LVIII.—*The Slow Oxidation of Methane at Low Temperatures.*

By WILLIAM A. BONE and RICHARD V. WHEELER.

THE mode in which a hydrocarbon burns in a supply of oxygen insufficient to completely oxidise it to carbon monoxide (or dioxide) and steam has been the subject of much controversy. The view, at one time generally held, that under such conditions the hydrogen burns in preference to the carbon, can hardly be reconciled with the results of experiments on the explosion of ethylene or acetylene with less than an equal volume of oxygen (Lean and Bone, *Trans.*, 1892, 61, 873; Bone and Cain, *Trans.*, 1897, 71, 26). These results indicate that the main reaction in the explosion wave may be represented by such equations as

From these and other similar experiments, it is sometimes argued that in a limited oxygen supply the carbon of a hydrocarbon burns preferentially to the hydrogen; it should, however, be pointed out that the evidence supporting this contention is wholly derived from

investigations of the oxidation of hydrocarbons at the high temperatures of the explosion wave. The present paper records the results of experiments on the slow combustion of methane in an oxygen supply just sufficient to oxidise the carbon to carbon monoxide, at temperatures where the velocity of the reaction is just appreciable. This line of inquiry is, we believe, entirely new.

The reasons for the selection of methane as the most suitable hydrocarbon for these studies were as follows: (1) it is the simplest saturated hydrocarbon, and its molecule contains only one carbon atom, (2) preliminary experiments showed that it can be maintained at 480° to 500° (temperatures considerably higher than those afterwards employed in the oxidation studies) for many days without undergoing the least change, and (3) a mixture of two volumes of methane with one of oxygen is non-explosive. This was the mixture used throughout our experiments.

In a preliminary series of experiments, the object of which was to determine the most suitable experimental methods for the inquiry, the mixture of methane (2 vols.) and oxygen (1 vol.) was circulated through a tube containing fragments of unglazed porcelain maintained at a constant temperature (between 400 and 450°) in a Lothar Meyer furnace. The apparatus involved, however, proved too complicated for experiments which necessarily extended over several days continuously; the results, it may be stated, indicated that a portion of the methane was burnt to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or carbon. We also tried maintaining the mixture at 300° to 350° in contact with palladium black, but the 'catalytic' effect of the metal introduced complications which made it difficult for us to follow the real cause of the reaction.*

We finally resorted to the simple expedient of sealing the mixtures of methane and oxygen, under atmospheric pressure, in cylindrical bulbs of boro-silicate glass with capillary ends; the bulbs were afterwards maintained at constant temperatures (between 300° and 400°) for several days in an air-bath, until the whole or a part of the oxygen had disappeared. The cooled bulbs were subsequently opened under mercury, any change in volume (always a contraction) noted, and the residual gas withdrawn for analysis. We were thus able to examine the gases at various periods during the oxidation of the methane at any given temperature, and we could hardly fail to detect the formation of a product at any stage of the oxidation which afterwards disappeared before the process was completed.

The interaction of two such gases as methane and oxygen in glass vessels at low temperatures being a surface phenomenon, the temperature

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at which its velocity is just appreciable, as well as the velocity at any other given temperature, will, to a certain extent, depend on the character of the surface. In our experiments, 300° was the lowest temperature at which any interaction could be detected after the lapse of two or three weeks. At 325° , however, the velocity was much greater; at 350° , in some instances, the whole of the oxygen disappeared within three or four days, whilst at 400° the oxidation was always completed in a single day. But we have so far been unable to measure the relative velocities of the reaction at different temperatures on account of the fact that, except at 400° , when the velocity is considerable, the influence of the 'surface factor' may be very different even in two bulbs of the same size, shape, and material. Thus, between 325° and 350° , an appreciable amount of oxidation always occurred within three days, but of a series of similar bulbs filled with the same mixture and heated in the same bath, some exhibited a greater amount of oxidation in two or three days than others did in a week or more. Nor does the 'surface factor' of a given bulb remain constant over two or three successive experiments with the same mixture; whether it would finally become constant after a long series of experiments is a point we are now investigating.

It is of course impossible, by any means at our command, to determine the precise manner in which the methane molecule is attacked by the oxygen, but we are able to discover what is the first distinct *stage* of the reaction. This first stage may, obviously, involve one of three things, namely:

(1) Selective combustion of hydrogen, thus,

(2) Selective combustion of carbon, thus,

(3) Simultaneous oxidation of carbon and hydrogen, thus,

The primary oxidation products (which it will be seen may include carbon, hydrogen, carbon monoxide, carbon dioxide, and steam) may, however, react with each other, or with the original constituents of the mixture. We had therefore, as an important part of our inquiry, to investigate the possibilities of such reactions occurring in our bulbs at temperatures between 300° and 400° . We will now briefly discuss the evidence so obtained.

The possible secondary reactions may be classified as follows:

(A), those in which free carbon may be involved, for example:

The evidence obtained shows that none of these reactions begin at temperatures between 300° and 400°.

A series of experiments with bulbs similar to those used in the oxidation studies have shown that steam and carbon monoxide can be maintained at 325° for a fortnight without the slightest change occurring. At 350°, no action could be detected within a week, but after ten days some 1.7 per cent. of carbon dioxide had been formed; at 400°, about the same amount of change occurred in a week. On the other hand, mixtures of equal volumes of hydrogen and carbon dioxide showed no signs of change when kept at 325° or 350° for a fortnight, or at 400° for a week.

The results of these experiments show that no complication arising from the interaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ enters into any of our experiments on the oxidation of methane.

We have found that moderately dry carbon monoxide and oxygen do not react between 300° and 400°; the formation of between 0.7 and 1.7 per cent. of carbon dioxide could usually be detected when the *moist* gases were maintained at 325°, 350°, or 400° for a week. The effects of this possible secondary change in the methane experiments are therefore practically negligible.

In 1895, V. Meyer and Raum (*Ber.*, 28, 2804) published the results of an investigation on the combination of the elements of electrolytic gas in glass bulbs, very similar to those used by us, at temperatures between 300° and 518°. At 300°, the formation of water could just be detected after 65 days; in the case of four out of five bulbs maintained at 350° for 5 days, a very small amount of combination occurred (between 0.5 and 1.9 per cent. only of the original gas had disappeared), whilst in the fifth bulb as much as 16.4 per cent. of the gases had combined.* At 448°, the combination was still very slow. We have carefully repeated these experiments, using bulbs which had previously been employed for heating the mixtures of

* Judging from our own experiments at this temperature, we are inclined to attribute this relatively large formation of water to some roughness of the inner surface of the bulb used either present originally or caused by a partial devitrification of the glass during the heating.

methane and oxygen. At 335° , we have never been able to detect the slightest formation of water from electrolytic gas within a week; at 350° , in six bulbs no combination took place in a week, although in the case of a seventh bulb, in which the glass had become devitrified at one end, the formation of water could be distinctly seen. At 400° , three bulbs exhibited no signs of change after three days; after a week, water could be distinctly seen in one bulb (nearly 40 per cent. of the mixture had combined), but none could be detected in the other two. Professor Dixon informs us that some years ago he maintained glass bulbs filled with electrolytic gas at 350° for several weeks, but was unable to detect any formation of water. Our own experience shows that hydrogen and oxygen, even when mixed in combining proportions and undiluted with other gases, do not within a week or two combine at 350° to any appreciable extent provided the glass surface with which the gases are in contact remains perfectly smooth. At 400° , however, we are on the border line where the formation of water may occasionally be recognised within a week, but hardly within three days; in our experiments with methane at this temperature, the whole of the oxygen always disappeared within a single day.

(E) We have also found that the following pairs of gases have no mutual action at temperatures between 350° and 400° (within a week or two). Methane and carbon dioxide; methane and steam; carbon monoxide and hydrogen.

It may therefore be taken for granted that no appreciable complication arising from possible secondary changes enters into our experiments on the oxidation of methane, the results of which may now be discussed.

We find that between 300° and 400° methane combines with oxygen with an enormously greater velocity than does hydrogen itself under the same conditions. We have followed the course of the oxidation in at least thirty cases, and although our mixtures never contained more than 1 volume of oxygen to 2 volumes of methane, *in no case have we been able to detect the liberation of free hydrogen or free carbon at any stage, from beginning to end, of the process.* The disappearance of oxygen was always accompanied, in the cooled products, by a corresponding diminution in volume, due to the formation of water. This formation of water could always be detected even in the initial stages of an experiment, when less than one-tenth of the oxygen originally present had disappeared; the amount of it increased as the oxidation proceeded, until the inner surface of the cooled bulb was completely wetted. Since these phenomena occurred at temperatures below that at which the elements of electrolytic gas combine (in similar bulbs) with any appreciable velocity, and since carbon dioxide and hydrogen do not react even at 400° , the natural

inference is that *water is one of the primary products of the partial oxidation of methane at these temperatures.*

At all stages of the oxidation, the gases in the bulbs contained (besides water vapour) carbon monoxide, carbon dioxide, unchanged methane, and, in some cases of course, oxygen. At no period have we been able to detect the formation of such products as methyl alcohol, formaldehyde, or formic acid; the carbon of that portion of the methane burnt always appeared in the products as carbon monoxide or dioxide. There was, however, no regularity in the ratio $\text{CO}_2:\text{CO}$ at any given period of the oxidation, except towards the end; during the earlier period, it usually varied between 1:7 and 1:3, but finally it approximated to a value between 1:2 and 1:1. Since the influence of the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ between 300° and 400° has been shown to be negligible, and that methane and carbon dioxide have no mutual action, our experiments point to the conclusion that *the first stage in the "partial" combustion of methane at low temperatures is a simultaneous oxidation of carbon and hydrogen to carbon monoxide and steam*, thus:

One curious feature about our results is the unexpectedly large proportion of carbon dioxide found in the gases at each stage, but especially towards the end of the oxidation. Now the rate at which carbon monoxide combines with oxygen, or reacts with steam, between 300° and 400° has been shown to be negligible; therefore we cannot explain the formation of any considerable quantity of carbon dioxide in an experiment on the supposition that carbon monoxide actually liberated during the primary oxidation is afterwards *gradually* transformed into the dioxide through the agency of steam and oxygen, or steam alone. The largest proportions of carbon dioxide were found in bulbs in which the mean rate of oxidation had been, for any particular temperature, fast; the two circumstances are, we are inclined to think, not unconnected. Further, we should perhaps state that our experiments suggest that the 'oxidation velocity' in a given case is accelerated after the first portions of the oxygen have disappeared, but this is a point which requires fuller investigation. We are inclined to take the following view of the formation of so much carbon dioxide. When the methane molecule is burnt, carbon monoxide and steam simultaneously come into being in an atmosphere containing oxygen. At the moment of their formation, these new molecules would be in an extremely labile and reactive condition, and it is probable that during this transitory 'labile period' a much more frequent exchange of oxygen would occur in the system $\begin{array}{c|c} \text{CO} & \text{OH}_2 \\ \text{CO} & \text{OH}_2 \end{array} \mid \text{O}_2$, than under ordinary circumstances. It is also conceivable that the 'lability' of such

a system would be influenced by the rate at which the methane succumbs to the attack of the oxygen.

EXPERIMENTAL.

I.—*The Preparation of Pure Methane.*

The preparation of pure methane by Gladstone and Tribe's method is always a tedious process; if, however, an aluminium-mercury couple be substituted for the zinc-copper pair, the result is much more satisfactory. In fact, the action of the aluminium-mercury couple on a mixture of methyl iodide and alcohol is so energetic that the reaction vessel must be well cooled by immersion in iced water at the outset of the preparation, or otherwise the evolution of the gas becomes too rapid, and is difficult to control. In addition to being contaminated with the vapours of the alcohol and iodide, the gas almost invariably contains a small quantity (2 or 3 per cent.) of hydrogen. This may be easily

FIG. 1.

removed, after the other impurities have been eliminated, in one of two ways, namely: (1) by passing the gas through a layer of 'oxidised' palladium black at 100° , or (2) by liquefaction of the methane in a bulb immersed in liquid air, when, of course, the hydrogen passes on. The details of the method are as follows:

The central bulb of the Wöhler U-tube A (Fig. 1) is filled with clean aluminium foil, cut into pieces about one-eighth of an inch square. A few c.c. of a mercuric chloride solution are poured on to the foil which, in the course of a minute or two, becomes coated with mercury. The liquid is then drained off, and the couple rapidly washed (twice) with methyl alcohol. About 30 grams of methyl iodide are then poured on to the couple. The tap funnel, B, containing a mixture of 2 to 3 parts by weight of methyl iodide and one part of methyl alcohol, is quickly inserted in one limb of the U-tube by means of a rubber cork. The other limb is immediately connected with the arrangement for washing the gas, consisting of (1) the worm C surrounded by iced

water, (2) worms D and E containing a strong solution of sodium methoxide in methyl alcohol, and (3) worm F containing strong sulphuric acid. The lower part of A should be immersed in iced water; on dropping the mixture from B on to the couple, a good evolution of methane is obtained. The air is swept out of the apparatus through the vertical branch of the three-way tap, G, before connection with the apparatus for the elimination of hydrogen is made. When oxidised palladium sponge is used for this purpose, it is placed in the small U-tube, H, which is immersed in boiling water. The gas is afterwards dried by passing it through the worm, K, containing sulphuric acid. Where palladium sponge is not available, the removal of traces of hydrogen can be effected by means of liquid air, the methane condensing to a colourless liquid as fast as it is evolved.

We have frequently tested the purity of the gas so prepared by explosion analyses; the following are the results in the cases of four typical samples:

	(1).	(2).	(3).	(4).
Volume of gas taken ...	58.00	44.40	66.25	57.0
Contraction C	115.8	89.2	130.0	112.0
Absorption A	57.95	44.5	65.3	56.3

II. *The Action of Heat on Methane.*

Since in the subsequent 'oxidation' experiments, mixtures of methane and oxygen were maintained at temperatures between 300° and 400° for, in some cases, as long as two or three weeks together, it was necessary to ascertain whether methane itself undergoes any change at temperatures at all near these limits. Accordingly, about 3 litres of pure methane were kept continuously circulating for six days and nights through a hard glass tube (about 0.75 metre long), packed with fragments of well-dried, unglazed porcelain, maintained at 480° in a Lothar Meyer furnace. In the circuit was a glass spiral, which, during the experiment, was kept surrounded by a freezing mixture. On examining the tube after the experiment, no blackening, or even discoloration of the porcelain, could be detected, nor could any liquid be seen in the glass spiral. The volume of the methane remained constant throughout the experiment, and analysis showed that it had undergone no change. Further experiments showed that only at 650—700° does methane begin to decompose, and even then very slowly.

III.—*The Oxidation Experiments.*

The mixtures of methane and oxygen (the latter prepared by heating recrystallised potassium chlorate in hard glass bulbs, and afterwards washing it through a strong solution of potassium hydroxide) were

made in a graduated glass holder over pure strong sulphuric acid. The methane in each case was determined analytically by an explosion method, and the oxygen by absorption with strongly alkaline pyrogallol (freshly prepared). Altogether five mixtures were used; the percentage composition of each, leaving altogether out of account the small amount of nitrogen present (namely, 1.0, 2.16, 0.95, 3.6, and 2.67 per cent. respectively),* is given below :

Mixture.	A.	B.	C.	D.	E.
Methane	69.0	66.66	67.44	66.80	66.90
Oxygen	31.0	33.34	32.56	32.20	33.10

Filling of the Bulbs.—The cylindrical Jena boro-silicate glass bulbs used in these experiments terminated at each end in a long capillary tube (1 mm. bore). They had a capacity of between 60 and 70 c.c. (length about 10 cm., diameter 3.5 cm.), except a few, somewhat larger (capacity 70 to 80 c.c.), used during the later stages of the research. Boro-silicate glass is eminently suited for the making of vessels in which gases are to be heated for long periods under pressure; in our own experiments the bulbs, filled at atmospheric pressure and temperature, could be maintained at 400° for, if necessary, many weeks without showing change in shape or capacity, or signs of devitrification. Similar bulbs made of ordinary soft or hard glass generally devitrified or burst when subjected to the same treatment. Further, boro-silicate glass possesses another great advantage over other kinds in that it withstands sudden changes of temperature.

Before being filled with the mixture under investigation, the inner surface of each bulb was thoroughly cleaned with hot strong nitric acid, and afterwards with distilled water. Each was subsequently dried in a current of hot air (dust free). A number of such clean, dry bulbs were connected in series, on the one hand, with the holder containing the mixture of methane and oxygen, and, on the other, through a drying tube to a Sprengel pump and manometer. When nearly vacuum, each bulb was strongly heated with a Bunsen burner and the exhaustion completed. As soon as the bulbs were cold, the mixture was admitted from the holder until the pressure in the apparatus was 2—3 mm. below the atmospheric; the capillaries of each bulb were then successively drawn out and sealed off in the blow-pipe.

Heating of the Bulbs.—The bulbs were heated, in batches of from 2 to 6 as required, in a special air-oven, the gas supply of which passed through a Stott's governor, and then through a Lothar Meyer regulator. The temperature was registered by a thermometer reading

* In order to make the results of the various experiments strictly comparable, we propose to adopt this course throughout the paper in tabulating the composition of the various gaseous mixtures under discussion. Since the nitrogen in each case was taken 'by difference,' the tabulated results will always add up to 100.

up to 500° , and we had no difficulty in keeping it practically constant for weeks together. The extreme variations on either side of the desired mean temperature were about 5° in the longest experiments; in the case of experiments extending over a few days only, the variations in temperature were even less.

Examination of the Bulbs after Heating.—As soon as each bulb was withdrawn from the air-bath, it was quickly cooled in water. The most superficial examination of the cold bulbs revealed two significant facts connected with the partial oxidation of the methane, namely, (1) no carbon had been deposited, and (2) the formation of a dew on the inner surface of the vessel. On standing such a bulb in a vertical position, the dew soon collected in the capillary as a colourless liquid.

The liquid was tasteless and odourless, it did not contain hydrogen peroxide, formaldehyde, or formic acid; it solidified in a freezing mixture, and the solid melted at 0° . It was, in short, water.

The bulbs were subsequently opened under mercury, and the gases withdrawn as follows:

A deep scratch having been made near the end of one of the capillaries of the bulb A (Fig. 2), the glass was nipped off under the surface of mercury contained in the cylinder, B. In each case, the mercury entered the bulb, partially filling it. After the lapse of half-an-hour, the level of the mercury inside the bulb (*a*) was marked (the levels inside and outside having been previously equalised). The open end

of the capillary was then forced into a stout rubber joint connected with the U-shaped capillary tube, C; the whole of this rubber joint and capillary had been previously filled with mercury as far as the tap D, through which connection was made with a Sprengel pump. All connections having been thoroughly exhausted, the tap, D, was opened, and the gas in A drawn off through the pump into tubes over mercury. Finally, the bulb, A, was detached, and its total volume, as well as the volume up to the mark *a*, determined. In this way, the contraction, due to the formation of water during the oxidation, was approximately measured; in all cases, it corresponded to the volume of oxygen which subsequent analysis showed had disappeared.

FIG. 2.

Analysis of the Residual Gases.—The analysis of the residual gases constituted the most important part of the work, for on their accuracy depends the proof that no free hydrogen was formed during the course of the oxidation. The apparatus used was that described by one of us at a meeting of the Society in 1898 (Proc., 1898, 14, 154), and a long experience of its working has shown that it admits of a high degree of accuracy.

In addition to a large amount of unchanged methane, the gases always contained carbon dioxide, carbon monoxide, and in some cases oxygen also. The last three were removed and estimated in the following order, namely (1), carbon dioxide by means of a strong solution of potassium hydroxide, (2) oxygen by means of a freshly prepared and strongly alkaline solution of pyrogallol, and (3) carbon monoxide by means of freshly prepared ammoniacal cuprous chloride, the gas being afterwards treated with dilute sulphuric acid before remeasurement. When the gases contained more than 5 per cent. of carbon monoxide, they were subjected to a second treatment with a fresh portion of the cuprous chloride solution. A series of trial experiments satisfied us that practically the whole of the carbon monoxide in such a mixture can be removed in this way; certainly never as much as 0.5 per cent. remains unabsorbed.

After removal of the three foregoing constituents, a measured portion of the residual gas was exploded with a large excess of oxygen, and the contraction in volume (*C*), and the absorption (*A*) when the products of explosion were treated with potassium hydroxide, determined. It is essential to the accuracy of such an analysis that the explosive mixture ($\text{CH}_4 + 2\text{O}_2$) should be largely diluted with excess of air, in order to avoid the oxidation of any nitrogen present, or deposition of carbon in the explosion vessel due to shock. In the case of these mixtures, we always added at least 100 volumes of diluents to every 50 to 60 volumes of the explosive mixture, and exploded the gases under half an atmosphere pressure. These precautions ensured the necessary conditions of accuracy.

From the ratio $\frac{C}{A}$ obtained in any case, we were able to determine whether the gases exploded contained hydrogen in addition to methane. This ratio for pure methane is, of course, 2.0, and for mixtures of methane and hydrogen would be greater (thus it would be 2.015 for a gas containing 99 per cent. of methane, and 1 per cent. of hydrogen, and trial experiments have shown that this quantity of hydrogen can be detected with certainty). An examination of the results of twenty-five different experiments detailed in the following paragraphs will show that in sixteen cases the ratio fell between 1.99 and 2.00; in seven other cases, it lay between 1.95 and 1.99, whilst in

two cases only (2·007 and 2·005 respectively) was it higher than 2·00. These numbers, therefore, prove the absence of free hydrogen in the oxidation products at all stages of the process.

Experiments at 300°.

The rate at which methane and oxygen combine at this temperature is very slow, so that it is hardly ever possible to detect any change unless the heating be continued over two or three weeks. The results of two experiments, in both of which the formation of water could be distinctly seen, are given below. The mixture employed was A (methane = 69·0 ; oxygen = 31·0) :

	Composition of dry gases after	
	14 days.	21 days.
Carbon dioxide	0·70	2·40
Carbon monoxide	3·85	6·40
Oxygen	27·10	21·40
Methane.....	68·35	69·80
$\frac{C}{A}$ for residual gas exploded.....	1·97	2·00

Experiments at 325°.

First Series.—Four bulbs filled, at 18° and 758 mm., with mixture D (methane = 66·8 ; oxygen = 33·2) and heated for 30 hours, 3, 6, and 11 days respectively. All showed the formation of water ; it will be seen that more oxygen had disappeared in the bulb heated 3 days than in the one in which the action had continued over 6 days. The analytical results are given below :

Duration of heating.	30 hours.	3 days.	6 days.	11 days.
Carbon dioxide	nil	1·66	0·90	2·30
Carbon monoxide	1·07	7·24	4·35	7·45
Oxygen	31·60	24·10	28·45	23·25
Methane	67·33	67·00	66·30	67·00
$\frac{C}{A}$ for residual gas exploded	2·00	2·00	2·00	2·00

Second Series.—Four bulbs filled, at 21° and 755 mm., with mixture E (methane = 66·9 ; oxygen = 33·1) and heated for 3, 7, 14, and 21 days respectively. Singularly enough, by far the greatest amount of interaction occurred in the bulb heated for 3 days ; indeed, the order according to 'rate of oxidation' is nearly the reverse of that

according to the duration of the heating. These experiments afford a good illustration of the point emphasised in the introduction, namely, that the influence of 'surface factor,' in the case of several exactly similar vessels, upon the velocity of a gaseous reaction is often enormously different. The analytical results are as follows :

Duration of heating.	21 days.	14 days.	6 days.	3 days.
Carbon dioxide	2.07	1.40	2.00	12.85
Carbon monoxide	5.50	5.00	6.15	16.30
Oxygen	25.60	25.70	24.10	(2.00)*†
Methane.....	66.83	67.90	67.75	(68.85)
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$\frac{C}{A}$ for residual gas exploded.....	2.00	1.985	1.987	1.985
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Experiments at 350°.

First Series.—Three bulbs filled with mixture E (methane = 66.9 ; oxygen = 33.1) at 22° and 747 mm., and heated for 24 hours, 66 hours, and a week respectively. Analyses of residual gases gave following results :

Duration of heating.	24 hours.	66 hours.	7 days.
Carbon dioxide	0.35	0.38	14.0
Carbon monoxide	2.05	2.90	16.3
Oxygen	31.38	30.35	0.9
Methane	66.22	66.37	68.8†
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$\frac{C}{A}$ for residual gas exploded.....	1.98	1.99	2.00
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Second Series.—Three bulbs filled with mixture E at 21° and 755 mm., and heated for 1, 3, and 7 days respectively. We would draw attention to the fact that the bulb heated 7 days exhibited a much smaller amount of oxidation than the one heated for the same time in the previous experiment. The analytical results for the residual gases were as follows :

Duration of heating.	1 day.	3 days.	7 days.
Carbon dioxide	0.40	2.80	2.25
Carbon monoxide	2.15	8.95	4.90
Oxygen	31.40	21.80	26.60
Methane	66.05	66.45	66.25
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$\frac{C}{A}$ for residual gas exploded.....	2.00	2.00	1.995
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* This number for oxygen is only approximate ; the same therefore applies to that given for methane.

† See footnote, p. 548.

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Third Series.—Six bulbs filled with mixture B (methane = 66.6; oxygen = 33.3) maintained at 350° for 13 days. In each case, practically the whole of the oxygen had disappeared, and a large quantity of water was produced. The contractions, on opening the bulbs under mercury, amount to between 30 and 33 per cent. of the original volume. The products of four of the bulbs were analysed, with the following results; attention is drawn to the large quantity of carbon dioxide produced in each case:

	(1).	(2).	(3).	(4).
Carbon dioxide	14.8	10.2	10.0	10.0
Carbon monoxide.....	16.0	23.6	21.5	22.2
Oxygen.....	nil	nil	0.3	nil
*Methane	69.2	66.2	68.2	67.8
$\frac{C}{A}$ for residual gas exploded	2.007	1.994	2.005	1.956

Experiments at 400°.

At this temperature, methane is rapidly oxidised, and differences due to surface factor in a series of similar bulbs tend to disappear. We have always found that the oxygen in our mixtures disappeared within a single day, and that the phenomena were altogether more regular than at lower temperatures. We would in this connection again point out that we have maintained bulbs containing electrolytic gas at 400° for 3 days, and in many cases a week, without finding any appreciable formation of water. The following are the analytical results from an experiment in which five bulbs filled with mixture C (methane = 67.44; oxygen = 32.56) at 20° and 750 mm. were heated for 1, 2, 4, and 11 days (two bulbs) respectively. The contraction observed on opening these bulbs under mercury amounted to as nearly as possible one-third of the original volume:

Duration of heating.	1 day.	2 days.	4 days.	11 days.	11 days.
Carbon dioxide	11.4	12.4	11.3	10.6	11.9
Carbon monoxide	18.4	17.0	17.6	18.9	18.6
*Methane	70.2	70.6	71.1	70.5	69.5
$\frac{C}{A}$ for residual gas exploded	1.95	1.99	2.00	2.00	2.00

* The percentage of methane in these products, and also in nearly all other experiments in which a large proportion (over 10 per cent.) of carbon dioxide was produced, is rather higher than it should be. We have reason to believe that this is caused by a small absorption of carbon dioxide by the alkali in the glass,

We are continuing this work and extending it to other hydrocarbons.

In conclusion, we desire to state that the expenses of this research have been defrayed out of grants received from the Government Grant Committee of the Royal Society.

THE OWENS COLLEGE,
MANCHESTER.