



## Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope<sup>1</sup>

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 ( $\epsilon$ ) 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 2878D 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.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.11 on Engineering Sciences of High Performance Fluids and Solids.

Current edition approved April 10, 1997. Published October 1997. Originally published as D 2879 – 70. Last previous edition D 2879 – 96.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 2878 Test Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils<sup>2</sup>

E 230 Temperature Electromotive Force (EMF) Tables for Standardized Thermocouples<sup>3</sup>

### 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,

$P_e$  = 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

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.03.

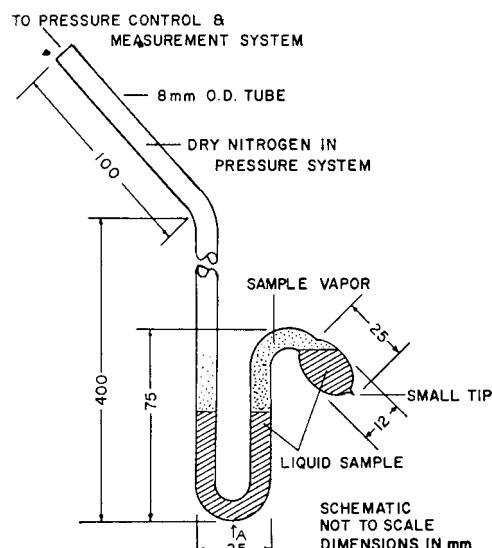


FIG. 1 Isoteniscope

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).

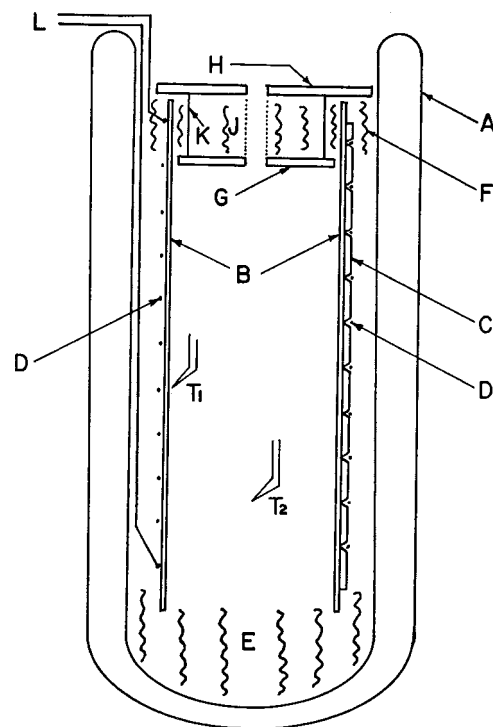
6.2 *Constant-Temperature Air Bath* (Fig. 2) for use over the temperature range from ambient to 748 K, controlled to  $\pm 2$  K in the zone occupied by the isoteniscope beyond point "A" (Fig. 1).

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
- T<sub>1</sub> Temperature-control thermocouple affixed to inside wall of Tube B.
- T<sub>2</sub> 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.