



Standard Test Method for Solubility of Fixed Gases in Low-Boiling Liquids¹

This standard is issued under the fixed designation D 3429; 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.

^{ε1} NOTE—Warnings were moved from notes to section text editorially December 2002.

1. Scope

1.1 This test method covers the determination of the solubilities of nonreactive gases such as nitrogen and helium in liquids that boil below 273 K. This test method is applicable at temperatures from 77 to 300 K from subambient pressure to 6.5 MPa (65 atm). This test method does not provide for analysis of the vapor phase in equilibrium with the liquid (see Section 3 for a description of terms).

1.2 This test method as written describes the procedures to be followed for determination of the solubilities of helium and nitrogen. If suitable modifications are made to the analytical measurements by gas chromatography, solubilities of other gases such as argon, hydrogen, oxygen, etc., can be determined.

1.3 The values stated in SI units are to be regarded as the standard. In cases where materials, products, or equipment are available in inch-pound units only, SI units are omitted.

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 6.1.2 and 7.1 and Annex A1.

2. Referenced Documents

2.1 ASTM Standards:

E 260 Practice for Packed Column Gas Chromatography²

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *carrier gas, n*—gas used to sweep samples through the gas chromatograph.

3.1.2 *test gas, n*—gas whose solubility is being determined.

3.1.3 *liquid or test liquid*—solvent for test gas.

3.1.4 *vapor, n*—vapor phase of test liquid.

3.1.5 *nonreactive gas, n*—gas that does not react chemically with the test liquid.

3.1.6 *elution, n*—the process of removing a material absorbed on the stationary phase of the gas chromatograph column by displacing it with the flowing carrier gas.

3.1.7 *fractionation, n*—change of composition caused by change of pressure.

4. Summary of Test Method

4.1 A sample of test liquid *A* is saturated with test gas *B* at specified temperature and pressure. A portion of the solution is withdrawn and vaporized in an evacuated sample container at room temperature. The concentration of gas *B* in the vaporized sample is determined by gas chromatography. It is necessary that the molar concentration of the gas in the sample container be the same as in the liquid phase. This will be true if fractionation of the sample is avoided while withdrawing it from the liquid phase, if no decomposition or polymerization of the test liquid occurs on vaporization, and if the vapor of the test liquid does not react with the walls of the sample container or connecting lines. It is also necessary that both the test gas and the vapor of the test liquid behave nearly ideally at 101 kPa (1 atm). If the above requirements are met, this test method will give estimates of solubility with an accuracy of $\pm 2\%$.

5. Significance and Use

5.1 The solubility of fixed gases in liquids is an important engineering parameter in the design of hydraulic systems. It is a measure of the amount of gas that can be released from solution when a system undergoes changes in pressure and temperature. Theoretical considerations permit approximate values of gas solubility to be computed with reasonable accuracy. Dissolved gases are separated and quantified chromatographically. The test method is restricted to use with low-boiling liquid samples.

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² *Annual Book of ASTM Standards*, Vol 03.06.

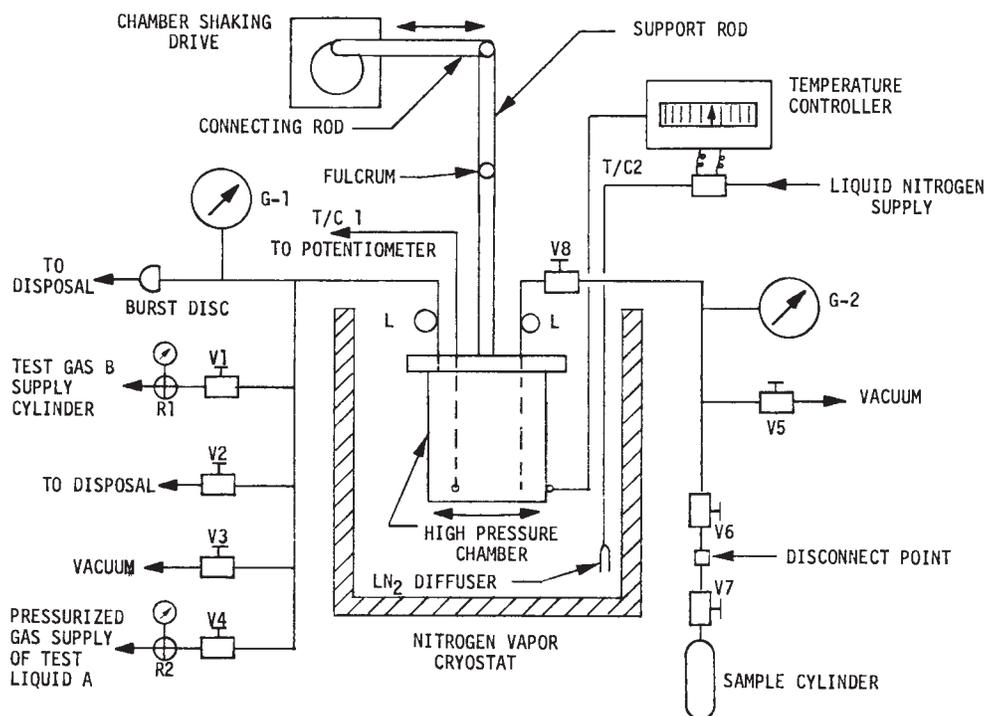
6. Apparatus

6.1 *Saturator and Sampler System*, suitable for the tests of low-boiling liquids and gases at various pressures and temperatures, shown schematically in Fig. 1. The system comprises four parts:

6.1.1 *High-Pressure Test Chamber*, with internal capacity of approximately (1 L) such as shown in Fig. 2. The lid of the test chamber is equipped with three ports. The first is to contain a thermocouple well, the second is for the addition of the test liquid and pressurization of the system with the test gas, and the third port is for withdrawal of the sample of solution from the liquid phase by means of an eductor tube which extends to the bottom of the chamber. The high-pressure assembly is mounted so that an oscillating motion in a horizontal plane can be applied to it mechanically with a frequency of 1 Hz (one cycle per second) and an amplitude of 0.02 m. Loops (pigtaills) are formed in the connecting metal lines to the test chamber to avoid undue stress.

6.1.1.1 An electric motor geared down to provide a shaft speed of about 60 rpm is convenient for providing the necessary agitation. An eccentric or connecting rod from the motor shaft to the support rod imparts an oscillating motion. Without agitation an excessive time is required for equilibrium to be established.

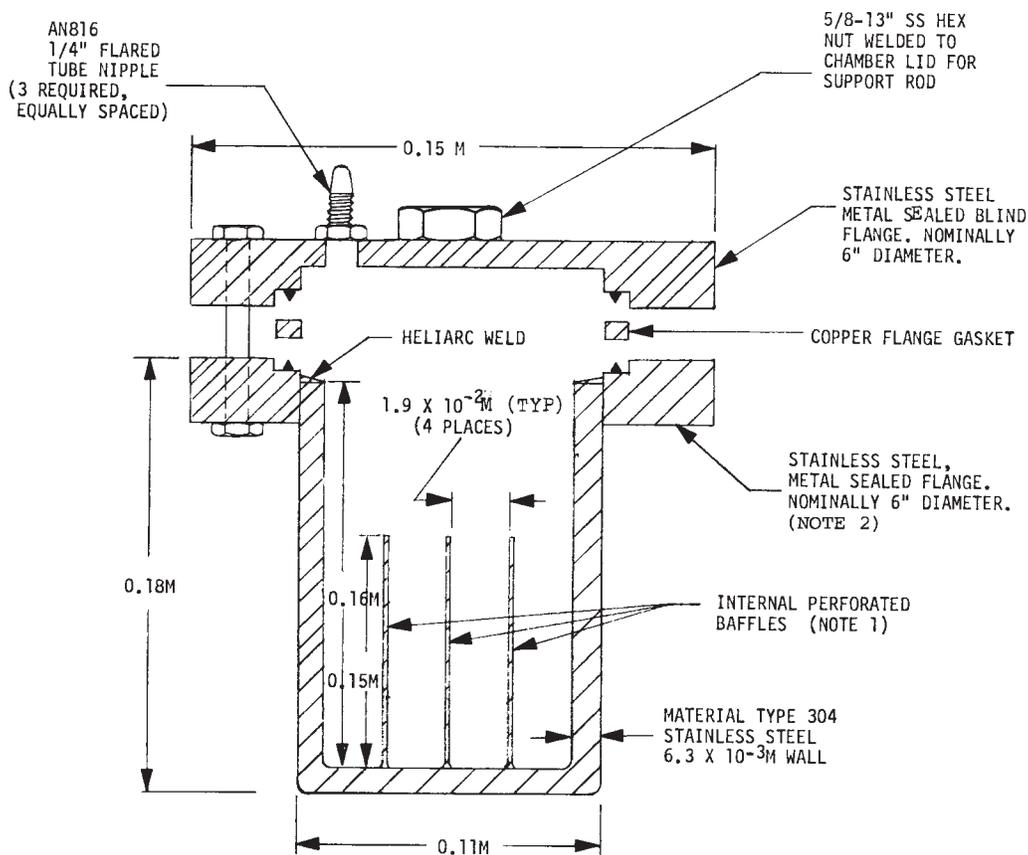
6.1.2 *Nitrogen Vapor Cryostat*, with suitable temperature measurement and control devices, to provide the low-temperature environment for the high-pressure test chamber. The cryostat consists of a cylindrical stainless steel Dewar or other suitable insulated container not less than 0.3 m in inside diameter and approximately 0.5 m in inside depth. A solenoid valve is used to admit liquid nitrogen to the cryostat. The liquid nitrogen cools the cryostat and its contents. The liquid nitrogen (**Warning**—See 7.1.) should be introduced through a diffuser, or in a fine stream behind a sheet metal baffle, so that liquid does not impinge directly on the test chamber or the controller thermocouple. The latter may be attached loosely to the side of the test chamber for convenience, but good thermal coupling to the chamber must *not* be made. Although the nitrogen vapor cryostat can undergo temperature excursions of several degrees, the test chamber will stabilize at a temperature that varies by only a few tenths of a degree because of its thermal inertia. To minimize heat transfer from outside of the apparatus and frost condensation, the top of the cryostat should be loosely covered with a lid of foamed glass or plastic, or other similar insulating material. (**Warning**—Extremely cold. Liberates gas that can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys. See A1.1.)



NOTE 1—All lines and fittings 300 series stainless steel.

1. V1 through V8—Stainless steel valves, metal-to-metal seat, bellows sealed 14 MPa (2000 psi) rating (V8 modified, see Fig. 3)
2. T/C-1—Copper-constantan thermocouple, test liquid temperature.
3. T/C-2—Copper-constantan thermocouple, vapor cryostat temperature controller.
4. G-1—Bourdon gage, 4½ or 6-in. size, Grade 3A (accuracy ±0.25 % of maximum reading), range 1.5 times highest desired system pressure.
5. G-2—Bourdon gage, 3½ to 6-in. size, Grade A or B (accuracy 2 % or better in the middle half of the scale, balance ± 3 % or better), compound range from 0 to 30 in. Hg and a gage pressure from 0 to 103 kPa (0 to 15 psi).
6. Burst Disk—Select to release at 50 % higher than maximum desired system pressure
7. Temperature Controller—Range 77 to 300 K, accuracy ±0.5 % full range
8. L—Loops in stainless steel lines for flexibility.
9. R1 and R2—Gas pressure regulators with pressure gage.

FIG. 1 Saturator Apparatus—Schematic



NOTE 1—All material 300 series stainless except flange gasket. Design of perforated baffles not critical but leave 6-mm diameter holes spaced on 20-mm centers are recommended. Baffles should be spot-welded to the inside of the chamber to prevent movement. The purpose of the baffles is to increase turbulence in the liquid and thereby increase the rate of solubility of gas in the test liquid.

NOTE 2—The conflat flange manufactured by the Varian Corp. of Palo Alto, CA, is suitable.

FIG. 2 Test Chamber Detail

6.1.3 *Vacuum and Pressurization Manifold*, required for initial evacuation of the test chamber, filling the chamber with the test liquid, and pressurizing the chamber with the test gas to the desired total pressure. The manifold is shown on the left side of Fig. 1.

6.1.3.1 The burst disk shown in Fig. 1 shall be of the type capable of withstanding an external pressure of 101 kPa (1 atm) when the system is evacuated.

6.1.3.2 The pump used to evacuate the apparatus shall be a good quality oil-filled mechanical pump capable of producing an ultimate vacuum of 0.1 Pa (10^{-6} atm) or better. If condensible vapors or reactive vapors are to be pumped, the pump shall be protected by a suitable absorber or cold trap. The pump shall run continuously for the duration of the test.

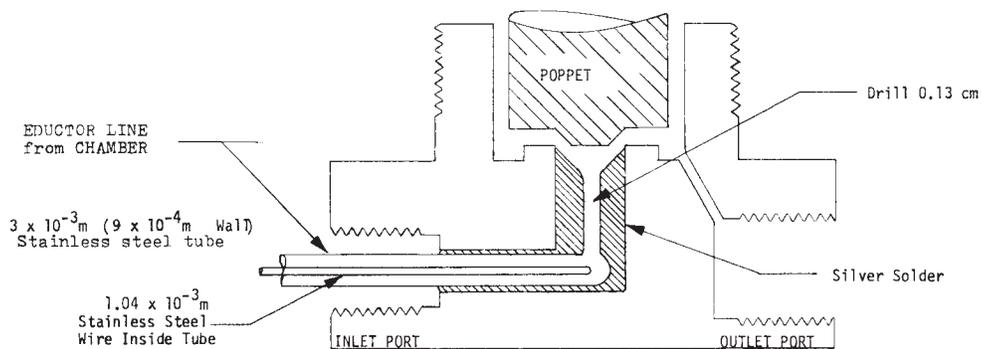
6.1.4 *Solution-Sampling System*—This system utilizes a 3-mm ($1/8$ -in.) outside diameter heavy-wall stainless steel eductor tube extending nearly to the bottom of the test chamber. The eductor tube end extending outside the chamber is connected to a valve just above the top of the cryostat, and the outlet of this valve leads to a sample cylinder or container of about 100-mL volume. Each time a sample is withdrawn from the liquid phase, the eductor tube and sampling valve must be purged, otherwise the liquid and vapor in the line will not necessarily be of equilibrium composition. To reduce the

amount of liquid lost through purging, the sample valve (V8 in Fig. 1) should be modified to reduce liquid holdup to a minimum. The details of this modification are shown in Fig. 3.

6.2 *Gas Chromatograph*, required for determination of the gas concentration in the sample. It must be equipped with a gas sampling valve. It is desirable that two different size loops be provided so that the sample size can be adjusted depending on the concentration of test gas to be determined. Sample loops of 0.5 and 2.0 mL are recommended. The gas chromatograph system must permit easy and rapid change of carrier gas and columns to suit a wide variety of analytical requirements. A thermal conductivity detector of the glass-coated bead type is recommended. The instrumentation should provide a variable attenuator for the detector signal so that a wide range of fixed gas concentrations may be accommodated. A suitable chart recorder, preferably equipped with integrator, should be provided. Alternatively, a digital readout may be used. A typical gas chromatograph is shown schematically in Fig. 4, and its power supply is shown in Fig. 5.

NOTE 1—Practice E 260 provides further description.

6.3 *Leak Testing*—All parts of the system should be tested with helium for leakage at a pressure 1.5 times test operating pressure and vacuum leak tested. The test should include



NOTE 1—Stainless steel wire extends from the position shown in the valve to the lower end of the eductor tube. The purpose of this modification is to reduce the volume of the valve upstream of the poppet to minimum. A valve with a blunt poppet, rather than a needle, is preferred for this service.

FIG. 3 Sampling Valve (V8) Modification

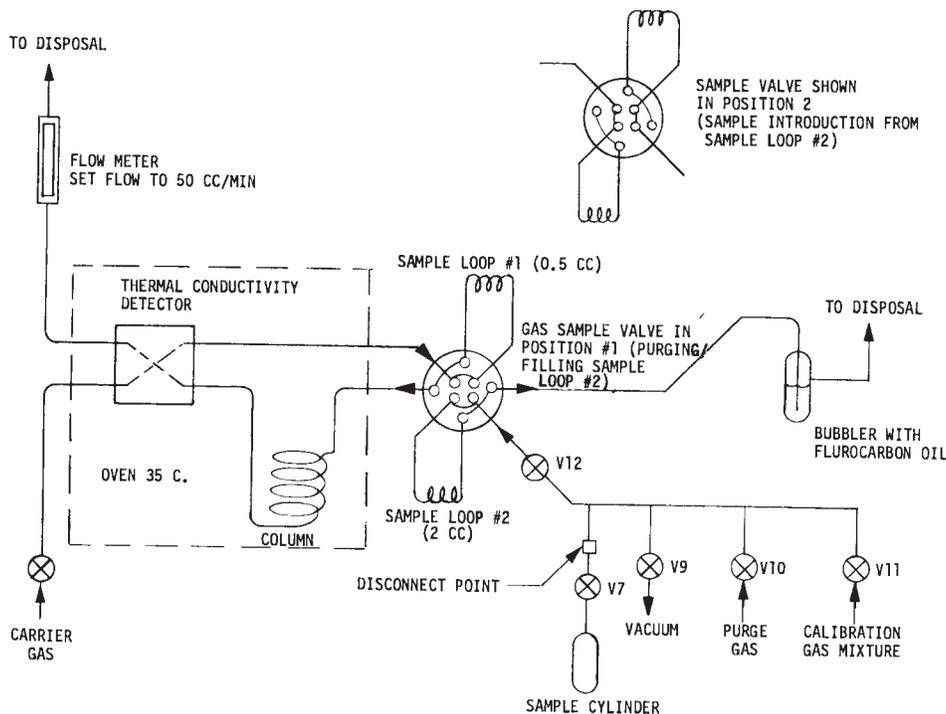


FIG. 4 Gas Chromatograph Schematic

external leaks and port-to-port leaks in valves. The total system maximum acceptable leak rate is 0.1 std cm³ atm/s. A mass spectrometer leak detector is suitable for the leak rate measurements.

7. Reagents and Materials

7.1 Calibration Mixtures—Gas Chromatography—For the determination of nitrogen solubility, one or more mixtures of nitrogen in helium are required for calibration of the gas chromatograph. Concentrations of 2% and 10% are recommended. The exact concentration of each mixture must be accurately known to ±1% of the absolute concentration of the minor constituent. Certified calibration mixtures are available from suppliers of commercial cylinder gases. For the determination of helium solubilities, mixtures of helium in nitrogen containing about 0.2% and 1.0% helium are recommended. The exact concentration should be known to ±1% of the

absolute mole fraction of the helium concentration. Nitrogen is used as the carrier gas when helium is the gas whose solubility is to be determined. Helium is used as the carrier gas when nitrogen solubility is being determined. (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.)

7.2 Column Materials—Because only two-component systems are analyzed and the boiling points of the test gas and liquid are relatively far apart, a relatively short column is sufficient to provide resolution. For most test liquids, a 0.2-m column of silica gel or molecular sieve will separate the test gas and test liquid. The column should be constructed of 6-mm (0.25-in.) thin-walled stainless steel tubing. Certain reactive test liquids, particularly the powerful oxidizers that contain fluorine, may react with the stationary phase materials to produce interferences. If this is the case, more elaborate columns must be used to afford resolution. Each combination

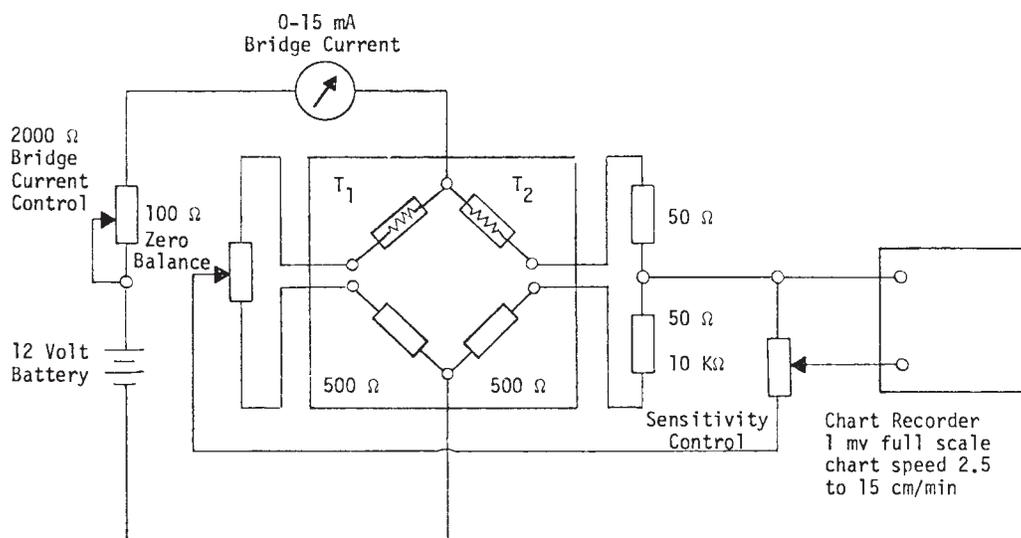


FIG. 5 Power Supply Schematic

of gas and liquid poses its own particular analytical problem and a certain amount of experimentation with stationary phase materials may be required. Table 1 contains a list of materials found appropriate for some typical test gas/liquid combinations.

7.3 *Gases, Compressed*—High-purity helium and nitrogen, or other test gases, are required for saturating the test liquids. The same gases are required for carrier gases in the gas chromatograph. (**Warning**—see 7.1.)

8. Safety Precautions

8.1 This procedure is applicable to determination of solubilities of gases in highly reactive or flammable test liquids at high pressure under cryogenic conditions. It is mandatory that adequate safety precautions be employed. All parts of systems at high pressure must be provided with suitable barricades to

prevent injury to operating personnel in the event of rupture of the equipment, and the portion of the eductor tube which is outside of the test chamber must be used in an explosion-proof hood.

9. Procedure

9.1 Evacuate the test chamber and the transfer manifold by opening the vacuum valve V3 (Fig. 1).

9.2 Set the temperature controller and cool the cryostat to a temperature near the temperature at which the solubility measurement is to be made. (**Warning**—see 6.1.2.)

9.3 Open valve V4 from the test vapor supply cylinder (**Warning**—see 7.1) and transfer sufficient vapor so that 100 to 200 mL of test liquid is condensed in the high-pressure test chamber.

TABLE 1 Typical Stationary Phase Materials for Chromatograph Columns

Test Gas/Liquid System	Carrier Gas	Column Description	Remarks
N ₂ /diborane	He	2 m molecular sieve ^A	Hydrogen, produced by reaction of diborane with moisture in column, produces initial downscale peak followed by N ₂ peak.
He/fluorine	N ₂		
He/FLOX	N ₂		
He/tetrafluorohydrazine	N ₂		
He/chlorine pentafluoride	N ₂	0.25 m 30 to 60 mesh soda lime	Soda lime absorbs HF and unreacted test liquid and protects
He/nitryl fluoride	N ₂	followed by 1.25 m molecular sieve.	detector sensing elements.
He/oxygen difluoride	N ₂		
N ₂ /oxygen difluoride	He		
N ₂ /tetrafluorohydrazine	He		
N ₂ /perchlorylfluoride	He		
He/ethane	N ₂		
He/propane	N ₂	0.2 m 28–200 mesh silica gel	
N ₂ /ethane	He		
N ₂ /propane	He		
He/ammonia	N ₂		
N ₂ /ammonia	He	1 m 60–80 mesh silica gel	Ammonia does not elute from column.
N ₂ /chlorine pentafluoride	He	1.25 m 30-mesh NaCl 0.25 m 60-mesh soda lime 0.75 molecular sieve ^B	NaCl is used in this case to convert halogen fluoride to chlorine. This eliminated interference due to production of oxygen in column.

^ALinde 13x molecular sieve has been found suitable for this purpose.

^BLinde 5A molecular sieve has been found suitable for this purpose.

9.3.1 The amount of liquid condensed may be estimated by weighing the test liquid supply cylinder during the vapor transfer. Alternatively, the volume of vapor can be measured in an auxiliary container of known volume connected to the manifold. The liquid volume is calculated from the known volume and the measured pressure of the vapor. If the test liquid has a critical temperature below ambient, the amount of vapor transferred is calculated from the pressure drop in the supply cylinder assuming that the volume of the cylinder is known or can be estimated. The calculations required are based on the perfect gas laws although such estimates are only approximate. The volume of liquid does not need to be known with great accuracy; $\pm 5\%$ is sufficient.

9.4 Adjust the set point of the controller until the desired temperature of the test liquid is reached as measured with a potentiometer connected to the leads of the measuring thermocouple.

9.4.1 The precision to which the temperature of the test liquid is measured is determined in part by the temperature coefficient of the solubility for the system being studied. In most cases, a determination of the temperature to ± 0.5 K will be adequate.

9.5 Start the agitation mechanism.

9.6 Open the test gas supply cylinder (**Warning**—See 7.1.) valve, *V1*, and fill the test chamber to the desired pressure as indicated by the Bourdon gage, *G1*. As the gas is absorbed by the test liquid the system pressure will drop slightly and more gas should be added to maintain the desired pressure indicated on *G1*.

9.7 Equilibrium of the test gas and its solution is indicated by a constant pressure reading on *G1*. This will take about 15 min for gases whose solubility does not exceed a few mole percent to reach equilibrium.

9.8 After equilibrium has apparently been attained continue agitation for an additional 5 min. Then take a sample of the liquid phase.

9.8.1 Stop agitation of the test chamber.

9.8.2 Evacuate the sample cylinder and connecting lines to the sampling valve, *V8*, by opening valve *V5* to the vacuum pump (valves *V6* and *V7* to remain open).

9.8.3 Close *V5* and regulate *V8* carefully to fill the sample cylinder to a maximum pressure of 101 kPa (1 atm) absolute pressure, as read on *G2*.

9.8.4 Fully close *V8* and pump out the sample cylinder through *V5* (see 6.1.2).

9.8.5 Repeat the filling of the sample cylinder followed by evacuation several times to ensure complete purging of the eductor tube and sample valve.

9.8.5.1 The purging of the eductor tube and sampling valve must ensure the rejection of all liquid or vapor initially contained in them. The number of successive fillings and evacuations of the sample cylinder may be calculated from the volume of the sample cylinder and the approximate volume of the eductor tube and valve body. With the construction recommended, three successive fillings and evacuations are sufficient to purge the sample line thoroughly.

9.8.6 After the final purging and evacuation, regulate valve *V8* to fill the sample cylinder to 150 kPa (1.5 atm) absolute pressure $\pm 10\%$.

9.8.7 Close valves *V6* and *V7* and disconnect the sample cylinder at the connection between the valves.

9.9 Attach the sample cylinder to the sample inlet manifold of the gas chromatograph and determine the fixed gas concentration in the sample as follows:

9.9.1 Evacuate the sample inlet manifold (Fig. 4) by opening the valve *V9* to the vacuum pump. (See 6.1.3.1 with for ultimate vacuum capabilities and protection of the pump from corrosive, reactive, or noncondensable vapors.)

9.9.2 Close valve *V9* to the vacuum pump and fill the manifold with sample gas by opening *V7*.

9.9.3 Slowly open the valve leading to the gas sample valve and allow gas to flow through the sample loop and escape through the bubbler until the loop has been purged and filled with a representative sample. A total flow of approximately 25 mL of sample will be adequate.

9.9.3.1 Prior to evacuation of the sample loop and backfilling with sample mixture it shall be established that the sample valve is completely leakfree under vacuum conditions. Most sample valves will leak slightly under vacuum after long use.

9.9.4 Immediately charge the sample to the chromatographic column by turning the sample through 90° . Allow time for elution of the fixed gas peak and the test liquid peak from the column. Record the fixed gas peak; the test liquid peak may be recorded if desired.

9.10 Reattach the sample cylinder to the apparatus and repeat the agitation of the test sample and contents for 15 min. Repeat the sampling and analysis in 9.8 and 9.9 until successive analyses agree. This will ensure that true equilibrium solubility has been attained.

9.11 Standardize the chromatograph by running a calibration mixture having nearly the same molar concentration of test gas as found in the sample. If possible, use the same setting of the attenuator and the same sample loop for sample and standard. Attach the cylinder containing the calibration standards to the sample inlet manifold and introduce to the sample loop as described in 9.9.

10. Calculation

10.1 Measure the peak areas due to the test gas in the sample and in the calibration standard using either a planimeter or an integrator attachment for the recorder. Peak areas may be expressed in any convenient units.

10.2 Calculate C_2 , the mole percent test gas in the sample, as follows:

$$C_2 = \frac{C_1 \times f \times P_2}{P_1} \quad (1)$$

where:

C_1 = mole percent test gas in calibration standard,

P_1 = peak area of standard,

P_2 = peak area of sample, and

f = normalizing factor calculated as follows:

$$f = \frac{S_1}{S_2} \times \frac{A_1}{A_2} \quad (2)$$

where:

- S_1 = gas sample loop size of standard, mL,
- S_2 = gas sample loop size of sample, mL,
- A_1 = attenuator setting for standard, and
- A_2 = attenuator setting for sample.

10.3 Calculate the gas solubility, V_c , reporting the results as the Ostwald coefficient, as follows:

$$V_c = \frac{C_2 (22\ 400) (T) d_T}{(100 - C_2 (MW_1) (273)) (P_T - P_V)} \quad (3)$$

where:

- C_2 = mole percent test gas in test sample,
- MW_1 = molecular weight of test liquid,
- d_T = density of test liquid at test temperature,
- T = test temperature, K,
- P_T = test pressure, and
- P_V = vapor pressure of test liquid at test temperature.

10.4 If desired, calculate the solubility, S_g , of the gas, expressing the results as millilitres (*STP*—standard temperature and pressure) per gram of solution, as follows:

$$S_g = \frac{\frac{C_2}{100} \times 22\ 400}{\frac{C_2}{100} \times MW_g + \frac{100 - C_2}{100} \times MW_l} \quad (4)$$

where:

- C_2 = mole percent gas in test sample,
- MW_g = gram molecular weight of test gas, and
- MW_l = gram molecular weight of test liquid,

10.5 If desired, calculate the Bunsen coefficient of solubility, B , as follows:

$$B = \frac{C_2 \times 22\ 400 \times d_T}{(100 - C_2) MW_l} \quad (5)$$

11. Precision and Bias

11.1 Because of the complex nature of this test method for solubility of fixed gases in low boiling liquids, there is not a sufficient number of volunteers to permit a cooperative laboratory program for determining the precision and bias. If the necessary volunteers can be obtained, a program will be undertaken at a later date.

12. Keywords

12.1 fixed gases; low-boiling liquids; solubility

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Liquid Nitrogen

Warning—Extremely cold. Liberates gas that may cause suffocation. Contact with skin causes burns or freezing, or both. Vapors may react violently with hot magnesium or aluminum alloys.

- Use with adequate ventilation.
- Avoid contact with skin or eyes.
- Do not taste.
- Do not put in closed or stoppered container.
- Do not enter storage areas unless adequately ventilated.

A1.2 Compressed Gases

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.

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