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Reference materials for calorimetry and differential thermal analysis

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1. Introduction

This publication is the result of the efforts of the ICTAC working group “thermochemistry” [1] during 1997–1998. It deals with reference materials (in abbreviated form: RM) for calorimetry and differential thermal analysis. It represents the updated version of two previous documents produced by the IUPAC Commission “Physicochemical Measurements and Standards”: the first was published in Pure and Applied Chemistry in 1974 [1] and the second in the book entitled “Recommended Reference Materials for the Realization of Physicochemical Properties” [2].

Calorimetry and differential thermal analysis are applicable to a wide range of scientific and technological research fields involving physical, chemical and biological processes. Calorimetry usually yields highly reproducible results which may, however, be inaccurate because of faulty calibration of the measurement system.

Calibration is a fundamental requirement for every thermoanalytical study. It requires the establishment of a quantitatively defined relationship between the value indicated by the measuring instrument and the correct value. The calibration of a modern calorimeter is achieved by the quantification of the produced signal when a known quantity of energy is generated within the system. Experimental conditions of calibration and measurement should be matched as closely as possible: not only the quantity of energy to be measured must be similar but the site and kinetics of generation and the temperature range (or the temperature of an isothermal system) should be as close as possible in both calibration and measurement experiments.

The energy of calibration should ideally be generated electrically but when the nature of the calorimetric system makes this difficult to achieve, then a reference material with a well established value of the property under study, preferably with a knowledge of the uncertainties of measurement, may be used as a calibrant. The word “material” is intended to include single substances, mixtures and devices. Whichever method of calibration is employed, reference materials are needed to check the results and to ensure that the calibrated calorimeter is applicable to the particular type of material, reaction, or process for which it is intended and is not subject to systematic errors.

During the past 50 years reference materials for calorimetry (mainly bomb, reaction and heat capacity) and for differential thermal analysis have been developed by national standardizing laboratories such as the National Institute of Science and Technology in the USA and through projects sponsored by bodies such as IUPAC, ICTAC, the Calorimetry Conference (USA), the Association Française de Calorimétrie et d’Analyse Thermique (AFCAT, France), the

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Gesellschaft für Thermische Analyse (GEFTA, Germany) and others. Ideally, a reference material should have been studied in several specialized laboratories and its properties established by measurements involving several techniques and critical evaluation of the corresponding results.

Reference materials recommended in this publication concern heat-capacity measurements, enthalpies of phase changes (fusion, transition, sublimation and vaporization), enthalpies of reaction and related processes (solid + solid, solid + liquid, liquid + liquid and gas + gas processes) and enthalpies of combustion (combustion of solids in oxygen, combustion of liquids in oxygen, combustion of solids in fluorine). In each of these sections the materials are classified as primary, secondary and tertiary reference materials and a definition for each of them is given. Some materials have their properties certified by, or their certification is traceable to, an authoritative national or international organization, agency or laboratory. These materials are called *certified reference materials*. When available, these materials have advantages over uncertified reference materials because source, lot, purity and uncertainties in the property value are defined.

A reference material should satisfy the following requirements: it must be easily obtainable in a pure state, quite stable, non-hygroscopic, non-volatile, easily brought into a suitable form for the measurement and physiologically harmless. In addition, reference materials must not react with the instrument material, the surrounding atmosphere and photoreactions must not occur.

In addition to updating existing reference materials found in previous editions on this subject, this publication identifies new reference materials. A total of 58 pure substances are proposed as reference materials for the measurement of enthalpies of phase change (29 for solid-solid or solid-liquid phase changes, 11 for solid-vapor phase changes and 18 for liquid-vapor phase changes) in comparison to the fourteen recommended in the previous issue [2]. As reference materials for the measurement of enthalpies of reaction and related processes, the ethanol + water system is proposed in addition to the materials previously published [2]. Four new pure substances and three candidates are proposed as reference materials for the measurement of enthalpies of solid combustion in oxygen.

The past three decades have seen a decline in activity in the traditional areas of precise calorimetry. Few additional measurements have become available with the high accuracy necessary for reference materials, although some new data have been published on existing substances. There are still gaps in the availability of reference materials in such important fields of calorimetry as the measurement of heat capacities of liquids and gases at high pressures, the measurement of enthalpies of solid + solid, solid + liquid and liquid + liquid processes especially those concerned with binary systems at high temperatures and pressures and ternary systems.

The introduction of each section is not intended to be comprehensive but reflects the present state of the art for the measurement under consideration. Many of the recommendations include a brief outline of the experimental methods available and the advantages and disadvantages of each method. Most of the recommendations include the following information for each recommended reference material: physical property, units, range of variables, physical state(s) within the range, apparatus used, recommended value, the names of contributors (to the previous and to this version), intended usage, source of supply, methods of preparation, pertinent physicochemical data and references.

The recommendations given in this publication are based on information from the literature up to the end of 1997, from correspondence with scientists in each discipline and from comments solicited from metrological bodies, national standards laboratories, manufacturers and suppliers. The recommended values in this document are the result of a careful evaluation by the contributors. The selected compounds and measurements reflect their best judgement. The temperatures in this work are reported in terms of the ITS-90 [3] unless otherwise stated. Molar masses of the elements are taken from the 1993 report of the IUPAC Commission on Atomic Weights and Isotopic Abundances [4]. Uncertainties associated with each measurement represent twice the overall standard deviation of the mean unless stated otherwise.

It should be observed that:

1. the recommended materials, in most instances, have not been checked independently by ICTAC;
2. the quality of material may change with time;

3. the quoted sources of supply may not be exclusive sources because no attempt has been made to seek out all possible alternatives;
4. ICTAC does not guarantee any material that is recommended.

Finally, I want to thank IUPAC for the permission given for the use in this publication of material from the previous issue [2] and all my colleagues who have contributed to this work. Their names are reported in the preliminary pages of this publication in the section “Contributors”. I am also indebted to Marie-Thérèse Vialle for secretarial assistance.

Raphaël Sabbah
Marseille, June 1998

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2. Reference materials for heat-capacity measurements

A review of reference materials for heat-capacity measurements has been made as an actualization of a previous work [1]. Recent information was searched through Chemical Abstracts, from January 1982 to June 1997. No precise experimental measurements have generally been performed in this period and only eight reports have been published recently for: α-aluminum oxide [2], copper [3], naphthalene [4], 1,4-dimethylbenzene [5,6], nitrogen [7] and carbon dioxide [8,9].

Although last revision considered to introduce indium and tungsten as reference materials, in the case of indium no experimental work on heat capacity has been made in the last period. In contrast, for tungsten two experimental sets of data have been obtained by acoustic levitation [10] and pulse-heating method [11]. Righini et al. [11] reported uncertainties of 4%. However, as a function of the temperature the values of heat capacity for tungsten are very similar to those of platinum and molybdenum. It seems not necessary, at this moment, that tungsten be suggested as a reference material.

To perform heat-capacity measurements, α-aluminum oxide remains as the reference material having the widest range of application for calibration and testing of calorimeters in the temperature range 10–2250 K. This compound is non-hygroscopic, non-volatile, chemically stable, relatively cheap, available in large quantities in a very high purity state, and resistant under oxidizing, neutral or weakly-reducing atmosphere. Being a thermal insulator, it is well suited for use with apparatus intended for heat-capacity measurements on poor conductors. In addition, α-aluminum oxide is available as a certified reference material and reusable samples are easy to clean and manipulate.

This review contains the recommended heat-capacity values for materials covering mainly the temperature range 10–500 K (see Fig. 1). The range includes: *solids* (aluminum oxide, platinum, copper, benzoic-acid, 2,2-dimethylpropane, molybdenum, naphthalene, diphenyl ether, heptane, hexafluorobenzene, polystyrene and poly(vinyl chloride); *liquids* (naphthalene, diphenyl-ether, heptane, polystyrene, poly(vinyl chloride), water, benzene, hexafluorobenzene and nitrogen); and *real gases* (hexafluorobenzene, water, benzene, nitrogen and carbon dioxide). The high-temperature range is covered just by three solid materials (aluminum oxide to 2250 K, platinum to 1500 K and molybdenum to 2800 K) and by two gases (nitrogen and carbon dioxide to 1000 K).

Reference materials are recommended for solid, liquid and gaseous phases in the following temperature ranges:

1. Solid: from 1 K (copper) to 2800 K (molybdenum).
2. Liquid: from 65 K (nitrogen) to 570 K (diphenyl ether).
3. Real gas: from 100 K (nitrogen) to 1000 K (nitrogen and carbon dioxide).

In most of the cases, the recommended values of heat capacity come from experimental measurements using adiabatic and Bunsen ice calorimeters. Values of heat capacity have been reported at the saturation vapor pressure for some solid and liquid materials (benzoic-acid, naphthalene, diphenyl-ether, heptane, water, benzene, hexafluorobenzene and nitrogen). For gases, heat-capacity values have been reported at

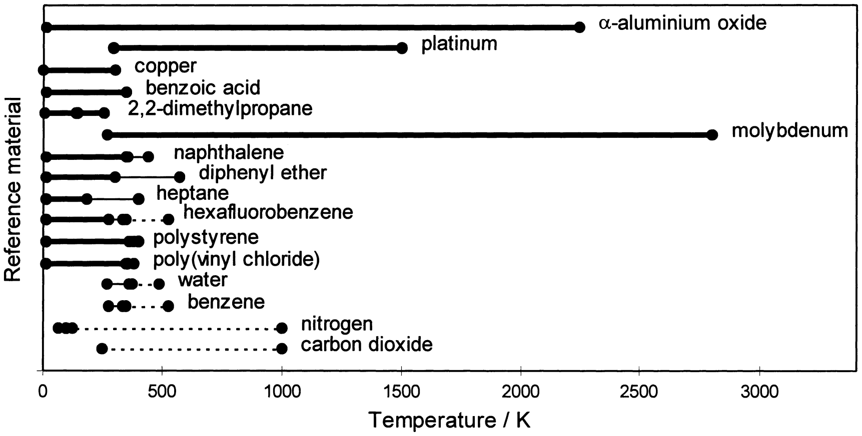

Fig. 1. Range of application of heat capacity reference materials: (▬ solid phase, — liquid phase; ..... gas phase).

different pressures (from 10 kPa to 50 MPa) and a heat-capacity value has been extrapolated to zero pressure (ideal gas).

A reference material proposed in last editions, 1,4-dimethylbenzene, was excluded in this revision. The reasons for this are:

1. some doubts in the scale of temperature in which the original values were reported [12],
2. recent results [5,6] that differ in some cases to 1% of the original values.

It should be convenient to have more additional experimental work to evaluate the reliability of heat capacity for this compound before it could be again recommended as reference material.

Fortunately, as shown in Fig. 2, the recommended substances cover a valuable heat-capacity range. Different molecular structures are in the origin of a wide range of heat-capacity values for the different reference materials at the same temperature (see Table 1).

In general, organic substances have high values of heat capacity, while low heat-capacity values correspond to inorganic materials. Calibration or testing of calorimeters must be performed using the appropriate reference material which should meet closely the conditions of experimental temperature, material phase and heat-capacity value to be determined.

Original data were revised for almost all the reference materials and recommended values of heat capacity and enthalpy are presented, as possible, according with the International Temperature Scale of 1990 (ITS-90) as described in Ref. [13], although in some cases Refs. [14,15] were also used. All recommended values are reported on the ITS-90 except for copper and liquid nitrogen. In these cases, equations are proposed instead of heat-capacity values. However, for these materials, corrections caused by changing temperature scale are smaller than inaccuracies given by the fitting.

Molar masses used by the original authors are indicated in the text for each reference material. Recommended values of heat capacity were corrected by using the molar masses of the elements taken from

Table 1
Some heat capacity values for the recommended materials[a]

Substance/T (K)	$C_{p,\mathrm{m}}/(\mathrm{J\,mol^{-1}\,K^{-1}})$			
	100	200	300	400
Aluminum oxide	12.852	51.12	79.43	96.10
Platinum			25.89	26.47
Copper	16.00	22.58	24.45	
Benzoic acid	64.01	102.89	147.68	
2,2-Dimethylpropane	17.20	28.02		
Molybdenum			23.96	25.09
Naphthalene	60.29	106.7	167.0	**235.8**
Diphenyl ether	84.42	143.08	218.18	**313.29**
Heptane	92.84	**201.32**	**225.53**	**270.08**
Hexafluorobenzene	86.98	157.0	**222.1**	*186.14*
Polystyrene	47.75	84.16	128.4	**201.0**
Poly(vinyl chloride)	26.8	43.0	59.4	
Water			**75.323**	*35.11*
Benzene			**136.5**	*115.11*
Nitrogen	**62.83**/*30.03*	*29.23*	*29.17*	*29.27*
Carbon dioxide			*37.5*	*41.4*

[a] Heat capacity values for liquid materials are in **bold** and for gases in *italic*.

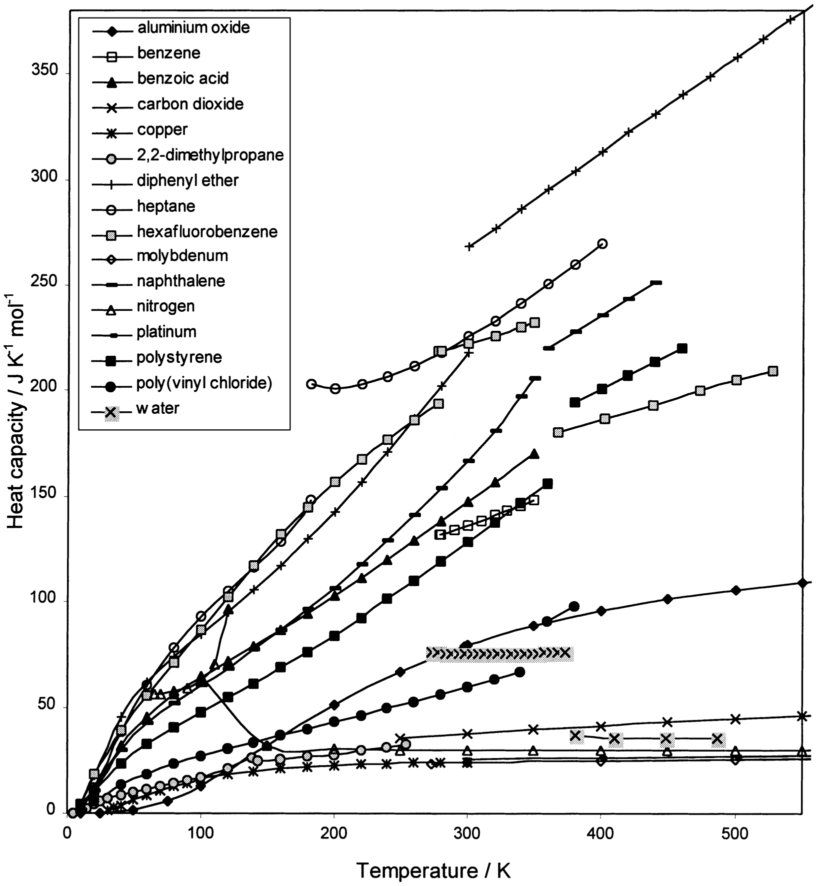

Fig. 2. Heat capacity of different reference materials as a function of the temperature.

the 1993 report of the IUPAC Commission on Atomic Weights and Isotopic Abundances [16].

Reference materials for the measurement of heat capacity have been classified as primary, secondary or tertiary reference material. A reference material is considered, in this section, as primary reference material when at least two independent adiabatic sets of experimental data are in good agreement, high purity samples are available (in most of the cases as reference materials) and the substance is thermochemically stable and non-hygroscopic in the range of application. This is the case of: α-aluminum oxide, benzoic acid, heptane, platinum and polystyrene. Secondary reference materials were considered as those for which there are two adiabatic sets of consistent experimental results but do not satisfy completely the criteria established for primary reference materials (copper and poly(vinyl chloride)). Another kind of secondary reference materials include those for which the criteria of purity and stability for primary reference materials are satisfied but just one adiabatic set of data is available (water, benzene, hexafluorobenzene, naphthalene and diphenyl ether). Tertiary reference materials were chosen as those for which reliable data have been reported from non-adiabatic measurements (2,2-dimethylpropane, nitrogen and carbon dioxide). Molybdenum is included in the last group because adiabatic measurements are available just in the range 300–700 K.

Throughout the text, the experimental uncertainties of the heat-capacity values are those claimed by the original authors. The deviation between these values (C_p) and the recommended values $(C_p)_r$, at the same temperature, represented by $[(C_p)–(C_p)_r]/(C_p)_r$, is also given. In the case for which the recommended heat capacity is given in terms of a polynomial, the uncertainty is represented by the standard deviation of the fitting.

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2.1. *In the solid state*

2.1.1. C_p *and H,* α*-aluminum oxide*

Physical property	heat capacity, enthalpy
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, C_p, m); $\mathrm{J\,mol^{-1}}$ (molar enthalpy, H_m); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_p); $\mathrm{J\,kg^{-1}}$ (specific enthalpy, h)
Recommended reference material	α-aluminum oxide (Al_2O_3): 101.9612 $\mathrm{g\,mol^{-1}}$; [1344–28–1]
Classification	primary RM
Range of variables	10–2250 K
Physical state within the range	solid
Apparatus used	adiabatic calorimeter, drop method using a Bunsen ice calorimeter
Contributors to the previous versions	J.D. Cox, S.S. Chang, D.A. Ditmars, G.T. Furukawa, J. Lielmezs, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.1.1.1. Intended usage Highly pure α-alumina (synthetic sapphire, corundum) is recommended for testing the performance of calorimeters [1–3] used for the measurement of the heat capacities of solids and liquids or for the measurement of the enthalpies of solids [4]. This material could also be used for the calibration of such calorimeters.

2.1.1.2. Sources of supply and/or methods of preparation A highly pure grade of α-alumina (SRM 720 with a certificate giving its measured enthalpy (relative to 0 K) and heat capacity from 10 to 2250 K is available from NIST. Samples of α-alumina of comparable purity can be obtained (without thermal certification) from Johnson Matthey. Sapphire disks of various thicknesses and diameters are available from Agate. Disks of 6 mm diameter and 0.5 mm thickness are suitable for differential scanning calorimetry. Other high purity material which might be suitable are also available from various commercial sources, e.g. Aldrich, Baker, etc.

2.1.1.3. Pertinent physicochemical data This material has no solid-solid transition in the quoted temperature range. Furukawa et al. [5] studied a sample of α-alumina with mass fraction purity of 0.9998–0.9999 assessed by spectrographic analysis. They employed adiabatic calorimetry in the temperature range 13–380 K and a drop method with a Bunsen ice calorimeter from 273 to 1170 K. Ditmars et al. [6] consolidated the results on a sample of comparable purity (SRM 720) in the temperature range 10–2250 K from C_p, m measured by automated adiabatic calorimetry [7] in the temperature range 8–375 K and from relative enthalpy measured by drop calorimeters of different designs [6,8] in the temperature range 273–2250 K. Results obtained by all these

Table 2
Original and corrected to ITS-90 values of heat capacity $C_{p,\mathrm{m}}$ and enthalpy H_m $(T)-H_\mathrm{m}$ (0 K) of α-aluminum oxide

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		H_m $(T)-H_\mathrm{m}$ (0 K) ($\mathrm{J\,mol^{-1}}$)	
	Original values	ITS-90	Original values	ITS-90
10	0.0091		0.023	
25	0.146	0.146	0.898	0.899
50	1.507	1.507	17.11	17.12
75	5.685	5.683	100.32	100.28
100	12.855	12.852	326.6	326.5
150	31.95	31.94	1433.1	1432.7
200	51.12	51.12	3519.9	3519.4
250	67.08	67.09	6490.3	6490.0
298.15	79.01	79.03	10 020	10 021
300	79.41	79.43	10 166	10 167
350	88.84	88.87	14 383	14 385
400	96.08	96.10	19 014	19 017
450	101.71	101.71	23 965	23 969
500	106.13	106.13	29 165	29 170
550	109.67	109.67	34 563	34 568
600	112.55	112.55	40 121	40 126
650	114.92	114.94	45 810	45 816
700	116.92	116.96	51 607	51 614
800	120.14	120.18	63 468	63 480
900	122.66	122.66	75 612	75 628
1000	124.77	124.62	87 986	87 986
1100	126.61	126.69	100 560	100 556
1200	128.25	128.47	113 300	113 313
1250	129.01	129.20	119 730	119 753
1300	129.74	129.85	126 200	126 231
1350	130.43	130.48	132 710	132 746
1400	131.08	131.13	139 240	139 277
1450	131.70	131.75	145 810	145 850
1500	132.29	132.35	152 410	152 453
1550	132.84	132.90	159 040	159 087
1600	133.86	133.42	165 700	165 750
1650	133.85	133.91	172 380	172 433
1700	134.31	134.38	179 080	179 136
1750	134.73	134.80	185 810	185 869
1800	135.13	135.20	192 550	192 613
1850	135.50	135.57	199 320	199 386
1900	135.85	135.92	206 100	206 171
1950	136.18	136.26	212 900	212 975
2000	136.50	136.58	219 720	219 799
2050	136.80	136.88	226 550	226 634
2100	137.10	137.18	233 400	233 488
2150	137.41	137.49	240 260	240 352
2200	137.73	137.82	247 140	247 237
2250	138.06	138.15	254 030	254 131

methods agree well in the overlap ranges. Values of heat capacity and enthalpy with temperatures (from [6]) are given in Table 2. Temperatures are reported in IPTS-68 above 13.81 K and in NBS-1965 provisional scale below 13.81 K [7]. Corrections of the values to the ITS-90, taking into account (T_{90}–T_{68}), d(T_{90}–T_{68})/dT and dC_p, m/dT values as described by Goldberg and Weir [9,10] are also given in the table, even if they are smaller than inaccuracies of experimental data [9,11].

The molar mass was taken as 101.9613 g mol^{-1}. The measurements made by Macleod [12] from 400 to 1250 K agree with the values in the table, except at the highest temperatures. Three more recent papers have reported experimental results on this material in the temperature ranges 298.15–1000 K [11], 300–550 K [13] and 80–400 K [14]. All of them are in agreement with the reference values in Table 2. No recent experimental values for temperatures over 1000 K are available.

Equations for C_p, m and $H_m(T)$–$H_m(0\,K)$ as functions of T (0–2200 K) have been given by Reshetnikov [15], Castanet [16] and Archer [17]. The values in Ref. [15] differ from those in Table 2 by about 0.2% in the range 100–1200 K and by 1% at 2100 K. Castanet [16] has made a critical review including almost all of the experiments performed until 1979, deviations of the obtained values from those in Table 2 are about 0.1% in the range 100–900 K, less than 1% in the range 900–2000 K and less than 2% over 2000 K. Archer's results [17] differ from values in Table 2 by about 0.05% from 150 to 900 K, 0.3% in the range 900–1900 K and less than 1.5% over 1900 K.

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2.1.2. *C_p and H, platinum*

Physical property	heat capacity, enthalpy
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{p,m}$); J mol^{-1} (molar enthalpy, H_m); J kg^{-1} K^{-1} (specific heat capacity, c_p); J kg^{-1} (specific enthalpy, h)
Recommended reference material	platinum (Pt): 195.08 g mol^{-1}; [7440-06-4]
Classification	primary RM
Range of variables	298.15–1500 K
Physical state within the range	solid
Apparatus used	drop calorimeter, laser flash calorimeter, pulse-heating calorimeter, temperature modulation methods
Contributors to the previous versions	J.T. Armstrong, J. Lielmezs, J.F. Martin, J. Rogez, R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.1.2.1. Intended usage Because of its high chemical stability, freedom from transitions, high melting point, $T_{fus} = 2045$ K [1], availability in high purity and low volatility at high temperatures, platinum is recommended for checking the accuracy of apparatus (especially those which use small quantities of material such as drop calorimeters and differential scanning calorimeters) for the measurement of enthalpy and heat capacity up to high temperatures.

2.1.2.2. Sources of supply and/or methods of preparation High purity platinum in wire form is available as SRM 680a from NIST. Samples of platinum of comparable purity can be obtained from Johnson Matthey; samples of platinum of mass fraction purity > 0.999 are available from various sources e.g. Goodfellow Metals, Material Research Corporation, Alfa, etc.

Table 3
IPTS-68 and corrected to the ITS-90 values of heat capacity $C_{p,\mathrm{m}}$ and enthalpy H_m $(T)-H_\mathrm{m}$ (298.15 K) of platinum

T (K)	$C_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})		H_m $(T)-H_\mathrm{m}$ (298.15 K) (J mol^{-1})	
	IPTS-68	ITS-90	IPTS-68	ITS-90
298.15	25.87	25.87	0	0
400	26.47	26.47	2669	2670
500	26.98	26.98	5337	5338
600	27.53	27.53	8065	8066
700	28.03	28.04	10 843	10 844
800	28.57	28.58	13 675	13 677
900	29.06	29.06	16 554	16 557
1000	29.54	29.50	19 479	19 478
1100	30.09	30.11	22 459	22 457
1200	30.58	30.63	25 490	25 491
1300	31.16	31.19	28 582	28 588
1400	31.71	31.72	31 720	31 727
1500	32.21	32.22	34 915	34 923

2.1.2.3. Pertinent physicochemical data The values for heat capacity recommended are those adopted by Hultgren et al. [1] which agree with the enthalpy measurements by drop calorimetry made by Kendall et al. [2] (339–1435 K), Jaeger et al. [3] (681–1665 K), Jaeger and Rosenbohm [4] (484–1877 K), and White [5] (373–1573 K) and by laser flash calorimetry made by Yokokawa and Takahashi [6] (80–1000 K). The molar mass was taken as 195.09 g mol^{-1}.

Table 3 gives values of the heat capacity and enthalpy (corrections to IPTS-68 and ITS-90 were made by using approximate equations given in Ref. [7] and Refs. [8,9], respectively).

Macleod [10] has measured the enthalpy of platinum in the temperature range 400–1700 K and has fitted the values with equations that lead to values of enthalpy and heat capacity in the range 300–1500 K which agree with Hultgren's selected values [1] within 1% below 1300 K and within 1.8% from 1300 to 1500 K. Results obtained by Vollmer and Kohlhass [11] and Macleod [10] by calorimetry, by Kraftmakher [12] and Seville [13] using modulation methods and by Righini and Rosso [14] using a pulse-heating method, show an enhancement in the heat capacity of platinum above 1500 K compared with the values reported in Refs. [1,3,4].

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2.1.3. C_p, copper

Physical property	heat capacity
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{p,\mathrm{m}}$); J kg^{-1} K^{-1} (specific heat capacity, c_p)
Recommended reference material	copper (Cu): 63.546 g mol^{-1}; [7440-50-8]
Classification	secondary RM
Range of variables	1–300 K
Physical state within the range	solid
Apparatus used	adiabatic calorimeter, isothermal calorimeter
Contributors to the previous version	J.D. Cox, J.W. Fisher, J. Lielmezs, D.L. Martin, J.F. Martin, R. Sabbah, R.L. Snowdon

Contributors to this version M. Campos, R. Patiño, L.A. Torres

2.1.3.1. Intended usage Copper is recommended for testing the performance of low-temperatures calorimeters used for the measurement of heat capacity of solids (and possibly liquids). For use below 20 K the copper must be of very high purity and degassed because very small (ppm) amounts of transition metal and hydrogen impurities may drastically affect the heat capacity [1]. Severe cold work may affect the heat capacity significantly, especially below 20 K [2]. At higher temperatures there may be no significant differences in the heat capacities of high purity and "workshop grade" copper. One such comparison has been made [3] showing a difference of 0.2% or less which is comparable with the scatter of the data.

2.1.3.2. Sources of supply and/or methods of preparation High purity degassed and annealed copper is available as Research Material RM5 from NIST.

2.1.3.3. Pertinent physicochemical data Copper was recommended as a reference material at low temperatures by the American Calorimetry Conference. Osborne et al. [4] analyzed the results available at the time and recommended the following Copper Reference Equation for use in the range 1–25 K:

$$C_{p,\mathrm{m}}/\mathrm{J\,mol^{-1}\,K^{-1}} = \Sigma A_N\,(T/\mathrm{K})^N \qquad (2.1.3.1)$$

where the six factors are:

$A_1 = 6.9434 \times 10^{-4}$
$A_3 = 4.7548 \times 10^{-5}$
$A_5 = 1.6314 \times 10^{-9}$
$A_7 = 9.4786 \times 10^{-11}$
$A_9 = -1.3639 \times 10^{-13}$
$A_{11} = 5.3898 \times 10^{-17}$

This applies to older temperature scales where the span 20–4.2 K was interpolated by the individual experimenter's gas thermometer and the 20 K calibration temperature and higher temperatures were on the NBS-1955 platinum thermometer scale and temperatures below 4.2 K on the 1958 ^{4}He vapor-pressure scale. Many laboratories still use such scales and the above equation is recommended in the 1–20 K range only (data above 20 K having since been shown to be in error). The scatter of raw data about the Copper Reference Equation was about ±0.6%.

The currently recommended temperature scale below 30 K is the EPT-76 scale which is very close to the Iowa State University T_x magnetic scale. The recommended reference equation for this conditions, in the 1–30 K range, is that of Holste et al. [5], being Eq. (2.1.3.1) with the following seven factors:

$A_1 = 6.9260 \times 10^{-4}$
$A_3 = 4.7369 \times 10^{-5}$
$A_5 = 1.9537 \times 10^{-9}$
$A_7 = 1.0869 \times 10^{-10}$
$A_9 = -1.9745 \times 10^{-13}$
$A_{11} = 1.3343 \times 10^{-16}$
$A_{13} = -3.2196 \times 10^{-20}$

The scatter of the raw data about this equation was ±0.1%. The difference between results obtained with the two recommended equation is roughly consistent with the known differences in the temperature scales. The smoothed heat capacity results from the two scales are closely similar at 20 K. It should be satisfactory to extrapolate the above equations below 1 K but sample impurity may cause divergence from these values as the temperature is reduced.

For measurements in the 30–300 K range on the IPTS-68 scale, the three data sets [3,6,7] are in reasonable agreement and Eq. (2.1.3.1) with the following fourteen factors is a good fit:

$A_0 = -0.1285753818 \times 10^{1}$
$A_7 = 0.3070527023 \times 10^{-10}$
$A_1 = 0.3098967121$
$A_8 = -0.1419198886 \times 10^{-12}$
$A_2 = -0.2924985792 \times 10^{-1}$
$A_9 = 0.4557519040 \times 10^{-15}$
$A_3 = 0.1418586260 \times 10^{-2}$
$A_{10} = -0.9894731263 \times 10^{-18}$
$A_4 = -0.3370489513 \times 10^{-4}$
$A_{11} = 0.1370529662 \times 10^{-20}$
$A_5 = 0.4856675621 \times 10^{-6}$
$A_{12} = -0.1074497377 \times 10^{-23}$
$A_6 = -0.4646773402 \times 10^{-8}$
$A_{13} = 0.3517161374 \times 10^{-27}$

Eq. (2.1.3.1) describes the recommended values by Furukawa [8] within ±0.3% in the 50–300 K range and within ±0.4% in the 30–50 K range. The revision of White and Collocott [9] leads to the conclusion that values recommended by Furukawa [8] remains as the more reliable. Experimental values obtained with a “tray” type calorimeter, reported more recently by Martin [10], are deviated from equation values just within ±0.2% in practically the entire range. Corrections to ITS 90, calculated as recommended by Goldberg and Weir [11], do not affect the equation because they are within ±0.06%.

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2.1.4. C_{sat}, *benzoic acid*

Physical property	heat capacity
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{\mathrm{sat,m}}$); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_{sat})
Recommended reference material	benzoic acid ($C_7H_6O_2$): 122.1234 g mol^{-1}; [65-85-0]
Classification	primary RM
Range of variables	10–350 K
Physical state within the range	solid
Apparatus used	adiabatic calorimeter
Contributors to the previous versions	J.D. Cox, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

Table 4
Original and corrected to ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ of benzoic acid

$C_{\mathrm{sat,m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		
T (K)	Original values	ITS-90
10	2.094	
20	11.06	11.07
40	31.70	31.70
60	45.79	45.79
80	55.82	55.82
100	64.01	64.01
120	71.53	71.52
140	79.01	79.00
160	86.70	86.69
180	94.65	94.65
200	102.88	102.89
220	111.42	111.43
240	120.26	120.27
260	129.31	129.33
280	138.44	138.47
300	147.64	147.68
320	156.87	156.92
350	170.70	170.76

2.1.4.1. Intended usage Benzoic acid is recommended for testing the performance of calorimeters used for the measurements of the heat capacity of solids from low temperatures to a little above ambient [1]. Use of the material in contact with base metal near to, or above, the melting point (395.52 K) is not recommended because of the material’s corrosive nature.

2.1.4.2. Sources of supply and/or methods of preparation It seems probable that samples of benzoic acid prepared as energy of combustion standards would also serve as heat-capacity standards [2]. These samples are available from Bureau of Analysed Samples, NIST and BDH.

2.1.4.3. Pertinent physicochemical data Arvidsson et al. [3] studied a sample of benzoic acid (energy of combustion standard SRM 39i from NIST, 39j at present) with a mole fraction purity of 0.99997 assessed by freezing point measurements on macrosamples. Values of the variation of $C_{p,\mathrm{m}}$ with temperature are given in Table 4. The molar mass was taken as 122.12 g mol^{-1}. Values refer to the solid in equilibrium with its vapor and were obtained with a small sample low-temperature adiabatic calorimeter. Temperatures are reported on IPTS-68 above 13.81 K. The calibration of the thermometer was extended below 13.81 K by the method of McCrackin and Chang [4].

Values reported by Ginnings and Furukawa [5] corrected to ITS-90 [6] agree with those in Table 4 within ±0.06% in the range 100–350 K. Values reported by Tatsumi et al. [7] agree with those in Table 4 within ±0.3 in the range 20–300 K. The agreement with other previous data [8,9] up to 300 K is good and gives strong support to the belief that the uncertainty of the measurements is better than ±0.1% above 60 K, ±0.3% between 15 and 60 K and about ±1% in the range 8–15 K.

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2.1.5. C_p, 2,2-dimethylpropane

Physical property	heat capacity
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{p,\mathrm{m}}$); J kg^{-1} K^{-1} (specific heat capacity, c_p)
Recommended reference material	2,2-Dimethylpropane (neopentane) (C_5H_{12}): 72.1503 g mol^{-1}; [463-82-1]
Classification	tertiary RM
Range of variables	(i) 5-139 K, (ii) 143-254 K
Physical state within the range	solid
Apparatus used	adiabatic calorimeter
Contributors to the previous versions	Y. Mashiko, R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.1.5.1. Intended usage 2,2-Dimethylpropane is recommended for testing the performance of calorimeters used for measuring the heat capacities of solids down to very low temperatures [1]. As the substance has a solid-solid transition [2] at (140.49 ± 0.05) K, temperatures in the vicinity of the transition point (139–142 K) should be avoided.

2.1.5.2. Sources of supply and/or methods of preparation A highly pure grade (mole fraction purity of 0.99997) sample of 2,2-dimethylpropane is available from API. Samples having, respectively, mole fraction and mass fraction purities of 0.9999 and 0.99 can be purchased from International Research Liaison Office, National Institute of Materials and Chemical Research (Japan) and Baker. The further purification of a sample of 2,2-dimethylpropane is possible by fractional distillation with treatment of the distillate by molecular sieve 5 A.

Table 5
Original and corrected to ITS-90 values of heat capacity $C_{p,\mathrm{m}}$ of 2,2-dimethylpropane

$C_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})		
T (K)	Original values	ITS-90
5	0.0662	
10	0.7655	
15	2.215	
20	3.953	
60	11.40	
70	12.62	
80	14.16	
90	15.68	15.64
100	17.19	17.20
120	21.23	21.24
138	26.14	26.12
143	24.61	24.58
160	25.64	25.61
180	26.92	26.90
200	28.02	28.02
220	29.53	29.54
240	31.22	31.24
254	32.84	32.87

2.1.5.3. Pertinent physicochemical data Enokido et al. [2] studied a sample of 2,2-dimethylpropane (the molar mass of which was taken as $72.151\,\mathrm{g\,mol^{-1}}$) the purity of which was established as mole fraction 0.99997 by calorimetric study of the melting behavior. Temperatures were reported on IPTS-48, below 90 K on NBS-55 scale and below 10 K on ^{4}He vapor-pressure scale [3].

Original experimental values of $C_{p,\mathrm{m}}$ were smoothed by the splines method; then, values of $C_{p,\mathrm{m}}$ were calculated at fixed temperatures and corrected to ITS-90 as described by Douglas [4] and Goldberg and Weir [5]. The results of this procedure are given in Table 5. Aston and Messerly [6] reported experimental heat-capacity values for 2,2-dimethylpropane in the range 13–278 K using a sample having a mole fraction purity of 0.9933. These values are deviated from those of Enokido et al. [2] within ±2% in all the temperature range.

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2.1.6. C_p and H, molybdenum

Physical property	heat capacity, enthalpy
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{p,\mathrm{m}}$); $\mathrm{J\,mol^{-1}}$ (molar enthalpy, H_m); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_p); $\mathrm{J\,kg^{-1}}$(specific enthalpy, h)
Recommended reference material	molybdenum (Mo): $95.94\,\mathrm{g\,mol^{-1}}$; [7439-98-7]
Classification	tertiary RM
Range of variables	273.15–2800 K
Physical state within the range	solid
Apparatus used	adiabatic calorimeter, drop method using a Bunsen ice calorimeter, high speed pulse calorimeter
Contributors to the previous versions	A. Cezairliyan, D. Ditmars, J. Lielmezs, J. Rogez, R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.1.6.1. Intended usage Pure molybdenum is recommended for testing the performance of calorimeters used for measuring the heat capacity or enthalpy of good thermally-conducting materials (solids and liquids) from 273 to 2800 K. Molybdenum has no known structural transitions within this temperature range but is oxidized rapidly in contact with air at temperatures above 773 K.

2.1.6.2. Sources of supply and/or methods of preparation Certified molybdenum samples (mass fraction purity of 0.9995) may be obtained from NIST as SRM 781-D2. Samples of molybdenum of comparable purity can be obtained from various sources e.g. Goodfellow Metals, Johnson Matthey, Materials Research Corporation, Alfa, Baker, etc.

2.1.6.3. Pertinent physicochemical data The relative enthalpy of NBS Standard Reference Material 781 has been measured by the drop method with two different calorimeters, a Bunsen ice calorimeter and an adiabatic calorimeter, in the temperature ranges 273–1173 K and 1173–2100 K, respectively. The uncertainties in the smoothed enthalpy data derived from these measurements are believed not to exceed ±0.6% at any temperature in these ranges. The heat capacity of the same material has also been measured in the temperature range 1500–2800 K using a millisecond-resolution pulse calorimetric technique with resistive self-heating. In the highest temperature range the smoothed heat-capacity data are believed to be uncertain by no more than ±3%. The details of the measurements and the results are given in Ref. [1]. The smoothed heat capacity and enthalpy results for the SRM 781 molybdenum are given in Table 6. The molar mass was taken as $95.94\,\mathrm{g\,mol^{-1}}$. These results are in good agreement with Hultgren's values [2].

Equations for $C_{p,\mathrm{m}}$ and $H_\mathrm{m}(T)-H_\mathrm{m}$ (273.15 K) or $H_\mathrm{m}(T)-H_\mathrm{m}$ (298.15 K) as functions of T have been

Table 6
IPTS-68 and corrected to ITS-90 values of heat capacity $C_{p,\mathrm{m}}$ and enthalpy H_m $(T)-H_\mathrm{m}$ (273.15 K) of molybdenum

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		H_m $(T)-H_\mathrm{m}$ (273.15 K) ($\mathrm{J\,mol^{-1}}$)	
	IPTS-68	ITS-90	IPTS-68	ITS-90
273.15	23.56	23.56	0	0
300	23.95	23.96	637.87	638.01
400	25.08	25.09	3093.4	3094.2
500	25.85	25.85	5642.2	5643.2
600	26.46	26.46	8258.7	8259.8
700	26.98	26.99	10 931	10 932
800	27.44	27.45	13 652	13 654
900	27.89	27.89	16 419	16 422
1000	28.37	28.34	19 232	19 232
1100	28.90	28.88	22 094	22 093
1200	29.49	29.55	25 013	25 016
1300	30.14	30.17	27 994	28 001
1400	30.86	30.87	31 044	31 052
1500	31.65	31.67	34 169	34 179
1600	32.50	32.52	37 376	37 388
1700	33.42	33.44	40 671	40 684
1800	34.42	34.44	44 062	44 077
1900	35.49	35.51	47 557	47 575
2000	36.65	36.68	51 163	51 184
2100	37.90	37.93	54 890	54 914
2200	39.24	39.27	58 746	58 773
2300	40.67	40.71	62 740	62 770
2400	42.21	42.25	66 884	66 918
2500	43.89	43.94	71 188	71 226
2600	45.88	45.93	75 673	75 717
2700	48.37	48.43	80 381	80 430
2800	51.57	51.65	85 371	85 427

given in Ref. [1]. In the range 500–1500 K values obtained from other sources and quoted in Refs. [1,2] are often in good agreement. Betz and Frohberg [3] determined the enthalpy of molybdenum by drop calorimetry in the range 2282–3383 K. Their results do not differ from the values in Table 6 by more than 1% up to 2650 K. Righini and Rosso [4], using a pulse-heating method, determined the heat capacity of molybdenum in the range 1300–2500 K. Cezairliyan [5] used the same technique in the range 1500–2800 K. Their results agree within ±0.5% with the values reported in Table 6 over most of the temperature range.

A review of experimental data by Desai [6] proposed recommended heat capacities and relative enthalpies in the range of temperature from 298.15 to 2897 K for molybdenum in the solid phase. Values corrected to ITS-90 [7,8] are in agreement with those in Table 6 within ±0.4% in all the temperature range.

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2.2. *In the solid and liquid states*

2.2.1. *C_{sat}, naphthalene*

Physical property:	heat capacity
Units:	J mol^{-1} K^{-1} (molar heat capacity, $C_{\mathrm{sat,m}}$); J kg^{-1} K^{-1} (specific heat capacity, c_{sat})
Recommended reference material:	Naphthalene ($C_{10}H_8$): 128.1735 g mol^{-1}; [91-20-3]
Classification	secondary RM
Range of variables:	(i) 10–350 K, (ii) 360–440 K
Physical state within the range:	(i) solid, (ii) liquid
Apparatus used:	adiabatic calorimeter
Contributors to the previous versions:	J.D. Cox, O. Riedel, R. Sabbah
Contributors to this version:	M. Campos, R. Patiño, L.A. Torres

2.2.1.1. Intended usage Naphthalene is recommended for testing the performance of calorimeters for measuring the heat capacities of solids and liquids [1].

2.2.1.2. Sources of supply and/or methods of preparation High purity samples of naphthalene can be obtained from API. Commercial samples with a mass fraction purity ≥ 0.99 are available from suppliers Aldrich, Fluka, etc. which can be used after further purification by zone-refining.

2.2.1.3. Pertinent physicochemical data McCullough et al. [2] examined a sample of naphthalene having a mole fraction purity of 0.99985 assessed by calorimetric study of the melting behavior. Values of $C_{\mathrm{sat,m}}$ for the solid in equilibrium with its vapor are given in Table 7. Measurements of temperature were made with platinum resistance thermometers calibrated on IPTS-48 and, below 90 K, on the provisional scale of NBS [3]. The molar mass was based on the 1951 International Atomic Weights. The uncertainty of the heat-capacity data was usually within ±0.1% to ±0.2%.

Recommended values are those of Ref. [2] corrected to ITS-90 [4,5] and for molar mass based on relative atomic masses of 1981 [6], and those from Ref. [7] as published in the original paper for the solid and liquid, respectively. All of these values were experimentally determined by adiabatic calorimetry.

Table 7
ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ of naphthalene

T_{90} (K)	$C_{\mathrm{sat,m}}$ (J mol^{-1}
Solid	
10	1.766
20	10.94
40	30.12
60	42.65
80	51.99
100	60.29
120	68.54
140	77.11
160	86.38
180	96.25
200	106.7
220	117.7
240	129.2
260	141.2
280	153.8
300	167.0
320	181.1
340	197.2
350	205.8
Liquid	
360	220.1
380	228.0
400	235.8
420	243.6
440	251.3

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2.2.2. C_{sat} *and H, diphenyl ether*

Physical property	heat capacity, enthalpy
Units	$\text{J mol}^{-1}\,\text{K}^{-1}$ (molar heat capacity, $C_{\text{sat,m}}$); J mol^{-1} (molar enthalpy, H_{m}); $\text{J kg}^{-1}\,\text{K}^{-1}$ (specific heat capacity, c_{sat}); J kg^{-1} (specific enthalpy, h)
Recommended reference material	diphenyl ether ($C_{12}H_{10}O$): 170.2108 g mol^{-1}; [101-84-8]
Classification	secondary RM
Range of variables	(i) 10–300.03 K, (ii) 300.03–570 K
Physical state within the range	(i) solid, (ii) liquid
Apparatus used	adiabatic calorimeter, drop method using a Bunsen ice calorimeter
Contributors to the previous versions	J.D. Cox, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.2.2.1. Intended usage Diphenyl ether is recommended for testing the performance of calorimeters [1,2] used for the measurement of the heat capacities of solids and liquids. Its relatively high boiling point (532 K) permits the use of this material over a wide range of temperatures and its ease purification and the inertness of the molten substance to most materials of construction are further points in its favor.

2.2.2.2. Sources of supply and/or method of preparation Commercial samples with a mass fraction purity of ≥ 0.99 are available from Aldrich, etc. which can be further purified by distillation and fractional crystallization. It is also necessary to remove the dissolved air and water from the sample before using it in calorimetric experiments.

2.2.2.3. Pertinent physicochemical data Furukawa et al. examined a sample of diphenyl ether with mole fraction purity of 0.999987 assessed by calorimetric study of the melting behavior. They determined the heat capacity between 18 and 360 K by adiabatic calorimetry and between 273 and 573 K by drop calorimetry [3,4]. Measurements of temperature were made with platinum resistance thermometers calibrated on the IPTS-48 and, below 90 K, on the provisional scale of the NBS [5]. The molar mass was taken as 170.20 g mol^{-1}.

Table 8 gives values of heat capacity and enthalpy for solid and liquid diphenyl ether under their own vapor pressure. It includes the original values [4] and those corrected to the ITS-90, as recommended by Douglas [6] and Goldberg and Weir [7].

The variation of the heat capacity of diphenyl ether with temperature is essentially linear in the liquid region, which is very useful property in a heat-capacity reference material. No more recent experimental values were found in the literature.

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2.2.3. C_{sat} *and H, heptane*

Physical property	heat capacity, enthalpy
Units	$\text{J mol}^{-1}\,\text{K}^{-1}$ (molar heat capacity, $C_{\text{sat,m}}$); J mol^{-1} (molar enthalpy, H_{m}); $\text{J kg}^{-1}\,\text{K}^{-1}$ (specific heat capacity, c_{sat}); J kg^{-1} (specific enthalpy, h)
Recommended reference material	Heptane (C_7H_{16}): 100.2040 g mol^{-1}; [142-82-5]
Classification	primary RM
Range of variables	(i) 10–182.59 K, (ii) 182.59–400 K
Physical state within the range	(i) solid, (ii) liquid
Apparatus used	adiabatic calorimeter, drop method using a Bunsen ice calorimeter
Contributors to the previous versions	J.D. Cox, T.B. Douglas, D.R. Douslin, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

Table 8
Original and corrected to ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ and enthalpy H_{m} (T)$-H_{\mathrm{m}}$ (0 K) of diphenyl ether

T (K)	$C_{\mathrm{sat,m}}$ (J mol^{-1} K^{-1})		H_{m} (T)$-H_{\mathrm{m}}$ (0 K) (J mol^{-1})	
	Original values	ITS-90	Original values	ITS-90
Solid				
10	3.283		8.272	
20	18.06		109.83	
40	45.44		763.18	
60	61.92		1848.2	
80	73.77		3208.8	
100	84.35	84.42	4791.8	4790.4
120	94.82	94.87	6582.5	6582.7
140	105.88	105.81	8588.3	6588.1
160	117.64	117.51	10 823	10 821
180	129.98	129.88	13 298	13 294
200	143.09	143.08	16 028	16 023
220	156.86	156.92	19 027	19 022
240	171.32	171.43	22 306	22 303
260	186.49	186.64	25 884	25 884
280	202.04	202.18	29 770	29 773
300	218.06	218.18	33 969	33 974
300.03	218.25	218.37	33 975	33 980
Liquid				
300.03	268.42	268.55	51 190	51 197
320	277.17	277.28	56 634	56 644
340	286.25	286.30	62 268	62 279
360	296.35	295.37	68 084	68 096
380	304.39	304.37	74 082	74 094
400	313.33	313.29	80 259	80 270
420	322.36	322.31	86 617	86 627
440	331.30	331.21	93 155	93 164
460	340.32	340.19	99 872	99 879
480	349.16	349.03	106 769	106 773
500	358.04	357.92	113 845	113 847
520	366.92	366.82	121 100	121 100
540	375.78	375.68	128 534	128 531
560	384.63	384.56	136 148	136 144
570	389.05	388.98	140 022	140 017

2.2.3.1. Intended usage Because it can be readily purified (especially with respect to non-hydrocarbon impurities), is chemically stable up to its critical temperature (540 K), can be easily distilled into or out of a calorimeter, exhibits no solid-solid transitions and comes rapidly to thermal equilibrium, heptane is recommended for testing the performance of heat-capacity calorimeters, especially those intended for measurements over the temperature range 10–400 K [1].

2.2.3.2. Sources of supply and/or methods of preparation Samples of heptane of suitable purity (mole fraction purity >0.999) can be obtained from API. Commercial samples with a mass fraction purity >0.999 are available from e.g. BDH, Fluka, etc. which can be further purified by distillation. It is also necessary to remove the dissolved air and water from the sample before using it in calorimetric experiments.

2.2.3.3. Pertinent physicochemical data Douglas et al. [2] measured the heat capacity of a sample of heptane of which the mole fraction purity was (0.99997 assessed by freezing-point determination. The molar mass was taken as 100.20 g mol^{-1}. Measurements of temperature were made with platinum

Table 9
Original and corrected to ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ and enthalpy H_{m} $(T)-H_{\mathrm{m}}$ (0 K) of heptane

T (K)	$C_{\mathrm{sat,m}}$ (J mol^{-1} K^{-1})		H_{m} $(T)-H_{\mathrm{m}}$ (0 K) (J mol^{-1})	
	Original values	ITS-90	Original values	ITS-90
Solid				
10	1.770		4.431	
20	11.80		65.25	
40	38.17		566.2	
60	60.48		1559.7	
80	78.28		2953.4	
100	92.77	92.84	4669.7	4667.9
120	105.20	105.25	6651.2	6651.0
140	116.83	116.74	8872.6	8872.0
160	129.03	128.88	11 328	11 325
180	145.13	144.69	14 054	14 013
182.59	148.58	148.44	14 430	14 424
Liquid				
182.59	203.15	203.05	28 452	28 444
200	201.31	201.32	31 973	31 964
220	202.74	202.83	36 008	36 000
240	206.47	206.61	40 097	40 091
260	211.73	211.90	44 277	44 275
280	218.23	218.36	48 574	48 575
300	225.44	225.53	53 010	53 013
320	233.25	233.32	57 598	57 603
340	241.67	241.68	62 349	62 355
360	250.63	250.60	67 276	67 283
380	260.10	260.06	72 392	72 398
400	270.13	270.08	77 708	77 714

resistance thermometers calibrated on the IPTS-48 and, below 90 K, on the provisional scale of the NBS [3]. Measurements were made by both adiabatic and drop calorimetry. Values of the heat capacity and enthalpy for solid and liquid heptane in equilibrium with their own vapor are given in Table 9, including correction (within ±0.1%) to the ITS-90 as described by Douglas [4] and by Goldberg and Weir [5].

The uncertainty of the listed values of heat capacity and enthalpy is about ±0.1% except below 50 K, where increasing tolerances must be allowed. Measurements were made by Schaake et al. [6], by Kalinowska et al. [7] and by Zhicheng et al. [8] using, respectively, an automatic calorimeter in the range 83–287 K, a semi-automatic calorimeter in the range 185–300 K and an automatic calorimeter in the range 200–380 K. The values of Kalinowska et al. and Zhicheng et al. are in excellent agreement with the results of Douglas et al. in the liquid region. The deviation of the values of Schaake et al. from the results of Douglas et al. is (0.2% in the range 110–287 K.

Recent revisions by Ruzicka et al. [9] and by Zabransky and Ruzicka [10] confirm that original values of Douglas et al. [2] remain the more reliable.

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Table 10
IPTS-68 and corrected to ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ and enthalpy H_{m} $(T){-}H_{\mathrm{m}}$ (0 K) of hexafluorobenzene

T (K)	$C_{\mathrm{sat,m}}$ (J mol^{-1} K^{-1})		H_{m} (T)$-H_{\mathrm{m}}$ (0 K) (J mol^{-1})	
	IPTS-68	ITS-90	IPTS-68	ITS-90
Solid				
10	4.43		11.0	
20	18.44	18.45	126	126
40	38.83	38.84	713	713
60	55.10	55.10	1654	1654
80	71.04	71.03	2916	2915
100	86.99	86.98	4496	4495
120	102.5	102.5	6393	6392
140	117.4	117.4	8592	8590
160	131.8	131.8	11 086	11 084
180	145.2	145.2	13 857	13 855
200	157.0	157.0	16 883	16 882
220	167.3	167.3	20 127	20 126
240	176.9	176.9	23 568	23 567
260	185.9	185.9	27 198	27 198
278.30	193.9	193.9	30 671	30 672
Liquid				
278.30	218.6	218.6	42 254	42 255
280	218.9	218.9	42 626	42 627
300	222.0	222.1	47 033	47 035
320	226.0	226.1	51 512	51 516
340	229.9	230.0	56 070	56 075
350	231.9	232.0	58 379	58 385

2.3. In the solid, liquid and real gas states

2.3.1. C_{sat} and H, hexafluorobenzene

Physical property	heat capacity
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{\mathrm{sat,m}}$); J mol^{-1} (molar enthalpy, H_{m}); J kg^{-1} K^{-1} (specific heat capacity, c_{sat}); J kg^{-1} (specific enthalpy, h)
Recommended reference material	hexafluorobenzene (C_6F_6): 186.0564 g mol^{-1}; [392-56-3]
Classification	secondary RM
Range of variables	(i) 10–278.30 K, (ii) 278.30–350 K, (iii) 335.15–527.15 K real gas at pressures up to 202.66 kPa
Physical state within the range	(i) solid, (ii) liquid, (iii) real gas
Apparatus used	adiabatic calorimeter, vapor-flow calorimeter
Contributor to the previous version	R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.3.1.1. Intended usage Hexafluorobenzene is recommended for testing the performance of calorimeters used for the measurements of the heat capacities of solids and liquids in equilibrium with their vapors and of vapors at pressures between 0 and 202.66 kPa.

2.3.1.2. Sources of supply and/or methods of preparation Commercial samples are available from BDH (with a mass fraction purity of 0.999), Aldrich, Fluka (with a mass fraction purity of $\geq$0.99) which can be further purified by preparative gas-liquid chromatography. It is also necessary to prevent the sample use in calorimetric experiments from being exposed to air and moisture.

2.3.1.3. Pertinent physicochemical data (i and ii) Messerly and Finke [1] examined a sample of hexafluorobenzene having a mole fraction purity of 0.9993 assessed by calorimetric study of the melting behavior. They determined the heat capacity between 13 and 342 K by adiabatic calorimetry. The values of heat capacity and enthalpy for solid and liquid

Table 11
IPTS-68 and ITS-90 heat capacities $C_{p,\mathrm{m}}$ of hexafluorobenzene in the gas phase

p (kPa)		$C_{p,\mathrm{m}}$ (T) (J mol^{-1} K^{-1})							
		T (K)							
		335.15	348.15	368.15	403.15	438.15	473.15	500.15	527.15
202.66	IPTS-68				190.53	195.74	201.81	206.32	210.55
202.66	ITS-90				190.58	195.77	201.82	206.33	210.56
101.32	IPTS-68			180.24	186.70	193.49	200.21	205.03	209.61
101.32	ITS-90			180.28	186.75	193.52	200.22	205.04	209.62
50.660	IPTS-68		173.24	177.47	185.01	192.39	199.38	204.49	209.14
50.660	ITS-90		173.30	177.51	185.06	192.42	199.39	204.50	209.15
37.996	IPTS-68	169.55	172.27	176.81					
37.996	ITS-90	169.60	172.33	176.85					
25.331	IPTS-68	168.48	171.47	176.29	184.33	192.04	199.23	204.52	209.08
25.331	ITS-90	168.53	171.53	176.33	184.38	192.07	199.24	204.53	209.09
19.000	IPTS-68	167.85							
19.000	IPTS-90	167.89							
12.667	IPTS-68	167.35	170.55						
12.667	ITS-90	167.40	170.61						
0 (ideal gas)	IPTS-68	166.27	169.70	174.95	183.40	191.45	198.76	204.09	208.78
0 (ideal gas)	ITS-90	166.32	169.76	174.99	183.45	191.48	198.77	204.10	208.79

hexafluorobenzene under their own vapor pressure are given in Table 10. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the IPTS-48 (revised text of 1960) [2] from 90 to 342 K and in terms of the provisional scale of the NBS below 90 K [3]. Corrections to IPTS-68 were introduced in the previous version [4] and subsequent corrections to ITS-90 were made as recommended by Goldberg and Weir [5].

From 30 to 350 K, the uncertainty of the results is estimated to be less than ±0.2%. In the premelting region and in the region 200–250 K where anomalous thermal behavior was observed, the uncertainty is estimated to be about ±0.5%. Below 30 K, the uncertainty of the individual measurements increases with decreasing temperature to ±1% near 12 K.

Results reported by Counsell et al. [6] for hexafluorobenzene are lower than those in Table 10, although deviations are within 1% from 10 to 300 K. The molar mass was taken as 186.057 g mol^{-1}.

As the difference between $C_{p,\mathrm{m}}$ and $C_{\mathrm{sat,m}}$ is barely significant, values in Table 10 for liquid hexafluorobenzene are also in agreement within 1% with values of $C_{p,\mathrm{m}}$ given in Ref. [7] in the range 278.3–350 K.

(iii) Experimental values obtained by Hossenlopp and Scott [8] using vapor-flow calorimetry are reported in Table 11 for the vapor heat capacity of hexafluorobenzene in the real and ideal gas states over large ranges of pressure and temperature (referred to the IPTS-68 and corrected to the ITS-90 as described in Ref. [4]).

The experimental uncertainty of the reported values is less than ±0.2%. The above sets of measurements agree to better than ±0.3% with those of Counsell et al. [6].

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2.4. *In the glass and liquid states*

2.4.1. *C_p, polystyrene*

Physical property	heat capacity
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{p,\mathrm{m}}$); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_p)
Recommended reference material	polystyrene (atactic): 104.1515 g mol^{-1} for –$CH_2CH(C_6H_5)$–; [9003-53-6]
Classification	primary RM
Range of variables	(i) 10–360 K, (ii) 380–460 K
Physical state within the range	(i) glass, (ii) liquid
Apparatus used	adiabatic calorimeter
Contributors to the previous version	S.S. Chang, R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.4.1.1. Intended usage Atactic polystyrene is recommended for testing the performance of differential scanning calorimeters used for measuring the heat capacity of polymers.

2.4.1.2. Sources of supply and/or methods of preparation Certified reference material (SRM 705a) for molecular weight and heat-capacity determinations is available from NIST. Polystyrene may also be obtained from Polysciences, Aldrich, BDH, etc.)

2.4.1.3. Pertinent physicochemical data Heat capacities of three Standard Reference Materials, SRM 705 for narrow molecular weight distribution (MWD) polystyrene [1], SRM 706 for broad MWD polystyrene [2] and SRM 1478 for narrow MWD polystyrene fraction [3] have been determined by adiabatic calorimetry for the temperature ranges 10–360 K, 20–470 and 6–380 K, respectively. The results of a large number of investigations were summarized by Gaur and Wunderlich [4]. The heat capacities in the glassy state below 340 K are insensitive to MWD and thermal history between ±1%. The heat capacity of the liquid above 370 K is highly reproducible for the individual sample. A kinetically influenced glass transition occurs around 370 K. The recommended values of $C_{p,\mathrm{m}}$ in the range 10–340 K were taken from Ref. [5] and are the same that in Ref. [1]. The heat capacities values above 340 K were taken from Refs. [2,4]. The molar mass of the repeating unit, –$CH_2CH(C_6H_5)$–; was taken as 104.152 g mol^{-1}.

Corrected values of $C_{p,\mathrm{m}}$ to ITS-90 were calculated as recommended by Douglas [6] and Goldberg and Weir [7] (see Table 12.

Table 12
Original and corrected to ITS-90 values of heat capacity $C_{p,\mathrm{m}}$ of polystyrene

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$) Original values	ITS-90
10	3.34	3.34
20	10.76	10.77
40	23.56	23.56
60	32.90	32.90
80	40.67	40.67
100	47.71	47.74
120	54.59	54.62
140	61.44	61.39
160	68.66	68.58
180	76.22	76.16
200	84.17	84.15
220	92.50	92.53
240	101.2	101.3
260	110.1	110.2
280	119.1	119.2
300	128.3	128.4
320	137.6	137.7
340	146.9	146.9
360	156.3	156.3
380	194.5	194.5
400	201.0	201.0
420	207.5	207.5
440	214.0	213.9
460	220.5	220.4

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2.4.2. C_p, poly(vinyl chloride)

Physical property	heat capacity
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{p,\mathrm{m}}$); $\mathrm{J\,g^{-1}\,K^{-1}}$ (specific heat capacity, c_p)
Recommended reference material	poly(vinyl chloride) (PVC): 62.4985 g mol^{-1} for –CH_2CHCl–; [9002-86-2]
Classification	secondary RM
Range of variables	(i) 10–350 K, (ii) 355–380 K
Physical state within the range	(i) glass, (ii) liquid
Apparatus used	adiabatic calorimeter
Contributors to the previous version	S.S. Chang, R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.4.2.1. Intended usage PVC is recommended for testing the performance of differential scanning calorimeters used for measuring the heat capacities of polymers.

2.4.2.2. Sources of supply and/or methods of preparation PVC may be obtained from Polysciences, Aldrich, Fluka, BDH, etc.

2.4.2.3. Pertinent physicochemical data Heat capacities for both bulk-polymerized and suspension-polymerized PVC have been determined by adiabatic calorimetry [1] after being subjected to various thermal and mechanical treatments. Heat capacity differences between quenched glass and annealed glass began to be observable (>0.1%) at 270 K, and reached 1% at 340 K. The influence of methods of polymerization of the heat capacity did not exceed 0.1%. A glass transition occurs around 355 K. Mechanical treatment may cause some energy to be stored. Others measurements [2,3] are summarized by Chang [1], with values deviated within 2% from 260 to 340 K and from 60 to 300 K, respectively. Gaur et al. [4] confirm that the values reported by Chang remain the more reliable. No recent experimental data were found in the literature.

Table 13 gives $C_{p,\mathrm{m}}$ of annealed bulk-polymerized PVC. Correction of heat capacities to ITS-90 [5] leads to the same original results in Ref. [1] (given in the IPTS-68). The molar mass of the repeating unit, -CH_2CHCl-, was taken as 62.499 g mol^{-1}. Heating unstabilized PVC to temperatures higher than 380 K results in thermal degradation and is therefore not recommended as reference material.

Table 13
Heat capacity $C_{p,\mathrm{m}}$ of poly(vinyl chloride)

T_{90} (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
10	1.81
20	5.92
40	13.4
60	18.8
80	23.1
100	26.8
120	30.3
140	33.6
160	36.7
180	39.9
200	43.0
220	46.2
240	49.4
260	52.6
280	56.0
300	59.4
320	62.9
340	67.0
360	91.1
380	98.1

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2.5. In the liquid and real gas states

2.5.1. C_p and C_{sat}, water

Physical property	heat capacity
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{p,\mathrm{m}}$ and $C_{\mathrm{sat,m}}$); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_p and c_{sat})
Recommended reference material	Water (H_2O): 18.0153 g mol^{-1}; [7732-18-5]
Classification	secondary RM

Range of variables	(i) 273.15–373.15 K liquid at 101.325 kPa pressure, (ii) 273.15–647.15 K liquid at the saturated vapor pressure, (iii) 361.80–487.20 K real gas at pressures up to 101.325 kPa
Physical state within the range	(i) and (ii) liquid, (iii) real gas
Apparatus used	adiabatic calorimeter, vapor-flow calorimeter
Contributors to the previous versions	J.D. Cox, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.5.1.1. Intended usage Since the beginning of calorimetry, water has been used as a reference material for heat capacity measurements [1], partly because it is universally available in high purity. Recently, it has also been used in differential scanning calorimetry [2].

2.5.1.2. Sources of supply and/or methods of preparation It is now possible to prepare by distillation of deionized water a sample having a high degree of purity.

2.5.1.3. Pertinent physicochemical data (i) Values of $C_{p,\mathrm{m}}$ (for a pressure of 101.325 kPa) for water are known with an uncertainty of ±0.01% to ±0.02% at close intervals of temperature (1 K). Values of the enthalpy of liquid water relative to the enthalpy at 273.15 K, a quantity useful in experiments using the method of mixtures, are also available at 1 K intervals of temperature [3].

Osborne et al. [3] measured the heat capacity of a sample of water, using a large adiabatic calorimeter especially designed to obtain the highest possible accuracy mentioned above. Values of both $C_{\mathrm{sat,m}}$ and $C_{p,\mathrm{m}}$ based on these measurements (with temperatures on IPTS-48) were presented by Ginnings and Furukawa [4]; these reference values were corrected to ITS-90 [5] and results are given in Table 14. A molar mass of 18.016 g mol^{-1} was used.

Recently Williams et al. [6] measured the specific heat of water in the range 280–350 K. Their data agreed with the values listed in Table 14 to within 0.2%.

(ii) Correlated values of $C_{\mathrm{sat,m}}$ and $H_{\mathrm{m}}(T)-H_{\mathrm{m}}$ (273.15 K) are available [7] at 1 K intervals of temperature covering the entire liquid range of water (273.15–647.15 K).

(iii) Values of the heat capacity of water vapor were obtained over large ranges of pressure and temperature by McCullough et al. [8]. The values on IPTS-68 in Table 15 were determined from their results, which were on IPTS-48 with 0°C = 273.16 K. According to the authors, the uncertainty of these data should not be greater than ±0.2%. Values of $C_{p,\mathrm{m}}$ at zero pressure in ideal gas state are interpolated from the statistically calculated values listed by Wagman et al. [9]. The values of heat capacity were corrected to ITS-90 as described by Goldberg and Weir [5].

The same conclusion is given by Sato et al. [10] after their revision to 1991. No recent experimental values were found in the literature.

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2.5.2. C_{sat}, benzene

Physical property	heat capacity
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{\mathrm{sat,m}}$); J kg^{-1} K^{-1} (specific heat capacity, c_{sat})
Recommended reference material	benzene (C_6H_6): 78.1136 g mol^{-1}; [71-43-2]

Table 14
IPTS-48 and ITS-90 values of the heat capacity $C_{\mathrm{sat,m}}$ and $C_{p,\mathrm{m}}$ of water in the liquid phase

T (K)	$C_{\mathrm{sat,m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	
	IPTS-48	ITS-90	IPTS-48	ITS-90
273.15	75.993	76.041	75.985	76.033
278.15	75.714	75.759	75.706	75.751
283.15	75.532	75.573	75.525	75.566
288.15	75.417	75.453	75.410	75.446
293.15	75.345	75.377	75.339	75.371
298.15	75.303	75.329	75.298	75.324
303.15	75.282	75.308	75.278	75.304
308.15	75.277	75.301	75.273	75.297
313.15	75.283	75.304	75.280	75.301
318.15	75.298	75.320	75.295	75.317
323.15	75.320	75.339	75.318	75.337
328.15	75.350	75.357	75.348	75.355
333.15	75.385	75.381	75.385	75.381
338.15	75.428	75.423	75.428	75.423
343.15	75.476	75.472	75.478	75.474
348.15	75.532	75.528	75.536	75.532
353.15	75.594	75.590	75.601	75.597
358.15	75.667	75.663	75.675	75.671
363.15	75.746	75.742	75.757	75.753
368.15	75.835	75.826	75.850	75.841
373.15	75.934	75.920	75.954	75.940

Table 15
IPTS-68 and ITS-90 values of heat capacity of water $C_{p,\mathrm{m}}$ in the gas phase

p (kPa)/T (K)	$C_{p,\mathrm{m}}$ (T) ($\mathrm{J\,mol^{-1}\,K^{-1}}$)									
	361.80		381.20		410.20		449.20		487.20	
	IPTS-68	ITS-90	IPTS-68	ITS-90	IPTS-68	ITS-90	IPTS-68	ITS-90	IPTS-68	ITS-90
101.32			36.82	36.82	35.84	35.84	35.47	35.47	34.44	35.44
47.36	35.65	35.66	35.19	35.19	34.94	34.94	35.02	35.02		
25.09	34.76	34.77	34.65	34.65	34.64	34.65	34.79	34.79	35.08	35.08
12.33	34.38	34.39	34.32	34.32						
0 (ideal gas)	33.95	33.96	34.09	34.10	34.33	34.34	34.69	34.69	35.07	35.07

Range of variables	(i) 279–350 K liquid at saturation pressure, (ii) 333–527 K real gas at pressures up to 202.65 kPa.
Classification	secondary RM
Physical state within the range	(i) liquid, (ii) real gas
Apparatus used	adiabatic calorimeter, vapor-flow calorimeter
Contributors to the previous versions	J.D. Cox, D.R. Douslin, J. Lielmezs, J.F. Martin, O. Riedel, R. Sabbah, D.R. Stull
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.5.2.1. Intended usage Because benzene is not corrosive, has excellent boiling characteristics and is easy to handle experimentally, it is recommended for testing the performance of vapor flow (non-adiabatic) calorimeters [1] for the measurement of the heat capacity of (i) liquids in equilibrium with their vapors and (ii) vapors at pressures between 0 (ideal gas state) and 202.65 kPa. Benzene must be carefully manipulated because is cancer suspect.

2.5.2.2. Sources of supply and/or methods of preparation High purity samples of benzene can be ob-

Table 16
Original and corrected to ITS-90 values of heat capacity $C_{\mathrm{sat,m}}$ of benzene in the liquid phase

	$C_{\mathrm{sat,m}}$ (J mol^{-1} K^{-1})	
T (K)	Original values	ITS-90
278.7	131.9	131.9
280	132.2	132.2
290	134.3	134.4
300	136.5	136.5
310	138.7	138.8
320	141.0	141.0
330	143.3	143.4
340	145.9	145.9
350	148.5	148.5

tained from API as well as from producers of high purity chemicals, e.g. BDH, Fluka, etc.

2.5.2.3. Pertinent physicochemical data (i) Using an adiabatic calorimeter, Oliver et al. [2] measured the heat capacity of sample of benzene having a mole fraction purity 0.99967, as assessed by a calorimetric study of the melting behavior. Their original data, obtained on the 1927 temperature scale, were fitted to give the following interpolated values for the molar heat capacity of liquid benzene at its saturation vapor pressure in the temperature range 278.67–340 K. The molar mass was taken as 78.113 g mol^{-1}. Corrected values of heat capacities to ITS-90 as recommended by Goldberg and Weir [3] are also included in Table 16. As the differences between $C_{p,\mathrm{m}}$ and $C_{\mathrm{sat,m}}$ are barely significant [4,5], the values in Table 16 are in agreement with those given at 298.15, 308.15 and 318.15 K in Ref. [4] and do not differ above 310 K from those given in Ref. [5] by more than 0.5%.

(ii) Experimental values obtained by Todd et al. [6] are reported in Table 17 for the vapor heat capacity of a sample of benzene (having a mole fraction purity of 0.9994 ± 0.0002, assessed by a freezing point method) in the real and ideal gas states over large ranges of pressure and temperature (referred to IPTS-68 and corrected to ITS-90 as described in Ref. [3]). The earlier values of $C^0_{p\mathrm{m}}$ reported in Ref. [7] are within 0.15% of a smooth curve drawn through the values given in Table 17. Part of the difference arises because "curvature corrections" in the extrapolation to zero pressure were not applied in the earlier work.

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2.5.3. C_p, nitrogen

Physical property	heat capacity
Units	J mol^{-1} K^{-1} (molar heat capacity, $C_{p,\mathrm{m}}$); J kg^{-1} K^{-1} (specific heat capacity, c_p)
Recommended reference material	nitrogen (N_2): 28.0135 g mol^{-1}; [7727-37-9]
Classification	tertiary RM
Range of variables	(i) 65–110 K liquid at saturation pressure, (ii) 100–1000 K real gas at pressures up to 40 MPa.
Physical state within the range	(i) liquid, (ii) real gas
Apparatus used	adiabatic calorimeter
Contributors to the previous versions	J.D. Cox, R.T. Jacobsen, R. Sabbah, D.R. Stull, L.A. Weber
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

2.5.3.1. Intended usage Nitrogen is recommended for testing the performance of calorimeters used for the measurements of the heat capacities of (i) liquids and liquified gases and (ii) gases and vapors.

2.5.3.2. Sources of supply and/or methods of preparation Nitrogen of suitable purity can be obtained commercially from various sources. Samples should be passed, at cylinder pressure, through a molecular sieve trap before being distilled into the calorimeter.

2.5.3.3. Pertinent physicochemical data The molar mass was taken as 28.016 g mol^{-1}. (i) The measurements of Giauque and Clayton [1] in the range

Table 17
IPTS-68 and ITS-90 values of the heat capacities $C_{p,\mathrm{m}}$ of benzene in the gas phase

p (kPa)	$C_{p,\mathrm{m}}$ (T) (J mol^{-1} K^{-1})								
	T (K)								
		333.15	348.15	368.15	408.15	438.15	473.15	500.15	527.15
202.65	IPTS-68				117.44	126.08	134.45	140.66	146.48
202.65	ITS-90				117.48	126.11	134.46	140.67	146.49
101.32	IPTS-68			106.39	115.85	124.99	133.79	140.09	145.99
101.32	ITS-90			106.42	115.88	125.02	133.80	140.10	146.00
50.662	IPTS-68		99.43	105.13	115.01	124.43	133.30	139.77	145.82
50.662	ITS-90		99.47	105.16	115.04	124.46	133.31	139.78	145.83
37.996	IPTS-68	94.68	99.06	104.88					
37.996	ITS-90	94.71	99.10	104.91					
25.331	IPTS-68	94.23	98.71	104.59	114.69	124.20	133.09	139.60	145.70
25.331	ITS-90	94.26	98.75	104.62	114.72	124.23	133.10	139.61	145.71
18.998	IPTS-68	94.00	98.53						
18.998	ITS-90	94.03	98.57						
12.666	IPTS-68	93.76	98.34	104.26	114.47				
12.666	ITS-90	93.79	98.38	104.29	114.50				
0 (ideal gas)	IPTS-68	93.32	97.99	103.98	114.29	123.93	132.94	139.47	145.59
0 (ideal gas)	ITS-90	93.35	98.03	104.01	114.32	123.96	132.95	139.48	145.60

65–78 K and of Weber [2] in the range 78–126 K on the gas-liquid two-phase system at its saturation vapor pressure can be expressed by the following equation within ±0.5%:

$$C_{\mathrm{sat}}/\mathrm{J\,mol^{-1}\,K^{-1}} = 88.619 - 1.3696x + 1.4443 \times 10^{-2}x^2 - 6.3700 \times 10^{-5}x^3 + 1.5580x/(126.2 - x)^{1/2} \qquad (2.5.3.1)$$

where $x = T$ (K). At temperatures above the normal boiling point, the data must generally be corrected for the presence of the vapor and for any PV work done (see Ref. [2]). Data of Wiebe and Brevoort [3] agree within 1% with the equation in the range 80–117 K. Corrections to ITS-90, calculated as recommended by Goldberg and Weir [4] do no affect the equation because they are within ±0.05% in the range 65–110 K.

(ii) Jacobsen and Stewart [5] reported calculated values for the heat capacity of nitrogen in the range 100–1000 K and 0.101325–40 MPa (Table 18). Values of $C^0_{p,\mathrm{m}}$ are also given. Corrections to ITS-90 were derived as described by Goldberg and Weir [4,6]. The calculated values at 0.101325 MPa are accurate to above ±0.1%, while the higher pressure, lower temperature values are estimated to be accurate to about ±1%, based upon comparisons with the dense-gas measurements of Ref. [2].

Revision of general thermodynamic properties of nitrogen [7] leads to the same results and describes the available data within ±3% in all the range of pressure and temperature. Perkins et al. [8] determined heat capacity using a sample of mole fraction 0.99999 and the technique of hot wire transient from 80 to 300 K and up to 70 MPa. The root-mean-square deviation between the experimental data and the calculated values in Ref. [6] is about 5%. Experimental data appear systematically higher at high pressure.

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Table 18
IPTS-68 and ITS-90 values of heat capacity of nitrogen in the gas phase

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)								
	p (MPa)	0	0.101325	1.0	5.0	10.0	15.0	20.0	40.0
100	IPTS-68	29.10	30.03	64.73	59.62	56.30	54.22	52.74	49.36
100	ITS-90	29.10	30.03	64.73	59.61	56.28	54.21	52.75	49.35
150	IPTS-68	29.11	29.37	32.13	67.00	80.11	62.49	56.07	48.46
150	ITS-90	29.11	29.37	32.13	67.00	80.11	62.48	56.06	48.46
200	IPTS-68	29.11	29.23	30.38	36.68	45.54	49.94	49.85	45.33
200	ITS-90	29.11	29.23	30.38	36.69	45.55	49.94	49.85	45.33
250	IPTS-68	29.11	29.18	29.82	32.80	36.41	39.22	40.88	41.44
250	ITS-90	29.11	29.18	29.82	32.80	36.41	39.22	40.88	41.44
300	IPTS-68	29.12	29.17	29.58	31.39	33.46	35.16	36.44	38.28
300	ITS-90	29.12	29.17	29.58	31.39	33.46	35.16	36.44	38.28
350	IPTS-68	29.16	29.20	29.48	30.71	32.09	33.26	34.19	36.09
350	ITS-90	29.17	29.21	29.49	30.72	32.10	33.27	34.20	36.10
400	IPTS-68	29.25	29.27	29.48	30.37	31.37	32.23	32.94	34.64
400	ITS-90	29.25	29.27	29.48	30.37	31.37	32.23	32.94	34.64
450	IPTS-68	29.39	29.40	29.56	30.24	31.00	31.66	32.23	33.69
450	ITS-90	29.39	29.40	29.56	30.24	31.00	31.66	32.23	33.69
500	IPTS-68	29.58	29.59	29.72	30.25	30.85	31.37	31.83	33.09
500	ITS-90	29.58	29.59	29.72	30.25	30.85	31.37	31.83	33.09
550	IPTS-68	29.82	29.84	29.94	30.36	30.84	31.27	31.65	32.74
550	ITS-90	29.82	29.84	29.94	30.36	30.84	31.27	31.65	32.74
600	IPTS-68	30.11	30.12	30.20	30.55	30.94	31.30	31.62	32.57
600	ITS-90	30.11	30.12	30.20	30.55	30.94	31.30	31.62	32.57
650	IPTS-68	30.42	30.43	30.50	30.79	31.12	31.42	31.69	32.52
650	ITS-90	30.42	30.43	30.50	30.79	31.12	31.42	31.69	32.52
700	IPTS-68	30.76	30.76	30.82	31.06	31.34	31.60	31.83	32.56
700	ITS-90	30.77	30.77	30.83	31.07	31.35	31.61	31.84	32.57
750	IPTS-68	31.09	31.10	31.15	31.35	31.59	31.81	32.01	32.66
750	ITS-90	31.10	31.11	31.16	31.36	31.60	31.82	32.02	32.67
800	IPTS-68	31.43	31.44	31.48	31.66	31.86	32.05	32.23	32.80
800	ITS-90	31.44	31.45	31.49	31.67	31.87	32.06	32.24	32.81
850	IPTS-68	31.76	31.77	31.81	31.96	32.14	32.30	32.46	32.97
850	ITS-90	31.77	31.78	31.82	31.97	32.15	32.31	32.47	32.98
900	IPTS-68	32.09	32.09	32.13	32.26	32.41	32.56	32.70	33.15
900	ITS-90	32.09	32.09	32.13	32.26	32.41	32.56	32.70	33.15
950	IPTS-68	32.40	32.40	32.43	32.55	32.69	32.81	32.93	33.34
950	ITS-90	32.35	32.35	32.37	32.49	32.63	32.75	32.87	33.28
1000	IPTS-68	32.70	32.70	32.72	32.83	32.95	33.06	33.17	33.54
1000	ITS-90	32.66	32.66	32.68	32.79	32.91	33.02	33.13	33.50

2.6. *In the real gas state*

2.6.1. *C_p, carbon dioxide*

Physical property	heat capacity
Units	$\mathrm{J\,mol^{-1}\,K^{-1}}$ (molar heat capacity, $C_{p,\mathrm{m}}$); $\mathrm{J\,kg^{-1}\,K^{-1}}$ (specific heat capacity, c_p)
Recommended reference material	carbon dioxide (CO_2): 44.0098 $\mathrm{g\,mol^{-1}}$; [124-38-9]
Classification	tertiary RM
Range of variables	250–1000 K real gas at pressures up to 50 MPa
Physical state within the range	real gas
Apparatus used	vapor-flow calorimeter, Tian-Calvet calorimeter
Contributor to the previous version	R. Sabbah
Contributors to this version	M. Campos, R. Patiño, L.A. Torres

Table 19
ITS-68 and IPTS-90 values of heat capacity $C_{p,\mathrm{m}}$ of carbon dioxide in the gas phase

T (K)	$C_{p,\mathrm{m}}$ (T) (J mol^{-1} K^{-1})										
	p (MPa)	0	0.01	0.05	0.1	0.5	1	5	10	25	50
250	IPTS-68	34.83	34.9	35.1	35.4	38.2	42.8	89.3	86.0	79.9	74.4
250	ITS-90	34.84	34.9	35.1	35.4	38.2	42.8	89.3	86.0	79.9	74.4
300	IPTS-68	37.21	37.2	37.3	37.5	38.7	40.3	79.0	131.0	88.1	77.3
300	ITS-90	37.23	37.2	37.3	37.5	38.7	40.3	79.0	131.0	88.1	77.3
350	IPTS-68	39.39	39.4	39.5	39.6	40.2	41.2	51.8	84.9	98.6	76.6
350	ITS-90	39.41	39.4	39.5	39.6	40.2	41.2	51.8	84.9	98.6	76.6
400	IPTS-68	41.33	41.3	41.4	41.4	41.9	42.5	48.2	58.4	85.6	74.7
400	ITS-90	41.35	41.3	41.4	41.4	41.9	42.5	48.2	58.4	85.6	74.7
450	IPTS-68	43.06	43.1	43.1	43.1	43.5	43.9	47.6	53.1	69.2	70.9
450	ITS-90	43.07	43.1	43.1	43.1	43.5	43.9	47.6	53.1	69.2	70.9
500	IPTS-68	44.61	44.6	44.6	44.7	44.9	45.2	47.9	51.5	61.6	66.9
500	ITS-90	44.62	44.6	44.6	44.7	44.9	45.2	47.9	51.5	61.6	66.9
550	IPTS-68	46.03	46.0	46.3	46.1	46.3	46.5	48.5	51.0	58.1	63.6
550	ITS-90	46.04	46.0	46.3	46.1	46.3	46.5	48.5	51.0	58.1	63.6
600	IPTS-68	47.32	47.3	47.3	47.4	47.5	47.7	49.2	51.1	56.3	61.1
600	ITS-90	47.33	47.3	47.3	47.4	47.5	47.7	49.2	51.1	56.3	61.1
650	IPTS-68	48.49	48.5	48.5	48.5	48.6	48.8	50.0	51.5	55.4	59.5
650	ITS-90	48.51	48.5	48.5	48.5	48.6	48.8	50.0	51.5	55.4	59.5
700	IPTS-68	49.56	49.6	49.6	49.6	49.7	49.8	50.8	51.9	55.0	58.4
700	ITS-90	49.59	49.6	49.6	49.6	49.7	49.8	50.8	51.9	55.0	58.4
750	IPTS-68	50.54	50.5	50.6	50.6	50.6	50.7	51.5	52.5	55.0	57.8
750	ITS-90	50.57	50.5	50.6	50.6	50.6	50.7	51.5	52.5	55.0	57.8
800	IPTS-68	51.43	51.4	51.4	51.5	51.5	51.6	52.3	53.1	55.1	57.5
800	ITS-90	51.46	51.4	51.4	51.5	51.5	51.6	52.3	53.1	55.1	57.5
850	IPTS-68	52.25	52.3	52.3	52.3	52.3	52.4	53.0	53.6	55.3	57.4
850	ITS-90	52.28	52.3	52.3	52.3	52.3	52.4	53.0	53.6	55.3	57.4
900	IPTS-68	52.99	53.0	53.0	53.0	53.1	53.1	53.6	54.2	55.6	57.4
900	ITS-90	53.00	53.0	53.0	53.0	53.1	53.1	53.6	54.2	55.6	57.4
950	IPTS-68	53.67	53.7	53.7	53.7	53.7	53.8	54.2	54.7	56.0	57.5
950	ITS-90	53.60	53.6	53.6	53.6	53.6	53.7	54.1	54.6	55.9	57.4
1000	IPTS-68	54.30	54.3	54.3	54.3	54.3	54.4	54.7	55.2	56.3	57.6
1000	ITS-90	54.25	54.2	54.2	54.2	54.2	54.3	54.6	55.1	56.2	57.5

2.6.1.1. Intended usage Carbon dioxide is recommended for testing the performance of calorimeters used for the measurements of the heat capacities of gases and vapors, especially calorimeters of the vapor-flow type.

2.6.1.2. Sources of supply and/or methods of preparation Carbon dioxide of suitable purity can be obtained commercially from various sources. As mentioned by Rivkin and Gukov [1], small amounts of nitrogen affect the heat capacity, so it is necessary to remove nitrogen from the sample before using it in calorimetric experiments.

2.6.1.3. Pertinent physicochemical data Altunin et al. [2] reported calculated values for the heat capacity of carbon dioxide from which are taken the values in Tables 19 and 20 for the real gas in the range 250–1000 K and 0.01–50 MPa. Values of $C^0_{p,\mathrm{m}}$ are also given. Corrections to ITS-90 were calculated as described by Goldberg and Weir [3,4].

Bottinga and Richet [5] calculated values of $C_{p,\mathrm{m}}$ for the real gas in the range 400–2100 K and 0.1–500 MPa and Bender et al. [6] gave experimental values in the range 233–473 K at pressures up to 1.5 MPa.

Ernst and Hochberg [7] measured heat capacities using a flow calorimeter and a sample with a mole fraction of 0.9999 in the range 333.15–393.15 K and up to 89.7 MPa. Dordain et al. [8] measured heat capacities using a Tian-Calvet calorimeter and a sample with a mole fraction of 0.99998 in the range 327.5–416.9 K,

Table 20
A summary of the melting (*M*), freezing (*F*), triple point (*T*) and transition temperatures (T_{trs}) of recommended reference materials

Substance	Transition temperature (K)	Phase change (K)	Classification
Metals			
Mercury		234.32 (*T*)	Primary
Gallium		302.91 (*M*)	Secondary
Indium		429.75 (*F*)	Primary
Tin		505.08 (*F*)	Primary
Bismuth		544.55 (*M*)	Secondary
Zinc		692.68 (*F*)	Secondary
Aluminum		933.47 (*F*)	Secondary
Inorganic substances			
Sodium nitrate	549	580 (*M*)	Tertiary
Lithium sulfate	851.43		Secondary
Organic substances			
2-Methylbutane		113.37 (*M*)	Primary
2-Methyl-1,3-butadiene		127.27 (*T*)	Secondary
Pentane		143.48 (*T*)	Primary
2,2,4-Trimethylpentane		165.80 (*T*)	Secondary
Cyclopentane	122.38, 138.06	179.72 (*T*)	Primary
Heptane		182.60 (*T*)	Primary
1,3-Difluorobenzene	187.3	204.08 (*T*)	Secondary
2,2-Dimethylpropane	140.51	256.76 (*T*)	Secondary
Hexafluorobenzene		278.30 (*T*)	Primary
Cyclohexane	186.25	279.81 (*T*)	Primary
Diphenyl ether		300.01(*T*)	Tertiary
Biphenyl		342.08 (*T*)	Primary
Naphthalene		353.35 (*T*)	Primary
Benzil		367.97 (*T*)	Secondary
Acetanilide		387.48 (*T*)	Secondary
Benzoic acid		395.50 (*T*)	Secondary
Diphenylacetic acid		420.41 (*T*)	Secondary
Triphenylene		471.02 (*T*)	Secondary
Hexachlorobenzene		501.83 (*T*)	Tertiary
Perylene		551.25 (*T*)	Secondary

up to 25.1 MPa. Both experimental results support the calculated values of Table 19 in the corresponding range with deviations within 2%. Values of Table 19 and experimental results, as function of pressure, are in agreement to describe the maxima of $C_{p,\mathrm{m}}$ isotherms and the shift to higher pressures with the increase of temperature.

References

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[2] S. Angus, B. Armstrong, K.M. de Reuck (Eds.), International Thermodynamic Tables of the Fluid State-3: Carbon Dioxide, Pergamon, Oxford, 1976.
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3. Reference materials for measurement of phase change enthalpies

The temperatures in this section are reported in terms of the ITS-90 [1,2] unless otherwise noted. Molar masses of the elements are adopted from the 1993 report of the IUPAC Commission on Atomic Weights and Isotopic Abundances [3]. Uncertainties associated with each measurement represents two standard deviations of the mean unless stated otherwise.

References

[1] H. Preston-Thomas, Metrologia 27 (1990) 3.

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3.1. Solid-solid or/and solid-liquid phase changes

A working group on “Calibration of Scanning Calorimeters” of the Gesellschaft für Thermische Analyse, Germany (GEFTA, [1]) has recommended that calibration substances for DSC and DTA instruments be based on adiabatically measured values. These recommendations have been followed in this compilation. Substances recommended as primary reference materials in this section were chosen on the basis of data obtained in at least two independent sets of adiabatic measurements and one DSC or DTA measurement which were in good agreement with each other. Other criteria such as availability, reproducibility, purity, thermodynamic stability, low toxicity and general non-volatility were also considered. Secondary reference materials are also proposed which do not rigorously meet all the criteria for primary reference materials, but are based on reliable data. To be recommended as a secondary reference material, good agreement between at least one set of measurements performed on an adiabatic calorimeter with data obtained on other instruments was necessary. These secondary reference materials offer a greater diversity in molecular structure and broaden the applicable temperature range. A designation of tertiary reference materials is also included in this compilation. To be included as a tertiary reference material, the material must have been recommended as a reference material, but either lacks adiabatic calorimetric data, a sufficient amount of confirmatory data or has been reported to exhibit some peculiarity in its thermochemical behavior. The reader should examine the pertinent thermochemical data presented for these compounds carefully before use.

The substances included in this compilation cover the temperature range 120–930 K as uniformly as possible. Metals pretreated with hydrogen and encapsulated in quartz covering the temperature range 1230–1768 K have also been proposed as reference materials for DSC and DTA measurements [2]. This technique is currently under assessment. Transition temperatures for a number of inorganic substances have been recommended by ICTAC as temperature reference materials for use in DTA and DSC studies. These materials and the enthalpy of transition which accompanies the transition are listed in Table 21 (at the end of this section). Other organic materials which have been recommended as reference materials but do not presently meet the criteria outlined above are listed in Table 22 (at the end of this section). These materials are not presently included in the main body of this section because of the lack of sufficient experimental data, poor agreement in the data available or for exhibiting properties that are not characteristic of good reference materials. In selection of fusion reference materials, the choice should be based on the temperature range and structural similarity of the reference materials to the samples being studied [3]. Recommended practices for both temperature and enthalpy calibrations of differential scanning calorimeters have been published [4,5].

References

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3.1.1. $\Delta_{fus}H$*, mercury*

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	mercury (Hg): 200.59 $\mathrm{g\,mol^{-1}}$; [7439-97-6]
Classification	primary RM
Range of variables	T: 234.32 K (T: triple point; fixed point material of the ITS-90)
Physical state within the range	liquid → solid

Apparatus used	isoperibol and adiabatic calorimeters, DSC
Recommended Value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (2295.3 \pm 0.8)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 11.4\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.1.1. Intended usage The use of mercury as a test material for differential scanning calorimetry has been suggested [1]. Mercury is a fixed point material for the ITS-90 [2].

3.1.1.2. Sources of supply and/or methods of preparation Certified samples are available from NIST (SRM 743). Other high purity material is available (Fluka: 99.9999%; Alfa: 99.999995%).

3.1.1.3. Pertinent physicochemical data A fusion enthalpy of $(2301 \pm 2)\,\mathrm{J\,mol^{-1}}$ and a fusion temperature of $(234.31 \pm 0.06)\,\mathrm{K}$ has recently been measured for mercury in an adiabatic calorimeter [2]. The fusion enthalpy of mercury has also been measured by DSC and the value obtained is in good agreement with the calorimetric value $(2295.3 \pm 0.8)\,\mathrm{J\,mol^{-1}}$ [3] recommended in the most recent edition of the JANAF tables [4]. The new results certify mercury as a primary reference material for differential scanning calorimetry. The uncertainty of the new results is within experimental error of the recommended value. The calorimetric value $(2295.3 \pm 0.8)\,\mathrm{J\,mol^{-1}}$ is retained as the recommended fusion enthalpy of mercury.

References

[1] J.E. Callanan, K.M. McDermott, E.F. Westrum Jr., J. Chem. Thermodyn. 22 (1990) 225.
[2] H. Preston-Thomas, Metrologia 27 (1990) 3.
[3] R.H. Busey, W.F. Giauque, J. Am. Chem. Soc. 75 (1953) 806.
[4] M.W. Chase Jr., J.R. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, 3rd ed., Part 2, J. Phys. Chem. Ref. Data Supplement 1 14 (1985) 1319.

3.1.2. $\Delta_{fus}H$, gallium

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	gallium (Ga): $69.723\,\mathrm{g\,mol^{-1}}$; [7440-55-3]
Classification	secondary RM
Range of variables	*M*: 302.91 K (*M*: melting point at 0.1 MPa; fixed point material of the ITS-90)
Physical state within the range	solid → liquid (0.1 MPa)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (5569 \pm 50)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 79.9\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.2.1. Intended usage The use of gallium as a test material for differential scanning calorimetry has been suggested by the German Society for Thermal Analysis, GEFTA. Gallium is a fixed point material for the ITS-90 [1]. Gallium should not be used with aluminum pans because of its tendency to form alloys [2]. The melt reacts with aluminum and is subject to strong supercooling.

3.1.2.2. Sources of supply and/or methods of preparation Certified samples are available from NIST (99.9999+%, SRM 1968). Other high purity material is available (Fluka: 99.999%; Alfa: 99.9999%).

3.1.2.3. Pertinent physicochemical data The fusion enthalpy of $(5569 \pm 50)\,\mathrm{J\,mol^{-1}}$ is a mean value of the most reliable measurements cited in the relevant literature [3–6].

References

[1] H. Preston-Thomas, Metrologia 27 (1990) 3.
[2] P.S. Nolan, H.E. Lemay, Thermochim. Acta 9 (1974) 81.
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3.1.3. $\Delta_{fus}H$, indium

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)

Recommended reference material	indium (In): 114.818 g mol^{-1}; [7440-74-6]
Classification	primary RM
Range of variables	F: 429.75 K (F: freezing point at 0.1 MPa; fixed point material of the ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (3286 \pm 13)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 28.6\ \mathrm{J\,g^{-1}}$
Contributors to the previous version	J.F. Martin, R. Sabbah, D.D. Sood, R. Venugopal
Contributor to this version	J. Chickos

3.1.3.1. Intended usage Indium has been recommended and used as a test reference material in apparatus employed in the measurement of fusion enthalpy [1,2]. This includes instruments such as adiabatic calorimeters [1,3] and differential scanning calorimeters [2]. Indium is a fixed point material for the ITS-90 [4].

3.1.3.2. Sources of supply and/or methods of preparation High purity material (99.999% or better) is available from a variety of commercial suppliers (Alfa, Fluka). Certified samples are available from NIST (99.9999+%, SRM 1971).

3.1.3.3. Pertinent physicochemical data Measurements of the triple point temperature and the enthalpy of fusion of an evacuated sample by adiabatic calorimetry have been reported on samples ($\geq$99.99 mol%) by Andon et al. [3] and most recently by Grønvold who reviewed previous measurements [1]. In a series of measurements on very pure samples (99.99995 mass%), Grønvold obtained a triple point of (429.75 ± 0.04) K and an enthalpy of fusion of $(3296 \pm 9)\ \mathrm{J\,mol^{-1}}$ using an adiabatic calorimeter. The uncertainty of $\pm 9\ \mathrm{J\,mol^{-1}}$ was determined by considering the 95% confidence interval of five determinations, $\pm 4\ \mathrm{J\,mol^{-1}}$, together with an estimated systematic error of $\pm 8\ \mathrm{J\,mol^{-1}}$. This fusion enthalpy of indium has been reviewed by the working group “Calibration of Scanning Calorimeters” of the Gesellschaft für Thermische Analyse, GEFTA [5]. Their recommended value, $(3286 \pm 13)\ \mathrm{J\,mol^{-1}}$, is within the uncertainty of the mean $(3287 \pm 25)\ \mathrm{J\,mol^{-1}}$ of the sixteen previous determinations reviewed by Grønvold and also within Grønvold’s uncertainty. The GEFTA value, $(3286 \pm 13)\ \mathrm{J\,mol^{-1}}$, is recommended for the fusion enthalpy of indium. The newer recommendations for the fusion enthalpy of indium are in good agreement with earlier values [6].

References

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3.1.4. $\Delta_{fus}H$, tin

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	tin (Sn): 118.710 g mol^{-1}; [7440-31-5]
Classification	primary RM
Range of variables	F: 505.08 K (F: freezing point at 0.1 MPa; fixed point material of the ITS-90)
Physical state within the range	liquid → solid (0.1 MPa)
Apparatus used	adiabatic calorimeter, drop method using a Bunsen ice calorimeter, DSC
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7170 \pm 43)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 60.4\ \mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.4.1. Intended usage The use of tin as a test material for differential scanning calorimetry has been suggested by the German Society for Thermal Analysis, GEFTA [1]. Tin is a fixed point material for the ITS-90 [2]. The melt reacts with aluminum and platinum [3].

3.1.4.2. Sources of supply and/or methods of preparation Certified samples are available from NIST (99.9995%, SRM 2220). Other high purity material is available (Fluka: 99.999%; Alfa: 99.9999%).

3.1.4.3. Pertinent physicochemical data The fusion enthalpy of (7170 ± 43) $\mathrm{J\,mol^{-1}}$ is a mean value of the most reliable measurements cited in the relevant literature [3–6]. The fusion enthalpy of tin has been reviewed by the working group “Calibration of Scanning Calorimeters” of the GEFTA [1,3].

References

[1] S.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger, W. Eysel, Thermochim. Acta 247 (1994) 129.
[2] H. Preston-Thomas, Metrologia 27 (1990) 3.
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3.1.5. $\Delta_{fus}H$, bismuth

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	bismuth (Bi): 208.9804 $\mathrm{g\,mol^{-1}}$; [7440-69-9]
Classification	secondary RM
Range of variables	M = 544.55 K (M: melting at 0.1 MPa; unsuitable for temperature calibration)
Physical state within the range	solid → liquid (0.1 MPa)
Apparatus used	adiabatic calorimeter, DSC
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (11250 \pm 439)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 53.8\,\mathrm{J\,g^{-1}}$)
Contributor to this version	J. Chickos

3.1.5.1. Intended usage The use of bismuth as a test material for differential scanning calorimetry has been suggested by the German Society for Thermal Analysis, GEFTA [1]. The melt reacts with aluminum.

3.1.5.2. Sources of supply and/or methods of preparation High purity material is available from several commercial sources (Fluka: 99.999%; Alfa: 99.9999%; J.T. Baker: 99.95+%).

3.1.5.3. Pertinent physicochemical data The fusion enthalpy (11250 ± 439) $\mathrm{J\,mol^{-1}}$ is a mean value of the most reliable measurements cited in the relevant literature [2–5].

References

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3.1.6. $\Delta_{fus}H$, zinc

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	zinc (Zn): 65.39 $\mathrm{g\,mol^{-1}}$; [7440-66-6]
Classification	secondary RM
Range of variables	F: 692.68 K (F: freezing point at 0.1 MPa; fixed point material of the ITS-90)
Physical state within the range	solid → liquid
Apparatus used	isothermal phase-change calorimeter, drop method using a Bunsen ice calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7026 \pm 80)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 107.4\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.6.1. Intended usage The use of zinc as a test material for differential scanning calorimetry has been suggested [1]. Zinc is a fixed point material for the ITS-90 [2].

3.1.6.2. Sources of supply and/or methods of preparation Certified samples are available from NIST (99.999%, SRM 2221b). Other high purity material is available (Fluka: 99.99%; Alfa: 99.9995%).

3.1.6.3. Pertinent physicochemical data A fusion enthalpy $(7026 \pm 80)\,\mathrm{J\,mol^{-1}}$ and a triple point temperature $(692.71 \pm 0.02)\,\mathrm{K}$ (corrected to ITS-90) has been measured for samples of zinc (SRM 2221a) in a method of mixtures isothermal phase-change calorimeter [1]. This enthalpy value while not comparing favorably with values recommended in three recent compilations, 7300 [3], (7322 ± 105) [4,5], and represents the first instance that both T_{fus} and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ were measured on the same sample using a single calorimetric technique at the purity cited above for the NIST sample. Ditmars notes that measurements of $\{H_{\mathrm{m}}(T) - H_{\mathrm{m}}(273.15\,\mathrm{K})\}$ in his work lies near the middle of the primary literature values for both solid and liquid zinc. The primary literature values of $\{H_{\mathrm{m}}(T) - H_{\mathrm{m}}(273.15\,\mathrm{K})\}$ for liquid zinc show significant scatter (±6%) and the discrepancy between these results and recent recommendations of $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ for zinc [3–5] may reflect the difficulty in selecting among divergent values. The recommended value is the value reported by Ditmars.

References

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3.1.7. $\Delta_{fus}H$, aluminum

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	aluminum (Al): $26.9815\,\mathrm{g\,mol^{-1}}$; [7429-90-5]
Classification	secondary RM
Range of variables	F: 933.47 K (F: freezing point at 0.1 MPa; fixed point material of the ITS-90)
Physical state within the range	liquid → solid (0.1 MPa)
Apparatus used,	adiabatic calorimeter Tian-Calvct calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (10740 \pm 247)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 398.1\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.7.1. Intended usage The use of aluminum as a test material for differential scanning calorimetry has been suggested by the German Society for Thermal Analysis, GEFTA [1]. The melt reacts strongly with platinum.

3.1.7.2. Sources of supply and/or methods of preparation Certified samples are available from NIST (SRM 1744). Other high purity material is available from commercial sources (Fluka: 99.999%; Alfa: 99.9997%).

3.1.7.3. Pertinent physicochemical data The fusion enthalpy of aluminum has been reviewed by the working group "Calibration of Scanning Calorimeters" of the GEFTA [1,2]. The fusion enthalpy $(10740 \pm 247)\,\mathrm{J\,mol^{-1}}$ is a mean value of the most reliable measurements cited in the relevant literature [3–5].

References

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3.1.8. $\Delta_{trs}H$, lithium sulfate

Physical property	enthalpy of transition
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	lithium sulfate$\cdot$ $H_2O(Li_2SO_4(H_2O)$: $127.9609\,\mathrm{g\,mol^{-1}}$; [10377-48-7]
Classification	secondary RM
Range of variables	T_{trs}: $851.43 \pm 0.25\,\mathrm{K}$ (T_{trs}: transition temperature, converted to ITS-90)
Physical state within the range	solid → solid (0.1 MPa)
Apparatus used	adiabatic calorimeter, dsc
Recommended value	$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (25070 \pm 1150)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 196.5\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.8.1. Intended usage The use of lithium sulfate as a calibrant for differential scanning calorimetry has been suggested by the German Society for Thermal Analysis, GEFTA [1]. The anhydrous salt is hygroscopic. It is recommended that the monohydrate be used and that the sample be backweighed after measurement. Dehydration occurs at temperatures in excess of 383 K and may cause violent agitation of the sample particles in the capsule. Do not use hermetically sealed capsules.

3.1.8.2. Sources of supply and/or methods of preparation High purity material as the monohydrate is available from commercial sources (Fluka: $\geq$99%; Alfa: 99.996%).

3.1.8.3. Pertinent physicochemical data The fusion enthalpy of lithium sulfate has been reviewed by the working group “Calibration of Scanning Calorimeters” of the GEFTA [1,2]. A solid to solid transition is observed at 851.43 K. A transition enthalpy $(25070 \pm 1150)\,\mathrm{J\,mol^{-1}}$ is recommended by GEFTA who reviewed the existing literature values 25564 [3], 25020 [4], 24460 [5], 25020 [6], 24650 [7], 25560 [8], 26100 [9]. The molar enthalpy of transition is based on a molecular weight of $109.94\,\mathrm{g\,mol^{-1}}$. Classification of lithium sulfate as a secondary reference material is based on the hygroscopic nature of the material and the precision of the measurements.

References

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3.1.9. $\Delta_{fus}H$ and $\Delta_{trs}H$, sodium nitrate

Physical property	enthalpy of fusion and transition
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$, specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	sodium nitrate ($NaNO_3$): $84.9947\,\mathrm{g\,mol^{-1}}$; [7631-99-4]
Classification	enthalpy of transition: tertiary RM; enthalpy of fusion: tertiary RM
Range of variables	T_{trs}: 549 K (T_{trs}: transition temperature); M: 580 K (M: melting temperature)
Physical state within the range	(i) solid → solid (0.1 MPa); (ii) solid → liquid (0.1 MPa)
Apparatus used	DSC
Recommended value	(i) $\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (3410 \pm 1548)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 40.1\,\mathrm{J\,g^{-1}}$; (ii) $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (15125 \pm 420)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 178.0\,\mathrm{J\,g^{-1}}$

Contributor to previous version	K.N. Roy, R. Sabbah, D.D. Sood
Contributor to this version	J. Chickos

3.1.9.1. Intended usage Sodium nitrate has been recommended as calibrant for differential scanning calorimetry [1–3]. The substance exhibits a solid-solid transition at 549 K and melts at 580 K. Sodium nitrate has been reported to be hygroscopic [2] and there is some question as to the possible influence of this transition on the reported enthalpy of melting [2,4]. The possibility of decomposition has also been mentioned [1].

3.1.9.2. Sources of supply and/or methods of preparation High purity material is available from a variety of commercial sources (Fluka: $\geq$99%; Alfa: 99.993%).

3.1.9.3. Pertinent physicochemical data The transition and fusion enthalpy of sodium nitrate has been measured by DSC. No adiabatic calorimetric measurements have been reported for the transition enthalpy of sodium nitrate. The following values for the enthalpy of transition have been reported: 3678 [2,5]; 3950 [2,6]; 728 [2,7]; 3849 $\mathrm{J\,mol^{-1}}$ [2,8]. Zeeb et al. reported a mean value of $(3410 \pm 1548)\,\mathrm{J\,mol^{-1}}$ on the basis of 23 DSC measurements. The enthalpy of fusion of sodium nitrate has been measured by several workers. Most measurements are not calorimetric measurements but DSC results. Lowings et al. [3] report a best value of $(15125 \pm 420)\,\mathrm{J\,mol^{-1}}$ (28 DSC measurements). The fusion enthalpy of sodium nitrate has been reinvestigated by Zeeb et al. [2] again by DSC and they report a mean enthalpy of $(15004 \pm 352)\,\mathrm{J\,mol^{-1}}$ (nine runs). Zeeb et al. also summarize a total of 11 previous determinations of the enthalpy of fusion of sodium nitrate. These earlier determinations result in a mean value of $(15157 \pm 758)\,\mathrm{J\,mol^{-1}}$. Kleppa and McCarty [9] measured the fusion enthalpy by reaction calorimetry and obtained a value of $(15464 \pm 268)\,\mathrm{J\,mol^{-1}}$. They also cite earlier work by Goodwin and Kalmus ($(15439 \pm 616)\,\mathrm{J\,mol^{-1}}$, [10]), and Sokolov and Shmidt ($(15046 \pm 16)\,\mathrm{J\,mol^{-1}}$, [11]). Most recently, Breuer and Eysel [1] reported a value of $(15750 \pm 220)\,\mathrm{J\,mol^{-1}}$ at 579.2 K by DSC (six runs). Sodium nitrate is designated presently as a tertiary reference material on the basis of the physical properties noted above and the lack of calorimetric data of sufficient precision. The recommended transition and fusion enthalpy values are the values reported by Zeeb et al. and Lowings et al., respectively. Uncertainties associated with the transition and fusion temperatures are not available.

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3.1.10. $\Delta_{fus}H$, 2-methylbutane

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	2-methylbutane, (C_5H_{12}): 72.1503 $\mathrm{g\,mol^{-1}}$; [78-78-4]
Classification	primary RM
Range of variables	M: (113.37 ± 0.10) K; (M: melting point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (5142 \pm 26)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 71.3\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.10.1. Intended usage 2-Methylbutane has been recommended and used as a reference material in the measurement of fusion enthalpies and fusion temperatures [1]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.10.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available from a variety of commercial suppliers (Aldrich: 99%; Fluka: 99.7+%; J.T. Baker: 99+%).

3.1.10.3. Pertinent physicochemical data Measurements by adiabatic calorimetry of the melting point and enthalpy of fusion of samples of 2-methylbutane (99.987 and 99.995 mol%) have been reported by Guthrie and Huffman [2] and Schumann et al. [3]. These workers report values of (113.37 ± 0.1) and (113.39 ± 0.1) K (IPTS-48) for the melting point temperature and (5156 ± 8) and (5130 ± 8) J mol^{-1} for the fusion enthalpy, respectively. These results are in good agreement with earlier values reported by Parks et al. of 112.6 K and 5114 J mol^{-1} [4]. More recently, the melting point and fusion enthalpy of 2-methylbutane has been measured by Sugisaki et al. [5] who report values of (113.36 ± 0.10) K and (5140 ± 4) J mol^{-1} on a sample of 99.986 mol%. The most recent measurements are those of Tan and Sabbah who report the triple point of 2-methylbutane (117.71 ± 0.06) K [1]. The recommended fusion enthalpy of (5142 ± 26) J mol^{-1} is the mean value from Refs. [2,3,5]. The recommended melting point is a mean value of the results reported by Guthrie and Huffman, and Schumann et al.

References

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3.1.11. $\Delta_{fus}H$, 2-methyl-1,3-butadiene

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	2-methyl-1,3-butadiene (C_5H_8): 68.1185 g mol^{-1}; [78-79-5]
Classification	secondary RM
Range of variables	T (127.27 ± 0.10) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (4877 \pm 132)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 71.6$ J g^{-1}
Contributor to this version	J. Chickos

3.1.11.1. Intended usage 2-Methyl-1,3-butadiene has been recommended as a reference material for low-temperature differential thermal analysis and differential scanning calorimetry [1]. The use of hermetically sealed samples is recommended for DTA and DSC studies.

3.1.11.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available (Aldrich: 99%; Fluka: 99.5+%). 2-Methyl-1,3-butadiene has a limited shelf-life.

3.1.11.3. Pertinent physicochemical data The fusion enthalpy of 2-methyl-1,3-butadiene has been measured by Bekkedahl and Wood using adiabatic calorimetry. A value of (4830 ± 30) J mol^{-1} was obtained [2]. Warfield and Petree [3] report an identical value. Messerly et al. [4] report a fusion enthalpy of (4925 ± 6) J mol^{-1} on a sample of (99.83 ± 0.08) mol% and a triple point of [(127.27 ± 0.10), IPTS-48] K also measured by adiabatic calorimetry. Tan and Sabbah have investigated the thermal properties of 2-methyl-1,3-butadiene using DTA [1]. A fusion enthalpy of (4864 ± 50) J mol^{-1} and a triple point of (127.23 ± 0.02) K was measured for their sample ((99.759) mol%). The recommended fusion enthalpy is the mean value from Refs. [2,4], (4877 ± 132) J mol^{-1}. Designation of 2-methyl-1,3-butadiene as a secondary reference material is prompted by the magnitude of the uncertainty associated with the two calorimetric measurements and the limited shelf-life of the material.

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3.1.12. $\Delta_{fus}H$, pentane

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\text{fus}}H_{\text{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\text{fus}}h$)
Recommended reference material	pentane (C_5H_{12}): 72.1503 g mol^{-1}; [109-66-0]
Classification	primary RM
Range of variables	T (143.48 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\text{fus}}H_{\text{m}} = (8409 \pm 20)$ J mol^{-1}; $\Delta_{\text{fus}}h = 116.5$ J g^{-1}
Contributor to this version	J. Chickos

3.1.12.1. Intended usage Pentane has been recommended as a reference material for low-temperature differential thermal analysis and differential scanning calorimetry [1]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.12.2. Sources of supply and/or methods of preparation Material of suitable purity is readily available. Commercial samples are available (J.T. Baker, Acros, Aldrich: 99+%; Fluka: 99.5+%).

3.1.12.3. Pertinent physicochemical data The fusion enthalpy of pentane has been measured by several different workers using adiabatic calorimetry. Much of this is early work. Parks and Huffman [2] and Timmermans [3] reported values of 8376 and 8368 J mol^{-1}, respectively, while Messerly and Kennedy [4] measured a value of (8415 ± 8) J mol^{-1}. More recently, Messerly et al. [5] report a fusion enthalpy of (8401 ± 5) J mol^{-1} on a sample of 99.86 mol%. A triple point of [143.47, IPTS-48] was determined from the temperature dependence on the fraction of sample melted. Using DTA, Tan and Sabbah [1] measured the triple point and fusion enthalpy of a sample of (99.858 ± 0.003) mol%. They obtained values of (143.46 ± 0.02) K and (8413 ± 14) J mol^{-1}, respectively. The mean value of the two most recent calorimetric studies, (8409 ± 20) J mol^{-1} is recommended for the fusion enthalpy of pentane. The triple point temperature is from Ref. [5].

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3.1.13. $\Delta_{fus}H$, 2,2,4-trimethylpentane

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\text{fus}}H_{\text{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\text{fus}}h$)
Recommended reference material	2,2,4-trimethylpentane, isooctane (C_8H_{18}): 114.2309 g mol^{-1}; [540-84-1]
Classification	secondary RM
Range of variables	T (165.80 ± 0.02) K (T: triple point temperature converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\text{fus}}H_{\text{m}} = (9212 \pm 16)$ J mol^{-1}; $\Delta_{\text{fus}}h = 80.6$ J g^{-1}

Contributor to this version	J. Chickos

3.1.13.1. Intended usage 2,2,4-trimethylpentane has been recommended as a reference material for low-temperature differential thermal analysis and differential scanning calorimetry [1]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.13.2. Sources of supply and/or methods of preparation Certified samples of 2,2,4-trimethylpentane are available (ORM: CRM043A). Commercial samples of suitable purity are available (Aldrich: 99.8%; Fluka, Acros: 99.5+%).

3.1.13.3. Pertinent physicochemical data The fusion enthalpy and melting point of 2,2,4-trimethylpentane has been measured using an adiabatic calorimeter by Pitzer [2]. A fusion enthalpy of $(9212 \pm 16)\,\mathrm{J\,mol^{-1}}$ was measured on a sample (99.99 mol%) melting at 165.79 K. Earlier Parks et al. [3] reported a fusion enthalpy of $(9043 \pm 20)\,\mathrm{J\,mol^{-1}}$. Tan and Sabbah [1] have investigated the thermal properties of 2,2,4-trimethylpentane using DTA. A fusion enthalpy of $(9084 \pm 96)\,\mathrm{J\,mol^{-1}}$ and a triple point of $(165.80 \pm 0.02)\,\mathrm{K}$ was measured for their sample (99.875 mol%). The triple point recommended for 2,2,4-trimethylpentane is taken from the work of Tan and Sabbah. The recommended fusion enthalpy is from the work of Pitzer.

References

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3.1.14. $\Delta_{fus}H$ *and* $\Delta_{trs}H$*, cyclopentane*

Physical property	enthalpy of fusion and transition
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$, specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	cyclopentane (C_5H_{10}): 70.1344 $\mathrm{g\,mol^{-1}}$; [287-92-3]
Classification	primary RM
Range of variables	(iii) T_{trs}: $(122.38 \pm 0.05)\,\mathrm{K}$; (ii) T_{trs} $(138.06 \pm 0.05)\,\mathrm{K}$; ($T_{\mathrm{trs}}$: transition temperature, converted to ITS-90); (i) T: $(179.72 \pm 0.05)\,\mathrm{K}$; ($T$: triple point temperature, converted to ITS-90)
Physical state within the range	solid(iii) → solid(ii); solid(ii) → solid(i); solid(i) → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC
Recommended value	$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (\mathrm{iii} \rightarrow \mathrm{ii})$ $(4881 \pm 12)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 69.6\,\mathrm{J\,g^{-1}}$; $\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (\mathrm{ii} \rightarrow \mathrm{i})$ $(345 \pm 3.7)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 4.9\,\mathrm{J\,g^{-1}}$; $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (605 \pm 7.2)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 8.6\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.14.1. Intended usage Cyclopentane has been recommended as a reference material for low-temperature differential thermal analysis and differential scanning calorimetry [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.14.2. Sources of supply and/or methods of preparation Material of suitable purity is available. (Fluka: 99.5% (material contains cyclopentene and has a limited shelf-life); Acros: 99+%).

3.1.14.3. Pertinent physicochemical data The recommended enthalpy values cited above are mean adiabatic calorimetric values obtained from Refs. [3–5]. Szasz et al. report values of $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (iii → ii) 4884.4; $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (ii → i) 342.7; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ 603.8 $\mathrm{J\,mol^{-1}}$. Douslin et al. report values of $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (iii → ii) 4884; $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (ii → i) 344.4; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ 608.9 $\mathrm{J\,mol^{-1}}$ and Aston et al. report values of $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (iii → ii) 4874; $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (ii → i) 346.4; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ 602 $\mathrm{J\,mol^{-1}}$. Recommended transition and fusion temperatures are from Ref. [1]. These results have been independently confirmed by DSC by Sarge et al. [2] who obtained the following mean values: $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (iii → ii) (5064 ± 112); $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (ii → i) (348 ± 18); $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (609 ± 28) J mol^{-1}. Rahm and Gmelin report slightly higher values by DSC: $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (iii → ii) (5195 ± 500), $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (ii → i) (661 ± 38); $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (615 ± 48) J mol^{-1} [6].

References

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3.1.15. $\Delta_{fus}H$, heptane

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	heptane (C_7H_{16}): 100.2040 g mol^{-1}; [142-82-5]
Classification	primary RM
Range of variables	T: (182.60 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (14023 \pm 19)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 140.0$ J g^{-1}
Contributor to this version	J. Chickos

3.1.15.1. Intended usage Heptane has been used as a reference material for low-temperature heat-capacity measurements [1] and has been used as a reference material for adiabatic calorimeters and for DTA [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.15.2. Sources of supply and/or methods of preparation Material of suitable purity is readily available (Aldrich: 99+%; Acros, Fluka: 99.5+%). Certified, high purity material 99.987% is available from NIST (SRM 1815a).

3.1.15.3. Pertinent physicochemical data The fusion enthalpy of heptane has been measured by several workers. A mean value of (14022.5 ± 19) J mol^{-1} has been reported by Douglas et al. (purity: (99.997 ± 0.002) mol%; T: 182.562 K (IPTS-48)) [3]. Other calorimetric values by Huffman et al. ((14037 ± 16.8) J mol^{-1}, T (182.55 ± 0.05) K (IPTS-48)) [4], and Van Miltenburg ((14061 ± 48) J mol^{-1}, 99.968 mol% [2]) are in good agreement. The NIST values for enthalpy and triple point are recommended [3].

References

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3.1.16. $\Delta_{fus}H$ and $\Delta_{trs}H$, 1,3-difluorobenzene

Physical property	enthalpy of fusion and transition
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); J g^{-1} or J kg^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$, specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	1,3-difluorobenzene ($C_6H_4F_2$): 114.0946 g mol^{-1}; [372-18-9]
Classification	secondary RM
Range of variables	(i) T_{trs}: (187.3 ± 1.4) K (T_{trs}: transition temperature, converted to ITS-90); (ii) T: (204.08 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	(i) solid → solid (in equilibrium with vapor); (ii) solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA

Recommended values	$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (827 \pm 3)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 7.3\,\mathrm{J\,g^{-1}}$; $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (8581 \pm 6)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 75.2\,\mathrm{J\,g^{-1}}$
Contributor to the previous version	R. Sabbah
Contributor to this version	J. Chickos

3.1.16.1. Intended usage 1,3-Difluorobenzene has been recommended for use as a reference material for testing the performance of calorimeters and for the measurement of the enthalpy of fusion [1]. The use of hermetically sealed samples is recommended. Calorimetric samples should avoid being exposed to air and moisture. Samples cooled faster than $2\,\mathrm{K\,min^{-1}}$ near 186 K were reported to supercool [2].

3.1.16.2. Sources of supply and/or methods of preparation Commercial samples with a high degree of purity are available (Aldrich, Fluka, Acros: 99+%).

3.1.16.3. Pertinent physicochemical data The transition and fusion enthalpy of 1,3-difluorobenzene has been measured by two groups. Messerly and Finke [2] using adiabatic calorimetry report a transition temperature of 186.77, a triple point of 204.03 K (IPTS-48) and transition and fusion enthalpies of (827 ± 3) and $(8581 \pm 6)\,\mathrm{J\,mol^{-1}}$, respectively. Sample purity (99.999 mol%) was assessed by a calorimetric study of the melting behavior. Using DTA, Tan and Sabbah [1] measured the transition temperature, triple point, transition and fusion enthalpies of a sample of (99.888 ± 0.08) mol%. They obtained values of (187.82 ± 0.16), (204.08 ± 0.02) K (ITS-90), (829 ± 4) and $(8597 \pm 42)\,\mathrm{J\,mol^{-1}}$, respectively, confirming earlier results. Both Tan and Sabbah and Messerly and Finke report identical triple points when the data is corrected to ITS-90. Messerly and Finke do not report probable uncertainties associated with their temperature measurements. The uncertainty associated with the triple point is from the results of Tan and Sabbah. The recommended transition temperature is the mean of the two values reported after correction to the ITS-90.

References

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3.1.17. $\Delta_{fus}H$ and $\Delta_{trs}H$, 2,2-dimethylpropane

Physical property	enthalpy of fusion and transition
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$, specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	2,2-dimethylpropane, neopentane (C_5H_{12}): $72.1503\,\mathrm{g\,mol^{-1}}$; [463-82-1]
Classification	secondary RM
Range of variables	(i) T_{trs}: (140.51 ± 0.10) K (T_{trs}: transition temperature, converted to ITS-90); (ii) T: (256.76 ± 0.01) K; (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended values	$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (2630.5 \pm 2.5)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 36.5\,\mathrm{J\,g^{-1}}$; $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (3096.2 \pm 2.5)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 42.9\,\mathrm{J\,g^{-1}}$
Contributor to the previous version	K.N. Roy, R. Sabbah, D. Sood
Contributor to this version	J. Chickos

3.1.17.1. Intended usage 2,2-Dimethylpropane has been recommended for testing the performance of calorimeters used in the measurement of fusion and transition enthalpies at temperatures around 140 and 250 K, respectively [1]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.17.2. Sources of supply and/or methods of preparation Material of suitable purity 99+% is available from Wiley Organics, API, CLARA, Matheson Gas Products. Additional purification is possible by fractionation through a 5 m spinning band column and treatment with molecular sieve 5A.

3.1.17.3. Pertinent physicochemical data Measurements by adiabatic calorimetry of the triple point, transition temperature and enthalpies of fusion and transition of a sample of 2,2-dimethylpropane (99.997 mol%) by Enokido et al., resulted in transition and triple point temperatures of (140.50 ± 0.10) K and 256.75 K and transition and fusion enthalpies of (2630.5 ± 2.5) and (3096.2 ± 2.5) J mol^{-1}, respectively [2]. Earlier work by Aston and Messerly reported transition and fusion enthalpies of (2577 ± 5) and (3256 ± 30) J mol^{-1}, respectively [3], based on a molar mass of 72.09 g mol^{-1}. The values reported by Enokido et al. have been recommended by the Commission of Physicochemical Measurements and Standards [1] and are recommended here also. Enokido et al. do not report an uncertainty associated with their determination of the triple point. A plot of temperature against the reciprocal of the fraction melted results in a linear correlation. Treatment of the data by linear regression and extrapolation to the pure solid reproduces their reported triple point. The standard error in the intercept associated with the regression analysis results in a value of (256.756 ± 0.001) K. The designation of 2,2-dimethylpropane as a secondary reference material is due solely to the lack of DSC or DTA data.

References

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3.1.18. $\Delta_{fus}H$, hexafluorobenzene

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	hexafluorobenzene (C_6F_6): 186.0564 g mol^{-1}; [392-56-3]
Classification	primary RM
Range of variables:	*T*: (278.30 ± 0.02) K (*T*: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (11588 \pm 13)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 62.3$ J g^{-1}
Contributor to the previous version	R. Sabbah
Contributor to this version	J. Chickos

3.1.18.1. Intended usage Hexafluorobenzene has been recommended for use as a reference material for testing the performance of calorimeters and for the measurement of the enthalpy of fusion [1].

3.1.18.2. Sources of supply and/or methods of preparation Material of suitable purity is readily available. Commercial samples with a high degree of purity are available (Aldrich: 99.9%; Fluka: 99.5+%). The use of hermetically sealed samples is recommended. Calorimetric samples should avoid being exposed to air and moisture.

3.1.18.3. Pertinent physicochemical data The fusion enthalpy of hexafluorobenzene has been measured by adiabatic calorimetry by three groups. Messerly and Finke [2] report a triple point of 278.30 K (IPTS-48) and a fusion enthalpy of (11586 ± 11) J mol^{-1} for a sample of 99.93 mol%. Counsell et al. [3] report a triple point of 278.25 K and a fusion enthalpy of (11590 ± 8) J mol^{-1} on a sample of 99.97 mol%. Paukov and Glukhikh [4] report a triple point of 278.14 K and a fusion enthalpy of (11435 ± 25) J mol^{-1} on a sample of 99.34 mol%. Using DTA, Tan and Sabbah [1] measured the triple point and fusion enthalpy of a sample of (99.861 ± 0.005) mol%. They obtained values of (278.20 ± 0.01) K and (11607 ± 70) J mol^{-1}, respectively, in best agreement with the results of Counsell et al. and Messerly and Finke. The mean value of these two calorimetric studies, (11588 ± 13) J mol^{-1} is recommended for the fusion enthalpy of hexafluorobenzene. The recommended triple point temperature is from Ref. [2]. Messerly and Finke do not report an uncertainty associated with their determination of the triple point. A plot of temperature against the reciprocal of the fraction melted results in a linear correlation. Treatment of the data by linear regression and extrapolation to the pure solid reproduces the reported triple point. The standard error in the intercept associated with the regression analysis results in a value of (278.30 ± 0.01) K.

References

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[4] I.E. Paukov, L.K. Glukhikh, Zh. Vses. Khim. Obshchestra im. D.I. Mendeleeva, 12 (1967) 236; (as cited in [2]).

3.1.19. $\Delta_{fus}H$ and $\Delta_{trs}H$, cyclohexane

Physical property	enthalpy of fusion and transition
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, molar enthalpy of transition, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$); $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,kg^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$, specific enthalpy of transition, $\Delta_{\mathrm{trs}}h$)
Recommended reference material	cyclohexane (C_6H_{12}): 84.1613 $\mathrm{g\,mol^{-1}}$; [110-82-7]
Classification	primary RM
Range of variables	(i) T_{trs}: (186.25 ± 0.02) K (T_{trs}: transition temperature, converted to ITS-90); (ii) T: (279.81 ± 0.04) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	(i) solid → solid (in equilibrium with vapor); (ii) solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended values	$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = (6713 \pm 74)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{trs}}h = 79.8\ \mathrm{J\,g^{-1}}$; $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (2652 \pm 71)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 31.5\ \mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.1.19.1. Intended usage Cyclohexane has been recommended as a reference material for low-temperature differential thermal analysis and differential scanning calorimetry [1,2]. The use of hermetically sealed samples in DSC and DTA work is recommended.

3.1.19.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available (Aldrich, Acros, Fluka: 99.5+%; J.T. Baker: 99%).

3.1.19.3. Pertinent physicochemical data The transition and fusion enthalpies and transition and melting points of cyclohexane have been measured by adiabatic calorimetry by Aston et al. and Ruehrwein and Huffman on samples of 99.905 and 99.985 mol%, respectively [3,4]. Transition temperatures (186.09 ± 0.05) and (186.1) K and corresponding transition enthalpies (6687 ± 12) and (6740 ± 3) $\mathrm{J\,mol^{-1}}$ were reported along with melting points and fusion enthalpies (279.84 ± 0.05) and (279.82 ± 0.05) K and (2627 ± 15) and (2677 ± 3) $\mathrm{J\,mol^{-1}}$, respectively. Although no experimental details are given, Ziegler and Andrews report transition and fusion enthalpies of 6820 and 2728 $\mathrm{J\,mol^{-1}}$ [5]. More recently, Stokes and Tomlins [6] measured the fusion enthalpy of a sample of cyclohexane (99.9993 mol%) from the pressure dependence of the melting point using the Clapeyron equation. They obtained the value (2727 ± 16) $\mathrm{J\,mol^{-1}}$ for the fusion enthalpy and measured a triple point of (279.83 ± 0.02) K. Tan and Sabbah have recently investigated the thermal properties of cyclohexane using DTA [1]. Transition and fusion enthalpies of (6792 ± 16) and (2677 ± 50) $\mathrm{J\,mol^{-1}}$ and a transition and triple point temperature of (186.24 ± 0.02) and (279.80 ± 0.04) K, respectively, were measured for their sample (99.979 mol%). The recommended value for the transition temperature is taken from the value reported by Tan and Sabbah. The recommended value for the triple point is taken as the mean of the values reported by Tan and Sabbah and Stokes and Tomlins (279.81 ± 0.04) K. The recommended transition and fusion enthalpies are mean values from the work of Aston et al. and Ruehrwein and Huffman.

References

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3.1.20. $\Delta_{fus}H$, diphenyl ether

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	diphenyl ether ($C_{12}H_{10}O$): 170.2108 $\mathrm{g\,mol^{-1}}$; [101-84-8]
Classification	tertiary RM
Range of variables	T: (300.01 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (17216 \pm 34)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 107.1\ \mathrm{J\,g^{-1}}$
Contributor to the previous versions	J.D. Cox, J.F. Martin, R. Sabbah
Contributor to this version	J. Chickos

3.1.20.1. Intended usage Diphenyl ether has been recommended as a test material for determining fusion enthalpies in classical (adiabatic, drop, ice and radiation) and differential scanning calorimetry [1]. It is available in high purity and appears inert to most materials encountered in calorimetry [2]. It is recommended that air and water be removed before using samples in calorimetric experiments and that the samples be hermetically sealed. Diphenyl ether has a tendency to supercool [1].

3.1.20.2. Sources of supply and/or methods of preparation High purity material is available from a variety of commercial suppliers (see phenyl ether, Acros, Aldrich, Lancaster: 99+%; Fluka: ≥98%) and can be readily purified [3].

3.1.20.3. Pertinent physicochemical data A sample of diphenyl ether, mole fraction of 0.999987 evaluated from the sample's melting behavior, resulted in the triple point temperature of (300.01±0.02) K and a fusion enthalpy of $(17216 \pm 34)\ \mathrm{J\,mol^{-1}}$ [2]. The fusion enthalpy and melting point have also been measured by DSC. Donnelly et al. [4] report a fusion enthalpy of 16159 $\mathrm{J\ mol^{-1}}$ and a melting point of 299.78 K. Diphenyl ether is classified as a tertiary reference material primarily because of the lack of sufficient data.

References

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3.1.21. $\Delta_{fus}H$, biphenyl

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	biphenyl ($C_{12}H_{10}$): 154.2114 $\mathrm{g\,mol^{-1}}$; [92-52-4]
Classification	primary RM
Range of variables	T: 342.08 K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (18574 \pm 4)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 120.4\ \mathrm{J\ g^{-1}}$
Contributor to this version	J. Chickos

3.1.21.1. Intended usage Biphenyl has been recommended as a test material for determining fusion enthalpies in differential scanning calorimetry [1]. It is recommended that samples be hermetically sealed for DSC and DTA work.

3.1.21.2. Sources of supply and/or methods of preparation Certified, high purity material (99.984%) is readily available from NIST (SRM 2222) or API Standard Reference Materials. High purity material is available from a variety of commercial suppliers (Aldrich: 99%; Fluka: 98+%). This material is expected to have an indefinite shelf-life under normal conditions. Biphenyl can be purified by vacuum distillation.

3.1.21.3. Pertinent physiochemical data The enthalpy of fusion of biphenyl has been evaluated by several groups. Workers at NIST report a certified value of $(18569 \pm 59)\,\mathrm{J\,mol^{-1}}$ and a melting temperature of $(342.41 \pm 0.54)\,\mathrm{K}$ as determined by DSC [1]. Chirico et al. using an adiabatic calorimeter [2] report a triple point and enthalpy of fusion of 342.098 K (IPTS-68) and $(18574 \pm 4)\,\mathrm{J\,mol^{-1}}$ (mole fraction 0.99983), respectively. Using DSC, O'Rourke and Mraw [3] measured a fusion temperature of $(342.2 \pm 1.0)\,\mathrm{K}$ and a fusion enthalpy of $(18580 \pm 31)\,\mathrm{J\,mol^{-1}}$ on a sample reported to be 99.9+ mol%. Reports by others (Schmidt: $18594\,\mathrm{J\,mol^{-1}}$ [4]; Ueberreiter and Orthmann: $18575\,\mathrm{J\,mol^{-1}}$ [5]; Spaght, Thomas and Parks: $18647\,\mathrm{J\,mol^{-1}}$ [6]) are all in good agreement with these results. The triple point and calorimetric fusion enthalpy reported by Chirico et al. are recommended.

References

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3.1.22. $\Delta_{fus}H$, naphthalene

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	naphthalene ($C_{10}H_8$): $128.1735\,\mathrm{g\,mol^{-1}}$; [91-20-3]
Classification	primary RM
Range of variables	T: $(353.35 \pm 0.04)\,\mathrm{K}$ (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (19\,061 \pm 80)\,\mathrm{J\,mol^{-1}}$; $148.7\,\mathrm{J\,g^{-1}}$
Contributors to the previous version	R. Sabbah, D.D. Sood, V. Venugopal
Contributor to this version	J. Chickos

3.1.22.1. Intended usage Naphthalene has been recommended as a calibrant for thermal analysis, especially for differential scanning calorimetry [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.22.2. Sources of supply and/or methods of preparation Certified, high purity material is readily available (ORM: LGC24024). Commercial samples are available from a variety of suppliers (Aldrich, Fluka: 99+%). Samples of higher purity can be obtained by zone refining.

3.1.22.3. Pertinent physicochemical data Measurements using adiabatic calorimetry on two samples of naphthalene, mole fraction ((0.9999), resulted in a triple point temperature of $(353.39 \pm 0.04)\,\mathrm{K}$ (IPTS-68) and a mean value of $(19\,061 \pm 80)\,\mathrm{J\,mol^{-1}}$ for the enthalpy of fusion [1]. This value is the mean of nine calorimetric measurements. This compares with the certificate values of $(19\,040 \pm 40)\,\mathrm{J\,mol^{-1}}$ and 353.38 K reported earlier for naphthalene by Connett [2]. Earlier adiabatic calorimetric measurements on naphthalene resulted in a fusion enthalpy of $(18\,979 \pm 8)\,\mathrm{J\,mol^{-1}}$ and a triple point of $(353.43 \pm 0.05)\,\mathrm{K}$ (IPTS-48) [3]. Other calorimetric fusion measurements include $19\,199\,\mathrm{J\,mol^{-1}}$ [4], and $18\,811\,\mathrm{J\,mol^{-1}}$ [5]. In a feasibility study to develop reference materials using differential scanning calorimetry, the fusion enthalpy of certified samples of naphthalene was investigated [6,7]. The fusion enthalpy of five hermetically sealed specimens measured by DSC resulted in a mean of (19 142 ± 109) J mol^{-1}. Repeated measurement of these same five samples four times reduced the observed fusion enthalpy to (19 099 ± 151) J mol^{-1}. Repeated runs also resulted in distorted peak shapes [6]. Other DSC measurements resulted in similar fusion enthalpies of (19 000 ± 800) J mol^{-1} [8], (19 120 ± 1000) J mol^{-1} [9]. The fusion enthalpy measured by Andon and Connett is recommended.

References

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3.1.23. $\Delta_{fus}H$, benzil

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion, $\Delta_{fus}H_m$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{fus}h$)
Recommended reference material	benzil ($C_{14}H_{10}O_2$): 210.2322 g mol^{-1}; [134-81-6]
Classification	secondary RM
Range of variables	*T*: (367.97 ± 0.02) K (*T*: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{fus}H_m$ = (23 546 ± 140) J mol^{-1}; 112.0 J g^{-1}
Contributors to the previous version	R. Sabbah, D.D. Sood, V. Venugopal
Contributor to this version	J. Chickos

3.1.23.1. Intended usage Benzil has been recommended as a calibrant for thermal analysis, especially for differential scanning calorimetry [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.23.2. Sources of supply and/or methods of preparation Certified high purity material is available (ORM: LGC2604). Commercial samples of suitable purity are available from a variety of suppliers (Aldrich: 98%; Acros: 99%; Fluka: 98%). Samples of higher purity can be obtained by zone refining.

3.1.23.3. Pertinent physicochemical data Measurements on two samples of benzil with a mole fraction of ≥0.9999, using an adiabatic calorimeter, resulted in the triple point (368.014 ± 0.02) K (IPTS-68), and a fusion enthalpy of (23 546 ± 140) J mol^{-1} [1]. This result, the mean of nine measurements on two samples, is in good agreement with an earlier report by Connett on the triple point and fusion enthalpy of benzil (368.02 K (23 550 ± 160) J mol^{-1}), used to certify the compound as a reference material [2]. Previously, a fusion enthalpy of 22 690 J mol^{-1} measured by differential scanning calorimetry was reported by Booss and Hauschildt [3]. A transition occurring at 84.07 K with an enthalpy change of 44.1 J mol^{-1} has also been reported [4]. The value reported by Andon and Connett is recommended.

References

[1] R.J.L. Andon, J.E. Connett, Thermochim. Acta 42 (1980) 241.
[2] J.E. Connett, Journées de Calorimétrie et d'Analyse Thermique 10 (1979) E1.1.
[3] H.J. Booss, H.R. Hauschildt, Fresenius Z. Anal. Chem. 261 (1972) 32.
[4] A. Dworkin, J. Chem. Thermodyn. 15 (1983) 1029.

3.1.24. $\Delta_{fus}H$, acetanilide

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion, $\Delta_{fus}H_m$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{fus}h$)
Recommended reference material	acetanilide (C_8H_9NO): 135.1656 g mol^{-1}; [103-84-4]

Classification	secondary RM
Range of variables	T: (387.48 ± 0.01) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (21\,653 \pm 22)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 160.2\,\mathrm{J\,g^{-1}}$
Contributors to the previous version	R. Sabbah, D.D. Sood, V. Venugopal
Contributor to this version	J. Chickos

3.1.24.1. Intended usage Acetanilide has been recommended as a calibrant for thermal analysis, especially for differential scanning calorimetry [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.24.2. Sources of supply and/or methods of preparation Certified, high purity material is available (ORM: LGC4002) and will also be available from NIST (SRM 141d, in preparation). Commercial samples of suitable purity are available from a variety of suppliers (Aldrich: 99.95+%; Acros: 99+%; Fluka: 99.5+%). Samples of higher purity can be obtained by zone refining.

3.1.24.3. Pertinent physicochemical data The measurement of five samples of acetanilide, mole fraction of 0.9997, resulted in the triple point of (387.525 ± 0.002) K (IPTS-68) and a fusion enthalpy of $(21\,653 \pm 22)\,\mathrm{J\,mol^{-1}}$ [1]. These results appears identical to an earlier report by Connett [2] used to certify the compound as a reference material. In a feasibility study to develop reference materials using differential scanning calorimetry, the fusion enthalpy of certified samples of acetanilide obtained from the National Physical Laboratory, Teddington, UK was investigated [3,4]. The fusion enthalpy of five hermetically sealed specimens measured by DSC resulted in a mean of $(22\,119 \pm 170)\,\mathrm{J\,mol^{-1}}$. Repeated measurement of these same five samples four times reduced the mean observed fusion enthalpy to $(22\,085 \pm 182)\,\mathrm{J\,mol^{-1}}$. Repeated runs on the same sample also resulted in distorted peak shapes.

References

[1] R.J.L. Andon, J.E. Connett, Thermochim. Acta 42 (1980) 241.

[2] J.E. Connett, Journées de Calorimétrie et d'Analyse Thermique 10 (1979) E1.1.

[3] J.E. Callanan, S.A. Sullivan, D.F. Vecchia, US NBS Special Publication 260-99, August 1985.

[4] J.E. Callanan, S.A. Sullivan, D.F. Vecchia, J. Res. Nat. Bur. Stand. 91 (1986) 123.

3.1.25. $\Delta_{fus}H$, benzoic acid

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	benzoic acid ($C_7H_6O_2$): $122.1234\,\mathrm{g\,mol^{-1}}$; [65-85-0]
Classification	secondary RM
Range of variables	T: (395.50 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DTA
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (18\,063 \pm 42)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 147.9\,\mathrm{J\,g^{-1}}$
Contributors to the previous versions	G.T. Armstrong, J.D. Cox, R. Sabbah, D.D. Sood, V. Venugopal
Contributor to this version	J. Chickos

3.1.25.1. Intended usage Benzoic acid has been recommended as a calibrant for enthalpies of fusion, adiabatic calorimetry and differential scanning calorimetry [1]. Benzoic acid attacks tin and copper at temperature near the melting point [2].

3.1.25.2. Sources of supply and/or methods of preparation Certified high purity material (99.9958%) is readily available from NIST (SRM 350a). Material prepared as a reference material for combustion measurements is suitable for calorimetric measurements. Commercial samples of suitable purity are available from a variety of suppliers (Aldrich, Acros: 99.5%; Fluka: 99.5+%). The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.25.3. Pertinent physicochemical data Using an adiabatic calorimeter, Andon and Connett measured the fusion enthalpy and triple point of a sample of benzoic acid, mole fraction >0.9999. The mean of nine measurements resulted in values of $(18\,063 \pm 42)\,\mathrm{J\,mol^{-1}}$ and $(395.527 \pm 0.002)\,\mathrm{K}$ (IPTS-68), respectively [1]. These results appears identical to an earlier report by Connett [2] used to certify the compound as a reference material. In an earlier study, Furukawa et al. [3] measured a fusion enthalpy of $(18\,000 \pm 200)$. These values are higher than the value reported by Sklyankin and Strelkov $(17\,800 \pm 80)$ [4]. Other report of the fusion enthalpy of benzoic acid include the DTA results of David [5] $(17\,400\,\mathrm{J\,mol^{-1}})$ and Pacor $(16\,230\,\mathrm{J\,mol^{-1}})$ [6]. The values reported by Andon and Connett are recommended. At present, benzoic acid is recommended as a secondary reference material primarily because of the poor agreement observed between the calorimetric values and those obtained by other methods.

References

[1] R.J.L. Andon, J.E. Connett, Thermochim. Acta 42 (1980) 241.

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3.1.26. $\Delta_{fus}H$, diphenylacetic acid

Physical property	enthalpy of fusion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	diphenylacetic acid ($C_{14}H_{12}O_2$): $212.2481\,\mathrm{g\,mol^{-1}}$; [117-34-0]
Classification	secondary RM
Range of variables	T: $(420.41 \pm 0.02)\,\mathrm{K}$ (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (31\,271 \pm 36)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{fus}}h = 147.3\,\mathrm{J\,g^{-1}}$
Contributors to the previous version	K.N. Roy, R. Sabbah, D.D. Sood
Contributor to this version	J. Chickos

3.1.26.1. Intended usage Diphenylacetic acid has been recommended as a calibrant for thermal analysis, especially for differential scanning calorimetry [1,2]. The use of hermetically sealed samples is recommended for DSC and DTA work.

3.1.26.2. Sources of supply and/or methods of preparation Certified high purity material is readily available (ORM: LGC2406). Commercial samples with a mass fraction (≥0.99) are available from a various suppliers (Aldrich, Acros: 99+%; Fluka: 98+%). Samples of higher purity can be obtained by zone refining.

3.1.26.3. Pertinent physicochemical data Five measurements of a sample of diphenylacetic acid, mole fraction of 0.9994, resulted in a triple point of $(420.441 \pm 0.001)\,\mathrm{K}$ (IPTS-68) and a fusion enthalpy of $(31\,271 \pm 36)\,\mathrm{J\,mol^{-1}}$ [1,2]. In a feasibility study to develop reference materials using differential scanning calorimetry, the fusion enthalpy of certified samples of diphenylacetic acid from the National Physical Laboratory, Teddington, UK [2] were measured. The measurement of five different hermetically sealed samples resulted in a mean value of $(31\,553 \pm 280)\,\mathrm{J\,mol^{-1}}$ [3,4]. Repeated measurement of the same five samples four times reduced the observed fusion enthalpy to $(31\,445 \pm 538)\,\mathrm{J\,mol^{-1}}$. Repeated runs exhibited distorted peak shapes.

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[2] J.E. Connett, Journées de Calorimétrie et d'Analyse Thermique 10 (1979) E1.1.

[3] J.E. Callanan, S.A. Sullivan, D.F. Vecchia, US NBS Special Publication 260-99, August 1985.

[4] J.E. Callanan, S.A. Sullivan, D.F. Vecchia, J. Res. Nat. Bur. Stand. 91 (1986) 123.

3.1.27. $\Delta_{fus}H$, triphenylene

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	triphenylene ($C_{18}H_{12}$): 228.2933 g mol^{-1}; [217-59-4]
Classification	secondary RM
Range of variables	T: (471.02 ± 0.06) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC, DTA
Recommended values	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (24\,744 \pm 8)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 108.4$ J g^{-1}
Contributor to this version	J. Chickos

3.1.27.1. Intended usage Triphenylene has been recommended as a reference material for differential thermal analysis and differential scanning calorimetry [1]. The use of hermetically sealed samples is recommended for DSC and DTA studies.

3.1.27.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available (Aldrich, Fluka: 98+%; Acros: 98%). Certified samples of triphenylene are also available (ORM: CRM27).

3.1.27.3. Pertinent physicochemical data The triple point and fusion enthalpy of triphenylene has been measured by adiabatic calorimetry by Wong and Westrum [2] on a 99.962 mol% sample. A triple point and fusion enthalpy of 471.01 K and $(24\,744 \pm 8)$ J mol^{-1}, respectively, was reported on their calorimetric sample. A similar study by Sabbah and El Watik [1] using DTA reported a triple point of (471.06 ± 0.06) K (IPTS-68) and a fusion enthalpy of $(24\,190 \pm 180)$ J mol^{-1} on a (99.85 ± 0.01) mol% sample. A DSC study of the thermal behavior of triphenylene by Casellato et al. [3] reported a melting point of (473.6 ± 0.4) K and a fusion enthalpy of $(25\,104 \pm 920)$ J mol^{-1}. The recommended fusion enthalpy is from the work of Wong and Westrum and the triple point from the report by Sabbah and El Watik.

References

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3.1.28. $\Delta_{fus}H$, hexachlorobenzene

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	hexachlorobenzene (C_6Cl_6): 284.7822 g mol^{-1}; [118-74-1]
Classification	tertiary RM
Range of variables	T: (501.83 ± 0.02) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	DSC, DTA
Recommended values	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (24\,960 \pm 800)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 87.6$ J g^{-1}
Contributor to this version	J. Chickos

3.1.28.1. Intended usage Hexachlorobenzene has been recommended as a reference material for differential thermal analysis and differential scanning calorimetry [1]. Hexachlorobenzene is *mutagenic* and a *cancer suspect agent*. The use of hermetically sealed samples is recommended for DSC and DTA studies.

3.1.28.2. Sources of supply and/or methods of purification Commercial samples of suitable purity are available (Aldrich, Acros: 99%; Fluka: 99+%). Certified samples of hexachlorobenzene are available (ORM: LGC1131).

3.1.28.3. Pertinent physicochemical data The transition and fusion enthalpies and transition and melting points of hexachlorobenzene have been studied by

DSC and DTA. Sabbah and An [2] report a melting point of (502.02 ± 0.02) K (IPTS-68) and a fusion enthalpy of (25 180 ± 740) J mol^{-1} by DTA on a (99.98 ± 0.003) mol% sample. A similar study by Sabbah and El Watik [1] reported a triple point of (501.87 ± 0.02) K (IPTS-68) and a fusion enthalpy of (24 960 ± 800) J mol^{-1} on a (99.969±0.002) mol% sample. Plato and Glasgow [3] report a melting point and fusion enthalpy of 505 K and 23 849 J mol^{-1} on a 99.99 mol% sample by DSC. In a similar DSC study, Donnelly et al. [4] report a fusion enthalpy of 24 534 J mol^{-1} and a melting point of 501.11 on a 99.99 mol% sample. Hexachlorobenzene is currently listed as a tertiary reference material due to the lack of adiabatic calorimetric data.

References

[1] R. Sabbah, L. El Watik, J. Therm. Anal. 38 (1992) 855.
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[3] C. Plato, A.R. Glasgow Jr., Anal. Chem. 41 (1969) 330.
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3.1.29. $\Delta_{fus}H$, perylene

Physical property	enthalpy of fusion
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of fusion, $\Delta_{\mathrm{fus}}h$)
Recommended reference material	perylene ($C_{20}H_{12}$): 252.3153 g mol^{-1}; [198-55-0]
Classification	secondary RM
Range of variables	T: (551.25 ± 0.01) K (T: triple point temperature, converted to ITS-90)
Physical state within the range	solid → liquid (in equilibrium with vapor)
Apparatus used	adiabatic calorimeter, DSC, DTA
Recommended values	$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (31\,874 \pm 84)$ J mol^{-1}; $\Delta_{\mathrm{fus}}h = 126.3$ J g^{-1}
Contributor to this version	J. Chickos

3.1.29.1. Intended usage Perylene has been recommended as a reference material for differential thermal analysis and differential scanning calorimetry [1]. The use of hermetically sealed samples is recommended for DSC and DTA studies.

3.1.29.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available (Aldrich: 99%; Fluka: 99+%). Certified samples of perylene are available (ORM: LGC1131, [2]). Purification is achieved by recrystallization (benzene, glacial acetic acid), sublimation and zone refining.

3.1.29.3. Pertinent physicochemical data The triple point and fusion enthalpy of perylene has been measured by Wong and Westrum [2] by adiabatic calorimetry. They report values of (550.94 ± 0.02) K and (31 874 ± 84) J mol^{-1}, respectively, on a sample of 99.97 mol%. A similar study by Sabbah and El Watik [1] using DTA reported a triple point of (551.29 ± 0.01) K (IPTS-68) and a fusion enthalpy of (32 580 ± 280) J mol^{-1} on a (99.889 ± 0.002) mol% sample. A DSC study of the thermal behavior of perylene by Casellato et al. [3] reported a melting point of (553.85 ± 0.3) K and a fusion enthalpy of (31 757 ± 1171) J mol^{-1}. The fusion enthalpy of Wong and Westrum and the triple point of Sabbah and El Watik are recommended.

References

[1] R. Sabbah, L. El Watik, J. Therm. Anal. 38 (1992) 855.
[2] W.-K. Wong, E.F. Westrum Jr., Mol. Cryst. Liq. Cryst. 61 (1980) 207.
[3] F. Casellato, C. Vecchi, A. Girelli, B. Casu, Thermochim. Acta 6 (1973) 361.

3.1.30. Other materials suggested as reference materials

The inorganic substances in Table 21 have been suggested as temperature reference materials for use in DTA and DSC studies. These materials are not recommended as reference materials at present for a variety of reasons including the lack of adiabatic calorimetric data, the potential for decomposition, the hygroscopic nature of the material and the lack of adequate reproducibility. The reader is encouraged to consult the references cited for specific details.

The organic substances in Table 22 have also been suggested as potential reference materials.

Table 21
A summary of other suggested inorganic reference materials

Substance	Transition temperature (K)	Melting point (K)	$\Delta_{\text{trs}}h$ ($J\,g^{-1}$)	$\Delta_{\text{fus}}h$ ($J\,g^{-1}$)	Reference
KNO_3	400.9		25.1		[1,2]
	403.2		45.2		[1]
	398.2		50		[1]
	403.2		50.5		[3]
AgI	422.2		27.9		[3]
	427.2		26.2		[4]
$RbNO_3$	439.2, 498.2, 558.2		26.2, 21.6, 8.7		[3]
	439.2, 501.2, 551.2		27.0, 18.5, 9.9		[3,4]
$AgNO_3$	441.2	484.2	13.4	71.4	[3]
	433.2	483.2	15	67.9	[3,5]
$KClO_4$	572.7		100.5		[1,6]
	571.2		93.8		[1]
	572.2		91.5		[1]
Ag_2SO_4	703.2		25.1		[1,7]
	699.2		41.9		[1]
	696.2		42.8		[1]
CsCl	749.2		17.2		[3]
	752.2		14.4		[1,4]
Quartz	846.2		8.4		[1,6]
	847.2		8		[1]
	849.2		9.3		[1]
K_2SO_4	856.2		46.1		[1,6]
	858.2		28.5		[1]
	859.2		29		[1]
K_2CrO_4	938.2		54.4		[1,3,6]
	947.2		33.9		[1]
	947.2		27		[1]
	941.2		35		[3]
	940.5		35.7		[3,8]

Table 22
A summary of other suggested organic reference materials

Substance	Reference
Adipic acid	[1,9]
Anisic acid	[10,11]
Benzanilide	[12]
2-Chloroanthraquinone	[10–12]
2-Chloropropane	[13]
Ethanol	[13,14]
Hexane	[13]
4-Iodobenzoic acid	[12]
1-Pentene	[13,15,16]
o-Terphenyl	[1,17]

These compounds are also not recommended for use at present either because of lack of data, lack of agreement of data from different laboratories or because of the thermal behavior observed. This table is included to provide impetus for further measurements.

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3.2. Solid-gas phase changes

The following protocol has been followed in identifying and ranking substances to be used as reference materials in sublimation enthalpy measurements. Substances recommended as reference materials in this document were chosen on the basis of data obtained by at least three independent sets of measurements that include a minimum of one calorimetric and one set of torsion and mass effusion measurements. Unlike other thermochemical measurements, uncertainties in sublimation enthalpies can be large, often several kJ or more, particularly for compounds exhibiting low volatility. It is not unusual to find large discrepancies between measurements made on the same compound. A statistical analysis of 191 independent experimental measurements on the sublimation enthalpies of 44 hydrocarbons resulted in a standard deviation of $\pm 7300\,\mathrm{J\,mol^{-1}}$ [1]. Using this uncertainty as a point of reference, compounds were selected as reference materials on measurements that displayed a standard deviation of less than $\pm 2000\,\mathrm{J\,mol^{-1}}$. The magnitude of each sublimation enthalpy was substantiated further by comparing the value obtained by direct measurement to that value approximated by addition of the fusion and vaporization enthalpies as described below. Additional criteria were applied to differentiate between primary, secondary and tertiary reference materials. The motivation for including the designation “tertiary reference material” was to identify measurements with some degree of reliability in pressure or temperature regimes not adequately covered by the other reference materials and to provide impetus for future work. Substances were selected and rated based on criteria such as relative volatility, availability, purity, thermodynamic stability and toxicity. Sublimation enthalpy measurements on these compounds were chosen on the basis of the track record of the laboratory reporting the work, the purity of the sample measured, the experimental details available, the general agreement between measurements, the number of available measurements, and the time frame of the measurements. While all measurements available at the time this report was written were considered, not all are included here. A significant number of measurements were excluded on the basis of the criteria cited above and on the subjective view of the compilers. Data reported prior to the 1950’s were generally avoided whenever possible. Finally, please note that all uncertainties reported in this section represent two standard deviations of the mean unless otherwise noted.

The ability of an experimental technique to measure vapor pressures or enthalpies in one pressure or temperature region does not by itself guarantee the same degree of accuracy in another. Systematic errors revealed by comparison of results obtained by different methods clearly establish the importance of documenting the accuracy of a series of measurements through the use of appropriate reference materials over the pressure and or temperature range employed. The approximate temperature-pressure regimes covered by the sublimation reference materials are summarized in Table 23 and illustrated in Fig. 3. Selection of the appropriate reference material is extremely important. The reference material chosen should be based on similarities in volatility to the compound being measured.

The sublimation enthalpy data evaluated in this section have been reported over the time frame 1922-present during which time several different temperature scales have been employed. The vapor pressure-temperature data were not corrected to the present temperature scale, ITS-90.

Corrections to 298.15 K from the temperatures of measurement have been included. In many instances, temperature adjustments have been applied by the authors reporting the work. If necessary, temperature corrections from the mean temperature of measurement, $\bar{T}$, to 298.15 K have been applied using Eqs. (3.2.1) and (3.2.2) [3]. These equations have been tested and found previously to provide good results [4,5]. The term $(C_p, \mathrm{m(s)})_{\mathrm{estd}}$ (298.15 K) refers to the heat capacity of the solid phase at 298.15 K and was estimated by group additivity [3]. When using Eq. (3.2.1), an uncertainty equal to one-third the magnitude of the total temperature adjustment was arbitrarily associated

Table 23
Temperatures and vapor pressures range of sublimation enthalpy reference materials

Substance	Temperature range (K)	Vapor pressure (Pa)	Classification
Benzoic acid ($C_7H_6O_2$)	298–383	0.1–360	Primary
Benzophenone (C_8H_8O)	307–385	0.3–130	Tertiary
Naphthalene ($C_{10}H_8$)	250–353	0.1–995	Primary
Ferrocene ($C_{10}H_{10}Fe$)	277–360	0.1–166	Primary
Biphenyl ($C_{12}H_{10}$)	278–363	0.1–70	Tertiary
Anthracene ($C_{14}H_{10}$)	338–360	0.1–1.0	Primary
Phenanthrene ($C_{14}H_{10}$)	315–335	0.1–1.0	Tertiary
trans-Stilbene ($C_{14}H_{12}$)	300–364	0.01–12	Tertiary
Pyrene ($C_{16}H_{10}$)	350–420	0.2–50	Secondary
1,3,5-Triphenylbenzene ($C_{24}H_{18}$)	365–450	0.001–6	Tertiary
Iodine (I_2)	273–387	4–12 600	Secondary

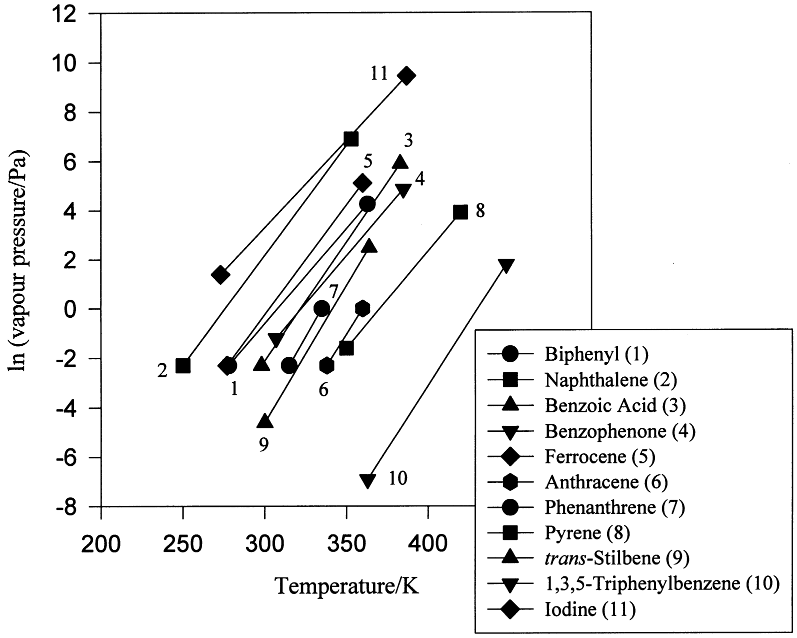

Fig. 3. The temperature-pressure domains covered by the sublimation enthalpy reference materials.

with the adjustment and was combined with the uncertainty associated with the experimental measurements in assessing the total uncertainty at 298.15 K

$$\Delta_{\rm sub}H_{\rm m}(298.15\,{\rm K})/{\rm J\,mol^{-1}} = \Delta_{\rm sub}H_{\rm m}(\bar{T}/{\rm K}) + [0.75 + 0.15(C_{p,\rm m}(s))_{\rm estd}/{\rm J\,mol^{-1}\,K^{-1}}(298.15\,{\rm K})][\bar{T}/{\rm K} - 298.15] \qquad (3.2.1)$$

$$\Delta_{\rm sub}H_{\rm m}(T_{\rm fus}) = \Delta_{\rm vap}H_{\rm m}(T_{\rm fus}) + \Delta_{\rm fus}H_{\rm m}(T_{\rm fus}) \qquad (3.2.2)$$

Eq. (3.2.2) was used to estimate sublimation enthalpies from the corresponding vaporization and fusion enthalpies of the solid. The experimental vaporization enthalpy was first adjusted from the mean temperature of measurement, $\bar{T}$ to the temperature, $T_{\rm fus}$, using Eq. (3.3.1) (see this Section 3.3). Addition of the fusion enthalpy followed by correction of the resulting sublimation enthalpy from $T_{\rm fus}$ to 298.15 K using Eq. (3.2.1) provided $\Delta_{\rm sub}H_{\rm m}$ (298.15 K).

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3.2.1. $\Delta_{sub}H$, benzoic acid

Physical property	enthalpy of sublimation
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of sublimation, $\Delta_{\rm sub}H_{\rm m}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of sublimation, $\Delta_{\rm sub}h$)
Recommended reference material	benzoic acid ($C_7H_6O_2$); 122.1234 $\mathrm{g\,mol^{-1}}$; [65-85-0]
Classification	primary RM
Range of variables	temperatures from 280 to 390 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\rm sub}H_{\rm m}$ (298.15 K) $= (89\,700 \pm 1000)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\rm sub}h$ (298.15 K) $= 734.5\ \mathrm{J\,g^{-1}}$
Contributor to the previous version	J.D. Cox
Contributor to this version	J. Chickos

3.2.1.1. Intended usage Benzoic acid has been recommended as a calibrant for enthalpy of sublimation measurements of substances having a vapor pressure of approximately 0.1 Pa at 298.15 K [1] or 10–360 Pa from $338 < T\ \mathrm{K} < 383$. The use of benzoic acid as a sublimation enthalpy reference material has been questioned because of the possibility of association of the acid in the gas phase [2,3]. However, it continues to be used as a reference material and all available experimental evidence suggests that it is a suitable reference material when measured under these specified conditions.

3.2.1.2. Sources of supply and/or methods of preparation Certified high purity material (99.9958%) is readily available from NIST (SRM 350a). Material prepared as a reference material for combustion measurements is suitable for calorimetric and vapor pressure measurements. Commercial samples of suitable purity are available from a variety of suppliers (Aldrich, Acros: 99.5+%; Fluka: 99.5+%).

3.2.1.3. Pertinent physicochemical data The vapor pressure and sublimation enthalpy of benzoic acid has been measured by a variety of different techniques and investigators. Despite the concern that the degree of dimerization of the acid in the gas phase can affect the sublimation enthalpy, reproducible results have been consistently obtained. Murata et al. [3] have reported that the degree of dissociation of the dimer in the saturated vapor to be higher than 0.997 at 298.15 K. Ribeiro Da Silva et al. have recently reported a summary of measurements of the sublimation enthalpy of thermochemical grade benzoic acid performed both in Utrecht and Oporto using a variety of techniques that included torsion effusion, mass effusion, spinning rotor and a diaphragm manometer over the temperature range 279–391 K. They obtain a mean value $(90\,460 \pm 2700)\ \mathrm{J\,mol^{-1}}$ which is consistent with most other literature values and suggests that the monomer-dimer dissociation does not have a significant thermochemical influence on the measurements [4]. Other recent reports of the sublimation enthalpy of benzoic acid including a variety of calorimetric measurements are summarized in Table 24. The mean sublimation enthalpy of $(89\,600 \pm 2750)$ from this table is comparable to $(89\,700 \pm 1000)\ \mathrm{J\,mol^{-1}}$ recommended by Cox [1] in 1974. Cox's value was based on earlier literature values. The difference between the two values is not statistically significant. The value recommended by Cox for benzoic acid $(89\,700 \pm 1000)\ \mathrm{J\,mol^{-1}}$ is retained.

De Kruif and Blok [7] have fitted the vapor pressure data of liquid benzoic acid available in the literature and have calculated a value for $\Delta_{\rm vap}H_{\rm m}$ (395.5 K) of $(69\,189 \pm 644)\ \mathrm{J\,mol^{-1}}$ at the melting point. Combining this with the recommended fusion enthalpy of $(18\,063 \pm 42)\ \mathrm{J\,mol^{-1}}$ (see Section 3.1.25) and adjusting the resulting sublimation enthalpy to 298.15 K using Eq. (3.2.1) and an es-

Table 24
Sublimation enthalpy of benzoic acid

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (T/K) ($\mathrm{J\,mol^{-1}}$)	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) ($\mathrm{J\,mol^{-1}}$)	Method	Purity (mol%)	Reference
	297–312	88 070 ± 420	TCM[a]	zrs[c]	[2]
87 750 ± 600	321	88 900 ± 600	Calorimetry	99.95	[3]
		90 460 ± 2700	See text	ts[d]	[4]
88 700 ± 1700	307–314	89 250 ± 1700	Mass effusion	ts[d]	[5]
87 450 ± 680	335	89 230 ± 1900	DSC[b]	99.997	[6]
89 450 ± 100	316–391	92 110 ± 500	Diaphragm manometry	99.9+	[7]
90 000 ± 2000	296–317	90 230 ± 2000[g]	Torsion, mass effusion	99.9+	[7]
90 350 ± 260	293–313	90 600 ± 400	Mass effusion	99.997	[8]
86 010 ± 830		89 000 ± 830	Calorimetry	sg[e]	[9]
86 180 ± 600	338–383	86 920 ± 800	Mass effusion	sg[e]	[9]
89 500 ± 340	298	89 500 ± 340	Calorimetry	NBS[f]	[10]
90 890[h]	291–307	90 910[g]	Mass effusion	na[i]	[11]

[a] Thermal conductivity manometry.
[b] Differential scanning calorimetry.
[c] Zone-refined sample.
[d] Thermochemical standard.
[e] Scintillation grade (Merck).
[f] NIST materials standard sample 39i.
[g] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for solid benzoic acid of 220 $\mathrm{J\,mol^{-1}\,K^{-1}}$.
[h] Uncertainty unavailable.
[i] Not available.

timated heat capacity for the solid $(C_{p,\mathrm{m}}(\mathrm{s}))_{\mathrm{estd}}$ (298.15 K) of 149 $\mathrm{J\,mol^{-1}\,K^{-1}}$ results in $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (89 500 ± 1630) $\mathrm{J\,mol^{-1}}$, in good agreement with the recommended value.

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3.2.2. $\Delta_{sub}H$, *benzophenone*

Physical property	enthalpy of sublimation
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	benzophenone ($C_{13}H_{10}O$); 182.2218 $\mathrm{g\,mol^{-1}}$; [119-61-9]
Classification	tertiary RM
Range of variables	temperatures from 307 to 385 K along the saturated vapor
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (93 770 ± 3540) $\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{sub}}h$ (298.15 K) = 514.6 $\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.2.2.1. Intended usage Benzophenone has been used to test and calibrate experimental setups for

Table 25
Sublimation enthalpy of benzophenone

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
95 070 ± 2000	305–320	95 570 ± 2020[a]	Diaphragm gauge	99.53	[1]
95 190 ± 1640	297–317	95 520 ± 1690	Torsion effusion	zrm[c]	[2]
93 890 ± 820	297–317	94 220 ± 860[a]	Mass effusion	zrm[c]	[2]
94 600 ± 1600	295–304	94 600 ± 1600[a]	TCM[b]	zrm[c]	[5]
93 350 ± 660	298	93 350 ± 660	Calorimetry	99.5+	[6]
95 000 ± 2600	293–318	95 230 ± 2600[a]	Torsion, mass effusion	na[d]	[1,7]
92 900 ± 1600	294–318	93 160 ± 1610[a]	Mass effusion	na[d]	[1,8]
92 000 ± 660	298	92 000 ± 660	Calorimetry	99+	[1,9]
89 960	298–318	90 290[a]	Mass effusion	na[d]	[10]

[a] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for solid benzophenone of 220 J mol^{-1} K^{-1}.
[b] Thermal conductivity manometry.
[c] Zone-refined material.
[d] An independent analysis of composition other than a physical property such as melting point is not available.

Table 26
Vaporization enthalpy of benzophenone

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
73 462 ± 200	320–386	78 320 ± 1600[a]	Diaphragm gauge	99.53	[1]
61 770 ± 400	474–505	78 700 ± 5700[a]	bp-p[b]	99.86	[11]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity for liquid benzophenone of 300 J mol^{-1} K^{-1}.
[b] Boiling point measured as a function of pressure.

measurement of vapor pressure and sublimation and vaporization enthalpies of substances exhibiting vapor pressures of approximately 0.1 Pa at 298.15 K and 0.3–130 Pa from $307 < T$ K < 385 [1,2]. The use of benzophenone as a reference material has been questioned because of the tendency to form a metastable solid phase [1,3]. However, it has been suggested as a useful calibrant for low vapor pressure measuring apparatus because of the tendency to easily supercool, thus permitting measurements on both the liquid and solid phase over the same temperature range.

3.2.2.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available from a variety of suppliers (Aldrich, Fluka: 99+%). Samples of higher purity are available from La Pine Scientific, Penta Mfg., Triple Crown America, and Accurate Chemical and Scientific.

3.2.2.3. Pertinent physicochemical data The vapor pressure and sublimation enthalpy of benzophenone has been measured by a variety of different techniques and investigators. De Kruif et al. [1] briefly review the available literature. A summary of the most recent measurements is provided in Table 25. A mean value of (93 770 ± 3540) J mol^{-1} is obtained which differs from 89 400 J mol^{-1} used by Pedley et al. [4]. Benzophenone is classified as a tertiary reference material at present, because some of the sublimation measurements reported in the literature are smaller in magnitude than those listed in Table 25. Since these values may have resulted from measurements made on the metastable solid state, it is not presently clear that this is the case.

The vaporization enthalpy of benzophenone has also been measured (Table 26). De Kruif et al. report a value of (73 462 ± 200) J mol^{-1} over the temperature range 320–386 K. Adjusted to the triple point temperature of 321 K, a vaporization enthalpy of (76 300 ± 1650) J mol^{-1} is obtained. Similarly, Dreisbach and Schader [11] report vapor pressure data from 474 to 579 K. Using a Clausius-Clapeyron treatment of the data from 474 to 505 K resulted in a vaporization enthalpy of (61 770 ± 400) J mol^{-1} which when adjusted to the triple point temperature afforded a value of (76 670 ± 5000) J mol^{-1}. Combining the mean vaporization enthalpy of (76 480 ± 2700) J mol^{-1}) with a fusion enthalpy of (18 194 ± 100) J mol^{-1} measured by adiabatic calorimetry [1], and adjusting the resulting sublimation enthalpy to 298.15 K according to Eq. (3.2.1), results in the value (95 450 ± 2700) J mol^{-1}, in agreement with the recommended value.

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3.2.3. $\Delta_{sub}H$, naphthalene

Physical property	enthalpy of sublimation
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	naphthalene ($C_{10}H_8$): 128.1735 g mol^{-1}; [91-20-3]
Classification	primary RM
Range of variables (solid)	temperatures 250–353 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (72 600 ± 600) J mol^{-1}; $\Delta_{\mathrm{sub}}h$ (298.15 K) = 566.4 J g^{-1}
Contributors to the previous versions	J.D. Cox, R. Sabbah
Contributor to this version	J. Chickos

3.2.3.1. Intended usage Naphthalene has been recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of solids around 10 Pa at 298.15 K [1–4]. Naphthalene has also been recommended as an alternative to ice as a reference material for vapor pressure measurements below $p = 1000$ Pa [1,2]. The use of naphthalene as a sublimation enthalpy reference should be restricted to measurements on compounds that exhibit vapor pressures in the range 0.1–995 Pa over the temperature range $250 < T$ K < 353.

3.2.3.2. Sources of supply and/or methods of preparation Certified, high purity material is readily available (ORM: LGC24024). Commercial samples are available from a variety of suppliers (Aldrich, Fluka: 99.9+%). Samples of higher purity can be obtained by zone refining.

3.2.3.3. Pertinent physicochemical data Chirico et al. [2] summarized the sublimation enthalpies of naphthalene measured from 280 to 340 K. A total of 10 values are reported at 298.15 K resulting in an average of (72 450 ± 1250) J mol^{-1} (Table 27). Considering only the data within three standard deviations from the mean results in a value of (72 626 ± 534) J mol^{-1} for nine values. Since this number is nearly identical to the value recommended previously [1], the recommended sublimation enthalpy of naphthalene is retained.

A value of (55 730 ± 2150) J mol^{-1} has been recommended for the vaporization enthalpy of naphthalene at 298.15 K [2,4,13–15]. Adjusting $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) to the melting point of naphthalene, 353.4 K, using Eq. (3.3.1) and an estimated heat capacity for the liquid of 205 J mol^{-1} K^{-1}, results in the value of (52 200 ± 3800) J mol^{-1}. Combining this with the recommended fusion enthalpy of (19 061 ± 80) J mol^{-1} (see Section 3.1.22) and readjusting the sublimation enthalpy back to 298.15 K ($(C_{p,\mathrm{m}}(\mathrm{s}))_{\mathrm{estd}}$ (298.15 K) = 157 J mol^{-1} K^{-1}) results

Table 27
Sublimation enthalpy of naphthalene

$\Delta_{sub}H_m$ (T/K) ($J\,mol^{-1}$)	T (K)	$\Delta_{sub}H_m$ (298.15 K) ($J\,mol^{-1}$)	Method	Purity (mol%)	Reference
		72 700 ± 400	Ebulliometer	99.93	[2]
	274–353	72 510 ± 280	Diaphram manometer	99.97	[4]
	230–260	72 680 ± 660	Knudsen gauge		[5]
72 050 ± 500	298.15	72 050 ± 500	Calorimetry	OAS[a]	[6]
73 000 ± 500	298.15	73 000 ± 500	Calorimetry	zrm[b]	[7]
	220–353	72 500	Transpiration	99.99	[8]
74 400 ± 1000	253–273	72 600 ± 1200	Torsion, mass effusion	zrm[b]	[9]
73 930 ± 600	271–284	72 800 ± 600	Mass effusion	99.95+	[10]
72 915 ± 740	244–256	72 920 ± 740	SRFG[d]	99.97	[11]
70 730 ± 2100	298.15	70 730 ± 2100[e]	Calorimetry	cg[c]	[12]

[a] Organic analytical standard grade.
[b] Zone-refined material.
[c] Calorimetric grade (Carlo Erba).
[d] Spinning rotor friction gauge.
[e] Not included in calculating the mean.

in a mean value of (72 604 ± 3915) $J\,mol^{-1}$ in good agreement with the recommended value.

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3.2.4. $\Delta_{sub}H$, *ferrocene*

Physical property	enthalpy of sublimation
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of sublimation $\Delta_{sub}H_m$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of fusion, $\Delta_{sub}h$)
Recommended reference material	ferrocene ($C_{10}H_{10}Fe$); 186.0344 $g\,mol^{-1}$; [102-54-5]
Classification	primary RM
Range of variables	temperatures from 277 to 360 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{sub}H_m$ (298.15 K) = (73 420 ± 1080) $J\,mol^{-1}$; $\Delta_{sub}h$ (298.15 K) = 394.7 $J\ g^{-1}$
Contributors to the previous version	J.D. Cox
Contributor to this version	J. Chickos

3.2.4.1. Intended usage Ferrocene has been recommended and used as a calibrant for enthalpies of sublimation measurements [1,2]. It should be used for measurements of substances exhibiting a vapor pressure of approximately 1.0 Pa at 298.15 K [1] or vapor pressures in the range of 0.1–166 Pa at $277 < T/\mathrm{K} < 360$.

3.2.4.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available from a variety of suppliers (Aldrich, Lancaster, Alfa: 98%; Fluka: >98%). Further purification can be achieved by recrystallization and sublimation at 373 K.

3.2.4.3. Pertinent physicochemical data The vapor pressure and sublimation enthalpy of ferrocene has been measured by a variety of different techniques and investigators. Some of the most recent measurements are listed in Table 28. The mean value of the entries listed is $(72\,950 \pm 2770)\,\mathrm{J\,mol^{-1}}$. Torres et al. [2] have critically reviewed all of the literature results reported to date which were measured by indirect methods. They recommend a weighted average value of $(73\,420 \pm 1080)\,\mathrm{J\,mol^{-1}}$ which is well within experimental error of the values cited in Table 28. This latter value is recommended for the sublimation enthalpy of ferrocene.

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3.2.5. $\Delta_{sub}H$, biphenyl

Physical property	enthalpy of sublimation
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	($C_{12}H_{10}$): 154.2114 $\mathrm{g\,mol^{-1}}$; [91-52-4]
Classification	tertiary RM
Range of variables	temperatures from 278 to 363 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, calorimetry, inclined piston
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) $= (82\,115 \pm 2130)\,\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{sub}}h$ (298.15 K) $= 532.5\,\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.2.5.1. Intended usage Biphenyl is recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus used in the measurement of the vapor pressures of solids that exhibit vapor pressures from 0.10 to 70 Pa at temperatures: $278 < T\ \mathrm{K} < 363$ [1].

3.2.5.2. Sources of supply and/or methods of preparation Certified high purity material (99.984%) is readily available from NIST (SRM 2222) or API Standard Reference Materials. High purity material is available from a variety of commercial suppliers (Aldrich: 99%; Fluka: 98+%). This material is expected to have an indefinite shelf life under normal conditions. Biphenyl can be purified by vacuum distillation [2].

3.2.5.3. Pertinent physicochemical data The sublimation enthalpy of biphenyl has been reported many times since the 1950's [1–8]. The reported values segregate into two sets; one set appears to center about a mean of $76\,000\,\mathrm{J\,mol^{-1}}$ [6–8] and the other about a mean of $82\,000\,\mathrm{J\,mol^{-1}}$. The most recent measurements appear in good agreement with each other and are consistent with the larger of the two values. The mean of the five measurements reported in Table 29 is $(82\,115 \pm 2130)\,\mathrm{J\,mol^{-1}}$ and is the recommended value. Biphenyl is presently considered a tertiary reference material.

The vaporization enthalpy of biphenyl has also been measured. Adjusting the values of $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$

Table 28
Sublimation enthalpy of ferrocene

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
72 510 ± 1800	292–300	72 390 ± 2000	Mass effusion	98+	[1]
74 600 ± 1600	280	74 300 ± 800	Mass effusion	99.99	[2]
73 200 ± 1400	298	73 200 ± 1400	Calorimetry	99.99	[2]
	294–302	70 300 ± 2000	Mass effusion	na[a]	[3]
72 070 ± 720	278–309	71 920 ± 720	Mass effusion	99.997	[4]
70 450 ± 460	330–360	72 260 ± 460	Diaphragm manometry	99+	[5]
73 390 ± 240	277–297	73 100 ± 240	Mass effusion	99+	[5]
75 900 ± 1400	277–297	75 610 ± 1400	Torsion effusion	99+	[5]
71 300 ± 2200	288–353	74 000 ± 4000	Torsion effusion		[6]
72 600 ± 2720	298–303	72 600 ± 2720	Mass effusion	na[a]	[7]
72 730 ± 1080	293–306	72 730 ± 1080	Mass effusion	na[a]	[8]

[a] An independent analysis of composition is unavailable.

Table 29
Sublimation enthalpy of biphenyl

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
81 520 ± 320	298	81 520 ± 320	Inclined piston	99.98	[1]
83 340 ± 920	283–338	83 720 ± 960[a,b]	Pressure gauge	99	[2]
81 755 ± 380	298	81 755 ± 380	Calorimetry	99.99	[3]
80 370 ± 3200	306–322	80 990 ± 3250[b]	Gas chromatography	na[c]	[4]
82 511 ± 810	288–314	82 600 ± 810[a,b]	Mass effusion	na[c]	[5]

[a] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.

[b] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for solid biphenyl of 192 J mol^{-1}.

[c] An independent analysis of composition other than a physical property such as melting point is not available.

Table 30
Vaporization enthalpy of biphenyl

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
61 762 ± 50	340	64 920 ± 130	Inclined piston	99.98	[1]
60 340 ± 500	333–393	66 285 ± 720[a,b]	Pressure gauge	99	[2]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity of 249 J mol^{-1} K^{-1} for liquid biphenyl.

[b] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.

(T K) from Table 30 to the melting point of biphenyl, 342 K, results in the mean value of (61 780 ± 440) J mol^{-1}. Combining this with the recommended fusion enthalpy of (18 574 ± 4) J mol^{-1} (see Section 3.1.21) and adjusting the resulting sublimation enthalpy back to 298.15 K, according to the protocol described above, results in a sublimation enthalpy of (81 650 ± 970) J mol^{-1}, in good agreement with the mean value reported above.

References

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3.2.6. $\Delta_{sub}H$, *anthracene*

Physical property	enthalpy of sublimation
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of sublimation $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	anthracene ($C_{14}H_{10}$) 178.2334 $\mathrm{g\,mol^{-1}}$; [120-12-7]
Classification	primary RM
Range of variables	temperatures from 338 to 360 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (103 360 ± 2670) $\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{sub}}h$ (298.15 K) = 579.9 $\mathrm{J\,g^{-1}}$
Contributor to this version	J. Chickos

3.2.6.1. Intended usage Anthracene is recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of solids that exhibit a vapor pressure between 0.1 and 1.0 Pa in the temperature range 338–360 K [1]. It has been used as a test substance by various investigators [2,3].

3.2.6.2. Sources of supply and/or methods of preparation Zone refined anthracene is readily available from a variety of commercial suppliers (Aldrich, Fluka: 99+%, Lancaster: 99.9%).

3.2.6.3. Pertinent physicochemical data The sublimation enthalpy of anthracene has been determined numerous times during the past 50 years [4]. Most values range from 85 000 to 105 000 $\mathrm{J\,mol^{-1}}$. Malaspina et al. [5] have summarized many of the early results. Pedley et al. [6] recommend a value of (101 700 ± 8400) $\mathrm{J\,mol^{-1}}$ for $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) while Kudchadker et al. [7] recommend a value of (100 900 ± 5600) $\mathrm{J\,mol^{-1}}$. Inclusion of more recent determinations of the sublimation enthalpy of anthracene increases the mean value slightly to (103 360 ± 2670) $\mathrm{J\,mol^{-1}}$. This is the recommended value. The uncertainty associated with each entry in the third column of Table 31 includes both the uncertainty associated with the measurements when available as well the uncertainty associated with the heat capacity corrections. Anthracene is evaluated as a primary reference material.

Vapor pressure as a function of temperature for liquid anthracene have been measured. The vaporization enthalpies are summarized in Table 32. A Clausius-Clapeyron treatment of the data was used to derive vaporization enthalpies at the mean temperature of measurement. The value, (59 210 ± 200) $\mathrm{J\,mol^{-1}}$, calculated from measurements made over the temperature range 496–555 K by Mortimer and Murphy [12], was adjusted to the melting point temperature, 488.9 K. This resulted in a vaporization enthalpy of (62 280 ± 410) $\mathrm{J\,mol^{-1}}$. Similarly, Nelson and Senseman [13] reported vapor pressure data from 500 to 583 K. A similar treatment of the data from 500 to 537 K afforded a vaporization enthalpy of (59 390 ± 2220) $\mathrm{J\,mol^{-1}}$. Adjusted to the melting point temperature (489 K) resulted in a value of (61 830 ± 2385) $\mathrm{J\,mol^{-1}}$. Combining the mean vaporization enthalpy, (62 060 ± 660) $\mathrm{J\,mol^{-1}}$ at 489 K with a fusion enthalpy of (29 372 ± 100) $\mathrm{J\,mol^{-1}}$ [14] and adjusting the resulting enthalpy to 298.15 K results in a sublimation enthalpy of (97 550 ± 4300) $\mathrm{J\,mol^{-1}}$ in agreement with the recommended value.

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Table 31
Sublimation enthalpy of anthracene

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
100 600 ± 2000	337–361	104 500 ± 3000	Torsion, mass effusion	zrm[b]	[1]
102 600 ± 2600	313–363	103 890 ± 2740[a]	Transpiration	99.9	[2]
101 035 ± 920	393	104 060 ± 2220[a]	Mass effusion	sg[c]	[5]
99 690 ± 1500	393	102 730 ± 2560[a]	Calorimetric	sg[c]	[5]
98 490 ± 1120[d]	342–359	100 200 ± 1600[a]	Mass effusion	na[e]	[8]
100 834 ± 600[d]	378–398	103 700 ± 2015[a]	Manometer	na[e]	[5,9]
103 390	303–373	104 670[a]	Mass effusion	na[e]	[10]
101 600 ± 4100	339–354	103 150 ± 4400[a]	Mass effusion	na[e]	[11]

[a] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity of 209 J mol^{-1} K^{-1} for the solid.
[b] Zone-refined material.
[c] Scintillation grade (Merck).
[d] The uncertainty evaluated from the data given in [8].
[e] An independent analysis of composition other than a physical property such as melting point is not available.

Table 32
Vaporization enthalpy of anthracene

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T/K) (J mol^{-1})	T (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
59 210 ± 200	496–555	78 150 ± 1122[a,b]	Isoteniscope	na[c]	[13]
59 390 ± 2220	500–537	77 700 ± 2385[a,b]	Isoteniscope	na[c]	[14]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity for liquid benzophenone of 280 J mol^{-1} K^{-1}.
[b] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.
[c] An independent analysis of composition other than a physical property such as melting point is not available.

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3.2.7. $\Delta_{sub}H$, phenanthrene

Physical property	enthalpy of sublimation
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	phenanthrene ($C_{14}H_{10}$): 178.2334 g mol^{-1}; [85-01-8]
Classification	tertiary RM
Range of variables	temperatures from 315 to 335 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (91 300 ± 2733) J mol^{-1}; $\Delta_{\mathrm{sub}}h$ (298.15 K) = 512.3 J g^{-1}
Contributor to this version	J. Chickos

3.2.7.1. Intended usage Phenanthrene is recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of solids that exhibit a vapor pressure between 0.1 and 1.0 Pa in the temperature range 315–335 K [1].

3.2.7.2. Sources of supply and/or methods of preparation Zone-refined phenanthrene as well as material at other purities are readily available from a variety of commercial suppliers (Aldrich: 99.5%, Alfa AESAR, Lancaster: 98%).

3.2.7.3. Pertinent physicochemical data The sublimation enthalpy of phenanthrene has been determined a number of times during the past 50 years. Most values range from 88 000 to 96 000 J mol^{-1} [2]. Pedley et al. [3] recommend a value of (91 300 ± 2200) J mol^{-1}

Table 33
Sublimation enthalpy of phenanthrene

$\Delta_{sub}H_m$ (T/K) ($J\,mol^{-1}$)	T (K)	$\Delta_{sub}H_m$ (298.15 K) ($J\,mol^{-1}$)	Method	Purity (mol%)	Reference
$90\,500 \pm 2000$	315–335	$92\,500 \pm 4000$	Torsion, mass effusion	97[a]	[1]
$87\,240 \pm 2200$	350	$90\,900 \pm 3400$	DSC[b]	99.5+	[4]
$90\,880 \pm 800$	298	$90\,880 \pm 800$	Calorimetry	99.97	[5]

[a] Contained <0.1% anthracene.
[b] Differential scanning calorimetry.

for $\Delta_{sub}H_m$ (298.15 K). The values listed in Table 33 are recent and appear to be reliable. A mean value of $(91\,420 \pm 1860)\,J\,mol^{-1}$ is obtained which is not significantly different from earlier recommendations. The recommendation of Pedley et al. is retained. Phenanthrene is presently designated as a tertiary reference material primarily because of the large spread of values reported in the literature [2]. The uncertainty assigned to the recommended value is the mean of the uncertainties reported in column 3 of Table 33.

The vaporization enthalpy of phenanthrene has been measured by Osborn and Douslin [6], Finke et al. [7], Mortimer and Murphy [9] and Nelson and Senseman [10]. Adjusting the vaporization enthalpies reported in Table 34 by Mortimer and Murphy [9] and Nelson and Senseman [10] to the triple point temperature, 372.4 K, using Eq. (3.3.1) and averaging the resulting values with the corresponding triple point values of $(70\,793 \pm 400)$ and $71\,210\,J\,mol^{-1}$ reported by Osborn and Douslin and Finke et al. results in a mean value of $(72\,510 \pm 3220)\,J\,mol^{-1}$. Addition of the fusion and transition enthalpies, $(16\,463 \pm 35)$ and $218\,J\,mol^{-1}$ (347.5 K), respectively [7,8], and adjusting the resulting sublimation enthalpy to 298.15 K using Eq. (3.2.1) results in a mean value of $(91\,570 \pm 3220)\,J\,mol^{-1}$, in good agreement with the recommended sublimation enthalpy.

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3.2.8. $\Delta_{sub}H$, *trans-stilbene*

Physical property	enthalpy of sublimation
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of sublimation, $\Delta_{sub}H_m$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of fusion, $\Delta_{sub}h$)
Recommended reference material	trans-stilbene, trans-1,2-diphenylethene ($C_{14}H_{12}$); 180.2493 $g\,mol^{-1}$; [103-30-0]
Classification	tertiary RM
Range of variables	temperatures from 300 to 364 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{sub}H_m$ (298.15 K) $= (101\,160 \pm 3460)\,J\,mol^{-1}$; $\Delta_{sub}h$ (298.15 K) $= 561.2\,J\,g^{-1}$
Contributor to this version	J. Chickos

3.2.8.1. Intended usage trans-Stilbene has been used to test and calibrate the experimental apparatus used for the measurement of vapor pressure, sublimation and vaporization enthalpies of substances having a vapor pressures of approximately 0.01–12 Pa from $300 < T\,K < 364$ [1]

Table 34
Vaporization enthalpy of phenanthrene

$\Delta_{vap}H_m$ (T/K) (J mol^{-1})	T (K)	$\Delta_{vap}H_m$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
68 980 ± 400[a]	373–423	77 250±3020[b]	Inclined piston	99.99	[6]
71 210	372	77 350[b]	Inclined piston	99.99	[7]
60 830 ± 313[a]	507–545	79 760 ± 6800[b]	Isoteniscope	na[c]	[9]
61 760 ± 1500[a]	505–538	80 360 ± 7350[b]	Isoteniscope	na[c]	[10]

[a] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.
[b] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for liquid phenanthrene of 279 J mol^{-1} K^{-1}.
[c] An independent analysis of composition is not available.

Table 35
Sublimation enthalpy of *trans*-stilbene

$\Delta_{sub}H_m$ (T/K) (J mol^{-1})	T (K)	$\Delta_{sub}H_m$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
99 050 ± 1930[a]	297–316	99 380 ± 1950	Spinning rotor	99.95	[1]
102 260 ± 28[a]	318–338	103 340 ± 720	Torsion, mass effusion	99.95	[1]
100 740 ± 1480[a]	342–364	102 730 ± 1990	Diaphragm manometer	99.95	[1]
99 200 ± 1600	298	99 200 ± 800	Calorimetry	BDH[d]	[5]
101 100 ± 680	317.5[b]	101 790 ± 970[c]	Mass effusion	na[e]	[1,6]
		102 090 ± 1680	TCM[f]	99.95	[1,7]
		99 600 ± 3400	Torsion effusion	na[e]	[1,8]

[a] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.
[b] Mean temperature of measurements.
[c] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for solid *trans*-stilbene of 220 J mol^{-1} K^{-1}.
[d] Sample from British Drug House.
[e] Not available.
[f] Thermal conductivity manometer.

3.2.8.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available from a variety of suppliers (Aldrich: 96%; Fluka, Lancaster: 97%). Higher purity and standard grade trans-stilbene is available from ChemService, Indofine Chem., or The Metron Group/THM. trans-Stilbene can also be recrystallized from ethanol and sublimed.

3.2.8.3. Pertinent physicochemical data The vapor pressure and sublimation enthalpy of *trans*-stilbene has been measured by a variety of different techniques. Van Ekeren et al. [1] briefly review the available literature. A summary of the most recent measurements is provided in Table 35. The mean value of (101 160 ± 3460) J mol^{-1} is recommended; this compares with the value (99 200 ± 800) J mol^{-1} recommended by Pedley et al. [2] trans-stilbene is presently recommended as a tertiary reference material.

The vaporization enthalpy of trans-stilbene can be calculated from the Antoine Constants reported for the temperature range 419–580 K [3]. Using these constants to calculate the vapor pressure from 419 to 449 K results in a vaporization enthalpy of 65 460 J mol^{-1} at 434 K. Adjusting the vaporization enthalpy to the melting point, 397.4 K, using Eq. (3.3.1) and an estimated heat capacity for the liquid at 298.15 K of 304 J mol^{-1}, provides the value 68 740 J mol^{-1}; addition of the fusion enthalpy (27 690 J mol^{-1}, [4]) and subsequent adjustment of the sublimation enthalpy to 298.15 K (using Eq. (3.2.1)) affords the value (100 000 ± 2620) J mol^{-1}, in good agreement with the recommended value. The uncertainty of (±2620) J mol^{-1} represents the uncertainty associated with the temperature adjustments only.

References

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3.2.9. $\Delta_{sub}H$, pyrene

Physical property	enthalpy of sublimation
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation, $\Delta_{\rm sub}H_{\rm m}$); J kg^{-1} or J g^{-1} (specific enthalpy of sublimation, $\Delta_{\rm sub}h$)
Recommended reference material	pyrene ($C_{16}H_{10}$): 202.2554 g mol^{-1}; [129-00-0]
Classification	secondary RM
Range of variables	temperatures from 350 to 420 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, transpiration, calorimetry
Recommended value	$\Delta_{\rm sub}H_{\rm m}$ (298.15 K) = (100 200 ± 3590) J mol^{-1}; $\Delta_{\rm vap}h$ (298.15 K) = 495.4 J g^{-1}
Contributor to this version	J. Chickos

3.2.9.1. Intended usage Pyrene is recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressure between 0.2 and 50 Pa in the temperature range 350–420 K [1].

3.2.9.2. Sources of supply and/or methods of preparation Certified high purity material is readily available (ORM: CRM177). Commercial samples are available from a variety of suppliers (Aldrich: 99%; Fluka: 99+%). Pyrene can be purified by recrystallized from *p*-dioxane and sublimed [2].

3.2.9.3. Pertinent physicochemical data The sublimation enthalpy of pyrene has been reported several times [3]. Pedley et al. [4] recommend a value of 100 200 J mol^{-1} for $\Delta_{\rm sub}H_{\rm m}$ (298.15 K). The sublimation enthalpy of pyrene was calculated for the Crystal I state in Ref. [5] from the vapor pressures reported from 398 to 423 K using a Clausius-Clapeyron treatment of the data. Similarly for Ref. [6], vapor pressure data from 353 to 393 K was used in calculating $\Delta_{\rm sub}H_{\rm m}$ (373 K). A mean value of (100 190 ± 3660) J mol^{-1} is derived for $\Delta_{\rm sub}H_{\rm m}$ (298.15 K) from an average of the first four entries. This value is not statistically significant from the value chosen by Pedley, which is retained as the recommended value. There are no experimental details presented in Ref. [7] listed in Table 36; this entry was not used in computing the mean.

The vaporization enthalpy of pyrene has also been measured on the supercooled liquid by Smith et al. [5] and for the liquid state by Sasse et al. [6]. The values in column 1 of Table 37 were calculated from a Clausius-Clapeyron treatment of the data. Adjustment of the enthalpy of vaporization to the melting point, 423.8 K, resulted in a mean value of (75 900 ± 1540) J mol^{-1}. Combined with a fusion enthalpy of (17 355 ± 4) J mol^{-1} [2] and adjusted to 298.15 K results in a mean value of (97 500 ± 1500) J mol^{-1}, in reasonable agreement with the recommended value.

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Table 36
Sublimation enthalpy of pyrene

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (*T*/K) (J mol^{-1})	*T* (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
97 675 ± 260[a]	384	100 545 ± 1930[b]	Calorimetry	99	[1]
97 470 ± 700[a]	348–419	100 340 ± 2040[b]	Mass effusion	99	[1]
93 965 ± 350[a]	398–423	97 726 ± 2530[b]	Inclined piston gauge	zrm[c]	[5]
99 308 ± 920[a]	353–393	102 151 ± 1910[b]	Pressure gauge	97+	[6]
97 900	314–454	100 741 ± 2840[b]	Transpiration	99.9	[7]

[a] Calculated by a Clausius-Clapeyron treatment of the vapor pressure-temperature data provided in the paper.

[b] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity of 217.8 J mol^{-1} K^{-1} for solid pyrene.

[c] Zone-refined material.

Table 37
Vaporization enthalpy of pyrene

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (*T*/K) (J mol^{-1})	*T* (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
76 510 ± 512	398–423	86 330 ± 3420[a,b]	Inclined piston gauge	zrm[c]	[6]
75 640 ± 1220	413–453	87 410 ± 4220[a]	Pressure gauge	97+	[7]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity of 295 J mol^{-1} K^{-1} for liquid pyrene (a value of 8 J mol^{-1} K^{-1} was used for an internal quaternary aromatic carbon) [8].

[b] Calculated from the vapor pressure of the supercooled liquid.

[c] Zone-refined material.

Table 38
Sublimation enthalpy of 1,3,5-triphenylbenzene

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (*T*/K) (J mol^{-1})	*T* (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
142 050 ± 2920	410–444	149 220 ± 7740[a]	Mass effusion	99	[1]
143 090 ± 600	410–444	150 260 ± 7200[a]	Calorimetry	99	[1]
143 600	363–408	148 460[a]	Mass effusion	na[b]	[2]
142 613	370–448	148 800[a]	Mass effusion	na[b]	[3]

[a] Sublimation enthalpy adjusted to 298.15 K using Eq. (3.2.1) and an estimated heat capacity for solid 1,3,5-triphenylbenzene of 366 J mol^{-1} K^{-1}.

[b] An independent analysis of composition other than a physical property such as melting point is not available.

3.2.10. $\Delta_{sub}H$, 1,3,5-triphenylbenzene

Physical property	enthalpy of sublimation
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of sublimation, $\Delta_{\mathrm{sub}}h$)
Recommended reference material	1,3,5-triphenylbenzene ($C_{24}H_{18}$): 306.4069 g mol^{-1}; [612-71-5]
Classification	tertiary RM
Range of variables	temperatures from 365 to 450 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes mass effusion, torsion effusion, calorimetry
Recommended value	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K) = (149 180 ± 1600) J mol^{-1}; $\Delta_{\mathrm{vap}}h$ (298.15 K) = 486.9 J g^{-1}
Contributor to this version	J. Chickos

3.2.10.1. Intended usage 1,3,5-Triphenylbenzene is recommended as a test material for the measurement of sublimation enthalpy to check the performance of calorimeters and apparatus for materials that exhibit a vapor pressure between 10^{-3} and 6 Pa in the temperature range 365–450 K [1–3]. It is one of a few compounds in this volatility range whose sublimation enthalpy has been reproducible.

3.2.10.2. Sources of supply and/or methods of preparation 1,3,5-Triphenylbenzene is available from a variety of commercial suppliers (Aldrich: 97%). Higher purity 1,3,5-triphenylbenzene is also available from The Metron Group/THM. 1,3,5-

Table 39
Vaporization enthalpy of 1,3,5-triphenylbenzene

$\Delta_{vap}H_m$ (T/K) ($J\,mol^{-1}$)	T (K)	$\Delta_{vap}H_m$ (298.15 K) ($J\,mol^{-1}$)	Method	Purity (mol%)	Reference
116 570 ± 2340	454–500	140 970 ± 5850[a]	Mass effusion	99	[1]
117 320 ± 1510	454–500	141 730 ± 5570[a]	Calorimetry	99	[1]
		139 950 ± 4000	C-GC[b]	99	[4]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity of 484 $J\,mol^{-1}\,K^{-1}$ for liquid 1,3,5-triphenylbenzene.

[b] Correlation-gas chromatography.

triphenylbenzene can be purified by recrystallization from glacial acetic acid and sublimation.

3.2.10.3. Pertinent physicochemical data The sublimation enthalpy of 1,3,5-triphenylbenzene has been reported several times in the past 50 years [1–3]. The mean value of the entries in Table 38 is (149 180 ± 1600) $J\,mol^{-1}$ and is the value recommended. 1,3,5-Triphenylbenzene is recommended as a tertiary reference material because of the limited amount data presently available.

The vaporization enthalpy of 1,3,5-triphenylbenzene has also been measured on the liquid by Malaspina et al. [1] by mass effusion and calorimetry and by correlation-gas chromatography by Chickos et al. ([4], Table 39). Adjustment of the enthalpy of vaporization to the melting point, 448.5 K, resulted in a mean value of (120 366 ± 1780) $J\,mol^{-1}$. Combined with a fusion enthalpy of (22 930 ± 600) $J\,mol^{-1}$ [1] and adjusted to 298.15 K results in a mean value of (151 660 ± 1780) $J\,mol^{-1}$ in reasonable agreement with the recommended value.

References

[1] L. Malaspina, G. Bardi, R. Gigli, J. Chem. Thermodyn. 6 (1974) 1053.

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3.2.11. $\Delta_{sub}H$, iodine

Physical property	enthalpy of sublimation
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of sublimation, $\Delta_{sub}H_m$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of fusion, $\Delta_{sub}h$)
Recommended reference material	iodine (I_2), 253.8089 $g\,mol^{-1}$; [7553-56-2]
Classification	secondary RM
Range of variables	temperatures from 273 to 387 K along the saturated vapor curve
Physical state within the range	solid → real saturated vapor
Apparatus used	includes transpiration, torsion effusion, calorimetry
Recommended value	$\Delta_{sub}H_m$ (298.15 K) = (62 440 ± 726) $J\,mol^{-1}$; $\Delta_{sub}h$ (298.15 K) = 246.0 $J\,g^{-1}$
Contributor to the previous version	R. Sabbah
Contributor to this version	J. Chickos

3.2.11.1. Intended usage Iodine has been suggested as a test material to calibrate calorimeters used for the measurement of sublimation enthalpies of substances exhibiting vapor pressures of 4–12 600 Pa from 273 to 387 K [1]. Corrosion experiments have shown that platinum is not attacked by iodine and gold becomes slightly tarnished after exposure. The tarnish disappears on standing in air. These metals and glass can be used to contain iodine [2]. Teflon is discolored after prolonged contact with iodine.

3.2.11.2. Sources of supply and/or methods of preparation Commercial samples of suitable purity are available from a variety of suppliers (Alfa: 99.999%; Aldrich: 99.999+%, Fluka, 99.8%; Lancaster: 99.5%).

3.2.11.3. Pertinent physicochemical data The values for the enthalpy of sublimation of iodine in the first column of Table 40 have been calculated from the original literature by plotting the natural logarithm

Table 40
Sublimation enthalpy of iodine

$\Delta_{sub}H_m$ (T/K) (J mol^{-1})	T (K)	T (K)	$\Delta_{sub}H_m$ (298.15 K) (J mol^{-1})	$\Delta_{sub}H_m$ (OK) (J mol^{-1})	Reference
62 572 ± 357	273–328	300.7	62 572	65 509	[1]
62 086 ± 1002	303–333	318.2	62 260	65 500	[2]
62 581 ± 430	273–323	298.2	62 581	65 509	[4]
60 182 ± 1059	339–387	359.1		65 567	[5]
62 291 ± 787	305–358	332		65 513	[6]

Table 41
Temperature and vapor pressure range of vaporization enthalpy reference materials

Substance	Temperature range (K)	Vapor pressure (Pa)	Classification
1-Propanol (C_3H_8O)	298–370	20E+3–135E+3	Primary
Pentane (C_5H_{12})	269–315	2.0E+4–1.2E+5	Primary
Hexafluorobenzene (C_6F_6)	290–377	7.5E+3–2.1E+5	Primary
Benzene (C_6H_6)	286–383	7.0E+3–2.4E+5	Primary
Hexane (C_6H_{14})	286–343	1.2E+4–1.0E+5	Primary
Heptane (C_7H_{16})	299–372	6.4E+3–1.0E+5	Primary
Octane (C_8H_{18})	326–400	7.7E+3–1.0E+5	Primary
Nonane (C_9H_{20})	344–425	6.4E+3–1.0E+5	Primary
Naphthalene ($C_{10}H_8$)	353–434	1.0E+3–2.3E+4	Secondary
Decane ($C_{10}H_{22}$)	268–348	1.7E+1–3.2E+3	Primary
Undecane ($C_{11}H_{24}$)	294–382	4.1E+1–6.4E+3	Primary
Dodecane ($C_{12}H_{26}$)	313–403	5.8E+1–7.3E+3	Primary
Tridecane ($C_{13}H_{28}$)	323–402	4.7E+1–3.7E+3	Primary
Tetradecane ($C_{14}H_{30}$)	344–422	7.6E+1–4.4E+3	Primary
Hexadecane ($C_{16}H_{32}$)	364–452	5.5E+1–4.7E+3	Primary
Octadecane ($C_{18}H_{38}$)	312–590	1.0E−1–1.0E+5	Primary
Eicosane ($C_{20}H_{42}$)	344–380	4.1E−1–9.1E+0	Primary
Water (H_2O)	273–647	6.1E+1–1.0E+5	Primary

of the vapor pressure against the reciprocal absolute temperature. The second column indicates the temperature range of the measurements and the third column is the mean temperature. The values for the sublimation enthalpy at absolute zero (fifth column) are taken from the JANAF Thermochemical Tables [3]. These values were calculated from the published vapor pressure data from 273 to 387 K using the thermodynamic functions of the condensed and gaseous phases described in the tables. The value cited by the JANAF Tables, $\Delta_{sub}H_m$ (298.15 K) = (62 440 ± 726) J mol^{-1}, is the recommended value. The uncertainty associated with this value, (±726 J mol^{-1}), is derived from the mean uncertainty associated in the slope of line obtained from the Clausius-Clapeyron treatment of the data listed in column 1 of Table 40. Iodine is considered as a secondary reference material primarily because of its reactivity and corrosive nature.

References

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3.3. *Liquid-gas phase changes*

Vaporization enthalpies have been the subject of two critical reviews and the selection of appropriate reference materials has taken advantage of this recent work [1,2]. Substances previously sug-

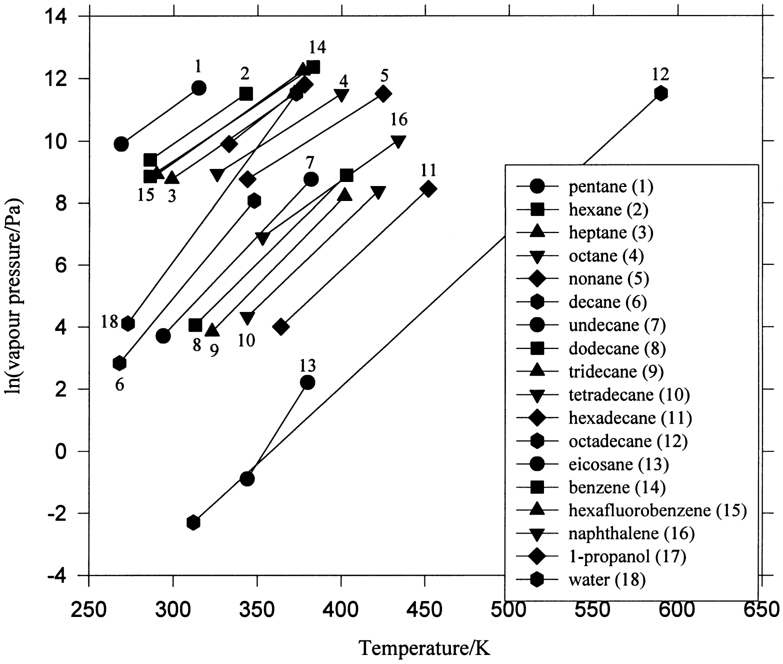

Fig. 4. The temperature-pressure domains covered by the reference materials for vaporization enthalpies.

gested as possible reference materials have been considered as have materials whose vaporization enthalpies have been the subject of numerous studies. Some vaporization enthalpies are reported as a function of temperature. Compounds were selected to cover the usual temperature–vapor pressure regimes normally encountered with these measurements. These domains are summarized in Table 41 and Fig. 4.

The vaporization enthalpy data evaluated in this section have been reported over the time period 1939 to present during which time several temperature scales have been employed. No attempt was made to correct the temperature-pressure data to the present temperature scale, ITS-90, although the vapor pressure data used for the n-alkanes have been corrected [2]. Adjustments to 298.15 K from the temperatures of measurement have been included. In most instances, temperature adjustments have been applied by the authors. Otherwise, temperature adjustments from the mean temperature of measurement, $\bar{T}$ to 298.15 K have been applied using Eq. (3.3.1) [3]. This equation has been tested and found to provide good results [4–5].

$$\begin{aligned}&\Delta_{\rm vap}H_{\rm m}(298.15\,{\rm K})/{\rm J\,mol^{-1}}\\&\quad=\Delta_{\rm vap}H_{\rm m}(\bar{T}/{\rm K})+[10.58+0.26(C_{p,{\rm m}}(1))_{\rm estd}/\\&\quad{\rm J\,mol^{-1}K^{-1}}(298.15\,{\rm K})][\bar{T}/{\rm K}-298.15]\qquad(3.3.1)\end{aligned}$$

The term $(C_{p,\rm m}(\rm l))_{\rm estd}$ ($\rm J\,mol^{-1}\,K^{-1}$) (298.15 K) refers to the heat capacity of the liquid phase at 298.15 K; this was estimated by group additivity [6]. An uncertainty of 15 $\rm J\,mol^{-1}$ was associated with the bracketed term in Eq. (3.3.1) [3].

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3.3.1. $\Delta_{vap}H$, 1-propanol

Physical property	enthalpy of vaporization
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of vaporization, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of vaporization, $\Delta_{\mathrm{vap}}h$)
Recommended reference material	1-propanol (C_3H_8O): 60.0959 $\mathrm{g\,mol^{-1}}$; [71-23-8]
Classification	primary RM
Range of variables	temperatures from 298 to 370 K along the saturated vapor curve
Physical state within the range	liquid → real saturated vapor
Apparatus used	calorimeter
Recommended value	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) $= (47\,450 \pm 100)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{vap}}h$ (298.15 K) $= 789.6\ \mathrm{J\,g^{-1}}$
Contributors to the previous version	R. Sabbah, D.D. Sood, V. Venugopal
Contributor to this version	J. Chickos

3.3.1.1. Intended usage 1-Propanol has been recommended and used as a material for testing the performance of calorimeters used in the measurement of vaporization enthalpies [1,2].

3.3.1.2. Sources of supply and/or methods of preparation Anhydrous high purity commercial samples are available from a variety of suppliers (Aldrich: 99.7%; Fluka: 99.8%). Exposure of samples used for calorimetric measurements to moisture in air should be limited. Storage over molecular sieves is recommended.

3.3.1.3. Pertinent physicochemical data Majer and Svoboda [3] have critically reviewed the vaporization enthalpy of 1-propanol. Vaporization enthalpies are available from 298 to 499 K. Errors in the values provided in Table 42 are believed less than 0.4%. Values at 298.15 and 370.3 K (boiling point, 0.1 MPa) are those recommended by Majer and Svoboda.

Table 42
Vaporization enthalpies of 1-propanol as a function of temperature

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T/K) $\mathrm{J\,mol^{-1}}$)	T (K)	Reference
47 450	298.15	[3]
46 840	308.2	[4]
46 370	313.2	[5]
45 020	333.3	[4]
44 870	333.3	[5]
44 500	338.2	[1]
43 880	343.9	[6]
43 630	348.2	[1]
43 150	353.7	[7]
41 440	370.3	[3]

References

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3.3.2. $\Delta_{vap}H$, hexafluorobenzene

Physical property	enthalpy of vaporization
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of vaporization, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of vaporization, $\Delta_{\mathrm{vap}}h$)
Recommended reference material	hexafluorobenzene (C_6F_6): 186.0564 $\mathrm{g\,mol^{-1}}$; [392-56-3]
Classification	primary RM
Range of variables	temperatures from 290 to 377 K along the saturated vapor curve
Physical state within the range	liquid → real saturated vapor
Apparatus used	includes ebulliometric apparatus, calorimeter
Recommended value	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) $= (35\,710 \pm 70)\ \mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{vap}}h$ (298.15 K) $= 191.9\ \mathrm{J\,g^{-1}}$
Contributors to the previous version	R. Sabbah
Contributor to this version	J. Chickos

3.3.2.1. Intended usage Hexafluorobenzene has been recommended as a test material for the measurement of vaporization enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of liquids. The pressure-volume-temperature relationships for hexafluorobenzene have been published as part of a set of IUPAC recommendations of reference materials [1]. Hexafluorobenzene can be used as a vaporization enthalpy reference to measure vapor pressures in the range 0.0075–0.21 MPa over the temperature range $290 < T/\mathrm{K} < 377$. Hexafluorobenzene has been suggested as a replacement for benzene because of its similar volatility, *non-toxicity* and stability. The anesthetic grade material has been found adequate for accurate measurements of thermodynamic properties [2].

3.3.2.2. Sources of supply and/or methods of preparation High purity commercial samples are available from a variety of suppliers (Aldrich: 99.9%; Fluka: 99.5+%). Exposure of samples used for calorimetric measurements to air and moisture should be limited.

3.3.2.3. Pertinent physicochemical data Majer and Svoboda [3] have critically reviewed the vaporization enthalpy of hexafluorobenzene. Vaporization enthalpies are available from 298 to 376 K. Errors in the recommended values are believed less than 0.1%. Table 43 provides a summary of some of the available data. Values at 298.15 and 353.3 K (boiling point, 0.1 MPa) are those recommended by Majer and Svoboda.

Table 43
Vaporization enthalpies of hexafluorobenzene as a function of temperature

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T/K) ($\mathrm{J\,mol^{-1}}$)	T (K)	Reference
35 710	298.15	[3]
35 540	300.6	[4]
34 450	315.9	[4]
34 440	316.0	[5]
33 340	333.4	[4]
33 170	333.4	[5]
31 660	353.3	[3]
31 680	353.4	[5]
31 670	353.4	[4]
29 830	376.5	[4]

References

[1] D. Ambrose, Pure Appl. Chem. 49 (1977) 1437.

[2] D. Ambrose, J. Chem. Thermodyn. 19 (1981) 1161.

[3] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series, No. 32, Blackwell, Oxford, 1985.

[4] I.A. Hossenlopp, D.W. Scott, J. Chem. Thermodyn. 13 (1981) 405.

[5] J.F. Counsell, J.H.S. Green, J.L. Hales, J.F. Martin, Trans. Faraday Soc. 61 (1965) 212.

3.3.3. $\Delta_{vap}H$, benzene

Physical property	enthalpy of vaporization
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of vaporization, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of vaporization, $\Delta_{\mathrm{vap}}h$)
Recommended reference material	benzene (C_6H_6): 78.11 $\mathrm{g\,mol^{-1}}$; [71-43-2]
Classification	primary RM
Range of variables	temperatures from 286 to 383 K along the saturated vapor curve
Physical state within the range	liquid → real saturated vapor
Apparatus used	includes ebulliometric apparatus, calorimeter
Recommended value	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) $= (33\,830 \pm 68)$ $\mathrm{J\,mol^{-1}}$; $\Delta_{\mathrm{vap}}h$ (298.15 K) $= 433.1\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	J.D. Cox, D.R. Douslin, J.F. Martin, K.N. Roy, R. Sabbah, D.D. Sood
Contributor to this version	J. Chickos

3.3.3.1. Intended usage Benzene has been recommended as a test material for the measurement of vaporization enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of liquids [1–3]. Benzene is a *cancer suspect agent* and proper precautions should be employed when using it. Benzene can be used as a vaporization enthalpy reference to measure vapor pressures in the range 0.007–0.24 MPa over the temperature range $286 < T/\mathrm{K} < 383$ [3].

Table 44
Vaporization enthalpies of benzene as a function of temperature

$\Delta_{\text{vap}}H_{\text{m}}$ (T/K) (J mol^{-1})	T (K)	Reference
34 090	293.2	[4]
33 830	298.15	[2]
33 330	307.2	[5]
32 800	318.2	[6]
31 620	338.2	[6]
30 830	351.8	[7]
30 720	353.3	[2]
30 500	360.5	[7]
30 210	365.7	[7]
26 260	377.6	[5]

3.3.3.2. Sources of supply and/or methods of preparation High purity commercial samples are available from a variety of suppliers (Aldrich, Fluka: 99.9+%).

3.3.3.3. Pertinent physicochemical data Majer and Svoboda [2] have critically reviewed the vaporization enthalpy of benzene and recommend it as a useful reference compound for testing vaporization calorimeters. The recommended values were determined from a large database originating from a diverse group of laboratories using a variety of different apparatus. Vaporization enthalpies are available from 293 to 478 K. Errors in the recommended values are believed less than 0.1% for data measured below the boiling point. Table 44 provides a summary of some of the available data. Values at 298 and 353.3 K (boiling point, 0.1 MPa) are those recommended by Majer and Svoboda.

References

[1] J.P. McCullough, D.W. Scott (Eds.), Experimental Thermodynamics. Vol. I: Calorimetry of Non-Reacting Systems, Chaps. 10, 11, Butterworths, London, 1968.
[2] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series, No. 32, Blackwell, Oxford, 1985.
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[4] N.L. Yarym-Agaev, N.N. Fedos'ev, K.G. Skorikov, Zh. Fiz. Khim. 11 (1949) 1257.
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3.3.4. $\Delta_{vap}H$, *n-alkanes*

Physical property	enthalpy of vaporization
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of vaporization, $\Delta_{\text{vap}}H$); J kg^{-1} or J g^{-1} (specific enthalpy of vaporization, $\Delta_{\text{vap}}h$)
Recommended reference materials	pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, hexadecane, octadecane, eicosane
Classification	primary RM
Physical state within the range	liquid → saturated vapor
Apparatus used	calorimeter
Recommended values	recommended $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) for the *n*-alkanes are given in Table 45
Contributor to this version	J. Chickos

3.3.4.1. Intended usage The *n*-alkanes, pentane to tetradecane, hexadecane, octadecane and eicosane are recommended as test materials for the measurement of vaporization enthalpies in checking the performance of calorimeters and apparatus used in the measurement of vapor pressures of liquids [1]. Recommended vapor pressure and temperature regimes associated with each compound are summarized in Table 41.

3.3.4.2. Sources of supply and/or methods of preparation Certified, high purity materials of some of the *n*-alkanes are available from ORM. Commercial samples of suitable purity are available from a variety of suppliers that include Aldrich, Fluka, and Acros.

3.3.4.3. Pertinent physicochemical data Various thermodynamic properties of the *n*-alkanes have been recently reviewed by Ruzika and Majer [1]. Their recommendations are summarized in Table 45. Recommended vaporization enthalpies at pressures from 0.1 to 0.1 MPa are also available. The reader is referred to Refs. [1,2] for further details. Vaporization enthalpies for pentane from 260 to 428 K, hexane from 298 to 444 K, heptane from 298 to 372 K, octane from 298 to 444 K, nonane from 298 to 368 K, decane from 298 to 444 K, undecane and dodecane at 298 K, tridecane from 298 to 348 K, tetradecane

Table 45
Recommended vaporization enthalpies at 298.15 K[a]

Alkane	Molar mass ($g\,mol^{-1}$)	Registry number	P_{sat} (298.15 K) (Pa)	$\Delta_{vap}H_m$ (298.15 K) ($J\,mol^{-1}$)	$\Delta_{vap}h$ ($J\,g^{-1}$)
Pentane	72.1503	[109-66-0]	6.84E+4	$26\,420 \pm 106$	366.2
Hexane	86.1772	[110-54-3]	2.02E+4	$31\,520 \pm 126$	365.8
Heptane	100.2040	[142-82-5]	6.10E+3	$36\,570 \pm 146$	365.0
Octane	114.2309	[111-65-9]	1.87E+3	$41\,560 \pm 166$	363.8
Nonane	128.2578	[111-84-2]	5.81E+2	$46\,550 \pm 186$	362.9
Decane	142.2847	[124-18-5]	1.82E+2	$51\,420 \pm 206$	361.4
Undecane	156.3116	[1120-21-4]	5.69E+1	$56\,580 \pm 566$	362.0
Dodecane	170.3384	[112-40-3]	1.80E+1	$61\,520 \pm 615$	361.2
Tridecane	184.3653	[629-50-5]	5.68E+0	$66\,680 \pm 667$	361.7
Tetradecane	198.3922	[629-59-4]	1.80E+0	$71\,730 \pm 717$	361.6
Hexadecane	226.4460	[544-76-3]	1.91E−1	$81\,350 \pm 813$	359.2
Octadecane	254.4997	[593-45-3]	2.01E−2[b]	$91\,440 \pm 1830$[b]	359.3
Eicosane	282.5535	[112-95-8]	2.09E−3[b]	$101\,810 \pm 2040$[b]	360.3

[a] From Ref. [1].

[b] Hypothetical values below the triple point.

from 298 to 358 K, and hexadecane at 298 K are also summarized in Ref. [2].

References

[1] R. Ruzika, V. Majer, J. Phys. Chem. Ref. Data 23 (1994) 1.

[2] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series, No. 32, Blackwell, Oxford, 1985.

3.3.5. $\Delta_{vap}H_m$, naphthalene

Physical property	enthalpy of vaporization
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of vaporization, $\Delta_{vap}H_m$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of vaporization, $\Delta_{vap}h$)
Recommended reference material	naphthalene ($C_{10}H_8$): 128.1735 $g\,mol^{-1}$; [91-20-3]
Classification	secondary RM
Range of variables (liquid)	temperatures from 353 to 434 K along the saturated vapor curve
Physical state within the range	liquid → real saturated vapor
Apparatus used	includes ebulliometer, diaphragm manometer, quartz helix gauge
Recommended value	$\Delta_{vap}H_m$ (298.15 K) $= (55\,650 \pm 2840)\,J\,mol^{-1}$; $\Delta_{vap}h$ (298.15 K) $= 434.2\,J\,g^{-1}$
Contributor to this version	J. Chickos

3.3.5.1. Intended usage Naphthalene is recommended as a test material for the measurement of vaporization enthalpy to check the performance of calorimeters and apparatus used in the measurement of vapor pressures of liquids. The use of naphthalene as a vaporization enthalpy reference should be restricted to measurements on compounds that exhibit vapor pressures in the range 10^{-3} to 0.023 MPa over the temperature range $353 < T/K < 434$.

3.3.5.2. Sources of supply and/or methods of preparation Certified high purity material is readily available (ORM: LGC24024). Commercial samples are available from a variety of suppliers (Aldrich, Fluka: 99+%). Samples of higher purity can be obtained by zone refining.

3.3.5.3. Pertinent physicochemical data (vaporization) The vaporization enthalpy of naphthalene has been reported by various laboratories [1–5]. The data is summarized in Table 46. Adjusted to 298.15 K, the vaporization enthalpies are all in good agreement resulting in a mean value of $(55\,730 \pm 2150)\,J\,mol^{-1}$. Naphthalene is presently recommended as a secondary reference material.

References

[1] R.D. Chirico, S.E. Knipmeyer, A. Nguyen, W.V. Steele, J. Chem. Thermodyn. 25 (1993) 1461.

Table 46
Vaporization enthalpy of naphthalene

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (*T*/K) (J mol^{-1})	*T* (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Method	Purity (mol%)	Reference
48 670 ± 300	400	54 840 ± 400	Ebulliometer	99.93	[1]
50 246 ± 150	353–388	55 027 ± 650^{a}	Diaphragm manometer	99.97	[2]
53 240 ± 2700	353–363	57 080 ± 3300^{a,b}	Pressure gauge	99+	[3]
50 520 ± 280	354–383	54 990 ± 2100^{a,b}	Quartz helix gauge	99.99	[4]
49 134 ± 630	400–434	56 720 ± 3600^{a,b}	bp-p^{c}	99.96	[5]

[a] Vaporization enthalpy adjusted to 298.15 K using Eq. (3.3.1) and an estimated heat capacity for liquid naphthalene of 205 J mol^{-1} K^{-1}.
[b] Calculated from the vapor pressures reported over the temperature range indicated by a Clausius-Clapeyron treatment of the data.
[c] Boiling point measured as a function of pressure.

[2] C.G. De Kruif, T. Kuipers, J.C. Van Miltenburg, R.C.F. Schaake, G. Stevens, J. Chem. Thermodyn. 13 (1981) 1081.
[3] K. Sasse, J. Jose, J.-C. Merlin, Fluid Phase Equilibria 42 (1988) 287.
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3.3.6. $\Delta_{vap}H$, *water*

Physical property	enthalpy of vaporization
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of vaporization, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$); J kg^{-1} or J g^{-1} (specific enthalpy of vaporization, $\Delta_{\mathrm{vap}}h$)
Recommended reference material	water (H_2O): 18.0153 g mol^{-1}; [7732-18-5]
Classification	primary RM
Range of variables	273–647 K along the liquid vapor saturation curve
Physical state within the range	liquid → real saturated vapor
Apparatus used	includes ebulliometric apparatus, calorimeter
Recommended value	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) = (43 990 ± 67) J mol^{-1}; $\Delta_{\mathrm{vap}}h$ (298.15 K) = 2441 J g^{-1}
Contributors to the previous versions	J.D. Cox, J.F. Martin, R. Sabbah, I. Wadsö
Contributor to this version	J. Chickos

3.3.6.1. Intended usage Despite poor boiling characteristics, its corrosive and conducting properties, water is recommended as a test material for testing the performance of calorimeters used in the measurement of vaporization enthalpies [1].

3.3.6.2. Sources of supply and/or methods of preparation Certified high purity commercial samples are available from a variety of suppliers (Aldrich, Fluka). It is also possible to prepare a sample of high purity by distillation of deionized water.

3.3.6.3. Pertinent physicochemical data Osborne et al. have studied the thermal properties of water in studies extending over a period of years [1]. The data in Table 47 has been extracted from a paper summarizing their results [2]. The reader is encouraged to consult the original work for data at other temperatures. Vaporization enthalpies are available from 273 to 647 K. The temperature scale which is not mentioned is believed to be ITS-27.

Table 47
Vaporization enthalpy of water as a function of temperature

T (K)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (*T*/K) (J mol^{-1})
273.15	45 054
298.15	43 990
313.15	43 350
333.15	42 482
353.15	41 585
373.15	40 657
393.15	39 684
413.15	38 643
433.15	37 518
453.15	36 304
473.15	34 962
493.15	33 468
513.15	31 809
533.15	29 930
553.15	27 795
573.15	25 300
593.15	22 297
613.15	18 502
633.15	12 966
647.15	2066

Table 48
Vaporization enthalpy of water at 298.15 K

$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (J mol^{-1})	Reference
43 990	[2]
43 980	[3]
43 980	[4]
44 020	[6]
44 040	[7]
44 060	[8]

The results reported in a more recent work [3,4] give $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ for water in the temperature range 298–398 K. The independent measurements of Osborne and Ginnings [5], Wadsö [6], Konícek [7] and Morawetz [8] at 298.15 K and of McCullough et al. [9] at 338 and 373 K are all in good agreement with the results in Table 47. To test the performance of an isothermal calorimeter designed to measure vaporization enthalpies at elevated temperatures and pressures, Parisod and Plattner [10] have measured the vaporization enthalpy of water in the range 573–633 K. Their results differ from those in Table 47 by less than 1%. A summary of the vaporization enthalpies of water reported at 298.15 K is given in Table 48. A mean value of $(44\,012 \pm 67)$ J mol^{-1} is obtained. The value previously recommended for water, 43 990 J mol^{-1}, falls within one standard deviation of the mean and is retained as the recommended value. An uncertainty of 67 J mol^{-1} is associated with the recommended value.

References

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[10] C.J. Parisod, E. Plattner, Rev. Sci. Instrum. 53 (1982) 54.

4. Reference materials for measurement of enthalpies of reaction and related processes

Reference materials for processes described as reaction, dissolution and dilution, except for reactions normally carried out in combustion bombs are included in this section. The entries have been classified according to the physical state of the substances.

Despite the role played by reference materials in the accuracy of calorimetric results and the work necessary to be carried out in the field of solid-solution calorimetry no relevant progress has been registered in recent years.

Potassium chloride is still currently used as a reference material for the enthalpy of solid-solution calorimetric determinations. It is available as a certified material and a detailed study of eventual sources of error was undertaken [1–3]. Data for the enthalpy of solution of potassium chloride in water for the reaction with a certain number of water molecules and at infinite dilution state are available [3–5]. Many authors use infinite dilution as standard state in the calibration of the calorimetric procedure and validation of the results. It is really the conventional standard state in solution chemistry. Thus it is useful to propose procedures to obtain enthalpy of solution at infinite dilution and to quote a reliable value. Data for the enthalpy of solution in a temperature range between 296 and 303 K were published [3].

Another classic reference material used for the enthalpy of solution measurements is tris(hydroxymethyl) aminomethane. The value for the enthalpy of reaction of this compound in 0.1 M hydrochloric acid has been quoted [2].

Sodium chloride [5] and 4-aminopyridine have been used for calorimetric calibration. Values for the enthalpy of solution of sodium chloride in water [6] and for the enthalpy of reaction of 4-aminopyridine with perchloric acid [7] have been determined. However, more detailed work undertaken with highly pure substances is necessary to be done before these substances can be recommended as reference materials.

The liquid-liquid systems include processes usually studied in enthalpy of mixing calorimeters with no or small vapor spaces (cyclohexane + hexane, 1,4-dioxane + tetrachloromethane, ethanol + water) or in reaction calorimeters (sulfuric acid solution + sodium hydroxide solution), as well as dilution reactions (sucrose solution, urea solution) which are of wide applicability but often particularly useful for checking the performance of liquid flow calorimeters including microcalorimeters.

The determination of the enthalpy of mixing of cyclohexane + hexane remains to be the most widely employed endothermic mixture for checking mixing calorimeters and it is well established. For exothermic systems, the mixture 1,4-dioxane + tetrachloromethane is used. The exothermic system ethanol + water has been added and proposed for checking the performance of calorimeters used in the measurement of the enthalpy of mixing of liquids at $T = 298.15$ K and $p = 0.1$ MPa. At temperatures above 298.15 K, several authors have obtained data at temperatures up to 548 K and pressures ranging from 0.40 to 20.00 MPa [8–11]. The ethanol + water system seems to be a strong candidate as a reference system for excess enthalpy at high temperatures and pressures. At the moment, the available data present experimental uncertainties between 1% and 2% which are still higher than those reported by authors working at 0.1 MPa. More experimental information for this system is required.

For dilution reaction, when viscous solutions are required, the dilution of sucrose solution is recommended and data are available for temperatures between 293.15 and 310.15 K [12]. The dilution of urea has advantages compared with the dilution of sucrose solution when less viscous solutions are required. Data for the dilution of solutions containing phosphate buffer (pH = 7) are also available which are useful to those studying biochemical reactions [13].

No new results have been reported in the literature for the well-established enthalpies of reaction of sulfuric acid solution + sodium hydroxide solution, hydrogen + oxygen, hydrogen + chlorine, and methane + oxygen.

Having in mind that chemical calibration is a prerequisite of quality assurance of accurate calorimetric results, much attention must be paid to this matter. Among others the following topics should be included in a research program:

1. Recommended procedure to be followed for obtaining the enthalpy of solution of potassium chloride in water at infinite dilution. Comparative study of uncertainties for the values quoted for this standard state with those obtained for the reaction with a certain number of water molecules should be performed.
2. Interlaboratory tests with potassium chloride and tris(hydroxymethyl)aminomethane in calorimetric solution processes in order to take information about the independence of instrument type and to quantify systematic and statistical uncertainties in calorimetric practice.
3. Study of substances which may be used as reference materials.
4. Validity of using reactions of reference substances with water for the calibration of calorimetric reactions in non-aqueous media.

Throughout this section, molar masses of the elements are adopted from the 1993 report of the IUPAC Commission on atomic Weights and Isotopic Abundances [14] and the uncertainty associated with numerical results represents twice the overall standard deviation of the mean.

References

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4.1. Solid–solid processes

4.1.1. $\Delta_r h^0$, Zirconium+barium chromate

Physical property	enthalpy of reaction
Units	$J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of reaction, $\Delta_r h^0$)
Recommended reference material	zirconium + barium chromate. (Zr): 91.2240 $g\,mol^{-1}$; [7440-67-7], ($BaCrO_4$): 253.3207 $g\,mol^{-1}$; [10294-40-3]
Classification	secondary RM
Range of variables	298.15 K is the temperature normally employed
Physical state within the range	solid + solid
Apparatus used	isoperibol calorimeter
Recommended value	$\Delta_r h^0 = (-1460 \pm 4.8)\,J\,g^{-1}$; $(-1632.3 \pm 7.3)\,J\,g^{-1}$; $(-1762 \pm 3.0)\,J\,g^{-1}$. These values refer to SRM 1651, 1652 and 1653, respectively (see Ref. [1])
Contributors to the previous versions	G.T. Armstrong, J.D. Cox
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4.1.1.1. Intended usage Heat-source (thermite-type, gasless) powders find use in defence and other applications. The “heating values” of production batches of such powders are determined by calorimetry (see Ref. [1] for other references) and it is desirable that the calorimeters used should be calibrated under conditions similar to those of the experiments on production materials. Agglomerate mixtures of zirconium and barium chromate are used to calibrate the calorimeters [1]. Such mixtures can be readily ignited, react completely in less than one second and generate very little gas.

4.1.1.2. Sources of supply and/or methods of preparation Standard values for the enthalpy of reaction were determined by using zirconium plus barium chromate mixtures supplied hitherto by the NBS (now NIST). Before use, heat-source powders of the types referred to above should be dried for 2 h at 344 K and 1.3 kPa pressure in a flat material container in an oven, which must contain no open heating coils, then cooled in a desiccator. General safety precautions in the handling of these powders are given in pages 4 and 5 of Ref. [1]. The mixtures used as reference material, SRM 1651, 1652 or 1653 are no longer supplied by NIST. They have to be prepared by the user following the procedure recommended in Ref. [1]. Zirconium as powder is available from Aldrich without any purity specification. Barium chromate is also purchased from Aldrich with the indication of 98+% purity.

4.1.1.3. Pertinent physicochemical data The specific enthalpy changes for solid-state reactions, when no air, oxygen or nitrogen are in contact with the samples of the batches of zirconium + barium chromate mixtures, were determined [1] at the NBS by means of an isoperibol calorimeter [2]. The samples were weighted in air. The values of $\Delta_r h^0$ are for SRM 1651, SRM 1652 and SRM 1653, respectively (-1460 ± 4.8); (-1632.3 ± 7.3) and $(-1762 \pm 3.0)\,J\,g^{-1}$.

References

[1] J.I. Minor Jr., G.T. Armstrong, Calorimetric Determination of Heating Values of Zirconium-Barium Chromate Heat-Source Powders as Reference Materials, NBS Report 9928, National Bureau of Standards, Washington, 1968.

[2] E.J. Prosen, W.H. Johnson, F.Y. Pergiel, J. Res. Nat. Bur. Stand. 62 (1959) 43.

4.2. Solid–liquid processes

4.2.1. $\Delta_r H^0$, α-silicon dioxide+hydrofluoric acid

Physical property	enthalpy of reaction in solution
Units	$J\,mol^{-1}$); $J\,kg^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of reaction, $\Delta_r H_m^0$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of reaction, $\Delta_r h^o$)
Recommended reference material	α-silicon dioxide (α-quartz; “low” quartz)+hydrofluoric acid (0.244 mass-fraction). (SiO_2): 60.0843 $g\,mol^{-1}$; [60676-86-0], (HF): 20.0063 $g\,mol^{-1}$ [7664-39-3].
Classification	secondary RM
Range of variables	298.15 K is the reference temperature usually employed

Physical state within the range	solid → liquid solution
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_r H_m^0 = (-141.93 \pm 0.07)$ kJmol^{-1}; $\Delta_r h^0 (-2362.2 \pm 1.1)$ J g^{-1}at 353.15 K
Contributors to the previous versions	J.D. Cox, A.J. Head, P.A.G. O'Hare, E.J. Prosen
Contributor to this version	M.L.P. Leitão

4.2.1.1. Intended usage Calorimeters [1,2] for the measurement of the enthalpies of solution of solids in hydrofluoric acid should be calibrated electrically. However, it is desirable to test the calorimetric procedure by dissolution of a solid of known enthalpy of reaction in solution. Many mineral substances dissolve rather slowly in hydrofluoric acid solution and to increase the rate of dissolution experiments are often conducted at temperatures higher than 298 K. For an experimental programme of this type, α-quartz is recommended as a test material.

4.2.1.2. Sources of supply and/or methods of preparation A sample of quartz with certificate of guarantee is available from Merck.

4.2.1.3. Pertinent physicochemical data Kilday and Prosen [3] have determined the enthalpy of reaction of α-quartz (as a standard reference material, SRM 1654 [4] proposed in the past by the NIST) with a solution containing hydrofluoric acid (mass fraction 0.244). The enthalpy of reaction was found to be (-141.93 ± 0.07) kJ mol^{-1} or (-2362.2 ± 1.1) J g^{-1} at 353.15 K. These values refer to a concentration of 5 g dm^{-3} of α-quartz in hydrofluoric acid and to a sample that passed a No. 200 sieve but was retained by a No. 400 sieve (particle size 37–74 μm). The equation representing the reaction and the process is:

$$\begin{aligned} &SiO_2(cr, \alpha\text{-quartz}) + 155[HF(3.44H_2O)](l) \\ &\quad = [H_2SiF_6 + 149HF](535.2H_2O)(l) \qquad (4.2.1.1) \end{aligned}$$

There is evidence that the enthalpy of reaction of α-quartz with hydrofluoric acid is dependent upon particle size, being more exothermic as the size decreases. Care should be taken at temperature and concentration significantly different from those referred [5,6].

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 9, 11, 14, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

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[5] B.S. Heminguay, R.A. Robie, J. Res. U.S. Geological Survey 5 (1977) 413.

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4.2.2. $\Delta_{sol}H^0$, potassium chloride

Physical property	enthalpy of solution
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of solution, $\Delta_{sol}H_m^0$); J kg^{-1} or J g^{-1} (specific enthalpy of solution, $\Delta_{sol}h^0$)
Recommended reference material	potassium chloride (KCl): 74.5 510 g mol^{-1}; [7447-40-7]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid → liquid solution
Apparatus used	adiabatic and isoperibol calorimeters
Recommended value	$\Delta_{sol}H_m^0$ (500 H_2O) = (17.584 ± 0.017) kJ mol^{-1}
Contributors to the previous versions	J.D. Cox, E.S. Domalski, A.J. Head, O. Riedel
Contributor to this version	M.L.P. Leitão

4.2.2.1. Intended usage Calorimeters [1,2] for the measurement of the enthalpies of solution of solids in liquids should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of solution of a solid in a liquid for which the value has been established. For an experimental programme involving endothermic dissolution, especially of a freelly solute substance dissolving in water, potassium chloride is recommended.

4.2.2.2. Sources of supply and/or methods of preparation KCl(cr) for solution calorimetry (SRM 1655) is available from NIST.

4.2.2.3. Pertinent physicochemical data Many determinations of the enthalpy of solution of potassium chloride in water have been made and the suitability of potassium chloride as a reference material for solution calorimetry has been discussed for a long time. The measurements were reviewed in 1977 by Montgomery et al. [3] who concluded that the most consistent results had been reported for potassium chloride dried at over 600 K.

The most thorough study has been published in 1980 by Kilday [4,5] who determined the enthalpy of solution in water of potassium chloride, NBS SRM 1655, in both isoperibol and adiabatic calorimeters, using this one to obtain data to provide the certified value of $(17.584 \pm 0.017)\,\mathrm{kJ\,mol^{-1}}$ for the standard molar enthalpy of the process

$$\mathrm{KCl\,(cr)} + 500\mathrm{H_2O(l)} = \mathrm{KCl(500H_2O)(l)} \quad (4.2.2.1)$$

The temperature coefficient of the reaction in the temperature range 296–303 K is given by $(\mathrm{d}\Delta_{\mathrm{sol}}\mathrm{H}^0/\mathrm{d}T) = (-154.8 \pm 6.4)\,\mathrm{J\,mol^{-1}K^{-1}}$

Results for the enthalpy of solution of SRM 1655 in water in the concentration range 0.005–0.14 $\mathrm{mol\,kg^{-1}}$ are also presented [5].

The value of $(17.47 \pm 0.07)\,\mathrm{kJ\,mol^{-1}}$ for the enthalpy of solution of KCl in 2000 H_2O was obtained in an interlaboratory experiment [6].

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 9, 11, 14, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

[3] R.L. Montgomery, R.A. Melaugh, C.-C. Lau, G.H. Meier, H.H. Chan, F.D. Rossini, J. Chem. Thermodyn. 9 (1977) 915.

[4] M.V. Kilday, J. Res. Nat. Bur. Stand. 85 (1980) 449.

[5] M.V. Kilday, J. Res. Nat. Bur. Stand. 85 (1980) 467.

[6] C. Günther, R. Pfestorf, M. Rother, J. Seidel, R. Zimmermann, G. Wolf, V. Schröder, J. Therm. Anal. 633 (1988) 359.

4.2.3. $\Delta_r H^0$, *tris(hydroxylmethyl)aminomethane*

Physical property	enthalpy of reaction in solution
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of reaction, $\Delta_r\mathrm{H}^0_\mathrm{m}$); $\mathrm{J\,kg^{-1}}$; or $\mathrm{J\,g^{-1}}$ (specific enthalpy of reaction, $\Delta_r h^0$)
Recommended reference material	tris(hydroxylmethyl)aminomethane. Common abbreviations: TRIS or THAM ($C_4H_{11}O_3N$): 121.1363 $\mathrm{g\,mol^{-1}}$; [77-86-1]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid → liquid solution
Apparatus used	isoperibol calorimeter
Recommended value	$\Delta_r\mathrm{H}^0_\mathrm{m} = (-29.770 \pm 0.032)\,\mathrm{kJ\,mol^{-1}}$; $\Delta_r h^0 = (-245.76 \pm 0.26)\,\mathrm{J\,g^{-1}}$ in HCl(aq) and $\Delta_r\mathrm{H}^0_\mathrm{m} = (17.177 \pm 0.023)\,\mathrm{kJ\,mol^{-1}}$; $\Delta_r h^0 = (141.80 \pm 0.19)\,\mathrm{J\,g^{-1}}$ in NaOH(aq) (see Ref. [3])
Contributors to the previous versions	G.T. Armstrong, J.D. Cox, A.J. Head, O. Riedel, C.E. Vanderzee
Contributor to this version	M.L.P. Leitão

4.2.3.1. Intended usage Calorimeters [1,2] for measuring the enthalpy of dissolution of a solid in a liquid (solution calorimeters) or the enthalpy of reaction of a solid with a relatively large volume of liquid (liquid-phase reaction calorimeters) should be calibrated electrically. It is good practice, however, to test the efficacy of the calorimetric procedure by measurement of the enthalpy of solution of a solid in a liquid, using a reaction for which the enthalpy has been determined by competent laboratories. Attested values exist for the enthalpy of solution at 298.15 K of crystalline TRIS in (a) 0.1 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid, an exothermic reaction, and (b) 0.05 $\mathrm{mol\,dm^{-3}}$ sodium hydroxide solution, an endothermic reaction. TRIS is recommended as a suitable material for testing solution calorimeters and liquid-phase reaction calorimeters which are to be employed for the study of rapid dissolutions or reactions.

4.2.3.2. Sources of supply and/or methods of preparation Tris(hydroxylmethyl)aminomethane, SRM 723 *c* in preparation as an anlytical reagent, can be purchased in the future from NIST.

Some authors reported problems in the purification of TRIS and evidenced energetic effects of mechanical strain. They recommended special attention on handling the compound when it is used as a calibrant of the calorimetric procedure [3,4].

4.2.3.3. Pertinent physicochemical data (a) The enthalpy of solution of TRIS in 0.1 mol dm^{-3} hydrochloric acid at 298.15 K (concentration 5 kg m^{-3}) has been extensively measured. Summaries of the values obtained are given in Refs. [5,6]. In spite of the variability found in the values for the enthalpy of the reaction of tris(hydroxymethyl)aminomethane with 0.1 M hydrochloric acid, this reaction continue to be the most used for checking the accuracy of the values when exothermic reactions are to be studied.

The value for the enthalpy of solution of TRIS at the concentration of 5 kg m^{-3} in 0.1 mol dm^{-3} HCl(aq) is (-245.76 ± 0.26) J g^{-1}. This value was recommended by the NBS (now NIST), for the SRM 724a sample [3]. TRIS is no longer available as a solution calorimetry standard from NIST. In the temperature range 293–303 K, the temperature coefficient of reaction is given by $(\mathrm{d}\Delta_r h^0/\mathrm{d}T) = (1.435 \pm 0.023)$ J g^{-1} K^{-1}.

(b) The enthalpies of TRIS in 0.05 mol dm^{-3} sodium hydroxide at 298.15 K (concentration 5 kg m^{-3}) was determined by Hill, Ojelund and Wadsö [7] as (141.90 ± 0.08) J g^{-1} and Prosen and Kilday [3] as (141.80 ± 0.19) J g^{-1}, whose value was used for the certification of NBS SRM 724a.

In the temperature range 293–303 K, the temperature coefficient of the enthalpy of reaction is given by $(\mathrm{d}\Delta_r h^0/\mathrm{d}T) = (1.025 \pm 0.025)$ J g^{-1} K^{-1}.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 9, 11, 14. Vol. II, Wiley, New York, 1962.
[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.
[3] E.J. Prosen, M.V. Kilday, J. Res. Nat. Bur. Stand. A 77 (1973) 581.
[4] C.E. Vanderzee, D.H. Vaugh, N.C. Haas, J. Chem. Thermodyn. 13 (1981) 1.
[5] R.L. Montgomery, R.A. Melaugh, C.-C. Lau, G.H. Meier, H.H. Chan, F.D. Rossini, J. Chem. Thermodyn. 9 (1977) 915.
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[7] J.O. Hill, G. Ojelund, I. Wadsö, J. Chem. Thermodyn. 1 (1969) 111.

4.2.4. $\Delta_r H^o$, 4-aminopyridine

Physical property	enthalpy of reaction in solution
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction, $\Delta_r H^0_m$); J kg^{-1}or J g^{-1} (specific enthalpy of reaction, $\Delta_r h^0$)
Recommended reference material	4-aminopyridine ($C_5H_6N_2$): 94.1161 g mol^{-1}; [504-24-5]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid → liquid solution
Apparatus used	adiabatic calorimeter
Recommended value	$\Delta_r H^0_m$(298.15 K) (kJ mol^{-1}) $= (-29.407 \pm 0.005)$ $-6.41 \pm 0.17)$ (c (mol dm^{-3})); $\Delta_r h^0$ (298.15 K) (J g^{-1}) $= (-312.46 \pm 0.05) - (68.1 \pm 1.8)$ (c (mol dm^{-3}))
Contributor to the previous version	G. Pilcher
Contributor to this version	M.L.P. Leitão

4.2.4.1. Intended usage Calorimeters [1,2] for the measurement of enthalpy of reaction of a solid with a relatively large volume of liquid (liquid-phase reaction calorimeters) or the enthalpy of reaction of a solid with a relatively large volume of liquid (liquid-phase reaction calorimeters) should be calibrated electrically. It is desirable, however, to test the calibration and calorimetric procedure by measurement of the enthalpy of solution of a solid in a liquid for which the enthalpy of reaction has been well established. The enthalpy of solution of crystalline 4-aminopyridine in 10% excess of aqueous perchloric acid at concentrations ≤ 0.05 mol dm^{-3} has been measured in three separate investigations with results in agreement. This reaction is recommended as a suitable exothermic test reaction for solution calorimeters when the experimental programme involves rapid dissolution or reaction in solution.

4.2.4.2. Sources of supply and or methods of preparation A suitable grade of 4-aminopyridine can be obtained by sublimation in vacuo of commercially available samples (e.g. Aldrich: 99%)

4.2.4.3. Pertinent physicochemical data Van Til and Johnson [3] measured the enthalpy of solution of 4-aminopyridine in water and the enthalpy of neutralization of that solution by aqueous acid at 298.15 K, from which the enthalpy of dissolution of the crystallline solid in the acid can be indirectly derived. Burchfield and Hepler [4] and Akello et al. [5] measured directly the enthalpy of solution of 4-aminopyridine(cr) in excess aqueous perchloric acid. Burchfield and Hepler found no dependence of the observed enthalpy on the amount of excess acid; an excess of 10% aqueous perchloric acid over the stoichiometric amount is recommended. The enthalpy of solution is a linear function of concentration of the solution produced and the direct determinations gave:

Burchfield and Hepler [4]:

$$\Delta_\mathrm{r} H^0_\mathrm{m}(298.15\,\mathrm{K})(\mathrm{kJ\,mol^{-1}}) = (-29.409 \pm 0.009) - (6.31 \pm 0.35)c\,(\mathrm{mol\,dm^{-3}}) \qquad (4.2.4.1)$$

Akello et al. [5]:

$$\Delta_\mathrm{r} H^0_\mathrm{m}(298.15\,\mathrm{K})(\mathrm{kJ\,mol^{-1}}) = (-29.392 \pm 0.011) - (6.83 \pm 0.29)c\,(\mathrm{mol\,dm^{-3}}) \qquad (4.2.4.2)$$

The results of Burchfield and Hepler [4] and Akello et al. [5] combined by least-squares analysis give recommended equations:

$$\Delta_\mathrm{r} H^0_\mathrm{m}(298.15\,\mathrm{K})(\mathrm{kJ\,mol^{-1}}) = (-29.407 \pm 0.005) - (6.41 \pm 0.17)c\,(\mathrm{mol\,dm^{-3}}) \qquad (4.2.4.3)$$

$$\Delta_\mathrm{r} h^0(298.15\,\mathrm{K})(\mathrm{J\,g^{-1}}) = (-312.46 \pm 0.05) - (68.1 \pm 1.8)c\,(\mathrm{mol\,dm^{-3}}) \qquad (4.2.4.4)$$

The standard deviation of the fit was 0.025 kJ mol^{-1} and the correlation coefficient 0.969. The recommended equations are based on measurements involving concentrations $\leq 0.05\,\mathrm{mol\,dm^{-3}}$. As this suitable over a range of concentrations, it has the advantage of permitting the testing of a particular calorimeter with a range of sample masses, hence a range of associated temperature rises.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 9, 11, 14, Vol. II, Wiley, New York, 1962.
[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.
[3] A.E. Van Til, D.C. Johnson, Thermochim. Acta 20 (1977) 177.
[4] T.E. Burchfield, L.G. Hepler, J. Chem. Thermodyn. 13 (1981) 513.
[5] M.J. Akello, M.I. Paz-Andrade, G. Pilcher, J. Chem. Thermodyn. 15 (1983) 949.

4.3. Liquid-liquid processes

4.3.1. $\Delta_{dil}H$, sucrose solution+water

Physical property	enthalpy of dilution
Units	J mol^{-1} (molar enthalpy of dilution, $\Delta_\mathrm{dil}H_\mathrm{m}$)
Recommended reference material	sucrose ($C_{12}H_{22}O_{11}$): 342.3001 g mol^{-1}; [57-50-1]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	aqueous solutions
Apparatus used	adiabatic twin calorimeter, flow microcalorimeter
Contributor to the previous versions	R.N. Golberg
Contributor to this version	M.V. Roux

4.3.1.1. Intended usage Calorimeters [1,2] for the measurement of enthalpies of mixing or dilution of aqueous solutions should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of mixing or dilution of solutions for which the value has been well established. The enthalpy of dilution of sucrose provides a means of detecting possible systematic

Table 49
Values of parameters for Eq. (4.3.1.1)

Reference	T (K)	A ($\mathrm{J\,kg\,mol^{-2}}$)	B ($\mathrm{J\,kg^2\,mol^{-3}}$)	Value of x
[3]	293.15	539.3	28.94	≤5.8
[3]	298.15	563.2	29.50	≤2.2
[3]	303.15	586.6	29.62	≤2.2
[4]	310.15	619.6	29.66	≤2.0

errors in calibration and measurements procedures, particularly when solutions of moderate viscosity are required.

4.3.1.2. Sources of supply and/or methods of preparation Suitable sample of sucrose may be obtained from a variety of suppliers (Aldrich, Fluka, BDH (under the denomination of "Aristar")). It is advised that freshly prepared solutions be used for the calorimetric measurements.

4.3.1.3. Pertinent physicochemical data Gucker and Pickard [3] measured the enthalpy of dilution of aqueous solutions of sucrose with an adiabatic twin calorimeter and gave the values of the relative apparent molal enthalpy, Φ_L, at 293.15, 298.15 and 303.15 K. Wadsö in numerous measurements using several types of calorimeters confirmed the results of Gucker et al. at 298.15 K. Using a 4-channel microcalorimetric system for the calorimetric measurements, he gave values for the relative apparent molal enthalpy, Φ_L, at 310.15 K. [4].

The results obtained from these authors are expressed by the following equation, the parameters of which are summarized in Table 49:

$$\Phi_L/\mathrm{J\,mol^{-1}} = Ax - Bx^2 \tag{4.3.1.1}$$

where $x = m$ ($\mathrm{mol\,kg^{-1}}$).

If the constants A and B are replaced by corresponding temperature dependent functions:

$$A(T) = -843.9 + 4.719T, \tag{4.3.1.2}$$

$$B(T) = -389 + 2.74T - 4.5\times10^{-3}T^2 \tag{4.3.1.3}$$

Φ_L can be calculated at different temperatures. These equations predict Φ_L values with an accuracy of about 1% for the temperature range 290–310 K.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 11, 14, 19, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

[3] F.T. Gucker, H.B. Pickard, R.W. Planck, J. Am. Chem. Soc. 61 (1939) 459. (Note that Gucker included some of the results of earlier investigations in his final equations.)

[4] L.-E. Briggner, I. Wadsö, J. Biochem. Biophys. Methods 22 (1991) 101.

4.3.2. $\Delta_{dil}H$, urea solution+water

Physical property	enthalpy of dilution
Units	$\mathrm{J\,mol^{-1}}$ (molar enthalpy of dilution, $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$)
Recommended reference material	urea (CH_4ON_2): 60.556 $\mathrm{g\,mol^{-1}}$; [57-13-6]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	aqueous solutions
Apparatus used	adiabatic twin calorimeter, twin-cell flow microcalorimeter
Contributors to the previous version	M.I. Paz-Andrade, G. Pilcher
Contributor to this version	M.V. Roux

4.3.2.1. Intended usage Calorimeters [1,2] for the measurement of enthalpies of mixing or dilution of aqueous solutions should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of mixing or dilution of solutions for which the value has been well established. The enthalpy of dilution of urea provides a means of detecting possible systematic errors in calibration and measurements procedures, particularly when solutions less viscous than those of sucrose are required.

4.3.2.2. Sources of supply and/or methods of preparation A suitable grade of urea is available as Standard Reference Material, no. 2152, from NIST and from BDH (under the denomination of "Aristar"). Other samples may be purified by recristallization from water or ethanol followed by intensive drying. The purity should be greater than 99.95 mol%. It is advised that freshly prepared solutions be used for the calorimetric measurements.

4.3.2.3. Pertinent physicochemical data Gucker and Pickard [3] measured the enthalpy of dilution of aqueous solutions of urea with an adiabatic twin calorimeter and gave the values of the relative apparent molal enthalpy, Φ_L, at 298.15 K. Their values are expressed by the following equation:

$$\Phi_\mathrm{L}/\mathrm{J\,mol^{-1}} = -359.37x + 28.52x^2 - 1.912x^3 + 0.06156x^4 \qquad (4.3.2.1)$$

where $x = m$ (mol kg^{-1}) for $x = 12$. For the conversion of cal$_{15}$ to joules, the value 1 cal$_{15}$ = 4.185 J was taken [4]. Egan and Luff [5] measured the enthalpy of solution of crystalline urea in water at 298.15 K and from their values an expression for Φ_L can be derived in excellent agreement with the results of Gucker and Pickard.

Paz-Andrade et al. [6] measured enthalpies of dilution of urea solutions in potassium phosphate buffer (pH 7.0, ionic strength 0.005 mol kg^{-1}) using a Beckman 190B twin-cell microcalorimeter. They obtained for the relative apparent molal enthalpy at 298.15 K:

$$\Phi_\mathrm{L}/\mathrm{J\,mol^{-1}} = -335.5x + 15.68x^2 - 0.2988x^3 \qquad (4.3.2.2)$$

where $x = m$ (mol kg^{-1}) for $x = 20$. The enthalpies of dilution in the pH phosphate buffer, which are of use to those studing biochemical reactions calorimetrically, differ only slightly from those in pure water.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 11, 14, 19, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

[3] F.T. Gucker, H.B. Pickard, J. Am. Chem. Soc. 62 (1940) 1464.

[4] F.D. Rossini (Ed.), Chemical Thermodynamics, Chap. 5, Wiley, New York, 1958.

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4.3.3. $\Delta_r H^0$, sulfuric acid solution+sodium hydroxide solution

Physical property	enthalpy of reaction in solution
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction, $\Delta_\mathrm{r} H^0_\mathrm{m}$); J kg^{-1} or J g^{-1} (specific enthalpy of reaction, $\Delta_\mathrm{r} h^0$)
Recommended reference materials	sulfuric acid solution + sodium hydroxide solution: 98.0795, 39.9971 g mol^{-1}; [7664-93-9], [1310-73-2]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	liquid + liquid
Apparatus used	isothermal reaction, isoperibol rotating-bomb combustion, and adiabatic solution calorimeters
Contributors to the previous versions	J.D. Cox, S.R. Gunn
Contributor to this version	M.V. Roux

4.3.3.1. Intended usage Calorimeters [1,2] for the measurement of enthalpies of reaction should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of a reaction for which the value has been well established. For an experimental program involving rapid exothermic reactions in solution, the reaction between sulfuric acid solution and excess sodium hydroxide solution, at defined concentrations, is recommended as a test reaction.

4.3.3.2. Sources of supply and/or methods of preparation Instructions for preparing the solutions of sulfuric acid and sodium hydroxide as calorimetric reactants have been given by Gunn [3,4].

4.3.3.3. Pertinent physicochemical data Gunn [3] has studied the enthalpy changes for the reactions between $H_2SO_4(8H_2O)$ and 2.5 mol of $NaOH(xH_2O)$, where x lays between 10 and 2580. By the use of a reaction calorimeter calibrated electrically Gunn [3] found the mean value $-(150.82 \pm 0.02)$ kJ mol^{-1} at 298.15 K for the enthalpy of the reaction:

$$\begin{aligned} &H_2SO_4(8H_2O)(1) + 2.5[NaOH(10H_2O)](1) \\ &\quad = [Na_2SO_4 + 0.5NaOH](35H_2O)(1) \qquad (4.3.3.1) \end{aligned}$$

Gunn et al. [4] found the mean value $-(150.80 \pm 0.02)$ kJ mol^{-1} for the same reaction at 298.15 K from the results of 42 experiments using three different rotating-bomb combustion calorimeters placed in three differents laboratories and calibrated by the combustion of benzoic acid. Prosen and Kilday [5] studied essentially the same process using an adiabatic vacuum-jacketed solution calorimeter calibrated electrically and found enthalpy values which were the same within the stated uncertainty.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 11, 14, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

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4.3.4. H^E, cyclohexane+hexane

Physical property	enthalpy of mixing
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of mixing, $\Delta_{mix}H_m$, or excess molar enthalpy of mixing, H_m^E); J kg^{-1} or J g^{-1} (specific enthalpy of mixing, $\Delta_{mix}h$, or excess specific enthalpy of mixing, h^E)
Recommended reference materials	cyclohexane+hexane ($C_6H_{12} + C_6H_{14}$): 84.1613, 86.1772 g mol^{-1}; [110-82-7], [110-54-3]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	liquid + liquid
Apparatus used	flow, batch and dilution calorimeters
Contributors to the previous versions	J.D. Cox, K.N. Marsh
Contributors to this version	A. Amengual, M.V. Roux

4.3.4.1. Intended usage Calorimeters [1,2] for the measurement of the enthalpies of mixing of liquids (equal to the excess enthalpies of the corresponding mixtures, H^E, since the enthalpy of mixing in an ideal system is zero) should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of mixing of two liquids for which the value of enthalpy of mixing has been well established. The liquid pair cyclohexane+hexane is recommended for this purpose, particularly for endothermic mixtures.

4.3.4.2. Sources of supply and/or methods of preparation The mass fraction purity of both cyclohexane and hexane should be greater than 99.95 mol%. Suitable samples of hexane may be obtained from Phillips Petroleum. Samples of cyclohexane may be obtained from a variety of suppliers (Aldrich, BDH).

4.3.4.3. Pertinent physicochemical data The enthalpy of mixing of (x) cyclohexane+(1-x) hexane is well fitted by a polynomial in the mole fraction x of cyclohexane of the form:

$$\begin{aligned} H^E(x) = x(1-x)(a_0 + a_1(1-2x) + a_2(1-2x)^2 \\ + a_3(1-2x)^3 \qquad (4.3.4.1) \end{aligned}$$

Measurements in the literature have varying degrees of accuracy. In the previous revision [3], Marsh analyzed a selected set of eight series of measurements made at 298.15 K with flow, batch and dilution calorimeters

Table 50

Coefficients a_i of the polynomial $H^E(x)$ at different temperatures and the value H^E_m of their maxima at mole fraction x_m (the numbers in parenthesis in column one are the references from which data have been taken to fit the polynomial and N is the total number of data)

Reference	T (K)	N	a_1	a_2	a_3	a_4	x_m	H^E_m(J mol^{-1})
[4–11]	298.15	275	864.59	−249.92	98.12	−30.65	0.576_1	221.0
[4–15]	298.15	402	864.63	−248.60	99.05	−34.97	0.575_9	221.0
[16]	288.15	48	917.62	−266.59	102.97	−30.50	0.576_3	234.6
[16]	318.15	48	752.14	−214.03	82.82	−30.14	0.574_9	192.1

[4–11]. Marsh's fitting led to the values of the coefficients a_i in the first row of Table 50.

In this revision, the series of measurements that have been used to determine the coefficients a_i have been selected according to the two following criteria: (i) x is given with at least four decimal digits and (ii) the standard deviation of the series, σ_H, is smaller than 1.1. The square of σ_H is the sum of $(H_i^E - H^E(x_i))^2$ divided by n–p, where H_i^E are the measured values at the mole fractions x_i, and n and p are the number of data points and the number of free coefficients in the polynomial $H^E(x)$ (4 in the present case) which are found by least squares for each series. The limit 1.1 has been taken because it is the largest standard deviation from Refs. [4–11] used in the previous revision. Among the revised literature, four more references [12–15] have been found to fulfill the above criteria. The coefficients a_i of the polynomial fitting the series in Refs. [4–15] are given in Table 50. They have been determined by least squares weighting the points from each reference with σ_H^{-2}. The maximum value of $H^E(x)$ at 298.15 K is 221.0 J mol^{-1} and occurs at $x_m = 0.575_9$. $H^E(x)$ fits the data with H equal to 0.6_6% of its maximun value. Our results agree with those of Marsh. Despite the fact that he reported the maximum at the cyclohexane mole fraction 0.579, the actual maximum of his polynomial is at 0.576_1. The mean difference between the values provided by his polynomial and ours is 0.04 J mol^{-1} with a maximum of 0.12 J mol^{-1}.

At temperatures different from 298.15 K no accurate measurements other than those reported in Ref. [16], and already used in Marsh's revision, have been found. The coefficients a_i, the position of the maximum and its value have been calculated for the data in Ref. [16] at 288.15 and 318.15 K. The results are given in Table 50. The position of the maximum is described by $x_m = -5 \times 10^{-5}$ (T (K)) + 0.5899 and H^E at the maximum by H^E_m(J mol^{-1}) = −1.4198 (T(K)) + 643.94.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 11, 14, 15, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

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[13] J.-P.E. Grolier, G.C. Benson, J. Chem. Thermodyn. 7 (1975) 89.

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[16] M.B. Ewing, K.N. Marsh, J. Chem. Thermodyn. 2 (1970) 295.

4.3.5. H^E, 1,4-dioxane+tetrachloromethane

Physical property	enthalpy of mixing
Units	J mol^{-1} or kJ mol^{-1} (molar enthalpy of mixing, $\Delta_{mix}H_m$, or excess molar enthalpy of mixing, H^E_m); J kg^{-1} or J g^{-1} (specific enthalpy of mixing, $\Delta_{mix}h$, or excess specific enthalpy of mixing, h^E)

Recommended reference materials	1,4-dioxane + tetrachloromethane ($C_4H_8O_2 + CCl_4$): 88.1063, 153.8218 g mol^{-1}; [123-91-1], [56-23-5]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	liquid + liquid
Apparatus used	flow, batch and dilution calorimeters
Contributor to the previous version	K.N. Marsh
Contributors to this version	A. Amengual, M.V. Roux

4.3.5.1. Intended usage Calorimeters [1,2] for the measurement of enthalpies of mixing of liquids (equal to the excess enthalpies of the corresponding mixtures, H^E, since the enthalpy of mixing in an ideal system is zero) should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of mixing of two liquids for which the value of the enthalpy of mixing has been well established. The liquid pair 1,4-dioxane + tetrachloromethane is recommended for this purpose, particularly for exothermic mixtures.

4.3.5.2. Sources of supply and/or methods of preparation The purity of both 1,4-dioxane and tetrachloromethane should be greater than 99.95 mol%. Suitable samples of both compounds may be obtained from a variety of suppliers (Aldrich and Riedel-de-Haën). Special care should be taken with tetrachloromethane as explained in Ref. [3]. Tetrachloromethane should not be exposed to light, since under certain conditions a radical reaction with release of energy can occur. 1,4-Dioxane + tetrachloromethane are toxic substances and proper precautions should be employed when using them.

4.3.5.3. Pertinent physicochemical data The measurements of the enthalpy of mixing of (x) 1,4-dioxane+$(1-x)$ tetrachloromethane found in the literature can be fitted by a polynomial in the mole fraction x of 1,4-dioxane of the form:

$$H^E(x) = x(1-x)(a_0 + a_1(1-2x) + a_2(1-2x)^2 + a_3(1-2x)^3) \tag{4.3.5.1}$$

The measurements at 298.15 K found in the literature have varying degrees of accuracy. In the previous revision [4] Marsh analyzed a selected set of four series of measurements made at 298.15 K with flow and dilution calorimeters [3, 5–7].

The series of measurements that have been used to determine the coefficients of the polynomial have been selected with the two following criteria: (i) x is given with, at least, three digits after the decimal and (ii) the standard deviation of the series, σ_H, is smaller than 1.0. The limits for these criteria have been taken to include data at least as good as those used in the previous revision. The square of σ_H is the sum $(H_i^E - H^E(x_i))^2$ divided by $n-p$, where H_i^E are the measured values at the mole fractions x_i, and n and p are the number of data points and the number of free coefficients in the polynomial $H^E(x)$ (four in the present case) which are found by least squares for each series. Five series of measurements from Refs. [3, 5–8] have been found to fulfill the above criteria. A total of 183 data points have been used to determine the coefficients a_i of the polynomial by least squares. Weighting the points from each reference with $\sigma_H{}^{-2}$, the following coefficients are obtained:

$$a_0 = -1007.20, \quad a_1 = 67.29, \quad a_2 = 168.79, \quad a_3 = 12.22 \tag{4.3.5.2}$$

$H^E(x)$ fits the data with σ_H equal to 0.6_6% of its minimun value. The minimum of the polynomial (4.3.5.1.) is -252.0 J mol^{-1} and occurs at the mole fraction $x = 0.514_3$.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 14, 15, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

[3] M.J. Costigan, L.J. Hodges, K.N. Marsh, R.H. Stokes, C.W. Tuxford, Aust. J. Chem. 33 (1980) 2103.

[4] A.J. Head, R. Sabbah, in: K.N. Marsh (Ed.), IUPAC Recommended Reference Materials for the Realization of Physicochemical Properties, Chap. 9, Blackwell, Oxford, 1987.

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4.3.6. H^E, *ethanol+water*

Physical property	enthalpy of mixing
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of mixing, $\Delta_{mix}H_m$, or excess molar enthalpy of mixing, H_m^E); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of mixing, $\Delta_{mix}h$, or excess specific enthalpy of mixing, h^E)
Recommended reference materials	ethanol+water ($C_2H_6O + H_2O$): 46.0690, 18.0153 $g\,mol^{-1}$; [64-17-5], [7732-18-5]
Classification	secondary RM
Range of variables	298.15 K and 0.1 MPa are the reference temperature and pressure normally employed
Physical states within the range	liquid + liquid
Apparatus used	isothermal dilution and flow calorimeters
Contributors to this version	J.A.R. Renuncio, M.V. Roux

4.3.6.1. Intended usage Calorimeters [1,2] for the measurement of the enthalpies of mixing of liquids (equal to the excess enthalpies of the corresponding mixtures, H^E, since the enthalpy of mixing in an ideal system is zero) should be calibrated electrically. However, it is desirable to test the calorimetric procedure by measurement of the enthalpy of mixing of two liquids for which the value of the enthalpy of mixing has been well established. The liquid pair ethanol + water is recommended for this purpose, particularly for exothermic mixtures.

4.3.6.2. Sources of supply and/or methods of preparation Pure ethanol and water (99.95 mol% or better) are available from many manufacturers, Aldrich among them. Sufficiently pure ethanol can be readily obtained by passing a distilled sample through Linde 3A molecular sieve immediately prior to use [3]. Water must be boiled to expel CO_2 prior to use.

4.3.6.3. Pertinent physicochemical data The enthalpy of mixing of (x) ethanol + (1−x) water is well fitted by a polynomial of the form:

$$H^E(x) = x(1-x)\sum_{A_n=0}^{n} A_n(1-2x)^{n-1}/[1-k(1-2x)] \qquad (4.3.6.1)$$

where A_n are the coefficients and k is a skewing factor which ranges from +1 to −1.

Measurements in the literature at T = 298.15 K and p = 0.1 MPa have various degrees of accuracy. Costigan et al. [3] measured the enthalpy of mixing of this system using three different isothermal displacement calorimeters and provided 103 measurements. The different runs agree within 0.2%. Data were fitted using a ten-parameter equation (nine linear terms and a skewing factor) with a standard deviation $\sigma = 1.2\,J\,mol^{-1}$. The coefficient values of the polynomial (4.3.6.1) are:

$$A_0 = -1628.5, \quad A_1 = -1365.7, \quad A_2 = -2414.0$$
$$A_3 = 232.0, \quad A_4 = 548.3, \quad A_5 = --4685.6,$$
$$A_6 = -7458.9, \quad A_7 = 3874.8, \quad A_8 = 6595.0,$$
$$k = 0.37.$$

The mixture ethanol + water has a minimun value $H_m^E = -776\,J\,mol^{-1}$, $x = 0.160$.

At T = 298.15 K and pressure above 0.1 MPa, flow calorimeters have been used by several authors [4–6]. Ott [4] compares the experimental data of Costigan [3] with data taken at 0.4 MPa and found that the pressure effect is small. The data exhibit similar accuracies to those reported by Costigan at 0.1 MPa.

At temperatures above 298.15 K, several authors [5–8] have obtained data at temperatures up to 548 K and pressures ranging from 0.40 to 20.00 MPa. Unfortunately, the available data do not agree between themselves, except for a few cases: 398 K and 15.00 MPa [5,8], 423 K and 5.00 MPa [6,8] and 473 and 5.00 and 15.00 MPa [6,8]. The available data present experimental uncertainties between 1% and 2% which are still higher than those reported by authors working at 0.1 MPa pressure. The ethanol + water system seems to be a strong candidate as a reference system for excess enthalpy at high temperatures and pressures. More experimental information for this system is required in the temperature and pressure ranges above mentioned.

References

[1] H.A. Skinner (Ed.), Experimental Thermochemistry, Chaps. 8, 9, 11, 14, 15, Vol. II, Wiley, New York, 1962.

[2] K.N. Marsh, P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol. IV: Solution Calorimetry, Blackwell, Oxford, 1994.

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4.4. Gas-gas processes

4.4.1. $\Delta_r H^0$, hydrogen+oxygen

Physical property	enthalpy of reaction
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar enthalpy of reaction, $\Delta_r H_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific enthalpy of reaction, $\Delta_r h^0$)
Recommended reference materials	hydrogen + oxygen ($H_2 + O_2$): 2.0159, 31.9988 $\mathrm{g\,mol^{-1}}$; [1333-74-0], [7782-44-7]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	gas + gas
Apparatus used	isothermal flame calorimeters
Recommended value	$\Delta_r H_m^0$ (298.15 K) $= -(285.830 \pm 0.042)$ $\mathrm{kJ\,mol^{-1}}$ for H_2O(l); $\Delta_r H_m^0$(298.15 K) $=-(241.814 \pm 0.042)$ $\mathrm{kJ\,mol^{-1}}$ for H_2O(g)
Contributors to the previous versions	J.D. Cox, A.J. Head
Contributor to this version	M.V. Roux

4.4.1.1. Intended usage Enthalpies of gas-phase reactions are generally measured by means of a flame calorimeter. Descriptions of such calorimeters, which may be operated isothermally, adiabatically or isoperibolically, are found in Refs. [1–3]. The energy equivalent of a gas-phase reaction calorimeter may be determined by the dissipation of measured amounts of electrical energy. In some calorimeter designs electrical calibration may be experimentally inconvenient and then the hydrogen + oxygen reaction (either in a flame or over a catalyst) affords a convenient means of calibrating the calorimeter. Alternatively, the hydrogen + oxygen reaction can be used to check the accuracy of an electrical calibration. Hydrogen burnt in oxygen was recommended as a Calibration and Test Material by the IUPAC Commision on Physicochemical Measurements and Standards in 1974 [4] and it is the only gas-gas reaction that is internationally agreed as being suitable for the calibration of gas-reaction calorimeters.

4.4.1.2. Sources of supply and/or methods of preparation Compressed hydrogen and oxygen of high purity are available from Air Liquide and other manufacturers.

4.4.1.3. Pertinent physicochemical data When a gas-reaction calorimeter is operated at a temperature close 298 K, most of the water formed by the hydrogen + oxygen reaction is a liquid and the liquid state would be the obvious reference state for water; allowance for the enthalpy of condensation of the water vapor in equilibrium with liquid water would be required. When the calorimeter is operated at a temperature above, say, 350 K it may be more convenient to adopt the gas state as the reference state for water; if the saturation vapor pressure was exceeded, allowance for the enthalpy of vaporization of liquid water would be required. The quantities necessary for these computations can be obtained from the work of the CODATA Task Group on key values for thermodynamics [5] which has selected the following values, based on experimetal work of Rossini, King and Armstrong and Keenan, Keyes, Hill and Moore

$$H_2(g) + 0.5\,O_2(g) = H_2O(l)\,\Delta_r H_m^0(298.15\,K) = -(285.830 \pm 0.042)\,kJ\,mol^{-1} \tag{4.4.1.1}$$

$$H_2(g) + 0.5\,O_2(g) = H_2O(g)\,\Delta_r H_m^0(298.15\,K) = -(241.814 \pm 0.042)\,kJ\,mol^{-1}. \tag{4.4.1.2}$$

References

[1] F.D. Rossini (Ed.), Experimental Thermochemistry, Chaps. 4, 13, Vol. I, Wiley, New York, 1956.

[2] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Chaps. 2, 3, 4, Academic Press, London, 1970.

[3] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chaps. 2, 3, 14, Pergamon, Oxford, 1979.

[4] J.D. Cox, Pure Appl. Chem. 40 (1974) 399.

[5] CODATA Recommended Key Values for Thermodynamics, 1977, J. Chem. Thermodyn. 10 (1978) 903.

4.4.2. $\Delta_r H^0$, hydrogen+chlorine

Physical property	enthalpy of reaction
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of reaction, $\Delta_r H_m^0$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific enthalpy of reaction, $\Delta_r h^0$
Recommended reference materials	hydrogen + chlorine ($H_2 + Cl_2$): 2.0159, 70.9054 $g\,mol^{-1}$; [1333-74-0], [7782-50-5]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	gas + gas
Apparatus used	isothermal flame calorimeters
Recommended value	$\Delta_r H_m^0$ (298.15 K) $= -(92.31 \pm 0.13)\,kJ\,mol^{-1}$ for HCl(g)
Contributors to the previous versions	J.D. Cox, O. Riedel, A.J. Head
Contributor to this version	M.V. Roux

4.4.2.1. Intended usage Enthalpies of gas-phase reactions are generally measured by means of a flame calorimeter. Descriptions of such calorimeters, which may be operated isothermally, adiabatically or isoperibolically, are found in Refs. [1–3]. The energy equivalent of a gas-phase reaction calorimeter may be determined by the dissipation of measured amounts of electrical energy. In some calorimeter designs electrical calibration may be experimentally inconvenient and then the hydrogen + oxygen reaction (either in a flame or over a catalyst) affords a convenient means of calibrating the calorimeter as recommended by the IUPAC Commission on Physicochemical Measurements and Standards in 1974 [4].

4.4.2.2. Sources of supply and/or methods of preparation Compressed hydrogen and chlorine of high purity are available from Air Liquide and other manufacturers.

4.4.2.3. Pertinent physicochemical data In some types of gas-reaction calorimeters the hydrogen chloride formed from the reaction between hydrogen and chlorine may remain in the calorimeter in the gas state. The following value, selected by the CODATA Task Group on key values for thermodynamics [5] will be applicable

$$0.5\,H_2(g) + 0.5\ Cl_2(g) = HCl(g)\,\Delta_r H_m^0(298.15\,K) = -(92.31 \pm 0.13)\,kJ\,mol^{-1}. \tag{4.4.2.1}$$

In other types of gas-reaction calorimeters hydrogen chloride may be conveniently absorbed in water placed initially within the calorimeter. In this case the enthalpy of formation of the hydrogen chloride at a determined finite dilution may be taken from Ref. [6], where tabulated values for the enthalpy of formation of the $HCl(xH_2O)(l)$, for x between 1 and ∞, are available.

References

[1] F.D. Rossini (Ed.), Experimental Thermochemistry, Chaps. 4, 13, Vol. I, Wiley, New York, 1956.

[2] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Chaps. 2, 3, 4, Academic Press, London, 1970.

[3] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chaps. 2, 3, 14, Pergamon, Oxford, 1979.
[4] J.D. Cox, Pure Appl. Chem. 40 (1974) 399.
[5] CODATA Recommended Key Values for Thermodynamics, 1977, J. Chem. Thermodyn. 10 (1978) 903.
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4.4.3. $\Delta_r H^0$, *methane+oxygen*

Physical property	enthalpy of reaction
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar enthalpy of reaction, $\Delta_r H_m^0$; $J\,g^{-1}$ (specific enthalpy of reaction, $\Delta_r h^0$)
Recommended reference materials	Methane + oxygen ($CH_4 + O_2$): 16.0428, 31.9988 $g\,mol^{-1}$; [74-82-8], [7782-44-7]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical states within the range	gas + gas
Apparatus used	isothermal flame calorimeters
Recommended value	$\Delta_r H_m^0$ (298.15 K) $= -(890.71 \pm 0.38)\,kJ\,mol^{-1}$
Contributor to the previous version	G.T. Armstrong
Contributor to this version	M.V. Roux

4.4.3.1. Intended usage Enthalpies of gas-phase reactions of gaseous fuels are generally measured by means of a flame calorimeter incorporating a burner in which gas is burnt in air or oxygen. Descriptions of such calorimeters, which may be operated isothermally, adiabatically or isoperibolically, are to be found in Refs. [1–5]. The energy equivalent of a gas-phase reaction calorimeter may be determined by the dissipation of measured amounts of electrical energy. In some calorimeter designs, electrical calibration may be experimentally inconvenient and then the hydrogen + oxygen reaction (either in a flame or over a catalyst) affords a convenient means for the calibration of the calorimeter as recommended by the IUPAC Commision on Physicochemical Measurements and Standards in 1974 [6]. Eiseman and Potter [2] propose the use of methane as calibrating gas when the calorimeter is to be used with gases having several times the heating value of the enthalpy of combustion of hydrogen.

4.4.3.2. Sources of supply and/or methods of preparation Compressed methane and oxygen of high purity are available from Air Liquide and other manufacturers.

4.4.3.3. Pertinent physicochemical data The certification of the pure methane is described by Armstrong [7]. The value for the enthalpy of combustion of the gas is based upon the measurements made by Rossini [8] and Prosen and Rossini [9] together with the measured composition of the gas and auxiliary data on non-ideality, temperature coefficient of the reaction and the partial pressure of water. Prosen and Rossini reported the value $-890.36\,kJ\,mol^{-1}$ which Armstrong [7] recalculated to obtain the value $-(890.31 \pm 0.29)\,kJ\,mol^{-1}$. Results in agreement with this figure have been published by Pittam and Pilcher [10] who found the value $-(890.71 \pm 0.38)\,kJ\,mol^{-1}$. All these values refer to a temperature of 298.15 K and to the gases in their standard states.

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5. Reference materials for measurement of enthalpies of combustion

This section involves the reference materials for calibration and testing of calorimeters devoted to the energy determination of reactions carried out in combustion bombs. The experimental measurements are related to a constant-volume system and from the energy of combustion the enthalpy of combustion is readily derived by means of the thermodynamic relation $\Delta H=\Delta U+p\Delta V$. Reference materials for enthalpies of combustion by flame calorimetry have been described in Section 4.4.

The precision of the obtained results with well-designed static- and rotating-bomb calorimeters is generally better than 0.01% and results of this order of accuracy can be obtained with highly purified C, H and O containing compounds. However, when other elements are present the accuracy is limited by the extent to which the stoichiometry of the bomb process can be controlled and determined. It is certainly true that far more inaccurate energies of combustion arise from incomplete combustion or from lack of a well-defined final state than from difficulties in the physical measurement of the energy of the bomb process. Reference materials have an important role to play in overcoming these problems.

Since the first document [1] of recommended reference materials approved in 1974, several new recommendations [2–4] have been published with literature searching to about 1980. In this version, the new measurements reported in literature up to 1997 have been investigated. The reference materials and their recommended values for energies of combustion measurements from various documents are listed in Table 51. Other compounds suggested as reference materials are also listed in this table.

The common desirable properties for reference materials in this section are easy availability, high purity, thermodynamic stability, non-hygroscopicity, non-volatility (for solid), completeness of combustion. In relation to these properties, sole benzoic acid is recommended as primary reference material in this compilation and is used to calibrate a combustion calorimeter; its energy of combustion was determined by using an electrically calibrated calorimeter. Substances recommended as secondary reference materials are test materials for checking the experimental methods used for different kinds of compounds and their values of the energy of combustion have been determined in at least two independent sets of precise measurements which were in good agreement with each other. The tertiary reference materials are materials which do not rigorously meet all the above criteria.

As above mentioned, benzoic acid remains as the unique primary reference material for calibrating bomb calorimeters. Some new determinations for highly pure samples confirm the rounded value “under standard bomb conditions” of $\Delta_c u=-26\,434\ \mathrm{J\,g^{-1}}$ which was already well established before.

Concerning the three reference materials proposed for the combustion of C, H, O, N containing compounds with relatively low nitrogen content, acetanilide has the advantage over hippuric acid because water-free samples are readily available. In addition Sato-Toshima et al. [5] found that nicotinic acid is difficult to burn completely with remarkable tendency to spatter. With regard to the reference materials for the combustion of C, H, O, N containing compounds with high nitrogen content, Aleksandrov et al. [6] suggested that 1,2,4-trizole can be used instead of urea.

4-Bromobenzoic acid and 2-iodobenzoic acid have been added as reference materials for the combustion of halogen compounds. Two values for 4-bromobenzoic acid are recommended corresponding to liquid bromine or $HBr(600H_2O)$ as the product of reference combustion reaction. No sufficient combustion calorimetry has been made on the 4-iodobenzoic acid. As a substitute, the energy of combustion of 2-iodobenzoic acid has been satisfactorily measured and thus is tentatively recommended as the reference material for the combustion of iodine-containing compounds.

No reference materials for the combustion of C, H, O, Cl/Br containing compounds with relatively high Cl/Br content have been recommended here. The uncertainty of the energy of combustion for these compounds is large due to (i) the low specific energy of combustion, (ii) the difficulty of complete combustion that requires the use of relatively large amounts of auxiliary material with a high hydrogen content, and (iii) the large correction of energy associated to the side reducing reaction of the free halogen formed during conbustion. Therefore, high precision calorimeter with tantalum-lined bomb is necessary to study these

Table 51
The recommended results of $-\Delta_c u^0$ (J g^{-1}) from various documents[a]

Reference Materials	Cl.[b]	Ref. [1]	Ref. [2]	Ref. [3]	Ref. [4]	This work
Combustion of solids in oxygen						
Benzoic acid[c]	P	26 434		26 434	26 434	26 434 ± 1
Succinic acid	S	12638.0 ± 1.6	12638.0 ± 1.6	12638.0 ± 1.6	12638.0 ± 1.6	12638.0 ± 1.6
Hippuric acid	T	23 548		23 548	23 548	23544.2 ± 3.8
Acetanilide	S		31234.0 ± 5.6	31 234 ± 7		31234.0 ± 5.0
Nicotinic acid	T		(22185.6 ± 4.6)		22 186	22186.3 ± 3.0
1,2,4-Triazole	S					19204.2 ± 4.1
Urea	T	10 537	10540.1 ± 2.0	10 539 ± 5	10541.0 ± 0.4	10 539 ± 5
Thianthrene	S	33466.0 ± 5.2	33467.8 ± 3.5	33 468 ± 4	33 466	33 468 ± 4
4-Fluorobenzoic acid	S	21857.0 ± 5.2	21860.6 ± 4.3	21 861 ± 4	21862.4 ± 6.4	21 860 ± 4
Pentafluorobenzoic acid	T	12062.4 ± 4.8	(12060.4 ± 4.7)	12062.4 ± 4.8	12062.4 ± 4.8	12060.4 ± 4.8
4-Chlorobenzoic acid	S	19562.7 ± 3.2	19565.2 ± 2.7	19 567 ± 2	19562.7 ± 3.2	19566.4 ± 1.5
4-Bromobenzoic acid	T		(15 372 ± 10)		(15 372)	15367.0 ± 4.2[d] 15261.0 ± 4.2[e]
2-Iodobenzoic acid	T					12771.3 ± 2.4
Triphenylphosphine oxide	S		(35789.9 ± 6.0)	35 790 ± 6	(35 790)	35789.3 ± 4.5
Combustion of liquids in oxygen						
2,2,4-Trimethylpentane	S	47 712	47 706 ± 7	47 712	47 712	47 712 ± 12
(,(,(-Trifluorotoluene	T		23052.4 ± 2.6	23052.4 ± 2.6		23052.4 ± 2.6
Combustion of solids in fluorine						
Sulfur	T		(37885.0 ± 2.2)	37 915 ± 90		37946.1 ± 6.2
Tungsten	S		(9336.4 ± 3.8)	9335.9 ± 3.8		9336.5 ± 3.8
Candidates (combustion of solids in oxygen)						
Tris		20030.3 ± 3.4	(20030.3 ± 3.4)		20030.3 ± 3.4	
2,3,5,6-Tetrachloro-*p*-xylene			(16 089 ± 6)		(16 089)	
4-Iodobenzoic acid			(12 710 ± 6)		(12 710)	

[a] For candidate reference materials the values are placed in parentheses. If a sample is available as a reference material with a certified value of $\Delta_c u^0$ or $\Delta_c h^0$, use of the certified value is preferable.

[b] Cl. (classification), P (primary), S (secondary), T (tertiary).

[c] The certified values $-\Delta_c u$ (J g^{-1}) under "standard bomb conditions".

[d] Br_2 (l) is selected as the combustion product.

[e] HBr(600H_2O) (l) is selected as the combustion product.

compounds and more work using this technique is expected.

Kirklin and Domalski [7] reported the energy of combustion of triphenylphosphine oxide which is in excellent agreement with the previously recommended value. Thus it was confirmed that this compound is a good reference material for phosphorous-containing compounds.

Fluorine combustion calorimetry is a powerful method for studying the thermochemistry of many inorganic substances. Sulfur has been proposed as a reference material for this technique. The values of the energy of combustion of this material previously reported are not in agreement with each other in their uncertainty intervals. O'Hare et al. [8] have improved the precision of their measurements by using pure samples and refining their technique; they reported several good results. However, new precise determinations of this energy from other laboratories are encouraged.

Throughout this section, molar masses of the elements are taken from the 1993 report of the IUPAC Commission on Atomic Weights and Isotopic Abundances [9]. Unless otherwise noted the uncertainty of a measured value represents twice the overall standard deviation of the mean [10,11]. The weighted value x of a set of measured values of the combustion energy of a reference material is selected as the recommended value and is calculated using the equation $x = \sum_n (x_i/\sigma_i^2)/\sum_n (1/\sigma_i^2)$ where n is the number of measured values in this set; x_i and σ_i are the *i*th measured value and its uncertainty [12]. The uncertainty σ of this recommended value is calculated using the equation $\sigma = \left(\sum_n \sigma_i^{-2}\right)^{-1/2}$.

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5.1. *Combustion of solids in oxygen*

5.1.1. $\Delta_c U^0$, *benzoic acid*

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^o$)
Recommended reference material	benzoic acid ($C_7H_6O_2$): 122.1234 $\mathrm{g\,mol^{-1}}$; [65-85-0]
Classification	primary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static (or rotating) oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(26434 \pm 1)\ \mathrm{J\,g^{-1}}$ (under "standard bomb conditions")
Contributors to the previous versions	Yu.I. Aleksandrov, G.T. Armstrong, J.D. Cox, E.S. Domalski, H. Feuerberg, J. Franc, J. Head, C. Mosselman, B.N. Oleinik, O. Riedel
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5.1.1.1. Intended usage By international agreement, reached in 1934, benzoic acid is the principal reference material for measuring the energy equivalent of oxygen-bomb calorimeters. All these calorimeters have a closed chamber which contains compressed oxygen and the sample to be burnt and are provided with an electrical system for the ignition of the sample. The size, shape, material of construction, disposition of parts and usage of the bomb vary greatly [1–5]: some are used statically, some in a moving mode; some are used immersed in a fluid, some in contact with a metal block and some naked; some are intended for gram samples, some for milligram samples; some are used isoperibolically, some isothermally and some adiabatically.

Benzoic acid also serves in combustion calorimetry to kindle materials which are difficult to burn, to influence the overall stoichiometry of a combustion reaction and to test analytical procedures.

5.1.1.2. Sources of supply and/or methods of preparation Suitable grades of benzoic acid (designated as "thermochemical" or "calorimetric" standard) certified for the value of the energy of combustion are available from NIST as SRM 39j and other authoritative laboratories in UK, Russian Federation and China.

5.1.1.3. Pertinent physicochemical data From a thermodynamic viewpoint the standard specific energy of combustion of benzoic acid at 298.15 K is the key quantity, but since bomb-combustion reactions are conducted under conditions far from those of the thermodynamic standard state, a more practical quantity is $\Delta_c u$(cert.), the specific energy of combustion certified by a standardizing laboratory as the energy evolved when 1 g of benzoic acid burns under "standard bomb conditions" [1]. Determinations of $\Delta_c u$(cert.) are made using calorimeters which are calibrated by means of electrical energy. An extensive study of a single batch of benzoic acid (NBS 39i) has been made from which the weighted mean of four concordant determinations [6–9] is $-(26\,433.6 \pm 0.9)\ \mathrm{J\,g^{-1}}$. This value is in good agreement with the earlier assessment by Hawtin [10] of determinations (on various samples) made prior to 1966, *viz*. $-(26\,434.4 \pm 1.2)\ \mathrm{J\,g^{-1}}$, the value selected by Cox and Pilcher $-26434\ \mathrm{J\,g^{-1}}$ [1], the value selected by Aleksandrov et al. $-(26\,434.4 \pm 0.6)\ \mathrm{J\,g^{-1}}$ [5] and some new determinations for highly pure samples (mole fraction purity 0.99999) of benzoic acid (purified by zone melting method): $-(26\,433 \pm 5)\ \mathrm{J\,g^{-1}}$ [11], $-(26\,433.4 \pm 4.0)\ \mathrm{J\,g^{-1}}$ [12] and $-(26\,433.4 \pm 3.4)\ \mathrm{J\,g^{-1}}$ [13]. The rounded value of $-26\,434\ \mathrm{J\,g^{-1}}$ for the value of $\Delta_c u$(cert.) for benzoic acid is thus well established. Although this value relates to essentially pure benzoic acid, it is important to note that a given batch of benzoic acid to be used for the calibration of bomb calorimeters may not be pure provided it is homogeneous and has been properly certified. However, if it is not pure, it cannot be used for testing analytical procedures. When benzoic acid is used under conditions remote from "standard bomb conditions", it may be preferable to calculate the value appropriate to these conditions from the standard specific energy of combustion $\Delta_c u^0$, which is $20\ \mathrm{J\,g^{-1}}$ less negative than $\Delta_c u$(cert.) [1].

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5.1.2. $\Delta_c U^0$ succinic acid

Physical property	Energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	Succinic acid ($C_4H_6O_4$): 118.0892 $\mathrm{g\,mol^{-1}}$; [110-15-6]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static (or rotating) oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0(298.15\ \mathrm{K}) = -(12\,638.0 \pm 1.6)\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	Yu.I. Aleksandrov, J.D. Cox, H. Feuerberg, A.J. Head, B.N. Oleinik, E.F. Westrum Jr.
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5.1.2.1. Intended usage Energies of combustion in oxygen of most compounds containing no elements other than C, H, O can be accurately measured with the aid of a static-bomb calorimeter [1,2]. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion.

Succinic acid is recommended as a test material for the combustion calorimetry of C, H, O compounds, although one group of workers have reported difficulty in obtaining complete combustion [3].

5.1.2.2. Sources of supply and/or methods of preparation A suitable sample of succinic acid can be prepared from an analytical grade specimen (e.g. Fluka: 99.5+%, Aldrich: 99+%, Sigma: 99+%) by four recrystallizations from distilled water followed by an effective drying procedure, either by a two-stage pelleting technique [4] or by vacuum sublimation below 398 K [5].

5.1.2.3. Pertinent physicochemical data The energy of combustion of succinic acid has been measured many times. The studies on the removal of water from succinic acid indicate that many of the samples used in the earlier work may have contained water. Oleinik et al. [5] selected the value $-(12638.5 \pm 1.5)\,\mathrm{J\,g^{-1}}$ based on three determinations where the purity of the succinic acid had been well established and the criteria of good calorimetry had been met [5,7]. Their selected value is in very close agreement with the value $-(12638.0 \pm 1.6)\,\mathrm{J\,g^{-1}}$ selected by Vanderzee et al. [7] from a wider range of published results after rigorous critical evaluation and re-calculation of some values. A weighted mean [5,8], $-(12638.0 \pm 1.6)\,\mathrm{J\,g^{-1}}$, is selected as the recommended value at 298.15 K which refers to the reaction:

$$\mathrm{C_4H_6O_4(cr) + 3.5O_2(g) = 4CO_2(g) + 3H_2O(l)} \quad (5.1.2.1)$$

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5.1.3. $\Delta_c U^0$, hippuric acid

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U^0_m$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	hippuric acid ($C_9H_9O_3N$): 179.1754 $\mathrm{g\,mol^{-1}}$; [495-69-2]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static or rotating oxygen-bomb calorimeter (the latter is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(23544.2 \pm 3.8)\,\mathrm{J\,g^{-1}}$
Contributors to the previous versions	Yu.I. Aleksandrov, J.D. Cox, A.J. Head, B.N. Oleinik
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5.1.3.1. Intended usage Energies of combustion in oxygen of most compounds containing C, H, O, N can be measured with the aid of a rotating-bomb calorimeter [1,2]. It has been noticed [1] that the conversion of the formed nitrogen oxides into nitric acid is slow in the combustion experiment, so a static-bomb calorimeter can be used only for the compounds of low nitrogen content for which the nitric acid correction is small. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion. Hippuric acid was recommended for this purpose by Huffman [3] as a test material for the combustion calorimetry of C, H, O, N compounds which have a relatively low nitrogen content (below 10%).

5.1.3.2. Sources of supply and/or methods of preparation Hippuric acid of sufficient purity can be obtained by crystallization of commercial material (e.g. Sigma: 99%, Aldrich: 98%, Fluka: 97+%) from water [3,4]. Hubbard et al. [4] found from analyzing CO_2 in the combustion products that the recrystallized material retains water (mass fraction of 6×10^{-4}) after drying in vacuo and storage over phosphorus pentoxide. But An et al. [6] did not find any detectable amount of water in their sample by the same technique. Oleinik et al. [5] have shown that the water can be completely removed by zone sublimation provided that care is taken to avoid thermal decomposition to benzoic acid. The technique successfully used by Vanderzee and Westrum [7] for drying succinic acid does not appear to have been applied to hippuric acid and is worthy of trial.

5.1.3.3. Pertinent physicochemical data The energy of combustion of hippuric acid has been measured many times. However, the residual water in the sample of hippuric acid had not been taken seriously into account until the result of Hubbard et al. [4]. They determined the value of energy of combustion of hippuric acid, $-(23\,543.0 \pm 8.9)\ \mathrm{J\,g^{-1}}$, based on the mass of carbon dioxide produced. For a recrystallized sample An et al. [6] reported that the ratio of CO_2 (found)/CO_2 (calc.) is equal to (1.0001 ± 0.0002) and the value of energy of combustion of hippuric acid based on the mass of sample burnt is $-(23\,541.8 \pm 5.1)\ \mathrm{J\,g^{-1}}$, Oleinik et al. [5] reported a mean value of energy of combustion of two different samples, $-(23\,550.7 \pm 7.8)\ \mathrm{J\,g^{-1}}$. The first sample is obtained from zone sublimation and the second is a recrystallized sample. A water content of 0.0003 mole fraction in the second sample was found by means of acid titration analysis and a corresponding energy correction was used. The results of the three groups of workers were compatible and lead to a recommended value of $-(23\,544.2 \pm 3.8)\ \mathrm{J\,g^{-1}}$ for the specific standard energy of combustion at 298.15 K for the reaction

$$C_9H_9O_3N(\mathrm{cr}) + 9.75\,O_2(\mathrm{g}) = 9CO_2(\mathrm{g}) + 4.5H_2O(\mathrm{l}) + 0.5\,N_2(\mathrm{g}) \qquad (5.1.3.1)$$

Provided that the water content in the sample can be checked, especially by means of determination of the mass of carbon dioxide produced in combustion, hippuric acid fulfills the requirements of a test substance for the combustion calorimetry of compounds with a relatively low nitrogen content.

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5.1.4. $\Delta_c U^0$, acetanilide

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	acetanilide (C_8H_9ON): 135.1656 $\mathrm{g\,mol^{-1}}$; [103-84-4]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static or rotating oxygen-bomb calorimeter (the latter is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(31234.0 \pm 5.0)\ \mathrm{J\,g^{-1}}$
Contributors to the previous version	E.S. Domalski, A.J. Head
Contributor to this version	An Xu-wu

5.1.4.1. Intended usage Energies of combustion in oxygen of most compounds containing C, H, O, N can be measured with the aid of a rotating-bomb calorimeter [1,2]. It has been noticed [1] that the conversion of the formed nitrogen oxides into nitric acid is slow in the combustion experiment, so a static-bomb calorimeter can be used only for the compounds of low nitrogen content of which the nitric acid correction is small. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and their experimental procedure by combustion of a test material of known energy of combustion. Acetanilide was recommended for this purpose by Johnson [3]; it is a test material for the combustion calorimetry of C, H, O, N compounds.

5.1.4.2. Sources of supply and/or methods of preparation A suitable material of highly pure acetanilide is available from commercial source (e.g. Aldrich: 99.95%) or can be obtained by sublimation or zone refining [4] of an analytical grade reagent (e.g. Fluka: 99.5+%).

5.1.4.3. Pertinent physicochemical data Johnson [3] has determined the energy of combustion of acetanilide (NBS SRM 141B) using an adiabatic rotating-bomb calorimeter and reported a value of $-(31\,234.2 \pm 6.9)\,\mathrm{J\,g^{-1}}$. Sato-Toshima et al. [5] have verified Johnson's result and given a new value $-(31\,233.7 \pm 7.4)\,\mathrm{J\,g^{-1}}$ by using a conventional static-bomb calorimeter. Thus the mean value, $-(31\,234.0 \pm 5.0)\,\mathrm{J\,g^{-1}}$, is recommended as the specific energy of combustion of acetanilide at 298.15 K for the reaction:

$$C_8H_9ON(cr) + 9.75\,O_2(g) = 8CO_2(g) + 4.5H_2O(l) + 0.5\,N_2(g) \qquad (5.1.4.1)$$

This value is also supported by the value calculated from the enthalpy of the reaction between aniline and acetic anhydride and the enthalpies of formation of these two substances, viz. $-31\,234\,\mathrm{J\,g^{-1}}$ [6]. Acetanilide as a reference material for the combustion calorimetry of substances with relatively low nitrogen content offers advantages over hippuric acid in being readily available free from water.

References

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[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.
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5.1.5. $\Delta_c U^0$, nicotinic acid

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	nicotinic acid ($C_6H_5O_2N$): 123.1112 $\mathrm{g\,mol^{-1}}$; [59-67-6]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static or rotating oxygen-bomb calorimeter (the latter is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(22\,186.3 \pm 3.0)\,\mathrm{J\,g^{-1}}$
Contributor to this version	An Xu-wu

5.1.5.1. Intended usage Energies of combustion in oxygen of most compounds containing C, H, O, N can be measured with the aid of a rotating-bomb calorimeter [1,2]. It has been noticed [1] that the conversion of the formed nitrogen oxides into nitric acid is slow in the combustion experiment, so a static-bomb calorimeter can be used only for the compounds of low nitrogen content of which the nitric acid correction is small. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and their experimental procedure by combustion of a test material of known energy of combustion. Nicotinic acid was recommended for this purpose [1]; it is a test material for the combustion calorimetry of C, H, O, N compounds.

5.1.5.2. Sources of supply and/or methods of preparation A suitable material of highly pure nicotinic acid is available from NIST as SRM 2151 as a reference material for organic microanalysis or can be prepared by recrystallization and sublimation in vacuo [4] from commercial material (e.g. Fluka: 99.5+%).

5.1.5.3. Pertinent physicochemical data Johnson [3] has determined the energy of combustion of nicotinic acid (NBS SRM 141B) using an adiabatic rotating-bomb calorimeter and reported a value of $-(22\,185.6 \pm 4.6)\,\mathrm{J\,g^{-1}}$. Sato-Toshima et al. [4] have verified Johnson's result and given a new value, $-(22\,186.9 \pm 3.9)\,\mathrm{J\,g^{-1}}$, by using a conventional static-bomb calorimeter. Thus the mean value, $-(22\,186.3 \pm 3.0)\,\mathrm{J\,g^{-1}}$, is recommended as the specific energy of combustion of nicotinic acid at 298.15 K for the reaction:

$$\mathrm{C_6H_5O_2N(cr)} + 7.25\,\mathrm{O_2(g)} = 6\mathrm{CO_2(g)} + 2.5\mathrm{H_2O(l)} + 0.5\,\mathrm{N_2(g)} \qquad (5.1.5.1)$$

References

[1] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Pergamon, Oxford, 1979.

[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.

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5.1.6. $\Delta_c U^0$, *1,2,4-triazole*

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	1,2,4-triazole ($\mathrm{C_2H_3N_3}$): 69.0660 $\mathrm{g\,mol^{-1}}$; [288-88-0]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(19204.2 \pm 4.1)\,\mathrm{J\,g^{-1}}$
Contributor to this version	An Xu-wu

5.1.6.1. Intended usage Energies of combustion in oxygen of most compounds containing C, H, O and N of high content can be measured with the aid of a rotating-bomb calorimeter [1,2]. It has been noticed [1] that the conversion of the formed nitrogen oxides into nitric acid is slow in the combustion experiment, so a check for significant quantities of nitrogen oxides in the bomb-gas cannot be overlooked after the combustion experiment. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and of the experimental procedure by combustion of a test material of known energy of combustion. 1,2,4-Triazole is recommended as a test material for the combustion calorimetry of C, H, O, N compounds containing such a large proportion of nitrogen.

5.1.6.2. Sources of supply and/or methods of preparation A suitable material can be obtained by recrystallization from ethanol [3] of the analytical grade reagent (e.g. Fluka: 99+%).

5.1.6.3. Pertinent physicochemical data Jiménez et al. [3] determined the energy of combustion of a sample of 1,2,4-triazole for which the certified mass fraction purity was better than 0.999 and reported the value $-(1326.3 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$ at 298.15 K for the energy of the reaction:

$$\mathrm{C_2H_3N_3(cr)} + 2.75\,\mathrm{O_2(g)} = 2\mathrm{CO_2(g)} + 1.5\mathrm{H_2O(l)} + 1.5\,\mathrm{N_2(g)} \qquad (5.1.6.1)$$

This value is in good agreement with that determined by Aleksandrov et al., $-(1326.9 \pm 0.9)\,\mathrm{kJ\,mol^{-1}}$ [4]. A weighted mean value $-(19\,204.2 \pm 4.1)\,\mathrm{J\,g^{-1}}$ is recommended for the specific energy of combustion.

References

[1] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Pergamon, Oxford, 1979.

[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.

[3] P. Jiménez, M.V. Roux, C. Turrión, J. Chem. Thermodyn. 21 (1989) 759.

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5.1.7. $\Delta_c U^0$, *urea*

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\ kg^{-1}}$or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	urea (CH_4ON_2): 60.0556 $\mathrm{g\,mol^{-1}}$; [57-13-6]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(10\,539 \pm 5)\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	Yu.I. Aleksandrov, G.T. Armstrong, A.J. Head, B.N. Oleinik
Contributor to this version	An Xu-wu

5.1.7.1. Intended usage Energies of combustion in oxygen of most compounds containing C, H, O and N of high content can be measured with the aid of a rotating-bomb calorimeter [1,2]. It has been noticed [1] that the conversion of the formed nitrogen oxides into nitric acid is slow in the combustion experiment, so a check for significant quantities of nitrogen oxides in the bomb-gas cannot be overlooked after the combustion experiment. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and of the experimental procedure by combustion of a test material of known energy of combustion. Urea is recommended as a test material for the combustion calorimetry of C, H, O, N compounds containing such a large proportion of nitrogen that complete combustion can only be obtained by the use of auxiliary materials such as benzoic acid or paraffin oil.

5.1.7.2. Sources of supply and/or methods of preparation A suitable material can be obtained by recrystallization of the analytical grade reagent (e.g. Fluka: 99.5+%, Sigma: 99.5%). Urea with certified energy of combustion is obtained from NIST as SRM 2152.

5.1.7.3. Pertinent physicochemical data Johnson [3] determined the energy of combustion of NIST reference samples of urea (SRM 912) for which the certified mass fraction purity was 0.997 but probably approached 0.999, since he showed the moisture content to be considerably lower than the certified value. He used benzoic acid as the auxiliary material and reported the value $-(10540.6 \pm 2.8)\ \mathrm{J\,g^{-1}}$ at 298.15 K for the energy of the reaction:

$$CH_4ON_2(cr) + 1.5\,O_2(g) = CO_2(g) + 2H_2O(l) + N_2(g) \qquad (5.1.7.1)$$

Johnson's value is in good agreement with that $-10\,537\ \mathrm{J\,g^{-1}}$ selected by Cox and Pilcher [4] from the results of earlier studies in which the purity of the urea was not established and in which paraffin oil was used as the auxiliary substance. The agreement between determinations by different workers using different sources of urea and different auxiliary materials supports the use of urea as a reference material and the value $-(10539 \pm 5)\ \mathrm{J\,g^{-1}}$ (the uncertainty is estimated) is recommended for the specific energy of combustion. The use of urea has, however, been criticized (on the grounds of the alleged thermal instability and hygroscopicity) by Aleksandrov et al. [5], who suggest that 1,2,4-triazole would be a more suitable reference material for substances of high nitrogen content.

References

[1] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Pergamon, Oxford, 1979.

[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.

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[4] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
[5] Yu.I. Aleksandrov, T.R. Osipova, V.F. Ushcevich, S.V. Murashova, B.N. Oleinik, Termodin. Org. Soedin. Gor'kii 8 (1979) 65.

5.1.8. $\Delta_c U^0$, *thianthrene*

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	thianthrene ($C_{12}H_8S_2$): 216.3275 $\mathrm{g\,mol^{-1}}$; [92-85-3]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(33468 \pm 4)\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	J.D. Cox, E.S. Domalski, A.J. Head, O. Riedel
Contributor to this version	An Xu-wu

5.1.8.1. Intended usage Energies of combustion in oxygen of most organic compounds containing sulfur can be accurately measured with the aid of a platinum-lined rotating-bomb calorimeter [1–4]. To ensure formation of a well-defined final state, water should be placed in the bomb and sufficient gaseous nitrogen (not less than 2.5%) should be present in the compressed oxygen so that the nitrogen oxides formed during the combustion process may catalyze the oxidation of all the sulfur to the S^{VI} state. It is important to ensure that the ratio between the number of moles of combined hydrogen and of combined sulfur exceeds two in the combustion material. Thus for a compound with a high proportion of sulfur it may be necessary to burn an auxiliary hydrogen-containing compound to achieve the necessary hydrogen to sulfur ratio. The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and of the experimental procedure by combustion of a test material of known energy of combustion. Thianthrene is recommended as a test material for the combustion calorimetry of C, H, S compounds.

5.1.8.2. Sources of supply and/or methods of preparation A suitable sample of thianthrene can be prepared by recrystallization, sublimation and fraction freezing [5] or by zone refining [6] from commercial material (e.g. Aldrich: 99%). Material certified for enthalpy of combustion can be purchased from NIST as SRM 1656.

5.1.8.3. Pertinent physicochemical data The suitability of thianthrene as a reference material in combustion calorimetry of sulfur compounds is well established. The results of five concordant determinations of the energy of combustion have been summarized by Johnson [6]. All five values fall within the range 15 $\mathrm{J\,g^{-1}}$ and yield a weighted mean of $-(33468 \pm 4)\ \mathrm{J\,g^{-1}}$ at 298.15 K which applies to the reaction:

$$\begin{aligned} &C_{12}H_8S_2(\mathrm{cr}) + 17O_2(\mathrm{g}) + 228H_2O(\mathrm{l}) \\ &\quad = 12CO_2(\mathrm{g}) + 2[H_2SO_4(115H_2O)](\mathrm{l}) \end{aligned} \tag{5.1.8.1}$$

Masuda et al. [7] measured the combustion energy of thianthrene (a SRM 1656 sample of NIST (USA)) and found $-(33464 \pm 12)\ \mathrm{J\,g^{-1}}$; Sabbah and El Watik [8] also reported a result of $-(33484 \pm 12)\ \mathrm{J\,g^{-1}}$ (mean ± s.d.m.) using a micro-bomb calorimeter. These values are in agreement with the recommended value. The values for the energies of combustion for reactions in which the concentration of the final sulfuric acid solution is other than $H_2SO_4(115H_2O)$ may be deduced from tabulated enthalpy of formation data [9,10]. It should be noted that the differences between enthalpies of formation of $H_2SO_4(nH_2O)$ listed in [9] yield reliable enthalpies of dilution, although the enthalpies of formation should be made more negative by 335 $\mathrm{J\,mol^{-1}}$ to be compatible with CODATA 1977 values [11].

References

[1] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.
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[10] V.P. Glushko (Ed.), Termicheskie Konstanty Veshchestv, Vol. II, Akademiya Nauk SSSR, VINITI, Moscow, 1966, Table 17.
[11] CODATA Recommended Key Values for Thermodynamics, 1977, J. Chem. Thermodyn. 10 (1978) 903.

5.1.9. $\Delta_c U^0$, 4-fluorobenzoic acid

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	4-fluorobenzoic acid ($C_7H_5O_2F$): 140.1139 $\mathrm{g\,mol^{-1}}$; [456-22-4]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(21860 \pm 4)\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	Yu.I. Aleksandrov, J.D. Cox, E.S. Domalski, A.J. Head, B.N. Oleinik, O. Riedel
Contributor to this version	An Xu-wu

5.1.9.1. Intended usage Energies of combustion in oxygen of most organic compounds containing fluorine can be accurately measured with the aid of a platinum-lined rotating-bomb calorimeter [1–3]. Sufficient water should be placed in the bomb initially so that the solution of hydrofluoric acid obtained after the combustion may have a concentration of not more than 5 $\mathrm{mol\,dm^{-3}}$. The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion. 4-Fluorobenzoic acid is recommended as a test material for the combustion of C, H, O, F compounds. Combustion reactions of fluorine compounds in which the atomic ratio of hydrogen to fluorine is equal to or greater than unity differ from those of compounds in which the atomic ratio is less than unity. Thus the reactions of the former compounds yield hydrogen fluoride as the sole fluorine-containing product, whereas the reactions of the latter compounds yield hydrogen fluoride and carbon tetrafluoride. Therefore 4-fluorobenzoic acid serves as a test material only for C, H, O, F compounds with hydrogen to fluorine ratio equal to or greater than unity.

5.1.9.2. Sources of supply and/or methods of preparation A suitable sample may be obtained by zone refining [4,5] from commercial material (e.g. Aldrich: 99%, Sigma: 98%). Johnson and Prosen [6] have pointed out that salicylic acid is a possible contaminant of 4-fluorobenzoic acid which can remain undetected by several analytical methods; they therefore recommended determination of hydrogen fluoride in the combustion products. Pure sample can also be obtained from NIST as a microanalytical standard SRM 2143.

5.1.9.3. Pertinent physicochemical data The suitability of 4-fluorobenzoic acid as a reference substance in combustion calorimetry has been established by three groups of workers [4–6] who obtained concordant values for the energy of the reaction:

$$\begin{aligned} &C_7H_5O_2F(\mathrm{cr}) + 7O_2(\mathrm{g}) + 18H_2O(\mathrm{l}) \\ &\quad = 7\,CO_2(\mathrm{g}) + HF(20\,H_2O)(\mathrm{l}) \end{aligned} \qquad (5.1.9.1)$$

The published work has been assessed by Cox [7] who recommends the selected value of $-(21\,861 \pm 4)\ \mathrm{J\,g^{-1}}$ for the standard energy of combustion at 298.15 K based on $HF(50H_2O)(\mathrm{l})$ as the reaction product. When correcting to $HF(20H_2O)(\mathrm{l})$ as the reaction product, the recommended value is changed to $-(21\,860 \pm 4)\ \mathrm{J\,g^{-1}}$.

References

[1] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

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5.1.10. $\Delta_c U^0$, pentafluorobenzoic acid

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	pentafluorobenzoic acid ($C_7HO_2F_5$): 212.0758 $\mathrm{g\,mol^{-1}}$; [602-94-8]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(12060.4 \pm 4.8)\ \mathrm{J\,g^{-1}}$
Contributors to the previous versions	J.D. Cox, A.J. Head
Contributor to this version	An Xu-wu

5.1.10.1. Intended usage Energies of combustion in oxygen of most organic compounds containing fluorine can be accurately measured with the aid of a platinum-lined rotating-bomb calorimeter [1–3]. Sufficient water should be placed in the bomb initially so that the solution of hydrofluoric acid obtained after the combustion may have a concentration of not more than 5 $\mathrm{mol\,dm^{-3}}$. The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and the experimental procedure by the combustion of a test material of known energy of combustion. Pentafluorobenzoic acid is recommended as a test material for the combustion calorimetry of C, H, O, F compounds. Combustion reactions of fluorine compounds in which the atomic ratio of hydrogen to fluorine is greater than or equal to unity differ from those of compounds in which the atomic ratio is less than unity. Thus the former compounds yield hydrogen fluoride as the sole fluorine-containing product, whereas the latter compounds yield a mixture of hydrogen fluoride and carbon tetrafluoride. Therefore pentafluorobenzoic acid serves as a test material only for C, H, F, O compounds with an atomic ratio of hydrogen to fluorine less than unity.

5.1.10.2. Sources of supply and/or methods of preparation Cox et al. [4] showed that a suitable sample of pentafluorobenzoic acid could be obtained by zone refining of a commercial sample (e.g. Aldrich: 99%).

5.1.10.3. Pertinent physicochemical data Cox et al. [4] suggested there was a need for a reference material for the study of the combustion of compounds with a low hydrogen to fluorine ratio and showed that pentafluorobenzoic acid possessed the necessary properties. The value they reported and revised [5], viz. $-(12\,060.4 \pm 4.8)\ \mathrm{J\,g^{-1}}$, at 298.15 K relates to the reaction:

$$\begin{aligned} &C_7HO_2F_5(\mathrm{Cr}) + 5\,O_2(\mathrm{g}) + 102\,H_2O(1) \\ &\quad = 7\,CO_2(\mathrm{g}) + 5[\mathrm{HF}(20\,H_2O)](1) \end{aligned} \tag{5.1.10.1}$$

It will be noted that in conformity with common practice, the equation is written as though no carbon tetrafluoride is formed. In reality, considerable amounts of carbon tetrafluoride are formed unless a hydrogen-containing auxiliary compound is burnt along with the pentafluorobenzoic acid. If enough hydrogen-containing compound is taken to ensure that the hydrogen to fluorine atomic ratio greatly exceeds unity and if the two compounds are intimately mixed before combustion, then no carbon tetrafluoride will be formed. However, this causes the majority of the energy evolved to come from the auxiliary which is an undesirable state of affairs. Cox et al. chose to perform two series of experiments, in the first of which hydrocarbon oil, used as auxiliary, contributed about 40% of the heat, whilst in the second benzoic acid, used as auxiliary, contributed about 60% of the heat. In both series of experiments it was necessary to determine the amount of carbon tetrafluoride formed and to correct for it. The determination of the amount of carbon tetrafluoride was based on the shortfall between the number of moles of combined carbon taken and the carbon dioxide found after the combustion. It would be desirable for further measurements of the energy of combustion of pentafluorobenzoic acid to be made.

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[1] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

[2] H.A. Skinner (Ed.), Experimental Thermochemistry, Vol. II, Wiley, New York, 1962.

[3] S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Pergamon, Oxford, 1979.

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5.1.11. $\Delta_c U^0$, 4-chlorobenzoic acid

Physical property	energy of combustion
Units	J mol^{-1} or kJ mol^{-1} (molar energy of combustion, $\Delta_c U_m^o$); J kg^{-1}or J g^{-1} (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	4-chlorobenzoic acid ($C_7H_5O_2Cl$): 156.5682 g mol^{-1}; [74-11-3]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter (a tantalum-lined bomb is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(19566.4 \pm 1.5)$ J g^{-1}
Contributors to the previous versions	Yu.I. Aleksandrov, J.D. Cox, E.S. Domalski, A.J. Head, B.N. Oleinik, O. Riedel, S. Sunner
Contributor to this version	An Xu-wu

5.1.11.1. Intended usage Energies of combustion in oxygen of most organic compounds containing chlorine can be accurately measured with the aid of a rotating-bomb calorimeter [1–3]. In order that the sole chlorine-containing product should be a hydrochloric acid solution, sufficient reducing agent (e.g. arsenious oxide solution or hydrazine hydrochloride solution) should be placed in the bomb before combustion is initiated. There is evidence that arsenious oxide solution can oxidize and hydrazine hydrochloride solution can decompose before a combustion experiment under the conditions prevailing in some platinum-lined bombs. Experimenters should always check to see whether these reactions, which are catalyzed by the platinum liner, are occurring under their experimental conditions. These side reactions can always be avoided by replacing platinum with tantalum.

The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. Many workers, however, like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion. 4-Chlorobenzoic acid is recommended as a test material for the combustion calorimetry of C, H, O, Cl compounds with an atomic ratio of hydrogen to chlorine equal to or greater than unity.

5.1.11.2. Sources of supply and/or methods of preparation A sample of 4-chlorobenzoic acid of satisfactory purity may be obtained by repeated recrystallizations and vacuum sublimation of commercial material (e.g. Aldrich: 99%).

5.1.11.3. Pertinent physicochemical data The suitability of 4-chlorobenzoic acid as a reference substance for combustion calorimetry has been well established and the results of three groups of workers [4–6], which involved the use of both platinum-lined and tantalum-lined combustion bombs and both arsenious oxide and hydrazine hydrochloride as reducing agents, have been discussed by Cox [7]. The weighted mean calculated from these values of the energy of combustion is $-(19565.2 \pm 2.7)\,\mathrm{J\,g^{-1}}$ and applies to the reaction:

$$\begin{aligned} &C_7H_5O_2Cl(cr) + 7\,O_2(g) + 598\,H_2O(l) \\ &\quad = 7\,CO_2(g) + HCl(600\,H_2O)(l) \qquad (5.1.11.1) \end{aligned}$$

Aleksandrov et al. [8] selected six values as being the most reliable from the data determined before 1981 and calculated a mean value $-(19\,565 \pm 1.9)\,\mathrm{J\,g^{-1}}$. Later determination values, $-(19\,557.4 \pm 7.0)\,\mathrm{J\,g^{-1}}$ [9], $-(19\,572.7 \pm 7.7)\,\mathrm{J\,g^{-1}}$ [10], $-(19\,566.6 \pm 9.6)\,\mathrm{J\,g^{-1}}$ (mean ± s.d.m.) [11], $-(19\,579.6 \pm 3.3)\,\mathrm{J\,g^{-1}}$ (mean ± s.d.m.) [12] and $-(19\,573.2 \pm 4.9)\,\mathrm{J\,g^{-1}}$ [13] are in agreement with these selected values in their uncertainty intervals. From eleven concordant results we calculated a weighted mean, $-(19566.4 \pm 1.5)\,\mathrm{J\,g^{-1}}$, as the recommended value.

Values for the energies of combustion in which the concentration of the final hydrochloric acid solution is other than $HCl(600H_2O)$ may be derived from tabulated enthalpy of formation data [14,15]. It should be noted that the differences between enthalpies of formation of $HCl(nH_2O)$ listed in [14] yield reliable enthalpies of dilution although the enthalpies of formation should be made more positive by $79\,\mathrm{J\,mol^{-1}}$ to be compatible with CODATA (1977) values [16].

References

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5.1.12. $\Delta_c U^0$, 4-bromobenzoic acid

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U^0_m$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	4-bromobenzoic acid ($C_7H_5O_2Br$): 201.0195 $\mathrm{g\,mol^{-1}}$; [586-76-5]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter (a tantalum-lined bomb is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(15367.0 \pm 4.2)\,\mathrm{J\,g^{-1}}$ $\{Br_2(l)$ as the combustion product$\}$; $\Delta_c u^0$ (298.15 K) $= -(15261.0 \pm 4.2)\,\mathrm{J\,g^{-1}}$ $\{HBr(600H_2O)(l)$ as the combustion product$\}$
Contributor to this version	An Xu-wu

5.1.12.1. Intended usage Energies of combustion in oxygen of most organic compounds containing bromine can be accurately measured with the aid of a rotating-bomb calorimeter [1–3]. Sufficient reductant (e.g. arsenious oxide solution) is used in the practical combustion experiments to ensure that the sole bromine-containing product is hydrobromic acid in solution. However, Bjellerup [4] chose liquid bromine in its standard state as the product of standard combustion reaction to calculate the energy of combustion of bromocompounds. There is evidence that arsenious oxide solution can oxidize prior to combustion under the conditions prevailing in some platinum-lined bombs. Experimenters should always check to see whether this reaction which is catalyzed by the platinum liner is occurring under their experimental conditions. This side reaction can always be avoided by replacing platinum by tantalum.

The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. Many workers, however, like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion. 4-Bromobenzoic acid is recommended as a test material for the combustion calorimetry of C, H, O, Br compounds with an atomic ratio of hydrogen to bromine equal to or greater than unity.

5.1.12.2. Sources of supply and/or methods of preparation A suitable sample of 4-bromobenzoic acid can be obtained by repeated sublimation in vacuo at 373 K from commercial material [5] (e.g. Merck: >99% or Fluka: 99%).

5.1.12.3. Pertinent physicochemical data Bjellerup [4] determined the energy of combustion of pure 4-bromobenzoic acid with a little paraffin oil as an auxiliary substance by using a rotating-bomb calorimeter. The result, after corrections using recent auxiliary thermal data, was $-(15\,372 \pm 10)\,\mathrm{J\,g^{-1}}$ [3]. Ferrão et al. [6] also reported a value, $-(15\,366.4 \pm 4.6)\,\mathrm{J\,g^{-1}}$, which was obtained from burning a BDH sample without any auxiliary oil in a tantanum-lined rotating-bomb calorimeter. Both results are in agreement with each other. A weighted mean value, $-(15\,367.0 \pm 4.2)\,\mathrm{J\,g^{-1}}$, is recommended as the specific energy of combustion of 4-bromobenzoic acid at 298.15 K for the reaction:

$$\begin{aligned}&\mathrm{C_7H_5O_2Br(Cr) + 7.25\,O_2(g)}\\&\quad\mathrm{= 7CO_2(g) + 2.5H_2O(l) + 0.5\,Br_2(l)}\end{aligned} \quad (5.1.12.1)$$

Sabbah and Rojas Aguilar [5] confirmed the recommended value with their determined value, $-(15\,369 \pm 6)\,\mathrm{J\,g^{-1}}$ (mean ± s.d.m.).

Some research workers prefer to choose HBr-$(600H_2O)$ instead of liquid bromine as the product of combustion reaction so that the energy of combustion associated with the standard-states reaction is close to the experimentally determined quantity and the energy correction associated with the oxidation of hydrobromic acid to elemental bromine according to the following reaction can be avoided:

$$\mathrm{HBr(aq.) + 0.25\,O_2(g) = 0.5\,H_2O(l) + 0.5\,Br_2(l)} \quad (5.1.12.2)$$

After recalculation using recent auxiliary thermal data [7,8], the recommended specific energy of combustion of 4-bromobenzoic acid is changed to $-(15261.0 \pm 4.2)\,\mathrm{J\,g^{-1}}$ for the reaction (at 298.15 K):

$$\begin{aligned}&\mathrm{C_7H_5O_2Br(cr) + 7O_2(g) + 598\,H_2O(l)}\\&\quad\mathrm{= 7CO_2(g) + HBr(600\,H_2O)(l)}\end{aligned} \quad (5.1.12.3)$$

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5.1.13. $\Delta_c U^0$, 2-iodobenzoic acid

Physical property	energy of combustion
Units	$J\,mol^{-1}$ or $kJ\,mol^{-1}$ (molar energy of combustion, $\Delta_c U_m^0$); $J\,kg^{-1}$ or $J\,g^{-1}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	2-iodobenzoic acid ($C_7H_5O_2I$): 248.0200 g mol^{-1}; [88-67-5]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	static or rotating oxygen-bomb calorimeter (the latter is preferable)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(12771.3 \pm 2.4)\,J\,g^{-1}$.
Contributor to this version	An Xu-wu

5.1.13.1. Intended usage Energies of combustion in oxygen of most organic compounds containing iodine can be accurately measured with the aid of a static- or a rotating-bomb calorimeter [1,2]. A bomb lined with platinum should be used to eliminate significant corrosion. It has been found that the theoretical quantity of elemental iodine is formed in the combustion reaction and the quantity of iodic acid formed is negligibly small. The thermochemical corrections for the energy of sublimation of iodine in the gas phase and the energy of the solution of iodine in the liquid phase are relatively insignificant. However, the assumption that only elemental iodine is formed in the combustion reaction should be confirmed by determining the total amount of it in the bomb.

The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. Many workers, however, like to check the accuracy of the benzoic acid calibration and their experimental procedure by the combustion of a test material of known energy of combustion. 2-Iodobenzoic acid is recommended as a test material for the combustion calorimetry of C, H, O, I compounds.

5.1.13.2. Sources of supply and/or methods of preparation A sample of 2-iodobenzoic acid of satisfactory purity can be obtained by repeated sublimation in vacuo from commercial material (e.g. Aldrich: 99+%).

5.1.13.3. Pertinent physicochemical data Ribeiro da Silva et al. [3] determined the energy of combustion of 2-iodobenzoic acid by means of two methods: (a) using a rotating-bomb calorimeter (but without rotation) with 1 cm^3 of H_2O in the bomb before the combustion, (b) using a rotating-bomb calorimeter with 10 cm^3 of KI (aq, 0.9 mol dm^{-3}) in the bomb before the combustion. The energy equivalent of the rotating-bomb calorimeter was re-calibrated by a series of comparison experiments in which benzoic acid was burnt in the presence of a mass 1.0 g of solid iodine sealed in polyester bags and 10 cm^3 of KI (aq, 0.9 mol dm^{-3}). The obtained results (mean ± s.d.m.) are, respectively: (a) $-(12770.7 \pm 1.3)\,J\,g^{-1}$ and (b) $-(12774.9 \pm 1.8)\,J\,g^{-1}$. According to the convention of assignment of uncertainties to thermochemical data [1], the uncertainties of these two values were recalculated from the standard deviations of certified value of benzoic acid, of energy equivalent of the calorimeter and of combustion energy of 2-iodobenzoic acid: $\pm 3.2\,J\,g^{-1}$ and $\pm 4.4\,J\,g^{-1}$, respectively. An earlier determination was made by Karlsson and was corrected by Smith [4]: $-(12\,767 \pm 6)\,J\,g^{-1}$. An uncertainty of $\pm 6\,J\,g^{-1}$ was estimated by Cox [5] for Karlsson's result of 4-iodobenzoic acid. The same uncertainty was designated here for Karlsson's result of 2-iodobenzoic acid. The weighted mean calculated from these concordant values of the energy of combustion is $-(12771.3 \pm 2.4)\,J\,g^{-1}$ and applies to the reaction:

$$C_7H_5O_2I(cr) + 7.25\,O_2(g) = 7\,CO_2(g) + 2.5\,H_2O(l) + 0.5\,I_2(cr) \quad (5.1.13.1)$$

Recently Sabbah and Rojas Aguilar [6] reported a result $-(12793.7 \pm 6.9)\,J\,g^{-1}$ (mean ± s.d.m.) using a micro-bomb calorimeter.

References

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5.1.14. $\Delta_c U^0$, triphenylphosphine oxide

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	triphenylphosphine oxide ($C_{18}H_{15}OP$): $278.2903\,\mathrm{g\,mol^{-1}}$; [791-28-6]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	rotating oxygen-bomb calorimeter (with a gold crucible)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(35\,789.3 \pm 4.5)\,\mathrm{J\,g^{-1}}$
Contributor to the previous version	A.J. Head
Contributor to this version	An Xu-wu

5.1.14.1. Intended usage Combustion of organophosphorus compounds in earlier work did not attain the precision and accuracy associated with modern experimental thermochemistry, partly because complete combustion was often difficult to achieve and partly because a mixture of oxyacids of phosphorus was produced. Harrop and Head [1] applied the techniques of rotating-bomb calorimetry [2] to the combustion of triphenylphosphine oxide. The substance was burnt completely when supported on a gold dish (platinum was attacked). The phosphorus-containing reaction products determined by using a paper-chromatographic technique were either a mixture of orthophosphoric acid and polyphosphoric acids (when water was used in the bomb) or orthophosphoric acid alone (when perchloric acid was used). It is suggested that these techniques are likely to be applicable to other C, H, O, P compounds and that triphenylphosphine oxide would then be a suitable reference material for checking the experimental procedure employed.

5.1.14.2. Sources of supply and/or methods of preparation A suitable sample of triphenylphosphine oxide can be obtained by recrystallization and zone refining of commercial material (e.g. Fluka: 98+%, Aldrich: 98%).

5.1.14.3. Pertinent physicochemical data Harrop and Head [1] established that triphenylphosphine oxide fulfils the requirements of a reference material for combustion calorimetry and reported the value $-(35\,789.9 \pm 6.0)\,\mathrm{J\,g^{-1}}$ at 298.15 K for the specific energy of the reaction:

$$\begin{aligned} &C_{18}H_{15}OP(cr) + 22.5\,O_2(g) \\ &\quad = 18\,CO_2(g) + H_3PO_4(6\,H_2O)(l) \qquad (5.1.14.1) \end{aligned}$$

This value was revised slightly by using new auxiliary data to $-(35\,789 \pm 6)\,\mathrm{J\,g^{-1}}$ [3]. Kirklin and Domalski [3] confirmed the above result by using an aneroid adiabatic rotating-bomb calorimeter. Determination of the phosphorus-containing reaction products was improved by using ion chromatography instead of paper chromatography. Their reported value, $-(35\,789.6 \pm 6.8)\,\mathrm{J\,g^{-1}}$, is in excellent agreement with Harrop and Head's result. Therefore, a selected value, $-(35\,789.3 \pm 4.5)\,\mathrm{J\,g^{-1}}$ is recommended.

References

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5.2. Combustion of liquids in oxygen

5.2.1. $\Delta_c U^0$, 2,2,4-trimethylpentane

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)

Recommended reference material	2,2,4-trimethylpentane (C_8H_{18}): 114.2309 g mol^{-1}; [540-84-1]
Classification	secondary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	liquid
Apparatus used	static or rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(47\,712 \pm 12)$ J g^{-1}
Contributors to the previous versions	G.T. Armstrong, J.D. Cox, O. Riedel
Contributor to this version	An Xu-wu

5.2.1.1. Intended usage Energies of combustion in oxygen of most compounds containing no elements other than C, H can be accurately measured with the aid of a static-calorimeter [1–3]. The energy equivalent of the calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration and of the experimental procedure by the combustion of a test material of known energy of combustion. 2,2,4-Trimethylpentane is recommended as a test material for the combustion calorimetry of liquid hydrocarbons that require encapsulation (in glass or plastic [1–3]) before combustion. 2,2,4-Trimethylpentane therefore serves as a test material in the establishment of the calorific values of liquid gasoline fuels.

5.2.1.2. Sources of supply and/or methods of preparation A suitable sample can be obtained by fractional distillation of commercial products (e.g. Aldrich: 99.8%, Sigma: 99%).

5.2.1.3. Pertinent physicochemical data The value quoted by Cox and Pilcher [1] for the standard molar enthalpy of combustion of 2,2,4-trimethylpentane is $-(5461.4 \pm 1.5)$ kJ mol^{-1} at 298.15 K which applies to the reaction:

$$C_8H_{18}(l) + 12.5\,O_2(g) = 8\,CO_2(g) + 9\,H_2O(l) \tag{5.2.1.1}$$

The corresponding value of the standard specific energy of combustion is $-(47\,712 \pm 12)$ J g^{-1}.

References

[1] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

[2] F.D. Rossini (Ed.), Experimental Thermochemistry, Vol. I, Wiley, New York, 1956.

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5.2.2. $\Delta_c U^0$, *α,α,α-trifluorotoluene*

Physical property	energy of combustion
Units	J mol^{-1} or kJ mol^{-1} (molar energy of combustion, $\Delta_c U_m^0$); J kg^{-1} or J g^{-1} (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	α,α,α-trifluorotoluene ($C_7H_5F_3$): 146.1119 g mol^{-1}; [98-08-8]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	liquid
Apparatus used	rotating oxygen-bomb calorimeter
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(23052.4 \pm 2.6)$ J g^{-1}
Contributors to the previous version	J.D. Cox, A.J. Head
Contributor to this version	An Xu-wu

5.2.2.1. Intended usage Energies of combustion in oxygen of most organic compounds containing fluorine can be accurately measured with the aid of a platinum-lined rotating-bomb calorimeter [1–3]. Sufficient water should be placed in the bomb initially so that the solution of hydrofluoric acid obtained after the combustion may have a concentration of not more than 5 mol dm^{-3}. The energy equivalent of the rotating-bomb calorimeter will normally be established by combustion of the thermochemical-standard benzoic acid. However, it is desirable to check the accuracy of the benzoic acid calibration and the experimental procedure by the combustion of a test material of known energy of combustion. Combustion reactions of fluorine compounds in which the atomic ratio of hydrogen to fluorine is greater than or equal to unity differ from those in which the atomic ratio of hydrogen to fluorine is less than unity. Thus the former compounds yield hydrogen fluoride as the sole fluorine-containing product, whereas the latter compounds yield a mixture of hydrogen fluoride and carbon tetrafluoride. Cox proposed α,α,α-trifluorotoluene as a suitable reference material for the combustion of liquid C, H, F, (O, N) compounds containing moderate amounts of fluorine, which yield hydrogen fluoride as the sole fluorine-containing product and which need to be encapsulated before combustion [4].

5.2.2.2. Sources of supply and/or methods of preparation A very pure material could be obtained by fractional distillation [5] or by low-temperature zone refining [6] from commercial products (e.g. Aldrich: 99+%, Fluka: 99+%).

5.2.2.3. Pertinent physicochemical data Two separate determinations on material with mole fraction purity of 0.99999 have been made by Good et al. [5,7] using different methods of encapsulation (quartz ampules, necessitating the application of a thermal correction for attack by hydrofluoric acid, and polyester bags). No carbon tetrafluoride was detected in the reaction products. Kolesov et al. [8] made measurements on a sample of mole fraction purity 0.99984 (containing water as the only contaminant) and based the results on the mass of carbon dioxide produced. They used polyamide bags to encapsulate the sample for combustion and made two series of determinations using two different rotating-bomb calorimeters. Only a trace of carbon tetrafluoride was detected in the reaction products. From the three results Cox [4] selected a weighted mean, $-(23052.4 \pm 2.6)\,\mathrm{J\,g^{-1}}$, as the recommended value at 298.15 K for the standard energy of the reaction:

$$\begin{aligned} &C_7H_5F_3(l) + 7.5O_2(g) + 59\,H_2O(l) \\ &\quad = 7\,CO_2(g) + 3[HF(20\,H_2O)](l) \end{aligned} \tag{5.2.2.1}$$

Later, Erastov et al. [6] made a new determination for a sample of mole fraction purity greater than 0.9999. Terylene film bags were used to encapsulate the sample. The determined result, $-23058.6\,\mathrm{J\,g^{-1}}$, is concordant with the value recommended by Cox.

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5.3. Combustion of solids in fluorine

5.3.1. $\Delta_c U^0$, sulfur

Physical property	energy of combustion
Units	$\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$ (molar energy of combustion, $\Delta_c U_m^0$); $\mathrm{J\,kg^{-1}}$ or $\mathrm{J\,g^{-1}}$ (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	sulfur (rhombic): $32.066\,\mathrm{g\,mol^{-1}}$; [7704-34-9]
Classification	tertiary RM
Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	fluorine-bomb combustion calorimeter (with two-compartment reaction vessel)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(37946.1 \pm 6.2)\,\mathrm{J\,g^{-1}}$
Contributors to the previous version	J.D. Cox, A.J. Head
Contributor to this version	An Xu-wu

5.3.1.1. Intended usage Combustion calorimetry in fluorine is a powerful method for determining enthalpies of formation of a wide range of inorganic substances but it is a difficult technique. The restriction on materials of construction to those not attacked by fluorine, the need to use fluorine of higher purity than is normally available from commercial sources and the safety requirements, all make extra demands on the calorimetrist [1,2]. Fluorine-combustion calorimeters using high-pressure metal bombs are usually calibrated by means of the combustion of benzoic acid in oxygen. The considerable difference between the conditions used in calibration and in measurement makes the use of reference materials for combustion in fluorine particularly desirable. Sulfur has been proposed as a reference material for the combustion of substances which ignite spontaneously in fluorine and therefore require the use of a two-compartment bomb [1,3].

5.3.1.2. Sources of supply and/or methods of preparation Highly pure sample of sulfur may be obtained from commercial products (e.g. Fluka: 99.999+%, Aldrich: 99.998%). However, an analysis made recently by O'Hare et al. [4] showed that the earlier sulfur sample used (USBM-P1b, prepared at the NIST, asserted to be 99.999% pure) [5,6] contained 0.04% of unsuspected impurities and a purer sample of α, rhombic sulfur (the impurities were less than mass fraction 0.00001) can be obtained using a revised von Wartenberg technique with vacuum distillation [4]. Nevertheless, the energies of combustion of both the samples are concordant with each other and the uncertainty interval for the impure sample is a little larger due to the corrections for the impurities. Therefore a corresponding analysis of the commercial product is necessary before use.

5.3.1.3. Pertinent physicochemical data The earlier values have been reported for the standard energy at 298.15 K of the reaction:

$$S(\alpha,\ \text{rhombic}) + 3\,F_2(g) = SF_6(g) \qquad (5.3.1.1)$$

determined by fluorine combustion calorimetry using metal bombs: $-1214.3\,\text{kJ mol}^{-1}$ by Schröder and Sieben [7], $-(1213.1 \pm 1.3)\,\text{kJ mol}^{-1}$ by Leonidov et al. [8] and $-(1216.6 \pm 1.0)\,\text{kJ mol}^{-1}$ by O'Hare [5]. In addition, Hubbard et al. [1] reported an unpublished value of $-(1215.6 \pm 1.7)\,\text{kJ mol}^{-1}$ obtained by Gross and Hayman using glass reaction vessels. The lower precision associated with these values is due to the purity of sulfur and fluorine and the difficulties associated with fluorine-bomb calorimetry. O'Hare et al. have improved the precision of their measurements by using purer samples and refining their technique. Recently they determined [4] a value of $-(1216.68 \pm 0.26)\,\text{kJ mol}^{-1}$ for a new sample of sulfur (mole fraction purity 0.99999), re-determined a value of $-(1217.10 \pm 0.42)\,\text{kJ mol}^{-1}$ for the sample (USBM-P1b) and reported a revised value of $-(1216.71 \pm 0.48)\,\text{kJ mol}^{-1}$ based on the previous determination [6] of the sample (USBM-P1b). The three values are in good agreement with each other. (All the results quoted are based on the value $32.066\,\text{g mol}^{-1}$ for the molar mass of S) A weighted mean, $-(37\,946.1 \pm 6.2)\,\text{J g}^{-1}$, is selected as the recommended value for the specific energy of combustion of sulfur in fluorine. In addition, new precise determinations of this energy from other laboratories are encouraged.

References

[1] W.N. Hubbard, G.K. Johnson, V.Ya. Leonidov, in: S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chap. 12, Pergamon, Oxford, 1979.

[2] W.N. Hubbard, in: H.A. Skinner (Ed.), Experimental Thermochemistry, Chap. 6, vol. II, Wiley, New York, 1962.

[3] J.D. Cox, in: S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chap. 4, Pergamon, Oxford, 1979.

[4] P.A.G. O'Hare, S. Susman, K.J. Volin, S.C. Rowland, J. Chem. Thermodyn. 24 (1992) 1009.

[5] P.A.G. O'Hare, J.L. Settle, W.N. Hubbard, Trans. Faraday Soc. 62 (1966) 558.

[6] P.A.G. O'Hare, J. Chem. Thermodyn. 17 (1985) 349.

[7] J. Schröder, F.J. Sieben, Chem. Ber. 103 (1970) 76.

[8] V.Ya. Leonidov, V.S. Pervov, O.M. Gaisinskaya, L.I. Klyuev, Edokl. Akad. Nauk SSSR, Fiz. Khim. 211 (1973) 901.

5.3.2. $\Delta_c U^0$, *tungsten*

Physical property	energy of combustion
Units	J mol^{-1} or kJ mol^{-1} (molar energy of combustion, $\Delta_c U_m^0$); J kg^{-1} or J g^{-1} (specific energy of combustion, $\Delta_c u^0$)
Recommended reference material	tungsten (W): $183.84\,\text{g mol}^{-1}$; [7440-33-7]
Classification	secondary RM

Range of variables	298.15 K is the reference temperature normally employed
Physical state within the range	solid
Apparatus used	fluorine-bomb combustion calorimeter (with one- or two-compartment reaction vessel)
Recommended value	$\Delta_c u^0$ (298.15 K) $= -(9336.5 \pm 3.8)\ \mathrm{J\,g^{-1}}$
Contributors to the previous version	J.D. Cox, A.J. Head
Contributor to this version	An Xu-wu

5.3.2.1. Intended usage Combustion calorimetry in fluorine is a powerful method for determining enthalpies of formation of a wide range of inorganic substances but it is a difficult technique. The restriction on materials of construction to those not attacked by fluorine, the need to use fluorine of higher purity than is normally available from commercial sources and the safety requirements, all make extra demands on the calorimetrist [1,2]. Fluorine-combustion calorimeters using high-pressure metal bombs are usually calibrated by means of the combustion of benzoic acid in oxygen. The considerable difference between the conditions used in calibration and in measurement makes the use of reference materials for combustion in fluorine particularly desirable. Tungsten has been proposed as a suitable substance: in the solid state it is inert to highly purified fluorine at room temperature but undergoes smooth and virtually complete conversion to tungsten hexafluoride when heated [1,3]. Tungsten is suitable, therefore, for use in one- or two-compartment bombs and is also useful as an auxiliary material for the combustion of other substances in fluorine.

5.3.2.2. Sources of supply and/or methods of preparation Highly pure tungsten sheet and wire can be obtained from commercial products (e.g. Fluka: 99.99+%). For work of the highest accuracy it is important for complete analytical data to be provided so that thermal corrections for the combustion of impurities can be calculated.

5.3.2.3. Pertinent physicochemical data The two principal determinations, where both tungsten and fluorine were of high purity, gave results in close agreement at 298.15 K for the energy of the reaction:

$$\mathrm{W(s)} + 3\,\mathrm{F_2(g)} = \mathrm{WF_6(g)} \qquad (5.3.2.1)$$

viz. $\Delta_c U^0 = -(1716.8 \pm 1.7)\ \mathrm{kJ\,mol^{-1}}$ [4] and $-(1716.3 \pm 0.8)\ \mathrm{kJ\,mol^{-1}}$ [5], the molar mass of tungsten being taken as $183.85\ \mathrm{g\,mol^{-1}}$. A third determination, where the fluorine contained 1% of oxygen plus nitrogen [6], yielded a result consistent with the first two, $-(1717.5 \pm 2.1)\ \mathrm{kJ\,mol^{-1}}$. The weighted mean value $\Delta_c u^0$ (298.15 K) $= -(9336.5 \pm 3.8)\ \mathrm{J\,g^{-1}}$ is calculated from these three results as the recommended value for the specific energy of combustion of tungsten in fluorine.

References

[1] W.N. Hubbard, G.K. Johnson, V.Ya. Leonidov, in: S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chap. 12, Pergamon, Oxford, 1979.
[2] W.N. Hubbard, in: H.A. Skinner (Ed.), Experimental Thermochemistry, Chap. 6, Vol. II, Wiley, New York, 1962.
[3] J.D. Cox, in: S. Sunner, M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1: Combustion Calorimetry, Chap. 4, Pergamon, Oxford, 1979.
[4] P.A.G. O'Hare, W.N. Hubbard, J. Phys. Chem. 70 (1966) 3353.
[5] V.Ya. Leonidov, V.S. Pervov, L.I. Klyuev, O.M. Gaisinskaya, V.A. Medvedev, N.S. Nikolaev, Dokl. Akad. Nauk SSSR, Ser. Khim. 205 (1972) 349.
[6] J. Schröder, F.J. Sieben, Chem. Ber. 103 (1970) 76.

6. List of suppliers

- Accurate Chemical and Scientific Corp., 300, Shames Drive, Wesbury, NY 11590, USA, Website address: http://www.accurateantibodies.com/
- Agate Products Ltd, 2/4 Quintin Avenue Merton Park, London SW20 8LD, UK, E-mail: agate@bsnet.co.uk
- American Petroleum Institute, Standard Reference Materials, 2114 Doherty Hall, Carnegie-Mellon University, Pittsburgh, PA 15213-3890, USA, Website address: http://www.phillips 66.com/
- Bureau of Analysed Samples Ltd., Newham Hall, Newby, Middlesbrough, Cleveland TS8 9EA, UK, Website address: http://www.basrid.co.uk/

- ChemService, Inc, PO Box 3108, 660 Tower Lane, West Chester, PA, USA, Website address: http://www.chemservice.com/
- CLARA (Canadian Liquid Air, Ltd), 1155 Sherbrooke St West, Montreal, Que., H3A1H8 Canada, Website address: http://www.airliquide.com/
- Goodfellow Metals Ltd., Cambridge Science Park, Milton Road, Cambridge CB4 4DJ, UK, Website address: http://www.goodfellowcom/
- Indofine Chemical Co., PO Box 743, Sommerville, NJ 08876, USA, Website address: http://www.indofinechemical.com/
- International Research Liaison Office, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan, Website address: http://www.nimc.go.jp/
- Johnson Matthey Chemical Ltd., 74 Hatton Garden, London EC1P 1AE, UK, Website address: http://www.matthey.com/
- La Pine Scientific Co., PO Box 780, 13636 Western Avenue, Blue Island, IL 60406-0780, USA, Fax: +1-708-388-4084
- Materials Research Corporation, Route 303, Orangeburg, NY 10962, USA
- Matheson Gas Products, 932 Paterson Plank Rd, New Jersey 07073, USA
- Website address: http://www.nmg1.com/
- Metron Group/THM Inc., PO Box 736, Millburn, NJ 07041, USA, Website address: http://www.metrongroup.com/
- NIST (National Institute of Science and Technology), Office of Standards Reference Materials, Gaithersburg, MD 20899, USA, Website address: http://www.nist.gov/
- ORM (The Office of Reference Materials), Laboratory of the Government Chemist, Queens Road, Teddington, Middlesex TW11 0LY, UK, Website address: http://www.lgc.co.uk/
- Penta Mfg. Co., PO Box 1448, Fairfield, NJ 07007-1448, USA
- E-mail: pentamfg@msn.com
- Phillips Petroleum Co., Bartlesville, OK 74004, USA, Website address: http://www.phillips66.com/
- Polysciences, Inc., Warrington, PA 18976, USA, Website address: http://www.polysciences.com/
- Triple Crown America, 13 North Seventh St., Perkasie, PA 18944, USA, Fax: +1-215-453-2508
- Wiley Organics, 1245 South 6th Street, PO Box 640, Coshocton, OH 43812, USA, E-mail: abd@coshocton.com

Note:

- Some suppliers do not have a website address. In this case, we have given their e-mail address (if they have one) or their fax number.
- For finding the address of the general commercial suppliers (Acros, Air Liquide, Aldrich, J.T. Baker, Fluka, Lancaster, Sigma, etc.) readers are invited to consult the corresponding catalogs.