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Vapor pressure by DSC: extending ASTM E 1782 below 5 kPa

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Abstract

In 1996, American Society for Testing and Materials (ASTM) Method E 1782–96, Standard Test Method for Determining Vapor Pressure by Thermal Analysis received final approval and was published as a standard method. For vapor pressure measurements by DSC, the method requires use of hermetic-type sealable pans with a single pinhole ≤125 μm (50–75 μm recommended) in the center of the lid. Pinholes of this size produce generally acceptable results over the 5 kPa to 2 MPa operational pressure range of the method. However, as the minimum recommended pressure is approached, boiling endotherms become increasingly broad. Recent efforts using larger pinholes (175–375 μm) have shown improved peak sharpness and elimination of leading edge curvature when pinhole size is increased as pressure is reduced. This need for increased pinhole diameter at lower pressures is consistent with orifice selections used in effusion studies. Optimization of pinhole size as a function of pressure may extend the practical operational range of ASTM E 1782 to permit rapid vapor pressure determination to at least 0.2 kPa.

Keywords: Differential scanning calorimetry (DSC); Differential thermal analysis (DTA); Vapor pressure; Pinhole lids; Boiling endotherm

1. Introduction

Differential thermal analysis (DTA) instrumentation with the thermocouple-inserted glass capillary configuration is ideally suited for measurement of boiling points at a variety of pressures [1–3]. Fig. 1 illustrates a typical sharp DTA endotherm resulting from isothermal boiling as a specimen vaporizes under equilibrium conditions. The boiling point is defined as the extrapolated peak onset temperature and is taken at the intersection of tangents to the curve. Attempts to perform similar experiments with differential scanning calorimetry (DSC) were initially unsuccessful due to excessive mass loss of the specimens prior to reaching the equilibrium boiling temperature. This mass loss arises from extensive pre-boiling vaporization promoted by the large surface-to-volume ratios of specimens in DSC containers. Use of crimped DSC containers was ineffective for retarding pre-boiling vaporization and did not permit attainment of isothermal boiling conditions. Hermetic-type sealable pans did prevent specimen loss but the resulting self-pressurization caused boiling point elevation and multiple, erratic boiling endotherms.

Introduction of a pinhole to the lid of the hermetic-type DSC pan has been reported [4–7] to control the rate at which the specimen vapor was removed

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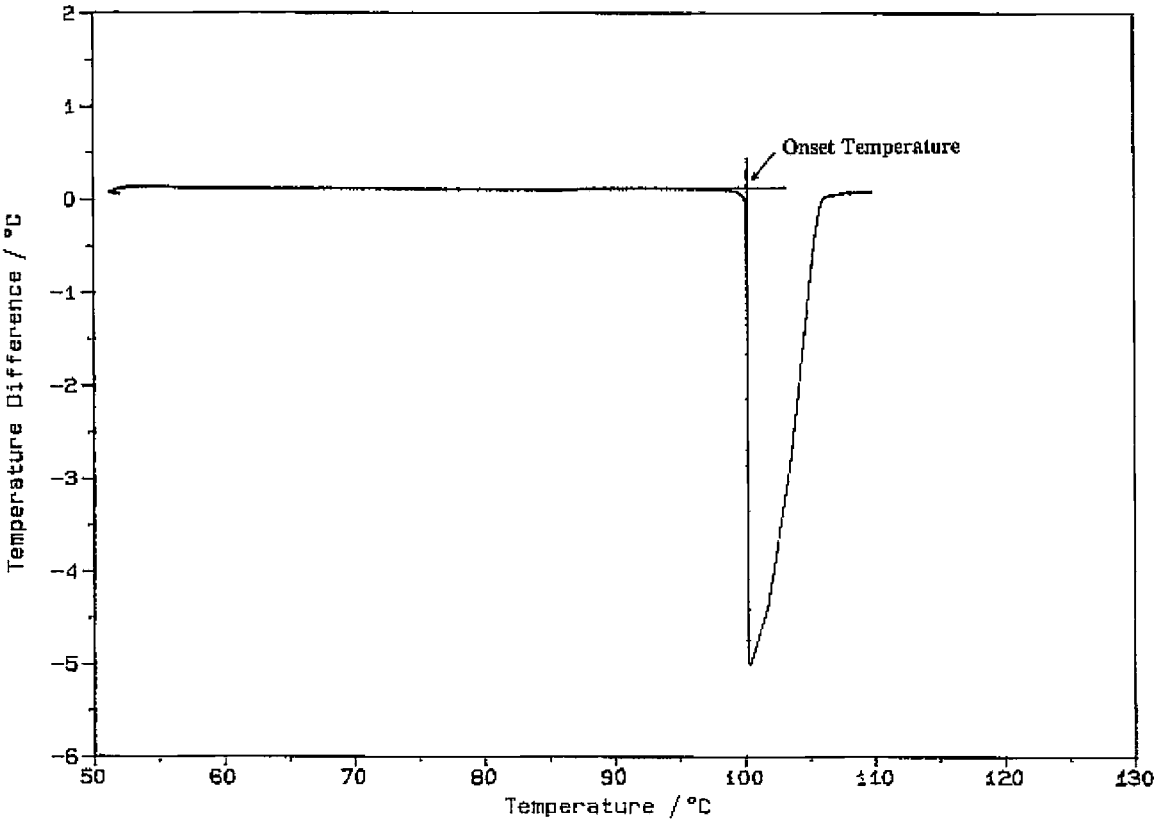

Fig. 1. DTA boiling endotherm for water at 100.9 kPa.

from the pan and subsequently produced boiling endotherms approaching the shape and accuracy of those generated using DTA. Not all pinholes, however, yielded acceptable results. Studies conducted in conjunction with ASTM task group E37.01.05 suggested a relationship existed between the effectiveness of a given pinhole size to achieve a "capillary equivalent" peak shape and the heating rate employed [6]. Similarly, these studies found artifacts in the DSC curve shape when recorded at extremes of pressure/vacuum [6,8]. ASTM E 1782–96 Standard Test Method for Determining Vapor Pressure by Thermal Analysis was eventually published in 1996 recommending pinholes between 50 and 75 μm for DSC and limiting the pressure range to 5 kPa to 2 MPa. The lower pressure limit was established from observations of increasingly significant broadening of the boiling endotherms near or below this pressure. Typical results for water under these conditions are shown in Fig. 2.

Within the working pressure range of ASTM E 1782–96 it was determined from Inter-laboratory studies [9] that pinholes between 25 and 125 μm provided comparable levels of equilibrium when a heating rate of 5 °C/min or slower is employed. The series of boiling endotherms for DIMP given in Fig. 3 illustrates the difficulty of employing ASTM E 1782 protocol beyond its recommended pressure range. As the test pressure approaches and exceeds the recommended lower limit, the endotherm becomes increasingly broad with the recommended pinholes. This broadening is indicative of a loss of vapor–liquid equilibrium conditions normally associated with boiling. Further deterioration of peak shape at even lower pressures complicates accurate determination of the peak onset temperature (boiling point) from the intersection of tangents to the curve. These endotherms at very low pressure are symptomatic of the difficulties previously encountered using DSC for boiling points without the

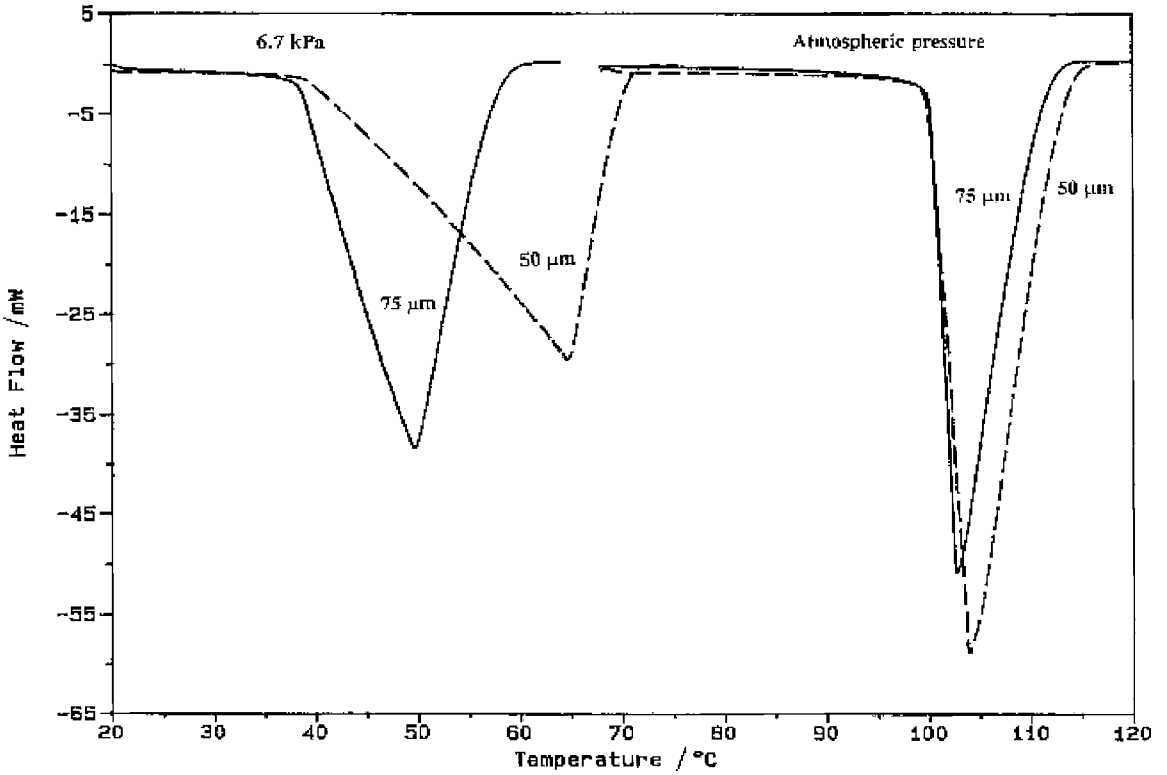

Fig. 2. DSC boiling endotherms for water within current ASTM E 1782 parameters (pressure range and pinhole size).

pinhole (see discussion by Jones and Seyler [6]) where extensive pre-boiling vaporization led to specimen depletion. Additionally, it was noted at pressures below the 5 kPa limit that the apparent boiling temperature decreases less than expected with a change in applied pressure. This would result in significant curvature in the vapor pressure curve.

It is generally desirable to generate vapor pressure data over as wide a range as possible including the temperature/pressure conditions of interest. Extension of the allowable pressure range of ASTM E 1782 is not possible without eliminating or minimizing those factors causing the peak broadening. Closer examination of the endotherms for water in Fig. 2, where two different size pinholes (50 and 75 μm) were used within the required ≤125 μm range, suggests that use of the larger pinhole at pressures near the 5 kPa limit yields the sharper peak. This re-examination of low pressure data led to limited studies of the effect of larger (>125 μm) pinhole diameters on boiling peak sharpness at pressures between 5 and 0.2 kPa. The results of these efforts are reported here.

2. Experimental

The experimental configuration for this work has been described previously [5] and is also shown in Fig. 2 of ASTM E 1782–96. Measurements were completed on a TA Instruments 2200 DSC and 910 Cell Base equipped with a standard DSC cell in accordance with the procedure specified in ASTM E 1782. System vacuum was achieved using a rotary vane pump with coarse and fine pressure regulators to hold the vacuum constant to ±0.01 kPa during boiling. Cell pressure was measured using an absolute mercury manometer. Hermetic-type sealable aluminum pans with single laser drilled pinholes (Kalbsey Corp., Carbon, IN) of 50, 75, 175, 250, and 375 ± 12 μm diameter were used. A heating rate of 5 °C/min, a sample size of 2 μl,

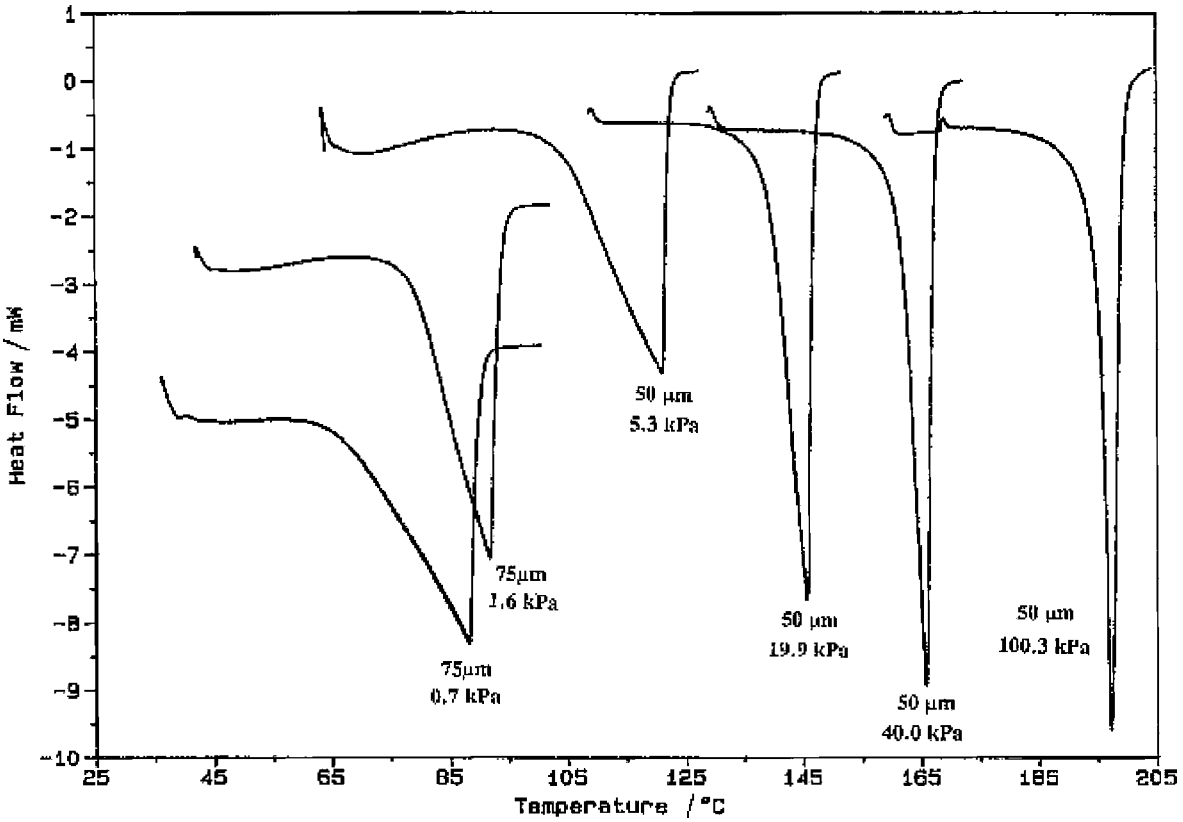

Fig. 3. DSC boiling endotherms for DIMP using recommended pinholes at pressures between 0.7 and 100.3 kPa.

and a pressure range of atmospheric pressure down to 0.2 kPa were employed. A very thin layer of conductive grease was applied between the specimen pan bottoms and the DSC stage to minimize thermal resistances at reduced pressures. Test materials included water, diisopropyl methyl phosphonate (DIMP) and dimethyl methyl phosphonate (DMMP).

3. Results

Emergence of data, such as that shown in Fig. 2, provided a pathway to extend the use of DSC to lower pressures. Boiling endotherms for water at 6.7 kPa (near the 5 kPa lower method limit) using five different pinhole sizes (50, 75, 175, 250, and 375 μm) illustrate the improvement in peak shape with larger pinholes as pressure is reduced (Fig. 4). Although the increased pinhole size improves peak shape by minimizing broadening, it also increases undesirable pre-boiling vaporization. This suggests that optimizing pinhole size selection requires consideration of both of these factors.

Measurements with DIMP and DMMP were completed covering the instrument operational pressure range, including pressures below those recommended in ASTM E 1782 using the larger 175, 250, and 375 μm pinholes. Both series (shown in Figs. 5 and 6) further illustrate the retention of peak sharpness with the use of larger pinholes at lower pressures.

Quantitative assessment of the improvement in peak shape can be achieved by comparing the slope of the leading edge of boiling endotherms. Table 1 contains the slopes and extrapolated onset temperatures for the water endotherms at 6.7 kPa (shown in Fig. 4) and for DMMP endotherms measured at 0.7, 0.8, and 0.9 kPa with various pinhole sizes. Unfortunately comparison of the water results to published values [10] does not

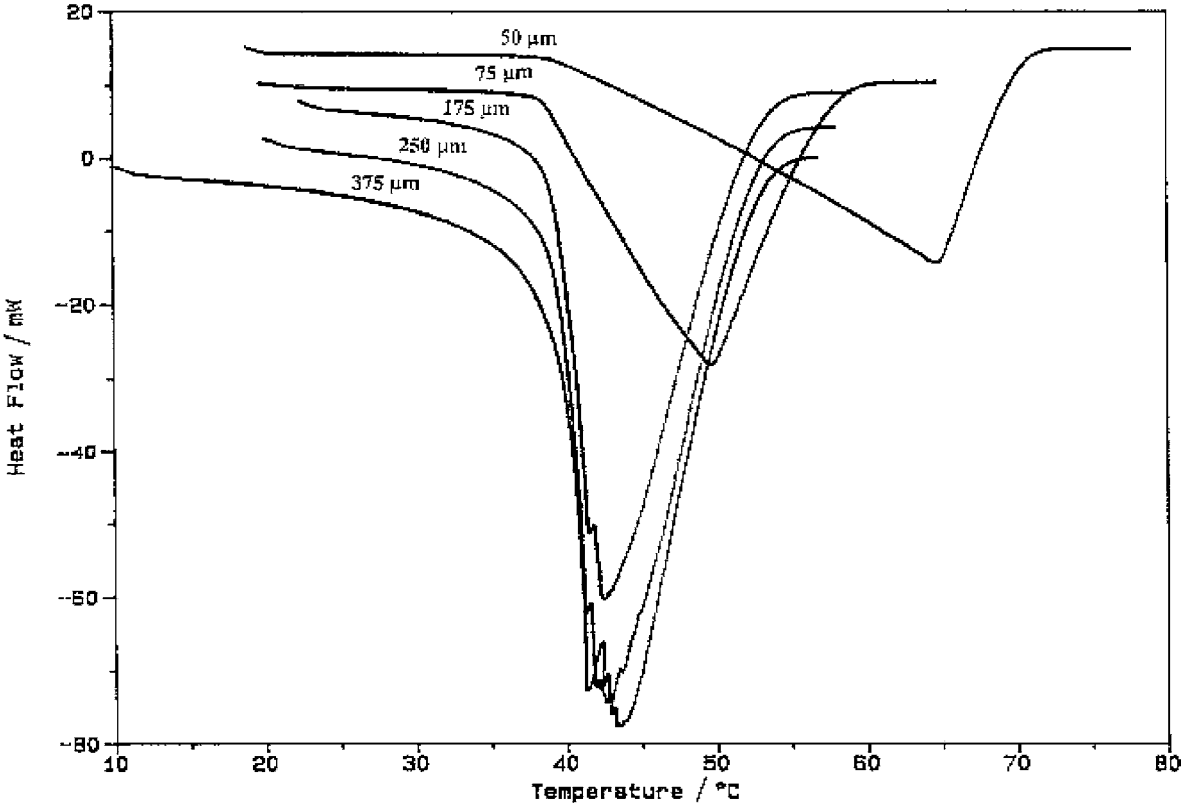

Fig. 4. DSC boiling endotherms for water with various pinhole sizes at 6.7 kPa.

indicate which pinhole gives the most accurate boiling point. All of the water onset temperatures agree with the literature within the ±1 °C accuracy of the method. The slope of the leading edge of the boiling endotherm is significantly steeper for the larger pinholes indicating much sharper peaks and a return to equilibrium conditions. These data point to the slope as a possible criterion that could be incorporated into ASTM E 1782 to optimize pinhole size as a function of pressure. This limited data set suggests a preliminary value of at least −3 mW/°C as an acceptable slope. However, a wider variety of materials should be studied before such a criterion is included in ASTM E 1782.

These results suggest that the shape of the boiling endotherm depends on factors controlling escape of sample molecules from the DSC container. With this method, boiling is detected at the temperature where the specimen partial pressure inside the DSC container equals the applied pressure outside the container. At the boiling point, the specimen reaches vapor–liquid equilibrium when the rate of vaporization equals the rate of condensation inside the container. The pinhole allows the vapor molecules saturating the inside of the container to escape. As vapor molecules leave the container, they are replenished until the liquid specimen is depleted. If the rate at which molecules leave the container equals the rate of generation of additional vapor molecules, a sharp peak results. The vertical leading edge of the boiling endotherm reflects isothermal conditions. Any deviation from this vertical leading edge reflects the extent to which these two processes are not balanced.

At pressures within the recommended range, escape of vapor through the pinhole is assumed to be a diffusion process where a large number of molecules are leaving the pan simultaneously. The recommended pinhole sizes appear to allow satisfactory balance of

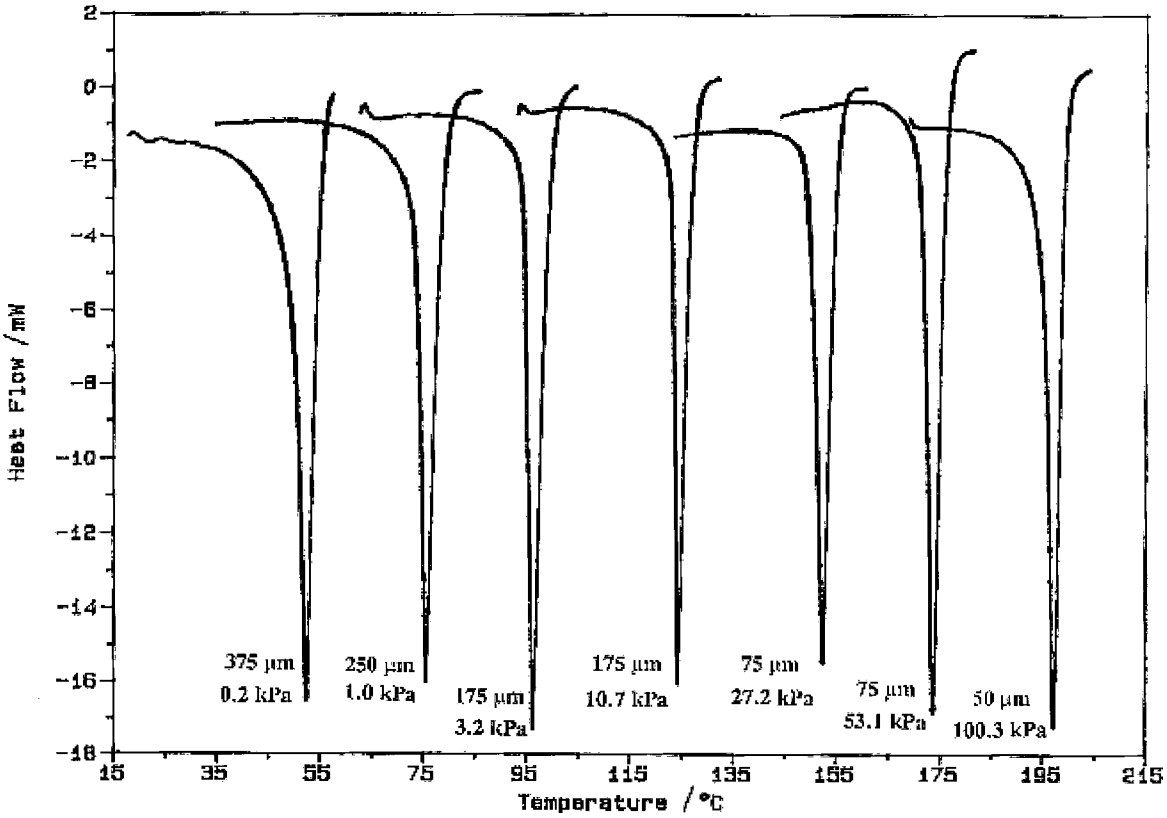

Fig. 5. Improved DSC boiling endotherms for DIMP with larger pinholes at pressures between 0.2 and 100.3 kPa.

the vaporization/vapor removal processes. However, this is clearly not the case as pressure is reduced. For boiling point measurements at low pressures, these processes occur with significantly fewer molecules. The observed peak broadening (deviation from a vertical leading edge) suggests that vapor molecules are not leaving the container as rapidly as they are being generated. It is postulated that this is due to the pinhole being too small. With fewer molecules present, the probability of any vapor molecule finding the pinhole to escape is reduced. This gives rise to self-pressurization inside the container and elevates the boiling temperature. Increasing the size of the pinhole restores the balance between the competing vaporization/vapor removal processes which yields a sharp boiling endotherm.

This low pressure behavior is consistent with practices for Knudsen effusion measurements. As pressures are lowered, the orifice of Knudsen effusion vessels is increased to maintain an appropriate relationship to the mean free path length of vapor molecules under study [11]. Knudsen vapor pressure measurements are carried out at much lower pressures and are subject to many constraints including elimination of molecular collisions as the material moves through the orifice. Obviously, the DSC measurements do not meet these criteria, but the results do suggest that the low pressure measurements may be approaching a regime where effusion rather than diffusion is the controlling mechanism. If this is the case, use of larger pinholes at low pressures appears appropriate.

If the key to retention of peak sharpness is balancing the vaporization/vapor escape processes, then use of a larger pinhole may only be one means of extending the pressure range of ASTM E 1782. The larger pinhole appears to allow more vapor molecules to escape at low pressures thereby preventing container pressurization and peak broadening. An alternative

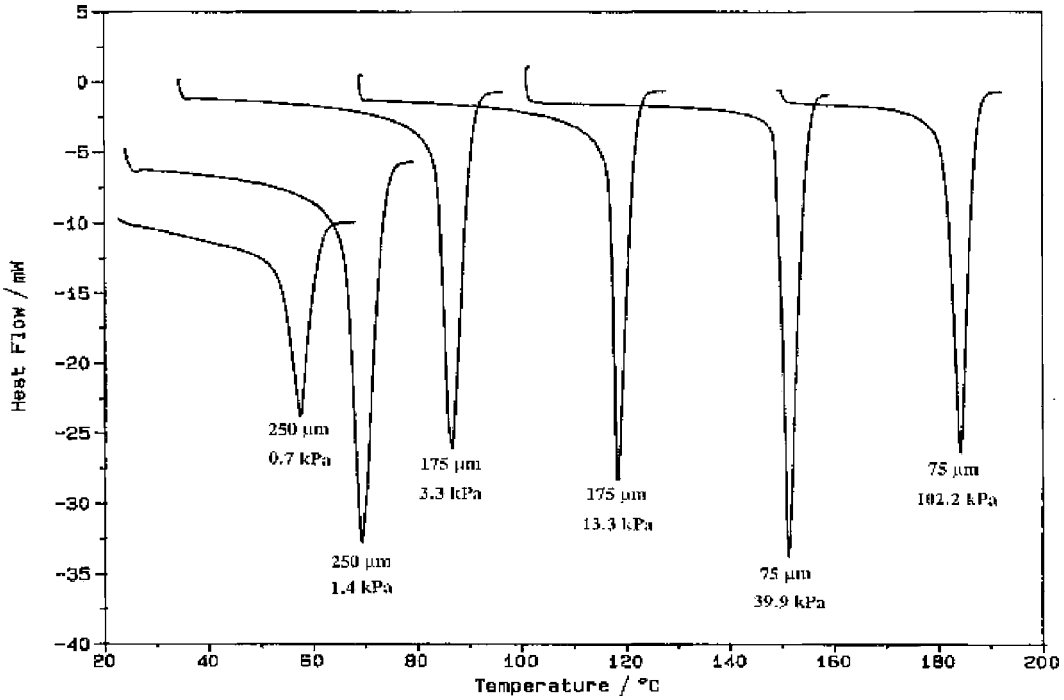

Fig. 6. Improved DSC boiling endotherms for DMMP with larger pinholes at pressures between 0.7 and 102.2 kPa.

Table 1
Effect of pinhole diameter on peak shape and onset temperature

Pressure (kPa)	Pinhole (mm)	Slope (mW/°C)	Onset temperature (°C)
Water[a]			
6.7	50	−1.1	39.1
6.7	75	−3.4	38.2
6.7	75	−6.5	38.8
6.7	175	−24.1	38.9
6.7	250	−23.4	39.0
6.7	375	−28.9	39.2
DMMP			
0.9	75	−0.3	63.5
0.9	175	−3.6	59.2
0.9	250	−5.0	59.2
0.8	75	−0.4	56.7
0.8	175	−3.5	57.0
0.8	250	−5.5	57.0
0.7	25	−0.0	79.7
0.7	75	−0.1	58.3
0.7	75	−0.3	56.3
0.7	175	−3.2	54.1
0.7	250	−2.9	53.2
0.7	375	−4.8	54.7

[a] Literature value: 38.2 °C at 6.7 kPa.

for balancing these processes may be use of a slower heating rate to slow vaporization. If this rate could be balanced with the escape of molecules through the recommended pinholes, peak shape should improve. This is an area for further study.

Finally, these results indicate that the use of a narrow range of pinhole lids limits the pressure range over which reliable vapor pressure data can be generated by DSC. It appears that using a combination of different size pinhole lids (increasing size as pressure is reduced) may maximize the measurable range for application of ASTM E 1782. By employing pinholes larger than those currently recommended by ASTM E 1782 at the lowest pressures, the peaks remained sharp throughout and the peak onset temperature continued to decrease with decreasing pressure in a regular fashion. These successful results support extension of the recommended pressure range and increase of the recommended pinhole size in ASTM E 1782. The results also suggest that peak slope may be used as a criterion from which one can determine at what pressure it will be necessary to change pinhole size for a given material.

4. Conclusions

Three liquids including water, diisopropyl methyl phosphonate, and dimethyl methyl phosphonate were studied at pressures near or below the 5 kPa lower limit recommended by ASTM E 1782–96, Standard Test Method for Determining Vapor Pressure by Thermal Analysis. Use of pinholes larger than the recommended limit of 125 μm significantly reduced peak broadening and improved the temperature accuracy of transitions. This need to increase the pinhole size at progressively lower pressures parallels practices in Knudsen effusion measurements and suggests the controlling mechanism of the pinhole changes from that of diffusion to that of effusion. Self-pressurization of the specimen container has been offered to explain the observed peak broadening and reduced transition temperature sensitivity to pressure reductions when ASTM recommended pinholes are utilized at pressures below the 5 kPa method lower limit. Extension of the useful pressure range recommended in ASTM E 1782 for DSC may be possible with use of multiple size pinholes applicable at different pressure intervals.

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