EVALUATION OF A BIOLOGICAL ANEROID MICROBOMB CALORIMETER WITH CALCIUM CARBIDE

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ABSTRACT

A robust, inexpensive commercial microbomb combustion calorimeter, which has previously only been used with biological samples, has been evaluated for applications involving inorganic materials. The calorimeter has been calibrated extensively using N.P.L. standardised benzoic acid, and has been evaluated with calcium carbide. Measurements on the combustion of calcium carbide were made using the carbide alone, and using benzoic acid, graphite and calcium as addition agents. The calorimeter is shown to have an uncertainty of $\pm 1.3\%$ (2 × standard deviation of mean) in calibration. The measurements on the combustion of calcium carbide have a total uncertainty of the order of $\pm 7\%$ (2 × standard deviation of mean), which is shown to be too large to permit any significant determination of the enthalpy of formation of the carbide. The potential applications of this calorimeter are outlined.

INTRODUCTION

In recent years interest has been shown in the accurate determination of enthalpies of combustion of samples of biological and organic materials which are available with the required purity only in small quantities. This limited supply of pure material for experimental purposes has led to the development of several models of microbomb combustion calorimeters[1-10]. There often exists a need to make measurements on small samples of material, apart from those named above, in research in other fields such as chemical metallurgy and inorganic chemistry. In particular, a requirement existed in the Department of Metallurgy at Manchester University to be able to measure enthalpies of combustion of small samples of carbide materials prepared by vapour phase deposition techniques. It was decided, therefore, to investigate the use of an inexpensive commercial aneroid microbomb calorimeter in order to evaluate the potential of the instrument for either accurate measurements on small samples of carbide materials, or as a convenient robust piece of equipment for the undergraduate laboratory. The calorimeter is based on the design of Phillipson[9] and has previously been used only for biological and organic materials.

The selection of the carbide for the trial investigation was based on a desire to perform a useful measurement on a material which did not produce too complicated a reaction residue. It was anticipated that a residue consisting of non-stoichiometric oxides or mixtures of lower and higher valency oxides would not be suitable for a preliminary investigation. It was decided, therefore, to investigate a sample of calcium carbide, which fulfils these requirements, and is important in that there are no reliable published data on the direct measurement of the enthalpy of combustion. The present accepted value for the standard enthalpy of formation of calcium carbide, -59.0 ± 8.4 kJ mol^{-1}, was obtained by Ruff and Josephy[11] in 1926 from the measurement of the enthalpy of solution of calcium carbide in hydrochloric acid. Kameyama and Inque[12] obtained the value of -44.4 kJ mol^{-1} by a solution calorimetric technique. Recently, Faircloth et al.[13] measured the dissociation pressure of calcium carbide by the Knudsen method, from which the standard enthalpy of formation was obtained as -54.8 ± 6.3 kJ mol^{-1}. In addition the enthalpy of formation of calcium carbide is of interest to metallurgists because of the reported formation of this compound by slag-metal reactions at high temperatures in steel-making processes where thermodynamic predictions would not indicate this to be possible[14].

EXPERIMENTAL

Microbomb calorimeter

Figure 1 shows the microbomb combustion calorimeter system (manufactured by Newham Electronics Ltd., London), which is of the aneroid non-adiabatic type, and consists essentially of a miniature bomb enclosure, a stand and heat transfer ring,

Fig. 1. The aneroid micro-bomb calorimeter.

and a cylindrical stainless steel jacket. The bomb, when placed in the stand, rests in close contact with the inner surface of a thin copper ring, which acts as the hot junction of an eight junction thermopile. A massive block of aluminium, situated beneath the copper ring, acts as the cold junction, and the output from the thermopile (upto 1 mV) is connected to a recording potentiometer. A highly polished cylindrical stainless steel jacket covers the bomb to reduce any effects due to the passage of air currents. The ignition of the sample is achieved by means of a condenser discharge which provides a constant energy input for each experimental determination.

The high pressure bomb vessel consists of two stainless steel parts which can be screwed together. The pressure seal in this unit is a "Teflon" O-ring. On assembly the internal cavity is spherical and has a capacity of approximately 8.0 ml. The upper part of the bomb carries the pressurising valve, the two terminals of the firing circuit and a stainless steel specimen pan.

Calorimetric measurements

Standard combustion calorimeter operation was used in all the calorimetric measurements. The bomb was flushed with pure oxygen, in order to remove traces of nitrogen from the reaction vessel, prior to filling to the working pressure of 30 atm. This pressure was used after an initial series of experiments, in which the oxygen pressure was 10 and 20 atm, had shown incomplete combustion of the standard benzoic acid.

The final calibration of the calorimeter was carried out by combusting N.P.L. standardised benzoic acid (sample B.C.S. No. 190j) under a variety of experimental conditions in order that any effects due to the initial temperature of the bomb or the sample size could be determined.

Measurements were made on the combustion of calcium carbide which was pelletised and loaded in the calorimetric vessel in an inert atmosphere dry box before filling the vessel with pure oxygen. X-ray and chemical analyses of the reaction residues of the initial experiments indicated that complete combustion had not occurred, and so the use of addition agents was investigated. Experiments were carried out in which varying percentages of benzoic acid, spectrographically pure graphite and 99% pure calcium were added to the calcium carbide with the aim of achieving complete combustion without adding too many complications to the reaction residue.

Analysis of materials

Attempts were made to prepare pure calcium carbide in the laboratory using a direct synthesis technique and using a method which involved the passage of acetylene through calcium dissolved in liquid ammonia[15], however, both of these failed to produce a material which was substantially better than commercially available calcium carbide. Consequently, a homogenised sample of commercial material was used for the evaluation of the calorimeter. It was realised that the impurity levels in this material were too high to allow an accurate absolute value of the enthalpy of formation to result from the series of measurements because of the uncertainties from

the analysis which would require to be combined with any measured values. However, the use of a homogenised batch of this material would permit the evaluation of the calorimeter for the measurement of energies of combustion.

The sample of calcium carbide was analysed using X-ray diffraction to establish the phases present, a wet analytical technique based on the method of Edwards[16] for the measurement of gases evolved on hydrolysis, atomic absorption spectrophoto-metry for the determination of total calcium in the sample, a combustion technique for the determination of free carbon, a thermogravimetric technique for the determination of moisture and the "nitro-sulphuric" method for silicon determination.

The analysis of the combustion residues was carried out by an X-ray diffraction technique and by a thermogravimetric method which used a sensitive automatic thermobalance to determine weight changes on heating at temperatures of 800 and 1000°C under inert and oxidising atmospheres. This technique was evolved because the X-ray examination of the residues of the preliminary combustion experiments indicated that in some cases calcium carbonate and calcium carbide were present. The residue was first heated to 800°C, in high purity argon, when the carbonate decomposed to give lime and carbon dioxide whilst leaving the remaining carbide virtually unchanged. On admitting oxygen to the system, and raising the sample temperature to 1000°C, the remaining carbide was then oxidised to lime and the consequent weight change could be associated with this reaction. X-ray examination of the residues after this treatment showed no evidence of calcium carbonate or calcium carbide.

RESULTS

Calibration of the calorimeter

Preliminary trials were carried out to investigate the effect of the initial tempera-ture of the bomb on the reproducibility of measurement of the energy of combustion of
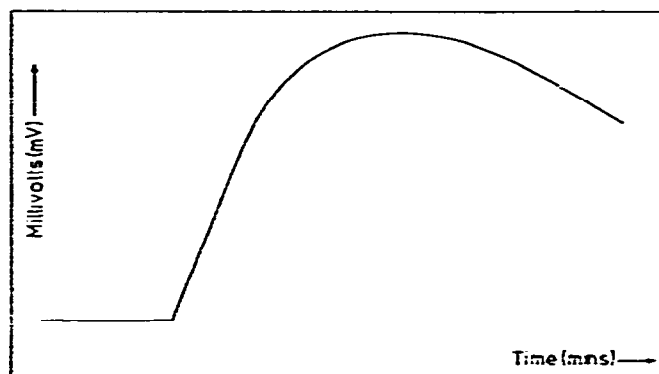

Fig. 2. Typical relationship between temperature and time for calibration and combustion experi-ments.

benzoic acid, because the recommended procedure for the calorimeter required that the bomb vessel be cooled to below the temperature of the cold junction block prior to ignition. In effect, altering the intial temperature of the bomb has the effect of changing the sign and slope of the baseline obtained in the time–temperature curve before ignition of the sample. It very soon became apparent that in order to obtain maximum reproducibility in measurement, it was necessary to ensure that a horizontal portion occurred on the time–temperature relationship for the pre-ignition part of the experiment. Consequently, all further measurements were made after suitably cooling the bomb prior to ignition to yield the form of the time–temperature curve shown in Fig. 2. Dickinson's extrapolation method was then used to determine the corrected peak height (temperature rise) for each experiment.

Figure 3 shows the relationship between corrected peak height and mass of benzoic acid for samples sizes ranging from 6–28 mg. It can be seen that a straight line, which passes through the origin, is obtained. These data yield an energy equivalent of 778.3 ± 5.4 J mV^{-1} (standard deviation of mean of 23 measurements) for the calorimeter.
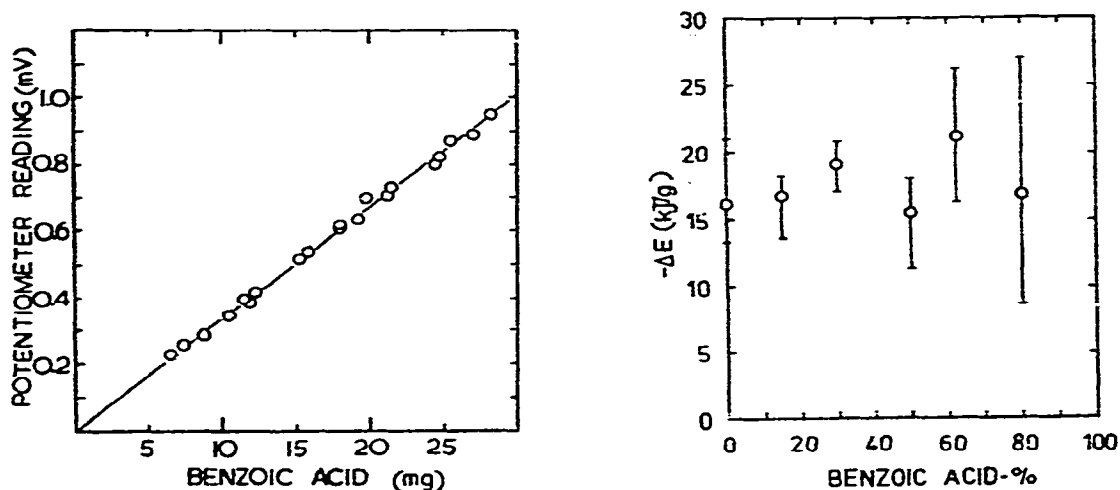

Fig. 3. Relationship between mass of benzoic acid and thermopile output obtained during calibration.

Fig. 4. Relationship between apparent energy of combustion of calcium carbide and wt.% benzoic acid added to sample.

Combustion of calcium carbide

Use of addition agents

Benzoic acid. Figure 4 shows the relationship between energy evolved per gram of calcium carbide and the wt. % benzoic acid in the sample. It can be seen that the errors associated with the measurements increase dramatically as the proportion of benzoic acid increases. This is because the experimental error from the measurement of the whole amount of energy liberated in each experiment is ascribed to a successively smaller quantity of carbide and hence the % uncertainty increases. The addition of

benzoic acid gives an increase in the energy evolved per gram of carbide for low additions, which at first sight appears to indicate a more complete combustion reaction, however, at larger additions the errors associated with the carbide make the measurements less meaningful. X-ray analysis of the reaction residues showed that successively larger amounts of calcium hydroxide were combined with the lime as the amount of benzoic acid was increased.

Graphite. The effect of additions of graphite (up to 40 wt. %) on the energy evolved per gram of carbide is shown in Fig. 5. It can be seen that increasing amounts of graphite give increasing apparent energies of combustion of the carbide. Additions greater than 40 wt. % were not used because of the difficulties associated with the pelletization of such mixtures. X-ray diffraction analysis of the combustion residues showed an increase in the amount of calcium carbonate as the proportion of graphite was increased.
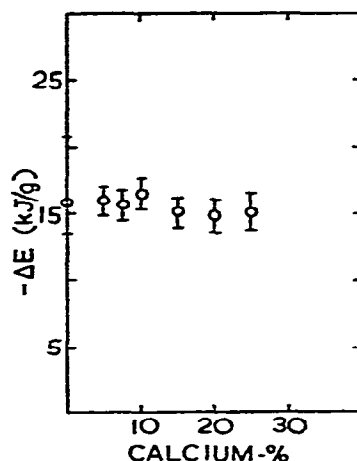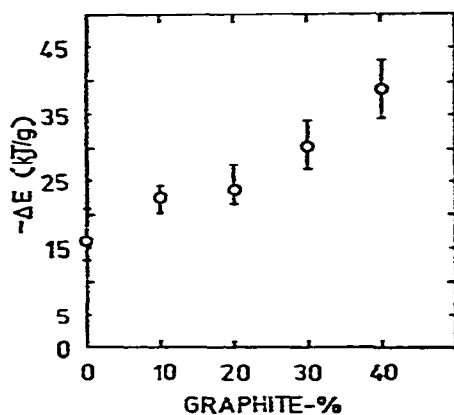

Fig. 5. Relationship between apparent energy of combustion of calcium carbide and wt.% graphite added to sample.

Fig. 6. Relationship between apparent energy of combustion of calcium carbide and wt.% calcium added to sample.

Calcium. The apparent energy of combustion of calcium carbide, determined with the addition of various amounts of calcium metal to the sample, is shown in Fig. 6. It can be seen that the addition of calcium does not significantly affect the energy evolved per gram of carbide, and this, along with the fact that X-ray analysis still indicated the presence of unburnt carbide along with carbonate and oxide, shows that these additions did not significantly help to achieve complete combustion.

Calcium carbide alone. The results obtained with the use of the various addition agents did not show significant advantages over the use of calcium carbide alone, and so a series of measurements were made on the sample of carbide. These measurements are presented in Table 1 where the total energy evolved is reported along with the necessary corrections for the formation of calcium carbonate, for the dissociation

TABLE 1

COMBUSTION EXPERIMENTS ON CALCIUM CARBIDE

Sample mass (mg)	Mass CaC_2 (mg)	Mass unburnt CaC_2 (mg)	Total energy evolved (J)	Corrections (J)				Apparent energy combustion CaC_2 (kJ g^{-1})
				Decomposition of $Ca(OH)_2$	Combustion of free C	Formation of $CaCO_3$	Combustion of SiC	
22.3	17.6	6.1	275.53	0.90	16.83	6.91	10.22	21.08
22.8	18.0	4.8	339.34	0.92	17.25	8.12	10.55	23.04
23.5	18.6	2.4	334.70	0.95	17.71	8.54	10.84	18.46
23.5	18.6	4.0	349.09	0.95	17.71	8.96	10.84	21.45
25.4	20.1	3.2	355.71	1.01	19.22	10.59	11.60	18.69
25.5	20.2	4.8	386.06	1.05	19.28	10.97	11.76	22.48
27.6	21.8	6.8	393.06	1.11	20.85	8.12	12.69	23.48

of calcium hydroxide originally present in the sample, for the combustion of free carbon and silicon carbide which were present in the sample, and for the amount of unburnt calcium carbide found in the residue. The thermodynamic values used in these corrections were taken from Kubaschewski et al.[17].

Analysis of carbide

The analysis of the commercial calcium carbide gave the following result: $CaC_2 = 79.01$ wt. %; $Ca(OH)_2 = 4.07$ wt. %; $CaO = 6.98$ wt. %; free $C = 8.45$ wt. %; $SiC = 1.48$ wt. %.

DISCUSSION

Calorimeter calibration

The calibration data shown in Fig. 3 indicate that, within the sample mass range investigated, the energy equivalent of the calorimeter remains constant, and hence a single calibration is sufficient for the sample sizes recommended for the calorimeter. The calibration gave an energy equivalent of 778.3 ± 10.8 J mV^{-1} ($\pm$ twice the standard deviation). The reproducibility in this energy equivalent agrees with that originally claimed for a calorimeter of this type[9] and is comparable with that of other microcalorimeters[3], but is considerably worse than that typically obtained with large-scale combustion calorimeters[18]. The low reproducibility obtained with the microbomb calorimeter reflects a variety of experimental parameters which include the small sample size and hence the increased associated percentage weighing errors; the simplicity of the temperature measurement system, which could be improved by the use of an ice-point cold junction for the thermopile, and reproducibility of the chart recorder; and any variations in firing energy from the condenser discharge system. The lack of a facility for the collection of product gas for analysis, also adds an extra unknown to the experimental system. Nevertheless, the determined energy equivalent does have a standard deviation better than ± 1% as claimed in the original work on the calorimeter.

Calcium carbide combustion

Effect of addition agents

Benzoic acid. Figure 4 shows that the apparent energy of combustion of calcium carbide increases with the addition of benzoic acid. Initially it appeared that this increase was due to the benzoic acid burning and helping to sustain the combustion reaction of the carbide. However, X-ray analysis of the residues showed that this was not the complete explanation. Additional diffraction lines due to calcium hydroxide appeared in the diffraction patterns of the residues, and the intensity of the lines increased as the percentage of benzoic acid in the pellet increased. The extra energy liberated during the combustion reactions, therefore, was associated with the reaction of the freshly prepared calcium oxide with the water produced by the combustion of benzoic acid ($\Delta H^{\circ}_{298} = -994.4 \pm 6.3$ kJ mol^{-1} calcium hydroxide).

As outlined in the Results section, the errors associated with the apparent energy

of combustion of the carbide, when high percentages of benzoic acid were present, caused the measurements to have little significance. This clearly illustrates the effect of having to associate all the experimental uncertainties with a small fraction of carbide in the pellet. Such situations arise in the use of both filler additions and combustion aids.

Graphite. It can be seen from Fig. 5 that the addition of up to 20 wt. % graphite to calcium carbide caused little change in the apparent energy of combustion of the carbide. The X-ray diffraction patterns obtained from the combustion products of these samples resembled very closely those obtained for the combustion of the carbide alone. With additions of 30 and 40 wt. % graphite to the carbide, the apparent energy of combustion increased greatly. In these cases, X-ray diffraction revealed an increase in the intensity of lines of calcium carbonate as the proportion of graphite in the sample increased. It is apparent, therefore, that the increases in apparent energy of combustion are not because of a more complete combustion of the carbide but are due to the additional exothermic side-reaction between calcium oxide and the large quantity of carbon dioxide generated by the combustion of the graphite ($\Delta H_{298}^{\circ} = -1207.5 \pm 2.9$ kJ mol^{-1} calcium carbonate).

Calcium. Figure 6 shows that the addition of up to 25 wt. % calcium to calcium carbide does not alter the apparent energy of combustion of calcium carbide. Additions greater than 25 wt. % were not used because the increased vigour of the combustion reaction caused melting of the sample pan. X-ray analysis of the residues showed that although the combustion reaction occurred more strongly with the addition of calcium, complete combustion of the carbide was not achieved. The reason for incomplete combustion is probably that the reaction took place violently in a short space of time before all the carbide had time to react. Thus, calcium did not behave as an ideal addition agent, which should allow the whole of the sample to be burned by prolonging the reaction time or sustaining the flame uniformly throughout the pellet. However, as the experimental data suggest, the main reaction in this case was free from any undesirable side-reactions.

Calcium carbide alone. The combustion data obtained for calcium carbide are presented in Table 1 where the corrections for impurities, side-reactions and incomplete combustion are also made. Using the Washburn correction[19] and other data compiled at the Bureau of Standards[20] these data yield an enthalpy of combustion at 298 K of -1361.1 kJ mol^{-1} calcium carbide with an uncertainty of ± 95.0 kJ (2 × standard deviation). The overall uncertainty associated with this enthalpy is larger than the reproducibility figure given above because of the low purity of the starting material. Hence, when the uncertainty of the analysis of the carbide is taken into consideration, and the enthalpy of combustion recalculated to give the maximum departure from the above value, an extra uncertainty of the order of ± 2.5 kJ mol^{-1} is introduced, which makes the calculation of the enthalpy of formation of calcium carbide of no significance ($\Delta H_f^{\circ} = -61.1 \pm 99.6$ kJ mol^{-1} at 298 K) although this value, with its large uncertainty, does agree with the data obtained by solution calorimetry[11]. It is apparent that the greatest uncertainty arises from the calorimetric

measurement itself (a standard deviation of mean $\pm 3.5\%$), which may arise, in part, from inhomogeneity of the carbide sample and deterioration of the sample during preparation. The technique of plotting the amount of carbon in the combustion product against the observed energy of combustion, which was recently proposed by Johnson et al.[21] to account for the fact that in the case of incomplete combustion the composition of the unburnt carbide may be different from the starting material[22], was not used with these data because of the low reproducibility of the measurements.

The earlier work[9] using a calorimeter of this design for biological samples reported a "precision" of better than 2.5% by comparing the measurements of combustion of a variety of animal species with this calorimeter with data determined in a separate device[3] for the same sample material. However, the calibration data and experimental measurements in this work were reported with an uncertainty of $\pm$ the standard deviation of the mean, rather than $\pm$ twice the standard deviation as used in most bomb calorimetric data[23]. Also the separate experimental errors do not appear to have been combined in the normal way[23]. The calorimeter has given combustion data for calcium carbide with a similar standard deviation to that obtained for the biological material, however, when the real requirement is to combine the experimental measurements with other thermodynamic data in order to calculate enthalpies of formation, the uncertainty of the measurements is too large. Nevertheless, the situation may be envisaged where an overall uncertainty of the order of $\pm 5\%$ is better than no data at all for extremely small specimens and this calorimeter should fulfil this role.

The experimental convenience of the calorimeter makes it an ideal instrument for the undergraduate laboratory where demonstration rather than absolute accuracy is required. It also seems a very suitable instrument for "degree of combustion" experiments with materials prior to investigation in a larger, more sophisticated piece of equipment.

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