Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 432 (2005) 169–176
thermochimica acta
www.elsevier.com/locate/tca

About models and methods to describe chip-calorimeters and determine sample properties from the measured signal

G.W.H. Höhne*, W. Winter

Ifa GmbH, Gehrnstr. 49, 89081 Ulm-Jungingen, Germany

Received 1 December 2004; received in revised form 3 February 2005; accepted 5 February 2005
Available online 4 March 2005

Abstract

Different models used to describe chip-calorimeters and to simulate their thermal behavior are presented together with the physical basics of heat transfer. Different methods to deconvolute the measured signals are explained. One model example for a certain chip-calorimeter is given in more detail to show the procedure.

Keywords: Calorimetry; Model; Chip-calorimeter; IC calorimeter; Heat capacity

---

1. Introduction

During the last years so-called chip- or IC-calorimeters have more and more been used to measure caloric and other thermal properties of small samples. They are even suitable to measure the respective properties of thin films. The advantages of these very small calorimeters are the small size, a low thermal inertia, a rather small time constant and a high sensitivity. However, the theory of such calorimeters and the mathematics for the deconvolution of the sample properties from the measurements is much more complicated than for common calorimeters. The pathway of the heat flow cannot be approximated by a one-dimensional model and the heat capacity of the sample is often in the same order of magnitude as the heat capacity of the calorimeter "cell", which in many chips consists only of a very thin silica membrane. In classical calorimeters the "cell" is much larger in mass and heat capacity than the sample. This is done to avoid an influence of the sample on the sensitivity of the calorimeter and free the calibration factor from sample properties.

At those times, when the classical calorimeters were built, no computers existed and all evaluation was done by hand. Therefore there was a need for simple formulas and methods to calculate the quantities of interest from the measured curves. The construction of the calorimeters was such to give a signal strictly proportional to the heat flow rate into the sample itself with a "calibration factor" almost not influenced by the heat transfer to the sample and its heat capacity. The price to be paid for this comfort was a rather low sensitivity of the calorimeter, with a need of large samples, and large time constants in the range from some seconds up to many minutes in the case of very sensitive "micro calorimeters".

Nowadays PCs in laptop size are available for everyone with a computing power comparable to mainframe computers filling a large room in the seventies. With this hardware and modern computer algebra systems it became possible for everyone to solve even complicated differential equation systems and calculate the quantities of interest. It is possible to calculate the heat flow rate into the sample in dependence of the sample temperature "online" during the measurement proceeds. Such techniques enable the scientist to construct very sensitive, small calorimeters with low time constants in the millisecond region and get reliable results even for very small samples and fast processes. This opens the door to caloric properties as well as to thermodynamics of thin films.

The aim of this review article is to give a detailed overview over suitable methods used in practice and explain the line

---

* Corresponding author.
E-mail address: g.w.h.hoehne@tue.nl (G.W.H. Höhne).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.02.008

of proceeding on the basis of commercially available chip-calorimeters. In the last chapter one possible way to model a commercial chip-calorimeter is presented as an example. This is, of course, not the only way to model such calorimeters, it may, however, serve as a guideline for other setups as well as an example for the power and success of this type of modeling.

2. Models and methods

2.1. Physical basics

Heat and heat flow rates are determined in most of the calorimeters by measuring temperatures or temperature differences. Heat needs temperature gradients to flow. For the transport of energy in form of heat Fourier's law is valid:

$$\mathbf{J}_q = -\boldsymbol{\lambda} \cdot \operatorname{grad} T \tag{1}$$

where $\mathbf{J}_q$ the energy (heat) flux vector, $\boldsymbol{\lambda}$ the thermal conductivity tensor and T the temperature. For the one-dimensional case and stationary conditions this vector equation simplifies to

$$\phi = -\frac{\boldsymbol{\lambda} a}{\Delta x}\Delta T \tag{2}$$

where ϕ is the heat flow rate, a the cross section area, Δx the length of the heat conducting path and $\Delta T = T_{\text{sample}} - T_{\text{furnace}}$ the temperature difference along this path. This equation is the fundamental equation for classical calorimetry. The construction principle of the calorimeters is done in such a way, that this simple equation becomes valid. The heat flow rate is proportional to the measured temperature difference with the proportionality coefficient K the so-called "calibration factor" of this calorimeter:

$$\phi = -K\,\Delta T \tag{3}$$

where K is the apparent thermal conductance of the (one-dimensional) heat flow pathway. The reciprocal quantity $1/K = R_{\text{th}}$ is the (apparent) thermal resistance of the heat conducting path.

As mentioned before the measured quantity to determine the heat flow rate in calorimeters is the temperature. Therefore the knowledge of the temperature field in dependence on position and time is of great importance. An important equation in this context is the "heat conduction equation":

$$\frac{\partial T}{\partial t} = D_{\text{th}}\nabla^2 T \quad \text{with} \quad D_{\text{th}} = \frac{\boldsymbol{\lambda}}{\rho c_p} \tag{4}$$

where D_{th} is the thermal diffusivity, ρ the density, c_p the specific heat capacity and ∇^2 the Laplace operator. It is assumed, that D_{th} does not depend on temperature or time, a simplification which normally holds for practical purposes. This partial differential equation describes the time dependent diffusion of the temperature (i.e. the change of the temperature field) in a uniform condensed medium via energy transport. A wave-like solution of the differential equation has the form:

$$T = T_0 \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \tag{5}$$

with ω is the angular frequency, $\mathbf{k}$ the wave vector and $\mathbf{r}$ the radius vector. Eq. (5) is a solution of the differential Eq. (4) if $D_{\text{th}}k^2 = i\omega$, this describes the so-called dispersion relation for that case.

In the one-dimensional semi-infinite case when the temperature at $z = 0$ is varied periodically with time like

$$T(0, t) = T_A \cos\omega t \tag{6}$$

the solution reads (for details see textbooks of thermal physics):

$$T(z, t) = T_A \exp\left(-\frac{z}{\delta}\right)\cos\left(\omega t - \frac{z}{\delta}\right) \tag{7}$$

with $\delta = (2D_{\text{th}}/\omega)^{1/2}$ a characteristic length. Eq. (7) characterizes a highly damped periodic wave; at a penetration depth of $z = \delta$ the original temperature amplitude T_{A} is reduced by $1/e$. This is a distance equal to the wavelength divided by 2π.

Another solution of the differential Eq. (4) for this one-dimensional case describes the time development of the temperature in response on a pulse $Q\delta(0, t)$ which at $t = 0$ has the form of a Dirac delta function localized at $x = 0$:

$$T(x, t) = \theta(t)\frac{2q}{\rho c_p}(4\pi D_{\text{th}}t)^{-1/2}\exp\left(-\frac{x^2}{4D_{\text{th}}t}\right) \tag{8}$$

where q is the density (per unit area) of the heat-pulse at the surface. The function has the shape of a (half) Gaussian curve. It can be shown that the width of the temperature distribution increases proportional to $(D_{\text{th}}t)^{1/2}$.

For the two- and three-dimensional case, respectively, Eq. (8) changes somewhat:

$$\begin{aligned} T_2(\mathbf{r}, t) &\propto (t)^{-1}\exp\left(-\tfrac{r^2}{4D_{\text{th}}t}\right) \\ T_3(\mathbf{r}, t) &\propto (t)^{-3/2}\exp\left(-\tfrac{r^2}{4D_{\text{th}}t}\right) \end{aligned} \tag{9}$$

The curve at a certain time t is still Gaussian type but points in the direction of the radius vector $\mathbf{r}$ rather than in x direction, whereas the decrease at a certain position becomes faster with increasing number of dimensions.

An exact solution of the partial differential Eq. (4) in three dimensions for given boundary and initial conditions is generally not possible and another way to describe the heat transport behavior of chip-calorimeters has to be found.

2.2. The one-dimensional heat flow path method

In the early time of calorimetry the calorimeters were constructed in such a way that the heat flux pathway is linear. Both plane and radial symmetric solutions were used in practice to get a one-dimensional or quasi one-dimensional heat flow pathway. The famous pioneer Tian derived the following equation which connects the measured temperature difference ΔT with the heat flow rate ϕ for this case:

$$\phi(t) = C_p\beta + \phi_r(t) = -\frac{\Delta T(t)}{R_{th}} - \frac{\tau}{R_{th}}\frac{d\Delta T(t)}{dt} \tag{10}$$

where ϕ_r is the heat flow rate of any reaction in the sample, C_p the heat capacity, $\beta = dT/dt$ the heating rate and $\tau = R_{th}C_p$ the time constant of the temperature relaxation. This is a differential equation for the measured ΔT signal. From this equation follows that ΔT is generally *not* proportional to the heat flow rate to/from the sample. Only in the case of stationarity (where $d\Delta T/dt = 0$) and in absence of thermal events in the sample ($\phi_r = 0$), the proportionality holds and Eq. (10) simplifies to Eq. (3).

However this equation describes a very simplified case, both quantities R_{th} and C_p are effective (apparent) quantities, they contain not only sample properties, but even contributions of the sample container, the support and the calorimetric cell. To get the heat flow rate into the sample, which is the quantity of interest in calorimetry, a twin arrangement with two calorimeters, one for the sample and one for the reference is often used. The two identical calorimeters, with an identical but empty sample container on the reference side, are placed together in one heating device (furnace). In the case of ideal symmetry the differential signal (i.e. $\phi_S - \phi_R$) reproduces the heat flow into the sample, all other contributions no longer apply this way. If we write down Eq. (10) for the sample and the reference side separately and subtract both from one another, we get, after some simplifications an equation which looks similar to Eq. (10), but now with the heat flow rate into the sample $\phi_S - \phi_R = \phi_{sample}$ (the quantity of interest) on the left hand side and with another temperature difference, namely $\Delta T = T_{sample} - T_{reference}$, on the right hand side. R_{th} and τ are the same for both sides if perfect symmetry is assumed. Therefore Eq. (10) can be used as well to model all differential (scanning) calorimeters with a one-dimensional heat flow pathway.

The solution of such a linear differential equation of 1st order for a heat pulse (or temperature step) event reads:

$$\Delta T(t) = k_1 \exp\left(-\frac{t}{\tau}\right) \tag{11}$$

This is a relaxation equation; the measured temperature difference drops exponentially towards zero, whereas the original event is a heat pulse (temperature step). The relaxation method allows determining the time constant τ of the calorimeter easily from the temperature step answer of the calorimeter. With that value, Eq. (11) is known and it is possible to deconvolute the real heat flow rate function produced by the sample from the measured heat flow rate function via Fourier transform and division in Fourier space followed by inverse Fourier transform [1,2]. It is also possible to introduce the measured $\Delta T(t)$ function into Eq. (10) and calculate the sample heat flow rate this way.

The model can be improved further by dividing the thermal path into several thermal resistances and heat capacities in series. This results in a linear differential equation of higher order, the solution for a heat pulse (temperature step answer) is now a sum of exponential functions with different time constants and different factors:

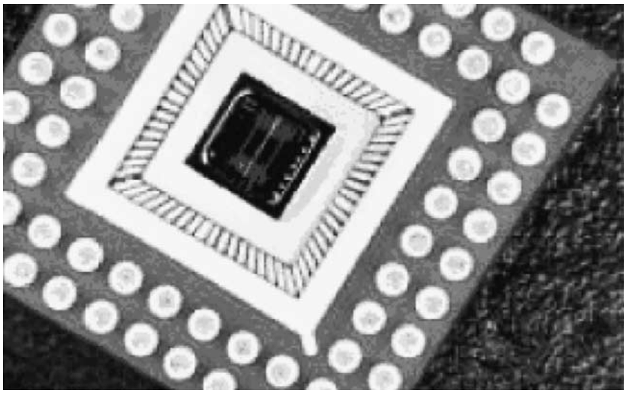

Fig. 1. Chip-calorimeter LCM-2506 from Xensor Integration [6].

$$\Delta T(t) = k_0 + k_1\,e^{-(t/\tau_1)} + k_2\,e^{-(t/\tau_2)} + k_3\,e^{-(t/\tau_3)} + \cdots \tag{12}$$

In practice, in the case of not too complex models with too many parameters, the different parameters can again be determined from suitable calibration experiments. One possibility is to perform a pulse like thermal event and measure the calorimeter response. With proper curve fitting algorithms it is in some cases possible to calculate the respective parameters properly.

However, the one-dimensional method is an approximation only. The advantage of a rather simple mathematical model is linked with the disadvantage of a rather massive calorimeter cell to get a sample-independent calibration factor and a large thermal resistance for high sensitivity. As a result the response time (time constant) and the heat relaxation time (thermal lag) are large as well which makes these common calorimeters unsuited to measure fast events in small samples and thin films. For such purposes chip- or IC-calorimeters have been developed with response times in the millisecond region, but for these calorimeters the one-dimensional approximation for the heat flow pathway is seldom sufficient to give precise results and improved models have to be applied.

2.3. Network models

A calorimeter is always a three-dimensional thing and the pathway of the energy from the heater to the sample is never only one-dimensional. In reality there is a whole network of pathways where the heat can flow from the hotter to the colder parts of the calorimeter. This is in particular true for chip-calorimeters like that shown in Fig. 1. It is often possible to divide the calorimetric setup into different parts of a certain (apparent) heat capacity which are connected together with thermal conductance of a certain (apparent) conductivity. This results in a three-dimensional network of capacities (nodes) and thermal resistances (paths) which can serve as an approximation of the real setup. The finer the subdivision is done the better is the approximation for the calorimeter. In the limit of infinite fine subdivision, the network reproduces the reality exactly. This so-called finite elements method (FEM) is, however, well known and often used in engineering to calculate mechanical and thermal behavior of constructs of different kind but needs often a higher computing expense.

The mathematical procedure of the FEM method starts from the energy conservation law: for every node the change of the stored energy equals the difference of incoming and outgoing heat fluxes. There are contributions from exchanged heat, caused by temperature differences toward the neighbor nodes, and from heat production or consumption caused by reactions or transitions inside the node (latent heat). For every node a differential equation like Eq. (10) can be formulated, which contains all exchanged, produced and stored heat flow rates, the heat capacity of the node and the temperature differences against all neighbor nodes together with the respective thermal resistances. For a not too large number of nodes this system of linear differential equations can be simplified and solved in a way to result in an equation which connects the heat flow rate into the sample (or the sample heat capacity) with the measured temperatures or temperature differences. We shall present an example of such a network approximation in the application section below. It should be mentioned that some powerful computer algebra systems exist on the market which can be very helpful to get reliable results. It is clear, that the mathematical solution of the system of differential equations becomes the more difficult the higher the number of nodes and equations is. It is a good idea to restrict the number of nodes to a minimum by clever modeling of the essential parts of the calorimetric setup and by a decision in advance which thermal pathways are dominant and which may be neglected.

Anyway, the solution got this way contains the heat capacity of all nodes of the model as well as the thermal resistances of their connections. Some of these are known from material databases if the respective material is known, other are unknown and have to be determined properly in adequate calibration experiments. The properties of the nodes belonging to the calorimeter itself are, as a rule, fixed and do not change for different experiments, whereas the properties of the sample and its thermal connection to the calorimeter are, of course, not constant but change from measurement to measurement.

The method described so far is, however, an approximation of the reality only. The result is therefore not exact and careful error evaluation must be done to determine the uncertainty of the respective calorimetric results. A more professional way to model the calorimetric setup takes care of the finite element method which divides the equipment into a sufficient number of sufficient small pieces (nodes) connected in three dimensions. This results again in a system of differential equations, which in practice are approximated by a system of linear equations, where the differentials are substituted by (small) differences. This system of equations can be evaluated recursively using the methods of numerical matrix algebra. It is obvious, that this method is expensive and needs some experiences to be successful. However, powerful professional software is available which helps the user with all details starting from automatic modeling of the finite elements, up to calculation of the temperature and heat flow fields, both for stationary and time dependent cases, for all thinkable initial and boundary conditions. This way it is easily possible to extract the heat flow rate into the sample, as well as at any position of the setup. Nowadays FEM software runs easily on modern PCs but is, of course not cheap and the user has to invest a lot of time to gain experiences. Furthermore the material properties (heat capacities and thermal conductivities) must be known for every part of the equipment, it is not possible to determine such properties this way. The only way is to compare the simulated results with the measured ones and see whether these fit together.

2.4. Linear response methods

The methods presented so far start from a known calorimetric setup with known properties and calculate the temperature and/or the heat fluxes at, say, sample position. Methods founded on the theory of linear response [2,3] start from the measured thermal response of the equipment with and without sample and calculate the heat flow rate into the sample (and other quantities) from those functions.

Within linear response theory any system is described as a box with an “input” and an “output”. The system reacts on a certain input (stimulus) with a certain output (response). Special input functions are the step-function and the pulse-function, the respective output functions are the step-response and the pulse-response, respectively. The step- and pulse-functions can be transformed into one-another by differentiation and integration, respectively. The same is true for the respective response functions.

The Fourier-transformed pulse-respond function is called transfer function of the system; it plays an important role in transfer theory. For linear systems it is known that the overall transfer function of a network can be calculated from the transfer functions of the individual components. The overall transfer function of components connected in series is the product of the individual transfer functions. If the components are connected in parallel the total transfer function is the sum of the transfer functions of the individual components.

For calorimeters the input function (stimulation) is often the temperature as a function of time and the output function (response) is the measured heat flow rate (more precise a voltage proportional to it). As mentioned before this signal is generally not the heat flow rate into the sample, which is the quantity of interest, but delayed in time and “smeared” in the case of thermal events inside the sample. To get the true sample properties we take advantage of the transfer functions of the setup (both with and without sample). The respective transfer functions are gotten by producing a heat pulse (or temperature step) inside the sample or on the sample site in the empty calorimeter and measuring the resulting heat flow rate response in time. Such pulses can be caused by Laser flashes or sudden crystallization of (heavily) supercooled pure substances. Fourier transform yields the respective transfer functions. What the heat flow concerns, the calorimeter and the sample are connected in series and the respective functions have to be multiplied to get the total transfer function. To get the sample transfer function the total transfer function has to be divided by the transfer function of the empty calorimeter. Inverse Fourier transform of the result yields the pulse response of the sample itself which allows calculation of thermal properties as thermal resistance and apparent heat capacity.

If we know the transfer function of a calorimetric setup we are able to calculate the true heat flow rate into the sample from the measured one. The procedure is the same as before, the measured heat flow rate function has to be Fourier-transformed, divided by the transfer function of the setup and re-transformed again.

3. Application examples

3.1. Examples from literature

Some of the above mentioned methods have been used to model conventional calorimeters and their heat transfer behavior, for details see Ref. [2]. The mostly used method was that, taking care of the one-dimensional heat flow pathway and using a twin arrangement and measure the differential heat flow rate. This method has also been applied to a chip-calorimeter by Allen and co-workers [4]. For a single chip-calorimeter the (one-dimensional) relaxation method was applied but in a somewhat modified form to include not only heat conduction but even radiation heat exchange [5].

However, the one-dimensional approximation can generally not be used for common chip-calorimeters, because most chip-calorimeters, even those available on the market [6,7] are originally not constructed for this purpose. The heater does, in many cases, not cover the whole area below the sample, and the chip, as well as the thermometer (thermocouples), are not radial-symmetric constructed (see Fig. 1). As a result the RC-network is more complex and the one-dimensional method adds only up to a rather poor approximation of the truth, nevertheless the one-dimensional approximation has successfully been used in practice (see e.g. Refs. [8,9,17]). Other authors used simple or more complex RC networks in two or three dimensions to model chip-calorimeters [10–13]. In the case of more complex models they solved the system of equations with computer algebra systems [12]. Even the more expensive FEM method has successfully been used to model chip-calorimeters [14]. Also method of linear response was applied, both for simple and more detailed models, in particular when temperature-modulated or pulse techniques were used [10,15,16]. All methods used have both advantages and disadvantages and no one can generally be recommended, because the respective chip-calorimeters and applications are too different. The scientist has to decide what method is most suitable for the current purpose. We shall give an example in what follows which may serve as a guideline how to come to a suitable compromise between mathematical expense and precision of the model.

3.2. Detailed example

Details of the chip-calorimeter presented here have been published before [11]. The basis of the calorimeter is the chip LCM-2506 from Xensor Integration [6] (Fig. 1). This chip consists of a thin silicone membrane in a thicker silicone rim. In the middle of the membrane is a (one-dimensional) heater between it and the rim a thermopile is integrated to measure the temperature difference between the sensitive center of the membrane and the rim. An integrated diode temperature sensor allows measuring the temperature of the rim separately. Fig. 2 shows a schematic drawing of the left to right cross section through the chip. The silicone rim is glued into a ceramic pin-grid array (PGA). In the real calorimeter the chip is connected top down (with the heater bottom side of the membrane) to a silver furnace which can be precisely temperature controlled. The calorimeter can be driven (i) conventionally, by heating the furnace linearly in time, (ii) isothermally, keeping the furnace temperature constant and (iii) in pulse mode, using the heater of the membrane to produce heat pulses or temperature steps. In every case the temperature difference signal from the thermopile and the temperature of the rim are measured as functions of time.

3.2.1. The model

The construction of this chip and the calorimetrical setup is certainly not one-dimensional and not cylinder-symmetric either. Even the simplest possible model for this chip-calorimeter contains several heat paths and nodes (Fig. 3). One node (F) replaces the furnace and the ceramic frame, which are thermally connected. The temperature of the furnace T_F is controlled and therefore given, furthermore the heat capacity (C_F) of this massive part is assumed to be infinite. One node (M) replaces the membrane with the heater and the hot junctions of the thermopile; it is thermally coupled to the rim (R) as well as to the furnace, the latter by convection and radiation heat transfer. The rim, in turn, is glued and thus coupled to the chip frame. On top of the membrane the sample (S) is positioned, but it is coupled to the furnace too (again via convection and radiation heat transfer). The different R_{ik} characterize the apparent thermal resistances of the five different pathways where the heat can flow. The C_i characterize the apparent heat capacities of the respective nodes.

The system of equations, describing the thermal behavior of this simplest possible network model, is obtained from the physical condition, that for every node the sum of all thermal fluxes must be zero (conservation of energy) and that for every loop the sum of temperature differences must

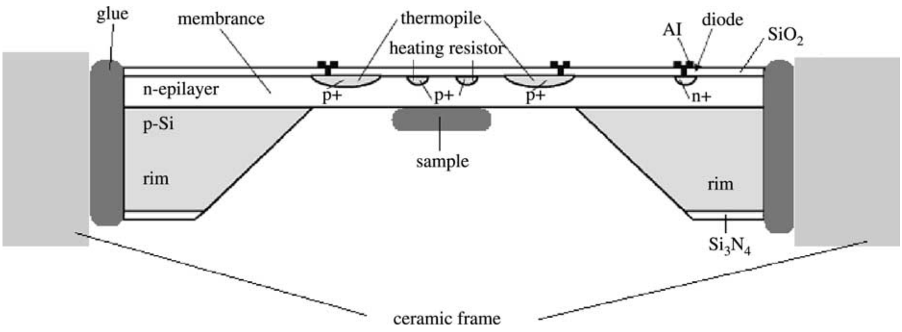

Fig. 2. Cross section scheme of the LCM-2506 chip according to [6].

be zero too. Therefore the following set of equations can be established using Fourier's law (in the one-dimensional form of Eq. (2)):

$$\begin{aligned}
&C_\mathrm{M}\frac{\mathrm{d}T_\mathrm{M}}{\mathrm{d}t}-\frac{T_\mathrm{M}-T_\mathrm{R}}{R_\mathrm{RM}}-\frac{T_\mathrm{M}-T_\mathrm{S}}{R_\mathrm{MS}}-\frac{T_\mathrm{M}-T_\mathrm{F}}{R_\mathrm{FM}}=\phi_\mathrm{heater}\\
&C_\mathrm{R}\frac{\mathrm{d}T_\mathrm{R}}{\mathrm{d}t}-\frac{T_\mathrm{R}-T_\mathrm{F}}{R_\mathrm{FR}}-\frac{T_\mathrm{R}-T_\mathrm{M}}{R_\mathrm{RM}}=0\\
&C_\mathrm{S}(t)\frac{\mathrm{d}T_\mathrm{S}}{\mathrm{d}t}+T_\mathrm{S}\frac{\mathrm{d}C_\mathrm{S}(t)}{\mathrm{d}t}-\frac{T_\mathrm{S}-T_\mathrm{F}}{R_\mathrm{FS}}-\frac{T_\mathrm{S}-T_\mathrm{M}}{R_\mathrm{MS}}=0\\
&T_\mathrm{F}(t)=T_0+\beta_0 t
\end{aligned}\tag{13}$$

and in addition the trivial relations:

$$\begin{aligned}
(T_\mathrm{M}-T_\mathrm{F})&=(T_\mathrm{M}-T_\mathrm{R})+(T_\mathrm{R}-T_\mathrm{F})\\
&=(T_\mathrm{M}-T_\mathrm{S})+(T_\mathrm{S}-T_\mathrm{F})
\end{aligned}$$

which hold for the respective time derivatives as well.

The equation system (13) links the given quantities ϕ_heater and T_F with the unknown (apparent) heat capacity of the sample $C_\mathrm{S}(t)$, the temperatures T_M, T_R and T_S. In the present form there are only three equations for four variables and in addition seven originally unknown parameters R_{ik} and C_i, the problem cannot be solved without further simplifications or additional conditions. One possibility is to measure the signal of the thermopile and introduce $\Delta T=T_\mathrm{M}-T_\mathrm{R}$ into the system as a known quantity. Now the system of equations can, in principle, be solved for, say, the apparent heat capacity of the sample $C_\mathrm{S}(t)$ in dependence of the given furnace temperature $T_\mathrm{F}(t)$, heater power $\phi_\mathrm{heater}(t)$ and thermopile signal $\Delta T(t)$, if the values of the other parameters can be determined somehow.

The system is, of course still rather complex and a solution not easy to get, so it is a good idea to try to simplify the system and estimate the magnitude of the parameters. In a first step the thermal resistance R_FR between the rim and the PGA was considerably reduced using a special glue with high thermal conductivity (containing silver powder) instead of the originally epoxy glue. As a result R_FR becomes very low and $(T_\mathrm{R}-T_\mathrm{F})$ can be neglected or $T_\mathrm{R}=T_\mathrm{F}=T_0+\beta t$. The system of equations can now be simplified, but the parameters are still unknown.

3.2.2. *The chip-calorimeter without sample*

The R_{ik} and C_i of the nodes belonging to the chip itself can be determined in experiments without sample. In this case the right hand node in the model (Fig. 3) can be dropped and the set of Eq. (13) for the empty chip-calorimeter simplifies:

$$\begin{aligned}
&C_\mathrm{M}\frac{\mathrm{d}T_\mathrm{M}}{\mathrm{d}t}-\frac{T_\mathrm{M}-T_\mathrm{R}}{R_\mathrm{RM}}-\frac{T_\mathrm{M}-T_\mathrm{F}}{R_\mathrm{FM}}=\phi_\mathrm{heater}(t)\\
&C_\mathrm{R}\frac{\mathrm{d}T_\mathrm{R}}{\mathrm{d}t}-\frac{T_\mathrm{R}-T_\mathrm{F}}{R_\mathrm{FR}}-\frac{T_\mathrm{R}-T_\mathrm{M}}{R_\mathrm{RM}}=0\\
&T_\mathrm{F}(t)=T_0+\beta_0 t
\end{aligned}\tag{14}$$

This system can be solved for the initial condition of constant and equal temperatures $T_\mathrm{M}=T_\mathrm{R}=T_\mathrm{F}=0$ and a step-like heater power function $\phi_\mathrm{heater}(t)$ and yield a function of the following form for the measured signal:

$$\Delta T(t)=T_\mathrm{M}(t)-T_\mathrm{R}(t)=k_1\,\mathrm{e}^{-k_2 t}+k_3\,\mathrm{e}^{-k_4 t}+k_5 \tag{15}$$

where the five constants k_1 to k_5 are rather complex linear algebraic combinations of the five parameters R_RM, R_FM, R_FR, C_M and C_R. The number can be reduced if we assume that the rim is thermally very well connected to the PGA (furnace), then R_FR becomes almost zero and C_R nearly infinite. The other parameters can be estimated from known material properties of the chip and laws of conduction and radiation heat transfer. For example we calculated [11] the membrane resistance $R_\mathrm{RM}=131\,(T/300)^{4/3}\,\mathrm{K\,W^{-1}}$ and that of the air layer above and below the membrane $R_\mathrm{FM}=9.2\times10^4\,(5.35+0.07T)^{-1}\,\mathrm{K\,W^{-1}}$. For, say, a temperature of 70 °C (343 K) this results in values of $R_\mathrm{RM}=160\,\mathrm{K\,W^{-1}}$ and

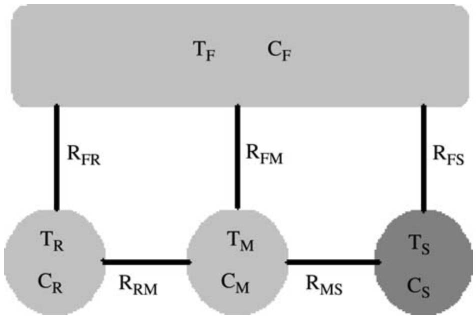

Fig. 3. Network model of the chip-calorimeter with four nodes and five heat conducting paths.

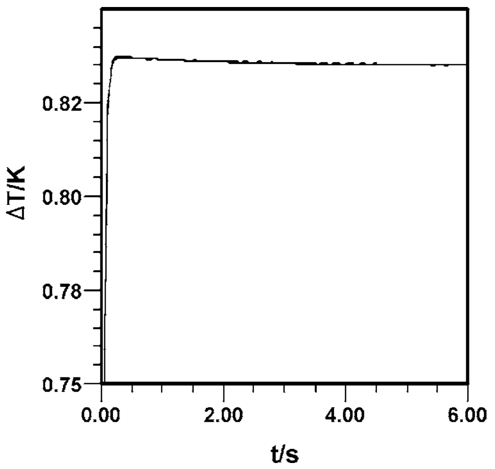

Fig. 4. Measured and simulated step response function of the calorimeter without sample (the difference is smaller than the width of the line, both curves are almost one on top of the other).

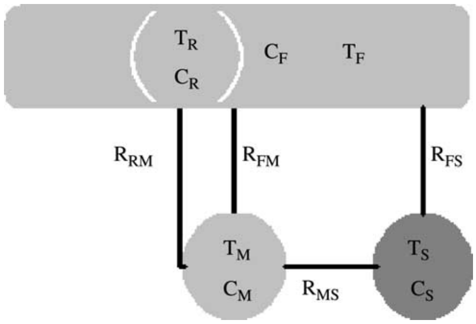

Fig. 5. Simplified network model of the chip-calorimeter with three nodes and three thermal paths.

$R_{\mathrm{FM}} = 3200\,\mathrm{K\,W^{-1}}$. The additional heat exchange via radiation from the membrane to the surrounding furnace can be estimated to a value of 10^{-5} W for a temperature difference of 0.8 K. This will not change the above calculated effective thermal resistance between the membrane and the furnace very much and can therefore be neglected. C_{M} on the other hand can be approximated to a value of about $5 \times 10^{-5}\,\mathrm{J\,K^{-1}}$.

These numbers are, of course, only rough approximations of the truth. To get more precise values, temperature steps are performed by switching an electrical power of 0.005 W to the heater and measure the resulting $\Delta T(t)$ function. The parameters k_i of Eq. (15) are fitted to match the measured function (see Fig. 4) using suitable evaluation software (in our case Origin) and realistic starting values of the k_i (which are calculated using the above mentioned equations connecting the k_i with the R_{ik} and C_i) and the above estimated values at 70 °C. The resulting best fit determined the five k_i of Eq. (15). With these values the algebraic system of equations connecting the model parameters was solved numerically using the Macsyma software and a weighted parameter variation procedure. This needs a lot of trial and error (the different parameters influence the measured pulse response function in different manner) before some experience is gained. However, the fit procedure resulted in the following parameter values for the empty chip at 70 °C: $R_{\mathrm{RM}} = 164\,\mathrm{K\,W^{-1}}$, $R_{\mathrm{FM}} = 2430\,\mathrm{K\,W^{-1}}$, $R_{\mathrm{FR}} = 12\,\mathrm{K\,W^{-1}}$, $C_{\mathrm{M}} = 0.00019\,\mathrm{J\,K^{-1}}$ and $C_{\mathrm{R}} = 0.145\,\mathrm{J\,K^{-1}}$. These values are somewhat temperature dependent, but almost fixed for the respective chip.

With the step response method and the named procedure such values can be determined for every other temperature as well, also during linear heating of the furnace. The fit function reproduces the measured $\Delta T(t)$ function sufficiently well (see Fig. 4) and the above simple model can therefore be used to describe our empty chip-calorimeter properly. Furthermore the above mentioned assumptions that the rim is very well connected with the furnace could be confirmed: C_{R} is 3 orders of magnitude larger than C_{M} and the resistance R_{FR} is much lower than the other resistances.

3.2.3. *The chip-calorimeter with sample (a simplified model)*

These findings enable to simplify the model as shown in Fig. 5: the rim (R) is now considered as part of the furnace with $T_{\mathrm{R}} = T_{\mathrm{F}}$, furthermore the two parallel resistances R_{RM} and R_{FM} can be considered as one apparent resistance $\bar{R}_{\mathrm{FM}}$. For this modified model the system of Eq. (13) simplify to the following system describing the heat flow rate balance of the nodes M and S and the temperature of the furnace F:

$$\begin{aligned}
&C_{\mathrm{M}}\frac{\mathrm{d}T_{\mathrm{M}}}{\mathrm{d}t} - \frac{T_{\mathrm{M}} - T_{\mathrm{S}}}{R_{\mathrm{MS}}} - \frac{T_{\mathrm{M}} - T_{\mathrm{F}}}{\bar{R}_{\mathrm{FM}}} = \phi_{\mathrm{heater}}(t)\\
&C_{\mathrm{S}}(t)\frac{\mathrm{d}T_{\mathrm{S}}}{\mathrm{d}t} + T_{\mathrm{S}}\frac{\mathrm{d}C_{\mathrm{S}}(t)}{\mathrm{d}t} - \frac{T_{\mathrm{S}} - T_{\mathrm{F}}}{R_{\mathrm{FS}}} - \frac{T_{\mathrm{S}} - T_{\mathrm{M}}}{R_{\mathrm{MS}}} = 0\\
&T_{\mathrm{F}}(t) = T_0 + \beta_0 t
\end{aligned} \tag{16}$$

which connects the apparent heat capacity of the sample $C_{\mathrm{S}}(t)$ with the heater power and the measured thermopile signal $\Delta T = T_{\mathrm{M}} - T_{\mathrm{R}}$. Some of the parameters are already determined, from the step response experiments with the empty calorimeter. Assuming a thin sample on top of the membrane, the resistance R_{FS} (concerning the convection and radiation) of this model should be about the same as R_{FM} of the empty calorimeter ($2430\,\mathrm{K\,W^{-1}}$) and $\bar{R}_{\mathrm{FM}} = (1/164 + 1/2430)^{-1} = 154\,\mathrm{K\,W^{-1}}$. These and the remaining unknown parameters R_{MS} (together with the time independent C_{S}) can be determined precisely with the same method again, but now using the model including the sample.

3.2.4. *The time independent solution*

If we assume that we perform the heater power steps in regions where no reactions and transitions occur in the sample, C_{S} can be considered as constant within the time of such a step experiment and $\mathrm{d}C_{\mathrm{S}}/\mathrm{d}t$ can be neglected. For this special case the equation system (16) looks like the system (14) but with different parameters. Therefore the solution for isothermal conditions has the form of Eq. (15) again and the parameters can be determined in the same way as before and yield again

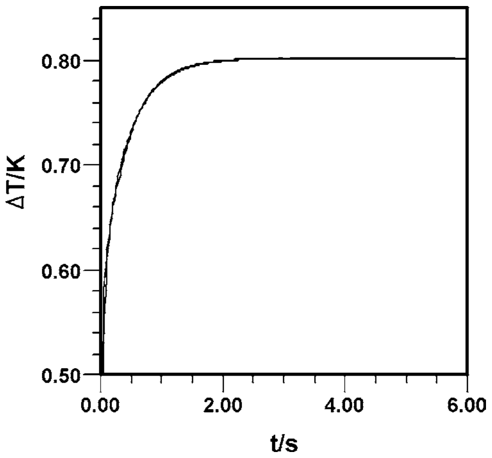

Fig. 6. Measured and simulated step response function of the calorimeter containing a sample of 0.52 mg PCL on a 0.5 mg Al-foil (the difference is smaller than the width of the line, both curves are almost one on top of the other).

a sufficient nice fit (see Fig. 6). As a result we got the following values for a sample of 0.5 mg of poly-caprolactone (PCL) (in a thin Al-foil to avoid contamination of the chip-calorimeter): $R_{FS} = 1150\,\mathrm{K\,W^{-1}}$, $R_{FM} = 163\,\mathrm{K\,W^{-1}}$, $R_{MS} = 310\,\mathrm{K\,W^{-1}}$ and $C_M = 0.00019\,\mathrm{J\,K^{-1}}$. From the measured $C_S = 0.00122\,\mathrm{J\,K^{-1}}$ the specific heat capacity of the PCL sample can be calculated (if we take the heat capacity of the involved Al-foil into account) and yields $C_p(\mathrm{PCL}) = 1.7\,\mathrm{J\,g^{-1}\,K^{-1}}$ at room temperature which is not far from the literature value of $1.8\,\mathrm{J\,g^{-1}\,K^{-1}}$. R_{MS} contains the thermal resistance between membrane and the Al-foil as well as the thermal resistance between foil and sample. This value differs, of course for different samples (ca. 20 %) and must be determined with the named pulse method in temperature regions without processes both in front and after regions of transitions to see possible changes.

3.2.5. The general solution

With the results from the step response method, which can be repeated at every moment (or temperature) outside of the region of reactions and transitions in the sample, it is now possible to solve the differential equation system (16)—at least numerically—and get the apparent heat capacity of the sample in dependence of the measured thermopile signal $\Delta T(t)$. It is also possible to simulate the thermopile signal for a given thermal event in the sample, or to simulate the response on a step- or pulse-like heater power stimulus. The powerful modern computer mathematics software is a very suitable tool to solve the mathematical problems which may develop. For the above described model the, of course, very complex solution could be calculated without larger problems, we desist, however, from presenting it here: The equations would fill a whole page and looks very different for every case (chip type and problem). These formulas are therefore of no general value, the form is often that of an integral equation with terms of exponential time behavior.

4. Conclusions

It has been shown that several methods exist and have successfully been used to describe the thermal behavior of the micro- or nano-calorimeters constructed on chip or IC basis. With these methods it is also possible to calculate the heat capacity of the sample from the measured signal. This is also possible during thermal events producing latent heat in the sample and causing a so-called excess heat capacity and thus a time-dependent apparent heat capacity curve. The pulse- or step-response method has proved to be a powerful tool to determine the model parameters by fitting the expected function to the measured step (or pulse) response function. A modern computer technique together with powerful software allows solving also rather complex problems (equation systems) without larger difficulties. This enables to construct very small and sensitive calorimeters with time constants in the millisecond region and determine thermal properties even of thin films without the need of a differential measurement with twin calorimeters like in conventional DSC.

References

[1] W. Hemminger, G.W.H. Höhne, Calorimetry, Fundamentals and Practice, Verlag Chemie, Weinheim, Deerfield Beach, Basel, 1984.
[2] G.W.H. Höhne, W. Hemminger, H.J. Flammersheim, Differential Scanning Calorimetry, 2nd revised and enlarged edition, Springer-Verlag, Berlin, Heidelberg, New York, 2003.
[3] G.W.H. Höhne, J.E.K. Schawe, Thermochim. Acta 229 (1993) 27.
[4] M.Yu. Efremov, E.A. Olson, M. Zhang, S.L. Lai, F. Schiettekatte, Z.S. Zhang, L.H. Allen, Thermochim. Acta 412 (2004) 13.
[5] D.W. Denlinger, E.N. Abarra, K. Allen, P.W. Rooney, M.T. Messer, S.K. Watson, F. Hellman, Rev. Sci. Instrum. 65 (4) (1994) 946.
[6] Xensor Integration, 2601 DE Delft, The Netherlands, http://www.xensor.nl.
[7] IPHT, 07702 Jena, Germany, http://ipht-jena.de.
[8] A.W.V. Herwaarden, P.M. Sarro, J.W. Gardner, P. Bataillard, Sens. Actuators A 43 (1994) 24.
[9] S. Adamovsky, A.A. Minakov, C. Schick, Thermochim. Acta 403 (2003) 55.
[10] J. Lerchner, G. Wolf, A. Torralba, V. Torra, Thermochim. Acta 302 (1997) 201.
[11] W. Winter, G.W.H. Höhne, Thermochim. Acta 403 (2003) 43.
[12] J. Lerchner, G. Wolf, C. Auguet, V. Torra, Thermochim. Acta 415 (2004) 9.
[13] C. Auguet, J. Lerchner, V. Torra, G. Wolf, J. Therm. Anal. Cal. 71 (2003) 951.
[14] H. Reichl, A. Heuberger (Eds.), Micro System Technologies'94, VDE-Verlag, Berlin, Offenbach, 1994, pp. 773–782.
[15] F. Fominaya, T. Fournier, P. Gandit, J. Chaussy, Rev. Sci. Instrum. 68 (11) (1997) 4191.
[16] M. Merzlyakov, Thermochim. Acta 403 (2003) 65.
[17] B. Revaz, D. O'Neil, L. Hull, F. Hellman, Rev. Sci. Instrum. 74 (2003) 4389.