



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

This standard is issued under the fixed designation D2879; 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.

This standard has been approved for use by agencies of the Department of Defense.

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 D2878, 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 **WARNING**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Ma-

terial Safety Data Sheet (MSDS) for details and EPA's website—<http://www.epa.gov/mercury/faq.htm>—for additional information. Users should be aware that selling mercury or mercury containing products into your state or country may be prohibited by law.

1.5 *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 warning statements, see 6.10, 6.12, and Annex A2.

2. Referenced Documents

2.1 ASTM Standards:²

D2878 Test Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils

E230 Specification and Temperature-Electromotive Force (EMF) Tables for Standardized Thermocouples

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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

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

3.2 Symbols:

C = temperature, °C,

K = temperature, K,

p = pressure, Pa or torr,

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.

t = time, s,

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

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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.

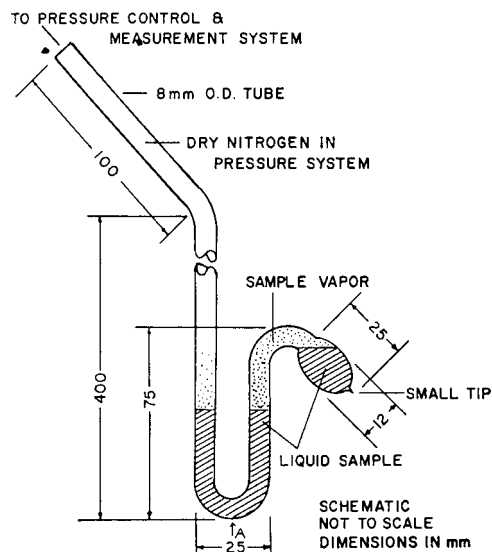


FIG. 1 Isoteniscope

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 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

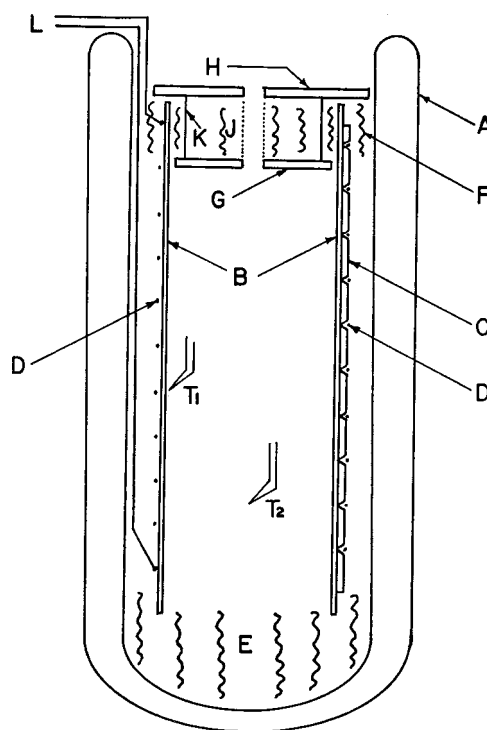
6.1 *Isoteniscope* (Fig. 1).

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 *Pressure Measurement Instrumentation*—Pressure transducers of suitable ranges are the preferred means for the measurement of pressure in the gas handling system. Alternatively bourdon-type vacuum gauges or liquid manometers may be used. Note that more than one gauge or transducer may be required for use over the range of 2.00 kPa (15 torr) to 101 kPa (760 torr) for pressures.



- 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 gauge, 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.
- L Heater leads connected to power output of temperature controller.
- T₁ Temperature-control thermocouple affixed to inside wall of Tube B.
- T₂ Temperature-indicating thermocouple affixed to isoteniscope.

FIG. 2 Constant-Temperature Air Bath

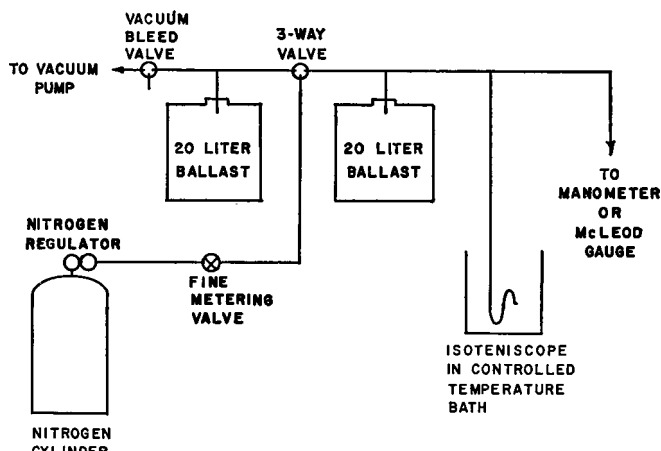


FIG. 3 Vacuum and Gas Handling System

6.6 *McLeod Vacuum Gauge*—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 Specification and Temperature Electromotive Force Tables E230.

6.10 *Nitrogen*—pre-purified grade. (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A2.1.)

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

6.12 *Alcohol Lamp*—(**Warning**—Flammable. Denatured alcohol cannot be made nontoxic. See A2.2.)

7. Hazards

7.1 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**—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.) 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 gauge. Break the vacuum with nitrogen (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.). Repeat the evacuation and purge of the system twice to remove residual oxygen.

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 lamp until it just boils (**Warning**—Flammable. Denatured alcohol cannot be made nontoxic. See A2.2.). Continue for 1 min.

NOTE 3—During the initial evacuation of the system, it may be necessary to cool volatile samples to prevent boiling or loss of volatiles.

NOTE 4—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 a transducer, gauge, or liquid manometer of appropriate range to measure the pressure in the gas handling system. Use the McLeod gauge 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).

8.4.1 It is extremely important that adjustments of the nitrogen pressure be made frequently and carefully. If the nitrogen pressure is momentarily too great, a bubble of nitrogen may pass through the manometer and mix with the sample vapor. If the nitrogen pressure is momentarily too low,

a bubble of sample vapor may escape. If either action occurs, the test is terminated immediately and restarted from 8.3.

NOTE 5—Because the densities of samples to be tested by this procedure are usually of the order of or less than 1 g/mL, small errors in the final adjustment of the liquid level in the manometer have a negligible effect on the measured values of vapor pressures above 133 Pa (1 torr = 1mmHg).

8.5 Increase the temperature of the constant-temperature bath 25 K. As the temperature rises, maintain pressure balance in the system in the manner described in 8.4. When temperature equilibrium is reached, make a final adjustment of pressure to establish balance. Read and record the system pressure. Repeat at intervals of 25 K until the system pressure exceeds 101 kPa (760 torr).

8.6 Plot the logarithm and the measured vapor pressure at each temperature versus the reciprocal of the absolute temperature, (K)⁻¹.

NOTE 6—Three or four-cycle semilog graph paper is useful for making this type of plot.

8.7 If the slope of the vapor pressure curve at its low-temperature end indicates that the sample contains fixed gases as a result of incomplete degassing, one of three procedures must be followed. (For examples, see Fig. 4 and Fig. 5.)

8.7.1 Repeat the determination of vapor pressure in the manner described in 8.1-8.7, but employ a more vigorous degassing procedure. This procedure is recommended for pure compounds and mixtures that do not have a vapor pressure greater than 133 Pa (1 torr) at 323 K.

NOTE 7—In general, vapor pressure determinations are made after both temperature equilibrium in the air bath and pressure equilibrium in the isoteniscope and measuring system are attained. However, when a sample begins to decompose, the observed vapor pressure of the sample usually increases even at constant temperature. In such cases, the measured pressure of the system is no longer a function only of the temperature and

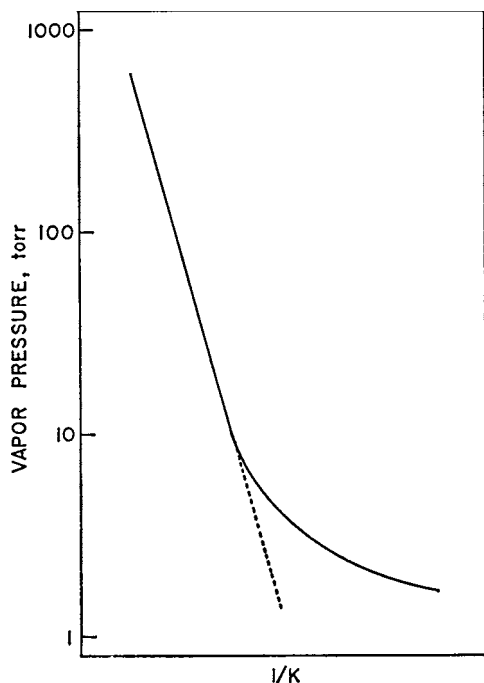


FIG. 4 Log P_e versus 1/K with Linear Region

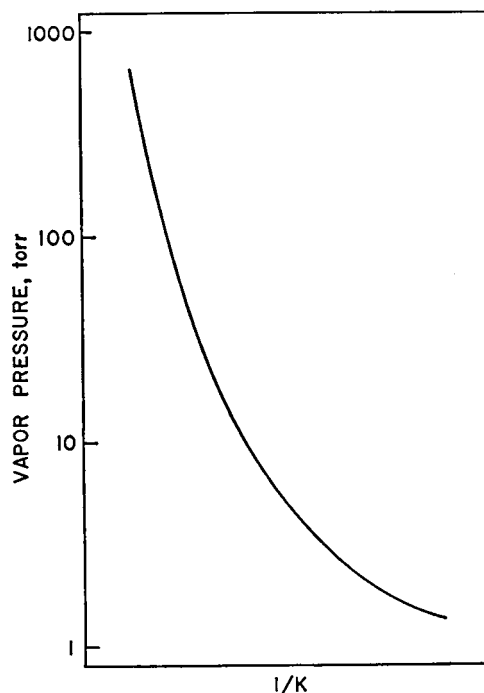


FIG. 5 Log P_e versus 1/K Without Linear Region

is not a vapor pressure in the usual sense of the term. It is sometimes useful to continue to take pressure readings even after a system has become unstable. In such cases, the pressure reading is taken after temperature equilibrium is reached in the air bath, regardless of whether a stable pressure balance can be maintained.

8.7.2 In many cases, despite the presence of fixed gases in the sample, the plot of the vapor pressure may be linear over a rather wide range of temperature (see Fig. 4). Extrapolate the linear section to lower temperatures to estimate the vapor pressure even though the presence of fixed gases prevents the direct determination. Extrapolation over more than one decade of pressure is not recommended.

8.7.3 If the lack of a suitable region of linearity prevents the use of the procedure described in 8.7.2 (see Fig. 5), the following arithmetic correction procedure is used: Assume that the pressure at the lowest temperature, K₁, at which measurements were made is predominantly due to fixed gases. Calculate the pressure that would be developed at constant volume if this volume of fixed gases were to be heated to the temperature, K₂, of the next data point.

$$P_{a2} = P_{a1} \times K_2/K_1 \quad (2)$$

Repeat this procedure for each data point. Calculate the corrected vapor pressure of the sample by subtracting each value of P_a from the corresponding P_e for each successive data point.

$$P_c = P_e - P_a \quad (3)$$

9. Calculation and Report

9.1 Plot the logarithms of the calculated values of the corrected vapor pressure versus the reciprocal of the absolute temperature in the manner described in 8.6.

9.2 From the plot of the logarithm of the corrected vapor pressure versus the reciprocal of the absolute temperature, read

the smoothed values of the vapor pressure at the desired temperature intervals. Report these values as the vapor pressure of the sample at the indicated temperatures.

9.3 Use the plot of the logarithm of the corrected vapor pressure versus the reciprocal of absolute temperature to determine the initial decomposition temperature of the sample. The initial decomposition temperature is that temperature at which the vapor pressure plot first deviates from linearity. Report this value as the initial decomposition temperature of the sample.

NOTE 8—The initial deviation from linearity is usually due to an increase in rate of pressure rise. A decrease in rate of pressure rise may be observed if the sample undergoes reactions such as polymerization. The vapor-pressure curve above the initial decomposition temperature is not necessarily linear or even approximately linear. Do not confuse nonlinearity due to the presence of fixed gases (see 9.3) with that caused by the

decomposition of the sample. Some samples do not decompose under the conditions of the test. In those instances the vapor-pressure curve is practically linear except for low-temperature deviations due to residual quantities of fixed gases.

10. Precision and Bias

10.1 Because of the complex nature of Test Method D2879 for vapor pressure-temperature relationship and because of the expensive equipment involved, there is not a sufficient number of volunteers to permit a comprehensive laboratory program for determining the precision and bias. If the necessary volunteers can be obtained, a program will be undertaken at a later date.

11. Keywords

11.1 decomposition temperature; initial decomposition temperature; isoteniscope; liquids; vapor pressure

ANNEXES

(Mandatory Information)

A1. ALTERNATIVE METHOD FOR DETERMINATION OF DECOMPOSITION TEMPERATURE

A1.1 Scope

A1.1.1 This annex describes a procedure for the determination of the decomposition temperature of liquids whose vapor pressure can be measured in the apparatus described in the standard method.

A1.2 Summary of Test Method

A1.2.1 Dissolved and entrained gases are removed from the sample in the same manner described in the standard method. The isothermal rate of pressure change with respect to time is measured for several temperatures above the expected decomposition temperature of the sample. The logarithms of the rates of pressure rise are plotted against the reciprocals of the absolute temperatures at which the rates were measured. The decomposition temperature is defined as the temperature at which the rate of pressure increase of the sample is equivalent to a rise of 67 kPa (500 torr) in 10 h (1.85 Pa/s).

A1.3 Procedure

A1.3.1 Determine the vapor pressure and initial decomposition temperature of the sample in accordance with the procedures described in Sections 8 and 9 of the standard method of test.

A1.3.2 If the sample is found to have an initial decomposition temperature that falls within the range of pressures and temperatures covered by the data in A1.3.1, fill an isoteniscope with a fresh quantity of sample and remove the dissolved fixed gas from it in accordance with the procedures described in 8.2. Prepare the isoteniscope for test as described in 8.3. Place the

filled isoteniscope in the constant-temperature bath maintained at a temperature at which a rate of pressure increase greater than 1.85 Pa/s (0.0139 torr/s) will be obtained. Maintain pressure balance in the system in the manner described in 8.4 until the isoteniscope and its contents reach temperature equilibrium. As soon as temperature equilibrium is attained, measure the system pressure at selected intervals of time until a constant rate is given by successive measurements.

A1.3.3 Repeat the determination of rate of pressure rise in accordance with A1.3.2 at temperature intervals of 10 to 15 K until a total of three or four determinations have been made.

A1.4 Calculation

A1.4.1 Plot the logarithm of the measured rates of pressure rise versus the reciprocal of the absolute temperature. Draw the best straight line through the data.

A1.4.2 Determine the temperature at which the rate of pressure rise is equal to 1.85 Pa/s (0.0139 torr/s). Report that temperature as the decomposition temperature of the sample.

A1.4.3 The interval between measurements is selected so that a minimum pressure change of approximately 2.66 kPa (20 torr) occurs during each interval.

A1.4.4 If the pressure in the sample chamber of the isoteniscope reaches 101 kPa (760 torr) as a result of the accumulation of decomposition products, the balancing gas pressure may be reduced slightly to allow some of these products to bubble through the manometer section of the isoteniscope. When the pressure has been reduced to a workable level, the system can be rebalanced and rate measurement resumed.

A2. WARNING STATEMENTS

A2.1 Nitrogen

Warning—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

Keep cylinder valve closed when not in use.

Use with adequate ventilation.

Do not enter storage areas unless adequately ventilated.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Never drop cylinder. Make sure cylinder is supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only. Do not use for inhalation purposes.

A2.2 Alcohol

Warning—Flammable. Denatured alcohol cannot be made nontoxic.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor or spray mist.

Avoid contact with eyes and skin.

Do not take internally.

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