Designation: D1016 – 05 (Reapproved 2015)

Standard Test Method for
Purity of Hydrocarbons from Freezing Points[1]

This standard is issued under the fixed designation D1016; 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 sampling and determination of purity of essentially pure compounds for which the freezing points for zero impurity and cryoscopic constants are given.[2] The compounds to which the test method is applicable are: (**Warning**—Extremely flammable liquids and liquefied gases.)

n-butane
isobutane
n-pentane
isopentane
n-hexane
n-heptane
n-octane
2,2,4-trimethylpentane
methylcyclohexane
isobutene
1,3-butadiene
isoprene(2-methyl-1,3-butadiene)
benzene
toluene (methylbenzene)
ethylbenzene
o-xylene (1,2-dimethylbenzene)
m-xylene (1,3-dimethylbenzene)
p-xylene (1,4-dimethylbenzene)
styrene (ethenylbenzene)

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

1.3 *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 Sections 1, 6, 8, and 10 – 26.

NOTE 1—This test method covers systems in which the impurities form with the major component a substantially ideal or sufficiently dilute solution, and also systems which deviate from the ideal laws, provided that, in the latter case, the lowering of the freezing point as a function of the concentration is known for each most probable impurity in the given substance.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1015 Test Method for Freezing Points of High-Purity Hydrocarbons

3. Summary of Test Method

3.1 After measurement of the freezing point of the actual sample, purity can be calculated from the value of the determined freezing point and the values given for the freezing point for zero impurity and for the applicable cryoscopic constant or constants.[4]

3.2 For the equilibrium between an infinitesimal amount of the crystalline phase of the major component and a liquid phase of the major component and one or more other components, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase is expressed by the equation:[5]

$$-\ln N_1 = -\ln(1 - N_2) = A(t_{f0} - t_f)[1 + B(t_{f0} - t_f) + \ldots] \quad (1)$$

where:

N_1 = mole fraction of the major component,
N_2 = $(1 - N_1)$ = sum of the mole fractions of all the other components,
t_f = freezing point, in degrees Celsius, of the given substance (in which the mole fraction of the major component is N_1), defined as the temperature at which an infinitesimal amount of crystals of the major component is in thermodynamic equilibrium with the liquid phase (see Note 3 of Test Method D1015),
t_{f0} = freezing point for zero impurity, in degrees Celsius, for the major component when pure, that is, when $N_1 = 1$ or $N_2 = 0$,

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical and Chemical Methods.

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[2] Numerical constants in this test method were taken from the most recently published data appearing in "Tables of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," or *ASTM DS 4A*, *Physical Constants of Hydrocarbons C_1 to C_{10}*, or both, prepared by the American Petroleum Institute, Research Project 44.

[3] 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.

[4] For a more complete discussion of this test method, see Glasgow, A. R., Jr., Streiff, A. J., and Rossini, F. D., "Determination of the Purity of Hydrocarbons by Measurement of Freezing Points," *Journal of Research* , JRNBA, National Institute of Standards and Technology, Vol 35, No. 6, 1945, p. 355.

[5] For details, see Taylor, W. J., and Rossini, F. D., *"Theoretical Analysis of Time-Temperature Freezing and Melting Curves as Applied to Hydrocarbons," Journal of Research*, JRNBA, Nat. Bureau Standards, Vol 32, No. 5, 1944, p. 197; also Lewis, G. N., and Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," 1923, pp. 237, 238, McGraw-Hill Book Co., New York, NY.

A = first or main cryoscopic constant, in mole fraction per degree, and

B = secondary cryoscopic constant, in mole fraction per degree.

Neglecting the higher terms not written in the brackets, Eq 1 can be transformed to the equation:

$$\log_{10} P = 2.00000 - (A/2.3026)(t_{f0} - t_f)[1 + B(t_{f0} - t_f)] \quad (2)$$

where:

P = purity of the given substance in terms of mole percent of the major component.

4. Significance and Use

4.1 The experimental procedures and physical constants provided by this test method, when used in conjunction with Test Method D1015, allow the determination of the purity of the material under test. A knowledge of the purity of these hydrocarbons is often needed to help control their manufacture and to determine their suitability for use as reagent chemicals or for conversion to other chemical intermediates or finished products.

5. Apparatus

5.1 *Sampling Apparatus,* as shown in Fig. 1, for withdrawing liquefied gases (for example, 1,3-butadiene) from pressure storage cylinders.

5.2 *Distilling Apparatus,* as shown in Fig. 2, for removing small amounts of polymer from low-boiling compounds (for example, 1,3-butadiene) by simple distillation at atmospheric pressure.

5.3 *Distilling Apparatus,* as shown in Fig. 3, for removing small amounts of polymer from compounds with boiling points near room temperature (for example, isoprene) by distillation at atmospheric pressure.

5.4 *Vacuum Distilling Apparatus and Transfer Trap,* as shown in Fig. 4, for removing dissolved air and large amounts of polymer from a compound (for example, 1,3-butadiene or styrene), by repeated freezing and evacuation, followed by distillation of the compound in vacuum in a closed system.

6. Materials

6.1 *Carbon Dioxide Refrigerant*—Solid carbon dioxide in a suitable liquid. (**Warning**—Extremely cold (−78.5 °C). Liberates heavy gas which can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys.) Acetone is recommended. (**Warning**—Extremely flammable. Harmful if inhaled. High concentrations can cause unconsciousness or death. Contact can cause skin irritation and dermatitis. Use refrigerant bath only with adequate ventilation!)

6.2 *Liquid Nitrogen or Liquid Air*—(**Warning**—Extremely cold. Liberates gas which can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys.) For use as a refrigerant. If obtainable, liquid nitrogen is preferable because of its safety.

6.2.1 Use liquid nitrogen refrigerant only with adequate ventilation. If liquid air is used as a refrigerant, it is imperative that any glass vessel containing hydrocarbon or other combustible compound and immersed in liquid air be protected with a suitable metal shield. The mixing of a hydrocarbon or other combustible compound with liquid air due to the breaking of a glass container would almost certainly result in a violent explosion. If liquid nitrogen is used as a refrigerant, no hydrocarbon sample should ever be permitted to cool below the condensation temperature of oxygen (−183 °C at atm). This would not be likely to occur in normal operation, but might occur if the apparatus were left unattended for some time.

7. Procedure

7.1 Measure the freezing point as described in Test Method D1015, using the modifications and constants given in Sections 8 – 26 of this test method for the specific compounds being examined.

NOTE 2—The estimated uncertainty in the calculated value of the purity as referred to in Sections 8 – 26 is not equivalent to the precision defined in RR:D02-1007.

8. *n*-Butane[6] (**Warning**—Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.)

8.1 Determine the freezing point from freezing curves, with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

8.2 The method of obtaining the samples shall be as follows: Assemble the apparatus for obtaining the sample as shown in Fig. 1, but with no lubricant on the ground-glass joints and with the valve at the bottom of the cylinder, so that sampling is from the liquid phase. Attach to *C* an absorption tube containing anhydrous calcium sulfate or other suitable desiccant (except magnesium perchlorate) so that water is not introduced into the system (Note 3). Fill the flask *F* with the carbon dioxide refrigerant to within about 51 mm (2 in.) of the top. After about 20 min or 30 min, when the system will have cooled sufficiently, remove the absorption tube and begin the collection of liquid *n*-butane by opening the valve *K* and adjusting the needle valve *J* so that the sample is collected at a rate of 1 mL to 2 mL (liquid)/min in the condensing tube *E*.

NOTE 3—However, if some water does condense with the hydrocarbon, the freezing point will not be affected significantly because of the extremely low solubility of water in the hydrocarbon at the freezing point of the latter.

8.3 Assemble the freezing point apparatus. Place the cooling bath in position around the freezing tube (*O* in Fig. 1 of Test Method D1015), letting the temperature as read on the platinum thermometer reach about −80 °C when all the sample has been collected.

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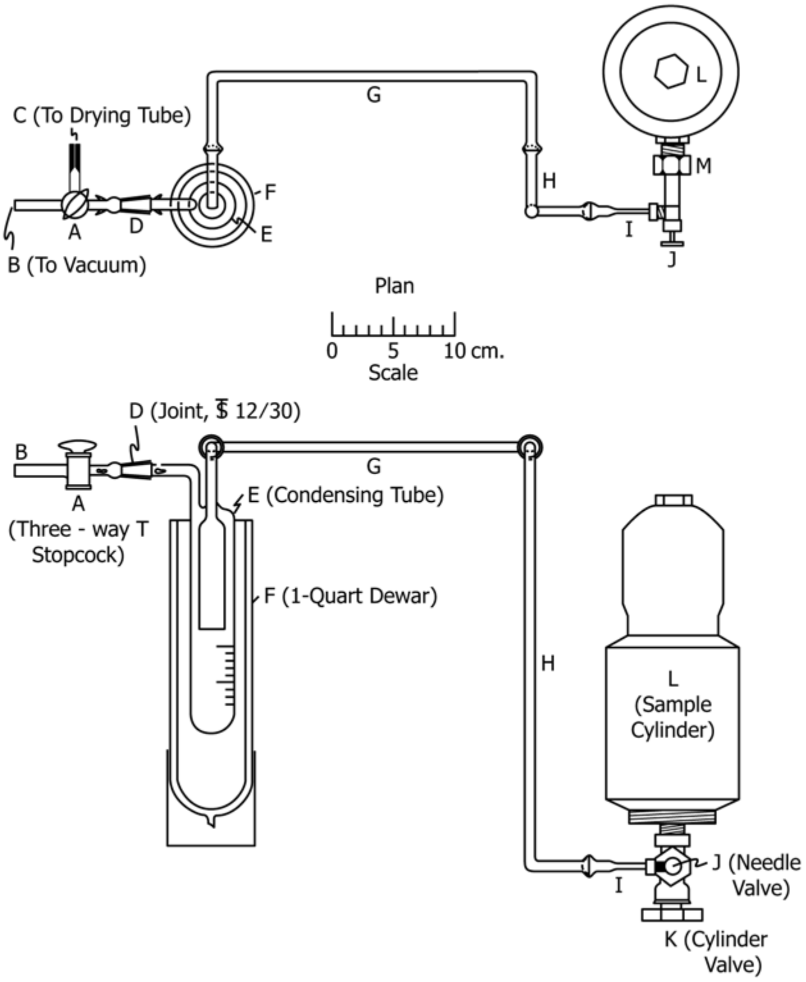
[6] For further details, see Glasgow , A. R., Jr., et al. "Determination of Purity by Measurement of Freezing Points of Compounds Involved in the Production of Synthetic Rubber," *Analytical Chemistry*, ANCHA, Vol 20, 1948, p. 410.



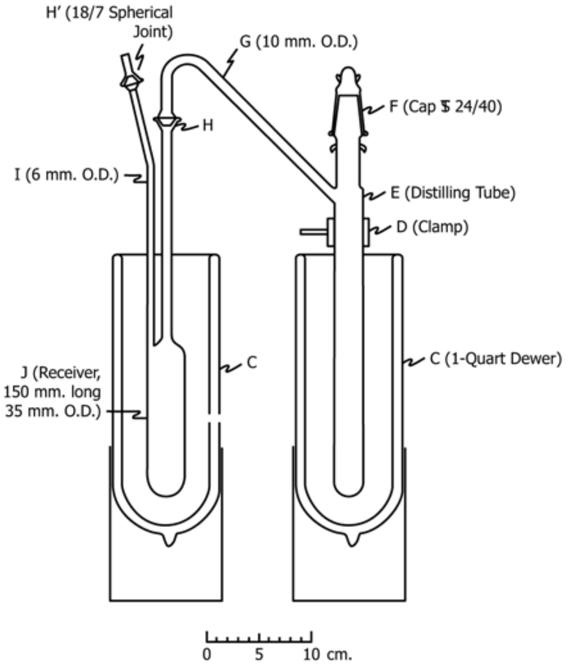
A—Three-way T stopcock, borosilicate glass (similar to Corning Pyrex No. 7420).
B—Connection to vacuum for purging and for evacuating system *CDEGHI*.
C—Capillary tube for venting, to which drying tube is also connected.
D—Joint, standard taper, 12/30, borosilicate glass.
E—Condensing tube, borosilicate glass.
F—Dewar flask, 1 qt size, borosilicate glass (similar to American Thermos Bottle Co. No. 8645).
G—Tubing, borosilicate glass, 10 mm in outside diameter, with spherical ground-glass joints, 18/7.
H—Tubing, silicate glass, 10 mm in outside diameter, with spherical ground-glass joints, 18/7.
I—Metal connection, brass spherical male joint at one end fitting to connection to needle valve at other end.
J—Needle valve, brass.
K—Valve on cylinder containing hydrocarbon material.
L—Standard cylinder containing hydrocarbon material.
M—Fitting to connect needle valve *J* to valve *K* on cylinder.

FIG. 1 Apparatus for Obtaining Sample

8.4 When 50 mL of liquid (temperature about −80 °C) has been collected in the condensing tube, close the valve *K* (Fig. 1) and allow the liquid which has collected at *I* to warm and transfer to the condensing tube (Note 4). Replace the attaching tubes *G* and *D* on the condensing tube by caps. The liquid sample is now ready for introduction into the freezing tube (*O* in Fig. 1 of Test Method D1015).

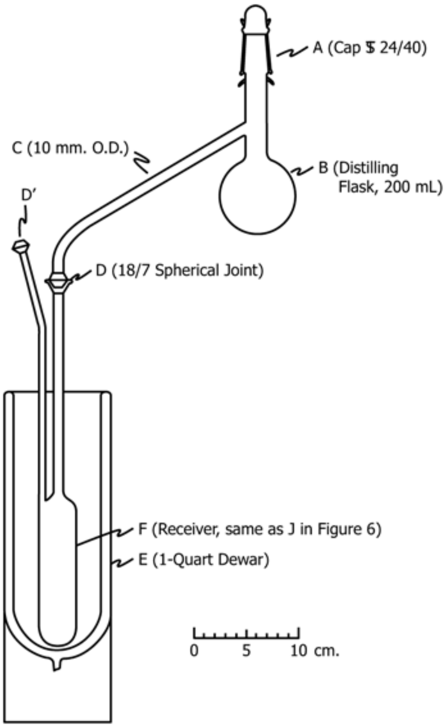
NOTE 4—In case the original sample contained water, there will remain at *I* some water that may be discarded after the hydrocarbon portion has been collected as outlined above.

8.5 When the temperature of the platinum thermometer is near −80 °C, remove the condensing tube (*E* in Fig. 1) from the Dewar flask. Wrap a cloth around the upper portion of the condensing tube (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), and after removing the caps on the condensing tube, raise the stopper holding the platinum thermometer, and pour the sample through the tapered male outlet of the condensing tube into the freezing tube (*O* in Fig. 1 of Test Method D1015). Quickly replace the stopper holding the platinum thermometer,



C—Dewar vessel, 1 qt capacity, borosilicate glass.
D—Clamp.
E—Distilling tube, borosilicate glass, 25 mm in outside diameter.
F—Standard-taper ground-glass joint, 24/40 borosilicate glass.
G—Tubing, 10 mm in outside diameter, borosilicate glass.
H, H′—Spherical ground-glass joints, 18/7, borosilicate glass.
I—Tubing, 6 mm in outside diameter, borosilicate glass.
J—Receiver, 35 mm in outside diameter, 150 mm in length, borosilicate glass.

FIG. 2 Simple Distilling Apparatus for Normally Gaseous Substances



A—Standard-taper, ground-glass joint, 24/40, borosilicate glass
B—Distilling flask, round bottom, 200-mL capacity, borosilicate glass.
C—Tubing, 10 mm in outside diameter, borosilicate glass.
D, D′—Spherical ground-glass joints, 18/7, borosilicate glass.
E—Dewar flask, 1 qt capacity, borosilicate glass.
F—Receiver, same as *J* in Fig. 2.

FIG. 3 Simple Distilling Apparatus for Normally Liquid Substances

and start the stirrer, with dry air flowing into the upper portion of the freezing tube through *M* (Fig. 1 of Test Method D1015).

8.6 Because the material is normally gaseous at room temperature, care should be taken in disposing of the sample safely.

8.7 For *n*-butane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f\,0} = -138.362\ °\text{C} \pm 0.025\ °\text{C} \tag{3}$$

and the cryoscopic constants are:

$$A = 0.03085\ \text{mole fraction}/°\text{C and} \tag{4}$$

$$B = 0.0048\ \text{mole fraction}/°\text{C}. \tag{5}$$

8.8 The cryoscopic constants given in 8.7 are applicable to samples of *n*-butane having a purity of about 95 mole % or better, with no one impurity present in an amount that exceeds its eutectic composition with the major component.

8.9 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

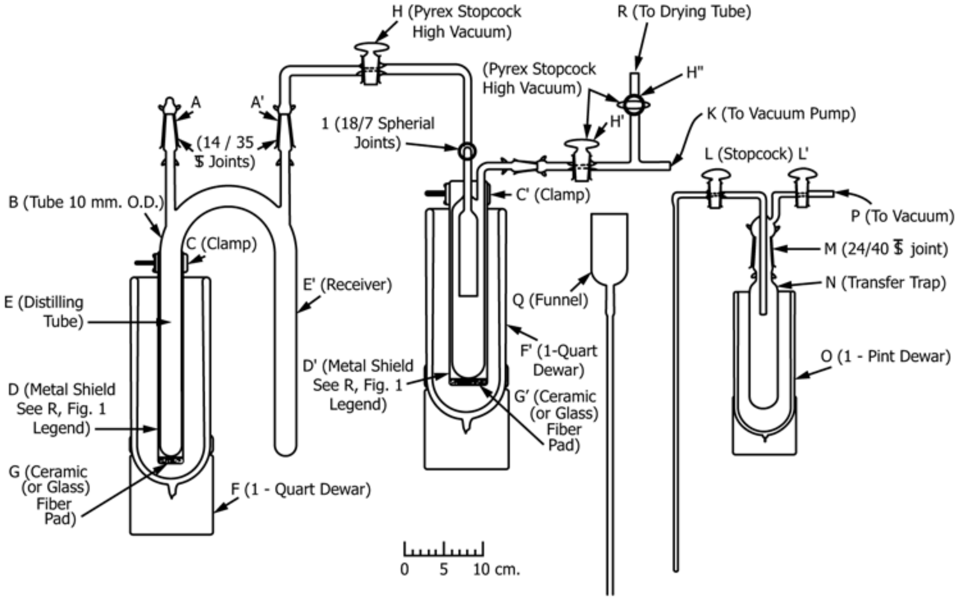
Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.08
99.0 to 99.5	0.09
98 to 99	0.10
97 to 98	0.12
96 to 97	0.15
95 to 96	0.20

9. Isobutane[6] (Warning—Extremely flammable gas under pressure. Vapor reduces oxygen available for breathing.)

9.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

9.2 Obtain the samples as follows: Assemble the apparatus for obtaining the sample as shown in Fig. 1, but with no lubricant on the ground-glass joints and with the valve at the bottom of the cylinder, so that sampling is from the liquid phase. Attach to *C* an absorption tube containing anhydrous calcium sulfate or other suitable desiccant (except magnesium perchlorate) so that water is not introduced into the system (Note 3). Fill the flask *F* with the carbon dioxide refrigerant to within about 51 mm (2 in.) of the top. After about 20 min or 30 min, when the system will have cooled sufficiently, remove the absorption tube and begin the collection of liquid isobutane by opening the valve *K* and adjusting the needle valve *J* so that the sample is collected at a rate of 1 mL to 2 mL (liquid)/min in the condensing tube *E*.

9.3 Assemble the freezing point apparatus. Place the cooling bath in position around the freezing tube (*O* in Fig. 1 of



A, A′—Standard-taper ground-glass joints, 14/35 borosilicate glass.
B—Tubing, 27 mm in outside diameter, borosilicate glass.
C, C′—Clamp.
D— Brass cylinder, 273 mm (10¾ in.) in length, 28.6 mm (1⅛ in.) in inside diameter; for precautions in use of liquid nitrogen and liquid air, see *R* in legend to Fig. 1 of Test Method D1015 and Notes 2 and 3 of Test Method D1015.
D′— Brass cylinder, 254 mm (10 in.) in length, 47.6 mm (1⅞ in.) in inside diameter, (see D above).
E—Original sample.
E′—Distilled sample.
F, F′—Dewar flask, 0.0009 m^3 (1 qt) capacity, borosilicate glass.
G and G′—Ceramic (or glass) fiber pad.
H, H′, H′—Stopcock, ground for high vacuum, borosilicate glass.
I—Spherical ground-glass joint, 18/7, borosilicate glass.
J—Condensing tube, used as trap (see *E* in Fig. 1).
K—Connection to vacuum system.
L, L′—Stopcock, ground for high vacuum, borosilicate glass.
M—Standard-taper ground-glass joint, 24/40 borosilicate glass.
N—Receiver withdrawal, 36 mm in outside diameter, borosilicate glass.
O—Dewar flask, 0.0005 m^3 (1 pt) capacity, borosilicate glass.
P—Connection to vacuum.
Q—Funnel with extension, 4 mm in inside diameter, borosilicate glass.
R—Connection to drying tube, borosilicate glass.

FIG. 4 Apparatus for Simple Vacuum Distillation

Test Method D1015), letting the temperature as read on the platinum thermometer reach about −80 °C when all the sample has been collected.

9.4 When 50 mL of liquid (temperature about −80 °C) has been collected in the condensing tube, close the valve *K* (Fig. 1) and allow the liquid which had collected at *I* to warm and transfer to the condensing tube (Note 4). Replace the attaching tubes, *G* and *D* , on the condensing tube by caps. The liquid sample is now ready for introduction into the freezing tube (*O* in Fig. 1 of Test Method D1015).

9.5 When the temperature of the platinum thermometer is near −80 °C, remove the condensing tube (*E* in Fig. 1) from the Dewar flask. Wrap a cloth around the upper portion of the condensing tube (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), and after removing the caps on the condensing tube, raise the stopper holding the platinum thermometer, and pour the sample through the tapered male outlet of the condensing tube into the freezing tube (*O* in Fig. 1 of Test Method D1015). Quickly replace the stopper holding the platinum thermometer and start the stirrer, with dry air flowing into the upper portion of the freezing tube through *M* (Fig. 1 of Test Method D1015).

9.6 Because of the fact that the material is normally gaseous at room temperature, care should be taken in disposing of the sample safely.

9.7 For isobutane, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -159.605\ °\mathrm{C} \pm 0.025\ °\mathrm{C} \quad (6)$$

and the cryoscopic constants are:

$$A = 0.04234 \text{ mole fraction/°C and} \quad (7)$$

$$B = 0.0057 \text{ mole fraction/°C}. \quad (8)$$

9.8 The cryoscopic constants given in 9.7 are applicable to samples of isobutane having a purity of about 95 mole % or better, with no one impurity present in an amount that exceeds its eutectic composition with the major component.

9.9 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.10
99.0 to 99.5	0.11
98 to 99	0.12
97 to 98	0.14
96 to 97	0.16
95 to 96	0.20

10. *n*-Pentane (Warning —Extremely flammable liquid. Harmful if inhaled. Vapors can cause flash fire.)

10.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

10.2 To obtain the sample, cool the container and *n*-pentane to near 0 °C and transfer a sample of about 60 mL (liquid at the given temperature) to a graduated cylinder which has been kept refrigerated slightly below 0 °C. The sample is now ready for introduction into the freezing tube, which should be precooled to near −80 °C.

10.3 For *n*-pentane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -129.730\ °C \pm 0.015\ °C \tag{9}$$

and the cryoscopic constants are:

$$A = 0.04906 \text{ mole fraction/°C and} \tag{10}$$

$$B = 0.0042 \text{ mole fraction/°C.} \tag{11}$$

10.4 The cryoscopic constants given in 10.3 are applicable to samples of *n*-pentane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

10.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.07
99.0 to 99.5	0.08
98 to 99	0.09
97 to 98	0.10
96 to 97	0.12
95 to 96	0.14

11. Isopentane (**Warning**—Extremely flammable liquid. Harmful if inhaled. Vapors can cause flash fire.)

11.1 Determine the freezing point from melting curves with the double helix stirrer, with a cooling bath of liquid nitrogen (or liquid air) to obtain the slurry of crystals and liquid, and a warming bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point, by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

11.2 To obtain a sample, cool the container and isopentane to near 0 °C and transfer a sample of about 65 mL (liquid at the given temperature) to a graduated cylinder which has been kept refrigerated slightly below 0 °C. The sample is now ready for introduction into the freezing tube which should be precooled to near −80 °C.

11.3 For isopentane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -159.905\ °C \pm 0.015\ °C \tag{12}$$

and the cryoscopic constants are:

$$A = 0.04829 \text{ mole fraction/°C and} \tag{13}$$

$$B = 0.0058 \text{ mole fraction/°C.} \tag{14}$$

11.4 The cryoscopic constants given in 11.3 are applicable to samples of isopentane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount which exceeds the composition of the eutectic with the major component.

11.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.07
99.0 to 99.5	0.08
98 to 99	0.09
97 to 98	0.10
96 to 97	0.12
95 to 96	0.14

12. *n*-Hexane (**Warning**—Extremely flammable. Harmful if inhaled. Can produce nerve cell damage. Vapors can cause flash fire.)

12.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

12.2 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of a pipet or by pouring into a graduated cylinder.

12.3 For *n*-hexane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -95.322\ °C \pm 0.010\ °C \tag{15}$$

and the cryoscopic constants are:

$$A = 0.04956 \text{ mole fraction/°C and} \tag{16}$$

$$B = 0.0039 \text{ mole fraction/°C.} \tag{17}$$

12.4 The cryoscopic constants given in 12.3 are applicable to samples of *n*-hexane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

12.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

13. *n*-Heptane (**Warning** —Flammable. Harmful if inhaled.)

13.1 Determining the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

13.2 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of a pipet or by pouring into a graduated cylinder.

13.3 For *n*-heptane, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -90.581 \ \ °C \pm 0.010 \ °C \tag{18}$$

and the cryoscopic constants are:

$$A = 0.05065 \text{ mole fraction/°C and} \tag{19}$$

$$B = 0.0033 \text{ mole fraction/°C.} \tag{20}$$

13.4 The cryoscopic constants given in 13.3 are applicable to samples of *n*-heptane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

13.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

14. *n*-Octane (**Warning** —Flammable. Harmful if inhaled.)

14.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of carbon dioxide refrigerant at a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

14.2 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of a pipet or by pouring into a graduated cylinder.

14.3 For *n*-octane the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -56.764 \ °C \pm 0.010 \ °C \tag{21}$$

and the cryoscopic constants are:

$$A = 0.05329 \text{ mole fraction/°C and} \tag{22}$$

$$B = 0.0031 \text{ mole fraction/°C.} \tag{23}$$

14.4 The cryoscopic constants given in 14.3 are applicable to samples of *n*-octane having a purity of about 95 mole % or better, with the usual impurities and with no impurity present in an amount that exceeds the composition of its eutectic with the major component.

14.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

15. 2,2,4-Trimethylpentane (**Warning**—Extremely flammable. Harmful if inhaled. Vapors can cause flash fire.)

15.1 For samples having a purity greater than about 99.5 mole %, determine the freezing point from melting curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), and a warming bath of solid carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

15.2 For samples having a purity less than about 99.5 mole %, determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

15.3 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of pipet or by pouring into a graduated cylinder.

15.4 For 2,2,4-trimethylpentane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -107.373 \ °C \pm 0.010 \ °C \tag{24}$$

and the cryoscopic constants are:

$$A = 0.04032 \text{ mole fraction/°C and} \tag{25}$$

$$B = 0.0043 \text{ mole fraction/°C.} \tag{26}$$

15.5 The cryoscopic constants given in 15.4 are applicable to samples of 2,2,4-trimethylpentane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

15.6 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

16. Methylcyclohexane (**Warning**—Flammable. Harmful if inhaled.)

16.1 Determine the freezing point from melting curves with the double helix stirrer, with a cooling bath of liquid nitrogen (or liquid air) to obtain the slurry of crystals and liquid, and a warming bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

16.2 Obtain a sample of 60 mL (measured at room temperature) directly from the original container by pouring into a graduated cylinder.

16.3 For methylcyclohexane, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -126.596\ °C \pm 0.015\ °C \tag{27}$$

and the cryoscopic constants are:

$$A = 0.03779 \text{ mole fraction/°C and} \tag{28}$$

$$A = 0.0032 \text{ mole fraction/°C.} \tag{29}$$

16.4 The cryoscopic constants given in 16.3 are applicable to samples of methylcyclohexane having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of the eutectic with the major component.

16.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

17. Isobutene[6] (**Warning**—Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.)

17.1 Determine the freezing point from freezing curves, with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

17.2 Obtain the samples as follows: Assemble the apparatus for obtaining the sample as shown in Fig. 1, but with no lubricant on the ground-glass joints and with the valve at the bottom of the cylinder, so that sampling is from the liquid phase. Attach to *C* an absorption tube containing anhydrous calcium sulfate or other suitable desiccant (except magnesium perchlorate) so that water is not introduced into the system (Note 3). Fill the flask *F* with the carbon dioxide refrigerant to within about 51 mm (2 in.) of the top. After about 20 min or 30 min, when the system will have cooled sufficiently, remove the absorption tube and begin the collection of liquid isobutene by opening the valve *K* and adjusting the needle valve *J* so that the sample is collected at a rate of 1 mL to 2 mL (liquid)/min in the condensing tube *E*.

17.3 Assemble the freezing point apparatus. Place the cooling bath in position around the freezing tube (*O* in Fig. 1 of Test Method D1015), letting the temperature as read on the platinum thermometer reach about −80 °C when all the sample has been collected.

17.4 When 50 mL of liquid (temperature about −80 °C) has been collected in the condensing tube, close the valve *K* (Fig. 1) and allow the liquid which has collected at *I* to warm and transfer to the condensing tube (Note 4). Replace the attaching tubes *G* and *D* on the condensing tube by caps. The liquid sample is now ready for introduction into the freezing tube (*O* in Fig. 1 of Test Method D1015).

17.5 When the temperature of the platinum thermometer is near −80 °C, remove the condensing tube (*E* in Fig. 1) from the Dewar flask. Wrap a cloth around the upper portion of the condensing tube (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), and after removing the caps on the condensing tube, raise the stopper holding the platinum thermometer, and pour the sample through the tapered male outlet of the condensing tube into the freezing tube (*O* in Fig. 1 of Test Method D1015). Quickly replace the stopper holding the platinum thermometer and start the stirrer, with dry air flowing into the upper portion of the freezing tube through *M* (Fig. 1 of Test Method D1015).

17.6 Because of the fact that the material is normally gaseous at room temperature, care should be taken in disposing of the sample safely.

17.7 For isobutene, the freezing point for zero impurity, in air at 1 atm, is as follows:

$$t_{f0} = -140.337\ °C \pm 0.020\ °C \tag{30}$$

and the cryoscopic constants are:

$$A = 0.04044 \text{ mole fraction/°C and} \tag{31}$$

$$B = 0.005 \text{ mole fraction/°C.} \tag{32}$$

17.8 The cryoscopic constants given in 17.7 are applicable to samples of isobutene having a purity of about 95 mole % or better, with no one impurity present in an amount that exceeds its eutectic composition with the major component.

17.9 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.08
99.0 to 99.5	0.09
98 to 99	0.10
97 to 98	0.12
96 to 97	0.15
95 to 96	0.20

18. 1,3-Butadiene[6] (**Warning**—Extremely flammable liquefied gas under pressure. May form explosive peroxides upon exposure to air. Harmful if inhaled. Irritating to eyes, skin, and mucous membranes.)

18.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

18.2 Obtain the samples as follows: Assemble the apparatus for obtaining the sample as shown in Fig. 1, but with no lubricant on the ground-glass joints and with the valve at the bottom of the cylinder, so that sampling is from the liquid phase. Attach to *C* an absorption tube containing anhydrous calcium sulfate or other suitable desiccant (except magnesium perchlorate) so that water is not introduced into the system (Note 3). Fill the flask *F* with the carbon dioxide refrigerant to within about 51 mm (2 in.) of the top. After about 20 min or 30 min, when the system will have cooled sufficiently, remove the absorption tube and begin the collection of liquid 1,3-butadiene by opening the valve *K* and adjusting the needle valve *J* so that the sample is collected at a rate of 1 mL to 2 mL (liquid)/min in the condensing tube *E*.

18.3 Assemble the freezing point apparatus. Place the cooling bath in position around the freezing tube (*O* in Fig. 1 of Test Method D1015), letting the temperature as read on the platinum thermometer reach about −80 °C when all the sample has been collected.

18.4 When 50 mL of liquid (temperature about −80 °C) has been collected in the condensing tube, close the valve *K* (Fig. 1) and allow the liquid, which has collected at *I*, to warm and transfer to the condensing tube (Note 4). Replace the attaching tubes *G* and *D* on the condensing tube by caps. The liquid sample is now ready for introduction into the freezing tube (*O* in Fig. 1 of Test Method D1015).

18.5 In some cases, it will be desirable to remove the dimer, other C_8 hydrocarbons, and higher polymer from the sample of 1,3-butadiene before determining the purity. For this removal, the procedure is as follows: Assemble the apparatus shown in Fig. 2 with a small amount (10 ppm to 100 ppm) of tertiary butyl catechol or other suitable inhibitor placed in the bottom of the distilling tube *E*, with no lubricant on the ground-glass joints. It is also desirable to place at the bottom of the flask a piece of carborundum or other suitable material to prevent bumping. Make a connection to the atmosphere through an absorption tube (as previously described in this section) at *H*' so that entering air is freed of carbon dioxide and water. Place a bath containing carbon dioxide refrigerant around the distilling tube *E*, and also around the receiver *J* so that the small entrance and exit tubes of *J* are covered with at least 5 cm of the bath. After about 20 min to 30 min, when the system will have precooled sufficiently, disconnect the connection to the atmosphere at *H*', remove the cap *F*, and introduce the liquid butadiene (temperature near −80 °C) by pouring through a precooled funnel (such as *Q* in Fig. 4 which may be cooled without contamination by liquid air or liquid nitrogen) into the distilling tube. Grease the cap *F* and replace immediately after the introduction of the sample. Then distill the material by removing the bath from the distilling tube and allowing it to warm in contact with the air of the room. Distillation is complete when the distilling tube has warmed to room temperature. Disconnect the receiver with the bath around it, cap it at *H* and *H*', and transfer 50 mL (liquid at about −80 °C) of the liquid butadiene to the freezing tube by pouring through *I* in a manner similar to that described for a sample collected in the condensing tube.

18.6 When the temperature of the platinum thermometer is near −80 °C, remove the condensing tube (*E* in Fig. 1) or the receiver (*J* in Fig. 2) from the Dewar. Wrap a cloth around the upper portion of the condensing tube or receiver (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), and after removing the caps on the condensing tube or receiver, raise the stopper holding the platinum thermometer, and pour the sample through the tapered male outlet of the condensing tube or the exit tube *I* of the receiver into the freezing tube (*O* in Fig. 1 of Test Method D1015). Quickly replace the stopper holding the platinum thermometer and start the stirrer, with dry air flowing into the upper portion of the freezing tube through *M* (Fig. 1 of Test Method D1015).

18.7 Because of the fact that the material is normally gaseous at room temperature, care should be taken in disposing of the sample safely.

18.8 For 1,3-butadiene, the freezing point for zero impurity, in air at 1 atm, is

$$t_{f0} = -108.902\ °\mathrm{C} \pm 0.010\ °\mathrm{C} \tag{33}$$

and the cryoscopic constants are:

$$A = 0.03560 \text{ mole fraction/°C and} \tag{34}$$

$$B = 0.0053 \text{ mole fraction/°C.} \tag{35}$$

18.9 The cryoscopic constants given in 18.8 are applicable to samples of 1,3-butadiene having a purity of about 95 mole % or better, with no one impurity present in an amount that exceeds its eutectic composition with the major component.

18.10 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.09
95 to 96	0.10

19. Isoprene (2-Methyl-1,3-Butadiene)[6] (Warning—Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.)

19.1 For samples having a purity greater than about 98 mole %, determine the freezing point from melting curves, with the double helical stirrer, with a cooling bath of liquid nitrogen (or liquid air), and a warming bath of carbon dioxide refrigerant, with the jacket of the freezing tube open to the high vacuum system during the entire melting part of the curve, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

19.2 For samples having a purity less than about 98 mole %, determine the freezing point from freezing curves, with either the aluminum cage stirrer or the double helical stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

19.3 The method of obtaining the sample is as follows: When the material is in a cylinder, assemble the apparatus shown in Fig. 1, with a suitable lubricant on the ground-glass joints, and with the valve below the body of the cylinder so that the sample is obtained from the liquid phase. Evacuate the system by connecting, through heavy-walled tubing, the opening *B* to a vacuum line. After evacuation, close the stopcock *A* to the outlets *B* and *C*, and collect the sample of isoprene (55 mL, liquid, at about −80 °C) in the refrigerated condensing tube *E*, in which was previously placed a small amount (about 10 ppm to 100 ppm) of tertiary butyl catechol or other suitable inhibitor. The sample as thus collected will contain the bulk of any dimer present in the original material. The sample, including substantially all of the dimer, is now ready for introduction into the freezing tube, which should be precooled to near −100 °C. When the isoprene is contained in capped bottles or sealed ampoules, cool the container and isoprene to near 0 °C and transfer a sample of about 65 mL (liquid at the given temperature) to a graduated cylinder which has been kept refrigerated slightly below 0 °C. The sample, including such amount of dimer and higher polymer as was originally present, is now ready for introduction into the freezing tube, which should be precooled to near −100 °C.

19.4 In most cases, it will be desirable to remove the dimer and higher polymer from the sample of isoprene before determining the purity. For this removal, the procedure is as follows: Assemble the apparatus shown in Fig. 3 with no lubricant on the ground-glass joints *D* and *D*'. Place a small amount of tertiary butyl catechol or other suitable inhibitor (about 10 ppm to 100 ppm) in the receiver *F* and a larger amount (about 100 ppm to 1000 ppm) in the distilling flask *B*. It is also desirable to place at the bottom of the flask *B* a piece of carborundum or other suitable material to prevent bumping. Place a cooling bath of water-ice around the distilling flask *B* and a bath containing carbon dioxide refrigerant around the receiver *F*. Make a connection to the atmosphere at *D*' through which the air is first freed of carbon dioxide and water, using a tube containing Ascarite and anhydrous calcium sulfate or other suitable desiccant. Introduce the sample (at 0 °C) into the flask *B*, place the cap *A* in position with a suitable lubricant between the grindings, and remove the connection to the atmosphere at *D*'. Place a water bath (at 40 °C to 50 °C) around the flask *B* and distill the material into *F*. Stop the distillation when a small residue remains in *B* with the water bath at 50 °C. Detach the receiver *F* at *D* and cap at *D* and *D*' with the bath containing carbon dioxide refrigerant still surrounding it. Remove the sample, with the upper portion of the container wrapped with a cloth (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), from the flask *E*, remove the caps and introduce the sample into the freezing tube, previously precooled to near −100 °C, by pouring through *D*'. For the procedure for introducing the sample into the tube, see 18.6 on 1,3-butadiene.

19.5 If the sample contains a very large amount of dimer and polymer, then the simple preceding procedure outlined will not suffice because the required distilling temperature will be too high, and a more complicated procedure is used, as follows: Assemble the apparatus shown in Fig. 4, with inhibitor placed in the distilling tube and receiver (plus some carborundum in the distilling tube to prevent bumping) as previously described in 19.4, and with all the ground joints except that at *A* lubricated. Place a cooling bath of carbon dioxide refrigerant around the distilling tube *E*. Permit air, freed of carbon dioxide and water, to enter the system through *RH" H'H* in order to compensate for the change in volume. When the sample is cooled, remove the cap *A* and introduce the sample through the funnel *Q*, which has been precooled with liquid air or liquid nitrogen. Then lubricate the cap *A* and close the stopcocks *H, H',* and *H*". Place liquid air or liquid nitrogen around the condensing tube *E* (Fig. 1), which serves as a trap, and also replace the carbon dioxide refrigerant around the distilling tube *E* (Fig. 4) with liquid nitrogen or liquid air. After the isoprene has solidified, evacuate the system by opening *H* and *H*' to the vacuum system. Close the stopcocks *H* and *H*' and remove the bath from *E* to allow the material to melt and release dissolved air. Crystallize the material again and evacuate the system as before. Repeat the process again, if necessary, to remove substantially all the air. (If any hydrocarbon has been caught in the trap *J*, it should be distilled back into the tube *E*, with the stopcock *H* open and *H*' closed.) Distill the material into *E*' by placing carbon dioxide refrigerant around the receiver and a water-ice bath around *E* (after the latter has warmed to near 0 °C). Halt the distillation when the transfer of material into the receiver has substantially halted, by admitting air (freed of water and carbon dioxide) into the system through *RH" H'H*. Remove the sample from the receiving tube *E* with the withdrawal receiver *N*. Evacuate the system *LMNL*, with *L*' open and *L* closed, through *P* and then close the stopcock *L*'. Surround the receiver *N*' by carbon dioxide refrigerant. Remove the material by inserting the inlet tube at *L* into the receiver and then opening the stopcock *L*. This procedure avoids loss by evaporation. Then introduce the material into the freezing tube, previously precooled to near −100 °C, by pouring through the tapered joint at *M*. For the procedure for introducing the sample into the tube, see 18.6 on 1,3-butadiene.

19.6 For isoprene (2-methyl-1,3-butadiene), the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -145.964\ °C \pm 0.020\ °C \tag{36}$$

and the cryoscopic constants are:

$$A = 0.0330\ \text{mole fraction}/°C\ \text{and} \tag{37}$$

$$B = 0.0030\ \text{mole fraction}/°C. \tag{38}$$

19.7 The cryoscopic constants given in 19.6 are applicable to samples of isoprene having a purity of about 95 mole % or better, with no one impurity present in an amount that exceeds the eutectic composition with the major component.

19.8 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.08
99.0 to 99.5	0.10
98 to 99	0.12
97 to 98	0.15
96 to 97	0.20
95 to 96	0.25

20. Benzene (**Warning**—Poison. Carcinogen. Harmful or fatal if swallowed. Extremely flammable. Vapors can cause flash fire. Vapor harmful, can be absorbed through skin.)

20.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point and with crystallization induced immediately below the freezing point by means of a cold rod.

20.2 Obtain a sample of 50 mL (measured at room temperature) directly from the original container by means of a pipet or by pouring into a graduated cylinder. Then filter the sample directly into the freezing point tube (*O* in Fig. 1 of Test Method D1015), through silica gel to remove water. See 9.3, and Fig. 5 of Test Method D1015.

20.3 For benzene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = 5.531 \ \ °C \pm 0.010 \ °C \tag{39}$$

and the cryoscopic constants are:

$$A = 0.01523 \text{ mole fraction/°C and} \tag{40}$$

$$B = 0.0032 \text{ mole fraction/°C.} \tag{41}$$

20.4 The cryoscopic constants given in 20.3 are applicable to samples of benzene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

20.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.02
99.0 to 99.5	0.03
98 to 99	0.04
97 to 98	0.05
96 to 97	0.06
95 to 96	0.08

21. Toluene (**Warning**—Flammable. Vapor harmful.)

21.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air), with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

21.2 A sample of 50 mL (measured at room temperature) is obtained directly from its original container by means of a pipet or by pouring into a graduated cylinder.

21.3 For toluene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -94.965 \ °C \pm 0.012 \ °C \tag{42}$$

and the cryoscopic constants are:

$$A = 0.02508 \text{ mole fraction/°C and} \tag{43}$$

$$B = 0.0019 \text{ mole fraction/°C.} \tag{44}$$

21.4 The cryoscopic constants given in 21.3 are applicable to samples of toluene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

21.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.03
99.0 to 99.5	0.04
98 to 99	0.05
97 to 98	0.06
96 to 97	0.08
95 to 96	0.10

22. Ethylbenzene (**Warning**—Flammable. Vapor harmful.)

22.1 Determine the freezing point from melting curves with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid air) to obtain the slurry of crystals and liquid, and a warming bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

22.2 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of a pipet or by pouring into a graduated cylinder.

22.3 For ethylbenzene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -94.949 \ °C \pm 0.015 \ °C \tag{45}$$

and the cryoscopic constants are:

$$A = 0.03471 \text{ mole fraction/°C and} \tag{46}$$

$$B = 0.0029 \text{ mole fraction/°C.} \tag{47}$$

22.4 The cryoscopic constants given in 22.3 are applicable to samples of ethylbenzene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

22.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.08
97 to 98	0.10
96 to 97	0.12
95 to 96	0.14

23. *o*-Xylene (**Warning**—Flammable. Vapor harmful.)

23.1 The freezing point is determined from freezing curves with the cage stirrer, with a cooling bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

23.2 A sample of 50 mL (measured at room temperature) is obtained directly from its original container by means of a pipet or by pouring into a graduated cylinder.

23.3 For *o*-xylene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -25.167\ °C \pm 0.005\ °C \quad (48)$$

and the cryoscopic constants are:

$$A = 0.02659 \text{ mole fraction/°C and} \quad (49)$$

$$B = 0.0030 \text{ mole fraction/°C}. \quad (50)$$

23.4 The cryoscopic constants given in 23.3 are applicable to samples of *o*-xylene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

23.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.02
99.0 to 99.5	0.03
98 to 99	0.04
97 to 98	0.05
96 to 97	0.06
95 to 96	0.08

24. *m*-Xylene (Warning —Flammable. Vapor harmful.)

24.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of solid carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

24.2 Obtain a sample of 50 mL (measured at room temperature) directly from its original container by means of a pipet or by pouring into a graduated cylinder.

24.3 For *m*-xylene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -47.844\ °C \pm 0.020\ °C \quad (51)$$

and the cryoscopic constants are:

$$A = 0.02741 \text{ mole fraction/°C and} \quad (52)$$

$$B = 0.0027 \text{ mole fraction/°C}. \quad (53)$$

24.4 The cryoscopic constants given in 24.3 are applicable to samples of *m*-xylene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

24.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.05
99.0 to 99.5	0.06
98 to 99	0.07
97 to 98	0.08
96 to 97	0.10
95 to 96	0.12

25. *p*-Xylene (Warning —Flammable. Vapor harmful.)

25.1 Determine the freezing point from freezing curves with the cage stirrer, with a cooling bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point, by seeding with crystals. (Crystallization may also be induced with a cold rod, but the recovery from undercooling will not be as rapid.)

25.2 Obtain a sample of 50 mL (measured at room temperature) directly from the original container by means of a pipet or by pouring into a graduated cylinder. The sample is then filtered directly into the freezing point tube, (*O* in Fig. 1 of Test Method D1015), through silica gel to remove water. See 9.3 and Fig. 5 of Test Method D1015.

25.3 For *p*-xylene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = 13.258\ °C \pm 0.012\ °C \quad (54)$$

and the cryoscopic constants are:

$$A = 0.02509 \text{ mole fraction/°C and} \quad (55)$$

$$B = 0.0028 \text{ mole fraction/°C}. \quad (56)$$

25.4 The cryoscopic constants given in 25.3 are applicable to samples of *p*-xylene having a purity of about 95 mole % or better, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the major component.

25.5 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.03
99.0 to 99.5	0.04
98 to 99	0.05
97 to 98	0.06
96 to 97	0.08
95 to 96	0.10

26. Styrene (Ethenylbenzene)[6] (Warning—Flammable. Vapor harmful.)

26.1 Determine the freezing point from freezing curves with the cage stirrer, with cooling bath of carbon dioxide refrigerant, with a cooling rate of 0.3 °C/min to 0.8 °C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

26.2 Obtain a sample of 50 mL (measured at room temperature) directly from the original container by means of a pipet or by pouring into a graduated cylinder.

26.3 If the previous treatment or storage condition of material was such that dimerization or polymerization may have occurred, the dimer or polymer should be removed by a simple vacuum distillation (Fig. 4), using the same procedure as described under isoprene (see 19.5) except that carbon dioxide refrigerant is used to refrigerate the receiver and the sample is distilled at room temperature.

26.4 For styrene, the freezing point for zero impurity, in air at 1 atm, is:

$$t_{f0} = -30.610\ °C \pm 0.008\ °C \quad (57)$$

and the cryoscopic constants are:

$$A = 0.02365 \text{ mole fraction/°C and} \quad (58)$$

$$B = 0.0044 \text{ mole fraction/°C}. \quad (59)$$

26.5 The cryoscopic constants given in 26.4 are applicable to samples of styrene having a purity of not less than about 95 mole %, with the usual impurities and with no one impurity present in an amount that exceeds the composition of its eutectic with the main component.

26.6 The estimated uncertainty in the calculated value of the purity is as follows, in mole %:

Calculated Purity, mole %	Uncertainty, plus or minus, mole %
Over 99.5	0.04
99.0 to 99.5	0.05
98 to 99	0.06
97 to 98	0.07
96 to 97	0.08
95 to 96	0.09

27. Precision and Bias

27.1 *Precision*—The precision for this test method is governed by the precision of Test Method D1015. Test Method D1015 must be used for the freezing point determinations in this test method.

27.2 *Bias*—The bias for this test method is governed by the bias of Test Method D1015. Test Method D1015 must be used for the freezing point determinations in this test method.

28. Keywords

28.1 crystallization; freeze point; LPG; pure hydrocarbons; purity

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