

DESIGN AND USE OF ANEROID BOMB CALORIMETERS

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(1) The object of a bomb calorimeter is to absorb the heat released from an accurately measured amount of chemical reaction and convert it into a temperature rise which can be measured with corresponding accuracy. Questions associated with the chemical reaction are often difficult, but will not be discussed here. This paper is concerned with the purely physical questions associated with the temperature rise. It is also concerned, in part, with the physical problem of producing a comparable temperature rise by introducing accurately measured Joule heat within the calorimeter. This procedure is necessary when the calorimeter is used for evaluating a thermochemical standard material, such as benzoic acid, with the intention of using it to measure the equivalents of other bomb calorimeters in which heat will be generated by combustion only.

Reasons will be put forward for believing that aneroid bomb calorimeters are capable of higher accuracy than conventional calorimeters in which the heat is absorbed in well stirred water. It will be contended that aneroid calorimeters can be designed which are simpler, and quicker in use, than stirred-water calorimeters.

(2) Apart from chemical considerations, the first requirement of a calorimeter is that its equivalent should be repeatable every time it is assembled, except for small variations in mass of substance, platinum, fuse and auxiliary material for which corrections can be made. The presence in the conventional calorimeter of water, whose heat of evaporation is very high, means that great care must be taken in design and assembly to minimize the evaporation and condensation of water, and to reproduce in every experiment any movements of water which are unavoidable.

(3) The rate of transfer of heat \dot{Q} between the calorimeter and its surroundings, during the period of the experiment, must obey an unchanging law such as $\dot{Q} = k(T - T_c)$ where T is the temperature of the thermometer in the calorimeter, and k and T_c remain constant throughout the experiment. Corrections can be applied, for example, if T in the equation differs for part of the time from the temperature of the thermometer; but errors are unavoidable if k and T_c do not remain constant.

It is clearly an advantage if k is small, and this is best achieved by evacuating the space between the calorimeter and its outer jacket, and by lengthening the electrical leads which cross this space. Vacuum spaces are not usually possible round stirred-water calorimeters.

As to the problem of keeping k constant, investigations by White¹ and others have shown that k is affected mainly by water vapour movement and by convection of air in the space surrounding the calorimeter. The

width of this space must be limited to 1 cm if it is not evacuated, and convection is still not fully eliminated, with the consequence that the temperature of the calorimeter must be kept within 1 to 1.5°C of its outer jacket. Convection in the air turns out to be the factor which restricts the permissible temperature rise in stirred-water bomb calorimetry to about 2°C.

(4) A calorimeter must reach a uniform temperature within 5 to 10 minutes after heat is generated within it. If a steel bomb is used, the only way to achieve such quick equilibrium is by surrounding it with well stirred water. There is only one metal, namely silver, whose thermal diffusivity is high enough for equally quick equilibrium to be reached without using stirred water, as *Table 1* shows. The values for the duration of the middle

Table 1. Duration of middle period in bomb calorimeter

Type	Mass of benzoic acid (g)	Diffusivity (cm ² /sec)	Middle period	
			Combustion (min)	Electrical (min)
Steel bomb in stirred water	1.3	—	10	11.5
Silver (Ag 92.5, Cu 7.5) bomb	0.2	1.6	5	8.5
Silver bomb (estimated)	1.3	1.6	10	13.5
Copper bomb (0.05% Te)	1.0	1.1	14	—
Brass bomb } estimated from surface tem-	1.3	0.34	90	—
Steel bomb } perature changes	1.3	0.12	300	—

period, during which equilibrium is being reached in the calorimeter, are approximately proportional to the inverse of its thermal diffusivity.

(5) *Figure 1* shows the construction of a small silver bomb calorimeter made at the National Physical Laboratory. The oxygen space is 97 ml, and 0.2 g of benzoic acid burns completely in oxygen at a pressure of 25 atm, producing a temperature rise of 3.5°C. A 1 in 5 scale model withstood an internal pressure of 500 atm without permanent deformation. The mass of silver is about 5.5 kg, and its equivalent is 1350 J/°C. A manganin heater of 10Ω is fixed inside the bomb to allow electrical determination of the equivalent.

The heat transfer coefficient, k , is 1.2 J °C⁻¹ min⁻¹. This is about 0.025 of the k of stirred-water calorimeters, but these have about seven times the equivalent of the silver bomb and are used with a rather smaller temperature rise. The standard deviation of individual estimates of the equivalent, the bomb being dismantled and reassembled each time, was less than 1 part in 7000. The standard deviation of individual estimates of the heat of combustion of benzoic acid, involving one combustion and one electrical experiment, was less than 1 part in 5000.

An interesting technical innovation is the method of filling the bomb with oxygen through a stainless steel hypodermic tube, pushed through the neoprene O-ring which seals the bomb. The O-ring reseals after the hypodermic tube is withdrawn. A full account of this bomb calorimeter will be shortly submitted for publication⁴.

(6) Under the rigorous conditions needed for the determination of the heat of combustion of thermochemical standard benzoic acid, it was found

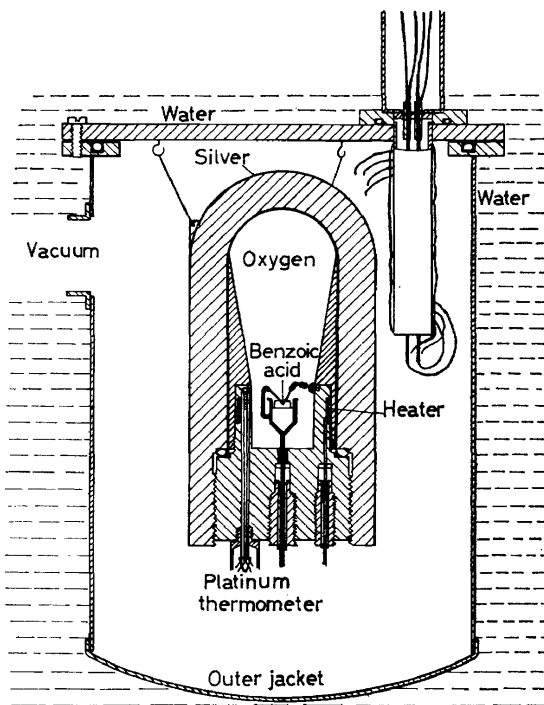


Figure 1. Aneroid bomb calorimeter

that the silver bomb produced results at least twice as quickly as a conventional stirred-water calorimeter. For routine determinations of the heats of formation of organic compounds, the silver bomb should again save time. For determinations of less than 0.1 per cent accuracy, the saving of time may be less noticeable, because about 30 min is needed for pumping the vacuum space and 30 min for filling with oxygen.

The chemical reactions associated with the combustion of sulphur compounds and other materials require a bomb to be rotated and turned over. The necessary mechanical power can, without too much difficulty, be transmitted into the vacuum space of an aneroid bomb calorimeter, or it can be generated there. Since the vacuum space can be quite large, the mechanical problems should indeed be easier in the vacuum round an aneroid bomb than in the water round a steel bomb.

Because of the difficulty of making stirred-water calorimeters of low heat capacity, it is possible that there may be special uses for small silver bomb calorimeters such as the one described. On the other hand there is no reason, except the cost of the silver, to prevent the construction of much larger silver bombs.

(7) The heat of combustion of benzoic acid under standard bomb conditions has just been estimated by the N.P.L. silver aneroid bomb calorimeter to be 26431.7 J/g, with a standard error of 2.2 J/g. This may be compared with the eleven most recently published estimates of the same

constant³, whose weighted mean value is 26435.5 J/g with a standard error of 1.0 J/g.

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