

MANUEL A.V. RIBEIRO DA SILVA
M.^a DORES M.C. RIBEIRO DA SILVA
GEOFFREY PILCHER *

Departamento de Química
Faculdade de Ciências
Universidade do Porto
4000 Porto, Portugal



THE CONSTRUCTION, CALIBRATION AND USE OF A NEW HIGH-PRECISION STATIC-BOMB CALORIMETER

A new high-precision static-bomb calorimeter, based on the well established Dickinson design, has been constructed in Porto. The energy equivalent of the calorimeter was determined to a precision (standard deviation of the mean) of $\pm 0.004\%$, using the combustion of benzoic acid (B.D.H. Thermochemical Standard). For measurements, the amount of compound burned was determined from the mass of carbon dioxide produced. The standard energy of combustion of 3-methylcatechol was determined in Porto as $-\frac{1}{2}\Delta U_c^\circ/M \text{ (J.g}^{-1}\text{)} = 28217.7 \pm 0.9$ in agreement with the value from measurements made independently in Manchester of $-\frac{1}{2}\Delta U_c^\circ/M \text{ (J.g}^{-1}\text{)} = 28216.9 \pm 1.9$.

* Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

INTRODUCTION

Measurement of enthalpies of combustion in oxygen is of fundamental importance in determining enthalpies of formation of organic compounds. Although in some instances, enthalpies of formation are derived from enthalpies of other reactions, e.g. hydrogenation, hydrolysis, halogenation; in these cases the auxiliary data needed to derive the required enthalpy of formation are determined from enthalpies of combustion. For organic compounds of low reactivity, combustion calorimetry is the appropriate method for determining their enthalpies of formation.

For solids or liquids, the combustion reaction is carried out under a high pressure of oxygen in a pressure vessel (bomb) and the thermodynamic quantity derived from this experiment at constant volume is the standard molar energy of combustion, ΔU_c° . The standard molar enthalpy of combustion, ΔH_c° is calculated from ΔU_c° using

$$\Delta H_c^\circ = \Delta U_c^\circ + \Delta nRT$$

where Δn is the increase in the number of moles of gaseous species resulting from the combustion reaction.

The conventional type of high-precision static-bomb calorimeter is based upon the design due to Dickinson [1] in which the bomb is placed in a vessel containing efficiently stirred water, the temperature of which is measured by a stable and sensitive thermometer. This paper describes a calorimeter of this type, designed for making measurements to a precision better than $\pm 0.01\%$. Such precision is required when determining small differences between enthalpies of formation, which are themselves derived as differences between the enthalpies of combustion of the compounds and the enthalpies of formation of the products of combustion, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

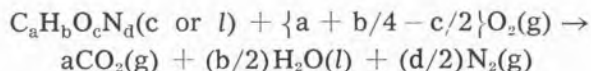
The experimental techniques must also be designed to minimise systematic errors. The energy equivalent of the calorimeter was

determined using the combustion of B.D.H. Thermochemical Standard benzoic acid and the experimental conditions for calibration, e.g. the initial and final temperatures and the length of the experiment were kept as close as possible to the corresponding conditions for measurements.

Since the pioneering work of Dickinson in 1915, there have been many developments in the techniques of bomb calorimetry [2], but these have not resulted in a significant improvement in the precision and accuracy of measurement. It seems probable that the factor limiting the overall accuracy is the precision to which the chemistry of the combustion reaction can be analysed and hence defined. As the energy change depends only on the initial and final states of the system, these states must be thermodynamically defined.

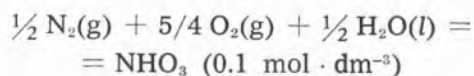
The *initial state* consists of the sample, solid or liquid, the oxygen which may contain a small quantity of nitrogen impurity, and the water originally placed in the bomb. The substance under investigation should be present as a single phase and should be of high purity. Corrections to compensate for impurities can occasionally be made but they are undesirable since they create additional uncertainty.

For compounds containing C, H, O and N, the experimental objective is to derive the standard molar enthalpy change for the reaction



Approximately, 90 % of the nitrogen in a compound will appear in the combustion products as elemental nitrogen; the remainder forms aqueous nitric acid determined by titration of the bomb washings after the combustion experiment. Jessup [3] has shown that no appreciable amount of nitric acid is lost on slowly releasing the gas from the bomb or by flushing the bomb with pure oxygen, provided ca. 1 cm³ of water is present in the bomb. Several workers [4, 5] have shown that nitrous acid formation is gener-

ally too small to be significant but if required it may be determined colorimetrically with Griess' reagent [6]. The energy correction for production of nitric acid is based on $\Delta U^0/(\text{kJ}\cdot\text{mol}^{-1}) = -59.7$ [7] for the formation of nitric acid according to

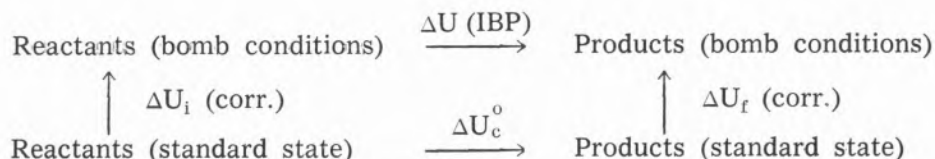


Some combustion experiments result in a small residue of carbon, requiring a correction of 33 kJ.g⁻¹ [8] for this incomplete combustion. If the carbon residue is small and confined to the crucible, this correction can be made with reasonable accuracy. If however, a large carbon residue is formed, especially on the bomb walls, the experimental result must be rejected. Experience has shown [9] that no carbon monoxide is formed in a clean combustion, but a large carbon residue is usually associated with formation of carbon monoxide.

The amount of substance burned may be determined from its mass by assuming complete combustion and the absence of non-carbonaceous impurities, particularly water. An alternative method is to determine the amount of substance burned from the mass of carbon dioxide produced, after, correction for that formed from the combustion of auxiliary materials such as the cotton used for ignition. This method was introduced by Jessup [3] and Prosen and Rossini [10] and is now widely used in high-precision bomb calorimetry. It has the advantage of minimising systematic errors which may arise from impurities in the sample and this method was used in this work.

To derive the standard molar energy of combustion it is necessary to correct the observed energy of combustion to obtain the corresponding value for all reactants and products to be in their standard states. The first comprehensive treatment of this problem was made by Washburn [11]. In this work a more recent development of Washburn's treatment was used for the calculation [12].

The principle of the Washburn corrections is apparent from the following cycle at 298.15 K.



The standard molar energy of combustion (ΔU_c°) is derived from the energy of the isothermal bomb process [$\Delta U \text{ (IBP)}$] by

$$\Delta U_c^\circ = \Delta U \text{ (IBP)} + \{ \Delta U_i \text{ (corr.)} - \Delta U_f \text{ (corr.)} \}$$

The total correction to the standard state

$$\Delta U_\Sigma = \{ \Delta U_i \text{ (corr.)} - \Delta U_f \text{ (corr.)} \}$$

is often relatively small because the $\Delta U \text{ (corr.)}$ terms enter the expression with opposite signs. The individual correction terms may be relatively large and are comprised essentially of the compression energies of the materials in the bomb including the gases, the energies of solution of the gases in the liquid phases present in the bomb and the energy of vaporisation of the water above the bomb solutions required to saturate the gaseous phase. After making the appropriate corrections for the minor energy changes, such as ignition, formation of nitric acid and formation of any carbon residue, the standard molar energy and the standard molar enthalpy of combustion are derived as previously described.

EXPERIMENTAL

APPARATUS

The combustion bomb, figure 1, is a twin-valve bomb, type 1105, Parr Instrument Company, Illinois, USA. It is made of Car-

penter 20 Cb3 stainless steel, has an internal volume of 0.34 dm³ and wall thickness 6.7 mm, sufficient to withstand more than 200 atm

pressure. The bomb head rests on a wide bevelled rim at the top of the bomb body where it is sealed by a rubber O-ring. When the screw cap, H, is tightened, positive metal to metal contact between the bomb head and body ensures the sealing ring to be well protected from the combustion flame. The bomb body has three metal legs, 1 cm high, to allow free circulation of water under the bomb. The bomb head is equipped with two valves, for inlet, A, and for outlet, B. Oxygen

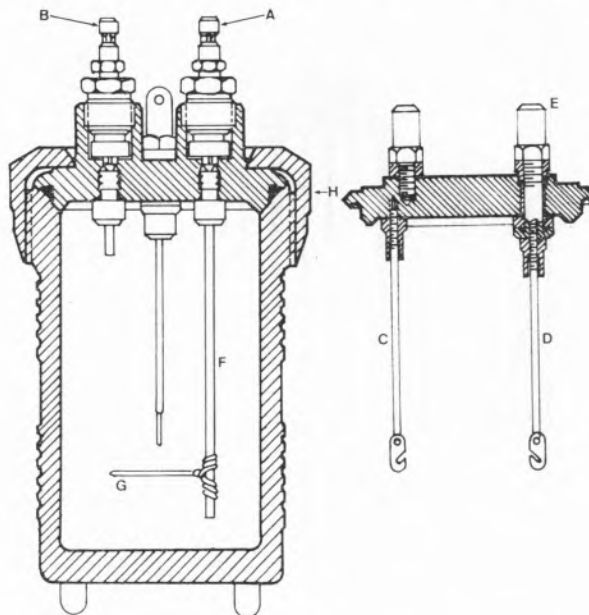


Fig. 1

Combustion Bomb

enters through the tube, F, below the crucible to ensure minimum disturbance of the crucible contents when filling or flushing the bomb. The gas connections are made with snap couplings which slip over the top of the valve

needle stems. The insulated electrode, D, is provided with an external terminal, E; the other electrode, C, is earthed to the bomb head. For ignition, a length of fine platinum wire (0.05 mm diameter) is connected between these electrodes. The sample is placed in a platinum crucible held in the platinum-10 % iridium support loop, G, attached to the bottom of the inlet tube.

Figure 2 shows the calorimeter system; the calorimeter can, A, is made of copper and is chromium plated. It consists of a cylinder,

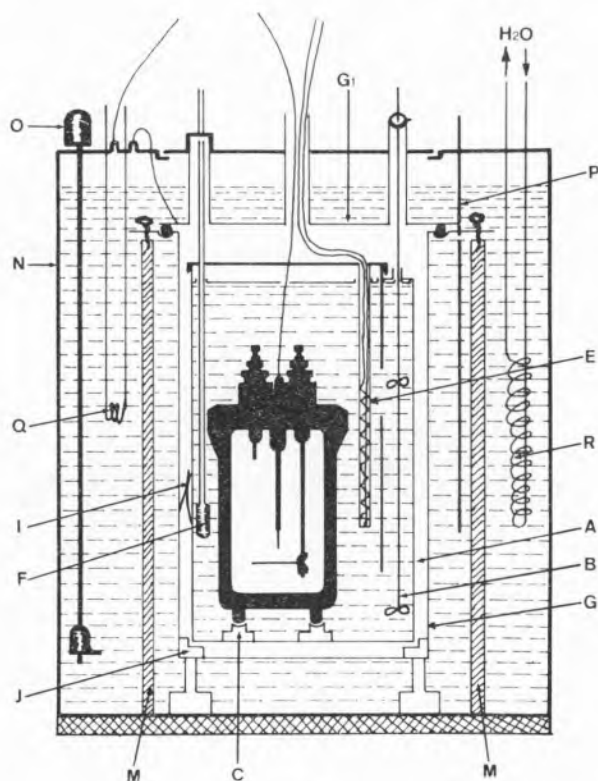


Fig. 2

The Static-Bomb Calorimeter System

14 cm diameter, 26 cm height, fitted with a vertical side tube with openings into the main cylinder at the top and bottom. The stirrer, B, is located in this side tube so that the water in the can is circulated over the bomb. The stirrer has two four-bladed propellers, is held in a bearing above the side tube and is rotated at 8 Hz using a flexible drive con-

nection to the stirrer shaft from a constant speed induction motor. The tightly fitting lid of the can is also made of chromium-plated copper and contains a small hole for the ignition lead sealed with a rubber gasket and a larger hole to admit the quartz thermometer. A copper tube, 1.5 cm diameter, 18 cm length, is attached to the underside of the lid and holds the calorimeter heater, E, a $320\ \Omega$ resistance. The bomb is held in a fixed central position in the can using the brass support, C, which rests on the bottom of the can.

The isothermal jacket, G, has the same shape as the calorimeter can but is 2 cm larger in overall dimensions to provide a uniform 1 cm air gap for all surfaces. The calorimeter can is centrally secured in the jacket by supporting it on three Perspex feet, J, 1 cm high, fixed at the bottom of the well. A small steel spring, I, placed between the calorimeter and the jacket provides the earth return for the ignition circuit. The jacket lid, G₁, is made watertight by an O-ring seal and is provided with three tubes, one for the quartz thermometer, F, one for the calorimeter stirrer shaft and one for the electrical leads to the calorimeter. The jacket is placed inside a cylindrical tank, N, diameter 40 cm, height 40 cm, which contains ca. 40 dm³ of water. The jacket is positioned vertically using two screws attached to the metal pillars, M; thus after assembly the jacket is submerged in the thermostatted water. The water in the tank is circulated by a centrifugal pump, O, and the temperature is controlled at ca. 301.5 K to $\pm 10^{-4}$ K with a temperature controller, Tronac PTC 41, by means of a probe, P, a heater, Q, and a cooling coil, R.

PROCEDURE

The solid sample is pelleted and weighed in the platinum crucible. A cotton thread fuse is attached to the platinum ignition wire and placed in contact with the pellet. 1 cm³ of water is added to the bomb which is then twice filled with oxygen to 10 atm and the

pressure released before filling to 30 atm at room temperature. The bomb is then lowered on to its stand in the calorimeter to which 3119.6 g of water has been added. After checking for leaks, the calorimeter is finally assembled and placed in the isothermal jacket which is then submerged in the thermostat. The calorimeter temperature is raised to 297.7 K using the calorimeter heater; then the system is allowed to equilibrate for approximately 20 minutes.

The calorimeter temperature was measured to 10^{-4} K at intervals of 20 s using a Hewlett-Packard quartz thermometer (HP-2804A) and recorded by a thermal printer (HP-5150A). The temperature profile for each experiment was divided in the customary manner into a fore-period (ca. 14 min.), main-period (ca. 10 min.) and an after-period (ca. 14 min.). The temperature readings were processed using a Commodore 8096 microcomputer to calculate ΔT_{ad} , the temperature rise that would have occurred in the calorimeter if the system were adiabatic with no work of stirring. The method of calculation was based on that described by Coops, Jessup and Van Nes [8].

The sample was ignited at 298.150 ± 0.002 K: the electrical energy for ignition was determined from the change in potential across a 1400 μ F capacitor when discharged, from an initial voltage of ca. 41 V, through the platinum ignition wire.

After the calorimetric experiment, the apparatus was disassembled and the bomb removed for analysis of the combustion products. The mass of carbon dioxide produced by the combustion was determined in all measurements on compounds and also in some calibration experiments to check the analytical method.

The Pyrex absorption tubes are shown in figure 3. They consist of two parts, the absorption body and the cover: aluminium cones are sealed into the sockets at the ends of the tubes using epoxy resin. The cones are equipped with O-rings so that the tubes can be connected in series with greaseless gas-tight joints. The body of the tube is

packed with Carbosorb (B.D.H. 12-20 mesh) contained within pads of glass wool. As Carbosorb expands on absorption of carbon dioxide, a thin glass wool rope is threaded through the centre of the absorbent to prevent blockage. The cover tubes are filled with magnesium perchlorate (B.D.H. 14-22 mesh)

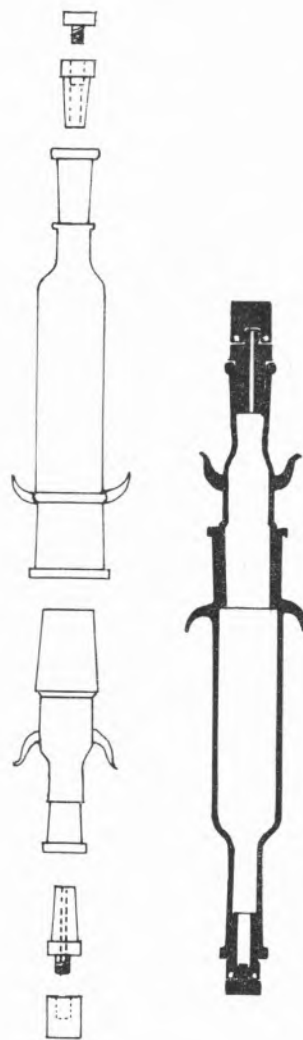


Fig. 3

Carbon Dioxide Absorption Tube

again between glass wool pads, to absorb the water liberated when Carbosorb absorbs carbon dioxide. The two parts of the absorption tube are joined by a cone and socket sealed with Apiezon wax.

Before use the absorption tubes are flushed with oxygen and all weighings are made with oxygen in the tubes. The tubes are weighed on an analytical balance to $\pm 10^{-5}$ g and remain on the balance for 30 min. to attain equilibrium. The bomb exit gases are discharged at ca. $150 \text{ cm}^3 \text{ min}^{-1}$ at atmospheric pressure through a large drying tube containing magnesium perchlorate before entering the absorption tubes. When the pressure in the bomb has fallen to atmospheric, the bomb is then flushed with oxygen at ca. $150 \text{ cm}^3 \text{ min}^{-1}$ for 30 min. to collect the remaining carbon dioxide. The tubes are sealed and left overnight before reweighing. The mass of carbon dioxide is calculated from the increase in weight of the tubes by multiplying by the factor 1.0045, previously derived by Rossini [13].

The bomb is then opened and the interior surfaces checked for signs of carbon deposits; if these are observed the experimental result is discarded. If a small residue of carbon is present in the crucible, it is determined from the change in weight on heating the crucible to red heat.

The bomb top, fittings and interior walls are washed with distilled water and the nitric acid determined by titration of the washings with NaOH (0.04 mol dm^{-3}) using methyl red indicator.

CALIBRATION

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (B.D.H. Thermochemical Standard, Batch No. 55504/01) having a specific energy of combustion under standard bomb conditions of $-\Delta U_c/(\text{J.g}^{-1}) = 26433.9 \pm 3.6$ [14].

The standard bomb conditions refer to combustion under 30 atm of oxygen at 298.15 K when the mass of the sample, m_s , and the mass of water, m_w , added to the bomb are related to the internal volume of the bomb, V , by $m_s/g = m_w/g = 3V/\text{dm}^3$. For small deviations from these conditions, the calorific

value can be calculated from the certificate value of applying a factor f , given by [8]

$$f = 1 + 10^{-6} [20 \{ (P/\text{atm}) - 30 \} + 42 \{ (m_s/g) (\text{dm}^3/V) - 3 \} + 30 \{ (m_w/g) (\text{dm}^3/V) - 3 \} - 45 \{ (T/K) - 298.15 \}]$$

where P is the initial oxygen pressure and T is the temperature to which the combustion reaction is referred. For the average conditions applying to the calibration of this calorimeter, the specific energy of combustion of the benzoic acid is the same as the certificate value.

The total energy equivalent is considered as the sum of two parts, ϵ (calor), the energy equivalent of the standard calorimetric system with the bomb empty and ϵ_c , the energy equivalent of the bomb contents. The combustion reaction is assigned to 298.15 K, and as ignition was carried out at this temperature, ϵ_c refers to the energy equivalent of the bomb contents for the final system and is given by [8]

$$\epsilon_t/(\text{J.K}^{-1}) = 21.0 n_{\text{O}_2} + 4.18 m_w + 2.28 m_s + 0.136 m_{\text{pt}}$$

where n_{O_2} is the number of moles of oxygen initially placed in the bomb and m_{pt} is the mass of the platinum crucible. The energy equivalent is calculated from

$$(\epsilon (\text{calor}) + \epsilon_t) \Delta T_{\text{ad}} = m_s (-\Delta U_c) + \Delta U (\text{cotton}) + \Delta U (\text{HNO}_3) + \Delta U (\text{ign.}) - \Delta U (\text{carbon})$$

where $m_s (-\Delta U_c)$ is the energy of combustion of the benzoic acid pellet, $\Delta U (\text{cotton})$ is the energy of combustion of the cotton thread fuse given by $-m^{\text{III}} (\Delta U_c^0/M (\text{cotton}))$. The cotton thread used has an empirical formula $\text{CH}_{1.686} \text{O}_{0.843}$ and a specific energy of combustion $\Delta U_c^0/M (\text{cotton})/(\text{J.g}^{-1}) = -16240$ [8]. $\Delta U (\text{HNO}_3)$ is the energy correction for the formation of nitric acid, $\Delta U (\text{ign.})$ is the

electrical ignition energy and ΔU (carbon) is the energy correction associated with a small carbon residue in the crucible. The mass of water added to the calorimeter differed slightly for each experiment resulting in small changes in the total energy equivalent. The average mass of water added was 3119.6 g and the calibration experiments were corrected to give the energy equivalent, ϵ (calor) corresponding to this mass of water. The results of eight calibration experiments

a compound measured using the Porto bomb calorimeter for which the results have been checked by independent measurements using the Manchester bomb calorimeter.

3-Methylcatechol (Lancaster Syntheses Limited) was purified by repeated sublimation *in vacuo* and the purity checked by ir spectroscopy and C, H microanalyses. The purification process was repeated until the combustion results were consistent and the carbon dioxide recovery ratio was satisfac-

Table 1
Calibration of Porto Static-Bomb Calorimeter

	1	2	3	4	5	6	7	8
m_s (BA)/g	1.15376	1.16269	0.96045	1.03541	0.95964	0.99587	0.94996	0.99770
m^{III} (cotton)/g	0.00550	0.00469	0.00407	0.00534	0.00406	0.00436	0.00451	0.00405
$\Delta T_{ad}/K$	1.92133	1.93515	1.59858	1.72483	1.59726	1.65787	1.58203	1.66062
$\epsilon_f/(J.K^{-1})$	17.4	17.6	17.1	17.3	17.1	17.2	17.1	17.2
Δm (H ₂ O)/g	0.0	0.1	0.2	0.0	0.2	0.3	0.1	0.0
m_s (BA) $(-\Delta U_c)/J$	30498.4	30735.0	25388.4	27369.9	25367.0	26325.1	25111.1	26373.1
ΔU (cotton)/J	89.3	76.2	66.1	86.7	65.9	70.8	73.2	65.8
ΔU (HNO ₃)/J	4.4	2.6	1.7	1.9	1.9	4.0	2.4	2.7
ΔU (ign.)/J	0.5	0.6	0.8	0.6	0.6	0.4	0.5	0.6
ΔU (carbon)/J	0.0	6.6	0.0	0.0	0.0	0.0	0.0	0.0
ϵ (calor)/(J.K ⁻¹)	15905.2	15902.1	15906.8	15902.6	15906.8	15905.8	15903.3	15905.9

are given in table 1, in which the terms are as previously defined and additionally, Δm (H₂O)/g is the deviation of the mass of water added to the calorimeter from 3119.6. The mean value and standard deviation of the mean were

$$\epsilon \text{ (calor)}/(J.K^{-1}) = 15904.8 \pm 0.7 (\pm 0.004 \%)$$

3-METHYLCATECHOL

The results for 3-methylcatechol are presented here as they constitute one example of

tory. The ratio of the mass of carbon dioxide observed to that calculated from the mass of sample was 0.9996 ± 0.0001 .

The results obtained using the Porto calorimeter are given in table 2. The specific energy of combustion was calculated from

$$\{\Delta U_c^0/M \text{ (compound)}\} = (m')^{-1} \{\Delta U \text{ (IBP)} + \Delta U \text{ (HNO}_3) + \Delta U \text{ (ign.)} - \Delta U \text{ (carbon)} + \Delta U_{\Sigma} + \Delta U \text{ (cotton)}\}$$

where ΔU (IBP) is the energy change of the isothermal bomb process at 298.15 K. The mean value and the standard deviation of

Table 2
Combustion of 3-Methylcatechol in Porto Static-Bomb Calorimeter

	1	2	3	4	5
m (CO ₂ , total)/g	2.43048	2.64305	2.43874	2.58733	2.62621
m ^I (compound)/g	0.97597	1.06189	0.97990	1.03985	1.05604
m ^{III} (cotton)/g	0.00580	0.00540	0.00465	0.00465	0.00430
ΔT _{ad} /K	1.73636	1.88792	1.74216	1.84861	1.87642
ε _i /(J.K ⁻¹)	16.2	16.3	16.2	16.3	16.3
ε _f /(J.K ⁻¹)	17.6	17.9	17.7	17.8	17.9
Δm (H ₂ O)/g	0.0	0.3	0.1	0.2	0.2
-ΔU (IBP)/J	27648.0	30064.0	27741.1	29437.2	29880.0
ΔU (HNO ₃)/J	3.5	3.2	3.1	4.4	3.0
ΔU (ign.)/J	0.5	0.4	1.1	0.3	0.9
ΔU (carbon)/J	8.3	8.3	5.0	6.6	13.2
ΔU _Σ /J	17.7	19.5	17.7	19.0	19.3
ΔU (cotton)/J	94.2	87.7	75.5	75.5	69.8
-ΔU _c ⁰ /M (compound)/(J.g ⁻¹)	28218.6	28215.3	28215.8	28220.0	28218.9

the mean for the specific energy of combustion was

$$\begin{aligned} \{ -\Delta U_c^0 / M (\text{compound}) \} / (\text{J.g}^{-1}) &= \\ &= 28217.7 \pm 0.9 \quad (\pm 0.003 \%) \end{aligned}$$

Combustion measurements were made in Manchester on a sample of 3-methylcatechol purified in the same manner as described above. The calorimeter has been reported [15], and was calibrated using the NBS Benzoic Acid Reference Sample 39i giving ε (calor)/(J.K⁻¹) = 15298.99 ± 0.56 [14]. The results are presented in table 3 in which the terms are as previously defined. The mean value with the standard deviation of the mean was { -ΔU_c⁰/M (compound) }/J.g⁻¹ = 28216.9 ± 1.9 (± 0.007 %), in agreement with the value obtained using the Porto calorimeter.

It is reasonable to accept these two sets of results as representing a single determination

of this energy of combustion, giving a weighted mean value with the standard deviation of the mean, { -ΔU_c⁰/M (compound) }/ (J.g⁻¹) = 28217.4 ± 0.9 (± 0.003 %). Accepting the average error for the calibration of the two calorimeters, ± 0.004 %, and the uncertainty in the certificate value for benzoic acid, ± 0.006 %, a total standard deviation of ± 0.008 % is obtained and in accord with normal thermochemical practice, this is doubled for the standard molar energies and enthalpies of combustion. The relative molar mass of 3-methylcatechol is 124.130 g mol⁻¹; hence -ΔU_c⁰(c)/(kJ.mol⁻¹) = 3502.2 ± 0.5, and -ΔH_c⁰(c)/(kJ.mol⁻¹) = 3505.4 ± 0.5. With ΔH_f⁰(CO₂, g)/(kJ.mol⁻¹) = -393.51 ± 0.13 and ΔH_f⁰(H₂O, l)/(kJ.mol⁻¹) = -285.83 ± 0.04 [16], the standard molar enthalpy of formation of crystalline 3-methylcatechol is derived, ΔH_f⁰(c)/(kJ.mol⁻¹) =

Table 3
Combustion of 3-Methylcatechol in Manchester Static — Bomb Calorimeter

	1	2	3	4
m (CO ₂ , total)/g	2.79184	2.52083	2.72785	2.45187
m ^I (compound)/g	1.12359	1.01400	1.09747	0.98650
m ^{III} (cotton)/g	0.00284	0.00274	0.00267	0.00275
$\Delta T_{ad}/K$	2.07477	1.87363	2.02788	1.82204
$\varepsilon_i/(J.K^{-1})$	14.4	14.3	14.4	14.2
$\varepsilon_f/(J.K^{-1})$	16.0	15.7	15.9	15.6
$\Delta m (H_2O)/g$	-0.1	-0.2	0.2	0.1
$-\Delta U$ (IBP)/J	31770.6	28689.5	31055.1	27901.7
$\Delta U (HNO_3)/J$	11.6	11.8	16.3	9.0
ΔU (ign.)/J	1.1	1.1	1.1	1.1
ΔU (carbon)/J	9.9	0.0	0.0	6.6
$\Delta U_{\Sigma}/J$	22.1	19.6	21.5	19.0
ΔU (cotton)/J	46.0	44.6	43.3	44.6
$-\Delta U_c^0/M$ (compound)/(J.g ⁻¹)	28212.8	28217.4	28222.1	28215.4

$= -392.5 \pm 1.1$. This result together with values for other alkyl-substituted catechols are being separately reported [17].

Received 6 June 1984

ACKNOWLEDGEMENTS

We thank NATO, Research Grant 1709 (Porto and Manchester Universities) and Junta Nacional de Investigação Científica and Tecnológica, Lisboa (Research contract 220.80.32, Porto University) for financial support. We also thank Instituto Nacional de Investigação Científica, Lisboa for partial financial support to a research project of the Chemical Research Centre, Porto University.

REFERENCES

- [1] H.C. DICKINSON, *Bull. Bur. Standards*, **11**, 189 (1915).
- [2] "Experimental Chemical Thermodynamics", Vol. 1, "Combustion Calorimetry", S. Sunner and M. Mansson, I.U.P.A.C., Pergamon Press, Oxford, 1979.
- [3] R.S. JESSUP, *J. Res. Nat. Bur. Standards*, **21**, 475 (1938).
- [4] E.J. PROSEN, *Nat. Bur. Standards Report No. 1119*, Washington, D.C. (1951).
- [5] G. WADDINGTON, W.N. HUBBARD and D.W. SCOTT, *J. Phys. Chem.*, **58**, 152 (1954).
- [6] A.I. VOGEL, "A Text-book of Quantitative Inorganic Analysis", p. 641, Longmans, Green and Company, London (1951).
- [7] D.D. WAGMAN, W.H. EVANS, V.B. PARKER, R.H. SCHUMM, I. HALOW, S.M. BAILEY, K.L. CHURNEY and R.L. NUTTALL, *J. Phys. Chem. Ref. Data*, **11** (1982): supplement no. 2.
- [8] J. COOPS, R.S. JESSUP and K. VAN NES, "Experimental Thermochemistry", Vol. 1, Chapter 3, F.D. Rossini editor: Interscience, New York (1956).
- [9] E.J. PROSEN and F.D. ROSSINI, *J. Res. Nat. Bur. Standards*, **27**, 289 (1941).
- [10] E.J. PROSEN and F.D. ROSSINI, *J. Res. Nat. Bur. Standards*, **33**, 255 (1944).

- [11] E.W. WASHBURN, *J. Res. Nat. Bur. Standards*, **10**, 525 (1933).
- [12] W.N. HUBBARD, D.W. SCOTT and G. WADDINGTON, "Experimental Thermochemistry", Vol. 1, Chapter 5, F.D. ROSSINI, editor: Interscience, New York (1956).
- [13] F.D. ROSSINI, *J. Res. Nat. Bur. Standards*, **6**, 19 (1931).
- [14] G. PILCHER, J. BICKERTON and M.D.M.C. RIBEIRO DA SILVA, *J. Chem. Thermodynamics*, **16**, 401 (1984).
- [15] J. BICKERTON, G. PILCHER and G. AL-TAKHIN, *J. Chem. Thermodynamics*, **16**, 373 (1984).
- [16] CODATA, *J. Chem. Thermodynamics*, **10**, 903 (1978).
- [17] M.D.M.C. RIBEIRO DA SILVA, M.A.V. RIBEIRO DA SILVA and G. PILCHER, *J. Chem. Thermodynamics*, **16**, 1149 (1984).

SUMÁRIO

Descreve-se a construção de um novo calorímetro de combustão de alta precisão, com bomba estática, baseado no modelo de Dickinson. O equivalente energético do calorímetro foi determinado com a precisão (desvio padrão da média) de $\pm 0.04\%$, usando a combustão do ácido benzóico (Padrão Termoquímico B.D.H.). Nas medições experimentais, a quantidade de composto queimado é determinada a partir da massa de dióxido de carbono produzido. A energia de combustão padrão do 3-metilcatecol foi determinada no Porto como $-\{\Delta U_c^\circ/M\}/(J.g^{-1}) = 28217.7 \pm 0.9$ em excelente concordância com o valor obtido em Manchester, em medições independentes de $-\{\Delta U_c^\circ/M\}/(J.g^{-1}) = 28216.9 \pm 1.9$.