Power balanced Differential Scanning Analysis for the characterization of phase transitions in Indium and Zinc

H. J. d'Nóbrega

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Abstract

In this work, a power balanced Differential Scanning Calorimetry technique is used to study two samples of Indium and Zinc and the effect of the sampling rate β in the quality of the measurments. We concluded that, up to a sampling of 5°C min⁻¹, its decrease affects positively the exactness of the obtained information. The qualitative results resembled those expected for exothermal and endothermal phase transitions, when sample and reference places are interchanged. An unknown sample was analysed with two scannings, the second, with smaller β being needed to clarify the processes involved.

Quantitatively, we determined the fusion point of Indium with error no greater than 2.8% and of Zinc, with analogous error of 1.75%, and the enthalpy associated with the fusion of a sample of both those elements $\Delta H_{\text{fus}}^{1^{\circ}\text{C}\min^{-1}} = 2787.6\text{mJ}, \ \Delta H_{\text{fus}}^{5^{\circ}\text{C}\min^{-1}} = 619.8\text{mJ}, \ \Delta H_{\text{sol}}^{5^{\circ}\text{C}\min^{-1}} = 615.0\text{mJ}.$

1 Introduction

1.1 Thermodynamic analysis techniques

The advent of nanotechnology came associated to an increasing need for techniques that allow a relatively fast, accurate and versatile thermodynamic and kinetic characterization of materials.

One of many techniques that aim for such goal is the DSC (Differential Scanning Calorimetry). Care is needed when consulting specialized literature, where distinction is often not made between power compensated and heat flux DSC.

Both techniques are based on the balance of a physical quantity between a calibration reference and the sample one wishes to characterise.

In a heat-flux DSC (HF-DSC) (Fig.1, on the right), the sample and the reference have a different variation of temperature, when heated by the same source. Such variation is recorded and converted into the sample's enthalpy change after calibration of characteristic parameters of the mechanism's state equations. Differential Thermal Analysis (DTA) is, in principle, very similar to HF-DSC.



Figure 1: On the left, a PC-DSC setup, with two furnaces (one for each crucible) and the differential measure of the power given to each sample to keep them thermalised. On the right, a HF-DSC setup, featuring one furnace and the differential temperature measurement (in a DTA, there is no path p, so neither contact between sample and reference nor heat conduction occur).

However, in a power-compensated DSC (PC-DSC, Fig.1, on the left), an automatic adjustment of the samples's heater power is performed so that $\Delta T_{S,R} =$ 0, the difference in supplied power (by two independent sources) being, in modulus, the power released or absorved by the sample. A thermal analysis controler (TAC) guarantees the desired thermal power balance between the samples and the computations may be carried out in a control unit such as a computer.

Studies regarding the fusion latent heat, the fusion temperature and the heat capacity of a sample may be conducted using a DSC. Throughout this text, DSC will be used to abreviate both the PC-DSC technique and the equipment based on it indescriminately.

1.2 Specificities of DSC measurements

The determination of the measurement baseline is a very important step [1] in the process. It represents the expected DSC curve in the absence of any transition or reaction [4], and is directly linked to the heat capacity of the sample. It is, therefore, necessary to subtract from all data the appropriate baseline, measured in the corresponding range of temperatures.

After this step is performed, the data may still not be presented with respect to a horizontal baseline, as will be mentioned in Sec.1.3. Care must be made when extracting information from these tilted thermograms - a correction of temperature is needed, as can be seen in Fig.2.

Also in Fig.2, the enthalpy variation during the process is negative and corresponds to the area in grey. If the process is a solidification, the fusion temperature must be extrapolated from the intersection between the linear fit of the decrease in differential flux and the fitted baseline.

Another important feature of DSC is the $\beta = \frac{dT}{dt}$ parameter, which corresponds to the temperature interval swept by the DSC in a certain time interval – usually a minute. The influence of this parameter in the thermograms may be studied for a sample with well documented thermodynamic quantities.

Considering that the DSC provides information regarding the time derivative of the enthalpy H, it may be derived that [5], after performing the baseline correction (with T_1 and T_2 as in Fig.2)



Figure 2: Corrections to be performed when extracting information from a thermogram with a non horizontal baseline.

$$\Delta H = \int_{T_1}^{T_2} \frac{1}{\beta} \left(\frac{dH}{dt}\right)_{\text{data}} corr dT.$$
(1)

1.3 Exothermal and endothermal reactions

The analysis performed using the DSC technique also provides information regarding the energetic classification of a given reaction, such as a physical state transition.

In fact, provided that the process occurs at constant pressure [2], one may say that the enthalpy variation upon occuring the reaction is negative for exothermal and positive for endothermal processes.

The expected thermogram provided by DSC may be qualitatively derived considering that what is read at a given time is the difference in terms of energy flow between sample and reference.

Until a chemical or physical transition occurs, a linear behaviour is to be expected, which may reflect the way their heat capacities at constant pressure, $c_{p,sample}$ and $c_{p,ref.}$ are changing with temperature.

If a process occurs to the sample, which results in heat emission, a increase in the differential measure is to be expected (or a decrease, if the difference is computed symetrically, as the sample and reference switch places in the DSC). An upward peak is the result of such process and $\Delta H > 0$.

2 Experimental setup

The experiments were carried out using a PC-DSC 7 by Perkin-ElmerTM(PE) coupled with a PE TAC 7/DX and a computer PE PC series DSC as a control unit.



Figure 3: Photograph of the PE DSC7. Samples (S) and references (R) in their respective crucibles, and the places F for samples (on the right) and reference (on the left) to be placed.

The experimental setup used was photographed for further reference (Fig.3).

3 Experimental method

The first part of the experiment consisted of the analysis of two identified samples, one consisting of Indium (Id) and the other consisting of Zinc (Zn).

Those samples were prepared from a small amount (of the order of the centigram, according to previous works [3]), and placed in a small crucible, with a diameter of about 1cm, after which they were pressed and sealed in order to prevent leakage.

In order to investigate how the sampling ratio β affected the quality of the measured data, we changed this parameter and perform consecutive measures for the same material. The temperature scanning ranges and sampling rates may be read from Tab.1.

Instead of determining a baseline each time we changed a parameter, we measured three baselines, corresponding to $\beta = 1, 5, 10^{\circ} \text{C min}^{-1}$ and performed a linear regression on the appropriate data from each of these baselines, so that a new, extrapolated, baseline could be computed considering the desired β and range of temperatures.

There was a need to perform a second regression in order to compute the ΔH for the phase transitions. We chose a polynomial fit of the fifth degree, as we had no theoretical insight on the dependence and wished to obtain reasonable accuracy – it was represented in blue in Figs.5-4. An interpolation of the thermogram points was performed for the same purpose. All this data processing was aided by OriginTM 9.1's fitting, interpolation and integration gadgets.

The Id and Zn samples were already prepared for analysis. A crucial detail of this experiment, helpful for the understanding of the thermograms shown, is the fact that sample and reference were not placed where they usually should be in order to obtain positive values when the sample is releasing heat, but interchanged. The consequences of this will be further developped.

For the second part of the experiment, a qualitative study of a known sample was performed, choosing a crucible from the available set and using the DSC to determine its thermogram. No information being known at the time, it was chosen to perform a first scan with $\beta = 200^{\circ}$ C min⁻¹, followed by a second scan with increased sampling rate and in the interesting temperature range provided by the first scan.

4 Experimental results

4.1 Indium (In) sample

The indium sample was analysed with two sampling rates, and the results are presented in Tab.1. The thermograms are shown in Figs.5 and 6.



Figure 4: The same temperature range is shown for the fusion (on the right) and the solidification (on the left) of the Zn sample, with a scanning rate of 5° C min⁻¹.

Ref.	$T_{\rm range}[^{\rm o}{\rm C}]$	β [°C min ⁻¹	$T_f[^{\mathrm{o}}\mathrm{C}]$	$\Delta H[\mathrm{mJ}]$
I1	150 - 180	5	161	2702.37
I2	150 - 180	1	157.5	2787.6
$\mathbf{Z1}$	410 - 440	10	427.67	619.5
Z2	410 - 440	1	426.31	619.43
Z3	410 - 440	5	426.83	619.77
$\mathbf{Z4}$	440 - 410	5	425.58	-615.00

Table 1: Measurements performed with the DSC, with variation of the analysed material, the sampling rate and the temperature ranges. The far left column identifies the assigned code to each dataset (I for Indium and Z for Zinc).



Figure 5: Enthalpy variation as a function of temperature for the heating of In sample with $\beta = 5^{\circ} \text{C} \text{min}^{-1}$.



Figure 6: Enthalpy variation as a function of temperature for the heating of In sample with $\beta = 1^{\circ} C \min^{-1}$.

Considering the nominal value for the indium fusion temperature, $T_{f,\text{nom}} = 156.6^{\circ}C$, the error percentages were computed, giving 2.8% and 0.57% – the best result for the smaller tested β .

Regarding the fusion latent heats, the estimated mass of the sample was computed from the measure of $\Delta H = mL_f$ and the nominal value of the latent heat of fusion for Indium, $L_{f,\text{In}} = 28.47 \text{mJ} \text{ mg}^{-1}$. We derived $m_{I1} = 94.92mg$ and $m_{I2} = 97.91mg$.

Considering the process by which the samples were prepared 3, we did not have access to the true mass of the sample, and can only criticize the obtained m in terms of rough estimations based on the density of In and the volume to which it was compressed [3]. The experimental order of magnitude of m seems to approach these estimates. Considering the interchanged sample and reference (Sec.3), the decrease in power flux determines $\Delta H > 0$ and the phase transition is exothermal, as is expected for the fusion of a substance.

4.2 Zinc (Zn) sample

The analysis performed was essentially the one performed on the In sample.



Figure 7: Enthalpy variation as a function of temperature for the heating of Zn sample with $\beta = 10^{\circ} \text{C min}^{-1}$.

Based on $T_{f,\text{nom}} = 419.5^{\circ}C$, we derived errors that varied with the sampling rate, consisting of 1.95%, 1.62%, 1.75% and 1.45% for trials Z1, Z2, Z3 and Z4, respectively. In this case, β didn't introduce a clear bias on the obtained data for small enough rate, given that trial Z2 has results with exactness between Z3 and Z4, which use the same $\beta = 5^{\circ}\text{Cmin}^{-1}$. It is possible, however, to say that the quality of the data improves from a rate of $10^{\circ}\text{Cmin}^{-1}$ to $5^{\circ}\text{Cmin}^{-1}$.

As a result, it is clearly advised to use scanning rates of this order in order to perform a first scan and identify thermal zones of potential interest, given that the effects of a phase transition ara not lost, only given with a greater error margin.



Figure 8: Enthalpy variation as a function of temperature for the heating of Zn sample with $\beta = 1^{\circ} C \min^{-1}$.

Using $L_{f,Zn} = 118 \text{mJ} \text{mg}^{-1}$, we derived the masses of the Zn sample (in miligrams): $m_{Z1} = 5.25$, $m_{Z2} =$ 5.253, $m_{Z3} = 5.249$ and $m_{Z4} = 5.212$. It is possible to conclude that all measurements are in the order of magnitude considered in previous works.

Aditionally, in order to observe an endothermal reaction, after Z3, instead of choosing to return the sample to the initial temperature for removal, we set the DSC to scan the temperature range decreasingly. The results are shown in Fig.4. As is expected (again, considering the experimental conditions discussed in Sec.3), heat is released during the fusion and the opposite occurs during the solidification.

There is an expected agreement between the measured quantities for heating and cooling, within the uncertainty. A difference in the fusion temperature between heating and cooling may be the result of phase transition conditions and not an experimental error.

4.3 Analysis of an unknown sample

The analysis of an unknown sample was performed with two different scanning rates, that can be read from Fig.9.

The first trial resulted in apparently interesting phenomena in the [300-450]°C range. A second trial showed that such phenomena were not recorded for



Figure 9: Thermogram of an unknown sample; on the right, a first scanning of temperatures in the range [100-500]°C with $\beta = 100^{\circ}$ C min⁻¹, on the left, a second scanning in the range [300,450]°C with $\beta = 10^{\circ}$ C min⁻¹.

a smaller β , thereby keeping us from furthering their investigation. It is possible that the sample may have become thermally inert in that range, with causes unknown to the investigation group. The other possibility – less likely – is that the large β for the first scanning resulted in false positives.

5 Conclusive remarks

In this work, several aspects of thermodynamic analysis techniques were introduced, such as DTA, HF-DSC and PC-DCS, with focus in the latter. The influence of the sampling rate β in this sort of measurement technique was qualitatively evaluated, having been concluded that a smaller β provides more reliable information, at leat up to 5

The trials were performed differently than normal, as the sample and reference were not placed in their "correct" furnace, but in the opposite. The effects of this misplacement were observed as the peaks recorded for phase transitions were pointing oppositely to where they usually should for a given reaction according to the sign of ΔH .

The melting points obtained agreed with the nominal ones within experimental uncertainty; in terms of ΔH for phase transitions, the mass of samples computed from that data and the latent heats of Indium and Zinc also seemed to be within the order of magnitude of previous estimations for those quantities.

The DSC proved to be a very interesting equipment when looking for a characterization of thermal properties of a sample, having resulted in a relatively fast and accurate analysis, so long as the scanning rate is propperly chosen.

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