A PLASTIC CAPSULE TECHNIQUE FOR THE COMBUSTION CALORIMETRY OF VOLATILE OR CHEMICALLY REACTIVE COMPOUNDS: THE HEAT OF COMBUSTION OF POLYTHENE

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INTRODUCTION

A considerable number of compounds of current thermochemical interest are either volatile or chemically reactive or both. The precise calorimetry of such compounds is fraught with difficult technical problems. This is specially so for combustion heat studies in a bomb calorimeter. Here it is of vital importance:

(a) to prevent chemical change or contamination of the pure sample at any time prior to ignition;
(b) to prevent evaporation of the sample during the weighing process or thereafter;
(c) to ensure, in so far as may be compatible with (a) and (b), that the conditions for complete combustion of the sample are optimum.

There have been several approaches to these problems, but the most efficacious and widely used has been to introduce the substance (usually a liquid) into glass ampoules of suitable size and then to seal these[1–5]. Such sealed ampoules completely satisfy conditions (a) and (b) above, but they have a number of disadvantages. The technique of manufacturing and filling them requires considerable skill, and, even at best, is a hit-and-miss affair. They have to be strong enough to withstand the pressure (30–40 atm) of oxygen in the bomb without bursting and yet not so strong that they fail to break on ignition of the auxiliary burning substance. In general, they fail to satisfy condition (c) in that the risk of explosion and incomplete combustion is fairly high[3–5]. An ingenious way of minimizing these latter difficulties is due to Thompson[6]. Again, sealing of the ampoules is a very delicate operation since it is liable to cause a certain amount of decomposition of the sample. Finally, there is always the danger that the melting glass may occlude some intermediate products of the combustion, though apparently this does not in general occur to any significant extent[5].

The above considerations have led us to search for a straightforward and reliable alternative to the glass ampoule technique, and we believe we have found such in the following simple method for making closed polythene capsules of any desired size or shape.

EXPERIMENTAL PROCEDURE

The raw material for the method is polythene (Imperial Chemical Industries, Ltd "Alkathene") sheet 0·2 mm thick. This is heat-softened

and vacuum-formed round suitable brass moulds with the aid of the set-up illustrated in *Figure 1(a)*. A is a cylindrical vacuum box fitted with a

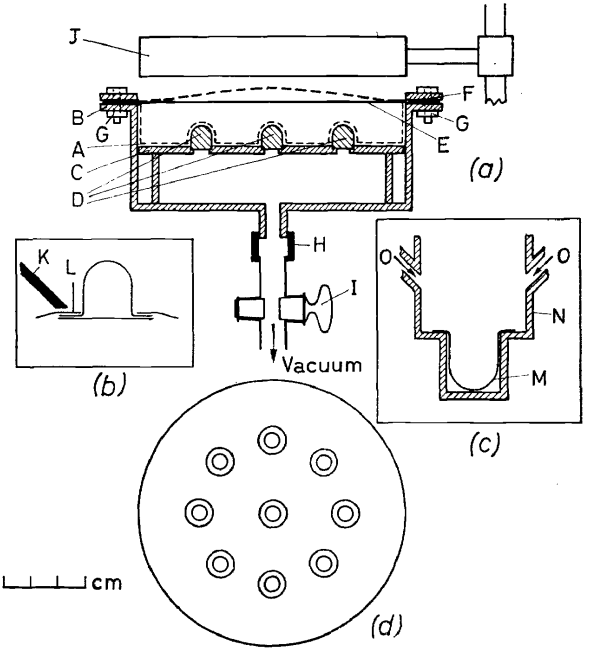

Figure 1

flange B. It is made of hard-drawn brass 1 mm thick. C is the brass platform carrying the nine moulds. It is a sliding-fit for A and is shown in plan in (*d*). The moulds, D, fit snugly into 1 cm-diameter grooves in the platform, as indicated. Under each mould is a 0·5 cm-diameter perforation. The polythene sheet E is clamped as a diaphragm on top of A with the aid of a flat ring F and four wing-nuts, two of which are shown at G. H is a piece of pressure tubing and I a glass tap. J is a 250 W heating element. We actually use an Osram infra-red lamp (I.R.R. 48 P.F.). It is mounted to swivel in the horizontal plane so that it may be swung quickly over and away from the polythene.

The procedure is as follows.

When all is ready the tap I is *closed* and the pump started. J is then switched on and swung into position about 3 cm directly above the diaphragm. Owing to the expansion of the air in the box the polythene swells up slightly as it is heated. This is indicated by the dotted line in *Figure 1(a)* and is an important feature of the method. Without this slight pressure build-up the softening polythene would sag down and foul the moulds before it is quite ready for vacuum-forming. The correct moment for removing the heat and applying the vacuum by opening tap I can be gauged easily by the eye: it is the moment at which the polythene has become quite transparent. On application of the vacuum, the poly-

thene quickly " forms " round the moulds as shown by the dotted line. The moulded sheet is then removed and the capsules cut out with a cork-borer of suitable diameter (1·5 cm). Polythene lids are heat-sealed on the capsules by applying a soldering iron K *via* a " Fluon "-coated glass cloth L, as indicated in *Figure 1(b)*.

The simplest method of charging the capsules with liquids is to use a hypodermic syringe. A small puncture is first made in the lid and the liquid injected through a second puncture. These punctures may then be sealed with a drop of molten polythene from a flaming piece of welding rod. It is quite easy with practice to seal the punctures with a mass of molten polythene that is small and reproducible within narrow limits. Its contribution to the heat output can thus be estimated reliably. For compounds which are susceptible to attack by atmospheric vapours or light, the above operations may be performed readily in an inert atmosphere, such as dry nitrogen, in a dark room. The capsules may be charged with volatile or reactive solids with the aid of the apparatus shown in *Figure 1(c)*. The capsule, M, without its lid, is placed in the brass container, N, as shown. The system is swept out with dry nitrogen *via* the two inlets, O. A suitable quantity of the solid sample is then transferred to M, the nitrogen counter-current being maintained the while. Finally, the lid is dropped into place and heat-sealed to the capsule as before.

The successful application of the present technique demands a precise knowledge of the heat of combustion of polythene. We have determined this under standard conditions with the apparatus described in an earlier paper[7]. The results are given in *Table 1* (1 cal = 4·1840 abs. joules).

Table 1. Heat of combustion of polythene

Vacuum weight of polythene (g)	*Total* (cal)	*I.C.** (cal)	*B.A.*† (cal)	*Polythene* (cal)	(kcal/g)
0·066484	− 3145·84	15·91	− 2423·47	− 738·28	11·105
0·092032	− 3460·87	16·44	− 2455·00	− 920·32	11·108
0·077026	− 3244·82	15·56	− 2404·89	− 855·49	11·107
0·065572	− 3105·87	15·83	− 2393·70	− 728·00	11·102
				Mean = 11·106	
				Δ = ± 0·004	

* I.C. = isothermal correction.
† B.A. = contribution to the total heat of the benzoic acid used as an auxiliary burning substance.

DISCUSSION

The present technique has obvious advantages over those involving glass, including even some of the most recent and elegant[5, 8, 9]. Among these advantages are the following:

(1) A large number of capsules almost identical in size, shape and weight can be made in a short space of time and without the need for any special skill.

(2) The size and shape of the capsules can be varied readily by changing the moulds.

(3) The capsules never burst before ignition as they are more than strong enough to withstand the pressure in the bomb.

(4) They are readily combustible and thus serve the purpose of an auxiliary burning substance, although they do not invariably eliminate the need for the latter.

(5) The fuse wires can be fixed at the neck of the capsules so that they have prolonged burning contact with the sample. The conditions for complete combustion are thereby enhanced.

(6) Polythene is resistant to attack by most chemicals at ordinary temperatures. The need, except in very special circumstances, for such as quartz ampoules[10] is thereby removed.

We thank Mr M. A. H. Lanyon, I.C.I. Ltd (Plastics Division) for valuable advice on the vacuum-forming procedure. R.G.M. is grateful to the Ministry of Education, N.I., for a Research Maintenance Grant.

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