Designation: D2766 – 95 (Reapproved 2009)

Standard Test Method for
Specific Heat of Liquids and Solids[1]

This standard is issued under the fixed designation D2766; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope

1.1 This test method covers the determination of the heat capacity of liquids and solids. It is applicable to liquids and solids that are chemically compatible with stainless steel, that have a vapor pressure less than 13.3 kPa (100 torr), and that do not undergo phase transformation throughout the range of test temperatures. The specific heat of materials with higher vapor pressures can be determined if their vapor pressures are known throughout the range of test temperatures.

1.2 The values stated in SI units are to be regarded as the standard. The values given 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *specific heat*—the ratio of the amount of heat needed to raise the temperature of a mass of the substance by a specified amount to that required to raise the temperature of an equal mass of water by the same amount, assuming no phase change in either case.

3.2 *Symbols:*

T_f = temperature of hot zone, °C,
T_c = initial temperature of calorimeter, °C,
T' = $T_f - T_c$ = temperature differential, °C,
R_1 = resistance of nominal 1-Ω standard resistor,
R_{100} = resistance of nominal 100-Ω standard resistor,
$R_{10\,000}$ = resistance of nominal 10 000-Ω standard resistor,
E_1 = emf across nominal 1-Ω standard resistor,
E_{100} = emf across nominal 100-Ω standard resistor,
$E_{10\,000}$ = emf across nominal 10 000-Ω standard resistor,
t_c = time of application of calibration heater current, s,
q = total heat developed by calibration heater, cal,
ΔE_c = total heat effect for container, mV,
ΔE_s = total heat effect for sample + container, mV,
Δe_c = total heat effect for calibration of calorimeter system during container run, mV,
Δe_s = total heat effect for calibration of calorimeter system during sample run, mV,
ΔH_c = total enthalpy change for container changing from T_f to T_c,
ΔH_T = total enthalpy change for sample plus container changing from T_f to T_c,
ΔH_s = total enthalpy change for sample changing from T_f to T_c,
F = calorimeter factor,
W = weight of sample corrected for air buoyancy
d_f = density of sample at T_f,
d_c = density of sample at T_c,
V_T = total volume of sample container,
V_f = volume of sample vapor at T_f,
V_c = volume of sample vapor at T_c,
P_f = vapor pressure of sample at T_f,
P_c = vapor pressure of sample at T_c,
N_f = moles sample vapor at T_f,
N_c = moles sample vapor at T_c,
N = moles sample vapor condensed,
ΔH_v = heat of vaporization of sample,
R = gas constant, and
K = heat of vaporization correction.

3.3 *Units:*

3.3.1 The energy and thermal (heat) capacity units used in this method are defined as follows:

1 cal (International Table) = 4.1868 J

1 Btu (British thermal unit, International Table) = 1055.06 J

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[1] This test method is under jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.L0.07 on Engineering Sciences of High Performance Fluids and Solids (Formally D02.1100).
Current edition approved Oct. 1, 2009. Published November 2009. Originally approved in 1968. Last previous edition approved in 2005 as D2766–95(2005). DOI: 10.1520/D2766-95R09.

[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.

1 Btu/lb °F = 1 cal/g °C
1 Btu/lb °F = 4.1868 J/g K

3.3.2 For all but the most precise measurements made with this method the rounded-off value of 4.19 J/cal can be used as this is adequate for the precision of the test and avoids the difficulty caused by the dual definition of the calorie.

4. Summary of Test Method

4.1 The enthalpy change, ΔH_c, that occurs when an empty sample container is transferred from a hot zone of constant temperature to an adiabatic calorimeter at a fixed initial temperature is measured for selected hot zone temperatures evenly spread over the temperature range of interest.

4.2 The enthalpy change, ΔH_T, that occurs when a container filled with the test specimen is transferred from a hot zone of constant temperature, T_c, to an adiabatic calorimeter at a fixed initial temperature is measured for selected hot-zone temperatures evenly spread over the temperature range of interest.

4.3 The net enthalpy change per gram of sample is then expressed as an analytical power function of the temperature differential T. The first derivative of this function with respect to the actual temperature, T_f, yields the specific heat of the sample as a function of temperature. Actual values of the specific heat may be obtained from solutions of this equation which is valid over the same range of temperatures over which the total enthalpy changes, ΔH_T, were measured.

5. Significance and Use

5.1 The specific heat or heat capacity of a substance is a thermodynamic property that is a measure of the amount of energy required to produce a given temperature change within a unit quantity of that substance. It is used in engineering calculations that relate to the manner in which a given system may react to thermal stresses.

6. Apparatus

6.1 *Drop-Method-of-Mixtures Calorimeter*, consisting essentially of a vertically mounted, thermostatically controlled, tube furnace and a water-filled adiabatic calorimeter. The furnace is mounted with respect to the calorimeter in such a way that it may be swung from a remote position to a location directly over the calorimeter and returned rapidly to the remote position. The sample container may thus be dropped directly into the calorimeter with a minimum transfer of radiation from furnace to calorimeter. Details of construction are shown in Fig. 1.

6.2 *Sample Container*—A stainless steel sample container with a polytetrafluoroethylene seal suitable for use at temperatures up to 533 K (500°F) is shown in Fig. 2.

6.3 *Potential Measuring Devices* (two required), potential measuring device capable of measurement of up to 1 V with a precision of 10^{-6} V or a potentiometer assembly with sensitivity of at least 1 µV or a digital multimeter with equivalent sensitivity, range, and a minimum of six digit resolution is acceptable. A direct reading digital temperature indicating device may be substituted for the potential measuring device
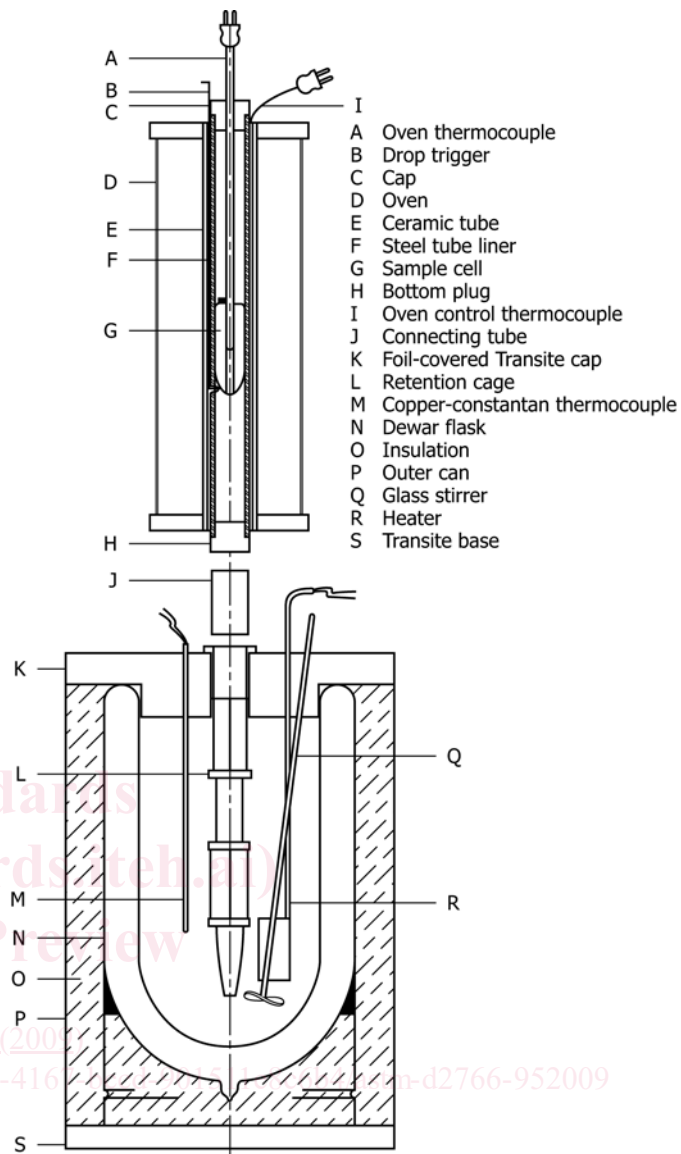

A	Oven thermocouple
B	Drop trigger
C	Cap
D	Oven
E	Ceramic tube
F	Steel tube liner
G	Sample cell
H	Bottom plug
I	Oven control thermocouple
J	Connecting tube
K	Foil-covered Transite cap
L	Retention cage
M	Copper-constantan thermocouple
N	Dewar flask
O	Insulation
P	Outer can
Q	Glass stirrer
R	Heater
S	Transite base

FIG. 1 Specific Heat Apparatus

for the purpose of measuring the temperature of the capsule while in the tube furnace. See Fig. 3.

6.4 *Resistor*, 1-Ω precision type.[3,4]

6.5 *Resistor*, 100-Ω precision type.[3,4]

6.6 *Resistor*, 10 000-Ω precision type.[3,4]

6.7 *Amplifier*, zero centered range, linear response with preset ranges to include ±25 µV, ±100 µV, ±200 µV, ±500 µV, ±1000 µV, and ±2000 µV; with error not to exceed ±0.04 % of output; with zero drift after warm-up not to exceed ±0.5 µV offset within which drift will not exceed ±0.2

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[3] 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.

[4] The sole source of supply of the apparatus known to the committee at this time is Models 9330/1, 9330/100, 9330/10K, Guildline Instruments, Inc., 103 Commerce St., Ste 160, Lake Mary, FL 32795-2590.
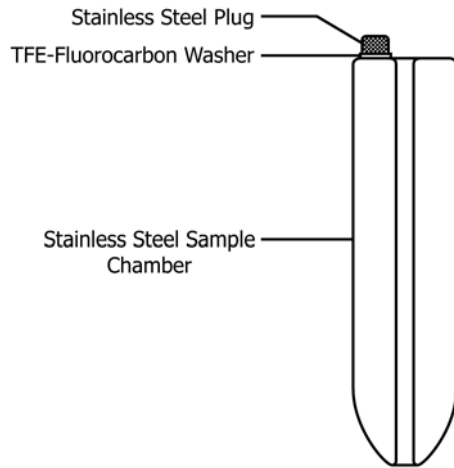
Stainless Steel Plug —

TFE-Fluorocarbon Washer —

Stainless Steel Sample Chamber —

FIG. 2 Specific Heat Sample Cell

µV/min. Equivalent instrumentation with different fixed potential ranges is acceptable provided the same overall potential ranges are covered.

6.8 *Strip Chart Recorder,* with nominal 25 cm chart, ±5 mV, zero center.

6.9 *Binding Posts,* low thermal emf-type, with provision for guard circuit.

6.10 *Rotary Switch,* low thermal emf-type, with provision for guard circuit.

6.11 *Thermistor Bridge.* [3,5]

6.12 *Thermistor.* [3,5]

6.13 *Thermocouple,* copper-constantan, stainless steel sheath, 3.2 mm ($^1/_8$ in.) in outside diameter. [3,6]

6.14 *Power Supply,* 24 V dc.

NOTE 1—Two 12 V automobile batteries in series have proved satisfactory as a power supply. They should be new and fully charged.

6.15 *Power Supply,* constant-voltage, for potentiometer. [3,7]

6.16 *Standard Cell,* unsaturated cadmium type, for potentiometer. [3,8]

7. Calibration

7.1 The enthalpy change, ΔH_c, that occurs when an empty sample container is transferred from the tube furnace at a fixed temperature into the adiabatic calorimeter is not a function only of the composition of the container and the temperature difference between the furnace and the calorimeter. Because heat losses occur as the results of both conduction and radiation from the container during the transfer process, some heat is also transferred by radiation to the calorimeter at the same

time. The measured value of ΔH_c as a function of temperature serves a dual purpose: (*1*) it provides the value of container enthalpy change that must be deducted from ΔH_T to determine ΔH_S; (*2*) simultaneously it affords a correction term that cancels out the effect of conduction and radiation that occur during sample transfer.

7.2 The following procedure is used to determine ΔH_c at each selected temperature for each sample container over the temperature range of interest (Note 3): Bring the empty sample container to a constant temperature in the vertical tube furnace. Monitor its temperature with the copper-constantan thermocouple that is fitted into the center well of the container. While the container is equilibrating, adjust the temperature of the calorimeter by cooling or warming it as required to bring it to a temperature just below the selected initial starting point (Note 4). Adjust the thermistor bridge so that it will have zero output at the selected initial temperature. Any changes of this bridge setting will require recalibration of the system. The amplified output of the thermistor bridge is displayed on the recorder (Note 5). As the calorimeter approaches the selected starting temperature, the output of the bridge becomes less negative and approaches zero (the starting temperature). Just before the output reaches zero, determine the temperature of the capsule by reading the output of the copper-constantan thermocouple to the nearest 1 µV (Note 6). At the moment the calorimeter temperature passes through the selected starting temperature, swing the vertical furnace over the calorimeter and drop the sample container into the calorimeter. Return the furnace immediately to its rest position. As the calorimeter warms, adjust the potentiometer bias to bring the recorded temperature trace on scale. Record the temperature until it resumes a nearly linear drift. Then determine the total heat effect, measured in millivolts, by taking the algebraic sum of the initial and final potentiometer biases and the extrapolated differences in the temperature traces (Note 7). In order to determine the exact energy equivalent of the millivolt change measured during the drop of the container, it is necessary to perform a heater run. This run is made after every drop as the calibration of the system is a function of the size of the heat effect as well as of the water content of the calorimeter. Since the rate of energy input from the electrical heater is of necessity much smaller than that encountered in the drop itself, it is not possible to duplicate the heat effect of the drop exactly. Instead, adjust the temperature of the calorimeter so that the bias of the potentiometer is such that an electrical heat effect of known size will occur over a range intermediate between the initial and final points of the drop (Note 8). During the heater run, measure the current through the heater and the potential drop across the heater by monitoring the potentials across standard resistors R_1 and R_{100}. Measure the time interval of application of heat to the nearest 0.1 s, and determine the change in potential due to the electrical heat effect by taking the algebraic sum of the initial and final potentiometer biases and the extrapolated initial and final temperatures.

NOTE 2—If organic materials are to be studied, it is suggested that fifteen determinations of ΔH_c made at roughly equal intervals over the temperature range from 311 to 533 K (100 to 500°F) will suffice in most instances.

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[5] The sole source of supply of the apparatus known to the committee at this time is VWR, Welch Div., Chicago, IL, under the following catalog number: Thermistor Bridge—No. S-81601; Thermistor—No. S-81620.

[6] The sole source of supply of the apparatus known to the committee at this time is Thermocouple Products Co., Inc., Villa Park, IL.

[7] The sole source of supply of the apparatus known to the committee at this time is No. 245G-NW-19, Instrulab, Inc., Dayton, OH.

[8] The sole source of supply of the apparatus known to the committee at this time is Eppley Laboratory, Inc., Newport, RI.