Applications

Measurement of vapor pressure curves and the enthalpy of vaporization of liquids by HPDSC

Dr. Samuele Giani

Measurement of the boiling point of a liquid at different pressures allows you to determine its vapor pressure curve. Besides this, the enthalpy of vaporization of the liquid can be determined from such measurements using the Clausius–Clapeyron equation. In this article, we show how such measurements are performed in a high-pressure DSC using water as an example.

Introduction

The boiling point of a liquid depends on the pressure of the surroundings: the lower the pressure the lower the temperature at which the liquid boils.

For example, on Mount Everest, the air pressure is only about 325 mbar and water boils at about 70 °C and not at 100 °C like at sea level. The pressure dependence of the boiling point can be easily measured by high-pressure DSC (HPDSC).

The enthalpy of vaporization can also be determined from such measurements using the Clausius–Clapeyron equation [1].

The Clausius–Clapeyron equation describes the relationship between the vapor pressure of a substance, p, and the temperature at which it boils, T:

$$\ln(p) = L - \frac{\Delta H}{R} \cdot \frac{1}{T} \qquad (1)$$

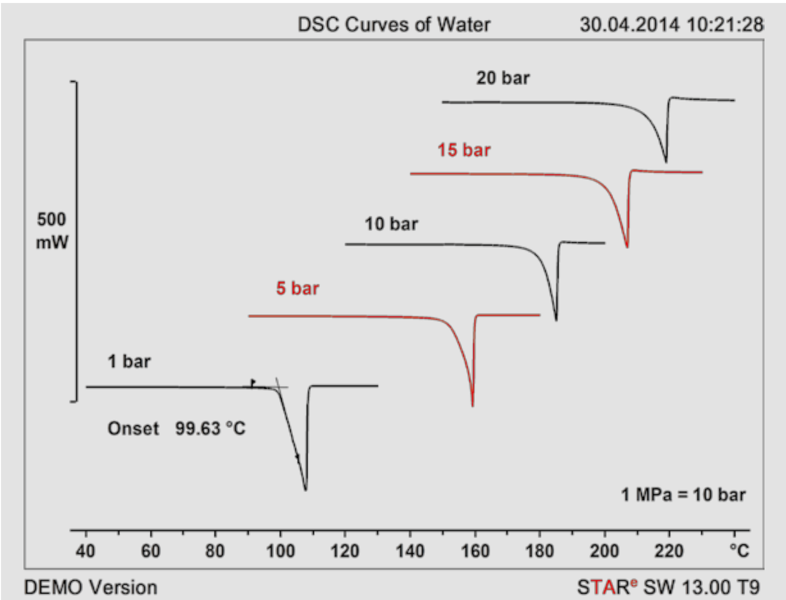

Figure 1.
DSC curves of water at different pressures. The onset temperature of the vaporization peak corresponds to the boiling point.

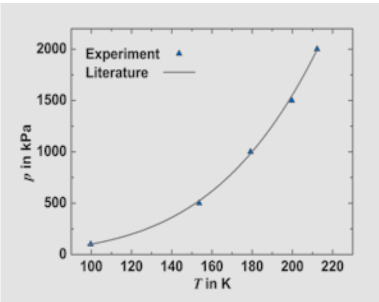

Figure 2.
Black: vapor pressure curve for water between 100 and 220 °C.
Blue: experimental results from HPDSC measurements.

Here ΔH stands for the enthalpy (heat) of vaporization, L is a substance-specific constant, and R is the universal gas constant, 8.314 J/(mol K). In this article, we use water as an example and show how boiling points can be measured by HPDSC at different pressures and how the enthalpy of vaporization can be calculated from this data.

Experimental details

The measurements were performed using an HP DSC 1 equipped with an FRS 5 sensor and a PC10 pressure controller. The evaporation of a liquid leads to DSC curves with broad endothermic peaks. The evaporation must be suppressed as far as possible to obtain a sharp vaporization peak and thus allow an accurate determination of the boiling point.

To do this, the crucibles are sealed with a lid in which a small hole has been pierced. Investigations of an ASTM task group showed that the optimum size of the hole depends on the pressure. At pressures above 1 bar, diameters of 50 µm are recommended [2, 3].

For our measurements, we used aluminum crucibles that were sealed with a lid with a 50-µm hole (ME 51119873). The sample weight was typically 2 mg and the heating rate 5 K/min. Nitrogen was used as the pressurizing gas.

Results

Figure 1 shows the measurement curves recorded at different pressures. The boiling point corresponds to the onset temperature of the vaporization peak. At the boiling point, the vapor pressure of the liquid equals the external pressure.

The applied pressure therefore corresponds to the vapor pressure of the liquid at the temperature at which it boils.

In Figure 2, the temperature dependence of the vapor pressure of water is displayed together with the results from our measurements.

The figure shows that there is good agreement between the measured values and the literature values.

Closer inspection of the DSC curves in Figure 1 at higher pressures shows a small exothermic peak immediately after the vaporization peak. This peak is due to the reaction of water vapor with aluminum [4]. To suppress this reaction, inert crucibles must be used, for example gold crucibles or gold-plated aluminum crucibles.

The black curve in Figure 3 shows the vaporization peak measured in an aluminum crucible at a pressure of 20 bar. The small exothermic peak after the vaporization peak can be clearly seen. If the same measurement is performed (red curve) in a gold-plated aluminum crucible (ME 51142973), the baseline is as expected flat after vaporization.

The broader vaporization peak obtained with the gold-plated aluminum crucible is due to the fact that a lid with a 50-µm hole is not available for this crucible. Instead of this, a lid was used that was pierced manually with a needle with a nominal diameter of 100 µm. The four-times-larger pin hole allowed much more water to evaporate before the water actually boiled and thus led to a broader vaporization peak.

Figure 4 displays a plot of the natural logarithm of the vapor pressure as a function of the reciprocal boiling point. According to the Clausius–Clapeyron relationship (see equation 1), the enthalpy of vaporization can be determined from the slope of the curve. This yields a value of 40.0 kJ/mol for water and agrees well with the literature value of 40.1 kJ/mol.

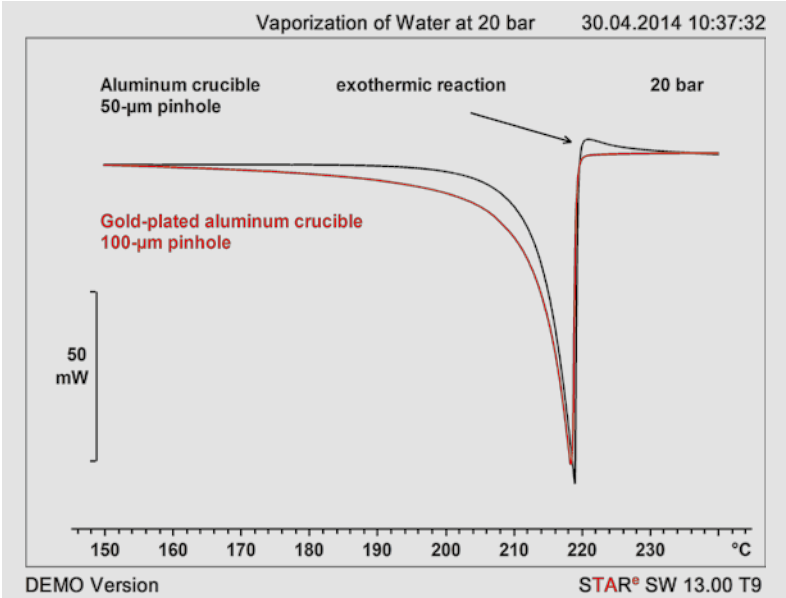

Figure 3.
Vaporization peak of water at 20 bar in aluminum and gold-plated aluminum crucibles.

Conclusions

The vapor pressure curves of liquids can be easily determined by HPDSC. To do this, the boiling point of the liquid is measured in crucibles sealed with a pierced lid at different pressures.

The vaporization enthalpy can also be determined from such measurements using the Clausius–Clapeyron equation. Using water as an example, we have shown that the resulting vapor pressure curve and the vaporization enthalpy agree well with the literature values.

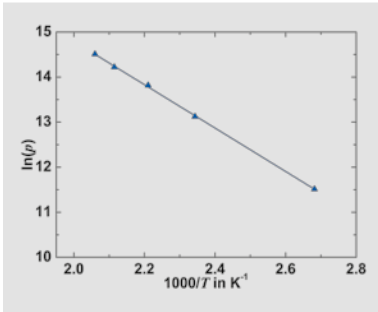

Figure 4.
The Clausius–Clapeyron diagram for water.

References

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[3] B. Perrenot, P. de Valliere, G. Widmann, Journal of Thermal Analysis (1992), 381–390)

[4] R.J. Seyler, R. Moody, ASTM Special Technical Paper 1326 (1997), 212–231