On the Equation of State of Propellant Gases

A. D. Crow and W. E. Grimshaw

Phil. Trans. R. Soc. Lond. A 1932 **230**, 39-73
doi: 10.1098/rsta.1932.0002

II. *On the Equation of State of Propellant Gases.*

By A. D. Crow *and* W. E. Grimshaw, *Research Department, Woolwich.*

(*Communicated by* Sir George Hadcock, F.R.S.)

(Received July 30, 1930—Read November 20, 1930.)

(Plate 1.)

Introduction.

Comparatively little experimental work has been carried out with modern apparatus in connection with the measurement of pressures developed by the gases resulting from the explosion of colloidal propellants.

Petavel,* using Service cordite, Mark I, has made observations of the effect on the recorded pressures of the nature of the enclosure and of the rate of pressure rise for low densities of loading. More recently, Muraour† and Burlot‡ in France have conducted experiments at higher densities of loading and with a variety of differing propellant compositions.

The present investigation was undertaken with a view to extending the work of Petavel to wider and more stringent conditions, and to formulating an explicit expression for the equation of state. The work has necessitated the design of special recording apparatus; and the procedure has been to measure the pressures given by various explosives at various densities of loading, to derive from these the pressures that would have been observed had there been no energy losses, and to compare the values so derived with those ascertained from the propellant compositions, using relevant kinetic and thermo-dynamical data.

Part I.—Apparatus and Experimental Methods.

The explosion vessel.

The vessel, of which a detailed drawing is given in fig. 1, was constructed some years ago in the Royal Gun Factory. It was built up in the same way as a piece of ordnance of an inner tube, with an outer jacket shrunk over. Some time before the inception of

---

* 'Phil. Trans.,' A, vol. 205, pp. 357–398 (1905).

† 'Mémorial des Poudres et Salpêtres,' vol. 20, pp. 323–329 (1923).

‡ *Ibid.*, vol. 21, pp. 411–489 (1924).

[Published February 13, 1931.

the present series of experiments, the vessel was relined by boring out the old worn inner tube and inserting a new one. For this reason, the strength is reduced and expansions under pressure are somewhat greater than they would have been in the original condition.

The inside diameter of the vessel is 5·6 cm. at the breech (open) end, and 5·4 cm. at the closed end, the outside diameter being 28 cm. The breech is closed by a screwed

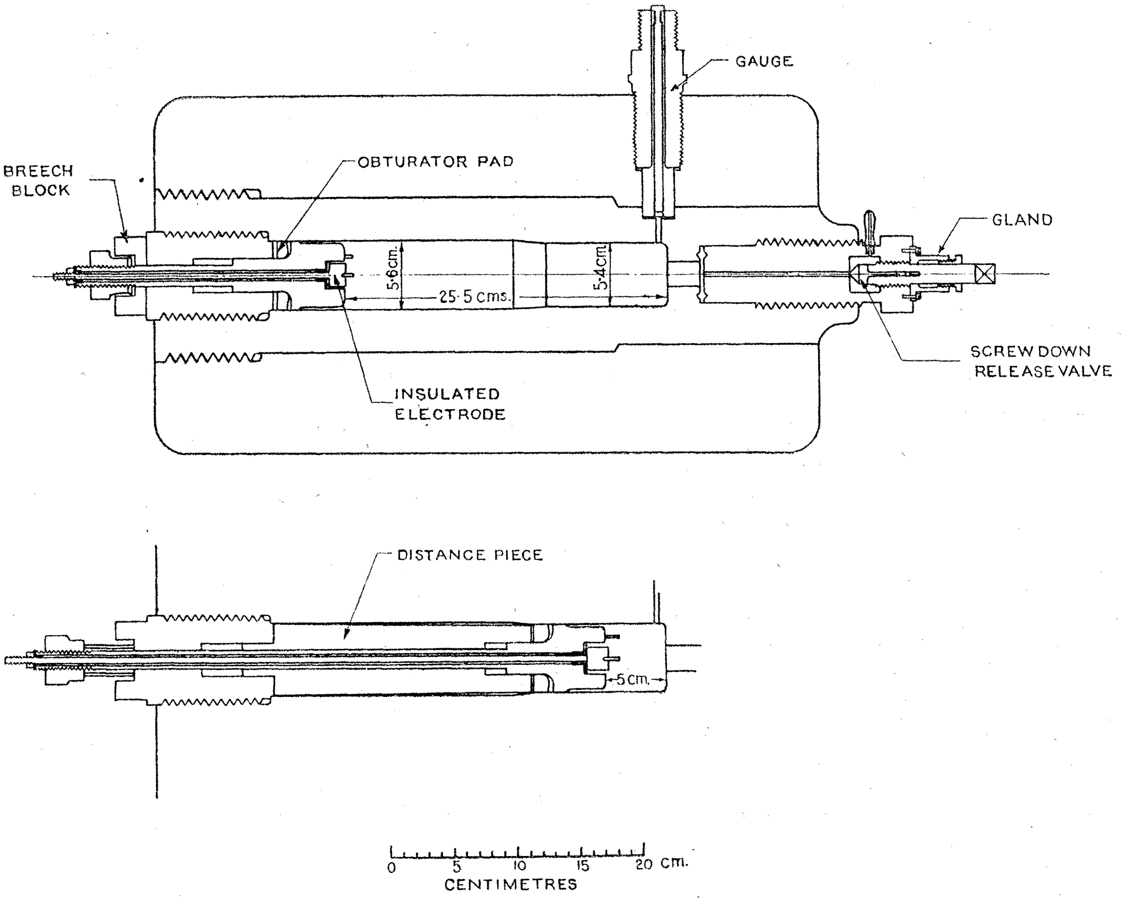


Fig. 1.—Closed Vessel—General Arrangement.

Breech block with extension piece for small capacity.

block, and gas sealing is effected in the same way as in a gun, by a slow cone pad obturator. The breech screw is bored through; and sliding in it is a vent-axial block, the inner end of which has a mushroom head just fitting into the vessel with bare clearance. Between the inner face of the mushroom head and the breech screw is an annular pad of asbestos and tallow enclosed in a canvas cover, and protected on each side by a tin disc. The thickness of the uncompressed pad is 1 cm. and the surface of the vessel on which its periphery seats is slightly coned, so as to avoid damage when inserting and removing the block.

Gas pressure on the mushroom head of the vent-axial compresses the pad, forcing it outwards against the wall of the vessel, and forming an efficient seal. The outer end of the stalk of the vent has a screw thread and a nut bearing on the outer face of the breech screw. By tightening this up an initial pressure is exerted on the pad and sealing is assured in the early stages of burning. After a new pad has been fully compressed several times, it becomes practically perfectly elastic, and the compression for any given pressure is always the same.

The vent-axial is bored out to take the insulated electrode for the firing current; this is a steel rod, 0·6 cm. diameter, with a solid head 1·5 cm. diameter. The mushroom head of the vent-axial is bored out 1·9 cm. diameter to take the head of the electrode, which seats on a mica washer; the annular space between head and hole is packed tightly with a mixture of mineral jelly and whitening, which is an efficient insulator, and, if properly packed, hardens under the influence of heat and pressure to an impervious mass. The head of the electrode is held down on the mica washer by screwing up a nut on the outer end of the rod. Steel pins inserted into the head of the electrode and the mushroom head of the vent serve to secure the firing fuze wire. Firing current is taken from 250 volt mains.

The arrangement described leaves a chamber whose length is 25·5 cm. and capacity 649 cm.^{3}, the surface exposed to the gases being 656·8 cm.^{2}

To provide an additional capacity use is made of a second vent-axial, otherwise similar but with a longer stalk, fitting into the same breech screw, but having a distance piece 20 cm. long between the breech screw and the pad. The latter is 5·4 cm. in diameter instead of 5·6 cm., and seats on the smaller diameter of the vessel, reducing the length of chamber to 5 cm. and the capacity to 130·7 cm.,^{3} surface 251·6 cm.^{2} The closed end of the vessel is bored out to take two screwed plugs for recording instruments. The radial one takes a spring gauge, and the axial one a screw-down valve for releasing the gases. Alternatively, the piezo-electric gauge referred to later fits into the axial boring whilst the radial one takes a release valve.

After loading, the vessel is exhausted through the release valve, which, to hold the vacuum, is fitted with a gland on the spindle; the vessel is then filled with a mixture of two parts of acetylene to twenty-five parts of air, the proportions being arranged for complete oxidation. The mixture is admitted from a gasholder under a pressure of about 30 cm. of water.

The temperature reached, even with initial cooling, is sufficient to ensure simultaneous ignition of the propellant over the whole surface, without setting up initial wave pressures in the vessel, the disposition of the charge also conducing to this end. By this means the burning is made more regular and conditions more uniform than if the charge were ignited by a flash at one end. To make certain of ignition at all times, the gas requires a fairly powerful initial impulse, and this is provided by blowing a fuze wire threaded through a primer, composed of sticks of small diameter cordite weighing 0·324 gms., together with a strand of dry guncotton yarn about 2 cm. long.

The cooling effect of the walls of the vessel is such that the pressure developed by the burning gas is too small to be recorded by the high-pressure spring gauge, though it is certainly not negligible. Before beginning the day's programme of firing, the temperature of the vessel is raised to at least 20° C. by a " warmer " round, and is kept between the limits of 20° and 30° C., water cooling being resorted to when necessary. Between the limits mentioned, the variation in pressure is within the experimental error of the gauge. Accumulations of water are removed before loading, and the air pump reduces the moisture present to a quantity which is practically constant.

The spring manometer.

The manometer used throughout the experiments, illustrated in fig. 2, was designed by C. M. **Balfour** and constructed in the Research Department, Woolwich. At the start of the investigation, **Petavel**'s spring gauge* was tried, but was found to have certain disadvantages, particularly in connection with the use of knife-edges for the mirror control. As the result of extended experiment the present design has been evolved, following the general principles resorted to by **Petavel**. The working member is a tube of Nickel-Chrome-Molybdenum steel, 0·604 cm. diameter inside, and 0·856 cm. diameter outside, having at one end a stout collar forming part of it, by which it is held in place. The inside surface of the tube is lapped out and a piston extending almost the full length is screwed in from the end opposite to the collar. Gas pressure acting

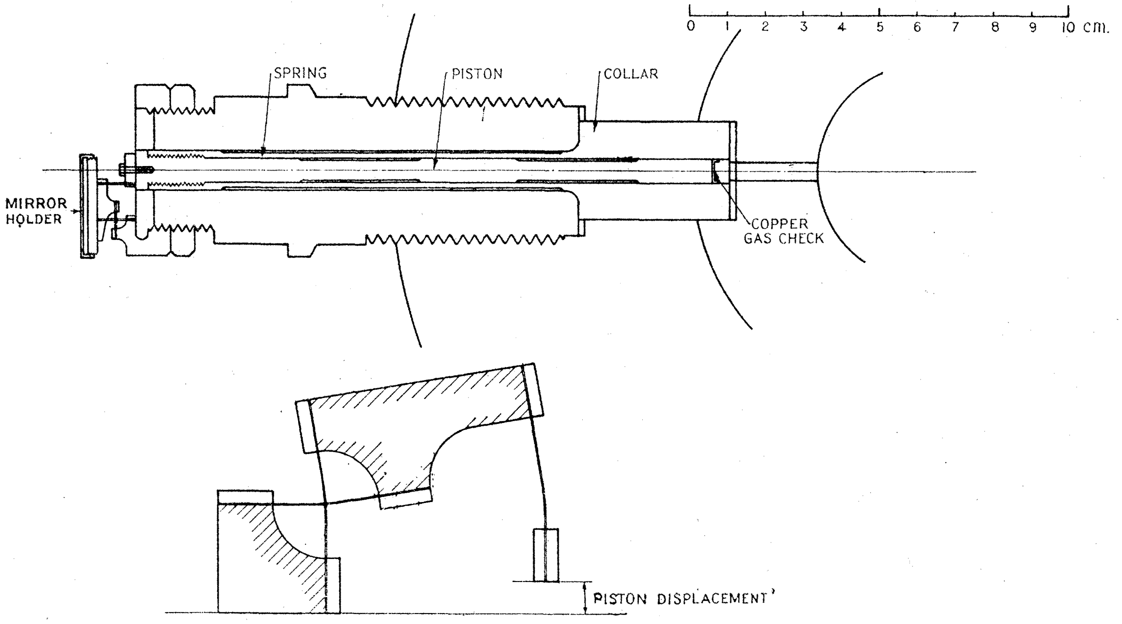


Fig. 2.—Spring Gauge.

Mirror-holder in deflected position.

---

* **Petavel**. 'Phil. Trans.,' A, vol. 205, p. 363 (1914).

on the end of the piston extends the tube, and causes the free end to move outwards. The effective length of the tube from the face of the collar to the screwed head of the piston is 8·6 cm.

The clearance between the piston and the tube is fairly large, of the order of 0·0025 cm. and, in addition, the piston is backed off, leaving only short portions in the middle and at each end of the full diameter; in this way friction is practically eliminated. Gas sealing is effected by a small cup of soft copper inserted into the tube over the end of the piston and lightly expanded with a steel punch and hammer. A flange on the piston head is accurately faced to fit on the outer face of the tube, forming an additional safeguard against gas leakage, an occurrence which is rare. Any slight initial stress that may be left in the tube by the expanding process is removed by giving the assembled piston and spring a sharp tap on a wooden bench. The tubular spring is held in place by a hollow screwed plug sliding over it and butting against the face of the collar. The inner face of the collar is forced against a copper washer seated in the vessel making a gas seal. The plug screws into the radial boring in the closed vessel, with its axis in the horizontal plane. After firing a round the gauge is removed from the vessel, dismantled and carefully cleaned, and a freshly annealed copper gas check inserted. Piston and gas check are lubricated freely with sperm oil.

At a working pressure of 4000 kg./cm.^{2} the extension of the spring is about 0·018 cm. This is slightly more than would be expected from its dimensions, but the excess seems to be due to elastic deformation of other parts of the instrument. The total movement is magnified optically, the mirror control system being shown in fig. 2 on an enlarged scale with the angular deflection greatly exaggerated. The suspension consists of a group of flat spring steel strips, two of which similar in dimensions are set parallel with each other, one connecting the mirror holder with the piston head, the other connecting it with a fixed base, which is a nut screwing on to the head of the gauge body. This is the magnifying arrangement devised by E. M. EDEN* for use in the "millionth" comparator at the National Physical Laboratory, but as in that form for present purposes it lacks lateral stiffness the spring attached to the fixed base has been stiffened by two others of the same length and thickness, but half the width, set one on each side of it, in a plane at right angles to it. One end of each is fixed to the base and the other to a projection on the mirror holder, the group of three springs forming the familiar crossed spring suspension.† The spring strips are fixed in direction at each end by cover plates and yield to movement of the piston by bending, approximately, into arcs of similar circles. The angular displacement of the mirror holder is closely proportional to the piston displacement so long as the latter is small in comparison with the distance between the parallel springs.

This form of control offers little resistance to piston movement, whilst independent movement of the mirror in any direction is resisted by at least one spring strip acting

---

* "Dictionary of Applied Physics," vol. 3, p. 627.

† "Dictionary of Applied Physics," vol. 3, p. 625.

as a strut, and these latter can be made as stiff as desired by choosing suitable proportions. In the instrument they are 0·62 cm. wide, 0·025 cm. thick, with an unsupported length of 0·5 cm. The distance between the parallel strips is 1 cm., and under working conditions, the magnifying factor is quite constant over the range of angular displacement involved, the natural frequency of the gauge when carrying a stainless steel mirror 2·5 cm. in diameter being not less than 2800. This is quite high enough to enable the instrument to follow even the shortest times of burning of the order of 15×10^{-4} sec. without undue oscillation, although the damping is small.

Recording arrangements.

The arrangements are shown in fig. 3, and present no unusual features, except for a method of obtaining a continuous time trace following the pressure curve.

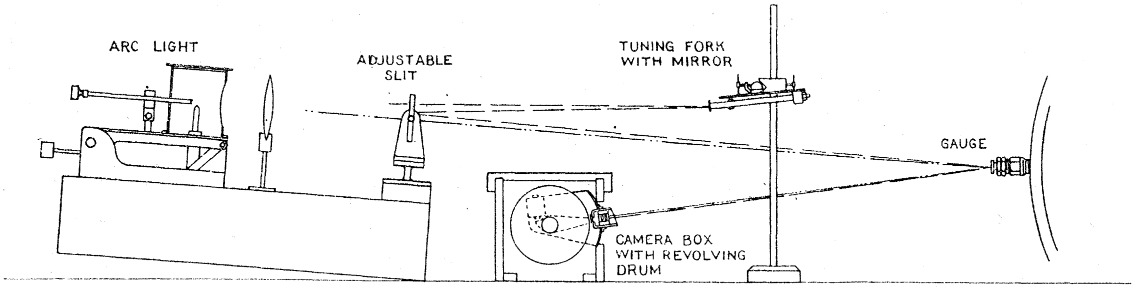


Fig. 3.—Recording Apparatus for General Arrangement.

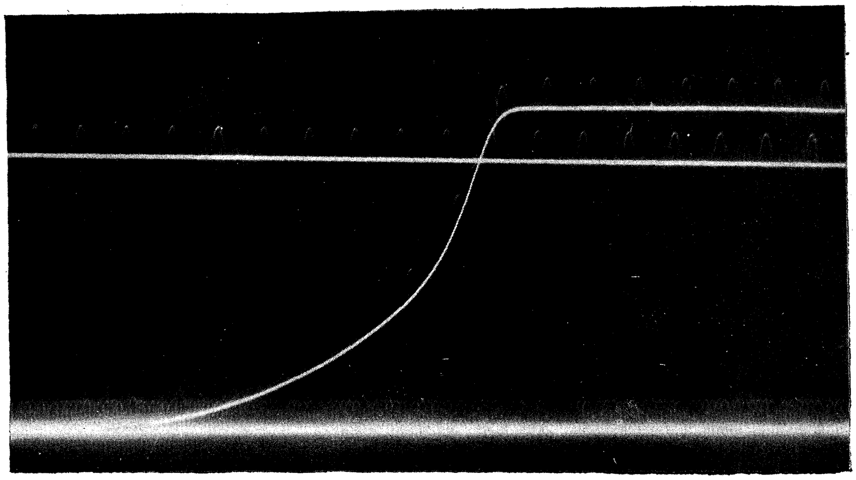
—— · · —— · · —— Path of Ray giving Pressure Trace.

—— —— —— —— Path of Ray giving Time Trace.

Records are obtained on a photographic film attached to a drum in a light-tight case, directly coupled to a small electric motor, the axis of the drum being horizontal. A stainless steel concave mirror on the gauge, of focal length 80 cm., forms an image on the drum of a vertical slit illuminated by an arc light. This image is condensed to a point by a cylindrical lens in front of the drum 10 cm. long and 2 cm. focal length. Behind the lens is a shutter operated by an electro-magnet and opened by a double pole switch at the instant the firing circuit is closed. A relay worked by a screw-thread on the drum spindle closes the shutter at any desired interval after the piston of the gauge has started to move, thus keeping the record clear of the greater part of the pressure-time trace after maximum pressure. The relay circuit includes a small lamp on the switch board, the extinction of which indicates to the operator that the charge has fired. The distance between the drum and the mirror is 154 cm. and the maximum height of a record at the top pressure is about 5·5 cm. The elastic movement of the gauge is therefore magnified rather more than 300 times.

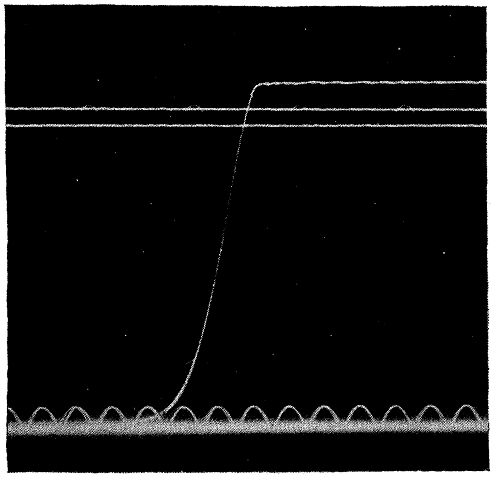
By reason of the wide range of conditions with which the gauge has to deal a constant speed motor cannot be employed. Moreover a time trace covering only a portion of

A.



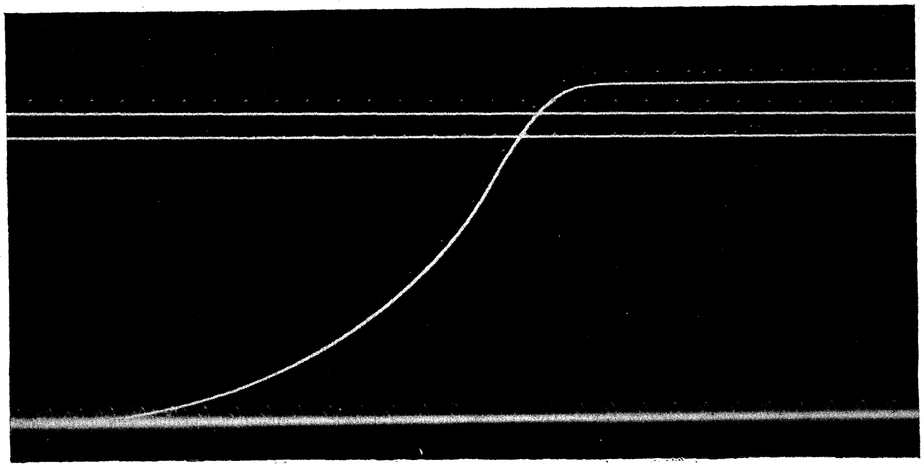
B (3). Large capacity, $\Delta = 0{\cdot}2211$.

B.



C (1). Large capacity, $\Delta = 0{\cdot}2211$.

C.



C (3). Small capacity, $\Delta = 0{\cdot}2211$.

D.

C (2). Large capacity, $\Delta = 0{\cdot}0420$.

Fig. 4.—Typical Records.

one revolution of the drum might not be adequate to interpret a record in which the time is fairly long, so the device shown in fig. 3 is used. A tuning fork of frequency 500, maintained by a microphone capsule, carries a concave mirror of 30 cm. focal length, which is illuminated by the upper part of the vertical slit, and forms an image of it on the front face of the slit plate itself. One side of the slit is formed of a stainless steel flat, and the whole slit is mounted in such a way that it can be rotated about vertical and horizontal axes. It is locked in such a position that the light coming from the fork mirror is reflected back to the gauge mirror and thence to the drum, forming there a second image by the side of the pressure trace. Vibration of the fork causes this image to trace out a sine-curve on the drum; and as only one side of the slit plate reflects the peaks alone of this sine-curve appear on one side of the pressure trace, following it throughout the whole time the shutter is open.

Some typical records reproduced from direct contact prints are shown in fig. 4 (Plate 1).

Manometer calibration.

The manometer was calibrated using the recording arrangements described above up to a pressure of 4000 kg./cm.^{2} on the dead weight tester illustrated (two elevations) in fig. 5.* The press follows normal design in balancing pressure against a known load. It was specially constructed for the Research Department, Woolwich, by the Budenberg Gauge Company, Ltd., and is capable of precise and reliable working up to a pressure of 5000 kg./cm.^{2} The spring gauge calibration was found linear over the range, the factor converting the height of the record to pressure being 728. To verify static functioning of the manometer over the range of experimental conditions encountered, a preliminary investigation was carried out in the large capacity of the closed vessel, using for comparison the piezo-electric gauge described below. Various considerations, for example, gas release, space, and lighting made it impossible to take simultaneous observations with the spring manometer and the piezo-electric gauge. Charges of a standard lot of cordite M.D. in consequence were fired round for round, giving pressures

---

* The dead-weight tester is hydraulically operated, the fluid being castor oil. Pressure is set up by the plunger K which operates on the fluid by means of the gearing and screw shown. The fluid channels, which are small, connect both with the gauge under test (attached at F) and with the column supporting the weighing apparatus AB. The latter comprises a number of separate discs, each of weight 10·16 kg., which rest on a rotating saddle, the whole being raised by the pressure of the oil on a piston of cross-sectional area 0·06452 cm.^{2} Each removable disc therefore corresponds to a pressure of 157·5 kg./cm.^{2}

The method of use is first to close the escape valve E, open valve C and fill with oil by the hand-pump H. Valve C is then closed, and pressure is set up by the handwheel until the sleeve AB carrying the weights is just lifted, care being taken that the sleeve and the weights are kept rotating slowly. Pressure is released by opening E, thus permitting the oil to escape through pipe I to the reservoir G.

Valve D is used only when the pressure is of such magnitude as to require more than one full stroke of K. On being temporarily closed the arrangement enables K to be returned for a second stroke.

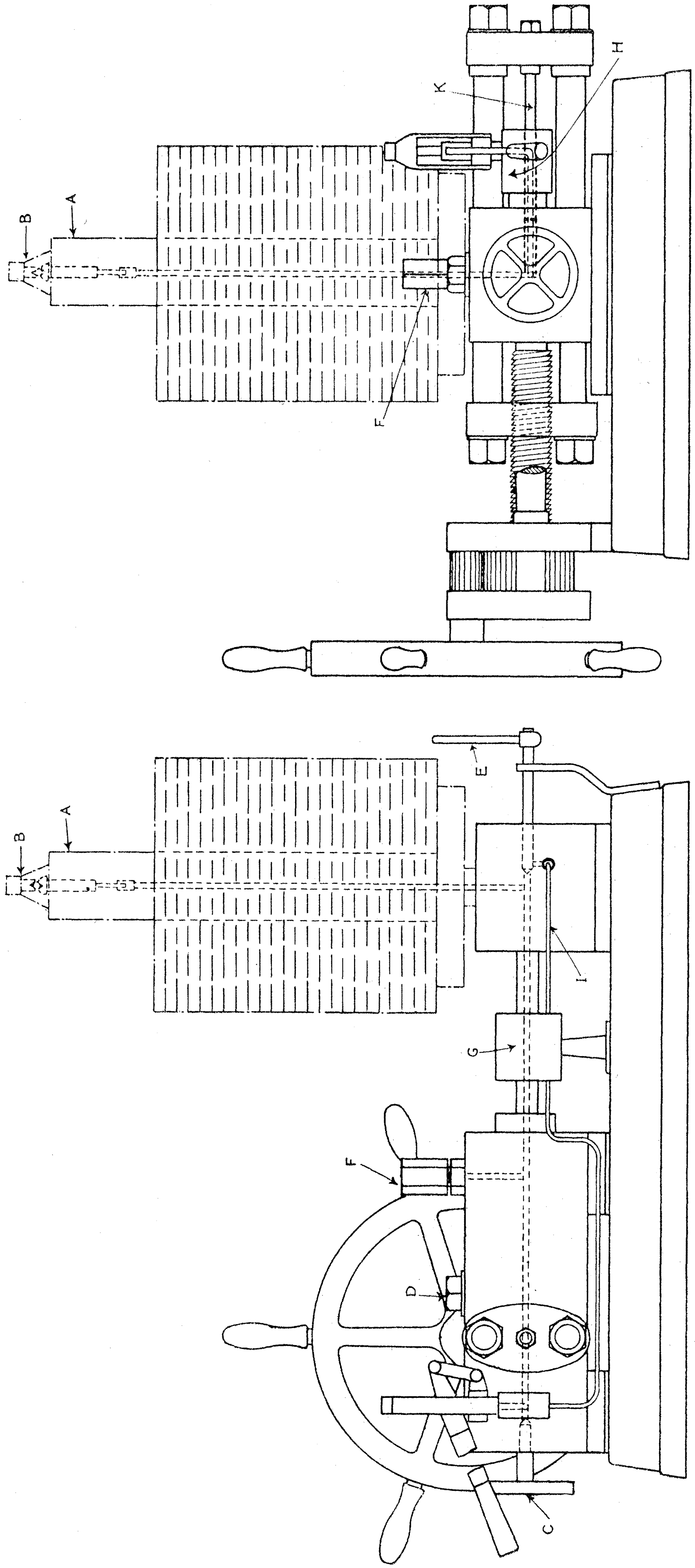


FIG. 5.

ranging from 261 kg./cm.^{2} to 3586 kg./cm.^{2}, comparative readings being shown graphically in fig. 6. It will be seen that the relation between the spring manometer record heights and the pressures measured by the piezo-electric gauge is one of direct proportionality, the conversion factor in this case being 724·4, or within 0·5 per cent. of the figure given

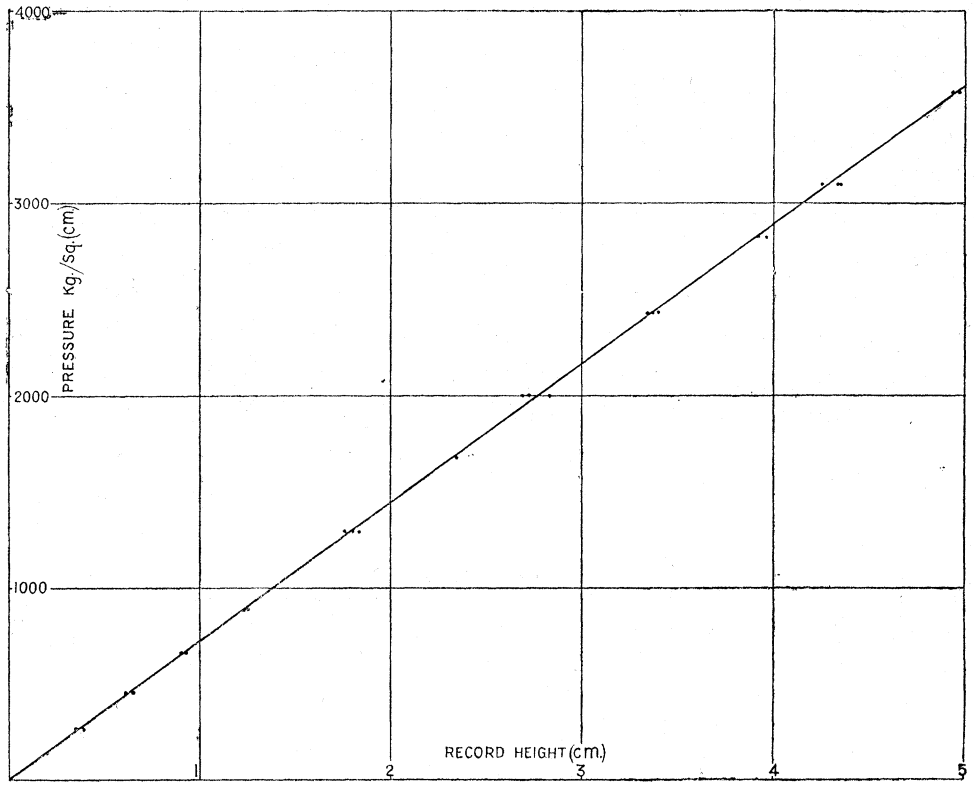


Fig. 6.—Calibration of Spring Manometer against Piezo-electric Gauge.

by the static calibration of the spring manometer. The piezo-electric gauge was employed for this dynamic test since by its nature there is absence of mechanical lag and also of friction.

The piezo-electric gauge.

The principle underlying the design of the gauge* was first suggested by J. J. Thomson, who demonstrated the possibilities of the application of the piezo-electric properties of certain types of crystal to the measurement of rapidly fluctuating pressures. The system was later developed by the Admiralty for the measurement of pressures of under-water explosions.† In applying the principle to pressure measurement in the closed vessel the design of the gauge is complicated by reason of the duration and magnitude of the temperatures and pressures involved.

---

* The gauge was designed by G. E. Condliffe, late of the Research Department, Woolwich, and forms the subject matter of British Patent No. 312502/28.

† Keys, 'J. Franklin Inst.,' vol. 196, pp. 576–591 (1923).

Details of the gauge are shown in fig. 7, which is drawn to scale. The body of the gauge A is turned from " Vibrac " steel threaded externally to screw into the explosion vessel, and to seat on a copper washer. The centre electrode B, shaped as shown, is insulated from the body of the gauge by the ebonite tube D and the mica washers M_1 and M_2. F is a steel disc of the same diameter as the end of B, a short split pin soldered into its centre fitting tightly into a corresponding hole in B. The flat thin steel plate P_1 is soldered into F, and the tourmaline crystal C, appropriately cut, is placed as shown, with another flat thin steel plate P_2 on the opposite side to P_1. P_2 is put into contact with the body of the gauge through the short steel spring V, which is soldered to it and to another small plate as shown. Insulation of the centre electrode system, which includes the face of the crystal in contact with P_1, is effected by means of the mica washers M_3. The crystal is held in place by the shaped ebonite supporting pieces E E. The space G surrounding and below the crystal is filled with an insulating medium composed of pure non-vulcanised Para rubber dissolved in white vaseline, and the end of the gauge is closed by the leather disc W, care being taken to exclude all air bubbles from G. When used in the explosion vessel W is covered with luting to protect it from the hot gases. To ensure good contact between the faces of the crystal and the plates P_1 P_2 the faces are first coated by sputtering from a silver cathode in a vacuum chamber, and the coating so obtained is reinforced by a further coating of copper, deposited electrolytically.

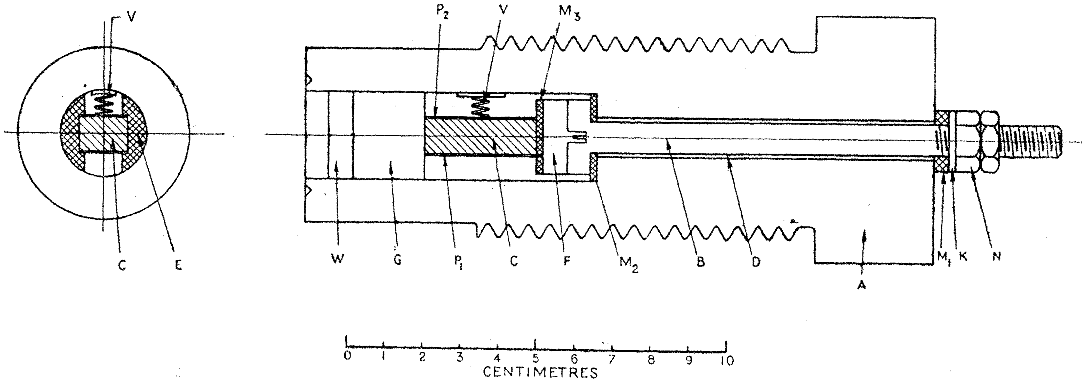


FIG. 7.—Piezo-electric Gauge.

The adoption of this form of mounting for the crystal results in considerable loss in natural frequency, which is now governed by the size of the container and the nature of the filling rather than by the crystal itself. It is, however, of sufficiently high order for the most rapid pressure rises in the experiments, and the design possesses the advantages that the full pressure is applied to the crystal and that there is no risk of mechanical breakdown due to non-uniform distribution of pressure over the surface.

Calibration of the gauge was carried out by measuring the charge produced by the sudden release of a known pressure, obtained by means of the dead-weight tester referred

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

to previously, the quantity of charge being indicated by the throw of a ballistic galvanometer. The gauge is screwed into an adaptor, which in turn is screwed into the body of the press. The adaptor is provided with a valve which can be opened quickly, thereby releasing the applied pressure, measurements with the arrangement adopted showing that the pressure is completely released in less than 0·01 second. The quarter-period of the ballistic galvanometer used is over three seconds and its sensitivity about 250 cm. per 10^{-6} coulomb. With the Budenberg press very high pressures can easily be held for a minute without variation; in consequence the accuracy of the calibration practically reduces to the accuracy with which the galvanometer deflection can be read, approximately to 0·05 cm. in 25 cm. or 0·2 per cent. Readings can be taken very quickly and a large number of observations have been made up to pressures of 4000 kg./cm.^{2} Within the accuracy indicated the relation between pressure and the charge developed has been found to be linear. Calibrations were carried out before, during, and after the series of firings in the closed vessel, with identical results. The sensitivity of the gauge is $8·67 \times 10^{-11}$ coulombs per kg./cm^2; the dimensions of the crystal being 3·05 cm. × 1·27 cm. × 1·02 cm.

The piezo-electric gauge was used in conjunction with a cathode-ray oscillograph of the A. B. Wood* type, being connected across one pair of deflecting plates, one plate and the closed vessel itself being earthed. The electrical capacity of the gauge, connecting leads, and oscillograph system is about 400 $\mu\mu f$, the sensitivity of the instrument being about 0·025 cm. per volt P.D. between the deflecting plates with an accelerating P.D. of the cathode beam of 3000 volts. The maximum deflection which can be recorded is about 2·5 cm., so that a full scale deflection can be obtained with a pressure in the region of 500 kg./cm.^{2} For higher pressures the capacity of the system is increased by loading in condensers. The movement of the cathode beam across the photographic plate on the time axis is effected by feeding the output of a rotating potentiometer through one of the electro-magnetic control coils of the oscillograph, the speed being arranged to give a single sweep across the plate in about half a second. The shutter is opened one second before firing the propellant charge, and closed about two seconds afterwards.

Part II.—Experimental Values and Derived Uncooled Pressures.

For the experiments three propellants were specially manufactured; a nitrocellulose powder, a cordite with 70 per cent. nitrocellulose and 30 per cent. nitroglycerine, and a hot ballistite with 40 per cent. nitrocellulose and 60 per cent. nitroglycerine. Each propellant was pressed in the shape of long cords, three sizes of cord being manufactured for each type of composition, nine samples of varying specification thus being available for experiment. Full details of the composition of each propellant are given in Part III.

---

* Wood, 'J. Inst. Elect. Eng.,' vol. 63, pp. 1046–1055 (1925).

Firings were carried out with each type at densities ranging from 0·0263 to 0·2479 (0·0263 to 0·2211 in the case of the ballistite samples) in each of the two capacities available, the larger having a volume of 649 cm.^{3} and a surface area of 656·8 cm.^{2} and the smaller a volume of 130·7 cm.^{3} with a surface area of 251·6 cm.^{2}. The density of loading Δ* has been taken throughout to include in the charge weight C the weight (0·324 gm.) of the primer referred to in Part I. The following table shows the charge weights for the respective densities of loading for the two capacities used in the experiments :—

TABLE I.

Δ (gms./cm.^{3}).	Volume 649 cm.^{3} C. (gms.).	Volume 130·7 cm.^{3} C. (gms.).
0·2479	160·9	32·40
0·2211	143·5	28·90
0·2049	133·0	26·78
0·1819	118·1	23·77
0·1546	100·3	20·21
0·1344	87·23	17·57
0·1066	69·28	13·93
0·0755	49·00	9·87
0·0585	37·97	7·65
0·0420	27·26	5·49
0·0263	17·07	3·44

At least two rounds were fired at each density of loading, and pressure-time curves were recorded in every case, the whole of the experimental data being incorporated in columns 1 to 4 of Table II, mean values being quoted for pressures and times to maximum pressure.

Examination of the values discloses features to which attention was drawn by PETAVEL, namely, the diminution in recorded pressure as the duration of the explosion becomes extended, and the effect on the recorded pressure of varying the ratio of wall surface to charge weight fired; these effects can clearly be attributed only to energy losses occurring during combustion. To arrive at the pressure which would have been developed, had there been no such loss of energy, it is necessary to examine in some detail the circumstances of the phenomenon.

Energy loss.

When the gases are given off from the burning surface of the propellant they impinge on the relatively cool walls of the vessel, and are cooled thereby in addition to imposing elastic stress in the steel of the vessel. Energy loss then is due to heat conduction and

---

[*] Δ is defined as the ratio of the charge weight in gms. to the volume of the enclosure in cm.^{3}.

to work done at the surface, and the amount of energy lost by the contained gases must be represented by the amount of heat that has crossed the surface of the vessel, together with the work done at the surface. Moreover, to refer the pressures corrected for heat and work losses to standard conditions a further adjustment is necessary, on account of the increase in the volume of the vessel brought about by the compressive action of the gases on the walls of the vessel. Equating, then, the energy loss of gas to the work done on the walls, together with the heat conducted across the surface, we have, if T_0 be the uncooled temperature, T the average temperature of the gas complex at the instant of maximum pressure, then

$$\text{Energy loss of gas} = C\,(T_0 - T)\,.\,s$$

where C is the charge weight in grams, and s is the mean specific heat of the gas complex over the region concerned.

To estimate the amount of work done on the walls, account has to be taken of the nature of the steel of the vessel, the build of the vessel, and the amount of compression of the obturator pads and the adaptors. The effective strength of the vessel has been assumed to be that of the liner only, since relining has taken place after original manufacture. The pad compressions were measured at various pressures by direct experiment. Detailed measurements have been made of the protrusion of the vent axial, the rounded corners, and various departures from plan.

The following results* have been obtained for pressure p kg./cm.^{2} where S is the wall surface :—

		Large capacity.	Small capacity.
Fractional volume increment	=	$3 \cdot 21 \times 10^{-6}\, p$	$13 \cdot 50 \times 10^{-6}\, p$
Work in calories	=	$3 \cdot 70 \times 10^{-8}\, p^2\, S$	$8 \cdot 18 \times 10^{-8}\, p^2 S$

To arrive at an expression for the quantity of heat conducted across the surface, it is to be remarked that the gas conditions inside the vessel during the combustion period differ essentially from those obtaining when the solid propellant has all been converted into gas. At the surface of the propellant grain a change of state is taking place with evolution of gas, so that intermolecular conditions during the explosion are more than ordinarily chaotic and the problem of heat change in consequence cannot be regarded from the viewpoint of normal conduction and convection. As the molecules are released

---

* In computing the values quoted, the increase in volume due to the expansion of the walls of the vessel under the pressure of the explosion has been calculated from the formula given by Love (' Mathematical Theory of Elasticity ' (2nd Edition), p. 142), assuming the effective outside diameter of the vessel to be that of the liner. Additional volume increment arising from the pad compression has been allowed for by direct measurement, and the increase in volume with the smaller capacity, due to the compression of the adaptor and to the stretching of the walls behind the adaptor face, has been calculated from the steel constants of the vessel.

at the grain surface they rush towards the walls, impulsive actions in collisions tending to equalise matters, so that the gas already present in the vessel acts as a mechanism for transferring excess action at the grain surface to the walls where the heat losses actually occur. The temperature distribution in the gas complex is clearly non-uniform, though, having regard to the order of times involved, the gradient is probably slight. The assumption of a suitable average temperature T (lower than the temperature of explosion T_0) throughout the combustion phase should in consequence lead to a correction of the right order of magnitude. Taking this average temperature to be that obtaining at the instant of maximum pressure, the problem has been considered as one of linear transfer of heat across an interface, the temperature on one side of which remains constant.*

The normal equation for heat conduction through a uniform body is :—

$$\rho c \frac{\partial \theta}{\partial t} = \kappa \cdot \frac{\partial^2 \theta}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ is the density, c the specific heat and κ the conductivity of the material.

Writing

$$z = x \sqrt{\frac{\rho c}{2\kappa t}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

---

* A direct treatment of this kind can be accepted as applicable and adequate only so long as the main transfer of heat through the gas complex is by convection, *i.e.*, while the gas density is increasing through propellant combustion, conduction effects in the gas being of secondary importance only. The time durations at issue are at most of the order of 0·1 sec. and can be so low as 0·002 sec., while the gas density variations during the times range from 0 to some 0·25 gms./cm.^{3}.

After maximum pressure, *i.e.*, in effect after the propellant has been completely converted into gas, the gas density remains constant, and convection ceases. A modified set of circumstances consequently arises, since there is then heat conduction through the gas complex, now at constant density, together with heat conduction through the steel, as previously considered. In these conditions, as is well known, resistance to flow of heat from the gas body to the wall surface is very much influenced by the thermal state of the layer of gas contiguous to the surface, and allowance has to be made for this fact in any general treatment. From inspection of cooling curves, *i.e.*, pressure-time curves obtained after maximum pressure, it can be ascertained that heat losses by cooling take place comparatively slowly, the modifying influence of the intervening gas layer being clearly at work. A phenomenon of this nature is likely to come more and more into prominence as abstraction of energy by the walls in the form of work, together with convection effects, cease, as the densities of loading are diminished, and as the propellant sizes are increased, times being more and more prolonged.

At the densities of loading resorted to, and with the propellant sizes employed, the layer effect modification, even if operative during the short interval of the convection phase, has been regarded as negligible. Support is lent to this moreover in that, for the higher densities of loading, on the values from which most reliance is placed, the main pressure correction arises from the work term, the heat correction term being comparatively small. This may be verified using equations (6A) and (6B) with $\sqrt{t} = 0$. It may be concluded therefore that though the corrections resulting from the treatment adopted are not strictly accurate, they are quite sufficiently so for practical purposes.

we have, assuming θ a function of z,

$$\frac{d^2\theta}{dz^2} = -z \cdot \frac{d\theta}{dz}, \quad \dots \dots \dots \dots \quad (3)$$

and the solution of equation (1) to comply with the initial conditions is

$$\theta = \theta_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\left(\frac{\kappa t}{\rho c}\right)}}} e^{-w^2}\, dw \right], \quad \dots \dots \dots \quad (4)$$

where θ is the excess temperature at a point x in the steel at any time t and θ_0 is the initial temperature difference of the two sides of the interface. The rate of heat flow per unit area across the interface is therefore $\theta_0 \sqrt{\frac{\kappa\rho c}{\pi t}}$, and the quantity of heat crossing in time t is $2\theta_0 \sqrt{\frac{\kappa\rho c t}{\pi}}$.

Writing $a = 2\sqrt{\frac{\kappa\rho c}{\pi}}$, there results

$$\mathrm{C}\,(\mathrm{T}_0 - \mathrm{T}) \,.\, s = bp^2\mathrm{S} + (\mathrm{T} - \mathrm{T}_w)\, a\mathrm{S}\sqrt{t}, \quad \dots \dots \dots \quad (5)$$

where T_w is the initial temperature of the wall surface at the start of the explosion, and b takes the values quoted above for the large and small capacity respectively.

At the high temperatures encountered, for a given density of loading, if p be the observed and p_0 the uncooled pressure, p/p_0 is equal to T/T_0.*

We have therefore :—

$$1 - \frac{p}{p_0} = \frac{bp^2\mathrm{S}}{\mathrm{CT}_0 s} + \frac{a}{s}\left(\frac{p}{p_0} - \frac{\mathrm{T}_w}{\mathrm{T}_0}\right)\sqrt{t} \cdot \frac{\mathrm{S}}{\mathrm{C}},$$

whence

$$p_0 = \frac{p\left(1 + \frac{a}{s} \cdot \frac{\mathrm{S}}{\mathrm{C}}\sqrt{t}\right)}{1 - \frac{bp^2\mathrm{S}}{\mathrm{CT}_0 s} + \frac{\mathrm{T}_w}{\mathrm{T}_0} \cdot \frac{a}{s} \cdot \frac{\mathrm{S}}{\mathrm{C}} \cdot \sqrt{t}}. \quad \dots \dots \dots \quad (6)$$

For the various propellants under investigation, T_0 ranges from 2750° K to 4170° K, and s from 0·30 to 0·40. In the application of the formula it, however, suffices to take mean values, having regard to the magnitude of the correction involved. T_0 has therefore been assumed equal to 3500° K throughout, and s equal to 0·35. The initial wall temperature T_w, which cannot be directly measured at the instant the explosion proper starts, has been taken to be 350° K, this being some 50° K above the value prior to the ignition of the primer and acetylene-air mixture.

---

* *Cf.* Part IV, equations (13) and (15).

Applying the correction for fractional volume increment, since p has been measured in an expanded volume, and taking $a = 0{\cdot}01775$, we have for the two vessels :—

Large capacity—

$$p_0 = \frac{p\,(1 + 3{\cdot}21 \times 10^{-6}\,p)\,(\mathrm{C} + 33{\cdot}3\,\sqrt{t})}{\mathrm{C} + 3{\cdot}33\,\sqrt{t} - 1{\cdot}984 \times 10^{-8}\,p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6\text{A})$$

Small capacity—

$$p_0 = \frac{p\,(1 + 13{\cdot}5 \times 10^{-6}\,p)\,(\mathrm{C} + 12{\cdot}76\,\sqrt{t})}{\mathrm{C} + 1{\cdot}276\,\sqrt{t} - 1{\cdot}681 \times 10^{-8}\,p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6\text{B})$$

For the above formulæ every constant with the exception of a has been calculated from *a priori* considerations. The value taken for a has been ascertained from a detailed analysis of the observed pressures and times for all the propellants, and leads to a value for the conductivity of steel under the conditions of approximately $0{\cdot}00027$ for the localised skin effects at issue. There does not appear to be any direct experimental method of verifying this figure, and the degree to which confidence can be attached to the formulæ developed above for deriving uncooled from observed pressures rests in the following considerations :—

(1) An energy summation effect is in question, and a relationship is established, based on the law of conservation.

(2) The work and expansion terms are calculated on the known nature build and details of the closed vessel.

(3) The occurrence of $\sqrt{t}$ in the algebraic form for the heat conduction renders the term highly sensitive for the small order times involved.*

(4) The value accorded to T is related specifically to the conditions of each experimental firing by the expression $\mathrm{T} = \mathrm{T}_0 p/p_0$, the value of p being the pressure observed at the end of combustion. In effect this assumes that the average temperature of the gas is constant during the explosion, and that it can be represented by the temperature to which the gas attains at the end of combustion. The value cannot be strictly true at the start, but becomes more nearly so as the explosion proceeds, and is exact at the end.

(5) Subject to the preceding considerations, it has to be ascertained that one value can be found for a applicable in each capacity and to all the various circumstances of the explosions, such that for any propellant fired at any density of loading in either capacity the values of p_0 derived by the two formulæ respectively from the observed values of p in the different capacities are the same numerically, or at least the same order of magnitude. More searching requirements for one

---

* For the higher values of Δ, to a first approximation, the cooling formula leads to the relationship $(p_0 - p) \propto \mathrm{S}p\,\sqrt{t}/\mathrm{C}$, a result which may be compared with the values given for $\Delta = 0{\cdot}20$ by Muraour—" L'influence du refroidissement dans la mesure des pressions explosives," ' Mémorial des Poudres et Salpêtres,' vol. 20, pp. 323–329.

a priori unknown constant to satisfy it would seem difficult to devise, and particularly so, having regard in certain of the cases to the orders of corrections involved.

(6) That the value deduced for κ is much less than that observed at ordinary temperatures is consistent with the known tendency of the conductivity of steel to decrease with increasing temperature.

Uncooled pressures.

In the application of the formulæ a real difficulty lies in the assessment of the duration of the explosion. The figures tabulated are means of all the observations made at each density of loading and with each type of propellant ; and within the limits of measurement no systematic difference is observable between times for corresponding conditions in the large and in the small capacity.

The explanation would seem to be that the gas density ρ at any instant is practically uniform throughout the vessel, but that at the immediate propellant surface where the change of state is taking place the temperature is the uncooled temperature T_0. The rate of burning consequently, which varies with the pressure, at the grain surface varies as ρT_0, and is consequently unaffected by the nature of the enclosure. To standardise conditions and to exclude elements of uncertainty at each end of the time-rise of pressure, the time of the explosion has been measured in every case from a point on the curve corresponding to one-fiftieth of the total height of the record to a point corresponding to forty-nine fiftieths of the total height.

The values of p_0 calculated on this basis are entered in columns 5 to 7 of Table II below.

Table II.—Experimental and derived uncooled pressure values.

N. (1) Nitrocellulose—cord diameter, 0·071 cm.

Δ (gms./cm.^{3}).	Time. (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0054	3309	3115	3395	3347	3371
0·2211	0·0065	2862	2707	2940	2909	2924
0·2049	0·0071	2616	2523	2688	2714	2701
0·1819	0·0081	2227	2167	2296	2332	2314
0·1546	0·0094	1857	1764	1924	1911	1917
0·1344	0·0104	1572	1507	1636	1642	1639
0·1066	0·0119	1199	1125	1261	1245	1253
0·0755	0·0139	803	762	862	875	868
0·0585	0·0153	613	583	673	695	684
0·0420	0·0167	419	397	478	505	491
0·0263	0·0184	257	228	317	328	322

TABLE II—(continued).

N. (2) Nitrocellulose—cord diameter, 0·215 cm.

Δ (gms./cm.^{3}).	Time (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0135	3284	3033	3396	3306	3351
0·2211	0·0160	2803	2633	2905	2879	2892
0·2049	0·0176	2539	2407	2638	2640	2639
0·1819	0·0194	2202	2082	2296	2293	2294
0·1546	0·0232	1813	1674	1891	1866	1878
0·1344	0·0260	1509	1395	1601	1575	1588
0·1066	0·0303	1137	1074	1235	1246	1240
0·0755	0·0362	781	693	874	852	863
0·0585	0·0401	553	495	641	644	642
0·0420	0·0444	367	345	450	493	471
0·0263	0·0489	214	172	294	290	292

N. (3) Nitrocellulose—cord diameter, 0·554 cm.

Δ (gms./cm.^{3}).	Time (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0405	3134	2906	3287	3247	3267
0·2211	0·0440	2696	2501	2841	2809	2825
0·2049	0·0470	2422	2268	2562	2562	2562
0·1819	0·0520	2076	1918	2212	2188	2200
0·1546	0·0610	1677	1550	1809	1804	1806
0·1344	0·0705	1429	1304	1566	1556	1561
0·1066	0·0860	1068	929	1206	1164	1185
0·0755	0·1090	680	586	816	808	812
0·0585	0·1255	495	430	631	650	640
0·0420	0·1450	328	271	460	471	465
0·0263	0·1685	167	135	276	293	284

C. (1) 70/30 Cordite—cord diameter, 0·066 cm.

Δ (gms./cm.^{3}).	Time (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0031	3694	3561	3781	3830	3805
0·2211	0·0033	3226	3118	3302	3342	3322
0·2049	0·0035	2967	2813	3039	3008	3023
0·1819	0·0038	2544	2462	2607	2627	2617
0·1546	0·0043	2085	2014	2143	2153	2148
0·1344	0·0048	1770	1718	1824	1843	1833
0·1066	0·0059	1361	1315	1413	1425	1419
0·0755	0·0076	917	885	969	988	978
0·0585	0·0092	708	668	762	769	765
0·0420	0·0103	493	465	548	564	556
0·0263	0·0140	285	258	343	356	349

TABLE II—(continued).

C. (2) 70/30 Cordite—cord diameter, 0·328 cm.

Δ (gms./cm.³).	Time (secs.).	p (kg./cm.²).		p_0 (kg./cm.²).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0125	3722	3484	3849	3819	3834
0·2211	0·0132	3213	3046	3328	3331	3329
0·2049	0·0139	2904	2767	3011	3030	3020
0·1819	0·0151	2531	2385	2635	2616	2625
0·1546	0·0172	2059	1967	2156	2172	2164
0·1344	0·0193	1758	1654	1854	1846	1850
0·1066	0·0234	1332	1241	1424	1419	1421
0·0755	0·0305	912	838	1011	1017	1014
0·0585	0·0365	668	597	769	767	768
0·0420	0·0449	444	403	545	578	561
0·0263	0·0560	250	222	351	384	367

C. (3) 70/30 Cordite—cord diameter, 0·890 cm.

Δ (gms./cm.³).	Time (secs.).	p (kg./cm.²).		p_0 (kg./cm.²).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2479	0·0375	3660	3377	3841	3793	3817
0·2211	0·0396	3122	2937	3287	3311	3299
0·2049	0·0417	2818	2660	2977	3010	2993
0·1819	0·0453	2400	2282	2550	2600	2575
0·1546	0·0516	1980	1852	2126	2147	2136
0·1344	0·0579	1658	1520	1807	1794	1800
0·1066	0·0702	1249	1131	1395	1394	1394
0·0755	0·0915	802	704	951	953	952
0·0585	0·1095	580	495	728	732	730
0·0420	0·1347	359	310	498	532	515
0·0263	0·1680	180	140	301	307	304

B. (1) 40/60 Ballistite—cord diameter, 0·064 cm.

Δ (gms./cm.³).	Time (secs.).	p (kg./cm.²).		p_0 (kg./cm.²).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2211	0·0016	3378	3125	3448	3326	3387
0·2049	0·0018	3030	2866	3093	3048	3070
0·1819	0·0020	2559	2531	2612	2685	2648
0·1546	0·0023	2118	2044	2165	2166	2165
0·1344	0·0026	1862	1744	1908	1851	1879
0·1066	0·0030	1375	1332	1414	1420	1417
0·0755	0·0037	926	913	963	989	976
0·0585	0·0045	710	685	749	761	755
0·0420	0·0059	484	463	528	539	533
0·0263	0·0079	261	243	301	314	307

TABLE II—(continued).

B. (2) 40/60 Ballistite—cord diameter, 0·430 cm.

Δ (gms./cm.^{3}).	Time (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2211	0·0091	3271	3118	3375	3391	3383
0·2049	0·0104	2937	2841	3035	3093	3064
0·1819	0·0111	2518	2481	2609	2705	2657
0·1546	0·0128	2125	1999	2214	2192	2203
0·1344	0·0137	1769	1712	1851	1889	1870
0·1066	0·0169	1328	1304	1416	1471	1443
0·0755	0·0229	904	862	1000	1024	1012
0·0585	0·0278	666	643	764	808	786
0·0420	0·0325	454	417	554	571	562
0·0263	0·0523	230	235	333	402	367

B. (3) 40/60 Ballistite—cord diameter, 1·200 cm.

Δ (gms./cm.^{3}).	Time (secs.).	p (kg./cm.^{2}).		p_0 (kg./cm.^{2}).		
		Large capacity.	Small capacity.	Large capacity.	Small capacity.	Mean.
0·2211	0·0196	3208	3079	3339	3405	3372
0·2049	0·0223	2945	2789	3076	3095	3085
0·1819	0·0247	2537	2410	2661	2689	2675
0·1546	0·0275	2059	1972	2176	2222	2199
0·1344	0·0312	1736	1649	1853	1883	1868
0·1066	0·0397	1342	1232	1463	1458	1460
0·0755	0·0514	852	828	972	1052	1012
0·0585	0·0702	627	586	757	815	786
0·0420	0·0861	391	354	513	560	536
0·0263	0·1229	197	167	310	340	325

Reviewing the figures for the uncooled pressures, it will be seen that while there is general agreement for the majority of the observations, there is a definite tendency at the lower densities of loading for the small capacity values to be higher than those for the larger capacity. In this connection, it must be recalled that the recording manometer was necessarily designed to compete with conditions represented by the application of a load of some 4000 kg./cm.^{2} in a time of the order of 2×10^{-3} second. Its sensitivity consequently is considerably diminished where pressures of the order of 300 kg./cm.^{2} and below are in question, since although the mean spring readings can be accepted over the whole range within a spread of ± 25 kg./cm.^{2}, such a variation, while of little moment at the top end of the scale, becomes of consequence at the lower end. Again, no account has been taken of the initial cooled pressure arising from the combustion of the strand of gun-cotton and of the acetylene-air igniting mixture, which is probably of the order of 15 kg./cm.^{2} at the start of burning of the propellant charge proper. An adjustment on this account would again affect the derived pressures at low densities more than at the top end, and more so in the small capacity than in the large. Finally, the formulæ adopted are in the nature of things most suitable for first order adjustments, and it will be observed that in some instances at the low densities of loading they have been applied in conditions where the corrections attain the order of 100 per cent. of the observed values. In most cases, however, the difference between corresponding mean values of p_0 lies within the spread given by the corresponding observed individual values of p, this spread being occasioned not only by reason of the considerations advanced above, but also by actual charge-to-charge variation of propellant of the same nominal composition.

Arrangements are in hand to investigate the region below 500 kg./cm.^{2} with specially designed apparatus and recording devices.

PART III.—CALCULATION OF THE TEMPERATURE OF EXPLOSION.

Heats of formation and mean molecular heats.

To calculate the temperature of explosion and the nature of the gas complex at the temperature of explosion, it is necessary to know the constituents of the explosive, their heats of formation, the heats of formation of the constituent gases, the mean molecular heats at constant volume of the gases over the range of temperature involved, and the control equation of the water-gas reaction. The heats of formation employed* (carbon amorphous) are tabulated below :—

TABLE III.—Heats of formation at constant pressure (C amorphous).

Chemical compound.	Formula.	Heat of formation per gm. at 15° C.	Heat of formation per gm. mol. at 15° C.
Guncotton	$C_{24}H_{29}N_{11}O_{42}$	630	720,000
Collodion	$C_{24}H_{31}N_9O_{38}$	684	720,000
Nitroglycerine	$C_3H_5N_3O_9$	420	95,340
Diphenylamine	$C_{12}H_{11}N$	— 325	— 54,900
Acetone	C_3H_6O	1120	65,000
Water	H_2O	3800	68,400
Steam	H_2O	3222	58,000
Carbon dioxide	CO_2	2210	97,240
Carbon monoxide	CO	1040	29,120

---

* The values tabulated are those accepted in the Research Department, Woolwich, on the results of numerous basic determinations.

The ascertainment of the values to be taken for the mean molecular heats has been a matter of some difficulty. From normal temperatures up to 2000° K., the values are known with some certainty, but between 2000° K. and 4000° K., which is the region at issue for the present purpose, comparatively little experimental data exist.

Recent research* has suggested two types of molecule to account for the band spectrum of CO_2, a straight and a bent model, the observed C_v having values nearer to those calculated for the straight model at normal temperatures, trending towards those calculated for the bent as the temperature increases from 273° K. to 473° K., and lying between the pair of calculated values at the higher temperatures. The values calculated on the hypothesis of the bent type are lower than those of the straight, and the model is inherently more probable. PIER and BJERRUM, in calculating values for $\bar{C}_v$ for CO_2 make use of the NERNST-LINDEMANN modification of the EINSTEIN method of computing molecular heats, and quote two illustrations where in the first instance the wave-lengths are taken as 14·7 μ, 6·2 μ, and 6·2 μ respectively, and in the second case, 14·7 μ, 4·3 μ, and 2·7 μ respectively. The values of $\bar{C}_v$ computed by the latter method are lower than those given in the first case, and lie between the observed values and those calculated from the bent model; moreover, the wave-lengths so used are those observed in spectroscopic analysis. These values have been accepted as a basis for computing $\bar{C}_v$ for CO_2 in the present investigation, and the same principle has been adopted for computing $\bar{C}_v$ for CO and N_2, and for H_2; namely, using the NERNST-LINDEMANN form and accepting as best values where available the wave-lengths observed or indicated spectroscopically. The appropriate formulæ† are :—

CO_2—

$$\bar{C}_v = 1\cdot987\,\{3 + \phi\,[2\cdot7] + \phi\,[4\cdot3] + \phi\,[14\cdot7]\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

CO and N_2—

$$\bar{C}_v = 1\cdot987\,\{2\cdot5 + \phi\,[2\cdot4]\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

H_2—

$$\bar{C}_v = 1\cdot987\,\{2\cdot5 + \phi\,[2\cdot0]\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

where

$$\phi\,[\lambda] = \tfrac{1}{2}\left\{\frac{x}{e^{x} - 1} + \frac{\frac{1}{2}x}{e^{\frac{1}{2}x} - 1}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

and $x = 14{,}580/\lambda\,T_0$, T_0 being measured in °K.

The case of H_2O is not susceptible to similar treatment, since the molecular heat increases with temperature at a rate greater than would be predicted from quantum considerations. To fit experimental values, BJERRUM has given the following formula :—

$$\bar{C}_v = 1\cdot987\,\{3 + 2\,\phi\,[1\cdot3] + \phi\,[3\cdot6]\} + \left(\frac{T_0}{3100}\right)^4$$

where T_0 is measured in °K.

---

* *Cf.* FOWLER, "Statistical Mechanics," p. 64.

† *Cf.* LEWIS, "System of Physical Chemistry," vol. 3, chap. 4.

This formula is in good agreement with observed values up to 3000° K, but shows a distinct tendency to over-calculate for values of T_0 above this figure. It is probable that the T_0^4 term is too severe as a correction for high values of T_0.

As an alternative to Bjerrum's formula the following expression is proposed :—

$$\overline{C}_v = 6 + \frac{7}{15} \cdot \frac{t}{1000} + \frac{16}{45} \cdot \left(\frac{t}{1000}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

where $\overline{C}_v$ is the mean molecular heat at constant volume between 0° C. and t° C. Comparison between experimental values and those given respectively by formula (11) and Bjerrum's formula is shown in Table IV.

Table IV.—Comparison between observed and calculated values of $\overline{C}_v$ for H_2O (gas).

t° C.	$\overline{C}_v$. Calculated. (Formula (11)).	$\overline{C}_v$. Calculated. (Bjerrum).	$\overline{C}_v$. Observed.	Observer.
	(110° C. — t° C.)		(110° C. — t° C.)	
620	6·51	6·55	6·51	Holborn and Henning.
1000	6·92	6·95	6·95	,, ,,
1327	7·35	7·36	7·40	,, ,,
	(18° C. — t° C.)		(18° C. — t° C.)	
1811	8·03	7·99	7·92	Pier
2110	8·59	8·54	8·54	,,
2377	9·14	9·14	9·37	,,
2663	9·8	9·9	10·0	Bjerrum
2908	10·4	10·7	10·5	,,
3060	10·8	11·3	10·9	,,

The other gases under consideration at normal temperatures are well removed from their liquefying points ; H_2O, on the other hand, in the region of 373° K approximates to a vapour. It has been suggested* that the abnormal rate of increase of the molecular heat may possibly be connected with a depolymerisation of any bimolecules present, though at high temperatures this should be negligible. Alternatively McCrea† has advanced the hypothesis that where H_2O alone is concerned the observed high molecular heat is due to dissociation taking place as the temperature increases above a critical value. The values for C_v proposed by McCrea for the undissociated molecule lead to

---

* Lewis, *loc. cit.*

† 'Proc. Camb. Phil. Soc.,' vol. 23, pp. 942–950 (1927).

values of $\bar{C}_v$ appreciably below those given in Table V for the region of t in excess of 1200° C; values which cannot be made to agree with the observational data obtained in the present investigation. In the particular case of a propellant gas complex, if dissociation of H_2O molecules occur the consequences are reflected in the other gases so that the H_2O content as calculated refers to undissociated molecules,* to which formula (11) must be held to apply, as also the experimental data given in Table IV. Values for $\bar{C}_v$ between 0° C and t° C for temperatures ranging from 2000° C. to 4000° C. are tabulated below for the various gases.

Table V.—Mean molecular heats at constant volume between 0° C. and t° C.

t° C.	$\bar{C}_v$.			
	CO_2.	CO and N_2.	H_2.	H_2O.
2000	9·99	5·73	5·58	8·36
2100	10·04	5·76	5·61	8·55
2200	10·09	5·79	5·64	8·75
2300	10·13	5·82	5·67	8·96
2400	10·17	5·85	5·70	9·17
2500	10·21	5·88	5·73	9·39
2600	10·25	5·90	5·75	9·62
2700	10·29	5·93	5·78	9·85
2800	10·33	5·95	5·80	10·09
2900	10·37	5·98	5·83	10·34
3000	10·41	6·00	5·85	10·60
3100	10·45	6·02	5·87	10·86
3200	10·49	6·04	5·89	11·13
3300	10·53	6·06	5·91	11·41
3400	10·56	6·08	5·93	11·70
3500	10·59	6·10	5·95	11·99
3600	10·62	6·12	5·97	12·29
3700	10·65	6·14	5·99	12·59
3800	10·67	6·15	6·01	12·91
3900	10·69	6·17	6·03	13·23
4000	10·71	6·18	6·04	13·56

The equilibrium equation for the water-gas reaction.

In establishing the formula for dissociative equilibria, use has been made of the foregoing expressions for $\bar{C}_v$, and applying the normal van't Hoff formula, we arrive at the following relationship for the concentration constant K_c :—

$$\begin{aligned}\log_{10} K_c &= \log_{10} \frac{(H_2O)\,(CO)}{(CO_2)\,(H_2)} \\ &= 2{\cdot}5333 + 0{\cdot}03832 \times 10^{-3}T_0 + 0{\cdot}03884 \times 10^{-6}T_0^2 \\ &\qquad - 0{\cdot}0696 \log_{10} T_0 - \frac{2241{\cdot}6}{T_0} + \Phi, \quad . \quad . \quad (12)\end{aligned}$$

---

* *Cf.* Henderson and Hassé, 'Proc. Roy. Soc.,' A, vol. 100, p. 468 (1922).

where

$$2\,\Phi = \log_{10}\left[\overset{\text{Product}}{(1-4)}\,(1-e^{-x})\,(1-e^{-\frac{1}{2}x})\right] - \log_{10}\left[(1-e^{-x_5})\,(1-e^{-\frac{1}{2}x_5})\right],$$

the values of x in the product (1 — 4) being given by $\lambda_1 = 2\cdot0$, $\lambda_2 = 2\cdot7$, $\lambda_3 = 4\cdot3$, $\lambda_4 = 14\cdot7$, the value for x_5 being given by $\lambda_5 = 2\cdot4$, the constant of integration corresponding to a value of $K_c = 1$ for $T_0 = 1125°$ K.* It will be observed that the value 2·5333 is not far removed from the figure that would have been computed on the basis of NERNST's hypothesis in connection with "solid" reactions at 0° K. Values of K_c between 1000° K. and 4200° K. are given in the following table :—

TABLE VI.—Values of K_c between 1000° K. and 4200° K.

T_0 (°K.).	K .	T_0 (°K.).	K_c.	T_0 (°K.).	K_c.
1000	0·52	2100	5·05	3200	10·4
1100	0·89	2200	5·50	3300	10·9
1200	1·27	2300	5·96	3400	11·45
1300	1·66	2400	6·42	3500	12·0
1400	2·05	2500	6·88	3600	12·6
1500	2·45	2600	7·35	3700	13·15
1600	2·86	2700	7·83	3800	13·65
1700	3·28	2800	8·32	3900	14·2
1800	3·71	2900	8·82	4000	14·8
1900	4·15	3000	9·33	4100	15·4
2000	4·60	3100	9·85	4200	16·0

YAMAGA† has carried out a detailed survey of the various expressions proposed for evaluating the equilibrium constant for the water-gas reaction. Of the nine forms considered by him he concludes that only three formulæ can be accepted as sufficiently representative for the high temperatures experienced in propellant explosions.

The three expressions are :—

A.—HABER's *second formula.*‡

$$\log_{10} K_c = -\frac{2170}{T_0} + 0\cdot979 \log_{10} T_0 - 1\cdot082 \times 10^{-3}\,T_0 + 1\cdot734 \times 10^{-7}\,T_0{}^2 - 0\cdot02858.$$

B.—YAMAGA's *first formula* (PIER's *molecular heats*).

$$\log_{10} K_c = -\frac{2196}{T_0} + 0\cdot60 \log_{10} T_0 - 0\cdot773 \times 10^{-3}\,T_0 + 0\cdot092 \times 10^{-6}\,T_0{}^2 + 0\cdot0065 \times 10^{-9}\,T_0{}^3 + 0\cdot8930.$$

---

* For the evidence for this value, *cf.* HABER, "Thermodynamics of Technical Gas Reactions," p. 121 *et seq.*

† YAMAGA, "The Equilibrium of Gases in the Reaction of Explosives," 'Proc. Int. Math. Congress,' Toronto, Canada, 1924.

‡ 'Z. Phys. Chem.,' vol. 68, p. 731 (1910).

C.—YAMAGA'S *second formula* (BJERRUM'S *molecular heats*).

$$\log_{10} K_c = -\frac{2190\cdot4}{T_0} + 0\cdot1086\left(\frac{T_0}{3100}\right)^4$$

$$-0\cdot4343\,\{F(2\cdot0)+2F(5\cdot0)+F(8\cdot1)-F(2\cdot4)-2F(1\cdot3)-F(3\cdot6)\}+2\cdot30.$$

where

$$F(\lambda) = \tfrac{1}{2}\left[\frac{3x}{2} - \log_{10}(e^x - 1) - \log_{10}(e^{\frac{1}{2}x} - 1)\right]$$

x being as defined in formula (12).

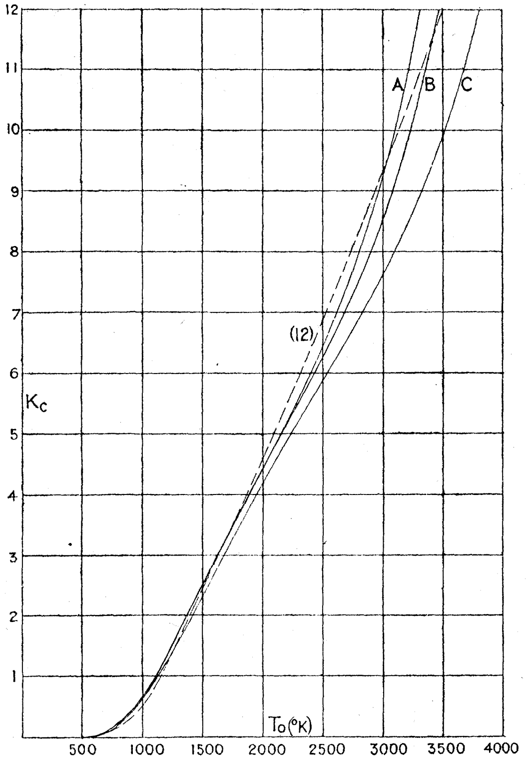


FIG. 8.—Water Gas Equilibrium, $K_c = \frac{(H_2O)(CO)}{(CO_2)(H_2)}$.

The comparison between the values calculated by formulæ A, B, C and (12) is shown diagrammatically in fig. 8. It will be seen that the values for K_c given by formula (12) lie very close to those given by formula A up to a temperature of 3000° K, and trend towards the values computed by formula C as the temperature increases above this figure.

Propellant compositions and calorimetric values.

The percentage compositions of the propellants used are set out in Table VII.

(The nitro-cellulose is composed of a mixture of gun cotton ($C_{24}H_{29}N_{11}O_{42}$) and collodion ($C_{24}H_{31}N_9O_{38}$), the N content depending on the proportions used.)

Samples of each propellant were fired in a calorimetric bomb (800 cm.^{3} volume) at a density of loading of 0·1, and the calorimetric values (water liquid) were determined.* Previous experience with gas analyses under these conditions has shown that the products "freeze" at a temperature corresponding to a value of K_c lying between 2·4 and 2·6. In addition, the percentage of methane formed is in general less than 0·2, and no correction consequently has been made on this account.

TABLE VII.—Propellant compositions.

Lot.	Cord diameter (cm.)	Nitro-cellulose.	N content per cent.	Nitro-glycerine $C_3H_5N_3O_9$.	Stabiliser $C_{12}H_{11}N$.	Volatile matter C_3H_6O.	Moisture H_2O.
N (1)	0·071	97·10	12·6	—	0·47	—	2·43
N (2)	0·215	96·90	12·6	—	0·46	2·14	0·50
N (3)	0·554	94·80	12·6	—	0·45	4·25	0·50
C (1)	0·066	71·03	13·2	28·74	—	0·23	—
C (2)	0·328	70·16	13·2	28·67	—	1·17	—
C (3)	0·890	68·91	13·2	28·79	—	2·30	—
B (1)	0·064	40·43	12·6	59·40	—	0·17	—
B (2)	0·430	40·49	12·6	59·35	—	0·16	—
B (3)	1·200	40·57	12·6	59·26	—	0·17	—

Using the heats of formation given in Table III, and accepting a value of 2·5 for K_c, the heat liberated per gram (water liquid) has been calculated for the respective propellants, and the comparison between calculated and observed values is set out in the following table :—

TABLE VIII.—Comparison between observed and calculated calorimetric values.

Lot.	Calorimetric value (water liquid) in cals./gm.	
	Observed.	Calculated.
N (1)	936	934
N (2)	896	891
N (3)	831	831
C (1)	1250	1246
C (2)	1220	1217
C (3)	1170	1185
B (1)	1470	1447
B (2)	1465	1447
B (3)	1460	1446

---

* The determinations were carried out by T. C. SUTTON, of the Research Department, Woolwich.

Calculation of T_0.

The water-liquid calorimetric values are used as a check on the heats of formation taken and on the chemical compositions. For the calculation of T_0 the water-gaseous calorimetric values are required, together with the nature of the gas-complex at the temperature of explosion. The method of calculation follows normal practice,* and may be illustrated by consideration of B (1). In the first place, the composition is expressed in gm. atoms per gram of the respective elements C, H, N and O, and the heat of formation of the propellant is calculated from the chemical analysis. A probable value of T_0 can be deduced from the observed water-liquid calorimetric value. This furnishes a trial value for K_c for ascertaining the composition of the gas complex at temperature T_0, whence can be obtained the heat evolved by the formation of the gases adjusted to constant volume conditions, and to the water-gaseous calorimetric value. Using the values tabulated for mean molecular heats at constant volume the heat contents can be computed for a range of temperatures, and a value of T_0 is obtained to correspond to the water-gaseous calorimetric value. If this value of T_0 is not in agreement with the value of K_c taken, an adjustment is made by inspection, the process being repeated until consistent values of T_0 and K_c for the water-gas reaction are secured.

Lot B (1)—*Calculation of* T_0.

The nitro-cellulose used has a 12·6 per cent. N content. The specification per gram is therefore :—

$$\frac{0\cdot4 \times 0\cdot4043}{1143} C_{24}H_{29}N_{11}O_{42} + \frac{0\cdot6 \times 0\cdot4043}{1053} C_{24}H_{31}N_9O_{38}$$
$$+ \frac{0\cdot5940}{227} C_3H_5N_3O_9 + \frac{0\cdot0017}{58} C_3H_6O,$$

or in gm. atoms/gm. :—

$$0\cdot016863 \, (C) + 0\cdot024504 \, (H) + 0\cdot011480 \, (N) + 0\cdot038277 \, (O).$$

The heat of formation per gram of propellant = 519·2 cals./gm. Assuming a value of 15·8 for K_c, corresponding to $T_0 = 4170°$ K, approximately, the constitution of the gases in gm. mols./gm. is :—

$$0\cdot009708 \, (CO_2) + 0\cdot007155 \, (CO) + 0\cdot000546 \, (H_2) + 0\cdot011706 \, (H_2O)$$
$$+ 0\cdot005740 \, (N_2),$$

giving (Σ gm. mols.)/gm. = 0·034855.

Adjusting to constant volume conditions the heat evolved by formation of the gases per gram of propellant = 1850·5 cals./gm., the calorimetric value (water-gaseous) being in consequence 1331·3 cals./gm. This value of the heat contents corresponds

---

* *Cf.* Henderson and Hassé, *loc. cit.*, p. 465 *et seq.*

to a temperature $T_0 = 4172°$ K. The results of calculation per gram of propellant for the whole of the propellants used are assembled in the following table :—

TABLE IX.—Gas composition and temperature of explosion (T_0).

Lot.	Gas (gm. mols./gm.).						T_0 (°K).
	CO_2.	CO.	H_2.	H_2O.	N_2.	(Σ gm.mols.)/gm.	
N (1)	0·004335	0·017432	0·004463	0·010543	0·004373	0·041146	2998
N (2)	0·003649	0·019174	0·005611	0·009398	0·004363	0·042195	2927
N (3)	0·003200	0·020244	0·006979	0·008827	0·004269	0·043519	2758
C (1)	0·007140	0·011946	0·001370	0·011214	0·005241	0·036911	3781
C (2)	0·006607	0·012771	0·001676	0·011272	0·005195	0·037521	3706
C (3)	0·005964	0·013748	0·002016	0·011367	0·005144	0·038239	3617
B (1)	0·009708	0·007155	0·000546	0·011706	0·005740	0·034855	4172
B (2)	0·009709	0·007155	0·000546	0·011704	0·005739	0·034853	4172
B (3)	0·009699	0·007176	0·000558	0·011698	0·005737	0·034868	4170

PART IV.—THE EQUATION OF STATE.

On general dynamical grounds at high temperatures where molecular cohesion effects are negligible and where it can be assumed that the molecules are effectively spherical in shape the equation of state of a gas mixture takes the form*

$$p_0 = \lambda\,(\Delta + \eta\,\Delta^2 + a\eta^2\,\Delta^3 + \ldots) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

The gases under investigation are in all cases a complex of CO_2, CO, N_2, H_2 and H_2O, and the conditions of aggregation are those of dissociative equilibrium. In equation (13) we have therefore in the units used that λ varies as the product of (Σ gm. mols)/gm. and T_0, the term (Σ gm. mols.)/gm. having reference to the fact that the control for dissociative equilibrium conditions is the water-gas reaction,

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

the value of (Σ gm. mols.)/gm. remaining invariant for a given propellant composition, but the gm. mols. of the respective constituents varying with the temperature.

A close approximation to equation (13) can be obtained by writing it in the form

$$p_0 = \lambda \Big/ \left(\frac{1}{\Delta} - \eta\right) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

which is formally identical with the NOBLE and ABEL equation. There is, however, an important difference in the physical interpretation of their form and that used here, in that NOBLE and ABEL introduced the term η to take account of the solid products occurring with the type of explosive with which they were dealing, no allowance being

---

* *Cf.* JEANS, "The Dynamical Theory of Gases," p. 172. BOLTZMANN by the method of the virial calculates the value of *a* as $\frac{5}{8}$ (*cf.* Vorlesungen über Gastheorie, vol. II, § 51).

made by them for the volume occupied by the molecules of the gas.* In the present connection η, by the Kinetic Theory of gases, must be four times the volume of the molecules contained in 1 gm. of the gas complex. The mean derived uncooled pressures entered in Table II have been analysed on the basis of equation (14) and lead to the following best fitting values for λ and η :—

TABLE X.—Experimental values of λ and η.

Lot.	λ.	η.
N (1)	10,560	0·94
N (2)	10,394	0·94
N (3)	10,090	0·94
C (1)	11,938	0·93
C (2)	11,974	0·93
C (3)	11,791	0·93
B (1)	12,148	0·91
B (2)	12,209	0·91
B (3)	12,256	0·91

Using the foregoing values of λ and η in equation (14), the fit is shown in Table XI.

TABLE XI.—Comparison between observed uncooled pressures and those derived from equation (14), using Table X.

(i) Nitro-cellulose.

Δ (gms./cm.^{3}).	p_0 (kg./cm.^{2}).					
	N (1).		N (2).		N (3).	
	Obs.	Derived.	Obs.	Derived.	Obs.	Derived.
0·2479	3371	3413	3351	3359	3267	3261
0·2211	2924	2947	2892	2901	2825	2816
0·2049	2701	2680	2639	2638	2562	2561
0·1819	2314	2317	2294	2280	2200	2214
0·1546	1917	1910	1878	1880	1806	1825
0·1344	1639	1625	1588	1599	1561	1552
0·1066	1253	1251	1240	1231	1185	1195
0·0755	868	859	863	845	812	820
0·0585	684	654	642	644	640	625
0·0420	491	462	471	455	465	441
0·0263	322	285	292	280	284	272

---

* PETAVEL, *loc. cit.*, p. 385.

TABLE XI.—(continued).

(ii) 70/30 Cordite.

Δ (gms./cm.^{3}).	p_0 (kg./cm.^{2}).					
	C (1).		C (2).		C (3).	
	Obs.	Derived.	Obs.	Derived.	Obs.	Derived.
0·2479	3805	3846	3834	3858	3817	3799
0·2211	3322	3323	3329	3333	3299	3282
0·2049	3023	3022	3020	3031	2993	2985
0·1819	2617	2613	2625	2621	2575	2581
0·1546	2148	2156	2164	2162	2136	2129
0·1344	1833	1834	1850	1839	1800	1811
0·1066	1419	1413	1421	1417	1394	1395
0·0755	978	970	1014	973	952	958
0·0585	765	739	768	741	730	730
0·0420	556	522	561	523	515	515
0·0263	349	322	367	323	304	318

(iii) 40/60 Ballistite.

Δ (gms./cm.^{3}).	p_0 (kg./cm.^{2}).					
	B (1).		B (2).		B (3).	
	Obs.	Derived.	Obs.	Derived.	Obs.	Derived.
0·2211	3387	3362	3383	3379	3372	3392
0·2049	3070	3060	3064	3075	3085	3087
0·1819	2648	2648	2657	2661	2675	2671
0·1546	2165	2186	2203	2197	2199	2205
0·1344	1879	1860	1870	1870	1868	1877
0·1066	1417	1434	1443	1441	1460	1447
0·0755	976	985	1012	990	1012	994
0·0585	755	751	786	755	786	757
0·0420	533	531	562	533	536	535
0·0263	307	327	367	329	325	330

In determining the values for λ and η, weight has been given to the pressures corresponding to densities of loading above 0·0585 for the reasons quoted at the end of Part II. It will be noted that at the lower densities of loading there is in some cases a tendency for the smoothed figures to be below the observations.

The quantities λ and η determined in this way are essentially inter-connected and must be accepted together, but the values obtained can most conveniently be discussed separately. Theoretically, the quantity λ is directly ascertainable from the thermodynamical data given in Table IX, the relationship* giving λ for pressures expressed as kg./cm.^{2} being :—

$$\lambda = 84\cdot80 \{(\Sigma \text{ gm. mols.})/\text{gm.}\} T_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

Comparison between the values of λ given by experiment and by equation (15) is shown below :—

TABLE XII.—Experimental and theoretical values of λ.

Lot.	λ.		Ratio (Observed to Calculated).
	Observed.	Calculated.	
N (1)	10,560	10,460	1·010
N (2)	10,394	10,473	0·992
N (3)	10,090	10,178	0·991
C (1)	11,938	11,835	1·009
C (2)	11,974	11,791	1·016
C (3)	11,791	11,729	1·005
B (1)	12,148	12,331	0·985
B (2)	12,209	12,330	0·990
B (3)	12,256	12,330	0·994

As regards the values for λ given by equation (15), uncertainty can enter only in connection with the molecular heat values tentatively accepted as most probably accurate on the reasons already adduced, these being based on conditions quite distinct from those of the present investigation. The agreement now established between the values for λ as calculated on the assumed molecular heats and as derived from the pressure observations lends strong support to the arguments used, and it would seem that the present method of pressure measurement with adjustment for cooling, together with the application of relevant thermo-dynamic formulæ furnishes an indirect method for assessing temperatures and molecular heats within the region in question, namely, between 2700° K. and 4200° K.

Discussion of the co-volume and the equation of state.

The accepted practice among writers on ballistics has been to assume that the co-volume η is proportional to (Σ gm. mols.)/gm. The highest determined value of η is 0·94 for the N propellants, the average (Σ gm. mols.)/gm. being 0·042287, the ratio being 22·23. The lowest determined value is 0·91 for the B propellants, the corresponding figure for (Σ gm. mols.)/gm. being 0·034859, the ratio being 26·08. It appears, therefore, that a simple relationship of this type can hold to a first approximation only, and it becomes necessary to appeal to other considerations for the physical interpretation of η.

---

* In evaluating the constant, the number of cm.^{3} occupied by 1 gm. mol. of a gas at N.T.P. has been taken as 22,412, the relative density of Hg as 13.596, and the absolute zero of temperature as —273·09° C.

From the form of equation (14) η must be four times the volume of the molecules contained in 1 gm. of the gas complex. The difficulty lies in assessing the magnitude of the respective molecule volumes at the temperatures encountered. It is known that the sphere of action of the molecules shrinks in size under increasing temperature conditions,* reaching in the limit a "hard kernel" value. An upper limit to the hard kernel molecular radius ($\frac{1}{2}\sigma_\infty$) can be evaluated from a knowledge of the maximum density of the substance when in the solid or liquid state. A lower limit can be determined on the basis of the Mossotti hypothesis from the di-electric constant, the molecule being regarded as a sphere which is a perfect conductor of electricity, the value of ($\frac{1}{2}\sigma_\infty$) obtained in this manner corresponding to the radius of the electrical structure. Intermediate values are given by SUTHERLAND's formula†—

$$\sigma = \sigma_\infty \left[1 + \mathrm{C}/\mathrm{T}_0\right]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which derives values for C and σ_∞ from viscosity, heat conduction and gaseous diffusion measurements of σ at various temperatures. In applying the data in the present connection a difficulty is encountered in that limiting values are not known for the H_2O molecule. The broad inference, however, from the general trend of the observations is that molecules of differing nature but of equal size under one temperature condition will be very nearly of equal size under a second temperature condition (the size diminishing with increasing temperature). The H_2O molecule has, therefore, been taken for calculation purposes to be the same size as the CO_2 molecule under corresponding temperature conditions.

Both the upper limit for ($\frac{1}{2}\sigma_\infty$) given by density measurements and that calculated from SUTHERLAND's formula lead to limiting values for η which are far too high. The limiting values given by the dielectric constant method‡ can be calculated from the formula :—

$$\mathrm{L}tg\,(\eta) = 4 \times 6{\cdot}062 \times 10^{23} \times \tfrac{4}{3}\pi \times \Sigma\left[(\tfrac{1}{2}\sigma_\infty)^3 \,.\, g\right] = 1{\cdot}0157 \times 10^{25} \times \Sigma\left[(\tfrac{1}{2}\sigma_\infty)^3 \,.\, g\right] \quad (17)$$

where the summation extends over the number of gm. mols./gm. of each constituent of the gas complex, $6{\cdot}062 \times 10^{23}$ being Loschmidt's number, and g symbolising individual gm. mols./gm. The mean values for each propellant are assembled in Table XIII.

TABLE XIII.—Comparison between experimental and mean limiting values of η.

Composition.	η.		Ratio.
	Experimental.	Limit (hard kernel).	
Nitrocellulose	0·94	0·877	1·072
Cordite	0·93	0·863	1·078
Ballistite	0·91	0·847	1·074

---

* *Cf.* JEANS, "The Dynamical Theory of Gases," Chaps. 11 and 14.

† 'Phil. Mag.,' vol. 36, p. 507 (1893) ; JEANS, *loc. cit.*

‡ The values of the dielectric constants used are those determined at ordinary temperatures.

The ratio between the hard kernel dielectric values and those observed is substantially constant, and assuming that at these high temperatures each type of molecule is affected in the same way by the temperature, the inference is that the molecular radii are in each case some 2·5 per cent. greater than the limiting values given by the dielectric constant method. The co-volume η can therefore be calculated directly from the analysis of (gm. mols.)/gm. for each gas complex from the formula*—

$$\eta = 1\cdot092 \times 10^{25} \times \Sigma \left[(\tfrac{1}{2}\,\sigma_{\infty})^3 \,.\, g \right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

It is interesting to note that within the limits of the experiments, the ratio between the experimental and the hard kernel values of η is invariant over the whole range of temperature. From the preceding the explicit formulation of the equation of state of a propellant gas complex is :—

$$p_0 = \frac{84\cdot80\,\{(\Sigma \text{ gm. mols.})/\text{gm.}\}\,.\,T_0}{\dfrac{1}{\Delta} - 1\cdot092 \times 10^{25} \times \Sigma \left[(\tfrac{1}{2}\,\sigma_{\infty})^3 \,.\, g \right]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

In considering the form of the equation, it may be observed that the gases under investigation are probably the nearest approach to certain types of matter in a stellar condition that it is possible to obtain and experiment with terrestrially. The density of the gas complex approaches that of a light mineral oil, temperatures attain some 4000° K, and pressures reach 3800 kg./cm.². In these conditions the spheres of action of the molecules have been shown to be slightly greater than the volumes of their electrical structures.

SUMMARY.

The aim of the investigation has been to formulate an expression for the equation of state of the gases resulting from explosions of propellant of known chemical composition. With this end in view it has been found necessary :—

(1) To evolve adequate methods for the measurement of pressure in the conditions encountered ;

(2) To investigate in detail the nature of, and to establish an expression for, the energy losses arising from the cooling of the hot gases at the wall surface of the vessel, together with the work absorbed in wall stress ;

(3) To re-formulate in the light of the latest available data expressions for assessing the molecular heats at constant volume of the various constituents of the gas complex, for temperatures ranging from 2700° K. to 4200° K. ;

(4) To re-calculate the equilibrium constant for the water-gas reaction over the range of temperatures involved ;

(5) To utilise the experimental evidence available for determining the effective volume occupied by the gas molecules.

---

* The respective values of $(\frac{1}{2}\sigma_{\infty}) \times 10^8$ used in the calculations are as follows :—

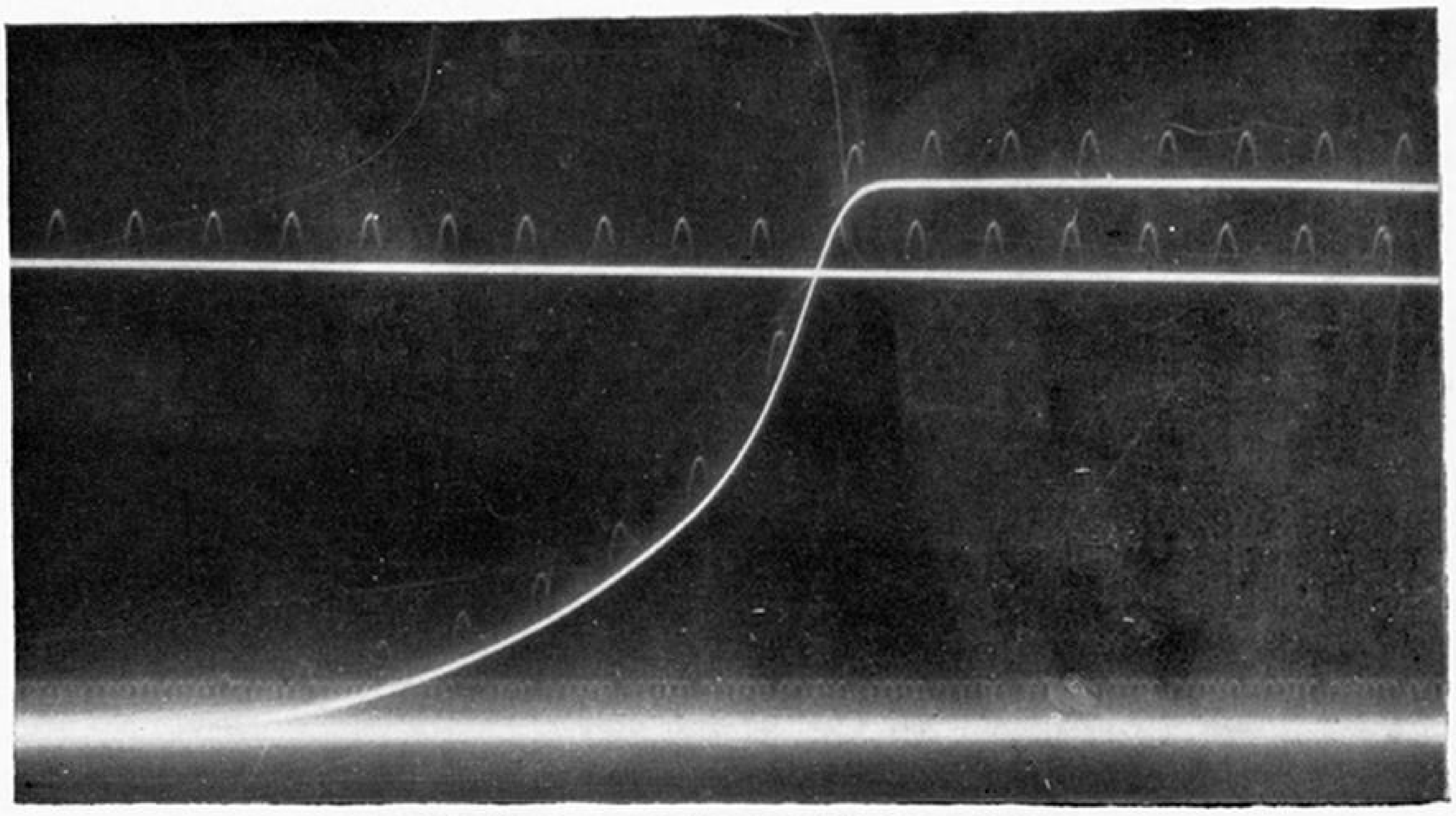
$CO_2 = 1\cdot40$; $H_2O = 1\cdot40$; $CO = 1\cdot26$; $N_2 = 1\cdot20$; $H_2 = 0\cdot92$.

Agreement to within 2 per cent. has been established for the quantity (λ) (the *ballistic force* of the propellant), between the values derived from direct experiment and those obtained from thermodynamical considerations; and it has been shown that the co-volume (η) can be evaluated from the constituents of the gas complex by using the hard kernel values of the molecular radii (dielectric constant method) increased by some 2·5 per cent.

The investigation has been restricted to the consideration of propellants in the gaseous state; the question of the intrinsic rates of burning for present purposes entering only implicitly in connection with total times of combustion.

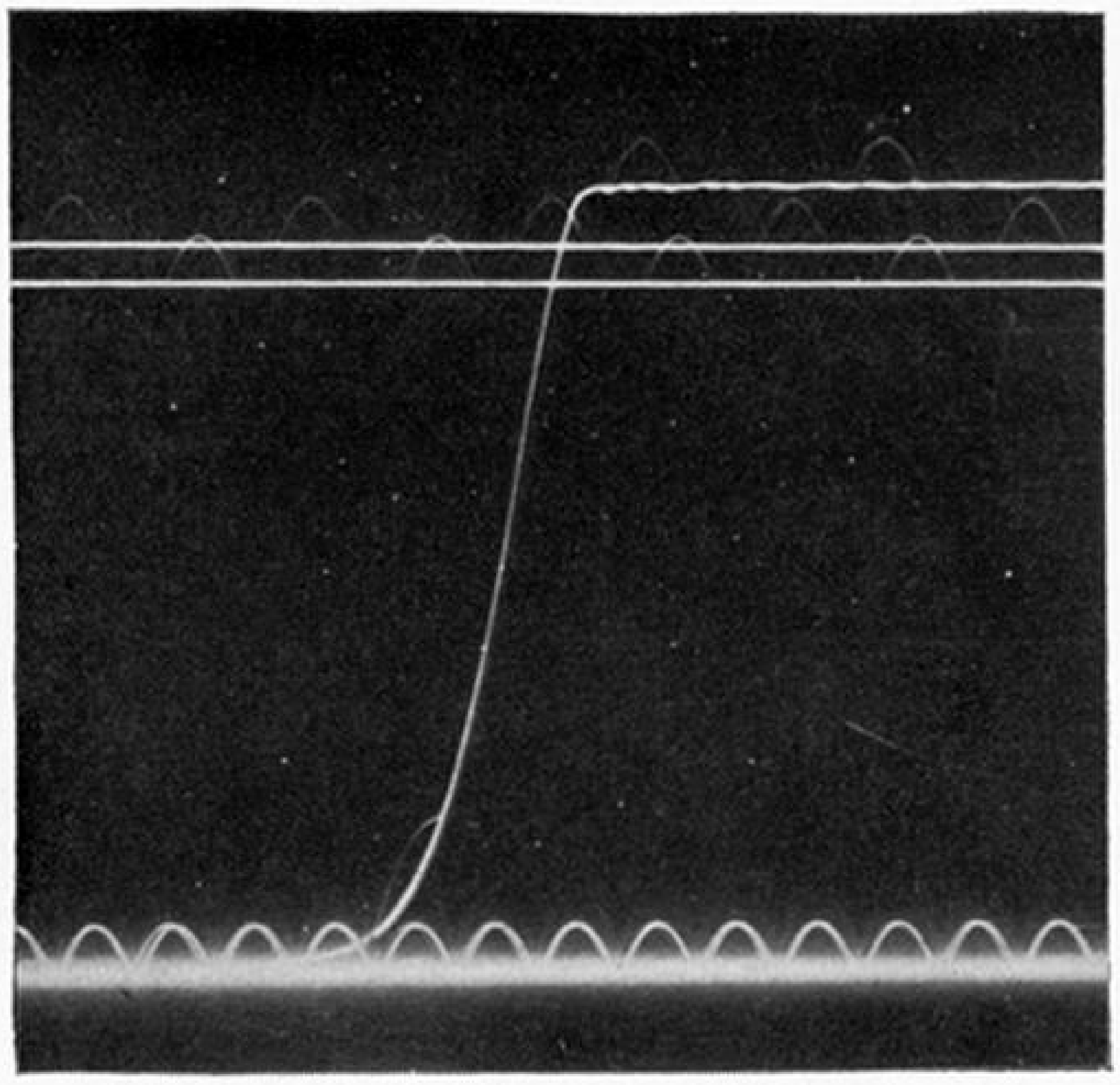
In conclusion, we wish to extend our thanks to Mr. J. G. Madden, Mr. C. M. Balfour and other members of the scientific staff who have assisted in the conduct of the experimental work, and to Brigadier R. K. Hezlet and Commander A. C. Goolden for affording us special facilities for carrying out the work and their interest in it. We desire also to acknowledge the courtesy of the Director of Artillery, the Director of Naval Ordnance, and the Ordnance Committee in approving publication.

A.



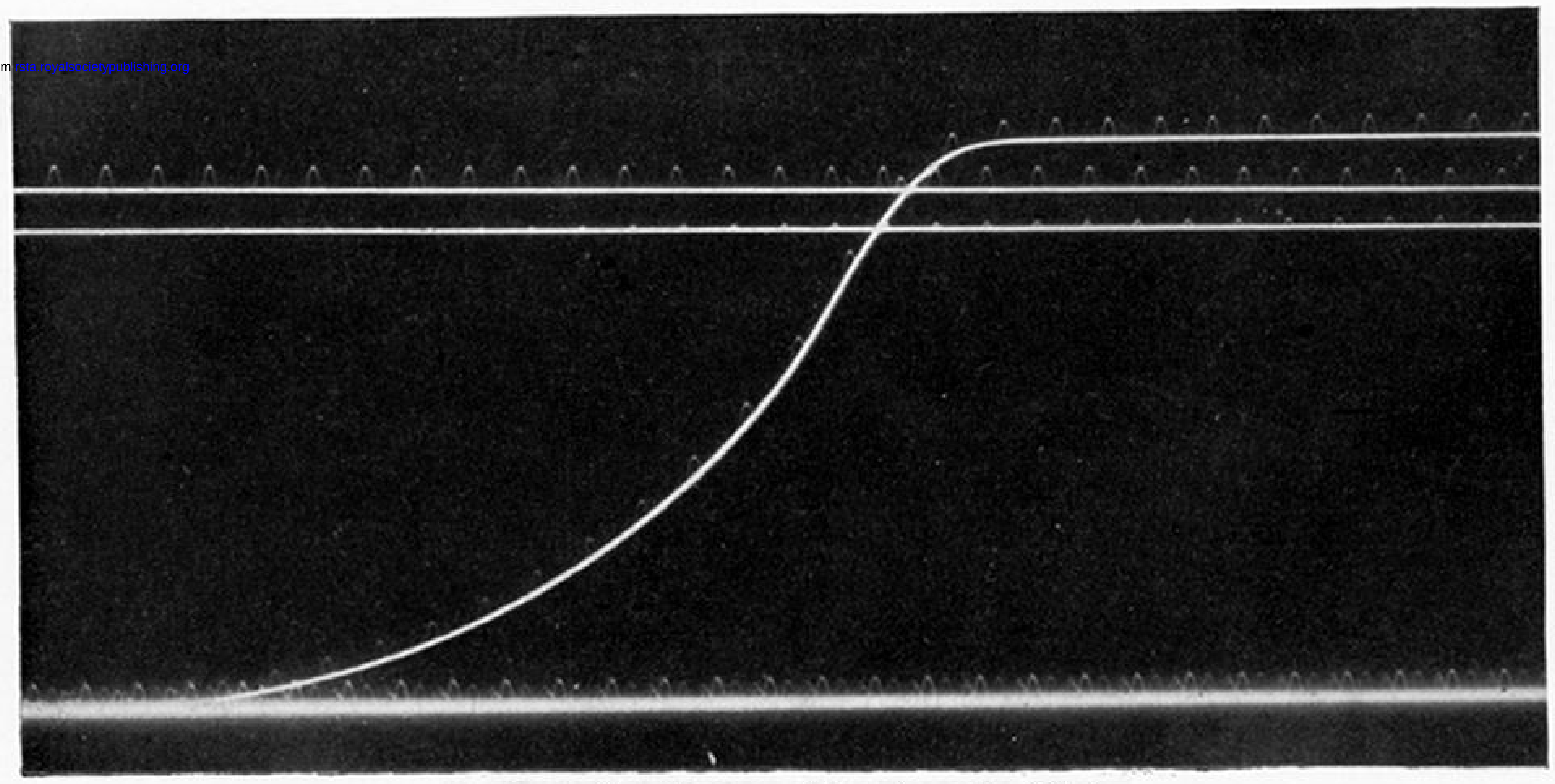
B (3). Large capacity, $\Delta = 0 \cdot 2211$.

B.



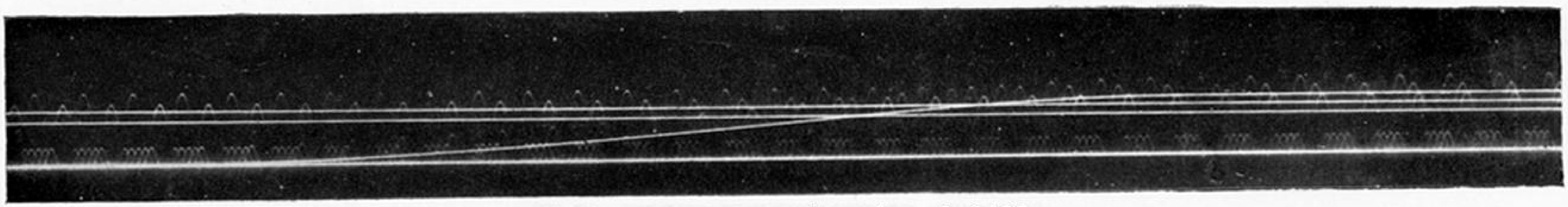
C (1). Large capacity, $\Delta = 0 \cdot 2211$.

C.



C (3). Small capacity, $\Delta = 0 \cdot 2211$.

).



C (2). Large capacity, $\Delta = 0 \cdot 0420$.

FIG. 4.—Typical Records.

[*Facing p.* 44.