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

Gaseous Combustion at High Pressures

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X. *Gaseous Combustion at High Pressures.*

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Contents.

Introduction.

In continuation of my previous work upon the mechanism of combustion,* I was enabled, in 1906, with the aid of funds provided by the Government Grant Committee to instal at Leeds University a complete apparatus for the study of gaseous

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* 'Trans. Chem. Soc.,' 1902, vol. 81, p. 535; 1903, vol. 83, p. 1074; 1904, vol. 85, pp. 693 and 1637; 1905, vol. 87, pp. 910 and 1232; 1906, vol. 89, pp. 652, 660, 939 and 1614.

[Published July 31, 1915.

explosions under high initial pressures. The present memoir contains a description of the installation, together with the principal results obtained therewith up to the time of my leaving Leeds in 1912, when the apparatus was removed to the Imperial College of Science and Technology, London.

My previous work (*loc. cit.*) had enabled me to put forward a new theory of the mechanism of hydrocarbon combustion, based on an experimental study of the whole range of conditions between slow combustion at relatively low temperatures and explosive combustion (including detonation) at initial pressures of between 270 and 1180 mm.

It was important, from several points of view, to carry the matter still further by examining the behaviour of certain explosive mixtures (which may be regarded as "crucial mixtures" in reference to the various theories of hydrocarbon combustion recently under discussion) when exploded under high initial pressures.

In addition to the above, important information has been gained as to the distribution of oxygen between methane and hydrogen or carbon monoxide, respectively, when mixtures containing insufficient oxygen for complete combustion are fired under high initial pressures; from such facts can be deduced the relative affinities of these gases for oxygen in flame combustion, as well as certain conclusions concerning the mechanism of the combustion of hydrogen and of carbon monoxide.

Finally, a study of the pressure curves obtained in a series of experiments in which methane, hydrogen, and carbon monoxide, respectively, were separately exploded with sufficient air to complete the primary oxidation in each case, has definitely proved that there is no direct (if any) relation in such cases between the relative times required for the attainment of the maximum pressure and the relative affinities of the respective combustible gases for oxygen.

The points adumbrated in the foregoing paragraphs will be discussed more fully in the paper.—W.A.B.

Part I.—Apparatus and Experimental Method.

The apparatus was specially designed by Prof. J. E. Petavel, F.R.S., for the accurate investigation of the mechanism of gaseous combustion under high initial pressures, using mixtures of known composition whose constituents have been prepared on a laboratory scale in a considerable degree of purity. The complete installation includes, therefore, means and apparatus (1) for preparing, purifying, and storing fairly large quantities (25 to 50 litres) of the various gases; (2) for separately compressing each gas into steel cylinders up to pressures of between 50 and 100 atmospheres; (3) for exploding accurately prepared mixtures under known initial pressures in steel bombs of different shapes and capacities so as to obtain reliable data for the interpretation of the chemical changes involved; and (4) for obtaining complete graphs of the pressure changes involved in the explosions of simple gaseous mixtures of known chemical composition.

(A). *Preparation and Purification of Gases.*

The gases employed in the experiments were prepared in quantities of from 25 to 50 litres at a time, briefly as follows:—

Hydrogen by the action of pure dilute sulphuric acid upon the electrolytic "crescent" zinc (guaranteed 99·98 per cent. purity), supplied by Brunner Mond and Co., Ltd.; the gas was thoroughly washed through a series of Erlenmeyer flasks containing a hot alkaline solution of potassium permanganate, which treatment reduced hydrocarbon impurity to a negligible point.

Carbon Monoxide by dropping commercial formic acid (95 per cent.) into warm sulphuric acid and subsequently scrubbing the gas in a coke tower with a spray of strong caustic soda solution.

*Methane** by the action of dilute hydrochloric acid upon aluminium carbide, and subsequent liquefaction of the washed and dried gas in a cylindrical glass receiver immersed in liquid air. The liquid hydrocarbon was finally fractionated, the first and last tenths being rejected.

*Ethane** by the decomposition of zinc ethide (supplied by KAHLBAUM) with water, and subsequent liquefaction of the washed gas and fractionation of the liquid, as in the case of methane.

*Ethylene** by the interaction of ethyl alcohol and syrupy phosphoric acid, of specific gravity 1·75, at 200° C. to 220° C. (NEWTH'S method. 'Trans. Chem. Soc.,' 1901, vol. 79, p. 915), and subsequent liquefaction and fractionation, as in the cases of methane and ethane.

Oxygen by gently heating recrystallised potassium permanganate and washing the resulting gas with strong caustic potash solution.

The purified gases were collected over a mixture of equal volumes of glycerine and water in large glass holders each of 15 to 20 litres capacity, from whence they were subsequently drawn into the cylinder of the compressing pump.

(B). *The Compression Cylinder and Pump.*

This part of the installation provides for the separate compression of each gas in a steel cylinder over glycerine and water. Fig. 1 represents the cylinder, A (internal capacity about 2½ litres), which was machined out of a mild steel forging and closed at either end by a special type of valve. The upper valve, B, serves for the admission of the gas from the holder, and is so constructed that as soon as the cylinder is full of gas the holder may be shut off by a movement which simultaneously opens connection with one or other of the high-pressure storage cylinders into which the gas is sent after compression. The lower valve, C, is provided with fairly wide

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* The purity of the above-mentioned hydrocarbons was in each case established by a careful explosion analysis with an excess of pure oxygen.

passages to facilitate the outflow of the compressing liquid into a special graduated reservoir underneath the experimental table during the inflow of the gas from the holder; the same valve on being closed to the said reservoir simultaneously opens connections with the compressing pump.

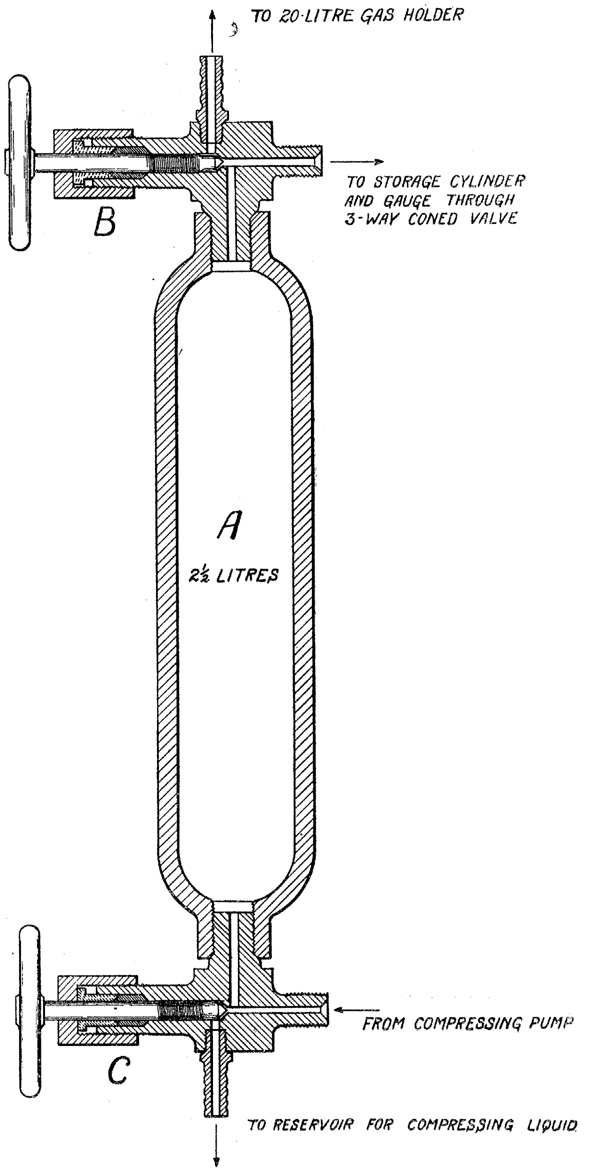

Fig. 1.

The compressing pump (fig. 2) is constructed out of an iron casting into which is fitted a bronze valve body and piston. It has two valves—inlet, A, and outlet, B,—and also a third valve, C, for releasing any gas which may accidentally become imprisoned in the head of the pump. The valves are all of bronze and easily accessible for cleaning purposes. The piston, which is worked by means of a hand lever about 12 inches long, is 0·5 inch in diameter with a stroke of 1·5 inches, and it is easily capable of giving a pressure of 100 atmospheres, if required.

The function of the pump is to raise the mixture of glycerine and water from the reservoir below the table (into which the liquid is discharged by gravity flow during the admission of the gas into the compression cylinder) and to force it into the compression cylinder, whereby the gas is compressed and also transferred under pressure into its proper storage cylinder. The mixture of glycerine and water is thus kept in constant movement during the cycle of operations involved in the compression of the gas, being alternately run out from the bottom of the compression cylinder as each successive charge of gas is being drawn into the system from the large storage holder, and afterwards pumped back into the compression cylinder during the compression of each charge and its transference under pressure to its small storage cylinder. This cycle of operations is controlled by the two valves of the compression cylinder and the entrance valve to the storage cylinder.

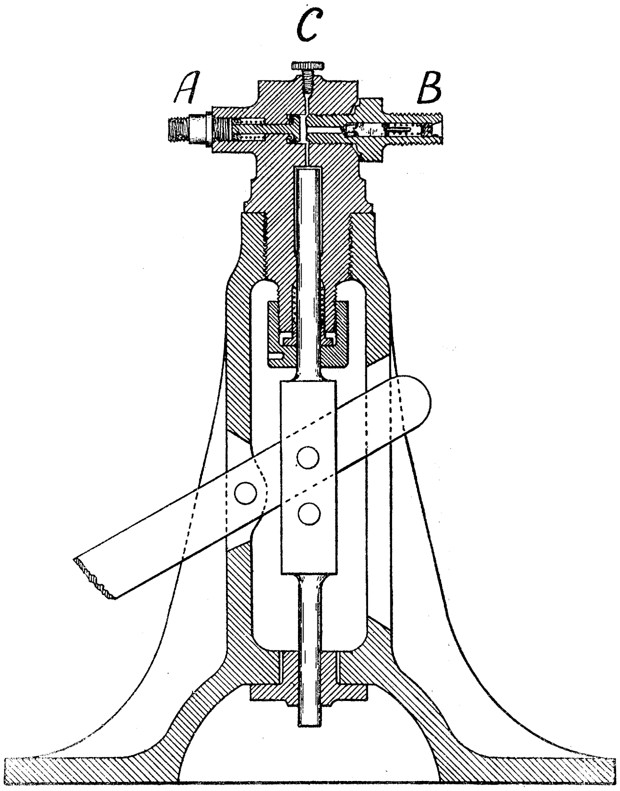

Fig. 2.

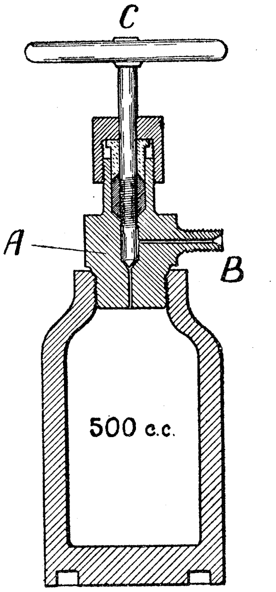

Fig. 3.

(C). *The Storage Cylinders.*

The storage cylinders, of which there are four in the installation, have each a capacity of about 500 c.c. ; the body of each cylinder (fig. 3) is constructed out of a mild steel forging, and is fitted with a bronze-coned valve, A, provided with a union joint, B, and controlled by the handwheel, C. Each cylinder is held by two studs in a cast-iron base which is bolted down to the experimental table. The joints and valves of the cylinders are so accurately made that even hydrogen may be stored in them at a pressure of 100 atmospheres for months together without appreciable loss.

(D). *The Explosion Bombs.*

Two explosion bombs are included in the installation, the one of cylindrical bore and approximately 103 c.c. internal capacity, and the other having a spherical cavity of approximately 275 c.c. capacity, as follows :—

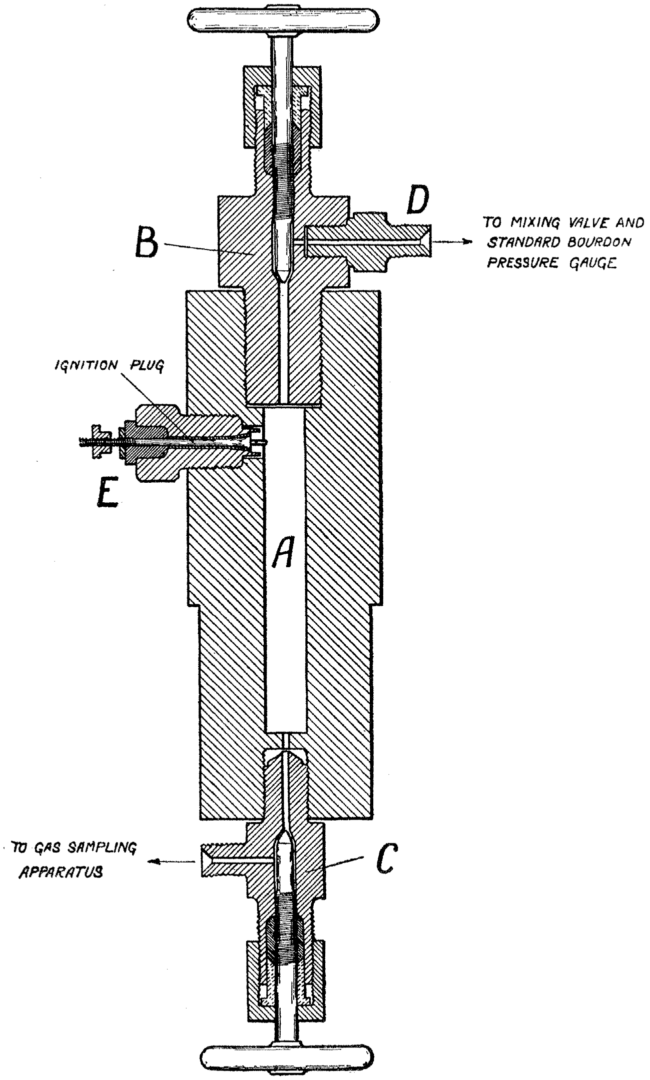

Fig. 4.

(1) *The Cylindrical Bomb* (Bomb A, fig. 4) was machined from a solid forging of open-hearth steel and accurately bored along its axis so as to make an explosion chamber, A, 1 inch in diameter and 8 inches long (capacity *circa* 103 c.c.). It is

fitted with two (upper and lower) coned valves, B and C; by means of the upper valve, B, connections are made, through the union joint, D, and an external four-way "mixing valve" (shown in plan in fig. 8 and in elevation in fig. 7) with (1) a standard Bourdon pressure gauge and (2), each of three storage cylinders. The lower valve, C, serves as a convenient outlet through which samples of the various gaseous mixtures and products were collected for analysis in glass tubes over mercury.

The shell of the vessel is bored, about an inch below the top valve, for the reception of a special joint, E, carrying the ignition plug. This plug is insulated by means of an ivory cylinder through whose axis there passes a steel spindle, the end of which forms one electrical pole, the body of the explosion vessel forming the other.

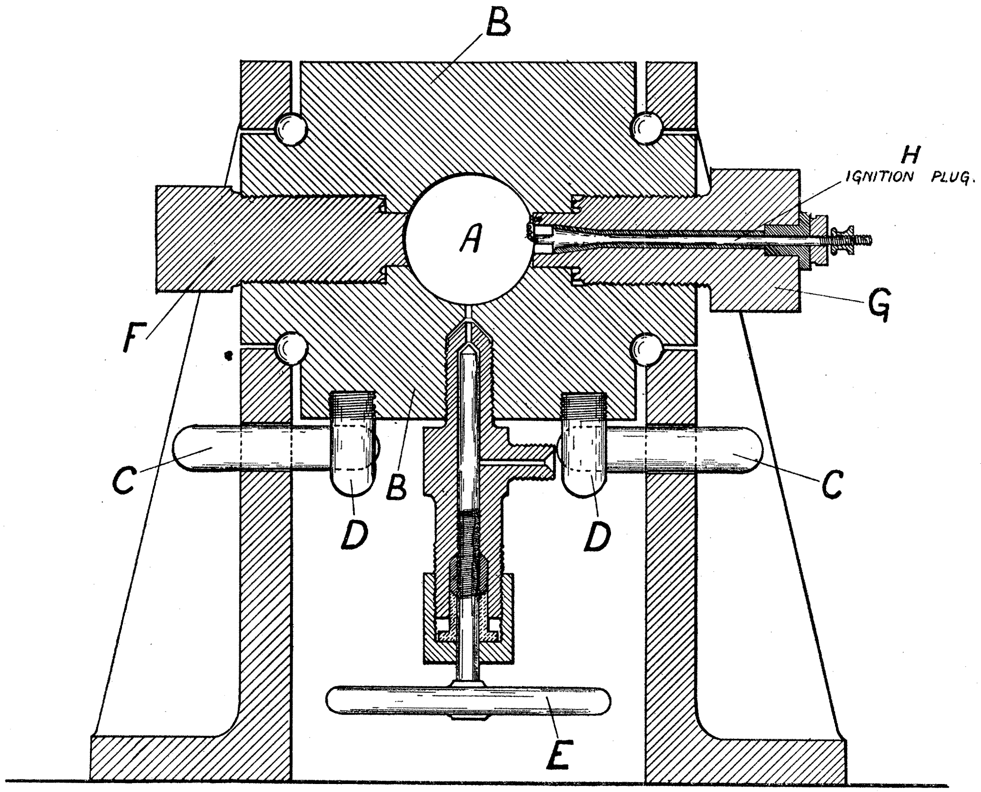

Fig. 5.

Ignition is effected electrically by the fusion of a short length of thin platinum wire bridged between the spindle and the outer steel screw of the plug.

All joints in the explosion vessel are "metal to metal" and are so accurately machined as to be absolutely tight at a test pressure of 1000 atmospheres. The bomb itself is securely held in a vertical position by four bolts in a massive iron casting, which in turn is bolted down to the experimental table. In order to ensure the perfect mixing of the constituents of a given explosive mixture before firing it, the explosion chamber contains a perfectly smooth bronze sphere of $\frac{7}{8}$ inch diameter which, after the gases have been introduced, is caused to roll up and down the chamber about 200 times by subjecting the vessel when in a horizontal position to a slight rocking motion. This is an important precaution in experiments of this kind, the omission of which may vitiate the results owing to imperfect mixing of the charge and stratification effects.

(2) *The Bomb with Spherical Explosion Cavity* (Bomb B, figs. 5 and 6) was likewise machined from a solid forging of open-hearth acid steel, out of the centre of which was cut the spherical cavity, A, 3 inches in diameter (capacity approximately 275 c.c.). The body, B B, of the bomb is cylindrical in outline, its axial length being 10·25 inches, and its diameter 8 inches; it is mounted on a cast-iron stand by means of ball bearings which permit of a rapid rotational motion of the bomb on its axis in order to ensure an effective mixing of its gaseous contents before an explosion. C, C, are steel stops which may be inserted against the plugs, D, D, when it is desired to keep the body of the bomb at rest.

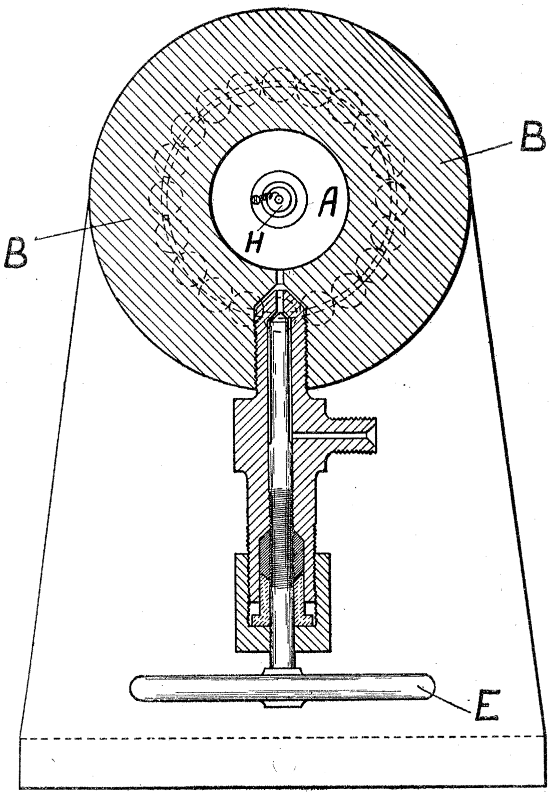

Fig. 6.

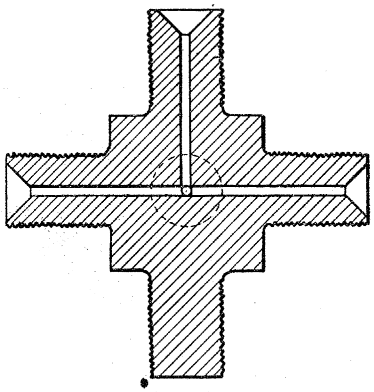

Fig. 7.

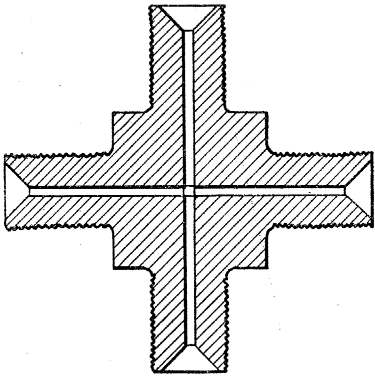

Fig. 8.

The bomb is fitted with the coned valve, E, and a plug, F, and also with a special joint, G, carrying an insulated ignition plug, H, of similar design to that used in the case of the aforesaid cylindrical bomb A. All joints are metal to metal, and capable of holding up a pressure of 1000 atmospheres, which was the testing pressure to which the bomb and all its fittings was submitted.

(E). *The Standard Bourdon Pressure Gauges.*

Three standard pressure gauges, of the Bourdon type, made by Messrs. Schaffer and Budenberg, Ltd., of Manchester, registering up to 30, 60, and 90 atmospheres, respectively, were used during the research to measure the pressures of the original mixtures fired, and of the cooled products after an explosion. These gauges were re-standardised at frequent intervals during the research by direct comparison against a mercury column at the makers' factory. The installation also includes three other Bourdon gauges, each registering up to 100 atmospheres, for ascertaining the pressures in the various storage cylinders at any time.

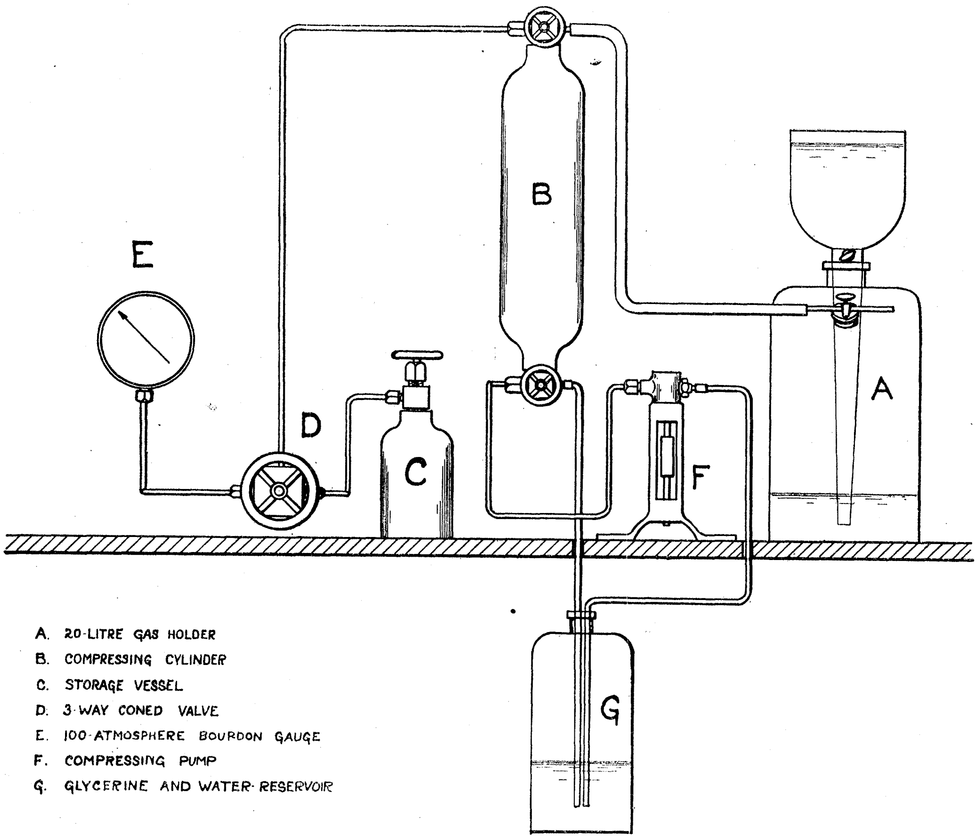

Fig. 9.

(F). *Diagram and Plan of the Installation.*

The general arrangement of the installation will be understood from figs. 9, 10, and 11, respectively, which show diagrammatically, the relation of its various parts, and the plan of the experimental table and its connections. Fig. 9 shows, in elevation, the arrangement for compressing the gases into their respective storage cylinders.

Figs. 10 and 11, show, in plan and elevation respectively, the general arrangement and connections of the storage cylinders, valves, mixing valve, and explosion bomb on the experimental table.

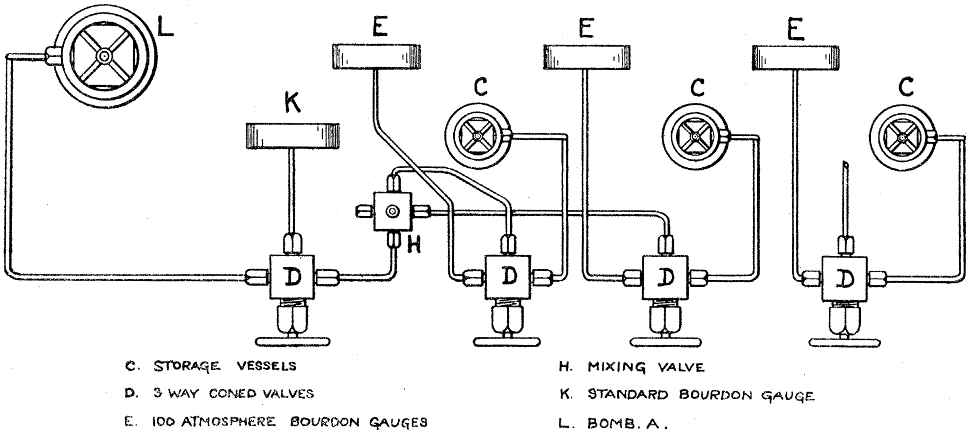

Fig. 10.

Figs. 12 and 13, show, in plan and sectional elevation, one of the coned valves employed in connecting up the various parts of the installation.

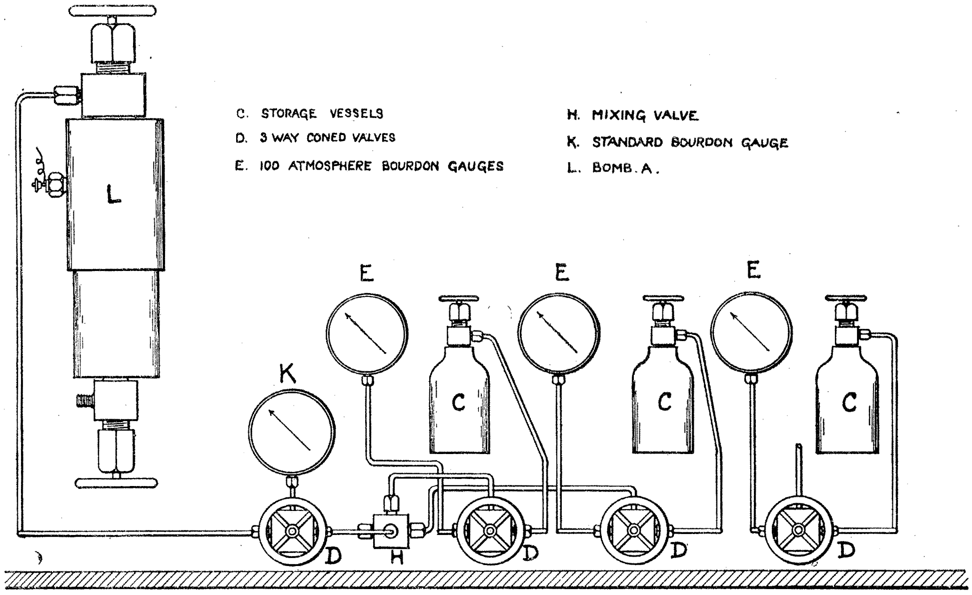

Fig. 11.

(G). *The Recording Manometer.*

For the pressure experiments described in Part VII. of the paper, the spherical bomb, B, was fitted with a recording manometer designed by Prof. J. E. PETAVEL, F.R.S.[*]

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[*] ‘Phil. Trans., 1905, A, vol. 397, pp. 361 to 364.

(fig. 14). Full details as to the experimental procedure in such a case will be found in the section of the paper referred to.

(H). *Gas Sampling and Analysis Arrangements.*

Samples of the orginal mixture fired, as well as of the exploded products in each experiment were drawn off, through one of the coned valves of the particular explosion bomb used, into tubes over mercury, and were subsequently analysed over mercury in an apparatus embodying the Frankland-McLeod principles specially designed by Prof. Bone for rapid and accurate work.*

The whole of the installation described under the preceding Sections A to D, inclusive, as well as the recording manometer and the chronograph used in the pressure experiments described hereafter in Part VII., were made by Mr. C. W. Cook, of Manchester, from designs kindly furnished by Prof. J. E. Petavel, F.R.S., to whom the authors desire to express their obligations. Figs. 12 and 13 (showing the 3-way coned valve), 14 (the manometer), and 15 (the chronograph), appeared in the memoir on "The Pressure of Explosives: Experiments in Solid and Gaseous Explosives," published by Prof. Petavel in the 'Philosophical Transactions' in 1905,† and are only reproduced here for the sake of completeness. Fig. 2 (the compression pump) also appeared in a later paper published by Prof. Petavel in 1908.‡

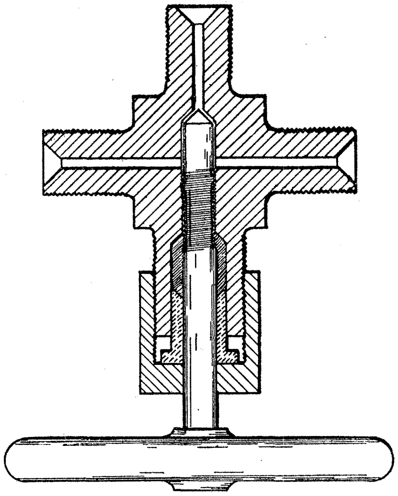
Fig. 12.

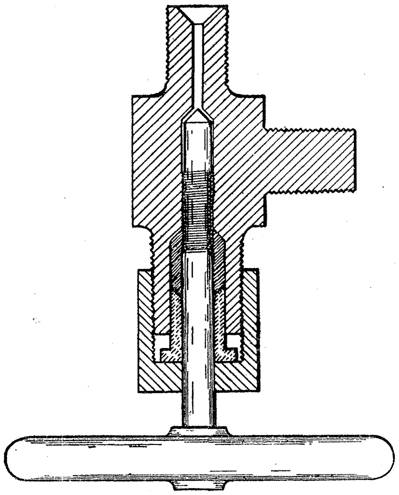
Fig. 13.

The two bombs, A and B, used by the authors (figs. 4 and 5) are similar in design to those shown on pp. 368 and 370 of Prof. Petavel's first memoir (*loc. cit.*), but differ from his in dimensions, internal capacities, the arrangements of the valves, and the position of the firing plug.

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* 'Proceedings Chemical Society,' 1898, vol. 14, p. 154.

† 'Phil. Trans.,' A, vol. 205, pp. 357 to 398.

‡ 'Physikalische Zeitschrift,' vol. IX, p. 75.

Experimental Method.

Before each experiment the bomb was thoroughly tested by filling it with either air or hydrogen up to from 30 to 50 atmospheres pressure, and in no case was an experiment proceeded with unless this pressure was held without appreciable loss for a period of twelve hours. At frequent intervals, also, during the investigation, each bomb was tested by exploding in it mixtures of oxygen with excess of hydrogen (the initial partial pressure of the oxygen varying usually from 3 to 10 atmospheres). In the rare event of the observed diminution in pressure exceeding the partial pressure of the oxygen multiplied by 3·0, a circumstance which might be due either to a slight outleakage at one of the valves during the explosion or to the occurrence of rust on the walls of the explosion chamber, the test was repeated until a satisfactory result was obtained. As an indication of the degree of accuracy obtainable when such mixtures are exploded in the apparatus, the following summary of the first 22 tests carried out with bomb A, are given below :—

	Limits.			
(1) Initial partial pressure of the oxygen varied between.	3	and	10 atmospheres.	
(2) Ratios between partial pressures of the hydrogen and oxygen in the mixture fired varied between.	3·0	„	8·75	„
(3) Ratio of pressure fall on explosion to initial partial pressure of oxygen varied between	2·85	„	3·07*	„

After a successful preliminary test with either hydrogen or air, and a thorough drying out of the explosion chamber by means of a current of dry air, the bomb and its connections, right up to the standard gauge and the storage cylinders, were exhausted by means of a Geryk pump. It was then filled up to about 5 atmospheres pressure with one of the constituents (usually the oxygen) of the particular explosive mixture under investigation, and after blowing off the excess of pressure, the bomb and its connections were once more exhausted. The first constituent of the proposed mixture was thereupon slowly admitted to the bomb from its storage cylinder until the standard Bourdon gauge indicated the desired pressure. The admission valve of the bomb was then closed and the excess pressure in the outside system between it and the gauge and storage cylinders blown off by momentarily unscrewing the union joint nearest to the bomb. The connections up to the bomb were then repeatedly swept out and finally filled at high pressure (exceeding that of the gas already in the bomb) with the second constituent of the proposed mixture, which was immediately afterwards slowly admitted to the bomb, up to its desired partial pressure, by suitable manipulation of the proper valves. The contents of the bomb were then submitted to

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* In 14 out of the 22 experiments this ratio was 3·0 exactly.

a thorough mixing process, after which a sample of the mixture was withdrawn through the bottom valve for subsequent analysis. In cases where the mixture under investigation was one of three constituents, the first two (one of which was always the oxygen) were first of all mixed in the bomb in their proper proportions, and this first mixture was always checked by analysis before the third constituent was added. Moreover, in all such cases, the special mixing device was brought into play after the addition of each constituent so as to ensure perfect homogeneity and accuracy in composition of the final mixture exploded.

Immediately before firing the mixture, the connections between the admission valve of the bomb and the standard gauge were filled up with oxygen to a pressure just below that of the mixture in the bomb; on momentarily opening the admission valve a little of the mixture in the bomb would pass outwards into the connections, and the gauge would within two or three seconds record the exact pressure (*i.e.*, to within 0·1 atmosphere) of the mixture remaining in the bomb. On again closing the admission valve a moment later the pressure indicated by the gauge *plus* one atmosphere (since the gauge readings were pressures *above* the atmospheric pressure) would be the "observed initial firing pressure."

After firing the mixture, the excess pressure in the connections between the admission valve of the bomb and the gauge was blown off, and then, after opening the valve of the bomb, the gauge reading was once more recorded. This reading was subsequently multiplied by a factor (the numerical value of which had been previously accurately determined by actual trial) representing the ratio of the whole volume of the bomb *plus* outside system, up to and including the tube of the gauge (now occupied by the products of explosion), to that of the bomb; the reading so multiplied *plus* 1·0 atmosphere would thus accurately represent the actual pressure of the cold gaseous products in the bomb after the explosion.

In cases where the mixture fired in the bomb contained constituents which would deviate from Boyle's law at high pressures more than the diatomic gases hydrogen, oxygen, and carbon monoxide (which for all practical purposes may be considered as deviating equally within the limits of pressure covered by the experiments included in this memoir) the "observed initial firing pressures" were subject to a certain correction on this account. In the cases of methane and ethylene, the values for PV as determined by Pouillet for pressures between 1 and 40 atmospheres were used in calculating the "correction" to be applied in any particular case. In the case of ethane, however, for which no authentic data could be found in scientific literature, a set of values were determined by direct comparison of the actual volumes (1) of hydrogen and (2) of ethane, respectively, measured at 15° C. and 760 mm., required to fill up bomb, A, to certain definite pressures, *e.g.*, 5, 10, 15, 20 and 25 atmospheres, respectively. The various pressures tabulated in the subsequent part of this paper represent the experimental pressures after due "correction" for deviations from Boyle's law in each particular case.

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

PART II.—THE EXPLOSION OF METHANE WITH LESS THAN ITS OWN VOLUME OF OXYGEN.

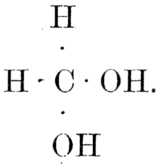
(With Mr. HAMILTON DAVIES, B.Sc.)

It has been known since DALTON'S time that at ordinary pressures methane cannot be exploded with much less than its own volume of oxygen. DALTON thus described the behaviour of a mixture of equal volumes of methane and oxygen on explosion (New System, Part II., p. 446):—"*If 100 measures of carburetted hydrogen be mixed with 100 measures of oxygen (the least that can be used with effect), and a spark passed through the mixture, there is an explosion without any material change of volume: after passing a few times through lime water, it is reduced a little, manifesting signs of carbonic acid. This residue is found to possess the characters of a mixture of equal volumes of carbonic oxide and hydrogen.*"

In the light of my work on the slow combustion of methane[*] this result is best expressed by the following equations:—

(i.) $$CH_4 + O_2 = [CH_2O + H_2O] = CO + H_2 + H_2O.$$

(ii.) $$CO + OH_2 \rightleftharpoons CO_2 + H_2,$$

or, in other words, the immediate result of the interaction of the hydrocarbon and oxygen is the formation of formaldehyde and steam—probably due to the thermal decomposition of *dihydroxymethane*  $\overset{H}{\underset{OH}{H \cdot C \cdot OH}}$. The formaldehyde at once decomposes, yielding equal volumes of carbon monoxide and hydrogen, and afterwards, as the system $CO + H_2 + H_2O$ is cooling, the reversible change $CO + OH_2 \rightleftharpoons CO_2 + H_2$ comes into play. It is to be noted that there is no deposition of carbon in such an explosion.

By employing such high initial pressures as were at our command with the new apparatus, it is possible to explode mixtures of methane with even as little as half its own volume of oxygen. The behaviour of a series of mixtures between the limits $2CH_4 + O_2$ and $CH_4 + O_2$ has been studied with results of considerable interest.

First Series. (*Bomb* A.)

Taking the experiments in their proper sequence, the results obtained by firing mixtures of methane with as nearly as possible half its own volume of oxygen in bomb, A, at initial pressures gradually increasing from 8·5 up to 31·25 atmospheres,

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[*] BONE and WHEELER, 'Trans. Chem. Soc.,' 1902, vol. 81, p. 535; 1903, vol. 83, p. 1074.

will first of all be considered. So far as could be judged from the character of the sound emitted, the explosion at initial pressures up to 16·5 atmospheres was not very violent; at 21·69 atmospheres the sound was distinctly more audible, and at 31·25 atmospheres a sharp metallic click, indicative of detonation, was heard. Carbon was deposited and steam abundantly formed in all experiments; there was always a permanent increase in pressure (20 to 30 per cent.) on explosion, the ratio, p_2/p_1, increasing regularly with the initial pressure. It is also noteworthy that, although much of the original methane remained unchanged, there was never the slightest trace of either acetylene or ethylene in the products.

The principal observations are given in Table I.

Second Series. (*Bomb* B.)

In the next series of experiments (Table II.) the same mixture was exploded, at initial pressures between 10 and 20 atmospheres in the large spherical bomb, B.

Third Series. (*Bomb* A.)

In this series of experiments (Table III.) the effect of gradually increasing the proportion of oxygen between the limits $2CH_4+O_2$ and CH_4+O_2 was investigated. The initial pressure was nearly the same (12·6 to 12·75 atmospheres) throughout the series. The most noteworthy fact brought to light was the total cessation of any separation of carbon after the proportion of oxygen exceeded the limit $3CH_4+2O_2$.

In interpreting the results given in Tables I. to III. it is important to distinguish between (1) the primary oxidation of the hydrocarbon, which is an exceedingly rapid process, and is probably completed during the short interval between ignition and the attainment of maximum pressure; and (2) certain probable secondary interactions whose influence may extend far into the subsequent long cooling period. For it is only these latter which would be affected by variations in the rate of cooling down from the maximum temperature.

With regard to the primary oxidation, the results with the mixture $2CH_4+O_2$ are obviously inconsistent with any idea of a preferential burning, whether of carbon or of hydrogen. If, however, it be supposed that the oxygen initially enters the methane molecule, forming unstable "hydroxylated" molecules, which then decompose, it becomes necessary to consider the probabilities of the direct formation of $CH_3.OH$ and $CH_2(OH)_2$, respectively, and the nature of their respective decomposition products at high temperatures, together with the magnitude of the corresponding heat changes.

Incidentally, the "hydroxylation" theory, which the author's previous researches has shown to be consistent with all the known chemical data concerning hydrocarbon combustion, is also indirectly supported on the physical side by Prof. W. M. Thornton's recent observations on the electrical ignition of the paraffin hydrocarbons in

TABLE I.—Explosion of Mixtures $2CH_4+O_2$ in Bomb A at Initial Pressures between 8·5 and 31·25 atmospheres.

Experiment No.	1			2			3			4			5		
Pressures in atmospheres, p_1	8·533			13·62			16·45			21·69			31·26		
Pressures in atmospheres, p_2	10·147			16·435			20·48			28·00			40·87		
p_2/p_1	1·19			1·207			1·245			1·292			1·306		
Original mixture,	Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.	
CH_4	65·9	5·633		67·0	9·126		67·0	11·02		66·5	14·43		65·75	20·55	
O_2	34·1	2·900		33·0	4·494		33·0	5·43		33·5	7·26		34·25	10·71	
Gaseous products,	Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.	
CO_2	2·70	0·281		2·95	0·484		2·70	0·55		3·35	0·94		3·80	1·59	
CO	26·55	2·766		25·90	4·258		26·40	5·42		26·45	7·41		27·30	11·41	
CH_4	16·95	1·766		18·90	2·609		14·90	3·05		15·55	4·34		16·25	6·80	
H_2	51·20	5·334		55·25	9·084		56·00	11·46		54·65	15·31		50·40	21·07	
	C.	H.	O.	C.	H.	O.	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	5·633	11·266	2·900	9·126	18·252	4·494	11·02	22·04	5·43	14·43	28·86	7·26	20·55	41·1	10·7
Units in gaseous products	4·813	8·866	1·664	7·351	14·302	2·613	9·02	17·56	3·26	12·69	23·99	4·64	19·80	34·7	7·3
Difference, atmospheres	0·82	2·4	1·236	1·77	3·95	1·88	2·00	4·48	2·17	1·74	4·87	2·62	0·74	6·4	3·4
Difference, per cent	14·5		42·6	19·4		42	18		40	12		36	3·6		32
Ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ in products	4·45			3·76			3·78			2·56			2·24		
Character of sound heard on firing the gases	Almost inaudible.									Distinctly audible.			Sharp metallic click.		

In the above as in all subsequent tables:—

p_1 = The corrected initial firing pressure of the dry "nitrogen free" gases.

p_2 = The corrected final pressure of the cooled "nitrogen free" products.

TABLE II.—Explosion of Mixture $2CH_4+O_2$ in Bomb B.

Experiment No.	6			7			8			9		
Corrected pressures in atmospheres p_1	10·107			9·426			19·90			19·325		
Corrected pressures in atmospheres p_2	14·390			12·404			27·147			26·424		
p_2/p_1	1·424			1·31			1·364			1·368		
Corrected partial pressures of original mixtures, atmospheres CH_4	6·728			6·316			13·35			12·810		
Corrected partial pressures of original mixtures, atmospheres O_2	3·379			3·110			6·55			6·515		
Partial pressures, gaseous products,* atmospheres CO_2	0·3723			0·397			0·764			0·650		
Partial pressures, gaseous products,* atmospheres CO	4·0440			3·329			7·413			7·508		
Partial pressures, gaseous products,* atmospheres CH_4	1·344			1·510			3·210			2·494		
Partial pressures, gaseous products,* atmospheres H_2	8·630			7·168			15·760			15·770		
	C.	H.	O.	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	6·728	13·456	3·379	6·316	12·63	3·11	13·35	26·7	6·55	12·81	25·62	6·51
Units in gaseous products	5·760	11·318	2·394	5·236	10·19	2·06	11·38	22·18	4·47	10·65	20·76	4·40
Difference	0·968	2·138	0·985	1·080	2·44	1·05	1·97	4·52	2·08	2·16	4·86	2·11
Per cent. difference	14·4		29·1	17·1		33·8	14·3		31·6	16·9		32·4
Ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$	2·58			2·65			2·67			3·3		

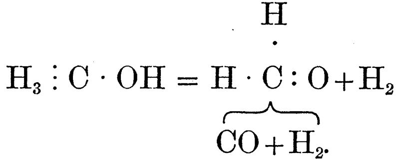
* N.B.—There was never any trace of either acetylene or ethylene in the products.

TABLE III.—Explosion of Mixtures of varying Composition between $2CH_4+O_2$ and CH_4+O_2 in Bomb A at Initial Pressure 12·7 atmospheres.

Experiment No.	10			11			12			13		
Pressures in atmospheres p_1	12·74			12·72			12·68			12·61		
Pressures in atmospheres p_2	15·05			18·10			17·30			14·10		
p_2/p_1	1·18			1·42			1·36			1·12		
Original mixture	Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.	
Original mixture CH_4	67·15	8·55		59·3	7·54		55·75	7·09		50·8	6·40	
Original mixture O_2	32·85	4·19		40·7	5·18		44·25	5·59		49·2	6·21	
Gaseous products	Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.		Per cent.	Partial pressures, atmospheres.	
Gaseous products CO_2	3·10	0·47		2·70	0·49		3·85	0·67		7·45	1·05	
Gaseous products CO	25·40	3·83		35·60	6·44		37·25	6·44		38·50	5·44	
Gaseous products CH_4	16·60	2·50		4·65	0·84		2·25	0·39		nil	nil	
Gaseous products H_2	54·90	8·26		57·05	10·32		56·65	9·80		54·05	7·60	
	C.	H.	O.	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	8·55	17·10	4·19	7·54	15·08	5·18	7·09	14·18	5·59	6·40	12·80	6·21
Units in gaseous products	6·80	13·26	2·38	7·77	12·00	3·71	7·50	10·58	3·89	6·49	7·60	3·77
Difference atmospheres	1·70	3·84	1·81	—	3·08	1·47	—	3·60	1·70	—	5·20	2·44
Difference per cent.	20		43·2			28·4			30·4			38·2
Ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ in products	3·65			3·75			3·43			3·4		
Remarks	Explosions almost inaudible; carbon deposited.			Explosion distinctly audible. No carbon deposited.						Very violent explosion with sharp metallic click. No carbon deposited.		

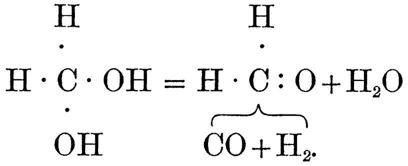
air.* Prof. THORNTON's experiments on the ignition by the continuous current of such hydrocarbon-air mixtures have proved that if I is the least igniting current and p the percentage of gas in the mixture, the ratio I/p is nearly proportional to the number of hydrogen atoms in the molecule, a fact which suggests that the initial attack of the oxygen is directed upon the hydrogen atoms in the hydrocarbon molecule; and inasmuch as any supposition of a preferential burning, in the old sense, of hydrogen is clearly inadmissible on chemical grounds, the "hydroxylation" theory seems to be the only satisfactory substitute.

With regard to the thermal decomposition of methyl alcohol, $CH_3.OH$, it now is definitely established that at high temperatures it is resolved ultimately into carbon monoxide and hydrogen, without any deposition of carbon or steam formation, in accordance with the following scheme:—†



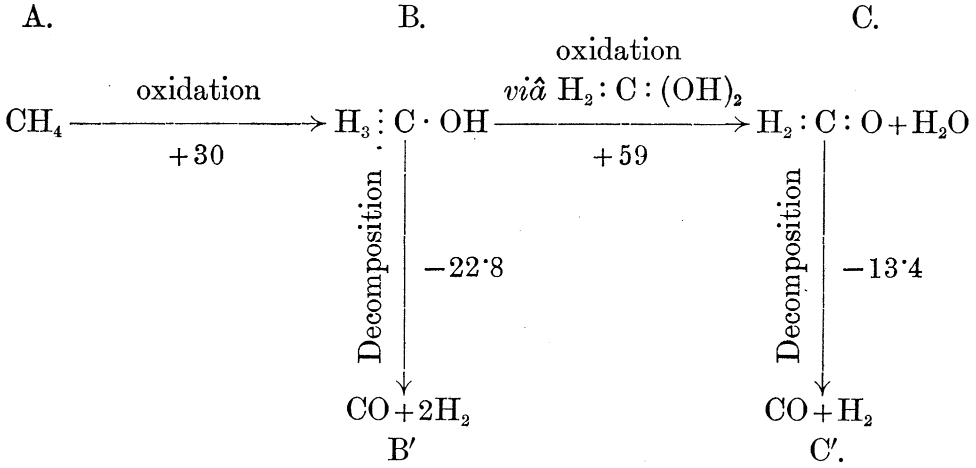
$$\mathrm{H_3} \vdots \mathrm{C\cdot OH} = \underbrace{\mathrm{H}\cdot\overset{\mathrm{H}}{\dot{\mathrm{C}}}:\mathrm{O}}_{\mathrm{CO+H_2.}} + \mathrm{H_2}$$

And with regard to dihydroxymethane, $CH_2(OH)_2$, there is little doubt but that at high temperatures it is ultimately resolved into carbon monoxide, hydrogen, and steam, as follows:—



$$\mathrm{H}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\dot{\underset{\cdot}{\mathrm{C}}}}}\cdot\mathrm{OH} = \underbrace{\mathrm{H}\cdot\overset{\mathrm{H}}{\dot{\mathrm{C}}}:\mathrm{O}}_{\mathrm{CO+H_2.}} + \mathrm{H_2O}$$

If now, the above facts be combined with the corresponding thermal changes, expressed in kilogram-centigrade units per gram-molecule, the scheme for the primary oxidation of methane may be represented as follows:—



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* 'Roy. Soc. Proc.,' 1914, A, vol. 90, pp. 272–280.

† BONE and DAVIES, 'Trans. Chem. Soc.,' 1914, vol. 106, pp. 1691–1696.

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

From which it is evident that the passage from A to B involves an evolution of 30 heat units, of which 22·8 would be absorbed if the transition B to B′ supervened, whereas the further passage from B to C involves an evolution of 59 heat units, of which only 13·4 would be absorbed during the transition C to C′. Hence, it might be expected that, whenever circumstances are favourable or permit, the transition A to B would be immediately followed by B to C, rather than by B to B′. Or, in other words, there would usually be a strong tendency for a "non-stop" run from A to C through B, that is, without any thermal decomposition in passing through B. The last-named, although not precluded, would only occur exceptionally. Moreover, it may be pointed out that the thermal decomposition of CH_3OH(B to B′) involves a slightly greater heat absorbtion than the resolution of methane itself into its elements (namely, $-22·8$ for methyl alcohol, as against $-22·7$ for methane) and that, therefore, heat liberated by oxidation (A to B or B to C) would be just as likely to decompose any residual methane as it would the methyl alcohol formed in passing through B. This consideration is of importance in connection with the course of events when methane is exploded with considerably less than its own volume of oxygen.

Any theory must, however, be capable of accounting for the following outstanding facts, namely (1) the ultimate formation of large quantities of both carbon and steam in the explosion of the mixture $2CH_4+O_2$; (2) the disappearance of carbon from the products when the proportion of oxygen in the mixtures exploded exceeds 40 per cent.; and (3) the occurrence of oxides of carbon and steam in the products of all the mixtures fired.

There is no difficulty in explaining, on the lines of the hydroxylation theory, the facts comprised under (1) and (3), especially in view of the strong tendency there would always be for a non-stop passage from CH_4 to $CH_2(OH)_2$, without any breaking down at the intermediate $CH_3.OH$ stage.

In the case of the equimolecular mixture, CH_4+O_2, the primary oxidation may thus be represented as a single transaction,

$$CH_4+O_2 = [H_2:C:(OH)_2] = \underbrace{H_2:C:O}_{CO+H_2,}+H_2O$$

involving the formation of steam but no separation of carbon. The facts observed with the mixture $2CH_4+O_2$, may also be explained on the supposition that in the primary oxygen attack half of the methane molecules are directly transformed into $CH_2(OH)_2$, and that the heat so liberated is sufficient to decompose part of the other half of the methane into its elements, the remainder being found intact after the explosion.

To explain the non-separation of carbon when the mixture $3CH_4+2O_2$, was exploded, it must be supposed that whilst one-third of the methane is directly transformed into $CH_2(OH)_2$, the other two-thirds cannot, for lack of oxygen, get beyond the $CH_3.OH$

stage, and that, therefore, the subequent thermal decompositions are restricted to those of such hydroxylated molecules as $CH_3.OH$ and $CH_2(OH)_2$ which do not involve any separation of carbon.

The above view of the matter is also consistent with another notable fact, namely, that in the case of mixtures intermediate between $2CH_4+O_2$, and CH_4+O_2 (*vide* Table III.) the *minimum* proportion of the oxygen appearing as steam in the products is found, not with $2CH_4+O_2$, as might at first appear likely, but with $3CH_4+2O_2$.

During the relatively long cooling period, which follows the attainment of the maximum explosion temperature, the following secondary interactions may come into play, namely: (*a*) the reversible change $CO+OH_2 \rightleftharpoons CO_2+H_2$; and, in the case of mixtures containing less oxygen than $3CH_4+2O_2$, (*b*) the interaction of steam and carbon $C+OH_2 = CO+H_2$; or, possibly (*c*) some slight interaction between methane and steam.

In this connection the recently published work of G. W. ANDREW on the "Water Gas Equilibrium in Hydrocarbon Flames,"* may be cited as proving that in a system containing only CO_2, CO, H_2, and H_2O, rapidly cooling down from the high temperatures prevailing in hydrocarbon flames, the equilibrium ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ adjusts itself automatically with the temperature until a point between 1500° C. and 1600° C. on the cooling curve is reached (corresponding to a value $K = 4{\cdot}0$, approximately), after which no further re-adjustment occurs. He also found that the adjustment of the equilibrium is not greatly influenced even when relatively large quantities of methane and carbon are found in the final products.

The results of our experiments, 1 to 3 inclusive, with the mixture $2CH_4+O_2$, where the initial pressures, 8·5 to 16·5 atmospheres were not sufficient for detonation, and in which the ratios $\frac{CO \times OH_2}{CO_2 \times H_2}$ in the final products varied between 4·45 and 3·76 only, confirm ANDREW'S conclusions. But in experiments 4 and 5, where with initial pressures 21·69 and 31·25, respectively, the mixtures detonated, the much lower ratio $\frac{CO \times OH_2}{CO_2 \times H_2} = 2{\cdot}56$ and 2·24, respectively, indicated some intervention of the separated carbon in the chemical interaction during the cooling period; there is nothing, however, in the results suggestive of any appreciable intervention of methane.

This conclusion is also borne out by the following figures relating to the mixture $2CH_4+O_2$, which show the ratio "R" which the sum of the oxygen as H_2O, *plus* half the oxygen as CO_2 in the products (assuming the CO_2 to have arisen wholly from the interaction $CO+OH_2 \rightleftharpoons CO_2+H_2$) bears to the total oxygen originally present in the mixtures fired in our experiments. The deviation of this ratio from 0·5 may be regarded as a measure of the participation of separated carbon in the secondary interactions during the respective cooling periods.

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* 'Trans. Chem. Soc.,' 1914, vol. 105, pp. 444–456.

EXPERIMENTS with Mixture $2CH_4+O_2$ in Bomb A.

Experiment No.	Initial pressure in atmospheres.	k.	R.
1	8·53	4·45	0·473
10	12·74	3·65	0·487
2	13·62	3·76	0·472
3	16·45	3·78	0·450
4	21·69	2·56	0·420
5	31·25	2·24	0·400

In the case of experiments with the mixture $2CH_4+O_2$, in bomb B, where, owing to the much smaller wall-surface per unit volume of mixture exploded, the maximum temperature would be somewhat higher, and the cooling period longer, than in the corresponding experiments in bomb A, the ratios "R" varied between 0·400 and 0·346.

PART III.—EXPERIMENTS SHOWING THE RELATIVE AFFINITIES OF METHANE AND HYDROGEN FOR OXYGEN IN EXPLOSIONS, AND CONCLUSIONS ARISING THEREFROM AS TO THE MODE OF COMBUSTION OF HYDROGEN.

(With Messrs. HAMILTON DAVIES and H. H. GRAY.)

The observations made during the preceding experiments that there is no deposition whatever of carbon when mixtures of composition intermediate between $3CH_4+2O_2$ and CH_4+O_2 are exploded under pressure, opened up the possibility of comparing the relative affinities of methane and hydrogen for oxygen under the conditions of homogeneous flame combustion, in the manner hereinafter to be described.

The theoretical importance of such a comparison is enhanced by the fact that it provides not only a basis for the discussion of the question whether or not the known rates of flame propagation through explosive mixtures of different combustible gases are governed by their relative affinities for oxygen, but also affords decisive evidence as to the mode of combustion of hydrogen in explosions.

Ever since Sir HUMPHREY DAVY'S experiments on flame, the combustibility of hydrogen has been considered superior to that of methane, and, as a matter of fact, not only is the ignition temperature in air of hydrogen (580° C. to 590° C.) lower than that of methane (650° C. to 750° C.),* but also the rates of inflammation (*i.e.*, of

* H. B. DIXON and H. F. COWARD, 'Trans. Chem. Soc.,' 1909, vol. 95, p. 519.

propagation of flame by conduction) of mixtures of hydrogen and air are much higher than those of methane-air mixtures. Thus, according to Le Chatelier.*

Hydrogen-Air Mixtures.

Hydrogen per cent. . .	10	20	30	40	50	60	70
Metres per second . . .	0·60	1·95	3·30	4·37	3·45	2·30	1·10

Methane-Air Mixtures.

Methane per cent.	6	8	10	12	14	16
Metres per second	0·03	0·23	0·42	0·61	0·36	0·10

Moreover, also, H. B. Dixon has shown that the rate of detonation of electrolytic gas, 2817 metres per second, is greater than the fastest rate for any mixture of methane and oxygen, namely 2528 metres per second for the equimolecular mixture CH_4+O_2.†

But inasmuch as ignition temperatures and rates of explosion are known to be governed chiefly by physical factors, such as heats of combustion, specific heats and molecular weights of products, and (possibly also) ionisation effects, nothing can be deduced from such data as to the relative affinities of the gases for oxygen. On the chemical side, however, certain experiments carried out, in the year 1856, by Landolt‡ in Bunsen's laboratory, in which the partly burnt products of a coal gas flame were sucked off for analysis through a fine platinum tube at different vertical heights (0, 10, 20, 30, 40, 50 mm.) along the vertical axis of the flame (100 mm. in height) have been cited as proving the vast superiority of the affinity of hydrogen over that of methane for oxygen in flames. Landolt, it is true, concluded that with regard to the different constituents of coal gas :—"*Der Wasserstoff ist unter allen Gasarten diejenige, welche am leichtesten verbrennt, es nimmt daher derselbe auch in der Flamme am schnellsten ab; etwas langsamer verschwindet das Grubengas, und zuletzt kommen die schweren Kohlenwasserstoffe, deren Verbrennung hauptsächlich erst in der oberen Hälfte der Flamme vor sich geht.*"

The circumstance that Landolt employed a platinum tube of narrow bore, fixed along the vertical axis of the flame, for the withdrawal of the partly burnt products, is in itself sufficient to vitiate his conclusion, inasmuch as recent researches in my laboratory have proved that in "surface combustion" (*e.g.*, in contact with firebrick at 500° C.) the usual order of the affinities of various combustible gases for oxygen in flames are entirely reversed.

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* 'Leçons sur le Carbone,' p. 279.

† Bakerian Lecture, 'Phil. Trans.,' 1893, vol. 184, pp. 177, 181.

‡ 'Habilitationsschrift, Breslau,' 1856; 'Pogg. Ann.,' vol. 99, 1856, pp. 389 to 417.

On the other hand, it has been proved in my previous researches upon hydrocarbon combustion: (1) that in slow combustion in borosilicate glass bulbs at temperatures between 300° C. and 400° C., methane, ethane, ethylene and acetylene are all oxidised at a much faster rate than is either hydrogen or carbon monoxide,* and (2) that on exploding such mixtures as $C_2H_4+H_2+O_2$ or $C_2H_2+2H_2+O_2$, the hydrocarbon is burnt in preference to hydrogen,† facts which are at variance with LANDOLT'S conclusion.

The possibility of deducing from our bomb experiments a direct comparison between the relative affinities of methane and hydrogen in explosions arose from the fact that the primary oxidation of methane involves a direct transition from CH_4+O_2 to $CH_2(OH)_2$, which latter breaks up into, ultimately, $CO+H_2+H_2O$, without any deposition of carbon. Whence it follows that if mixtures, $CH_4+O_2+xH_2$, be exploded, the division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (*i.e.*, direct oxidation) may be deduced from the proportion of the original methane found intact in the final products, provided always that there is no separation of carbon, which in fact is never observed in such circumstances.

The experimental method consisted, therefore, in exploding a series of mixtures $CH_4+O_2+xH_2$, in which the hydrocarbon and oxygen were initially present in as nearly as possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 8, and determining from the percentage of the original methane remaining intact in each case (1) the oxygen distribution when $x = 2$, and (2) the influence upon such distribution of successive equal increments of x up to 8. And in order to determine the possible influence of the walls of the explosion vessel upon the results, parallel series of experiments were carried out in each of the two bombs, A and B.

In each case the mixture exploded with a distinctly audible sound, which diminished in intensity as the proportion of hydrogen x increased, until with the mixture $CH_4+O_2+8H_2$ only a faint puff could be heard. In no case was there any separation of carbon.

Before discussing the bearing of the results upon the matter under investigation, it will be convenient to detail and summarise them in the following tabulated form. (Tables IV. to VIII. inclusive.)

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* 'Trans. Chem. Soc.,' 1902, vol. 81, pp. 538 and 539; 1904, vol. 85, p. 694.

† *Ibid.*, 1906, vol. 89, pp. 669 and 670, also 'Proc. Royal Institution,' 1908–10, vol. 19, pp. 73 to 87.

TABLE IV.—Explosion of Mixture $CH_4+O_2+2H_2$ in Bomb A.

Experiment No.	14	15	16	17
p_1	18·004	18·335	19·625	48·85
p_2	18·0136	18·2473	19·454	48·149
p_2/p_1	1·0005	0·995	0·991	0·986
Partial pressures in original mixture in atmospheres	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CH_4 . .	4·469	4·706	4·834	11·80
H_2 . .	8·863	9·007	10·030	24·93
O_2 . .	4·672	4·622	4·761	12·12
Partial pressures in gaseous products in atmospheres	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CO_2 . .	0·3672	0·3367	0·394	1·164
CO . .	4·2960	4·2960	4·470	10·910
H_2 . .	13·1300	13·410	14·320	35·520
CH_4 . .	0·2204	0·2046	0·270	0·555
$\frac{CO \times OH_2}{CO_2 \times H_2}$	4·01	4·16	3·6	3·0
Per cent. distribution of oxygen deduced from unburnt CH_4 — to CH_4 . .	95·31	95·70	94·74	95·6
to H_2 . .	4·69	4·30	5·26	4·4

Per cent.

Mean distribution of oxygen $\begin{cases} \text{to } CH_4 = 95{\cdot}34. \\ \text{to } H_2 \;\; = \;\; 4{\cdot}66. \end{cases}$

TABLE V.—Explosion of Mixture $CH_4+O_2+4H_2$ in Bomb A.

Experiment No.	18	19	20	21	22	23
p_1	20·50	21·206	29·39	31·36	37·07	71·6
p_2	18·5258	19·3907	26·280	28·14	34·387	67·70
p_2/p_1	0·9038	0·9147	0·8942	0·8973	0·9276	0·9456
Partial pressures in original mixtures in atmospheres	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CH_4	3·51	3·888	4·79	5·20	6·26	12·1
H_2	13·41	13·61	19·75	20·80	24·71	47·1
O_2	3·58	3·708	4·85	5·36	6·10	12·4
Partial pressures in gaseous products in atmospheres	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CO_2	0·1432	0·2011	0·270	0·32	0·358	0·87
CO	2·836	2·889	3·780	4·21	4·976	10·86
H_2	14·840	15·450	21·38	22·68	27·770	53·55
CH_4	0·7066	0·8506	0·85	0·93	1·283	2·42
$\frac{CO \times OH_2}{CO_2 \times H_2}$	[5·47]	3·90	3·23	3·65	3·38	2·93
Per cent. distribution of oxygen deduced from unburnt CH_4: to CH_4	80·83	78·47	82·65	83·0	81·0	81·0
to H_2	19·17	21·53	17·35	17·0	19·0	19·0

Per cent.
Mean distribution of oxygen to CH_4 = 81·0.
to H_2 = 19·0.

Table VI.—Explosion of Mixture $CH_4+O_2+6H_2$ in Bomb A.

Experiment No.	24	25	26	27
p_1	22·15	41·767	40·923	32·967
p_2	18·20	34·021	33·393	27·229
p_2/p_1	0·8217	0·8145	0·8160	0·8260
Partial pressures in original mixture	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CH_4	2·84	5·448	5·030	4·080
H_2	16·47	30·910	30·800	24·770
O_2	2·84	5·409	5·093	4·117
Partial pressures in gaseous products	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CO_2	0·11	0·246	0·172	0·152
CO	1·45	2·772	2·724	2·340
H_2	15·33	28·28	28·050	23·03
CH_4	1·31	2·723	2·447	1·707
$\frac{CO \times OH_2}{CO_2 \times H_2}$	3·53	3·11	4·23	4·01
Per cent. distribution of oxygen deduced from unburnt CH_4 to CH_4	54·3	52·57	54·2	59·3
to H_2	45·7	47·43	45·8	40·7

Per cent.

Mean distribution of oxygen $\begin{cases} \text{to } CH_4 = 54{\cdot}9. \\ \text{to } H_2 \;\; = 45{\cdot}1. \end{cases}$

TABLE VII.—Explosion of Mixture $CH_4+O_2+8H_2$ in Bomb A.

Experiment No.	28	29	30
p_1	39·135	49·656	50·09
p_2	29·9723	38·6634	38·6622
p_2/p_1	0·7659	0·779	0·772
	atmospheres.	atmospheres.	atmospheres.
Partial pressures in original mixture CH_4	3·859	5·038	5·02
H_2	31·390	39·580	40·16
O_2	3·886	5·038	4·91
	atmospheres.	atmospheres.	atmospheres.
Partial pressures in gaseous products CO_2	0·1243	0·1724	0·1592
CO	1·104	1·551	1·512
H_2	25·870	33·570	33·170
CH_4	2·874	3·370	3·821
$\frac{CO \times OH_2}{CO_2 \times H_2}$	2·42	2·35	2·16
Per cent. distribution of oxygen deduced from unburnt CH_4 to CH_4 .	30·0	33·8	30·4
to H_2 .	70·0	66·2	69·6

Per cent.

Mean distribution of oxygen $\begin{cases} \text{to } CH_4 = 31·4. \\ \text{to } H_2 \;\; = 68·6. \end{cases}$

TABLE VIII.—Explosion of Mixture $CH_4+O_2+xH_2$ in Bomb B.

Experiment No.	31	32	33	34	35	36	37	38	39
x	2	2	2	4	4	6	6	6	6
p_1	18·314	21·12	17·118	24·152	26·258	35·109	35·658	34·406	34·974
p_2	18·1204	21·082	17·1492	23·1858	25·398	31·505	32·067	30·946	30·998
p_2/p_1	0·989	0·998	1·002	0·960	0·967	0·897	0·899	0·899	0·886
Partial pressures in original mixture	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CH_4	4·424	5·48	4·528	4·361	4·614	4·544	4·638	4·195	4·565
H_2	9·486	10·08	8·080	15·430	17·030	25·870	26·400	25·910	25·950
O_2	4·404	5·56	4·510	4·361	4·614	4·695	4·620	4·301	4·459
Partial pressures in gaseous products	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.	atmospheres.
CO_2	0·339	0·470	0·3566	0·255	0·304	0·217	0·198	0·223	0·224
CO	4·049	5·168	4·250	3·742	4·071	3·321	3·306	3·190	3·082
H_2	13·61	15·290	12·400	18·800	20·600	26·74	27·34	26·32	26·44
CH_4	0·1224	0·154	0·1426	0·3888	0·423	1·227	1·223	1·213	1·252
$\frac{CO \times OH_2}{CO_2 \times H_2}$	3·75	3·77	4·21	3·52	3·05	2·95	3·47	3·12	2·98
Per cent. distribution of oxygen deduced from unburnt CH_4 to CH_4	97·33	97·20	96·90	91·1	90·82	73·0	73·6	71·1	72·6
to H_2	2·77	2·80	3·10	8·9	9·18	27·0	26·4	28·9	27·4
Mean percentage of oxygen to hydrogen	2·9			9·0		27·4			

The mean results of the foregoing experiments, so far as the distribution of oxygen between methane and hydrogen is concerned, are summarised as follows :—

TABLE IX.—Mixtures $CH_4+O_2+xH_2$.

x.		2.	4.	6.	8.
		Per cent.	Per cent.	Per cent.	Per cent.
Bomb A	O_2 to CH_4	95·34	81·0	54·9	31·4
	O_2 to H_2	4·66	19·0	45·1	68·6
Bomb B	O_2 to CH_4	97·1	91·0	72·6	—
	O_2 to H_2	2·9	9·0	27·4	—

It is at once evident from the results with the mixture $CH_4+O_2+2H_2$ that *the affinity of methane is at least twenty to thirty times greater than that of hydrogen for oxygen in explosions.* The actual distribution of oxygen when a particular mixture is exploded is undoubtedly influenced to some extent by the walls of the containing vessel but not by the absolute initial pressure. The influence of the containing walls would presumably disappear after a certain limiting ratio of area/volume is attained, and, had the resources at our disposal permitted, it would have been interesting to have made further experiments with a still larger bomb than B. An examination of the summarised results in Table IX. leads to the important conclusion that *the influence of successive increases in x, the volume ratio of H_2 to CH_4 in the mixture exploded, upon the actual oxygen distribution is for a given vessel proprotional to x^2.* This can hardly mean other than that in explosion flames hydrogen is *directly* burnt to steam as the result of trimolecular impacts,

$$2H_2+O_2 = 2H_2O.$$

PART IV.—EXPERIMENTS ON THE RELATIVE AFFINITIES OF METHANE AND CARBON MONOXIDE FOR OXYGEN IN EXPLOSIONS.

(With Messrs. HAMILTON DAVIES and H. H. GRAY.)

The success of the experiments described in the preceding section led us to make a similar attempt to determine the division of oxygen between methane and carbon monoxide when mixtures of the general composition CH_4+O_2+xCO are exploded under pressure. In this we were not completely successful, owing to a slight separation of carbon in the explosions whenever x exceeded 3·0 or thereabouts. Provided, however, that x did not exceed this limit, no carbon was deposited during the explosion, and such experiments may be given in detail as quite reliable so far as the question of the oxygen distribution between the two inflammable constituents is concerned.

Explosion of Mixture CH_4+O_2+3CO *in Bomb A.*

The results of the following two very concordant experiments in which the mixture was exploded, in bomb A, at an initial pressure of about 24 atmospheres, may be recorded as typical of the series. All that could be heard of the explosion was a faint squeak, and although on afterwards opening the bomb there was a trace of carbon on the firing wire, no carbon at all had been deposited on the bomb itself during the explosion. Condensation of moisture from the products could be detected, and the explosion was accompanied by a small increase of pressure. The results showed that between 8 and 9 per cent. only of the original oxygen had, during the initial "oxidation" stage of the explosion, combined with the carbon monoxide; the remainder had reacted with the methane. The results are tabulated as follows:—

TABLE X.—Explosion of CH_4+O_2+3CO in Bomb A.

Experiment No.		40	41
		atmospheres.	atmospheres.
Pressures in atmospheres	p_1	23·6	23·25
	p_2	25·2	24·70
p_2/p_1		1·068	1·063
		atmospheres.	atmospheres.
Partial pressures in original mixture	CH_4	4·32	4·70
	CO	14·60	13·85
	O_2	4·68	4·70
		atmospheres.	atmospheres.
Partial pressures in the gaseous products	CO_2	2·23	2·29
	CO	16·85	16·39
	H_2	5·78	5·57
	CH_4	0·34	0·45
$\frac{CO \times OH_2}{CO_2 \times H_2}$		3·17	3·34
Per cent. distribution of oxygen deduced from unburnt CH_4	to CH_4	92·0	91·0
	to CO	8·0	9·0

Explosion of CH_4+O_2+6CO *in Bomb A.*

In three other experiments (Nos. 42 to 44, inclusive), mixtures approximating to CH_4+O_2+6CO, were exploded in bomb A, but on account of there being a slight deposition of carbon during the explosion, which might conceivably have somewhat affected the accuracy of the determination of the oxygen distribution, we do not propose to publish them in detail, but for purposes of comparison with experiments

40 and 41, we may give the following summarised figures, from which it will be seen that there was practically no change in pressure after explosion and that approximately 20 per cent. of the original methane remained intact in the final products :—

TABLE XI.

Experiment No.	42	43	44
p_1 atmospheres	35·25	38·25	38·95
p_2 atmospheres	35·30	37·95	38·60
p_2/p_1	1·00	0·995	0·991
Percentage of the original methane unburnt	23·9	17·5	20·3

Explosion of Mixture CH_4+O_2+2CO *in Bomb B.*

The following two experiments with a mixture CH_4+O_2+2CO, were carried out in bomb B, for purposes of comparison with the corresponding experiments with the mixture $CH_4+O_2+2H_2$ (*vide* Table VIII., p. 303). There was no deposition of carbon during the explosion, but some moisture condensed on cooling, and the final pressure was approximately 9 per cent. greater than that of the original mixture. Taking the mean of the two experiments, 4·7 per cent. of the original methane remained intact in the products, as compared with an average of 2·9 per cent. in the corresponding experiment with the mixture $CH_4+O_2+2H_2$

TABLE XII.

Experiment No.		45	46
p_1 atmospheres		20·90	19·44
p_2 atmospheres		22·66	21·33
p_2/p_1		1·085	1·097
Partial pressures in the original mixture, atmospheres . . .	CH_4	5·184	4·870
	CO	10·470	9·831
	O_2	5·248	4·743
Partial pressures in the gaseous products, atmospheres . . .	CO_2	1·963	1·758
	CO.	14·110	13·260
	H_2.	6·320	6·106
	CH_4	0·266	0·207
$\frac{CO \times OH_2}{CO_2 \times H_2}$		3·64	3·56
Per cent. distribution of oxygen deduced from unburnt CH_4	to CH_4	94·9	95·7
	to CO	5·1	4·3

Explosion of CH_4+O_2+6CO *in Bomb B.*

Two experiments were carried out with this mixture in bomb B, but again a slight deposition of carbon occurred during the explosion, and therefore only the following summarised results need be given. There was practically no change in pressure in the cooled products, and approximately 16 to 17 per cent. of the original methane survived the explosion, as compared with an average of 27·4 per cent. in the corresponding experiments with the mixture $CH_4+O_2+6H_2$ (*vide* Table VIII., p. 303).

TABLE XIII.

Experiment No.	47	48
p_1 atmospheres	43·13	42·75
p_2 atmospheres	43·50	43·26
p_2/p_1	1·009	1·012
Per cent. of the original CH_4 unburnt . . .	16·3	17·1

Review of Results.

It is important to compare the results obtained with the foregoing CH_4+O_2+xCO mixtures, not only amongst themselves, but also with the results of the corresponding experiments with the $CH_4+O_2+xH_2$ mixtures.

In the first place, it is evident that the affinities of either hydrogen or carbon monoxide are greatly inferior to that of methane for oxygen in explosion flames; thus it may be inferred from the experiments with $CH_4+O_2+2H_2$ that the ratio of the affinities CH_4/H_2 is of the order 20 or 30 to 1 at least, and probably higher, if the influence of the walls of the containing vessel could be entirely eliminated.

Owing to the uncertainty of our knowledge as to the precise mechanism of the combustion of carbon monoxide in explosions, that is to say, as to the extent and character of the intermediary action of steam, it is perhaps difficult to assign, even approximately, any numerical relation between the affinities of methane and carbon monoxide for oxygen in flames. Nevertheless, it may be pointed out, without laying undue stress on the fact, that when the mixtures, initially containing methane, hydrogen or carbon monoxide, and oxygen in stochiochemical proportions (*i.e.*, $CH_4+O_2+2H_2$ and CH_4+O_2+2CO), were exploded under similar conditions in bomb B, the carbon monoxide was apparently more effective than hydrogen in pulling away oxygen from the predominating affinity of the hydrocarbon. From the theoretical standpoint it would probably be well worth while to undertake a further extended study of the matter in larger explosion vessels than we have employed, although it would be both a costly and a laborious enterprise.

Whereas, in the case of hydrogen, the influence of successive increments in x, the volume ratio of the other combustible constituent to methane in the mixture exploded, upon the actual oxygen distribution is proportional to x^2, in the case of carbon monoxide, it is more nearly proportional to x. This points to some fundamental difference between the modes of combustion of the two gases in flames; thus whilst the evidence is strongly in favour of the supposition that hydrogen is burnt directly to steam as the result of trimolecular collisions $2H_2+O_2 = 2H_2O$, the results with mixtures CH_4+O_2+CO seem to require some different supposition, such, for instance, as an intermediary action of steam.

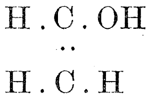
Part V.—Experiments with Mixtures of Ethylene, Hydrogen and Oxygen of the Type $C_2H_4+O_2+xH_2$.

(With Messrs. H. H. Gray and J. B. Dawson.)

It has long been known that when ethylene is exploded with its own volume of oxygen there is a doubling of the volume in the cooled products, with the formation of principally carbon monoxide and hydrogen, but without any separation of carbon or condensation of steam, substantially in accordance with the empirical equation

$$C_2H_4+O_2 = 2CO+2H_2.$$

It has also been shown that the addition to such a mixture of hydrogen sufficient to bring its composition up to $C_2H_4+O_2+H_2$, does not cause any separation of carbon on explosion, although there results a slight condensation of steam on cooling.*

That the above facts do not really imply a preferential combustion of carbon (as some have supposed) was proved by a study of the behaviour of a mixture $3C_2H_4+2O_2$, which on explosion gives rise to large quantities of both carbon and steam, together with methane, acetylene, hydrogen and oxides of carbon. Indeed, the facts harmonise very well with the hydroxylation theory, which would require the intermediate formation of *monohydroxyethylene*  $\begin{array}{c}\mathrm{H\,.\,C\,.\,OH}\\ \cdot\cdot\\ \mathrm{H\,.\,C\,.\,H}\end{array}$, a substance which on thermal decomposition would yield H_2O and $\vdots CH$ residues, the latter subsequently either (i.) undergoing hydrogenation to CH_4 in an atmosphere sufficiently rich in

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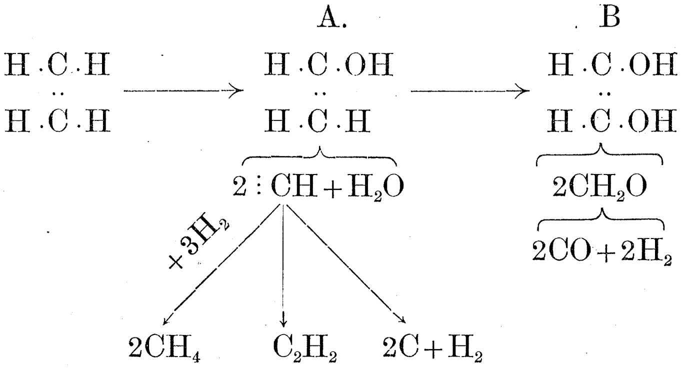
* Bone and Drugman, 'Trans. Chem. Soc.' 1906, vol. 89, pp. 669 to 671.

hydrogen; or (ii.) uniting with each other forming acetylene; or (iii.) decomposing into carbon and hydrogen, according to the experimental conditions.*

In the presence of a sufficient oxygen supply, however, there is a "non-stop" run through the *monohydroxy* to the *dihydroxy* stage which, on subsequent thermal decomposition, would give rise, first of all to formaldehyde, and then to carbon monoxide and hydrogen. The scheme of the "oxygen attack" is as follows, with the proviso that no decomposition occurs in "running through" stage A when there is sufficient oxygen to complete the transition to stage B.



It occurred to us that it would be of great interest to study the behaviour of mixtures $C_2H_4+O_2+xH_2$ in the bomb apparatus at initial high pressures, because successive additions of hydrogen would, according to the above scheme, operate in two distinct ways, namely (i.) by participating, more and more, in proportion to its active mass, in the initial oxygen distribution, it would prevent some of the hydrocarbon completing the A to B transformation, and so bringing about some decomposition at A; and (ii.) by participating in any "A" decomposition in such a manner as to "hydrogenise" the ⁝CH residues, and so counteracting, and perhaps even suppressing altogether, separation of carbon.

Such a twofold influence would be marked by (i.) an increasing steam and methane formation in the products with successive initial additions of hydrogen; and (ii.) a restraint or even total prevention of carbon deposition.

On actually putting matters to the experimental test it was found possible to add as much hydrogen as would correspond to $C_2H_4+O_2+8H_2$ without causing any deposition of carbon whatever on explosion, and is it probable that an even larger proportion of hydrogen could have been added without producing such a result. Progressive additions of hydrogen did, indeed, have the anticipated effects in regard to steam and methane formation as the following results will illustrate; there was, however, never any trace of acetylene found in the products.

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* See also BONE and COWARD on "The Thermal Decomposition of Hydrocarbons," 'Trans. Chem. Soc.,' 1908, vol. 93, pp. 1198 to 1225.

TABLE XIV.

Experiment No. . . .	49	50	51	52
Mixture	$C_2H_4+O_2+2H_2$	$C_2H_4+O_2+4H_2$	$C_2H_4+O_2+6H_2$	$C_2H_4+O_2+8H_2$
p_1 atmospheres	20·84	26·00	40·67	49·0
p_2 atmospheres	29·40	29·43	46·2	45·0
p_2/p_1	1·41	1·132	1·135	0·918
Per cent. of original carbon appearing as CH_4 in products	7·65	22·4	26·9	43·5
Per cent. of original oxygen appearing as H_2O in products (approximately) . .	4·0 to 6·5	18	27 to 42	36 to 46

PART VI.—THE EXPLOSION OF ETHANE WITH ITS OWN VOLUME OF OXGYEN.

(With Dr. HERBERT H. HENSTOCK.)

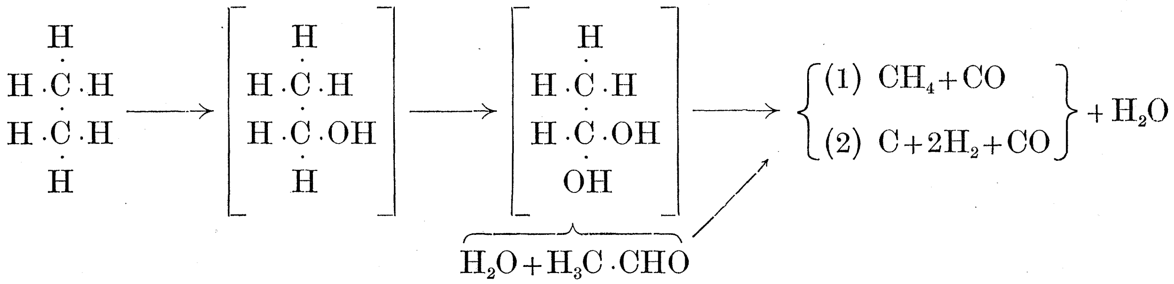
Owing to its crucially important bearing on the theory of hydrocarbon combustion, the behaviour of an equimolecular mixture of ethane and oxygen on explosion has been the subject of much investigation and discussion in recent years.

According to the now discarded theory of a preferential burning of carbon, such a mixture should, on explosion, give rise to carbon monoxide and hydrogen without any separation of carbon or steam formation, in accordance with the equation,

$$C_2H_6+O_2 = 2CO+3H_2;$$

and, inasmuch as carbon monoxide and hydrogen are, to all intents and purposes, mutually inert in flames, the final result should be unaffected by variations in initial pressure, or by the rate of cooling of the products for the maximum pressure of explosion.

It has, however, been shown that the behaviour of the said mixture is not at all in accordance with the requirements of the theory in question, inasmuch as it always gives rise on explosion to large quantities of free carbon, methane, steam, and aldehydic vapours, as well as oxides of carbon and hydrogen, just as would be expected from the standpoint of the hydroxylation theory, according to which there would be a "non-stop" run, through $C_2H_5.OH$, to $C_2H_4(OH)_2$, which would then decompose, yielding first acetaldehyde and steam, the acetaldehyde then breaking down into carbon, hydrogen, methane and carbon monoxide, in accordance with the scheme.



$$\begin{array}{c}H\\H\cdot C\cdot H\\H\cdot C\cdot H\\H\end{array}\longrightarrow\left[\begin{array}{c}H\\H\cdot C\cdot H\\H\cdot C\cdot OH\\H\end{array}\right]\longrightarrow\underbrace{\left[\begin{array}{c}H\\H\cdot C\cdot H\\H\cdot C\cdot OH\\OH\end{array}\right]}_{H_2O+H_3C\cdot CHO}\longrightarrow\left.\left\{\begin{array}{l}(1)\ CH_4+CO\\(2)\ C+2H_2+CO\end{array}\right.\right\}+H_2O$$

This conclusion was endorsed, in general terms, by Prof. H. B. DIXON in his Presidential Address to the Chemical Society in 1910, as the result of his own independent observations on the rate of detonation of a mixture $C_2H_6+O_2$.*

The modes of decomposition of dihydroxyethane and acetaldehyde at high temperatures, and the nature of the resulting products are such as would permit of the play of several secondary interactions, such for instance as (i.) $CO+OH_2 \rightleftharpoons CO_2+H_2$, and (ii.) $C+OH_2 = CO+H_2$, during the cooling period of an explosion. And therefore it is to be expected that the final result in any particular case will depend upon (i.) the maximum flame temperature and the rate of the subsequent cooling therefrom, which conditions are in turn governed by such factors as initial pressure, and (ii.) the phase attained by the explosion (*i.e.*, "inflammation" or "detonation"), and (iii.) the area and nature of the cooling surface per unit volume presented by the walls of the containing vessel.

The dependence of the final result upon such conditions is well illustrated by the following tabulated records (Table XV.) of the behaviour of a mixture $C_2H_6+O_2$ (i.) when inflamed at less than atmospheric pressure in glass vessels presenting very different areas of cooling surfaces to a given volume of the combining gases, and (ii.) when detonated in a leaden coil at initial pressures of 900 to 1200 mm.

It is thus seen (1) that the rapid cooling of the exploded gases in (*a*) favoured the survival of steam, aldehydes, and unsaturated hydrocarbons; (2) that the longer duration of the flame in (*b*) greatly increased the separation of carbon, at the expense of the saturated hydrocarbons and aldehyde, whilst it also favoured the secondary reduction of steam by carbon; and (3) that the much higher temperatures and pressures attained in detonation, whilst militating against the survival of aldehyde and unsaturated hydrocarbons, was chiefly effective in promoting the secondary reduction of steam by carbon. Nevertheless, even in detonation, as much as 17 to 20 per cent. of the original oxygen appeared as steam in the final products.

The foregoing considerations led us to study in detail the behaviour of the same mixture when exploded in bomb A, under various initial pressures between 10 and 40

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* 'Trans. Chem. Soc.' 1910, vol. 97, p. 665.

atmospheres, with results which are set forth in Table XVI. In all cases there was a marked deposition of carbon, and condensation of steam on cooling, but, as was anticipated, an increase in the initial pressure tended, on the whole, to diminish the proportion of both these results. The ratios p_2/p_1, in the different experiments varied between 1·85 and 2·05.

TABLE XV.—Explosion of Mixture $C_2H_6+O_2$.

Experimental conditions.	Inflammation in				
	(*a.*) *Long glass tube.* 1·5 metre long. 20 mm. internal diameter. Volume = 470 c.c. Area of walls = 940 cm.^{2}	(*b.*) *Glass globe.* Internal diameter = 8·5 cm. Volume = 320 c.c. Area of walls = 226 cm.^{2}		(*c.*) Detonation in lead coil. 20 metres long. 36 mm. internal diameter. Volume = 3100 c.c.	
	mm.	mm.	mm.	mm.	mm.
p_1	701	448	685	906	1180
p_2	1018	724	1187	1700	2240
p_2/p_1	1·45	1·61	1·73	1·86	1·90
Per cent. composition of gaseous products: CO_2 . . .	4·20	4·00	3·40	1·65	1·80
CO . . .	34·80	34·10	36·10	39·00	39·10
C_2H_2 . .	5·00 } 7·65	2·25	0·15	1·20	0·90
C_2H_4 . .	2·65			0·50	0·50
CH_4 . . .	8·85	6·85	7·25	6·65	7·70
H_2 . . .	44·50	52·80	53·05	51·00	50·00
Per cent. of original carbon deposited . .	7·6	19	17	5·3	3
Per cent. of original oxygen appearing as H_2O, &c., in condensable products .	37·8	32·8	27·5	20	17
Remarks . . .	Luminous flame travelled at approximately 0·5 metre per second. Each successive layer of the burning gas remained incandescent $\frac{1}{20}$ to $\frac{1}{30}$ second. Products gave strong aldehydic reaction; much steam condensed on cooling.	Lurid flame filled the globe and was of longer duration than in (*a*). Products gave faint aldehydic reaction, and steam condensed on cooling.		Coil filled cold; then its temperature was raised to 98° C. before the mixture was detonated; afterwards apparatus cooled by immersion in cold water.	

Another very notable and significant feature was the complete absence of both acetylene and ethylene from the final products, which, however, always contained considerable quantities of methane, even at the highest pressures. Such facts point to a sufficient violence in the explosion to shatter completely any unsaturated hydrocarbon or acetylene, if indeed such were momentarily found in the flame, and afford also another striking proof of the great stability of methane at the highest explosion temperatures.

TABLE XVI.—Explosion of Mixture $C_2H_6+O_2$ at High Pressures in Bomb A.

Experiment No.		53	54	55	56	57
p_1 atmospheres.		10·9	14·77	18·55	25·21	39·65
p_2 atmospheres.		20·56	27·93	37·22	51·72	73·4
p_2/p_1		1·88	1·89	2·0	2·05	1·85
Partial pressures in original mixture in atmospheres	C_2H_6 . . .	5·54	7·55	9·20	12·67	20·15
	O_2 . . .	5·36	7·22	9·35	12·54	19·50
Partial pressures in gaseous products in atmospheres	CO_2 . . .	0·570.	0·95	1·04	1·31	3·15
	CO . . .	7·525	9·80	14·14	19·49	27·35
	H_2 . . .	10·830	14·50	19·76	27·25	34·7
	CH_4 . . .	1·635	2·68	2·28	3·67	8·2
Per cent. carbon deposited		11·7	10·9	5·0	3·4	4·0
Per cent. of original oxygen appearing as H_2O in the final products		19·0	19·0	13·1	11·8	13·8

PART VII.—PRESSURE EXPERIMENTS.

The foregoing experiments (Part III.) having proved the absence of any direct connection between the relative affinities of methane, hydrogen and carbon-monoxide, respectively, for oxygen, in homogeneous flame combustion, and the rates of flame propagation through explosive mixtures, in which the combining gases are present in proportions corresponding to the effective primary reactions concerned, it now remained to prove whether or not such chemical factors determine the rates of attainment of the maximum pressures in explosions.

It had been our original intention to obtain optical records of the complete pressure curves, both *before* and *after* the attainment of maximum pressure, when the "primary" mixtures CH_4+O_2, $2H_2+O_2$, and $2CO+O_2$, respectively, are exploded at high initial pressures. But in this we were not entirely successful, owing to the excessively short intervals between ignition and the attainment of the maximum pressure, more particularly in the case of the fastest burning of the mixtures referred to, namely, $2H_2+O_2$. It was decided, therefore, to limit the investigations to the study of corresponding "air" mixtures, whose composition may, for all practical purposes, be written—

$$CH_4+O_2+4N_2,$$

$$2H_2+O_2+4N_2,$$

$$2CO+O_2+4N_2.$$

The experimental method consisted in firing such mixtures at initial pressures of from 45 to 50 atmospheres in the spherical bomb, B, to which was attached a Petavel recording manometer with its optical accessories.

The action of this manometer depends on the principle that the time period θ of a vibrating system may be expressed in terms of W the weight of its moving parts, and A the force required to produce unit deflection therein, as follows,

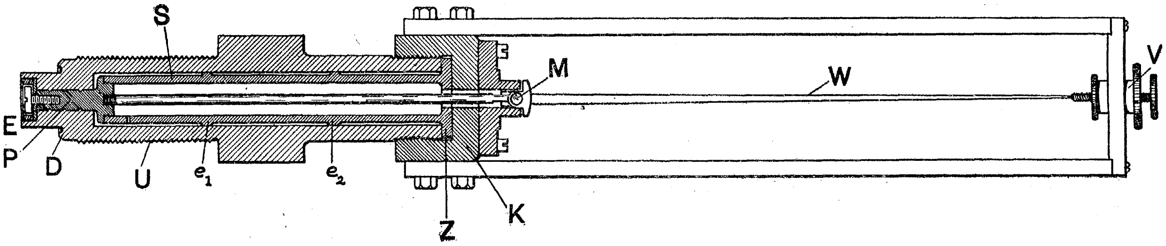

Fig. 14.

$$\theta = 2\pi\sqrt{\frac{W}{Ag}},$$

and in order to make θ as short as possible, consistent with a sufficiently great strength (W) to withstand the sudden development of extremely high pressures, the controlling force (A) brought into play per unit length of motion is made as great as possible, by using the stiffest spring obtainable. This means, of course, that the actual motion produced in the spring by the explosion is exceedingly small, but for recording purposes this is magnified by a special optical device, which focuses a point source of light on to a rapidly revolving drum, to which is attached a sensitive photographic film.

The following description of the instrument (fig. 14) used in our experiments is taken, with slight modifications, from Prof. PETAVEL'S memoir on "The Pressures of Explosions."*

The gauge is screwed into the explosion chamber by means of the thread, U. A gas-tight joint is formed by the ring, D, on the manometer pressing against a flat ledge in the enclosure. The end of the gauge from D to E fits well in the walls of the explosion chamber, and the joint is thus protected from the direct effect of the explosion. The spring, S, about 5 inches in length, is tubular in shape, and to prevent any buckling it is made to fit closely the cylinder, in which it is contained, in two places e_1 and e_2. The spring is fixed at its other end, Z, being held in position by the nut, K, whilst at its other end it is free and supports the piston, P.

The mirror, M (which in our experiments was of silvered glass with a focal length of about 2·5 feet), is attached to a lever, and at the outset of an experiment is kept in the zero position by means of the stretched piano wire (gauge 25), W; adjustment of the zero is effected by means of the screw, V. The distance between the knife edges of the mirror holder in our experiments was one thirty-second of an inch.

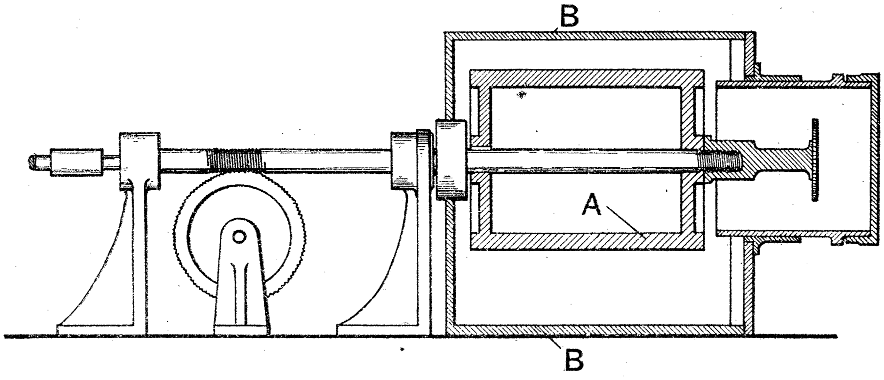

Fig. 15.

The sources of light employed by us was the crater of an electric arc in which the carbons were at right angles, and the beam was reflected by the mirror on to a sensitive photographic film fixed on to the drum, A, of the chronograph (fig. 15), also designed by Prof. PETAVEL (*loc. cit.*).

This drum (diameter = 8·8 cms.) which was usually rotated at a constant speed of between 200 and 600 revolutions per minute by means of an electric motor, was enclosed in a light-tight aluminium casing, BB, provided with a longitudinal slit, the width of which could be adjusted to suit the particular experimental conditions, and which could also be closed when required. An electrically-controlled tuning fork, giving 100 to 200 vibrations per second, was used as a time indicator; the fork being so placed that each vibration momentarily interrupted the light falling on to the photographic film, thus producing a dotted record on the resulting pressure curve.

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* 'Phil. Trans.,' 1905, A, vol. 205, p. 363.

The results of two typical experiments with each of the three mixtures are recorded in Table XVII., whilst figs. 16, 17 and 18, reproduce the corresponding pressure curves, from the moment of ignition until far into the cooling period after the attainment of maximum pressure, in each case, for one experiment with each mixture.

TABLE XVII.—Pressure Experiments.

Experiment No. . .	58	59	60	61	62	63
Mixture fired	$2H_2 + O_2 + 4N_2$		$CH_4 + O_2 + 4N_2$		$2CO + O_2 + 4N_2$	
Per cent. composition of mixture fired . . .	$H_2 = 29{\cdot}6$ $O_2 = 14{\cdot}5$ $N_2 = 55{\cdot}9$	$H_2 = 29{\cdot}7$ $O_2 = 14{\cdot}3$ $N_2 = 56{\cdot}9$	$CH_4 = 16{\cdot}7$ $O_2 = 17{\cdot}1$ $N_2 = 66{\cdot}2$	$CH_4 = 16{\cdot}8$ $O_2 = 16{\cdot}8$ $N_2 = 66{\cdot}4$	$CO = 28{\cdot}1$ $O_2 = 14{\cdot}0$ $N_2 = 57{\cdot}9$	$CO = 28{\cdot}03$ $O_2 = 14{\cdot}60$ $N_2 = 57{\cdot}37$
Initial pressure p_i in atmospheres . . .	53·0	50·0	44·9	50·0	51·0	49·8
Maximum explosion pressure in atmospheres p_m	425·0	400·0	240·0	280·0	423·0	420·0
Final pressure of cold products in atmospheres p_f	30·5	28·74	47·1	51·7	42·6	41·46
Ratio p_m/p_i	8·0	8·0	5·35	5·6	8·3	8·4
Ratio p_f/p_i	0·575	0·575	1·049	1·034	0·832	0·837
Time required for attainment of maximum pressure in seconds .	0·011	0·010	0·05	0·08 about	0·10	0·10

It is evident, from the above records, that the hydrogen-air mixture is by far the "fastest burning" of the three mixtures investigated, the maximum pressure being reached in approximately one-tenth of the time taken in the case of the slowest burning carbon-monoxide mixtures (0·01 as compared with 0·10 seconds).

The time required for the attainment of maximum pressure in the case of the methane air mixtures (0·05 to 0·08 seconds) was at least five times as long as that required in the case of the hydrogen-air mixtures, notwithstanding the fact that the affinity of methane is something like twenty times as great as that of hydrogen for oxygen in flames. Apparently, therefore, there is no direct relation between the actual rate at which the potential energy of an explosive mixture is transferred on explosion as sensible heat to its products, and the magnitude of the chemical affinity between its combining constituents.

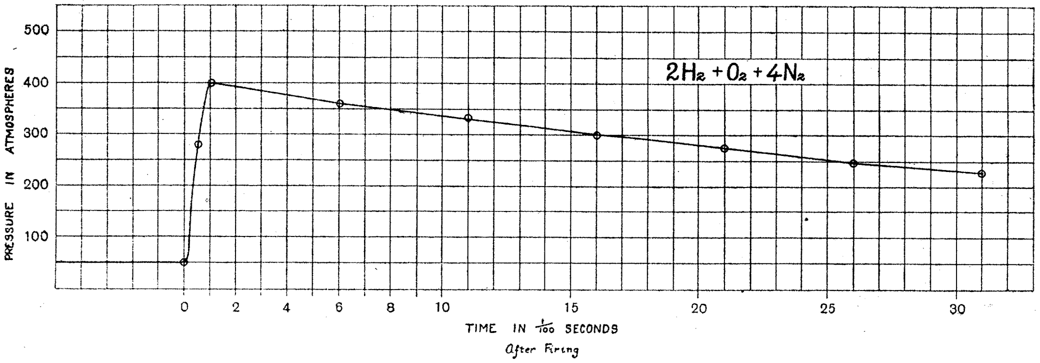

Fig. 16.

Attention may be drawn to the extreme slowness of the cooling after the attainment of maximum pressure in such explosions, a circumstance which has been observed by previous workers in other similar cases of gaseous explosion. This was particularly marked in the case of the methane-air mixtures, in which there was

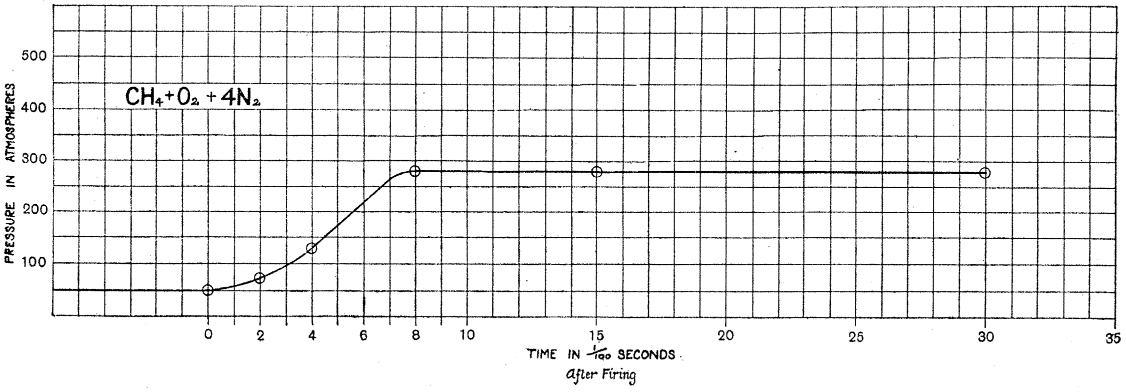

Fig. 17.

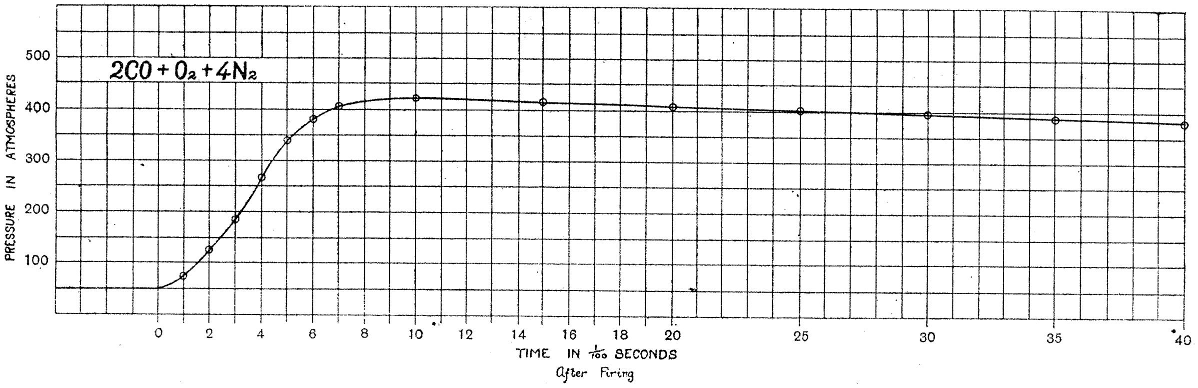

Fig. 18.

hardly any appreciable cooling during an interval of 0·22 seconds after the attainment of maximum pressure. This circumstance may possibly be attributed to (1) the combustion taking place in well defined chemical stages, and also to (2) the operation of the exothermic secondary interaction between carbon monoxide and steam during the cooling period. The cooling is rather more rapid in the case of the carbon monoxide-air mixture, and still more so in the case of the hydrogen-air mixture. The last named would appear to be a simple cooling curve uninfluenced by chemical combination.

Our thanks are due to the Government Grant Committee of the Society for liberal grants out of which the cost of the expensive apparatus employed on the work has been defrayed.