Gaseous Combustion at Medium Pressures. Part I. Carbon Monoxide-Air Explosions in a Closed Vessel. Part II. Methane-Air Explosions in a Closed Vessel

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VIII. *Gaseous Combustion at Medium Pressures. Part I.—Carbon Monoxide-Air Explosions in a Closed Vessel. Part II.—Methane-Air Explosions in a Closed Vessel.*

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During the past five years a programme of research involving air-fuel explosions in a closed vessel has been in progress at the National Physical Laboratory for the Engineering Research Board of the Department of Scientific and Industrial Research. Among the experimental results obtained, those relating to Carbon Monoxide and Methane were considered likely to be of interest to the Society, and form the subject of the present communication.

Of the two investigations described, the first gives experimental data on the respective influences of hydrogen-air and water vapour on a carbon monoxide-air explosion, and the second relates to explosions of methane and air over a comparatively wide range of initial temperature and pressure.

PART I.—CARBON MONOXIDE-AIR EXPLOSIONS IN A CLOSED VESSEL, WITH SPECIAL REFERENCE TO THE EFFECT OF ADDITIONS OF (*a*) HYDROGEN-AIR AND (*b*) WATER VAPOUR.

When Bone and Haward published their interesting experiments* showing, *inter alia*, the marked influence of a small proportion of H_2-air on a CO-air explosion at an initial pressure of 50 atmospheres and at atmospheric initial temperature, it was suggested by the Engine Sub-Committee of the Aeronautical Research Committee that a similar series of experiments, at initial pressures corresponding to engine conditions, should be put in hand at the National Physical Laboratory. Mr. H. T. Tizard made the further suggestion that, at the same time, the effect of water vapour additions to a CO-air mixture should be investigated.

In carrying out these suggestions three series of explosions were performed at an initial pressure of 76·8 lbs. per square inch (absolute), and at an initial temperature of 50° C., a pressure-time record being obtained of each explosion.

The mixtures in the respective series were :—

(1) $2(mH_2 + nCO) + O_2 + 3\cdot8N_2$, where m and n are variable, but $m + n = 1$; water vapour content less than 1 in 2000.

* 'Roy. Soc. Proc.,' A, vol. 100 (1921).

(2) $2CO + O_2 + 3 \cdot 8N_2$, with water vapour additions varying from $0 \cdot 3$ to $2 \cdot 4$ volumes per 100.

(3) A repetition and extension of (1), including the addition of $1 \cdot 2$ volumes of water vapour per 100 of mixture.

Apparatus and Experimental Procedure.

(1) *The Explosive Mixture.*—The comparatively dry explosive mixture was prepared in bulk in a high-pressure gas cylinder and drawn off as required for explosion in an electrically heated steel vessel (7 ins. diameter by 8 ins. long—surface corroded—*vide* fig. 1) provided with a spark gap ($\frac{1}{2}$ mm.) at the centre and fitted with a manometer (*vide* fig. 2) for giving a pressure time record of the explosion.*
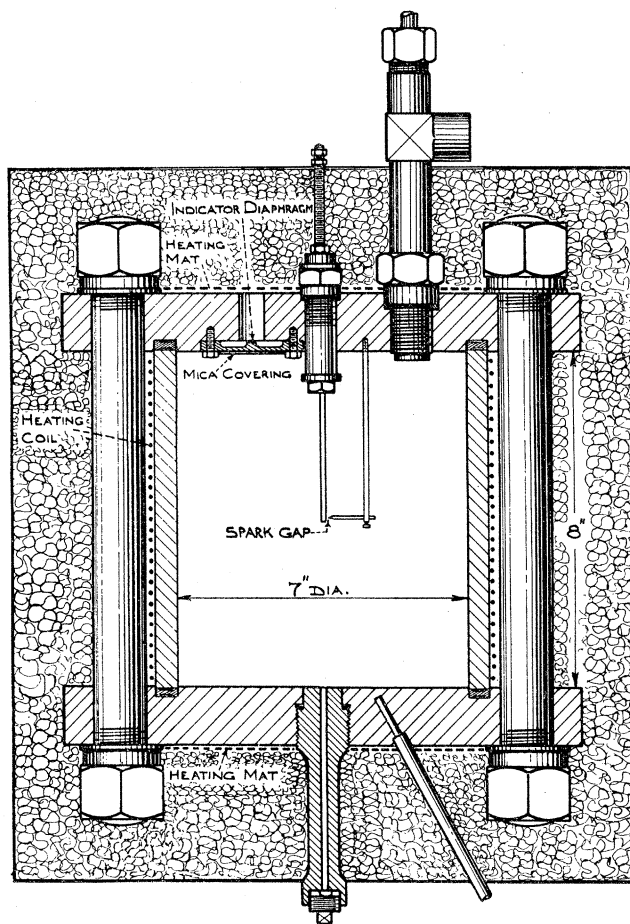

FIG. 1.—Mild-steel explosion vessel.

By using two mixing cylinders, one of which contained a " complete combustion " mixture of hydrogen and air, and the other a similar mixture of carbon monoxide and

* For further details of apparatus reference should be made to 'Aeronautical Research Committee Reports and Memoranda,' No. 902 (H.M. Stationery Office).

air, further " complete combustion " mixtures of these mixtures could readily be obtained by making successive additions to the CO-air cylinder from the H_2-air cylinder. Thus, at the start of a series, separate H_2-air and CO-air mixtures were available for the separate H_2-air and CO-air explosions and, at the finish, sufficient H_2-air mixture remained for further explosions of that mixture to check the constancy of the recording apparatus.
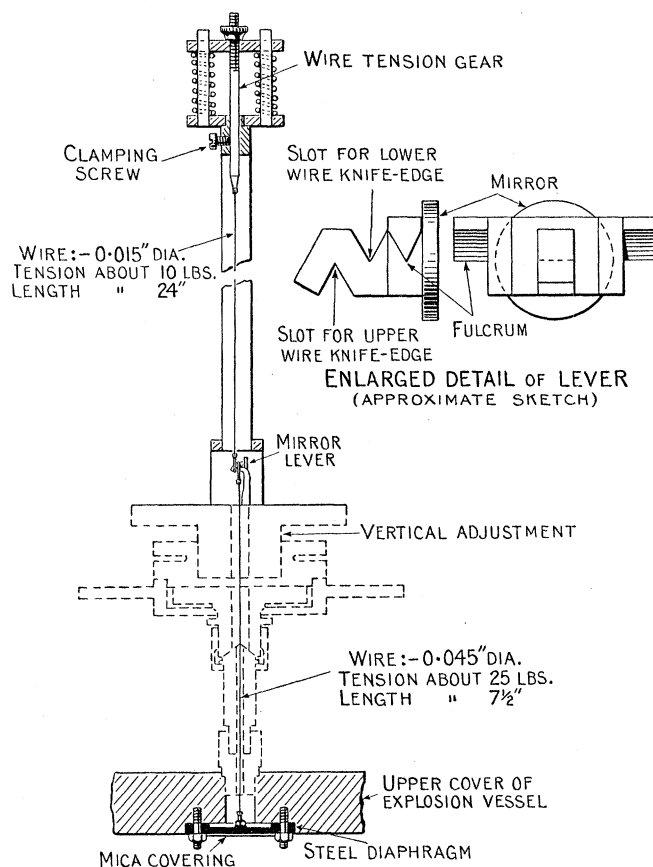

FIG. 2.—Optical indicator.

The primary CO-air and H_2-air mixtures were made up at an initial pressure of about 17 atmospheres, and were sampled, analysed and adjusted until of the desired " complete combustion " composition. The subsequent mixtures of these mixtures were analysed and their composition determined from a mean of the analysis and pressure-mixing figures.

As to humidity, the mixtures were comparatively dry, as they were prepared largely from high-pressure gases, the water vapour content being estimated at less than 1 in 2000 (by volume). In the text such mixtures are sometimes referred to as " dry," to distinguish them from those to which water vapour additions were made.

The carbon monoxide was kindly supplied by Prof. BURSTALL (Birmingham University), who states that the gas was prepared by the well-known method of adding formic acid

to strong sulphuric acid.   The process was carried out in electrically heated silica flasks, and the gas generated was cooled, scrubbed with sodium hydrate, passed through two washing flasks to an iron gas-holder, then compressed into storage cylinders to about 120 atmospheres pressure.   The consignment used for these experiments was analysed, after receipt, and its composition appeared to be :—

	Per cent.
CO	97·3
H_2	0·2
CO_2	0·2
O_2	0·4
N_2 (by difference)	1·9
	100·0

As the gas was by no means odourless, but had a smell suggesting acetylene, it was tested for C_2H_2 (and other heavy hydrocarbons) by fuming sulphuric acid, but no appreciable amount was detected.   For the hydrogen determination it was necessary to analyse comparatively large volumes of the CO ; in four cases 170 c.c. were taken and in one case 680 c.c.   After absorbing the CO and O_2 by a hydrochloric acid solution of cuprous chloride, the remnant gases were treated with caustic potash—supplied with oxygen in the form of air—and passed over palladium in order to remove the hydrogen by fractional combustion.   Successive determinations gave values decreasing from 0·33 per cent. to 0·13 per cent.

A confirmation of the CO analysis was sought by exploding CO-air mixtures of varying strength in a small glass explosion vessel and noting the contraction in volume and the CO_2 formed, but the former measurement exceeded that due to the oxidation of the CO and small volume of H_2 by from 0 to nearly 3 per cent.   This effect may be due to the formation of oxides of nitrogen.

For the H_2-air mixtures, the hydrogen was the same as that used in previous work and was a particularly pure sample supplied by the British Oxygen Company.   The original analysis showed a purity of about 99·5 per cent.

When water vapour was added to the mixture the addition was made to each explosion vessel charge, the apparatus illustrated in fig. 3 being used.   The procedure in this case was to charge the explosion vessel to atmospheric pressure with " dry " mixture (valve A being closed), couple up the water vessel containing the weight of water to be evaporated, set dry mixture flowing slowly through junction box into the explosion vessel, open valve A and apply Bunsen burner to evaporate the water, close valve A and charge the vessel rapidly with dry mixture, until within a pound or two of the desired pressure, making the final pressure adjustments slowly.

The junction box, to which the water vessel was coupled and through which the " dry " mixture flows on its way to the explosion vessel, was maintained at about

110° C. The slow flow of mixture during the evaporation was designed to carry the water vapour into the explosion vessel, and the subsequent rapid flow to cause sufficient turbulence to mix water vapour and " dry " gas. Although the method was by no means perfect for obtaining a homogeneous mixture, it gave fairly consistent results and appeared to be sufficiently accurate for the purpose.
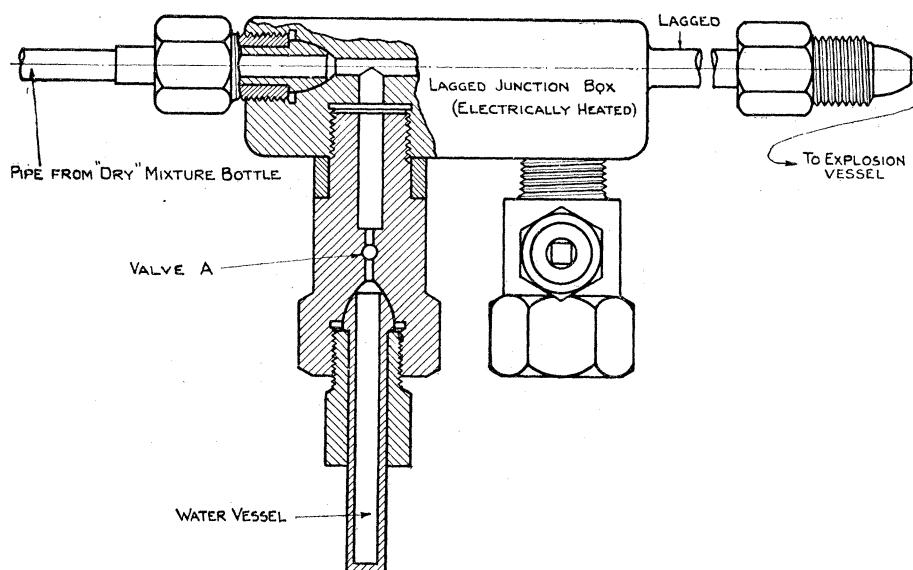

FIG. 3.—Apparatus for introducing water vapour.

Of the three series of explosions carried out, the first consisted of comparatively dry " complete combustion " mixtures of H_2 and air and of CO and air and of mixtures of these, the approximate mixture compositions being :—

		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
H_2-air	..	100	0·2	4·1	8·0	11·9	24·8	49·7
CO-air	..	0	99·8	95·9	92·0	88·1	75·2	50·3

These mixtures were exploded at an initial pressure of 76·8 lbs. per square inch (absolute) and at an initial temperature of 50° C., and pressure-time records obtained.

In the second series an explosion of nearly dry CO-air mixture was followed by explosions of the same mixture to which varying amounts of water vapour had been added—the initial pressure and temperature being the same as in the first series. The water vapour addition per 100 volumes of " dry " mixture varied from 0·3 to 2·56 volumes, but since the charge would be completely saturated by 2·38 volumes—the latter figure represents the maximum water vapour content before explosion.

Finally, a third series of explosions was put through for the purpose of checking the

first series and of obtaining information on the effect of a constant water vapour addition to mixtures of CO-air and H_2-air.   The mixture range was also extended to include

	Per cent.
H_2-air	2·2
CO-air	97·8

(2) *Pressure-Time Explosion Records.*—To record the pressure a solid-rimmed steel diaphragm was fitted flush with the inner surface of the cover of the explosion vessel. The diaphragm deflection—magnified over 1000 times—was recorded on sensitised paper, attached to a rotating drum having a peripheral speed of about 1 metre a second. In order to protect the diaphragm from temperature distortion during the early part of the explosion and cooling, a mica and thin sheet-metal cover was provided.   As the maximum diaphragm deflection was of the order of a couple of thousandths of an inch, inertia effects were eliminated.   The manometer was calibrated—*in situ*—against a standard pressure gauge, compressed air being used for the purpose.   The high-frequency vibration (about 1100 per second) shown on some of the Records (*vide* No. 558, fig. 5) is the natural period of the optical lever under the action of the two strained wires. The time-scale was indicated automatically on the cooling curves by means of tuning-fork interceptions of the light.

Experimental Results.

The results of the first series are given in Table I, and superimposed pressure-time records are shown in fig. 4.   Parts of the actual records (they are too long for complete reproduction) have been reproduced photographically to a reduced scale in fig. 5.

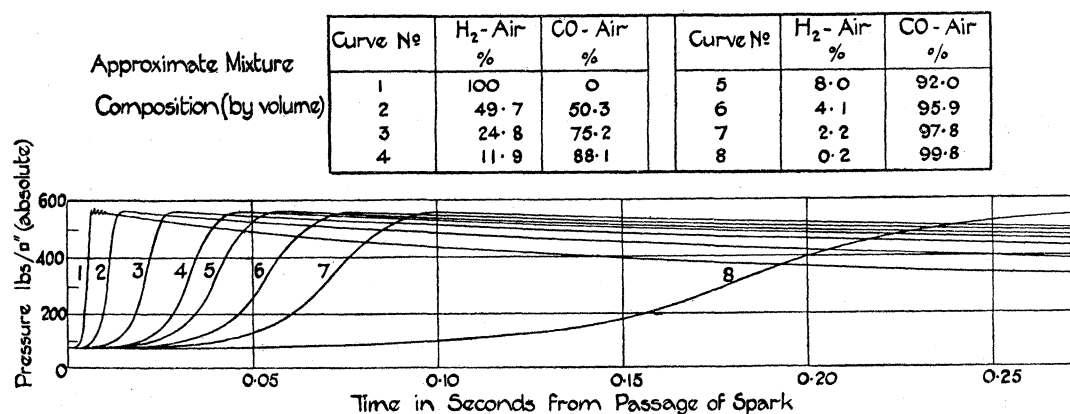| Approximate Mixture Composition (by volume)	Curve Nº	H_2-Air %	CO-Air %	Curve Nº	H_2-Air %	CO-Air %
	1	100	0	5	8·0	92·0
	2	49·7	50·3	6	4·1	95·9
	3	24·8	75·2	7	2·2	97·8
	4	11·9	88·1	8	0·2	99·8

FIG. 4.—Superimposed pressure-time records of " dry " mixtures of H_2-air and CO-air.

Table II applies to the second and third series.   Superimposed explosion records of the second series are given in fig. 8.   One record of the third series, that for the 2·2 per cent. H_2-air, is included in figs. 4 and 5.

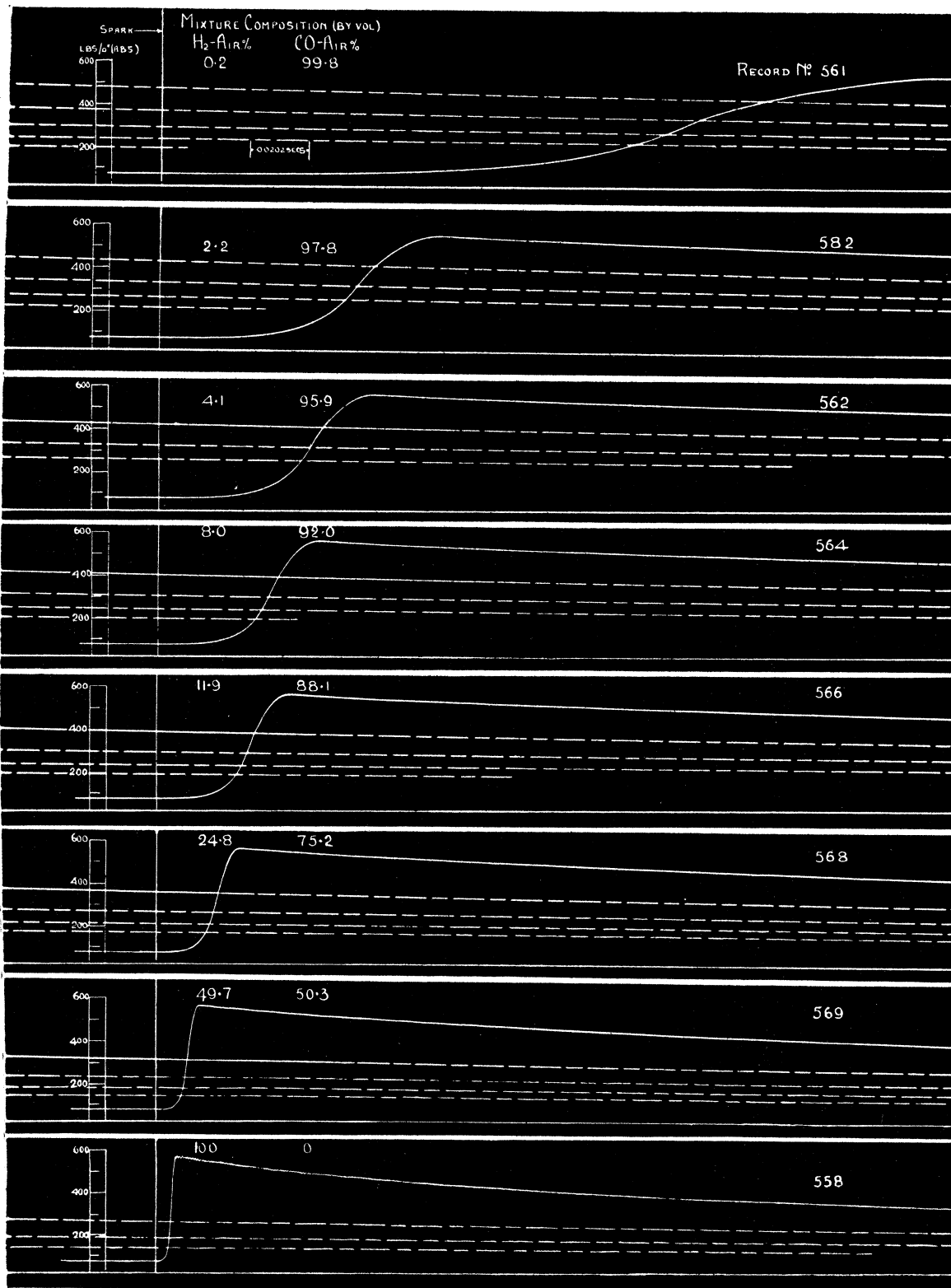FIG. 5.

The bracketed figures given in Tables I and II for the H_2-air explosions should be taken together; they indicate that a pressure very slightly less than the maximum was reached about 1/1000 seconds before the recorded maximum.

(I) *Effect of H_2-Air Additions to a CO-Air Mixture, the Mixture being Comparatively Dry.* (a) " *Explosion Time.*"—The influence of H_2-air additions to a CO-air mixture is clearly seen in figs. 4, 5 and 6.
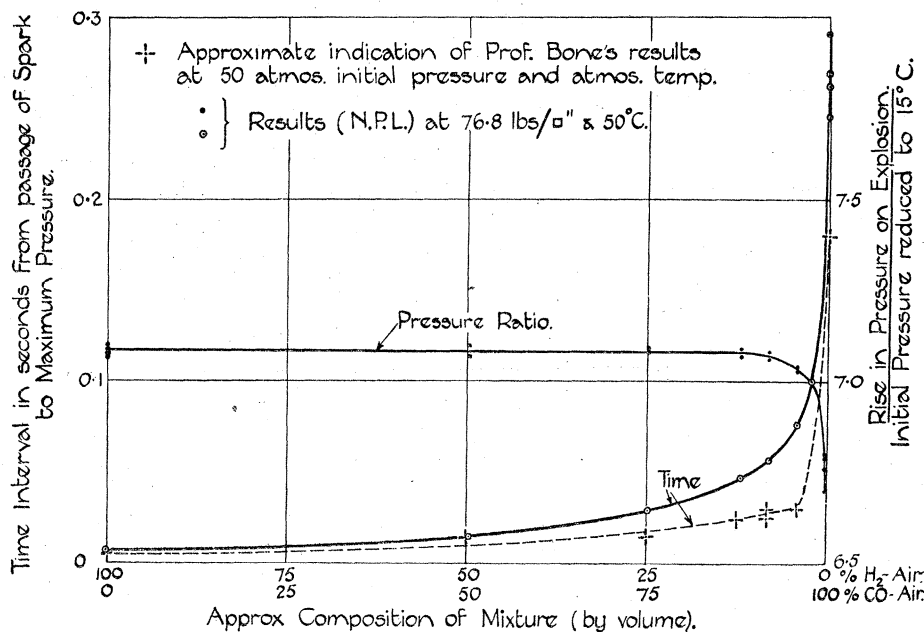

FIG. 6.—Effect of addition of H_2-air to a nearly dry CO-air mixture.

Just over 2 per cent. of H_2-air in the mixture reduces the explosion time from about 0·26 seconds to 0·1 seconds, and 4 per cent. reduces it to 0·076 seconds. With the latter percentage Prof. BONE, working at an initial pressure of 50 atmospheres and at atmospheric temperature, obtained a still greater effect, the explosion time being reduced from 0·18 to 0·03 seconds. Prof. BONE's results are indicated by the dotted curve in fig. 6.

In the present experiments, the " explosion time " for the " dry " CO-air mixture varied considerably. Thus, in Explosions 792–794 (Records 559–561), Table I, and 806 (Record 573), Table II, this interval varied from 0·246 to 0·29. This is probably due to slight variations in the humidity. Explosion 792 took place after a couple of H_2-air explosions, and it is possible that a trace of water vapour still existed, say, in the mica insulation of the sparking plug and in the joints of the explosion vessel. For each succeeding CO-air explosion the traces of water vapour from such sources would become less, and the explosion time tend to increase, as is the case. Explosion 806 was the first of a new series, and the explosion vessel was probably still drier. Considerable difficulty was experienced in igniting this charge by the " single " spark, the fourth

attempt being successful. After Explosion 814, it was intended to finish the water vapour series with a " dry " CO-air explosion, but as two attempts to fire the charge were without avail, the idea was abandoned. Prof. BONE, in his experiments, mentioned variations in the explosion time of the CO-air mixture and attributed it to slight changes in the hygroscopic state.

(b) *Maximum Explosion Pressures.*—It is of considerable interest to note that with all " dry " mixtures of H_2-air and CO-air the maximum explosion pressures are nearly the same and equal to that of the undiluted H_2-air mixture, whereas the undiluted " dry " CO-air mixture gave a maximum about 4 per cent. lower (*vide* page 340, on effect of water vapour addition). Prof. BONE,[*] however, obtained an 8 per cent. higher maximum with the CO-air mixture than with the H_2-air mixture, mixtures of which the thermal equivalents of the total energy were approximately the same. When comparing his maximum pressures for mixtures of H_2-air and CO-air (ranging from 390 to 427 atmospheres) the variations in their thermal equivalents, due to irregularities in mixture composition, must be borne in mind.

(c) *" Cooling " Curves.*—Prof. BONE remarked in connection with this high-pressure work :—

(1) With H_2-air, cooling commenced almost immediately after the attainment of the maximum pressure.

(2) With CO-air it was delayed for quite an appreciable time interval thereafter, showing that heat energy was still being liberated long after the maximum temperature had been reached.

(3) Subsequent cooling after the attainment of maximum pressure was very much slower in the CO-air than in the H_2-air explosions. In the former not only was there an interval of about $0 \cdot 05$ seconds during which the maximum pressure was fully maintained, but also subsequently the pressure fell at only half the rate it had done in the latter.

The present low-pressure experiments, however, show that the interval during which a constant maximum pressure is maintained is of the order of $0 \cdot 004$ seconds in the case of the dry CO-air mixture, and varies from $0 \cdot 001$ seconds to zero as the percentage of H_2-air increases.

Typical " cooling " curves have been plotted in fig. 7 in which zero time corresponds to the attainment of maximum pressure (*i.e.*, the cessation of rise).

(II) *The Influence of the Addition of Water Vapour to a CO-Air Mixture.* (a) *" Explosion Time."*—In spite of some uncertainty as to the thoroughness of the mixing of the water vapour and CO-air, the results of this series of experiments showed definitely that water vapour additions had a marked influence on the character of the explosion curve. Four of the explosion records, Nos. 573, 580, 578, and 575 are shown

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[*] *Loc. cit.*
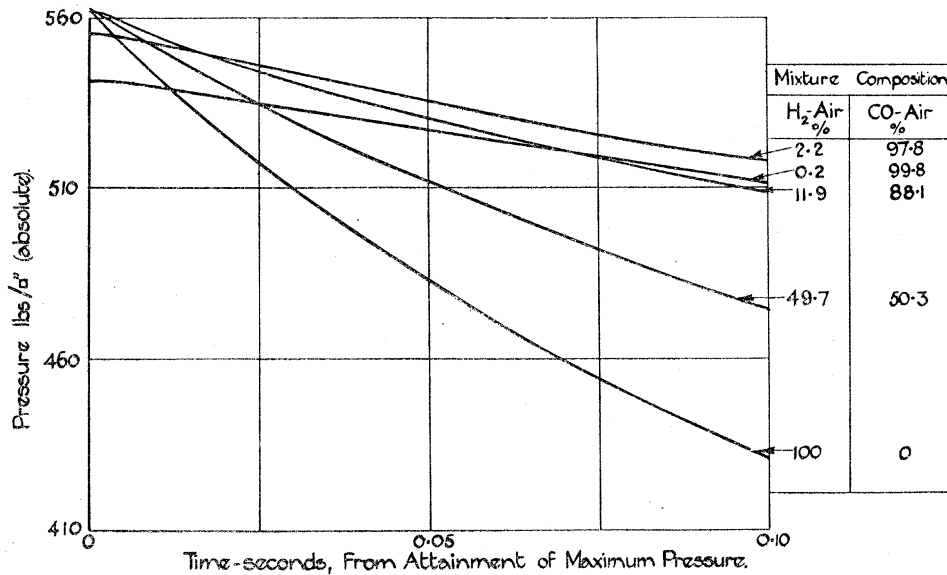
FIG. 7.—Typical cooling curves for nearly dry explosive mixtures.

superimposed in fig. 8.   The addition of 0·3 volume of water vapour to 100 volumes of comparatively dry CO-air mixture reduced the explosion time from about 0·29 to 0·16 second, whereas an addition of 1·68 volumes was associated with an " explosion time " of about 0·095.   The largest quantity of water vapour added was 2·56 volumes per 100 of mixture, but as the charge (at 50° C.) would be saturated by 2·38 volumes, the surplus would not be effective until after combustion had commenced.
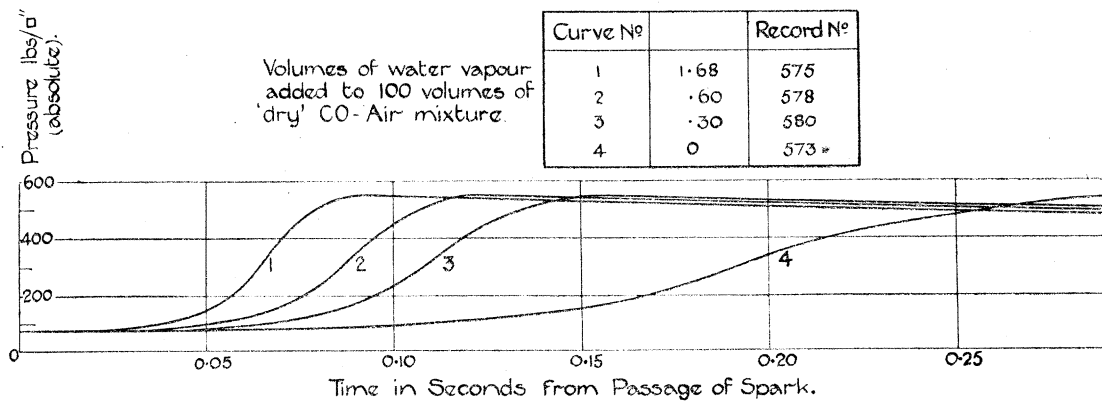
FIG. 8.—Superimposed pressure-time records, showing effect of water-vapour additions to nearly dry CO-air mixture.

(b) *Maximum Explosion Pressures.*—From the first portion of Table II it will be observed that the addition of 0·3 volume of water vapour results in the maximum pressure being increased by more than 2 per cent., and by doubling this water vapour addition (0·6 volume) a further increase of about 1 per cent. is obtained.

Although water vapour additions varied from 0·3 to 2·56 (2·38) volumes per 100 of

nearly dry CO-air mixture, the maximum explosion pressures show less than 1 per cent. variation, the decrease in the thermal equivalent of the mixture being apparently largely counteracted by other effects.

(c) " Cooling " Curves.—From figures given in Table II it will be observed that the pressure drop during 1/10 second from the attainment of maximum pressure varies from 29 lbs. per square inch for the " dry " CO-air mixture to 40 lbs. per square inch for the mixture containing about 1·7 per cent. of water vapour and 42 lbs. per square inch for 2·6 per cent.   The presence of water vapour leads to an increase in the apparent rate of cooling.

(d) Identical Explosion Records.—In comparing the pressure-time curves it was of interest to discover that almost identical explosion records were produced by :—

(1) The addition of 1·21 volumes of water vapour to 100 volumes of nearly dry CO-air mixture (Record 577, Table II).

(2) The addition of 2·1 per cent. of nearly dry H_2-air to nearly dry CO-air (Record 582, Table II).

For convenience of comparison, these records are shown superimposed in fig. 9, the
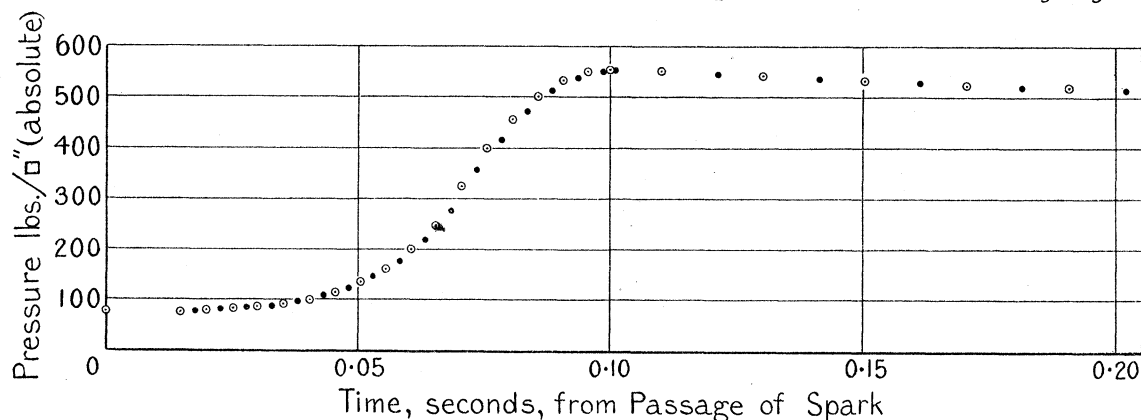
FIG. 9.—Superimposed pressure-time explosion records.

plain points applying to Record 577 and the encircled points to Record 582. If no nitrogen compounds were formed during combustion the composition of the products in the two cases would be :—

	CO_2 per cent.	H_2O per cent.	N_2 per cent.
(1)	33·98	1·46	64·56
(2)	33·76	0·76	65·48

The charge masses are slightly different.

2 z 2

(III) *The Effect of a Constant Water Vapour Addition to CO-Air and H_2-Air and Mixtures of These.*—In this series about 1·23 volumes of water vapour were added to each 100 volumes of " dry " mixture, giving a humidity corresponding to atmospheric air saturated at 10° C.

(a) *Explosion Time.*—In the plotted observations in fig. 10 it will be noticed that the
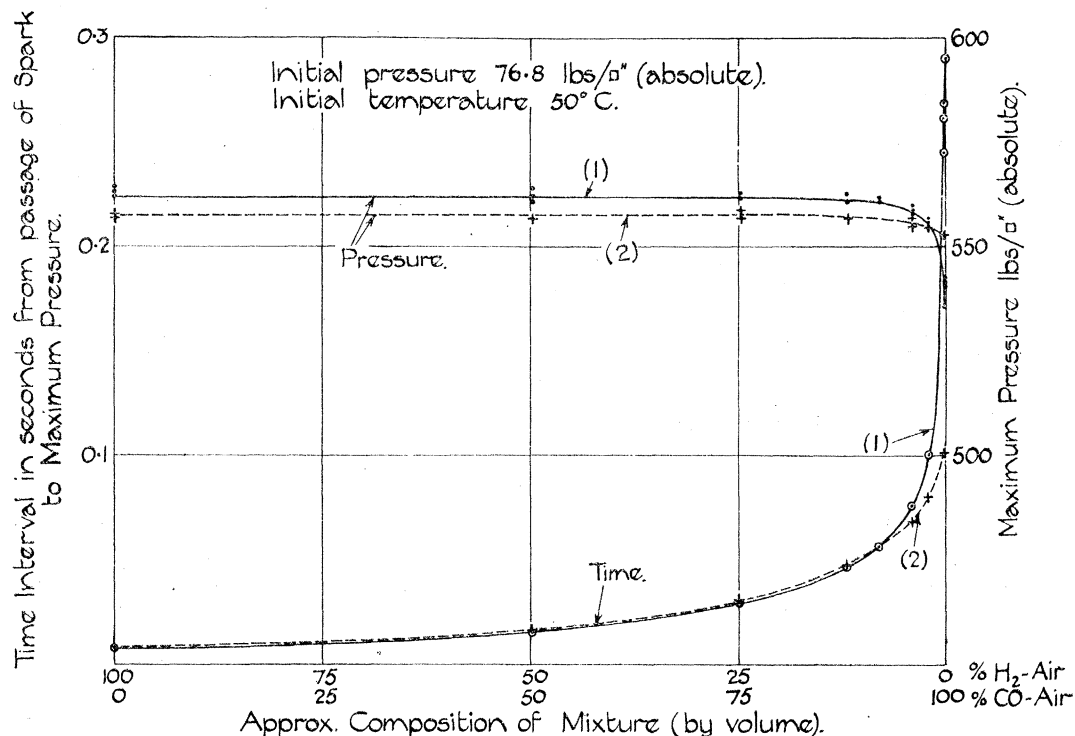
FIG. 10.—Carbon monoxide-air and hydrogen-air mixtures. (1) dry; (2) with about 1·2 per cent. of water vapour.

" explosion time " is reduced by the water vapour addition when the mixture contains less than 8 per cent. of H_2-air, but slightly increased for greater percentages. In recent experiments the usual effect of slight water vapour additions to air-hexane, air-benzene and air-methane mixtures has been found to be a slight increase in the explosion time and a slight reduction in the maximum explosion pressure.

(b) *Maximum Explosion Pressures.*—Referring again to fig. 10, the addition of the given quantity of water vapour reduces the maximum pressure by slightly under 1 per cent. for all H_2-air CO-air mixtures in which the H_2-air exceeds about 8 per cent.; below 8 per cent. the reduction decreases until with a 2 per cent. H_2-air addition the " dry " and " wet " mixtures give the same maximum. Below 2 per cent. the " wet " mixture gives a higher maximum, as previously noted in connection with CO-air water vapour series.

(c) *" Cooling " Curves.*—Comparing the " cooling " curves for the " wet " and " dry " mixtures, the addition of water vapour sets up :—

(1) An increase in the apparent rate of cooling for mixtures containing 2 per cent. of H_2-air.

(2) A lesser increase when the H_2-air percentage is 4.

(3) A very slight increase when the percentage is 12.

(4) No appreciable effect when the H_2-air percentage is 25 or more.

Roughly, where the maximum pressure curves in fig. 10 are parallel, the water vapour addition has no effect on the rate of cooling, but from the point where they commence to converge the effect increases. In other words, where the " wet " mixture maximum pressure exceeds about 99 per cent. of the dry mixture maximum the rate of cooling is affected. Were it not for large variations in the explosion time in this region it might be concluded that more chemical energy had been converted into heat energy at the " start " of cooling.

(IV) *Comparison of Water Vapour Effects when the Water Vapour was* (1) *directly added,* (2) *produced by the combustion of* H_2-*Air.*—The experiments already detailed allow a comparison to be made as to the influence of the water vapour when due to (1) the direct addition of water vapour to the " dry " CO-air mixture, and (2) the addition of H_2-air to the dry CO-air mixture.

The composition of the dry combustion products (exhaust gas) will not be quite the same in the two cases, owing to the introduction of nitrogen in the H_2-air, but the difference in composition is not sufficient to have much effect on the specific heat. For the curves plotted in fig. 11, therefore, the dry " exhaust gas " is of constant composition in curves (1), but varies slightly in the case of curves (2) and (3).
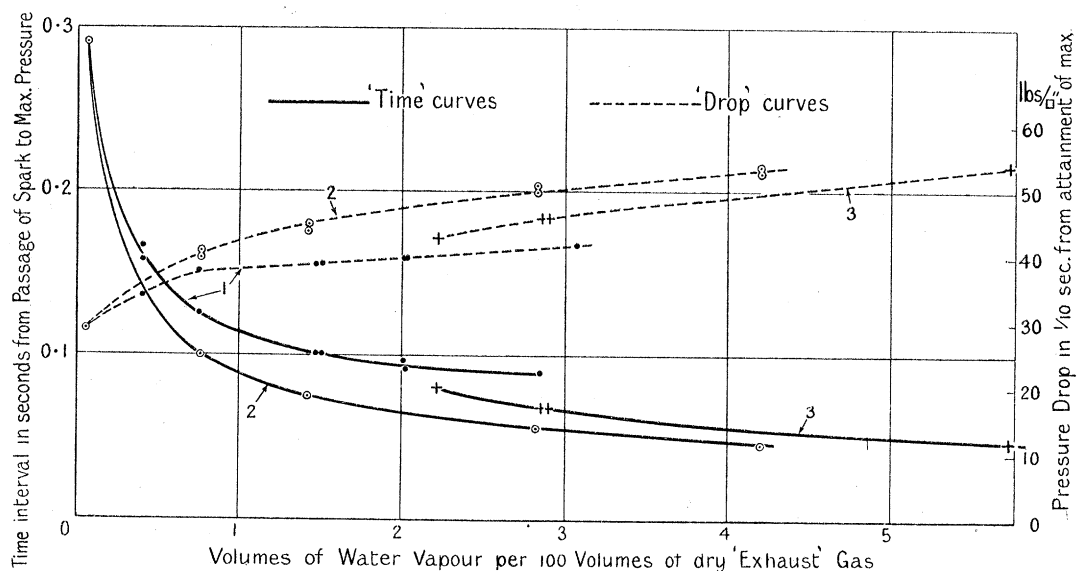
FIG. 11.—Effect of water vapour, due to an addition to the carbon monoxide-air mixture of—

    Curve 1.—Water vapour mainly.

    Curve 2. Hydrogen-air.

    Curve 3. Water vapour (about $1 \cdot 5$) plus hydrogen-air (remainder).

Referring to fig. 11, the " explosion time " curves indicate that the shortening of that interval due to the addition of H_2-air is greater than that due to the direct addition

of water vapour for the same water content of the products.   That is, the H_2-air has a greater effect than that due to its yield of water vapour.

As to the pressure drop in 1/10 second after the attainment of maximum pressure, it will be observed that for the same water vapour content in the " exhaust gas " the drop was considerably greater in the case of the H_2-air addition than when the water vapour was directly added.

PART II.—METHANE-AIR EXPLOSIONS IN A CLOSED VESSEL OVER A WIDE RANGE OF INITIAL TEMPERATURE AND PRESSURE.

In these experiments on mixtures of Methane and Air, the effect of variations in the fuel-air ratio was first examined, the explosions being carried out at a constant initial temperature of 100° C. and a constant initial pressure of 95 lbs. per square inch (absolute).

This was followed by a series of experiments at initial temperatures varying from atmospheric to 400° C., and at initial pressures ranging from 30 to 171 lbs. per square inch (absolute), the mixture ratio being maintained constant.

Apparatus and Experimental Procedure.—The apparatus has already been described in Part I.   The methane was obtained from South Wales, and proved to be exceptionally pure for a natural product.   From analyses made in a Macfarlane and Caldwell apparatus using an explosion vessel, the composition was estimated to be :—

	Per cent.
CH_4	98·1
CO_2	0·6
CO	0·2
H_2	0·0
O_2	0·0
Residue, assumed to be N_2	1·1
	100·0

The mixture was prepared (in bulk) from highly compressed air and compressed methane, and was therefore comparatively dry.   The air-fuel ratio was usually determined from the subsequent analysis of a sample of the mixture, but in one or two cases where such determinations were lacking or were obviously incorrect, other means, such as calculation from mixing pressures, were employed.

In the experiments in which products of combustion (exhaust gas) were added to the mixture, the procedure was to retain in the explosion vessel the desired quantity of combustion products of the previous explosion and to add to these products the

fresh mixture. No mechanical stirring was provided for thoroughly mixing the exhaust gas and the new charge, but from two consecutive explosions (Records 486A and 486B, Table V), in which the same percentage of exhaust gas was added, the results were so similar as to suggest satisfactory mixing rather than very consistent stratification. In this connection it should be noted that, owing to the high water vapour content in the combustion products, there will be a tendency in the high-pressure experiments at 100° C. for slight condensation to persist on the internal surface of the explosion vessel when the final temperature (of, say, 102 or 103° C.) is reached. As the exhaust gas is discharged this water will evaporate, and thus slightly increase the water vapour content of the residual exhaust that is retained for diluting the new charge. The effect is small and occurs only in the 100° C. series at the initial pressure of 95 lbs. per square inch.

As already explained, the prepared air-methane mixture was comparatively dry, and in order to make certain that the practical absence of water vapour was not leading to incorrect conclusions from the internal-combustion engine standpoint, a small quantity—about 1·3 per cent. by volume—of water vapour was added in some cases, as shown in the tabulated results. The water vapour was introduced by the method described in Part I.

Experimental Results.

(1) *The Effect of Variations in the Air-fuel Ratio at Constant Initial Pressure and Temperature.*—In this series explosions were carried out at an initial pressure of about 95 lbs. per square inch (absolute) and at an initial temperature of 100° C. for a range of air-methane mixtures in which the percentage of the latter constituent varied from 12·1 per cent. to 7·3 per cent. It was intended to start the series with a richer mixture; but the one prepared, containing about 13·2 per cent. of methane, failed to ignite under the action of the single spark, and it was only after the primary " make-and-break " had been agitated possibly a hundred times that an explosion, with a very long " explosion time," was observed to take place.

On the weak mixture side it was noticed that combustion products containing free oxygen smelt strongly of nitric acid, and their analysis gave a smaller percentage of O_2 than that computed, or than that given by explosions of the mixture in a small glass explosion vessel. Further, the composition of the products of combustion of strong mixtures varied with the size of the explosion vessel: thus the analysis (A) below applies to an explosion of a 9·9 per cent. mixture at an initial temperature of 100° C. in the large steel explosion vessel, whereas (B) applies to a similar mixture exploded in a small glass explosion vessel at atmospheric temperature.

	CO_2 per cent.	CO per cent.	H_2 per cent.
(A)	10·8	1·2	1·0
(B)	10·5	1·65	0·7

The results of this series, and of some experiments carried out later, are set out in Table III, and some pressure-time records are shown in fig. 12.
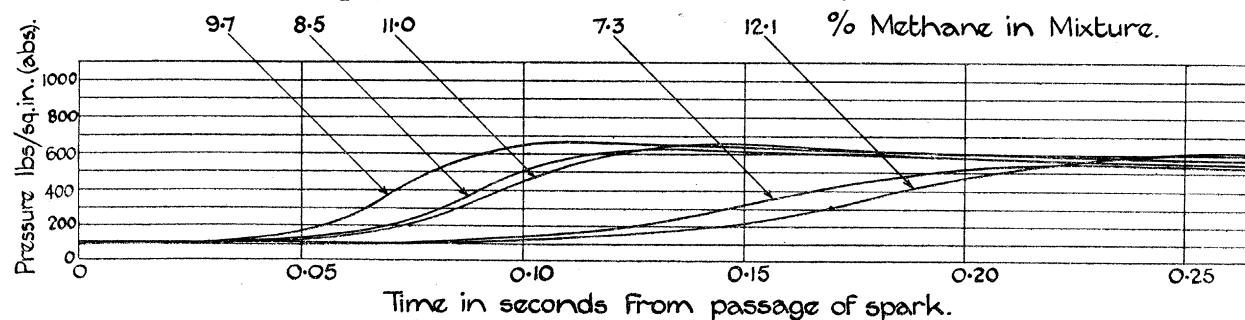
FIG. 12.—Variation of mixture strength.   Methane-air mixtures.

From the pressure-time records of fig. 12 and the curves of fig. 13, the relation of the maximum pressure and the " explosion time " to the air-fuel ratio can readily be seen.
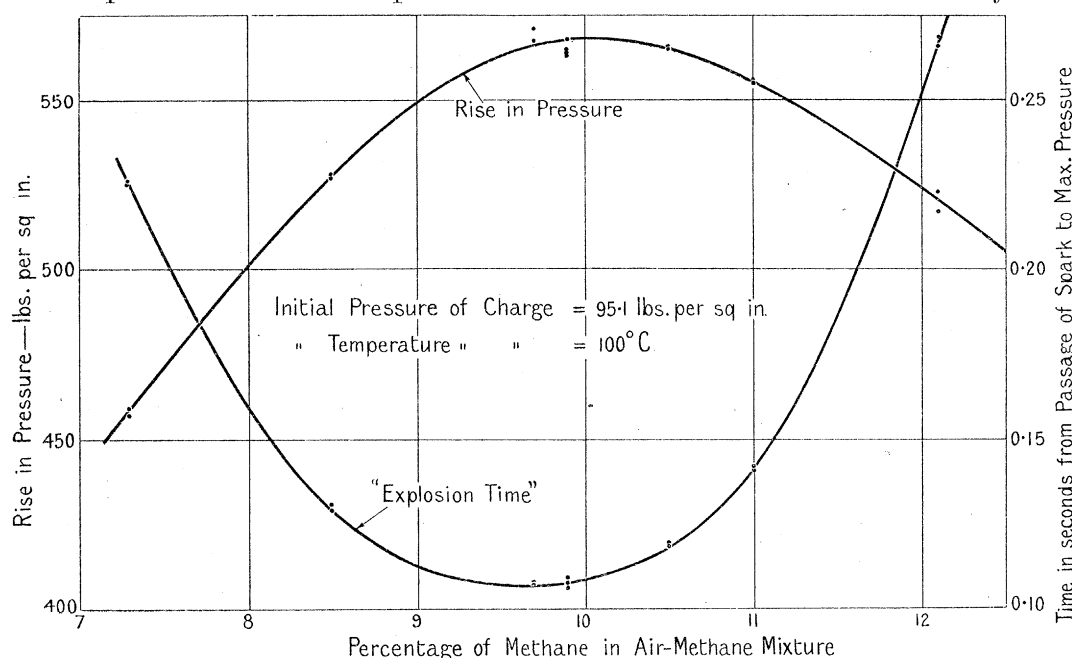
FIG. 13.

Mixtures containing from $9 \cdot 7$ to $10 \cdot 5$ per cent. of CH_4 give sensibly the same pressure rise on explosion, whereas the explosion time is a minimum in the region of the $9 \cdot 7$ per cent. mixture.   A "complete combustion" mixture would contain nearly $9 \cdot 5$ per cent. of methane.

(2) *The Effect of Variations in the Initial Temperature and the Initial Pressure at Constant Mixture Ratio.*—In this series of experiments the initial temperatures were varied from atmospheric to 400° C., and at each temperature the charge density was varied over the range corresponding to 2 to 5 atmospheres at 15° C.   The mixture contained about $9 \cdot 9$ per cent. of methane throughout.   The range of initial temperature is limited by the ignition of the charge by the *heated* walls of the explosion vessel.   The

upper temperature of 400° C. is the highest initial temperature so far attained ; it compares with 300° C. for hydrogen* and for benzene, and 230° C. for hexane and for petrol.† It must be noted, however, that at this upper temperature of 400° C. there was a continual creep of the indicator zero, rendering calibrations and pressure determinations liable to inaccuracy. The effect of diluting the mixture with about 6 per cent. of exhaust gas and about 1·2 per cent. of water vapour was examined for initial temperatures of 100° C. and above.

The results of the experiments are given in Tables IV, V and VI. As before, the maximum temperatures have been computed on the assumption that :—

$$\text{Max. temp. (abs.)} = \frac{\text{initial temp. (abs.)} \times \text{max. pressure}}{\text{volume ratio} \times \text{initial pressure}}.$$

The volume ratio was found by experiment to be 1·007.

In fig. 14 a number of the pressure-time records have been reproduced.
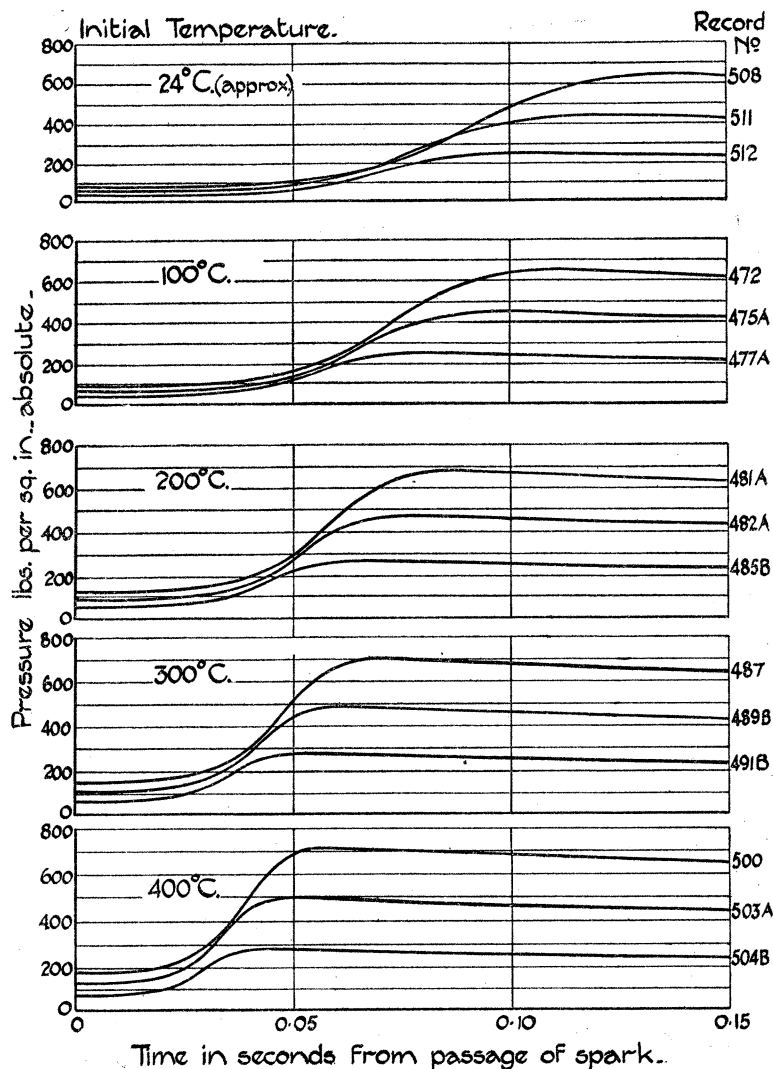
FIG. 14.—Explosion records. Variation of initial pressure and temperature. 9·9 per cent. methane.

* " Air Hydrogen Explosions in Closed Vessels," 'Aeronautical Research Committee,' R. & M. 902.
† " Closed Vessel Explosions," 'Aeronautical Research Committee,' R. & M. 979.

From figs. 15 and 16 and Tables IV, V and VI, it will be observed that the " explosion time," *i.e.*, the interval from the passage of spark to the attainment of maximum pressure,
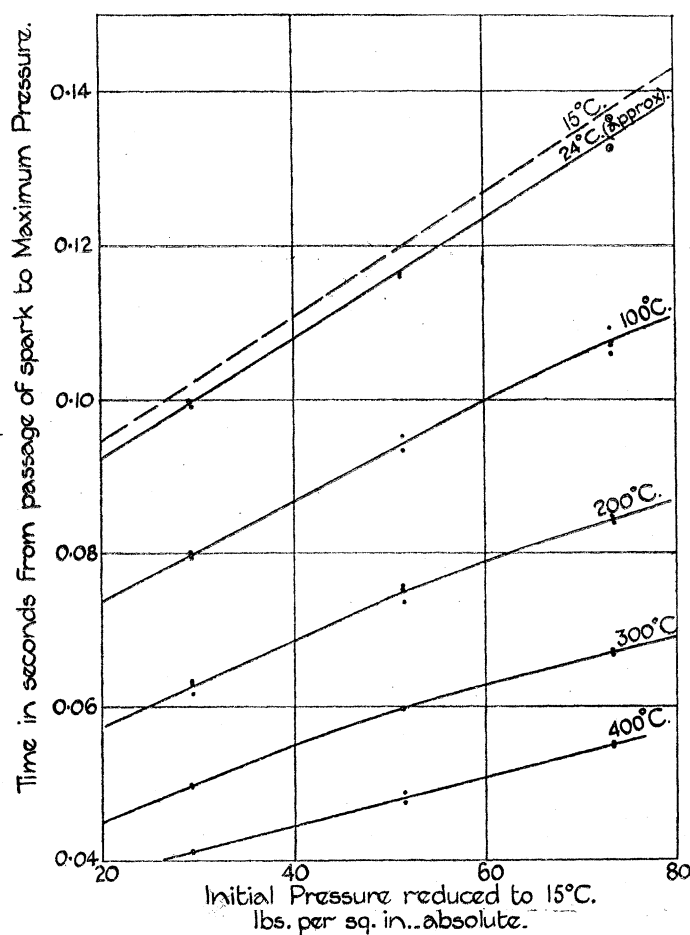
Fig. 15.—Methane-air mixture.   9·9 per cent. methane.

is increased by (1) increasing the charge density, (2) decreasing the initial temperature, (3) adding a diluent such as water vapour or combustion products. In fig. 15 the " explosion " times have been plotted on what is equivalent to a density base (*i.e.*, initial pressure reduced to 15° C.), whereas in fig. 16 a pressure base has been adopted.

The relation of " rise of pressure " on explosion to initial pressure is shown in fig. 17, and the following figures, which are the means of those given in the Tables, show the relation of pressure rise to density at the initial temperatures stated :—

Initial pressure reduced to 15° C.	Average rise of pressure at initial temperatures given.				
	24° C.	100° C.	200° C.	300° C.	400° C.
73·4	568	565	565	554	547
51·4	394	394	394	385	375
29·3	222	222	223	216	213
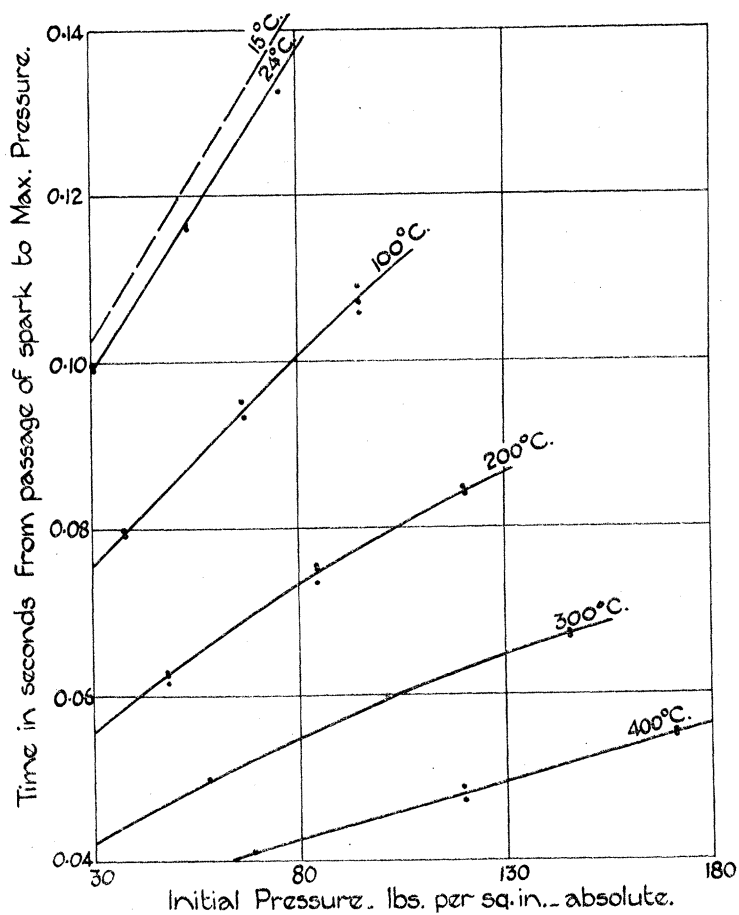
FIG. 16.—Methane-air mixture.   9·9 per cent. methane.
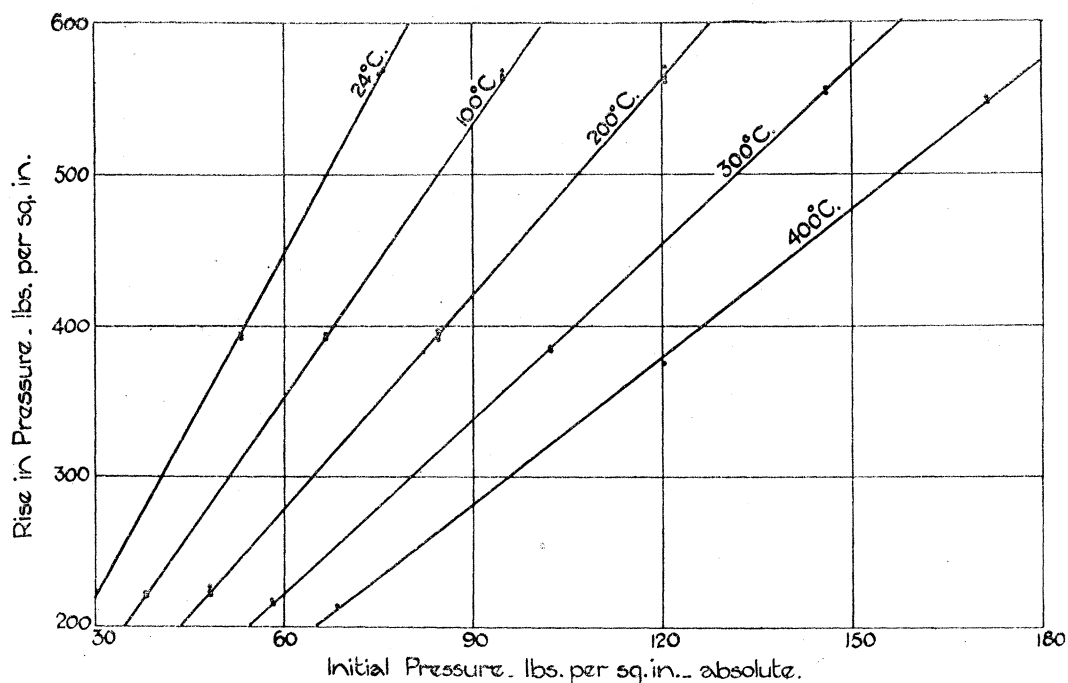
FIG. 17.—Methane-air mixture.   9·9 per cent. methane.

3 A 2

The variation of specific heat with temperature is apparently masked by other factors.

As to the effect of diluting the mixture by the addition of 6·3 volumes of combustion products per 100 of air-methane, it will be found, on plotting, that the pressure rise given by the diluted mixture is 94·5 per cent. of that given by the undiluted. The percentage of air-methane contained in the former mixture is 94·1 per cent.

TABLE I.—Carbon Monoxide-Air, Hydrogen-Air Mixtures. Initial Temperature 50° C.

Record number.	Per cent. of H₂-air in mixture (remainder CO-air) approx.	Composition of mixture, per cent. by volume.					Pressures in explosion vessel.						Temperatures in explosion vessel.		Time intervals.	
		CO.	H₂.	O₂.	N₂.	CO₂.	Initial pressure, lbs. per sq. inch (Abs.).	Initial reduced to 15° C., lbs. per sq. inch (Abs.).	Maximum pressure, lbs. per sq. inch (Abs.).	Rise, lbs. per sq. inch.	Pressure 1/10 sec. after maximum, lbs. per sq. inch (Abs.).	$\frac{\text{Rise}}{\text{Initial}}$ at 15° C.	Approximate maximum.* °C.	Rise. °C.	Spark to maximum. Seconds.	Commencement of rise to maximum. Seconds.
557	100	0	29·35	14·65	55·9	0·1	76·8	68·5	563 (560)	486 (483)	430	7·09	2500	2450	0·0072 (0·0062)	0·0056 (0·0046)
558							76·8	68·5	562 (561)	485 (484)	431	7·08	2495	2445	0·0075 (0·0064)	0·0062 (0·0051)
559	0·2	29·3	0·05	14·6	56·0	0·05	76·8	68·5	542	465	512	6·79	2395	2345	0·2457	0·2048
560							76·8	68·5	543	466	513	6·80	2400	2350	0·2621	—
561							76·8	68·5	541	464	510	6·77	2390	2340	0·2693	0·2326
562	4·1	28·2	1·2	14·6	55·9	0·1	76·9	68·5	559	482	514	7·04	2480	2430	0·0759	0·0645
563							76·9	68·6	560	483	516	7·04	2480	2430	0·0766	0·0659
564	8·0	27·05	2·35	14·6	55·9	0·1	76·8	68·5	562	485	512	7·08	2495	2445	0·0566	0·0482
565							76·8	68·5	561	484	510	7·06	2490	2440	0·0564	0·0485
566	11·9	25·85	3·50	14·6	55·95	0·1	76·8	68·5	563	486	508	7·09	2500	2450	0·0465	0·0383
567							76·8	68·5	563	486	508	7·09	2500	2450	0·0468	0·0393
568	24·8	22·1	7·3	14·6	55·9	0·1	76·8	68·5	563	486	495	7·09	2500	2450	0·0293	0·0239
569	49·7	14·75	14·6	14·6	55·95	0·1	76·9	68·6	564	487	475	7·10	2500	2450	0·0155	0·0123
570							76·9	68·6	562	485	473	7·07	2490	2440	0·0157	0·0125
571	100	0	29·35	14·65	55·9	0·1	76·9	68·6	564 (561)	487 (484)	430	7·10	2500	2450	0·0075 (0·0065)	0·0059 (0·0049)
572							76·9	68·6	562 (560)	485 (483)	430	7·07	2490	2440	0·0074 (0·0064)	0·0058 (0·0048)

* Assuming maximum temperature (abs.) = initial temperature (abs.) $\times \dfrac{\text{maximum pressure}}{\text{initial pressure}} \times \dfrac{100}{85\cdot4}$

TABLE II.—Carbon Monoxide Air, Water Vapour, Hydrogen-Air Mixtures. Initial Temperature 50° C.

Record number.	Per cent. of H₂-air in mixture (remainder CO-air) approx.	Composition of mixture, per cent. by volume.					Volumes of water vapour added per 100 volumes of mixture.	Pressures in explosion vessel.						Temperatures in explosion vessel.		Time intervals.	
		CO.	H₂.	O₂.	N₂.	CO₂.		Initial pressure, lbs. per sq. inch (Abs.).	Initial reduced to 15° C., lbs. per sq. inch (Abs.).	Maximum pressure, lbs. per sq. inch (Abs.).	Rise, lbs. per sq. inch.	Pressure 1/10 sec. after maximum, lbs. per sq. inch (Abs.).	Rise / Initial at 15°C.	Approximate maximum.* °C.	Rise. °C.	Spark to maximum. Seconds.	Commencement of rise to maximum. Seconds.
573	0·2	29·3	0·05	14·7	55·85	0·1	0	76·8	68·5	536	459	507	6·70	2370	2320	0·2902	0·2488
574							1·67	76·8	68·5	552	475	512	6·94	2440	2390	0·0970	0·0861
575							1·68	76·8	68·5	552	475	512	6·94	2440	2390	0·0920	0·0765
576							1·24	76·8	68·5	553	476	514	6·95	2445	2395	0·1015	0·0859
577							1·21	76·8	68·5	553	476	514	6·95	2445	2395	0·1010	0·0832
578							0·60	76·8	68·5	552	475	514	6·94	2445	2395	0·1259	0·1056
579							0·30	76·8	68·5	548	471	514	6·88	2425	2375	0·1663	0·1382
580							0·30	76·8	68·5	549	472	515	6·89	2430	2380	0·1579	0·1358
581							2·56 (2·38)	76·8	68·5	551	474	509	6·92	2430	2380	0·0901	0·0773
582	2·2	28·7	0·65	14·7	55·85	0·1	0	76·8	68·5	556	479	516	7·00	2470	2420	0·1000	0·0850
583							0	76·8	68·5	557	480	*516	7·01	2475	2425	0·1002	0·0860
584							1·23	76·8	68·5	555	478	512	6·98	2455	2405	0·0808	0·0709
585	4·1	28·1	1·2	14·7	55·9	0·1	0	76·8	68·5	558	481	514	7·02	2475	2425	0·0756	0·0632
586							1·24	76·8	68·5	557	480	511	7·01	2465	2415	0·0684	0·0574
587							1·21	76·8	68·5	555	478	509	6·98	2455	2405	0·0686	0·0584
588	11·8	25·85	3·45	14·7	55·9	0·1	0	76·8	68·5	561	484	508	7·07	2490	2440	0·0470	0·0387
589							1·24	76·8	68·5	557	480	503	7·01	2465	2415	0·0475	0·0391
590							0	76·8	68·5	561	484	507	7·07	2490	2440	0·0473	0·0385
591	24·8	22·0	7·25	14·7	55·95	0·1	0	76·8	68·5	562	485	495	7·08	2495	2445	0·0291	0·0234
592							1·24	76·8	68·5	559	482	491	7·04	2475	2425	0·0300	0·0242
593							1·23	76·8	68·5	557	480	490	7·01	2465	2415	0·0301	0·0242
594	49·8	14·7	14·6	14·65	55·95	0·1	0	76·8	68·5	561	484	472	7·07	2490	2440	0·0151	0·0127
595							1·23	76·8	68·5	557	480	469	7·01	2465	2415	0·0156	0·0126
596							1·23	76·8	68·5	557	480	468	7·01	2465	2415	0·0160	0·0132
597	100	0	29·4	14·65	55·90	0·05	0	76·8	68·5	562	485	431	7·08	2495	2445	0·0075	0·0060
598							1·22	76·8	68·5	558	481	427	7·02	2470	2420	0·0078	0·0062
599							1·23	76·8	68·5	557	480	426	7·01	2465	2415	0·0076	0·0060

* Assuming maximum temperature (abs.) = initial temperature (abs.) $\times \dfrac{\text{maximum pressure}}{\text{initial pressure}} \times \dfrac{\text{volume before combustion}}{\text{volume after combustion}}$.

TABLE III.—Effect of Variations in Mixture Strength. Air-Methane Mixtures.

Record number.	Approximate composition of mixture parts by volume.		Volumes of diluent added per 100 volumes of air-methane mixture.	Partial analysis of cooled products of combustion.			Pressures in explosion vessel.							Initial temperature of charge. °C.	Time intervals.	
	CH₄.	Air.*		CO₂ per cent.	O₂ per cent.	CO per cent.	Initial lbs. per sq. inch (Abs.).	Initial reduced to 15°C., lbs. per sq. inch (Abs.).	Maximum lbs. per sq. inch (Abs.).	Rise, lbs. per sq. inch.	1/10 sec. after maximum lbs. per sq. inch (Abs.).	Maximum / Initial.	Rise / Initial at 15°C.		Spark to maximum pressure. Seconds.	Commencement of rise to maximum pressure. Seconds.
448	12·1	87·9	—	7·2	0	6·5	95·1	73·4	618	523	561	6·50	7·13	100	0·2659	0·2266
449			—	7·2	0	6·4	95·1	73·4	612	517	557	6·43	7·04	100	0·2683	0·2265
450	11·0	89·0	—	8·8	0	4·2	95·2	73·5	651	556	579	6·84	7·56	100	0·1406	0·1222
451			—	8·7	0	4·2	95·2	73·5	650	555	578	6·83	7·55	100	0·1419	0·1229
452			1·2 steam	8·9	0	4·1	95·1	73·4	639	544	570	6·72	7·41	100	0·1538	0·1375
453			1·1 steam	8·8	0	4·1	95·1	73·4	637	542	568	6·70	7·38	100	0·1509	0·1311
460	10·5	89·5	—	9·7	0	2·9	95·2	73·5	661	566	585	6·94	7·70	100	0·1193	0·1031
461			6·4 "exhaust"	—	—	—	95·2	73·5	660	565	583	6·93	7·69	100	0·1180	0·1011
462			—	9·7	0	2·9	95·2	73·5	617	522	556	6·48	7·10	100	0·1729	0·1477
463			1·2 steam	9·7	0	2·9	95·2	73·5	647	552	576	6·80	7·51	100	0·1289	0·1101
472	9·9	90·1	—	10·7	0	1·0	95·0	73·3	658	563	583	6·93	7·68	100	0·1069	0·0916
473A			6·3 "exhaust"	—	—	—	95·0	73·3	660	565	585	6·95	7·71	100	0·1090	0·0918
473B			—	10·8	0	1·1	95·0	73·3	622	527	559	6·55	7·19	100	0·1533	0·1313
474			1·3 steam	10·8	0	1·0	95·0	73·3	650	555	578	6·84	7·57	100	0·1193	0·1007
495	9·9	90·1	—	10·8	0	1·2	95·0	73·3	663	568	591	6·98	7·75	100	0·1058	0·0917
506	9·9	90·1	—	10·8	0	1·3	95·1	73·4	659	564	589	6·93	7·68	100	0·1072	0·0907
507			—	10·8	0	1·3	95·1	73·4	660	565	590	6·94	7·70	100	0·1071	0·0909
454	9·7	90·3	—	11·2	0	0·4	95·1	73·4	666	571	594	7·00	7·78	100	0·1065	0·0917
455			—	11·2	0	0·5	95·1	73·4	662	567	588	6·96	7·72	100	0·1077	0·0930
456	8·5	91·5	—	10·4	2·0	0	95·2	73·5	623	528	559	6·54	7·18	100	0·1288	0·1091
457			—	10·4	2·0	0	95·2	73·5	622	527	559	6·53	7·17	100	0·1306	0·1101
458	7·3	92·7	—	8·8	4·8	0	95·0	73·3	558	457	506	5·81	6·23	100	0·2259	0·1957
459			—	8·7	4·9	0	95·1	73·4	554	459	507	5·83	6·25	100	0·2256	0·1918

* The volume of air includes impurities introduced with the methane.

TABLE IV.—Variation in Initial Temperature and Pressure. Air-Methane (9·9 per cent.) Mixture.

Record number.	CH₄	Air.*	Volumes of diluent added per 100 volumes of air-methane mixture.	CO₂ per cent.	O₂ per cent.	CO per cent.	Initial lbs. per sq. inch (Abs.).	Initial reduced to 15°C, lbs. per sq. inch (Abs.).	Maximum lbs. per sq. inch (Abs.).	Rise, lbs. per sq. inch.	Pressure 1/10 sec. after maximum lbs. per sq. inch (Abs.).	Rise Initial at 15°C.	Initial °C.	Approximate maximum °C.	Approximate rise °C.	Spark to maximum pressure. Seconds.	Commencement of rise to maximum pressure. Seconds.
508	9·9	90·1	—	10·7	0	1·2	75·5	73·5	642	567	573	7·71	22·9	2225	2200	0·1364	0·1154
509			—	10·7	0	1·2	75·8	73·5	644	568	575	7·73	24·2	2235	2210	0·1325	0·1126
510			—	10·8	0	1·3	53·1	51·3	447	394	388	7·68	25·3	2220	2195	0·1160	0·0956
511			—	—	—	—	53·0	51·3	446	393	388	7·66	24·6	2215	2190	0·1163	0·0963
512			—	—	—	—	30·3	29·3	252	222	209	7·58	24·7	2185	2160	0·0997	0·0778
513			—	10·7	0	1·3	30·3	29·4	252	222	209	7·55	24·3	2180	2155	0·0990	—
472	9·9	90·1	—	10·7	0	1·0	95·0	73·3	658	563	583	7·68	100	2290	2190	0·1069	0·0916
473A			—	—	—	—	95·0	73·3	660	565	585	7·71	100	2300	2200	0·1090	0·0918
473B			6·3 " exhaust "	10·8	0	1·1	95·0	73·3	622	527	559	7·19	100	2150	2050	0·1533	0·1313
474			1·3 H₂O	10·8	0	1·0	95·0	73·3	650	555	578	7·57	100	2260	2160	0·1193	0·1007
475A			—	10·8	0	1·2	66·7	51·5	459	393	398	7·63	100	2275	2175	0·0950	0·0773
475B			1·3 H₂O	—	—	—	66·7	51·5	453	386	392	7·49	100	2245	2145	0·1047	0·0885
476A			—	—	—	—	66·7	51·5	460	394	399	7·65	100	2280	2180	0·0933	0·0812
476B			6·3 " exhaust "	—	0	—	66·7	51·5	434	367	379	7·13	100	2140	2040	0·1316	0·1108
477A			—	10·8		1·1	38·1	29·4	260	222	215	7·55	100	2255	2155	0·0795	0·0616
477B			1·3 H₂O	—		—	38·1	29·4	258	218	212	7·41	100	2215	2115	0·0871	0·0731
478			—	—		—	38·1	29·4	259	221	214	7·52	100	2245	2145	0·0798	0·0614
479			6·2 " exhaust "	—		—	38·1	29·4	247	209	205	7·11	100	2130	2030	0·1070	0·0851
495	9·9	90·1	—	10·8	0	1·2 (h)	95·0	73·3	663	568	591	7·75	100	2315	2215	0·1058	0·0917
506	9·9	90·1	—	10·8	0	1·3	95·1	73·4	659	564	589	7·68	100	2295	2195	0·1072	0·0907
507			—	10·8	0	1·3	95·1	73·4	660	565	590	7·70	100	2295	2195	0·1071	0·0909

* The volume of air includes impurities introduced with the methane.

(h) In this exhaust sample the hydrogen content was determined and found to be 1 per cent.

TABLE V.—Variation in Initial Temperature and Pressure. Air-Methane (9·9 per cent.) Mixture.

Record number.	CH₄.	Air.*	Volumes of diluent added per 100 volumes of air-methane mixture.	CO₂ per cent.	O₂ per cent.	CO per cent.	Initial lbs. per sq. inch (Abs.).	Initial reduced to 15°C., lbs. per sq. inch (Abs.).	Maximum lbs. per sq. inch (Abs.).	Rise, lbs. per sq. inch.	Pressure 1/10 sec. after maximum lbs. per sq. inch (Abs.).	Rise ÷ Initial at 15°C.	Initial °C.	Approximate maximum °C.	Approximate rise °C.	Spark to maximum pressure Seconds.	Commencement of rise to maximum pressure Seconds.
480A	9·9	90·1	1·3 H₂O	10·9	0	1·1	120·6	73·4	682	561	606	7·64	200	2385	2185	0·0844	0·0749
480B				10·9	0	1·1	120·6	73·4	677	556	603	7·57	200	2365	2165	0·0929	0·0809
481A			4·9 " exhaust "	—	—	—	120·6	73·4	684	563	613	7·67	200	2390	2190	0·0838	0·0726
481B				10·8	0	1·1	120·6	73·4	662	541	593	7·37	200	2305	2105	0·1086	0·0914
482			4·7 " exhaust "	—	—	—	84·4	51·4	477	393	416	7·64	200	2380	2180	0·0750	0·0669
483A				10·8	0	1·1	84·4	51·4	475	391	415	7·61	200	2370	2170	0·0734	0·0637
483B			1·3 H₂O	10·8	0	1·1	84·4	51·4	458	374	402	7·28	200	2275	2075	0·0940	0·0847
484A			1·4 H₂O	—	—	—	84·4	51·4	470	386	410	7·51	200	2345	2145	0·0797	0·0692
484B			4·8 " exhaust "	10·8	0	1·1	48·2	29·3	269	221	225	7·54	200	2350	2150	0·0615	0·0528
485A				—	—	—	48·2	29·3	267	219	224	7·47	200	2330	2130	0·0682	0·0576
485B			4·8 " exhaust "	—	—	—	48·2	29·3	270	222	226	7·58	200	2360	2160	0·0628	0·0525
486A				—	—	—	48·2	29·3	260	212	219	7·24	200	2260	2060	0·0770	0·0612
486B				—	—	—	48·2	29·3	260	212	220	7·24	200	2260	2060	0·0771	0·0618
496A	9·9	90·1	6·3 " exhaust "	10·9	0	1·2 (h)	120·6	73·4	684 (b)	563 (b)	620 (b)	7·67 (b)	200	2390 (b)	2190 (b)	0·0845(b)	0·0729(b)
496B				10·9	0	1·1	120·6	73·4	659	539	595	7·34	200	2295	2095	0·1183	0·1020
497				—	—	—	120·6	73·4	691	570	619	7·77	200	2420	2220	0·0843	0·0728
498A			6·3 " exhaust "	—	—	—	84·4	51·4	481	397	422	7·72	200	2405	2205	0·0754	0·0649
498B				—	—	—	84·5	51·4	461	377	407	7·33	200	2290	2090	0·1019	0·0902
499A			6·3 " exhaust "	—	—	—	48·2	29·3	274	226	233	7·71	200	2395	2195	0·0626	0·0511
499B			6·3 " exhaust "	—	—	—	48·2	29·3	263	215	223	7·34	200	2290	2090	0·0819	0·0654

* The volume of air includes impurities introduced with the methane.

Volume ratio determinations—(1) 1·0063, (2) 1·0072, (3) 1·0072 } Mean 1·007.

(b) Abnormal pressure-time record.

(h) In this exhaust sample the hydrogen content was determined and found to be 1·1 per cent.

TABLE VI.—Variation in Initial Temperature and Pressure.   Air-Methane (9·9 per cent.) Mixture.

Record number.	CH₄.	Air.*	Volumes of diluent added per 100 volumes of air-methane mixture.	CO₂ per cent.	O₂ per cent.	CO per cent.	Initial lbs. per sq. inch (Abs.).	Initial reduced to 15°C., lbs. per sq. inch (Abs.).	Maximum lbs. per sq. inch (Abs.).	Rise. lbs. per sq. inch.	Pressure 1/10 sec. after maximum lbs. per sq. inch (Abs.).	Rise / Initial at 15° C.	Initial. °C.	Approximate maximum. °C.	Approximate rise. °C.	Spark to maximum pressure. Seconds.	Commencement of rise to maximum pressure. Seconds.
487	9·9	90·1	—	11·0	0	1·0	145·9	73·3	699	553	626	7·54	300	2455	2155	0·0667	0·0575
488A			—	—	—	—	145·9	73·3	701	555	627	7·57	300	2460	2160	0·0671	0·0591
488B			6·3 " exhaust "	10·9	0	1·1	145·9	73·3	671	525	603	7·16	300	2345	2045	0·0923	0·0820
489A			1·3 H₂O …	11·0	0	1·1	145·9	73·3	692	546	618	7·45	300	2425	2125	0·0735	0·0648
489B			—	11·0	0	1·1	102·3	51·4	487	385	426	7·49	300	2435	2135	0·0596	0·0502
490A			—	—	—	—	102·3	51·4	486	384	425	7·47	300	2430	2130	0·0597	0·0512
490B			6·2 " exhaust "	—	—	—	102·3	51·4	467	365	412	7·10	300	2325	2025	0·0806	0·0692
491A			1·3 H₂O …	10·9	0	1·0	102·3	51·4	481	379	420	7·37	300	2400	2100	0·0643	0·0550
491B			—	—	—	—	58·2	29·2	275	217	233	7·43	300	2415	2115	0·0497	0·0405
492A			—	—	—	—	58·2	29·2	273	215	231	7·36	300	2395	2095	0·0496	0·0405
492B			6·7 " exhaust "	—	—	—	58·2	29·2	261	203	223	6·95	300	2280	1980	0·0674	0·0564
493			1·3 H₂O …	—	—	—	58·2	29·2	270	212	227	7·26	300	2365	2065	0·0540	0·0446
500	9·9	90·1	—	11·1	0	0·9	171·5	73·4	718	546	638	7·44	400	2525	2125	0·0552	0·0474
501A			—	—	—	—	171·5	73·4	719	548	642	7·47	400	2530	2130	0·0548	0·0465
501B			6·3 " exhaust "	11·0	0	1·1	171·5	73·4	687	516	616	7·03	400	2405	2005	0·0731	0·0659
502A			1·3 H₂O …	11·2	0	0·9	171·5	73·4	708	536	633	7·30	400	2485	2085	0·0578	0·0507
502B			—	11·1	0	1·0	120·1	51·4	495	375	433	7·30	400	2480	2080	0·0487	0·0409
503A			—	—	—	—	120·1	51·4	495	375	432	7·30	400	2480	2080	0·0473	0·0408
503B			6·3 " exhaust "	—	—	—	120·1	51·4	477	357	419	6·95	400	2380	1980	0·0550	0·0475
504A			1·3 H₂O …	—	—	—	120·1	51·4	489	369	428	7·18	400	2450	2050	0·0512	0·0431
504B			—	—	—	—	68·5	29·3	282	213	237	7·27	400	2480	2080	0·0410	0·0360

* The volume of air includes impurities introduced with the methane.