Calorimetry

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1 Introduction

Dynamic calorimeters are ideal for investigating the thermal effects that occur in materials. These devices have two pans (sample holders), one for a reference specimen and one for the measured specimen. During the measurement, the temperature of the two pans is increased linearly in time. The coefficient of this linear function is called the rate of heating.

The output signal is proportional to the difference of the powers needed to increase the temperatures of the pans linearly in time. This means that if a process occurs in the measured sample that involves heat absorption or heat loss, a positive or negative peak will appear in the signal. From the position and the shape of the peak, one can deduce what kind of transition occurred, as well as calculate many parameters that are specific for that. For instance, the temperature of the transition point, the heat needed for the transition, or the activation energy.

These devices are commonly used for the investigation of chemical reactions and phase transitions occurring in liquids and solids. Their great advantage over conventional calorimeters is that they require a much smaller quantity of material ($10 - 100$mg), and that they can give information about the thermal phenomenon rapidly and over a larger range of temperature. The sensitivity of the device depends on the phenomenon being examined, but is usually between $0.1 - 1$mW.

There are two types of dynamic calorimeters, the Differential Temperate Analyser (DTA) and the Differential Scanning Calorimeter (DSC). These differ in the manner of the feedback that controls the temperatures of the pans. This will be discussed later in more details. For now, let us simply say that in a DTA the output signal is approximately proportional to the temperature difference that results from the different warming of the two samples. Using this signal and the properties of the device and the sample, the required power difference for the prescribed heating has to be determined. In a DSC, on the other hand, the obtained signal is directly proportional to the power difference needed for the heating.

It should be noted that there are other scanning devices for the investigation of the thermal properties of materials. For instance, the thermogravimeter (TGA) that detects the weight change of the specimen, or the thermal mechanical analyser (TMA), which

detects its volume change. These will not be used in our measurement and thus will not be discussed.

2   The principle of the operation of the DSC

This summary of the principle of the operation of the DSC is based on the work of O'Neill (1964), Grey (1968) and Kemény (1984).
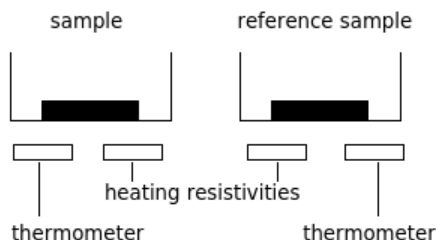

Figure 1: A schematic sketch of a DSC.

As shown on Fig.1, the measured and the reference sample are placed in platinum-iridium sample holders, which are heated from the bottom. The temperature of each of the samples is measured using platinum resistance thermometers.

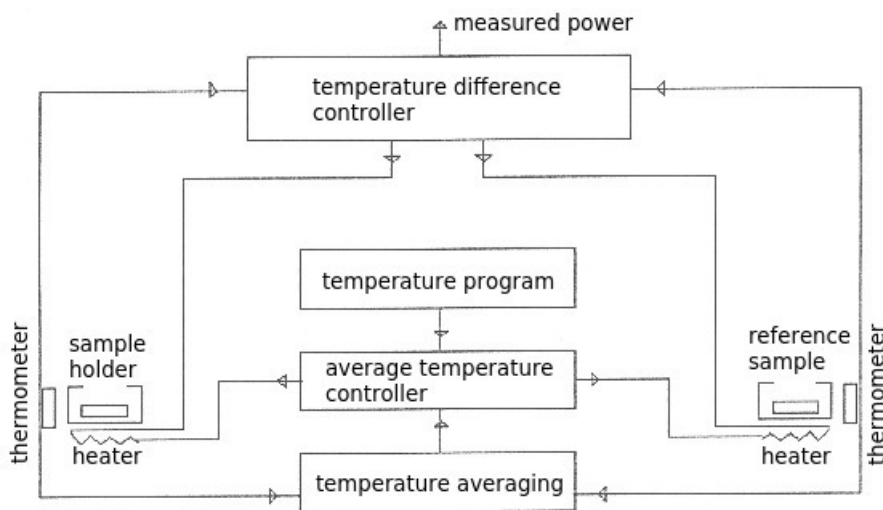The two heaters are controlled using a double loop feedback circuit, as shown in Fig.2.

Figure 2: The feedback system of a DSC.

The first loop controls the average heating power, so that the average of the temperatures measured on the resistance thermometers would change linearly in time, according to the pre-set heating rate. The other loop offsets the heating power of each heater in relation to the mean power. This W power shift is proportional to the temperature

difference of the two thermometers and its sign is set to decrease the temperature difference. This method is called power compensation. As will be discussed in details, this makes the power difference proportional to the temperature difference.

There is another way to decrease the temperature difference. This can be considered a further development of the regular DTA. The two specimens are placed in one single, temperature-controlled heater, and are connected to each other with a good heat conductor. This results in the reduction of the temperature difference. Such an apparatus is commonly referred to as a "heat flow DSC". We mark that it became available due to the rapid development of electronics, as the measurement of lower thermoelectric voltages became possible. Only the power-compensated DSC will be introduced in detail, but its operation principles and the measurement methods can be easily applied to the heat flow DSC.

2.1   Heat currents in the samples

Heat flows from the heater to the sample only if the temperature of the heater differs from the temperature of the sample. Let T_{hm} and T_{hr} denote the temperature of the heater of the measured sample and the temperature of heater of the reference sample, and let T_m and T_r denote the temperature of the measured sample and the reference sample, respectively. According to Newton's law, the $\frac{dq_m}{dt}$ and $\frac{dq_r}{dt}$ powers flowing into the samples are

$$\frac{dq_m}{dt} = \frac{T_{hm} - T_m}{R_m^*} \tag{1}$$

$$\frac{dq_r}{dt} = \frac{T_{hr} - T_r}{R_r^*}, \tag{2}$$

where R_m^* and R_r^* denote the heat resistivity between the samples and the heaters.

If a chemical reaction or a phase transition that results in heat absorption or loss occurs in the measured sample, the balance-sheet equation of the power is

$$\frac{dh}{dt} = c_m \frac{dT_m}{dt} - \frac{dq_m}{dt} + w_m, \tag{3}$$

where c_m is the heat capacity of the sample, dh/dt is the rate of the enthalpy change and w_m is the heat loss of the sample. As the reference sample is thermally inert, the previous balance-sheet equation for it is

$$0 = c_r \frac{dT_r}{dt} - \frac{dq_r}{dt} + w_r, \tag{4}$$

where c_r is the heat capacity of the reference sample, and w_r is its heat loss.

Let the $P_m^0(T)$ and $P_r^0(T)$ functions respectively denote the power required to have T temperature in both heaters, if the sample holders are empty. If the samples are present, the required $P_m(T)$ and $P_r(T)$ powers are

$$P_m(T_m) = P_m^0(T_{hm}) + \frac{dq_m}{dt} \tag{5}$$

and

$$P_r(T_r) = P_r^0(T_{hr}) + \frac{dq_r}{dt}. \tag{6}$$

The first feedback loop changes the average temperature according to the set heating program (heating rate), ie.

$$\frac{T_{\mathrm{hm}} + T_{\mathrm{hr}}}{2} = T_{\mathrm{h}} = vt + T_0, \tag{7}$$

where v is the heating rate, T_0 is the starting temperature and t is the time elapsed.

The other feedback loop means that the $P_{\mathrm{m}} - P_{\mathrm{r}} = W$ difference is proportional to the $T_{\mathrm{hm}} - T_{\mathrm{hr}}$ temperature difference, ie.

$$W = -K(T_{\mathrm{hm}} - T_{\mathrm{hr}}). \tag{8}$$

Usually, it is assumed that the properties of the two pans are approximately the same. Therefore, if we introduce the

$$\Delta T_{\mathrm{h}} = T_{\mathrm{hm}} - T_{\mathrm{hr}}. \tag{9}$$

$$\Delta T = T_{\mathrm{m}} - T_{\mathrm{r}}. \tag{10}$$

$$\frac{2}{R} = \frac{\mathrm{d}P_{\mathrm{m}}^0}{\mathrm{d}T}(T_{\mathrm{h}}) + \frac{\mathrm{d}P_{\mathrm{r}}^0}{\mathrm{d}T}(T_{\mathrm{h}}) \tag{11}$$

$$\Delta P(T_{\mathrm{h}}) = P_{\mathrm{m}}^0(T_{\mathrm{h}}) - P_{\mathrm{r}}^0(T_{\mathrm{r}}) \tag{12}$$

notations and take the difference of Eq.5 and Eq.6, and use Eq.8,

$$\frac{\mathrm{d}q_{\mathrm{m}}}{\mathrm{d}t} - \frac{\mathrm{d}q_{\mathrm{r}}}{\mathrm{d}t} = -K\Delta T_{\mathrm{h}} - \frac{1}{R}\Delta T_{\mathrm{h}} + \Delta P = -\frac{1}{R_{\mathrm{eff}}}\Delta T_{\mathrm{m}} + \Delta P \tag{13}$$

is a good approximation.

$\frac{\mathrm{d}q_{\mathrm{m}}}{\mathrm{d}t}$ and $\frac{\mathrm{d}q_{\mathrm{r}}}{\mathrm{d}t}$ can be eliminated from Eq.1-4 and Eq.13, assuming that $T_{\mathrm{h}} - \frac{T_{\mathrm{m}} + T_{\mathrm{r}}}{2}$ (the difference of the average temperature of the heaters and of the samples) is small. In this case, neglecting the

$$\left(\frac{1}{R_{\mathrm{m}}^*} - \frac{1}{R_{\mathrm{r}}^*}\right)\left(T_{\mathrm{h}} - \frac{T_{\mathrm{m}} + T_{\mathrm{r}}}{2}\right) \tag{14}$$

second-order term, and introducing the $\frac{2}{R^*} = \frac{1}{R_{\mathrm{m}}^*} + \frac{1}{R_{\mathrm{r}}^*}$ notation, we get

$$-\frac{1}{R_{\mathrm{eff}}}\Delta T_{\mathrm{h}} + \Delta P = \frac{1}{R^*}\Delta T_{\mathrm{h}} + \frac{T_{\mathrm{m}} - T_{\mathrm{r}}}{R^*} \tag{15}$$

$$c_{\mathrm{m}}\frac{\mathrm{d}T_{\mathrm{m}}}{\mathrm{d}t} + \frac{\mathrm{d}h}{\mathrm{d}t} = \frac{T_{\mathrm{h}} - T_{\mathrm{m}}}{R_{\mathrm{m}}^*} + \frac{\Delta T_{\mathrm{h}}}{R_{\mathrm{m}}^*} - w_{\mathrm{m}} \tag{16}$$

$$c_{\mathrm{r}}\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t} = \frac{T_{\mathrm{h}} - T_{\mathrm{r}}}{R_{\mathrm{r}}^*} + \frac{\Delta T_{\mathrm{h}}}{R_{\mathrm{r}}^*} - w_{\mathrm{r}}. \tag{17}$$

In most cases one can assume that

$$(c_{\mathrm{m}} - c_{\mathrm{r}})\frac{\mathrm{d}}{\mathrm{d}t}\frac{T_{\mathrm{m}} + T_{\mathrm{r}}}{2} - (c_{\mathrm{m}} - c_{\mathrm{r}})\frac{\mathrm{d}T_{\mathrm{h}}}{\mathrm{d}t} \ll (c_{\mathrm{m}} - c_{\mathrm{r}})\frac{\mathrm{d}T_{\mathrm{h}}}{\mathrm{d}t}. \tag{18}$$

Then T_{m} and T_{r} can be eliminated from Eq.17 and in Eq.18. Using the notations

$$c = \frac{c_{\mathrm{m}} + c_{\mathrm{r}}}{2}, \tag{19}$$

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$$w_{\mathrm{bas}}(T) = -\Delta P + w_{\mathrm{r}} - w_{\mathrm{m}} \tag{20}$$

we get

$$(c_{\mathrm{m}} - c_{\mathrm{r}})v + c\frac{\mathrm{d}\Delta T_{\mathrm{h}}}{\mathrm{d}t} + \frac{\mathrm{d}h}{\mathrm{d}t} = -\frac{1}{R_{\mathrm{eff}}}\Delta T_{\mathrm{h}} - w_{\mathrm{bas}}(T). \tag{21}$$

If R_{eff} as a function of temperature is known, one can use the measured ΔT_{h} signal to calculate $w = -\frac{\Delta T_{\mathrm{h}}}{R_{\mathrm{eff}}}$ (which has the dimension of power), then using Eq.21 one will end up with

$$(c_{\mathrm{m}} - c_{\mathrm{r}})v + \frac{\mathrm{d}h}{\mathrm{d}t} + cR_{\mathrm{eff}}\frac{\mathrm{d}w}{\mathrm{d}t} + w_{\mathrm{bas}}(T) = w. \tag{22}$$

This can be taken as the basic equation that describes the operation of the DSC. If the characteristic time that describes the time evolution of $(c_{\mathrm{m}} - c_{\mathrm{r}})v + \frac{\mathrm{d}h}{\mathrm{d}t}$ is much larger than the $\tau = \frac{1}{cR_{\mathrm{eff}}}$ relaxation time of the calorimeter, then the third term of the left-hand side of Eq.22 can be neglected and the measured w power is

$$w = (c_{\mathrm{m}} - c_{\mathrm{r}})v + \frac{\mathrm{d}h}{\mathrm{d}t} + w_{\mathrm{bas}}(T). \tag{23}$$

When sudden changes occur, for instance the heating rate is changed, the term containing the time differential of the power yields easily observable transients on the output curve. But these usually do not carry important information about the sample.

It is obvious that if the two samples are completely the same and no processes that would result enthalpy change take place, then the output signal is the term denoted by $w_{\mathrm{bas}}(T)$. It is called the baseline. It vanishes only if the sample holders are exactly the same, which is never true, of course. This means that in precise measurements, the baseline must be determined somehow. This is not easy as the baseline contains the properties of the whole device and the heat loss of the samples, and is usually not exactly the same even for two consecutive heating processes.
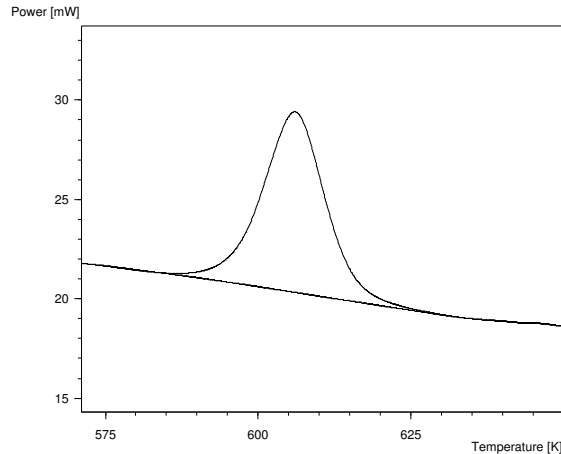

Figure 3: Recrystallisation of Fe-B metallic glass. First and second heating.

If the sample undergoes an irreversible transition during the first heating process, and no transition takes places during the second, then the latter is a good approximation of the baseline (Fig.3). A typical instance for this is the recrystallisation of metallic glasses.
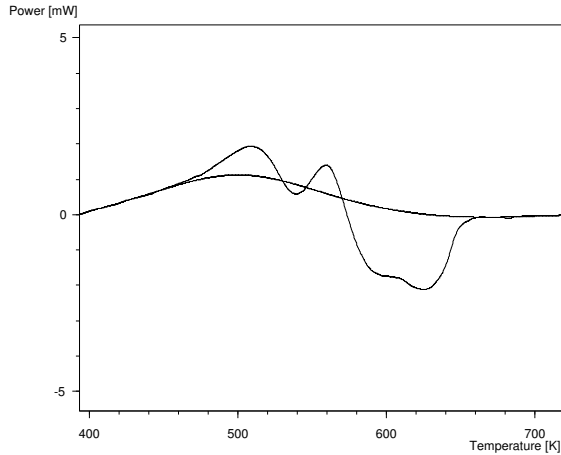
Figure 4: A typical thermogram showing precipitation and dissolution in an Al-Mg-Zn alloy, with the baseline drawn.

In any other case, the baseline has to be determined graphically, under assumption that it is a smooth curve. For most cases, the determination is obvious. But sometimes even the direction of the process is impossible to determine, so that one has to guess the properties of the process from other measurements before the baseline can be determined. A such measured curve and the baseline is shown in Fig.4. (It should be noted that even if the curve of the second heating process can be taken as a baseline, one might need to slightly correct it, as the specific heat of the sample might have changed.)

The calibration of the device is also important. As previously mentioned, the output signal is proportional to the difference of the temperatures of the two sample holders. To determine the heat capacity of the sample and the rate of enthalpy change, $R_{\mathrm{eff}}(T)$ has to be known. If it can be considered constant at a given temperature, then its value can be determined with calibration measurements, performed on samples of already known transition heat. This usually means measuring the heat of fusion of a pure material. Due to the power compensation of the device, $R_{\mathrm{eff}}(T)$ is largely independent of the thermal properties of the calorimeter, as

$$\frac{1}{R_{\mathrm{eff}}} = K + \frac{1}{R} \tag{24}$$

and the value of K is set to be much larger than $\frac{1}{R}$. Therefore, in a DSC

$$R_{\mathrm{eff}} = \frac{1}{K}. \tag{25}$$

This means that the power calibration is independent of the temperature and nearly constant in time. In other words, in a DSC the output signal is proportional to the difference of the powers that flow into the samples.

The above can be applied to the DTA with $K = 0$. In this case, however $R_{\mathrm{eff}} = R$, which means that the multiplier needed for the power calibration is determined by the thermal properties of the calorimeter. Consequently R_{eff} is usually temperature-dependent. So for a quantitative measurement it has to be calibrated at more tem-

peratures. This is not much of a problem, if $R_{\text{eff}} = R$ is constant in time at given temperatures, which, however, is not easy to achieve. Also, above 1000ºC the separate heating of the two sample holders is not solved yet. So all high-temperature calorimeters are DTAs. It should be noted that calorimeters that are not power compensated but can be easily calibrated, are also often called DSCs. To distinguish them from regular DSCs, these are called heat flow DSCs.

3 Studying transitions with a DSC

DSCs are suitable for the investigation of numerous types of transitions, but the different types require substantially different evaluation procedures. Some procedures that are common in metallic physics are introduced below.

3.1 Determining the parameters of melting

Determining the melting point and the heat of fusion of a material – or, in the case of an alloy, drawing the phase diagram – is a common problem. It's especially important since – as has been mentioned before – determining the melting point and the heat of fusion are used to calibrate the device.
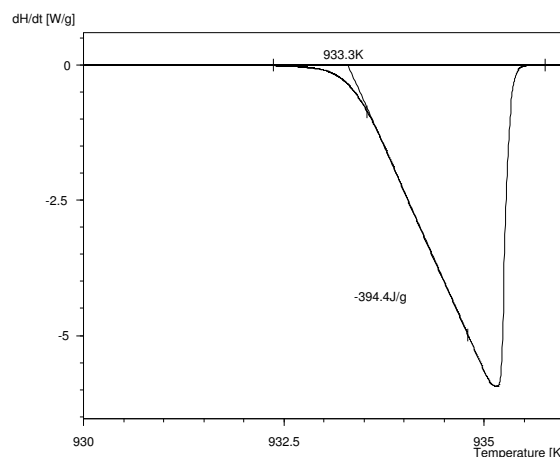

Figure 5: A thermogram measured when melting a pure material (Al).

Considering finite heat conductivity between the heater and the sample, melting the material always results in a peak of finite width, even for very pure samples, since to melt the entire sample, a finite, non-zero amount of time has to elapse.

The melting curve of a very pure sample is shown in Fig.5. The first, entering part of the peak is approximately linear. Then, after the sample is melted, the signal suddenly drops back to zero. Since the enthalpy change as a function of time cannot be given explicitly when a melting is examined, to determine the shape of the thermogram we have to turn to Eq.15 - 17 instead of Eq.23. Expressing T_{r} from Eq.15 and substituting

it into Eq.17 one finds

$$\frac{1}{R_{\text{eff}}}\Delta T_{\text{h}} - c_{\text{r}}\left(\frac{R}{R_{\text{eff}}} + 1\right)\frac{\text{d}\Delta T_{\text{h}}}{\text{d}t} = \frac{1}{R_{\text{r}}^{*}}\left(T - T_{\text{m}}\right) - w_{\text{r}} - \Delta P. \tag{26}$$

The second term on the left-hand side of the equation can usually be neglected, so (using the same notations as before)

$$w = -\frac{1}{R_{\text{r}}^{*}}(T - T_{\text{m}}) + w_{\text{bas}}. \tag{27}$$

As the T_{m} temperature of the measured sample is constant until the end of the fusion, the output signal changes proportionally to the heating program temperature. The slope of the $w(T)$ curve is determined by the heat transfer between the sample and the sample holder, so it doesn't contain relevant information. When the fusion ends, T_{m} stops being constant, and the output signal drops back to the value determined by Eq.23. This can be described with an exponential function with a time constant that corresponds to the device. As the heat capacity of the solid and the liquid phase differ, the measured output signals before and after the fusion are also slightly different.

The melting point is obviously exactly at that point where the peak starts. But since this point can not be determined precisely, it is practical to consider the intersection point of the baseline and the linear function fitted onto the entering part of the peak to be the melting point (see Fig.5).

From Eq.23, the heat of fusion is the time integral of the $w(t)$ curve, normed with the mass of the sample.

It should be noted that during the first melting the heat resistivity between the sample and the holder may change due to the change in the geometry of the sample. In such cases it is expedient to melt the sample again and use the latter thermogram.

The curves of alloys and of pure materials differ from each other. As melting starts at solidus temperature and ends at liquidus temperature, the width of the peak is mainly influenced by these two temperatures, not the heat transfer coefficient. We will discuss the phase diagrams of alloys and their determination later.

The measurement error of the melting point is of the order of 0.1^{o}C, and of the fusion heat is a few percent.

3.2   Measuring specific heat

If no transition takes place, Eq.23 is simplified to

$$(c_{\text{m}} - c_{\text{r}})v + w_{\text{bas}}(T) = w \tag{28}$$

So the difference of the output signal and the baseline is proportional to the difference of the heat capacities of the samples. This means that one can measure the heat capacity, thus the specific heat of the sample. If one records two thermograms, one with and the other without the sample, and takes their difference, the result will be proportional to the heat capacity of the sample as a function of the temperature (Eq.28). But for this, one has to assume that the baselines are the same in the two measurements. This can be done if only an estimate is required, but to calculate the exact value of the specific

heat, the change of the baseline must be considered. One can eliminate this uncertainty through the so-called modulated DSC method. This means that a sinusoidal signal of 0.01Hz frequency and 1ºC amplitude is added to the linear heating program. Then a modulated component appears on the output along with the previously discussed, slowly varying signal (see Fig.6).
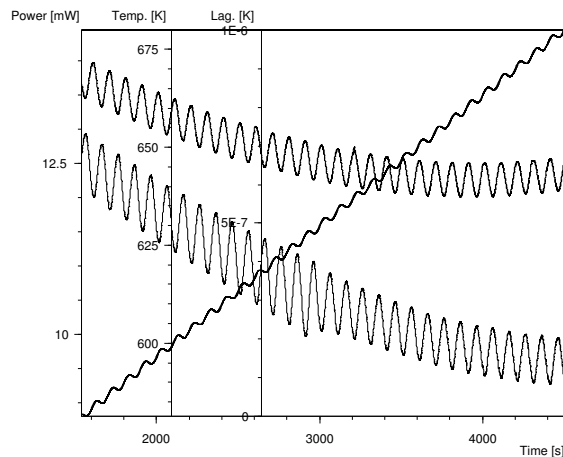

Figure 6: The measured modulated signal of a Ni sample (lower curve) and of an empty sample holder (upper curve) and the program temperature.

Eq.28 changes to

$$(c_{\mathrm{m}} - c_{\mathrm{r}})(v + A\omega\cos(\omega t)) + w_{\mathrm{bas}}(T) = w \tag{29}$$

where A is the amplitude and ω is the angular frequency of the modulation. So the amplitude of the modulated component is proportional to the difference of the heat capacities of the two samples. To obtain the specific heat of the measured specimen, the value of c_{r} must be known. To determine this, one has to make an other measurement with empty sample holder, and evaluate the difference of the two signals. Such a measurement of a nickel specimen near the Curie point is shown in Fig.7 and Fig.8.

3.3   Separation of reversible and irreversible processes

Besides the precise measurement of specific heat, the modulation method can also be extremely useful in separating the reversible and irreversible processes that occur in the sample. With the regular method, the output signal is the sum of the reversible and the irreversible heat. One can separate these by stopping the heating, letting the sample cool down a bit, then heating it up again – the second heating's curve will only contain the reversible heat. Modulation "automates" this process. It would be a good approximation to say that the mean of the modulated signal yields the irreversible heat, while its amplitude yields the reversible heat.

A typical curve of a modulated measurement (performed on chrome-based metallic glass) is shown in Fig.9. It is worth noting that on the non-evaluated figure, the increase
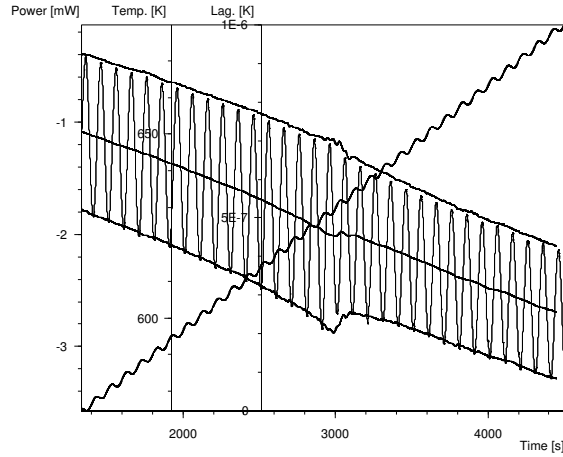
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Figure 7: Modulated measurement of a Ni sample near the Curie-temperature.
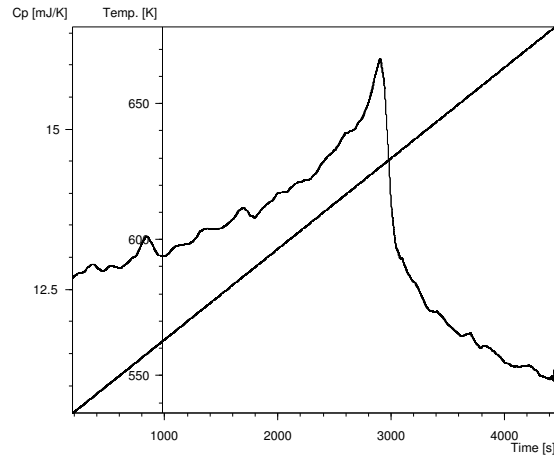

Figure 8: Change of the specific heat of Ni near the Curie-temperature.

in specific heat at the glass transition temperature is very hard to observe. After evaluation, however, it becomes apparent. This illustrates the effectiveness of the modulated method quite well.

3.4   Thermally activated processes

A process is thermally activated if a system, whose state corresponds to a local minimum of free enthalpy, overcomes a potential barrier with thermal fluctuations, thus reaching a state of lower potential. The processes occurring in solids are usually thermally activated. Typical examples include the crystallization of metallic glasses and the deposition and solution of precipitations in solid solutes.

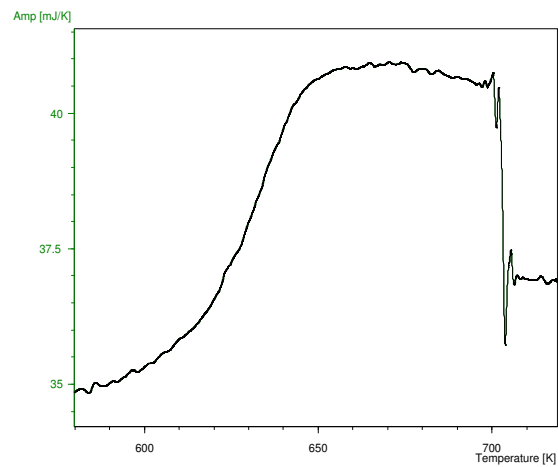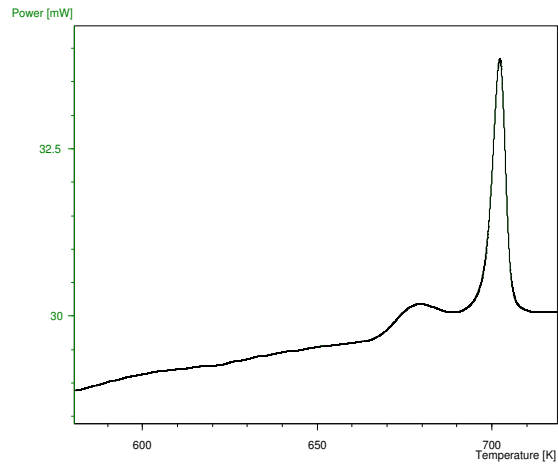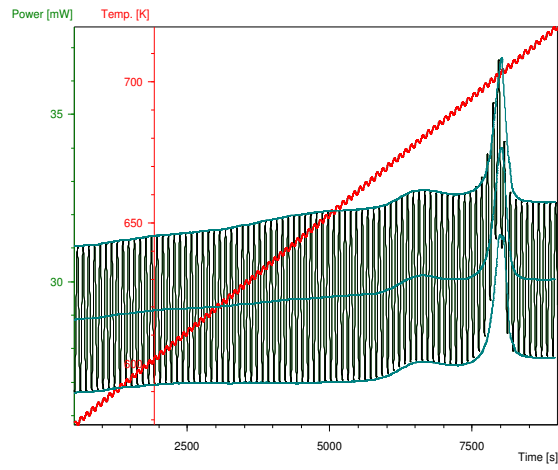During the transition, one can observe the appearance and growth of a new phase.

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Figure 9: Modulated measurement of a Cr-based metallic glass (top figure). The irreversible heat that indicates recrystallisation (middle figure). The reversible heat, which increases relatively rapidly at the glass-transition temperature (bottom figure).

At t time, let $v(t_0, t)$ denote the volume of the grain that appeared at t_0. In the sample

of V volume the V_2 volume of the transformed phase as a function of time is

$$V_2 = V \left\{ N_0 v(0,t) + \int_0^t I(t') v(t',t) dt' \right\} \tag{30}$$

where N_0 is the density of the grains at the beginning and $I(t)$ is the probability of a new nucleation occurring. This does not take into account that growing grains may overlap. This problem was solved by Johnson, Mehl, Avrami and Kolmogorov using the so-called extended volume hypothesis. In the hypothesis Eq.30 was taken to be true, but it stood for a hypothetical, extended volume instead of the real volume. Between the V_2 real and the V_{ex} extended volume the

$$dV_2 = \left(1 - \frac{V_2}{V} \right) dV_{\text{ex}} \tag{31}$$

relation was assumed. This means that at constant temperature, at t time the transformed $C(t,T) \frac{V_2}{V}$ fraction is determined as

$$-\ln(1-C) = \left\{ N_0 v(0,t) + \int_0^t I(t') v(t',t) dt' \right\}. \tag{32}$$

If the right-hand side of Eq.32 is a simple power-law function of time at constant temperature, the equation is called Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetics. Then the transformed fraction is

$$C(t,T) = 1 - \exp\left\{ -(kt)^n \right\}, \tag{33}$$

where k is a temperature-dependent constant and n is an exponent characteristic to the process. In a thermally activated process,

$$k = Z \exp\left\{ -\frac{Q}{RT} \right\} \tag{34}$$

where Q is the activation energy of the process, Z is the so-called frequency factor and R is the universal gas constant.

Eq.33 and Eq.34 mean that these transitions can be described with three parameters: the activation energy, the frequency factor and the exponent.

Of course, the above expression for $C(t,T)$ holds only if the process is isothermal, which is not the case of DSC measurements. To be able to measure the parameters, Eq.33 has to be generalized for non-isothermal processes.

It would be possible to use the momentary temperature at t time instead of a constant temperature in Eq.34. This method is in practice, but Kemény *et al.* have showed that this is completely formal and can not be justified with any physical principles. Instead, they suggested a method based on the isokinetic hypothesis. Here it is assumed that the rate of transition depends only on the momentary temperature and the already transformed fraction, but not any previous thermal changes to the sample.

To calculate the $C(t,T)$ transformed fraction in a non-isothermal process, we start from Eq.33:

$$g(C(t)) = kt \tag{35}$$

where
$$g(C) = |-\ln(1-C)|^{1/n}. \tag{36}$$

Eq.35 can be generalized in the manner of the isokinetic hypothesis: it can be modified to be local, ie.
$$\Delta g(C(t)) = k(T(t))\Delta t. \tag{37}$$

Then the transformed fraction (in a non-isothermal measurement) is

$$C(t) = 1 - \exp\left\{\left[\int_0^t k(T(t'))dt'\right]^n\right\}. \tag{38}$$

Specifically in a DSC the heating rate is constant, ie.

$$T(t) = vt + T_0, \tag{39}$$

where v is the heating rate and T_0 is the starting temperature.

A DSC measures the $\frac{dh}{dt}$ enthalpy rate. If one norms it (ie. divides by) the total change of enthalpy (the area under the peak), not the transformed fraction but the $\frac{dc}{dt}$ rate of transformation is obtained. Certainly, this holds only if the transition undergoes in a single step, or the different processes do not overlap and each can be normed with its area, respectively.

As $C(t)$ in Eq.38 is a very complicated function of the Q, Z and n parameters, it is very difficult to determine them from the measured curves. Especially when the transition consists of more steps.

Often one wants to determine only the activation energy (which is perhaps the most important parameter). It can be solved in a very easy way. Using Eq.38 it can be shown that the v heating rate and the $T_{\max}$ temperature respecting to the maximum of the $\frac{dc}{dt}$ curve can be related as

$$\ln(v) = a - 1.052\frac{Q}{R}\frac{1}{T_{\max}}, \tag{40}$$

where the a parameter is independent of v, and depends only on Q, Z and n. A consequence of Eq.40 is that in case of thermally activated processes the higher the heating rate is, the higher temperature the peak corresponds to. It can be easily observed in measurements, as shown in Fig.10.

We mention that the peak shift can be interpreted thusly: if the heating rate is higher, the system spends less time in a given ΔT temperature interval. This means that then less amount of material can transform to the other state. Thus the transition occurs "later".

It is important to note that due to the peak shift thermograms of different materials can be compared only if the heating rates were the same.

Eq.40 means that if one makes more thermograms of the same sample with different heating rates, and plots $\ln(v)$ as a function of $T_{\max}$, a linear function is obtained. From its slope and y-intercept the activation energy and a can be calculated. If the transition undergoes in more steps, thus multiple peaks are present, then each peak's respective activation energy must be calculated. Fig.11 shows the $1/T_{\max} - \ln(v)$ curve of the set of measurements shown in Fig.4.
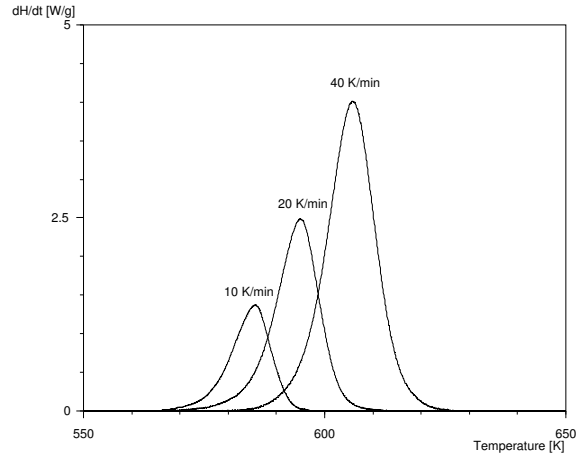
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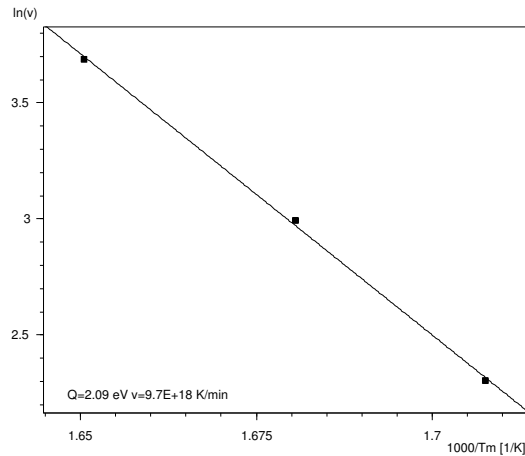Figure 10: Thermograms of Fe-B metallic glass with different heating rates.

Figure 11: $1/T_{\max} - ln(v)$ curve.

4   Determination of phase diagrams of alloys

The DSC is suitable for determining the phase diagrams of alloys. First, let us summarize the thermodynamics of binary alloys (ie. alloys of two components).

Most of the time when solids are being measured, pressure is kept at a constant value (usually atmospheric pressure), while temperature is the control parameter that changes in time. In such a case, the thermodynamic potential describing the system is the $G = U - TS + pV$ free enthalpy (where U is the internal energy, T is the temperature, S is the entropy, p is the pressure and V is the volume).

We note that the $F = U - TS$ free energy is often used instead of the free enthalpy. It is possible if the experiment is performed under not large pressure and on a solid,

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since

$$dG - dF = pdV + Vdp = \left(V + p\frac{\partial V}{\partial p_T}\right)dp + \frac{1}{V}\frac{\partial p}{\partial T_p}pVdT$$
$$= V\left(1 - \frac{V}{\kappa}\right)dp + \beta pVdT, \tag{41}$$

where κ is the isothermal compressibility and β the coefficient of thermal expansion. As dp is zero, the two thermodynamic potentials are the same if $pv\beta$ is small. As β is small for solids, the former holds for atmospheric pressure.

If the amount of each components is not constant, the change in internal energy is

$$dU = TdS - pdV + \mu_A dN_A + \mu_B dN_B, \tag{42}$$

where μ_A and μ_B are the chemical potentials of, and N_A and N_B the number of particles of the A and B components, respectively. Thus the change in free energy is

$$dG = -SdT + Vdp + \mu_A dN_A + \mu_B dN_B. \tag{43}$$

According to the general rule, the internal energy for these systems is

$$U = TS - pV + \mu_A N_A + \mu_B N_B. \tag{44}$$

Using this and the definition of the free enthalpy

$$G = \mu_A N_A + \mu_B N_B. \tag{45}$$

It is practical to use the $g = G/(N_A + N_B)$ free enthalpy of a single atom (specific free enthalpy). Using Eq.45, g is

$$g = \mu_A c + \mu_B(1 - c), \tag{46}$$

where $c = \frac{N_A}{N_A + N_B}$ is the concentration of the A-type atoms. (The two chemical potentials depend on the concentration, of course.) Using Eq.44 and Eq.45, the change of g is

$$dg = -sdT + \frac{1}{n}dp + (\mu_A - \mu_B)dc \tag{47}$$

where $s = S/(N_A + N_B)$ is the specific entropy and $n = (N_A + N_B)/V$ is the particle density. So the derivative of the specific free enthalpy with respect to the concentration and at constant temperature and pressure is

$$\left(\frac{\partial g}{\partial c}\right)_{T,p} = \mu_A - \mu_B. \tag{48}$$

If the concentration dependence of the specific free enthalpy is known, then using Eq.46 and Eq.48, the chemical potential of the two components can be easily determined graphically: the value of the line that is tangential to the $g(c)$ curve at the point of the given concentration is μ_B at $c = 0$ and μ_A at $c = 1$ (see Fig.12).

A homogeneous, single-phase system containing multiple components may be unstable in some cases due to the interaction of the components: the system may separate into two or more phases. In the following, we examine the thermodynamic conditions of two phases being in equilibrium in a binary alloy at a given temperature.

It is known from thermodynamics that a system is in a state of equilibrium at constant temperature and pressure if the total free enthalpy of the system is at a minimum. So
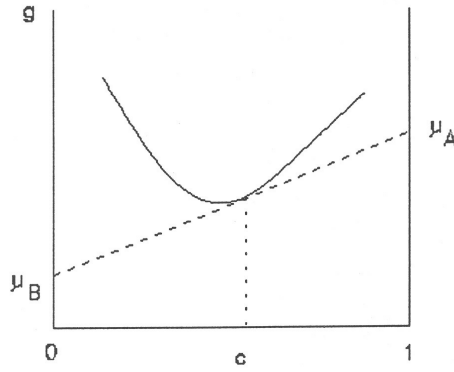
Figure 12: Determination of the chemical potential in a binary system using the concentration dependence of the specific free enthalpy.

first let us look at the conditions of decreasing free enthalpy if the system separates into two phases, one with c_1 concentration and f volume fraction and the other with c_2 concentration and $1 - f$ volume fraction. The free enthalpy of the separated system is

$$g_s = fg(c_1) + (1 - f)g(c_2). \tag{49}$$

Of course, the mean concentration has to remain the same, ie.

$$c = fc_1 + (1 - f)c_2. \tag{50}$$

So, after eliminating the volume fraction, we get

$$g_s = \frac{c}{c_1 - c_2}(g(c_1) - g(c_2)) + \frac{c_1 g(c_1) - c_2 g(c_2)}{c_1 - c_2}. \tag{51}$$

So g_s as a function of the c concentration is a line that goes through the $(c_1, g(c_1))$ and $(c_2, g(c_2))$ points. This means that (as can be seen in Fig.13/a), if the $g(c)$ curve is convex downward at every points, then separating will always increase the free enthalpy. Otherwise, the free enthalpy can decrease (see Fig.13/b). So a condition of separation is that the specific free enthalpy curve must have a concave part.

If the free enthalpy curve has to minimums (as in Fig.13/b), then the minimum free enthalpy can be achieved if the g_s line is the mutual tangential of the two minimums, ie. the dashed line in Fig.13/b. Thus, the two equilibrium concentrations are the concentrations corresponding to the two points of tangency. This means that if the mean concentration falls between these two points, in equilibrium the system will always separate into two phases with concentrations corresponding to the two points of tangency. The volume fraction of the phases can be determined from Eq.50. We note that (as has been previously shown) the chemical potentials of each components is always the intersection point of the tangential line and the $c = 0$ and $c = 1$ axes. The consequence of the mutual tangential is that the chemical potential of a component is the same in
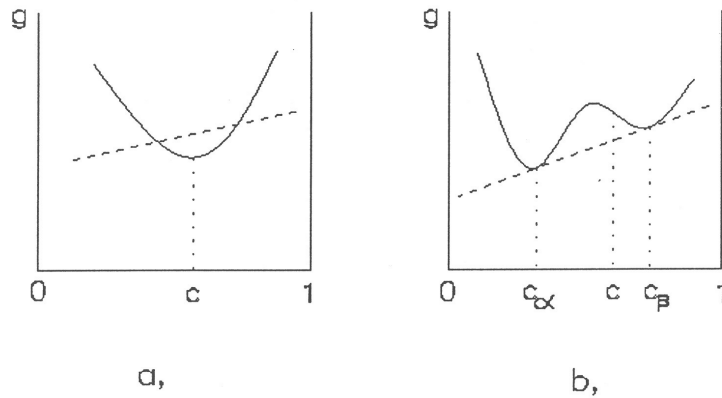
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Figure 13: Free energy curves with one (a) and two (b) minimums.

the two phases. This is in accordance with the general principle that in equilibrium the intensive state quantities are the same.

Since free enthalpy is temperature-dependent, the concentrations of the equilibrium phases also change with the temperature. Above a certain temperature, the free enthalpy curve has only one minimum, hence a single-phase system is formed. The possible phases are commonly represented on a so-called phase diagram. The phase diagram gives the concentrations of the equilibrium phases as a function of the temperature. For a simply behaving binary material, it is like Fig.14. If the concentration-temperature data pair falls into the area marked $\alpha + \beta$, the system will separate into α and β phases.
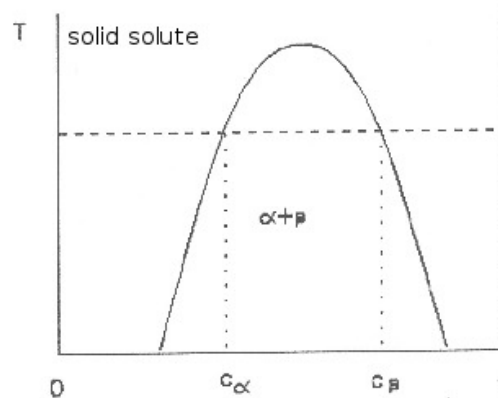

Figure 14: Phase diagram of a simple binary material.

The spatial distribution of the phases strongly depends on the history of the sample, and is also heavily influenced by the surface tension and the diffusion coefficient. Therefore, the morphology cannot be determined through thermodynamic considerations alone. In a state of minimum energy, the phase boundary would be a sphere, but in practice it can be hardly achieved.
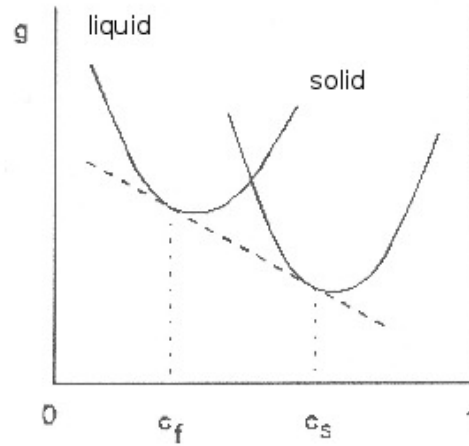

Figure 15: Free enthalpy of the liquid and the solid phase as a function of the concentration.

We must also discuss (partially) melted binary systems. If we plot the free enthalpy curves of the solid and the liquid phase as a function of the concentration (Fig.15), then – with similar considerations as before – it should be clear that the system may reach a free enthalpy minimum in a way that both a liquid and a solid phase are present. Like before, the tangency points of the mutual tangential line yield the concentrations of the phases. In the simplest case this gives the phase diagram shown in Fig.16. The upper curve is called liquidus and the lower is called solidus. Above the liquidus, only liquid phase, and under the solidus only solid phase is present. Between them the liquid and solid phase are in equilibrium.

Real systems can be described with a combination of the phase diagrams in Fig.14 and Fig.16. One of the most important ones is the so-called eutectic phase diagram, which is shown in Fig.17. Its speciality is that there is a certain value of concentration (marked by the dashed line) where the solid and liquid phases cannot be in equilibrium. So if the material is melted, then above the melting point only the liquid phase will be present, similarly to pure materials. There are many other types of phase diagrams, but these are not considered here.

Phase diagrams can be measured very accurately with a DSC. For this, the best is to use a heating rate of about 1K/min. Fig.18 shows a thermogram recorded using an Sn-Pb alloy. Similarly to the melting of pure materials, the solidus and liquidus temperature are at the intersection points of the baseline and the linear functions fitted onto the entering and the exiting segments of the curve.
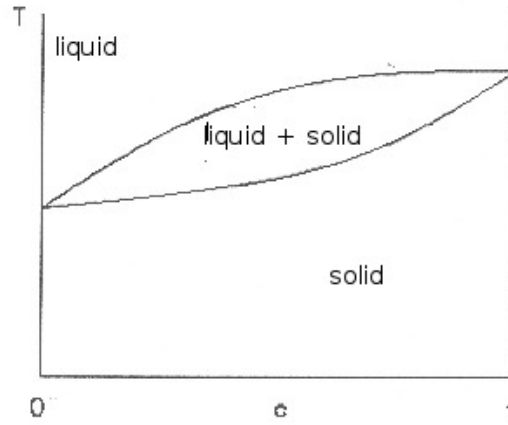
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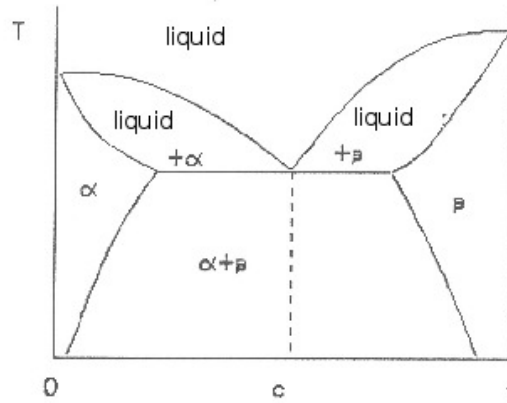Figure 16: Phase diagram if both liquid and solid phase are present.

Figure 17: Phase diagram of an eutectic material.

5 Usage of the PERKIN-ELMER type DSC

The PERKIN-ELMER type DSC is one of the most widely used calorimeters. Without any additional devices, these DSCs can be used in the temperature range of 350-1000K. With a complementary cooling system 200K can be achieved. Moreover, when cooled with liquid nitrogen, even 100K can be achieved, but this makes the measurement very complicated and long-drawn.

The temperature scale can be altered to degrees of Celsius. In this case, the maximum attainable temperature is 1000^oC. However, such high temperatures significantly reduce the lifetime of the machine and should therefore be avoided if possible.

The rate of heating can be set to any value between 0.01 and 320K/min. The most suitable rate strongly depends on the properties of the measured material. As a rule of thumb, rates above 5K/min are not practical for determining the melting point and the
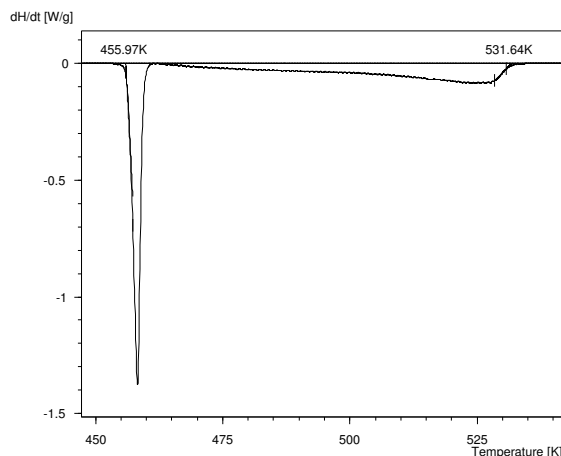
Figure 18: Thermogram of a Sn-Pb alloy.

phase diagram, since the lower the rate is, the more precise the measurement will be. Thus the rate should be chosen as low as possible. For solid phase transitions a rate in the range of 5 and 80K/min is the most suitable. The highest value, 320K/min is suitable only for reaching the starting temperature and for rapid cooling.

A general principle is that the higher the rate, the higher the measured signal is, since the enthalpy of the transition has to flow in in a shorter time. This means that processes with low transition heat can be better observed at higher rates. However, higher rate gives a larger uncertainty of the baseline.

The sensitivity of the calorimeter is of the order of mW. This means that since the samples should have a mass of $10 - 100$mg, an enthalpy change rate of 0.1W/g is the minimum that can be measured. Of course, observability also depends on the temperature range: a process with a wider temperature range is more difficult to distinguish from the baseline than a process of the same rate but narrower temperature range.

In a PERKIN-ELMER 2 type calorimeter the shape of the baseline can be electronically controlled.

First of all, the K in Eq.8 is weakly temperature-dependent, and that dependency is variable. Secondly, in the second feedback circuit a function that is linear in time and has a variable parameter is added to $K(T_{\mathrm{m}} - T_{\mathrm{r}})$. Thus, one can set the baseline to have an S-shape. This means that the starting, ending and mean power are all zero.

The baseline can be controlled with the potentiometers labelled ZERO, SLOPE and DT BALANCE. ZERO shifts the level of the output signal. SLOPE changes its slope and DT BALANCE changes its curvature. However, the exact effect these have on the signal depends on the temperature range involved, as well as the heating rate. Therefore, one can only set the baseline with precision by recording it multiple times and determining the effect of DT BALANCE and SLOPE. For a detailed review of adjustment, see the PERKIN-ELMER DSC USER MANUAL.

Finally, an important warning: to protect the device, one should always place the samples into the sample holders and not anywhere else; otherwise the sample could form an alloy with the materials of the calorimeter.