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Treatment of a Power Compensated Scanning Calorimeter by the Field Equation of Heat Conduction

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Abstract

The theoretical treatment of a scanning calorimeter usually is performed by investigating electrical analog circuits with discrete elements like capacitors and resistors. In this paper the system is considered as being continuous and thus is treated by the field equation of heat conduction. We shall calculate the shape of temperature and the signal in the cases of no thermal event, an exothermal reaction, an endothermal phase transition. The latter is assumed to happen in a thin and a thick sample where the phase boundary moves across it. All solutions are derived by analytical methods.

1. Introduction

In the common textbooks about calorimetry such as [2] the theoretical treatment is performed by models consisting of discrete elements i.e. the theoretical calculation of the signal is based upon electric analogue circuits containing capacitors and resistors. The calorimetric device, however, should be considered as being continuous and thus the treatment should be performed by the equation of heat conduction [3,4]. In spite of some critical remarks with respect to this well known field equation [1] refering to the nonlinearities caused by the dependence of the heat conductivity and the heat capacity on temperature we shall apply this equation here because of an easy mathematical framework. In order to get a more basical understanding of the heat transport we shall restrict ourselves to almost simple one dimensional models of a power scanning calorimeter [2] which is heated by a constant rate. The models shall be treated only by applying analytical methods i.e. by Laplace transformation [4,5,6]. The calorimetric device is illustrated schematically in fig.1.

The equipment consists of a reference and of a sample system which are almost identical. At the bottom ($z = 0$) they are heated by a constant increase β of temperature. The sample system is kept at the same temperature as the reference system. Thus any difference in the power used for heating has to be due to any thermal events in the sample system. The sample system consisting of the sample itself and of the sample holder which

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belongs to the calorimetric equipment is represented only by a homogeneous rod. This is a rather large simplification but a more detailed model consisting of two parts one representing the sample holder and the other one representing the sample cannot be resolved actually by analytical methods [1].

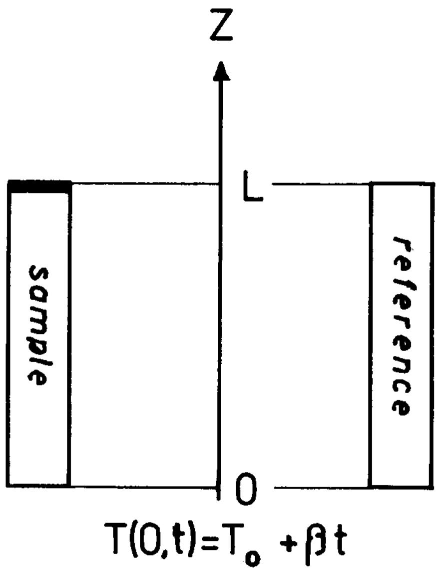

Fig.1: Schematical illustration of a power compensated calorimeter

Anyway the treatment by the simple model will give some new aspects. We shall calculate the shape of temperature and the signal in those cases where no thermal event, an exothermal event and an endothermal one happen. The latter will also be discussed for the case of a thick sample where a phase boundary is moving across it.

2. An Almost General Solution of the One Dimensional Field Equation By Laplace Transformation

Assuming a homogeneous system with constant heat conductivity and heat capacity the field equation is a linear partial differential equation [1,4,5]

$$\nabla^2 T(\mathbf{r},t) = \alpha \frac{\partial T(\mathbf{r},t)}{\partial t} \tag{2,1}$$

In the case of one dimensional transport (2,1) is simplified as

$$\frac{\partial^2 T(z,t)}{\partial z^2} = \alpha \frac{\partial T(z,t)}{\partial t} \tag{2,2}$$

where α denotes the inverse thermal diffusivity. The Laplace transformation [1] with respect to the time t yields an inhomogeneous ordinary differential

$$\frac{\partial^2 T(z,s)}{\partial z^2} - \alpha s\, T(z,s) = -\alpha\, T(z,0) \tag{2,3}$$

equation T(z,0) denotes the initial shape of temperature. The general solution of (2,3) is given as where $T_{inh}(z,s)$ denotes one particular solution of the inhomogeneous equation (2,3). The latter can be obtained by the Laplace transformation with respect to z which yields an algebraic equation.

$$(k^2 - \alpha s)\, T_{inh}(k,s) = -\alpha\, T(k,s) \tag{2,5}$$

According to the theorem of convolution the transformation back into the regime of z yields

$$T_{inh}(z,s) = -\frac{\alpha}{\sqrt{\alpha s}} \int_0^z \sinh \sqrt{\alpha s}\,(z-z')\; T(z',0)\; dz' \tag{2,6}$$

The integration constants A, B have to be determined from the boundary conditions at z - 0, z - L, respectively. Because of the constant increase of temperature at z - 0

$$T(0,t) = T_0 + \beta t \tag{2,7}$$

(2,4) is obtained as

$$T(z,s) = T(0,s) \cosh \sqrt{\alpha s}\, z + B \sinh \sqrt{\alpha s}\, z - \frac{\alpha}{\sqrt{\alpha s}} \int_0^z \sinh \sqrt{\alpha s}\,(z-z')\; T(z',0)\; dz' \tag{2,8}$$

The second integration constant B depends on the physical problem one is dealing with.

2.1. Shape of Temperature And Signal Without Any Thermal Event

The heat conductor is adiabatically isolated at z - L. Assuming the initial shape of temperature as being uniform

$$T(z,0) \equiv 0 \tag{2,9}$$

one obtains

$$T(z,s) = T(0,s) \underbrace{\frac{\cosh\sqrt{\alpha s}\,(L-z)}{\cosh\sqrt{\alpha s}\,L}}_{\gamma(z,s)} \qquad (2,10)$$

The transformation back into the regime of time t is given by the convolution of $T(0,t) - \beta t$ with $\gamma(z,t)$

$$\gamma(z,t) = \frac{\pi}{\alpha L^2} \sum_{n=0}^{\infty} (2n+1)\,\sin(2n+1)\frac{\pi}{2}\frac{z}{L}\; e^{-y_n^2 t} \qquad (2,11)$$

where y_n^2 is defined as

$$y_n^2 = \frac{(2n+1)^2\pi^2}{4\alpha L^2} \qquad (2,12)$$

Thus one gets by carrying out the convolution

$$T(z,t) = \beta t - \alpha\beta L z\left(1-\frac{z}{2L}\right) + \frac{16\alpha L^2}{\pi^3}\sum_{n=0}^{\infty}\frac{\sin(2n+1)\frac{\pi}{2}\frac{z}{L}}{(2n+1)^3}\; e^{-y_n^2 t} \qquad (2,13)$$

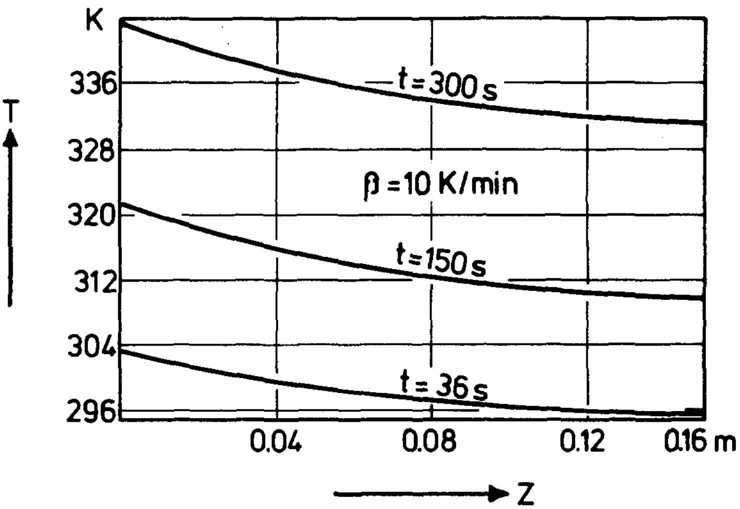

Fig.2: Parabolic shapes of temperature of an enlarged model of the sample holder with the sample. The model consists of a rod of copper heated at one boundary and adiabatically isolated at the other one.

The solution converges to a parabolic shape of temperature. The exponentials are caused by switching on the heater at the time $t = 0$ where the shape of temperature has been uniform. In fig. 2 this shape of temperature is illustrated for large values of time. The gradient of temperature vanishes at $z = L$ because of the boundary condition of adiabatical isolation.

The signal is obtained by calculating the heat flow at $z = 0$

$$J(0,t \to \infty) = -\lambda F \frac{\partial T(0,t \to \infty)}{\partial z} \tag{2,14}$$

where λ, F denote the heat conductivity and the cross sectional area, respectively, and by subtracting the heat flow of the reference. Thus one obtains the well known result

$$\Delta J(t \to \infty) = \beta \Delta C \tag{2,15}$$

ΔC denotes the difference of heat capacity between the sample and the reference.

2.2. Shape of Temperature And Signal in the Case of an Exothermal Event

Now we assume that a thermal event - e.g. an exothermal chemical reaction - happens which is described by the boundary heat flow

$$J(L,t) = -\lambda F \frac{\partial T(L,t)}{\partial z} \tag{2,16}$$

Additionally we assume the intial shape of temperature as being parabolic as is illustrated in fig.2. So one gets from (2,6), (2,8) with the help of the boundary condition (2,16)

$$T(z,s) = T(0,s) \frac{\cosh \sqrt{\alpha s}\,(L-z)}{\cosh \sqrt{\alpha s}\, L} - \frac{1}{\lambda F} \frac{\sinh \sqrt{\alpha s}\, z}{\sqrt{\alpha s} \cosh \sqrt{\alpha s}\, L} J(L,s) -$$

$$\frac{\sinh \sqrt{\alpha s}\, z}{\sqrt{\alpha s} \cosh \sqrt{\alpha s}\, L} \frac{\partial T_{inh}(L,s)}{\partial z} + T_{inh}(z,s) \tag{2,17}$$

The calculations are considerably simplified by subtraction of the temperature of the reference, where $J(L,s)$ vanishes. Thus it is obtained

$$\Delta T(z,s) = -\frac{1}{\lambda F} \frac{1}{\sqrt{\alpha s}} \frac{\sinh \sqrt{\alpha s}\, z}{\cosh \sqrt{\alpha s}\, L} J(L,s) \tag{2,18}$$

This result enables us to calculate the signal

$$\Delta J(s) = -\lambda F \frac{\partial \Delta T(0,s)}{\partial z} = \frac{1}{\cosh \sqrt{\alpha s}\, L} J(L,s) \tag{2,19}$$

Hence the signal is a linear response of the production of heat

$$\Delta J(t) = \int_0^t G(t-t')\ J(L,t')\ dt' \qquad (2,20)$$

with the G(t) function [7]

$$G(t) = \frac{\pi}{\alpha L^2} \sum_{n=0}^{\infty} (-1)^n\ (2n+1)\ e^{-\frac{(2n+1)^2 \pi^2}{4 \alpha L^2} t} \qquad (2,21)$$

For some applications it should be useful to know the real temperature of the sample i.e. the temperature at z - L - e.g. for chemical reactions where the rate constant depends on temperature. This requires the transformation of (2,18) back into the regime of time and adding the parabolic shape of the reference temperature. Thus it is yielded

$$T(z,t) = T_0 + \beta t - \alpha \beta L z \left(1 - \frac{z}{2L}\right) - \frac{2}{C} \sum_{n=0}^{\infty} (-1)^n \sin(2n+1)\frac{\pi}{2}\frac{z}{L} \int_0^t e^{-\frac{(2n+1)^2 \pi^2}{4 \alpha L^2}(t-t')}\ J(L,t')\ dt' \qquad (2,22)$$

T_0 denotes the apparent onset temperature of the reaction which measured by the calorimeter whereas $T_0 - \alpha \beta L^2/2$ denotes the real temperature of the sample at that time.

2.3. Endothermal Transition

The endothermal transition is divided into two intervals of time: $t < t_0$ where the transition happens and $t > t_0$ where the transition has stopped but where the signal decreases back to the base line.

2.3.1. Shape of Temperature And Signal During the Transition

Now an endothermal event in a thin sample situated at z - L is assumed which is described by an isothermal boundary condition at z - L. Furthermore it is assumed that the uniform shape of temperature at the beginning when the calorimeter has been switched on is forgotten. Thus we have the parabolic shape of temperature (2,13) as an initial condition. According to the isothermal boundary condition at z - L one finds with the help of (2,8)

$$\frac{T_u}{s} = T(0,s)\ \cosh\sqrt{\alpha s}\,L + B\ \sinh\sqrt{\alpha s}\,L - \frac{\alpha}{\sqrt{\alpha s}} \int_0^z \sinh\sqrt{\alpha s}\,(L-z')\ T(z',0)\ dz' \qquad (2,23)$$

where T_u denotes the true temperature of the transition. This yields the Laplace transformed shape of temperature:

$$T(z,s) = T(0,s)\,\frac{\sinh\sqrt{\alpha s}\,(L-z)}{\sinh\sqrt{\alpha s}\,L} + \frac{T_u}{s}\,\frac{\sinh\sqrt{\alpha s}\,z}{\sinh\sqrt{\alpha s}\,L} +$$

$$\frac{\alpha \sinh\sqrt{\alpha s}\,z}{\sqrt{\alpha s}\,\sinh\sqrt{\alpha s}\,L}\int_0^L \sinh\sqrt{\alpha s}\,(L-z')\;T(z',0)\;dz' -$$

$$\frac{\alpha}{\sqrt{\alpha s}}\int_0^z \sinh\sqrt{\alpha s}\,(z-z')\;T(z',0)\;dz' \qquad (2,24)$$

The initial shape of temperature consists of the steady state terms of (2,13)

$$T(z,0) = T_0 - \alpha\beta L z\left(1-\frac{z}{2L}\right) \qquad (2,25)$$

where T_0 denotes the temperature of the transition indicated by the calorimeter. The integrals have been evaluated in the appendix. So one finds after a lot of calculation

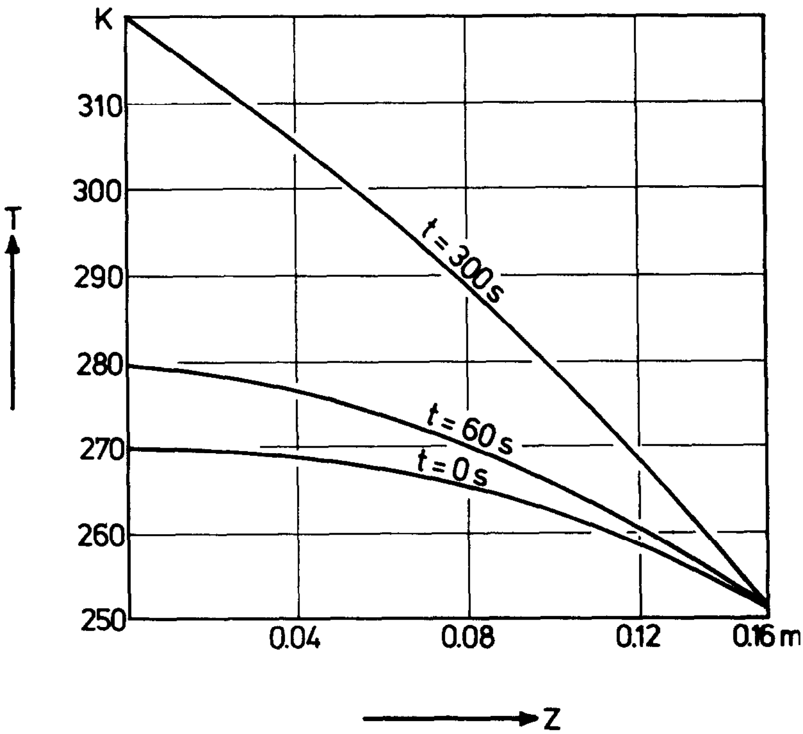

Fig 3: Time dependent cubic parabola describing the shape of temperature of the same rod of copper which is heated at one boundary and kept isothermal at the other one.

The initial shape of temperature consists of the steady state terms of (2,13)

$$T(z,0) = T_o - \alpha\beta L z\left(1-\frac{z}{2L}\right) \tag{2,25}$$

where T_o denotes the temperature of the transition indicated by the calorimeter. The integrals have been evaluated [7]. So one finds after a lot of calculation

$$T(z,s) = T(0,s) - \frac{\beta}{s^2}\frac{\sinh\sqrt{\alpha s}\,z}{\sinh\sqrt{\alpha s}\,L} - \frac{\alpha\beta L z}{s} + \frac{\alpha\beta z^2}{2s} \tag{2,26}$$

After the transformation back into the regime of time the shape of temperature is obtained as a Fourier series in z which has to be calculated. Thus one yields

$$T(z,t) = T_o + \beta t\left(1-\frac{z}{L}\right) - \frac{5}{6}\alpha\beta L z + \frac{\alpha\beta z^2}{2} - \frac{1}{6}\frac{\alpha\beta z^3}{L}$$
$$-\frac{2\alpha\beta L^2}{\pi^3}\sum_{n=1}^{\infty}\frac{\sin n\pi\left(1-\frac{z}{L}\right)}{n^3}\, e^{-\frac{n^2\pi^2}{\alpha L^2}t} \tag{2,27}$$

The last term is associated with the onset of the thermal event and vanishes for large times. This shape of temperature one obtains for large values of time is illustrated in fig.3.

From (2,27) one gets the heat flow into the sample which is the original desmeared thermal event and which performs the phase transition.

$$J(L,t) = \frac{\lambda A}{L}\beta t + \frac{1}{3}C\beta - \frac{2C\beta}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\, e^{-\frac{n^2\pi^2}{\alpha L^2}t} \tag{2,28}$$

The heat flow at z = 0 is determined as

$$J(0,t) = \frac{\lambda A}{L}\beta t + \frac{5}{6}C\beta - \frac{2C\beta}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\, e^{-\frac{n^2\pi^2}{\alpha L^2}t} \tag{2,29}$$

This heat flow performs the heating of the calorimeter and the phase transition in the sample. The difference

$$J(0,t) - J(L,t) = \frac{1}{2}C\beta - \frac{4C\beta}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\, e^{-\frac{(2n+1)^2\pi^2}{\alpha L^2}t} \tag{2,30}$$

is stored in the calorimeter and causes the increase of temperature. It is quite elucidating that only one half of the heat capacity appears in (2,30) for large periods of time: the reason is the shape of temperature illustrated in fig.3 which means that only a part of the sample system is heated. From (2,29) one obtains the total signal of the calorimeter

$$\Delta J(t) = J(0,t) - J_{ref}(0,t) = \frac{\lambda A}{L}\beta t + \Delta C\beta - \frac{1}{6}C\beta - \frac{2C\beta}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\, e^{-\frac{n^2\pi^2}{\alpha L^2}t} \tag{2,31}$$

ΔC denotes the difference of the heat capacity between the system of the sample and the reference. According to (2,15) the term $\Delta C\beta$ represents the base line. It should be emphasized that the term $-1/6\,C\beta$ does not appear in the classical treatments. Hence the straight part of the signal which is represented by the term $\lambda A/L\,\beta t$ does not intersect the baseline at $t = 0$ but lateron at $t > 0$. This could be a reason that the obvious onset temperature T_O estimated from the signal is too large.

2.3.2. Relaxation After the Phase Transition

After the endothermal phase transition the upper boundary at $z = L$ is adiabatically isolated just as before the phase transition. Hence the integration constant B of eq. (2,8) is given as

$$B = -\,T(0,s)\,\frac{\sinh\sqrt{\alpha s}\,L}{\cosh\sqrt{\alpha s}\,L} + \frac{\alpha}{\sqrt{\alpha s}}\int_0^L \cosh\sqrt{\alpha s}\,(L-z')\;T(z',0)\;dz' \tag{2,32}$$

The initial shape of temperature is obtained from (2,24) for $t\to\infty$

$$T(z,0) = T_o + \beta t_o\left(1-\frac{z}{L}\right) - \frac{4}{3}\alpha\beta L z + \frac{\alpha\beta z^2}{2} + \frac{\alpha\beta z^3}{3L} \tag{2,33}$$

After a lot of calculation one gets the Laplace Transform of the shape of temperature

$$T(z,s) = T(0,s) + \frac{1}{s}\left(\frac{\beta t_o}{L} + \frac{4}{3}\alpha\beta L\right)\left(\frac{\sinh\sqrt{\alpha s}\,z}{\sqrt{\alpha s}\,\cosh\sqrt{\alpha s}\,L} - z\right) + \frac{1}{s}\left(\frac{\alpha\beta z^2}{2} - \frac{\alpha\beta z^3}{3L}\right) + \frac{2\beta z}{L s^2} - 2\,\frac{\sinh\sqrt{\alpha s}\,z}{\sqrt{\alpha s}\,\cosh\sqrt{\alpha s}\,L}\left(\frac{\alpha\beta L}{s} + \frac{\beta}{L s^2}\right) \tag{2,34}$$

The transformation back into the regime of time has been performed in [7] Hence the shape of temperature is obtained as

$$T(z,t) = T_o + \beta t_o + \beta t - \alpha\beta L z\left(1-\frac{z}{2L}\right) - \left(\beta t_o - \frac{2}{3}\alpha\beta L^2\right)\frac{8}{\pi^2}\sum_{n=0}^{\infty}(-1)^n\,\frac{\sin(2n+1)\frac{\pi}{2}\frac{z}{L}}{(2n+1)^2}\,e^{-\frac{(2n+1)^2\pi^2}{4\alpha L^2}t} \;\; \frac{64\,\alpha L^2}{\pi^4}\sum_{n=0}^{\infty}\frac{\cos(2n+1)\frac{\pi}{2}\left(1-\frac{z}{L}\right)}{(2n+1)^4}\,e^{-\frac{(2n+1)^2\pi^2}{4\alpha L^2}t} \tag{2,35}$$

Obviously (2,31) converges to the well known parabolic shape of temperature (2,13) as it should be. From (2,31) the signal is determined as

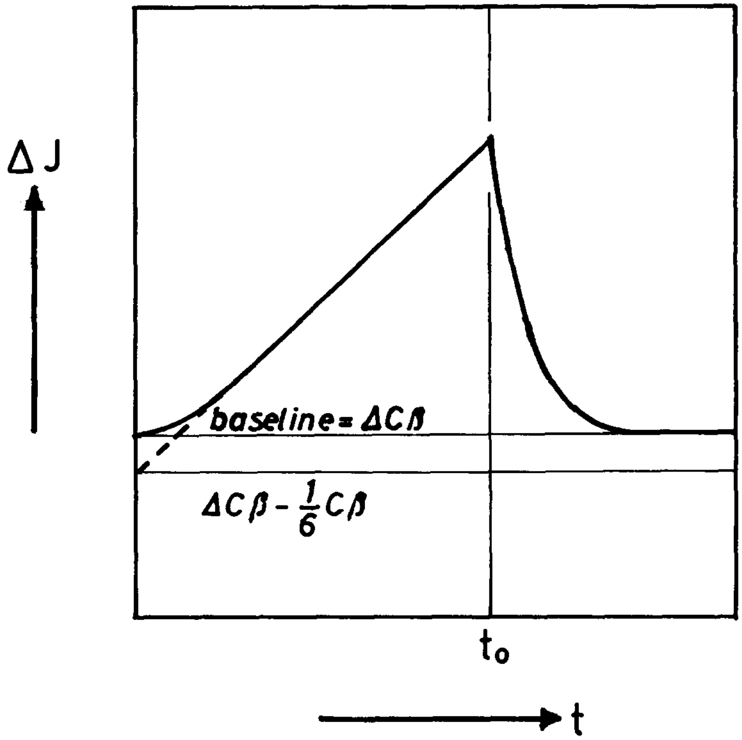

Fig. 4: Signal of the calorimeter during and after the endothermal transition. The straight part of the curve intersects the ΔJ axis below the baseline in contrast to the classical treatments.

$$\Delta J(t) = \Delta C\beta + \frac{4}{\pi}\left(\frac{\lambda A}{L}\beta t_0 - \frac{2}{3}C\beta\right)\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\, e^{-\frac{(2n+1)^2\pi^2}{4\alpha L^2}t}$$

$$- \frac{32}{\pi^3}C\beta\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^3}\, e^{-\frac{(2n+1)^2\pi^2}{4\alpha L^2}t} \qquad (2,36)$$

In fig. 4 the signal during the transition and afterwards during the period of relaxation is illustrated.

2.3.3 Endothermal Transition with a Moving Phase Boundary

In a thick sample one has to take into account that the melting cannot take place all over the sample but that it will start in regions near the heater. It will go on by a moving boundary between the liquid and the solid phase the position of which depends on the heat already transported into the sample, i.e.

$$J(L(t),t) = h\ m = h\rho V = h\rho A L(t) \tag{2,37}$$

h denotes the mass specific enthalpy of melting, m, V the increase of mass and of volume of the molten phase, respectively. In fig.5 the one dimensio-

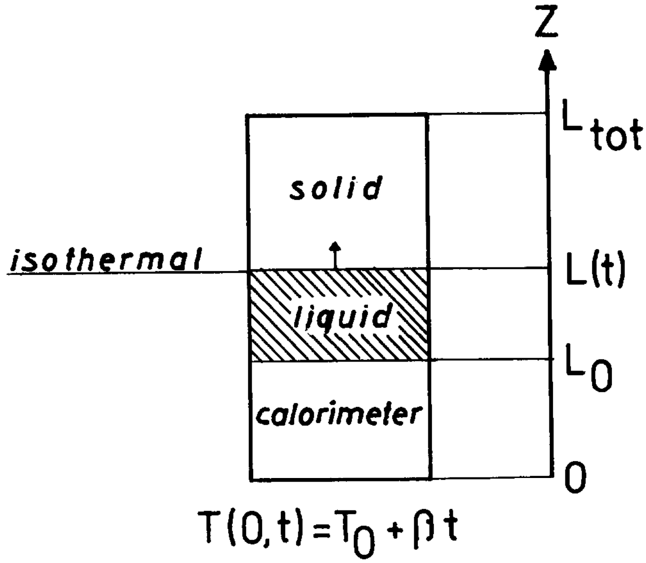

Fig. 5: One dimensional model of melting of a thick sample with moving boundary between the liquid and the solid phase.

nal model of melting of a thick sample is illustrated. This model is not very realistic because it is assumed that the heat conducting sample holder, the liquid and the solid phase do not differ in the heat conductivity and the specific heat capacity. A more detailed model would require, however, resolving the field equation of an inhomogeneous heat conducting rod which cannot be achieved by analytical methods only [1].

Inserting Fourier's law into (2,37) yields after integration

$$L(t) = L_0 - \frac{\lambda}{h\rho} \int_0^t \frac{\partial T(L(t),t')}{\partial z}\, dt' \tag{2,38}$$

This integral equation cannot be resolved exactly because the integrand is the solution of the field equation with the time dependent isothermal boundary condition L(t). It can be resolved approximately for slow heating rates, however. In this case there is time enough to get a shape of temperature corresponding to a fixed boundary at each moment. So one inserts the solution of the thin sample (2,28) into the differential equation (2,37)

$$J(L(t),t) = \frac{\lambda A}{L(t)}\beta t + \frac{1}{3}c\rho A\beta L(t) - \frac{2c\rho A\beta}{\pi^2}L(t)\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{n^2\pi^2}{\alpha L(t)^2}t}$$
$$= h\rho A\dot{L}(t) \qquad (2,39)$$

This differential equation is nonlinear and inhomogeneous. It cannot be resolved exactly because of the exponentials containing the function L(t). So the series of exponentials has to be neglected which means that the part of length L_0 belonging to the calorimeter is sufficiently short. Thus one yields the differential equation

$$\left(\frac{1}{2}\frac{d}{dt} - \frac{1}{3}\beta\frac{c}{h}\right)L(t)^2 = \frac{\lambda}{h\rho}\beta t \qquad (2,40)$$

as a differential equation which is linear in $L^2(t)$. The solution is given as

$$L(t) = \sqrt{\left(L_0^2 + \frac{9\lambda h}{2c^2\rho\beta}\right)e^{\frac{2c\beta}{3h}t} - \frac{3\lambda}{c\rho}t - \frac{9\lambda h}{2c^2\rho\beta}} \qquad (2,41)$$

From this result one easily calculates the signal of the calorimeter

$$\Delta J(t) = \frac{\lambda A}{L(t)}\beta t + \frac{5}{6}c\rho A\beta L(t) - C_{ref}\beta \quad (t < t_0) \qquad (2,42)$$

C_{ref} denotes the heat capacity of the reference system. After the phase transition there is the period of relaxation where the signal decreases down to the base line. During this period the signal is given by (2,36) where L denotes the total constant length L_{tot} and the length of the liquid phase after the transition. In fig.6 the signal of the calorimeter is illustrated.

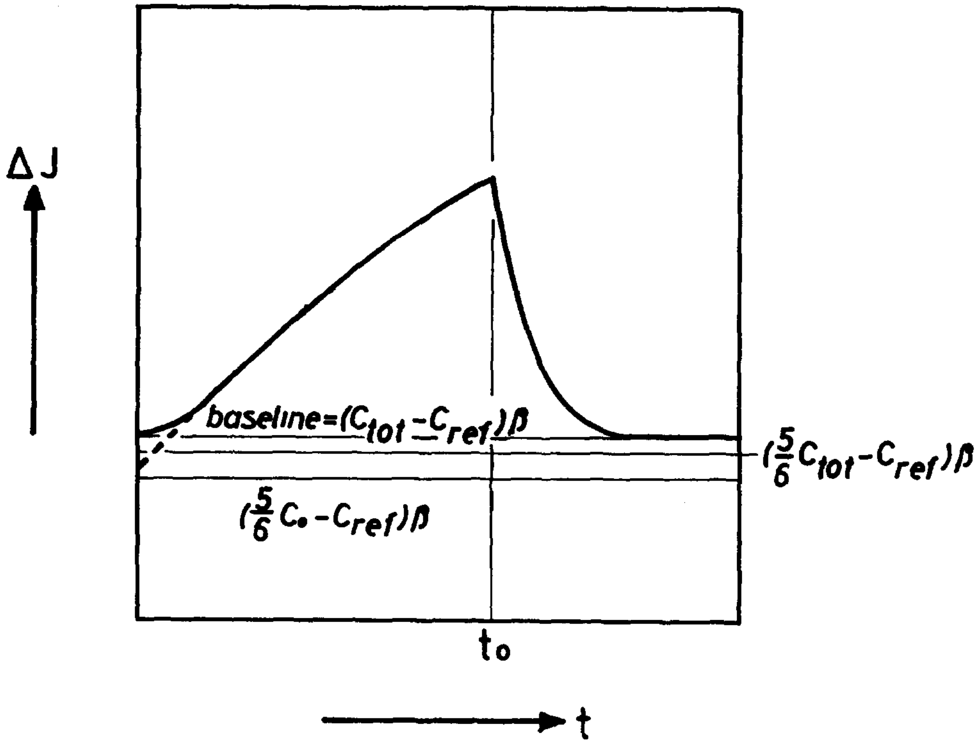

Fig. 6: Signal of the calorimeter versus time or the indicated temperature $T(0,t) = T_o + \beta t$

2.3.4. Discussion

The results derived for the simple model reveal some new aspects compared with the common treatments [1] which are illustrated in fig.7. The latter shows the signal during the transition according to (2,31) (2,42), respectively. According to (2,13) the initial shape of temperature at the beginning of the transition is parabolic. So the obvious temperature of the transition T_o is too large compared with the true one T_u. A further reason why this temperature is overestimated from the signal is the following: the straight part of the signal $\Delta J(t)$ does not intersect the ΔJ-axis at the base line $\Delta C \beta$ but at the value $\Delta C \beta - 1/6\, C \beta$. This means more physically spoken: there is some more heat needed for the transition which causes a certain increase of the signal and there is less heat as before the transition needed for heating the sample system because the temperature remains constant at the upper boundary $z = L$. Hence the increase of the signal at the beginning is weak and the obvious temperature T_o might be overestimated. The balance of energy yields for the total heat of transition

$$Q = \int_0^{t_0} J(L,t)\, dt = \int_0^{t_0} (\Delta J(t) - \Delta C\,\beta)\, dt + \int_{t_0}^{\infty} (\Delta J(t) - \Delta C\,\beta)\, dt \qquad (2,43)$$

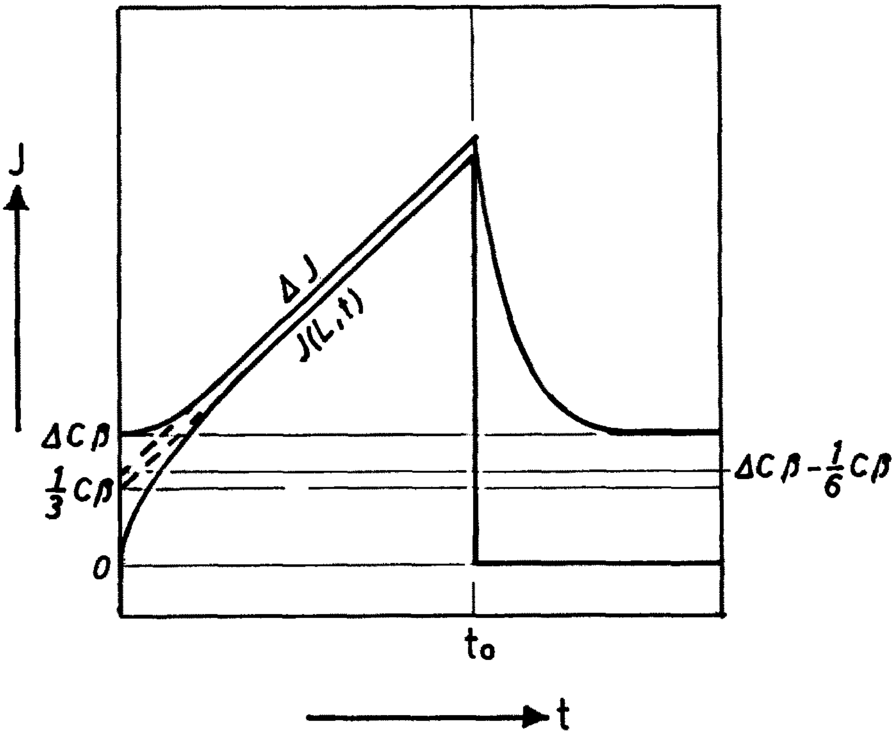

Fig. 7: Signal ΔJ(t), desmeared heat flow J(L,t) during and after an endothermal transition.

3. Final Remarks

The shapes of temperatures and the signals have been calculated for the cases of

a) no thermal event

b) an exothermal event

c) an endothermal event in a thin sample

d) an endothermal event in thick sample with a moving phase boundary We yielded the following result for large periods of time where the phenomena due to any initial shape of temperature are negligeably small

a) parabolic shape of temperature, the baseline of the signal ΔJ differs from zero if the sample and the reference system are of different heat capacity

b) the shape of temperature and the signal depend on the heat production as linear responses i.e. they are obtained as the convolution integral of the original thermal event with the G-functions that have been calculated from the one dimensional model.

c) The shape of temperature is a time dependent cubic parabola. In contrast to the classical treatments the signal intersects the ΔJ axis below the base-line as is illustrated in fig. 5,6,7. This shift may cause an error in the temperature of the transition estimated from the signal. The enthalpy of the transition is not influenced, however.

d) In contrast to c) the signal does not increase constantly during the transition but the increase becomes weaker in time because the sample itself becomes "longer".

An interesting result is the shifting of the signal during the endothermal transition mentioned above which may also lead to modifications of the methods how to obtain the base line during that period of time for those cases where the new and the old phase differ in heat capacity. For instance we do not want to deal with that problem because the model of the homogeneous rod is too simple and it is not very realistic. A more detailed model consisting of an inhomogeneous rod cannot be resolved exactly, however, i.e. the Laplace transforms can be calculated but the only problem is the transformation back into the regime of time. We do hope, however, to get the exact solution in the surroundings of three particular cases with respect to the heat conductivity and heat cpacity of both phases.

4. References:

1 H. Hoff, Can. J. Phys. 68 (1990) 198

2 W. Hemminger, G. W. Höhne, Calorimetry, Fundamentals and Practise, Verlag Chemie, Weinheim, 1983

3 H. S. Carslaw, J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, Oxford, 1959

4 U. Grigull, H. Sandner, Waermeleitung, Springer-Verlag, Berlin, 1979

5 O. Foellinger, Laplace- und Fouriertransformation, AEG-Telefunken, Berlin, Berlin 1979

6 J. G. Hobrook, Laplace transforms for electronic engineers, Pergamon Press Ltd., Oxford, 1966

7 to be published elsewhere but is now available on request