



Designation: E1782 – 22

Standard Test Method for Determining Vapor Pressure by Thermal Analysis¹

This standard is issued under the fixed designation E1782; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a procedure for the determination of the vapor pressure of pure liquids or melts from boiling point measurements made using differential thermal analysis (DTA) or differential scanning calorimetry (DSC) instrumentation operated at different applied pressures.

1.2 This test method can be used for the temperature range 273 K to 773 K (0 °C to 500 °C) and for pressures between 0.2 kPa to 2 MPa. These ranges may differ depending upon the instrumentation used and the thermal stability of materials tested. Because a range of applied pressures is required by this test method, the analyst is best served by use of instrumentation referred to as high pressure differential thermal instrumentation (HPDSC or HPDTA).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. (See also [IEEE/ASTM SI 10](#).)

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- [E473 Terminology Relating to Thermal Analysis and Rheology](#)
- [E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)
- [E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers](#)
- [E1142 Terminology Relating to Thermophysical Properties](#)
- [E2071 Practice for Calculating Heat of Vaporization or Sublimation from Vapor Pressure Data](#)
- [E3142 Test Method for Thermal Lag of Thermal Analysis Apparatus](#)
- [IEEE/ASTM SI 10 Standard for Use of the International System of Units \(SI\) The Modern Metric System](#)

3. Terminology

3.1 *Definitions:*

3.1.1 The following terms are applicable to this test method and can be found in either Terminology [E473](#) or Terminology [E1142](#): *boiling pressure, boiling temperature, differential scanning calorimetry (DSC), differential thermal analysis (DTA), vapor pressure, vaporization point, vaporization temperature.*

3.2 *Symbols:*

3.2.1 *A, B, C*—Antoine vapor pressure equation (**1**)³ constants (log₁₀, kPa, K):

$$\text{Antoine vapor pressure equation: } \text{Log}_{10} P = A - B/(T + C)$$

where:

P = vapor pressure, kPa,
T = temperature, K, and
A, B, and C = constants.

4. Summary of Test Method

4.1 In thermal analysis, a physical property of a material is measured either as a function of time at a specified constant temperature, or more frequently, as a function of temperature under conditions of a fixed rate of temperature change. The measured property is the dependent variable and the measured temperature is the independent variable. A specimen in an appropriate container is heated at a constant rate within a DTA or DSC instrument operated under an applied constant vacuum/

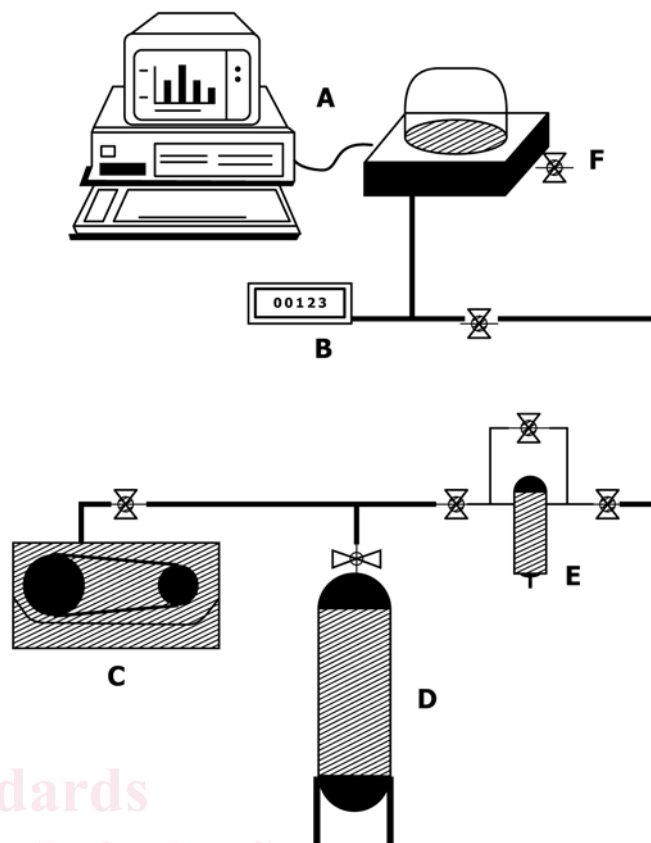
³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

pressure between 0.2 kPa and 2 MPa until a boiling endotherm is recorded. Boiling is observed at the temperature where the specimen partial pressure equals the pressure applied to the test chamber. The pressure is recorded during observation of the boiling endotherm and the boiling temperature is recorded as the extrapolated onset temperature. This measurement is repeated using new specimens for each of five or more different pressures covering the pressure range of interest. The pressure-temperature data are fitted as $\text{Log}_{10} P$ and $1/T$ (K^{-1}) to the Antoine vapor pressure equation (see Fig. 1). Vapor pressure values required for specific reports are then computed from the derived equation.

4.2 The capability of the assembled system after calibration shall be periodically checked by using this test method on high purity water as a reference substance and comparing the derived vapor pressure data with the NBS/NRC steam tables attached as Appendix X1. For pressures below 5 kPa, operation of the assembled system may be checked using 1-octanol (2).

5. Significance and Use

5.1 Vapor pressure is a fundamental thermophysical property of a liquid. Vapor pressure data are useful in process design and control, in establishing environmental regulations for safe handling and transport, for estimation of volatile organic content (VOC), and in deriving hazard assessments.



NOTE 1—“A,” DSC/DTA instrument; “B,” pressure transducer; “C,” pressure/vacuum source; “D,” pressure stabilizer; “E,” pressure regulator; and “F,” relief valve.

FIG. 2 Schematic of Apparatus

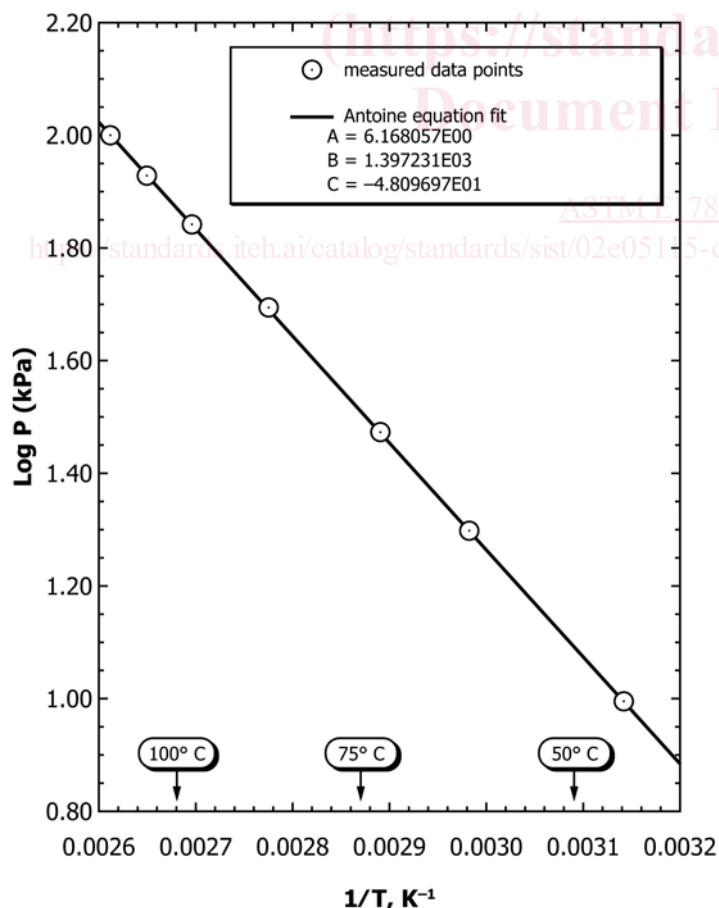


FIG. 1 Vapor Pressure Curve with Experimental Data and Antoine Equation Fit

Vapor pressure and boiling temperature data are required for Safety Data Sheets (SDS). The enthalpy of vaporization may also be estimated from the slope of the vapor pressure curve (see Practice E2071).

6. Interferences

6.1 This test method involves the continuous monitoring of the specimen temperature within the test chamber's enclosed environment of a flowing, static, or self-generated gaseous atmosphere (or vacuum) during execution of the stipulated procedure. In DSC and DTA apparatus, the temperature sensor utilized to measure the specimen temperature is not in direct contact with the specimen but is in fixed close thermal contact assumed to be representative of the specimen, such that the measured temperature is that of the temperature sensor itself and the actual specimen temperature will lag behind this measured temperature during heating or cooling. The magnitude of this temperature offset depends upon a number of systematic and random factors including but not limited to type and size of sensor, rate of temperature change, size and thermal conductance of the specimen, specimen container, and temperature sensor, and the interfacial contact resistances between the temperature sensor and the specimen container and between the specimen and the specimen container during the measurement. To obtain the correct specimen temperature, the DSC or DTA apparatus must be temperature calibrated at

equivalent experimental conditions so that the recorded temperature correctly indicates the specimen temperature.

6.2 Temperature sensors are subject to degraded performance with age and exposure to the DSC or DTA test chamber atmosphere. It is therefore imperative that the apparatus is temperature calibrated regularly.

6.3 This test method is limited to materials that exhibit a single sharp boiling endotherm under the conditions outlined in this test method.

6.4 Oxidation, pyrolysis, or polymerization of condensed organic materials retained at temperatures above their ambient boiling point may be encountered at elevated pressures. This is observed as an exotherm or a significantly broadened endotherm, or both, and shall not be considered a valid pressure-temperature datum point. Use of an inert gas for elevated pressures or for back-filling after evacuation of the sample chamber is recommended to minimize the risk of oxidation.

6.5 Partial blockage of the pinhole in the DSC container can occasionally be encountered. This may be observed as noise spikes on the boiling endotherm and shall not be considered a valid pressure-temperature datum point

7. Apparatus

7.1 *Differential Scanning Calorimeter (DSC) or Differential Thermal Analyzer (DTA)*—Multiple generations of differential scanning calorimeters and differential thermal analyzers from numerous commercial suppliers, as well as in-house custom apparatus, utilizing a variety of temperature and heat flow sensors in various configurations may be available to the user. While all such apparatus capabilities may not be equivalent, for purposes of this test method, any DSC or DTA instrumentation that meets the following criteria should be able to generate acceptable results.

7.1.1 The essential equipment required to provide the minimum instrument capability of this test method includes (see Fig. 2):

7.1.1.1 *DSC/DTA Test Chamber*, composed of a furnace(s) to provide uniform controlled heating of a specimen and reference at a constant rate within the 273 K to 773 K temperature range of this test method; a temperature sensor to provide an indication of the specimen/furnace temperature to ± 0.01 K; a differential sensor to detect a difference (temperature or heat flow) between the specimen and reference equivalent to 5 mW; and a means of sustaining an inert gas or vacuum test chamber environment at pressures above and below ambient.

7.1.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits to ± 1 K at a rate of temperature change of 5 K/min constant within ± 1 %.

7.1.1.3 *Recording Device*, to provide a means of acquiring, storing and displaying measured or calculated signals or both. The minimum output signals are heat flow, temperature and time.

7.1.2 *Pressure/Vacuum System*, consisting of:

7.1.2.1 *A pressure vessel*, or similar means of sealing the test chamber at any applied absolute pressure within the 0.2 kPa to 2 MPa range of this test method.

7.1.2.2 *Source of Pressurized Gas*, or vacuum capable of sustaining a regulated inert gas pressure to the test chamber of between 0.2 kPa and 2 MPa.

7.1.2.3 *Pressure Transducer(s)*, to measure the pressure in the test chamber to within 1 % including any temperature dependence of the transducer(s) over the range of 0.2 kPa to 2 MPa.

NOTE 1—Distance (or dead volume) between the pressure transducer and the specimen in the test chamber should be minimized to ensure accurate recording of the pressure at the time of boiling.

7.1.2.4 *Pressure Regulator*, or similar device to adjust the applied pressure in the test chamber to ± 2 % of the desired value.

7.1.2.5 *Ballast*, or similar means to maintain the applied pressure in the test chamber constant to ± 1 %.

7.1.2.6 *Valves*, to control delivery of the inert gas/vacuum to the test chamber or to isolate components of the pressure/vacuum system, or both. Valves shall be rated in excess of the 2 MPa upper pressure limit of this test method.

7.1.3 *Containers*, (pans, capillary tubes, etc.) that are inert to the specimen and reference materials and which are of suitable structural shape and integrity to contain the specimen and reference in accordance with the following specific requirements:

7.1.3.1 It is imperative that the containers used in this test method are capable of retaining the specimen in a manner that minimizes specimen loss through vaporization prior to boiling and that promotes the development of vapor-liquid equilibrium at boiling. When both conditions are met a sharp endotherm with minimal baseline curvature at the onset will be observed.

NOTE 2—Studies by ASTM task group E37.01.05 and others (3-5) have determined glass cylindrical containers of 2 mm to 4 mm inside diameter by 25 mm long are suitable for thermocouple inserted style DTA instruments; and a hermetic sealable pan (approximately 40 μ L vol) with a single pinhole in the center of the lid is suitable for DSC instruments with nominal heating rates of 5 K/min. Use of a progression of pinhole sizes ranging from approximately 50 μ m to 350 μ m is recommended in order to retain boiling endotherm sharpness over the full pressure range of this method. Typically, the sharpest boiling endotherm for a sample will be produced at atmospheric pressure with a small (50 μ m to 75 μ m) pinhole. As pressure is reduced, increasingly larger pinholes should be used to minimize endotherm broadening. Use of large pinholes (350 μ m) at pressures as low as 0.2 kPa has been shown to produce boiling endotherms of comparable sharpness to atmospheric pressure endotherms. Use of heating rates other than 5 K/min are not recommended for this test method. Higher rates may result in some self-pressurization of the specimen and lesser rates will extend measurement times and will tend to promote preboiling vaporization.

7.2 Auxiliary equipment considered useful in conducting this test method include:

7.2.1 A coolant system that can be coupled directly with the controller to the furnace to hasten its recovery from elevated temperatures or to sustain a subambient temperature to within ± 1 K of a lower limit temperature.

7.2.2 A balance to weigh specimens or specimen containers, or both, to ± 0.1 mg.

7.2.3 A syringe or micropipet to deliver liquid specimens of 1 μL to 5 $\mu\text{L} \pm 10\%$.

7.2.4 Pressure relief valve to prevent accidental overpressurization in the pressure system. A rating of 10 % in excess of the upper use pressure is suggested provided it does not exceed the maximum working pressure rating of any individual component in the system.

8. Precautions

8.1 Safety Precautions:

8.1.1 Pressures in addition to ambient are employed in this test method. Ensure that the pressure/vacuum system is certified for operation at the extremes of pressure encountered with this test method. Incorporation of a pressure relief device is recommended.

8.1.2 Adequate provisions shall be available for retention and disposal of any spilled mercury if mercury-containing pressure devices are employed.

9. Sampling

9.1 Typical specimen sizes used for individual pressure measurements are 1 mg to 5 mg of solid or 1 μL to 5 μL of liquid. Similar size specimens should be used for each individual measurement of a given sample.

9.2 Samples are assumed to be tested as received. Report any special sampling or pretreatment used with this test method.

10. Calibration

10.1 Prior to installation, the temperature sensors used in DSC or DTA apparatus are calibrated under isothermal conditions where static equilibrium is achieved. Thermal analysis apparatus temperature calibration is performed under assumed linear rates of temperature change where dynamic equilibrium is obtained between the test specimen and the temperature sensor. Such temperature calibration compensates for the temperature offset between the specimen temperature and that of the temperature sensor arising from their lack of direct intimate contact. With temperature calibration in dynamic equilibrium, it is essential that as many variables as practical are fixed and repeatable, duplicating the conditions for subsequent analysis studies. Perform calibration according to Test Method E967, using the environment, heating rate, and specimen containers intended for this test method. Accomplish temperature calibration at ambient pressure with a calibrant(s) that represents the temperature range to be used for subsequent testing.

NOTE 3—The effect of pressure on the melting temperature of pure materials used to calibrate the temperature axis has been shown to be $<0.01\text{ K}$ at the maximum pressure of this method (6). The effects of vacuum on the heat transfer characteristics and subsequent thermal lag of various differential thermal instruments (DSC and DTA) have not been established. From general experiences these effects should not alter the temperature axis calibration by more than 1 K at the minimum pressure of this test method.

10.2 The temperature offset between the specimen and the temperature sensor changes linearly with rate of temperature change for rates employed in this test method. The slope of this

relationship is the thermal lag and its determination permits temperature calibration determined at one rate of temperature change to be adjusted to that of another rate of temperature change. Using the same calibrant material, purge gas and flow rate as that used to calibrate the temperature axis of the instrument, repeat for two additional rates of temperature change following the procedure given in Test Method E3142 to determine the thermal offset.

10.3 Regular calibration of the temperature axis and determination of the thermal lag is necessary for making good temperature based measurements using DSC or DTA. The interval between calibrations is dependent upon a variety of factors. Follow the instrument manufacturer's guidelines. For testing requiring parameters outside those routinely used for calibration and thermal lag determination or if an apparent change in the equipment is noted, it is necessary to temperature calibrate the apparatus. Use the same variables during calibration that will be used for the subsequent testing.

10.4 Calibrate the pressure transducer according to the recommendations of the manufacturer or similar appropriate procedure.

11. Procedure

11.1 Place the specimen and inert reference in suitable containers (see 7.1.3) into the test chamber.

NOTE 4—If hermetic sealable DSC pans with pinholed lids are used, make sure there is no sample material on the outer surfaces of the container and that a good hermetic seal is accomplished. Either will result in preboiling vaporization that at least partially negates the function of the pinhole. Be certain, also, that the pinhole is free of dirt or debris.

NOTE 5—For DSC vacuum operation, use of a thin layer of conductive paste between the pan and the furnace is recommended to retain sensitivity and resolution.

11.2 Seal the test chamber and apply the desired pressure.

NOTE 6—It is recommended to flush residual oxygen from the test chamber by either purging for several minutes with inert gas or by evacuation and back-filling with inert gas.

11.3 Allow the pressure to stabilize and equilibrate the test chamber at a start temperature which shall be at least 30 K below the expected boiling temperature to ensure stable temperature control and baseline.

11.4 Heat the specimen and reference at a constant rate of 5 K/min, recording the DSC/DTA curve until the vaporization is complete.

11.5 Record the absolute pressure in the test chamber at the time the boiling endotherm is observed.

NOTE 7—Most pressure gauges report pressure relative to ambient pressure. In such cases, the measured pressure shall be added to or subtracted from atmospheric pressure measured by a barometer to obtain absolute pressure.

11.6 Restore the test chamber to ambient conditions upon completion of the heating curve.

11.7 Repeat 11.1 – 11.6 with a new specimen at each of four or more additional pressures throughout the pressure range capability of the equipment.

NOTE 8—A minimum of five measurements at different pressures are

required for this test method. Additional measurements should improve the fit of the Antoine vapor pressure equation and reduce the uncertainty of the Antoine constants used to calculate the vapor pressure curve.

12. Calculation

12.1 Determine and tabulate each boiling temperature (as T_o or T_e in Fig. 3) along with its corresponding observed pressure, P .

NOTE 9—Traditionally, the extrapolated onset temperature (T_o) of an endotherm recorded by DSC is used as the transition temperature; the peak maximum temperature (T_e) is used for thermocouple inserted DTA configurations. The convention employed during temperature calibration shall be used for these calculations.

12.2 If necessary, correct the observed pressures and temperatures by the amount determined from the calibrations. Plot the logarithms of pressure ($\log_{10}P$) versus the reciprocal of the absolute temperature ($1/T, K^{-1}$). Examine this plot for any abrupt deviation from linearity as evidence of instability.

NOTE 10—Deviations from linearity (curvature) due to expected decreases in enthalpy of vaporization with temperature (Antoine equation “ C ” constant negative) should not be confused with the abrupt deviation due to decomposition or polymerization. Curvature of normal data is barely perceptible.

12.3 Calculate the Antoine vapor pressure equation constants: A , B , and C retaining all available decimals using a nonlinear least-squares regression program to fit the Antoine equation, $\text{Log}_{10} P = A - B/(T + C)$ to the corrected pressure-temperature data points. Data for which any of the fitted Antoine equation constants fall outside of ranges given in Note 11 shall be rejected.

NOTE 11—This test method uses the SI units of Kelvin for temperature instead of the traditional use of Celsius. The only effect of this change is to make the “ C ” constant of the Antoine equation a negative value. Antoine equation constants (for \log_{10} , kPa, and K units) typically fall in these ranges:⁴ A , 4.9 to 7.8; B , 750 to 3000; and C , -235 to -3. If a nonlinear least-squares regression program is not available, a multilinear least-squares regression program may be used for Antoine equation fitting

⁴ These ranges were determined by examination of Antoine equation literature and databanks, for example, see Refs (1) and (7).

by making these variable transformations:⁵ $a = A$; $b = A * C - B$; and $c = -C$. The fitting equation, now linear in the parameters, is:

$$t * \log_{10} P = a * t + b + c * \log_{10} P$$

12.4 Using the Antoine equation with constants determined in 12.3, compute a table of pressure-temperature data pairs encompassing the range of conditions tested including the boiling point temperatures for pressures of 1000 kPa, 101.32 kPa (760 torr), and 10 kPa and the vapor pressure at 293.15 K (20.00 °C).

13. Report

13.1 Report the following information:

13.1.1 Sample identity, purity (if known or determined, as well as how it was determined), and source;

13.1.2 A table of the corrected pressure-temperature data points;

13.1.3 The Antoine vapor pressure equation constants A , B , and C rounded to the nearest 0.000001;

13.1.4 A table of the computed pressure-temperature data including the boiling point temperatures at 1000 kPa, 101.32 kPa (760 torr), and 10 kPa rounded to the nearest 0.1 K, and the vapor pressure at 293.15 K (20.00 °C) rounded to the nearest 0.1 kPa;

13.1.5 A graphic presentation of the vapor pressure curve including the regression fit to the Antoine vapor pressure equation;

13.1.6 Any abrupt deviation from linearity in the vapor pressure curve and the temperature of its occurrence; and

13.1.7 The specific dated version of this test method used.

14. Precision and Bias

14.1 *Interlaboratory Study (ILS)*—An interlaboratory study for measurement of vapor pressure by this test method was conducted in 1995. Two materials were studied: *n*-heptane and distilled water. Each of six laboratories measured vapor pressure data for *n*-heptane; each of six laboratories measured vapor pressure data for distilled water. Practice E691 was followed for the ILS design and for the analysis of the data.

14.2 *Test Results*—The precision information given below is for duplicate determinations of vapor pressure data calculated from the derived Antoine equations as described in 12.3.

14.3 *Precision*—The terms repeatability and reproducibility given below are used as specified in Practice E177. Standard deviations among study results may be calculated by dividing the third and fourth table columns by 2.8.

14.3.1 *Precision for n-Heptane:*

	ILS Average	Repeatability	Reproducibility	NIST Data
Boiling point (K) at 1000 kPa	467.7	11.3	19.1	474.3
Normal Boiling point (K) at 101.325 kPa	371.2	2.0	3.5	371.6
Boiling point (K) at 10.0 kPa	308.3	3.2	3.6	308.5
Vapor pressure (kPa) at 293.15 K	4.9	0.9	1.0	4.7

⁵ This procedure was described in Ref (8).

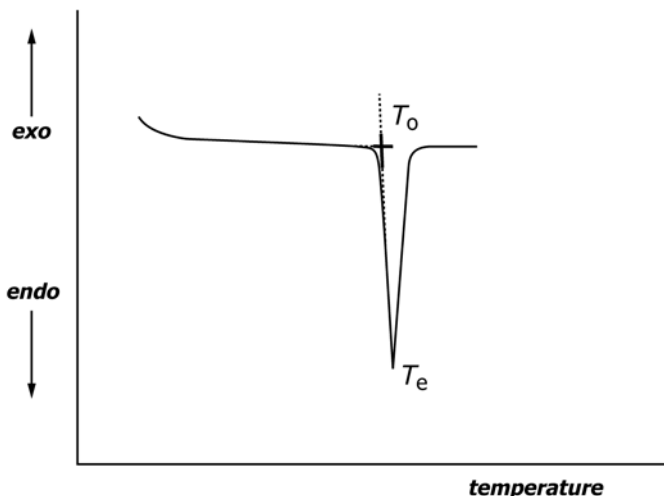


FIG. 3 Boiling Endotherm from DSC/DTA Instrumentation with: extrapolated Onset, T_o and Peak Maximum, T_e