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BSI Standards Publication

Fine ceramics (advanced ceramics, advanced technical ceramics) — Thermophysical properties of ceramic composites — Determination of specific heat capacity

National foreword

This British Standard is the UK implementation of EN ISO 19628:2021. It is identical to ISO 19628:2017. It supersedes BS EN 1159-3:2003 and BS ISO 19628:2017, which are withdrawn.

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A list of organizations represented on this committee can be obtained on request to its committee manager.

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Fine ceramics (advanced ceramics, advanced technical ceramics) - Thermophysical properties of ceramic composites - Determination of specific heat capacity (ISO 19628:2017)

Céramiques techniques - Propriétés thermophysiques des composites céramiques - Détermination de la capacité thermique specifique (ISO 19628:2017)

Hochleistungskeramik - Thermophysikalische Eigenschaften von keramischen Verbundwerkstoffen - Bestimmung der spezifischen Wärmekapazität (ISO 19628:2017)

This European Standard was approved by CEN on 22 February 2021.

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European foreword

The text of ISO 19628:2017 has been prepared by Technical Committee ISO/TC 206 "Fine ceramics" of the International Organization for Standardization (ISO) and has been taken over as EN ISO 19628:2021 by Technical Committee CEN/TC 184 “Advanced technical ceramics” the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2021, and conflicting national standards shall be withdrawn at the latest by September 2021.

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Endorsement notice

The text of ISO 19628:2017 has been approved by CEN as EN ISO 19628:2021 without any modification.

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www .org/directives).

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This document was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Thermophysical properties of ceramic composites — Determination of specific heat capacity

1 Scope

This document describes two methods for the determination of the specific heat capacity of ceramic matrix composites with continuous reinforcements (1D, 2D, 3D).

Unidirectional (1D), bi-directional (2D) and tridirectional (XD, with $2 < x \leq 3$).

The two methods are:

- method A: drop calorimetry;
- method B: differential scanning calorimetry.

They are applicable from ambient temperature up to a maximum temperature, depending on the method: method A can be used up to 2 250 K, while method B is limited to 1 900 K.

NOTE Method A is limited to the determination of an average value of the specific heat capacity over a given temperature range and can give a larger spread of results.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 19634, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Ceramic composites — Notations and symbols*

IEC 60584-1, *Thermocouples — Part 1: Reference tables*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 19634 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www .org/obp

3.1
specific heat capacity
C_p
amount of heat required to raise the temperature of a mass unit of material by 1 K at constant temperature and pressure

$$C_p = \frac{1}{m}\frac{dQ}{dT}$$

where Q is the heat required for a test-piece of mass m.

3.2
mean specific heat capacity
$\overline{C}_\mathrm{p}$
amount of heat required to raise the temperature of a mass unit of a material from temperature T_1 to temperature T_2 at a constant pressure, divided by the temperature increase ($T_2 - T_1$) expressed in K

3.3
representative volume element
RVE
minimum volume which is representative of the material considered

4 Method A – drop calorimetry

4.1 Principle

A test piece is dropped from a conditioning chamber at a constant temperature T_1 to another chamber at a constant temperature T_2.

The mean specific heat capacity is determined from the measured amount of heat required to maintain the temperature constant in the second chamber. Transfer of the test piece shall be done under conditions as close as possible to adiabatic conditions.

4.2 Apparatus

4.2.1 Drop calorimeter, there are several types of drop calorimeters. They include one (or more) conditioning chambers and measuring chambers, which can be operated under controlled atmosphere and which are all equipped with a temperature control system that allows a temperature stability of less than 1 K.

The conditioning chamber shall have a homogeneous temperature zone size greater than the test specimen size. The measuring chamber shall have a homogeneous temperature zone of a sufficient length to accept several specimens and a sufficient thermal inertia to limit the temperature disturbance, due to the drop.

Heat transfer by radiation during the drop shall be avoided as far as possible.

4.2.2 Balance, with an accuracy of 0,1 mg for test pieces over 10 mg and an accuracy of 0,01 mg for test pieces below 10 mg.

4.2.3 Temperature detectors, thermocouples in accordance with IEC 60584-1 shall be used for the measurement of temperature up to 1 920 K.

For higher temperatures, infrared detectors or any other suitable device may be used.

4.2.4 Data acquisition system, the sampling period during the test shall be less than 0,5 s.

4.3 Standard reference materials

Standard reference materials which can be used for calibration purposes are listed in Annex B.

4.4 Test specimens

The test specimens shall be representative of the material.

This criterion is generally met by test specimens containing the maximum number of representative volume elements compatible with the volume of the crucible. If this number is less than five, several solutions are possible:

a) the test specimens should have an exact number of representative volume elements;

b) the material should be cut into specimens; a number of similar test specimens should be tested and an average value determined.

4.5 Calibration of calorimeter

4.5.1 General

Calibration of calorimeters may be done according to two different methods. The first consists of dissipating a known amount of thermal power using a calibrated resistor introduced in the second chamber of the calorimeter. In the second method a reference specimen with known specific heat capacity is dropped according to the procedure described in 4.6.

4.5.2 Electrical calibration

The calibration factor is the ratio of a known amount of thermal power dissipated in the resistor to the steady-state calorimetric output signal, and is measured at temperature T_2.

NOTE 1 The method using power dissipation in a resistor is limited to 1 350 K.

NOTE 2 This method can only be used if the sensitivity of the calorimeter is not affected by the filling of the measuring chamber.

4.5.3 Calibration using standard reference material

This calibration is called “drop calibration”. A specimen made of a standard reference material with a known specific heat capacity is dropped according to the test procedures described in 4.6. (See Annex B for standard reference material.) The calibration factor is determined according to Annex A.

4.6 Test procedures

4.6.1 Test without a crucible

4.6.1.1 Test with drop calibration

The test without a crucible and with drop calibration is done in the following order:

R, T, R, T, R, T, R

where

R is the test of standard reference material;

T is the test of test specimen.

Carry out each test as described in 4.6.3.

4.6.1.2 Test with electrical calibration

The test without a crucible and with calibration using power dissipation in a resistor is done in the following order:

— calibration of calorimeter;

— test on three test specimens.

Carry out each test as described in 4.6.3.

NOTE The avoidance of interaction between the test specimen and the calorimetric conditioning and measuring chambers can require the use of a sealed crucible.

4.6.2 Test with a crucible

4.6.2.1 General

The mass of all empty crucibles used for the test shall not differ by more than 5 %.

4.6.2.2 Test with drop calibration

The test with a crucible and with drop calibration is carried out in the following order:

C, C + R, C + T, C, C + R, C + T, C, C + R, C + T, C

where

C is the test with the empty crucible;

C + R is the test of crucible plus standard reference material;

C + T is the test of crucible plus test specimen.

Carry out each test as described in 4.6.3.

4.6.2.3 Test with electrical calibration

The test with a crucible and with calibration using power dissipation in a resistor is done in the following order:

— calibration of calorimeter;

— carry out the following sequence:

C, C + T, C, C + T, C, C + T, C

where

C is the test with the empty crucible;

C + T is the test with crucible plus test specimen.

Carry out each test as described in 4.6.3.

4.6.3 Description of test

The test piece (test specimen, standard material or empty crucible) and reference material shall be dried at (110 ± 5) °C until the difference in weight of two successive weighings is lower than 0,2 mg:

— measure the mass when a crucible is not used with an accuracy of ± 0,1 mg or ± 0,1 %, whichever is the smaller;

— when a crucible is used, measure the mass of each assembly dropped (empty crucible, crucible and standard reference material, crucible and test specimen);

- place the test piece (test specimen, standard material or empty crucible) in the conditioning chamber at temperature T_1 and wait for a sufficient period (around 15 min) to reach thermal equilibrium of the test piece with its environment;
- measure T_1 and T_2;
- start recording the calorimetric signal before the test piece is dropped;
- drop the test piece;
- stop the recording when the steady-state output signal is reached.

4.7 Calculations

4.7.1 General

The change in heat Q corresponding to the drop of the test piece is related to the area A under the calorimetric output signal by the following equation.

$$Q = K \cdot A$$

where K is the calorimeter calibration factor.

4.7.2 Determination of the calorimetric calibration factor

4.7.2.1 Electrical calibration

See Annex A.

$$K = \frac{\text{heat dissipated}}{\text{area under the calorimetric output signal}} = \frac{H}{A}$$

4.7.2.2 With standard reference material

See Annex B.

4.7.3 Determination of mean specific heat capacity $\overline{C_\mathrm{p}}$

The mean specific heat capacity is determined using the following formula:

$$\overline{C_\mathrm{p}}(T_1, T_2) = \frac{1}{m_\mathrm{i}} \frac{Q_\mathrm{i}(T_1, T_2)}{(T_2 - T_1)}$$

where

T_1	is the initial temperature at which test pieces are conditioned;
T_2	is the calorimeter temperature;
$Q_\mathrm{i}(T_1, T_2)$	is the heat variation between T_1 and T_2;
m_i	is the mass of the test piece, determined by weighing;
$\overline{C_\mathrm{p}}(T_1, T_2)$	is the mean specific heat capacity between T_1 and T_2.

The subscript i has a different meaning depending on the type of test piece:

- i = c for an empty crucible;
- i = t for a test piece;
- i = t + c for a test piece and crucible.

without crucible

$$\overline{C_{\mathrm{pt}}} = \frac{K \cdot A_{\mathrm{t}}}{m_{\mathrm{t}}\left(T_2 - T_1\right)}$$

with crucible

$$\overline{C_{\mathrm{pt}}} = \frac{K\left(A_{\mathrm{c+t}} - A_{\mathrm{c}}\right)}{m_{\mathrm{t}}\left(T_2 - T_1\right)}$$

where

A_{t} is the value of integration of calorimetric output signal of test specimen;

A_{c} is the value of integration of calorimetric output signal of crucible;

$A_{\mathrm{c+t}}$ is the value of integration of calorimetric output signal of test specimen plus crucible.

5 Method B – differential scanning calorimetry

5.1 Principle

5.1.1 General

The method consists in measuring the difference in power needed to raise the temperature of the test specimen in its crucible and of an empty identical crucible using the same heating programme, which may be stepwise heating or continuous heating.

Stepwise heating allows only the determination of the mean specific heat capacity $\overline{C_{\mathrm{p}}}\left(T_1, T_2\right)$ over a temperature range (T_1,T_2), whereas continuous heating allows determination of the specific heat capacity C_{p} at a given temperature.

5.1.2 Stepwise heating method

The mean specific heat capacity $\overline{C_{\mathrm{p}}}\left(T_1, T_2\right)$ is measured in a temperature interval defined by two isothermal levels, T_1 and T_2. The heat, Q_{E}, which is necessary to change the temperature from T_1 to T_2 is determined by integrating the thermal power, P_{E}, with respect to time. The corresponding heat, Q_{E}, is:

$$Q_{\mathrm{E}} = \int_o^t P_{\mathrm{E}} dt = (m_{\mathrm{t}} \overline{C_{\mathrm{p}}}(T_1, T_2) + C_{\mathrm{c}} + C_{\mathrm{o}})(T_2 - T_1)$$

where

m_{t}	is the mass of the test specimen;
$\overline{C_{\mathrm{p}}}(T_1, T_2)$	is the mean specific heat capacity of the test specimen;
C_{o}	is the heat capacity of the calorimeter;
C_{c}	is the heat capacity of the crucible.

Another experiment for the determination of the baseline is performed using an identical imposed heating sequence with the empty crucible. The corresponding heat, Q_{B}, is given by:

$$Q_{\mathrm{B}} = \int_o^t P_{\mathrm{B}} dt = \left[C_{\mathrm{c}} + C_{\mathrm{o}}\right](T_2 - T_1)$$

From the above equations, the mean specific heat capacity can be calculated as:

$$\overline{C_{\mathrm{p}}}(T_1 - T_2) = \frac{Q_{\mathrm{E}} - Q_{\mathrm{B}}}{m_{\mathrm{t}}(T_2 - T_1)}$$

5.1.3 Continuous heating method

Temperature is increased linearly versus time at a constant heating_rate ß. Using the same notation as in 5.1.2, the thermal power P_{E} supplied to the system at every moment is:

$$K \cdot S_{\mathrm{c+t}} = \left(m_{\mathrm{t}} C_{\mathrm{p}} + C_{\mathrm{c}} + C_{\mathrm{o}}\right)\beta$$

Another experiment for the determination of the baseline is performed with the empty crucible. The corresponding thermal power is given by

$$K \cdot S_{\mathrm{c}} = (C_{\mathrm{c}} + C_{\mathrm{o}})\beta$$

The specific heat capacity can be calculated from:

$$C_{\mathrm{p}} = \frac{K(S_{\mathrm{c+t}} - S_{\mathrm{c}})}{m_{\mathrm{t}}\beta}$$

where

K	is the calibration factor;
S_{c}, $S_{\mathrm{c+t}}$	are the output signals;
$K \cdot S_{\mathrm{c}}$ and $K \cdot S_{\mathrm{c+t}}$	are the thermal powers supplied to the system.

5.2 Apparatus

5.2.1 Differential scanning calorimeter.

5.2.1.1 There are two types of differential scanning calorimeters operating on power compensation and heat flux principles, both designed to operate under adiabatic conditions.

Both comprise two measuring cells housed in a furnace which provides overall system heating. One cell contains the test specimen and its crucible, the other contains an empty crucible only.

5.2.1.2 Power compensation type: each cell has an additional heater to compensate for the temperature variations from the overall heating programme. The power which is supplied to either cell heater to maintain equal temperatures during heating is measured.

5.2.1.3 Heat flux type: power is exchanged between each cell and its respective surrounding during the heating programme. The difference in power exchange between the two cells is measured.

5.2.2 **Balance**, with an accuracy better than 0,1 mg.

5.2.3 **Temperature detectors**, thermocouples in accordance with IEC 60584-1 shall be used for the measurement of temperature.

5.2.4 **Data acquisition system**, the time duration between two successive measurements shall be less than 0,5 s.

5.3 Standard reference materials, SRM

Standard reference materials shall be used for calibration. An example is given in Annex B.

5.4 Test specimens

The test specimens shall be representative of the material.

This criterion is generally met by test specimens containing the maximum number of representative volume elements compatible with the volume of the crucible. If this number is less than five, several solutions are possible:

a) the test specimens should have an exact number of representative volume elements;

b) the material should be cut into pieces, and a number of similar test pieces should be tested and an average value determined.

5.5 Temperature calibration

A temperature calibration curve for the furnace using the same heating rate as for the determination of the specific heat capacity is established by using the melting points of standard reference materials (see, for example, Annex C).

Thermocouples shall be calibrated in accordance with IEC 60584-1.

5.6 Test procedure for the determination of C_p

5.6.1 General

Depending on the necessity or not of using a calibration factor K for the calorimeter, two methods can be used:

Method 1: measurements requiring the knowledge of the K factor; in this case, care shall be taken in order to ensure that the calibration is valid for all the measurements to be taken.

NOTE Generally, this can be done by running a test using a test specimen with well-known properties.

Method 2: measurements requiring the use of a reference standard material during a series of tests.

5.6.2 Method 1: Measurements requiring the knowledge of the K factor

5.6.2.1 Determination of the K factor

The calibration factor K is obtained by electrical calibration. It is determined from the ratio of a known amount of power dissipated in a resistor to the steady-state calorimetric output signal.

5.6.2.2 Measurements with the specimen for the determination of the C_p

5.6.2.2.1 General

A series of measurements shall always be referenced to a baseline measurement performed under experimental conditions identical to the other measurements in the series. The type of crucible used depends on the type of test specimen and on the temperature range, and shall be the same for the series of measurements. The mass of all empty crucibles used in the series shall not differ by more than 5 %.

5.6.2.2.2 Test sequence for the stepwise heating method (see Figure 1)

5.6.2.2.2.1 Generation of the baseline

See Figure 1.

a) weigh the two empty crucibles to the nearest 0,1 mg;

b) place the two crucibles in the calorimeter;

c) set the calorimeter heating rate, initial and final temperature, and cooling rate;

NOTE Generally, the heating rate is in the range 1 K/min to 20 K/min.

d) heat to an initial temperature, and wait for the temperature to be stabilized at the initial temperature;

e) heat at a constant rate to final temperature of the first step while recording the calorimeter output signal, until the final temperature is reached and stabilized in order to obtain a baseline;

f) repeat c) to e) for the number of steps required;

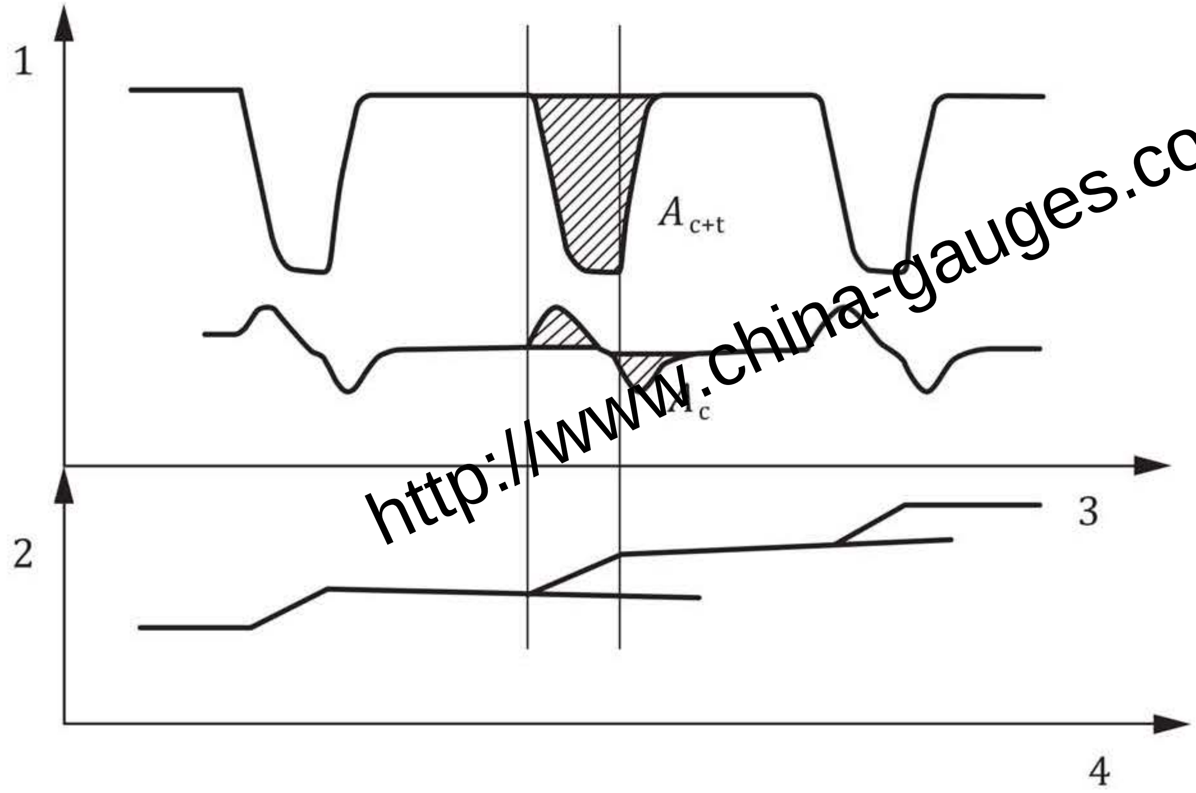
g) cool down to initial temperature;

h) remove the crucibles from the measurement cell.

5.6.2.2.2.2 Measurements using a test specimen

See Figure 1.

Weigh the test specimen and place it in the crucible to be located in the measurement cell. Repeat operations b) to h) from 5.6.2.2.2.1 on generation of the baseline. Repeat this procedure for a minimum of three test specimens.



Key

1	output signal
2	temperature
3	time
4	time

Figure 1 — Stepwise heating method (with calibration factor)

5.6.2.2.3 Test sequence for the continuous heating method

5.6.2.2.3.1 Generation of the baseline

See Figure 2.

a) weigh the two empty crucibles to the nearest 0,1 mg;

b) place the two crucibles in the calorimeter;

c) set the calorimeter heating rate, initial and final temperature, and cooling rate;

NOTE Generally, the heating rate is in the range 1 K/min to 20 K/min.

d) heat to an initial temperature, and wait for the temperature to be stabilized at the initial temperature;

e) heat at a constant rate to final temperature of the first step, while recording the calorimeter output signal, until the final temperature is reached and stabilized in order to obtain a baseline;

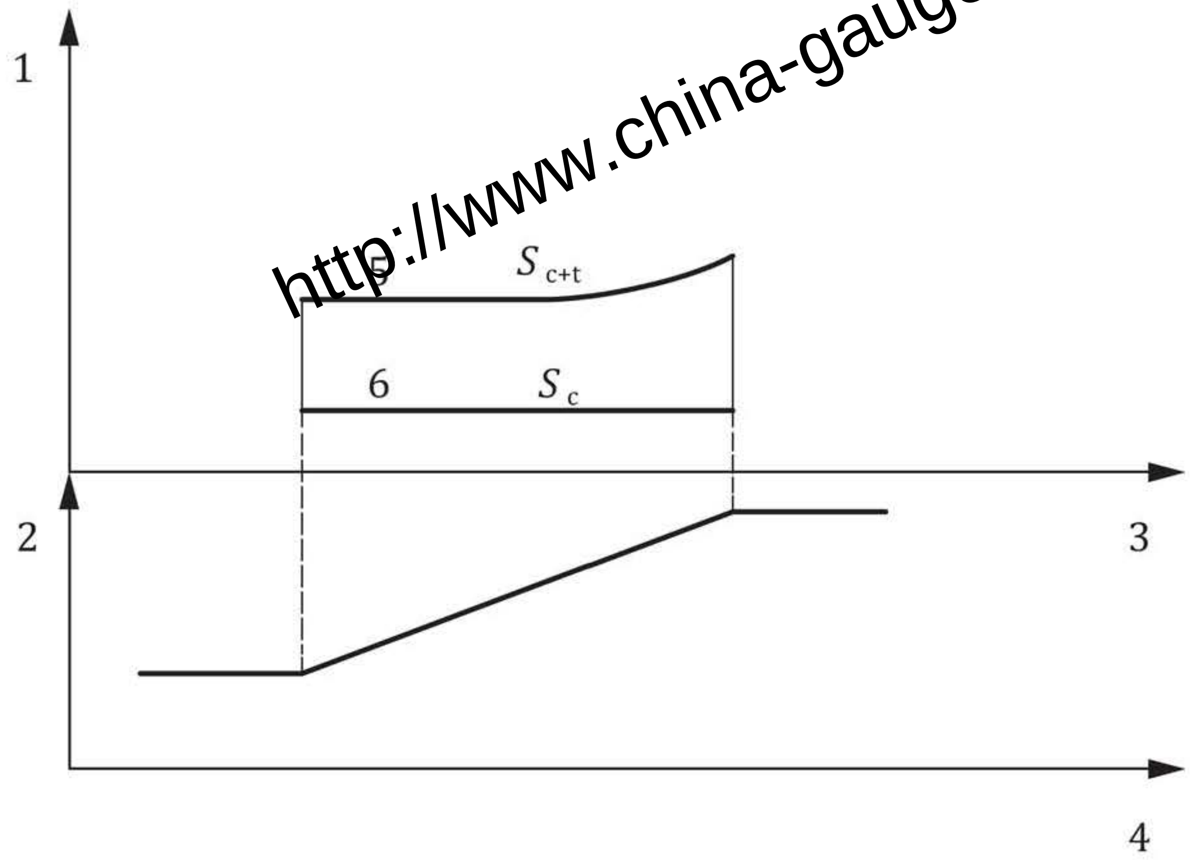
f) cool down to initial temperature;

g) remove the crucibles from the measurement cell.

5.6.2.2.3.2 Measurements using a test specimen

See Figure 2.

Weigh the test specimen and place it in the crucible to be located in the measurement cell. Repeat operations b to g of the above paragraph on generation of the baseline. Repeat this procedure for a minimum of three test specimens.



Key

1	output signal	4	time
2	temperature	5	test piece
3	time	6	baseline

Figure 2 — Continuous heating method (with calibration factor)

5.6.3 Method 2: measurements requiring the use of a reference standard material (SRM)

5.6.3.1 General

The two methods described in 5.6.3.2 and 5.6.3.3 each require:

- measurements with two empty crucibles for the generation of the baseline;
- measurements with one empty crucible and one crucible with the SRM;
- measurements with one empty crucible and one crucible with the test specimen.

5.6.3.2 Test sequence for the stepwise heating method

5.6.3.2.1 Generation of the baseline

See Figure 3.

a) weigh the two empty crucibles to the nearest 0,1 mg;

b) place the two crucibles in the calorimeter;

c) set the calorimeter heating rate, initial and final temperature and cooling rate;

NOTE Generally, the heating rate is in the range 1 K/min to 20 K/min.

d) heat to an initial temperature, and wait for the temperature to be stabilized at the initial temperature;

e) heat at a constant rate to final temperature of the first step, while recording the calorimeter output signal, until the final temperature is reached and stabilized in order to obtain a baseline;

f) repeat c) to e) for the number of steps required;

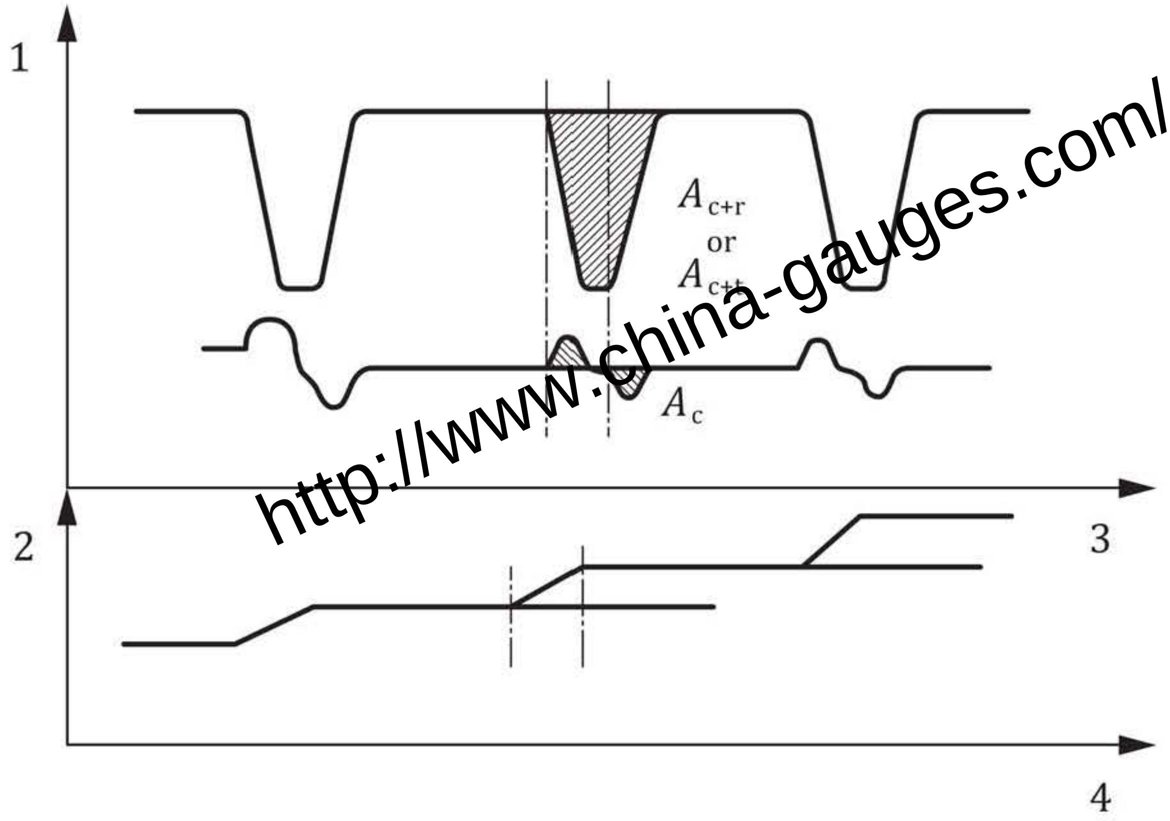
g) cool down to initial temperature;

h) remove the crucibles from the measurement cell.

5.6.3.2.2 Measurement with a test specimen or with a SRM

See Figure 3.

Weigh the test specimen or the SRM and place it in the crucible to be located in the measurement cell. Repeat operations b) to h) from 5.6.3.2.1 on generation of the baseline. Repeat this procedure for a minimum of three test specimens.



Key

1	output signal
2	temperature
3	time
4	time

Figure 3 — Stepwise heating method (with standard reference material)

5.6.3.3 Test sequence for continuous heating method

5.6.3.3.1 Generation of the baseline

See Figure 4.

a) weigh the two empty crucibles to the nearest 0,1 mg;

b) place the two crucibles in the calorimeter;

c) set the calorimeter heating rate, initial and final temperature, and cooling rate;

NOTE Generally, the heating rate is in the range 1 K/min to 20 K/min.

d) heat to an initial temperature, and wait for the temperature to be stabilized at the initial temperature;

e) heat at a constant rate to final temperature of the first step, while recording the calorimeter output signal, until the final temperature is reached and stabilized in order to obtain a baseline;

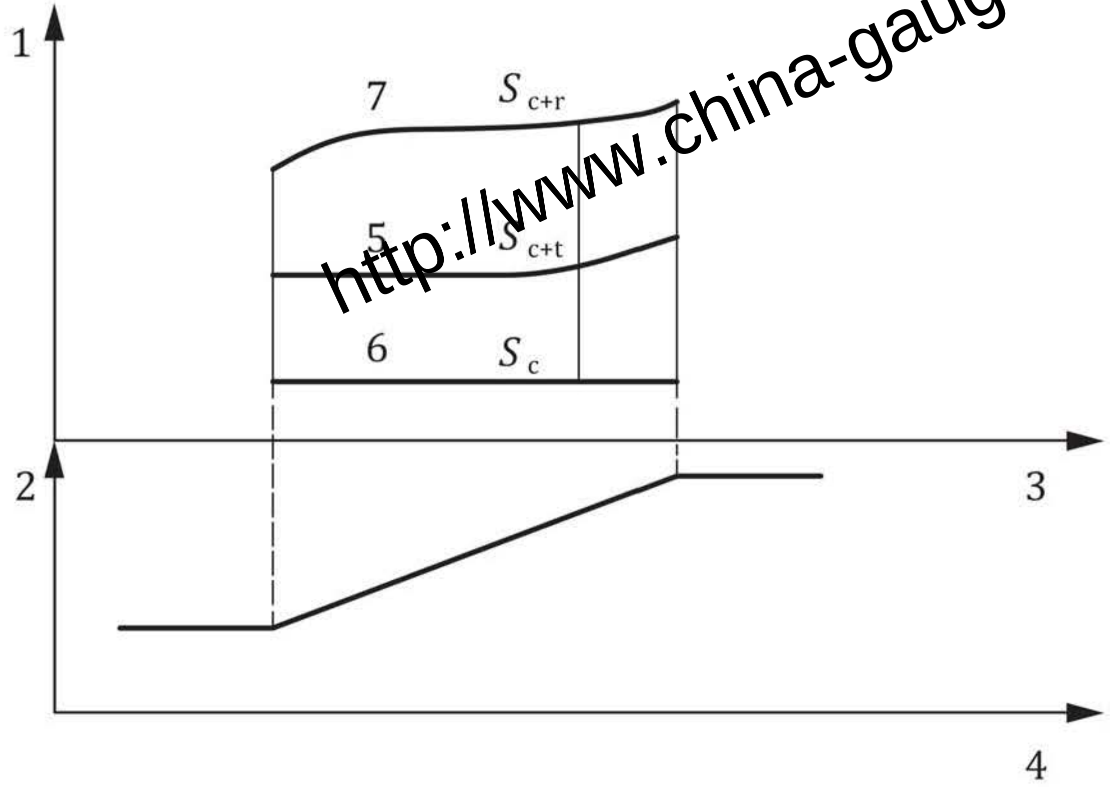
f) cool down to initial temperature;

g) remove the crucibles from the measurement cell.

5.6.3.3.2 Measurements using a test specimen or an SRM

See Figure 4.

Weigh the test specimen or the SRM and place it in the crucible to be located in the measurement cell. Repeat operations b) to g) from 5.6.3.3.1 on generation of the baseline. Repeat this procedure for a minimum of three test specimens.



Key

1 output signal
2 temperature
3 time
4 time
5 test piece
6 baseline
7 reference

Figure 4 — Continuous heating method (with standard reference material)

5.7 Calculation of results

5.7.1 Method requiring the knowledge of the *K* factor

5.7.1.1 Stepwise heating method

See Figure 1.

The use of a computer with adapted software greatly simplifies data acquisition and treatment, and is recommended.

For the considered temperature interval, the shaded areas, *A*, are the integrals of the output signal, s, with respect to time.

For the baseline run with an empty crucible, one obtains:

$$\overline{K} \cdot A_c = (C_c + C_o)(T_2 - T_1)$$

For crucible plus test specimen:

$$\overline{K} \cdot A_{c+t} = (m_t \overline{C_{pt}} + C_c + C_o)(T_2 - T_1)$$

From these two equations one obtains:

$$\overline{C_{pt}}(T_1, T_2) = \frac{\overline{K}(A_{c+t} - A_c)}{m_t(T_2 - T_1)}$$

where

$\overline{K}$	is the mean calorimeter calibration factor for the temperature range T_1 to T_2, in watts per volt ($W.V^{-1}$);
C_o	is the heat capacity of the calorimeter, in joules per kelvin ($J.kg^{-1}.K^{-1}$);
C_c	is the heat capacity of the crucible, in joules per kelvin ($J.kg^{-1}.K^{-1}$);
$\overline{C_{pt}}$	is the mean specific heat capacity of the test specimen, in joules per kilogram and per kelvin ($J.kg^{-1}.K^{-1}$);
m_t	is the mass of the test specimen, in kilograms (kg).

5.7.1.2 Continuous heating method

See Figure 2.

Using the same notations as in 5.7.1.1 plus C_{pt} as the specific heat capacity of the test specimen, one obtains for each temperature:

— for the empty crucible:

$$KS_c = (C_c + C_o)\beta$$

— for crucible plus test specimen:

$$KS_{c+t} = (m_t C_{pt} + C_c + C_o)\beta$$

The specific heat capacity of the test specimen for each temperature, T, is then obtained from:

$$C_{pt} = \frac{K(S_{c+t} - S_c)}{m_t \cdot \beta}$$

where

β	is the constant heating rate in $(K\,.\,s^{-1})$;
K	is the calibration factor at a temperature, T;
S_c, S_{c+t}	are the output signals of the calorimeter in volts (V).

5.7.2 Method using an SRM

5.7.2.1 Stepwise heating method

See Figure 3.

The use of a computer with adapted software greatly simplifies data acquisition and treatment, and is recommended.

For the considered temperature interval, the shaded areas, A, are the integrals of the output signal, s, with respect to time.

For the baseline run with an empty crucible, one obtains:

$$\overline{K}A_{\mathrm{c}}=(C_{\mathrm{c}}+C_{\mathrm{o}})(T_2-T_1)$$

— for crucible plus test piece:

$$\overline{K}A_{\mathrm{c+t}}=(m_{\mathrm{t}}\overline{C_{\mathrm{pt}}}+C_{\mathrm{c}}+C_{\mathrm{o}})(T_2-T_1)$$

— for crucible plus reference piece:

$$\overline{K}A_{\mathrm{c+r}}=(m_{\mathrm{r}}\overline{C_{\mathrm{pr}}}+C_{\mathrm{c}}+C_{\mathrm{o}})(T_2-T_1)$$

where

$\overline{K}$	is the mean calorimeter calibration factor in watts per volt (W.V^{-1});
C_{o}	is the heat capacity of the calorimeter in joules per kilogram and per kelvin (J.kg^{-1}.K^{-1});
C_{c}	is the heat capacity of the crucible in joules per kilogram and per kelvin (J.kg^{-1}.K^{-1});
$\overline{C_{\mathrm{pt}}}$	is the mean specific heat capacity of the test piece in joules per kilogram and per kelvin (J.kg^{-1}.K^{-1});
$\overline{C_{\mathrm{pr}}}$	is the mean specific heat capacity of the reference piece in joules per kilogram and per kelvin (J.kg^{-1}.K^{-1});
m_{t}	is the mass of the test specimen in kilograms (kg);
m_{r}	is the mass of the standard reference material in kilograms (kg).

The mean specific heat capacity of the test piece is then obtained from:

$$\overline{C_{\mathrm{pt}}}(T_1,T_2)=\overline{C_{\mathrm{pr}}}\frac{m_{\mathrm{r}}(A_{\mathrm{c+t}}-A_{\mathrm{c}})}{m_{\mathrm{t}}(A_{\mathrm{c+r}}-A_{\mathrm{c}})}$$

5.7.2.2 Continuous heating method

See Figure 4.

Using the same notations as in 5.7.2.1 plus C_{pt} as the specific heat capacity of the test specimen and C_{pr} as the specific heat capacity of the standard reference material, one obtains for each temperature:

— for the empty crucible:

$$KS_{\mathrm{c}} = (C_{\mathrm{c}} + C_{\mathrm{o}})\beta$$

— for crucible plus test specimen:

$$KS_{\mathrm{c+t}} = (m_{\mathrm{t}} C_{\mathrm{pt}} + C_{\mathrm{c}} + C_{\mathrm{o}})\beta$$

— for crucible plus standard reference material:

$$KS_{\mathrm{c+r}} = \left(m_{\mathrm{r}} C_{\mathrm{pr}} + C_{\mathrm{c}} + C_{\mathrm{o}}\right)\beta$$

The specific heat capacity of the test specimen for each temperature, *T*, is then obtained from:

$$\overline{C_{\mathrm{pt}}} = \overline{C_{\mathrm{pr}}} \frac{m_{\mathrm{r}}\left(S_{\mathrm{c+t}} - S_{\mathrm{c}}\right)}{m_{\mathrm{t}}\left(S_{\mathrm{c+t}} - S_{\mathrm{c}}\right)}$$

where

β	is the constant heating rate in ($K_S{}^{-1}$)
K	is the calibration factor at a temperature, T
S, $S_{\mathrm{c+t}}$, $S_{\mathrm{c+r}}$	are the output signals of the calorimeter in volts (V).

6 Test report

The test report shall contain at least the following information:

a) name of the testing establishment;

b) date of the test; a unique identification of the report and of each page, the customer's and signatory's names and addresses;

c) reference to this document, i.e. "Determined in accordance with ISO 19628";

d) type of method of measurement used;

e) brief details of the equipment used, or any procedures adopted, including necessary deviations;

f) calibration procedures if applicable;

g) material type, manufacturing code, batch number;

h) methods of production of test specimens from supplied material (if appropriate);

i) relevant test parameters (as required for each test);

j) results of individual tests on required number of test specimens;

k) mean results and standard deviation (if required);

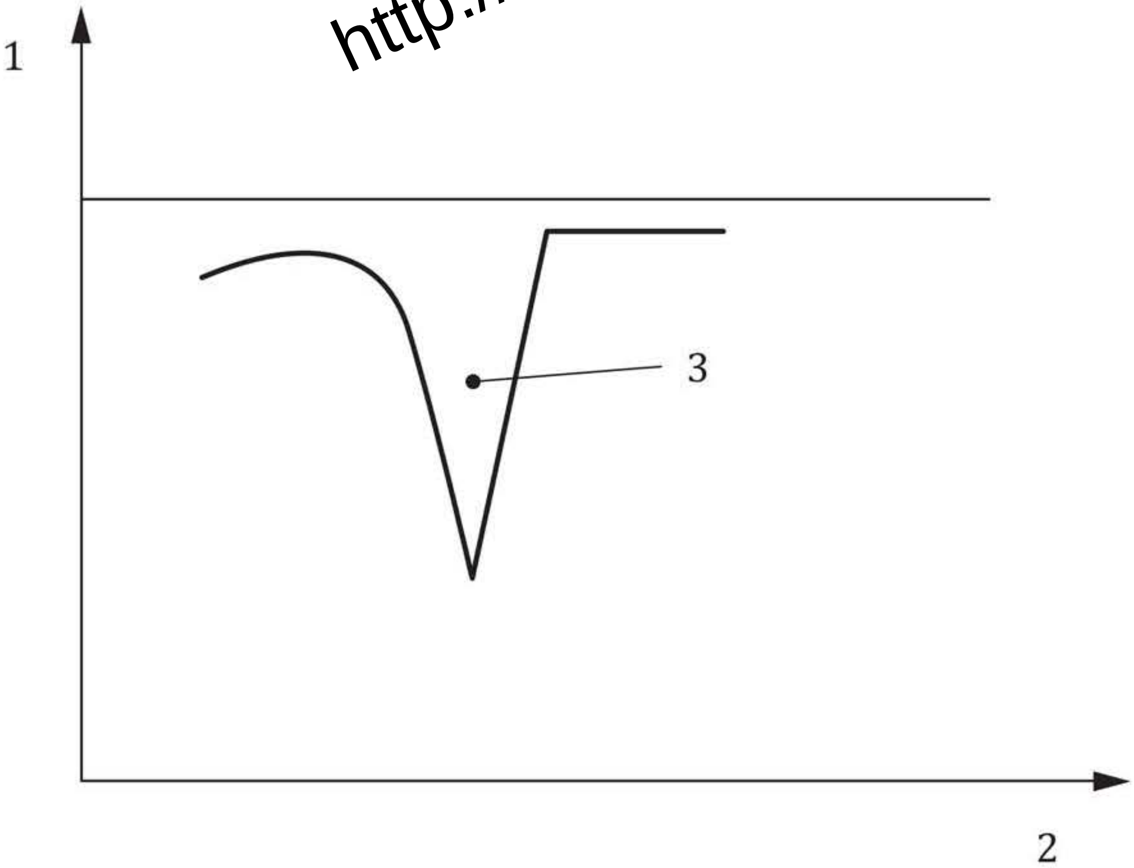
l) comments about the test or the test results;

m) value of specific heat capacity at each required temperature, or value of the mean specific heat capacity between two temperatures calculated on at least three test specimens.

Annex A
(normative)

Drop calorimetry – determination of the calibration factor using standard reference material

A test specimen made from a standard reference material (mass m_r) is dropped from a temperature T_1 into the calorimeter at temperature T_2. Figure A.1 shows an example of a heat dissipation curve on a reference material.



Key

1 output signal
2 time
3 A_r in µV . s

Figure A.1 — Heat dissipation curve as a function of time

The calibration factor K of the calorimeter at temperature T expressed in watt/volts is equal to:

$$K = \frac{H_r}{A_r}$$

where

A_r is the area under the peak in volt seconds;

H_r is the amount of heat required for the reference test specimen to heat from temperature T_1 to temperature T_2.

The calibration coefficient K varies with temperature and shall be measured for each temperature.

Annex B
(informative)

Standard reference material

The most convenient standard reference material, for this method the α-alumina or sapphire, certified by the National Institute of Science and Technology of USA (NIST) under reference SRM 720 up to 2 250 K.

This Standard Reference Material (SRM) is intended for use in calibrating or checking calorimeters used to measure either enthalpy or heat capacity within the range of 10 to 2 250 K.

The material furnished is synthetic sapphire cylinders, cut from centerless-ground rods grown by the Vernieul process and obtained from the Union Carbide Corporation.

The enthalpy and heat-capacity data have been derived from high-temperature enthalpy and low-temperature heat-capacity measurements. These data are presented in both tabular and equation format.

The enthalpy values are accurate to ± 0,1 % from 70 to 1173 K and the heat-capacity values have an accuracy ranging from ± 0,1 % at 70 K to ± 0,3 % at 1 200 K. Below 70 K, the inaccuracy in heat-capacity and enthalpy values increase gradually to ± 10 % at 10 K, because, with decreasing temperature, the heat capacity of sapphire diminishes at a much faster rate than does that of the sample container (mainly copper). The precision of the heat-capacity measurement between 100 and 380 K is estimated to be ± 0,02 %. The precision of the enthalpy measurement from 273,15 to 1 173 K is estimated to be 0,02 %. For the temperature range 1 173 to 2 250 K, the precision of the enthalpy measurement is estimated to be ± 0,03 %, and the accuracy of the measured enthalpy is estimated to be ± 0,2 %, to a large extent reflecting the uncertainty in temperature measurements at these high temperatures. Above 1 700 K, a detectable weight loss was observed in an open container due to evaporation of material.

Relative enthalpy and heat capacity[b]

Temp[a] K	**H_T-$H_{0\ K}$** J-mol^{-1}	**C_p** J-mol^{-1}·K^{-1}
10	0,023	0,009 1
15	0,115	0,030 7
20	0,364	0,073 2
25	0,898	0,146
30	1,905	0,265
35	3,646	0,443
40	6,460	0,697
45	10,77	1,046
50	17,11	1,507
60	38,18	2,793
70	74,68	4,592
80	131,7	6,901
90	214,2	9,679
100	326,6	12,855
110	472,4	16,347

[a] Temperatures expressed on IPTS-68 scale.

[b] Molecular weight = 101,961 3.

Relative enthalpy *(continued)*

Temp[a] K	H_T–$H_{0\ K}$ J-mol^{-1}	C_p J-mol^{-1}·K^{-1}
	654,3	20,07
130	874,3	23,95
140	1133,7	27,93
	1 433,1	31,95
160	1 772,7	35,95
170	2 152,0	39,90
	2 570,3	43,75
190	3 026,7	47,50
200	3 519,9	51,12
210	4 048,7	54,61
220	4 611,6	57,95
230	5 207,1	61,14
240	5 833,9	64,18
250	6 490,3	67,08
260	7 175,0	69,82
270	7 886,3	72,12
273,15	8 115,6	73,21
280	8 622,8	74,87
290	9 383,2	77,20
298,15	10 020	79,01
300	10 166	79,41
310	10 971	81,51
320	11 796	83,49
330	12 641	85,37
340	13 503	87,16
350	14 383	88,84
360	15 280	90,45
370	16 192	91,97
380	17 119	93,41
390	18 060	94,78
400	19 014	96,08
410	19 982	97,32
420	20 961	98,50
430	21 951	99,62
440	22 953	100,69
450	23 965	101,71
460	24 987	162,68
470	26 018	103,60
480	27 059	104,48
490	28 108	105,33
500	29 165	106,13

[a] Temperatures expressed on IPTS-68 scale.

[b] Molecular weight = 101,961 3.

Relative enthalpy *(continued)*

Temp[a] K	**H_T-$H_{0\ K}$** J-mol^{-1}	**C_p** J-mol^{-1}·K^{-1}
510	30 230	106,90
520	31 303	107,64
530	32 383	108,35
540	33 470	109,02
550	34 563	109,67
560	35 663	110,29
570	36 769	110,89
580	37 881	111,46
590	38 998	112,02
600	40 121	112,55
610	41 249	113,06
620	42 382	113,55
630	43 520	114,02
640	44 663	114,48
650	45 810	114,92
660	46 961	115,35
670	48 117	115,76
680	49 276	116,16
690	50 440	116,55
700	51 607	116,92
720	53 953	117,64
740	56 313	118,32
760	58 685	118,96
780	61 071	119,56
800	63 468	120,14
820	65 876	120,69
840	68 295	121,21
860	70 724	121,71
880	73 163	122,20
900	75 612	122,66
920	78 070	123,11
940	80 536	123,55
960	83 011	123,97
980	85 495	124,37
1 000	87 986	124,77
1 020	90 486	125,16
1 040	92 992	125,53
1 060	95 507	125,90
1 080	98 028	126,26
1 100	100 560	126,61
1 120	103 090	126,95

[a] Temperatures expressed on IPTS-68 scale.

[b] Molecular weight = 101,961 3.

Relative enthalpy *(continued)*

Temp[a] K	H_T–$H_{0\ K}$ J-mol^{-1}	C_p J-mol^{-1}·K^{-1}
1 140	105 640	127,29
1 160	108 180	127,61
1 180	110 740	127,94
1 200	113 300	128,25
1 250	119 730	129,01
1 300	126 200	129,74
1 350	132 710	130,43
1 400	139 240	131,08
1 450	145 810	131,70
1 500	152 410	132,29
1 550	159 040	132,84
1 600	165 700	133,36
1 650	172 380	133,85
1 700	1 790,80	134,31
1 750	1 858,10	134,73
1 800	1 925,50	135,13
1 850	1 993,20	135,50
1 900	2 061,00	135,85
1 950	2 129,00	136,18
2 000	219 720	136,50
2 050	226 550	136,80
2 100	233 400	137,10
2 150	240 260	137,41
2 200	247 140	137,23
2 250	254 010	138,06

[a] Temperatures expressed on IPTS-68 scale.

[b] Molecular weight = 101,961 3.

Below 273,15 K, the heat-capacity values were calculated from a spline function fitted to the heat-capacity data over three temperature intervals and employing polynomials, Pn (n = 1,2,3) of the form:

$$Pn = \sum_{i=0}^{6} \frac{A_1}{\mathrm{i}\,!}\left(T - T_0\right)$$

45,0 K > $T \geq$ 8,61 K:	T_0 = 8,61 K	A_3 = +0,450 764E-02
	A_0 = −0,514 7E+01	A_4 = −0,514 64E-03
C_p = exp (P_1) J-mol^{-1}·K^{-1}	A_1 = +0,341 27E+00	A_5 = +0,397 864E-04
	A_2 = −0,333 446E-01	A_6 = −0,152 136E-05

125,0 K > $T \geq$ 45,0 K:	T_0 = 40,0 K	A_3 = +0,951 73E-04
	A_0 = +0,696 6E+00	A_4 = −0,359 10E-05

$C_p = P_2$ J-mol^{-1}·K^{-1} A_1 = +0,593 87E-01 A_5 = −0,649 8E-07

A_2 = +0,403 57E-02 A_6 = +0,408 9E-08

273,15 K > $T \geq$ 125,0 K: T_0 = 125,0 K A_3 = −0,839 67E-04

A_0 = +0,219 93E+02 A_4 = +0,191 33E-05

$C_p = P_3$ J-mol^{-1}·K^{-1} A_1 = +0,388 53E+00 A_5 = −0,317 78E-07

A_2 = +0,139 55E-02 A_6 = +0,295 62E-09

Above 273,15 K, enthalpy and heat-capacity values were derived from the following equation:

$$H_1\text{-}H_{273,15} = \mathrm{A}T^{-2} + \mathrm{B}T^{-1} + \mathrm{C}\ln T + \mathrm{K} + \mathrm{D}T + \mathrm{E}T^2 + \mathrm{F}T^3 + \mathrm{G}T^4 + \mathrm{H}T^5 \text{ J-mol}^{-1}$$

A = +6,625 3E+07 E = −8,575 16E-02

B = −4,542 38E+06 F = +4,299 063E-05

C = −5,475 599E+04 G = −1,151 92E-08

K = +2,581 970 2E+05 H = +1,263 51E-12

D = +2,574 076E+02

Low-temperature measurements from 10 to 380 K were made with a vacuum adiabatic calorimeter [1.2] operated automatically under the control of a minicomputer. Enthalpy measurements at 18 temperatures from 273 to 1 173 K were made by the drop method using a Bunsen ice calorimeter [3.4]. From 1173 to 2 250 K, enthalpy measurements were made with an adiabatic receiving calorimeter [5.6]. All temperatures are expressed on the IPTS-68 scale. In the correction of specimen mass data for atmospheric buoyancy, a density of 3,97 g.cm^{-3} for α-AI_2O_3 was assumed. The functions presented were fitted by the method of least squares to these data. The tabulated values were calculated using these functions.

An occasional particle may contain an end smear due to the method employed in cutting the material. These smears do not contribute significantly to the enthalpy values given in this certificate. However, it is recommended that the material be heated to 1 000 °C in air prior to heat-capacity measurements below 350 K. Microprobe analyses indicate small quantities of chloride, titanium, calcium, silicon, iron, copper, and zinc on the surfaces. Spectrographic examination indicates the purity of the bulk material to be at least 99,95 + percent, with the major impurities being magnesium, calcium, chromium, iron, silicon, and titanium. Examination by atomic absorption spectrometry for magnesium, indicated as the major impurity by the above tests, shows that the surface contamination by this element amounts to 1 ppm, or less, and that the bulk material contains 10 ppm, or less, of magnesium. In addition, the material absorbs a small amount (30 ppm or less, presumably moisture) of weight on the ground surfaces on exposure to room air, and may require heating in an inert atmosphere, if this amount of moisture is of concern. Combustion analysis in oxygen indicates the material contains on the order of 10 ppm or less of carbonaceous material calculated as carbon.

Annex C
(informative)

Materials for calorimeter calibrations

Table C.1 gives the temperatures and heat of fusion for a selection of metallic reference materials.

Table C.1 — Temperatures and heat of fusion for a selection of metallic reference material

Material	Temperature (°C)	Heat of fusion ($J{\cdot}g^{-1}$)
Indium	156,4	28,4
Tin	231,8	56,1
Lead	327,4	24,7
Zinc	419,4	111,2
Aluminium	660	395
Silver	962	104,5
Gold	1 064	64
Nickel	1 455	299
Palladium	1 554	162

Bibliography

[1] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

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