Designation: E659 – 15

Standard Test Method for Autoignition Temperature of Chemicals[1]

This standard is issued under the fixed designation E659; 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.

INTRODUCTION

This test method is one of several methods developed by ASTM Committee E27 for determining the hazards of chemicals. It is designed to be used in conjunction with other tests to characterize the hazard potential of the chemical under test.

1. Scope

1.1 This test method covers the determination of hot- and cool-flame autoignition temperatures of a liquid chemical in air at atmospheric pressure in a uniformly heated vessel.

NOTE 1—Within certain limitations, this test method can also be used to determine the autoignition temperature of solid chemicals which readily melt and vaporize at temperatures below the test temperature and for chemicals that are gaseous at atmospheric pressure and temperature.

NOTE 2—After a round robin study, Test Method D2155 was discontinued, and replaced by Test Method E659 in 1978. See also Appendix X2.

1.2 *This standard should be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2155 Test Method for Determination of Fire Resistance of Aircraft Hydraulic Fluids by Autoignition Temperature

D2883 Test Method for Reaction Threshold Temperature of Liquid and Solid Materials

E659 Test Method for Autoignition Temperature of Liquid Chemicals

3. Terminology

3.1 *Definitions:*

3.1.1 *ignition, n*—the initiation of combustion.

3.1.1.1 *Discussion*—Ignition, which is subjective, is defined for this test method as the appearance of a flame accompanied by a sharp rise in the temperature of the gas mixture. The determination is made in total darkness because some flames, such as cool-flames, are observed with difficulty.

3.1.2 *autoignition, n*—the ignition of a material commonly in air as the result of heat liberation due to an exothermic oxidation reaction in the absence of an external ignition source such as a spark or flame.

3.1.3 *autoignition temperature, n*—the minimum temperature at which autoignition occurs under the specified conditions of test.

3.1.3.1 *Discussion*—Autoignition temperature is also referred to as spontaneous ignition temperature, self-ignition temperature, autogenous ignition temperature, and by the acronyms AIT and SIT. As determined by this test method, AIT is the lowest temperature at which the substance will produce hot-flame ignition in air at atmospheric pressure without the aid of an external energy source such as spark or flame. It is the lowest temperature to which a combustible mixture must be raised, so that the rate of heat evolved by the exothermic oxidation reaction will over-balance the rate at which heat is lost to the surroundings and cause ignition.

3.1.4 *cool-flame, n*—a faint, pale blue luminescence or flame occurring below the autoignition temperature (AIT).

3.1.4.1 *Discussion*—Cool-flames occur in rich vapor-air mixtures of most hydrocarbons and oxygenated hydrocarbons. They are the first part of the multistage ignition process.

3.1.5 *ignition delay time, n*—the time lapse between application of heat to a material and its ignition. It is the time in seconds between insertion of the sample into the flask and ignition. It is maximum at the minimum autoignition temperature and also referred to as ignition lag.

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[1] This test method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.04 on Flammability and Ignitability of Chemicals.

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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.

4. Summary of Test Method

4.1 A small, metered sample of the product to be tested is inserted into a uniformly heated 500-ml glass flask containing air at a predetermined temperature. The contents of the flask are observed in a dark room for 10 min following insertion of the sample, or until autoignition occurs. Autoignition is evidenced by the sudden appearance of a flame inside the flask and by a sharp rise in the temperature of the gas mixture. The lowest internal flask temperature (T) at which hot-flame ignition occurs for a series of prescribed sample volumes is taken to be the hot-flame autoignition temperature (AIT) of the chemical in air at atmospheric pressure. Ignition delay times (ignition time lags) are measured in order to determine the ignition delay-ignition temperature relationship.

4.2 The temperatures at which cool-flame ignitions are observed or evidenced by small sharp rises of the gas mixture temperature are also recorded along with the corresponding ignition delay times. The lowest flask temperature at which cool-flame ignition occurs is taken to be the cool-flame autoignition temperature (CFT). Similarly, observations are made of any nonluminous preflame reactions, as evidenced by a relatively gradual temperature rise which then falls off to the base temperature. The lowest flask temperature at which these reactions are observed is the reaction threshold temperature (RTT).

NOTE 3—The hot-flame autoignition, cool-flame autoignition, and reaction threshold temperatures obtained by this test method approximate those temperatures obtained by Test Method D2883 for hot-flame reaction, cool-flame reaction, and reaction threshold, respectively.

5. Significance and Use

5.1 Autoignition, by its very nature, is dependent on the chemical and physical properties of the material and the method and apparatus employed for its determination. The autoignition temperature by a given method does not necessarily represent the minimum temperature at which a given material will self-ignite in air. The volume of the vessel used is particularly important since lower autoignition temperatures will be achieved in larger vessels. (See Appendix X2.) Vessel material can also be an important factor.

5.2 The temperatures determined by this test method are those at which air oxidation leads to ignition. These temperatures can be expected to vary with the test pressure and oxygen concentration.

5.3 This test method is not designed for evaluating materials which are capable of exothermic decomposition. For such materials, ignition is dependent upon the thermal and kinetic properties of the decomposition, the mass of the sample, and the heat transfer characteristics of the system.

5.4 This test method can be employed for solid chemicals which melt and vaporize or which readily sublime at the test temperature. No condensed phase, liquid or solid, should be present when ignition occurs.

5.5 This test method is not designed to measure the autoignition temperature of materials which are solids or liquids at the test temperature (for example, wood, paper, cotton, plastics, and high-boiling point chemicals). Such materials will thermally degrade in the flask and the accumulated degradation products may ignite.

5.6 This test method can be used, with appropriate modifications, for chemicals that are gaseous at atmospheric temperature and pressure.

5.7 This test method was developed primarily for liquid chemicals but has been employed to test readily vaporized solids. Responsibility for extension of this test method to solids of unknown thermal stability, boiling point, or degradation characteristics rests with the operator.

6. Apparatus

6.1 *Furnace*—An electrically heated crucible furnace or fluidized sand bath of appropriate internal geometry and dimensions to contain the test flask and which will maintain a uniform temperature within the flask shall be used. A furnace with a cylindrically shaped interior, 5 in. (12.7 cm) in inside diameter, and 7 in. (17.8 cm) deep is minimal for this purpose. It should be capable of attaining a temperature of 600°C or higher.

6.2 *Temperature Controller*—A temperature control system, capable of controlling the temperature in the furnace to within ±1°C at temperatures up to 350°C, and to within ±2°C above 350°C, is required. Temperatures are monitored at the bottom, side, and neck of the flask by means of three external thermocouples. Heating adjustments are made when necessary in order to maintain uniform temperature within the flask. If a controller is not available, temperature control may be achieved by the use of suitable autotransformers or rheostats, thermocouples, and a suitable potentiometer.

6.3 *Test Flask*—The test flask shall be a commercial 500-ml borosilicate round-bottom, short-necked boiling flask.

6.3.1 The flask is closely wrapped in reflective metal foil, such as aluminum, to promote temperature uniformity, and is suspended in the furnace so as to be completely enclosed with the top of the neck being inset below the top of the insulated cover (see Fig. 1).

6.3.2 The flask is suspended in the furnace or sand bath by means of a thick insulating holder, the bottom of which is also covered with reflective metal foil.

6.4 *Hypodermic Syringe*—A 500 or 1000-µl hypodermic syringe equipped with a 6-in., No. 26 or finer stainless steel needle, and calibrated in units of 10 µl should be used to inject liquid samples into the heated flask. It is suggested that a needle with a right-angle bend be used so that the operator's fingers can be kept away from the flask opening.

6.5 *Balance*—A laboratory balance capable of weighing to the nearest 10 mg shall be used for preparing samples that are solid at room temperature. Sample weights will range from 10 to 1000 mg.

6.6 *Powder Funnel*—A 60-mm filling funnel is used to aid the insertion of solid samples into the flask. It is suggested that a holder such as a small buret clamp be used so that the operator's fingers can be kept away from the flask opening.

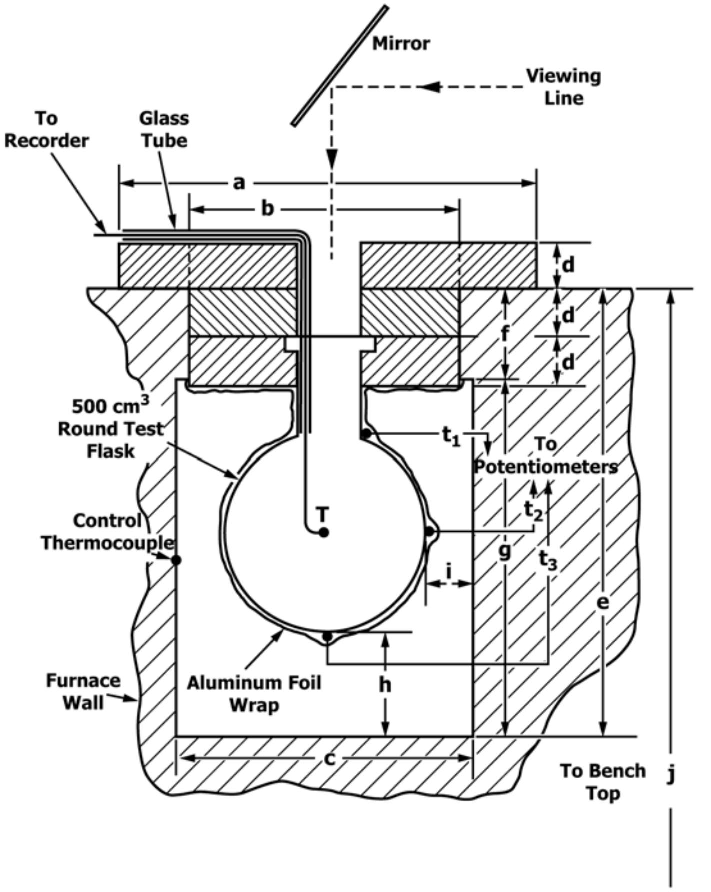

FIG. 1 Autoignition Temperature Apparatus

6.7 *Thermocouple*—A fine Chromel-Alumel thermocouple (36 B and S gage) is used for measuring the gas temperature (T) inside the flask. Position the tip of the thermocouple at the center of the flask. Thermocouples should be calibrated against standard temperatures or a standard thermocouple, and should be rechecked frequently. Iron-constantan thermocouples are to be avoided because they may promote catalytic oxidation on the iron-oxide surface. External flask temperatures are measured with a No. 20 B and S gage or finer thermocouple mounted at the top (t_1), middle (t_2), and bottom (t_3) of the flask.

6.8 *Recording Potentiometer*—A fast response (1 s or less for full scale pen travel) variable range and variable chart speed recording potentiometer shall be used for recording the signal from the internal gas thermocouple (T). An X–Y recorder has been found suitable for this purpose.

6.9 *Timer*—A stop watch or electric timer (preferably foot-switch operated) calibrated in 0.1 or 0.2-s units shall be used to determine the time lag before ignition (time interval between the instant of sample insertion and that of ignition as evidenced by the appearance of the flame). If visual ignition is difficult to observe, the temperature-time recorder trace may be used to estimate the time lag.

6.10 *Mirror*—A 6-in. mirror or other suitable size, mounted above the flask so that the observer may see into the flask without having to be directly over it.

6.11 *Hot-Air Gun*—A suitable hot-air gun may be used to purge the product gases after a reaction is completed and before the next test. A temperature-controlled, hot-air guncan reduce testing time if used to aid in achieving the desired flash temperature between trials and upon insertion of clean test flasks.

7. Safety Considerations

7.1 No explosion hazard is encountered in conducting the determination as outlined in Section 7. However, flames are occasionally emitted well above the top of the flask. Thus, the operator should always use a mirror for observation of the flask interior. The use of a right-angle syringe and, for solids, the use of a holder for the powder funnel will remove the hands from the immediate vicinity of the flask opening.

7.2 It is recommended that the apparatus be installed in a fume hood or be equipped with an exhaust duct to prevent exposure to potentially toxic combustion and decomposition products. All tests with toxic chemicals should involve the use of adequate exhaust ventilation.

7.3 Determinations normally should not be made on potential or known explosive or propellant materials. Where such AIT information is required, the determinations should be made remotely behind a barricade.

8. Procedure

8.1 *Temperature Control*—After the internal flask temperature (T) has reached the desired temperature, adjust the temperature controller to maintain this temperature within the designated limits and allow the system to equilibrate.

8.2 *Lighting*—The lighting before sample insertion should be very subdued. Extinguish the lights as the sample is inserted. Cool-flame tests are generally conducted in total darkness. Eyes should be totally dark-adapted for optimum observation of cool flames.

8.3 *Sample Addition:*

8.3.1 *Liquids*—Inject 100 µl of the sample to be tested into the flask with the hypodermic syringe and quickly withdraw the syringe. Extinguish the lights as the sample is injected.

8.3.2 *Solids*—Insert a 100-mg sample by pouring it from the weighing vessel through the powder funnel which is inserted in the neck of the flask. Quickly withdraw the powder funnel and extinguish the lights.

8.3.3 *Gases*—Inject 100 mg of the sample to be tested into the flask with a syringe (or other means such as one described in Appendix X4) and quickly withdraw the syringe. Extinguish the lights as the sample is injected.

NOTE 4—Ideal gas law, with the average molecular weight of the injected gas, may be used to determine the necessary volume of the test gas to be drawn into the syringe.

NOTE 5—For low molecular weight gases, it may be more appropriate to select the initial test gas volume to be drawn into the syringe from the stoichiometric concentration or from (LFL+UFL)/2. In that case, the search approach provided in 8.5.3 will need to be modified accordingly.

NOTE 6—Low molecular weight gases require addition of large volumes that are appreciable fraction of the test flask volume. In order to minimize the escape of the test gas from the opening, added gas may need to be cooled or liquefied prior to injection.

8.4 *Time Measurement*—Start the timer as the sample is inserted into the flask, and also mark this on the recorder trace. In most cases, the recorder trace of the interior thermocouple will indicate the time of sample injection as a cooling spike.

8.5 *Observations and Subsequent Trials—*Observe the inside of the test flask in total darkness by means of the mirror placed at an appropriate angle above the flask.

8.5.1 If ignition is not observed in 10 min, consider the concentration of the sample tested to be nonflammable at the gas temperature in the flask (Note 7). Completely purge the flask with the hot-air gun. Reset the timer and recorder. Repeat the test at a higher temperature (about 30°C). Allow time for attainment of thermal equilibrium between trials. An elapsed time of 10 min is sufficient. Shorter intervals may be employed for preliminary trials. Thermal equilibrium should be ensured for final trials.

NOTE 7—Most materials ignite in less than 10 min. However, some chemicals (such as saturated cyclic organics) do exhibit long delay times. Initial tests may be conducted employing shorter delay times, but final trials should be based on a 10-min test time.

8.5.2 If positive ignition occurs, stop the timer and record the time interval between sample insertion and ignition as the ignition delay time. Lower the test temperature 30°C and repeat the entire procedure until autoignition is no longer obtained. Narrow the test interval to 3°C and determine the break point between ignition and nonignition.

8.5.3 Repeat the procedure using a larger sample, 150 µl or 150 mg. If ignition occurs at a lower temperature with the increased sample size, repeat the process again using larger samples (200 and 250 µl or mg) until the minimum autoignition temperature is obtained. If ignition occurs only at a higher temperature using the larger samples (those above 100 µl or 100 mg or 0.1 g), then repeat the process using small samples (70 µl or mg, and finally, 50 µl or mg).

8.5.4 Use a new flask for tests on each product. Should the flask become visibly coated with residue before the completion of tests for a given product, conduct the final series of tests with a new flask.

8.6 *Autoignition*—Autoignition is usually evidenced in these tests by hot flames of various colors, usually yellow, red, or blue, but sometimes by cool flames that appear as faint bluish glows which are visible only in total darkness. Normally, the hot flames produce sharp temperature rises of at least a few hundred degrees or more, whereas, the cool flames are accompanied by rises of less than 100°C. Cool flames generally occur at lower flask temperatures than hot flames but may form over an intermediate temperature range, so that the lowest temperature at which any ignition occurs should be recorded. Below these ignition temperatures, nonluminous preflame reactions may occur and are distinguishable by rather weak temperature rises that are barely detectable in some instances.

8.7 *Data—*Record the test temperature, atmospheric pressure, quantity of sample used, ignition delay time, and temperature rise. A plot of ignition delay time versus temperature may be made to assist in determining the autoignition temperature.

8.7.1 A plot of the logarithm of the delay time versus the reciprocal of the absolute temperature normally results in a straight line passing through both the autoignition and cool-flame test results.

9. Report

9.1 The report shall include the following information:

9.1.1 Description of the sample including its physical state at atmospheric conditions.

9.1.2 Atmospheric conditions (barometric pressure, ambient temperature, and relative humidity) pressure at the time and place where tests were conducted.

9.1.3 Hot-flame autoignition temperature, AIT (°C).

9.1.4 Quantity of the sample that resulted in the lowest AIT in the test series.

9.2 The report may also include the following information:

9.2.1 Cool-flame autoignition temperature, CFT (°C).

9.2.2 Reaction threshold temperature, RTT (°C) for preflame reaction.

9.2.3 Corresponding time lags.

10. Precision

10.1 The following criteria should be used for judging the acceptability of results (95 % confidence):

10.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than 2 % of the temperature in degrees Celsius.

10.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if the two results differ by more than 5 % of the temperature in degrees Celsius.

APPENDIXES

(Nonmandatory Information)

X1. APPARATUS

X1.1 Dimensions

X1.1.1 Fig. 1 is a cut-away diagram of a typical test flask installation in a commercial pot-type crucible furnace. Other furnaces or laboratory sand baths capable of maintaining the required temperature uniformity are satisfactory. The following dimensions are for a Heavy-Duty Laboratory Crucible Furnace:[3]

(a)	7 in.	(17.8 cm)
(b)	5 in.	(12.7 cm)
(c)	5½ in.	(14.0 cm)
(d)	1 in.	(2.5 cm)
(e)	10 in.	(25.4 cm)
(f)	1⅞ in.	(4.8 cm)
(g)	8⅛ in.	(20.6 cm)
(h)	2½ in.	(6.4 cm)
(i)	¾ in.	(1.9 cm)
(j)	17 in.	(43.2 cm)

X1.2 Insulated Cover

X1.2.1 The insulated cover is fabricated from mineral insulating block as a split unit to facilitate test flask removal and installation. The cover bottom is lined with aluminum foil.

X1.3 Thermocouples

X1.3.1 Test temperature thermocouple (T) is a bare 36-gage chromel-alumel (Type K) junction located at the center of the test vessel. Proper placement of the junction is facilitated by inserting the leads through properly shaped small diameter glass tubing. The glass tubing should not extend below the flash shoulder into the spherical portion of the flask to avoid flame quenching effects. This thermocouple is fed to the recording potentiometer (see 5.8).

X1.3.2 External flask temperatures are measured with thermocouples t_1, t_2, and t_3 located outside the test vessel and beneath the aluminum foil wrap. These thermocouples can be monitored by a suitable strip chart recorder or manual potentiometer. If the temperature uniformity of the test set-up has been adequately established, as in X1.5, the routine use of exterior thermocouples is not necessary. The three exterior thermocouples are required if a multiple top, sidewall, and bottom heater system is employed to obtain flask temperature uniformity.

X1.3.3 A furnace control thermocouple may be contained in the flask cavity. In the furnace illustrated in Fig. 1, the thermocouple is inset in the face of the furnace refractory, as are the heating elements.

X1.4 Flask Location

X1.4.1 If furnace depth permits, the top of the flask neck should be recessed beneath the top of the insulated cover, positioning the flask near the furnace heater center line, as in Fig. 1. The resulting optimum flask location and minimal heat loss, and the use of the aluminum foil flask overwrap result in excellent flask temperature uniformity.

X1.5 Temperature Uniformity

X1.5.1 The temperatures in Table X1.1 were obtained with the furnace configuration shown in Fig. 1; this furnace contains vertical heaters set in the furnace sidewall around the entire circumference.

TABLE X1.1 Temperature Uniformity

Test Temperature (T), °C	External Flask Temperature, °C		
	t_1	t_2	t_3
81	81	82	82
232	232	236	235
343	342.3	349	347
505	504.5	512	509.5

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[3] The Lindberg Model 56621, available from laboratory equipment suppliers, has been found satisfactory for this purpose. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

X2. EFFECT OF VOLUME ON AIT

X2.1 Numerous investigators[4] have noted that the larger the test vessel the lower is the autoignition temperature. Thus, caution is indicated in applying the temperatures derived by this test method to practical situations.[5,6]

X2.2 The determination of the vessel volume effect involves repeating these procedures in three or more test volumes, such as 250, 500, 1000 and 5000 ml, of the same geometry. A plot of autoignition temperature versus logarithm of the vessel volume can be helpful in estimating the AITs at other volumes.

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[4] Setchkin, N. P., "Self-Ignition Temperatures of Combustible Liquids," Research Paper 2516, *Journal of Research*, National Bureau of Standards, Vol 53, No. 49, 1954.

[5] Zabetakis, M. G., Scott, G. S., and Kennedy, R. E., *Autoignition of Lubricants at Elevated Pressures*, U.S. Bureau of Mines RI 6112, 1962.

[6] Kuchta, J. M., "Summary of Ignition Properties of Jet Fuels and Other Aircraft Combustible Fluids," *Technical Report AFAPL-TR-70*, Air Force Aero Propulsion Laboratory, September 1975.

X3. EFFECT OF PRESSURE ON AIT

X3.1 Increasing the pressure also lowers the AIT, as has been confirmed by numerous investigators.

X4. AN APPARATUS THAT HAS BEEN USED FOR GAS/VAPOR ADDITION

X4.1 An apparatus that has been used for gas/vapor addition is shown in Fig. X4.1.

NOTE X4.1—Rapid, reproducible, and accurate delivery of the test gas is essential for the accuracy of the test results, because the test method seeks to find the lowest AIT corresponding to the optimal (worst case) concentration of the test sample.

X4.2 The setup seen in Fig. X4.1 is comprised of the following items:

X4.2.1 *Sample Vessel*—A vessel of sufficient size shall be used to prepare the gas/vapor mixtures to be tested.

X4.2.2 *Heater and Temperature Controller*—A heating system with a temperature controller shall be used to heat the sample vessel to the desired temperature for preparation of the gas/vapor mixtures. The piping leading from the sample vessel to the test flask shall also be heated to at least the temperature

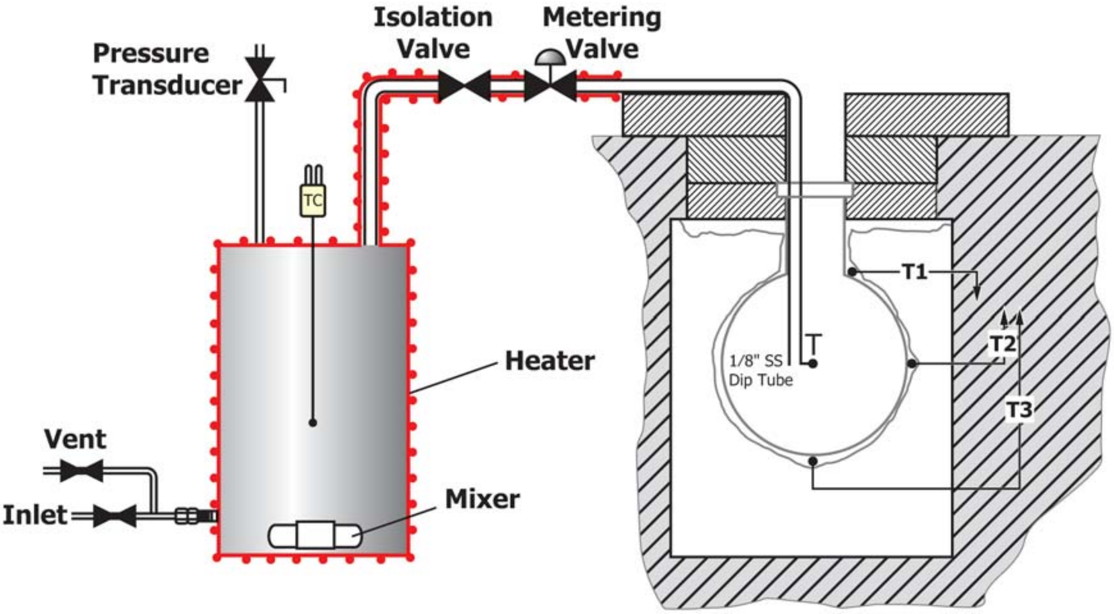

FIG. X4.1 Gas Addition Apparatus

of the sample vessel to minimize condensation within the lines during the sample addition to the test flask.

X4.2.3 *Thermocouple*—A fine gage thermocouple is used to monitor the temperature inside the sample vessel.

X4.2.4 *Pressure Transducer*—A pressure transducer is used for both preparation of the gas mixture inside the sample vessel as well as measuring the change in pressure during the addition of mixture to the test flask.

X4.2.5 *⅛ in. Stainless Steel Dip Tube*—A stainless steel tube having a maximum OD of ⅛ in. shall be used for addition of the gas/vapor mixture to the test flask. The dip tube shall be inserted along the side of the flask and its outlet is positioned in the center of the axial direction of the spherical flask.

X4.2.6 *Quarter Turn Isolation Valve and Check Valve*—An isolation valve shall be used to supply and cutoff the sample mixture from the sample vessel to the test flask. A check valve may be required to be installed between the sample vessel and the test flask to minimize flow back into the sample vessel to minimize.

X4.2.7 *Mixer*—A mixing device shall be incorporated in the sample vessel for tests with multiple component mixtures. During the course of the test, the mixer should be on to help keep the gas/vapor mixture homogenous and minimize any stratification between the components.

X4.2.8 *Flow Meter*—A flow meter or metering valve is used in conjunction with a quarter-turn shut off valve to finely control the amount of sample injected into the test flask.

X4.3 The following test procedure has been used for gas and gas/vapor mixtures:

X4.3.1 The mixture to be tested is to be prepared in the sample vessel through partial pressure addition of each component or by another suitable means. The sample vessel shall be heated if necessary in order to obtain the desired concentration of each component in the mixture.

X4.3.2 Inject a specified amount of the mixture into the test flask (for example, 0.1 psi; actual amount will be dependent on the sample vessel size) by opening the isolation valve between the sample vessel and the test flask. Monitor the amount added to the flask through the change in the pressure reading on the sample vessel. An approximate sample quantity can be calculated from the measured pressure difference in the sample vessel, assuming the mixture behaves as an ideal gas and knowing the volume and temperature of the sample vessel.