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THERMAL EXPLOSION OF UNSTABLE COMPOUNDS
EXPERIMENTAL EQUIPMENT AND METHODS

by

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FIRE

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SUMMARY

A detailed description is given of equipment used to determine minimum temperatures for thermal explosion of unstable compounds. Measurements of heat transfer coefficients controlling the explosion are also reported.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

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INTRODUCTION

The purpose of this note is to place on record details of the experimental equipment and methods developed for a study of thermal explosion in unstable compounds. An investigation in which the equipment was used is reported elsewhere[1].

The experimental objective was the determination of the minimum ambient temperatures for the self-heating to explosion of unstable compounds in charges of given shape but varying size. The substances to be examined were generally expected to have explosive powers considerably less than for ~~explosive powers considerably less than for~~ explosives proper, and to be more likely to deflagrate than to detonate. Their properties in these respects would be determined as far as possible beforehand by the usual methods. For safety purposes, however, it was assumed that detonation would occur and appropriate precautions were taken.

Two pieces of equipment are described in the note. One is a vented electric furnace for the study of relatively small samples at higher temperatures and the other, for larger samples at lower temperatures, is an adaptation of the use of expendable heating jackets with a fluid heating medium as previously described by Merzhanov and others[2-4]. Details are also given of measurements of relevant heat transfer coefficients.

Detailed engineering drawings are not now available, but the following descriptions of the equipment should be sufficient to enable similar equipment to be constructed. The main requirements are that the temperature within a working space should be uniform and controllable within close limits for long periods with a minimum of attention and, for safety, the equipment should be operable by remote control when charged and be capable of venting a deflagration safely or, if necessary, of permitting an occasional detonation. Otherwise modifications of the designs can be made as desired to suit special requirements or local workshop resources.

VENTED FURNACE

General

The general arrangement of the furnace and control equipment is shown in Plate 1. A vertical electric tube furnace, counterpoised and working on spring-loaded runners between parallel vertical guides, can be lowered over a frame-work supporting a container for the compound to be tested together with necessary thermocouples, and also with aluminium foil bursting discs clamped between rings at four levels. When the furnace is lowered, the charge container and thermocouples are confined within a working space 18.3 cm (7³/16") in diameter and 28.4 cm (11³/16") in length contained by the furnace wall and the two inner bursting discs. Guard spaces above and below the work space are closed by the upper and lower bursting discs and contain loose piles of pieces of crinkled aluminium foil as additional thermal insulation. Further details of the furance and centre support are given later.

The main supporting structure is of welded steel. With the lower ends of the guides fixed to the steel table top, the rigidity was such that no difficulty was experienced in preserving the alignment of the furnace and the central support.

The furnace and counterweight were suspended from a roller chain passing over sprockets, one of which was driven by a reversible geared motor for raising and lowering the furnace by remote control. The furnace travel was determined by limit switches.

Plate 1 shows the furnace at the development stage. Later, the whole structure was enclosed in a hut to shield the furnace from major draughts and so improve the control, and also to contain any fragments of the charge container if the charge were to detonate (see further below).

Central support

Details of the central support, and of the furnace(see further below), are shown in vertical section in Fig. 1. Apart from the square base plate (see Plate 1) the structure has cylindrical symmetry. The figure is drawn approximately to scale and, as such, is a sufficient guide to suitable dimensions for constructional purposes. The support was made from mild steel and was cadmium plated.

In order to simplify the drawing, fixings are not shown but it may be noted that the assembly of flanges and spacers (carrying the gasket and the terminals) at the lower end was held together by recessed screws into the ends of the short inner supporting tube. The whole assembly was located in the recess in the base plate by a peg (not shown) and was held by clamps (not shown) on the base plate which engaged the lowermost flange.

Four pairs of rings held bursting discs of 0.025 mm (0.001") hard aluminium foil (A m Fig. 1). The lower member of each pair was welded to each of the four support rods ($^5/16$" diameter), while the top member was a loose sliding fit on the rods. A further, single, ring was welded to the support rods in a convenient position to support a tripod for the charge container in the working space. A series of holes round the outer circumference of this ring and the lower rings, vertically aligned, were provided for thermocouple and other service leads to be taken out, through small bore "pyrex" tubes, to terminals on the "paxolin" ring above the base plate (these tubes and terminals can be seen in Plate 1). The thin paxolin piece immediately below the flange supporting the gasket was drilled to the inner diameter of the pyrex tubes only and so acted as support.

The base plate was bolted over a central hole, of full vent diameter, in the steel table top (Plate 1). Lateral movement was provided so that the whole assembly could be centred with respect to the furnace before being finally bolted down. Axial alignment with the furnace was adjusted by packing-pieces under the base plate.

Furnace

The tube furnace shown in Plate 1 was one that had been designed for other purposes and was used here primarily to obtain guidance on the require-ments for a final design suitable for the study of unstable compounds. The final design is shown in vertical section in Fig. 1.

The furnace had a double liner made from two cylinders rolled from 0.635 cm ($\frac{1}{4}$") mild steel plate and butt welded. The inner liner, which covered only the central working section, was machined to be a close fit inside the outer liner. Grooves were cut in the wall of the inner liner, on two diameters at right angles, to form pockets for control thermocouples. The clearance between the inner liner and the central support when the furnace was lowered was about 0.8 mm ($^1/32$").

The furnace winding, covering the outer liner to within $\frac{3}{4}$" of each end, consisted of 16 S.W.G. 80/20 Nickel chromium alloy and was graduated as follows:

3" at each end, 37 turns at 12.3 t.p.i., with a centre section
of 12" having 75 turns at 6.25 t.p.i.

The total resistance was 50 ohms. The winding was electrically insulated from the steel liner by $^1/32$" of 'Micanite' covered by $^1/32$" of asbestos paper. The furnace leads, and tappings to the winding sections were taken out to a junction box at the rear of the furnace (not shown).

The furnace liner was supported between the end plates by insulating bushes of asbestos wood, with allowance for thermal expansion, and the whole was held together by four tie bars (not shown) between the end plates. The space between the liner and the outer casing was filled with dried vermiculite insulation.

The four sets of leads from the control thermocouples, were taken out through holes in the top plate of the furnace under an annular cover and thence to an electrically heated ('Sunvic') reference junction (42.3°C) fixed to the back of the furnace (not shown) where connection was made to copper leads from the control panel.

The top of the furnace was closed by an aluminium foil bursting disc, B in Fig. 1, held in place by a loose ring in which was fitted a disc of expanded polystyrene insulation 1.27 cm ($\frac{1}{2}$") thick. This closure, and the asbestos gasket at the lower end, sealed the interior of the furnace when it was lowered over the central support. In order to reduce disturbance of the temperature, an insulating cover was supported against the lower open end when the furnace was in the raised position.

The furnace, complete with the reference junction and side members carrying the runners (Plate 1) weighed 81 Kg (178 lb.). In the final version, the furnace and counterweight were fixed to the roller-chain suspension ($^5/16$" x $\frac{1}{2}$" 'motorcycle' chain) by half-links and not the Bowden cable shown in Plate 1. The drive motor was a 250 volt, single phase, fractional horsepower AC. motor with condenser starter and a reduction gear giving a torque of 0.23 kg fm (20 lb/in) at 5 r.p.m. Operation was by a reversing switch on the control panel, a pilot light on the control panel indicating when the furnace was moving between the limit switches.

Power supply and Temperature control

Flexibility was desirable in the power supply to the furnace since it was likely to be required to operate, within close limits, at temperatures ranging from about 50°C to 350°C. The power was controlled by an auto-transformer from the mains supply and a variable resistance connected in series with the furnace and the output of the transformer. The resistance was short-circuited by the temperature controller during the 'on' cycle of operation and, by suitable adjustment of the transformer and resistance, approximate equality of the 'on' and 'off' cycles, required for optimum control, could be readily achieved.

The temperature controller/indicator was an electronic type arranged for proportional control with a four minute cycle. A switch providing the appropriate series/parallel connection of the four control thermocouples in the furnace, allowed the controller to operate at either 200°C or 400°C F.S.D.

At 80°C, control was obtained to within about ± 0.3 degC at the centre of the working space.

Temperature distribution

In the absence of stirring, the temperature within the working space of the furance operating under steady conditions, was within ± 0.8 degC of the value at the centre at distances of about 5 cm above and below the centre, the differences increasing to several degC towards the upper and lower bursting discs enclosing the working space.

A circulating fan, driven _via_ a long shaft by an electric motor below the furnace table and supported in the working space in a 'Teflon' bearing, was therefore fitted. With the fan in operation, the temperature at most points tested within the working space was then within ± 0.5 degC of the value at the centre.

Safety

Advice was obtained to the effect that, allowing reasonable factors of safety, 40-60 g of organic peroxide could be allowed to explode in a 7" diameter mild steel tube with $\frac{1}{4}$" walls[5]. The double-walled liner finally adopted for the furnace provided an additional margin of safety for these amounts.

In an investigation of the thermal explosion of dry benzoyl peroxide in open-topped cylindrical containers of 23 S.W.G. Aluminium, the explosions were usually deflagrations which blew out the bursting discs in the furnace and left the container undamaged[2]. On one occasion, however, a charge of 28 g in a container 4.1 cm diameter, exposed for 22 hours to a temperature 7 degC above the critical value for thermal explosion, exploded with sufficient violence to fragment the container. The fragments and the distorted container support ($\frac{1}{8}$" brass) are shown in Plate 2 together with an undamaged container. There was no noticeable damage to the furnace or central support.

As a precaution against failure of the furnace suspension a 4" x 2" wooden beam was placed across the main supporting framework immediately below the furnace when it was in the raised position and charges were being prepared for test.

Operation

In determining a critical temperature for thermal explosion of a charge of given size, the furnace was first adjusted to a given steady temperature - as indicated by a thermocouple located near the centre of the working space.

Then the charge container, on a wire support, was placed in position with a differential thermocouple, sheathed in a closed 'Pyrex' capillary, supported at its centre to indicate a temperature change with respect to the furnace. A second differential couple was tied to the outer surface of the container. After raising and lowering the furnace to insert the charge, it was found that the furnace temperature recovered to the pre-set value within a period of one hour. The temperature in the working space (with ice point reference) and the output of the differential thermocouples were recorded continuously during a test. Occasional checks on the furnace temperature were made with a potentiometer. Tests were repeated with fresh charges at different furnace temperatures until the critical temperature for thermal explosion had been bracketed as closely as desired.

In general, the furnace was found to be satisfactory in use and capable of stable operation for periods of the order of weeks. Occasionally, however, drifts or 'jumps' in temperature occurred of up to about 1 degC. The origin of these was not satisfactorily determined, but there was some indication that they were due to minor faults in the temperature measurement system rather than in the control. The only major drawback was the long time required for the furnace to stabilise following a large alteration in the operating temperature; because of this, adjustment to a particular temperature could take several hours.

EQUIPMENT FOR LARGER SCALE EXPLOSIONS

As indicated in the Introduction, the method of determining the minimum temperatures for thermal explosion of larger charges, up to 800 g of organic peroxide, was based on that used by Merzhanov and others in which the charge was heated in expendable jackets through which a fluid medium was circulated at constant temperature. The relevant temperatures for the work on organic peroxides[1] were well below $100^{\circ}C$, so water could be used as the heating medium.

The general arrangement of the equipment used is shown diagramatically in Fig. 2 with, inset, details of the disposition of the peroxide charge in the heating jacket. Most of the system was assembled from commercially available parts and requires only brief description.

The water was heated by a 1 Kw heater in a 20 gal. galvanised steel tank which was fitted with a cover and lagged. A 10 gal. feed tank and ball valve were provided to make up losses due to evaporation through the apertures in the cover. A $\frac{1}{4}$ H.P. stirrer was fitted and the temperature was controlled to within about $\pm$ 0.05 degC by a toluene thermoregulator with proportioning head and electronic relay.

The water was circulated to the heating jacket through $\frac{3}{4}$" B.S.P. pipe (length 25 ft, see below), by a centrifugal pump (delivery 10 g.p.m. at a head of 5 ft).

Three gate valves AA and B, Fig. 2, were provided so that the water could be circulated through the jacket or by-passed through B. The jacket and all the pipework were lagged with 1 in resin-bonded fibreglass insulation protected from the weather by an outer wrapping of 'polythene' sheet. With an outside air temperature of $9^{o}C$ and a water temperature of $60-70^{o}C$, the drop in water temperature between the tank and the heating jacket was 0.2 degC.

The heating jackets, Fig. 2 inset, were made from 18 S.W.G. mild steel sheet with welded joints, the side arms being short lengths of $\frac{3}{4}$" B.S.P. pipe. They were intended to be expendable in the event of violent explosion and were constructed to minimum standards but, in fact, they suffered no damage from the explosion of the benzoyl peroxide paste studied[1]. The dimensions were such that the internal depth was twice the internal diameter and an air gap of 2-4 mm was allowed between the jacket and the open-topped cylindrical container (22-24 S.W.G. aluminium) for the peroxide charge, the latter being supported by ceramic spacers. Separate heating jackets were, of course, required for each size of container. The closure consisted of two discs of expanded polystyrene ($\frac{1}{2}$ in thick), P, wrapped in aluminium foil spaced as shown in Fig. 2, topped by a plug of cotton wool. The polystyrene discs were perforated for the two thermocouples, T, sheathed with 'pyrex', one at the centre and the other at the outside edge of the charge. A complete assembly ready for test is shown in Plate 3.

The thermocouples were connected to record the temperature rise in the charge with respect to the heating jacket, and the reference junctions were usually taped directly to the surface of the jacket under the lagging. The stability in the reference junctions obtained with this arrangement was not entirely satisfactory and it was found, in some later check tests, that the provision of a tube in the water jacket, R, Fig. 2 inset, to contain the reference junctions warranted the extra fabrication involved.

Safety

These larger scale explosion tests were performed in an outdoor explosion cell shown in plan in Fig. 3. The cell was constructed of 9" reinforced brickwork, 6' 6" high, and the section shown hatched in Fig. 3 was provided with a roof of 6" reinforced concrete. The cell was intended mainly to contain fragments in the event of the charge detonating, but the open section also provided safe venting for possible vapour explosion of solvent or flammable decomposition products.

The heating jacket was supported on a light table in the roofed section and the valves controlling the water circulation (AAB in Fig. 2) were immediately outside the cell in a box provided with a lock, the key of which was carried by the operator.

The water heating equipment and recorders were contained in a hut at a distance of 20 ft from the wall carrying the valve box.

The only material tested in the cell was a paste of benzoyl peroxide in dimethyl phthalate[1]. The 'explosion' of this material was a relatively slow deflagration leading to forceful ejection of the contents of the charge container (see marks on roof in Plate 3) but no damage was done to the container or to the heating jacket.

MEASUREMENT OF HEAT-TRANSFER COEFFICIENTS

Aluminium cylinders in vented furnace

The surface heat transfer coefficients, h, for the aluminium containers in the stirred air of the working space in the vented furnace were estimated from measurements of the heat transfer coefficients for solid aluminium cylinders of similar dimensions and surface finish. The cylinders were heated electrically at a known power input by small heaters in central cavities (0.6 cm diameter) and the steady-state temperature difference between the cylinder surface and the air in the working space was measured by means of a differential thermocouple. Measurements were made on two sizes of cylinder with a length to diameter ratio of 1.7, and heat transfer coefficients for other sizes were estimated by fitting the following equation for heat and mass transfer from small spheres, due to Ranz and Marshall[6], to the observations:-

$$N_{Nu} = 2 + 0.6\ N_{Pr}^{\frac{1}{3}}\ N_{Re}^{\frac{1}{2}} \tag{1}$$

The results obtained are given in the following table:-

Diameter cm	Energy input cal/s	Temp Diff degC	$\dfrac{h}{cal\ cm^{-2}\ s^{-1}\ degC^{-1}}$	N_{Nu}	N_{Re} equation (1)	Velocity cm/s
3.8	3.48	2.6	8.1 x 10^{-4} ⎫			
			⎬ 46*	6660	368	
3.8	7.95	5.3	8.8 x 10^{-4} ⎭			
2.8	6.96	8.0	9.5 x 10^{-4}	38	4500	338

*Based on mean value of h for the two results.

Tabulated data for air[7] was used to calculate the Nusselt number, N_{Nu}, from the experimental results and, taking the Prandtl number, N_{Pr}, as 0.72, the Reynolds number, N_{Re}, was calculated from equation (1). Again using the appropriate data for air[7], the velocity characteristic of the air stirring was calculated from the Reynolds number.

The mean value of this velocity, 353 cm/s, was then used in equation (1) for purposes of estimating heat transfer coefficients for other sizes (Table 1 of reference 1). The contributions of convection and radiation to the total heat transfer were not separated in making these estimates since, for a surface temperature $5^{o}C$ in excess of the furnace temperature and an emissivity as high as 0.2 for bright aluminium, the radiative transfer was estimated to be only 5 per cent of the convective transfer.

Heat transfer in heating jackets

In order to estimate heat transfer coefficients for the aluminium containers in the heating jackets used for the larger-scale explosions, measurements were made of the steady temperature difference obtained when a container was filled with transformer oil which was stirred and heated electrically. The arrangement of the container in the jacket was as shown in Fig. 2 inset, except that a tube to accommodate the stirrer spindle, and the electrical leads to a heating coil in the oil, passed through the closure.

For the container 4.1 cm diameter the steady temperature difference was 4.9 ± 0.2 degC for an energy input of 4.3 cal/s. This corresponds to a heat transfer coefficient for all surfaces of the container (filled to a depth of 1.6 x diameter[1]) of 4.2×10^{-4} cal $cm^{-2} s^{-1}$ degC^{-1}.

The air gap between the container and the inner wall of the jacket was 3.5 mm; the ratio of the outer and inner diameter for this annular space being 1.17. For heat transfer in air between infinite concentric cylinders with this ratio of diameters, the Rayleigh number is of order 10^{5} and, therefore[7], heat transfer is conductive. Calculating a heat transfer coefficient, for both conduction and radiation, across an air gap of 3.5 mm, and assuming an emissivity of 0.6 for an oil contaminated aluminium surface[8], the value obtained is 3.3×10^{-4} cal $cm^{-2} s^{-1}$ degC^{-1}. This is in reasonable agreement with the measured value for the 4.1 cm container.

For all other containers except one, the air gap was 3.5 mm and the coefficient measured for the 4.1 cm container was used. The exception was the 2.8 cm container for which the air gap was 1.9 mm and the heat transfer coefficient was estimated by calculation to be about 6×10^{-4} cal $cm^{-2} s^{-1}$ degC^{-1}.
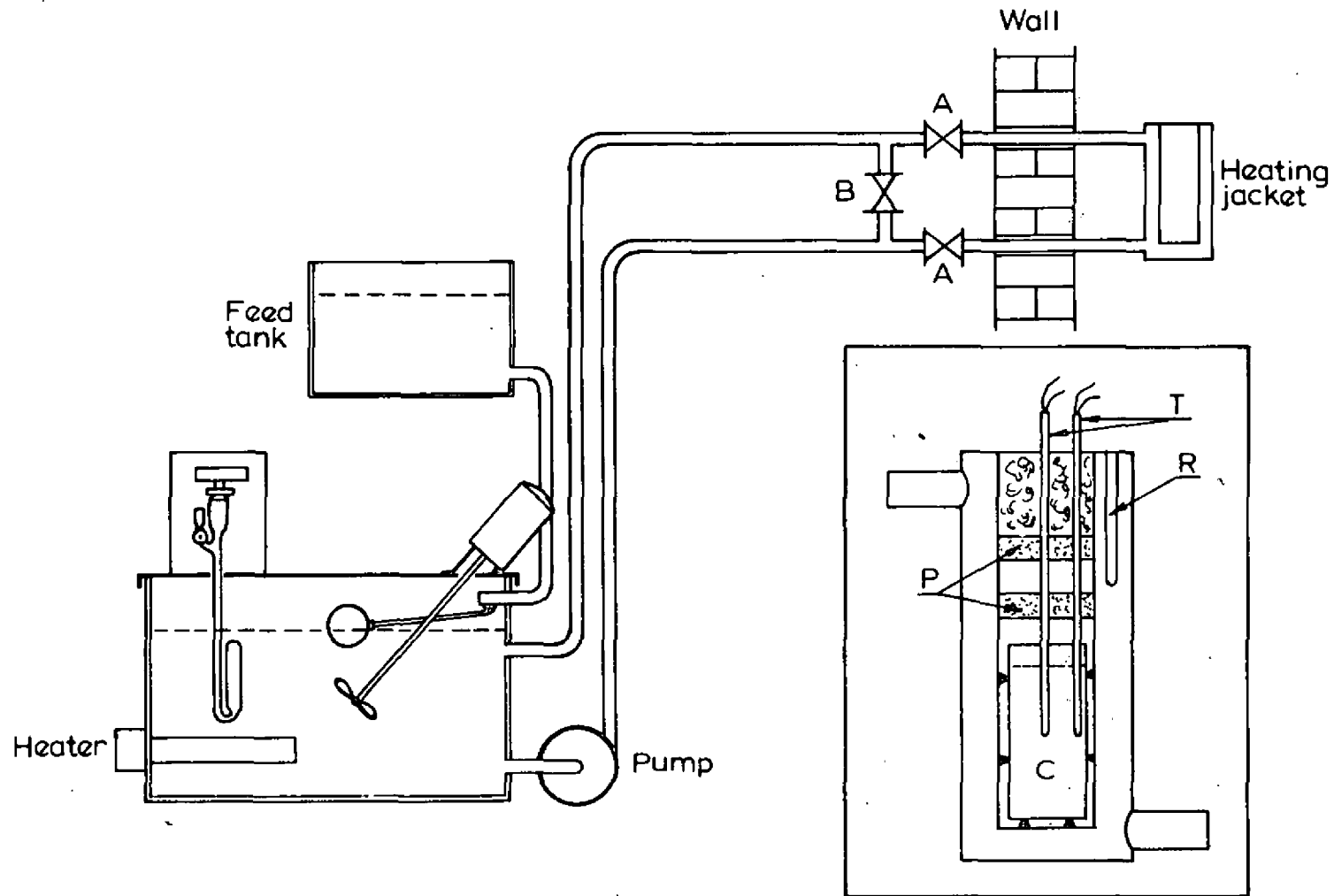
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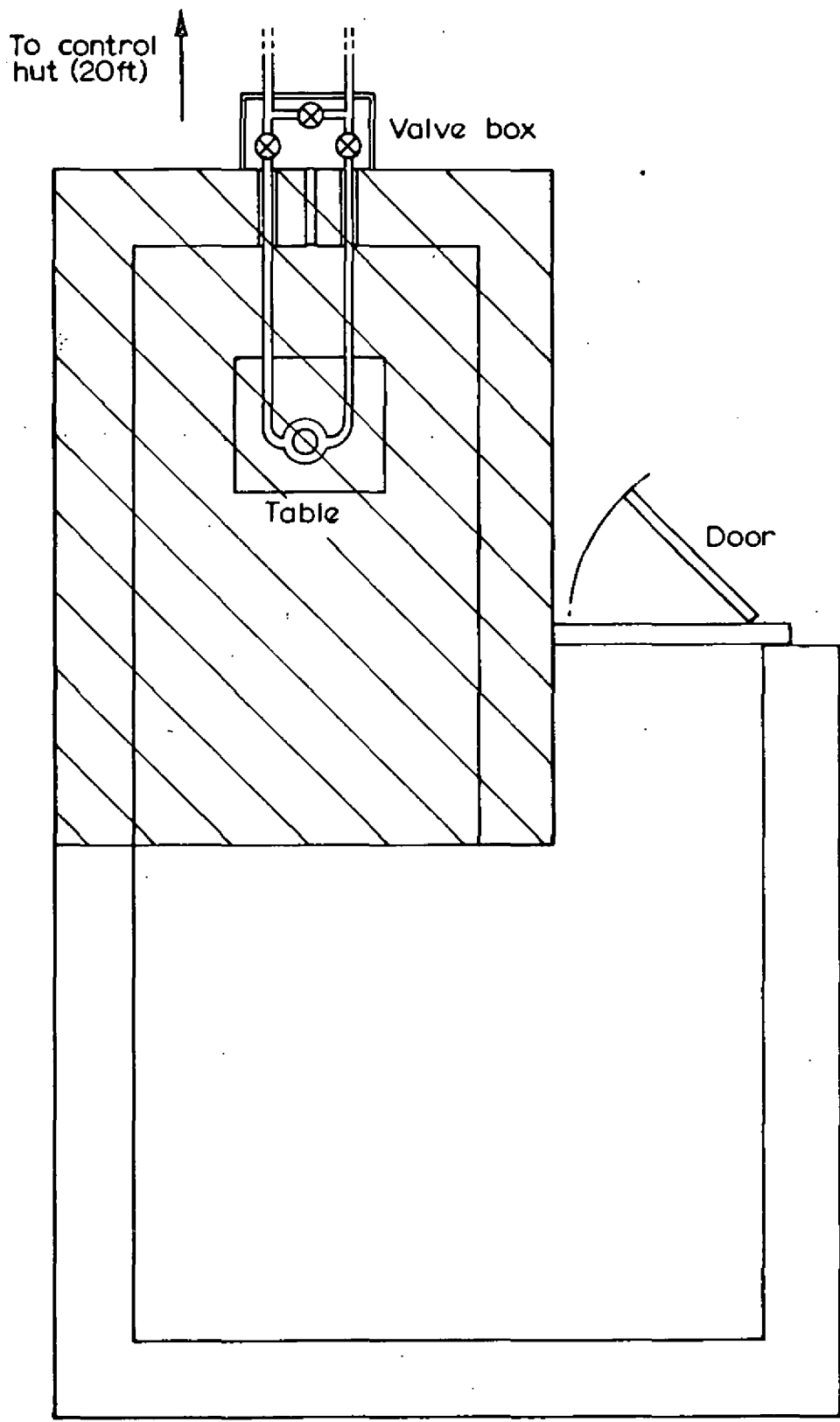
B

A

A

A

A

A

Insulating bush

Thermocouple pocket

Clearance $\frac{1}{32}''$

Inner steel liner

Outer steel liner

Outer case

Insulating bush

Asbestos gasket

Paxolin

Base plate

Scale

0   6in
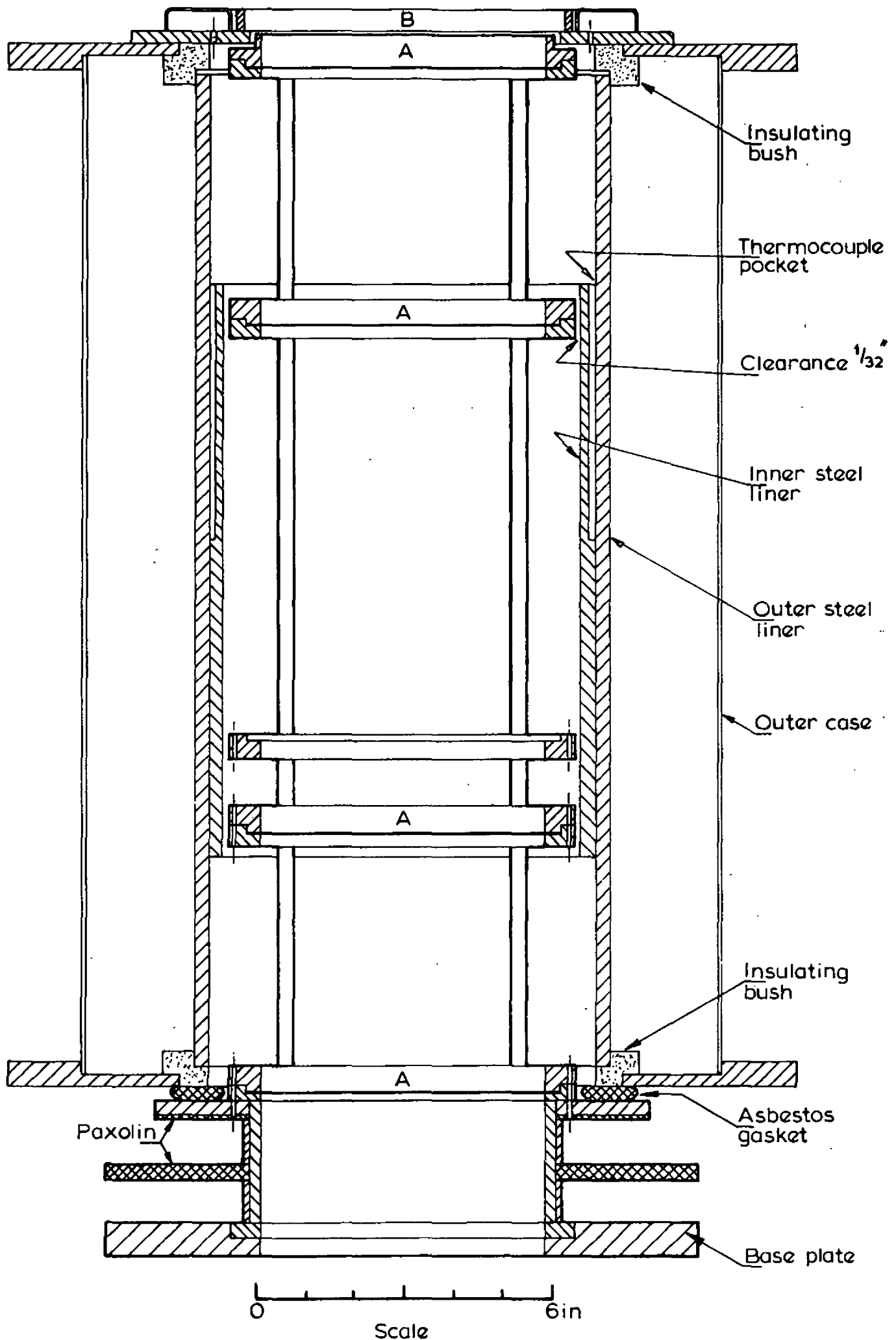
Vertical section — for lettering see text

FIG. 1. FURNACE AND CENTRAL SUPPORT

FIG. 2. EQUIPMENT FOR LARGER SCALE EXPLOSIONS

To control hut (20ft)
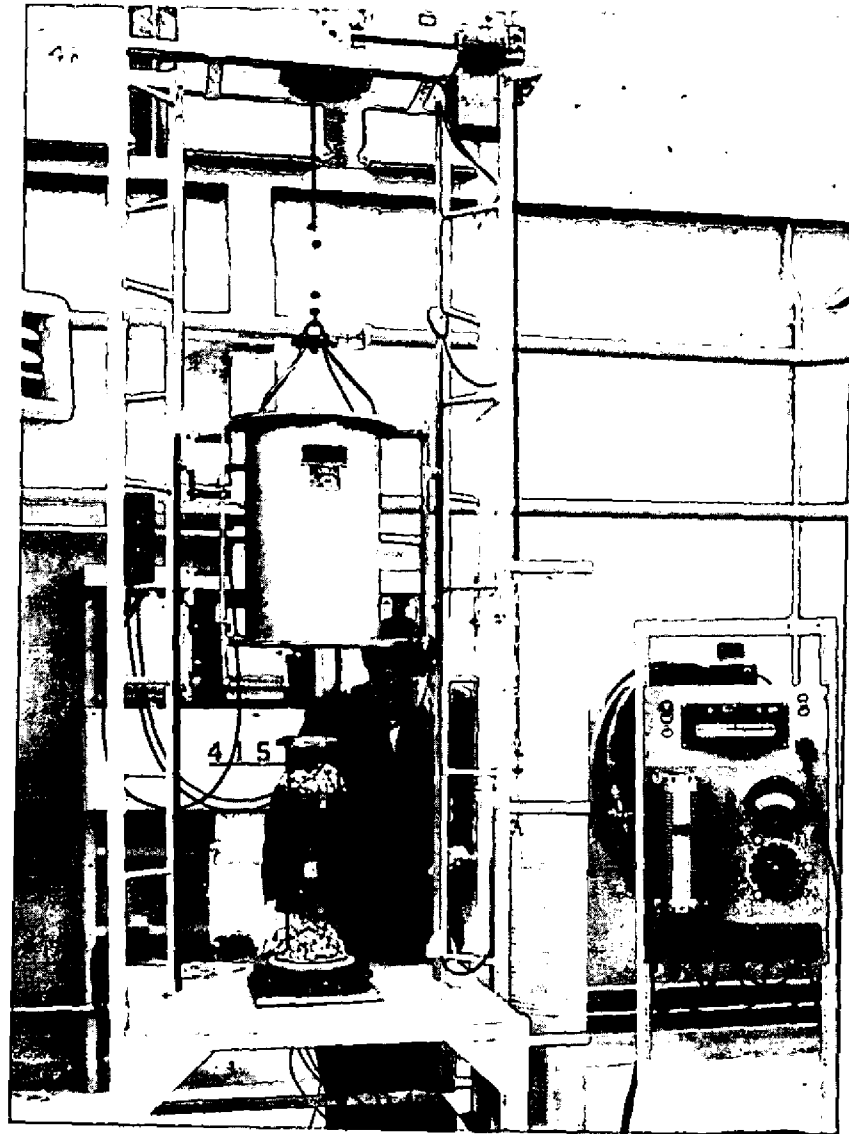
Valve box

Table
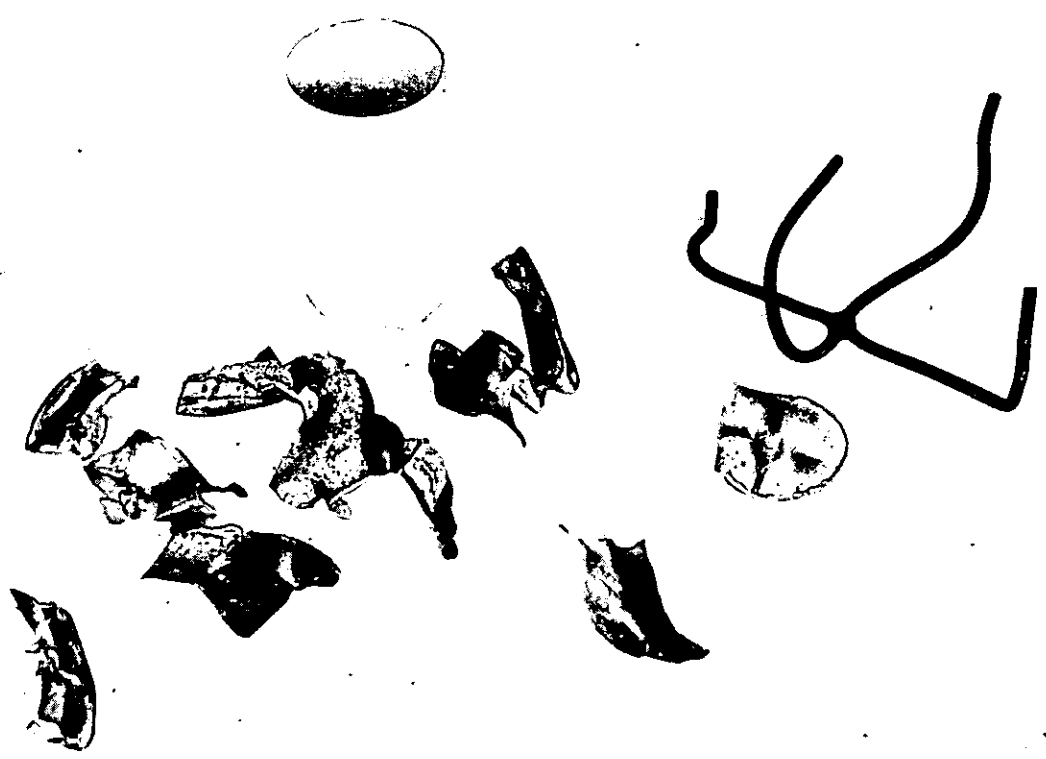
Door

Scale

3ft

Hatched section roofed

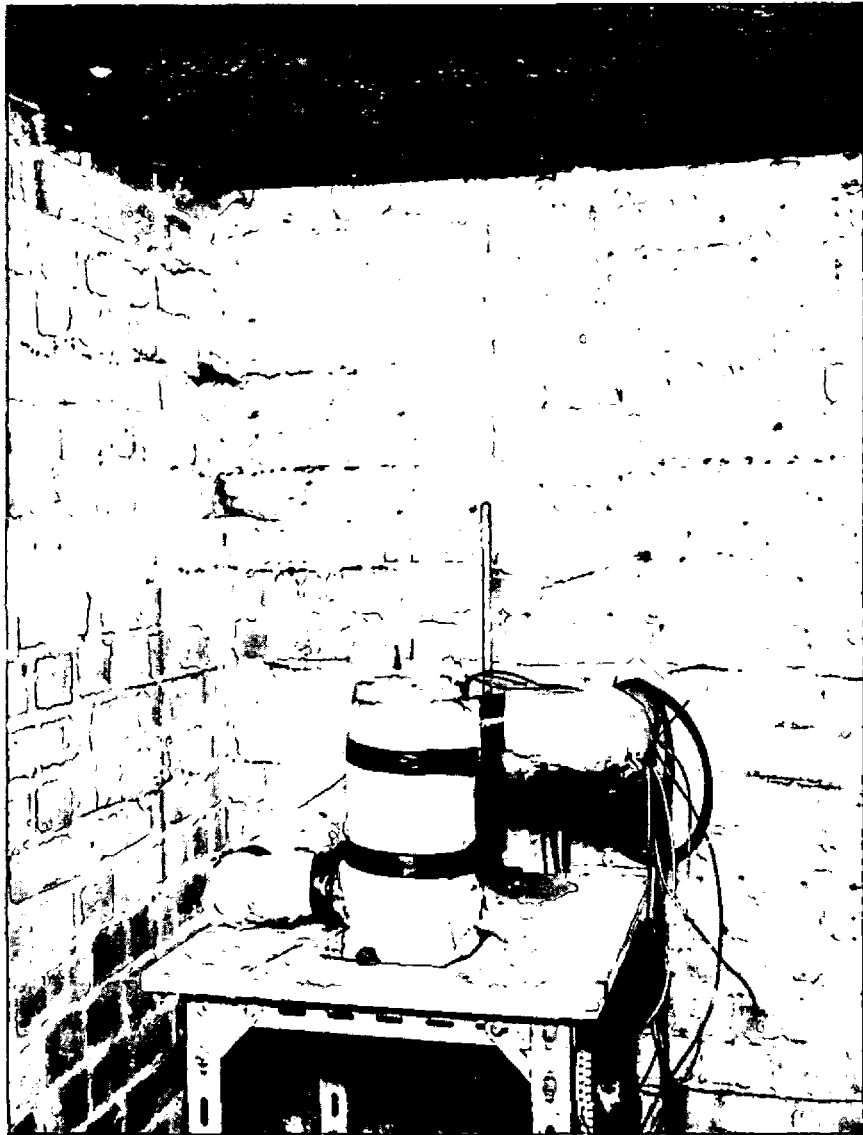FIG. 3. PLAN OF EXPLOSION CELL

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VENTED ELECTRIC FURNACE FOR
THERMAL EXPLOSION STUDIES

PLATE 1

DAMAGE DUE TO SUPERCRITICAL EXPLOSION OF
BENZOYL▮ PEROXIDE

PLATE 2

HEATING ARRANGEMENT FOR LARGER
SCALE EXPLOSION STUDIES

PLATE 3