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COMMISSION ON PHYSICOCHEMICAL
MEASUREMENTS AND STANDARDS
SUB-COMMISSION ON CALIBRATION AND TEST MATERIALS

RECOMMENDED REFERENCE MATERIALS FOR THE REALIZATION OF PHYSICOCHEMICAL PROPERTIES

EDITOR: E. F. G. HERINGTON

Recommendations approved 1974

LONDON
BUTTERWORTHS

PHYSICAL CHEMISTRY DIVISION
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EDITOR: E. F. G. HERINGTON

SECTION: GENERAL INTRODUCTION

COLLATOR: J. P. CALI

1. PREAMBLE

There are many measuring systems and instruments in use today which yield results whose uncertainty of measurement and limits of error cannot be established without the employment of materials with known properties. The materials used for this purpose are called reference materials (see below). The IUPAC Commission I.4† having realized the importance for industry and science of materials with known properties prepared a 'Catalogue of physicochemical standard substances'[1] which is a list of samples certified by National Standardizing Laboratories.

However, it was realized by members of Commission I.4 that a more comprehensive compilation was needed and the Commission has set up a Sub-Commission (for members see ‡) on Calibration and Test Materials under the chairmanship of Professor H. Kienitz to study this problem. This Sub-Commission has examined the steps necessary in the selection and specification of reference materials for use in various types of physicochemical measurement, and the present recommendations are the first results of the Sub-Commission's labours. This General Introduction to the Recommendations has been prepared by Dr J. P. Cali at the invitation of the Sub-Commission, who have appointed Dr E. F. G. Herington as editor for the Recommendations.

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Sections of the Recommendations will appear as they become available; thus the Sections: Enthalpy (collated by Dr J. D. Cox), Optical Rotation (collated by Drs I. Brown and J. E. Lane), Surface Tension (collated by Drs I. Brown and J. E. Lane), and Optical Refraction (collated by Drs I. Brown and J. E. Lane) are issued with this General Introduction to the whole series.

2. CLASSES OF MATERIALS FOR USE IN CALIBRATION AND TEST PROCEDURES

Various names, which are often inconsistent and linguistically confusing, are in use for classes of materials employed in calibration and test procedures. For example, a well characterized material used for these purposes is, in various parts of the world, referred to as a standard sample, as a standard reference material, as a reference sample or as a test substance. The name used in this work is reference material defined as a material whose properties have been well characterized (preferably with a knowledge of the uncertainties of measurement). The word material here is intended to include single substances, mixtures and devices, but this last group will constitute only a minor portion of these Recommendations. As pure substances are materials of definite and usually known chemical composition they are usually more easily characterized than mixtures and are therefore frequently the materials of choice as reference materials.

Two main classes of reference materials for physicochemical measurement are proposed: Primary Substances (PS), and Calibration and Test Materials (CTM) with a sub-class of the latter termed Certified Reference Materials (CRM).

2.1. Primary Substances (PS)

The word primary is used in the sense of fundamental or basic. These are substances required for the realization of measurement scales. In science today these scales are those associated with the base or derived units of the Système International (SI)[2]. The relationship between the scale and the primary substance is immanent in the substance itself. Thus, the second is realized by counting (in essence) 9 192 631 770 transitions of the two hyperfine levels of the ground state of caesium-133. The ground state transitions are, of course, an inherent property of the substance called caesium-133. Primary substances are invariably required to be 'pure'; in reality the samples are, in many instances, purified to a degree which reflects the present purification state-of-art. Should different samples of a substance in this class differ somewhat in purity, then the resulting variations would cause small and accountable variations in the realization of the property. Samples of these PS should meet at least one of the following two criteria: they should be certified as to purity, stability, conditions for use by an authoritative and highly competent laboratory, or else the substance should be obtainable in a pure state by a method of preparation and purification that is well documented, tested and proven so that certification is unnecessary. Examples of PS are a certified sample of gold to realize the 1968 International Practical Temperature Scale and a certified sample of krypton-86 to realize the metre. An example of a

PS which could in principle be used without certification is water, for use in the realization of the temperature 273.16 K.

2.2. Calibration and Test Materials (CTM)

This class of reference materials contains by far the largest number of members. These materials may be used to calibrate instruments to ensure that the numerical values obtained for a measured property are accurate (within the uncertainty limits required) or to realize a practical scale which cannot be defined directly in terms of the base or derived SI units. The need for such a scale may arise because of the complexity of the situation or because of lack of basic knowledge; an example is the definition of the fading hour. Materials of this class may also be used to check methods of analysis or to test whether a method is satisfactory. They also provide a means for quality control or for testing some property of apparatus or process.

Most CTM used in the world today are not certified and the Sub-Commission has frequently had to recommend use of uncertified materials, which may either require purification by the user or be available in adequate purity from reliable sources.

However, samples of some CTM have been characterized and have had their properties certified by an authoritative national or international organization, agency or laboratory and these are called Certified Reference Materials (CRM) for the purpose of these Recommendations. When available CRM are likely to have several advantages over uncertified CTM because they often have smaller uncertainties in the values of their properties, and moreover such specimens are usually available over a long period. Further they often provide a convenient method for the transfer of a value of a property from a standardizing laboratory to a working laboratory. For example, samples of benzoic acid certified with respect to calorific value are often used in this manner.

3. PURPOSE AND SCOPE OF THE RECOMMENDATIONS

Effective communication in science and technology is maintained in large part through the use of numerical data obtained by measurement. The efficiency of this communication system depends upon the extent to which independent measuring systems yield results related to a common frame of reference. It is therefore useful to consider some features of satisfactory measurement systems.

The SI has now been accepted internationally as a rational, self-consistent system of units. There must be a means to realize in practice the SI, and both the definitions of units and the methods used to realize them, including the choice and specification of the relevant PS, are the responsibility of the Comité International des Poids et Mesures (CIPM) working with the International Unions and with the National Standards Laboratories. PS are essential for the realization of the base units of the SI and they find use in many laboratories. In much scientific and technological work it may be inconvenient to realize a unit of the SI directly; instead it may be more convenient to transfer a unit from a standardizing laboratory to a working laboratory either by the use of a CRM or by the use of a CTM with a well documented value of a physical property: an example is the use of water as a density standard. There must also be means for testing the performance of equipment and the reliability of methods. In such studies the accuracy as well as the reproducibility of results is often important. Moreover, it is often necessary to re-check the performance of instruments and methods from time to time. Organizations concerned with this type of work are Professional Societies, Standards Bodies (e.g. ISO, ASTM), Government Agencies and Laboratories, and Industrial Associations. For all this work CTM and CRM are invaluable.

4. PRESENTATION OF THE INFORMATION

Information on Recommended Reference Materials will be issued in separate Sections each with an introduction by a designated member of the Sub-Commission. Recommendations given in each Section are based on information from the literature, from correspondence with scientists in each discipline and from comments solicited from standards groups and bodies, national certifying laboratories, manufacturers and suppliers. The assessment of the gathered information was first made by the designated member of the Sub-Commission and then, insofar as practicable, by the Sub-Commission as a body. It is the intention of the Sub-Commission to revise from time to time the information given in the Recommendations and users are invited to send suggestions for improvement and extension of the Recommendations to the Secretary of Commission I.4.

The following principles have been adopted for the presentation of the recommendations. The SI is used as far as is practicable but if it has been necessary to employ traditional units, the conversion factor to the SI is stated. Recommendations by the ISO and by the IUPAC on the use of the SI have been followed[3, 4]. For numerical values the publication 'The values of the fundamental constants for chemistry'[5] and the table of atomic weights adopted by the IUPAC[6] have been employed.

4.1. Arrangement of Each Section

The introduction to each Section is not intended to be exhaustive but reflects the present state-of-the-art for the measurement under consideration, with special emphasis (where appropriate) on industrial applications.

The tables which follow the introduction include the following information for each recommended material: physical property, units, range of variables, physical state(s) within range, class of reference material, the names of contributors, intended usage, source of supply and/or methods of preparation, pertinent physicochemical data, references. The following provisos apply to the information on sources of supply: (a) the recommended materials, in most instances, have not been checked independently by the IUPAC; (b) the quality of material may change with time; (c) the quoted sources of supply may not be exclusive sources because no attempt has been made to seek out all possible alternative sources; (d) the IUPAC does not guarantee any material that is recommended.

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[1] 'Catalogue of physicochemical standard substances', *Pure Appl. Chem.* **29**, 597 (1972).

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[3] International Organization for Standardization *Recommendation R 1000*, 'Rules for the use of the International System of Units and a selection of the decimal multiples and submultiples of the SI Units', Geneva (1969).

[4] 'Manual of symbols and terminology for physicochemical quantities and units', *Pure Appl. Chem.* **21**, 1–44 (1970).

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PHYSICAL CHEMISTRY DIVISION

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EDITOR: E. F. G. HERINGTON

SECTION: ENTHALPY

COLLATOR: J. D. COX

CONTENTS

REFERENCE MATERIALS FOR ENTHALPY MEASUREMENT. INTRODUCTION

The need for calibration and test materials in enthalpy measurements, i.e. in calorimetry, has been recognized by experimentalists for many years. Indeed in earlier times the use of water for the definition of certain energy units (e.g. the ‘mean’ and ‘15°’ calories) indicated the heavy dependence of calorimetry on a material standard. After the renaissance of calorimetry in the nineteen-twenties the importance of water as a calibration material declined: experimentalists increasingly preferred to use as their energy unit either the joule, realized electrically, or a version of the calorie defined in terms of the joule and not in terms of the properties of water.

Many types of calorimeter can be calibrated electrically with the necessary accuracy, and this procedure is always to be commended. However, bomb calorimeters require calibration to very high accuracy and the necessary electrical equipment is not available in many laboratories. There is thus a need for a calibration material to transfer the energy unit from a standardizing laboratory: benzoic acid has served as the sole recommended calibration material for bomb calorimetry since its recommendation for this role by the Union Internationale de Chimie in 1934, *vide infra*. Some of the other materials described below can also be used to calibrate certain types of calorimeter, in the circumstance that the design of the calorimeter makes electrical calibration difficult or inconvenient. But, generally, the materials to be described are intended to permit the testing of calorimeters or calorimetric procedures.

Of course it is feasible to test one's equipment or procedure by the use of any homogeneous sample that may be available, but this practice can at best only indicate the precision of one's measurements: to establish their accuracy (i.e. their freedom from significant systematic errors) the use of a sample with known physicochemical properties is required.

The following is a résumé of the categories of calorimetric measurement covered by the present set of recommended calibration and test materials.

I. REFERENCE MATERIALS FOR HEAT-CAPACITY MEASUREMENTS

Measurements of heat capacities of materials are made within the temperature range 1–3000 K, and there is need for a set of test materials that encompasses this wide range. The set should include materials in the solid, liquid and gaseous states, to match the state of matter under investigation, but should exclude materials that undergo chemical change or exhibit any but the simplest phase behaviour.

Of the materials listed, one (copper) is intended for use at very low temperatures and two others (platinum and molybdenum) are intended for use at very high temperatures. α-Alumina is a solid test material of special importance, as it is stable over a very wide temperature range; *n*-heptane and water are important liquid test materials. All the gaseous test materials mentioned are recommended for use at low pressures only; no gaseous test material for use at high pressures is recommended at this time.

II, III AND IV. REFERENCE MATERIALS FOR ENTHALPY-OF-TRANSITION MEASUREMENTS

Materials for the following types of transition are included: solid to liquid (melting); liquid to saturated vapour (vaporization); solid to saturated vapour (sublimation). No recommendation is made for materials to serve as standards for solid-to-solid transitions, although there is a definite need for calibration or test materials of this type (e.g. in differential scanning calorimetry) but measurements of the necessary accuracy on suitable materials are lacking. For a similar reason, the materials recommended as test materials for melting, vaporization and sublimation cover a narrower temperature range than would be desirable.

V AND VI. REFERENCE MATERIALS FOR ENTHALPY-OF-REACTION AND FOR ENTHALPY-OF-SOLUTION MEASUREMENTS

In the present context it is undesirable to draw a hard and fast distinction between the dissolution of a solute in a solvent and the reaction of a substance with a liquid reagent resulting in the formation of a solution, and the dilution of a solution from one concentration to another. All three processes normally involve an enthalpy change, though the magnitude of the change tends to be larger for processes involving chemical reaction. The enthalpy change may be positive or negative in sign, and the choice of test (or calibration) system will often be dictated by the sign of the enthalpy change under investigation; the substance tris-(hydroxymethyl)aminomethane can be used as a test material of either positive or negative enthalpy of solution by appropriate choice of liquid reagent. Another factor influencing the choice of test system is the speed at which solution takes place: if slow dissolution is under investigation, the system α-quartz plus hydrofluoric acid may well commend itself; if fast dissolution is under investigation the use of other systems, detailed below, would be preferable.

VII. REFERENCE MATERIALS FOR ENERGY-OF-COMBUSTION MEASUREMENTS

Note that the materials listed for energy-of-combustion measurements (i.e. measurements of ΔU, reaction at constant volume) can also serve as reference materials for enthalpy-of-combustion measurements (i.e. measurement of ΔH, reaction at constant pressure) because the relation between ΔU and ΔH is $\Delta H = \Delta U + p\Delta V$, and $p\Delta V$ can invariably be estimated with the necessary accuracy.

The special status of benzoic acid in the calibration of bomb calorimeters has already been commented upon. Recent measurements on one particular batch of benzoic acid showed encouragingly high concordance between several laboratories, but since material is available from various sources and since each batch must be replaced from time to time, continued vigilance will be needed to ensure the quality of this calibration material.

A range of reference materials for combustion calorimetry of substances of differing chemical compositions is needed because chemical factors often determine the overall accuracy of bomb-calorimetric experiments. Thus a calorimetrist will select a chlorine-containing test material when studying the combustion of organochlorine compounds, and so on; he may use the chlorine-containing test material not only to check his calorimetric procedure but also to develop methods for the control of the stoichiometry of the reactions taking place within the bomb, and methods used for the analysis of the products.

Reference was made above to the desirability of selecting a test material which has properties similar to those of the material under investigation. Unless this is done and unless the use of the test material is restricted to the range of variables listed, there can be no certainty as to the validity of the test.

The detailed information presented on the following pages was assembled during 1969–1972 with the cooperation of calorimetrists in many countries. It is hoped that the information given on any one recommended calibration or test material is reasonably complete, though there may well be sources of supply additional to those listed. However, it is recognized that yet further calibration or test materials are desirable, to cover the complete needs of calorimetrists. For example, further enthalpy-of-transition materials would be useful, covering solid-state transitions and melting, vaporization and sublimation at temperatures outside the ranges to which the present recommendations apply; again, more enthalpy-of-reaction materials would be useful, covering bromo-, iodo- and phosphorus-compounds. Hopefully, further recommendations can be made in the coming years.

I/1

Physical property: Heat capacity, enthalpy
Units: J mol^{-1} K^{-1} (molar heat capacity); J mol^{-1} (molar enthalpy)
J kg^{-1} K^{-1} (specific heat capacity); J kg^{-1} (specific enthalpy)
Recommended reference material: α-aluminium oxide (Al_2O_3)
Range of variables: 10–2000 K
Physical state within the range: solid
Class: Calibration and Test Material; Certified Reference Material
Contributors: J. D. Cox, D. A. Ditmars, G. T. Furukawa, J. F. Martin, O. Riedel, D. R. Stull

Intended usage:
Highly pure α-alumina (synthetic sapphire, corundum) is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of solids and liquids[1] or of calorimeters used for the measurement of the enthalpies of solids[2]. This material could also be used for the calibration of such calorimeters.

Sources of supply and/or methods of preparation:
A highly pure grade of α-alumina with a certificate giving its measured enthalpy (relative to 0 K) and heat capacity from 273.15 to 2250 K is available from supplier (M). Samples of α-alumina of comparable purity can be obtained (without thermal certification) from supplier (K).

Pertinent physicochemical data:
This material has no solid–solid transitions in the quoted temperature range. Furukawa *et al.*[3] studied a sample of α-alumina that had been assessed as 99.98–99.99 per cent pure by spectrographic analysis. They employed adiabatic calorimetry in the temperature range 13–380 K. Ditmars and Douglas[6], and West and Ishihara[6], using drop calorimeters of different designs, measured the relative enthalpy of a sample of comparable purity (SRM 720) in the temperature ranges 273.15–1173.15 K and 1173.15–2250 K,

respectively. Results obtained by all three methods agree very well in the overlap ranges. Following are values of C_p with temperatures on the International Practical Temperature Scale of 1968 with 0°C = 273.15 K. The

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J mol}^{-1}\,\text{K}^{-1}}$
10	0.0094	250	67.05	600	112.55
25	0.1417	300	79.41	700	116.92
50	1.492	350	88.84	800	120.14
75	5.671	400	96.08	900	122.66
100	128.5	450	101.71	1000	124.77
150	31.95	500	106.13	1100	126.61
200	51.13	550	109.67	1200	128.25

relative molecular mass was taken as 101.9612. The measurements made by Macleod[4] agree with the values in the table, except at the highest temperatures.

Values of $H_T^\circ - H_0^\circ$, needed when α-alumina is used in drop calorimetry, are also available[6]. Equations for C_p and $H_T^\circ - H_0^\circ$ as functions of T (0–2200 K) have been given by Reshetnikov[5]. The values he reports for $H_T^\circ - H_0^\circ$ differ from those in reference 6 by up to 0.3 per cent in the range 273.15 to 1200 K.

REFERENCES

[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. I: *Calorimetry of Non-reacting Systems*, Chapters 5 and 9. Butterworths: London (1968).

[2] Ibid., Chapter 8.

[3] G. T. Furukawa, T. B. Douglas, R. E. McCoskey and D. C. Ginnings, *J. Res. Nat. Bur. Stand.* **57**, 67 (1956).

[4] A. C. Macleod, *Trans. Faraday Soc.* **63**, 300 (1967).

[5] M. A. Reshetnikov, *Russ. J. Phys. Chem.* **43** (9), 1254 (1969).

[6] NBS Certificate for Standard Reference Material 720. See also D. A. Ditmars and T. B. Douglas, *J. Res. Nat. Bur. Stand.* **75A**, 401 (1971).

I/2

Physical property: Heat capacity; enthalpy
Units: J mol^{-1} K^{-1} (molar heat capacity); J mol^{-1} (molar enthalpy)
J kg^{-1} K^{-1} (specific heat capacity); J kg^{-1} (specific enthalpy)
Recommended reference material: Platinum (Pt)
Range of variables: 298–2000 K
Physical state within the range: solid
Class: Calibration and Test Material; Certified Reference Material
Contributor: G. T. Armstrong

Intended usage:
Because of its high chemical stability, freedom from transitions, high melting point, availability in high purity, low volatility at high temperatures, platinum is recommended for checking the accuracy of apparatus for the measurement of enthalpy and heat capacity up to high temperatures.

Sources of supply and/or methods of preparation:
High-purity platinum in wire form ($<$ 10 p.p.m. total of eleven common metals and oxygen) is available as SRM 680 from supplier (M).

Pertinent physicochemical data:
The values of 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] (681–1664 K), Jaeger and Rosenbohm[4] (484–1877 K), and White[5] (373–1573 K). Hultgren's values for the heat capacity and enthalpy relative to 298.15 K are as follows.

$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{H_T - H_{298.15\,\mathrm{K}}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{H_T - H_{298.15\,\mathrm{K}}}{\mathrm{kJ\,mol^{-1}}}$
298.15	25.8	0	1200	30.7	25.52
400	26.5	2.67	1300	31.3	28.62
500	27.0	5.34	1400	31.8	31.77
600	27.5	8.07	1500	32.3	34.97
700	28.0	10.84	1600	32.8	38.22
800	28.6	13.68	1700	33.3	41.53
900	29.1	16.56	1800	33.8	44.89
1000	29.6	19.49	1900	34.4	48.30
1100	30.2	22.48	2000	34.9	51.76

Recently Macleod[6] has measured the enthalpy of platinum in the temperature range 400–1700 K. His results for the high temperature measurements agree well with those in the above table, but there are slight discrepancies for temperatures below 1000 K. Macleod considers that the values of $H_T – H_{298.15\,\mathrm{K}}$ given in the table above for 298.15 K $< T <$ 1000 K, are too high.

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1. R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, Wiley, New York (1963): 'Supplement for Platinum': (1969).
2. W. B. Kendall, R. L. Orr and R. Hultgren, *J. Chem. Engng Data*, **7**, 516 (1962).
3. F. M. Jaeger, E. Rosenbohm and J. A. Bottema, *Proc. Acad. Sci. Amst.* **35**, 763 (1932).
4. F. M. Jaeger and E. Rosenbohm, *Proc. Acad. Sci. Amst.* **30**, 1069 (1927).
5. W. P. White, *Phys. Rev.* **12**, 436 (1918).
6. A. C. Macleod, *J. Chem. Thermodynamics*, **4**, 391 (1972).

I/3

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} or mJ mol^{-1} K^{-1} (molar heat capacity)
Recommended reference material: Copper (Cu)
Range of variables: 1–25 K
Physical state within the range: solid

Class: Calibration and Test Material: Certified Reference Material
Contributors: J. D. Cox; J. F. Martin

Intended usage:
Copper is recommended for testing the performance of cryogenic calorimeters[1], and for intercomparing results between different laboratories that are concerned with thermal measurements in the very low temperature range, where the establishment of reliable temperature scales is difficult.

Sources of supply and/or methods of preparation:
Samples of a specially prepared grade of copper are available from supplier (C).

Pertinent physicochemical data:
Osborne *et al.*[2] studied a sample of copper designated as rod No. 1 of sample T-1.1 from the 1965 Calorimetry Conference Copper Standard. The sample had been prepared from 99.999 + per cent High Purity Copper by further treatment at the Argonne National Laboratory. The germanium resistance thermometer was calibrated between 0.85 and 2.3 K using ^{3}He vapour pressure, between 2.1 and 4.2 K using ^{4}He vapour pressure, between 4.2 and 25 K using a ^{4}He gas thermometer, and near 20 K using normal H_2 vapour pressure. The heat capacity of copper in the range 1–25 K is expressed by the equation below, taking the relative atomic mass as 63.54.

$$C_p/\text{mJ mol}^{-1}\,\text{K}^{-1} = \sum_{i=1}^{n} A_i T^{2i-1}$$

where $A_1 = 6.9434 \times 10^{-1}$ $A_4 = 9.4786 \times 10^{-8}$
$A_2 = 4.7548 \times 10^{-2}$ $A_5 = -1.3639 \times 10^{-10}$
$A_3 = 1.6314 \times 10^{-6}$ $A_6 = 5.3898 \times 10^{-14}$

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[1] J. P. McCullough and D. W. Scott (editors). *Experimental Thermodynamics*, Vol. I: *Calorimetry of Non-reacting Systems*, Chapter 7. Butterworths: London (1968).

[2] D. W. Osborne, H. E. Flotow and F. Schreiner, *Rev. Sci. Instrum.* **38**, 159 (1967).

I/4

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Succinic acid ($C_4H_6O_4$)
Range of variables: 5–320 K
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, O. Riedel

Intended usage:
Succinic acid is recommended for testing the performance of calorimeters used for the measurement of heat capacity of solids from low temperatures to a little above ambient[1]. The substance exhibits no thermal anomalies in the solid state[2].

Sources of supply and/or methods of preparation:
A suitable sample of succinic acid can be prepared from analytical-reagent grade material by four recrystallizations from distilled water[2]. An effective drying procedure for the crystals so produced has been described[2].

Pertinent physicochemical data:
Vanderzee and Westrum[2] measured C_p of a sample of succinic acid that was carefully tested for its water content (0.003 per cent). The relative molecular mass was taken as 118.090 for the values in the following table.

$\frac{T}{K}$	$\frac{C_p}{\text{J mol}^{-1}\text{ K}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{J mol}^{-1}\text{ K}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{J mol}^{-1}\text{ K}^{-1}}$
5	0.100	100	68.58	220	118.8
10	0.812	120	77.70	240	127.4
20	5.937	140	86.19	260	136.0
40	25.48	160	94.35	280	144.8
60	43.89	180	102.4	300	153.8
80	57.83	200	110.5	320	163.1

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[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. 1: *Calorimetry of Non-reacting Systems*, Chapters 5 and 6. Butterworths: London (1968).

[2] C. E. Vanderzee and E. F. Westrum, *J. Chem. Thermodynamics*, **2**, 681 (1970).

1/5

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Benzoic acid ($C_7H_6O_2$)
Range of variables: 10–340 K
Physical state within the range: solid
Class: Calibration and Test Material; Certified Reference Material
Contributors: J. D. Cox, J. F. Martin, O. Riedel, D. R. Stull

Intended usage:
Benzoic acid is recommended for testing the performance of calorimeters used for the measurement 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 (395.5 K) is not recommended, because of the material's corrosive nature.

Sources of supply and/or methods of preparation:
The sample of benzoic acid used to establish the heat capacity[2] had been specially prepared as a thermometric standard[3]. It seems probable that samples of benzoic acid prepared as energy-of-combustion standards would also serve as heat-capacity standards.

Samples of energy-of-combustion (thermochemical) standard benzoic acid are available from suppliers (A), (D), (E), and (M).

Pertinent physicochemical data:
Furukawa *et al.*[2] studied a sample of benzoic acid that had been assessed as 99.997 mol per cent pure by time–temperature freezing-point measurements[3]. The following values relate to the solid in equilibrium with its vapour, with the relative molecular mass taken as 122.12. The results of measurements made by isoperibolic calorimetry and reported by Cole *et al.*[4] agree with those in the table except for the values for the lowest temperature. The adiabatic measurements made by Osborne *et al.*[5] and by Rybkin *et al.*[6] also agree with those in the table.

$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\text{K}^{-1}}$
10	1.923	120	71.51	240	120.22
20	11.00	140	79.09	260	129.24
40	31.68	160	86.75	280	138.40
60	45.88	180	94.70	300	147.66
80	55.85	200	102.89	320	156.96
100	63.93	220	111.40	340	166.22

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[2] G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Res. Nat. Bur. Stand.* **47**, 256 (1951).
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[5] D. W. Osborne, E. F. Westrum and H. R. Lohr, *J. Amer. Chem. Soc.* **82**, 2737 (1955).
[6] N. P. Rybkin, A. K. Baranyuk and M. P. Orlova, *Third International Conference on Chemical Thermodynamics*, Baden, Book VIII, page 30 (1973).

1/6

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: 2,2-Dimethylpropane (C_5H_{12})
Range of variables: (i) 4–139 K; (ii) 142–254 K
Physical state within the range: solid
Class: Calibration and Test Material
Contributor: Y. Mashiko

Intended usage:
2,2-Dimethylpropane (neopentane) 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 140.50 ± 0.05 K, the temperature range round the transition point (say 139–142 K) should be avoided when this material is used for the testing of calorimeters.

Sources of supply and/or methods of preparation:
Samples of 2,2-dimethylpropane of suitable purity can be prepared[2] from 99.5 per cent pure material [e.g. from material from supplier (N)] by fractional

distillation, with treatment of the distillate by Molecular Sieve 5A. Samples are also available from supplier (B).

Pertinent physicochemical data:

Enokido *et al.*[2] studied a sample of 2,2-dimethylpropane which they assessed as 99.997 mol per cent pure by melting-point measurements made with an adiabatic calorimeter. A selection from their measured values of C_{sat} is given below, with the relative molecular mass taken as 72.151. Their results for the temperature range 60–139 K are slightly lower and for temperatures near 250 K are much lower than those reported by Aston and Messerly[3]. Probably the less pure specimen used by the latter workers was responsible for considerable premelting.

$\frac{T}{K}$	$\frac{C_{sat}}{J\ mol^{-1}\ K^{-1}}$	$\frac{T}{K}$	$\frac{C_{sat}}{J\ mol^{-1}\ K^{-1}}$	$\frac{T}{K}$	$\frac{C_{sat}}{J\ mol^{-1}\ K^{-1}}$
4.141	0.1532	81.405	60.17	161.296	107.8
6.409	0.7063	101.293	72.93	180.398	112.8
10.043	3.249	120.903	89.70	201.904	117.7
20.164	16.78	139.014	111.3	220.360	123.6
61.576	48.37	—	—	239.880	130.6
		142.424	110.0	254.044	137.5

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[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. I: *Calorimetry of Non-reacting Systems*, Chapters 5, 6 and 7. Butterworths: London (1968).

[2] H. Enokido, T. Shinoda and Y. Mashiko, *Bull. Chem. Soc. Japan*, **42**, 84 (1969).

[3] J. G. Aston and G. H. Messerly, *J. Amer. Chem. Soc.* **58**, 2354 (1936).

I/7

Physical property: Heat capacity, enthalpy
Units: J mol^{-1} K^{-1} (molar heat capacity); J mol^{-1} (molar enthalpy)
J kg^{-1} K^{-1} (specific heat capacity); J kg^{-1} (specific enthalpy)
Recommended reference material: Molybdenum (Mo)
Range of variables: 273–2500 K (good data available 1200–2100 K)
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: A. Cezairliyan, D. Ditmars

Intended usage:

Pure molybdenum is recommended for testing the performance of calorimeters for measuring the heat capacity or enthalpy of solids and liquids from 273–2500 K by drop or pulse calorimetry. Molybdenum has no known structural transitions within this temperature range but it is oxidized rapidly in contact with air at temperatures above 500°C.

Sources of supply and/or methods of preparation:

Molybdenum samples of purity 99.5 per cent may be purchased from supplier (H). A suitable sample, but not certified, can be obtained from supplier (M).

For thermal measurement below 900°C it is recommended that the metal be first annealed at a temperature above 900°C for several hours.

Pertinent physicochemical data:

Kirillin *et al.*[1] have measured the relative enthalpy of a sample of 99.95 per cent purity for the temperature interval 700–2400°C by drop calorimetry. These authors give the following equation for the relative enthalpy, and estimate the errors in their measurements not to exceed ± 0.9 per cent below 2000°C. Temperatures are expressed on the International Practical Temperature Scale of 1948.

$$(H_t - H_{0^\circ\mathrm{C}})/\mathrm{kJ\ kg^{-1}} = 0.2498(t/^\circ\mathrm{C}) + 2.96 \times 10^{-5}(t/^\circ\mathrm{C})^2 + 3.2 \times 10^{-9}(t/^\circ\mathrm{C})^3$$

Heat capacity values calculated from this equation join acceptably with existing low-temperature data[2] and agree well for temperatures above 1 700°C with measurements made by Cezairliyan[3], who measured the heat capacity by pulse calorimetry using a sample of 99.9+ per cent purity (major impurities, Cu, Ni, Zr: sample annealed at 1400 K; density, 10.2 g cm^{-3}). Ishihara and Douglas have completed enthalpy measurements[4] on a sample of at least 99.8 per cent purity for the temperature range 1170 to 2100 K. The results of measurement agree with those reported by Kirillin *et al.* within the latter's estimate of error. Additional accurate measurements for the range 273–2 500 K are in progress at the National Bureau of Standards.

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[3] A. Cezairliyan, *J. Res. Nat. Bur. Stand.* **74A**, 65 (1970).

[4] S. Ishihara and T. B. Douglas, *NBS Rep. No. 10481*, page 59, US Govt Printing Office: Washington, DC (1971).

I/8

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Naphthalene ($C_{10}H_8$)
Range of variables: (i) 10–350 K; (ii) 357–371 K
Physical states within the range: (i) solid; (ii) liquid
Class: Calibration and Test Material
Contributors: J. D. Cox, O. Riedel

Intended usage:

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

Sources of supply and/or methods of preparation:

Naphthalene samples of certified high purity can be obtained from suppliers (B) and (F).

Pertinent physicochemical data:
McCullough *et al.*[2] examined a sample of naphthalene which they assessed as of 99.985 mol per cent purity by calorimetric study of the melting behaviour. From their results the following table of values of C_{sat} for the solid in equilibrium with its vapour were derived with temperatures expressed on the International Practical Temperature Scale of 1948, with 0°C = 273.16 K.

$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\,\text{K}^{-1}}$
10	1.766	120	68.50	240	129.1
20	10.94	140	77.17	260	141.1
40	30.12	160	86.48	280	153.7
60	42.65	180	96.33	300	166.9
80	51.99	200	106.71	320	181.1
100	60.25	220	117.72	340	197.2
				350	205.8

McCullough *et al.*[2] also measured the heat capacity of liquid naphthalene in equilibrium with its vapour. The following equation is valid for 357–371 K.

$$C_{\text{sat}}(\text{l})/\text{J mol}^{-1}\,\text{K}^{-1} = 80.383 + 0.3873\,(T/\text{K})$$

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[2] J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe and G. Waddington, *J. Amer. Chem. Soc.* **61**, 1105 (1957).

1/9

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Diphenyl ether ($C_{12}H_{10}O$)
Range of variables: (i) 10–300.01 K; (ii) 300.01–570 K
Physical states within the range: (i) solid; (ii) liquid under its own vapour pressure
Class: Calibration and Test Material
Contributors: J. D. Cox, J. F. Martin, O. Riedel, D. R. Stull

Intended usage:
Diphenyl ether is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of solids and liquids[1]. Its relatively high boiling point permits the use of this material over a wide range of temperature and its ease of purification and the inertness of the

molten substance to most materials of construction are further points in its favour.

Sources of supply and/or methods of preparation:
Samples of diphenyl ether of suitable purity can be obtained from supplier (F) and samples of 'perfume-grade' can be obtained from supplier (G).

Pertinent physicochemical data:
Furukawa *et al.*[2,3] examined a sample of diphenyl ether which they assessed as 99.9987 mol per cent pure by adiabatic melting-point studies. They determined the heat capacity between 18 and 360 K by adiabatic calorimetry and between 273 and 573 K by drop calorimetry. In the drop calorimetric measurements, a Bunsen ice calorimeter was used to receive the specimen; the factor relating energy to mass of mercury drawn in was taken as 270.46 J g^{-1}. The values in the following table assume that the relative molecular mass is 170.20.

Solid				Liquid			
T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_{sat}/J mol^{-1} K^{-1}	T/K	C_{sat}/J mol^{-1} K^{-1}
10	3.283	160	117.64	300.01	268.42	460	340.32
20	18.06	180	129.98	320	277.17	480	349.16
40	45.44	200	143.09	340	286.25	500	358.04
60	61.92	220	156.86	360	295.35	520	366.92
80	73.77	240	171.32	380	304.39	540	375.78
100	84.35	260	186.49	400	313.33	560	384.63
120	94.82	280	202.04	420	322.36	570	389.05
140	105.88	300	218.06	440	331.30		
		300.01	218.25				

REFERENCES

[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. I: *Calorimetry of Non-reacting Systems*, Chapter 5, 6 and 9. Butterworths: London (1968).

[2] G. T. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, *J. Res. Nat. Bur. Stand.* **46**, 195 (1951).

[3] D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.* **75**, 522 (1953).

I/10

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: *n*-Heptane (C_7H_{16})
Range of variables: (i) 10–182.59 K; (ii) 182.59–400 K
Physical states within the range: (i) solid; (ii) liquid under its own vapour pressure
Class: Calibration and Test Material

Contributors: J. D. Cox, T. B. Douglas, D. R. Douslin. J. F. Martin.
O. Riedel, D. R. Stull

Intended usage:
n-Heptane is recommended for testing the performance of heat-capacity calorimeters, especially those intended for measurements over the temperature range[1] 10–400 K. The sample may be introduced into the calorimeter vessel either by pouring or by distillation[2]. There are no solid–solid transitions, and the material comes to thermal equilibrium rapidly.

Sources of supply and/or methods of preparation:
Samples of *n*-heptane of suitable purity can be obtained from suppliers (B) and (F).

Pertinent physicochemical data:
Douglas *et al.*[5] measured the heat capacity of a sample of *n*-heptane that had been assessed as 99.997 mol per cent pure by freezing-point determinations. Measurements were made by both adiabatic[3] and drop[4] calorimetry. The results in the following table are corrected[7] to the International Practical Temperature Scale of 1968 for temperatures above 90 K, with 0°C = 273.15 K, but with the NBS-55 provisional temperature scale used below 90 K. The relative molecular mass is taken as 100.20. Measurements of C_p made from 1947 to 1954 at the US Bureau of Mines Laboratory, Bartlesville, have been summarized in a *Bulletin*[6]; information on further measurements made since 1954 is available from the US Bureau of Mines Energy Research Center. Bartlesville, Oklahoma 74003, USA.

Solid				Liquid			
$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat}}}{\text{J mol}^{-1}\text{K}^{-1}}$
10	1.77	100	92.85	182.59	203.05	300	225.49
20	11.80	120	105.27	200	201.30	320	233.26
40	38.17	140	116.75	220	202.81	340	241.64
60	60.48	160	128.90	240	206.59	360	250.57
80	78.28	180	145.02	260	211.86	380	260.01
		182.59	148.48	280	218.32	400	270.02

REFERENCES

[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. 1: *Calorimetry of Non-reacting Systems*, Chapters 5, 6 and 9. Butterworths: London (1968).

[2] D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.* **75**, 522 (1953).

[3] R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde and N. Bekkedahl, *J. Res. Nat. Bur. Stand.* **35**, 39 (1945).

[4] Reference 1, Chapter 8.

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[6] J. P. McCullough and J. F. Messerly, 'The use of *n*-heptane as a reference substance for low-temperature calorimetry', *US Bur. Min. Bull. No. 596* (1961).

[7] T. B. Douglas, *J. Res. Nat. Bur. Stand.* **73A**, 451 (1969).

I/11

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} or J g^{-1} K^{-1} (specific heat capacity)
Recommended reference material: 1,4-Dimethylbenzene (*p*-xylene, C_8H_{10})
Range of variables: 273–573 K
Physical state within the range: liquid in equilibrium with its vapour
Class: Calibration and Test Material
Contributors: J. D. Cox, D. R. Stull

Intended usage:
1,4-Dimethylbenzene is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of liquids in equilibrium with their vapours.

Sources of supply and/or methods of preparation:
Samples of 1,4-dimethylbenzene of suitable purity can be obtained from suppliers (B) and (F).

Pertinent physicochemical data:
Corruccini and Ginnings[1] studied a sample of 1,4-dimethylbenzene that had been assessed as 99.93 mol per cent pure by a freezing-point method. Their experimental method involved the use of a drop calorimeter, with a Bunsen ice calorimeter to receive the specimen. The factor used to relate energy to mass of mercury displaced from the Bunsen ice calorimeter was 270.42 ± 0.06 J g^{-1}. From their measurements of relative enthalpy they derived the following values of specific heat capacity.

$\frac{\theta}{^\circ C}$	$\frac{C_{sat}}{J\,g^{-1}\,K^{-1}}$	$\frac{\theta}{^\circ C}$	$\frac{C_{sat}}{J\,g^{-1}\,K^{-1}}$
0	1.6460*	160	2.1853
13.2	1.6790†	180	2.2619
20	1.6974	200	2.3414
40	1.7564	220	2.4271
60	1.8200	240	2.5225
80	1.8882	260	2.6296
100	1.9606	280	2.7501
120	2.0351	300	2.8840
140	2.1100		

* Value for undercooled liquid.
† Value for liquid at the melting point.
The interpolated value of C_{sat} at 25°C is 1.7118 J g^{-1} K^{-1}.

REFERENCE

[1] R. J. Corruccini and D. C. Ginnings, *J. Amer. Chem. Soc.* **69**, 2291 (1947).

I/12

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)

Recommended reference material: Water (H_2O)
Range of variables: (i) 273–373 K at 101 325 Pa pressure
(ii) 273–647 K at the saturated vapour pressure
Physical state within the range: liquid
Class: Calibration and Test Material
Contributors: J. D. Cox, J. F. Martin, O. Riedel, D. R. Stull

Intended usage:
Water is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of liquids. In liquid heat-capacity calorimetry it is usually preferable to calibrate the calorimeter using electrical energy. Some workers, however, prefer to calibrate with the aid of a liquid of accurately known C_p, and water has long been used for this purpose. Values of C_p for this liquid are known to an accuracy of 0.01–0.02 per cent at close intervals of temperature (1 K). Values of the enthalpy of liquid water relative to the enthalpy at 0°C, a quantity useful in experiments by the method of mixtures, are also available[1] at 1 K intervals of temperature. Correlated values of C_{sat} and $H_T - H_{273.16\,K}$ are available[2] at 1 K intervals of temperature, covering the entire liquid range of water (273–647 K).

Sources of supply and/or methods of preparation:
The method employed for the preparation of a sample used for measurement has been given[1].

Pertinent physicochemical data:
Osborne *et al.*[1] measured the heat capacity of a sample of water and based on these measurements, values of both C_{sat} and C_p for a pressure of 101 325 Pa were presented in molar units by Ginnings and Furukawa[3]. The relative molecular mass was taken as 18.016.

θ / °C	C_{sat} / J mol^{-1} K^{-1}	C_p^* / J mol^{-1} K^{-1}	θ / °C	C_{sat} / J mol^{-1} K^{-1}	C_p^* / J mol^{-1} K^{-1}
0	75.993	75.985	50	75.320	75.318
5	75.714	75.706	55	75.350	75.348
10	75.532	75.525	60	75.385	75.385
15	75.417	75.410	65	75.428	75.428
20	75.345	75.339	70	75.476	75.478
25	75.303	75.298	75	75.532	75.536
30	75.282	75.278	80	75.594	75.601
35	75.277	75.273	85	75.667	75.675
40	75.283	75.280	90	75.746	75.757
45	75.298	75.295	95	75.835	75.850
50	75.320	75.318	100	75.934	75.954

* p = 101 325 Pa.

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[3] D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.* **75**, 522 (1953).

I/13

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Benzene (C_6H_6)
Range of variables: (i) 279–390 K liquid at saturation pressure
(ii) 333–527 K real gas at pressures up to 101 325 Pa
Physical states within the range: (i) liquid; (ii) real gas
Class: Calibration and Test Material
Contributors: J. D. Cox, D. R. Douslin, J. F. Martin, O. Riedel, D. R. Stull

Intended usage:
Benzene is recommended for testing the performance of calorimeters[1] used for the measurement of the heat capacity of (i) liquids in equilibrium with their vapours, (ii) vapours at pressures between 0 and 101 325 Pa.

Sources of supply and/or methods of preparation:
Benzene samples of suitable purity can be obtained from suppliers (B) and (F).

Pertinent physicochemical data:
Oliver *et al.*[2] measured the heat capacity of a sample of benzene which they assessed as 99.967 mol per cent pure by a calorimetric study of the melting behaviour. From a smooth curve drawn through a plot of their experimental data they obtained the following values for the molar heat capacity of liquid benzene at its saturation vapour pressure. The values of C_{sat} in this and the following table are expressed in J mol^{-1} K^{-1}. Values starred are from Ref. 3.

T/K	278.7	280	290	300	310	320	330
C_{sat}	131.9	132.2	134.3	136.5	138.7	141.0	143.3
T/K	340	350	360	370	380	390	
C_{sat}	145.9	148.5	151.0*	153.6*	156.4*	159.3*	

Various workers[4, 5, 6] have made accurate measurements of the vapour heat capacity of highly purified benzene samples, and from these measurements Douslin *et al.*[5] selected the following values for the real gas.

p/Pa				T/K				
	333.15	348.15	368.15	403.15	438.15	473.15	500.15	527.15
101 325			106.39	115.86	124.99	133.79	140.09	145.99
50663		99.43	105.13	115.01	124.43	133.31	139.77	145.82
37977	94.68	99.06	104.88					
25 331	94.23	98.71	104.60	114.69	124.20	133.09	139.60	145.70
18998	94.01	98.53						
12666	93.76	98.35	104.27	114.47				
0	93.33	98.00	104.01	114.31	123.95	132.95	139.48	145.59

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[1] J. P. McCullough and D. W. Scott (editors), *Experimental Thermodynamics*, Vol. I: *Calorimetry of Non-reacting Systems*, Chapters 5, 6 and 10. Butterworths: London (1968).

[2] J. D. Oliver, M. Eaton and H. M. Huffman, *J. Amer. Chem. Soc.* **70**, 1502 (1948).

[3] J. F. Martin, private communication to J. D. Cox.
[4] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.* **15**, 565 (1947).
[5] J. L. Hales, J. D. Cox and E. B. Lees, *Trans. Faraday Soc.* **59**, 1544 (1963).
[6] D. R. Douslin, I. A. Hossenlopp and S. S. Todd, private communication to J. D. Cox.

I/14

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Nitrogen (N_2)
Range of variables: (i) 65–125 K liquid at saturation pressure
(ii) 100–1000 K real gas at a pressure of 101 325 Pa
Physical states within the range; (i) liquid; (ii) real gas
Class: Calibration and Test Material
Contributors: J. D. Cox, D. R. Stull

Intended usage:
Nitrogen is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of (i) liquids and liquefied gases. and (ii) gases and vapours.

Sources of supply and/or methods of preparation:
Nitrogen of suitable purity can be obtained by the chemical treatment of commercial nitrogen, followed by fractional distillation[1]. Alternatively. nitrogen of suitable purity can be obtained by the reaction

$$8NH_3 + 3Br_2 = 6NH_4Br + N_2$$

followed by chemical purification and distillation[2].

Pertinent physicochemical data:
The relative molecular mass was taken as 28.016.
(i) The measurements made by Wiebe and Brevoort[1], and by Giauque and Clayton[2] of the C_p of liquid nitrogen at its saturation vapour pressure can be expressed by the following equation.

$$C_{sat}/\text{J mol}^{-1}\,\text{K}^{-1} = 98.133 - 30.5473 \times 10^{-1}(T/\text{K}) + 7.3491 \times 10^{-2}(T/\text{K})^2 - 7.4368 \times 10^{-4}(T/\text{K})^3 + 27.9119 \times 10^{-7}(T/\text{K})^4$$

(ii) Hilsenrath *et al.*[3] considered both experimental and statistically calculated values of the heat capacity of nitrogen gas. The following values relate to the real gas at 101 325 Pa pressure.

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
100	30.04	400	29.27	700	30.76
150	29.34	450	29.41	750	31.10
200	29.22	500	29.59	800	31.44
250	29.18	550	29.84	850	31.76
300	29.17	600	30.12	900	32.10
350	29.20	650	30.43	950	32.40
				1000	32.70

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I/15

Physical property: Heat capacity
Units: J mol^{-1} K^{-1} (molar heat capacity)
J kg^{-1} K^{-1} (specific heat capacity)
Recommended reference material: Carbon disulphide (CS_2)
Range of variables: 325–502 K with pressures from 0 to 101 325 Pa
Physical states within the range: (i) ideal gas (ii) real gas
Class: Calibration and Test Material
Contributors: J. D. Cox, D. R. Stull

Intended usage:
Carbon disulphide is recommended for testing the performance of calorimeters used for the measurement of the heat capacities of gases and vapours, especially calorimeters of the vapour-flow type[1]. This material is recommended because the experimentally derived values[2] of the molar heat capacity at zero pressure, C_p°, can be compared with values calculated by statistical mechanics, thus permitting a check on systematic errors of measurement.

Sources of supply and/or methods of preparation:
Suitable material can be obtained by fractional distillation of 'CP Grade' carbon disulphide[2].

Pertinent physicochemical data:
Waddington *et al.*[2] used a sample of carbon disulphide that had been assessed as 99.98 mol per cent pure by a time–temperature freezing-point method. They obtained the following values of C_p, where the temperatures quoted are expressed on the 1948 International Practical Temperature Scale and the relative molecular mass was taken as 76.142. The values of C_p at zero pressure (i.e. C_p°) in the table below, obtained by extrapolation of the results of measurement at higher pressures, are in good agreement with values for the ideal gas calculated from spectroscopic data by statistical

p/Pa	C_p/J mol^{-1} K^{-1}				
	T/K 325.65	T/K 367.65	T/K 407.10	T/K 453.35	T/K 502.25
101 325	48.44	49.40	50.32	51.59	T/K 52.56
48 129	47.53	—	—	—	—
25027	47.16	48.64	49.85	51.23	52.31
0 (Ideal gas)	46.76	48.40	49.71	51.12	52.23

mechanics. The fundamental constants used in the statistical calculations were the 1951 values. Statistically calculated values of C_p° are also available[2] for 200, 273.15 and 298.15 K and for the temperature range 300–1500 K at intervals of 100 K.

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II/1

Physical property: Enthalpy of fusion (melting), ΔH_m
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion)
Recommended reference material: Benzoic acid ($C_7H_6O_2$)
Range of variables: fixed point, $T_{\text{triple point}} = 395.52$ K
Physical states within the range: solid → liquid (in equilibrium with the vapour)
Class: Calibration and Test Material
Contributors: G. T. Armstrong, J. D. Cox

Intended usage:
Benzoic acid is recommended for testing calorimeters used for the measurement of enthalpies of fusion, for example, adiabatic calorimeters[1] or differential scanning calorimeters; it could also be used for the calibration of calorimeters of the latter type.

Benzoic acid attacks tin and copper[2] at temperatures near the melting point and its use as a test (or calibration) material is therefore recommended only when the acid is in contact with inert materials.

Sources of supply and/or methods of preparation:
A suitable grade of benzoic acid is available from supplier (M).

Pertinent physicochemical data:
Furukawa *et al.*[2] studied a sample of benzoic acid which they assessed as 99.997 mol per cent pure by calorimetric study of the melting behaviour. From three experiments they found a value of 18.007 ± 0.003 kJ mol^{-1} for the enthalpy of fusion at the triple point temperature, but because the molten acid attacked the metal of the calorimeter during the experiments they preferred a more cautious expression of the accuracy of the results and therefore record 18.00 ± 0.01 kJ mol^{-1}.

A re-determination of the enthalpy of fusion, without the complication of corrosive attack on the calorimeter, would be desirable.

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II/2

Physical property: Enthalpy of fusion (melting), ΔH_m
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion)
J kg^{-1} or J g^{-1} (specific enthalpy of fusion)
Recommended reference material: Diphenyl ether ($C_{12}H_{10}O$)
Range of variables: fixed point, $T_{\text{triple point}} = 300.01 \pm 0.01$ K
Physical states within the range: solid → liquid (in equilibrium with the vapour)
Class: Calibration and Test Material
Contributors: J. D. Cox, J. F. Martin

Intended usage:
The use of diphenyl ether as a test material for equipment used for the determination of enthalpies of fusion is suggested. Such apparatuses include adiabatic calorimeters[2], drop calorimeters, ice calorimeters[3,4] radiation calorimeters[5], and apparatuses using dynamic methods such as differental scanning calorimeters.

The use of diphenyl ether as the working substance in a modified Bunsen calorimeter has been advocated[1,6].

It has been shown[1] that diphenyl ether can be prepared in a state of extremely high purity and that it is relatively stable in contact with the tin lining of a sample container, and with a Monel container.

Sources of supply and/or methods of preparation:
Samples of diphenyl ether of certified high purity can be obtained from supplier (F).

Pertinent physicochemical data:
Furukawa *et al.*[1] purified a sample by fractional distillation, then by 25 fractional crystallizations followed by repeated slow freezings while the specimen was evacuated to remove dissolved air and water. The impurity content as established by the melting behaviour was 0.0013 mol per cent. They report that the enthalpy of fusion is 17217 ± 17 J mol^{-1} (i.e. 101.15 ± 0.10 J g^{-1}) and they state that the uncertainty quoted (± 0.1 per cent) is a best estimate of the probable error and is not a statistically computed value.

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II/3

Physical property: Enthalpy of fusion (melting), ΔH_m
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of fusion)
J kg^{-1} or J g^{-1} (specific enthalpy of fusion)

Recommended reference material: Benzene (C_6H_6)
Range of variables: fixed point, $T_{\text{triple point}} = 278.68$ K
Physical states within the range: solid → liquid (in equilibrium with the vapour)
Class: Calibration and Test Material
Contributors: J. D. Cox, J. F. Martin

Intended usage:
The use of benzene as a test material for apparatuses employed for the measurement of enthalpies of fusion is suggested. Such apparatuses include adiabatic calorimeters[1], drop calorimeters, ice calorimeters[2,3], radiation calorimeters[4], and apparatuses using dynamic methods such as differential scanning calorimeters.

Sources of supply and/or methods of preparation:
Samples of benzene of certified high purity can be obtained from suppliers (B) and (F).

Methods for the purification of benzene have been given by Thorne *et al.*[5].

Pertinent physicochemical data:
The value for the enthalpy of fusion selected by Stull, Westrum and Sinke[7] is 9837 J mol^{-1}, i.e. 125.9 J g^{-1}.

Details of a determination of a value for the enthalpy of fusion, albeit with a result differing slightly from the selected value quoted above, have been given by Oliver *et al.*[6].

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III/1

Physical property: Enthalpy of vaporization, ΔH_v
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of vaporization)
J kg^{-1} or J g^{-1} (specific enthalpy of vaporization)
Recommended reference material: Benzene (C_6H_6)
Range of variables: 298–510 K along the liquid–vapour saturation curve
Physical states within the range: liquid → real saturated vapour
Class: Calibration and Test Material
Contributors: J. D. Cox, D. R. Douslin, J.F. Martin

Intended usage:
Modern methods for the determination of the enthalpies of vaporization of liquids, based either on direct measurement by calorimetry or on calculations using vapour pressure data, are described in monographs[1,2,3]. So far as

direct measurement is concerned, the normal practice is to measure electrical energy input to the calorimeter with the aid of appropriate physical standards. To check the efficacy of the measurement procedure it is recommended that benzene be used as a test material.

Sources of supply and/or methods of preparation:
Samples of benzene of purity greater than 99.9 mol per cent are available from various sources, e.g. suppliers (B) and (F).

Pertinent physicochemical data:
Douslin and Todd[4] have selected the following values for the enthalpy of vaporization for various temperatures expressed on the International Practical Temperature Scale of 1968, using published data together with some of their own unpublished values. The values of ΔH_v are expressed as kJ mol^{-1}. The uncertainty of a given value of ΔH_v is less than 0.01 kJ mol^{-1}.

T/K	298.099	307.207	314.088	324.441	332.298	353.242	377.582
ΔH_v	33.844	33.330	32.951	32.370	31.924	30.727	29.255

Lawrenson[5] has calculated values of ΔH_v from a correlation of published values of liquid and vapour properties of benzene. The values he derives for temperatures below 380 K are in good agreement with those given above; the values he derives for temperatures above 380 K are as follows:

T/K	390	410	430	450	470	490	510
ΔH_v	28.55	27.27	25.86	24.31	22.51	20.42	17.90

The uncertainty of a given value of ΔH_v should not exceed 0.2 kJ mol^{-1}.

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III/2

Physical property: Enthalpy of vaporization, ΔH_v
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of vaporization)
J kg^{-1} or J g^{-1} (specific enthalpy of vaporization)
Recommended reference material: Water (H_2O)
Range of variables: 0–340°C along the liquid–vapour saturation curve
Physical states within the range: liquid → real saturated vapour
Class: Calibration and Test Material
Contributors: J. D. Cox, J. F. Martin, I. Wadsö

Intended usage:
Modern methods for the determination of the enthalpies of vaporization of liquids, based either on direct measurement by calorimetry or on calculations using vapour pressure data, are described in monographs[1,2,3]. So far as direct measurement is concerned, the normal practice is to measure the electrical input to the calorimeter with the aid of appropriate physical standards. To check the efficacy of the measurement procedure it is recommended that water be used as a test material.

Sources of supply and/or methods of preparation:
McCullough *et al.*[4] utilized a sample prepared by distillation of deionized water from potassium permanganate.

Pertinent physicochemical data:
Osborne and co-workers[5] studied the thermal properties of liquid and real-gas water substance in researches extending over many years (see reference 1, Chapter 11). The following data have been extracted from a summarizing paper[5] and that paper should be consulted for values at closer temperature intervals, extending up to a temperature of 374°C.

θ/°C	ΔH_v/J g^{-1}	θ/°C	ΔH_v/J g^{-1}	θ/°C	ΔH_v/J g^{-1}
0	2500.8	120	2202.7	240	1765.6
25	2441.7	140	2144.9	260	1661.3
40	2406.2	160	2082.5	280	1542.8
60	2358.0	180	2015.1	300	1404.3
80	2308.2	200	1940.6	320	1237.6
100	2256.7	220	1857.7	340	1027.0

Independent measurements made by Wadsö at 25°C gave the value 2443.4 J g^{-1}. Osborne and Ginnings[7] made measurements at 25°C and obtained the value 2444.1 J g^{-1}. Measurements by McCullough *et al.*[4] made for the temperature 100°C gave the value 2256 J g^{-1}. It would seem therefore that the values given in the above table are accurate, to within ± 2 J g^{-1}.

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IV/1

Physical property: Enthalpy of sublimation, ΔH_s
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation)
J kg^{-1} or J g^{-1} (specific enthalpy of sublimation)
Recommended reference material: Benzoic acid ($C_7H_6O_2$)
Range of variables: temperatures near 298 K along the saturated vapour curve
Physical states within the range: solid → real saturated vapour
Class: Calibration and Test Material
Contributor: J. D. Cox

Intended usage:
Until recently, calorimetric measurements of the enthalpy of sublimation had rarely been attempted, although a newly developed method[1] gives promise of wide application. Most values of the enthalpy of sublimation to be found in the literature have been calculated from measured values of the saturated vapour pressure as a function of temperature, or from a combination of measured values of enthalpies of fusion of solids and the enthalpies of vaporization of liquids[2]. Whichever experimental approach is employed, it is important to check the efficacy of the method by the use of a test material, and benzoic acid is recommended for this purpose. Benzoic acid should be especially useful in a programme of measurements of the enthalpies of sublimation of solids having saturated vapour pressures around a pressure of 0.1 Pa at 298 K.

Sources of supply and/or methods of preparation:
Samples of benzoic acid of high purity are available from several sources, for example, from sources (A), (D), (E) and (M).

Pertinent physicochemical data:
Davies and Jones[3] derived the value 91.4 ± 1.4 kJ mol^{-1} for the enthalpy of sublimation at 363 K, from measurements of the saturated vapour pressure of crystalline benzoic acid in the temperature range 70–114°C. Colomina *et al.*[4] measured the vapour pressure of the crystalline acid at near-ambient temperatures by an improved Knudsen method, and calculated a value of 90.0 ± 0.3 kJ mol^{-1} for the temperature 25°C. Morawetz[5] obtained the value 89.5 ± 0.2 kJ mol^{-1} from calorimetric measurements at 25°C. Malaspina *et al.*[6] used a combined effusion–microcalorimetry apparatus to study the vaporization of crystalline benzoic acid (338–383 K). They report the following mean values for the enthalpy of sublimation at 298 K: 89.3 ± 0.4 kJ mol^{-1} by microcalorimetry; 89.0 ± 0.4 kJ mol^{-1} by second-law treatment of effusion measurements; 94.5 ± 0.3 kJ mol^{-1} by third-law treatment of effusion measurements. The inconsistency between the last of these values and the others may have arisen from the use of erroneous values of the Gibbs energy function. The recommended selected value from all these measurements is 89.7 ± 0.5 kJ mol^{-1} for the temperature 298.15 K.

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IV/2

Physical property: Enthalpy of sublimation, ΔH_s
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of sublimation)
J kg^{-1} or J g^{-1} (specific enthalpy of sublimation)
Recommended reference material: Naphthalene ($C_{10}H_8$)
Range of variables: temperatures near 298 K along the saturated vapour curve
Physical state within the range: solid → real saturated vapour
Class: Calibration and Test Material
Contributor: J. D. Cox

Intended usage:

Until recently, calorimetric measurements of the enthalpy of sublimation have rarely been attempted, though a newly developed method[1] gives promise of wide application. Most values of the enthalpy of sublimation to be found in the literature have been calculated from measurements of the saturated vapour pressure as a function of temperature, or from a combination of measured values of enthalpies of fusion of solids and the enthalpies of vaporization of liquids[2]. Whichever experimental approach is employed, it is important to check the efficacy of the method by use of a test material, and naphthalene is recommended for this purpose. Naphthalene should be especially useful in a programme of measurements of the enthalpies of sublimation of solids having saturated vapour pressures around a pressure of 10 Pa at 298 K.

Sources of supply and/or methods of preparation:

Naphthalene of certified high purity is obtainable from suppliers (B) and (F).

Pertinent physicochemical data:

Miller[3] combined his results of measurement of the saturated vapour pressure of solid naphthalene (230–260 K) with thermodynamic and statistico-mechanical values to obtain the mean value 72.68 ± 0.33 kJ mol^{-1} at 298 K for the enthalpy of sublimation. Morawetz[4] obtained the value 72.05 ± 0.25 kJ mol^{-1} for 298 K by direct calorimetric measurement. Irving[5] used a calorimetric method to determine the enthalpy of sublimation of samples of naphthalene from three different sources and found no significant inter-sample differences in the results. He reports the value 73.00 ± 0.25 kJ mol^{-1} for the temperature of 298 K. Ambrose and Lawrenson[6] derived the value 72.5 kJ mol^{-1} for the temperature 298 K from their assessed values of the vapour pressure of crystalline naphthalene.

The recommended value for the enthalpy of sublimation at 298 K is 72.5 ± 0.25 kJ mol^{-1}.

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V/1

Physical property: Enthalpy of reaction, ΔH_r°
Units: J kg^{-1} or J g^{-1} (specific enthalpy of reaction)
Recommended reference material: Zirconium + barium chromate
Range of variables: 25°C (298.15 K) is the temperature normally employed
Physical states within the range: solid + solid
Class: Calibration and Test Material; Certified Reference Material
Contributors: G. T. Armstrong, J. D. Cox

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 reference 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.

Sources of supply and/or methods of preparation:
Zirconium plus barium chromate mixtures of three distinct nominal heating values, viz. −350, −390 and −425 cal g^{-1} (1 cal = 4.1840 J) are available from supplier (M).

Before use, heat-source powders of the types referred to above should be dried for two hours at 71°C at 1.3 kPa pressure in a flat metal 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 on pages 4 and 5 of reference 1.

Pertinent physicochemical data:
The heating values (i.e. the specific enthalpy changes for solid-state reactions, when no air, oxygen or nitrogen are in contact with the samples) of three batches of zirconium + barium chromate mixtures were determined[1] at the National Bureau of Standards, Washington DC, by means of an isoperibol calorimeter[2]. The samples were weighed in air.

NBS Standard Reference Material 1651: Heating value −1460 ± 4.8 J g^{-1}
NBS Standard Reference Material 1652: Heating value −1632.3 ± 7.3 J g^{-1}
NBS Standard Reference Material 1653: Heating value −1762.0 ± 3.0 J g^{-1}

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V/2

Physical property: Enthalpy of reaction in solution, ΔH_r°
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction)
J kg^{-1} or J g^{-1} (specific enthalpy of reaction)
Recommended reference materials: Sulphuric acid solution + sodium hydroxide solution
Range of variables: 25°C (298.15 K) is the temperature normally employed
Physical state within the range: liquid
Class: Calibration and Test Material
Contributors: J. D. Cox, S. R. Gunn

Intended usage:
Calorimeters[1] for the measurement of enthalpies of reaction in solution 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 programme involving rapid exothermic reactions in solution, the reaction between sulphuric acid solution and excess sodium hydroxide solution, at defined concentrations, is recommended as a test reaction.

Sources of supply and/or methods for preparation:
Instructions for preparing solutions of sulphuric acid and sodium hydroxide as calorimetric reactants have been given by Gunn[2,3].

Pertinent physicochemical data:
Gunn[2] has studied the enthalpy changes for the reactions between $H_2SO_4(8H_2O)$ and 2.5 moles of $NaOH(xH_2O)$ where x lay between 10 and 2580. By the use of a reaction calorimeter calibrated electrically Gunn[2] found the mean value -150.82 ± 0.02 kJ mol^{-1} at 298.15 K for the enthalpy of the reaction

$$H_2SO_4(8H_2O)(l) + 2.5\,[NaOH\,(10H_2O)]\,(l) = [Na_2SO_4 + 0.5\,NaOH]\,(35H_2O)\,(l)$$

Prosen and Kilday[4] studied essentially the same process in an adiabatic, vacuum-jacketed solution calorimeter calibrated electrically, and found enthalpy values which were the same within the stated uncertainty. Gunn *et al.*[3] found the mean value -150.80 ± 0.02 kJ mol^{-1} for the same reaction at 298.15 K by the use of bomb calorimeters calibrated by the combustion of benzoic acid.

Near 25°C the temperature coefficient of the enthalpy of the reaction is given by $(d\Delta H_r^\circ/dT) = +88$ J K^{-1} mol^{-1}.

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V/3

Physical property: Enthalpy of reaction, ΔH_r°
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction)
J kg^{-1} or J g^{-1} (specific enthalpy of reaction)
Recommended reference materials: Hydrogen + oxygen
Range of variables: 25°C (298.15 K) is the temperature normally employed
Physical state within the range: gas
Class: Calibration and Test Material
Contributors: J. D. Cox, A. J. Head

Intended usage:
Enthalpies of gas-phase reactions are generally measured by means of a flow calorimeter incorporating either a burner or a solid catalyst. Descriptions of such calorimeters, which may be operated isothermally. adiabatically or isoperibolically, are to be found in references 1, 2 and 3. The energy-equivalent of a gas-phase reaction calorimeter may be determined by the dissipation of measured amounts of electrical energy, but in some designs of calorimeter 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. Alternatively the hydrogen + oxygen reaction can be used to check the accuracy of an electrical calibration. Indeed the hydrogen + oxygen reaction is the only gas–gas reaction that is internationally agreed as being suitable for the calibration of reaction calorimeters.

Sources of supply and/or methods of preparation:
Compressed hydrogen and oxygen of high purity are available from many manufacturers.

Pertinent physicochemical data:
When a gas-reaction calorimeter is operated at a temperature close to 298 K, most of the water formed by the hydrogen + oxygen reaction is liquid and the liquid state would be the obvious reference state for water; allowance for the enthalpy of condensation of the water vapour 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 vapour pressure were 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[4] which has selected the following values, based on experimental work by Rossini, King and Armstrong, and Keenan, Keyes, Hill and Moore:

$$H_2(g) + 0.5\ O_2(g) = H_2O\,(l), \quad \Delta H^\circ_{r,\,298.15\ K} = -285.830 \pm 0.042\ \text{kJ mol}^{-1}$$

$$H_2(g) + 0.5\,O_2(g) = H_2O(g), \quad \Delta H^\circ_{r,\,298.15\,K} = -241.814 \pm 0.042\ \mathrm{kJ\,mol^{-1}}$$

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[4] S. Sunner, *J. Chem. Thermodynamics*, 3, 1 (1971).

V/4

Physical property: Enthalpy of reaction, ΔH°_r

Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction)
J kg^{-1} or J g^{-1} (specific enthalpy of reaction)

Recommended reference materials: Hydrogen + chlorine

Range of variables: 25°C (298.15 K) is the temperature normally employed

Physical state within the range: gas

Class: Calibration and Test Material

Contributors: J. D. Cox, O. Riedel

Intended usage:

Enthalpies of gas-phase reactions are generally measured by means of a flow calorimeter incorporating either a burner or a solid catalyst. Descriptions of such calorimeters, which may be operated isothermally, adiabatically or isoperibolically, are to be found in references 1, 2 and 3. The energy-equivalent of a gas-phase reaction calorimeter may be established either by use of electric energy, or by use of the hydrogen + oxygen reaction. For checking the accuracy of a calibration, use of the hydrogen + chlorine reaction is recommended.

Sources of supply and/or method of preparation:

Compressed hydrogen and chlorine of high purity are available from many manufacturers.

Pertinent physicochemical data:

In some types of gas-reaction calorimeters the hydrogen chloride formed from the reaction between hydrogen and chlorine may leave the calorimeter in the gas state. The following value, selected by the CODATA Task Group on Key Values for Thermodynamics[4], will be applicable to a reaction conducted at low pressure:

$$0.5\,H_2(g) + 0.5\,Cl_2(g) = HCl(g), \quad \Delta H^\circ_{r,\,298.15\,K} = -92.31 \pm 0.13\ \mathrm{kJ\,mol^{-1}}$$

In other types of gas-reaction calorimeters hydrogen chloride may be conveniently absorbed in water placed initially within the calorimeter. The following value, selected by the CODATA Task Group[4], will then be relevant:

$$0.5\,H_2(g) + 0.5\,Cl_2(g) + \infty H_2O\,(l) = HCl(\infty H_2O)\,(l),$$
$$\Delta H^\circ_{r,\,298.15\,K} = -167.080 \pm 0.088\ \mathrm{kJ\,mol^{-1}}$$

Data needed to correct the above value from that for infinite dilution to that for finite dilution may be taken from references 5 or 6.

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V/5

Physical property: Enthalpy of reaction, ΔH_r°
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction)
J m^{-3} or GJ m^{-3} (volumetric enthalpy of reaction)
Recommended reference materials: Methane + oxygen ($CH_4 + O_2$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed but 60°F (15.555°C) is the commonly used temperature in some countries
Physical state within the range: real gas
Class: Calibration and Test Material
Contributor: G. T. Armstrong

Intended usage:
Heating values of gaseous fuels are customarily measured by means of a flow calorimeter in which the gas is burned in air or oxygen. Descriptions of such calorimeters are to be found in references 1 and 2. The enthalpy of combustion per unit volume is generally indicated on a chart. The calorimeter is usually run as a continuous-flow device and is most readily calibrated by occasional experiments with methane samples of known composition and heating value. Electrical calibration is essentially impossible. The calorimeters burn the gas in excess air at constant atmospheric pressure. The gas is metered by a wet test meter, hence the heating value observed is that of the gas saturated with water.

Sources of supply and/or methods of preparation:
Samples in gas cylinders of methane of good quality, certified as to the enthalpy of combustion, are available from supplier (J). The samples have been compared with a pure methane sample using a typical flow calorimeter. The heating value of the pure methane sample had been certified at the National Bureau of Standards, USA. The pure methane sample was obtained from supplier (L).

Pertinent physicochemical data:
The certification of the pure methane sample is described by Armstrong[3]. The value for the enthalpy of combustion of the real gas is based upon the measurements made by Rossini[4] and by Prosen and Rossini[5] 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 -212.80 kcal mol^{-1} (1 cal = 4.1840 J) which Armstrong[3] recalculated to obtain the value -890.31 ± 0.29 kJ mol^{-1}. Results in agreement with this figure have been published by Pittam and Pilcher[6], who found the value -890.71 ± 0.38 kJ mol^{-1}. All these values refer to a temperature of 298.15 K.

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[6] D. A. Pittam and G. Pilcher, *J. Chem. Soc. Faraday I*. **68**, 2224 (1972).

VI/1

Physical property: Enthalpy of reaction in solution, ΔH_r°
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of reaction)
J kg^{-1} or J g^{-1} (specific enthalpy of reaction)
Recommended reference materials: α-Silicon dioxide (α-quartz; 'low' quartz) + hydrofluoric acid (24.4 per cent by mass)
Range of variables: 25°C is the reference temperature usually employed but the actual temperature of certification in this instance is 353.15 K. Information is given to permit conversion of the value to 298.15 K.
Physical states within the range: solid → liquid solution
Class: Calibration and Test Material; Certified Reference Material
Contributors: J. D. Cox, E. J. Prosen

Intended usage:
Calorimeters[1] for the measurement of the enthalpies of solution of solids in hydrofluoric acid solution 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 25°C. For an experimental programme of this type α-quartz is recommended as a test material.

Sources of supply and/or methods of preparation:
A suitable sample of α-quartz with a certified[2] value for the enthalpy of reaction is available from supplier (M).

Pertinent physicochemical data:
Kilday and Prosen[3] have determined the enthalpy of reaction of α-quartz

(NBS Standard Reference Material 1654) with a solution containing 24.4 per cent (by mass) hydrofluoric acid. The enthalpy of reaction was found to be -141.93 ± 0.07 kJ mol^{-1} (i.e. -2362.2 ± 1.1 J g^{-1}). These values refer to a concentration of 5 g of α-quartz per 1000 cm^3 of hydrofluoric acid, and to a sample that passed a No. 200 sieve but was retained by a No. 400 sieve. The equation representing the reaction and solution process is

$$\mathrm{SiO_2(c,\alpha\text{-}quartz) + 155[HF(3.44\ H_2O)](l) = [H_2SiF_6 + 149HF](535.2\ H_2O)(l)}$$

The certificate[2] that accompanies the material available from supplier (M) gives instructions for the use of the material and provides references to other work. The temperature coefficient of the reaction is given by $(\mathrm{d}\Delta H_r^\circ/\mathrm{d}T) = -95.3$ J K^{-1} mol^{-1}. The effect on the enthalpy of reaction caused by small departures of the hydrofluoric acid concentration from the nominal 24.4 per cent can be allowed for by the use of the factor $-$ 79.6 J mol^{-1} (mass per cent HF)$^{-1}$.

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VI/2

Physical property: Enthalpy of solution, ΔH_s°
Units: J mol^{-1} or kJ mol^{-1} (molar enthalpy of solution)
J kg^{-1} or J g^{-1} (specific enthalpy of solution)
Recommended reference material: Potassium chloride (KCl)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical states within the range: solid → liquid solution
Class: Calibration and Test Material
Contributors: J. D. Cox, O. Riedel

Intended usage:
Calorimeters[1] 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 well established. For an experimental programme involving endothermic dissolution, especially of a freely soluble substance dissolving in water, potassium chloride is recommended.

Sources of supply and/or method of preparation:
Samples of potassium chloride of high purity are available from many chemical supply houses. Supplier (M) can provide a 'primary chemical' grade as SRM 999.

Pertinent physicochemical data:
Many studies of the suitability of potassium chloride as an enthalpy-of-solution test material have been made, and many values for the enthalpy have been published[2, 3, 4]. According to Gunn[5] the value for the enthalpy is somewhat dependent on the pretreatment given to the sample, and this factor may limit the accuracy with which the enthalpy can be specified. The modern values reported below all refer to the process carried out at 298.15 K, represented by the equation

$$\mathrm{KCl\,(c) + 200\,H_2O\,(l) = KCl\,(200\,H_2O)\,(l)}$$

Gunn[5] reported a value + 17.57 ± 0.02 kJ $\mathrm{mol^{-1}}$; Somsen, Coops and Tolk[2] reported + 17.51 ± 0.01 kJ $\mathrm{mol^{-1}}$; Irving and Wadsö[6] reported + 17.53 ± 0.01 kJ $\mathrm{mol^{-1}}$; Vasil'ev and Lobanov[3] reported + 17.54 ± 0.03 kJ $\mathrm{mol^{-1}}$ and Olofsson *et al.*[7] reported + 17.55 ± 0.03 kJ $\mathrm{mol^{-1}}$.

The recommended value is + 17.55 ± 0.04 kJ $\mathrm{mol^{-1}}$ where the ± term allows for the effect of various ways of preparing the sample. Near 25°C the temperature coefficient of the enthalpy of this reaction is given by $(\mathrm{d}\Delta H_s/\mathrm{d}T) = -\,145\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

The measurements made by Olofsson *et al.*[7] which actually relate to the reaction

$$\mathrm{KCl\,(c) + 450\,H_2O\,(l) = KCl\,(450\,H_2O)\,(l)}$$

were conducted at 25, 40, 55, 60, 87 and 117°C, with meticulous attention to detail; their remarks on the need to grind samples before drying them are noteworthy. A relation valid for a wide range of temperatures is given in reference 7.

The concentration dependence of the enthalpy can be deduced from the data presented by Lange and Monheim[8].

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[5] S. R. Gunn, *J. Phys. Chem.* **69**, 2902 (1965).

[6] R. J. Irving and I. Wadsö, *Acta Chem. Scand.* **18**, 195 (1964).

[7] G. Olofsson, S. Sunner, M. Efimov and J. Laynez, *J. Chem. Thermodynamics*, **5**, 199 (1973).

[8] E. Lange and J. Monheim, *Z. Phys. Chem.* **A150**, 349 (1930).

VI/3

Physical property: Enthalpy of reaction in solution, ΔH_r°
Units: J $\mathrm{mol^{-1}}$ or kJ $\mathrm{mol^{-1}}$ (molar enthalpy of reaction)
J $\mathrm{kg^{-1}}$ or J $\mathrm{g^{-1}}$ (specific enthalpy of reaction)
Recommended reference material: Tris(hydroxymethyl)aminomethane
($\mathrm{C_4H_{11}O_3N}$)
Common abbreviations: THAM or tris

Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical states within the range: solid → liquid solution
Class: Calibration and Test Material; Certified Reference Material
Contributors: G. T. Armstrong, J. D. Cox, A. J. Head, O. Riedel

Intended usage:
Calorimeters[1] 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. However, it is good practice to test the efficacy of the calorimetric procedure by measurement of the enthalpy of solution of a solid in a liquid, using a solid–liquid pair for which the enthalpy of solution has been determined by competent laboratories. Attested values exist for the enthalpy of solution at 25°C of crystalline THAM in (a) 0.1 M hydrochloric acid solution, and (b) 0.05 M sodium hydroxide solution. THAM is recommended as a suitable material for testing solution calorimeters and liquid-phase reaction calorimeters, when the experimental programme involves rapid dissolutions or reactions in solution.

Sources of supply and/or methods of preparation:
A suitable grade of THAM is available from supplier (M).

Pertinent physicochemical data:
(a) Dissolution of crystalline THAM in 0.1 M hydrochloric acid solution. The following values of the enthalpy (298.15 K) apply to a THAM concentration of 5 mg cm^{-3}, -245.47 ± 0.02 J g^{-1} (Gunn[2]), -245.54 ± 0.06 J g^{-1} (Hill, Ojelund and Wadsö[3]), -245.76 ± 0.26 J g^{-1} (Kilday and Prosen[4]). The uncertainty figure attached to the results reported by Kilday and Prosen[4] allows for inhomogeneity in the sample and for other possible systematic errors, in addition to calorimetric replication errors.
(b) Dissolution of crystalline THAM, in 0.05 M sodium hydroxide solution. The following values of the enthalpy (298.15 K) apply to a THAM concentration of 5 mg cm^{-3}, $+141.90 \pm 0.08$ J g^{-1} (Hill, Ojelund and Wadsö[3]), $+141.70 \pm 0.19$ J g^{-1} (Kilday and Prosen[4]). The uncertainty figure attached to the results reported by Kilday and Prosen[4] allows for possible errors in the analysis of the sodium hydroxide solution and for other possible systematic errors, in addition to calorimetric replication errors.

In the temperature range 293–303 K the temperature coefficient of the enthalpy of reaction[4] for condition (a) is $(\mathrm{d}\Delta H_{\mathrm{r}}^{\circ}/\mathrm{d}T) = +1.435 \pm 0.023$ J g^{-1} K^{-1}, and for condition (b) is $(\mathrm{d}\Delta H_{\mathrm{r}}^{\circ}/\mathrm{d}T) = +1.033 \pm 0.041$ J g^{-1} K^{-1}.

A relation valid for a wide range of temperature is given by Olofsson *et al.*[5]. Because of the sensitivity of the values of the enthalpies of reactions of type (b) to changes in concentration it is important to keep closely to the specified concentrations.

REFERENCES

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[5] G. Olofsson, S. Sunner, M. Efimov and J. Laynez, *J. Chem. Thermodynamics*, **5**, 199 (1973).

VI/4

Physical property: Enthalpy of mixing, ΔH^{E}
Units: J mol^{-1} (molar enthalpy of mixing)
J kg^{-1} or J g^{-1} (specific enthalpy of mixing)
Recommended reference materials: Cyclohexane + *n*-hexane (C_6H_{12} + C_6H_{14})
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: liquid
Class: Calibration and Test Material
Contributor: J. D. Cox

Intended usage:
Calorimeters[1] for the measurement of the enthalpies of mixing of liquids (equal to the excess enthalpies of the corresponding mixtures, since the enthalpy of mixing of an ideal mixture is zero), should be calibrated electrically. However, it is good practice to prove the efficacy of 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 cyclohexane + *n*-hexane has been recommended for this purpose by McGlashan and Stoeckli[2].

Sources of supply and/or method of preparation:
Suitable samples[3] of cyclohexane ('Research Grade') may be obtained from supplier (N). Suitable samples of *n*-hexane may be obtained from various supply houses, for example[3] 'AR Grade' can be obtained from supplier (I).

Pertinent physicochemical data:
Ewing *et al.*[3] have determined the enthalpy of mixing (298.15 K) by the use of three different apparatuses. The results for each series of experiments may be expressed by the following polynomial where the subscript 2 refers to *n*-hexane

$$H^{E}/\text{J mol}^{-1} = x_2(1 - x_2)[A + B(1 - 2x_2) + C(1 - 2x_2)^2 + D(1 - 2x_2)^3 + E(1 - 2x_2)^4]$$

The constants for their three series of experiments were

Series	A	B	C	D	E
1	864.67	249.51	99.06	33.22	—
2	865.09	249.32	92.77	35.31	9.00
3	864.55	247.70	99.92	35.46	

From these data the mean value of the maximum value of the enthalpy of mixing at 298.15 K is 221.0 J mol^{-1}, and this occurs at a mole fraction of *n*-hexane equal to 0.421.

According to McGlashan and Stoeckli[2] the maximum value of the enthalpy of mixing at 298.15 K is 221.4 J mol^{-1}, and this occurs at a mole fraction of *n*-hexane equal to 0.424. The equation given by these authors is similar in form to the above equation, with $A = 866.1$, $B = 249.4$, $C = 97.0$, $D = 31.8$ and $E = 0$. Near 25°C the temperature coefficient of the enthalpy of mixing at the maximum is given[4] by $(\mathrm{d}\Delta H^{\mathrm{E}}/\mathrm{d}\,T) = -1.39\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

REFERENCES

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[3] M. B. Ewing, K. N. Marsh, R. H. Stokes and C. W. Tuxford, *J. Chem. Thermodynamics*, **2**, 751 (1970).

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VI/5

Physical property: Enthalpy of dilution
Units: J mol^{-1} (molar enthalpy of dilution)
Recommended reference material: Sucrose ($C_{12}H_{22}O_{11}$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical states within the range: aqueous solutions
Class: Calibration and Test Material
Contributor: R. N. Goldberg

Intended usage:
Calorimeters[1] 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 errors in calibration and measurement procedures.

Sources of supply and/or methods of preparation:
A suitable grade of sucrose is available as Standard Reference Material No. 17a from supplier (M).

Pertinent physicochemical data:
The best data at present available are those given by Gucker *et al.*[2] who expressed values for the relative apparent molal enthalpy, φ_{L}, by the following equations:

$$\varphi_{\mathrm{L}}/\mathrm{J\ mol^{-1}} = 539.3\,m - 28.941\,m^2 \quad \text{at } 20^{\circ}\mathrm{C}\ (m \leqslant 5.9)$$
$$\varphi_{\mathrm{L}}/\mathrm{J\ mol^{-1}} = 563.2\,m - 29.50\,m^2 \quad \text{at } 25^{\circ}\mathrm{C}\ (m \leqslant 2.2)$$
$$\varphi_{\mathrm{L}}/\mathrm{J\ mol^{-1}} = 586.6\,m - 29.62\,m^2 \quad \text{at } 30^{\circ}\mathrm{C}\ (m \leqslant 2.2)$$

where m is the molality, i.e. the concentration expressed in mol kg^{-1}. These workers performed their measurements by means of an adiabatic twin-calorimeter and used Standard Reference Material No. 17 obtained from supplier (M).

The usefulness of the dilution of aqueous sucrose solutions for the testing of microcalorimeters is under examination in several different laboratories. The following dilutions are deemed to be of particular interest: 0.20 m to 0.10 m; 0.20 m to 0.066 m and 0.50 m to 0.25 m.

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VII/1

Physical property: Energy of combustion, ΔU_c°
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Benzoic acid ($C_7H_6O_2$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material; Certified Reference Material
Contributors: G. T. Armstrong, J. D. Cox, H. Feuerberg, J. Franc, B. N. Oleinik, O. Riedel
Intended usage:

By international agreement, reached in 1934, benzoic acid is the principal reference material for measuring the energy equivalent of oxygen-bomb calorimeters. These calorimeters all 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, 2, 3]: 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 difficult-to-burn materials, to influence the overall stoichiometry of a combustion reaction and to test analytical procedures.

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 suppliers (A) and (M). Samples certified by the National Physical Laboratory, UK are available from suppliers (D) and (E).

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 ΔU_{cert}, the specific energy of combustion certified by a national standardizing laboratory as the energy evolved when 1 g (mass *in vacuo*) of benzoic acid burns under 'standard bomb conditions'[1]. In 1966 Hawtin[4] made a statistical assessment of published values of ΔU_{cert}, finding the mean value -26434.4 ± 1.2 J g^{-1}. Other values, published since 1966, have been listed[5]. The newer values would reduce Hawtin's mean value very slightly, and it is reasonable to adopt the rounded value -26434 J g^{-1} as the value appropriate to pure benzoic acid. It is important to note, however, that a given batch of benzoic acid to be used for the calibration of a bomb calorimeter may not be chemically pure. Indeed it need not be pure provided it is homogeneous, but if it is not pure it cannot be used for testing analytical procedures. A value of ΔU_{cert} for each batch should be available from the suppliers. According to present knowledge[1]. the relation between ΔU_c° and ΔU_{cert} is

$$|\Delta U_{\text{cert}}| - |\Delta U_c^{\circ}| = 20 \text{ J g}^{-1}$$

Armstrong[6] has discussed possible sources of error in the calorimeters whose use led to $\Delta U_{\text{cert}} = -26434$ J g^{-1}.

Since benzoic acid does not establish the scales of joules per mole or joules per gram the term 'primary standard for calorimetry' is inappropriate: the role of benzoic acid is to transfer the measurement scale from national standardizing laboratories to other laboratories.

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VII/2

Physical property: Energy of combustion, ΔU_c
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Hippuric acid ($C_9H_9O_3N$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, A. J. Head

Intended usage:
Energies of combustion in oxygen of most compounds containing no elements but C, H, O, N can be accurately measured with the aid of a static bomb calorimeter[1,2,3]. The energy equivalent of the calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and their experimental procedure generally, by combustion of a test material of known energy of combustion. Hippuric acid was recommended for this purpose by Huffman[4]; it is a test material for the combustion calorimetry of C, H, O, N compounds, especially those that can be burned without being first sealed in a capsule.

Sources of supply and/or methods of preparation:
Three groups of investigators[4,5,6] prepared samples of hippuric acid for combustion calorimetry by recrystallization of good commercial material from water; other methods of purification were investigated by Huffman[4]. Recrystallized material may be dried *in vacuo* and stored over phosphorus pentoxide, but there is evidence[6] that material so dried may contain about 0.06 per cent of water; see also the following section.

Pertinent physicochemical data:
A study of the use of hippuric acid as a test material in combustion calorimetry showed it to be suitable in most respects[4], save that complete removal of water cannot be assured. Hubbard, Frow and Waddington[6] also found difficulty in completely removing water from a sample recrystallized from water and they therefore based their value for the energy of combustion on the mass of carbon dioxide formed rather than on the mass of sample taken. Cox and Pilcher[1] selected from published data the value $-23\,548$ J g^{-1} for the specific energy of combustion for the reaction

$$C_9H_9O_3N\,(c) + 9.75\,O_2\,(g) = 9\,CO_2\,(g) + 4.5\,H_2O\,(l) + 0.5\,N_2\,(g)$$

A more rigorous investigation of the suitability of hippuric acid to serve as a test material is desirable. In particular the problem of removal of water should be restudied and the method applied by Vanderzee and Westrum[7] to the drying of succinic acid is worthy of trial.

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[2] F. D. Rossini (editor), *Experimental Thermochemistry*, Vol. I. Wiley (Interscience): New York (1956).

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[7] C. E. Vanderzee and E. F. Westrum Jr, *J. Chem. Thermodynamics*, **2**, 681 (1970).

VII/3

Physical property: Energy of combustion, ΔU_c°
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Succinic acid ($C_4H_6O_4$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, H. Feuerberg, A. J. Head, E. F. Westrum Jr

Intended usage:
Energies of combustion in oxygen of most compounds containing no elements but C, H, O, N can be accurately measured with the aid of a static bomb calorimeter[1, 2, 3]. The energy equivalent of the calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and their experimental procedure generally, 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, especially those that can be successfully burned without being first sealed in a capsule.

Sources of supply and/or methods of preparation:
A suitable sample of succinic acid can be prepared[4, 5] from an analytical-grade specimen by four recrystallizations from distilled water, and an effective drying procedure is described.

Pertinent physicochemical data:
The energy of combustion of succinic acid has been measured many times. Cox and Pilcher's selected value is -12634 J g^{-1}. However, recent studies[4, 5] of the removal of water from succinic acid samples indicate that at least some of the measured values from which the selection was made relate to samples that may have contained residual water. Vanderzee, Månsson and Sunner[5] have reported the value -12639.3 ± 2.3 J g^{-1} and have re-assessed all values published up to 1972 to give the selected value -12638.0 ± 1.6 J g^{-1}. The reaction to which this value applies is

$$C_4H_6O_4\,(c) + 3.5\,O_2\,(g) = 4\,CO_2\,(g) + 3\,H_2O\,(l)$$

REFERENCES

[1] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press: London (1970).

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[4] C. E. Vanderzee and E. F. Westrum Jr, *J. Chem. Thermodynamics*, **2**, 681 (1970).

[5] C. E. Vanderzee, M. Månsson and S. Sunner, *J. Chem. Thermodynamics*, **4**, 533 (1972).

VII/4

Physical property: Energy of combustion, ΔU_c°

Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)

Recommended reference material: 4-Fluorobenzoic acid ($C_7H_5FO_2$)

Range of variables: 25°C (298.15 K) is the reference temperature normally employed

Physical state within the range: solid

Class: Calibration and Test Material

Contributors: J. D. Cox, A. J. Head, O. Riedel

Intended usage:

Energies of combustion in oxygen of most organic compounds containing fluorine can be accurately measured with the aid of a platinum-lined moving bomb calorimeter[1, 2, 3]. Techniques involving the use of static bomb calorimeters are less accurate. 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 a moving-bomb calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and the experimental procedure generally, 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, F, O compounds, especially those that can be successfully burnt without being sealed in a capsule initially. 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 only as a test material for C, H, F, O compounds with a hydrogen to fluorine ratio equal to or greater than unity.

Sources of supply and/or methods of preparation:

Good, Scott and Waddington[4] showed that a suitable sample of 4-fluorobenzoic acid could readily be obtained by zone refining of a commercial specimen. Highly pure samples of this acid are available from supplier (M).

Pertinent physicochemical data:

Good, Scott and Waddington[4] suggested that 4-fluorobenzoic acid had the properties required of a reference material in combustion calorimetry, and Cox, Gundry and Head[5] confirmed their suggestion. Good *et al.*[4] measured the energy of combustion of a sample assessed as 99.93 mol per cent pure and obtained the value $-21\,857 \pm 5.2$ J g^{-1}; Cox *et al.*[5] measured the energy of combustion of a sample assessed as 99.95 mol per cent pure and found the value $-21\,862.4 \pm 6.4$ J g^{-1}. These values refer to the reaction

$$C_7H_5FO_2\,(c) + 7\,O_2\,(g) + 18\,H_2O\,(l) = 7\,CO_2\,(g) + HF\,(20\,H_2O)\,(l)$$

Preliminary values[6] for two samples of 4-fluorobenzoic acid are in reasonable accord with those given above.

REFERENCES

[1] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press: London (1970).

[2] F. D. Rossini (editor), *Experimental Thermochemistry*, Vol. I. Wiley (Interscience): New York (1956).

[3] H. A. Skinner (editor), *Experimental Thermochemistry*, Vol. II. Wiley (Interscience): New York (1962).

[4] W. D. Good, D. W. Scott and G. Waddington, *J. Phys. Chem.* **60**, 1080 (1956).

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VII/5

Physical property: Energy of combustion, ΔU_c

Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)

Recommended reference material: Thianthrene ($C_{12}H_8S_2$)

Range of variables: 25°C (298.15 K) is the reference temperature normally employed

Physical state within the range: solid

Class: Calibration and Test Material

Contributors: J. D. Cox, A. J. Head, O. Riedel

Intended usage:

Energies of combustion in oxygen of most organic compounds containing sulphur can be accurately measured with the aid of a platinum-lined moving-bomb calorimeter[1,2,3]. Techniques involving the use of static bomb calorimeters are less accurate. 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 per cent) should be present in the compressed oxygen so that the nitrogen oxides formed during the combustion process may catalyse the oxidation of all the sulphur to the S^{VI} state. It is important to ensure that the ratio between the number of moles of combined hydrogen and of combined sulphur exceeds two in the combustion. Thus for a compound with a high proportion of sulphur it may be necessary to burn an auxiliary hydrogen-containing compound to achieve the necessary hydrogen to sulphur ratio. The energy equivalent of a moving-bomb calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and of the experimental procedure generally, 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, especially those that can be successfully burned without being enclosed initially in a capsule.

Sources of supply and/or methods of preparation:

Sunner and Lundin[4] synthesized a sample of thianthrene for use in combustion calorimetry. They purified the sample by recrystallization, sublimation and fractional freezing.

Pertinent physicochemical data:
The suitability of thianthrene as a test material in combustion calorimetry has been proved by Sunner and Lundin[4]. Cox and Pilcher[1] selected, from published data, the value − 33466 J g^{-1} which applies to the reaction

$$C_{12}H_8S_2(c) + 17O_2(g) + 228H_2O(l) = 12CO_2(g) + 2[H_2SO_4(115H_2O)](l)$$

A recent measurement[7] gave a value identical with this selected value. Values for the energies of combustion for reactions in which the concentration of the final sulphuric acid solution is other than H_2SO_4 (115 H_2O) may be deduced with the aid of tabulated heat-of-mixing data[5,6].

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[2] F. D. Rossini (editor), *Experimental Thermochemistry*, Vol. I. Wiley (Interscience): New York (1956).

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[6] V. P. Glushko (chief editor), *Termicheskie Konstanty Veshchestv*, Vol. II. Akademiya Nauk SSSR, VINITI, Table 17, Moscow (1966).

[7] G. T. Armstrong and W. H. Johnson, *Third International Conference on Chemical Thermodynamics*, Book VIII, page 55. Baden (1973).

VII/6

Physical property: Energy of combustion, ΔU_c°
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: 4-Chlorobenzoic acid ($C_7H_5ClO_2$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, A. J. Head, O. Riedel, S. Sunner
Intended usage:
Energies of combustion in oxygen of most organic compounds containing chlorine can be accurately measured with the aid of a platinum-lined moving-bomb calorimeter[1,2,3]. Techniques involving the use of static-bomb calorimeters are less accurate. In order that the sole chlorine-containing product should be a hydrochloric acid solution, sufficient reducing agent (e.g. arsenious oxide solution) should be placed in the bomb before combustion is initiated.

The energy equivalent of a moving-bomb calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and their experimental procedure generally, 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, Cl, O compounds with an atomic ratio of hydrogen to chlorine equal to or greater than unity.

Sources of supply and/or methods of preparation:
Suitable samples of 4-chlorobenzoic acid are expected to be available from supplier (M).

Pertinent physicochemical data:
It is well established that the combustion of an organochlorine compound in oxygen leads to some hydrogen chloride and some elemental chlorine. Reduction of the latter to hydrogen chloride (in solution) can be accomplished if a reducing solution is placed initially in the bomb. Cox and Pilcher[1] record two determinations of the energy of combustion of 4-chlorobenzoic acid: in one instance arsenious oxide solution was used as reductant, and in the other instance hydrazine hydrochloride solution was used as reductant. More recent collaborative work[4] between laboratories in Sweden and the USA involved the use of samples of two different origins and led to three distinct series of measurements. The suitability of 4-chlorobenzoic acid as a calorimetric standard substance was proved, and the value -19562.7 ± 3.2 $\mathrm{J\,g^{-1}}$ was established for the energy of combustion. This value applies to the reaction written below, and was obtained from experiments in which arsenious oxide solution was used as reductant.

$$C_7H_5O_2Cl\,(c) + 7\,O_2\,(g) + 598\,H_2O\,(l) = 7\,CO_2 + HCl\,(600\,H_2O)\,(l)$$

A preliminary value[5], for a National Bureau of Standards Reference Sample, is in reasonable accord with the value just quoted.

There is evidence that hydrazine hydrochloride solution can decompose, and that arsenious oxide solution can oxidize before a combustion experiment, under the conditions prevailing in a platinum-lined bomb. These unwanted reactions appear to be subject to catalysis and therefore experimenters should check to see that the reductant solutions they use are stable under their bomb conditions.

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[3] H. A. Skinner (editor), *Experimental Thermochemistry*, Vol. II. Wiley (Interscience): New York (1962).

[4] A. T. Hu, G. C. Sinke, M. Månsson and B. Ringnér, *J. Chem. Thermodynamics*, **4**, 283 (1972).

[5] G. T. Armstrong and W. H. Johnson, *Third Internatonal Conference on Chemical Thermodynamics*, Book VIII, page 55, Baden (1973).

VII/7

Physical property: Energy of combustion, ΔU_c°
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Tris(hydroxymethyl)aminomethane ($C_4H_{11}O_3N$)
Common abbreviations: THAM or tris
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, O. Riedel

Intended usage:
Energies of combustion in oxygen of most compounds containing no elements but C, H, O, N can be accurately measured with the aid of a static-bomb calorimeter[1, 2, 3]. The energy equivalent of the calorimeter will normally be established by combustion of 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. Tris(hydroxymethyl)-aminomethane is recommended as a test material for the combustion calorimetry of C, H, O, N compounds.

Sources of supply and/or methods of preparation:
A suitable grade of tris(hydroxymethyl)aminomethane is available from supplier (M).

Pertinent physicochemical data:
Laynez, Ringnér and Sunner[4] measured the energy of combustion of a sample of tris(hydroxymethyl)aminomethane, which had been estimated to be 99.96 ± 0.01 per cent pure by acidimetric titration. The samples studied (also reference 6) had a water content of less than 2×10^{-3} per cent by mass and a methanol content of less than 2×10^{-3} per cent by mass, after having been dried at 80°C for twelve hours. It is not clear whether encapsulation in polyester, as done by Laynez *et al.*[4], is essential. Laynez *et al.* report the value -20030.3 ± 3.4 J g^{-1}, i.e. -2426.41 ± 0.78 kJ mol^{-1}, where the ± figures are twice the overall standard deviations of the means. The values refer to the reaction

$$C_4H_{11}O_3N\,(c) + 5.25\,O_2\,(g) = 4\,CO_2\,(g) + 5.5\,H_2O\,(l) + 0.5\,N_2\,(g)$$

REFERENCES

[1] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press: London (1970).

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VII/8

Physical property: Energy of combustion, ΔU_c°
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Pentafluorobenzoic acid ($C_7HF_5O_2$)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributors: J. D. Cox, A. J. Head

Intended usage:
Energies of combustion in oxygen of most organic compounds containing fluorine can be accurately measured with the aid of a platinum-lined moving-bomb calorimeter[1,2,3]. Techniques involving the use of static-bomb calorimeters are less accurate. 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 a moving-bomb calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and the experimental procedure generally, 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, F, O compounds, especially those that can be successfully burnt without prior encapsulation. 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 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. Therefore pentafluorobenzoic acid serves only as a test material for C, H, F, O compounds with an atomic ratio of hydrogen to fluorine less than unity.

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 a commercial sample.

Pertinent physicochemical data:
Cox, Gundry and Head[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, viz. -12062.4 ± 4.8 J g^{-1}, relates to the reaction

$$C_7HF_5O_2\,(c) + 5\,O_2\,(g) + 102\,H_2O\,(l) = 7\,CO_2\,(g) + 5[HF(20\,H_2O)] \quad (1)$$

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, Gundry and Head chose to perform two series of experiments, in the first of which hydrocarbon oil, used as auxiliary, contributed about 40 per cent of the heat, whilst in the second benzoic acid, used as auxiliary, contributed about 60 per cent 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 number of moles of 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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VII/9

Physical property: Energy of combustion, ΔU_c
Units: J mol^{-1} or kJ mol^{-1} (molar energy of combustion)
J kg^{-1} or J g^{-1} (specific energy of combustion)
Recommended reference material: Urea (CH_4ON_2)
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: solid
Class: Calibration and Test Material
Contributor: G. T. Armstrong

Intended usage:

Energies of combustion in oxygen of most compounds containing no elements but C, H, O, N can be accurately measured with the aid of a static or a rotating bomb calorimeter[1,2,3]. The energy equivalent of the calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and of the experimental procedure generally, 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 difficulty is experienced in obtaining complete combustion.

Sources of supply and/or methods for preparation:
A suitable grade of urea is available from supplier (M).

Pertinent physicochemical data:
Johnson[4] has determined the energy of combustion of the NBS Reference Samples of urea and has tentatively ascribed the value $-10541 \pm 0.4\ \mathrm{J\ g^{-1}}$ to the specific energy of combustion for the reaction

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

Cox and Pilcher[1] reviewed the earlier work and selected a value equivalent to $-10537\ \mathrm{J\ g^{-1}}$ from a series of published values[5,6,7], the spread of which encompasses the above value.

A promoter for the combustion of urea, for which purpose benzoic acid is suitable, is necessary to obtain complete combustion. The urea samples thus test an experimeter's ability to measure difficult-to-burn substances containing C, H, O, N.

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VII/10

Physical property: Energy of combustion, ΔU_c°
Units: $\mathrm{J\ mol^{-1}}$ or $\mathrm{kJ\ mol^{-1}}$ (molar energy of combustion)
$\mathrm{J\ kg^{-1}}$ or $\mathrm{J\ g^{-1}}$ (specific energy of combustion)
Recommended reference material: 2,2,4-Trimethylpentane (C_8H_{18})
Range of variables: 25°C (298.15 K) is the reference temperature normally employed
Physical state within the range: liquid
Class: Calibration and Test Material; Certified Reference Material
Contributors: G. T. Armstrong, J. D. Cox, O. Riedel

Intended usage:
Energies of combustion in oxygen of most compounds containing no elements but C, H, O, N can be accurately measured with the aid of a static-bomb calorimeter[1,2,3]. The energy equivalent of the calorimeter will normally be established by combustion of thermochemical-standard benzoic acid. However, many workers like to check the accuracy of the benzoic acid calibration, and of the experimental procedure generally, 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[1,2,3]) before combustion. 2,2,4-Trimethylpentane therefore serves as a test material in the establishment of the calorific values of liquid gasoline fuels.

Sources of supply and/or methods of preparation:
A suitable grade of 2,2,4-trimethylpentane certified for the specific energy of combustion is available from suppliers (B) and (M).

Pertinent physicochemical data:
The value quoted by Cox and Pilcher[1] for the standard molar enthalpy of combustion of 2,2,4-trimethylpentane is -5461.37 kJ mol^{-1} which applies to the reaction

$$C_8H_{18}(l) + 12.5\,O_2(g) = 8\,CO_2(g) + 9\,H_2O(l)$$

The corresponding value of the standard specific energy of combustion is -47712 J g^{-1}.

An account of the determination of the energy of combustion of the actual sample of 2,2,4-trimethylpentane issued by the Office of Standard Reference Materials, NBS, has been given by Armstrong[4].

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PHYSICAL CHEMISTRY DIVISION
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RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

Recommendations approved 1974

EDITOR: E. F. G. HERINGTON

SECTION: OPTICAL ROTATION

COLLATORS: I. BROWN and J. E. LANE

CONTENTS

Reference materials for the measurement of optical rotation

REFERENCE MATERIALS FOR OPTICAL ROTATION MEASUREMENTS.

INTRODUCTION

The techniques of polarimetry and saccharimetry were formulated by Biot early in the nineteenth century and the methods and apparatus used are described in detail by Bates *et al.*[1], Heller[2] and Asmus[3]. Saccharimetry is extensively used in the sugar industry. The calibration materials which have been employed are sucrose solutions, dextrose solutions and quartz plates. These three materials are proposed as suitable calibration and test materials. Sucrose and dextrose are listed in the IUPAC 'Catalogue of Physicochemical Standard Substances'.

The conventional measures of optical rotation have been the specific optical rotatory power or specific optical rotation. That is the rotation in circular degrees given by a 10 cm thickness of liquid or solution containing 1 g of optically active material per millilitre. The customary symbol has been $[\alpha]^t_\lambda$ where t is the Celsius temperature and λ the wavelength of light used. A temperature of 20 °C and a wavelength 546.1 or 589.25 nm are usually used.

The conventional specific rotation for liquids is given by $[\alpha] = \alpha/l\rho$ and for solids in solution $[\alpha] = 100\alpha/lc$ where α is the rotation angle in circular degrees, l is the cell path length in dm, ρ is the density of the liquid in g ml^{-1} and c is the concentration of dissolved material in g/100 ml. For solids, degrees per millimetre have also been used.

From the above relations it can be seen that the conventional unit of specific rotation is deg ml g^{-1} dm^{-1}. In the sugar industry, measurements are made on the 'sugar scale' (°S) where 100°S is the rotation given by a 2 dm tube filled with 'normal' sucrose solution containing 26.000 g of sugar per 100 ml of solution at 20°C and $\lambda = 546.1$ nm. The quantity 100°S corresponds to an angle, α, of 40.763°; an angle which is also given by a 'normal' quartz plate (1.5934 mm thick).

The SI unit of angle is the radian, and McGlashan[4,5] has proposed the symbol α_m for the specific optical rotatory power with the unit rad m^2 kg^{-1}. This specific optical rotatory power is the rotation in radians given by a 1 m thickness of liquid or solution containing 1 kg of optically active solute per m^3 of solution. Thus

$$\alpha_m/\text{rad m}^2\text{ kg}^{-1} = [\alpha] \times \pi/180 \times 1.000028 \times 10^{-2}/\text{deg ml g}^{-1}\text{ dm}^{-1}$$

$$= [\alpha] \times 1.745378 \times 10^{-4}/\text{deg ml g}^{-1}\text{ dm}^{-1}$$

For sucrose the value of $[\alpha]^{20}_{546.1\text{nm}}/\text{deg ml g}^{-1}\text{ dm}^{-1}$ is 78.342 which corresponds to the value 1.3674×10^{-2} for $\alpha_m/\text{rad m}^2\text{ kg}^{-1}$. The SI unit rad m^2 kg^{-1} is inconveniently large and it is proposed that the unit mrad m^2 kg^{-1} be adopted thus

$$\alpha_m/\text{mrad m}^2\text{ kg}^{-1} = [\alpha] \times 0.1745378/\text{deg ml g}^{-1}\text{ dm}^{-1}$$

It should be noted that Heller[2] has suggested a unit, the Biot, which is 10.00028 times smaller than the proposed unit mrad m^2 kg^{-1}.

It would be desirable to have α_m values for calibration and test materials quoted for 25°C as well as for 20°C.

It is suggested that national laboratories who issue and/or certify samples of sucrose, dextrose or quartz plates as calibration and test materials should issue certificates with concentrations given in kg m^{-3} and with specific rotatory power given in mrad m^2 kg^{-1}.

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1

Physical property: Optical rotation, α_m
Unit: mrad m^2 kg^{-1}
Recommended reference material: Sucrose ($C_{12}H_{22}O_{11}$)
Range of variables: 20°C; wavelengths 546.1 nm, 589.25 nm
Physical state within the range: aqueous solution
Class: Certified Reference Material
Contributors: I. Brown, J. P. Cali, J. Franc, J. E. Lane, T. Plebanksi

Intended usage:
Sucrose can be used for calibration and for checking the performance of manually operated and automatically recording light polarimeters and saccharimeters employed for determination of the optical rotation of liquids or dissolved solids. Details of the apparatus and of the methods are available[1, 2, 3].

Sources of supply and/or methods of preparation:
Samples of sucrose are available from suppliers (B) and (C). As sucrose must be kept dry during storage to avoid the possibility of inversion, samples should be stored in sealed ampoules under vacuum or in dry inert gas.

Pertinent physicochemical data:
The following values of specific rotation were calculated from data given on National Bureau of Standards certificates for a sample of sucrose labelled SRM 17a. The values refer to a solution of concentration 260.00 kg m^{-3}.

$$\alpha^{20\,^\circ\mathrm{C}}_{\mathrm{m},\,546.1\,\mathrm{nm}}/\mathrm{mrad\,m^2\,kg^{-1}} = 13.674$$
$$\alpha^{20\,^\circ\mathrm{C}}_{\mathrm{m},\,589.25\,\mathrm{nm}}/\mathrm{mrad\,m^2\,kg^{-1}} = 11.612$$

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2

Physical property: Optical rotation, α_m
Unit: mrad m^2 kg^{-1}
Recommended reference material: Anhydrous dextrose (D-glucose) ($C_6H_{12}O_6$)
Range of variables: 20°C; wavelengths 546.1 nm, 589.25 nm
Physical state within the range: aqueous solution
Class: Certified Reference Material
Contributors: I. Brown, J. P. Cali, J. Franc, J. E. Lane

Intended usage:
D-Glucose can be used for calibration and for checking the performance of manually operated and automatically recording light polarimeters and saccharimeters employed for the determination of the optical rotation of

liquids and dissolved solids. Details of the apparatus and of the methods are available[1,2,3].

Sources of supply and/or methods of preparation:
Samples of D-glucose are available from supplier (B). Samples of D-glucose absorb moisture on the surface and this water can be removed by drying the specimen in vacuum at temperatures between 60 and 70°C.

Pertinent physicochemical data:
The following equation which expresses the specific rotation of dextrose solutions as a function of dextrose concentration, $c/\mathrm{kg\,m^{-3}}$, for the range 60 to 320 $\mathrm{kg\,m^{-3}}$ has been derived from data given on a National Bureau of Standards certificate applicable to dextrose sample SRM 41a.

$$\alpha^{20\,^\circ\mathrm{C}}_{\mathrm{m},\,546.1\,\mathrm{nm}}/\mathrm{mrad\,m^2\,kg^{-1}} = 10.827 + 0.0007430c$$

The following value of specific rotation for a wavelength of 589.25 nm which refers to a concentration of 40.0 $\mathrm{kg\,m^{-3}}$ was derived from the same source.

$$\alpha^{20\,^\circ\mathrm{C}}_{\mathrm{m},\,589.25\,\mathrm{nm}}/\mathrm{mrad\,m^2\,kg^{-1}} = 9.20$$

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3

Physical property: Optical rotation
Unit: mrad (i.e. milliradian for each individual plate)
Recommended reference material: Quartz control plates
Range of variables: 20°C; wavelengths 546.1 nm, 589.25 nm
Physical state within the range: solid
Class: Certified Reference Material
Contributors: I. Brown, J. Dyson, J. E. Lane

Intended usage:
Quartz control plates can be used for calibration and for checking the performance of saccharimeters employed for the determination of sucrose in solutions. These plates are normally calibrated in degrees of sugar. They could be calibrated in milliradians for use in the calibration of polarimeters. Details of the plates and an account of their uses are given in reference 1.

Sources of supply and/or methods of preparation:
Quartz control plates are available from suppliers (A) and (D). Certificates giving the rotation in degrees of sugar for individual plates from these suppliers are available from the National Physical Laboratory, Teddington, Middlesex, UK.

Pertinent physicochemical data:
Values of the optical rotation for individual plates are given in certificates issued with the plates.

REFERENCE

[1] F. J. Bates *et al.*, *US National Bureau of Standards Circular C440.* US Govt Printing Office: Washington, DC (1942).

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PHYSICAL CHEMISTRY DIVISION
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RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

Recommendations approved 1974

EDITOR: E. F. G. HERINGTON

SECTION: SURFACE TENSION

COLLATORS: I. BROWN and J. E. LANE

CONTENTS

REFERENCE MATERIALS FOR SURFACE TENSION MEASUREMENTS.

INTRODUCTION

Ever since Young[1] (1805) and Laplace[2] (1806) demonstrated that the pressure difference across a point on a surface is determined by the surface tension and the curvature of the surface at that point, it has been possible to measure surface tension precisely, and without the need for any form of calibration. However, for at least a century after Young's and Laplace's work, very few reliable measurements of surface tension were made. The major sources of error were (and these sources are often still present in modern measurements) the use of imprecise measuring techniques, the use of inappropriate mathematical expressions to calculate values of surface tension from the experimental observations and failure to exclude surface active impurities from the apparatus. Experimental work since 1910 by Richards and Carver[3] and by Harkins *et al.*[4,5] has shown how to avoid the errors arising from the first and last of these sources while correct mathematical expressions, and convenient methods for using them, have been developed by Laplace[2], Rayleigh[6], Bashworth and Adams[7], and Sugden[8,9].

Notwithstanding the earlier comment that the calibration of apparatus is unnecessary, nevertheless for many of the measuring methods calibration is convenient and often desirable because of difficulties in making accurate measurements of some dimensions of the apparatus. Water and benzene are recommended as suitable calibration materials. It is recommended that the symbol γ or σ be used to denote surface tension, and that the unit be mN m^{-1} (millinewton per metre). This unit gives the same number as the older c.g.s. unit of dyne cm^{-1}.

Methods of measurement

Excellent reviews of available methods have been given by Harkins and Alexander[5], Adam[10] and Adamson[11].

The capillary rise technique is the favoured absolute method and experimental details have been given by Richards and Carver[3]. Sugden[8] has given an accurate and convenient method for the calculation of values of the surface tension from capillary rise, and this method has recently been improved by Lane[12]. Absolute values of surface tension of common liquids can be measured to ±0.02 mN m^{-1} by the capillary rise method but this requires very accurate measurement of the capillary radius which is difficult to achieve. The problem can be avoided by the determination of the capillary radius by calibration with a liquid of known surface tension.

The maximum bubble pressure method is described by Sugden[9], and for properly formed tips has the advantage over the capillary rise method of being independent of contact angle. If the contact angle is $<90^\circ$, the bubble detaches from the outside of the tip; otherwise it detaches from the inside of the tip. The appropriate radius must be used for the calculation of the surface tension. Correction factors for the non-sphericity of the bubble have been given by Sugden[9], and in a more convenient and accurate form by Johnson and Lane[13]. The tip radii can also be determined by calibration. In this manner it is possible to obtain values of the surface tension reliable to ±0.1 mN m^{-1}.

A third reliable method employs the Wilhelmy vertical plate balance with a smooth plate[14–16]. Problems associated with rough plates have been discussed recently by Lane and Jordan[17] and also by Princen[18]. With smooth plates no special corrections are required for the calculation of surface tension. With care, absolute measurements of surface tension to ±0.05 mN m^{-1} can be achieved. No advantage is obtained by calibration with a liquid of known surface tension.

Many laboratories have used the du Nouy balance and a horizontal platinum ring but this method is not recommended, as uncertain correction factors have to be introduced, and the maximum force necessary to raise the ring is difficult to measure. These problems are discussed by Adam[10]. The drop-weight (or drop-volume) method is based on a dynamic measurement and thus lacks the precision of the other methods given above, all of which are static. However, it is particularly convenient for measuring the tension at a liquid/liquid interface. Suitable experimental arrangements are described by Harkins and Alexander[5]. Harkins and Brown[4] have determined empirically the values of the correction factors needed to calculate surface tension from the experimental data.

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1

Physical property: Surface tension
Unit: $\mathrm{mN\ m^{-1}}$ (millinewton per metre)
Recommended reference material: Water (H_2O)
Range of variables: 0 to 60°C
Physical state within the range: liquid
Class: Calibration and Test Material
Contributors: I. Brown, J. Franc, J. E. Lane

Intended usage:
Water can be used for the calibration and for the testing of apparatus used to measure surface tension.

Sources of supply and/or methods of preparation:
Purification by distillation, redistillation from alkaline permanganate and a third distillation from a trace of sulphuric acid is recommended by Harkins and Brown[1]. Because water is easily contaminated by surface active materials that are often present in air the apparatus and the water should be prepared immediately before measurements are made.

Pertinent physicochemical data:
Harkins and Alexander[2] have examined the surface tension data for the water/air interface as a function of temperature and find that values of surface tension can be calculated to within experimental error ($\pm 0.02\ \mathrm{mN\ m^{-1}}$) by means of the following equation

$$\gamma_{\mathrm{H_2O/air}}/\mathrm{mN\,m^{-1}} = 75.680 - 0.138\theta - 3.56 \times 10^{-4} \times \theta^2 + 4.7 \times 10^{-7} \times \theta^3$$

where the temperature (θ/°C) is restricted to the range $0 \leqslant (\theta/^{\circ}\mathrm{C}) \leqslant 60$.

This equation which gives the values 72.78 mN m^{-1} for 20°C and 72.01 mN m^{-1} for 25°C for the surface tension of the water/air interface can be used to calculate values for water prepared by the recommended method[1].

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2

Physical property: Surface tension
Units: mN m^{-1} (millinewton per metre)
Recommended reference material: Benzene (C_6H_6)
Range of variables: 10–60°C
Physical state within the range: liquid
Class: Calibration and Test Materials
Contributors: I. Brown, J. Franc, J. E. Lane

Intended usage:
Benzene can be used for the calibration and for the testing of apparatus used to measure surface tension.

Sources of supply and/or method of preparation:
Samples can be purified by shaking them with mercury and then with sulphuric acid. The samples should next be distilled and then should be fractionally frozen five times[1–3].

Pertinent physicochemical data:
The value of the surface tension of the benzene/air interface at 20°C is well established[1–4] as 28.88 ± 0.01 mN m^{-1}. A considerable amount of data for temperatures from 10–60°C has been collated by Young and Harkins[5], who produced the equation

$$\gamma_{\text{benzene/air}}/\text{mN m}^{-1} = 31.58 - 0.137\theta + 0.0001\,\theta^2$$

where θ is the temperature in °C. This equation gives values 28.88 mN m^{-1} for 20°C and 28.22 mN m^{-1} for 25°C. The values for 30°C given by Koefoed and Villadsen[6] and for 60°C given by Marechal[7] agree with values calculated from the equation to within ±0.03 mN m^{-1}. The data recorded by Donaldson and Quale[8] appear to be too low for temperatures above 20°C. The equation given above should produce values accurate to better than ±0.05 mN m^{-1} and can be used to calculate values for samples of benzene purified as described[1–3].

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RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

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SECTION: OPTICAL REFRACTION (REFRACTIVE INDEX)

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CONTENTS

INTRODUCTION

The symbol for refractive index recommended by the IUPAC[1] is n. A primary standard is not required for refractive index measurements because the refractive index of any liquid can be determined accurately by the use of the minimum deviation method described by Tilton and Taylor[2] which employs a carefully made hollow prism with the temperature controlled by a thermostat. However, such apparatus is usually not readily available, so that reference materials are required for the calibration of commercial refractometers. Most commercial refractometers are either critical angle instruments (e.g. the Abbe and the Pulfrich instruments) or are hollow prism instruments (e.g. the Hilger–Chance refractometer) but recently flow differential refractometers based on the Fresnel principle and hollow split prisms have become available.

One of the largest problems in the measurement of the refractive index of liquids precisely is the attainment of adequate control of the temperature of the sample. In some commercial instruments there are difficulties with the enclosure of the sample and such designs may allow evaporation of the liquid to occur which lowers the sample temperature and may cause changes in the concentration of mixtures. Inadequate closure may also cause the contamination of the sample by air or by water vapour. The most satisfactory methods of measurement are those based on the use of a hollow prism operated in a constant temperature enclosure. A good general description of the apparatus and methods for the measurement of refractive index has been given by Bauer and Lewin[3]. Additional useful information is given by Tilton[4], Tilton and Taylor[5] and Fishter[6].

Water is recommended to be the first choice as a calibration and test material for refractive index measurements of liquids. The refractive index of air-free water relative to that of dry air at temperatures from 0 to 60°C for light of 13 wavelengths has been measured with great care by Tilton and Taylor[2] with an uncertainty of less than 1 p.p.m. The differences between these values and those of another sample of purified water due to likely isotope variations are of the order of a few parts in 10^7.

Selected values of refractive index are given[7] for air-saturated water over the temperature range 0 to 60°C. These values are approximately three parts in 10^7 higher than those reported by Tilton and Taylor[2].

In the past the values for the refractive index of water given in the *International Critical Tables* have been widely used but these are based on the earlier measurements made by Flatow[8] and are in marked disagreement with the more recent values reported by Tilton and Taylor[2].

The temperature scale used by Tilton and Taylor in 1938 was the 'International Temperature Scale' and in the range 0 to 60°C it is identical with the International Practical Temperature Scale of 1948. This, however, differs from the present recommended scale, the International Practical Temperature Scale of 1968, by up to 0.01° in this temperature range. The temperature coefficient of the refractive index of water is approximately 1.7 p.p.m. per 0.01°. The values given by Tilton and Taylor have been recalculated for the wavelength 589.25 nm to give the table of values recommended by this IUPAC Commission. For example, for 50°C (t_{48}) Tilton and Taylor give for n_D the value 1.3290369 but the value for 50°C (t_{68}) which equals 50.01° (t_{48}) is 1.3290352.

When the accuracy of refractive index values required for calibration purposes is not greater than one in the fifth decimal place the values for water quoted by Tilton and Taylor[2] tabulated for temperatures relative to the International Practical Temperature Scale 1948 (IPTS 1948) may be used without alteration for temperatures relative to IPTS 1968. When a greater accuracy is required for temperatures expressed on IPTS 1968 the table of values provided here with the data sheets can be used for the wavelength 589.25 nm at temperatures in the range 0 to 60°C. Values on the IPTS 1968 can be obtained for other wavelengths by first converting the temperature to the IPTS 1948 and using this value in the equation (3) provided by Tilton and Taylor[2].

Various hydrocarbons with certified values for refractive index are available, for example, samples of 2,2,4-trimethylpentane can be obtained from suppliers (A), (C) and (D). Samples of hexadecane, *trans*-bicyclo[4,4,0]-decane, and 1-methylnaphthalene of certified refractive index are available from supplier (A). Certified samples of methylcyclohexane and toluene are available from supplier (A) and from National Laboratories[9] which can also supply cyclohexane. These Laboratories[9] provide samples with certified values of the refractive index (± 0.00003) for 20°C and for a wavelength of 589.25 nm.

Optical glasses might be thought to be the most suitable materials for use as calibration materials because they are stable and have very low temperature coefficients of refractive index. However, although they may be suitable for the calibration and testing of certain critical angle instruments they are not always suitable for use with hollow prism or flow instruments for which the use of a liquid may be essential. Moreover optical glasses can only be used to check high refractive index calibrations. Samples of optical glasses with their refractive index values certified by National Laboratories[9] are available and specimens can also be obtained from some manufacturers of optical components. For example, the National Physical Laboratory, Teddington, UK has supplied worked and calibrated standards to supplier (B).

For those observers who prefer solids to check the performance of their instruments, optical quality materials that could possibly be used for low refractive index settings are commercially available. Supplier (E) has issued a brochure that describes polycrystalline LiF ($n = 1.392$), CaF_2 ($n = 1.434$) and BaF_2 ($n = 1.476$). Synthetic SiO_2 ($n = 1.458$) is available from a number of companies. Samples of these materials would have to be certified by National Laboratories for their use as reference materials.

Four hydrocarbons are recommended as suitable calibration and test materials and these, together with water and an optical glass, form a group of calibration and test materials with refractive index values spaced at suitable intervals and covering a range of temperatures and wavelengths. The following data sheets give details of the properties of these materials.

REFERENCES

[1] *IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units.* Butterworths: London (1969).

[2] L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.* **20**, 419 (1938).

[3] N. Bauer and S. Z. Lewin, *Technique of Organic Chemistry*, Vol. I, *Physical Methods*, Part II, Third Edition, A. Weissberger (editor), p 1211. Interscience: New York (1960).

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1

Physical property: Optical refraction (refractive index), n
Unit: Dimensionless
Recommended reference material: Water (H_2O)
Range of variables: 0 to 60°C, wavelength 589.25 nm
Physical state within the range: liquid
Class: Calibration and Test Material
Contributors: I. Brown, H. Feuerberg, J. Franc, E. F. G. Herington, J. E. Lane, T. Plebanksi

Intended usage:

Water can be used for the calibration and for the testing of the performance of refractometers employed for measurements on liquids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Sources of supply and/or methods of preparation:

A suitable sample of purified, degased water can be prepared by the distillation of city water from a well steamed glass apparatus with the sample collected hot. Details are given by Tilton and Taylor[1]; the method recommended by Harkins and Brown[3] is also suitable.

Pertinent physicochemical data:

Values for the refractive index of air-free water at thirteen wavelengths and at temperatures from 0 to 60°C (IPTS 1948) are given by Tilton and Taylor[1]. The following table gives the refractive index for the sodium D line (589.25 nm) at one degree intervals over the temperature range 0 to 60°C where the temperatures refer to IPTS 1968. These values were calculated in the following way.

Temperatures on the IPTS 1948 corresponding to the temperatures at one degree intervals on the IPTS 1968 were calculated by the use of equation (1) which is a modification of equation (12) given by Bedford and Kirby[4].

$$t_{48} = t_{68} - 0.045(t_{68}/100)[(t_{68}/100) - 1][(t_{68}/419.58) - 1][(t_{68}/630.74) - 1] - t_{68}(t_{68} - 100)(\delta_{68} - \delta_{48})/[\delta_{68}(100 - 2t_{68}) + 10^4] \qquad (1)$$

where $(\delta_{68} - \delta_{48}) = 0.0049768$ and $\delta_{68} = 1.496334$. Then the required refractive index values were calculated for a wavelength of 589.25 nm by equation (2) given by Tilton and Taylor[1].

$$n_D^t = n_D^{20} - [\bar{B}/(\Delta t)^3 + \bar{A}(\Delta t)^2 + \bar{C}\Delta t]/10^7(t_{48} + \bar{D}) \qquad (2)$$

where $t = t_{48}$ (this equation only), $\bar{A} = 2352.12$, $\bar{B} = 6.3649$, $\bar{C} = 76087.9$ and $\bar{D} = 65.7081$; $n_D^{20} = 1.3329877$, $\Delta t = (t_{48} - 20)$. These values of the constants are given by Tilton and Taylor[1] on pages 443 and 449.

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[1] L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.* **20**, 419 (1938).
[2] N. Bauer and S. Z. Lewin, *Technique of Organic Chemistry*, Vol. I, *Physical Methods*, Part II, Third Edition, A. Weissberger (editor), p 1211, Interscience: New York (1960).
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[4] R. E. Bedford and C. G. Kirby, *Metrologia*, **5**, 83 (1969).

Refractive Index of Air-free Water
At temperatures from 0 to 60°C (IPTS 1968) and at wavelength 589.25 nm

t_{68}/°C	n_D	t_{68}/°C	n_D	t_{68}/°C	n_D
0	1.333 9493	20	1.332 9870	40	1.330 6084
1	9474	21	8965	41	4614
2	9397	22	8027	42	3121
3	9264	23	7055	43	1604
4	9077	24	6052	44	0064
5	8837	25	5017	45	1.329 8501
6	8546	26	3951	46	6916
7	8205	27	2855	47	5308
8	7812	28	1730	48	3677
9	7382	29	0575	49	2025
10	6902	30	1.331 9392	50	0352
11	6378	31	8180	51	1.328 8656
12	5812	32	6941	52	6940
13	5204	33	5675	53	5203
14	4556	34	4382	54	3444
15	3868	35	3062	55	1666
16	3142	36	1717	56	1.327 9867
17	2378	37	0346	57	8047
18	1577	38	1.330 8950	58	6208
19	0741	39	7529	59	4349
...	---	...	—	60	2470

2

Physical property: Optical refraction (refractive index), n
Unit: Dimensionless
Recommended reference material: 2,2,4-Trimethylpentane (C_8H_{18})
Range of variables: 20 to 30°C, 7 wavelengths 435.89 to 667.81 nm
Physical state within the range: liquid
Class: Certified Reference Material
Contributors: I. Brown, H. Feuerberg, J. Franc, E. F. G. Herington,
J. E. Lane, T. Plebanski

Intended usage:

Samples of 2,2,4-trimethylpentane can be used to calibrate and to check refractometers employed for measurements on liquids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Sources of supply and/or methods of preparation:

Samples with certificated values for the refractive index are available from suppliers (A), (C) and (D); see also reference 3.

Pertinent physicochemical data:

The following values of refractive index, which apply to an air-saturated sample available from supplier (A), were determined by the Optical Instrument Section of the National Bureau of Standards, USA. The uncertainty in these values is estimated to be ±0.00003.

Supplier (A), Sample 217X 99.968 ± 0.006 mol per cent pure

Wavelength/nm	20/°C	25/°C	30/°C
667.81	1.38916	1.38670	1.38424
656.28	1.38945	1.38698	1.38452
589.25	1.39145	1.38898	1.38650
546.07	1.39316	1.39068	1.38820
501.57	1.39544	1.39294	1.39044
486.13	1.39639	1.39389	1.39138
435.83	1.40029	1.39776	1.39523

The following are values of refractive index for a sample of 2,2,4-trimethylpentane available from supplier (C).

Supplier (C), Sample 217b 99.993 ± 0.002 mol per cent pure
Uncertainty of all values is less than 0.00002

Wavelength/nm	20/°C	25/°C	30/°C
667.81	1.38918	1.38672	1.38426
656.28	1.38947	1.38700	1.38454
589.25	1.39147	1.38900	1.38652
546.07	1.39318	1.39070	1.38822
501.57	1.39546	1.39296	1.39046
486.13	1.39641	1.39391	1.39140
435.83	1.40031	1.39778	1.39525

Supplier (D) provides samples of 2,2,4-trimethylpentane with values of refractive index determined with a dipping Carl Zeiss refractometer calibrated with glass plates[4] (see also reference 3). Thus a sample of 99.95 mole per cent purity, air-saturated, has a refractive index of 1.39139 ± 0.00003 at 20°C for a wavelength of 589.25 nm.

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3

Physical property: Optical refraction (refractive index), *n*
Unit: Dimensionless
Recommended reference material: Hexadecane ($C_{16}H_{34}$)
Range of variables: 20 to 100°C, 7 wavelengths 435.83 to 667.81 nm
Physical state within the range: liquid
Class: Certified Reference Material

Contributors: I. Brown, H. Feuerberg, J. Franc, E. F. G. Herington,
J. E. Lane, T. Plebanski

Intended usage:

Samples of hexadecane can be used to calibrate and to check refractometers employed for making measurements on liquids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Sources of supply and/or methods of preparation:

Samples of certificated refractive index are available from supplier (A).

Pertinent physicochemical data:

The following values of refractive index, which apply to an air-saturated sample available from supplier (A), were determined for temperatures of 20, 25 and 30°C by the American Petroleum Institute Research Project 6 at the Carnegie–Mellon University, and for 80 and 100°C by the Research Laboratory of the Sun Oil Company. The uncertainty in the values is estimated to be ±0.00008 for temperatures of 20, 25 and 30°C and ±0.0002 for 80 and 100°C. Values for other temperatures may be obtained by linear interpolation between the tabulated values.

Hexadecane available from supplier (A)
Supplier (A), Sample 568-X 99.96 ± 0·04 mol per cent pure

Wavelength/nm	20/°C	25/°C	30/°C	80/°C	100/°C
667.81	1.43204	1.43001	1.42798	—	—
656.28	1.43235	1.43032	1.42829	1.4078	1.3998
589.25	1.43453	1.43250	1.43047	1.4098	1.4017
546.07	1.43640	1.43436	1.43232	1.4117	1.4034
501.57	1.43888	1.43684	1.43480	—	—
486.13	1.43993	1.43788	1.43583	1.4150	1.4069
435.83	1.44419	1.44213	1.44007	1.4191	1.4108

REFERENCES

[1] L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.* **20**, 419 (1938).

[2] N. Bauer and S. Z. Lewin, *Technique of Organic Chemistry*, Vol. I, *Physical Methods*, Part II, Third Edition, A. Weissberger (editor), p 1211. Interscience: New York (1960).

4

Physical property: Optical refraction (refractive index), *n*
Unit: Dimensionless
Recommended reference material: *trans*-Bicyclo[4,4,0]decane ($C_{10}H_{18}$)
trans-Decahydronaphthalene
Range of variables: 20 to 100°C, 7 wavelengths 435.83 to 667.81 nm
Physical state within the range: liquid
Class: Certified Reference Material
Contributors: I. Brown, H. Feuerberg, J. Franc, E. F. G. Herington,
J. E. Lane, T. Plebanski

Intended usage:

Samples of *trans*-bicyclo[4,4,0]decane can be used to calibrate and to check refractometers employed for making measurements on liquids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Sources of supply and/or methods of preparation:

Samples of certificated refractive index are available from supplier (A).

Pertinent physicochemical data:

The following values of refractive index, which apply to an air-saturated sample available from supplier (A) were determined for temperatures of 20, 25 and 30°C by the American Petroleum Institute Research Project 6 at the Carnegie–Mellon University, and for 80 and 100°C by the Research Laboratory of the Sun Oil Company. The uncertainty in the values is estimated to be ±0.00008 for temperatures of 20, 25 and 30°C and ±0.0002 for 80 and 100°C. Values for other temperatures may be obtained by linear interpolation between the tabulated values.

trans-Bicyclo[4,4,0]decane available from supplier (A)
Supplier (A), Sample 561-X 99.98 ± 0.02 mol per cent pure

Wavelength/nm	20/°C	25/°C	30/°C	80/°C	100/°C
667.81	1.46654	1.46438	1.46222	—	
656.28	1.46688	1.46472	1.46256	1.4411	1.4324
589.25	1.46932	1.46715	1.46498	1.4434	1.4347
546.07	1.47141	1.46923	1.46705	1.4453	1.4367
501.57	1.47420	1.47200	1.46980	—	—
486.13	1.47535	1.47315	1.47095	1.4492	1.4409
435.83	1.48011	1.47789	1.47567	1.4536	1.4448

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5

Physical property: Optical refraction (refractive index), *n*
Unit: Dimensionless
Recommended reference material: 1-Methylnaphthalene ($C_{11}H_{10}$)
Range of variables: 20 to 100°C, 7 wavelengths 435.83 to 667.81 nm
Physical state within the range: liquid
Class: Certified Reference Material
Contributors: I. Brown, H. Feuerberg, J. Franc, E. F. G. Herington,
J. E. Lane, T. Plebanski

Intended usage:

Samples of 1-methylnaphthalene can be used to calibrate and to check refractometers employed for making measurements on liquids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Pertinent physicochemical data:

The following values of refractive index, which apply to an air-saturated sample available from supplier (A) were determined for temperatures of 20, 25 and 30°C by the American Petroleum Institute Research Project 6 at the Carnegie–Mellon University, and for 80 and 100°C by the Research Laboratory of the Sun Oil Company. The uncertainty in the values is estimated to be ±0.00008 for temperatures of 20, 25 and 30°C and ±0.0002 for 80 and 100°C. Values for other temperatures may be obtained by linear interpolation between the tabulated values.

1-Methylnaphthalene available from supplier (A)
Supplier (A), Sample 578-X   99.97 ± 0.03 mol per cent pure

Wavelength/nm	20/°C	25/°C	30/°C	80/°C	100/°C
667·81	1.60828	1.60592	1.60360	—	—
656.28	1.60940	1.60703	1.60471	1.5805	1.5710
589.25	1.61755	1.61512	1.61278	1.5882	1.5786
546.07	1.62488	1.62240	1.62005	1.5952	1.5855
501.57	1.63513	1.63259	1.63022	—	—
486.13	1.63958	1.63701	1.63463	1.6092	1.5990
435.83	—	1.65627	1.65386	1.6274	1.6172

REFERENCES

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6

Physical property: Optical refraction (refractive index), *n*
Unit: Dimensionless
Recommended reference material: 'Crown' optical glass
Range of variables: 20°C, wavelength 589.25 nm
Physical state within the range: solid
Class: Certified Reference Material
Contributors: I. Brown, J. Dyson, H. Feuerberg, J. Franc, E. F. G. Herington, J. E. Lane, T. Plebanski

Intended usage:

This optical glass can be used to calibrate and to check refractometers that are suitable for making measurements on solids. Details of methods and apparatus are given by Tilton and Taylor[1] and by Bauer and Lewin[2].

Sources of supply and/or methods of preparation:

Samples are available from supplier (D). Similar samples are probably available from optical manufacturers [e.g. supplier (B)] with values certified by National Laboratories.

Pertinent physicochemical data:

Samples of 'Crown' optical glass are available from supplier (D) with the following refractive index values at 20°C; 1.51840 ± 0.00002, 589.25 nm; 1.51850 ± 0.00002, 587.6 nm. These values were determined by absolute goniometric measurements on prisms from which the plates were cut[4].

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[3] *IUPAC Catalogue of Physicochemical Standard Substances*, Butterworths: London (1972).
[4] M. Tarasiuk and W. Wnukowski, *Pomiary Automatyka Kontrola*, **3**, 108 (1973).

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(A) API Standard Reference Materials,
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(B) Chance Pilkington Optical Works,
St Asaph, Flintshire (UK)

(C) Office of Standard Reference Materials,
US Department of Commerce,
National Bureau of Standards,
Washington DC 20234 (USA)

(D) Polish Committee of Standardization and Measures
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(E) Schott Optical Glass, Inc.,
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