



Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope¹

This standard is issued under the fixed designation D 2879; 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 covers the determination of the vapor pressure of pure liquids, the vapor pressure exerted by mixtures in a closed vessel at $40 \pm 5\%$ ullage, and the initial thermal decomposition temperature of pure and mixed liquids. It is applicable to liquids that are compatible with borosilicate glass and that have a vapor pressure between 133 Pa (1.0 torr) and 101.3 kPa (760 torr) at the selected test temperatures. The test method is suitable for use over the range from ambient to 748 K. The temperature range may be extended to include temperatures below ambient provided a suitable constant-temperature bath for such temperatures is used.

NOTE 1—The isoteniscope is a constant-volume apparatus and results obtained with it on other than pure liquids differ from those obtained in a constant-pressure distillation.

1.2 Most petroleum products boil over a fairly wide temperature range, and this fact shall be recognized in discussion of their vapor pressures. Even an ideal mixture following Raoult's law will show a progressive decrease in vapor pressure as the lighter component is removed, and this is vastly accentuated in complex mixtures such as lubricating oils containing traces of dewaxing solvents, etc. Such a mixture may well exert a pressure in a closed vessel of as much as 100 times that calculated from its average composition, and it is the closed vessel which is simulated by the isoteniscope. For measurement of the apparent vapor pressure in open systems, Test Method D 2878^{D 2878}, is recommended.

1.3 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 3, Note 4, and Note 5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2878 Test Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils²

E 230 Temperature Electromotive Force (EMF) Tables for Standardized Thermocouples³

3. Terminology

3.1 *Definition of Term Specific to This Standard*

3.2 *ullage*—that percentage of a closed system which is filled with vapor.

3.2.1 *Discussion*—Specifically, on Fig. 1, that portion of the volume of the isoteniscope to the right of point A which is filled with vapor.

3.3 *Symbols:*

C = temperature, °C,

K = temperature, K,

p = pressure, Pa or torr,

t = time, s,

P_c = experimentally measured total system pressure,

P_a = partial pressure due to fixed gases dissolved in sample,

P_c = corrected vapor pressure, Pa or torr.

$$K = C + 273.15 \quad (1)$$

4. Summary of Test Method

4.1 Dissolved and entrained fixed gases are removed from the sample in the isoteniscope by heating a thin layer of a sample at reduced pressure, removing in this process the minimum amount of volatile constituents from the sample.

4.2 The vapor pressure of the sample at selected temperatures is determined by balancing the pressure due to the vapor of the sample against a known pressure of an inert gas. The manometer section of the isoteniscope is used to determine pressure equality.

4.3 The initial decomposition temperature is determined from a plot of the logarithm of the vapor pressure versus the reciprocal of absolute temperature. The initial decomposition

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 14.03.

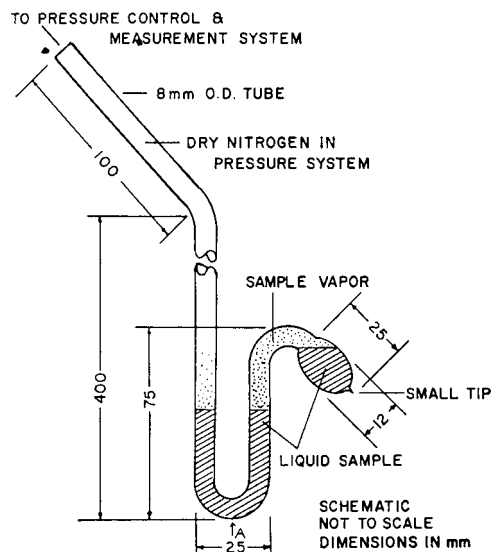


FIG. 1 Isoteniscope

temperature is taken as that temperature at which the plot first departs from linearity as a result of the decomposition of the sample. An optional method provides for the use of isothermal rates of pressure rise for this purpose (see Annex A1). These are measured at several temperatures and the logarithm of the rate of pressure rise is plotted versus the reciprocal of absolute temperature. The decomposition temperature of the sample is taken to be that temperature at which the rate of increase of pressure is sufficient to produce a rise of 185 Pa (0.0139 torr/s).

NOTE 2—Vapor pressures less than 133 Pa (1.0 torr), but greater than 13.3 Pa (0.1 torr) at a selected test temperature can be determined directly with reduced accuracy. In some cases the tendency of the sample to retain dissolved or occluded air may prevent direct determinations of vapor pressure in this range. In such cases, data points obtained at higher pressures can be extrapolated to yield approximate vapor pressures in this range.

5. Significance and Use

5.1 The vapor pressure of a substance as determined by isoteniscope reflects a property of the sample as received including most volatile components, but excluding dissolved fixed gases such as air. Vapor pressure, *per se*, is a thermodynamic property which is dependent only upon composition and temperature for stable systems. The isoteniscope method is designed to minimize composition changes which may occur during the course of measurement.

6. Apparatus

6.1 *Isoteniscope* (Fig. 1).

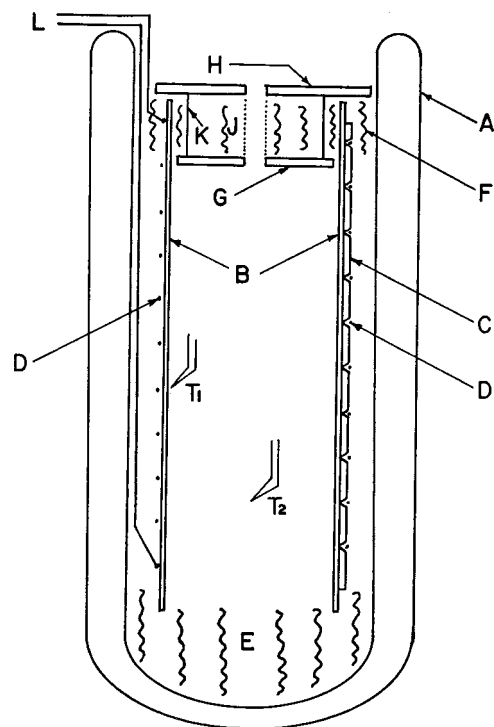
6.2 *Constant-Temperature Air Bath* (Fig. 2) for use over the temperature range from ambient to 748 K, controlled to ± 2 K in the zone occupied by the isoteniscope beyond point "A" (Fig. 1).

6.3 *Temperature Controller*.

6.4 *Vacuum and Gas Handling System* (Fig. 3).

6.5 *Mercury Manometer*, closed end, 0 to 101.3 kPa (0 to 760 torr) range.

NOTE 3—**Warning:** Poison. May be harmful or fatal if inhaled or



- A Dewar, strip silvered, 110 mm ID by 400 mm deep.
- B Borosilicate glass tube, 90 mm OD by 320 mm long.
- C Glass rod, 1/8-in. in diameter by 310 mm long. Three of these heater element holders are fused along their entire length to the outer surface of Tube B at 120-deg intervals. Slots cut into the fused glass rods on 3/8-in. centers serve as guides for the heating wire D.
- D Resistance wire, B. and S. No. 21 gage, spirally wrapped around Tube B and its attached guides.
- E Glass wool pad.
- F Glass wool pad for centering Tube B and sealing annular opening.
- G Lower plate of insulated isoteniscope holder. Transite disk 1/8 in. thick, loose fit in Tube B. With hole for isoteniscope.
- H Upper plate of insulated isoteniscope holder. Transite disk 1/8 in. thick, loose fit in Dewar A. With hole for isoteniscope.
- J Glass wool insulation between plates G and H.
- K Plate spacer rods.
- Heater leads connected to power output of temperature controller.
- L
- T₁ Temperature-control thermocouple affixed to inside wall of Tube B.
- T₂ Temperature-indicating thermocouple affixed to isoteniscope.

FIG. 2 Constant-Temperature Air Bath

swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A2.1.

6.6 *McLeod Vacuum Gage*, 0 to 2.00 kPa (0 to 15 torr), vertical primary standard type.

6.7 *Mechanical Two-Stage Vacuum Pump*.

6.8 *Direct Temperature Readout*, either potentiometric or electronic.

6.9 *Thermocouple*, in accordance with American National Standard for Temperature Measurement Thermocouples (ANSI C96.1) from Tables E 230.

6.10 *Nitrogen*, pre-purified grade.

NOTE 4—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A2.2.

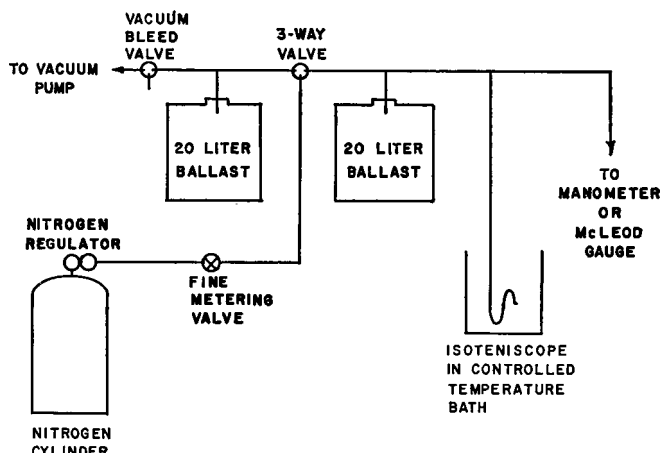


FIG. 3 Vacuum and Gas Handling System

6.11 Nitrogen Pressure Regulator, single-stage, 0 to 345 kPa gage (0 to 50 psig).

6.12 Alcohol Lamp.

NOTE 5—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

7. Hazards

7.1 The procedure requires measuring pressures with devices containing mercury (**Warning**—See Note 3). Spillage of this material creates a safety hazard in the form of toxic vapor in the room. This can be prevented by use of catchment vessels under the devices. If these fail, and the ventilation of the room during occupancy is below $0.01 \text{ m}^3 \text{ (s}\cdot\text{m}^2)$, $2 \text{ ft}^3\text{/min}\cdot\text{ft}^2$, thorough cleaning of the floor followed by inspection with a mercury vapor-detecting device is recommended. The following procedures for floor cleaning have been found effective:

7.1.1 A 5 % aqueous solution of sodium polysulfide penetrates well into porous surfaces, but should not be used on polished metal objects.

7.1.2 Sweeping with flowers of sulfur, or agricultural colloidal sulfur, is effective on nonporous floors.

7.1.3 Sweeping with granular zinc, about 20 mesh ($840 \mu\text{m}$) that has been rinsed in 3 % hydrochloric acid, is effective in catching macro-drops.

7.2 The apparatus includes a vacuum system and a Dewar flask (constant temperature air bath) that is subjected to elevated temperatures. Suitable means should be employed to protect the operator from implosion of these systems. These means include wrapping of vacuum vessels, use of safety shield in front of Dewar flask, and use of safety glasses by the operator.

8. Procedure

8.1 Add to the isoteniscope a quantity of sample sufficient to fill the sample bulb and the short leg of the manometer section (**Warning**—See Note 6) to point A of Fig. 1. Attach the isoteniscope to the vacuum system as shown in Fig. 3, and evacuate both the system and the filled isoteniscope to a pressure of 13.3 Pa (0.1 torr) as measured on the McLeod gage. Break the vacuum with nitrogen (**Warning**—See Note 7). Repeat the evacuation and purge of the system twice to remove residual oxygen.

NOTE 6—**Warning:** Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A1.1.

NOTE 7—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.

8.2 Place the filled isoteniscope in a horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section. Reduce the system pressure to 133 Pa (1 torr). Remove dissolved fixed gases by gently warming the sample with an alcohol (**Warning**—See Note 8) lamp until it just boils. Continue for 1 min.

NOTE 8—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

NOTE 9—During the initial evacuation of the system, it may be necessary to cool volatile samples to prevent boiling or loss of volatiles.

NOTE 10—If the sample is a pure compound, complete removal of fixed gases may readily be accomplished by vigorous boiling at 13.3 Pa (0.1 torr). For samples that consist of mixtures of substances differing in vapor pressure, this procedure is likely to produce an error due to the loss of volatile components. Gentle boiling is to be preferred in such cases. The rate of boiling during degassing may be controlled by varying both the pressure at which the procedure is carried out and the amount of heating. In most cases, satisfactory degassing can be obtained at 133 Pa (1 torr). However, extremely viscous materials may require degassing at lower pressures. Samples of high volatility may have to be degassed at higher pressures. In the event that the vapor pressure data indicate that the degassing procedure has not completely removed all dissolved gases, it may be necessary to apply a correction to the data or to disregard data points that are so affected (see 8.7). The degassing procedure does not prevent the loss of volatile sample components completely. However, the described procedure minimizes such losses, so that for most purposes the degassed sample can be considered to be representative of the original sample less the fixed gases that have been removed.

8.3 After the sample has been degassed, close the vacuum line valve and turn the isoteniscope to return the sample to the bulb and short leg of the manometer so that both are entirely filled with the liquid. Create a vapor-filled, nitrogen-free space between the bulb and the manometer in the following manner: maintain the pressure in the isoteniscope at the same pressure used for degassing; heat the drawn-out tip of the sample bulb with a small flame until sample vapor is released from the sample; continue to heat the tip until the vapor expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope.

8.4 Place the filled isoteniscope in a vertical position in the constant-temperature bath. As the isoteniscope approaches temperature equilibrium in the bath, add nitrogen to the gas-sampling system until its pressure equals that of the sample. Periodically adjust the pressure of the nitrogen in the gas-handling system to equal that of the sample. When the isoteniscope reaches temperature equilibrium, make a final adjustment of the nitrogen pressure to equal the vapor pressure of the sample. Pressure balance in the system is indicated by the manometer section of the isoteniscope. When the liquid levels in the manometer arms are equal in height, balance is indicated. Read and record the nitrogen pressure in the system at the balance point. Use the McLeod gage to measure pressures below 2.00 kPa (15 torr) and the mercury manometer for pressures from 2.00 kPa (15 torr) to 101 kPa (760 torr).