

DSC CALIBRATION DURING COOLING **A survey of possible compounds**

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Abstract

A number of compounds is investigated for DSC calibration during cooling. Adamantane and Zn show fast reversible transitions and can be applied both for temperature and for heat calibrations. A third compound, namely 4,4'-azoxyanisole, has a liquid crystal to isotropic liquid transition at 409 K. This compound can be used for temperature calibration. Heat calibration with this compound is more problematic because of the small heat effect and the construction of the baseline. Other compounds like NaNO₃, In, Hg and Pb, show a slight supercooling. Nevertheless they can be used for heat calibration. The use of large samples of NaNO₃ and In gives the possibility to construct the equilibrium onset temperatures of the cooling peaks, so these two compounds are also appropriate for temperature calibration on cooling.

Keywords: avoidance of sample/pan reactions, DSC calibration during cooling, influence of sample mass on crystallization behaviour, reversible transitions, supercooling

Introduction

DSC instruments are normally calibrated using compounds showing first order transitions with well known temperature and heat effect. These calibrations are made in the heating mode. Because of the existence of a time lag, the extrapolated onset temperature T_0 varies with the heating rate.

The greatest accuracy is reached with different heating rates and extrapolation to zero-heating rate [1, 2]. This is however a time-consuming method.

A faster method is to compare the investigated compound with some calibration compounds in the appropriate temperature region and with one constant heating rate (for instance 10 K min⁻¹). When the thermal mass of the applied samples does not differ too much, an identical time lag can be expected for all these samples, resulting into a fast practical calibration.

Calibration during cooling is more problematic, because most compounds show supercooling effects. Some compounds, however, show no supercooling and behave symmetrically during heating and cooling with the same rate. Application of these

compounds results in a fast calibration method, also applicable during cooling. When the applied DSC instrument behaves symmetrically during heating and cooling, which is the case for most heat flux instruments, the mean value $\langle T \rangle$ of the extrapolated onset temperatures T_0 of these compounds for heating and cooling with the same rate is constant and independent of the absolute value of the heating and cooling rate. This value $\langle T \rangle$ corresponds to the value of T_0 , determined by extrapolation to heating rate zero, but can be determined in a much faster way!

In preceding articles [3–5] three different compounds with symmetrical behaviour are mentioned, namely: adamantane ($C_{10}H_{16}$), 4,4'-azoxyanisole ($C_{14}H_{14}N_2O_3$) and Zn. Other compounds, like Hg and Pb, show slight supercooling, while Ga and Sn have a very large supercooling.

In this article the possible application of two other compounds is discussed, namely $NaNO_3$ and In. They show a supercooling effect, but smaller than Hg and Pb, and can give correct extrapolated onset temperatures during cooling, provided that the sample mass is large enough.

The relevant thermodynamic data for all these compounds are:

– Adamantane has a reversible solid-solid transition at 208.62 K, with $\Delta H = 24.78 \text{ J g}^{-1}$ [6, 7].

– Zinc melts at 692.677 K, with $\Delta H = 111.97 \text{ J g}^{-1}$ [1, 8].

– 4,4'-Azoxyanisole shows two transitions on heating: I, a melting reaction (solid \rightarrow liquid crystal) at about 389 K ($\Delta H = 112 \text{ J g}^{-1}$) and II, a liquid crystal \rightarrow isotropic liquid transition at about 409 K (ΔH is about 4 J g^{-1}) [3, 9, 10].

The first transition in the 4,4'-azoxyanisole curve (I) has a very large supercooling effect, but transition II is completely reversible. Application of this compound has some disadvantages because no exact calibration figures exist in literature and the heat effect of the second peak is very small. The measured value of this heat effect depends on the construction of the base line.

So this compound is certainly not an ideal substance for calibration purposes, but it was taken into account because no other appropriate compounds are known in this temperature range.

– $NaNO_3$ shows two transitions on heating: I, a solid \rightarrow solid transition at 549 K (temperature of peak maximum), with $\Delta H = 40.11 \text{ J g}^{-1}$ and II, a melting reaction at 580 K, with $\Delta H = 176.52 \text{ J g}^{-1}$ [11, 12].

As shown in Fig. 1, the first transition (I) cannot be used for calibration since the peak is very broad and asymmetrical, with only a small heat effect. The measured values are: peak temperature 548.79 K and $\Delta H = 37.40 \text{ J g}^{-1}$. The second transition (II), however, can well be applied for calibration during heating and cooling, since the supercooling effect is rather small (1.3 K at -10 K min^{-1}) so that for large amounts the equilibrium onset temperature can be determined by extrapolation of the equilibrium part of the cooling peak.

– In melts at 429.75 K, with $\Delta H = 28.62 \text{ J g}^{-1}$ [1, 2, 8].

Just like $NaNO_3$, also in this case the supercooling effect is small enough (2.3 K at -10 K min^{-1}) for application during cooling.

– Pb (600.61 K, $\Delta H=23.02 \text{ J g}^{-1}$) and Hg (234.32 K, $\Delta H=11.62 \text{ J g}^{-1}$) show higher supercooling (about 3 K at -10 K min^{-1}).

Therefore, even for large sample amounts, the extrapolated onset temperature is difficult to determine during cooling. So these two compounds are usable for enthalpy calibration during cooling, but not for temperature calibration.

– Ga (302.91 K, $\Delta H=79.87 \text{ J g}^{-1}$) shows a supercooling of about 25 K at -10 K min^{-1} .

So this compound cannot be used for DSC calibration during cooling, just like Sn, which has an even higher supercooling effect.

Recently (1999) Martens and Cruz-Pinto [13] discussed the temperature calibration of a DSC instrument on cooling.

They tested In, Pb and $\text{C}_{22}\text{H}_{26}\text{N}_2$ (a liquid crystal delivered by Merck, ref. CBOOA [13]), showing a transition at 379.5 K. The experiments were carried out on a Perkin Elmer DSC-7 instrument. The sample mass was 5–10 mg. The following supercooling figures (extrapolated to zero heating rate) were found:

In:	1.95 K
Pb:	2.17 K
$\text{C}_{22}\text{H}_{26}\text{N}_2$:	0.257 K

As will be shown, the figures for In and Pb agree rather well with our results.

Experiments and results

A DSC instrument from Rheometric Scientific (DSC-GOLD) was used with a liquid nitrogen cooling device for programmed cooling [3]. Temperature and DSC signal were calibrated at a heating rate of 10 K min^{-1} , using adamantane, Hg and Ga for the low temperature range, and In, Sn, Pb and Zn for the high-temperature range.

Samples of the test-substances were of the highest obtainable purity: the metals >99.999%, NaNO_3 better than 99.9%, and 4,4'-azoxyanisole and adamantane >99%. They are used without further purification.

The samples, except Hg, were contained in flat aluminium pans, with a mass of about 29 mg. Hg was measured in a hermetically sealed pan (mass 48 mg). In order to avoid chemical reactions between the aluminium pans and Ga, Pb and Zn, samples of these metals were embedded in 10–20 mg alumina (Al_2O_3) powder, except the large Pb sample (35 mg).

The sample amount was 2–14 mg, except for 4,4'-azoxyanisole. Because of the small heat effect a greater amount of this compound was taken, namely 25 mg. Also greater amounts of Pb (35 mg), In (24.9 mg) and NaNO_3 (8.5 mg) were measured.

An experiment consisted of subsequent heating and cooling of a sample with the same absolute rate, giving an endothermic peak on heating and an exothermic peak on cooling. As discussed before, the compound 4,4'-azoxyanisole has a transition I with a large heat effect at 389 K, followed by the reversible transition II with a small heat effect at 409 K. Particularly at high heating rates this could give problems. If such is the case, it is unlikely that the peak of transition II can be detected in the end

phase of the first peak (I) [8, 9]. However, this can be avoided because transition I has a great supercooling effect [3]. So after the first heating run the sample can be cooled down to below 373 K without solidification. The following experiments only show the peak of transition II, provided that the sample is not cooled down below 373 K.

The results of the experiments are given in Table 1 and in the Figures 1–5.

Table 1 Results of heating and cooling runs for various samples at several rates (K min^{-1}). The measured heat effect ΔH (J g^{-1}), the extrapolated onset temperature T_0 (K), the temperature difference ΔT and the mean value $\langle T \rangle$ between heating and cooling with the same rate, are given

Sample + mass/mg	Rate/ K min^{-1}	Heating		Cooling		$\Delta T/\text{K}$	$\langle T \rangle/\text{K}$
		T_0/K	$\Delta H/\text{J g}^{-1}$	T_0/K	$\Delta H/\text{J g}^{-1}$		
$\text{C}_{10}\text{H}_{16}$ Adamantane 5.350	10	208.71	24.66	207.49	-24.96	1.22	208.10
	5	208.30	23.48	207.80	-23.67	0.50	208.05
	1	208.05	22.59	208.02	-22.33	0.03	208.04
4,4'-azoxy- anisole 25.10	20	409.49	4.31	407.81	-4.32	1.68	408.65
	10	409.11	4.43	408.25	-4.28	0.86	408.68
	5	408.92	4.36	408.52	-4.13	0.46	408.72
	2	408.84	3.92	408.69	-	0.15	408.76
NaNO_3 2.446	10	578.21	168.23	577.12*	-165.12	1.09	-
NaNO_3 8.489	10	579.61	-**	578.85	-**	0.76	579.23
	5	579.19	173.93	578.96	-172.69	0.23	579.08
	1	578.57	171.73	578.59	-175.09	-0.02	578.58
Zn 2.487	10	691.89	111.94	690.54	-111.64	1.35	691.22
	5	691.38	111.74	690.70	-114.05	0.68	691.04
	1	691.19	111.18	690.93	-113.11	0.26	691.06
In 4.486	10	430.16	28.04	427.86*	-27.62	2.30	-
In 24.900	20	430.18	-**	429.33	-**	0.85	429.75
	10	429.96	27.51	429.54	-27.35	0.42	429.75
	5	429.86	27.44	429.71	-27.35	0.15	429.78
Pb 11.875	10	601.23	23.40	598.01*	22.71	3.22	-
Pb 35.200	10	600.16	23.63	597.27*	-**	2.89	-
Hg 13.65	10	234.20	11.42	231.11*	-11.33	3.09	-
	5	233.98	11.52	231.21*	-11.12	2.77	-
	2	233.75	11.60	231.31*	-10.50	2.44	-
Ga 2.339	10	303.06	76.98	278.49*	-77.76	24.57	-

*Not the extrapolated onset is given but the real temperature at the beginning of the crystallization

**These heat effects could not be determined, for reason of a too high DSC signal

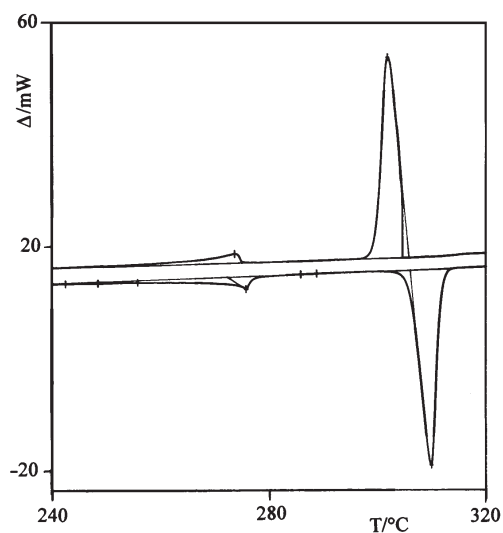


Fig. 1 Heating and cooling run of 8.489 mg NaNO_3 at 5 K min^{-1}

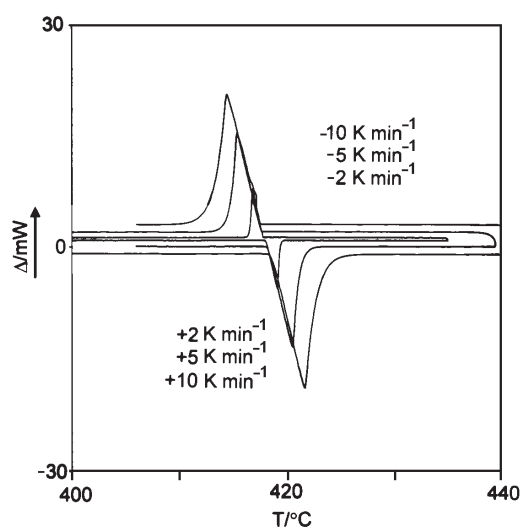


Fig. 2 DSC runs of 2.487 mg Zn, embedded in 10.7 mg alumina, with successive heating and cooling rates of 10, 5 and 1 K min^{-1} . (+2 and -2 in the figure must be: +1 and -1) Degrees centigrade ($^{\circ}\text{C}$)= $\text{K}-273.15$ Up=exothermic; Down=endothermic

Figure 2 shows that Zn behaves completely reversible during heating and cooling: the peaks are identical for heating and cooling at the same rate, with equal shape, peak height and surface area. The difference ΔT of the onset temperatures is small

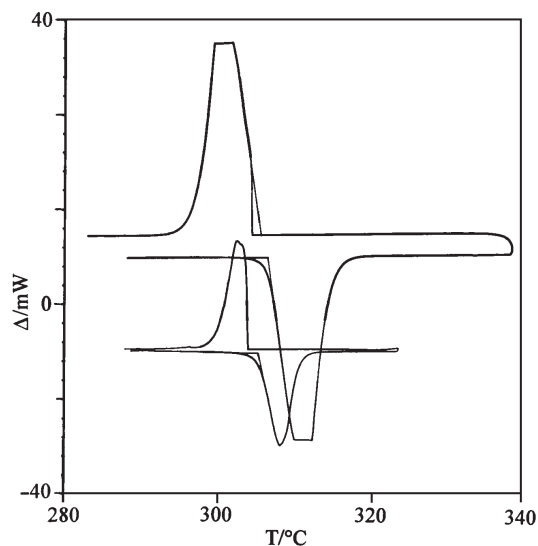


Fig. 3 Heating and cooling runs of 8.489 and 2.446 mg NaNO_3 at 10 K min^{-1} .

The small amount shows only supercooling at crystallization, but with the large sample amount the equilibrium onset temperature can easily be constructed for the crystallization reaction. At this high heating rate the DSC peak is cut off because the amplifier cannot handle these large DSC signals. This can be avoided by using lower heating rates (7 K min^{-1} , or lower)

and decreases with decreasing heating/cooling rate: about 1.3 K at 10 K min^{-1} , 0.68 K at 5 K min^{-1} and 0.26 K at 1 K min^{-1} .

The mean onset temperature $\langle T \rangle$ is nearly constant and varies between 691.04 and 691.22 K .

Table 1 shows that adamantane, just like Zn, is completely reversible [3].

Also, results of 4,4'-azoxyanisole are given in Table 1. The peak shape is not so sharp as is the case for Zn. This is caused by the fact that the value of the specific heat is larger in the liquid crystal range, than it is for the isotropic liquid [3]. This influences the peak shape at the lower temperature side, but the peak onset however is sharp and the extrapolated onset temperature T_0 can be determined very accurately.

The figures in Table 1 show that ΔT is small and varies from 1.68 K at 20 K min^{-1} to 0.15 K at 2 K min^{-1} .

The mean temperature $\langle T \rangle$ is rather constant and varies between 408.65 and 408.76 K (mean value of four experiments: 408.70 K). So this compound also shows a reversible behaviour.

In Fig. 3 two amounts of NaNO_3 are compared at 10 K min^{-1} , namely 2.446 and 8.489 mg .

The small sample shows only a supercooling peak during crystallization, but the large amount shows that during crystallization the equilibrium DSC peak is reached,

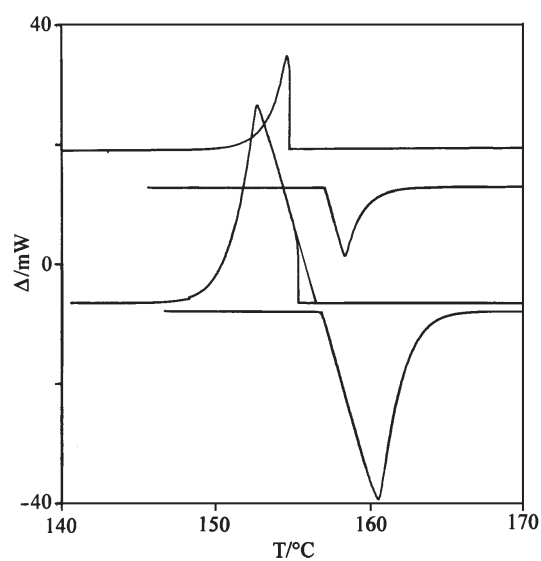


Fig. 4 Heating and cooling runs of 4.486 mg and 24.900 mg In at 10 K min^{-1} . Just like in Fig. 3, for the small amount only supercooling is found, but the large sample shows only a small supercooling effect, resulting into an easy construction of the extrapolated equilibrium onset temperature during cooling

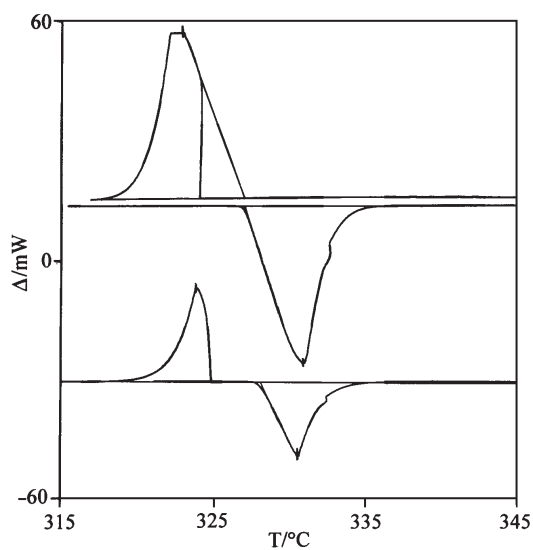


Fig. 5 Heating and cooling runs of 11.876 mg and 35.200 mg Pb at 10 K min^{-1} . Here the supercooling is too high for accurate determination of the equilibrium onset temperature during crystallization

after initial supercooling. From this equilibrium part of the DSC curve the extrapolated onset temperature can be constructed.

It can also be seen that a large sample amount combined with a high heating or cooling rate can give problems with the amplifier. From 7 K min^{-1} and lower this problem disappears, since the height of the DSC signal not only depends on sample mass and heat effect, but also on the heating rate.

This effect depends on the type of instrument. Perhaps, other instruments do not show problems with these high DSC signals?

From Table 1 it can be seen that for large samples the mean value $\langle T \rangle$ of the extrapolated onset temperatures varies from 578.58 (at 1 K min^{-1}) up to 579.23 K (at 10 K min^{-1}).

In addition, the results of heating experiments (10 K min^{-1}) with small and large samples show a slight difference between the extrapolated onset temperatures: 578.21 K for 2.446 mg and 579.61 K for 8.489 mg.

So more investigations are necessary in order to find out whether NaNO_3 indeed can be used for DSC calibration.

In Fig. 4 and Table 1 the results are given for the metal In (4.486 and 24.90 mg respectively).

From these figures it can be seen that In is a good sample for calibration during cooling, provided that the sample mass is large enough.

In Fig. 5 and Table 1 the results for Pb are given. The supercooling is too strong, so temperature calibration during cooling is difficult with this compound.

Hg behaves like Pb. Both compounds show medium supercooling effects (about 3 K at 10 K min^{-1}). Finally, the figures for Ga are given in Table 1.

In this case the supercooling is so large, that it is not advised to use it as a DSC calibration standard during cooling.

Similar arguments are applicable for Sn.

In most cases, the measured heat effects correspond rather well with the literature values, both during heating and during (super)cooling. Only at low rates occasionally somewhat lower values are measured. Possibly it can be explained by the more difficult construction of the baseline at low rates.

Also the measured supercooling of In and Pb corresponds rather well to the values found by Martens and Cruz-Pinto [13].

Conclusions

- For correct temperature calibration during cooling the temperature sensor must be in close thermal contact with the sample pan.
- For DSC calibration during cooling, compounds are needed with fast reversible transitions.
- Two compounds are very well suitable, namely adamantane and Zn.
- Adamantane has a reversible solid-solid transition at 208.62 K, with a heat effect of 24.78 J g^{-1} .

- Zn has a reversible solid-liquid transition (melting) at 692.677 K with a heat effect of 111.97 J g⁻¹.
- A third suitable compound is 4,4'-azoxyanisole, showing a reversible transition at 409.11 K, as measured during this investigation with a scan rate of 10 K min⁻¹, being the rate of the preliminary calibration of the instrument. It concerns the liquid crystal-isotropic liquid transition.
- Since the heat effect, belonging to the above-mentioned transition of 4,4'-azoxyanisole, is very small (ΔH is measured to be 4.25 J g⁻¹), experiments were performed using a large amount of sample (25 mg).
- Two compounds, namely NaNO₃ and In, show a so small supercooling (1 and 2 K respectively at 10 K min⁻¹) that they can be applied for DSC calibration during cooling, both for temperature and heat signal. A condition is that the sample mass is high enough for determination of the extrapolated onset temperatures.
- Two other compounds, namely Hg and Pb show a supercooling effect of about 3 K at 10 K min⁻¹. So they are initially less suitable for temperature calibration during cooling.
- The starting temperature of the (super)cooling peak, however, is found to be rather constant for Hg, namely 231.11 K at -10 K min⁻¹ and 231.31 K at -2 K min⁻¹.
- It would be worthwhile to investigate whether compounds with only a slight supercooling effect, could nevertheless be used for DSC calibration during cooling.
- In order to avoid reactions between aluminium sample pans and metal samples, it is advisable to embed Zn, Ga and Pb in alumina powder.

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