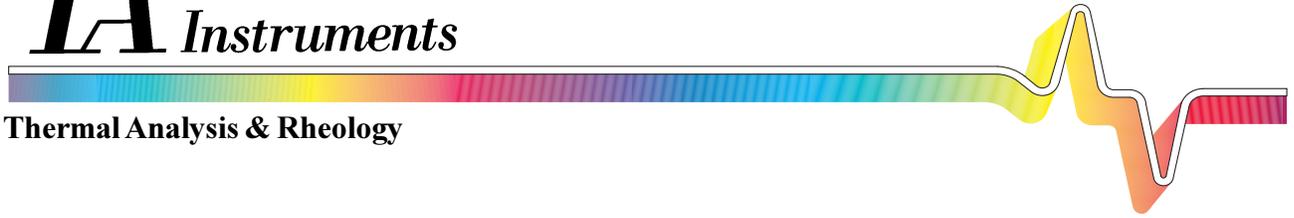


**TA** *Instruments*

Thermal Analysis & Rheology



## **Differential Scanning Calorimetry for Boiling Points and Vapor Pressure**

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## Abstract

Extensive vaporization of volatile specimens during heating in a differential scanning calorimeter (DSC) has limited the use of DSC for measuring boiling points or generating vapor pressure curves. This preboiling vaporization tends to broaden boiling endotherms, may exhaust the specimen before the actual boiling point, or can self-pressurize a sealed specimen. Recent efforts to increase the utility of DSC for studying volatile specimens have shown that a pinhole of 25 to 125  $\mu\text{m}$  diameter in a hermetic sealed container or capillary flask sample containers are both capable of establishing the vapor-liquid equilibrium necessary to minimize specimen loss and to develop sharp boiling endotherms. When used with heating rates of 5°C/min to 10°C/min in a pressure DSC, boiling temperature-pressure data pairs may be obtained over a typical pressure range of 7 kPa to 3 MPa. Fitting five or more of such T-p pairs with the Antoine equation:

$$\log P = A + B/(T+C); T \text{ in } ^\circ\text{C}$$

allows one to create a vapor pressure curve suitable for accurate interpolation of values. An examination of water in four laboratories using pinhole containers for differing portions of the pressure range 1 kPa to 7 MPa yielded T-p values within the 95% confidence limits of CRC Handbook tables.

## Introduction

Use of differential thermal analysis (DTA) to measure boiling points of pure liquids for determining their vapor pressure gained some notoriety during the 1960's (1-3). Experimenters recorded the temperature of the boiling endotherm at a number of imposed pressures typically at or below ambient pressure. Graphical methods such as those discussed by Thompson (4) converted these temperature pressure pairs into vapor pressure curves.

Unique to many of these early DTA instruments was the use of thermocouple inserted glass capillary tubes to contain the liquid specimens. This sample configuration minimized escape of vapors and tended to establish refluxing at the boiling temperature which insured the vapor-liquid equilibrium necessary for a sharp endotherm and an accurate determination of the boiling temperature.

In differential scanning calorimeters (DSC), measurements on volatile specimens were fraught with difficulties arising primarily from the relatively large surface-to-volume ratios of specimens in DSC containers. These difficulties are amplified by any purge used in the DSC measurements where, for open pans, the specimens volatilized quickly causing broad endotherms and often, depletion of the specimen before the actual boiling temperature was reached (Figure 1a). Hermetically sealable containers were introduced to prevent loss of specimen but they still suffered from broad, sometimes multiple, endotherms and the added problem of self-pressurization (Figure 1b). Addition of a pinhole in the lid of a volatile sample pan hermetically sealed was reported to result in sharp, accurate boiling endotherms (5) (Figure 1c). Farritor and Tao (6) further suggested placing a small metal ball over the pinhole to form in effect, a pressure release valve.

A 1976 review by Seyler (7) of the parameters affecting the determination of vapor pressure of pure liquids using differential thermal methods served as a basis for ASTM Committee E-37 on Thermal Methods to initiate efforts to establish a standard test method in the early 1980's. An interlaboratory test program conducted as part of this effort showed successful results were obtainable using DTA with thermocouple inserted capillary sample containers. However, despite the use of sealed specimens with pinholes in the lids, the DSC results lacked the precision and accuracy required for a standard method.

Use of DSC for measuring boiling points and determining vapor pressure received little further attention until 1992. Increasing health, safety and environmental concerns and more widespread availability of commercial pressure DSC equipment have encouraged reexamination of the DSC approach for establishing vapor pressure values. The discussion which follows highlights the successful description of DSC conditions necessary to improve the evaluation of volatile samples for boiling points and vapor pressure which has led to an ASTM draft method.

## Experimental

An informational study was conducted by four members of ASTM task group E37.01.05 which include A.B. Butrow, U.S. Army ERDEC (Aberdeen Proving Ground, MD), R.B. Cassel, Perkin-Elmer Corporation (Norwalk, CT), C.W. Schaumann, TA Instruments, Inc. (New Castle, DE), and R.J. Seyler, Eastman Kodak Company (Rochester, NY). Pinholes in the lids of hermetic sealed containers (15 $\mu$ L to 40 $\mu$ L volumes) with diameters of 25, 51, 76, 127, 254, and 508 $\mu$ m were tested in a partial matrix study. Other variables included heating rates of 5 $^{\circ}$ C/min, 10 $^{\circ}$ C/min, 20 $^{\circ}$ C/min, and 50 $^{\circ}$ C/min; specimen sizes from 0.2mg to 6mg; and pressure ranging from 1.3kPa to 7MPa of nitrogen. Materials used in this study included water, o-xylene, toluene, phenyl ether, ethylbenzene, dioxane, cyclohexane, and diethyl malonate. DSC instrumentation used in this study included a Mettler DSC 27HP, TA Instruments DSC 910 with HPDSC cell, Perkin-Elmer System 7 with HPDSC accessory, and Perkin-Elmer DSC2 with HPDSC accessory.

Capillary flask containers were evaluated in a TA Instruments DSC 910, a Seiko 210 DSC, and a Mettler DSC 27HP at a heating rate of 10 $^{\circ}$ C/min with 2.4mg to 5.4mg specimens of o-xylene, ethylbenzene, or water. Both the TA Instruments and Seiko instruments were operated at ambient pressure while the Mettler instrument was operated in the 10kPa to 2MPa nitrogen pressure range.

## Discussion

Use of DTA or DSC for vapor pressure studies is possible because of the unique thermodynamic conditions for boiling. When the temperature of a liquid is increased, the pressure of the vapor in equilibrium with the liquid increases as more of the surface molecules achieve sufficient kinetic energy to escape the condensed phase. When this vapor pressure equals the external pressure on the vapor space, the liquid boils isothermally at that temperature. If one changes the applied pressure, the temperature at which boiling occurs changes a corresponding amount. Since DTA and DSC instrumentation are intended to measure the temperatures of transitions in materials, determining vapor pressures by measuring the boiling temperature at several different pressures is a natural application of these differential thermal methodologies.

As already noted in the introduction, the application of DSC for measuring boiling points encountered difficulties because of the specimen geometry. Because the liquid has a vapor pressure below the boiling temperature, some fraction of the condensed phase will evaporate to satisfy the vapor-liquid equilibrium at the current temperature. This evaporative loss of the specimen will be controlled by the surface area of the specimen, the volume of the vapor space, and the material's vapor pressure determined by the temperature. In DSC the surface-to volume ratio promotes evaporation and both the internal furnace volume of a DSC and the use of a purge require a considerable fraction of the specimen to evaporate even at relatively low temperatures.

Encapsulating the specimen in a hermetic container eliminates the removal of material by the purge and reduces the volume of vapor space to a level that will only require a small percentage of a typical specimen mass to satisfy the vapor liquid equilibrium. The difficulty with the hermetic container is that it self pressurizes with heating which leads to broadening of the boiling endotherm, multiple endotherms, distortion of the container, or even rupture of the container. Even when a single endotherm is recorded, the actual pressure associated with the observed boiling temperature is not known and curvature in the leading edge of the endotherm adds to the uncertainty of the real boiling temperature.

While addition of a pinhole to otherwise hermetically sealed specimens appeared to be the solution to the DSC dilemma for volatile specimens, the large variability encountered in the interlaboratory test data encountered by ASTM E37 suggested the pinhole was not a satisfactory approach. In 1992 Perrenot, de Valliere, and Widman (8) defined conditions in the DSC leading to a "self generated atmosphere" which resulted in excellent peak shapes at pressures between 0.1MPa and 1.8 MPa for water. These conditions were achieved using a pinhole between 30 $\mu$ m and 50 $\mu$ m with approx. 2.5 mg specimens and a 1 $^{\circ}$ C/min heating rate. This pinhole size is significantly smaller than generally used previously and represents the key to success. It must be small enough to restrict diffusion of vapor molecules into the purge to a rate less than that through the vapor space inside the specimen container, yet be sufficiently large to minimize any self-pressurization.

Utilizing the concept of attaining “capillary equivalence, Jones and Seyler (9) literally coupled a short capillary stack to a glass specimen container to achieve the same diffusion limiting effects as the pinhole of Perrenot, et al. These 25uL volume flat-bottomed capillary flasks included an 11mm x 1mm i.d. capillary neck (Figure 2). Although the capillary diameter is much larger than the pinhole, it is compensated for by the greater length. Though technically acceptable for use with liquids, these capillary flasks would have required some modification to the furnace covers in many of the commercial DSC instruments or a reduction in the length of the capillary neck.

The reinstated ASTM task group E37.01.05 opted to reexamine the pinhole approach using the Perrenot, de Valliere, and Widman conditions as a reference. They undertook a partial matrix information study to verify the Perrenot, et al findings and to define practical limits for the experimental parameters used. This study indicated consistently sharp endotherms with no appreciable preboiling vaporization could be obtained when pinholes of 25 to 127µm diameter were employed with heating rates of 5°C/min to 10°C/min. Use of heating rates  $2 > 20^\circ\text{C}/\text{min}$  tended to reveal some distortion in the peaks and consistently higher temperatures indicative of overpressures within the specimen container. The larger diameter pinholes studied (254 to 508µm) yielded endotherms more typical of open pan configurations. It was, however, noted that considerable reduction in leading edge curvature of the endotherms for the 254µm pinhole was possible when heating rates in excess of 10°C/min were attempted.

More recently, Contreras, Girela, and Parera (10) reported pinhole diameters of 0.4mm were suitable for vapor pressure studies in the pressure range 0.7kPa to 40kPa. These pinholes are significantly larger than those examined in the ASTM study but smaller than typically employed previously. The success of these larger pinholes is their use of somewhat larger specimen sizes of 5 mg and heating rates of 15°C/min. These results actually confirm the ASTM findings that pinholes of diameter greater than 127µm may be successful if the heating rate is sufficiently fast to overcome vapor losses through the pinhole.

A final comment about the quality of the pinhole is worth mentioning. Figure 3 illustrates one of several distortions of the boiling endotherm which was encountered when other than “clean pinholes were used. Not only is it necessary to control the size of the pinhole but it is also necessary to insure a clean uniform opening. In recognition of these requirements, laser drilled pinhole lids with hole diameters between 51 and 76µm are now commercially available.

Caution should be taken when attempting to measure boiling points at pressures above ambient, especially for organic materials. As a general rule of thumb, one can anticipate the boiling point will increase 1°C for every 10kPa of pressure increase above ambient. Retaining many organics in the condensed phase much beyond their normal boiling point will result in decomposition. Similarly, addition of pressure will enhance the effective reactivity of oxygen at the sample surface. Care should be taken to avoid the presence of oxygen in the specimen vapor space when employing elevated pressures, particularly above 1MPa. Its presence will result in partial oxidation on heating and a change in the vapor pressure.

Another procedural complication which has been encountered is that of poor seals. These may result from a bad crimp or because of sample or other debris on the seal area of the hermetic containers. In such instances the pinhole size is effectively enlarged and conditions more like an open pan occur or multiple peaks are observed as liquid escapes from the seal area. Thus care should be taken to insure a clean seal area and a complete cold weld seal before initiating a measurement.

Putting these findings into practice allows one to conveniently measure the boiling point of pure liquids using DSC. Repeating the measurement at 5 or more pressures throughout the pressure range of interest results in a set of T-p data pairs which may be used to establish the vapor pressure of the material being investigated. A vapor pressure curve such as Figure 4 may be generated by simply plotting the T-p pairs as  $\log P$  vs  $1/T(\text{K})$ . It is, however, recommended that a curve be fitted to these data pairs. For narrow pressure ranges it is possible to perform a least squares fit of these points for a vapor pressure curve represented by the Clausius-Clapeyron equation (4).

$$A + B/T, T \text{ in K}$$

The vapor pressure curve is actually ‘S’ shaped between the triple point and the critical point. This curvature arises because the enthalpy of vaporization is not independent of temperature nor is the vapor necessarily an ideal gas at all

temperatures. Both the constancy of delta H and the ideal gas behavior are assumed for the Clausius Clapeyron equation and are the reason this straight line equation has led to serious extrapolation errors in predicting vapor pressure at temperature extremes. A better fit for vapor pressure curves is achieved with a nonlinear regression of logP vs 1/°C as the Antoine equation:

$$\log P = A + B/(T+C), T \text{ in } ^\circ\text{C}.$$

with typical values of the Antoine constants being A=6-7, B=1200-1700, and C=215-240. This improved fit is especially true for wider pressure ranges and is appropriate for studying materials between their triple point to 75% of their critical point (4).

Putting this all together, each of the four laboratories in the ASTM information study examined water over different portions of the pressure interval 1kPa to 7MPa as part of their individual contributions. Their combined results are shown in Figure 5 along with a fit of the CRC Handbook (11) values of water. All measured values were within the 95% confidence interval for the Antoine equation of the reference values. Back (12) recently reported repeated vapor pressure measurements of water over a narrower temperature range agreed within 2.4% of reference values. This success has led to a draft method for determining vapor pressure of pure liquids by DSC from ASTM E37.01.05.

## Recommendations

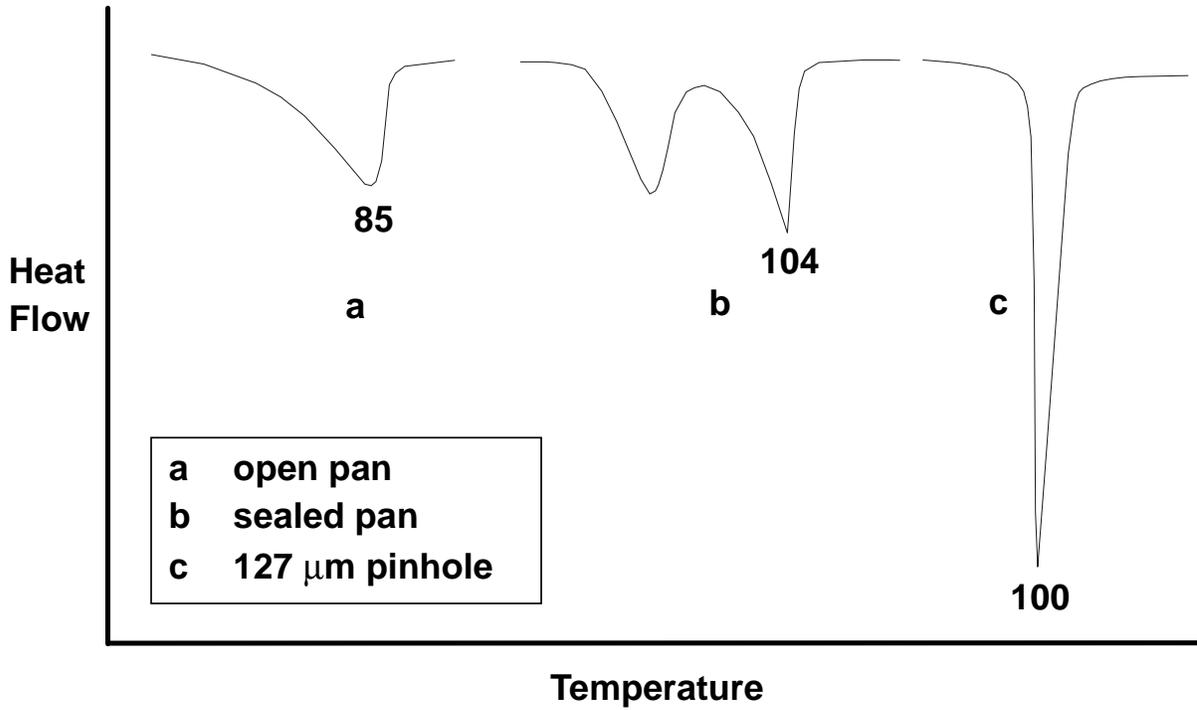
The historical difficulties encountered when attempting to measure the boiling point of pure liquids with DSC can be minimized by using hermetic containers with very small pinholes and moderately slow heating rates. Hermetic containers with a capacity of less than 50 µL, a specimen size of 2mg to 4mg, a heating rate of 5°C/min to 10°C/min, and a “clean” pinhole of diameter 25 to 127µm are the preferred experimental parameters for this application of DSC.

If these measurements are to be used to generate a vapor pressure curve, a minimum of 5 boiling point measurements should be determined at different pressures throughout the range of interest. A practical range of pressures for this approach is 7kPa to 2MPa. It is recommended the T-p pairs be fitted with a nonlinear regression of logP vs 1/T, °C to the Antoine equation.

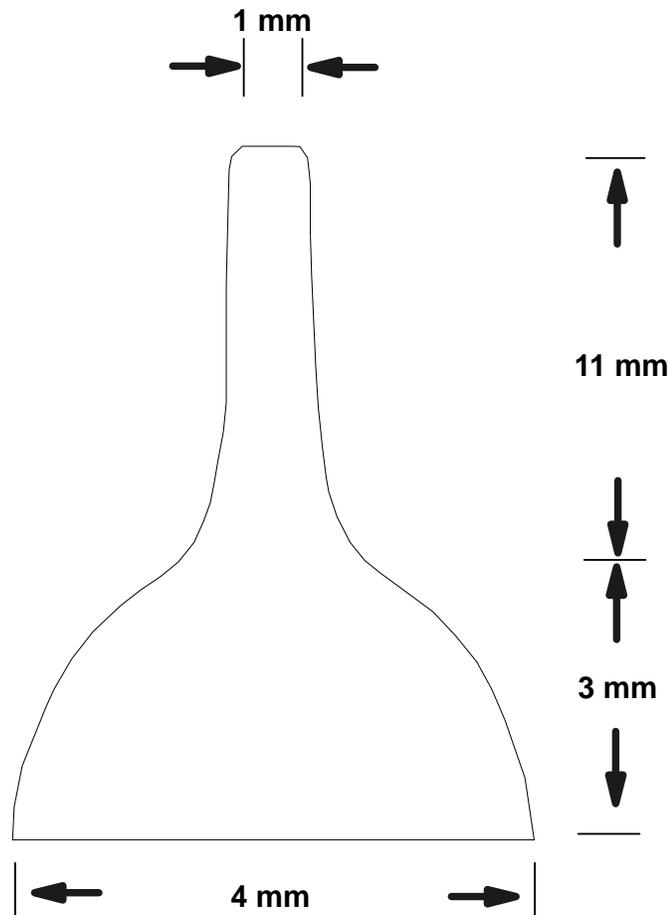
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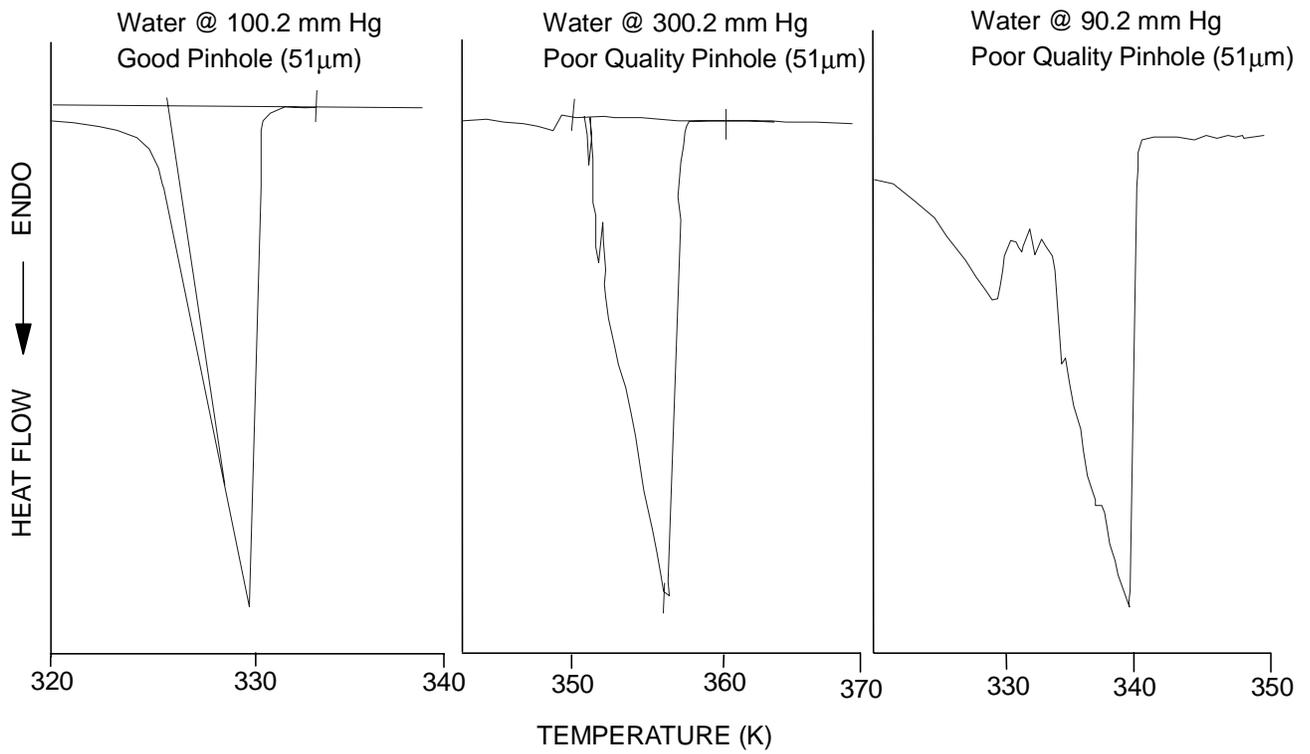
**Figure 1. EFFECT OF CONTAINER ON CURVE SHAPE**



**Figure 2. CAPILLARY FLASK FOR LIQUIDS IN DSC**



**Figure 3. EFFECT OF PINHOLE "CLEANLINESS"**



**Figure 4. VAPOR PRESSURE PLOT OF MEASURED POINTS WITH CLAUSIUS-CLAPEYRON FIT**

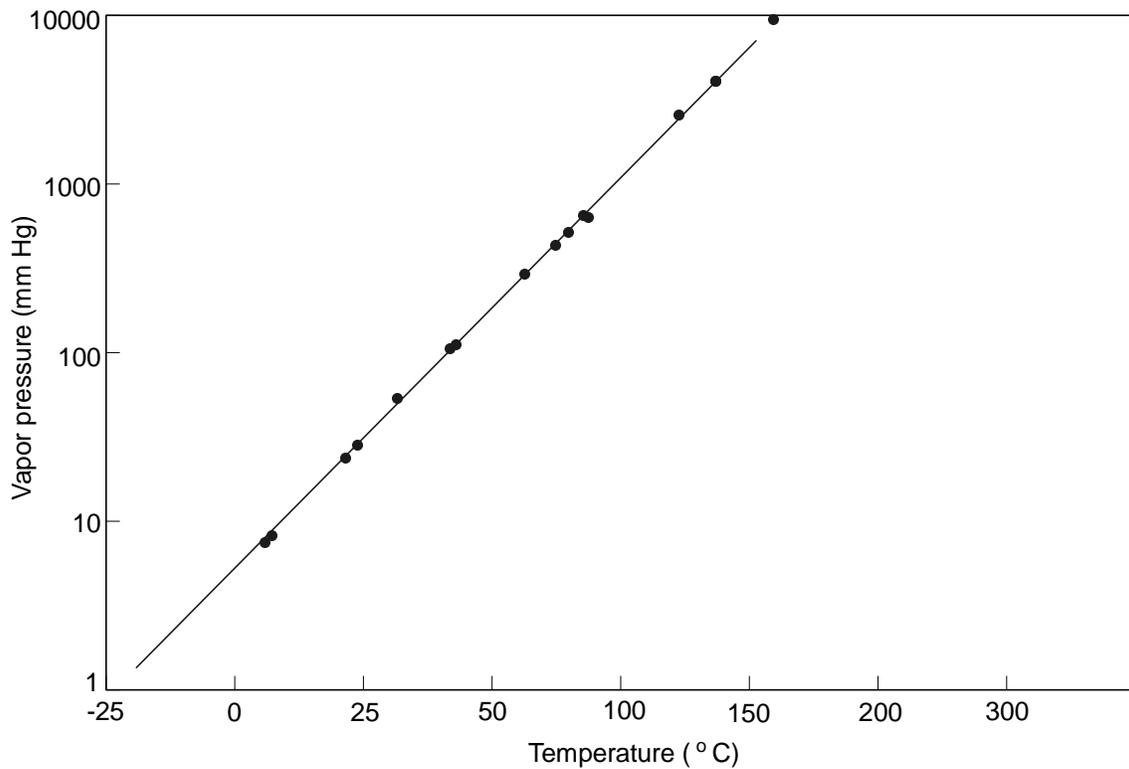


Figure 5. WATER VAPOR PRESSURE CURVE  
(Comparison to literature values)

