HIGH-RESOLUTION ADIABATIC SCANNING CALORIMETRY ON THE MELTING TRANSITION OF ICE

INTRODUCTION

Scanning calorimetric techniques allow to obtain continuously the evolution of the heat capacity at constant pressure C_p (T) in terms of the power P and the rate dT/dt.

$$C_p = \frac{dQ}{dT} = \frac{dQ/dt}{dT/dt} = \frac{P}{\dot{T}}$$

Adiabatic Scanning Calorimetry (ASC) : A constant power P is supplied to the sample and the resulting change in temperature $T(t)$ is measured as a function of time from which the rate dT/dt can be calculated. Combining the rate with the constant power results in $C_p(T)$. Moreover, the enthalpy $H(T)$ is easily obtained from the product of the power P and the time laps between the start of the run at t_0 and the time at which $T(t)$ was reached.

$$H(T) = P\left[t(T) - t(T_0)\right]$$

Differential Scanning Calorimetry (DSC) : A constant rate dT/dt is imposed via a constant power P_{ref} imposed on a known reference material. The power $P_s = dQ/dt$ on the sample has to be adjusted to follow the constant rate (of the reference). This becomes very difficult at very sharp transitions because large power changes have to be provided, which quite often results in time lags and temperature differences between the real and the detected transition and severe smearing out of the transition peak. The enthalpy $H(T)$ has to be derived from the integration of the $C_p(T)$ data.

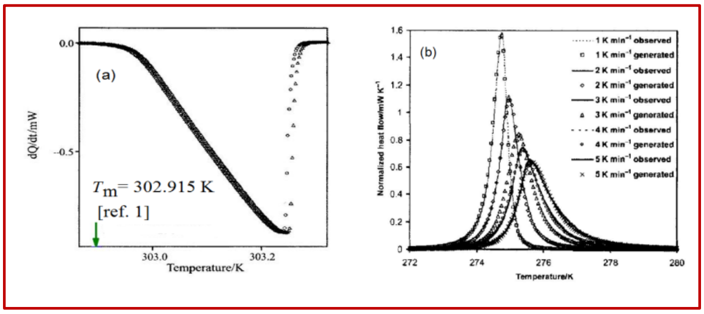
$$H(T) = \int_{T_0}^{T} C_p \, dT$$

RESULTS

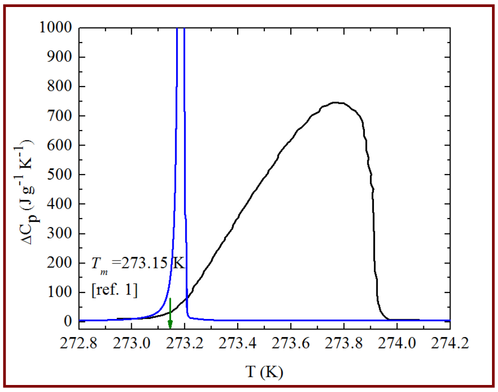
Sample measured **Water was purchased from Fisher Scientific [HPLC gradient grade, code W/0106/17, batch 0625273 (2006)] and it was measured as received without further treatment or purification.**

- **Melting transition temperature T_m = 273.15 K [1]**
- **Heat of fusion = 332.8 J g^{-1} [1]**

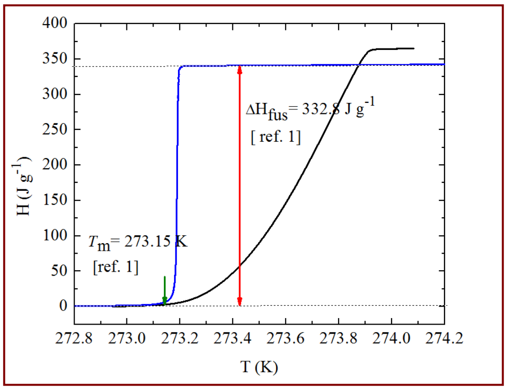
Measurement **A heating run with constant power of 150 µW in a Peltier-based ASC calorimeter on a 57.3 mg sample.**



(a) DSC power data from reference 2. Run on 7.40 mg of water using a constant rate of 1 mK/s [2]. (b) Reference 3.



Heat capacity ΔC_p. Black solid line: DSC data derived from dQ/dt data in the above figure from ref[2]. Blue solid line: ASC data from this work.



Enthalpy of fusion of water. Black solid line: DSC data derived from dQ/dt data in the top figure from reference [2]. Blue solid line: ASC data from this work.

CONCLUSIONS

- **The melting transition temperature agrees with the literature value within the temperature calibration of the calorimeter (about 25 mK).**
- **Excellent agreement with the value of heat of fusion quoted in the literature.**
- **The melting transition takes place in a more than 20 times narrower temperature interval (~30 mK) than the one quoted in DSC measurements (~0.70K). In DSC measurements, due to forcing a temperature ramp upon the sample, at a first-order phase transition there is a severe smearing out of the transition peak. In contrast, the evolution of the sample temperature in an ASC is fully natural and reflecting purely the thermodynamics of the material.**

REFERENCES

[1] American Institute of Physics Handbook, (third edition) D.E. Gray, Ed. (Mac Graw-Hill, 1972 New York, USA)

[2] H. Inaba, T. Saito, K. Tozaki, and H. Hayashi, Effect of the magnetic field on the melting transition of H_2O and D_2O measured by a high resolution and supersensitive differential scanning calorimeter, J. Appl. Phys. 96, 6127 (2004)

[3] V. T. Popa and E. Segal, Shape analysis of DSC ice melting endotherms: towards an estimation of the instrument profile, J. Therm. Anal. Cal. 69, 149 (2002)