J Therm Anal Calorim (2010) 99:939–945
DOI 10.1007/s10973-009-0555-9

Modernization and validation of an isoperibol rotating bomb calorimeter for the measurement of energies of combustion of sulphur compounds

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MEDICTA2009 Conference

Abstract A rotating bomb calorimeter belonging to the Laboratory of Chemistry and Process Engineering (UCP) at ENSTA ParisTech since the 1960s was modernized and re-set in order of service for the measurement of heats of combustion of sulphur-containing compounds. The parts of the calorimeter that were replaced concerned essentially the thermal regulation, firing system and data acquisition, while most of the mechanical organs were found to work perfectly. The apparatus was tested extensively and calibrated using standard benzoic acid. The standard energy of combustion of thianthrene was measured to validate the operating protocol for sulphur compounds.

Keywords Energy of combustion · Enthalpy of formation · Rotating bomb calorimetry · Sulphur compounds

Introduction

The knowledge of thermochemical data is required for several scientific and engineering applications, for instance, in computational thermochemistry, thermodynamics, process design or safety assessment. Combustion calorimetry is a rather widespread technique and has long been used for the determination of heats of combustion, which may be corrected to standard energies of combustion, and hence to standard enthalpies of formation, by applying the standard state correction calculation formalized by Washburn [1]. This method applies to organic substances containing C, H, O and N elements, as well as some non metal hetero-element such as B and Se [2] and metals such as Hg, Sc, Y, Sn, Hg and many others [3]. For sulphur, arsenic, silicon, phosphorus and halogen compounds, however, static bomb combustion calorimeters cannot be used because the final state of the reaction is not well defined [2]. After combustion of sulphur compounds, the sulphur trioxide and dioxide that are formed are absorbed by the water resulting from the combustion and form a heterogeneous deposit on the bomb's wall. Because of the high energy of dilution of sulphuric acid solutions, the errors resulting from assuming a homogeneous final state lead to excessive uncertainties. In the case of halogen or phosphorous compounds, the final state may contain various oxidation products in quantities that cannot be simply determined nor predicted. For these reasons, there is a relative lack of data concerning these classes of compounds that are of primary importance in many industrial fields, such as pharmaceuticals, pesticides, energetic materials, polymers and many others.

The principle of moving bomb calorimetry consists in transforming the calorimetric bomb into a stirred reactor where additional reactions, involving reactants in solution introduced in the bomb prior to the combustion, may be performed to bring the combustion products to a perfectly defined final state. Rotating bomb calorimeters were developed in the early twentieth century to allow efficient mixing of the reactants. In the 1950s, Hubbard et al. [4, 5], Waddington et al. [6] and Good et al. [7] described such apparatuses designed for the measurement of the combustion energy of sulphur and halogen compounds and an extension of the Washburn standard state correction to those compounds was described [5, 8].

Since they are not commercially available, those equipments are rare. Few rotating bomb calorimeters were

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constructed since the development of this technique, and even fewer are still in service. Nevertheless, several researchers have devoted their works to the determination of standard enthalpies of formation of sulphur and halogen compounds since the early 1960s [9–16]. Much more recently, Ribeiro da Silva and co-workers have published an impressive number of measurements obtained using a rotating bomb calorimeter over the past two decades [17–21]. Roux, Temprado and co-workers recently published several articles related to calorimetric and ab initio computational studies on sulphur compounds [22–26].

The present work is part of a program devoted to the development of predictive calculation of thermochemical properties of pure compounds in condensed phases [27–29]. Empirical predictive methods based on group contribution summation require considerable numbers of experimental data that are not always available. In order to extend the field of application of the methods developed for C, H, O and N compounds [28, 29] to other classes of chemicals, we have undertaken a program of experimental determinations of standard enthalpies of formation of solid compounds containing the elements C, H, O and S.

This article presents the modification of a rotating bomb calorimeter that was built in 1968 and used during more than 30 years at the department of energetic materials of the Ecole Nationale Supérieure de Techniques Avancées (ENSTA ParisTech, Paris, France) for measurements on compounds of interest in the field of armament and propelling. The calorimeter was fitted with new temperature regulation, data acquisition and ignition systems and submitted to several tests in order to validate its working features. The calorimeter was calibrated using standard benzoic acid and the protocol for the measurement of combustion energies of sulphur compounds was validated using thianthrene.

Modification of the calorimeter

The original apparatus

The isoperibolic rotating bomb calorimeter was built in 1968 by the mechanical workshops of the French Technical Direction for Terrestrial Armament (DTAT, Puteaux, France), using draughts from the National Argonne Laboratory (Chicago, USA). It was then used by Ducros et al. [30] for the determination of enthalpies of formation of substances involved in the composition of military explosives and propellants. These measurements were confidential and could not be published. Figure 1 is a photograph of the original calorimeter with its electric hardware (d, e), bucket (b) and calorimetric bomb (a). Its design is very close to that described by Waddington et al. in [6].

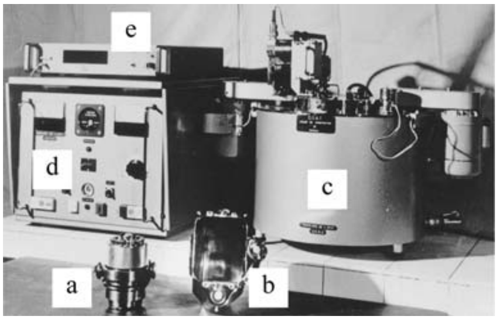

Fig. 1 General view of the rotating bomb calorimeter and its equipments

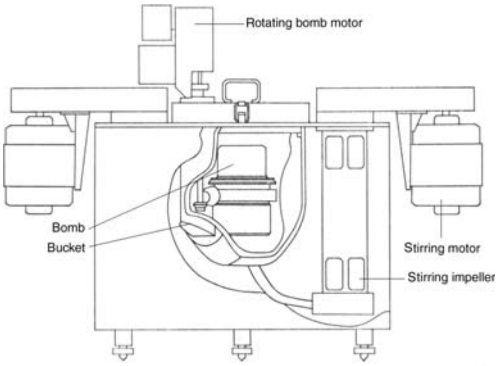

Fig. 2 Scheme of the calorimeter showing its main mechanical parts

All the mechanical parts of the calorimeter were used with no modification. It is composed of an external jacket filled with water that maintains a constant temperature around the calorimetric bucket, in which takes place the rotating bomb. Figure 2 presents a diagram of the calorimeter, showing the bomb placed "bottom-up" in the bucket. Two impellers force the circulation of the water inside the jacket and its cover to assure thermal homogeneity. A draught of the bucket is presented in Fig. 3. It is realized in nickel-platted copper, as well as the inner part of the jacket, in order to reduce radiating heat exchanges. Bomb rotation is transmitted via the axis (Ab) attached to the motor fixed on the jacket cover (Cj). The water in the bucket is stirred by an impeller (I) connected to a second motor via a belt-pulley. A resistor (not presented on the draught) can be used to warm the water in the bucket prior to experiment.

Figure 4 shows the 0.342 L stainless steel bomb, which is entirely lined with platinum to avoid corrosion reactions.

Temperature acquisition

Original temperature probes were tested before use. They consist of linearized thermistor composite sensors that deliver temperature measurements with a resolution of

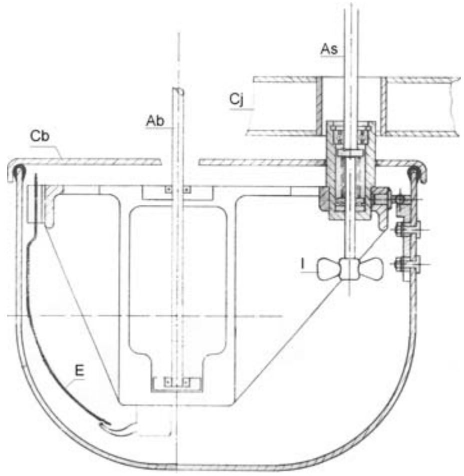

Fig. 3 Draught of the calorimetric bucket

Fig. 4 View of the calorimetric bomb

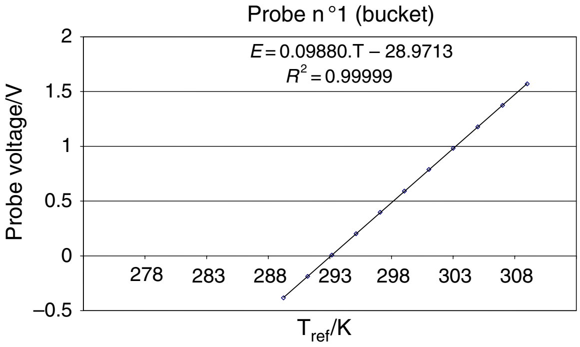

Fig. 5 Linearity test of a temperature probe

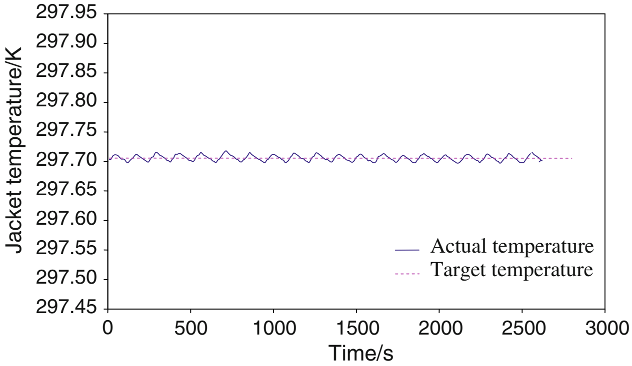

Fig. 6 Stability test of the external jacket temperature regulation

10^{-3} K. In order to assess the linearity of the response, we measured the voltage delivered by the probes plunged in a high precision bath, model 7008 from Hart Scientific, in the temperatures range 288–308 K. The reference temperature was measured using a PHP 601 thermometer connected to an AN5847C reference platinum probe from AOIP. As can be seen in Fig. 5 for the probe used in the measurement of the bucket temperature, the response is almost perfectly linear within the range of interest for combustion calorimetry.

A new acquisition system was developed. The probes are connected to voltage indicators equipped with digital outputs (ITI 20BD from AOIP). A program was realized to automatically acquire the digitalized signal and convert it to temperatures. The program also calculates the adiabatic temperature change at the end of an experiment.

Jacket thermal regulation

The thermal regulation of the jacket was originally performed via a contact thermometer driving a heating resistor. The heating power compensates for the heat sink provided by a constant flow of fresh water circulating in a streamer within the jacket. We used the jacket temperature indicator to automatically switch the resistor on or off, thus providing an efficient thermal regulation. As can be seen in Fig. 6, the jacket temperature could be maintained within ±0.02 K around the target value of 297.70 K during a combustion experiment.

Ignition system

A 100,000 μF capacitor charged to 35 V was used to fuse the 0.05 mm platinum wire attached to the electrodes in the bomb and provoke the ignition. The energy of ignition was then deduced from the voltage fall across the capacitor. Ignition was transmitted to the sample by a cotton thread ($CH_{1.774}O_{0.887}$), which energy of combustion was found equal to –16,945 J g^{-1}.

Calibration and validation tests

Materials and experimental protocol

Freshly distilled water was used to fill the calorimetric bucket. Oxygen was purchased from Air Liquide.

Samples were weighed on an AX205 DeltaRange® Mettler Toledo balance (inaccuracy: ±10 µg) and corrections from apparent mass to effective mass were applied using the densities measured with an AccuPyc 1330 gas pycnometer (Micromeritics). In each experiment, 10 mL of distilled water was placed in the bomb in order to ensure a well-defined thermodynamic equilibrium at the end of the combustion. The bucket was filled with (3770.0 ± 0.1) g of distilled water weighed on a Mettler Toledo PB8001-S balance having a resolution of 10^{-1} g. The bomb was charged with oxygen to $p = 3.04$ MPa and placed in the bucket. After inserting the bucket in the calorimeter, the water was warmed to a temperature close do 295.6 K by the auxiliary resistor prior to starting the experiment.

Temperature was recorded every 2.5 s during the whole experiment. The main period of acquisition started at the moment of the ignition and lasted for exactly 1,200 s. For each experiment, the bomb rotation was started 600 s after ignition. Temperatures were acquired for a period of 1,200 s before the ignition and another period of 1,200 s after the main period, in order to correct the measured temperature change for external heat exchanges. The adiabatic temperature change was calculated by the acquisition program at the end of each experiment. Figure 7 presents the evolution of the bucket temperature during a sample experiment.

The total acidity of the final solution was titrated by 0.5 molar NaOH and nitric acid content was deduced by subtracting the amount of sulphuric acid calculated assuming total conversion of sulphur to H_2SO_4. Nitric acid is formed by the oxidation of atmospheric nitrogen present in the bomb and which is required to catalyze full oxidation of sulphur. The enthalpy of formation of HNO_3 in solution was taken from [31].

Calibration

The calorimeter was calibrated by the combustion of one gram pellets of standardized benzoic acid [CAS No. 65-85-0] purchased from Parr, having a combustion energy of –(26,434 ± 3) J g^{-1} based on weight in vacuum. This value was corrected to actual experimental conditions according to the recommendations of Coops et al. [32], applying the correcting factor given by:

$$f = 1 + 10^{-6}\left[20(P-30) + 42\left(\frac{m_{ab}}{V} - 3\right) + 30\left(\frac{m_w}{V} - 3\right) - 45(T_i - 298.15)\right]$$

where P is the initial pressure in the bomb in atmospheres, m_{ab} the mass of benzoic acid in grams, V the volume of the bomb in litre, m_w the mass of added water in grams and T_i the initial temperature to which the combustion is referred. Table 1 presents the results of the seven calibration tests performed. The standard energy of combustion of the benzoic acid sample is converted to the combustion energy in the actual conditions of the experiments by applying the standard state correction ΔU_Σ calculated following the procedure given in [8], and then corrected from isothermal combustion at 298.15 K to actual combustion between the initial and final temperatures of experiment, taking into account the energy equivalent of the bomb content in the initial and final state, ε_i and ε_f respectively. The ignition energy ΔU_{ign}, the combustion energy of the cotton thread ΔU_{fuse} and the energy of formation of nitric acid ΔU_{HNO_3} are then added to obtain the overall combustion energy ΔU_{exp} that serves to determine the energy equivalent of the calorimeter EE. The average result was found to be (14748.7 ± 6.2) J K^{-1}. The quoted uncertainty is equal to twice the standard deviation of the mean; it represents 0.042% of the absolute value.

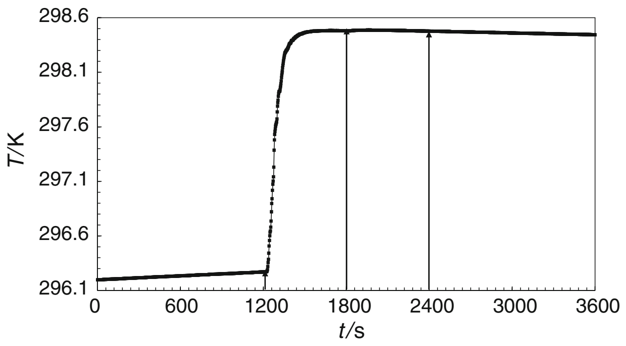

Fig. 7 Bucket temperature evolution versus time during an experiment

Validation tests

SRM 1656 standard thianthrene [CAS No. 92-85-3] purchased from the National Institute of Standards and Technology (NIST, USA), having a purity of 99.7% and a certified combustion energy of –(33,480 ± 9) J g^{-1}, was used to validate the measurement of combustion energies of sulphur compounds. The results obtained for five test combustions are reported in Table 2. The experimental energy variation of the calorimetric system is first converted to the isothermal energy variation at 298.15 K in the actual bomb conditions ΔU_{IBP} by taking into account the initial and final energy equivalent of the bomb content, ε_i and ε_f, respectively. ΔU_{IBP} also includes the ignition energy ΔU_{ign}. The combustion energy of the cotton thread ΔU_{fuse} and the energy of formation of nitric acid ΔU_{HNO_3} are then subtracted and finally, the standard state correction ΔU_Σ is applied, resulting in the massic energy of combustion of the sample in the standard state $\Delta_c u^o$. The mean value of –(33,465 ± 5) J g^{-1} is in agreement with the recommended value of

Table 1 Calibration tests

Exp. no.	1	2	3	4	5	6	7
m_{ab}/g	1.04391	1.00035	0.99899	0.98891	1.00852	0.99479	1.03807
m_{fuse}/g	0.00232	0.00238	0.00256	0.00232	0.00271	0.00202	0.00270
T_i/K	295.7022	295.5580	295.6114	296.1476	295.6358	296.2449	295.7202
T_f/K	297.5852	297.3708	297.4193	297.9265	297.4582	298.0286	297.5930
ΔT_{ad}/K	1.8751	1.7968	1.7953	1.7758	1.8115	1.7861	1.8649
ε_i/J.K^{-1}	16.15	16.10	16.10	16.09	16.11	16.09	16.15
ε_f/J.K^{-1}	17.35	17.25	17.25	17.22	17.27	17.23	17.34
ΔU_{ign}/J	1.10	0.90	0.60	1.00	1.00	1.00	1.10
f	1.000900	1.000901	1.000898	1.000873	1.000898	1.000869	1.000898
ΔU_{HNO_3}/J	0.6	0.6	0.6	0.6	0.6	0.6	0.6
ΔU_{fuse}/J	39.35	40.37	43.42	39.35	45.96	34.26	45.79
ΔU_{Σ}/J	21.96	20.94	20.92	20.69	21.14	20.81	21.83
ΔU_{exp}	27652.63	26500.67	26467.40	26196.23	26722.41	26346.77	27504.06
EE/J K^{-1}	14746.89	14748.90	14742.85	14751.54	14751.46	14750.59	14748.43
<EE>/J K^{-1}	14748.67 ± 6.16						

m_{ab}, mass of benzoic acid; m_{fuse}, mass of the cotton thread; T_i, initial temperature; T_f, final temperature; ΔT_{ad}, adiabatic temperature change; ε_i, energy equivalent of the contents of the initial state; ε_f, energy equivalent of the contents of the final state; f, correcting factor to experimental conditions of the energy of combustion of benzoic acid [32]; EE energy equivalent

Table 2 Results obtained for the combustion energy of thianthrene

Exp. no.	1	2	3	4	5
$m_{thianthrene}$/g	0.98536	0.87512	0.69138	0.59142	0.96939
m_{fuse}/g	0.00286	0.00233	0.00284	0.00262	0.00276
T_i/K	296.2695	296.5169	296.1928	296.2602	296.2689
T_f/K	298.4764	298.4770	297.7701	297.6185	298.4437
ΔT_{ad}/K	2.2338	1.9836	1.5691	1.3429	2.1976
ε_i/J K^{-1}	61.93	61.61	61.42	60.56	62.49
ε_f/J K^{-1}	61.03	60.74	60.65	59.76	61.69
ΔU_{ign}/J	1.00	0.97	1.06	1.32	1.45
ΔU_{IBP}/J	−33082.63	−29376.13	−23237.33	−19886.30	−32546.59
ΔU_{HNO_3}/J	48.49	39.48	48.16	44.43	46.80
ΔU_{fuse}/J	37.40	35.94	38.90	38.03	36.54
ΔU_{Σ}/J	20.59	18.59	13.48	12.38	20.55
$\Delta_c u^o$/J g^{-1}	−33466.26	−33460.69	−33464.65	−33464.31	−33467.13
$<\Delta_c u^o>$/J g^{-1}	−33465.11 ± 5.06				

$m_{thianthrene}$, mass of thianthrene; m_{fuse}, mass of the cotton thread; T_i, initial temperature; T_f, final temperature; ΔT_{ad}, adiabatic temperature change; ε_i, energy equivalent of the contents of the initial state; ε_f, energy equivalent of the contents of the final state; ΔU_{ign}, ignition energy; ΔU_{IBP}, energy of isothermal combustion in the actual bomb conditions, including the ignition energy; ΔU_{HNO_3}, energy of formation of nitric acid; ΔU_{fuse}, energy of combustion of the cotton thread; ΔU_{Σ}, standard state correction; $\Delta_c u^o$, standard massic energy of combustion

–(33,468 ± 4) J g^{-1} [33] and slightly lower than the certified value given by the NIST.

The confidence interval obtained for the measurements correspond to ±0.015% of the mean, which is much better than the uncertainty of temperature measurements of $\pm 10^{-3}$ K, that is, ±0.05% of the adiabatic temperature increase ΔT_{ad}. This is due to the fact that ΔT_{ad} is obtained from a great number of temperature measurements before, during and after the temperature rise, as can be seen on Fig. 7. It is obvious, however, that improving the resolution of the temperature probe would enhance the precision of measurements. In future works, the calorimetric bucket will be slightly modified so that it may accommodate the probe of a HP 2804A quartz thermometer having a resolution of 10^{-4} K.

Conclusions

A rotating bomb calorimeter, similar to the apparatus described more than 50 years ago by the inventors of this technique, has been modernized with great care to enhance its functionality while preserving its original qualities. In a next step, the calorimeter will be equipped with a quartz thermometer in order to gain one order of magnitude in the precision of temperature change measurements.

The calorimeter was calibrated and validated for the measurement of combustion energies of sulphur compounds using a standard method. The measurements that will be obtained, in complement to those published by other researchers, will be used for the development and testing of extended methods of computation of thermochemical properties of solids and liquids.

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