WILLIAM A. PRYOR, V. C. DAVIS, and MILTON AUSMAN
California Research Corp., Richmond, Calif.

A Microbomb with Rapid Heating and Variable Shaking

This reactor is useful for kinetic and equilibrium measurements at high temperatures and pressures

A PRESSURE REACTOR which can be rapidly heated and cooled, and agitated at variable speeds has many uses—e.g., in kinetic studies. These requirements eliminate use of a heating bath. Flow reactors sometimes solve these difficulties, but they use greater amounts of material and give kinetic data more difficult to interpret. Recently, an autoclave was described (*2*) with short heating and cooling times, but large temperature gradients probably exist along its walls.

To fill the need for a constant temperature, constant volume reactor, a bomb was constructed from standard stainless steel pressure tubing (Figure 1). The bomb is heated by passing alternating current at low voltage directly through its walls. It contains 7.9 cc. of free space, can be heated to 300° C. in 1.5 minutes, and can be violently agitated. Safe operating pressure is 6000 p.s.i. (ASME code book calculation; safety factor of at least four is allowed). The temperature gradient along the wall is ±1° C. in the region used.

The Microbomb

The bomb is a Type 316 stainless-steel tube, 14 inches long, $^5/_{16}$ inch in inside diameter, $^9/_{16}$ inch in outside diameter, and closed at each end by pressure caps (High Pressure Equipment Co., Erie, Pa., No. 15-AHF19). The ends of the caps are machined to fit in clamps on the shaker. Figure 2 shows these caps with a $^1/_{16}$-inch diameter thermocouple probe installed (High Pressure Equipment Co., 116-AT-11061-IC).

The larger mass of the caps plus other end losses makes the temperature at the end of the bomb much less than at the center. To lessen the temperature gradient along the length of the bomb, wall thickness is slightly reduced near each end, an amount depending on the operating temperature desired (Figure 2). This increases resistance and, consequently, heating at the ends of the bomb relative to the center and lessens heat flow from the bomb to the caps. The temperature gradient along the center $6^1/_4$ inches of the bomb is about 2° C. after this is done. These cuts in the bomb wall are not as deep as those made for the standard pressure tubing threads and, therefore, do not influence the pressure limitation placed on the bomb. The higher the operating temperature desired, the more the diameter must be reduced (Table I).

The liquid charge is restricted to the center portion of the bomb, where the temperature gradient is smallest, by use of carefully fitted Teflon plugs, 0.310 inch in diameter, $3^7/_8$ inches long, and with a $^1/_{16}$-inch hole in the center. One plug fits tightly on the thermocouple probe and the other on either stainless steel microtubing or on a second thermocouple. One end of each plug is machined to fit tightly into the inside of the pressure caps (Figure 2). The large coefficient of linear expansion of Teflon relative to stainless steel [20×10^{-5} (*7*) *vs.* 1.1×10^{-5} (*4*)] ensures that the ends are plugged tightly at reaction temperature and that the plugs do not move.

Filling and Use of the Bomb

To fill the bomb, one end is capped and the bomb clamped upright. Liquids are pipetted into the open tube, solids added directly from weighing pigs, and the bomb is sealed. Allowance must be made for volume expansion if temperatures are high. For example, 4.0 cc. of aqueous solution can be used for an operating temperature of 320° C. Small amounts of volatile liquids are added and removed while the bottom portion of the bomb is cooled in dry ice–acetone. In this way, 0.025 ml. of toluene can be added without losses. A valve can be added to the microtubing passing

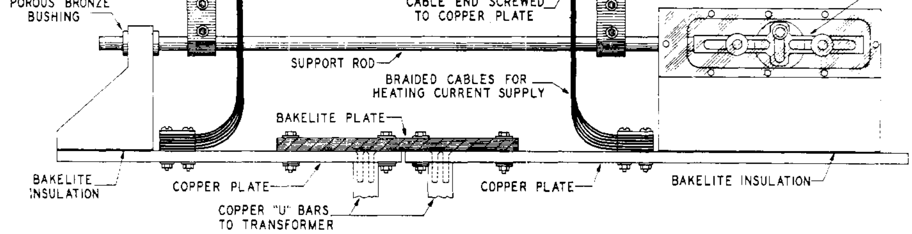

Figure 1. Bomb mounted in heater shaker. The bomb is 14 inches long

Table I. Temperatures at Various Positions on the Microbomb[a]

	Bomb 1, ° C.[b]	Bomb 2, ° C.[c]
In. from bomb center		
0	315.6	233.7
$2^5/_8$	314.9	...
$2^7/_8$	...	233.1
3	314.0	233.1
$3^1/_8$ (end of Teflon plug)	...	231.8
$3^1/_4$ (outside free space)	313.3	229.5
$5^1/_8$ (outside free space)	237.0	...
Inside thermocouple	316.2	234.2

[a] Measured with 4.0 g. water in bomb. [b] Diameter reduced 0.035 and 0.045 inch (Figure 2). [c] Diameter reduced 0.030 and 0.040 inch in the two zones (Figure 2).

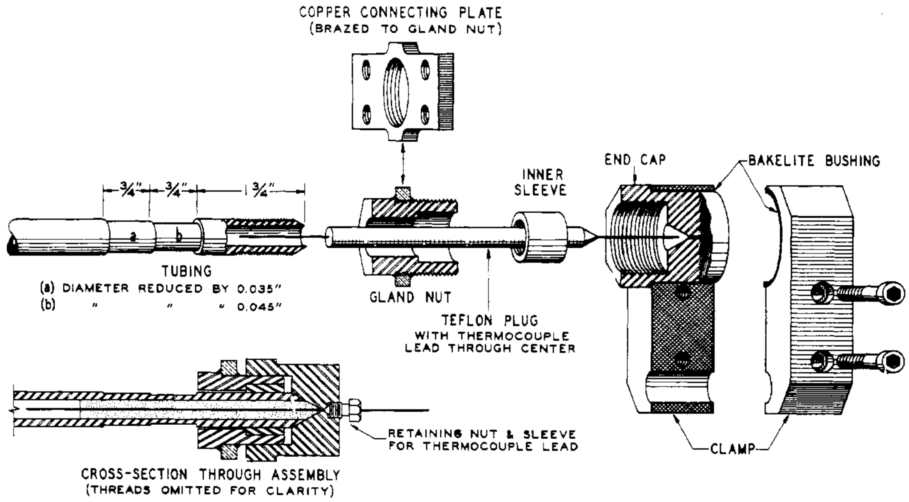

Figure 2. To lessen temperature gradients along the length of the bomb, wall thickness is slightly reduced near each end

through one cap so gas samples can be taken.

Temperature Control

Temperature is measured both with 30-gage IC thermocouples spot welded to the outside of the bomb and with the inside thermocouple probe. Agreement is within experimental error of the potentiometer (Table I). Automatic temperature control is achieved with a proportioning motor-driven Variac. This controller compares the electromotive force of the outside thermocouple with that of a reference, and converts the algebraic difference to alternating current. The current drives a phase sensitive motor to increase or decrease a Variac which controls the current in the primary of a low voltage transformer. The transformer has a bus-bar secondary rather than windings and this secondary leads directly to the bomb (Figures 1 and 3).

Absolute temperatures can be read to within a few degrees centrigrade using a sensitive potentiometer. Temperatures can be controlled to better than $\pm 0.5°$ C.

Passing alternating current directly through the bomb wall heats the bomb at 3° C. per second. The response of the motor-driver Variac is rapid, and the control temperature is not overshot. The bomb is cooled at 6° C. per second by blowing high pressure air along the bomb.

Heater-Shaker

Figure 1 shows the bomb clamped in the shaker and the insulation used to prevent heating current passing through the shaker assembly. The bomb is clamped to a horizontal rod with aluminum clamps which are insulated from the bomb with Bakelite inserts. The gland nuts have copper extensions braised on them, and a cluster of battery cables can be screwed into these extensions to carry the heating current (Figure 2). The battery cables carry up to 500 amperes at 1.5 volts from a transformer located directly under the bomb (Figure 3). This full current is used only while the bomb is being brought to temperature; 117 amperes at 0.53 volt holds the bomb at 288° C. A furnace for oxygen determinations has been reported *(5)* which uses metal tubes for burners. The tubes are heated by passing current through them just as is this microbomb.

The rod to which the bomb is clamped slides through porous bronze bushings and is shaken at up to 1500 cycles per minute over a variable stroke. The stroke can be set at $^1/_8$, $^1/_4$, $^1/_2$, or $^3/_4$ inch by adjusting a pin on a cam wheel. This cam is moved by a Scotch yoke which is attached directly to the shaking rod and is sealed in an oil-tight cage and lubricated with light oil (Figure 1). The cam is driven with a variable speed, direct-current motor. A glass model showed that shaking at about 1000 cycles per minute over a $^3/_4$-inch stroke homogenized two immiscible liquids.

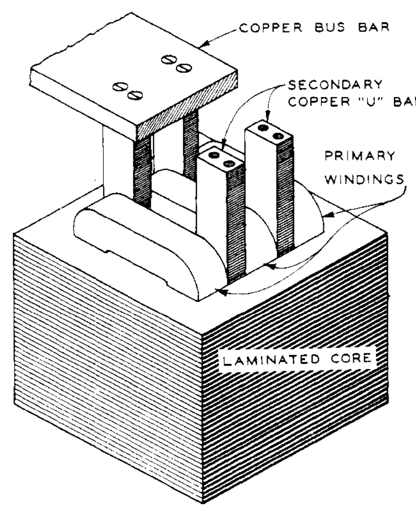

Figure 3. Rather than windings, the transformer has a secondary which leads directly to the bomb

Applications

This microbomb is useful whenever material must be heated to elevated temperatures for a precise length of time. This is frequently true of both kinetic and equilibrium measurements, and examples of each have been studied.

The major application has been a study of the oxidation of *m*-toluic to isophthalic acid by aqueous sulfur solutions at 250° to 300° C. *(3)*. Both kinetic and equilibrium measurements were made. Kinetic data on a small-batch scale were obtained despite the high temperature and pressure. Heat-up time is a negligible fraction of the time at reaction temperature, so the reaction could be started and stopped sharply. In this study the equilibrium distribution of sulfur species in various sulfur ions had to be known at reaction temperature. The bomb can be cooled fast enough to freeze the equilibrium, and measurements made at room temperature gave the concentrations present at reaction temperature.

In a second study, the hydrolysis at equilibrium of nylon polymers was measured at a series of elevated temperatures. Nylon and water were added to the bomb and the decrease in molecular weight was investigated as a function of time and temperature. The data showed the approach to equilibrium and its position. Here again, the short cooling time permitted measurements to be made at room temperature that apply to elevated temperatures. The rapid agitation also proved critical to mix water into the viscous polymer melt.

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