

From DSC curve to thermodynamic potential function

G.W.H. Höhne

Sektion für Kalorimetrie, Universität Ulm, Postfach 4066,
D-7900 Ulm

Abstract

The connections between DSC curves and thermodynamic potential functions are shown. It is easy to calculate the specific heat capacity and thus the potential functions from the heat flow rate in the case of steady state conditions, but in the region of phase transitions and reactions the relations are not so easy and special "desmearing" procedures have to be applied. Additional complications result from the non-uniform temperature field inside the sample. With this corrections included, DSC is a smart method to get the thermodynamic potential functions.

1. THEORY

The thermodynamic potential functions will be calculated from heat capacities, which in their turn are defined as

$$C_v(T) = |dQ/dT|_v \quad C_p(T) = |dQ/dT|_p \quad (1)$$

that is to say, as the amount of heat necessary to rise the temperature one Kelvin. Usually the amount of substance in question is chosen to be one mole for this definitions. The subscript indicates that the volume or the pressure has to be held constant during the measurement. The difference of these two quantities is

$$C_p - C_v = T \cdot V \cdot \alpha^2 / K \quad (2)$$

where V is the molal volume, α the isobaric thermal volume expansion coefficient and K the isothermal compressibility. For solid bodies this difference is often neglected, but also in this case C_p is 3 - 10 percent larger as C_v and these two quantities are not interchangeable for precise measurements.

From the heat capacities the thermodynamic potential functions can be calculated:

$$U(T) = \int C_v dT + \int (\partial U / \partial V)_T dV \quad (3)$$

$$H(T) = \int C_p dT + \int (\partial H / \partial p)_T dp \quad (4)$$

$$S(T) = \int (C_p/T) dT - \int V \alpha dp \quad (5)$$

$$F(T) = U(T) - T \cdot S(T) \quad (6)$$

$$G(T) = H(T) - T \cdot S(T) \quad (7)$$

To get the respective specific quantities (written in small capitals) they should be divided by the molal mass in question.

The calculations to get the potential functions are simple integrations and summations of the respective heat capacity functions if the volume or the pressure is held constant ($dV=0$ or $dp=0$) during the measurement. Thus the question arises how we can get these functions from the DSC curves.

Normally the output of a DSC is a heat flow rate function of time $\dot{\Phi}(t)$. As time and program temperature are linearly connected via $T_p = \beta t + T_0$ the output may also be given as a function of temperature namely T_p . But in heating and cooling mode the sample temperature T_s is different from the program temperature because of temperature gradients along the heat flow path.

Beside this discrepancy the specific heat capacity can be determined from the differential heat flow of the sample and baseline (empty pans) run

$$c_p(T) = \Delta\dot{\Phi}(T_s) / (\beta \cdot m_s) \text{ for open pans (p = const.)} \quad (8a)$$

$$c_v(T) = \Delta\dot{\Phi}(T_s) / (\beta \cdot m_s) \text{ for sealed pans (v = const.)} \quad (8b)$$

(β : heating rate, m : sample mass, $\Delta\dot{\Phi} = \dot{\Phi}_s - \dot{\Phi}_b$: steady state heat flow rate) and by integration of these equations we get the enthalpy or internal energy respective entropy.

$$H - H_0 = \Delta H = \int \Delta\dot{\Phi}(T_s) / (\beta \cdot m_s) dT = \int \Delta\dot{\Phi}(T_s) / m_s dt \text{ (p=const.)} \quad (9a)$$

$$U - U_0 = \Delta U = \int \Delta\dot{\Phi}(T_s) / (\beta \cdot m_s) dT = \int \Delta\dot{\Phi}(T_s) / m_s dt \text{ (v=const.)} \quad (9b)$$

$$S - S_0 = \Delta S = \int \Delta\dot{\Phi}(T_s) / (T_s \cdot \beta \cdot m_s) dT \text{ (p=const.)} \quad (9c)$$

and from these functions the remaining ones due to equations 6 and 7.

In the case, that the heat flowing into the sample is not only for warming up of it but also for other events, as for instance phase changes, we have to start from the first law of thermodynamics

$$dU = dQ + dW + \Sigma dE_i \quad (10)$$

where Q is the heat, W the work and E_i other energy forms (e.g. surface energy, deformation energy, chemical energy) exchanged during the process in question. Hence, taking dW as volume work $-pdV$, we get

$$dU = dQ - pdV + \Sigma dE_i \quad (11a)$$

and with the identity $H = U + pV$

$$dH = dQ + Vdp + \sum dE_i \quad (11b)$$

Integration yields the excess quantities of the process

$$\Delta H^e = \int dQ^e + \sum \int dE_i = \int \Delta \phi^e dt + \sum \int dE_i \quad (p=\text{const.}) \quad (12a)$$

$$\Delta U^e = \int dQ^e + \sum \int dE_i = \int \Delta \phi^e dt + \sum \int dE_i \quad (v=\text{const.}) \quad (12b)$$

As a result we find, that the integral over the excess heat flow rate (peak area) is equal to the change of the potential function only if there are no further energy forms changed during the process (all $dE_i=0$). This condition must be checked carefully in practice, it is not at all trivial especially in the case of phase transitions and chemical reactions where both surface energy and wetting may change non-neglectably.

Furthermore it should be reminded, that the differentials on the right side of equation 10 are no total ones. As a result the quantities on the right side of equation 12 may depend on the path the process is driven on, whereas the sum (the left side) is a difference of state functions and doesn't depend on the path of the process. In a dynamical calorimeter, as the DSC, the process in the sample is run away from equilibrium and the path may already change with the change of the heating rate. Thus the measured heat may depend on the heating rate, which must not be the case for any state function (e.g. ΔH).

Often it is not easy to determine the excess heat flow rate, especially in the case of chemical reactions, where c_p changes as the reactants and the reaction product are different materials with different heat capacity. Here a determination of the excess heat flow rate by drawing a straight line between the beginning and the end of the reaction is not

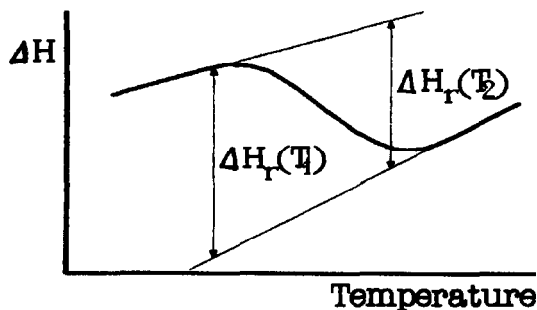


Figure Determination of the excess enthalpy of an reaction.

possible. Instead the reaction enthalpy can be determined from the integral over the c_p function between a starting and an end temperature, leading to the total enthalpy change between these temperatures. In this function the reaction enthalpy appears as a step change, which can be determined at every wanted temperature by extrapolation of the enthalpy function of the reactants and that of the product to the tempera-

ture in question. For precise determination of reaction enthalpies directly from DSC curves the reader is referred to literature [1].

2. PRACTICE

2.1 In absence of phase transitions

A DSC is a dynamical calorimeter where the temperature is changed during the measurement. As heat transport needs time, the sample reaches the program temperature later as the temperature sensor does. In other words there is a thermal lag between the temperature of the controller and the sample temperature. This lag increases with the heat flow, because of the proportional connection between the heat flow rate and the temperature gradient in question. Thus the difference between program temperature and true sample temperature depends on the heat flow rate and for that reason on the sample mass and on the heating or cooling rate (see Fig.1).

Another thermal lag originates from the temperature profile in thick samples. During steady state heating with constant rate there is a parabolic temperature profile [2] inside the sample with the average value depending on thickness d , thermal conductivity λ , density ρ and heating rate β

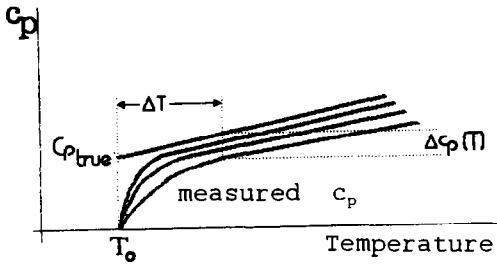


Figure 1. Thermal lag ΔT and its influence on calculated c_p for a thin sample. The measured curves differ in heating rate.

$$\Delta_s T = c_p \cdot \rho \cdot \beta \cdot d^2 / 3\lambda \quad (13)$$

$\Delta_s T$ is the temperature difference between the average temperature inside the sample and the temperature of the low border of the sample at the bottom of the pan. Comparing Fig. 1 with Fig. 2 this additional thermal lag is distinct.

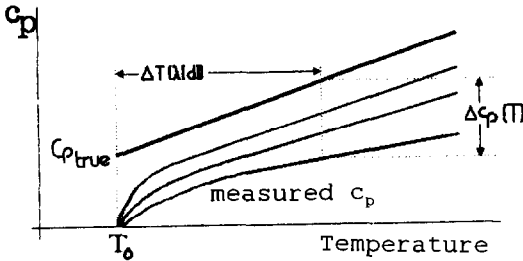


Figure 2. Thermal lag ΔT and its influence on calculated c_p for a thick sample. The measured curves differ in heating rate.

As can be seen from this figure the thermal lag causes a decrease of the calculated heat capacity due to the true one. The reason of this is the thermal lag in connection with the temperature dependence of the heat

capacity. The sample has a lower temperature as the plotted program temperature and thus the heat flow rate is also lower. Consequently the calculated heat capacity (see eq. 8) must be to small as well. Usually the temperature dependence of the heat capacity is rather weak and therefore the error low, but it should be considered for precision measurements.

2.2 With phase transition

If additionally a first order transition takes place in the sample, we find a peak in the measured curve. The connections between the result of the measurement and the potential function searched are as shown in Fig. 3. Obviously the DSC curve (i) and the heat capacity function of a first order transition (v) respective its integral (vi) differ distinctly and there are several steps (a - e) of "translation" necessary. The first three procedures are well known

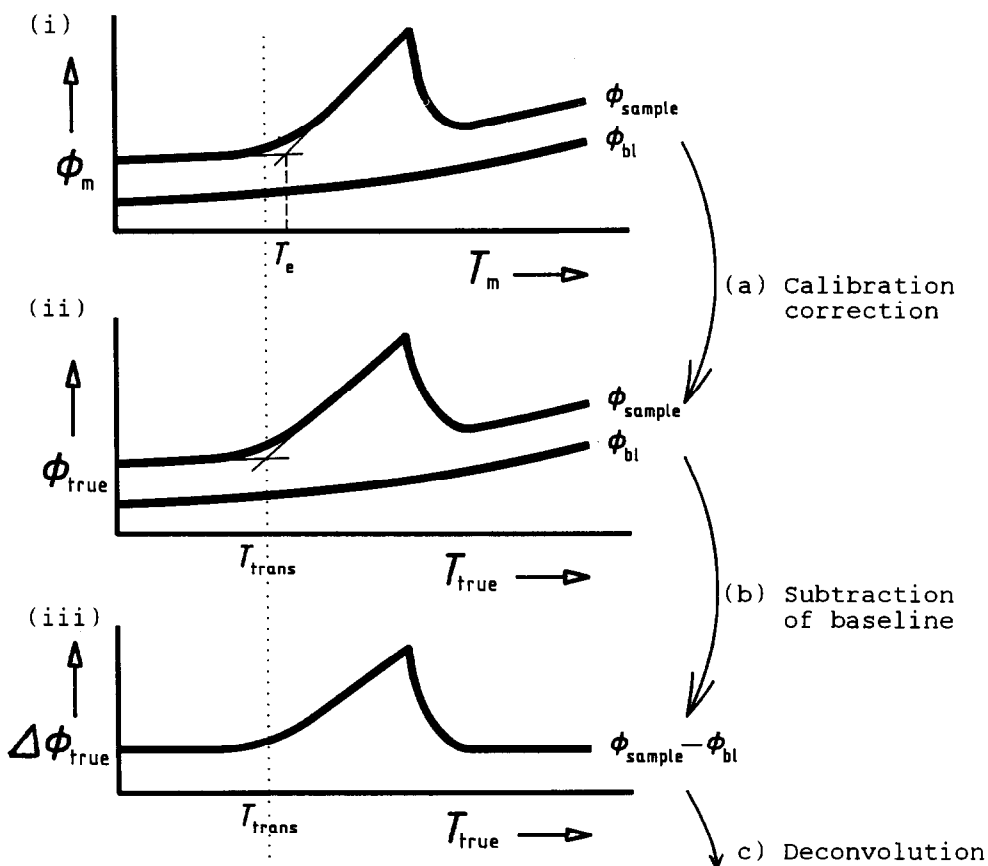


Figure 3. Procedures to come to thermodynamic potential functions from DSC heat flow rate curves.

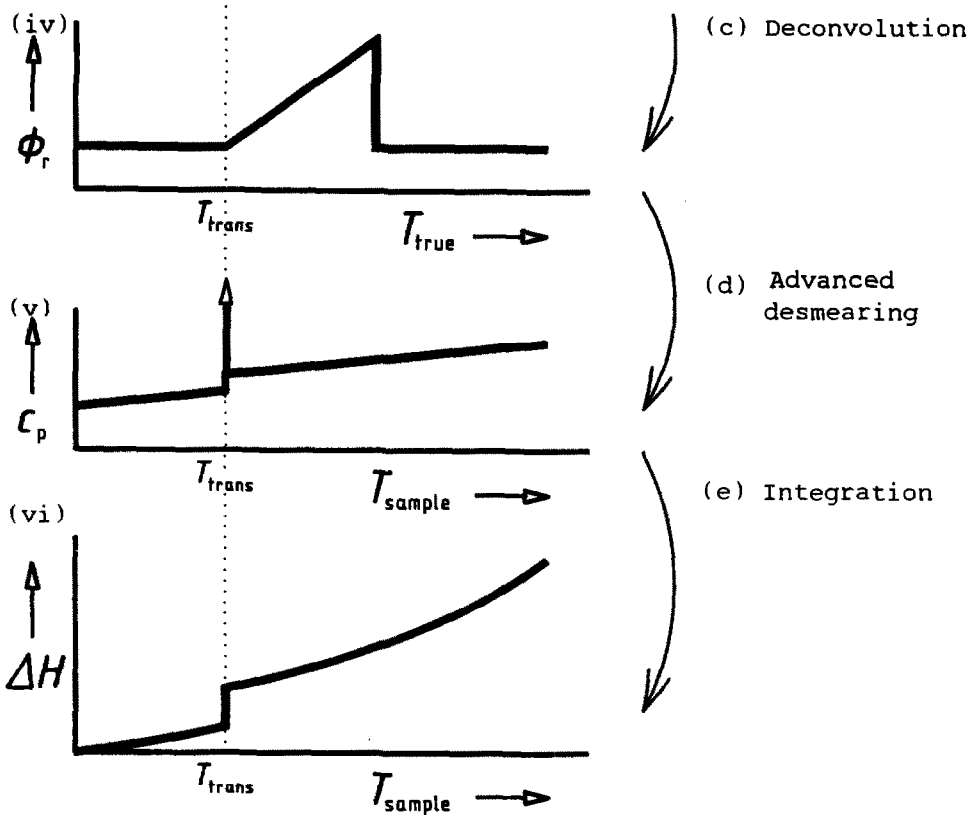


Figure 3 (continued).

- (a) correction of the heat flow and temperature scales due to the results of the calibration,
 (b) subtraction of the baseline,
 (c) "desmearing" (deconvolution) due to the falsification of the sample heat flow on the way through the apparatus.

Nevertheless, the curve got after these procedures (which should correct all influences of the apparatus on the measured heat flow) represents the first order phase transition (e.g. melting) as a triangle instead of a Dirac delta function as it should be. The reason for this is that the temperature of the sample doesn't change until phase transition is completed. As the program temperature proceeds during this time, the temperature gradient from DSC to sample increases linearly and thus the heat flow. The slope is proportional to the heat conductivity between DSC and sample.

Procedure (d) in Fig. 3 involves, beside the calculation of c_p with the aid of eq. 8a, a non-linear transformation of the temperature scale. In the case of a first order phase transition of a pure substance this transformation is rather simple

and aim at a compression of the temperature scale between T_1 and T_2 to one point T_{TRANS} (Fig. 4).

For a phase transition of a non-pure sample the procedure is not so simple and must be done with the theoretical background of the transfer theory (theory of linear response) coming out to a desmearing of the measured curve with the triangle function of the pure substance as apparatus function [3]. In Fig. 5 this is done and the resulting true c_p function can for instance be used to calculate the phase diagram or to determine the impurity in question.

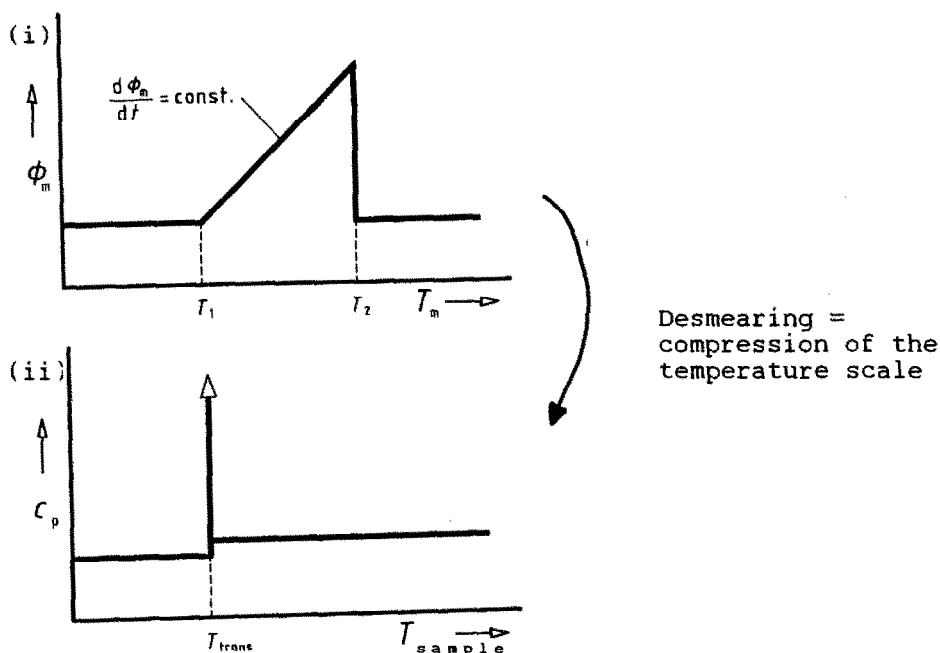


Figure 4. Desmearing of the melting peak of a pure substance: (i) DSC curve after correction of all apparative influences, (ii) calculated after transformation of the temperature scale.

Finally the procedure (e) is state of the art again. The integration may indeed also be done on c_p curves which are not desmeared due to procedure (d). In this case the resulting enthalpy curve is incorrect in the region of the phase transition and must not be taken for further thermodynamical evaluations in this region.

It should be emphasized that a finite thickness of the sample arises to an additional smearing of the curves in the case of a phase transition as well, as the melting zone is walking through the sample (due to the temperature profile) the melting peak is broadened additionally.

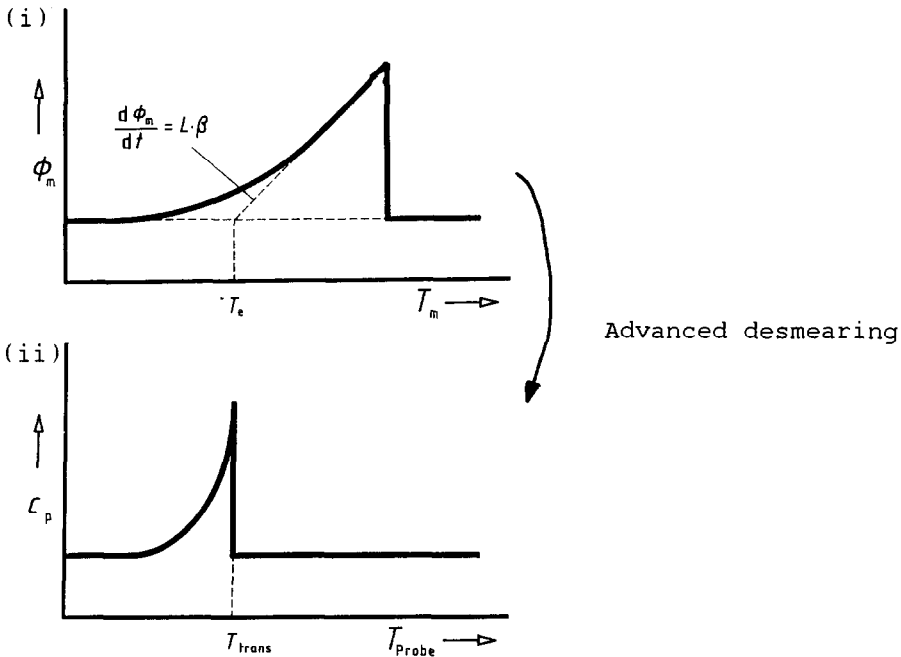


Figure 5. Desmearing procedure of the melting peak of an impure substance

2.3 Desmearing

The total procedure leading from the DSC curve to thermodynamical potential functions has been described above in principle. It looks to be rather complicated, but in fact most of it is state of the art in evaluation software. There is only the deconvolution of the apparatusive smearing and the desmearing of the sample influence on the heat flow rate curve which are not commonly used.

The deconvolution procedure for the apparatusive influence has been subject of research for a long time (see e.g. [4,5,6]) and shall be presented here only briefly. The mean idea is to solve the convolution integral

$$\phi_m(t) = \int \phi_r(t') \cdot a(t-t') dt' \quad (14)$$

for the reaction heat flow rate $\phi_r(t)$, with $\phi_m(t)$ being the measured heat flow rate and $a(t)$ the so called apparatus function. The latter is the answer of the apparatus on an impulse like event at the place of the sample, and can easily be determined by measuring the response of the DSC on very fast heat releasing processes as light flashes, crystallisation after supercooling of say an Indium grain, or heat impulses from an electrical heater.

The desmearing procedure of the sample influences is, as pointed out above, in general not an easy one, especially in case of first order phase transitions. Nevertheless, in the case of steady state conditions or transitions without latent heat (as the glass transition) it can be done.

One method depends on the fact, that the slope of the heat flow rate curve after switching from isothermal to scanning mode, or vice versa, is the response of the apparatus on a step change of the scanning rate and thus contains all necessary information on the heat transfer behaviour of both apparatus and sample [7]. If the linearity of the equipment is valid, the output function is also a convolution product of the searched desmeared function and the apparatus function derived from the heat flow rate curve between switching the scanning rate on and off and obtaining steady state conditions [7].

A considerable advantage of this desmearing method is the fact, that both apparative and sample influences can be desmeared in one procedure. Especially the falsification of the c_p function due to the thermal lag is also corrected at the same time. On the other hand the desmearing problem presented in figures 4 and 5 cannot be solved by this method.

3. CONCLUSIONS

The differential scanning calorimetry is a suitable method to determine thermodynamical potential functions, especially the heat capacity. But the experimenter has to pay attention to the smearing effects of both apparatus and sample. Especially the influence of the sample and the temperature profile inside of it on the measured curve should be noted. In case of large sample masses of bad heat conductivity and heating rates above 5 K/min the smearing effect may amount to several Kelvin.

On the other hand desmearing is easily possible with the aid of modern computer techniques and should be done as far as possible to get the true potential function, especially in the case of narrow transitions or reactions.

A desmearing is not necessary, if the expected corrections are obviously smaller than the certainty of the results aspired to. That is to say, if the thermal lag for instance causes an error in c_p determination of 0.2 percent and the measurement results in an uncertainty of say 3 percent, a desmearing is indeed meaningless. The same is valid for processes which are very broad in terms of temperature.

Taking this facts in consideration, the DSC is, nevertheless, a quick and elegant method to determine thermodynamic potential functions with an sufficient precision.

It is desirable to determine the heat capacity function more frequently instead of the heat flow rate curve, as it is the base of all thermodynamic evaluation and thus of more information. The DSC is indeed a method which enables researchers to do true calorimetry.

5. ACKNOWLEDGEMENTS

The author wish to thank Mike Richardson from NPL, Christoph Schick and Jürgen Schawe from Hochschule Güstrow for helpfull discussions. Furthermore my thank is adressed to the participants of the 8. Ulmer Kalorimetrietage who have incited this review by their persistent asking.

4. REFERENCES

- 1 M.J. Richardson in G. Allen (Ed.), Comprehensive Polymer Science Vol.1, Pergamon Press, New York, (1989), 894.
- 2 H. Hoff, Thermochim. Acta (1991) this issue.
- 3 G.W.H. Höhne et al., in preparation.
- 4 G.W.H. Höhne, Thermochim. Acta 22 (1978) 347.
- 5 K.-R. Loeblich, Thermochim. Acta 83 (1985) 99 and Thermochim. Acta 85 (1985) 263.
- 6 H.J. Flammersheim et al., Thermochim. Acta (1991) this issue.
- 7 J. Schawe and C. Schick, Thermochim. Acta (1991) this issue.