Measuring the enthalpy and temperature of melting

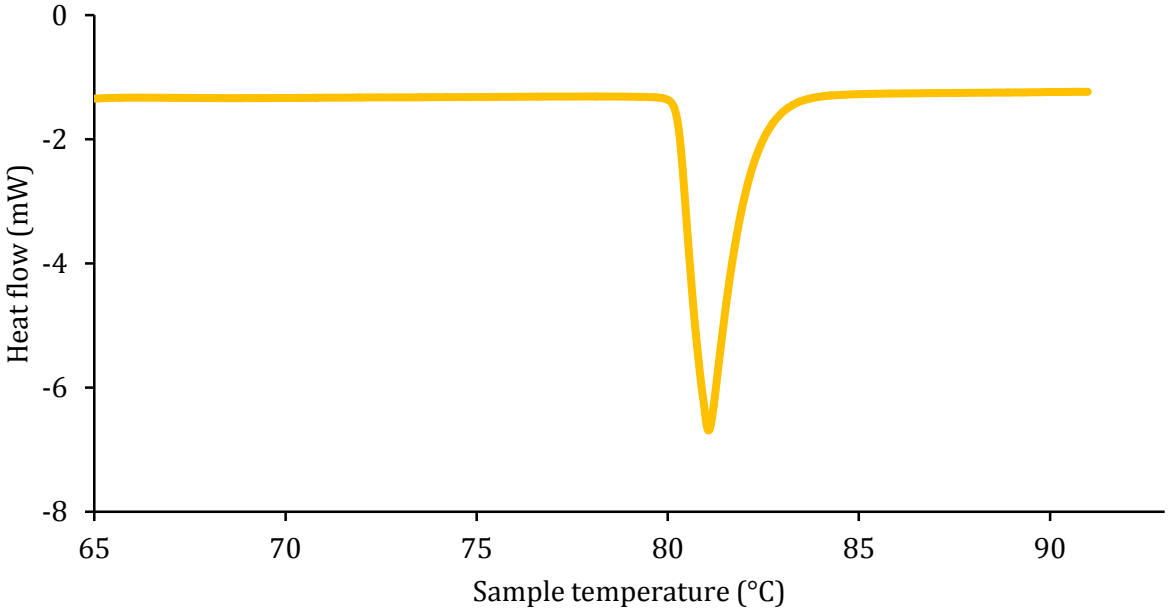
Introduction

The melting of a substance is the phase transition from a solid state to a liquid state, typically by the application of heat or pressure. The associated enthalpy and temperature are its characteristics and have been measured and recorded for many substances. **Those values are then useful for determining the purity of a body, as well as identifying compounds in a mixture.**

They are usually measured using Differential Scanning Calorimetry (DSC). The substance is placed in a cell, which is coupled with a reference cell left empty. The heat flow between the two cells is monitored while they are heated up. It is normally constant, until the melting occurs, as more heat is transferred to the cell containing the substance to make it melt.

Experimental details

- Method: ISO 11357-3:2011(E) standard for the determination of temperature and enthalpy of melting using DSC [1]
- Instrument: *Setaram* microSC, calibrated by Joule effect from −20 °C to 180 °C
- Sample: naphthalene
- Amount of sample: 4.00 mg
- Thermal profile: heating ramp at 1.2 K/min from 20 °C to 63 °C, then at 0.7 K/min from 63 °C to 93 °C
- Sample holder: standard 1 mL Hastelloy cells; the measurement cell contains the sample and the reference cell is empty

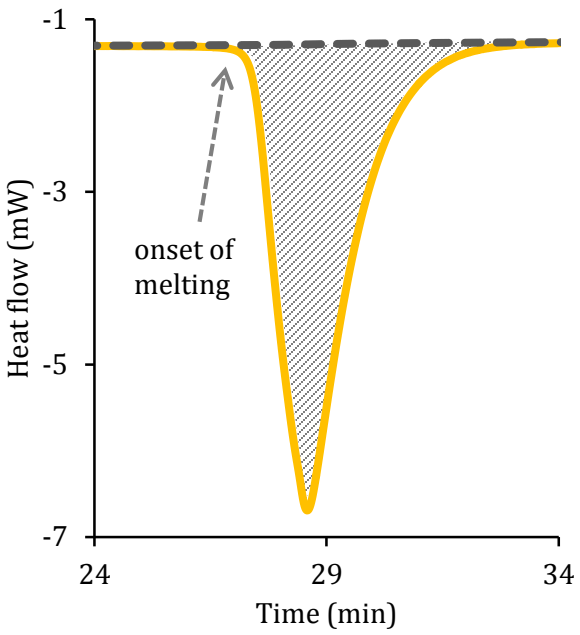


Variation of heat flow with respect to the temperature of naphthalene subjected to heating. Only the portion of the curve from 65 °C is shown here. A negative peak starting at 80 °C is observed: it is the sign of an endothermic process. The decreasing branch is a straight line, whereas the increasing branch back to the baseline is an exponential line: this is the typical shape of a melting peak for a pure substance.

Results

The two parameters associated with the melting, i.e. the enthalpy and the temperature, are calculated from the peak. The melting enthalpy, or enthalpy of fusion, is the area between the peak and the baseline when plotted with respect to the time, as shown on the right. The melting temperature for a pure body is defined as the temperature at the onset of the peak; it is found by geometric construction at the intersection between the baseline (here: a tangential sigmoid) and the tangent to the decreasing branch on the inflexion point.

The present naphthalene sample shows a melting enthalpy of 147.1 kJ/kg and a melting temperature of 80.3 °C, which are in agreement with the certified values from the Laboratory of the Government Chemist (LGC).



Conclusion

- The temperature and enthalpy of melting of a pure substance can be measured using differential scanning calorimetry (DSC) during a heating ramp at constant rate.
- The temperature range of the experiment should be carefully chosen, so that the melting takes place at least 15 min away from the limits of the heating ramp.
- The DSC has to be calibrated over the whole range of temperature of the experiment, in both temperature and heat flow, preferably using Joule effect for the latter as in the case of the present instrument.
- This technique can be applied to any pure substance and to mixtures too, provided that the melting of the components occur at distinct temperatures.

[1] *Plastics - Differential scanning calorimetry (DSC)* – Part 3: Determination of temperature and enthalpy of melting and crystallization, ISO 11357-3:2011(E)