tau_C) \frac{dq_{OUT}}{dt} + \frac{\alpha_C}{\alpha_{SMC} + \alpha_C} q_{OUT} \right] \end{aligned} \quad (57)$$

which has the same form as the equation derived previously, but without an explicit consideration of the differential mounting. The time constants are defined as follows: $\tau_C = C_C/(\alpha_C + \alpha_{SMC})$, $\tau_{SM} = C_{SM}/\alpha_{SMC}$.

A schematic diagram of the differential compensated calorimeter, where the sample is placed outside the feedback loop, is presented in Fig. 5. On the

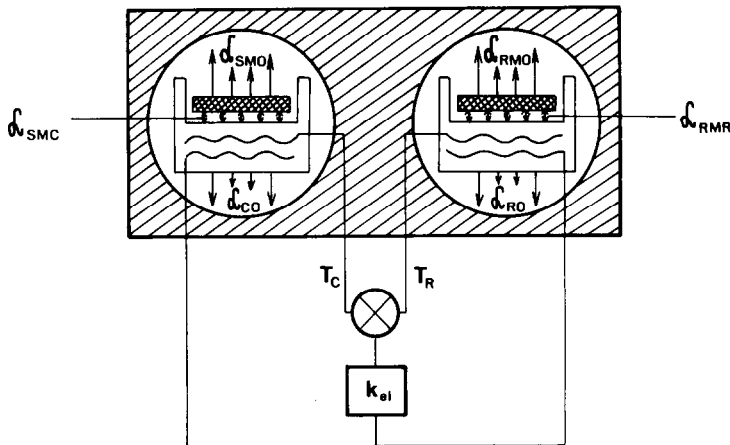


Fig. 5. A diagram of a differential power compensated calorimeter where the samples are outside the feedback loop.

basis of this model the following equations can be written

$$C_{SM} \frac{dT_{SM}}{dt} + \alpha_{SMC}(T_{SM} - T_C) + \alpha_{SM0}(T_{SM} - T_0) = q_{IN} \quad (58)$$

$$C_C \frac{dT_C}{dt} + \alpha_C(T_C - T_0) - \alpha_{SMC}(T_{SM} - T_C) = q_{OUT} \quad (59)$$

$$C_{RM} \frac{dT_{RM}}{dt} + \alpha_{RMR}(T_{RM} - T_C) + \alpha_{RM0}(T_R - T_0) = 0 \quad (60)$$

$$C_R \frac{dT_R}{dt} + \alpha_R(T_R - T_0) - \alpha_{RMR}(T_{RM} - T_R) = 0 \quad (61)$$

where α_{SM0} and α_{RM0} are the heat exchange coefficients between the sample and reference materials and the environment, respectively. As before, the measured signal is defined by eqn. (54). Using the same procedure, one can obtain the following equations for the measuring cell

$$\begin{aligned} \frac{C_{SM}C_C}{\alpha_{SMC}} \frac{d^2T_C}{dt^2} + \left[C_{SM} \frac{\alpha_C + \alpha_{SMC}}{\alpha_{SMC}} + C_C \frac{\alpha_{SMC} + \alpha_{SM0}}{\alpha_{SMC}} \right] \frac{dT_C}{dt} \\ + \left[\alpha_C + \alpha_{SM0} + \frac{\alpha_C \alpha_{SM0}}{\alpha_{SMC}} \right] T_C = q_{IN} + q_{OUT} \left(1 + \frac{\alpha_{SM0}}{\alpha_{SMC}} \right) + \frac{C_{SM}}{\alpha_{SMC}} \frac{dq_{OUT}}{dt} \end{aligned} \quad (62)$$

and for the reference cell

$$\begin{aligned} \frac{C_{RM}C_R}{\alpha_{RMR}} \frac{d^2T_R}{dt^2} + \left[C_{RM} \frac{\alpha_R + \alpha_{RMR}}{\alpha_{RMR}} + C_R \frac{\alpha_{RMR} + \alpha_{RM0}}{\alpha_{RMR}} \right] \frac{dT_R}{dt} \\ + \left[\alpha_R + \alpha_{RM0} + \frac{\alpha_R \alpha_{RM0}}{\alpha_{RMR}} \right] T_R = 0 \end{aligned} \quad (63)$$

Therefore, for differential mounting the equation is as follows

$$\begin{aligned}
 q_{\text{OUT}} = & -q_{\text{IN}} - \frac{\alpha_{\text{SM0}}}{\alpha_{\text{SMC}}} q_{\text{OUT}} - \frac{\alpha_{\text{SMC}} + \alpha_{\text{SM0}}}{\alpha_{\text{SMC}}} \tau_{\text{SM}} \frac{dq_{\text{OUT}}}{dt} \\
 & - \frac{(\alpha_{\text{SMC}} + \alpha_{\text{C}})(\alpha_{\text{SMC}} + \alpha_{\text{C}})}{k_{\text{el}} \alpha_{\text{SMC}}} \left\{ \tau_{\text{SM}} \tau_{\text{C}} \frac{d^2 q_{\text{OUT}}}{dt^2} + (\tau_{\text{SM}} + \tau_{\text{C}}) \frac{dq_{\text{OUT}}}{dt} \right. \\
 & \left. + \left[1 - \frac{\alpha_{\text{SMC}}^2}{(\alpha_{\text{SMC}} + \alpha_{\text{C}})(\alpha_{\text{SMC}} + \alpha_{\text{SM0}})} \right] q_{\text{OUT}} \right\} \quad (64)
 \end{aligned}$$

The time constants have the following definitions: $\tau_{\text{C}} = C_{\text{C}}/(\alpha_{\text{SMC}} + \alpha_{\text{C}})$, $\tau_{\text{SM}} = C_{\text{SM}}/(\alpha_{\text{SMC}} + \alpha_{\text{SM0}})$. When comparing eqn. (64) with that obtained by Randzio and Sunner, one can see that the differential mounting does not help very much when the sample and reference are not placed in the feedback loop. Independently of the gain of the feedback loop there will always be a static error related to the ratio between the heat exchange coefficients, α_{SM0} and α_{SMC} , and a dynamic error whose magnitude will depend on the ratio $(\alpha_{\text{SMC}} + \alpha_{\text{SM0}})/\alpha_{\text{SMC}}$ and on the time constant of the sample.

The above analysis is valid when compensation is only performed in the measuring cell. The reference cell is a pure reference. The proper setting of the value of U_0 (Fig. 4) permits both exothermic and endothermic effects to be compensated [20,21]. The above observations are correct, however, even when the recorded signal is a difference of powers developed in the reference and measuring cells [22]. It can be proved by analysing the terms in eqn. (64) which are not divided by k_{el} . If it is assumed that q_1 is the power developed in the measuring cell and q_2 that developed in the reference cell, then the recorded signal is

$$q_{\text{OUT}} = q_1 \left(1 + \frac{\alpha_{\text{SM0}}}{\alpha_{\text{SMC}}} \right) + \frac{C_{\text{SM}}}{\alpha_{\text{SMC}}} \frac{dq_1}{dt} - q_2 \left(1 + \frac{\alpha_{\text{RM0}}}{\alpha_{\text{RMC}}} \right) - \frac{C_{\text{RM}}}{\alpha_{\text{RMR}}} \frac{dq_2}{dt} \quad (65)$$

If it is once more assumed that the heat exchange coefficients and the time constants of both cells are equal (an ideal differential mounting), equation (65) is reduced to the form

$$q_{\text{OUT}} = \Delta q \left(1 + \frac{\alpha_{\text{SM0}}}{\alpha_{\text{SMC}}} \right) + \frac{C_{\text{SM}}}{\alpha_{\text{SMC}}} \frac{d(\Delta q)}{dt} \quad (66)$$

where $\Delta q = q_1 - q_2$. It is clear that the method of compensation, itself, does not eliminate the two terms which are independent of the gain of the feedback loop; only the proper placing of the sample in the calorimetric cell can result in an actual advantage of using the compensation method. Even if the sample is placed fully in the feedback loop, however, the reduction of the time constant cannot be very high since gain (k_{el}) is limited due to stability problems. As it has been shown experimentally [8], it is possible to use an additional dynamic corrector mounted in series with the feedback loop, as in

the diathermic method. However, the total reduction of the time constant is very similar to that in the diathermic method. Thus, from the point of view of dynamic errors in the time domain, described above, both methods (diathermic and compensated) have similar capabilities.

As far as dynamic errors in the parameter space are concerned, the compensation method is much more advantageous than the diathermic method. The output sensitivity function of a compensated calorimeter defined in the time domain and its Bode sensitivity function defined in the frequency domain are as follows

$$\sigma(t, \alpha_0) = \left. \frac{\partial q_{\text{OUT}}(t, \alpha)}{\partial \alpha} \right|_{\alpha_0} \quad (67)$$

$$S_{G_C}^{H_C}(s) = \left. \frac{\partial \ln H_C}{\partial \ln G_C} \right|_{G_{C,0}} = \left. \frac{\partial H_C/H_C}{\partial G_C/G_C} \right|_{G_{C,0}} = \left. \frac{\partial H_C}{\partial G_C} \right|_{G_{C,0}} \frac{G_{C,0}}{H_{C,0}} \quad (68)$$

By applying the same procedure as in the case of the diathermic calorimeter, the relationship between the sensitivity functions can be written as

$$\begin{aligned} \mathcal{L}\{\sigma(t, \alpha_0)\} &= \frac{\partial q_{\text{OUT}}(s, \alpha)}{\partial \alpha_j} = \frac{\partial H(s, \alpha) q_{\text{IN}}(s)}{\partial \alpha_j} \\ &= S_{G_C}^{H_C}(s) S_{\alpha_j}^{G_C}(s) \frac{H_{C,0}}{\alpha_{j,0}} q_{\text{IN}}(s) \end{aligned} \quad (69)$$

Integration of eqn. (68) gives the actual value of the output signal of the compensated calorimeter in terms of the complex frequency

$$q_{\text{OUT}}(s, \alpha) = q_{\text{OUT}}(s, \alpha_0) + \sum_{j=1}^l S_{G_C}^{H_C}(s) S_{\alpha_j}^{G_C}(s) q_{\text{OUT}}(s, \alpha_0) \frac{\Delta \alpha_j}{\alpha_{j,0}} \quad (70)$$

and, hence, an equation for the relative parameter-induced error is obtained

$$\delta_{\text{dyn},p} = \frac{q(s, \alpha) - q_{\text{OUT}}(s, \alpha_0)}{q_{\text{OUT}}(s, \alpha_0)} = S_{G_C}^{H_C}(s) \sum_{j=1}^l S_{\alpha_j}^{G_C}(s) \frac{\Delta \alpha_j}{\alpha_{j,0}} \quad (71)$$

When comparing eqn. (71), defining the relative parameter-induced error of the compensation method, with eqn. (44), defining a similar error of the diathermic method, one can see that in the former case an additional sensitivity function, $S_{G_C}^{H_C}(s)$, appears. On application of the compensation method to a calorimeter with one time constant (eqns. 21 and 49), this sensitivity function becomes

$$S_{G_C}^{H_C}(s) = \frac{1 + \tau_{C,0}s}{1 + \tau_{C,0}s + K_0} \quad (72)$$

and the relative parameter-induced error is described by eqn. (73)

$$\delta_{\text{dyn},p} = - \frac{\frac{\Delta \alpha_C}{\alpha_{C0}} (1 + 2\tau_{C,0}s) + \Delta \tau_C s}{1 + \tau_{C,0}s + K_0} \quad (73)$$

where K_0 is the total gain of the feedback loop at the nominal value of the heat exchange coefficient. Equation (73) was obtained by introducing eqns. (45), (46) and (72) into eqn. (71). It can be seen from eqn. (73) that in the compensation method the influence of changes in the time constant and heat exchange coefficient on the relative parameter-induced output error is reduced by a factor whose magnitude is determined by the gain of the compensation loop. This is the main advantage of the compensation method over the diathermic one.

LINEAR VARIATIONS OF INDEPENDENT THERMODYNAMIC VARIABLES

As stated above, linear variations of independent thermodynamic variables in scanning calorimetry are advantageous, since the description of the thermodynamic significance of the output signal is then easiest. As for power measurements, there are two methods of obtaining linear variations of independent thermodynamic variables: passive and active. Active programming is when the state of the interface directly influencing the substance under investigation is directly controlled according to a given set function of time. When this control is not direct, the programming is considered to be passive, for example, in the case of temperature programming, where the calorimetric block serves only as a heat sink and the temperature program is realized directly in the heating shield. In passive programming, it is very difficult to take into consideration all unforeseeable changes of the programmed variable, caused, for example, by the change in the sample under investigation. In the case of active programming, this change is automatically compensated at the dynamic precision, determined by the quality of the programming system. Another difficulty lies in obtaining a uniform variation of the independent thermodynamic parameter over the whole of the sample investigated. A more detailed analysis is given below on the basis of our calorimeter [20,23].

Linear variation of temperature

A large number of different systems of linear temperature programming have been described in the literature. The best are those in which the surface of heat exchange between the samples (reference and investigated) and the calorimetric block is directly and actively programmed. O'Neill had shown that in this case the calorimetric thermograms can be described quantitatively [1]. The best known example of such a design is the calorimeter of Watson et al. [24]. Unfortunately, this construction can give good results only for very small samples. If the samples are too large, the condition of temperature uniformity cannot be satisfied; but often in practice much

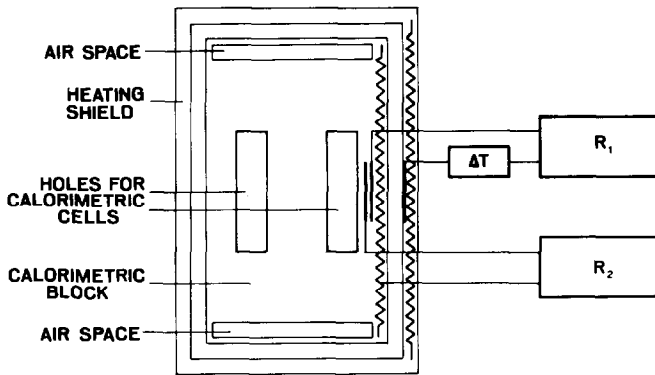


Fig. 6. A diagram of a thermostat with controlled heat exchange.

larger samples must be used. An example of a design of an actively programmed calorimetric thermostat for larger samples ($1-10 \text{ cm}^3$) and for large temperature intervals is schematically presented in Fig. 6 [25]. Only a model is presented to show some main features of the design. The essential concept is that the thermal action on the calorimetric cells is achieved through the formation of a heat exchange by direct control of the direction and intensity of thermal fluxes. The thermostat contains a privileged thermal circuit in which thermal resistance between the block and the environment is much smaller than the resistances of other possible thermal circuits. The privileged thermal circuit contains a controlled temperature source. This temperature source affects the thermal flux in the circuit such that the thermal gradient in the block is constant and small, and non-adiabatic conditions are maintained to ensure a continuous relationship between the set temperature of the block and the intensity of the thermal flux between the block and the heating shield. The above idea is achieved in the construction, since the cylindrical metal block with holes for calorimetric cells has a heater mounted on its whole lateral surface. Two temperature sensors are placed in the block near its heating surface. The bottom and top surfaces of the cylindrical block are passive and, to reduce the heat exchange through them, the thermal resistances are increased by horizontal air spaces. The calorimetric block is placed coaxially in the heating shield. The thermal resistance of the thermal path containing the block and the heating shield is much smaller than that of the thermal path through the bottom and top surfaces of the block. The heating elements of the block and heating shield are connected through control loops and are controlled by separate controllers. Together with two temperature sensors placed in the block and the heating shield, they form the temperature source which maintains the set value of thermal flux between the block and the heating shield. This flux is decided by choosing a set value of the temperature difference, $\Delta T = T_B - T_H$. The chosen value of ΔT must fulfil the following inequalities and must be as

small as possible

$$\frac{\alpha_C(T_C - T_B) + \alpha_R(T_R - T_B)}{\alpha_B} < \Delta T < \frac{\alpha_H(T_H - T_0)}{\alpha_B} \quad (74)$$

where T_B , T_H and T_0 are the temperatures of the block, heating shield and environment, respectively, α_B and α_H are the heat exchange coefficients between the block and the heating shield and the heating shield and environment, respectively. The second temperature sensor placed in the block controls the power developed in the heating element according to the desired time function: $T_B = T_B(t)$. Any change in heat fluxes coming from the calorimetric vessels is automatically compensated by the main loop and the temperature of the calorimetric block is maintained according to the actual program value. The actively programmed thermostat described has an additional advantage: it can be (and is) used as an isothermal thermostat for pressure-scanning [2] or volume-scanning calorimetric measurements.

Linear variations of pressure

Pressure as an independent thermodynamic variable has two advantages: it is an intensive parameter and the propagation of its local changes is very fast (especially in fluid medium) over the whole volume. These features enable a pressure program to be achieved with all the elements of the programming system placed outside the calorimeter, the calorimetric vessels being connected to it through pressure-proof capillaries. Thus, the pressure system consists of an internal part introduced into the calorimeter and an external part placed outside the calorimeter. The pressure in such a system can be varied either by changing the volume or temperature of the external part, the internal part being kept under strictly isothermal conditions. In both cases the programming system should be active, i.e., the executing element must be controlled by the difference between the actual value resulting from the program and the actual pressure in the system. When the pressure program is realized through passive programming, e.g., by linear variation of volume or temperature of the external part, then a volume change in the substance under investigation causes the program to become nonlinear, and the resulting calorimetric thermogram is distorted. An obvious example of such a situation was observed experimentally for the pressure-induced fusion of di-phenyl-ether [2]. Of course, even in the case of passive programming, one can obtain good results when the volume of the external part is a number of orders of magnitude larger than the volume of the internal part. A similar situation can be observed in temperature programming when the large heat capacity of the calorimetric block is insensitive to heat fluxes coming from the much smaller heat capacity of the substance under investigation. However, in both cases the inertia of such systems is very high and from both the energetic and safety points of view

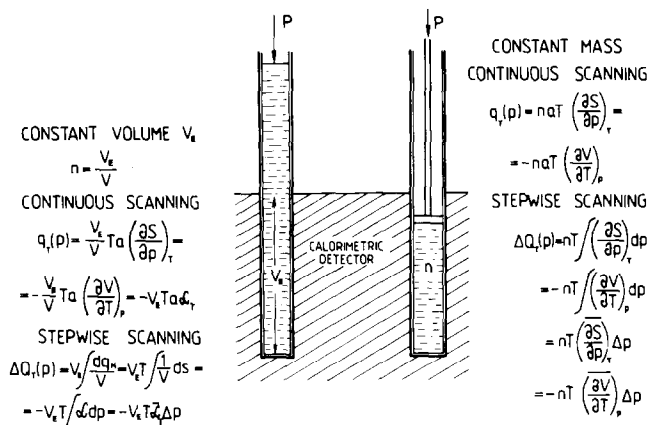


Fig. 7. A diagram and thermodynamic formulae for two methods of pressure transmission into the calorimetric vessels.

such systems are much less advantageous than the corresponding active systems.

The use of pressure as an independent thermodynamic variable has another characteristic feature: the method of its transmission into the sample under investigation has an enormous influence on the thermodynamic significance of the thermal effect generated or absorbed in the process [26]. There are two main methods of pressure transmission into the calorimeter: (1) through the liquid under investigation, or (2) by means of a piston placed in the calorimetric vessel. These two situations are schematically presented in Fig. 7. When pressure is transmitted through the liquid under investigation, its mass in the calorimetric vessel changes during the experiment; the volume, V_E , in which it is contained remains almost constant and is determined in a separate calibration procedure. When pressure is programmed as a linear function of time the power, in this particular case, is described by the following equation

$$q_T(p) = \pm \frac{V_E}{V} Ta \left(\frac{\partial S}{\partial p} \right)_T = - [\pm V_E Ta \alpha_T] \quad (75)$$

where α_T is the volume thermal expansion of the substance under investigation. When a similar experiment is performed with the use of a piston, the mass, expressed in numbers of moles, n , remains constant and the power is described by the following equation

$$q_T(p) = \pm naT \left(\frac{\partial S}{\partial p} \right)_T = - \left[\pm naT \left(\frac{\partial V}{\partial T} \right)_p \right] \quad (76)$$

Thus, it is clear that the experiment with constant mass gives information on the thermodynamic derivative itself, while that with constant experimental volume gives information on the ratio of the thermodynamic derivative to

the molar volume of the substance under investigation. In practice, in pressure-controlled calorimeters these two situations very often coexist, for example, when the substance investigated is placed in a bellows and the pressure is transmitted through a liquid [2].

For comparison, in Fig. 7 formulae are also given for the stepwise scanning of pressure (the integral form of pressure-controlled scanning calorimetry) called the piezothermal method by Ter Minassian and Pruzan [27]. It can be seen that in this case one obtains information on the mean values of thermodynamic quantities over the range of applied pressure steps. A similar situation exists in temperature-controlled scanning calorimetry [28].

THE SCANNING CALORIMETRY OF FIRST-ORDER PHASE TRANSITIONS

It has already been stated that the scanning calorimeter is an instrument which measures the power generated or absorbed by a process of linear variation of an independent thermodynamic variable. In the preceding paragraphs these two functions were analysed separately. In the practical experiment these functions must be considered together and should be correctly adapted to the actual metrological requirements. Powers $q_p(T)$, $q_V(T)$, $q_T(p)$, and $q_T(V)$ are the input signals and they are observable only by means of the calorimetric output signal. Thus, all deformations of the input signal by the calorimeter are very important in the interpretation of the results of a scanning calorimetry experiment. A detailed analysis is presented below for the case of a first-order phase transition of a pure substance induced by pressure and temperature. The analysis given by O'Neill [1] for temperature-induced fusion showed that the power of fusion developed in the calorimetric vessel for a small time increment can be described by the following equation

$$q_{p,\text{fus}}(T) = \frac{bt}{k_s} \quad (77)$$

In the case of pressure-induced fusion this power is described by the following equation [3]

$$q_{T,\text{fus}}(p) = \frac{at}{\left(\frac{dp}{dT}\right)_{T_\tau} k_s} \quad (78)$$

where $(dp/dT)_{T_\tau} = \Delta S/\Delta V|_{T_\tau}$ for the phase change in the substance investigated.

Equations (77) and (78) correctly describe the power of fusion to 1% error if the mass of the sample, m , placed in the calorimetric vessel fulfils the

following relation [3]

$$m \leq 0.01 A^2 \rho \lambda k_s \quad (79)$$

where A is the active area of heat exchange in the calorimetric vessel, ρ is the density of the liquid layer and λ is the liquid heat conductivity of the substance investigated. It is worth noting that the power of fusion described by eqns. (77) and (78) does not depend on the physical parameters of the substance investigated. On the other hand, the size of the sample depends not only on the heat exchange conditions in the calorimetric vessel ($A^2 k_s$) but also on the product ($\rho \lambda$) of the heat conductivity of the substance investigated and its density. Equations (77) and (78) describe the power absorbed during fusion in the calorimetric vessel; however, it is observable only by means of the calorimetric output signal. When investigating this problem more carefully, one should notice that eqns. (77) and (78) are very similar to eqn. (25), describing the model input signal analysed in this paper. The parameters r and d in eqn. (77) have the following physical meanings for temperature-induced fusion

$$r = \frac{b}{k_s} \quad \text{and} \quad d = \left(\frac{2mlk_s}{b} \right)^{1/2} \quad (80)$$

and for pressure-induced fusion (eqn. 78)

$$r = \frac{a}{k_s \left(\frac{dp}{dT} \right)_{T_T}} \quad \text{and} \quad d = \left[\frac{2mlk_s}{a} \left(\frac{dp}{dT} \right)_{T_T} \right]^{1/2} \quad (81)$$

where l is the specific heat of fusion of the substance under investigation. When introducing these quantities into eqn. (25), one can directly use the model considerations concerning the dynamic errors presented above. Of course, it must be assumed that the values of r and d remain constant during fusion. From a practical point of view, especially interesting are the two cases presented in Figs. 3a and in 3d. The figures have been made using reduced time (time divided by the main time constant of the calorimeter), so they have a universal meaning. One can also easily transform the abscissa to temperature or pressure values by using the rates of linear variations of these parameters. One can distinguish in Fig. 3a two important areas of dynamic error in the time domain: (1) the dynamic error in the course of fusion, and (2) the dynamic error after the end of fusion. From a practical point of view, the second area is of least importance, while the first one is of prime importance for the application of scanning calorimetry to purity determinations and, generally, to investigations of phase transitions. It is worth noting from Fig. 3a and eqn. (25), together with eqns. (80) and (81), that the time constant of the calorimetric vessel has an influence on both the shape of the thermogram of fusion and the value of the intercept of the straight stationary line of the thermogram with the time (pressure, temperature) abscissa.

Thus, use of this technique in comparative investigations always requires such standards for such quantities, so as to not change the time constant of the calorimeter with respect to the sample under investigation. Otherwise, errors are made in the determination of fusion parameters (temperature, pressure), which can even lead to the discovery of impurities in a pure substance, and vice versa, or to their interpretation as strange melting phenomena. The best technique is, however, to reduce the time constant of the calorimeter properly; as a result, not only are the dynamic errors during the course of fusion smaller, but also the dynamic error represented by the second area in Fig. 3a is reduced and the measurement time is shortened. From Fig. 3d one can make some conclusions concerning the dependence of the relative dynamic error on the experimental properties. It can be seen that the relative dynamic error is always reduced when the ratio d/τ_c is high. Therefore, from this point of view it is advantageous to reduce the time constant of the calorimeter as much as possible and to increase the period, d . Using eqns. (80), (81) and (28) or (30), one can choose, for a given experiment, a value of the rate of variation of a thermodynamic variable so as to minimise the dynamic error or to achieve a compromise between the dynamic precision needed and the time devoted to the experiment itself.

ACKNOWLEDGEMENT

This work has been carried out as a part of the Polish Academy of Sciences basic research program 03.10.1.7.2.

LIST OF SYMBOLS

A	active area of the calorimetric vessel (cm^2)
a	rate of linear variation of pressure (Pa s^{-1})
α	actual parameter vector
α_0	initial parameter vector
α_B	coefficient of heat exchange between the calorimetric block and heating shield (W K^{-1})
α_C	coefficient of heat exchange between the measuring vessel and thermostat (W K^{-1})
α_H	coefficient of heat exchange between the heating shield and outside environment (W K^{-1})
α_R	coefficient of heat exchange between the reference vessel and thermostat (W K^{-1})
α_{RM0}	coefficient of heat exchange between the reference material and environment (W K^{-1})
α_{RMR}	coefficient of heat exchange between the reference material and reference vessel (W K^{-1})

α_{SMC}	coefficient of heat exchange between the sample material and measuring vessel (W K^{-1})
α_{SM0}	coefficient of heat exchange between the sample material and environment (W K^{-1})
α_T	isobaric volume thermal expansion of the substance under investigation (K^{-1})
b	rate of linear variations of temperature (K s^{-1})
c	rate of linear variations of volume ($\text{cm}^3 \text{s}^{-1}$)
C_C, C_R	heat capacities of the measuring and reference vessels, respectively (J K^{-1})
C_{SM}, C_{RM}	heat capacities of the sample and reference materials, respectively (J K^{-1})
d	period of the input power evolution (s)
$\Delta_{\text{dyn},t}$	absolute dynamic error in the time domain
$\delta_{\text{dyn},p}$	relative parameter induced error
$\delta_{\text{dyn},t}$	relative quadratic error in the time domain
$G(s)$	transfer function of a passive system
$G_C(s)$	transfer function of the calorimeter
$G_d(s)$	complex dynamic gain of the calorimeter
H	molar enthalpy (J mol^{-1})
$H(s)$	transfer function of an active system
$H_C(s)$	transfer function of the power compensated calorimeter
j	imaginary number
K	total static gain of the calorimeter
k_{el}	static gain of the calorimetric amplifier (W K^{-1})
k_s	static gain of the calorimeter (K W^{-1})
l	specific heat of fusion of the substance under investigation (J g^{-1})
λ	heat conductivity of the substance under investigation in the liquid state ($\text{W cm}^{-1} \text{K}^{-1}$)
m	mass (g)
n	number of moles (mol)
ω	angular frequency (rad s^{-1})
p	pressure (Pa)
Q	molar heat (J mol^{-1})
q_{IN}	input power signal (W)
q_{OUT}	power output signal of the compensated calorimeter (W)
$q_p(T)$	isobaric molar power (W mol^{-1})
$q_T(p), q_T(V)$	isothermal molar powers (W mol^{-1})
$q_V(T)$	isochoric molar power (W mol^{-1})
r	rate of linear power variation (W s^{-1})
ρ	density of the liquid layer (g cm^{-3})
S	molar entropy ($\text{J mol}^{-1} \text{K}^{-1}$)
s	Laplace operator

$S_{\alpha_c}^{G_c}(s)$	sensitivity function of the diathermic calorimeter
$S_{\alpha_c}^{\tilde{G}_c}(s)$	sensitivity function of the diathermic calorimeter with respect to the heat exchange coefficient
$S_{\tau_c}^{\tilde{G}_c}(s)$	sensitivity function of the diathermic calorimeter with respect to the time constant
$S_{G_c}^H(s)$	sensitivity function of the compensation loop
$\sigma(t, \alpha_0)$	output sensitivity function defined in the time domain
T	temperature (K)
T_C, T_R	temperatures of the measuring and reference vessels, respectively (K)
T_{SM}, T_{RM}	temperature of the sample and reference materials, respectively (K)
T_T	temperature of the thermostat (K)
t	time (s)
τ_C, τ_R	time constants of the measuring and reference vessels, respectively (s)
τ_{RM}, τ_{SM}	time constants of the reference and sample materials, respectively (s)
θ	output signal of the differential diathermic calorimeter (K)
U	molar internal energy (J mol^{-1})
V	molar volume ($\text{cm}^3 \text{mol}^{-1}$)
V_E	internal volume of the calorimetric vessel (cm^3)

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