

## Thermal Analysis

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## Determining Vapor Pressure by Pressure DSC

**Introduction**

In many lines of work it is “normal” to smell the presence of semi-volatile solids and liquids, even though at higher concentrations these vapors may be considered hazardous. With greater consciousness of reducing hazards in the workplace has come a need to quantify the

volatility of laboratory substances in order to develop procedures for handling these materials safely. DTA, DSC and TGA have been used in the past to determine boiling points and to estimate vapor pressure.

**Purpose**

To develop a method to determine the vapor pressure of volatile materials using the high pressure accessory of the DSC 7. The test material reported here is water, which makes an ideal non-hazardous material for method development.

**Experimental**

In response to local energy fluctuations at the surface of a liquid or solid, molecules spontaneously transfer into the gaseous phase. In a closed vessel, at a given temperature an equilibrium will be established between material in the gas phase and in the condensed phase. As a material is heated, the pressure exerted by the volatile component – the vapor pressure – increases. Nineteenth century physical chemists worked out the relationships between the pressure, volume and temperature under these conditions, thus giving the underlying form for the equations to which the DSC data will be fitted.

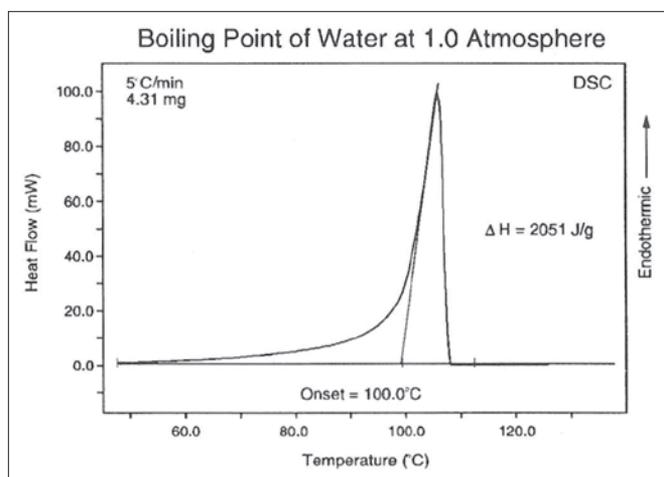


Figure 1. DSC curve of water heated in a vapor pressure (pin-hole) capsule. The extrapolated onset is the boiling temperature, in this case at 1 atmosphere external pressure.

If the material in a DSC pan is held at a constant pressure, then there will be an endothermic heat flow associated with the condensed material entering the vapor phase (Figure 1). When the vapor pressure of the sample exceeds the total pressure exerted on the sample by its surroundings, the material boils. With increasing temperature the rate of boiling will increase – along with the endothermic heat flow – until all the material is in the vapor phase. In fact, the material in the condensed phase will stay at the boiling temperature until all the material has boiled off. The flat leading edge of the endotherm represents the portion of the experiment where the sample temperature is constant at the boiling point and the calorimeter temperature is continuing to increase at the specified heating rate.

**Pressure Unit Conversions<sup>2</sup>**

0.01 mbar = 1 Pa =  $9.8692 \times 10^{-6}$  atm = 0.0075 mm Hg = 0.000145 psi = 0.0075 torr

atm = 760 torr = 14.696 psi = 1.01325 bar

100 torr = 1.934 psi = 0.132 atm = 1.133 bar

The isothermal boiling condition described above is obtained only when the vapor phase over the sample consists of 100% vapor of the volatile component. This will only be achieved after all the other gaseous material has been swept out by the boil-off. This is accomplished by encapsulating the sample in a pan which has a small hole. If the hole is not extremely small then all the material will evaporate before this condition is achieved. The results from several labs were best when using a low volume, hermetically sealed pan with a hole size between 50 and 125 microns, with a

sample size between 2 to 10 milligrams and a scan rate of 5 or 10 degrees per minute. It is also necessary that the hole size remain constant during the boiling process. The results of a multi-laboratory test were reported at the 1993 North American Thermal Analysis Society meeting.<sup>1</sup> They showed that the best results were obtained by laser drilled holes and that mechanically punched holes did not consistently maintain a constant hole size. PerkinElmer provides these laser-drilled pans under PerkinElmer Part No. N5190788.

In order to obtain the vapor pressure of a material at ambient pressure and temperature it is necessary to determine the boiling point at several pressures, then extrapolate back to ambient temperature. That is, several samples of the material are prepared in vapor pressure pans. A boiling point is obtained at each of several pressures.

These data are collected using a pressure DSC capable of being operated either at elevated pressure or under vacuum. For scientists with access to a PerkinElmer power compensation-type DSC, for example, the DSC 8000, this is accomplished through the use of a DSC High Pressure Cell accessory (PerkinElmer Part No. N5200001) and a DSC model-specific adaption kit. For this application, it is recommended that tap water or water from a cooled temperature bath be used to maintain the block temperature 10 °C to 20 °C below room temperature. Also, a pressure regulator capable of being read to an accuracy of  $\pm 1$  psi or better should be used. This is especially important for vacuum work.

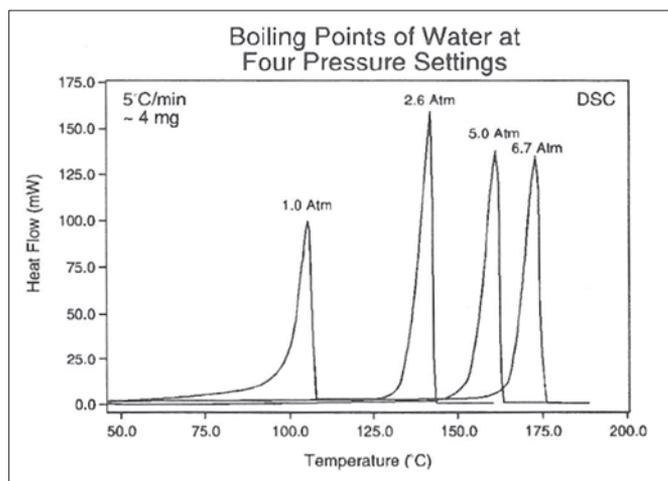


Figure 2. DSC curves of water at four elevated pressures using a pressure DSC accessory attached to a power compensation-type DSC.

In the inter-laboratory testing that was carried out, the boiling point of water was determined by each laboratory at several pressures. Typical experimental curves are shown in Figure 2. Other laboratories gathered data on water at higher and lower pressures, down to 100 torr. At low pressures the boiling curve is broadened due to the increased thermal resistance between the sample pan and the sample holder floor (because of the shortage of gas molecules to carry heat across this area).

At high pressures some laboratories reported evidence of an exothermic reaction of water with aluminium and exothermic decomposition of organic materials. In any case, the low pressure region is more important for the vapor pressure extrapolation.

Another phenomenon reported by most labs was an apparent overshooting of the baseline and/or baseline shift associated with boiling. This is believed to be due to a transitory change in the thermal conductivity of the sample surroundings. When this is observed it is recommended that the boiling point be obtained using the Onset calculation function – instead of Peak – so that the tangents can be independently selected.

Calibration is another experimental consideration. Temperature calibration was checked using indium at each pressure setting. The maximum correction required was  $\pm 0.40$  °C referenced to calibration at 1 atm.

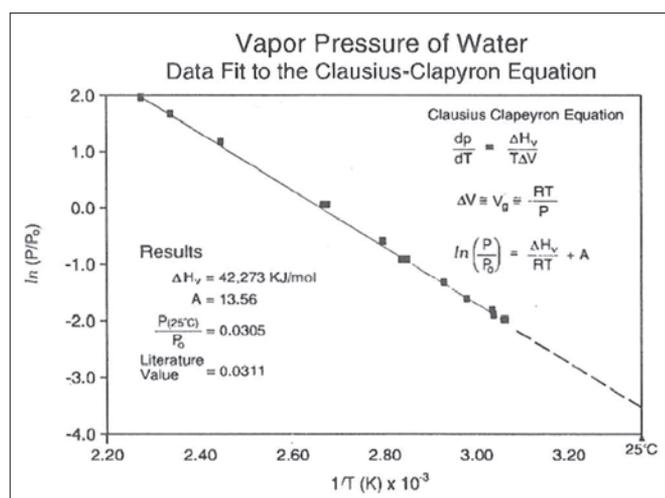


Figure 3. DSC data from various sources fitted to the Clausius-Claypron equation for calculating vapor pressure.

The first equation used to fit the temperature-pressure data is the Clausius-Clapeyron equation (Figure 3). The advantage of this equation is that it is directly derived from first principles.<sup>3</sup> Moreover, the parameters can be determined using a linear least squares fit. However, for various reasons there will be a curvature to the plot, which will lead to the potential for error in extrapolating the straight line fit.

The second equation used, the Antoine equation, is commonly used by those determining vapor pressure by the classical technique of ebulliometry. The Antoine equation is an empirical modification of Clausius-Clapeyron; it includes a third coefficient which effectively shifts the temperature scale. This creates curvature in the Log P versus 1/T plot, which allows a better fit of the data in the low pressure region.

There are two considerations to keep in mind when choosing an equation to fit the data. First, as a rule of thumb, the use of three parameters (i.e., the Antoine equation) instead of two should be avoided when there are 5 data points or less, for statistical reasons. Second, if there is a measurement error that becomes greater at low pressures, then the fitting of a curved line to the data (i.e., the Clausius-Clapeyron equation) will exaggerate the error and the result in a poor extrapolation in the low pressure direction.

The data were fitted to the Antoine equation and the coefficients solved for. This was accomplished using a similar least squares fit as above and using a series of successive approximations for the third parameter with the standard deviation of the fit as the goodness criterion. This step was carried out using all data from all participating laboratories.<sup>1</sup> See Figure 4 for results.

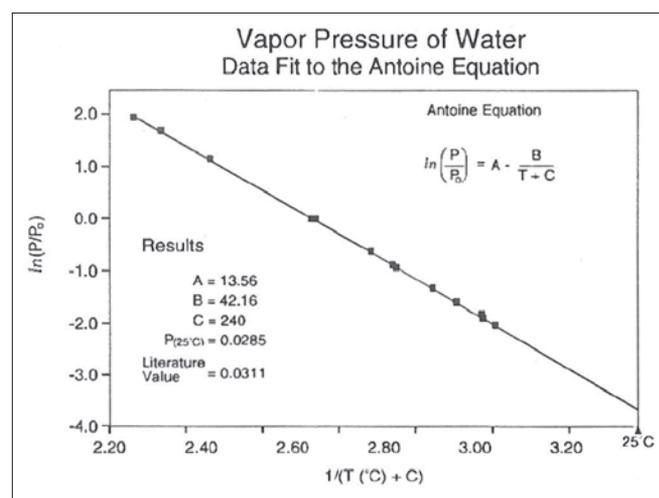


Figure 4. DSC data from various sources fitted to the Antoine variation of the Clausius-Claypron equation for calculating vapor pressure.

## Results

The water data were also compared to literature data from CRC Steam Tables.<sup>2</sup> And, finally, the data were extrapolated to 25 °C in order to demonstrate how this technique is used to predict vapor pressure at ambient temperature. For this system and the range of data taken, the best fit as obtained using the Clausius-Clapeyron equation. The heat of vaporization obtained from the plot, 42273 J/mole, is an average over the pressure range. It agrees well with the steam tables. For example, Hv (60 °C) = 42482 J/mole. From this fit the predicted partial pressure of water at 25 °C would be 0.0313; from steam tables it is found to be 0.0313.

As part of the ASTM® E-37 fact gathering effort, this technique was also successfully applied to ethyl benzene, a common laboratory solvent and diethyl malonate, a “simulant” for a toxic material such as a pesticide. For these two samples, there was more curvature in the Log P vs. 1/T plot, and the Antoine equation gave the superior fit.

## Conclusion

The techniques discussed in this report provide a good method for determining vapor pressure as a function of temperature. It requires the use of a pressure DSC cell operated primarily at subambient pressures. It employs special capsules with carefully controlled laser-drilled holes. Once the boiling point data has been obtained at several pressures, it can be extrapolated to estimate the vapor pressure at environmental temperatures. The method has been codified as a standard method from ASTM® (E 1782), which contains useful information on carrying out this analysis.

## References

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