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This report is prepared as a presentation for the Fourth International Conference on Chemical Thermodynamics, Baden, Austria, 3-7 September 1973. The complete description of the experiments will be presented in future publications which will receive general distribution.

Please consult the NBS Office of Technical Information and Publications to obtain the proper citations.

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**U. S. DEPARTMENT OF COMMERCE,** Frederick B. Dent, Secretary

**NATIONAL BUREAU OF STANDARDS,** Richard W. Roberts, Director

# Standard Reference Materials for Combustion Calorimetry

George T. Armstrong and Walter H. Johnson

## Abstract

Combustion measurements using a rotating bomb adiabatic aneroid calorimeter have been used to make a preliminary evaluation of ten substances as potential thermochemical reference materials for combustion of organic compounds containing N, S, Cl and F. p-chlorobenzoic acid, p-fluorobenzoic acid, and urea are recommended for acquisition, certification, and distribution. Thianthrene may also be suitable. For the ten substances including in addition to the above: o- and m-chlorobenzoic acids, o-fluorobenzoic acid, nicotinic acid, acettanilide, and creatinine, typical combustion data are given, showing corrections applied; and mean thermodynamic functions at 25°C are given together with error estimates. The results are compared with other work. Recommendations and a discussion of the role of standard reference materials for thermochemistry are given.

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# STANDARD REFERENCE MATERIALS FOR COMBUSTION CALORIMETRY[1]

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## 1.0 Introduction

Standard reference materials (SRM's) for combustion calorimetry serve two principal purposes. (1) A primary standard reference material provides a means of calibrating a calorimeter using a process similar to those which are to be studied with the calorimeter. The value for the energy of combustion determined in a national standardizing laboratory provides the experimentalist with a scale of measurement consistent with the energy scale of the measurement system. In the case of energy measurements this is the joule as established in the International System of Units. (2) A secondary standard reference material provides a well characterized material of a particular class of substances, which can be studied in many different laboratories. As the material is the same in all measurements, observed differences are due either to differences in technique or to differences in the calorimeters. If the experimental problems of measurement have been worked out by competent research workers in the field recommended procedures for use of the material may also be available. Such a material can be used by the experimentalist with some degree of confidence to establish his capability of making accurate measurements on substances of this class. The possibility of differences in performances of calorimeters may not be neglected. This is a less pronounced problem in bomb calorimetry than in some other calorimetric processes.

For many years benzoic acid has been available as a primary SRM. It was available for this purpose as early as 1911 from the U.S. National Bureau of Standards, Stratton (1911), and it, as well as other substances, had been used by Stohman, Kleber, Langbein, and Offenhaver (1893). Technologically the principal use of this standard has been for calibrating bomb calorimeters to be used in laboratories testing foods and other agricultural products, fuels, as well as other combustible materials and energy sources. The standard has permitted rapid, inexpensive determinations of heating values of moderate accuracy. However this particular SRM was found to be of good enough quality even for the most precise scientific studies of combustion energies, and its use throughout the

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[1] This paper is available as NBS Internal Report 73-158.

world in determining energies of combustion of pure substances has caused a large fraction of the total thermochemical data base to be derived from the certified energy of combustion.

Almost from the beginning, the desirability of secondary SRM's was recognized, but these materials have never been provided by a national standardizing laboratory to the extent requested. The subject was reviewed by Waddington (1956).

The reason secondary standard reference materials have not previously been provided is probably in large part an economic matter. NBS standard reference materials are sold at a price to compensate for their production, certification, and sale. An SRM of a general character, such as benzoic acid has a large enough market to permit sale at a very moderate price. However, despite the fact that a number of laboratories have a very urgent need for secondary SRM's, the actual number of potential users is quite small. The estimated number of users in any year may be of the order of ten for a particular standard reference material as specialized as a thermochemical standard. The great benefit to the thermochemical community and the improvement of the validity of thermochemical data are therefore important factors in justifying a series of materials.

Materials already in use for combustion calorimetry standards, and materials previously proposed for combustion standards are listed in Table 1, including both primary and secondary standards.

One purpose of a secondary SRM in thermochemistry is to give the user confidence in his ability to make accurate measurements after having calibrated his apparatus. This seems to be primarily a didactic use or a reassurance. The novice training to do bomb calorimetry would be reassured if, after calibrating his apparatus, he could then make measurements on a simple, straightforward process and obtain results that he could compare with known correct values. This is the primary argument used for another C, H, O compound such as succinic acid. A possible variation of such a material from benzoic acid is a significantly different specific enthalpy of combustion. The hydrocarbon, 2,2,4-trimethylpentane, gives the user an opportunity to test his skill at handling a volatile hydrocarbon. In this respect it is partially satisfactory, but still fails to cope with an important problem in petroleum test laboratories: the changing heat value of a volatile fuel mixture on standing, due to fractional vaporization of the more volatile components.

| Substance | | |
|---|---|---|
| hydrogen | $H_2(g)$ | flow calorimetry |
| methane | $CH_4(g)$ | flow calorimetry |
| 2,2,4-trimethylpentane | $C_8H_{18}(\ell)$ | volatile hydrocarbon |
| naphthalene | $C_{10}H_8(c)$ | formerly available |
| benzoic acid | $C_7H_6O_2(c)$ | transfer standard |
| sucrose | $C_{12}H_{22}O_{11}(c)$ | formerly available |
| salicylic acid | $C_7H_6O_3(c)$ | C, H, O-compound |
| succinic acid | $C_4H_6O_4(c)$ | |
| acetanilide | $C_8H_9NO(c)$ | N-compound |
| hippuric acid | $C_9H_9NO_3(c)$ | |
| urea | $CH_4N_2O(c)$ | |
| nicotinic acid | $C_6H_5NO_2(c)$ | |
| THMAM* | $C_4H_{11}NO_3(c)$ | |
| thianthrene | $C_{12}H_8S_2(c)$ | S-compound |
| thioglycolic acid | $C_2H_4O_2S(\ell)$ | |
| sym-diphenylthiourea | $C_{13}H_{12}N_2S(c)$ | |
| sulfanilamide | $C_6H_8N_2O_2S(c)$ | |
| benzotrifluoride | $C_7H_5F_3(\ell)$ | F-compound |
| p-fluorobenzoic acid | $C_7H_5O_2F(c)$ | |
| pentafluorobenzoic acid | $C_7HO_2F_5(c)$ | |
| m-trifluoromethylbenzoic acid | $C_8H_5O_2F_3(c)$ | |
| trichlorophenol | $C_6H_3OCl_3(c)$ | Cl-compound |
| m-chlorobenzoic acid | $C_7H_5O_2Cl(c)$ | |
| p-chlorobenzoic acid | $C_7H_5O_2Cl(c)$ | |
| o bromobenzoic acid | $C_7H_5O_2Br(c)$ | Br-compound |
| m-iodobenzoic acid | $C_7H_5O_2I(c)$ | I-compound |
| triphenylphosphine oxide | $C_{18}H_{15}OP(c)$ | P-compound |

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*tris(hydroxymethyl)aminomethane

Each additional element introduced into a compound also introduces new problems. These problems include (a) obtaining completeness of combustion; and (b) obtaining a definite set of products. Thus, for instance a compound containing little hydrogen may smoke or char because the flame is not hot enough to obtain complete combustion. This is a relatively simple problem in many cases, though troublesome. The techniques for obtaining more nearly complete combustion are well known (higher oxygen pressure, promoters, lighter weight crucible and other supports); also the techniques for determining that combustion is complete are known ($CO_2$ determination, CO determination, odor of products, absence of soot). Much more subtle problems are to establish the nature of the products and to devise experimental conditions such that a consistent and analyzable set of products is obtained, when other elements than C, H, O are present.

Typical problems are: (a) the formation of acid products when group V, VI, and VII elements are present, (b) the formation of elements in various oxidation states when multiple valency can occur. Acid products can be determined by titration, but if more than one acid is present the separate identification may be more difficult. Acid products may be corrosive to the calorimeter parts and side reactions may therefore occur. Various oxidation states lead to other analytical problems, as when $Cl_2$ may be formed along with HCl from organic chlorine compounds. The establishment of combustion conditions in which the complexity of the products is minimized is a reasonable goal because it simplifies the product analysis.

The problem of criteria for selection of suitable secondary reference materials does not have a simple answer. This becomes evident as soon as one tries to choose a substance for a particular class--fluorine compound--for example. Should the compound have a high proportion or a low proportion of fluorine? It turns out that if F is bound to C in the compound, the probability of finding $CF_4$ or other CF compounds in the products is increased. As found by Good, Scott, Waddington (1956) the amount of $CF_4$ is determined by the ratio of H to F in the combustion mixture--low H/F leading to high $CF_4$. As $CF_4$ is difficult to determine if $CO_2$ is also to be determined this presents a problem. One solution is to select a high-as well as a low-fluorine sample. This approach leads to conceptual difficulties because it increases the number of required samples and there is no discernable limit to such an increase. Any new set of conditions could require a different reference material.

A possible solution to this dilemma is to set a criterion of difficulty for problems to be solved by the use of a standard reference material. Thus an SRM for a given set of elements should exemplify a characteristic problem which must be solved in order to obtain satisfactory measurements.

An important function of reference materials is to help locate errors in measurements by different individuals, different procedures and different kinds of instruments. Thus too close adherence to a ritual procedure and common design of calorimeter is shortsighted and likely to obscure errors rather than reveal them.

Recognizing the importance of tracing errors in thermochemistry and of the important part reference materials may play in obtaining an internally self consistent set of thermochemical values inter-relating the chemical substances, the National Bureau of Standards undertook the preparation of a series of thermochemical standard reference materials containing the elements N, F, Cl, Br, I, S, and P, individually in organic compounds This is a preliminary report of the investigations that have been carried out in the study. The work involved collaboration between the Thermochemistry Section and the Office of Standard Reference Materials, which provided samples for study and some financial support for the work. The work that has been done is primarily a calorimetric study of the combustion energy of selected compounds which offer potentiality as standard reference materials.

## 2.0 Calorimeter

The calorimeter used in the experiments was designed , constructed and tested by Prosen and Johnson. It is an aneroid, vacuum-jacketed calorimeter with adiabatic shield, and rotating bomb. The calorimeter assembly is illustrated in figure 1. The bomb is shown in figure 2. A principal problem in an aneroid calorimeter is to obtain temperature distributions known well enough that heat transfer to the surroundings does not create a large error. The laminated construction is the design feature which solves this problem, when combined with the vacuum jacket and polished gold surfaces on bomb exterior and shield interior.

The calorimeter is a comparison device, comparing the energy of combustion of the substance under study with the energy of combustion of the reference substance, benzoic acid (NBS SRM 39i)[1]. The certificate value, 26.434 ± 0.003 $kJ \cdot g^{-1}$, was used for the energy of reaction of benzoic acid. On the basis of calibration measurements the energy equivalent of the calorimeter is about 2519 $J \cdot K^{-1}$, the value being determined accurately with an uncertainty (2 sdm) of about 0.005 percent for each series of experiments.

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[1] Standard reference materials listed with a number associated are available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

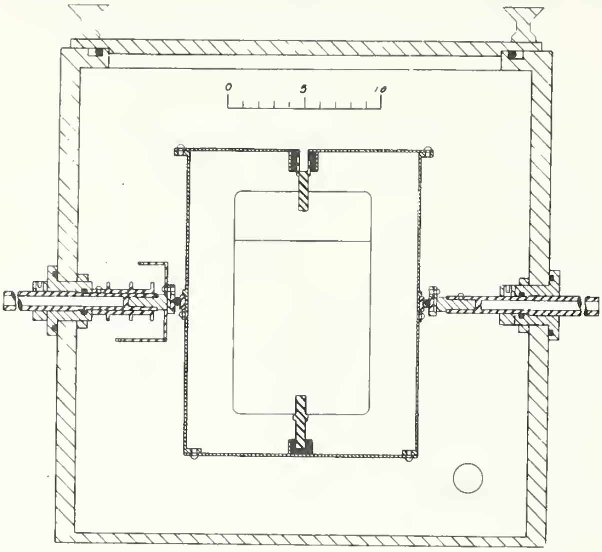

Figure 1. Schematic view of calorimeter assembly. (An early diagram) The outer, room-temperature, evacuated box is shown, with the rotating adiabatic shield. The shield rotates on two axes following a pre-programmed routine. The bomb, (see fig. 2 for detail), is contained within the adiabatic shield.

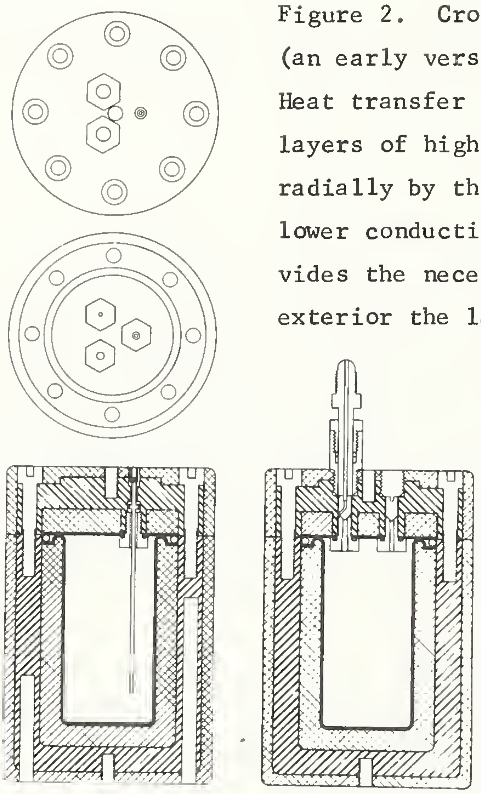

Figure 2. Cross section of aneroid calorimeter bomb (an early version) showing laminated construction. Heat transfer is aided laterally by inner and outer layers of high-conductivity metals, and hindered radially by the laminated construction and by the lower conductivity of the steel layer, which provides the necessary strength. From interior to exterior the laminations consist of platinum liner (about 1 mm), silver (about 12 mm), steel (about 12 mm), silver (about 7 mm), gold plate. The bomb is suspended within the adiabatic shield by two axial pins inserted in holes shown in top and bottom.

Temperatures are measured by a calibrated capsule-type platinum-resistance thermometer inserted in the bomb wall. Temperature differences between calorimeter bomb and adiabatic shield are measured by copper-constantan thermocouples. The output voltage is used to regulate the adiabatic shield temperature in such a way as to minimize the temperature difference. Small temperature drifts (due to thermometer heat) are observed in the bomb temperature during the rating periods, and these drifts are taken into account in calculating the temperature rise. Temperature rise values ranged from about one kelvin to about three kelvins and were reported to $10^{-6}$ K.

The energy equivalent of the standard calorimeter system was adjusted for variations in the average temperature of the experiments, for heat capacities of minor components added to the calorimeter, and for the heat capacities of the initial contents of the bomb. The first two adjustments amounted to less than one $J \cdot K^{-1}$. The heat capacities of the bomb contents, accurately calculated in each experiment, contributed 15 to 20 $J \cdot K^{-1}$, mostly due to the water added for dissolving acids formed.

The small energy equivalent of the calorimeter makes possible the use of comparatively small samples. Depending on the chemical constitution of the substance, samples of 0.1 to 0.7 g, releasing 2 to 8 kJ, are used to obtain the desired temperature increments of one to 3 K.

## 3.0 Experimental Studies

Typically a series of six experiments, with occasional variations of one or two in number, was made with each potential reference material. The experiments are discussed briefly below for each substance. A typical experiment is summarized for each substances in table 2. Data listed for each substance are experiment number; observed total heat, $Q_{obs}$; correction for ignition energy, $q_{ign}$; correction for decomposition of $HNO_3$, $q_N$; Washburn correction, $q_W$; correction for adjustment to standard final temperature, $q_{Tf}$; energy of standard reaction, $U_f - U_i$; mass of sample, $m_s$; specific standard internal energy of reaction at selected final temperature, $\Delta U_c^\circ$(at Tf). Special entries for some substances when listed are mentioned in the paragraph relating to the substance.

The reactions carried out approximated the stoichiometric equations listed in Table 3. The observed energy measurements were adjusted to correspond to these reactions. In Table 4 are given average thermodynamic quantities and uncertainties of these quantities corresponding to the equations in Table 3. The final temperature, Tf, to which the experimental reaction was referred, and the mean specific standard internal energy of combustion, $-\Delta U_c^\circ$, at Tf are given together with the number of experiments and the standard deviation of the mean. Also given are the molar standard internal energy of combustion, $\Delta U_c^\circ$, the molar standard enthalpy of combustion, $\Delta H_c^\circ$, and the molar standard enthalpy of formation,

### Table 2. Typical Experimental Data

| Substance | o-FBA[a] | o-ClBA[b] | acetanilide | urea | nicotinic acid | creatinine | thianthrene |
|---|---|---|---|---|---|---|---|
| Experiment No. | 233 | 329 | 440 | 434 | 354 | 502 | 538 |
| $Q_{obs}$, J | -2883.73 | -2554.19 | -8256.01 | -7887.68 | -7479.34 | -2879.51 | -7594.55 |
| $q_{ign}$, J | 1.06 | 0.86 | 0.91 | 0.89 | 0.95 | 1.01 | 1.20 |
| $q_N$, J | 0.76 | 0.23 | 15.97 | 26.26 | 18.13 | 12.27 | -9.91 |
| $q_{As}$, J | - | 12.02 | - | - | - | - | - |
| $q_{Pt}$, J | - | 0.17 | - | - | - | - | - |
| $q_{Aux}$, J | - | - | - | 434.61 | - | 339.90 | - |
| $q_{diln}$, J | - | - | - | - | - | - | 0.17 |
| $q_W$, J | 4.67 | 4.00 | 9.35 | 11.25 | 11.18 | 3.38 | 6.97 |
| $q_{Tf}$, J | -0.01 | .00 | -0.09 | -0.09 | 0.01 | -0.02 | - |
| $U^\circ_f - U^\circ_i$ | -2877.35 | -2536.91 | -8229.87 | -7414.76 | -7449.07 | -2522.97 | -7576.30 |
| $m_s$, g | 0.130899 | 0.128651 | 0.263557 | 0.703709 | 0.335815 | 0.122270 | 0.226366 |
| $\Delta u^\circ_c$ (at Tf), $J \cdot g^{-1}$ | -21981.45 | -19719.32 | -31226.16 | -10536.68 | -22182.06 | -20634.38 | -33469.26 |

[a] o-fluorobenzoic acid; [b] o-chlorobenzoic acid

Table 3. Reactions Studied

(1) $C_7H_5O_2F(c) + 7\ O_2(g) + 48\ H_2O(\ell) = 7\ CO_2(g) + [HF + 50\ H_2O](\ell)$

(2) $C_7H_5O_2Cl(c) + 7\ O_2(g) + 198\ H_2O(\ell) = 7\ CO_2(g) + [HCl + 200\ H_2O](\ell)$

(3) $C_8H_9NO(c) + 39/4\ O_2(g) = 8\ CO_2(g) + 9/2\ H_2O(\ell) + 1/2\ N_2(g)$

(4) $CH_4N_2O(c) + 3/2\ O_2(g) = CO_2(g) + 2\ H_2O(\ell) + N_2(g)$

(5) $C_6H_5NO_2(c) + 25/4\ O_2(g) = 6\ CO_2(g) + 5/2\ H_2O(\ell) + 1/2\ N_2(g)$

(6) $C_4H_7N_3O(c) + 21/4\ O_2(g) = 4\ CO_2(g) + 7/2\ H_2O(\ell) + 3/2\ N_2(g)$

(7) $C_{12}H_8S_2(c) + 17\ O_2(g) + 198\ H_2O(\ell) = 12\ CO_2(g) + 2[H_2SO_4 + 100\ H_2O](\ell)$

Table 4. Thermodynamic Quantities[a] and Uncertainties[b]

| Substance | Reaction No. | No. of Expts. | Tf °C | $-\Delta u_c^\circ$(at Tf) $J \cdot g^{-1}$ | sdm $J \cdot g^{-1}$ | $-\Delta U_c^\circ$(at 25°C) $kJ \cdot mol^{-1}$ | $-\Delta H_c^\circ$(at 25°C) $kJ \cdot mol^{-1}$ | $-\Delta H_f^\circ$(at 25°C) $kJ \cdot mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| o-fluorobenzoic acid | (1) | 6 | 26 | 21981.68 | 2.90 | 3079.95±0.92 | 3079.95±0.92 | 565.63±1.20 |
| p-fluorobenzoic acid (i) | (1) | 6 | 26 | 21860.78 | 1.47 | 3063.01±0.61 | 3063.01±0.61 | 582.57±0.98 |
| p-fluorobenzoic acid (ii) | (1) | 6 | 28 | 21866.21 | 1.91 | 3063.77±0.70 | 3063.77±0.70 | 581.81±1.04 |
| o-chlorobenzoic acid | (2) | 7 | 26 | 19719.33 | 1.43 | 3087.45±0.68 | 3087.45±0.68 | 405.07±0.81 |
| m-chlorobenzoic acid | (2) | 5 | 26 | 19594.70 | 1.02 | 3067.94±0.60 | 3067.94±0.60 | 424.58±0.74 |
| p-chlorobenzoic acid | (2) | 8 | 26 | 19571.31 | 1.35 | 3064.28±0.66 | 3064.28±0.66 | 428.24±0.79 |
| acetanilide | (3) | 6 | 28 | 31229.45 | 2.11 | 4221.69±0.84 | 4224.82±0.84 | 209.52±0.91 |
| urea | (4) | 6 | 28 | 10536.22 | 0.37 | 633.00±0.10 | 631.75±0.10 | 333.42±0.13 |
| nicotinic acid | (5) | 6 | 28 | 22182.56 | 0.90 | 2731.21±0.27 | 2730.58±0.27 | 345.07±0.36 |
| creatinine | (6) | 6 | 26 | 20641.83 | 3.33 | 2335.15±0.80 | 2334.53±0.80 | 239.92±0.82 |
| thianthrene | (7) | 5 | 28 | 33464.67 | 5.54 | 7239.21±2.61 | 7251.73±2.61 | -182.71 |

[a] Preliminary values. The quantities listed refer to the samples measured rather than to an idealized pure compound.

[b] Uncertainties in ΔUc and ΔHc (at 25°C) are estimated 95 percent confidence limits and include uncertainties in the standard value of benzoic acid, in the calibration, and other systematic errors. The uncertainty in ΔHf also includes uncertainties in the enthalpies of formation of other substances occurring in the reaction.

## Table 5. Comparative Values[a]

| Substance | Reference | $-\Delta H^\circ_c$ (at 25 °C)[b] and uncertainty kJ·mol$^{-1}$ | Difference from this work kJ·mol$^{-1}$ |
|---|---|---|---|
| o-fluorobenzoic acid | Good, Scott, Waddington (1956) | 3080.68±1.50 | -0.73 |
| p-fluorobenzoic acid | Good, Scott, Waddington (1956) | 3061.60±1.21 | +1.41 and +2.17 |
| p-fluorobenzoic acid | Cox, Gundry, Head (1964) | 3063.23±0.88 | -0.22 and +0.54 |
| o-chlorobenzoic acid | Smith, Bjellerup, Krook, Westermark (1953) | 3094.07±8.4 | -6.27[c] |
| m-chlorobenzoic acid | Smith, Bjellerup, Krook, Westermark (1953) | 3069.38±8.4 | -1.09[c] |
| p-chlorobenzoic acid | Bjellerup, Smith (1954) | 3065.62±1.67 | -0.99[c] |
|  | Hajiev, Agarunov (1968) | 3064.78±3.14 | -0.15 |
|  | Hu, Sinke, Månsson, Ringner (1972) | 3062.98±0.75 | 1.65 |
|  |  | 3062.77±1.05 | 1.86 |
|  |  | 3062.94±0.84 | 1.69 |
| acetanilide | Wadso (1962); Cox and Pilcher (1970) | 209.53±1.38[d] | -0.01 |
|  | Wadso (1962); Domalski (1972) | 210.45[e] | +0.93 |
| urea | Huffman (1940) | 631.78±0.17 | -0.03 |
|  | Sunner (1946) | 633.87±1.68 | -2.12 |
|  | Månsson and Sunner (1963) | 631.36±0.08 | +0.39 |
| nicotinic acid | - | - | - |
| creatinine | Huffman, Ellis, Fox (1936) | 2335.97±0.42 | -1.44 |
| thianthrene | Hubbard, Katz, Waddington (1954) | 7251.50±2.20 | +0.41[f] |
|  | Keith and Mackle (1958) | 7250.31±2.88 | +1.60[f] |

Table 5. Comparative Values[a] (cont.)

| Substance | Reference | $-\Delta H_c^\circ$(at 25°C) | Difference from this work $kJ\cdot mol^{-1}$ |
|---|---|---|---|
| thianthrene | Sunner and Lundin (1953); Sunner (1963) | 7252.08±1.17 | -0.17[f] |
| | Hu, Yen, Geng (1966) | 7252.54±2.18 | -0.63[f] |

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[a] Early values, prior to 1936 are of historical interest only.

[b] Values and uncertainties are those given by Cox and Pilcher (1970).

[c] Values for chlorobenzoic acids were adjusted 0.35 $kJ\cdot mol^{-1}$ for the difference between $[HCl + 200\ H_2O](\ell)$ and $[HCl + 600\ H_2O](\ell)$

[d] Enthalpy of formation computed by Cox and Pilcher from Wadsö reaction energy.

[e] Enthalpy of formation computed by Domalski from Wadsö reaction energy.

[f] Values for thianthrene were adjusted 0.18 $kJ\cdot mol^{-1}$ for the difference between $[H_2SO_4 + 100\ H_2O](\ell)$ and $[H_2SO_4 + 115\ H_2O](\ell)$

$\Delta H^\circ_f$, at 25 °C, for each substance, together with the respective uncertainties of these quantities.

In reducing the data atomic weights were taken from the 1969 table of atomic weights. Enthalpies of formation of other substances were taken from Wagman, et al (1968). Washburn corrections were made by computer program based on equations generally taken from appropriate chapters of Experimental Thermochemistry, Rossini (1956) and Skinner (1962). The adaptations were made by Shomate (for C, H, O, N compounds), and further modified by Armstrong, and by Prosen with respect to these compounds and to allow treatment of F compounds. The program for Cl compounds was provided by Månsson. No computer program for the S compound was available so that the calculations were made following Hubbard, Scott, and Waddington (1956).

## 4.0 Substances studied: characterization and observations.

The studies which were carried out were not performed on samples that would form the proposed reference materials, but on materials already available. In some cases these were substances already certified as standard reference materials for other purposes.

### 4.1 Fluorobenzoic acids

A sample of o-fluorobenzoic acid and a sample of p-fluorobenzoic acid(i) obtained from W. D. Good (U.S. Bureau of Mines, Bartlesville) and a commercial sample of p-fluorobenzoic acid(ii) (J. T. Baker, Ultrex No. 4979) were tested as potential fluorine containing thermochemical standards. The fluorobenzoic acids from Good were the same as used by Good, Scott, and Waddington (1956). The results obtained on the ortho-acid in this work and in the Bureau of Mines work do not differ significantly. The results on the two samples of the para-acid do not differ significantly from each other or from the work of Cox, Gundry, and Head (1964). They do not agree as well with the results of Good, Scott, and Waddington (1956).

### 4.2. Chlorobenzoic acids

O-chlorobenzoic acid used was an NBS microanalytical standard; the m-chlorobenzoic acid was a commercial sample (J. T. Baker, Ultrex No. 4976); and p-Chlorobenzoic acid was obtained from the Lund thermochemical laboratory, and was the sample used by Hu, Sinke, Månsson and Ringner (1972). Relatively large uncertainties are assigned by Cox and Pilcher (1970) to the work of Smith, Bjellerup, Krook, and Westermark (1953) on o-, and m-chlorobenzoic acids. The present results are well within these error limits. Bjellerup and Smith (1954) and Hajiev and Agarunov (1968) have reported measurements on p-chlorobenzoic acid which are in agreement with each other and with the present work. More recently Hu, Sinke, Månsson, and Ringner (1971) have reported three values determined in different calorimeters and which are at the limits of the combined errors.

In these experiments $As_2O_3$ was used to reduce chlorine formed in the combustion. The correction for this reaction of chlorine is listed in Table 2 as $q_{As}$. A difficulty was encountered in these experiments caused by the slow reaction of arsenious oxide with oxygen during the period after loading the bomb and before performing the heat measurement. This tended to cause an error in the determination of the amount of arsenic oxide formed during the reaction. It was found to be catalyzed by the platinum of the bomb lining in contact with the arsenious oxide solution. This difficulty was overcome by placing the arsenious oxide solution in a plastic container. A small correction, $q_{Pt}$, was applied for the formation of $H_2PtCl_6$ during the reaction.

### 4.3 Acetanilide ($C_6H_5NHCOCH_3$)

The sample measured was NBS SRM 141b,[1] certified as a material for microchemical analysis of C, H, and N. The sample is indicated by its certificate to be 99.99 mole percent pure, and to be non-hygroscopic It had been purified by fractional crystallization from the melt. The enthalpy of formation calculated from our combustion measurements is in close agreement with the value obtained by Wadsö (1962) on the basis of the liquid phase reaction of acetic anhydride and aniline as calculated by Cox and Pilcher (1970) but in less good agreement with the value calculated by Domalski from the same reaction using different auxiliary data

### 4.4. Urea (carbamide); ($(NH_2)_2CO$)

The sample used was NBS SRM 912,[1] a standard obtained from a commercial source and certified for use in clinical analysis procedures. The observed enthalpy of combustion is in good agreement with that reported by Huffman (1940), and Månsson and Skinner (1963). Urea requires an igniter to obtain consistent combustion. Using benzoic acid for this purpose, very good precision is obtained. The energy from this small amount of benzoic acid is listed in Table 2 as $q_{Aux}$. This sample had the best reproducibility of the samples tested.

### 4.5 Nicotinic acid (pyridine-3-carboxylic acid); ($NC_5H_4COOH$)

The sample used was NBS SRM 148,[1] certified for microdetermination of

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[1] See footnote p. 5.

C, H, N. Titrimetric assay indicates a purity of 99.99 ± 0.08 percent. No previous determinations have been made of the combustion energy. This sample gave clean reproducible combustions without a promoter.

### 4.6 Creatinine $(\mathrm{HN{=}\overline{CN(CH_3)CH_2CON}H}$

The sample used was NBS SRM 914[1], certified for use in calibration and standarization of procedures used in clinical analysis. Its composition (percent) is stated to be: purity (99.8), volatile matter (0.03), chloride (0.07), ash (0.003), insoluble matter (0.001). The sample required an igniter to obtain complete combustions. The reproducibility was substantially poorer than for the other nitrogen compounds tested and larger samples led to incomplete combustion. The results were at about the limits of stated experimental error from those reported by Huffman, Ellis, and Fox (1936).

### 4.7 Thianthrene $((C_6H_4)_2S_2)$

The sample was obtained commercially (Aldrich Chemical) and was zone refined with fifteen passes. The results were less reproducible than most of the other substances, but had about the same reproducibility as previously reported work. These measurements give an energy of combustion about midway between the results of Hubbard, Katz, and Waddington (1954) and of Hu, Yen, and Geng (1966). They are in good agreement with the results of Sunner (1963).

The thianthrene combustions led to a black finish on the platinum crucible, which on ignition led to a clean matte finish. The problem which this poses is not understood. The correction in Table 2, labeled $q_{diln}$ is the adjustment of the final solution to the standard concentration.

### 5.0 Recommendations:

The following tentative recommendations are made about the thermochemical reference materials program: (1) In the selection of a thermochemical reference material for comparative studies a criterion of difficulty should be used to insure that the reference material exemplifies a difficult problem characteristic of the class of substances it represents. (2) Urea is a reasonable reference material for nitrogen compounds because it requires an igniter to achieve consistent combustion, a problem characteristic of organic nitrogen compounds. (3) While p-chlorobenzoic acid and p-fluorobenzoic acid are low in halogens, the amount of experimental comparison work already done on them should be taken advantage of in selecting them as reference materials.

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[1] See footnote p. 5.

(4) Because the demand for thermochemical reference materials is likely to be light, the collection of reference materials certified for other purposes seems to be a reasonable source for the materials needed.
(5) Certification of thermochemical reference materials containing special elements should include references to work done on the same substance (the same or other batches) in other places as well as the standardizing laboratory. (6) Because the purposes of thermochemical reference materials include the discovery of sources of systematic or random errors, the use of rigidly defined procedures should not be overemphasized. Reasonable variations in procedures and instruments should be encouraged. (7) Comparison of the results of measurements made in this work with measurements made elsewhere on the same substances indicates that differences between laboratories/samples/procedures lead to differences of 0.01 to 0.05 percent between well qualified scientists. Absolute differences of 0.2 to 2 $kJ \cdot mol^{-1}$ are prevalent.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Combustion measurements using a rotating bomb adiabatic aneroid calorimeter have been used to make a preliminary evaluation of ten substances as potential thermochemical reference materials for combustion or organic compounds containing N, S, Cl and F. p-chlorobenzoic acid, p-fluorobenzoic acid, and urea are recommended for acquisition, certification, and distribution. Thianthrene may also be suitable. For the ten substances including in addition to the above: o- and m-chlorobenzoic acids, o-fluorobenzoic acid, nicotinic acid, acetanilide, and creatinine, typical combustion data are given, showing corrections applied; and mean thermodynamic functions at 25°C are given together with error estimates. The results are compared with other work. Recommendations and a discussion of the role of standard reference materials for thermochemistry are given.

17. KEY WORDS (Alphabetical order, separated by semicolons) Acetanilide; bomb calorimetry; calorimetry; chlorobenzoic acid; combustion; creatinine; fluorobenzoic acid; nicotinic acid; reference materials; thermochemical; thermochemical standards; thianthrene; urea.

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