



## Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters<sup>1</sup>

This standard is issued under the fixed designation E 968; 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.

### 1. Scope

1.1 This practice covers the heat flow calibration of differential scanning calorimeters over the temperature range from  $-130^{\circ}\text{C}$  to  $+800^{\circ}\text{C}$ .

1.2 Values given in SI units are to be regarded as the standard.

1.3 Computer or electronic based instruments, techniques or data manipulation equivalent to this practice may also be used.

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 whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See also Section 7.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

E 473 Terminology Relating to Thermal Analysis<sup>2</sup>

E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry<sup>2</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>2</sup>

### 3. Terminology

3.1 *Definitions*—Specific technical terms used in this practice are in accordance with Terminologies E 474 and E 1142.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *coefficient of variation, n*—a measure of relative precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

NOTE 1—The term quantitative differential thermal analysis refers to differential thermal analyzers that are designed to obtain quantitative or semiquantitative heat flow results. This procedure may also be used to calibrate such apparatus.

### 4. Summary of Practice

4.1 Differential scanning calorimeters measure heat flow

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Thermal Analysis Methods.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 1 Sapphire ( $\alpha - \text{Al}_2\text{O}_3$ ) Specific Heat Capacity<sup>A</sup>

Temperature, K	Specific Heat Capacity, J/g·K	Temperature, K	Specific Heat Capacity, J/g·K
140	0.2739	630	1.1184
150	3.3133	640	1.1228
160	0.3523	650	1.1272
170	0.3912	660	1.1313
180	0.4290	670	1.1353
190	0.4659	680	1.1393
200	0.5014	690	1.1431
210	0.5356	700	1.1467
220	0.5684	710	1.1503
230	0.6045	720	1.1538
240	0.6294	730	1.1572
250	0.6578	740	1.1604
260	0.6846	750	1.1604
270	0.7102	760	1.1667
280	0.7344	770	1.1698
290	0.7574	780	1.1727
300	0.7792	790	1.1756
310	0.7999	800	1.1784
320	0.8194	810	1.1811
330	0.8380	820	1.1839
340	0.8555	830	1.1864
350	0.8721	840	1.1890
360	0.8878	850	1.1914
370	0.9027	860	1.1939
380	0.9168	870	1.1962
390	0.9302	880	1.1986
400	0.9429	890	1.2008
410	0.9550	900	1.2031
420	0.9665	910	1.2053
430	0.9775	920	1.2074
440	0.9879	930	1.2095
450	0.9978	940	1.2115
460	1.0073	950	1.2135
470	1.0164	960	1.2153
480	1.0250	970	1.2174
490	1.0332	980	1.2194
500	1.0411	990	1.2212
510	1.0436	1000	1.2230
520	1.0379	1010	1.2249
530	1.0628	1020	1.2266
540	1.0674	1030	1.2284
550	1.0758	1040	1.2301
560	1.0819	1050	1.2318
570	1.0877	1060	1.2335
580	1.0934	1070	1.2351
590	1.0988	1080	1.2364
600	1.1039	1090	1.2383
610	1.1090	1100	1.2400
620	1.1138		

<sup>A</sup>Archer, D.G., *J. Phys. Chem. Ref. Data*, Vol 22, No. 8, pp. 1441–1453 (1993).

(power) into or out of a test specimen and provide a signal output proportional to this measurement. This signal often is recorded as a function of a second signal proportional to temperature or time. If this heat flow signal is integrated over

time, the resultant value is proportional to energy (or enthalpy or heat). To obtain the desired energy information, the observed instrument response (such as the area under the curve scribed) must be multiplied by a proportionality constant that converts the units of instrument output into the desired energy units. This proportionality constant is called the instrument calibration coefficient ( $E$ ). The value and dimensions (units) of  $E$  depend upon the particular differential scanning calorimeter and recording system being used and, moreover, may vary with temperature.

4.2 This practice consists of calibrating the heat flow response of a differential scanning calorimeter (that is, measuring the calibration coefficient) by recording the melting endotherm of a high-purity standard material (where the heat of fusion is known to better than  $\pm 1.5\%$  (rel)) as a function of time. The peak is then integrated (over time) to yield an area measurement proportional to the enthalpy of melting of the standard material.

4.3 Calibration of the instrument is extended to temperatures other than that of the melting point of the standard material through the recording of the specific heat capacity of a (second) standard material over the temperature range of interest. The ratio of the measured specific heat capacity at the temperature of interest to that of the temperature of calibration provides an instrument calibration coefficient at the new temperature.

4.4 Once the calibration coefficient at a given temperature is determined, it may be used to determine the desired energy value associated with an enthalpic transition in an unknown specimen at that temperature (see Method E 793).

## 5. Significance and Use

5.1 Differential scanning calorimetry is used to determine the heat or enthalpy of transition. For this information to be meaningful in an absolute sense, heat flow calibration of the apparatus or comparison of the resulting data to that of a known standard is required.

5.2 This practice is useful in calibrating the heat flow axis of differential scanning calorimeters or quantitative differential thermal analyzers for subsequent use in the measurement of transition energies and specific heat capacities of unknowns.

## 6. Apparatus

6.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes:

6.1.1 A *DSC test chamber*, composed of the following:

6.1.1.1 A furnace(s) to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate with the temperature range of  $-100$  to  $600^\circ\text{C}$ .

NOTE 2—This temperature range may be extended to higher and lower temperatures depending upon the capabilities of the apparatus.

6.1.1.2 A *temperature sensor*, to provide an indication of the specimen/furnace temperature to  $\pm 0.01\text{ K}$ .

6.1.1.3 A *differential sensor*, to detect a heat flow (power) difference between the specimen and reference equivalent to  $1\ \mu\text{W}$ .

6.1.1.4 A means of sustaining a *test chamber environment*, of an inert purge gas at a purge gas rate of 10 to 100 mL/min  $\pm 5\text{ mL/min}$ .

NOTE 3—Typically, 99.9+ % pure nitrogen, argon or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended and is essential for operation at subambient temperatures.

6.1.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of between 1 and 35 K/min constant to  $\pm 1\%$  and at an isothermal temperature constant to  $\pm 0.1\text{ K}$ .

6.1.3 A *recording device*, either digital or analog, capable of recording and displaying the heat flow (DSC curve) signal versus temperature, displaying any fraction including the signal noise.

6.1.4 *Containers*, (pans, crucibles, vials, etc. and associated lids), that are inert to the specimen and reference materials and that are of suitable structural shape and integrity to contain the specimen and reference.

NOTE 4—Most containers require special tool(s) for opening, closing or sealing. The specific tool(s) necessary to perform this action also are required.

6.1.5 *Cooling capability*, to achieve and sustain cryogenic temperatures, to hasten cool down from elevated temperatures, or to provide constant cooling rates, or a combination thereof.

6.1.6 Computer and software capability to perform the mathematical treatments of this method including peak integration.

6.2 A *balance*, with capacity of 100 mg to weight specimens, or containers, or both, to  $\pm 1\ \mu\text{g}$ .

## 7. Precautions

7.1 Toxic or corrosive effluents, or both, may be released when heating some material and could be harmful to personnel and apparatus.

## 8. Reagents and Materials

8.1 For the temperature range covered by many applications, the melting transitions of the following greater-than-99.9 % pure material may be used for calibration.

	Melting Temperature, $\text{K}^3$	Heat of Fusion, $\text{J/g}^4$
Indium	429.8	$28.42 \pm 0.36$

8.2 *Sapphire*, ( $\alpha\text{-Al}_2\text{O}_3$ ), 20 to 80 mg, solid disk.

## 9. Calibration

9.1 Perform any calibration procedures described by the manufacturer in the operations manual.

9.2 Perform a temperature signal calibration according to Practice E 967.

## 10. Procedure

10.1 *Calibration at a specific temperature*—The following

<sup>3</sup> Rossini, F. D., *Pure Applied Chemistry*, Vol 22, 1970, p. 557.

<sup>4</sup> Hultgren, R. et al, *Selected Values of Thermodynamic Properties of the Elements*, American Society of Metals, Metals Park, OH, 1973.