

TEMPERATURE CALIBRATION OF A HIGH-PRESSURE DSC FOR MEASUREMENTS IN AMMONIA

Dependence of calibration parameters on pressure

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In this paper the temperature calibration of a Mettler Toledo DSC27HP high-pressure DSC for measurements in an ammonia atmosphere is described. Measurements were performed on the melting process of three reference substances in golden crucibles: indium, tin and lead. The procedure described by the German Society for Thermal Analysis and Calorimetry, GEFTA, was applied: to correct for temperature gradients in the DSC-cell extrapolated onset temperatures of the endothermic melting peaks were measured as a function of heating rate to find by extrapolation the extrapolated onset temperature at zero heating rate, which should be a temperature corrected for temperature gradients. However, measurements performed at different pressures (between 1.5 and 8.4 bar) showed that the evaluated extrapolated onset temperatures at zero heating rate decreased with increasing pressure. This observation cannot be explained by the known dependence of melting temperatures on pressure. Therefore pressure dependence of the extrapolated onset temperatures must be caused by experimental issues. It is assumed that, although the results were extrapolated to zero heating rate, results are still influenced by temperature gradients in the DSC-cell. As a mean value, the extrapolated onset temperatures at zero heating rate decreased by 0.053°C when the pressure was raised by 1 bar. Since the software package does not allow for the pressure dependence of calibration parameters, measurement results must be corrected manually for this effect.

Keywords: calibration, high-pressure DSC

Introduction

Some years ago we started a project, in cooperation with the Energy Research Centre of The Netherlands, to investigate the thermodynamic properties of materials that can be used in high-temperature high lift chemical heat pumps. In particular we are interested in the solid complexes of inorganic salts with ammonia. This research is of interest because it may help significantly to reduce the amount of energy that is wasted in industry, and thus can help to reduce the amount of primary energy that is used. As an example, Spoelstra *et al.* [1] reported that in The Netherlands alone a quantity of industrial waste heat in the order of 110 PJ (i.e. $110 \cdot 10^{15}$ J/year) is actively cooled and dissipated into the environment. Unfortunately this enormous amount of heat is available at a temperature range of 50 to 150°C, whereas heat that is useful for industrial purposes must be available at a temperature of about 230°C (middle pressure steam). Using a well-designed heat pump a significant part of the waste heat can be lifted to higher temperatures; the other part of the waste heat will be dissipated into the environment at a lower temperature. Therefore the advantage is twofold: waste heat is partly upgraded to

useful heat, and thus helps saving primary energy sources, and the rest of the waste heat is dissipated into the environment at a lower temperature, which decreases the thermal pollution.

A chemical heat pump that is based on the reversible formation and decomposition of solid ammonia complexes of inorganic salts may well be adequate for this purpose. To design such an instrument and to optimise its efficiency, the thermodynamic properties of the materials are of great importance, as well as knowledge on the kinetics of the reactions. In our research project we decided to use high-pressure differential scanning calorimetry (HPDSC) to measure the stability regions of several solid ammonia complexes, together with the temperatures and heats of transition. The first results on lithium chloride ammonia complexes and magnesium chloride ammonia complexes have been published recently [2, 3].

For performing quantitative measurements using differential scanning calorimetry (DSC) it is important to calibrate the instrument for temperature as well as for heat flow. Much has been written about calibration procedures and reference substances. A couple of years ago a working group of the German Society for

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Thermal Analysis, GEFTA, published a series of papers on the temperature [4, 5] and the heat flow [6] calibration. A summary was published in reference [7]. The procedures and substances they proposed were adapted by the International Confederation for Thermal Analysis and Calorimetry (ICTAC), and in The Netherlands the Dutch Society for Thermal Analysis and Calorimetry (TAWN) recommends its members to use these procedures. It is this procedure that we used for calibrating our high-pressure DSC for use in an ammonia atmosphere. In this paper we focus on the temperature calibration.

In short, the GEFTA procedure indicates that in DSCs, when the sample is heated at a certain heating rate, there will be temperature gradients. Because the temperature sensor is always positioned outside the sample container, there will be a difference in the recorded temperature and the sample temperature. Since the temperature gradients will be greater when a higher heating rate is applied, this difference will depend on the used heating rate. For this reason the GEFTA procedure implies that transition temperatures of standard reference materials should be measured as a function of heating rate. The (un-calibrated) transition temperature that is corrected for temperature gradients is equal to the transition temperature at zero heating rate, and can be found by extrapolation of the experimental results.

The slope of the transition temperature vs. heating rate is sometimes called 'thermal lag'. This thermal lag may be used as a calibration parameter to estimate, after calibration, the zero heating rate transition temperature from real measurements. If best accuracy is needed, also during real measurements after calibration the transitions must be measured as a function of heating rate, so that extrapolation to zero heating rate is possible.

Experimental

The used high-pressure DSC is a Mettler Toledo DSC27HP. This, in fact, is a DSC mounted inside a stainless steel pressure cylinder. The DSC cell can be purged by a gas; the purge gas enters the DSC cell through a Brooks flow controller, model 5850S. From the DSC cell the gas flows into the pressure cylinder and then leaves the system through a Brooks pressure controller, model 5866. The flow controller and the pressure controller were calibrated for use with ammonia by the supplier (Brooks). With this setup the pressure during measurements can be kept constant, irrespective of the used temperature programme. The setup is schematically drawn in Fig. 1.

For the measurements golden aluminium crucibles were used, with a volume of about 40 μL and a mass of

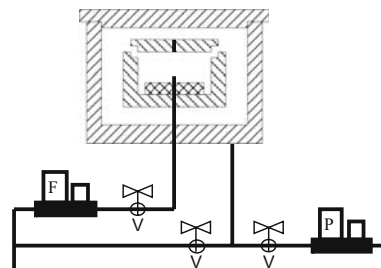


Fig. 1 Schematic drawing of the experimental setup. F – flow controller; P – pressure controller; V – valves

about 375 mg. A hole with a diameter of about 2 mm was drilled in the lids, which were placed loosely on the crucibles (i.e. the crucibles were not sealed). In all cases on the reference position of the DSC sensor an empty crucible was placed. On the sample position of the DSC sensor a crucible which contained a standard reference material was placed. As standard reference materials for the calibration we used indium, tin and lead. The materials were supplied by Mettler Toledo; the purity of all materials was indicated to be better than 99.999%. Small pellets of the materials were encapsulated in glass envelopes to prevent reaction of the materials with the golden crucibles and/or with the ammonia atmosphere. As a result, the reference materials are not exposed to the applied pressure in the DSC cell.

During all measurements the flow controller which regulated the flow rate of the ammonia purge gas was set to a value of 50 mL min^{-1} . The used ammonia gas was purchased from Hoekloos, The Netherlands, with an indicated purity greater than 99.98%. The pressure controller was set to a value between 1.5 and 8.4 bar. At each constant pressure a series of at least three measurements was performed at heating rates between 1 and 10 K min^{-1} . The extrapolated onset temperatures of the endothermic melting peaks at the different heating rates were used to find (from a linear fit) the extrapolated onset temperature at zero heating rate, which is assumed to be the (un-calibrated) melting temperature of the sample.

Results and discussion

The results of the (un-calibrated) extrapolated onset temperatures extrapolated to zero heating rate for the measurements in an ammonia atmosphere on indium, tin and lead are presented in Tables 1–3, respectively. The results are graphically represented in Figs 2–4, respectively.

It can clearly be observed that the obtained extrapolated onset temperatures at zero heating rate decrease on increasing pressure. The dependence on pressure seems to be linear. Linear regression for the three substances resulted in the following equations: for indium:

$$T_c(\beta \rightarrow 0, p)/^{\circ}\text{C} = 169.74 - 0.047p/\text{bar} \quad (1)$$

for tin:

$$T_c(\beta \rightarrow 0, p)/^{\circ}\text{C} = 247.66 - 0.056p/\text{bar} \quad (2)$$

for lead:

$$T_c(\beta \rightarrow 0, p)/^{\circ}\text{C} = 346.62 - 0.055p/\text{bar} \quad (3)$$

The decreasing temperature with increasing pressure is not caused by the pressure dependence of the transition. First, this is because in our experiments the samples are enclosed in glass envelopes, which implies that the applied pressure does not act on the samples. Second, if the samples would be subjected to increased pressures, the pressure-temperature relation along the equilibrium line would be given by the

Table 1 Result of the measurements on indium in an ammonia atmosphere. Note that the presented temperatures are un-calibrated results

Measurement series No.	p/bar	$T_c(\beta \rightarrow 0)/^{\circ}\text{C}$
1	2.0	169.69
2	7.0	169.41
3	4.5	169.50
4	2.0	169.64
5	8.4	169.32
6	6.0	169.42
7	7.5	169.42
8	4.5	169.49
9	3.0	169.60
10	1.5	169.69
11	3.5	169.56
12	5.0	169.56
13	7.0	169.45
14	3.0	169.55
15	4.0	169.54

Table 2 Result of the measurements on tin in an ammonia atmosphere. Note that the presented temperatures are un-calibrated results

Measurement series No.	p/bar	$T_c(\beta \rightarrow 0)/^{\circ}\text{C}$
1	8.0	247.19
2	5.0	247.38
3	2.0	247.53
4	6.5	247.28
5	3.5	247.45
6	1.5	247.57
7	3.5	247.46
8	2.0	247.58
9	6.0	247.39

Table 3 Result of the measurements on lead in an ammonia atmosphere. Note that the presented temperatures are un-calibrated results

Measurement series No.	p/bar	$T_c(\beta \rightarrow 0)/^{\circ}\text{C}$
1	5.0	346.29
2	3.0	346.46
3	7.0	346.23
4	1.5	346.54
5	4.0	346.41
6	2.0	346.50
7	6.0	346.32

Clausius–Clapeyron equation, which may be stated as (for example [8]):

$$\left(\frac{dp}{dT}\right)_{\text{eq. curve}} = \frac{\Delta_m S^*}{\Delta_m V^*} \quad (4)$$

where $\Delta_m S^*$ is the entropy change on melting and $\Delta_m V^*$ the volume change on melting. Since for the used reference substances both the entropy change and the volume change on melting are positive, an increasing melting temperature would be expected on increasing pressure. Our decreasing temperatures on increasing pressures therefore must be associated to

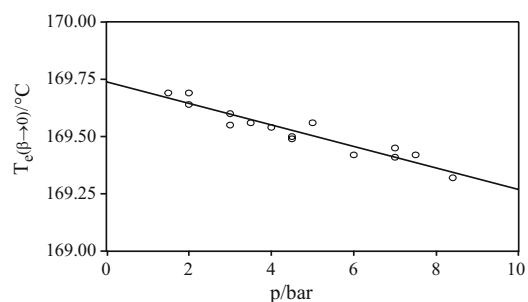


Fig. 2 Results of the measurements on indium in an ammonia atmosphere: (un-calibrated) extrapolated onset temperatures extrapolated to zero heating rate as a function of pressure

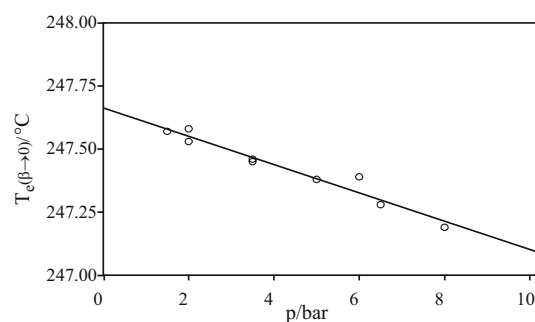


Fig. 3 Results of the measurements on tin in an ammonia atmosphere: (un-calibrated) extrapolated onset temperatures extrapolated to zero heating rate as a function of pressure

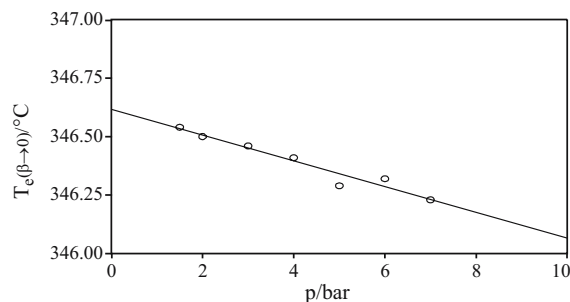


Fig. 4 Results of the measurements on lead in an ammonia atmosphere: (un-calibrated) extrapolated onset temperatures extrapolated to zero heating rate as a function of pressure

experimental issues. It is expected that the observed pressure dependence is caused by temperature gradients within our DSC. This would imply that, even though the values have been extrapolated to zero heating rate, there still remain temperature gradients within the DSC cell.

To verify whether the observed results are not specific for measurements in ammonia, we also performed some experiments in a nitrogen atmosphere. Unfortunately we could only use nitrogen gas from the network of pipes in our laboratory. For this reason the maximum pressure that could be used was 5 bar. The obtained results can be summarised as follows:

for indium:

$$T_e(\beta \rightarrow 0, p) / ^\circ\text{C} = 169.59 - 0.065p / \text{bar} \quad (5)$$

for tin:

$$T_e(\beta \rightarrow 0, p) / ^\circ\text{C} = 247.22 - 0.047p / \text{bar} \quad (6)$$

for lead:

$$T_e(\beta \rightarrow 0, p) / ^\circ\text{C} = 346.11 - 0.073p / \text{bar} \quad (7)$$

Clearly the observed tendency (decreasing extrapolated onset temperatures on increasing pressures) is the same in nitrogen as in ammonia. However, the temperature dependence of the degree to which the extrapolated onset temperatures at zero heating rate depend on pressure in nitrogen is not the same as in ammonia. Therefore this temperature difference is considered to be not significant.

For this reason, for measurements in an ammonia atmosphere, it is assumed that the extrapolated onset temperatures at zero heating rate linearly depend on the pressure and that the slope of this dependence is best given by the mean value of the slopes found for indium, tin and lead (Eqs (1)–(3)): $-0.053^\circ\text{C}/\text{bar}$. Since the software package does not allow for a pressure dependence of the calibration parameters, the instrument must be calibrated for one specific pressure. In our case we chose a pressure of 3 bar for this calibration. This implies that a manual correction must be made to tempera-

tures measured at pressures that differ from 3 bar: a value of $+0.053(p/\text{bar}-3)^\circ\text{C}$ must be added.

In the previous paragraphs we focused on the extrapolated onset temperatures extrapolated to zero heating rate. From this extrapolation to zero heating rate we also obtained values for the thermal lag. Within the experimental uncertainty we did not find a pressure dependence of the thermal lag values. As an average value, which we also use as the calibration parameter in the software, we found a value of 9 s.

Conclusions

From our observations it is concluded that recorded transition temperatures depend on the applied pressure although there is no physical reason for this dependence. It is therefore expected that the reason for the observed pressure dependence is that there are temperature gradients within the DSC-cell, even though the results have been extrapolated to zero heating rate. The software that is supplied for the control of the instrument and the evaluation of the results does not allow for pressure influence on the calibration. Therefore the instrument is calibrated for measurements at one specific pressure (in our case for a pressure of 3 bar). When real measurements are performed at a pressure p that differs from 3 bar, the results must be manually corrected by an amount that is equal to $+0.053(p/\text{bar}-3)^\circ\text{C}$.

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