

# Standard Test Method for Specific Heat of Liquids and Solids<sup>1</sup>

This standard is issued under the fixed designation D 2766; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

## 1. Scope

1.1 This test method covers the determination of the 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:

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer<sup>2</sup>

## 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,
$R_f$	= resistance of nominal 1- $\Omega$ standard resistor,

$R_{100}$	= resistance of nominal 100- $\Omega$ standard resistor,
$R_{10\ 000}$	= resistance of nominal 10 000- $\Omega$ standard resistor,
$E_1$	= emf across nominal 1- $\Omega$ standard resistor,
$E_{1\ 00}$	= emf across nominal 100- $\Omega$ standard resistor,
$E_{10\ 000}$	= emf across nominal 10 000- $\Omega$ standard resistor,
$t_c$	= time of application of calibration heater current, s,
$q$	= total heat developed by calibration heater, cal,
$\Delta E_c$	= total heat effect for container, mV,
$\Delta E_s$	= total heat effect for sample + container, mV,
$\Delta e_c$	= total heat effect for calibration of calorimeter system during container run, mV,
$\Delta e_s$	= total heat effect for calibration of calorimeter system during sample run, mV,
$\Delta H_c$	= total enthalpy change for container changing from $T_f$ to $T_c$ ,
$\Delta H_T$	= total enthalpy change for sample plus container changing from $T_f$ to $T_c$ ,
$\Delta H_s$	= 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,
$\Delta H_v$	= 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
1 Btu/lb °F = 1 cal/g °C
1 Btu/lb °F = 4.1868 J/g K

<sup>1</sup> This test method is under jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.11 on Engineering Science of High Performance Fluids and Solids.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

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,  $\Delta H_c$ , 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,  $\Delta H_T$ , 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,  $\Delta H_T$ , were measured.

**5. Significance and Use**

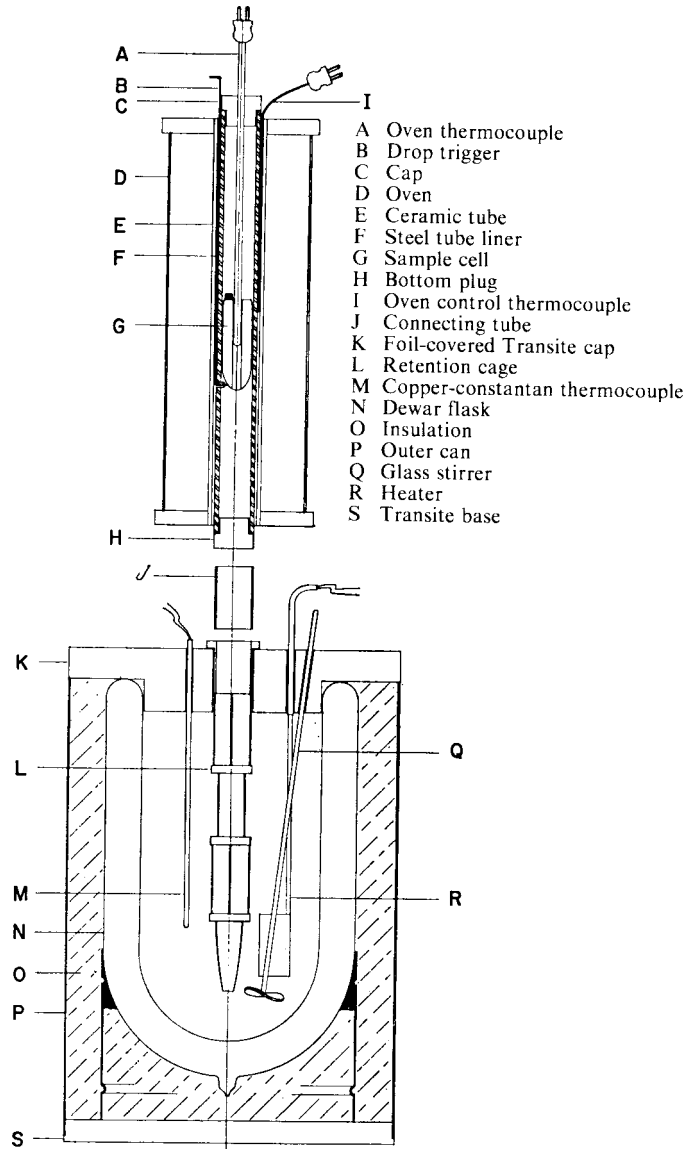
5.1 The specific heat or heat capacity of a substance is a thermodynamic property that is a measure of the amount of energy required to produce a given temperature change within a unit quantity of that substance. It is used in engineering calculations that relate to the manner in which a given system 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  $\mu$ V 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 for the purpose of measuring the temperature of the capsule while in the tube furnace. See Fig. 3.



**FIG. 1 Specific Heat Apparatus**

- 6.4 Resistor, 1- $\Omega$  precision type.<sup>3</sup>
- 6.5 Resistor, 100- $\Omega$  precision type.<sup>3</sup>
- 6.6 Resistor, 10 000- $\Omega$  precision type.<sup>3</sup>
- 6.7 Amplifier, zero centered range, linear response with preset ranges to include  $\pm 25 \mu$ V,  $\pm 100 \mu$ V,  $\pm 200 \mu$ V,  $\pm 500 \mu$ V,  $\pm 1000 \mu$ V, and  $\pm 2000 \mu$ V; with error not to exceed  $\pm 0.04\%$  of output; with zero drift after warm-up not to exceed  $\pm 0.5 \mu$ V offset within which drift will not exceed  $\pm 0.2 \mu$ V/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,  $\pm 5$  mV, zero center.
- 6.9 Binding Posts, low thermal emf-type, with provision for guard circuit.

<sup>3</sup> Models 9330/1, 9330/100, 9330/10K manufactured by Guidelines Instruments, Inc., 103 Commerce St., Ste 160, Lake May, FL 32795-2590. Equivalent instrumentation is acceptable.

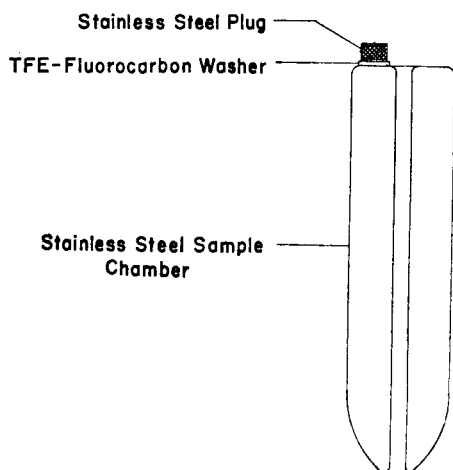


FIG. 2 Specific Heat Sample Cell

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

6.11 *Thermistor Bridge*.<sup>4</sup>

6.12 *Thermistor*.<sup>4</sup>

6.13 *Thermocouple*, copper-constantan, stainless steel sheath, 3.2 mm (1/8 in.) in outside diameter.<sup>5</sup>

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.<sup>6</sup>

6.16 *Standard Cell*, unsaturated cadmium type, for potentiometer.<sup>7</sup>

## 7. Calibration

7.1 The enthalpy change,  $\Delta H_c$ , 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  $\Delta H_c$  as a function of temperature serves a dual purpose: (a) it provides the value of container enthalpy change that must be deducted from  $\Delta H_T$  to determine  $\Delta H_S$ ; (b) 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  $\Delta H_c$  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  $\mu\text{V}$  (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  $\Delta H_c$  made at roughly equal intervals over the temperature range from 311 to 533 K (100 to 500°F) will suffice in most instances.

NOTE 3—The initial temperature is usually selected to be slightly lower than average room temperature so that calorimeter drift due to stirring and deviations from complete adiabaticity will result in a slow, almost linear drift through the selected starting temperature.

NOTE 4—Normally a 50  $\mu\text{V}$  full-scale setting of the amplifier is used and initial potentiometer bias is set at zero.

NOTE 5—Provided that an accurate calibration of the thermocouple is made prior to its use, it should be possible to determine the temperature to the nearest 0.1°C with accuracy.

NOTE 6—To compensate for differences in the initial and final rates of drift, it is good practice to extrapolate both initial and final rates to that

<sup>4</sup> Available from VWR, Welch Div., Chicago, Ill., under the following catalog number: Thermistor Bridge—No. S-81601; Thermistor—No. S-81620. Equivalent instrumentation is acceptable.

<sup>5</sup> Available from Thermocouple Products Co., Inc., Villa Park, IL. Equivalent instrumentation is acceptable.

<sup>6</sup> No. 245G-NW-19 manufactured by Instrulab, Inc., Dayton, Ohio, has been found satisfactory. Equivalent instrumentation is acceptable.

<sup>7</sup> A cell of this type, manufactured by Eppley Laboratory, Inc., Newport, RI, has been found satisfactory. Equivalent instrumentation is acceptable.

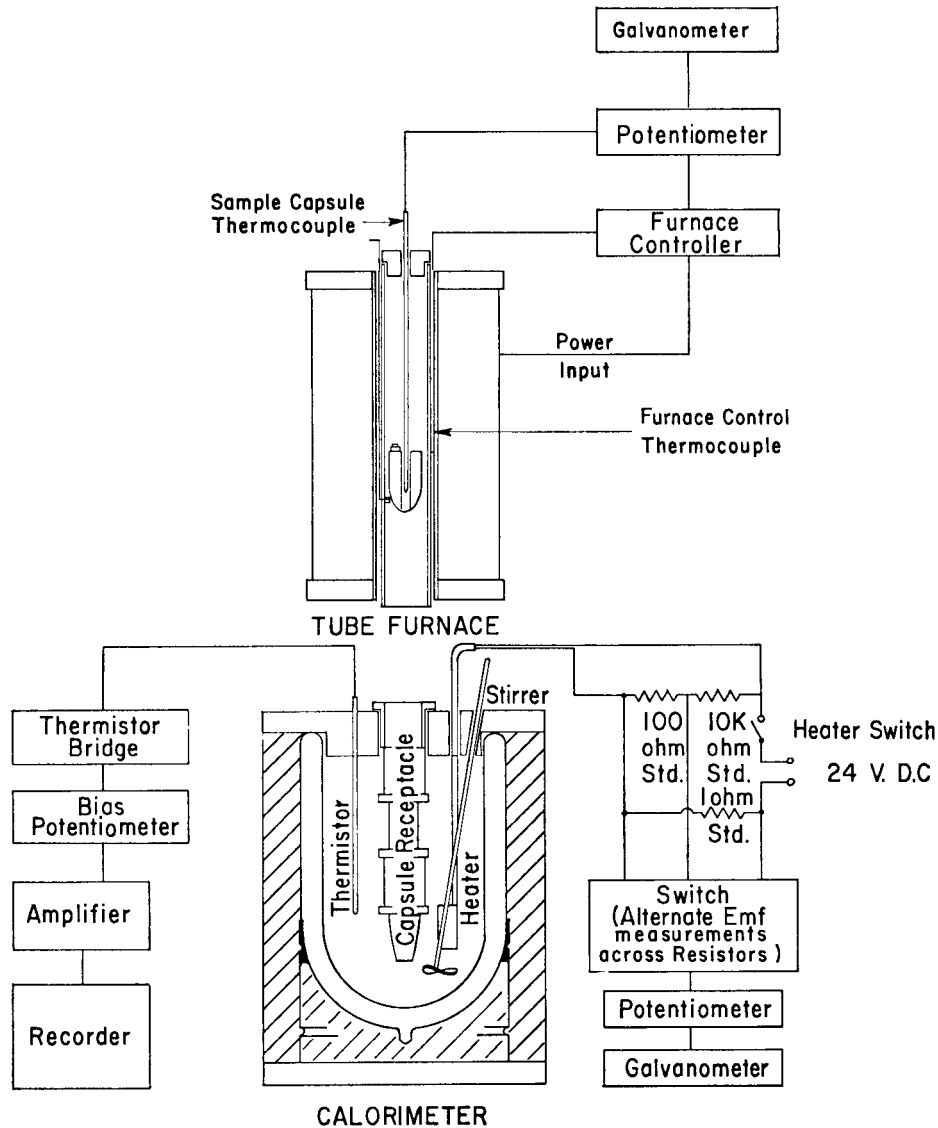


FIG. 3 Specific Heat Measuring and Control Circuit Diagram

point in time at which one half of the total heat effect has occurred. For the heat effect occurring after a drop, it has been found that one half of the total heat effect occurs so rapidly that no significant error occurs in extrapolating the final drift back to the initial time. For heater runs, it is necessary to make an empirical determination of the point at which one half of the heat effect has occurred in order to perform a proper extrapolation.

NOTE 7—Thus, if the total heat effect of the drop is found to be 8 mV and a heater run will cause a change of 2 mV, the initial bias of the heater run should be set at 3 mV so the final point will be 5 mV. This procedure compensates almost completely for the non-linearity of the thermistor. The error incurred if the procedure is followed is sufficiently small to be insignificant even if fairly large (for example, up to 0.5 mV) deviations from the mid-point are allowed.

7.3 Repeat the procedure described in 7.2 for each temperature at which it is desired to calibrate a given sample container.

### 8. Procedure

8.1 Fill the sample container with a weighed amount of the sample. Make appropriate air-buoyancy corrections in determining the weight of the sample following the principles given

in the Preparation of Apparatus section of Test Method D 1217. Repeat the procedure described in 7.2 for each temperature at which it is desired to determine the value of  $\Delta H_T$  for the filled sample container. The number of determinations needed will vary in accordance with the precision required in the result. Normally, a minimum of five determinations is needed over any given temperature range. Expected precision of five data points taken over the range from 311 to 533 K (100 to 500°F) is approximately 5%. Ten data points taken over the same range should produce precision in the result approaching 1%.

NOTE 8—The foregoing procedure is valid for samples that are stable and that have a vapor pressure less than 100 torr over the range of temperatures studied. A modified method for materials that have higher vapor pressures is given in Annex A1.

### 9. Calculation and Report

9.1 Calculate the value of  $\Delta H_c$  for each temperature as follows:

Calculate the energy developed in the electrical heater:

$$q = \frac{E_1}{R_1} \left[ \left( \frac{R_{100} + R_{10,000}}{R_{100}} \right) E_{100} - E_1 \right] \times t_c / 4.186 \quad (1)$$

Calculate the calorimeter factor:

$$F = q / \Delta e_c \quad (2)$$

Calculate the total heat effect in joules (calories):

$$\Delta H_c = F \Delta E_c \quad (3)$$

Plot the experimental values of  $\Delta H_c$  versus the temperature in deg C. Use a scale sufficiently large to allow  $\Delta H_c$  to be read to the nearest 4 J (1 cal) and the temperature to the nearest 0.1°C.

9.2 Calculate the value of  $\Delta H_T$  for each data point as follows:

$$F = q / \Delta e_s \quad (4)$$

$$\Delta H_T = F \cdot \Delta E_s \quad (5)$$

9.3 Calculate the value of  $\Delta H_s$  per gram of sample for each data point as follows:

$$\Delta H_s = (\Delta H_T - \Delta H_c) / W \quad (6)$$

9.4 Using the method of least squares analysis, derive an equation for  $\Delta H_s$  as a function of the temperature differential  $T'$ . The form of the equation shall be:

$$\Delta H_s = BT' + CT'^2 \quad (7)$$

where  $B$  and  $C$  are arbitrary constants given by the solutions of the following equations:

$$\sum_{i=1}^n (\Delta H_s)_i T'_i = B \sum_{i=1}^n T'_i{}^2 + C \sum_{i=1}^n T'_i{}^3 \quad (8)$$

$$\sum_{i=1}^n (\Delta H_s)_i T'_i{}^2 = B \sum_{i=1}^n T'_i{}^3 + C \sum_{i=1}^n T'_i{}^4 \quad (9)$$

9.5 Calculate the specific heat by differentiating the equation for  $\Delta H_s$  with respect to  $T'$ . Obtain an equation for specific heat as a function of  $T_f$  by substituting for the value of  $T'$  in the derivative of  $\Delta H_s$ . Use this equation to determine the values of specific heat of desired temperatures within the range of temperatures covered by the experimental data. The use of equations developed by this method for obtained extrapolated values of specific heat is not recommended.

NOTE 9—If a sample undergoes a phase transformation at a temperature within the range covered by the data points, a discontinuity will appear in  $\Delta H_s$ . In this case the procedures of 9.4 and 9.5 should be applied separately to the data points above and below the discontinuity. Additional data points may be necessary in order to produce a meaningful result. Extrapolation of a plot of  $\Delta H_s$  values to the temperature at which the discontinuity occurs provides a means for determining the heat effect involved in the phase transformation.

## 10. Precision and Bias

10.1 *Precision and Bias*—Because of the complex nature of the procedure for the determination of specific heat and because of the expensive equipment involved in the initial set-up of the procedure, there is not a sufficient number of volunteers to permit a cooperative laboratory program for determining the precision and bias of this test method. If the necessary volunteers can be obtained, a program will be undertaken at a later date.

## 11. Keywords

11.1 heating tests; specific heat

## ANNEX

### (Mandatory Information)

#### A1. PROCEDURE FOR DETERMINING HEAT CAPACITY OF MATERIALS HAVING VAPOR PRESSURES ABOVE 13.3 kPa (100 TORR)

A1.1 The following procedure must be followed in order to ensure that values of  $\Delta H_T$  do not include excessive amounts of heat liberated by the condensation of sample vapors. The correction described below is necessary only when the sample being tested has a vapor pressure greater than 13.3 kPa (100 torr) at the temperature of tests. When the vapor pressure exceeds 13.3 kPa (100 torr) for only part of a temperature range, the correction should be applied only to those points that fall into the high vapor pressure region.

A1.2 The vapor pressure of the sample must be known over the temperature range of interest and at the initial temperature of the calorimeter. The molar heat of vaporization may be determined from the average slope of a plot of the log of the vapor pressure versus reciprocal of absolute temperature using the Clausius-Clapeyron relation. Temperature variation of the heat of vaporization need not be taken into account. The average molecular weight of the sample vapor must also be known. If the exact molecular weight is not known, an approximate molecular weight determined from the approximate chain length expected in the sample shall be used.

A1.3 Accurately determine the total volume of the sample container. Using this value and the weight and the densities of the sample at  $T_f$  and  $T_c$ , calculate the volume of vapor in the capsule at the initial and final temperatures.

$$V_f = V_T - (W/d_f) \quad (A1.1)$$

$$V_c = V_T - (W/d_c) \quad (A1.2)$$

A1.4 From the values of  $V_f$  and  $V_c$  calculated above and the sample vapor pressures, determine the number of moles of vapor present at  $T_f$  and  $T_c$  and by difference, the number of moles of vapor that have condensed. Assume that the vapors obey the ideal gas law.

$$N = N_f - N_c = (P_f V_f / RT_f) - (P_c V_c / RT_c) \quad (A1.3)$$

A1.5 The correction,  $K$ , to be subtracted from  $\Delta H_T$  is then given by

$$K = N \times \Delta H_v \quad (A1.4)$$

A1.5.1 The magnitude of the correction,  $K$ , can be minimized by filling the capsule as completely as possible. Care

shall be taken not to have an entirely liquid-filled system which might rupture on heating.

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