THE OXIDATION OF METHANE

by

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A thesis submitted in
fulfilment of the
requirements for the
degree of Doctor of
Philosophy of Glasgow
University.

July, 1928.

It is a pleasant duty for the author to record his gratitude and indebtedness to Professor Gray, Royal Technical College, for his encouraging supervision, advice and constructive criticism during the course of the work.

The author also desires to thank the Governors of the Royal Technical College and the Carnegie Trust for the Universities of Scotland for grants which have allowed him to carry out this work.

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SUMMARY.

PART I.

In this section a comprehensive study of the combustion of methane by means of copper oxide has been carried out. The influence of temperature on the amount of methane burned by a constant weight of copper oxide has been investigated, together with a few preliminary experiments on the effect of varying the time of contact of the gas and the oxidising agent (pp.28-34).

Details of the effect of the addition of hydrogen or ethylene to the methane on the temperature of combustion of the latter hydrocarbon are given, together with figures illustrating the oxidation of the olefine by means of copper oxide (pp.35-45).

The activity of lead chromate, both precipitated and fused, in causing the oxidation of methane has been investigated, together with the effect of temperature on the oxidation of carbon monoxide by the fused salt (pp.46-55).

Details are then given of the effect of the addition of the following catalysts to the copper oxide in causing a decrease in the temperature of combustion of methane:-

1. Cuprous Chloride.......pp.56-62.
2. Vanadium Pentoxide.....pp.63-70.
3. Cobalt Oxide...........pp.71-73.
4. Nickel Oxide...........pp.74-77.
5. Manganese Dioxide......pp.78-81.

while in the case of vanadium pentoxide the effect of varying the amount of catalyst present has been studied.

Finally, the oxidation of methane by means of pumice impregnated with cobalt oxide has been investigated (pp.82-85).

In each case complete tables of results, from the point where no combustion takes place to the temperature at which all the hydrocarbon is completely oxidised, are given and the results shown graphically.

PART II.

In this section a study of the influence of catalysts in promoting the oxidation of methane, in a mixyure containing two volumes of methane and one volume of oxygen, has been undertaken. The influence of temperature on the quantities of methane oxidised to the various products of oxidation has been studied and the reaction between the two gases followed out until 25% of the methane supplied has been oxidised to carbon dioxide, this being the maximum value possible under the circumstances.

Details are given of the efficiencies of the following

catalysts in promoting the oxidation of methane by means of gaseous oxygen:-

1. Palladium Black on Asbestos......pp.112-115
2. Platinised Asbestos.............pp.116-119
3. Platinum Black on Asbestos.......pp.120-123
4. Copper on Pumice.................pp.124-128
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6. Vanadium Oxides on Pumice........pp.133-138
7. Cuprous Chloride on Pumice.......pp.139-148.

In all cases except the last, complete tables of results from the point at which oxidation commences or, in cases where this is below atmospheric temperature, from atmospheric temperature, are given and the results shown graphically.

PART III.

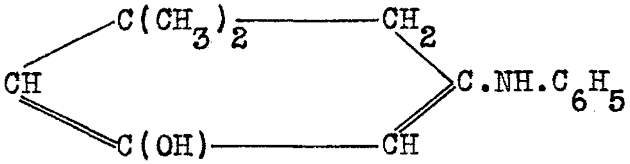
The influence of the time of contact in determining the amount of methane oxidised by means of copper oxide has been investigated in this section. Various types of apparatus have been considered and two main methods of procedure finally adopted. The results obtained by these methods have been fully analysed and two subsidiary investigations, suggested from the conclusions drawn from these results, have been carried out. These were investigations into the effects caused by varying the concentration of methane in the gaseous mixture and by varying the amount of surface of copper oxide exposed to the gas.

PART I.

THE INFLUENCE OF CATALYSTS IN PROMOTING THE OXIDATION OF METHANE BY MEANS OF COPPER OXIDE.

Introduction.

In many problems in fuel technology and organic chemistry where analyses by means of combustion are necessary the issue is partially dependent on the complete oxidation of methane, either by means of an oxidising agent which furnishes the oxygen necessary for oxidation or by means of an external supply of oxygen in the presence of an oxidation catalyst, the medium being heated to a suitable temperature. Many organic substances on decomposing give off large quantities of methane and it is well known that coals and oils evolve methane on heating. Thus Haas (1)* has drawn attention to the fact that certain basic compounds, derived from reduced benzene nuclei and having two methyl groups attached to the same carbon atom, of the type



yield an appreciable quantity of methane when heated with copper oxide in the Dumas absolute method of estimation of nitrogen and this methane, not being completely oxidised, is measured as nitrogen in the azotometer and leads to results which are 2% - 5% too high. Lambris (2) has described a very elaborate method for estimating nitrogen in such substances, involving the passage of the gas obtained, mixed with excess

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* The numbers refer to the bibliography at end of book.

oxygen, over a red-hot platinum spiral and then through a heated tube containing reduced copper to absorb the excess oxygen. Ths combustion thus takes place in two stages and all combustible gases, particularly methane, are burned, leaving pure nitrogen in the nitrometer.

Further, King and MacDougall (3), in the course of work on the determination of carbon and hydrogen in coal by Liebig's method, have shown that, even when oxygen is supplied from an external source, methane is not always completely oxidised by copper oxide, even at 800°C., as much as 0.3mgm. of the carbon in the coal escaping combustion in the form of methane, leading to an error of 0.15% in the carbon content value of the coal. They have also noted that methane is the gas which most easily escapes combustion, the higher paraffins being completely oxidised at lower temperatures and the unsaturated hydrocarbons at still lower temperatures.

Very little definite data seem available concerning the complete oxidation of methane with oxidising agents or with oxygen in the presence of a catalyst. In 1894, Phillips (4), in the course of work on the initial combustion temperatures of organic substances, mainly hydrocarbons, in oxygen in the presence of palladianised asbestos, found that methane commenced to burn at 404°- 414°C. under these conditions, while in the following year Campbell (5), using copper oxide alone and copper oxide impregnated with palladium as oxidising substances, found no combustion to take place, in either case, at 455°C., This observation was followed in 1896 by that of Dunstan and Carr (6) who found that in the estimation of nitrogen in aconitine methane was left unoxidised by a 60cm. column of copper oxide maintained at a red heat and that an increase in the rate of flow of the gases over the copper oxide caused a decrease in the amount of methane burned.

Four years later, Gautier (7), in an investigation on the combustion of various gases at great dilutions by means of copper oxide, found that methane, even at a dilution of 1 part in 4,000 parts of air, was not completely oxidised by passage through two tubes, each containing a 35cm. layer of copper oxide, maintained at a red heat. By passing a mixture of methane and oxygen in the proportions necessary for complete combustion, over palladianised asbestos, Denham (8), in 1905, gave the temperature of initial combustion as 514° - 546°C. and drew conclusions in agreement with those of Dunstan and Carr with respect to the influence of the rate of flow of the gases on the temperature of initial combustion.

In the following year Sabatier and Mailhe (9) claimed that, when methane mixed with oxygen was passed over incandescent copper oxide, the methane was almost completely oxidised, a little formaldehyde being formed. In the same year Haas (1) detected as much as 43% methane remaining unburned when that gas was passed over heated copper oxide, but no temperature observations are recorded. Finally, King and MacDougall (3) have found that methane is not always oxidised by copper oxide even at 800°C..

In the estimation of hydrogen, carbon monoxide and methane in gas analysis it is generally accepted that the preferential oxidation of hydrogen and carbon monoxide by means of oxidising agents such as copper oxide and the subsequent determination of methane, either by explosion or slow combustion with oxygen, gives greater satisfaction than methods which demand the use of acidic or ammoniacal solutions of cuprous chloride for determining carbon monoxide or of palladium sponge, palladianised asbestos or colloidal palladium solution for determining hydrogen. In the case of copper oxide the oxygen for combustion comes from the reagent itself so that the reagent lasts for practically an infinite number of determinations and is easily restored to activity, when partly reduced, by passing air over it when hot. It is evident that in these cases the hydrogen and carbon monoxide must be oxidised at a temperature high enough to ensure complete combustion and yet low enough to leave the methane unattacked.

While Hempel (10) was the first to suggest the use of the fractional combustion of mixed gases by means of palladium sponge in gas analysis, copper oxide was first employed by Jaeger in 1898 (11) for the fractional combustion of hydrogen in presence of methane. He found that hydrogen was completely oxidised when passed over copper oxide kept at a temperature of 250°C., at which temperature methane is unaffected, and recommended that the methane be oxidised by heating the copper oxide to bright redness.

Nesmjelow (12) extended Jaeger's method in 1909 to the fractional combustion of mixtures of hydrogen, carbon monoxide and methane by passing the gases over copper oxide at 250°C. when only the hydrogen and carbon monoxide are burned, while Ubbelholde and de Castro (13), two years later, recommended a temperature of 270°C. for the combustion of hydrogen and carbon monoxide and a red heat for that of methane, Taplay (14), in 1912, again recommended 270°C. for the oxidation of hydrogen but gave a fixed value of 850°C. for the oxidation of methane, while Worrel (15), a year later, used 250° - 260°C. for the former temperature and a red heat for the latter. In the same year Dennis (16) used a temperature of 270°C. for the combustion of hydrogen, but preferred to burn the methane by means of a platinum spiral, the objection to the use of copper oxide for methane being that prolonged heating of the combustion tube and repeated passage of the gas through it are necessary for the complete oxidation of the hydrocarbon.

Wibaut (17), in 1914, stated that the combustion of the gases is greatly accelerated if the copper oxide is mixed with sufficient cerium dioxide to produce a grayish white mixture. Taylor (18), in the same year, recommended a temperature of 275°C. for the combustion of hydrogen and carbon monoxide and stated that the maximum permissible temperature for these gases depends on the nature of the hydrocarbons present, and that with methane only, probably 300°C. is not too high, although if the gas contains higher homologues of methane, these may be oxidised at this temperature. Terrès and Manguin (19), a year later, stated that hydrogen is burned completely at 250°- 300°C.. They found that dry carbon monoxide by itself is only 90% - 94% oxidised at 300°C., that methane begins to burn at 310°C., this temperature being lowered a few degrees in presence of hydrogen, and that methane is completely burned at a red heat.

In 1916, in an exhaustive investigation into Jaeger's method of fractional combustion, Burrell and Oberfell (20) found that the method yielded trustworthy results for a large variety of gases by using temperatures of 275°- 300°C. for hydrogen and carbon monoxide and 800°C. for methane.

From the above short summary of the history of the progress of Jaeger's fractional combustion method of analysis, it is evident that a knowledge of the exact initial temperature of combustion of methane in presence of various oxidising agents would be exceedingly helpful, so that the method may be placed on a more certain footing as far as the combustion of methane is concerned, for, undoubtedly, the method seems capable of being used successfully in a variety of analyses which otherwise would necessitate more elaborate methods. With these facts in view and also owing to the fact that methane being left unoxidised in combustions may lead to serious errors in ultimate analyses, the following investigations on the temperatures of combustion of methane by copper oxide, in presence of various catalysts, were carried out.

GENERAL METHOD of PROCEDURE.

The general method of procedure adopted was to pass an approximately 5% mixture of methane, or other combustible gas, diluted with nitrogen and positively freed from oxygen, which could oxidise the methane during the process of combustion, and from any other combustible gas which might influence the temperature of the oxidising agent locally and so give an erroneous value for that particular temperature, over the oxidising medium. The methane burned was estimated by absorbing the carbon dioxide formed in caustic potash solution and the resulting gases examined quantitatively for combustible gases. The oxidising medium was heated to different temperatures in an electric furnace and these temperatures noted by means of a thermocouple.

The apparatus designed for these experiments is shown in the sketch Fig. 1 on page 10. It consisted of a 3½ litre aspirator bottle, E, to which was attached a simple device, BCD, which allowed gas to be delivered from the aspirator at a constant pressure, the method of operation of which will be explained later, and to which was attached by means of a two-way stopcock, F, a three-way stopcock, G. One limb of this stopcock was attached to an air purification system (which, for the sake of simplicity has not been shown in the sketch) consisting of

(1) a gas tower containing a small lower layer of cotton wool and calcium chloride and a large upper layer of soda lime,

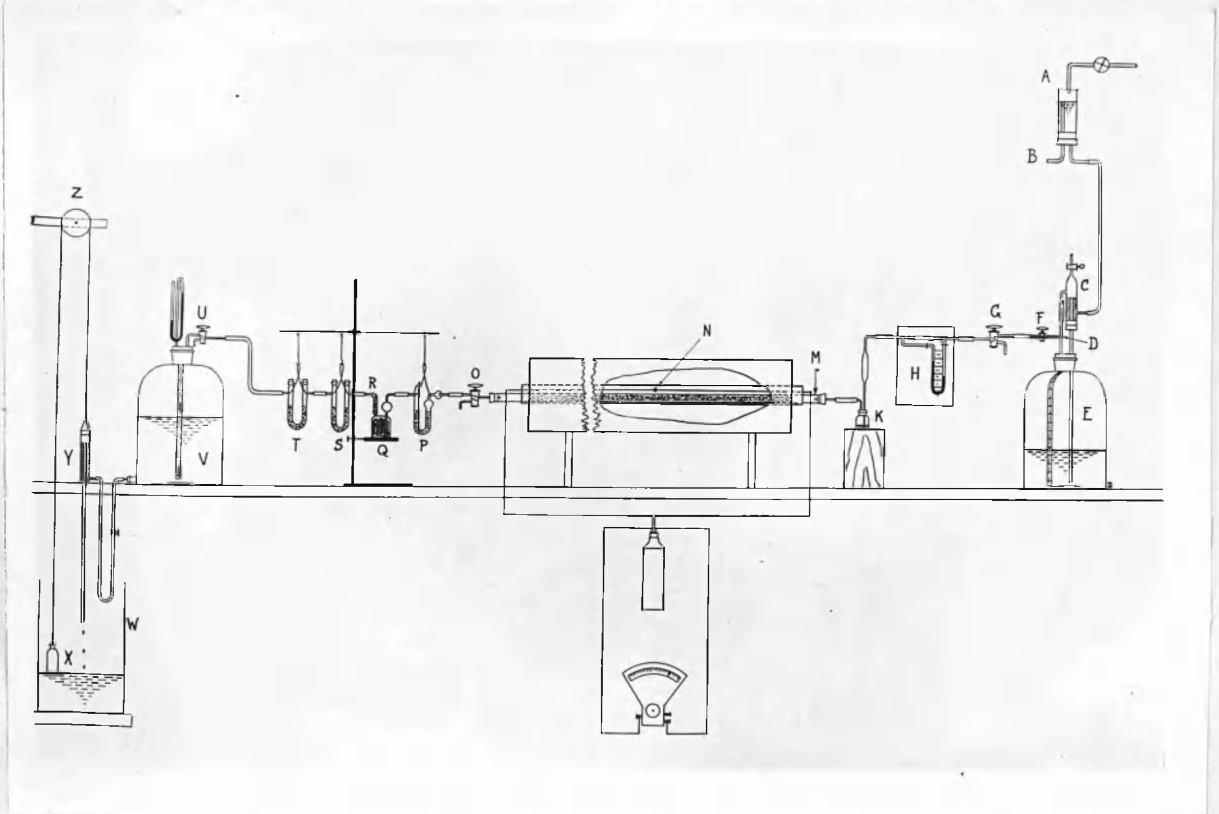

Fig. 1.

(2) a gas washing bottle containing a 50% solution of caustic potash in water,

(3) a T-piece safety-valve,

by means of which air from a compressed air pipe-line, after having been freed from carbon dioxide, could be swept through the apparatus.

Connected to the other side of G was a small differential gauge, H, containing water and mounted on a graduated scale. The jet connecting the two limbs of the gauge was calibrated as shown in Appendix I (page 202) so that a given fall in the pressure of the gas after passing through the jet could be converted to a corresponding rate of flow of gas by reference to a graph. Connected to the outlet side of H was a small wash-bottle, K, the inlet tube of which was drawn to a jet which just dipped below the surface of some concentrated sulphuric acid. This "bubbler" gave a visual indication of the rate of flow of gas and also served as a means for testing the apparatus for leaks.

The combustion tube, M, was of the usual type, made of hard glass, about 90cm. long and 1.25cm. internal diameter, with walls of at least 1mm. thickness. The oxidising material was placed centrally in the tube and the tube placed centrally in the furnace. The electric furnace used for heating the combustion tube and its contents was wound with nichrome wire, the temperature of which was controlled by means of an external rheostat in series with an ammeter, while the temperature of the oxidising agent was measured by using a nickel-nichrome thermocouple, the junction of which, N, was placed in the exact centre of the furnace tube, between the combustion tube and the furnace tube wall.

Connected to the posterior end of the combustion tube was a three-way stopcock, O, one limb of which was open to the atmosphere while the other was connected to the U-tube, P, which was filled with 8 - 32 mesh pumice moistened with concentrated sulphuric acid. The U-tube was, in turn, connected to a set of potash bulbs, Q, of the Landsiedl type, containing a 50% aqueous solution of potassium hydroxide, while the guard tube, R, contained, in order, layers of asbestos, solid caustic potash, asbestos, ignited calcium chloride and asbestos. The potash bulbs were followed by a second U-tube, S, containing ignited calcium chloride and a third U-tube, T, charged in the same manner as P. The last U-tube, T, was connected to a graduated $3\frac{1}{2}$ litre aspirator bottle, V, by way of the three-way capillary stopcock, U, while V, in turn, was connected to the levelling arrangement WXYZ, which enable the pressure of the gas in V to be kept practically constant. The confining liquid in the receiving aspirator was a cold saturated solution of magnesium chloride in water.

In an apparatus of this type it is extremely advantageous if the rate of flow of gas can be kept at a constant value and this can only be realised if the pressures of the gas supplied to and the gas collected from the system can be kept constant, provided, of course, that all other conditions remain unaltered. The use of the two constant pressure appliances, ABCD and WXYZ, which have been designed by Professor Gray (21,22), enable these conditions to be fulfilled.

In the first of these systems a constant flow of water from the main enters the constant level tube at A and excess water runs to waste at B. In order to expel the gas from the graduated aspirator water flows from the constant level tube AB, through the rubber connection to the weir, C, and thence overflows down the wide tube into the bottle, E. This influx of water causes the pressure of the gas to be increased to such an extent that it is forced through the stopcock, F, and thence through the system. The pressure of the gas in the aspirator, E, is governed by the "head" of water between A and C, since the gas in C is in direct communication with the gas in E, so that the "head" of water used to expel the gas from the aspirator is independent of the level of the water in the aspirator. By this means the gas in E is kept at a constant pressure and consequently is delivered at a constant rate throughout the experiment. This "head" of water necessary to force the gas through the system can be altered by altering the difference in levels in AB and C by raising the level tube AB.

The gas left the bottle, E, and passed through the stopcocks, F and G, to the differential gauge, H, which was set to the necessary difference in levels of the water in the two limbs by means of the constant level tube, AB, through the indicator, K, and over the oxidising mixture. The water formed by combustion was absorbed by the concentrated sulphuric acid in P and the carbon dioxide in Q. S was used as a second guard tube to the bulbs, Q, while T prevented water vapour from V being absorbed by S or R. The unabsorbed gases were collected in the aspirator, V, to which was connected the second constant pressure device, WXYZ.

The second arrangement enables a gas to be collected at a constant pressure, independent of whether the flow of gas is regular or not. V is connected to Y by means of a rubber tube and Y, in turn, is connected to a float, X, by means of a string passing over the pulley, Z. The vessel, W, contains the same liquid as is used as confining liquid in V and has an internal diameter equal to that of the aspirator, V. When gas enters V, liquid is forced out into Y and thence into W, so that the liquid level in W rises by the same amount as that in V has fallen. Thus X rises by this same amount and causes Y to fall by this amount also, so that the pressure in V is automatically brought back to its original value. In the experiments performed, the pressure in V was always kept slightly below atmospheric pressure in order to assist the passage of the gas through M, P, Q, S and T.

METHOD of MEASUREMENT of TEMPERATURE.

The temperature of the oxidising agent in use was measured by means of a nickel-nichrome thermoelectric couple placed between the interior wall of the furnace tube and the exterior wall of the combustion tube and arranged so that the junction of the two wires was immediately above the centre of the layer of oxidising agent. As indicated in the sketch, the free ends of the wires were taken to a cold junction, kept at 0°C. by means of broken ice in a vacuum flask, from which leads were taken in the usual manner to a high resistance galvanometer. The temperature of the oxidising agent was obtained by referring to the graph of temperature and e.m.f. developed, shown in Appendix II, page 205.

In Appendix II are tabulated results which demonstrate that when equilibrium is established, the temperatures in the centre of the layer of oxidising material and in that part of the furnace tube above this point become equal, so that an estimation of the temperature at the point shown by the junction of the couple in the sketch also gives an estimation of the actual temperature of the substance contained in the combustion tube. In view of this, provision was made, as is shown later (p. 22) to ensure the equalisation of the interior and exterior temperatures before an experiment was commenced.

From the details of the standardisation of the thermojunction, shown in Appendix II, it has been assumed that the temperatures quoted are correct to within 5°C.. Appendix II also contains details of an exploration of the variation of temperature along the furnace tube.

[illegible] only determined as shown in appendix III on page [illegible] found to be [illegible].

The gas from the storage bottle was introduced [illegible] sampling tube in the usual way and in quantity [illegible] the mercury below the stopcock, B, into the [illegible] tubing. A was then closed and then B. The [illegible] storage bottle was removed and a manometer, J, [illegible] place as shown in the diagram, while to the end of [illegible] funnel containing water was fixed. By turning [illegible] communication between the funnel and the mano[illegible] the manometer was filled with water and [illegible] closed. The levelling [illegible] was raised [illegible] stopcock [illegible] turned to give communication between [illegible] and then allowed to pass slowly into the stopcock, B. When the [illegible] had risen just above the stopcock, B was closed and the [illegible]

METHOD of CONDUCTING an EXPERIMENT.

The gas under observation was measured in a gas sampling tube which had been previously calibrated by means of mercury. The arrangement is shown in the sketch, Fig.2., on page 18. The volume contained by the sampling tube from the top of the stopcock, A, to the mark, M, on the lower capillary, accurately determined as shown in Appendix III on page 211, was found to be 202.1cc.

The gas from the storage bottle was introduced into the sampling tube in the usual way and in quantity sufficient to bring the mercury below the stopcock, B, into the capillary rubber tubing. A was then closed and then B. The connection to the storage bottle was removed and a manometer, F, attached in its place as shown in the diagram, while to the side limb of A a funnel containing water was fixed. By turning A to allow of communication between the funnel and the manometer, the manometer was filled with water and A closed. The levelling vessel, C, was raised, the stopcock, B, gradually opened to give communication between C and AB and the mercury allowed to rise slowly into the stopcock, B. When the mercury had risen just above the stopcock, B was closed and the screw-clip, D, tightened so that communication between the sampling tube and the levelling vessel was cut off. B was again opened and by adjustment of the screw-clip, E, the mercury was brought to the mark, M, the gas being now under a pressure greater than atmospheric. A was next opened to give communication between

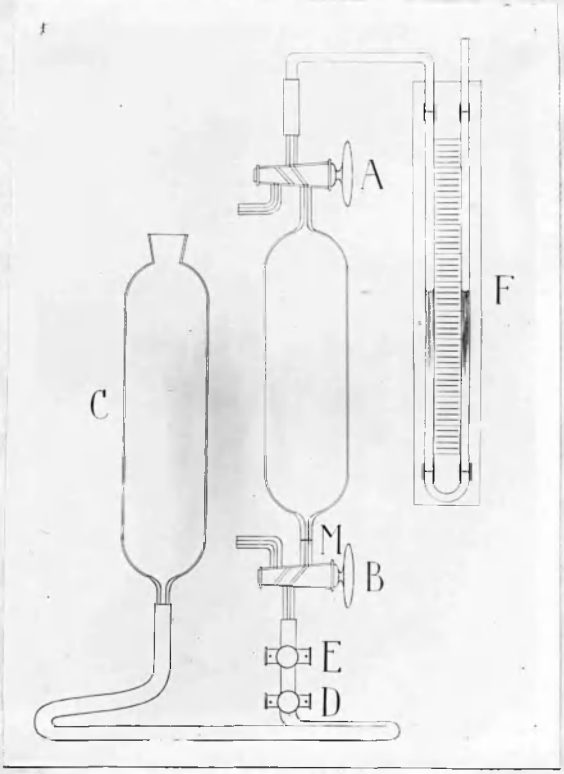

Fig. 2.

F and AB and, owing to the pressure exerted by the gas, the water was forced upwards from A and expelled from the open limb of F. When equilibrium was established the gas was still under a pressure greater than atmospheric, so that the water always completely filled the open limb of F while the other limb was only partially filled.

Water was then abstracted from the open limb by means of a piece of glass tubing, one end of which had been drawn into a capillary small enough to enter the tube of the manometer, until the two levels were of the same height, the gas now being under atmospheric pressure.

The apparatus was left thus, with AB in communication with the manometer, in a room, free from draughts and sources of heat, for half an hour, when final adjustments of E and F were made. A and B were then closed and the manometer detached, the gas sampling tube now containing 202.1cc gas (moist measured under the prevailing conditions of temperature and pressure.

The aspirator, E, (Fig.1. p.10) and its fittings were disconnected from the three-way stopcock, G, and the constant level device, AB, and the whole completely filled up with water until water overflowed at the stopcocks F and C, these stopcocks being closed in that order. The inlet stopcock, C, was then connected to a flask which had been generating nitrogen by the method described in Appendix IV, page 213, for a period of time sufficiently long to ensure all air had been expelled from the apparatus and its connections, the stopcock at the bottom of E opened and water allowed to flow out as nitrogen entered at C. A volume of nitrogen, considerably in excess of that necessary to give a 5% methane mixture with the methane contained in the 202.1cc. gas sampling tube, was collected, the various stopcocks closed and the nitrogen allowed to cool.

When quite cold, the nitrogen was allowed to stand beside the methane in the sampling tube for the half hour or more during which this latter gas was left before being measured. The methane was then measured out to give 202.1cc. of methane as already described and the upper stopcock of the gas sampling tube connected to the stopcock, C, of the aspirator. Water was then run into the aspirator by way of the lower stopcock and nitrogen expelled through C and the upper stopcock of the sampling tube into the atmosphere until the volume of nitrogen left was such that, together with the 202.1cc. of methane, would give a mixture containing approximately 5% of methane. The upper stopcock of the gas sampling tube was turned to give communication between the sampling tube and C and the methane driven over into the aspirator, from which water was allowed to flow through the bottom stopcock.

When all the methane had been transferred to the aspirator, C was closed and the total volume of gas in E noted. From these data the methane content of the gaseous mixture was determined, being given by

$$\frac{202.1 \times M}{V} \quad \% CH_4$$

where M is the percentage of methane in the stock gas used, the remainder being nitrogen, and V is the total volume in ccs. of the mixture (referred to hereafter as the Original Gas) contained in the aspirator E.

During the half hour necessary to ensure the equalisation of the temperatures of the two gases before mixing, the potash bulbs and the guard tube were weighed. Previously they had been carefully cleaned with a silk handkerchief and allowed to stand in the balance case for exactly half an hour, so that they were always weighed under the same conditions. The weights having been determined, the bulbs and tube were replaced in position in the general apparatus.

The mixed gases were thoroughly shaken in the aspirator, the aspirator placed in position and the constant level device, AB, connected up. Water was run into the aspirator and a few ccs. of gas expelled through F in order to displace the small amount of water retained in the free limb of that stopcock. F was then connected to the stopcock, G.

The stopcock, O, was turned to open the combustion tube to the atmosphere and the current for heating the furnace windings switched on. During the preliminary heating of the furnace a slow current of purified air from the compressed air main was fed in through G in order to reoxidise any material left reduced from the preceding experiment, and the clip between V and Y opened. Magnesium chloride solution was added to, or abstracted from, W until the manometer attached to the aspirator, V, registered a pressure of 2" water below atmospheric and if the flow of water from Y stopped completely in a few seconds, with the screw-clip full open, the apparatus was considered air-tight from the stopcock, O, onwards. During an experiment this screw-clip was left full open.

When the temperature of the furnace had nearly reached the value required, the current of air was stopped and a steady current of the methane mixture led through the tube by turning the stopcock, G, to connect F with H. This stream of gas was continued until the e.m.f. indicated by the thermocouple had become constant and an equilibrium over the whole apparatus had been established, when the stopcock, O, was closed in order to ascertain whether the apparatus was leaking or not. If the flow of bubbles in K stopped completely it was assumed that there was no leak in the apparatus from A to O.

The flow of gas was resumed and at a noted time the stopcock, O, was turned so that the gas entered the sulphuric acid U-tube, P, after leaving the combustion tube. At the same time the volume of gas in E was noted, together with the prevailing values of temperature (obtained from a thermometer suspended by the side of, and touching, E) and pressure. The level tube, AB, was regulated so that the pressure difference indicated by the differential gauge, H, was that corresponding to the required rate of flow of gas. The apparatus was then entirely automatic, provided a constant supply of water from A was maintained.

During the course of the combustion the temperature of the oxidising material, as registered on the scale of the galvanometer, was periodically noted, so that no deviation from the temperature at the beginning of the experiment should take place. In general, it was found that once an equilibrium had been established before the actual commencement of an experiment, there was no fluctuation in the value of the e.m.f. registered by the galvanometer.

If water became liable to collect at the cold posterior end of the combustion tube, a Bunsen was placed below this end to drive this water, as much as possible, into the sulphuric acid U-tube.

The flow of gas was allowed to continue until, in all, $1\frac{1}{2}$ - 2 litres had passed over the oxidising material. When the level of water in the aspirator,E, had reached a graduation mark on the scale, the stopcock, O, was turned to permit of communication between the combustion tube and the atmosphere and the time noted, together with fresh determinations of the volume, temperature and pressure of the gas in E.

Air, from the main connected to the stopcock, G, was now passed through the combustion tube at a considerable speed for about half an hour in order to flush the tube free from the combustible gas and its products. When this had been accomplished, the speed of the air was reduced to a speed approximately equal to that of the flow of gas during the experiment; the stopcock, O, was turned to connect the combustion tube to the absorption train and the apparatus left for about half an hour until sufficient air had passed through the system to clear out any combustible gas from the absorption system into the aspirator, V. The Resulting Gas, in all cases, thus contained air and consequently had a greater volume than that of the Original Gas from which it was obtained.

The air was then turned off, the stopcock, U, closed and the aspirator, V, disconnected from the absorption system.

Some confining liquid was transferred from W into Y until the levels of liquid in the limbs of the U-tube were the same; the volume of gas in V was either read off the graduated scale or determined by weighing W and its contents before and after the the experiment and the temperature and pressure of the gas noted as in the case of the Original Gas. The bulbs and U-tube, QRS, were disconnected, closed with plugs of rubber tubing, carefully cleaned as before and left in the balance case for half an hour before the plugs were removed and each vessel weighed.

The gas in the aspirator, V, which was termed the Resulting Gas, was allowed to remain quiescent for several hours, generally over night, to ensure homogeneity, a sample withdrawn for analysis and this carried out by means of Haldane's apparatus, carbon dioxide (if any) and combustibles being estimated.

The weight of combustible gas supplied was calculated from the data obtained from the aspirator, E, while from the increase in weight of the potash bulbs and attachments, due to the carbon dioxide absorbed, the weight of combustible gas burned was obtained. From the analysis of the Resulting Gas the weight of combustible gas remaining unchanged was determined. The sum of the second and third weights should be equal to the first and in this manner a balance was struck.

The water formed as a product of the combustion was not estimated owing to the difficulty of removing water from the limbs and bore of the stopcock, P.

The rate of flow of the gas was determined by dividing the volume of gas in ccs. passed over the material in the tube by the number of minutes necessary for it to do so, giving a value of the speed in ccs. per minute; from this value and the value for the volume of available space over the oxidising agent in the tube, obtained by the method described in Appendix V, page 216, the time of contact of gas and oxidising agent was determined. This value was kept as far as possible the same for each combustion of each series.

In all cases the International Atomic Weights for 1925 and Regnault's values for the tension of aqueous vapour were used. For the values of the densities of the various gases encountered during the experiments, the following figures, published by the United States Bureau of Standards (23) were adopted:-

Gas.	Weight of 1 litre of gas in gm..	Molecular Volume in litres.
Methane	0.7168	22.368
Ethylene	1.2604	22.248
Carbon Monoxide	1.2504	22.396
Carbon Dioxide	1.9769	22.259

METHOD of CALCULATION.

The following is the method of calculation. (taken from Expt. No.4 of the Methane - Fused Lead Chromate series, page 50):-

Original Gas.

202.1cc. gas containing 81.05% CH_4 and 18.95% N_2 were diluted with nitrogen to 3470cc., giving an Original Gas containing 4.72% CH_4.

Initial reading = 1090cc.

Final reading = 0

Gas used = 1090cc.

Temperature = 18.0°C.. Corrected pressure (i.e. corrected for the "head" of water between AB and C and for the vapour pressure of water.) = 782.4mm.

$$CH_4 \text{ supplied} = \frac{1.090 \times 4.72 \times 16.037 \times 782.4 \times 273}{100 \times 22.368 \times 760 \times 291} \text{gm.}$$

$$= \underline{\underline{.0355\text{gm.}}}$$

Time = 60min.. Rate of Flow = 18.1cc. per min.

$$\text{Time of Contact} = \frac{63.1}{18.1} \text{ min..}$$

$$= \underline{\underline{3.49\text{min..}}}$$

Weight of CO_2 formed = .0250gm..

CH_4 burned = .0092gm..

Resulting Gas.

Volume = 2800cc. at 18.0°C. and 759.0mm..(corrected.)

CH_4 content = 1.050%.

CO content = 0.350%.

$$CH_4 \text{ in gas} = \frac{2.800 \times 1.050 \times 16.037 \times 759.0 \times 273}{100 \times 22.368 \times 760 \times 291} \text{ gm..}$$

$$= \underline{\underline{.0197\text{gm..}}}$$

$$CO \text{ in gas} = \frac{2.800 \times 0.350 \times 28.005 \times 759.0 \times 273}{100 \times 22.396 \times 760 \times 291} \text{ gm..}$$

$$= .0115\text{gm.}$$

$$\equiv \underline{\underline{.0066\text{gm. } CH_4.}}$$

Balance.

CH_4 supplied	= 0.0355gm..	CH_4 burned to CO_2	= 0.0092gm..
Losses	= Nil	CH_4 burned to CO	= 0.0066gm..
		CH_4 unburned	= 0.0197gm..
	0.0355gm..		0.0355gm..

$\therefore$ CH_4 burned to CO_2 = 25.8%

CH_4 burned to CO = 19.1%

A. - METHANE and COPPER OXIDE.

The methane used for the following experiments was prepared by Grignard's method (24) as described in Appendix IV, page 213. The copper oxide was such that it passed through an 8 mesh to the linear inch sieve but was retained by a 32 mesh sieve; 250gm. of such copper oxide were used and filled centrally into the combustion tube, occupying 61.3cm. of its length and having an available space volume of 60.1cc. in contact with the copper oxide.

In 250gm. copper oxide there are available 50gm. oxygen. By burning 2 litres of a 5% methane mixture, i.e. 100cc. pure methane, 0.286gm. oxygen are consumed, so that for these experiments there are $\frac{50}{.286}$, or 175, times the necessary amount of oxygen available for complete combustion.

The following are the results obtained (Table I).

The results are grouped in the graph in Fig. 3.

TABLE

METHANE AND

Expt. No.	Temp. °C.	Original Gas.			Wt. of CO_2 formed. gm.
		Volume. cc.	% CH_4.	Wt. CH_4 supplied. gm.	
1.	495	1580	5.00	0.0535	Nil
2.	530	2000	5.10	0.0702	Nil
3.	560	1850	4.70	0.0596	Nil
4.	605	1850	5.01	0.0640	0.0520
5.	620	1800	5.93	0.0736	0.0806
6.	660	1800	5.80	0.0725	0.1360
7.	700	1600	5.83	0.0667	0.1736
8.	745	1760	5.27	0.0653	0.1778

I.

COPPER OXIDE.

Resulting Gas.		Methane Burned. gm.	Methane Unburned. gm.	% CH_4 Burned.	Rate of Flow in cc. per min.	Time of Contact. min.
Volume. cc.	% CH_4					
2760	2.84	Nil	0.0517	Nil	24.0	2.30
———	———Gas	Lost———	———	Nil	15.4	3.58
3400	2.55	Nil	0.0586	Nil	19.4	2.84
3640	1.84	0.0191	0.0449	29.8	18.5	2.98
3500	1.84	0.0296	0.0431	40.2	20.0	2.76
3100	1.10	0.0498	0.0230	68.8	22.5	2.45
3030	0.12	0.0633	0.0025	95.0	22.8	2.42
3380	Nil	0.0646	Nil	100.0	22.0	2.51

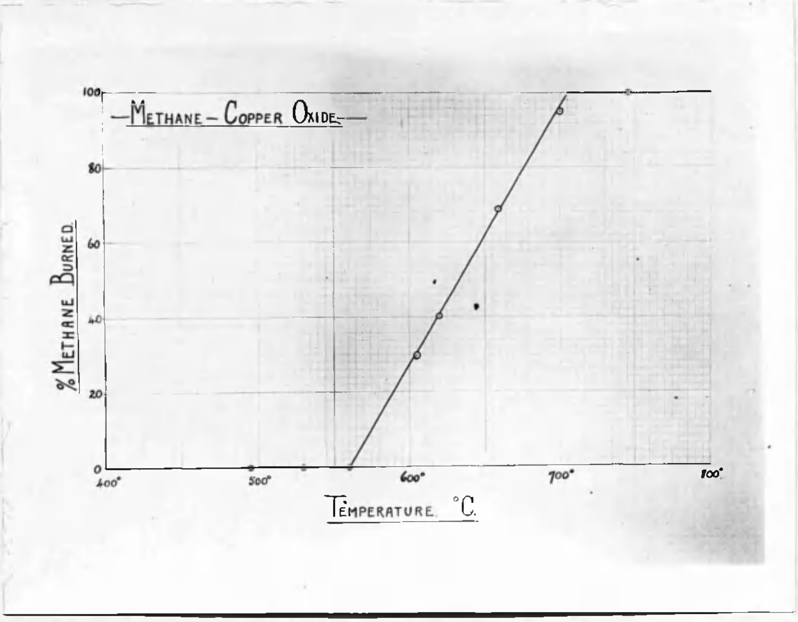

Fig. 3.

The following data (Table II) were obtained to find the effect of varying the rate of flow at a temperature several degress above that at which methane was completely oxidised and also at temperatures at which the hydrocarbon was left partially unattacked.

Conclusions.

From the results obtained it is seen that, under the conditions of the experiments, methane begins to burn at an appreciable rate in presence of copper oxide at 560°C. and is completely burned at 705°C., the amount burned at any temperature between those two limiting values being directly

TABLE

METHANE AND

Expt. No.	Temp. °C.	Original Gas.			Wt. of CO_2 formed. gm.
		Volume. cc.	% CH_4	Wt. CH_4 supplied. gm.	
9.	808	2000	5.01	0.0702	0.1906
10.	808	1270	5.32	0.0472	0.1270
11.	808	1600	4.88	0.0537	*0.1417
12.	700	1615	4.95	0.0520	0.1356
13.	700	1400	4.95	0.0465	0.1230
14.	700	680	5.02	0.0232	0.0628
15.	592	1340	5.02	0.0458	0.0920
16.	592	950	5.02	0.0330	0.0852

*0.1382gm. CO_2 absorbed by potash bulbs, 0.0035gm. unabsorbed by bulbs but obtained in residual gas.

II.

COPPER OXIDE.

Resulting Gas.		Methane Burned. gm.	Methane Unburned. gm.	% CH_4 Burned.	Rate of Flow in cc. per min.	Time of Contact. min.
Volume cc.	% CH_4					
3100	Nil	0.0693	Nil	100.0	33.3	1.66
2750	.023	0.0466	0.0004	98.8	42.3	1.30
3550	.029	0.0520	0.0007	96.8	53.3	1.03
2930	.091	0.0494	0.0017	95.0	14.3	3.86
2845	.038	0.0448	0.0007	96.4	7.96	6.93
1420	Trace	0.0229	Trace	100.	4.00	13.8
3840	.045	0.0335	0.0114	73.2	4.22	13.1
2835	.070	0.0311	0.0013	94.1	1.41	39.2

proportional to the temperature, provided the time of contact of hydrocarbon and copper oxide lies between 2.42 minutes and 2.98 minutes. This represents a much shorter period of contact than is usual in either a combustion for the determination of carbon and hydrogen by Liebig's method or the determination of nitrogen by the Dumas absolute method, so that if, in such combustions, the temperature of the copper oxide is kept above 705°C.* no trouble from the incomplete combustion of methane should be experienced.

The fact that good agreements in the amount of methane supplied and the amount accounted for as completely burned and unburned shows that the reaction

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

represented the final stage in the oxidation, no loss of methane resulting from the formation of an intermediate oxidation product.

With regard to the effect of varying the rate of flow of the gas, the results at 808°C. indicate that at this temperature increase in the rate of flow causes progressively a decrease in the amount of methane burned, as would be expected, but even at a speed of 42.3cc. per minute only very little methane is left unoxidised. At 53.3cc. per minute both oxidising and absorption systems break down completely, but it is worthy of note that it is the oxidising system which is

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* These temperatures, and corresponding temperatures in succeeding sections, have been obtained from the various graphs and are reported to the nearest multiple of 5°.

first affected by an increase in the rate of flow of gas.

At 700°C. a decrease in the rate of flow of gas from 22.8cc. per minute to 14.3cc. per minute has no effect on the efficiency of the oxidising system and even a further decrease to 7.96cc. per minute only very slightly increases the amount of methane burned; but when the value of the speed of the gas falls to 4.00cc. per minute practically all the hydrocarbon is completely oxidised.

At 592°C., where, with a speed of 18.20cc. per minute, 21.6% of the methane supplied is burned, a decrease in the rate of flow to 4.22cc. per minute raises the oxidising efficiency of the copper oxide to 73.2% and a decrease to 1.41cc. per minute gives an efficiency of 94.1%.

It is evident from these figures that the time factor in the oxidation of methane by means of copper under the conditions of the experiments is of prime importance; by prolonging sufficiently the time of contact at any temperature above 560°C. it should be possible to obtain complete combustion of the hydrocarbon. This factor is further exploited in Part III.

From the results at 700°C. it was decided to keep the rates of flow of the gas in subsequent experiments between 14 and 20cc. per minute, except in one special case which was carried out to find the effect of adding another combustible gas to the methane nitrogen mixture. Further, it was found impossible to keep the rate of flow constant throughout each series of combustions, owing to the varying resistance to flow offered by the sulphuric acid U-tube and the potash bulbs, but the rate of flow was kept as nearly constant as possible and certainly between the limiting speeds of 14 and 20cc. per minute.

B. - METHANE-HYDROGEN and COPPER OXIDE.

Gautier (7) has drawn attention to the fact that when hydrogen is mixed with a methane-air mixture and passed over copper oxide at a red heat, more methane is oxidised than when hydrogen is absent, while Charitschkoff (25), in burning away the hydrogen from a methane-hydrogen mixture by means of oxygen in presence of palladianised asbestos, has found that an appreciable part of the methane always undergoes combustion. In this latter case, however, the temperature at which the hydrogen burns is not raised, so that the combustion of the methane must be due to the great heating effect of the burning hydrogen which raises the temperature locally to that at which methane burns.

In view of these facts it was decided that the effect of mixing hydrogen with the methane nitrogen mixtures used in the last series of experiments should be investigated.

The methane-hydrogen mixtures were prepared by the action of water on aluminium carbide as described in Appendix IV, page 214 , the copper oxide used being the same as that used for methane alone.

The following are the results obtained (Table III), these being collected in the graph in Fig. 4.

TABLE

METHANE - HYDROGEN

Expt. No.	Temp. °C.	Original Gas.				Wt. CO_2 formed gm.
		Volume cc.	% CH_4	% H_2	Wt. CH_4 supplied gm.	
1.	519	1950	4.63	1.80	0.0597	Nil
2.	523	2100	2.08	0.14	0.0305	Nil
3.	600	2000	7.12	0.90	0.0972	0.0778
4.	610	1720	7.12	0.90	0.0732	0.0912
5.	621	2000	3.95	4.68	0.0535	0.0668
6.	635	2070	5.61	5.45	0.0794	0.1428
7.	673	570*	5.61	5.45	0.0221	0.0592
8.	756	1950	4.79	1.89	0.0623	0.1708
9.	770	2500	3.79	11.9	0.0634	0.1746
10.	840	2180	3.99	6.97	0.0576	0.1582

*Stopped owing to potash bulbs

III.

and COPPER OXIDE.

Resulting Gas.		Methane Burned gm.	Methane Unburned gm.	% Methane Burned.	Rate of flow cc. per min.	Time of Contact min.
Volume cc.	% CH_4					
3500	2.68	Nil	0.0596	Nil	10.00	5.51
3600	1.25	Nil	0.0300	Nil	8.42	6.56
2800	3.72	0.0283	0.0689	29.1	7.86	6.98
2300	2.60	0.0332	0.0395	45.4	8.39	6.47
2600	1.62	0.0261	0.0276	48.8	7.85	6.98
1950	2.06	0.0520	0.0264	65.5	7.60	7.25
1150	Nil	0.0216	Nil	100.0	-	-
3100	Nil	0.0621	Nil	100.0	10.80	5.10
3500	Nil	0.0635	Nil	100.0	13.50	4.08
2240	Nil	0.0574	Nil	100.0	14.50	3.80

becoming choked with bicarbonate.

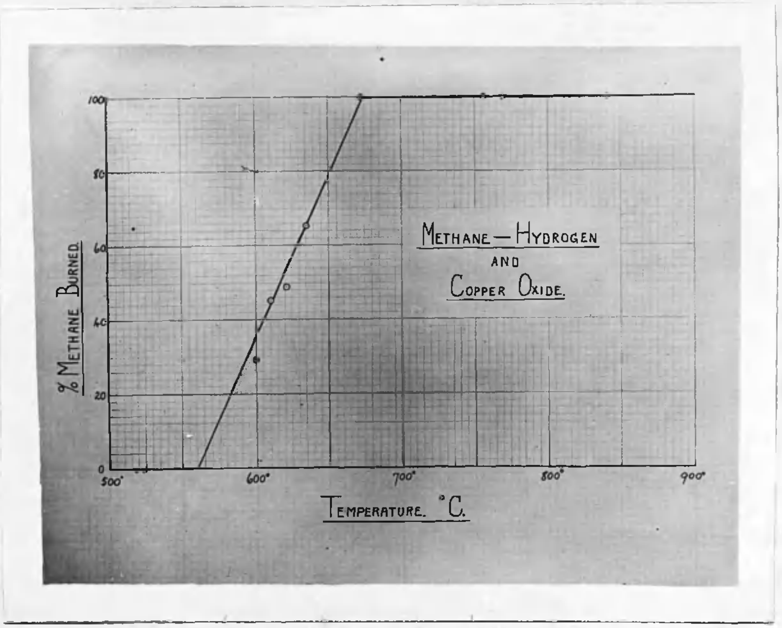

Fig. 4.

Conclusions.

The data obtained show that the presence of hydrogen in methane-nitrogen mixtures causes the methane to be oxidised at appreciably lower temperatures, a mixture containing approximately equal volumes of hydrogen and methane giving complete combustion at 675°C., while with methane alone, some hydrocarbon remains unattacked at 700°C., even when the time of contact is increased to over 13 minutes. (cf. Expts. 13 and 14, page 31).

The above data, together with these obtained from the combustion of similar mixtures of methane and ethylene, illustrate that the addition of another combustible gas to the methane-nitrogen mixtures causes a greater increase in the amount of methane burned the nearer the temperature is to that at which complete combustion takes place.

C. - (a) ETHYLENE and COPPER OXIDE and
(b) METHANE-ETHYLENE and COPPER OXIDE.

It is a well-known fact that in the estimation of oxygen in gases by absorption with yellow phosphorus, the presence of even a few hundredths of a per cent. of ethylene completely prevents the oxidation of the phosphorus. The rôle of catalytic poison played by ethylene was early recognised in the history of catalysis, Henry (26) in 1825 having noted that this hydrocarbon acts as an inhibiting catalyst on platinum sponge in contact catalysis in fractional combustion.

Campbell (5) has shown that ethylene has an initial combustion point of 315° - 325°C. in presence of copper oxide and King and MacDougall (3) have detected appreciable quantities of unsaturated hydrocarbons in the gas collected from the analysis of coal involving the passage of the products of distillation over copper oxide maintained at 350°C..

Owing to its comparatively large solubility in water (27) and its reaction with sulphuric acid, the combustion of ethylene could not be examined in the general apparatus as it was arranged for the combustion of methane. The original gas mixture was supplied from a $1\frac{1}{2}$ litre aspirator bottle fitted with a levelling tube containing mercury as confining liquid. The levelling tube was kept at a constant height above the aspirator and mercury poured in almost continuously. This method, of course, did not give a constant rate of flow of gas and the values given under this heading are consequently the average values during the experiment. The bubbler, K, was filled with 50% caustic potash solution and the U-tubes, P, S and T, with granular calcium chloride saturated with carbon dioxide, in order to overcome the difficulty consequent on the solubility of ethylene in sulphuric acid.

The ethylene used was prepared by Newth's method (28) and analysed over mercury by means of Bone and Wheeler's apparatus, both by absorption by bromine water and by explosion. The copper oxide used was the same as that used for methane alone.

Ethylene was estimated in the Resulting Gas by means of Haldane's apparatus, which, for this purpose, was fitted with an extra absorption pipette containing bromine water.

The results are shown in Table IV and are collected in the graph in Fig. 5. They show that ethylene has an initial combustion point of 310° C., a value in close agreement with that obtained by Campbell (supra.) and that at 400° C. ethylene is completely oxidised to carbon dioxide and water.

Experiments on the effect of adding ethylene to a methane-nitrogen mixture were now carried out, the ethylene being added in a quantity such thst the ratio of methane to ethylene was about the same as that in which these two gases occur in ordinary coal gas. The same apparatus and methods

TABLE

ETHYLENE AND

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Resulting Gas.	
		Volume. cc.	% C_2H_4	Weight of Ethylene supplied. gm.		Volume cc.	% C_2H_4
1.	260	990	6.83	0.0817	Nil	1300	5.10
2.	315	920	9.08	0.0986	0.0110	1050	7.43
3.	330	745	5.59	0.0512	0.0178	1050	3.44
4.	350	850	5.12	0.0560	0.0550	1050	3.00
5.	360	1020	7.30	0.0889	0.1270	1050	3.94
6.	383	950	4.66	0.0541	0.1472	1150	0.47
7.	400	900	4.52	0.0487	0.1502	1000	Nil
8.	447	1400	5.74	0.0943	0.2966	1500	Nil
9.	505	1050	5.89	0.0707	0.2222	1100	Nil

IV.

COPPER OXIDE.

Ethylene Burned. gm.	Ethylene Unburned. gm.	Ethylene Burned. %	Rate of Flow (Mean.) cc. per min.	Time of Contact (Mean.) min.
Nil	0.0801	Nil	8.0	6.9
0.0035	0.0941	3.5	6.8	8.1
0.0057	0.0442	11.1	5.7	9.7
0.0175	0.0389	31.3	8.1	6.8
0.0405	0.0494	46.0	7.3	7.6
0.0469	0.0068	86.7	7.0	7.9
0.0479	Nil	100.0	7.2	7.7
0.0945	Nil	100.0	9.3	5.9
0.0708	Nil	100.0	6.2	8.9

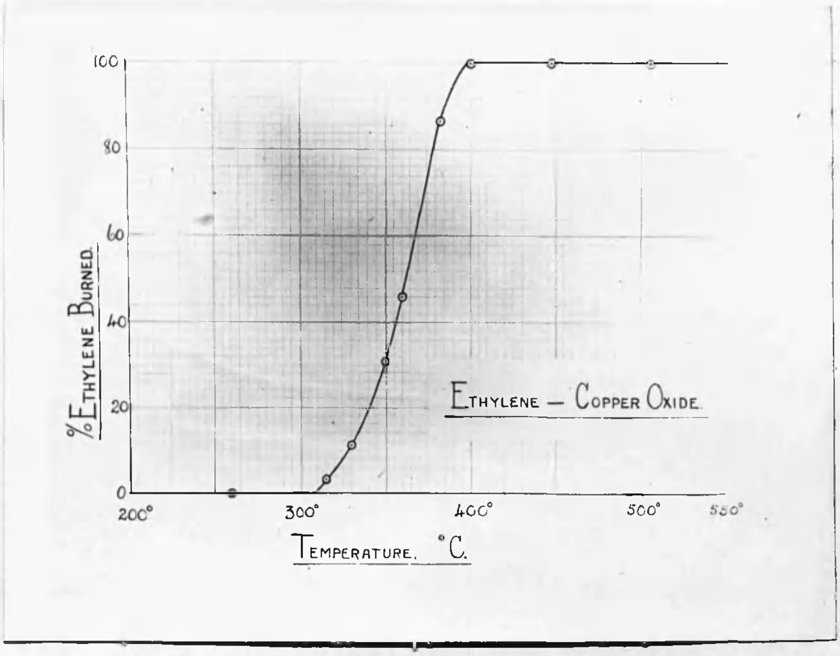

Fig. 5.

of analysis were used as with ethylene.

The following example shows the method of calculation.

CH_4 supplied = 0.0464gm. C_2H_4 supplied = 0.0068gm.

CH_4 left = 0.0214gm. C_2H_4 left = 0.0000gm.

$\therefore CH_4$ burned = 0.0250gm. $\therefore C_2H_4$ burned = 0.0068gm.

$\therefore CO_2$ from CH_4 = 0.0682gm. $\therefore CO_2$ from C_2H_4 = 0.0213gm.

Total CO_2 formed = 0.0895gm..

CO_2 actually obtained = 0.0888gm..

$$CH_4 \text{ burned} = \frac{0.0250}{0.0464} \times 100\%$$

$$= \underline{\underline{54.0\%}}$$

C_2H_4 burned = 100.0%

The following data were obtained (Table V), the results being grouped in the graph in Fig. 6.

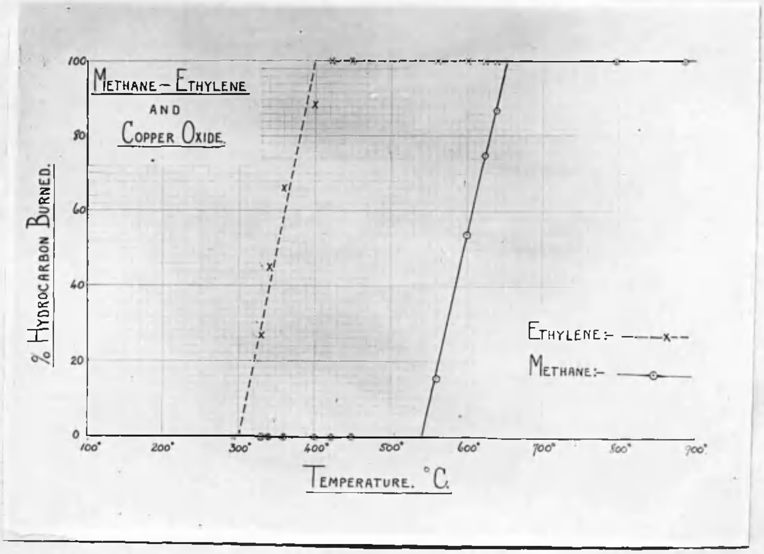

Fig. 6.

Conclusions.

The above results show that ethylene, instead of preventing or inhibiting the combustion of methane, acts as a promoter, causing the temperature necessary for initial combustion to be lowered from 560° C. to 545° C. while the temperature of complete combustion is lowered by 50°, to 655° C.,

TABLE

METHANE-ETHYLENE and

Expt. No.	Temp. °C.	Original Gas.					Weight of CO_2 formed. gm.	Resulting	
		Volume. cc.	% CH_4	% C_2H_4	Methane supplied. gm.	Ethylene supplied. gm.		Volume. cc.	% CH_4
1.	295	970	5.20	0.54	0.0337	0.0062	Nil	1670	3.00
2.	330	1085	6.42	0.53	0.0465	0.0068	*	1900	3.58
3.	340	990	5.66	0.58	0,0373	0.0068	0.0098	1620	3.45
4.	360	1180	6.11	0.51	0.0475	0.0070	0.0143	2830	2.55
5.	400	1200	6.22	0.52	0.0491	0.0072	0.0201	2400	3.10
6.	422	1280	5.44	0.45	0.0462	0.0066	0.0210	2150	3.24
7.	450	1130	3.76	0.31	0.0290	0.0041	0.0168	2400	1.88
8.	560	1105	6.53	0.54	0.0474	0.0070	0.0424	1850	3.29
9.	600	1300	5.47	0.45	0.0464	0.0068	0.0888	1460	2.29
10.	625	1200	5.80	0.48	0.0464	0.0068	0.1161	2000	0.87
11.	640	1065	5.25	0.43	0.0373	0.0055	0.1078	2050	0.36
12.	795	1200	5.39	0.45	0.0423	0.0062	0.1345	1860	Nil
13.	885	1180	5.57	0.46	0.0428	0.0063	0.1366	1780	Nil

* Bulbs broken while cleaning before weighing.

V.

COPPER OXIDE.

Gas.								
% C_2H_4	Methane burned. gm.	Ethylene burned. gm.	Methane unburned. gm.	Ethylene unburned. gm.	Methane burned. %	Ethylene burned. %	Mean Rate of Flow. cc./min.	Mean Time of Contact. min.
0.32	Nil	Nil	0.0335	0.0063	Nil	Nil	13.0	4.24
0.22	-	0.0018	0.0455	0.0050	Nil	26.8	15.5	3.56
0.20	Nil	0.0031	0.0371	0.0040	Nil	45.6	11.6	4.75
0.002	Nil	0.0046	0.0475	0.0008	Nil	66.0	16.8	3.28
0.025	Nil	0.0064	0.0489	0.0005	Nil	88.8	15.0	3.68
Nil	Nil	0.0067	0.0462	Nil	Nil	100.0	10.7	5.15
Nil	Nil	0.0050	0.0295	Nil	Nil	100.0	18.8	2.93
Nil	0.0074	0.0070	0.0400	Nil	15.6	100.0	15.1	3.65
Nil	0.0250	0.0068	0.0214	Nil	54.0	100.0	18.5	2.98
Nil	0.0348	0.0068	0.0116	Nil	74.9	100.0	15.0	3.68
Nil	0.0324	0.0055	0.0049	Nil	87.0	100.0	15.2	3.63
Nil	0.0423	0.0062	Nil	Nil	100.0	100.0	15.0	3.68
Nil	0.0428	0.0063	Nil	Nil	100.0	100.0	17.0	3.24

owing, probably, to the same reason as that recorded under the methane-hydrogen mixtures.

The temperature of combustion of ethylene in this case cannot safely be commented upon, owing to the small quantities of that hydrocarbon used and the consequent larger experimental error.

D. - METHANE - LEAD CHROMATE.

Fused lead chromate as an oxidising agent for the combustion of organic compounds has been widely used, either alone or mixed with red lead as recommended by de Roode (29), the only objection recorded being that such an oxidising agent requires continually to be renewed, although Ritthausen (30) claims that reduced lead chromate may be purified and regenerated by ignition in a stream of oxygen, which gas is absorbed until complete regeneration ensues. Haas (1) successfully used the fused chromate in obtaining the complete combustion of methane in circumstances where copper oxide failed to oxidise as much as 43% of the hydrocarbon.

The following experiments were carried out with pumice impregnated with lead chromate, prepared as follows:-

65gm. 4 - 8 mesh pumice were digested with concentrated sulphuric acid for 3 hours, drained and washed with boiling water until the washings were neutral to litmus. The pumice was dried, ignited, cooled and covered with a solution containing 30gm. potassium chromate in distilled water. An aqueous solution of 50gm. lead nitrate was then added, the mixture gently boiled for 2 hours and allowed to stand overnight. Next morning the excess lead chromate was washed off, the impregnated pumice warmed with water and drained until free from potassium salts, dried and gently ignited. The weight of impregnated pumice obtained was

76gm. so that 11gm. lead chromate had been taken up.

66.6cm. length of the combustion tube were filled with the impregnated pumice which was kept in position by two 1cm. plugs of asbestos. In all 50gm. impregnated pumice, containing 7.2gm. lead chromate, were used, giving an excess of 1.75 times the amount necessary to oxidise completely two litres of a 5% methane mixture. The available space over the pumice was 62.8cc..

In order to regenerate the oxidising agent after each combustion, the impregnated pumice was heated in a stream of oxygen for at least 3 hours at 808°C., or 36° below the melting point of lead chromate (31).

The methane used was prepared from magnesium methyl iodide by Grignard's method and the experiments carried out in the manner described under methane and copper oxide.

The results obtained are shown in Table VI, which demonstrates that even at 592°C. no combustion took place and that at higher temperatures, where some oxidation did occur, the hydrocarbon was not completely oxidised, traces of carbon monoxide being obtained in the Resulting Gas in each of the three experiments where any oxidation took place. Further, since the experiments are arranged in the order in which they were carried out, it is evident that reduced lead chromate is not regenerated by a stream of oxygen at 808°C., even after an exposure to this gas for 5 hours.

TABLE

METHANE AND LEAD

Expt. No.	Temp. °C.	Original Gas.			Wt. of CO_2 formed. gm.
		Volume. cc.	% CH_4	Wt. CH_4 supplied. gm.	
1.	403	1800	4.89	0.0602	Nil
2.	480	1300	4.89	0.0435	Nil
3.	592	1360	6.13	0.0571	Nil
4.	729	1100	6.13	0.0470	0.0425
5.	757	1630	4.93	0.0556	0.0454
6.	795	1500	4.93	0.0511	0.0386

VI.

CHROMATE ON PUMICE.

Resulting Gas.		Methane	Methane	Methane	Rate of Flow.	Time of
Volume. cc.	% CH_4	burned. gm.	unburned. gm.	burned. %	cc. per min.	Contact. min.
2590	3.53	Nil	0.0606	Nil	25.7	2.44
3200	2.05	Nil	0.0435	Nil	27.1	2.32
3130	2.76	Nil	0.0574	Nil	22.7	2.77
3250*	1.42	0.0156	0.0312	33.2	26.8	2.35
2790*	2.07	0.0167	0.0387	29.9	23.3	2.70
2860*	1.90	0.0142	0.0364	27.7	21.4	2.93

* Resulting Gases contained traces of Carbon Monoxide.

For these reasons recourse was made to fused lead chromate as an oxidising agent. 247gm. fused lead chromate (4 - 8 mesh) were used, occupying 66.6cm. length of the tube and having an available space of 63.1cc. over the oxidising agent. Assuming the oxygen available for oxidation of the methane is represented by

$$2PbCrO_4 \rightarrow 2PbO + Cr_2O_3 + 3O.$$

there was present 137 times the amount of lead chromate necessary for the complete oxidation of 2 litres of a 5% methane mixture.

The tube was heated to 400°C. and air passed for 2 hours before use. After each combustion the lead chromate was heated to 808°C. in a stream of oxygen for at least two hours.

The following table indicates the results obtained and these are grouped in the graph in Fig. 7.

Again the experiments are arranged in the order in which they were carried out. The graph shows that in presence of fused lead chromate methane is initially oxidised at 530° - 535°C. but complete oxidation does not take place until a temperature of 710°C. is attained. Further, at temperatures above 600°C. appreciably large quantities of the methane are oxidised only to carbon monoxide which remains unattacked until the temperature reaches 640°C., above which temperature the amount of carbon monoxide remaining gradually diminishes until at 710°C. the hydrocarbon is completely oxidised to

TABLE

METHANE AND

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	443	1350	4.89	0.0448	Nil	2900
2.	500	1490	5.31	0.0549	Nil	3000
3.	600	2070	4.71	0.0673	0.0210	*
4.	640	1090	4.72	0.0355	0.0250	2800
5.	687	1500	5.04	0.0517	0.0990	2800
6.	709	1310	5.04	0.0458	0.1216	3000
7.	709	1650	4.76	0.0513	0.1408	2895
8.	765	1580	4.89	0.0524	0.1428	3150
9.	685	2950	5.03	0.1017	0.2062	**

* Gas lost owing to manometer blowing out.

** Gas not collected, but passed into palladium chloride solution to confirm presence of carbon monoxide.

VII.

FUSED LEAD CHROMATE.

-ing Gas.		Methane burned to CO$_2$. gm.	Methane burned to CO. gm.	Methane unburned. gm.	Methane burned to CO$_2$. %	Methane burned to CO. %	Rate of Flow. cc.p. min.	Time of Contact. min.
% CH$_4$	% CO							
2.35	Nil	Nil	Nil	0.0449	Nil	Nil	15.0	4.21
2.67	Nil	Nil	Nil	0.0546	Nil	Nil	16.6	3.80
--	--	0.0077	--	--	11.4	--	17.2	3.67
1.05	0.35	0.0092	0.0068	0.0197	25.8	19.1	18.1	3.49
0.42	0.33	0.0363	0.0062	0.0079	70.2	12.0	15.0	4.21
Nil	0.043	0.0443	0.0009	Nil	97.0	2.0	13.1	4.82
Nil	Nil	0.0513	Nil	Nil	100.0	Nil	18.1	3.49
Nil	Nil	0.0524	Nil	Nil	100.0	Nil	15.8	3.99
--	--	0.0752	--	--	74.0	--	--	--

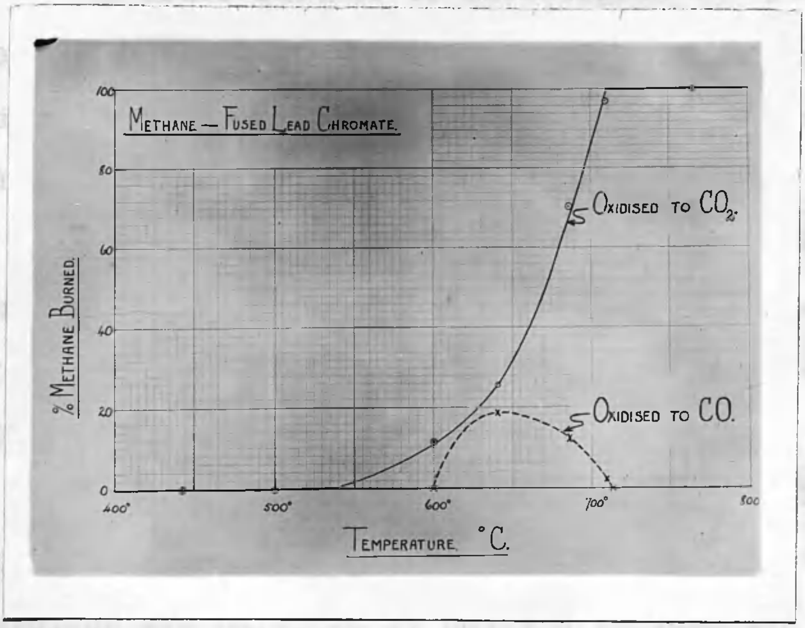

Fig. 7.

carbon dioxide and water.

In experiment 9 the lead chromate which had been used for experiments 1 - 8 was replaced by a fresh charge of 247gm. and the Resulting Gas, instead of being collected and analysed, was passed into a solution of palladium chloride to confirm the presence of carbon monoxide by Potain and Drouin's palladium chloride test (32). This test was decidedly positive, a heavy black precipitate of palladium being obtained, leaving the supernatant liquid perfectly colourless. The high percentage of methane burned in experiment 9 (74.0%) as compared with the value at 685°C. given by the graph (65.0%)

also shows that lead chromate can not be regenerated by the treatment described after it has become reduced.

In order further to investigate the persistence of carbon monoxide in the above series of experiments, the influence of temperature on the reaction between that gas and fused lead chromate was examined. 253gm. fused lead chromate (4 - 8 mesh) were used, filling 65.0cm. length of the tube and having an available space of 53.9cc.. Following the same reasoning as with methane, this amount of lead chromate is 433 times the necessary amount.

The carbon monoxide used was prepared by dropping formic acid (D = 1.2) on to concentrated sulphuric acid. The gas evolved was purified by passage through two gas washing bottles containing alkaline pyrogallol. The gas was analysed in Bone and Wheeler's apparatus both by absorption with ammoniacal cuprous chloride solution and by explosion with oxygen, while the Resulting Gas was analysed by slow combustion in Haldane's apparatus.

The results are given in Table VIII and are represented graphically in Fig. 8. The graph shows that carbon monoxide, although having an initial combustion point of 100°C., is not completely oxidised below 615°C.. For this reason it would appear that in the oxidation of methane by lead chromate a large amount of carbon monoxide is formed at the hottest part of the tube and this gas, being swept to the cooler parts of the tube, where the rate of oxidation is much slower, is left

TABLE

CARBON MONOXIDE AND

Expt. No.	Temp. °C.	Original Gas.			Weight of
		Volume. cc.	% CO.	CO supplied. gm.	CO_2 formed. gm.
1.	c.50	1640	5.23	0.1058	Nil
2.	182	1480	5.23	0.0941	0.0260
3.	205	1950	5.23	0.1239	0.0422
4.	416	1840	5.33	0.1130	0.1114
5.	485	1810	5.43	0.1169	0.1384
6.	592	1900	5.40	0.1196	0.1744
7.	628	1440	5.40	0.0919	0.1480

VIII.

FUSED LEAD CHROMATE.

Resulting Gas.		Carbon Monoxide burned. gm.	Carbon Monoxide unburned. gm.	Carbon Monoxide burned. %	Rate of Flow. cc. per min.	Time of Contact. min.
Volume. cc.	% CO.					
3040	2.88	Nil	0.1048	Nil	17.9	3.01
2990	2.25	0.0166	0.0785	17.6	19.2	2.80
*	--	0.0269	--	21.7	19.5	2.76
3180	1.16	0.0709	0.0417	62.7	20.2	2.67
3150	0.80	0.0881	0.0291	75.4	17.9	3.01
3980	0.15	0.1110	0.0066	92.8	19.8	2.72
3210	Nil	0.0940	Nil	100.0	19.4	2.78

* Gas lost owing to manometer sucking in overnight.

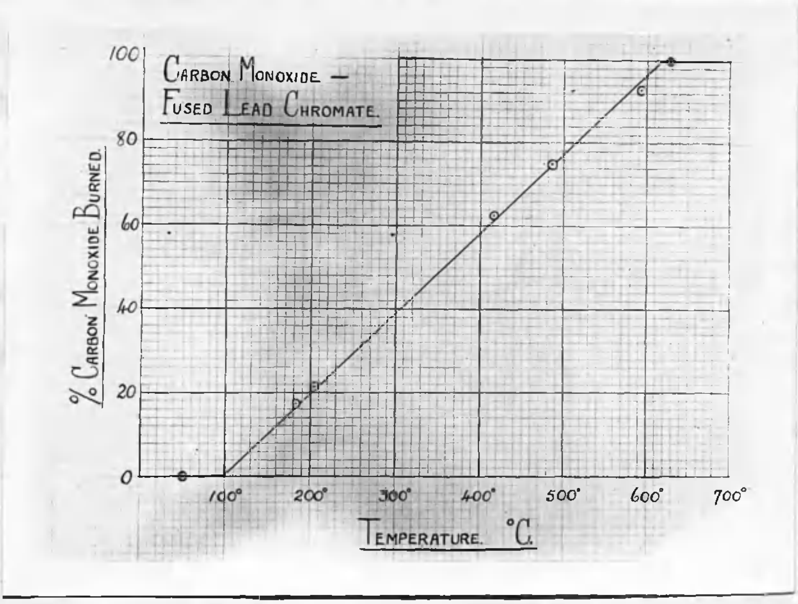

Fig. 8.

partially unattacked and unchanged carbon monoxide appears in the Resulting Gas.

The curve shown in Fig. 8 illustrates clearly the influence of the time of contact on the amount of oxidation taking place. It is possible that with a sufficiently long time of contact of carbon monoxide with fused lead chromate, complete oxidation to carbon dioxide will take place just above 100°C..

Conclusions.

While causing methane initially to burn at a much lower temperature than copper oxide, fused lead chromate has nothing to recommend it as opposed to copper oxide in view of the fact that the temperature of complete combustion is practically the same as that with copper oxide.

Since fused lead chromate, when once reduced in the combustion tube, cannot be regenerated in situ and since it is liable to oxidise methane to the carbon monoxide stage and no further, the use of this salt as an oxidising agent in combustion analyses is not to be recommended.

E. - METHANE and COPPER OXIDE IMPREGNATED with CUPROUS CHLORIDE.

The use of cuprous chloride as a catalyst in promoting the complete oxidation of methane by means of copper oxide has been suggested by Dunstan and Carr (6) and by Haas (1), but no data with reference to the influence of temperature on the efficiency of the catalyst or the danger of the evolution of hydrochloric acid have been recorded. The following experiments were carried out with a view to repairing these deficiencies.

Preparation of Impregnated Copper Oxide.

250gm. freshly ignited copper oxide (8 - 32 mesh) were evaporated to dryness, with constant stirring, with an aqueous suspension containing 40gm. cuprous chloride and the dry mass gently ignited.

260gm. of the impregnated oxide were used, occupying 67.0cm. length of the combustion tube and having an available space of 62.8cc., and the mass ignited in a stream of oxygen at 400°C., several degrees below the melting point of cuprous chloride (33), for 6 hours. This gave a mixture containing $\frac{45}{.286}$, or 157, times the necessary amount of copper oxide required for the complete combustion of the hydrocarbon and containing 13.8% cuprous chloride.

The methane and nitrogen were prepared as before and the method adopted was that described under Methane and Copper Oxide.

The following results were obtained, these being shown in the graph in Fig. 9.

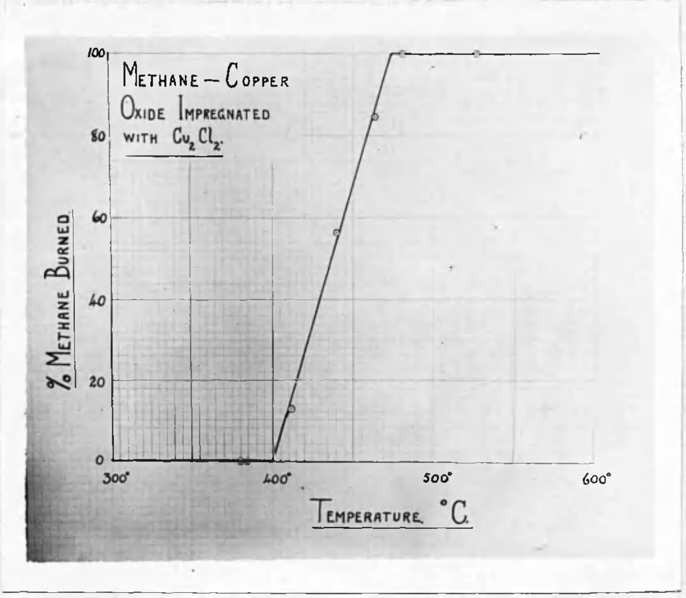

Fig. 9.

The graph shows that under the conditions of the experiments, methane begins to be oxidised at 400°C. and complete combustion takes place under the prevailing conditions at 475°C., 230° below the corresponding temperature obtained when copper oxide was used alone. At the temperatures shown in the table no trouble from hydrochloric acid was encountered.

With a view to finding the effect of prolonged activity on the life of cuprous chloride as a catalyst, the

TABLE

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	380	1300	5.42	0.0481	Nil	3500
2.	384	1450	4.76	0.0454	Nil	2910
3.	412	1360	5.42	0.0496	0.0172	*
4.	440	1360	5.55	0.0520	0.0800	3300
5.	463	1210	5.55	0.0452	0.1046	3050
6.	480	1370	5.18	0.0488	0.1308	3050
7.	525	1410	5.18	0.0500	0.1354	3250

* Gas lost owing to manometer sucking in overnight.

IX.

IMPREGNATED WITH CUPROUS CHLORIDE.

-ing Gas.	Methane burned. gm.	Methane unburned. gm.	Methane burned. %	Rate of Flow. cc. per min.	Time of Contact. min.
% CH_4					
2.07	Nil	0.0475	Nil	22.8	2.76
2.37	Nil	0.0444	Nil	15.4	4.06
--	0.0063	--	12.7	15.1	4.16
1.02	0.0293	0.0224	56.4	17.6	3.57
0.32	0.0384	0.0061	84.9	14.6	4.30
Nil	0.0478	Nil	100.0	15.2	4.13
Nil	0.0493	Nil	100.0	14.1	4.45

following experiment was carried out.

The tube containing the copper oxide and cuprous chloride was heated to 515°C. and air and a gaseous mixture containing 60.6% CH_4, 29.4% H_2 and 10.0% N_2 passed alternately over the oxidising agent, the temperature being altered for each passage of the combustible gas. The exit gases, after passing through the sulphuric acid U-tube were passed directly into a solution of silver nitrate acidified with concentrated nitric acid. By this means the cuprous chloride was subjected to a process involving the oxidiation of 1.49gm. methane and 0.090gm. hydrogen which together required 16% of the copper oxide in the tube for complete oxidation, while the formation of hydrochloric acid could easily be detected. The results are shown in Table X.

After this series of combustions a determination to ascertain whether the activity of the catalyst had decreased was carried out, with the following results.

4.99% CH_4 MIXTURE.

Expt.No.	Temp. °C.	Wt.Methane Supplied. gm.	Wt.Methane Burned. gm.	Wt.Methane Unburned. gm.	Methane Burned %	Rate of Flow. cc. per min.	Time of Contact. min.
8	500	0.0519	0.0307	0.0202	59.1	14.4	4.36
9	795	0.0493	0.0491	Nil	100.0	16.1	3.90

TABLE X.

PASSAGE OF METHANE-HYDROGEN MIXTURE OVER IMPREGNATED COPPER OXIDE.

Volume of Gas. cc.	Time of Passage. min.	Rate of Flow. cc. per min.	Temp. °C.	Presence or Absence of Hydrochloric Acid.
900	67	12.0	515-530	No HCl
Air	60	-	530-515	-
1070	60	17.8	515-530	No HCl
Air	88	-	530-20	-
300	26	11.1	575-580	No HCl
Air	26	-	580-660	-
270	21	12.8	660-665	Little HCl
Air	61	-	665-755	-
560	30	18.7	755-765	Much HCl
Air	66	-	765-810	-
310	30	10.3	810-813	Much HCl

It is thus evident that the catalyst had lost much of its activity after prolonged use, the efficiency, measured by the amount of methane oxidised, having dropped by about 40% at 500°C.. The good balance in the various weights of methane obtained in the experiment carried out at 795°C. shows that at high temperatures where copper oxide alone gives complete combustion, cuprous chloride does not give any liberation of hydrochloric acid during the combustion of methane when this gas is used alone.

Conclusions.

(1) Impregnation of copper oxide with cuprous chloride materially reduces the temperature of combustion of methane from that obtained with copper oxide alone.

(2) At temperatures above 650°C. hydrogen reduces the chloride and gives free hydrogen chloride. This renders cuprous chloride unsuitable for use in carbon and hydrogen estimations carried out at these temperatures unless special precautions are taken, but it may advantageously be used for nitrogen estimations by the absolute method and possibly for carbon and hydrogen estimation at temperatures below 650°C., at which temperature any methane which may be formed is completely oxidised.

Nitrogen estimations on mesityl oxide phenylthiosemicarbazone, carried out in this College, were always high when copper oxide was used alone, owing to the incomplete combustion of methane, but on impregnating the copper oxide with cuprous chloride, satisfactory results were obtained.

(3) Owing to the fact that cuprous chloride melts at 430°C. (supra.) it will be advantageous to conduct experiments as little above 475°C.,,at which temperature complete combustion of methane is obtained, as is possible in order to prevent loss of activity owing to the catalyst running to the bottom of the tube.

[illegible] n pentoxide is the best oxidation cat [illegible] paration of phthalic anhydride anth [illegible] thraquinone from naphthalene, anthrac [illegible] ively, while Weiss and Downs (75) hav [illegible] the partial oxidation of benzene by [illegible] de as a catalyst in circumstances in [illegible] sinum give complete oxidation to carb [illegible]

Nevertheless it was thought that i [illegible] vanadium pentoxide successfully as a [illegible] t in promoting the oxidation of metha [illegible]

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F. - METHANE and COPPER OXIDE IMPREGNATED with VANADIUM PENTOXIDE.

Although vanadium pentoxide is a very active oxidation catalyst, its greatest use in this respect seems to be restricted to the production of intermediate oxidation products; for example, it is largely adopted as a catalyst in the oxidation of aniline to aniline black as reported by Witz (34) and Gouillon (35), while several patents have been taken out in respect to its use in the preparation of acetic acid from acetaldehyde (36, 37). Gibbs (38) has found that vanadium pentoxide is the best oxidation catalyst for use in the preparation of phthalic anhydride, anthraquinone and phenanthraquinone from naphthalene, anthracene and phenanthrene respectively, while Weiss and Downs (39) have obtained maleic acid by the partial oxidation of benzene by using vanadium pentoxide as a catalyst in circumstances in which cerium oxide and platinum give complete oxidation to carbon dioxide and water.

Nevertheless it was thought that it might be possible to use vanadium pentoxide successfully as a complete oxidation catalyst in promoting the oxidation of methane by copper oxide and, in order to investigate this matter, the following experiments were carried out.

Preparation of Impregnated Copper Oxide.

In using this catalyst two separate quantities of impregnated copper oxide were prepared, each containing a different proportion of vanadium pentoxide, and these used to ascertain the effect of varying the amount of catalyst present in the mixture. In the first case 15gm. ammonium vanadate were made into a cream with water, the suspension diluted and evaporated to dryness, with constant stirring, with 265gm. freshly ignited 8 - 32 mesh copper oxide. 245gm. of the resultant mixture were placed centrally in the combustion tube, occupying 60.3cm. of its length and heated to 550°C., about 100°C. below the melting point of vanadium pentoxide (40) in a stream of oxygen for 8 hours. This gave a mixture containing $\frac{46}{.286} = 161$ times the amount of copper oxide necessary for the complete oxidation of 2 litres of a 5% methane mixture. The available space over the oxidising mixture was 62.0cc. and the mixture so prepared contained 4.2% V_2O_5 by weight.

The figures for the other mixture prepared were:-

Weight of NH_4VO_3	3.5gm.
Weight of CuO	250gm.
Weight of mixture used	245gm.
Length of tube occupied	60.5cm.
CuO present = $\frac{47}{\cdot 286}$ =	164 times necessary amount.
Available space	59.2cc.
% V_2O_5 in mixture	1.0%

The methane and nitrogen were prepared by the methods described under methane and copper oxide.

The following are the results obtained with the 4.2% mixture, the figures being grouped in the graph in Fig. 10 and tabulated in Table XI.

TABLE

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	443	1220	5.36	0.0449	Nil	2850
2.	503	1200	5.64	0.0467	0.0100	2740
3.	555	1650	4.95	0.0562	0.0358	3100
4.	592	1500	5.10	0.0527	0.0574	2950
5.	592	1420	4.76	0.0450	0.0475	2945
6.	629	1440	5.10	0.0522	0.0882	3010
7.	671	1240	5.64	0.0485	0.1266	3140
8.	705	1600	5.36	0.0588	0.1622	2120

XI.

IMPREGNATED WITH 4.2% VANADIUM PENTOXIDE.

- ing Gas. % CH_4	Methane burned. gm.	Methane unburned. gm.	Methane burned. %	Rate of Flow. cc. per min.	Time of Contact. min.
2.36	Nil	0.0448	Nil	15.4	4.03
2.44	0.0037	0.0436	7.9	15.2	4.08
2.15	0.0130	0.0445	23.1	17.3	3.58
1.63	0.0209	0.0321	39.7	13.9	4.46
1.46	0.0173	0.0277	38.5	15.9	3.90
0.87	0.0324	0.0185	62.0	15.2	4.08
0.098	0.0461	0.0021	95.2	15.7	3.95
Nil	0.0591	Nil	100.0	15.8	3.93

The graph shows that, in the case of the 4.2% mixture, methane begins to burn at 445°C. and complete oxidation is obtained at 675°C., or 30° below the corresponding temperature obtained with copper oxide alone.

In order to test the life of the vanadium pentoxide as a catalyst, about 2¼ litres of a gas containing 58.4% CH_4, 28.0% H_2 and 13.6% N_2 were passed, intermittently with air over the oxidising mixture according to the scheme in Table XII, p. 67. The oxidising mixture was now subjected to an ordinary combustion at a point on the curve to ascertain if the catalyst had deteriorated in any way. Such a combustion gave the following results:-

Expt. No. 9.

Temp.	665°C.
Original Gas. Volume	2140cc.
% CH_4	5.10%
Weight CH_4 supplied	0.0719gm.
Weight of CO_2 formed	0.1748gm.
Resulting Gas. Volume	3140cc.
% CH_4	0.43%
Weight of CH_4 burned	0.0637gm.
Weight of CH_4 unburned	0.0092gm.
% CH_4 burned	88.2%
Rate of Flow	16.8cc. per min.
Time of Contact	3.63min..

TABLE XII.

PASSAGE OF METHANE-HYDROGEN MIXTURE OVER IMPREGNATED COPPER OXIDE.

Volume of Gas. cc.	Time of Passage. min.	Rate of Flow. cc. per min.	Temp. °C.
450	22	20.4	710-720
Air	92	-	720-715
500	42	12.2	715-720
Air	49	-	720-710
400	28	14.3	710-720
Air	28	-	720-715
400	29	13.8	715-720
Air	-	-	720-20
400	34	11.8	710-720
Air	78	-	720-710
400	34	11.8	710-720
Air	-	-	720-20

Since the value for 665°C. obtained from the graph is 88.0% it is evident that vanadium pentoxide does not deteriorate with use as an oxidation catalyst.

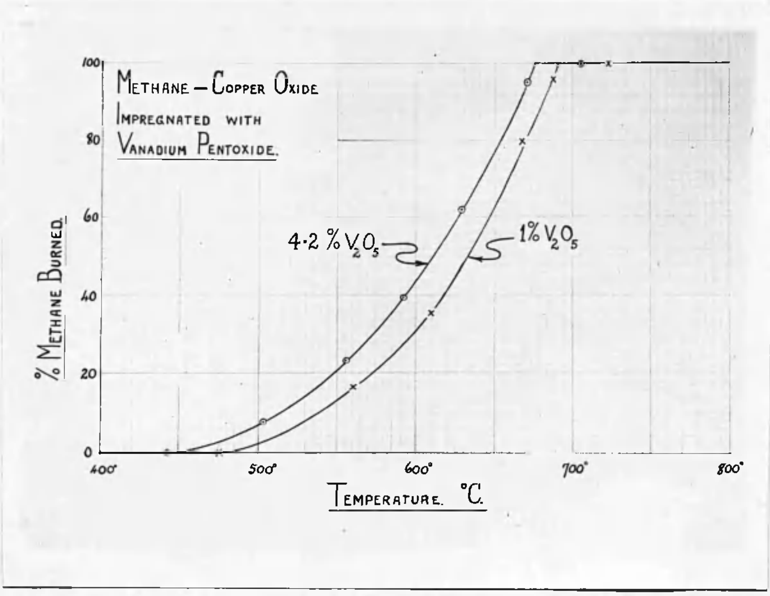


Fig. 10.

The results obtained with the 1% vanadium pentoxide-copper oxide mixture are detailed in Table XIII while they are collected in the graph in Fig. 10.

The graph gives for the initial combustion temperature 475°C., or 30° above the temperature given by the 4.2% mixture, and for the temperature at which complete combustion takes place, 690°C., 15° above the corresponding temperature obtained with the 4.2% mixture.

TABLE

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	475	1350	4.93	0.0444	Nil	3030
2.	560	1745	5.12	0.0611	0.0270	3700
3.	610	1180	14.20	0.1133	0.1100	3610
4.	668	1150	14.20	0.1084	0.2362	2550
5.	688	1430	5.35	0.0505	0.1330	2980
6.	723	1490	5.35	0.0535	0.1494	3010

XIII.

IMPREGNATED WITH 1% VANADIUM PENTOXIDE.

-ing Gas.		Methane burned.	Methane unburned.	Methane burned.	Rate of Flow.	Time of Contact.
	% CH_4	gm.	gm.	%	cc. per min.	min.
	2.21	Nil	0.0436	Nil	18.0	3.29
	2.10	0.0099	0.0513	16.2	16.9	3.48
	3.11	0.0403	0.0732	35.6	16.9	3.48
	1.36	0.0861	0.0228	79.5	17.7	3.35
	0.084	0.0485	0.0016	96.0	17.5	3.37
	Nil	0.0544	Nil	100.0	17.7	3.35

Conclusions.

From the results obtained it is evident that vanadium pentoxide may be successfully used as an oxidation catalyst in the complete combustion of methane by means of copper oxide and that the efficiency of the catalyst is a function of the amount present. The catalyst has the advantage that it does not deteriorate after prolonged use.

G. - METHANE and COPPER OXIDE IMPREGNATED with COBALTO - COBALTIC OXIDE, Co_3O_4.

Although until recent years the use of metallic oxides as catalysts in the oxidation of organic compounds has been limited almost exclusively to copper oxide, Sabatier and Mailhe (9) have shown that cobaltous oxide has catalytic properties entirely comparable with those of finely divided platinum, since methane, mixed with oxygen and caused to impinge on a surface of cobaltous oxide at 200°C. is almost completely oxidised, a little formaldehyde being formed. Almost simultaneously Matignon and Trannoy (41) showed that this oxide could be used as a catalyst in producing a "lampe sans flamme" by causing the combustion of methyl alcohol vapour on a surface of cobaltous oxide.

Since these two catalytic uses of cobaltous oxide yielded such successful results it was decided to study the use of this oxide as a catalyst in promoting the oxidation of methane by means of copper oxide.

Preparation of Impregnated Copper Oxide.

23.6gm. $Co(NO_3)_2.6H_2O$ (sufficient to give 5gm. CoO) were dissolved in water in an evaporating basin and 250gm. freshly ignited 8 - 32 mesh copper oxide added. The whole mass was slowly evaporated to dryness, with constant stirring, and the dry mixture gently ignited.

217gm. of the mixture were introduced into the combustion tube, occupying 65.0cm. of its length and heated in a current of air for 6 hours at 614°C.. All traces of oxides of nitrogen and water were driven off in less than two hours. This gave a mixture containing $\frac{43}{.286}$, or 150, times the necessary amount of copper oxide and containing 2.0% CoO. The available space in contact with the impregnated copper oxide was 61.9cc..

Although the oxide of cobalt produced by heating cobalt nitrate is at first cobaltous oxide (CoO), Kalmus (42) and others have shown that the stable oxide formed by heating cobaltous oxide in air or oxygen is cobaltocobaltic oxide (Co_3O_4), so that in the experiments carried out the actual catalyst would be the latter oxide.

The results obtained are given in Table XIV and are collected in the graph in Fig. 11. These show that the initial combustion temperature of methane is reduced by 270° to 290°C. while the temperature at which complete combustion takes place is 650°C., or 55° below that obtained with copper oxide alone, adequate proof that the oxidation of methane is greatly promoted by this catalyst.

Conclusions.

Cobaltocobaltic oxide may be successfully used as a catalyst in promoting the oxidation of methane by means of copper oxide.

TABLE

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-	
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.	
1.	250	1450	5.04	0.0507	Nil	3340	
2.	420	1520	5.12	0.0574	0.0128	3400	
3.	490	1260	5.08	0.0444	0.0222	3150	
4.	550	1990	5.08	0.0687	0.0544	3340	
5.	600	1660	5.35	0.0590	0.1066	2280	
6.	640	1360	5.35	0.0483	0.1226	2550	
7.	733	1860	4.93	0.0616	0.1700	3250	

XIV.

IMPREGNATED WITH 2% COBALT OXIDE.

-ing Gas.	Methane burned. gm.	Methane unburned. gm.	Methane burned. %	Rate of Flow. cc. per min.	Time of Contact. min.
% CH_4					
2.25	Nil	0.0503	Nil	18.2	3.40
2.26	0.0047	0.0517	8.2	17.9	3.46
1.71	0.0081	0.0356	18.2	19.4	3.19
2.18	0.0198	0.0480	28.9	18.2	3.40
1.37	0.0388	0.0197	65.8	18.2	3.40
0.28	0.0447	0.0046	92.5	17.9	3.46
Nil	0.0620	Nil	100.0	18.6	3.33

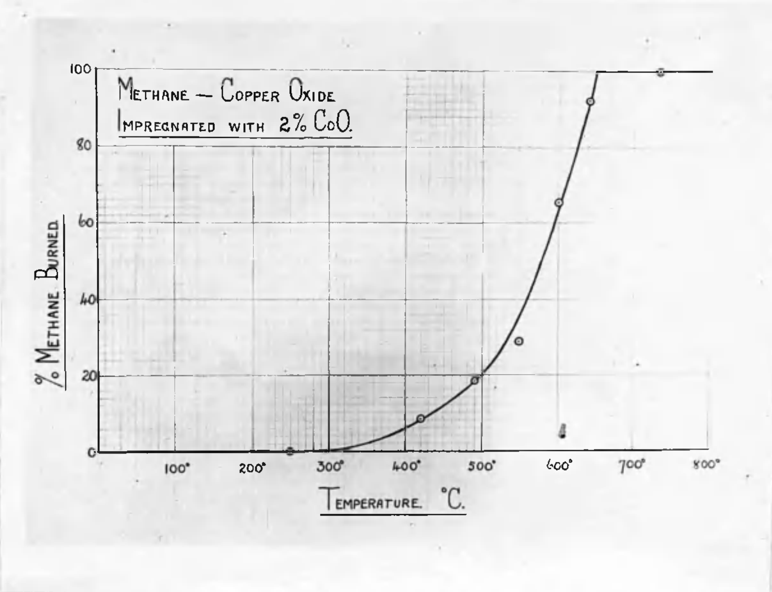

Methane — Copper Oxide
Impregnated with 2% CoO.
% Methane Burned
Temperature °C.
0
20
40
60
80
100
100°
200°
300°
400°
500°
600°
700°
800°

Fig. 11.

H. - METHANE and COPPER OXIDE IMPREGNATED with NICKELOUS OXIDE.

Although nickel oxide is perhaps better known as a hydrogenation catalyst, the idea was entertained that this oxide may be advantageously used as an oxidation catalyst in view of the success of the cobalt oxide as shown in the last section. Boudouard (43) has reported that both nickel and cobalt oxides oxidise carbon monoxide completely and more rapidly than ferric oxide, while Sabatier and Mailhe (9) have shown that nickel oxide gives almost complete oxidation of hydrocarbons in presence of oxygen, a little formaldehyde being formed. Matignon and Trannoy (41) have successfully used nickel oxide in place of cobalt oxide in their lamp without flame.

Preparation of Impregnated Copper Oxide.

23.6gm. $Ni(NO_3)_2.6H_2O$ - sufficient to give 5gm. NiO - were dissolved in an evaporating basin, 250gm. freshly ignited 8 - 32 mesh copper oxide added, the whole mass well mixed and slowly evaporated to dryness with constant stirring. The dry mixture was introduced into the combustion tube, occupying 64.1cm. of its length, and ignited in a current of air at 621°C. for 6 hours, all traces of oxides of nitrogen having been expelled in less than 2 hours. This gave a mixture containing 2.0% NiO and $\frac{50}{.286}$, or 175, times the necessary amount of copper oxide. The space over the oxidising mixture was 64.5cc..

According to Caven and Lander (44), NiO is stable at high temperatures, so that in this case the mixture contains 2% nickelous oxide as such.

The results are shown in Table XV, from which the graph in Fig. 12 has been constructed.

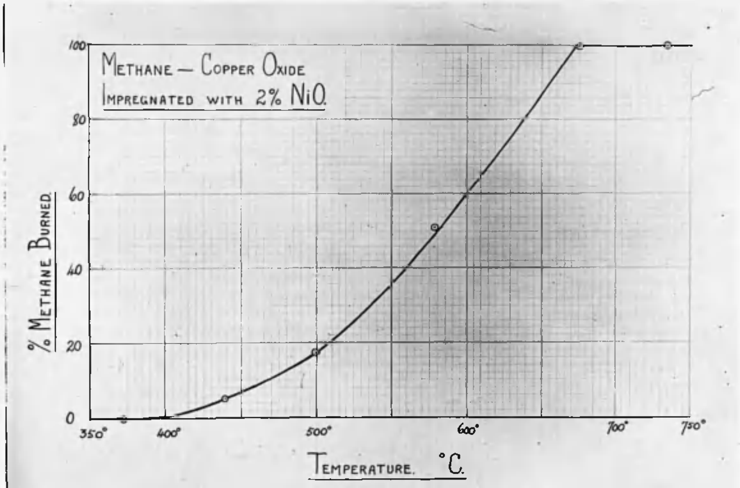


Fig. 12.

The date show that the initial combustion temperature of methane is 395°C. or 165° below the figure for copper oxide alone, while the minimum temperature of complete combustion is reduced by 30° to 675°C..

TABLE

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	372	1250	5.12	0.0443	Nil	2950
2.	439	1610	4.19	0.0462	0.0064	3050
3.	499	1590	4.19	0.0460	0.0218	3270
4.	578	1980	4.89	0.0653	0.0916	2990
5.	675	1340	4.89	0.0444	0.1214	3060
6.	734	1850	5.04	0.0634	0.1738	3060

XV.

IMPREGNATED WITH 2% NICKEL OXIDE.

-ing Gas.	Methane burned. gm.	Methane unburned. gm.	Methane burned. %	Rate of Flow. cc./min.	Time of Contact. min.
% CH_4					
2.18	Nil	0.0429	Nil	18.6	3.46
2.08	0.0023	0.0434	5.0	19.7	3.28
1.75	0.0079	0.0380	17.3	19.1	3.38
1.67	0.0334	0.0324	51.1	19.5	3.31
Trace	0.0442	Trace	100	18.4	3.51
Nil	0.0633	Nil	100.0	19.9	3.24

Conclusions.

Although not so efficient a catalyst as cobaltocobaltic oxide, nickel oxide may successfully be used as an oxidation catalyst in promoting the oxidation of methane by means of copper oxide.

K. - METHANE and COPPER OXIDE IMPREGNATED with MANGANESE DIOXIDE.

In their investigations on the combustion of organic substances on surfaces which acted as catalysts Matignon and Trannoy (41) found that while the oxides of cobalt and nickel gave results with methyl alcohol only, manganese dioxide was able to maintain incandescence when other organic compounds were used. Sabatier and Mailhe (9) also found that in aiding the combustion of hydrocarbons catalytically manganese dioxide had properties quite comparable with those of finely divided platinum.

In recent years the catalytic oxidation of carbon monoxide has occupied the attention of American chemists. This oxidation may be brought about by metals such as platinum and palladium, but the time of contact necessary for complete oxidation is comparatively great. It has been found that mixtures of certain oxides are much more effective as catalysts and may bring about the complete oxidation of carbon monoxide at ordinary temperatures with a surprisingly short time of contact. In this respect a mixture of manganese dioxide and copper oxide has been found to be exceedingly efficient, in fact, Lamb, Scalione and Edgar (45) have found that such a mixture, containing only 1% manganese dioxide, developes so much heat with a mixture of carbon monoxide and hydrogen that not only is the former gas completely oxidised but also part of the latter. An exhaustive survey of this work is given by Bray and his collaborators in the Journal of the American Chemical Society (46).

In the catalytic oxidation of ammonia Piggot (47) has shown that a mixture of manganese dioxide and copper oxide in the ratio 60:40 has an efficiency of over 90% at 800°C..

These facts prompted the idea that manganese dioxide may prove an efficient catalyst in the work under consideration.

Preparation of Impregnated Copper Oxide.

11.4gm. $MnCl_2.4H_2O$ (sufficient to give 5gm. MnO_2) were dissolved in water, a little ammonium chloride solution added and bromine water added until the solution developed a permanent yellow colour. A slight excess of ammonia was then added and the solution warmed. The precipitated manganese dioxide was filtered off, washed with distilled water until free from halide and washed into an evaporating basin containing 250gm. freshly ignited 8 - 32 mesh copper oxide covered with distilled water. The mixture was then slowly evaporated to dryness, with constant stirring and gently ignited.

227gm. of the mixture were used, occupying 65.0cm. length of the combustion tube in which it was ignited in a current of air for 6 hours at 700°C.. The mixture used contained 2.0% MnO_2 and $\frac{45}{.286}$, or 157, times the necessary amount of copper oxide, while the available space in contact with the oxidising medium was 57.8cc..

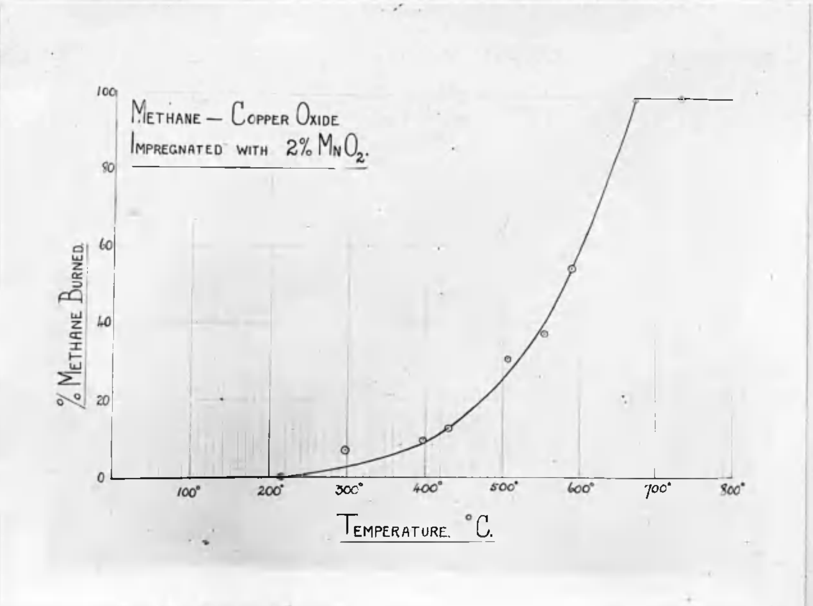
According to Wright and Luff (48) the oxide of manganese stable at high temperatures is mangano - manganic oxide, Mn_3O_4, so that in this case the catalyst was really this latter oxide.

The results obtained are shown in Table XVI and are collected in the graph in Fig. 13. These show that the initial combustion point of methane is reduced by 345° to 215° and the temperature of complete combustion by 30° to 675° C..

Conclusions.

The results obtained show that impregnation of copper oxide with manganese dioxide considerably reduces the temperature of combustion of methane and that such a mixture may be advantageously used in cases where trouble from the non - oxidation of methane arises.

Fig. 13.



T A B L E

METHANE AND COPPER OXIDE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	215	1340	5.18	0.0467	Nil	3210
2.	297	1340	5.18	0.0469	0.0086	3060
3.	398	1450	5.45	0.0529	0.0138	3480
4.	430	1440	5.45	0.0525	0.0174	3410
5.	506	1310	5.83	0.0492	0.0418	3480
6.	556	1460	5.83	0.0579	0.0758	*
7.	590	1470	5.77	0.0586	0.1352	3255
8.	672	1595	4.89	0.0530	0.1448	2890
9.	733	1750	5.12	0.0606	0.1640	3120

* Gas lost owing to aspirator emptying.

XVI.

IMPREGNATED WITH 2% MANGANESE DIOXIDE.

-ing Gas.		Methane burned.	Methane unburned.	Methane burned.	Rate of Flow.	Time of Contact.
	% CH_4	gm.	gm.	%	cc. per min.	min.
	2.18	Nil	0.0469	Nil	17.9	3.23
	2.18	0.0031	0.0436	6.7	18.6	3.11
	2.08	0.0050	0.0466	9.5	17.7	3.26
	2.07	0.0063	0.0457	12.1	19.2	3.01
	1.50	0.0152	0.0327	31.0	18.5	3.12
	-	0.0276	-	47.7	18.5	3.12
	0.42	0.0493	0.0090	54.6	18.0	3.21
	0.025	0.0528	0.0004	99.6	20.1	2.87
	Nil	0.0598	Nil	100.0	18.2	3.18

L. - METHANE and COBALTO - COBALTIC OXIDE.

In view of the success of cobalto-cobaltic oxide as a catalyst in reducing the temperature of complete combustion of methane by as much as 55°C., it was decided to investigate the effect of temperature on the oxidation of methane by this oxide alone, deposited on pumice. For this purpose, 86.0gm. $Co(NO_3)_2.6H_2O$ were mixed with 75gm. 4 - 8 mesh purified pumice, melted and evaporated, with constant stirring, until the whole mass was dry. This gave 135gm. mixture. 82.5gm. of this mixture were used, occupying 65.0cm. length of the combustion tube and heated to 250°C. for 3 hours and then to 750°C. for 6 hours with air passing.

Calculated as cobaltous oxide, CoO, 11.2gm. in all were used, containing 2.4gm. oxygen, i.e. $\frac{2.4}{.286}$, or 8.4 times the necessary amount of oxygen. The volume of space in contact with the oxidising medium and its carrier was 93.6cc..

The results are tabulated in Table XVII and grouped in the graph in Fig. 14. These show that the initial combustion point of methane is 250°C., or 40° below that obtained with the oxide mixed with copper oxide, while the lowest temperature of complete combustion is 705°C., or 55° above the corresponding temperature for the cobalt oxide - copper oxide mixture and equal to the value obtained with copper oxide alone.

TABLE

METHANE AND PUMICE

Expt. No.	Temp. °C.	Original Gas.			Weight of CO_2 formed. gm.	Result-
		Volume. cc.	% CH_4	Methane supplied. gm.		Volume. cc.
1.	219	1610	5.08	0.0553	Nil	3390
2.	403	1500	5.08	0.0501	0.0092	3120
3.	500	1540	5.20	0.0534	0.0132	3200
4.	541	1550	5.20	0.0540	0.0176	3360
5.	591	1640	4.92	0.0543	0.0294	3110
6.	639	1600	4.76	0.0519	0.0697	2960
7.	685	1640	4.92	0.0558	0.1268	3200
8.	715	1600	4.76	0.0508	0.1400	3200

XVII.

IMPREGNATED WITH COBALT OXIDE.

-ing Gas.	Methane	Methane	Methane	Rate of Flow.	Time of
% CH_4	Burned. gm.	Unburned. gm.	Burned. %	cc. per min.	Contact. min.
2.48	Nil	0.0547	Nil	18.6	5.04
2.41	0.0033	0.0476	6.7	17.4	5.38
2.40	0.0048	0.0494	9.0	18.1	5.18
2.23	0.0064	0.0484	11.9	18.9	4.96
2.17	0.0107	0.0440	19.7	18.8	4.98
1.44	0.0248	0.0282	47.7	17.8	5.26
0.50	0.0462	0.0105	82.8	18.2	5.15
Nil	0.0510	Nil	100.0	18.0	5.21

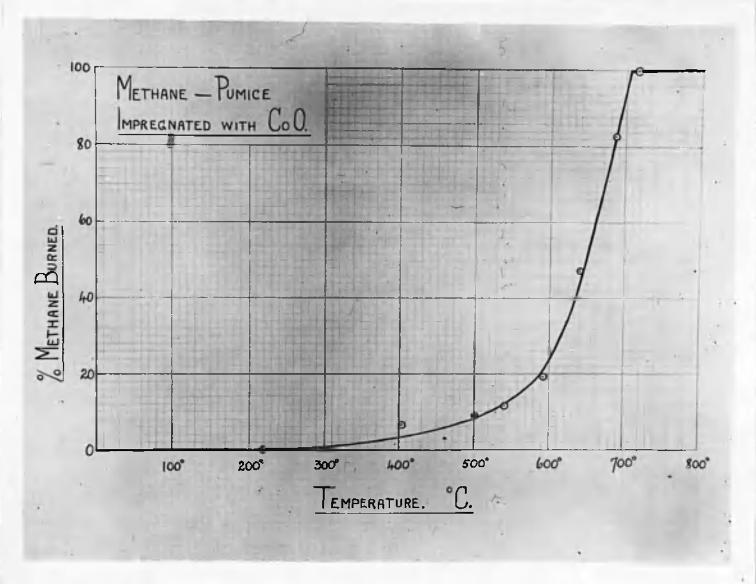


Fig. 14.

Conclusions.

Cobalt oxide may be successfully used as an oxidising agent in organic combustions, being completely comparable with copper oxide in this respect.

The fact that the lowest temperature of complete combustion of methane obtained with cobalt oxide is 55° above the corresponding temperature for the cobalt oxide - copper oxide mixture undoubtedly shows that the action of cobalt oxide in lowering the temperature of combustion of methane with copper oxide, when mixed with this latter oxide, is catalytic.

GENERAL CONCLUSIONS.

From a study of the work carried out in this section it is concluded that cuprous chloride, vanadium pentoxide, cobalt oxide, nickel oxide and manganese dioxide may all be used successfully as catalysts for promoting the oxidation of methane by copper oxide, the efficiency of the catalyst being a function of the amount present in the case of vanadium pentoxide and probably also in the other cases.

As an easy mode of comparing the efficiencies of the various catalysts used the graphs in Fig. 15 and Fig. 16 have been prepared. In the first of these all the straight line graphs have been collected and in the second all the curves, together with the graph obtained when copper oxide was used alone.

The fact that the curves obtained can be divided into two such distinct classes is worthy of consideration, especially when it is noted that in Fig. 15 are placed all the graphs obtained as the result of the investigation on the effect of the addition of another combustible gas to the methane - nitrogen mixture, together with the graph obtained by the use of cuprous chloride as a catalyst. The effect of adding either hydrogen or ethylene to methane is to reduce the temperature of combustion of the latter hydrocarbon, most probably owing to the fact that the combustion of the more easily oxidised gas generates sufficient heat locally to

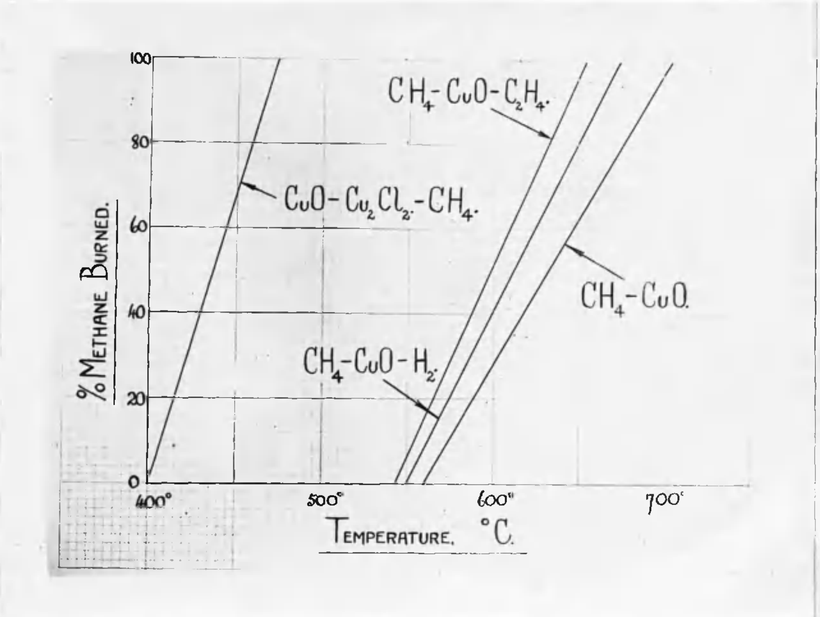

% Methane Burned.
0
20
40
60
80
100
400°
500°
600°
700°
Temperature. °C.
CH4-CuO-C2H4.
CuO-Cu2Cl2-CH4.
CH4-CuO.
CH4-CuO-H2.

Fig. 15.

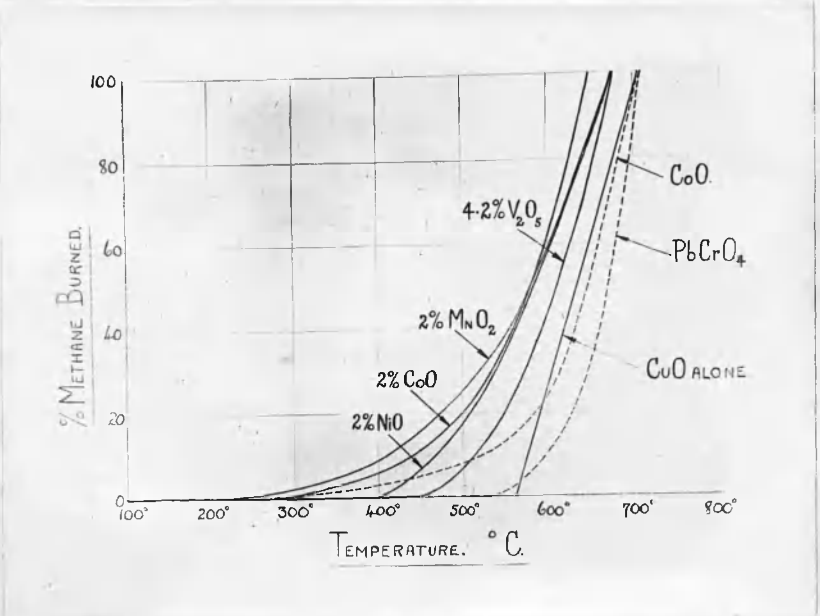
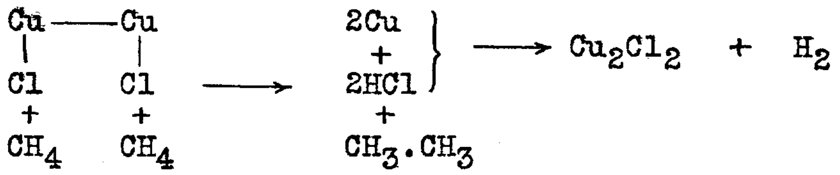

% Methane Burned.
0
20
40
60
80
100
100°
200°
300°
400°
500°
600°
700°
800°
Temperature. °C.
CoO.
PbCrO4
4·2% V2O5
2% MnO2
2% CoO
2% NiO
CuO alone

Fig. 16.

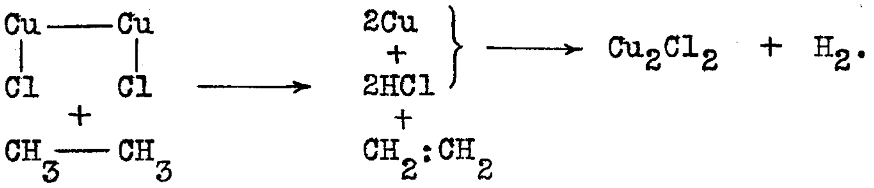
cause the oxidation of the methane to take place.

This explanation, however, does not apply to the question of the function of cuprous chloride although the result produced is similar and since this catalyst produces a different type of curve from any of the other catalysts studied, it is evident that, catalytically, cuprous chloride functions in a manner completely different from the others. It is possible that in the case of all the other catalysts it is the activity of the copper oxide which is increased on the addition of the catalyst, while with cuprous chloride, the reactivity of the methane, rather than that of the copper oxide, is increased.

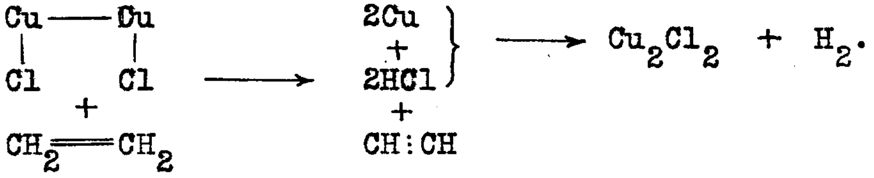
There is a possibility that cuprous chloride reacts with methane and progressively dehydrogenates this hydrocarbon with the formation of ethane, ethylene and possibly acetylene, which hydrocarbons are more easily oxidised by copper oxide than methane and, when mixed with this paraffin, lower its temperature of combustion. This dehydrogenation may be made clear by the following scheme which clearly shows the possible formation of hydrochloric acid and its subsequent conversion to hydrogen:-



$$\begin{matrix}\mathrm{Cu} & \text{---} & \mathrm{Cu}\\ | & & |\\ \mathrm{Cl} & & \mathrm{Cl}\\ + & & +\\ \mathrm{CH_4} & & \mathrm{CH_4}\end{matrix} \longrightarrow \begin{array}{l}\left.\begin{matrix}2\mathrm{Cu}\\ +\\ 2\mathrm{HCl}\end{matrix}\right\}\longrightarrow \mathrm{Cu_2Cl_2} \quad + \quad \mathrm{H_2}\\ \quad + \\ \mathrm{CH_3.CH_3}\end{array}$$



$$\begin{array}{c}\mathrm{Cu}-\mathrm{Cu}\\ |\qquad|\\ \mathrm{Cl}\qquad\mathrm{Cl}\\ +\\ \mathrm{CH_3}-\mathrm{CH_3}\end{array} \longrightarrow \begin{array}{c}\left.\begin{array}{c}2\mathrm{Cu}\\+\\2\mathrm{HCl}\end{array}\right\}\\+\\\mathrm{CH_2{:}CH_2}\end{array} \longrightarrow \mathrm{Cu_2Cl_2} + \mathrm{H_2}.$$



$$\begin{array}{c}\mathrm{Cu}-\mathrm{Cu}\\ |\qquad|\\ \mathrm{Cl}\qquad\mathrm{Cl}\\ +\\ \mathrm{CH_2}=\mathrm{CH_2}\end{array} \longrightarrow \begin{array}{c}\left.\begin{array}{c}2\mathrm{Cu}\\+\\2\mathrm{HCl}\end{array}\right\}\\+\\\mathrm{CH{:}CH}\end{array} \longrightarrow \mathrm{Cu_2Cl_2} + \mathrm{H_2}.$$

This scheme provides for the formation of hydrogen and ethylene, both of which, when mixed with methane, produce straight line graphs with copper oxide. This hypothesis is submitted without proof.

With regard to the efficiency of the various catalysts studied, it is seen that cuprous chloride is by far the most efficient, but this efficiency decreases greatly if the catalyst is heated above its melting point (430°C.). The determination of carbon and hydrogen by combustion over copper oxide with cuprous chloride as catalyst should not be carried out at temperatures above 650°C., at which temperatures free hydrogen chloride is formed by the action of free hydrogen, unless provision is made for the oxidation of this gas and the subsequent fixation of the chlorine. Below 650°C. no free hydrogen chloride is obtained and, since all methane is completely oxidised at 475°C. the catalyst may be advantageously used for carbon and hydrogen estimations between these limits of temperature. In nitrogen estimations no precautions as to the oxidation of hydrogen chloride are necessary and cuprous chloride may be considered an ideal catalyst for these déterminations.

Reference to Fig. 16 demonstrates that the most efficient catalyst studied in this group is cobalt oxide, the remainder, in order of efficiency being manganese dioxide, nickel oxide and vanadium pentoxide. This is in complete agreement with the results of Yant and Hawk (49) who, in 1927, published details of an investigation into the activity of various metal and metal oxide catalysts in promoting the oxidation of methane by means of air. Of the four catalysts mentioned above, the influence of vanadium pentoxide was not studied, but the order of efficiency of the other catalysts obtained by these authors was cobalt oxide, manganese dioxide and nickel oxide.

It may be recorded that the work carried out in this section (Part I) was completed before the results of Yant and Hawk were published and that, although the two investigations only differ in respect of the fact that in one of them air and in the other copper oxide, is used as the source of oxygen, no notice of this work was obtained until the paper referred to was published.

The addition of another combustible gas, such as hydrogen or ethylene, to methane materially promotes the oxidation of the latter hydrocarbon for the reason stated above. Ethylene, although acting as a negative catalyst or a catalytic poison in some cases, does not act as such in the combustion of methane by copper oxide. Owing to its greater heat of combustion per unit volume, ethylene effects a greater reduction in the temperature of combustion of methane than does hydrogen.

The use of fused lead chromate as an oxidising agent in combustion analyses is not to be recommended, owing to the possibility of the incomplete oxidation of methane to carbon monoxide and to the fact that, once reduced, it cannot be regenerated in situ by heating in a current of oxygen even at 800°C.. Further, the graph shows that it is inferior to copper oxide in causing the complete combustion of methane.

Cobalt oxide used alone, whilst initially oxidising methane at a much lower temperature than copper oxide, is practically only equal in efficiency to this latter oxide at the point where complete combustion takes place.

The final conclusion is that for general use at any temperature a mixture of copper oxide and cobalt oxide provides the best safeguard, at present known, against the incomplete combustion of methane.

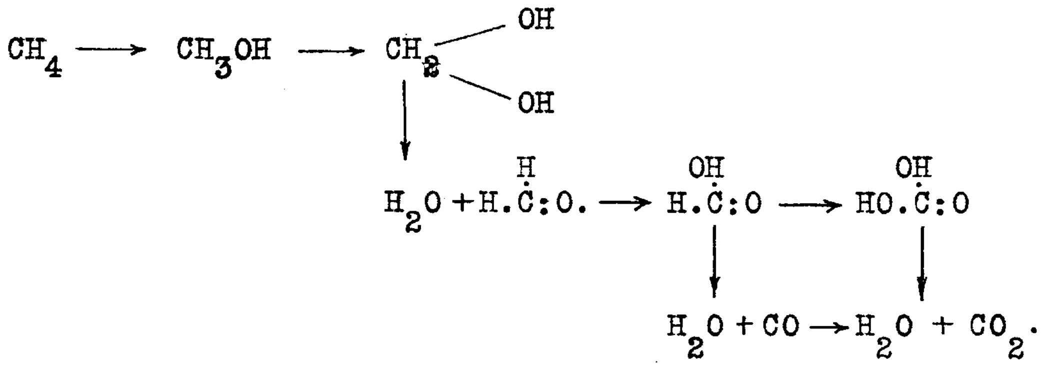
PART II.

THE INFLUENCE OF CATALYSTS IN THE OXIDATION OF METHANE BY HALF ITS VOLUME OF OXYGEN.

Introduction.

During the course of his experiments on flame, Davy, in 1817 (50), discovered that combustible gases slowly combined with oxygen at temperatures below their ignition points. This led him to enquire whether the temperature of such slow combination, while lower than that necessary to produce flame, might be high enough to render solid bodies incandescent. By introducing a warm platinum wire into mixtures of air with coal gas, ethylene, carbon monoxide, hydrogen or prussic acid, he discovered that the wire became red hot and remained so until almost all the oxygen had been consumed. Thus Davy discovered the well-known phenomenon of Catalytic Combustion.

Since Otto (51) in 1898 claimed to have produced methyl alcohol, formaldehyde and formic acid by the action of ozone on methane, the partial oxidation of methane by means of gaseous oxygen, with and without the aid of catalysts, has proved to be the subject of many experiments. In 1902, Bone and R. V. Wheeler (52) carried out, on the oxidation of methane by means of a deficiency of oxygen, a series of experiments which, with others, led to the formulation of the Hydroxylation Theory of Hydrocarbon Combustion propounded by Professor Bone. According to this theory, when a hydrocarbon is oxidised, there is a tendency for the hydrogen atoms successively to be oxidised to hydroxyl groups, yielding hydroxylated molecules which may, or may not, be stable under the conditions of the experiment. If stable, such hydroxylated compounds may be isolated, but if not, they will decompose into simpler products, which products may undergo further oxidation by hydroxylation. In the case of methane the stages in the oxidation are given by the following scheme, in which vertical arrows represent stages of thermal decomposition and horizontal arrows stages of oxidation:-



According to this scheme it should be possible to obtain methyl alcohol, formaldehyde, formic acid, carbon monoxide, carbon dioxide and water by the controlled oxidation of methane.

That Bone's work on the oxidation of hydrocarbons opened up a new area of investigation is evident by the large number of contributions to the literature of the controlled oxidation of hydrocarbons that has been published since 1902.

In 1906, Lance and Elsworthy (53) claimed to have obtained methyl alcohol by oxidising methane with such oxidising agents as

(a) hydrogen peroxide
(b) hydrogen peroxide and ferrous sulphate (Fenton's reagent)
(c) hydrogen peroxide and persulphuric acid
and (d) persulphuric acid,

while von Unruh (54), in 1907, obtained chiefly formaldehyde, although methyl alcohol and formic acid were also formed in small quantities, by the oxidation of methane by means of air or oxygen in presence of tan bark.

Fernekes (55) heated a mixture of methane and air, in a specially constructed burner, to such an extent that formaldehyde was produced. The outer envelope of gas issuing from the burner was allowed to become ignited, whilst external air was excluded from the inner gases and complete combustion was prevented by baffling the stream of gas against a cooling surface.

Traun (56) obtained methyl alcohol and formaldehyde by oxidising methane by means of carbon dioxide. The mixed gases were passed through a constricted pipe heated to 500° - 700°C. at the constriction and the gaseous reaction products quickly cooled. The yield of formaldehyde was about 56% and the formation of methyl alcohol was favoured by a slower passage of the gases through the tube. The yield of formaldehyde was increased to 70% by adding ammonia to the reacting gases, whereby hexamethylene - tetramine, a compound more stable than formaldehyde, was formed.

In 1922, Blair and T. S. Wheeler commenced a very thorough investigation into the oxidation of hydrocarbons with special reference to the production of formaldehyde. Using methane as the hydrocarbon they (57) confirmed work carried out by Otto (supra) and Drugman (58) on the production of formaldehyde by the interaction of methane and ozone, giving a series of quantitative investigations in place of the latter two authors' qualitative results. By using a modification of Bone and R. V. Wheeler's method of circulating methane with a deficiency of oxygen through a heated tube, they obtained more promising yields of formaldehyde (59) as an outcome of which they established the following two quantitative relations:-

(1) Under the conditions of the experiment the yield of formaldehyde varies inversely as the temperature and as the time of heating.

(2) With shorter times of heating, equimolecular mixtures give the higher yields of formaldehyde; for longer times of heating, excess hydrocarbon mixtures are better.

A full summary of the results is to be found in a booklet published by H.M. Stationery Office (60).

Berl and Fischer (61) studied the partial oxidation of methane by means of various oxidising agents, supplied in quantities less than that required for complete combustion, by passing the mixed gases through a heated tube containing silica as catalyst. The main products, using air as oxidising agent, were oxides of carbon and a little formaldehyde.

Tropsch and Roelen (62) drew conclusions similar to those given by T. S. Wheeler and Blair on the production by formaldehyde by the partial oxidation of methane. In this case methane and oxygen were passed through a quartz tube containing no catalyst. Medvedev (63) experimented with gold, platinum and oxides of nickel, aluminium, copper, silver, lead and cerium as catalysts on an asbestos base in the oxidation of methane to formaldehyde and showed that at low rates of flow only carbon dioxide was formed. At higher speeds, however, formaldehyde was produced, in one case over 58% of the methane decomposed being oxidised to formaldehyde.

A patent has recently been taken out for the production of methyl alcohol and formaldehyde by the action of catalysts on methane - oxygen or methane - ozone mixtures under pressure at a red heat, such catalysts being pumice, brick fragments, slag, asbestos, sand, quartz, etc..(64).

It is seen that, for economic reasons, most of the above investigations have been concerned with the production of formaldehyde by the partial oxidation of methane and, with the exception of a few notes by T. S. Wheeler and Blair (59), no quantitative results on the influence of catalysts on the acceleration of the complete oxidation of methane by means of oxygen are available. In order to compare the efficiencies of several of the more common oxidation catalysts, the following investigations were carried out.

GENERAL METHOD of PROCEDURE.

In this series of experiments the method adopted was to circulate, at practically a uniform rate in a closed system, modelled on that devised by Bone and R. V. Wheeler in their researches on the oxidation of hydrocarbons at low temperatures (52), a gaseous mixture containing approximately two volumes of methane and one volume of oxygen over the catalyst, the temperature of which was varied for each experiment. The original and final gaseous mixtures were analysed and the wash waters examined qualitatively. Before and after each experiment pressure readings were noted and the results calculated by Bone and R. V. Wheeler's method of partial pressures (52).

The apparatus used is shown in the sketch in Fig. 17 on page 100. It consisted of a glass bulb, A, of about 500cc. capacity and containing a few ccs. of distilled water, so that the gases entering the combustion tube were always saturated with water vapour at the temperature indicated by the thermometer immersed in the water jacket which surrounded the bulb. This jacket and the cooling coil at the exit end of the combustion tube were carefully screened from heat radiated from the furnace by means of the thick asbestos screens shown in the sketch. Connected to the bulb, A, was a three-way stopcock, B, which allowed the gases to be passed through the combustion tube or bye-passed directly to the circulation pump. The combustion tube was contained centrally in the electric furnace and a layer of 20cm. of catalyst placed centrally in the tube. This ensured that the catalyst, over its whole length, was maintained at a uniform temperature, (cf. Appendix II, p. 210) this temperature being determined by the nickel-nichrome thermocouple shown, the junction of which, as in the last series of experiments, was placed in the centre of the furnace tube between the combustion tube and the furnace tube wall and immediately over the centre of the layer of catalyst.

After passing over the catalyst, the gaseous mixture was passed through the glass worm, C, which was immersed in melting ice and which contained a little distilled water to absorb any soluble intermediate oxidation products and in which there also condensed any water formed during the reaction.

The gases were circulated by the automatic Sprengel pump, D, which forced them into the return tube, E, behind which was placed a millimeter scale (not shown in sketch) on which the pressure of the gas in the system could be noted before and after each experiment. The return tube was connected to the bulb, A, and the apparatus closed by the stopcock, F, through which the system was first of all evacuated, the Original Gas introduced and the sample of Residual Gas withdrawn for analysis.

In Bone and R. V. Wheeler's original apparatus, all joints, with the exception of those at the ends of the combustion tube, which were made with heavy rubber pressure tubing, were sealed in a blowpipe flame, but in the apparatus

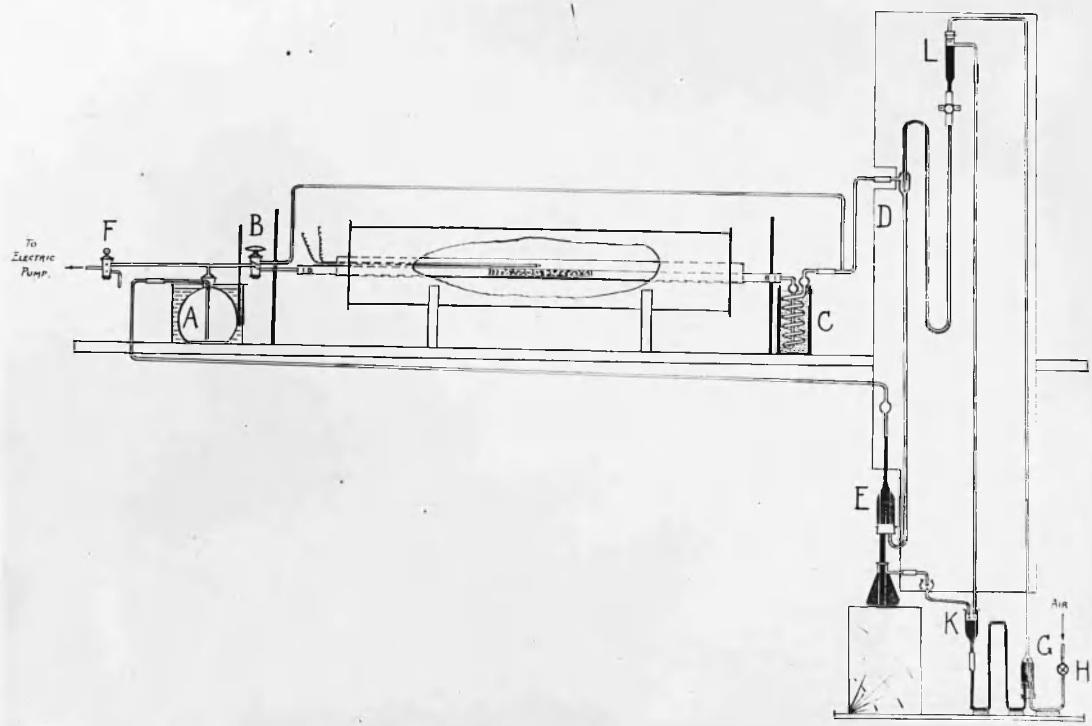


Fig. 17.

described more rubber connections were employed for the sake of ease in disconnecting the worm in order to examine its contents and in replacing the combustion tube and catalyst at the end of each series of experiments. All such rubber connections were made of heavy rubber pressure tubing and liberally coated with amyl acetate collodion, while the combustion tube was connected up by means of two tightly-fitting rubber stoppers and these similarly coated with collodion. In such an apparatus the amount of leakage, tested under a vacuum, was never greater than 10mm. in 5 hours.

The automatic working of the Sprengel pump was obtained by means of the device shown, the power for which was supplied by compressed air. The mercury elevator, G, consisted of a jet connected to a compressed air main through the valve, H; this jet was enclosed in a small cylinder which tapered to a narrow bore tube immediately above the jet and which was connected to a mercury reservoir, K, into which all the mercury from the pump finally returned. The mercury in G was elevated by a steady current of air which first of all broke the mercury into short columns and then forced it up the narrow glass tube into the reservoir, L, connected to the pump. This reservoir was fitted with an overflow tube which led to the mercury reservoir, K. During an experiment the elevator was made to function at such a rate that mercury continually passed from the reservoir, L, to the receiver,,K, by way of the overflow tube, so that the "head" of mercury necessary for the working of the pump remained practically constant.

On leaving the pump the mercury passed through the enlarged part of the return tube, E, into the Buchner flask immediately below: this flask contained sufficient mercury completely to fill the return tube when the system was evacuated. The mercury then passed into the small thistle funnel and on to the receiver, K.

By this means, under the power supplied by air under a pressure of a few pounds, the pump was rendered automatic.

The average rate of flow of gas obtained from the pump, measured by the time required for it to pass one litre of air at atmospheric pressure, before being assembled in the apparatus, was found to be 50cc. per minute and for purposes of calculation of times of contact of gas and catalyst this figure was adopted. The method of estimating the available space in contact with the catalyst and its carrier was the same as that used in Part I and is described in Appendix V, page 216.

The total volume of the apparatus, determined roughly by measuring the volumes of the component parts, was about 800cc., while the volume of the bye-pass tube was 10cc.. Assuming the pump to cause a circulation of 50cc. per minute, this means that the gases would be circulated 18 - 20 times in 5 hours, the duration of one experiment.

The methane used for the experiments was prepared by Grignard's method (24) as detailed in Appendix IV, page 213, while the oxygen was obtained from cylinders of that gas, being washed with caustic soda solution before use. The gaseous mixtures of methane and oxygen were rendered homogeneous by shaking and were stored over a saturated solution of magnesium chloride. These were analysed over mercury in Bone and Wheeler's apparatus.

METHOD of CONDUCTING an EXPERIMENT.

The system was evacuated through the stopcock, F, by means of an electrically driven oil pump, the stopcock, B, being turned from time to time to communicate alternately with the combustion tube and the bye-pass tube, until the pressure recorded by the return tube scale differed from atmospheric by the tension of aqueous vapour at the temperature given by the thermometer placed against the reservoir bulb. The methane-oxygen mixture, of known composition, was then fed in through F until the pressure of the gas was approximately two-thirds of an atmosphere, and the pressure on the return tube scale, the atmospheric pressure and the temperature, t°C., indicated by the thermometer, noted.

The Sprengel pump was started and the gases circulated through the bye-pass tube while the furnace was heating up. When the furnace had attained the required temperature, the gases were circulated through the combustion tube and the time noted. Each experiment was allowed to run for five hours and once every hour the gases were bye-passed for five minutes in order to sweep the gas from the bye-pass tube.

During the circulation the pump was allowed to circulate the gases as quickly as possible, the speed being approximately 50cc. per minute. The temperature generally showed a tendency to increase at the outset of an experiment and to decrease towards the end, but by judicious use of the rheostat controlling the current supplied to the furnace it was possible to control the temperature to within ±5°C..

At the end of five hours the furnace current was switched off and the gases circulated through the bye-pass tube until the furnace had cooled down. During the process of cooling, the seal of water in the worm prevented the products of the reaction, which took place in the combustion tube during this period of cooling, from mixing with the main volume of gas. The products of the reaction, which took place in the combustion tube during the period of heating of the furnace, did mix with the rest of the gas, but this period was much the shorter of the two.

When "all cold", generally after having been left overnight, the water surrounding the reservoir, A, was brought to t°C. again, the gases circulated for about an hour and fresh determinations of the pressure indicated by the return tube scale and of the atmospheric pressure made.

A sample of gas was then withdrawn through F and analysed in Bone and Wheeler's apparatus over mercury while the contents of the worm were washed out into a clean beaker and the resulting solution tested for methyl alcohol, formaldehyde and formic acid by the following method:-

A portion of the washings was examined for formaldehyde by means of Wright's rosaniline test (65); the remainder was distilled over caustic soda solution or potassium cyanide solution to fix the formaldehyde and the distillate divided into two portions. The first was examined for methyl alcohol by Wright's method (ibid.) and the second allowed to remain in contact with clean magnesium turnings for several hours and the resulting solution subsequently tested for formaldehyde. The U. S. Pharmacopoeia Test using resorcinol (66) was employed to confirm the presence of formaldehyde when found by the rosaniline test.

METHOD of CALCULATION.

For purposes of calculation and reporting of results all gases were calculated to nitrogen free gas. The method of calculation was that of Partial Pressures used by Bone and R. V. Wheeler (52) in their circulation experiments.

Owing to the fact that it was necessary to leave the apparatus overnight, generally for a period of over 16 hours before making the final pressure reading and withdrawing a sample of gas for analysis, it is probable that, during this long interval, the amount of air leaking into the apparatus would be quite appreciable, so that, in the calculation of results, the consumption of oxygen has not been followed out in the scheme of partial pressures. This omission was further desirable since some of the catalysts studied themselves absorb oxygen. The oxygen leaking in during this quiescent period, except in a few isolated cases, would not participate in the reaction so that the final results would not be appreciably affected.

In cases where free hydrogen was obtained in the Residual Gas no back - calculation to an equivalent amount of methane was necessary for this gas since no free carbon was detected in any of the experiments. This means that any hydrogen obtained in the Residual Gas had been formed (indirectly,) from methane by the liberation of carbon compounds, all of which are accounted for in the scheme of partial pressures.

The following example is taken from Experiment No. 6 of the Palladium Black series of experiments.

Original Gas contained $53.9\% CH_4$, $29.0\% O_2$, $17.1\% N_2$,

or as nitrogen free gas $65.1\% CH_4$, $34.9\% O_2$.

Original Pressure = 679mm..

Partial Pressure of CH_4 in Original Gas (Nitrogen free)

= (679 x 0.651)mm. = 442mm..

Residual Gas (Nitrogen free) contained

$20.9\% CO_2$, $3.5\% CO$, $3.9\% O_2$, $71.7\% CH_4$.

Final Pressure = 429mm..

Partial Pressure of CO_2 = (429 x .209)mm. = 90mm. ≡ 90mm. CH_4.
" " " CO = (429 x .035)mm. = 15mm. ≡ 15mm. CH_4.
" " " CH_4 = (429 x .717)mm. = 307mm. = 307mm. CH_4.

Partial Pressure of CH_4 supplied = 442mm.
" " " CH_4 left unoxidised = 307mm.
" " " CH_4 oxidised = (442-307)mm. = 135mm.
" " " CH_4 oxidised to gaseous products = (90 + 15)mm. = 105mm.
" " " CH_4 oxidised to liquid* products = (135-105)mm. = 30mm.

Methane oxidised to CO_2 = $(\frac{90}{442} \times 100)\%$ = 20.3%.
" " " CO = $(\frac{15}{442} \times 100)\%$ = 3.4%.
" " " liquid* = $(\frac{30}{442} \times 100)\%$ = 6.8%.
Total Methane oxidised = 30.5%.

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* i.e. to oxidation products containing carbon absorbed by the water in the worm. This also includes all errors.

General Considerations.

According to Bone's theory of the mechanism of hydrocarbon combustion (52), the oxidation of methane in these experiments should follow the course

$$CH_4 \longrightarrow CH_3OH \longrightarrow HCHO \longrightarrow HCOOH \longrightarrow CO \longrightarrow CO_2,$$

so that there is the possibility of any one of the above oxidation products being isolated provided it is stable under the conditions of the experiments. The thermal decomposition of the above products is a factor which enters into the scheme of oxidation as well as their susceptibility to oxidation in the absence of catalysts.

The following data illustrate the facts known in respect to these factors.

Methane.

Bone and Coward (67) have shown that the rate of decomposition of methane is inappreciable below 700°C..

Methyl Alcohol.

Ipatiew (68), in his well-known researches on the decomposition of alcohols in contact with hot solids, found that on passing the vapour of methyl alcohol through a combustion tube heated to 880°C. it underwent a slow decomposition to "oxymethylene" (CH_2O) and a gas containing carbon monoxide, hydrogen and methane, while Bone and Davies (69) obtained similar gaseous products at 650°C.. No carbon was deposited in any of the experiments. These facts, together with the fact that methyl alcohol vapour is very easily oxidised to formaldehyde by means of gaseous oxygen, render the isolation of methyl alcohol in these experiments almost impossible.

Formaldehyde.

According to Gautier (70), when formaldehyde is passed through a red hot tube of porcelain it decomposes according to the equation:-

$$HCHO = H_2 + CO.$$

Bone and Smith (71) have confirmed this at 400°C., but also found traces of methane at this temperature. These investigators found that at 700°C. formaldehyde was almost completely decomposed into hydrogen and carbon monoxide, but even at 1125°C. some aldehyde was left undecomposed.

The isolation of formaldehyde in quantity from the oxidation of methane by such experiments necessitates a gaseous linear velocity of about 20cm. per second according to Tropsch and Roelen (62), so that if any formaldehyde is obtained in the experiments it will appear mainly at low temperatures, owing to the comparatively slow rate of flow of the gases (50cc. per minute) in the apparatus used.

Formic Acid.

T. S. Wheeler and Blair (59) have shown that formic acid decomposes into carbon monoxide and water comparatively easily, so that there is very little possibility of this acid being obtained.

Oxides of Carbon.

Carbon monoxide and carbon dioxide are very stable and should be the chief products, if not the sole products, at high temperatures, the amount of carbon monoxide remaining decreasing with increase in temperature.

Thus the main products expected, without the use of catalysts, are formaldehyde, carbon monoxide and carbon dioxide, although catalysts may aid the decomposition or oxidation of the first two compounds.

A. - PALLADIUM BLACK on ASBESTOS.

Kuznezov (72) has shown that palladium black decomposes formaldehyde almost completely into carbon monoxide and hydrogen at 300°C., but the result depends largely on the physical condition of the catalyst, while Sabatier and Mailhe (73) have found that at 245°C. palladium gives almost complete dehydrogenation of formic acid into carbon dioxide and hydrogen, an observation which has been confirmed by Zelinsky and Glinka (74). Fester and Brude (75), by passing carbon monoxide over palladium, found this gas was decomposed into free carbon and carbon dioxide even at 65°C..

These data would point to the production of large quantities of carbon dioxide and carbon monoxide with possibly a little formaldehyde at low temperatures.

Preparation of Impregnated Asbestos.

12gm. asbestos, which had previously been boiled with concentrated hydrochloric acid and ignited, were mixed with a solution of palladium chloride, excess of sodium formate solution and enough sodium carbonate solution to keep the mixture alkaline, added. The mixture was gently boiled until the supernatant liquid became colourless, when this solution was decanted. The asbestos was subsequently washed until free from salts, dried and ignited. The weight of palladium deposited on the asbestos was 0.108gm.. In all, only 3gm. impregnated asbestos, containing 0.027gm. palladium, were used, having an available space of 15.5cc. in contact with it. This gives an anerage time of contact of gas and catalyst of 0.31 minutes per circulation.

The following are the results obtained (Table XVIII). These are collected on the graph in Fig. 18, which shows that even at ordinary temperatures palladium black causes methane

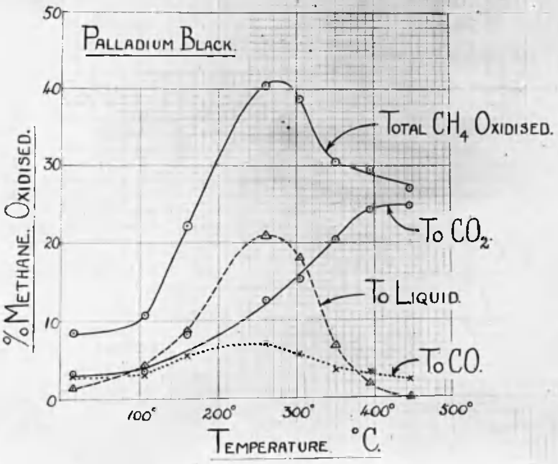

Fig. 18.

and oxygen slowly to combine, the chief products being the oxides of carbon with a little formaldehyde. As the temperature increases there is a rapid increase in the quantity of hydrocarbon oxidised to formaldehyde until a maximum of

TABLE

PALLADIUM BLACK ON ASBESTOS-

Expt. No.	Temp. °C.	Original Gas.				Residual -			
		Press. mm.	Methane		% O_2	Press. mm.	Methane		Carbon
			%	Partial Press. mm.			%	Partial Press. mm.	%
1.	17	574	63.3	363	36.7	554	59.9	332	2.4
2.	107	521	63.3	330	36.7	501	58.7	294	2.4
3.	160	554	63.3	352	36.7	529	51.8	274	5.4
4.	260	506	63.3	333	36.7	400	49.8	198	10.5
5.	303	612	63.3	388	36.7	358	66.2	237	16.5
6.	350	679	65.1	442	34.9	429	71.7	307	20.9
7.	394	739	65.1	481	34.9	485	70.2	340	23.8
8.	447	557	65.1	362	34.9	365	72.3	264	24.7

XVII.

-METHANE -- OXYGEN.

- Gas				% Methane Oxidised				Products Identified in Wash Waters.
Dioxide	Carbon Monoxide							
Partial Press. mm.	%	Partial Press. mm.	% O_2	To CO_2	To CO	To Liquid	Total	
13	2.1	12	35.6	3.6	3.2	1.7	8.5	H.CHO
12	2.0	10	36.9	3.6	3.0	4.2	10.8	H.CHO
29	3.6	19	39.2	8.1	5.5	8.5	22.1	H.CHO
42	5.9	24	33.8	12.6	7.1	20.8	40.5	H.CHO
59	6.2	22	11.1	15.2	5.7	18.0	38.9	H.CHO
90	3.5	15	3.9	20.3	3.4	6.8	30.5	H.CHO
116	3.4	16	2.6	24.2	3.3	1.9	29.4	H.CHO
90	2.2	8	0.8	24.8	2.2	Nil	27.0	-

approximately 21% is reached at 260°C., above which the yield of formaldehyde rapidly decreases until at 400°C. only a trace is left undecomposed.

The quantities of carbon monoxide formed at the end of the reactions vary only between small limits, the amount of this oxide obtained increasing slowly to 7.0% at 260°C. and falling from this point as the temperature is increased until at 447°C. only 2.2% of the hydrocarbon supplied is obtained as this oxidation product.

As is to be expected, the yield of carbon dioxide increases with increase in temperature until the maximum yield obtainable with a mixture of two volumes of methane and one volume of oxygen, viz., 25%, is obtained about 450°C..

Conclusions.

From the results obtained palladium black appears to be a very efficient catalyst for promoting the oxidation of methane, only traces of intermediate oxidation products being obtained above 400°C. in circumstances where the maximum possible yield of carbon dioxide is 25%.

B. - PLATINISED ASBESTOS.

In 1905, during the course of an exhaustive investigation into the methods of hydrogenation involving the use of finely divided metals, Sabatier and Senderens (76) found that platinum sponge decomposes methyl alcohol completely into formaldehyde and hydrogen at 250°C., but the formaldehyde is almost immediately further decomposed into carbon monoxide and hydrogen, only traces being left unattacked. Trillat (77), by passing the vapour of methyl alcohol mixed with air over a heated platinum spiral, under conditions which precluded the decomposition of the products of oxidation, found that, as the temperature of the wire was increased from 200°C., there were formed firstly formaldehyde and a little methylal; at a dull red heat formic acid was obtained together with increased amounts of formaldehyde and methylal: at a cherry red heat these decreased and the proportion of carbon dioxide subsequently increased with increase of incandescence.

Sabatier and Mailhe (73) found that platinum belongs to the class of catalysts which dehydrogenate formic acid and yield only a trace of formaldehyde, the principal products being carbon dioxide and hydrogen. They also showed that platinum caused complete decomposition in this manner at 215°C.. This was later confirmed by Mailhe and do Godon. (78).

Thus, since platinum causes the decomposition or oxidation of methyl alcohol, formaldehyde and formic acid at such low temperatures, the principal products obtained by the catalytic oxidation of methane under the conditions of the experiments should be the oxides of carbon. If formaldehyde or formic acid are obtained these will only appear in the products below 200°C..

Preparation of Catalyst.

The platinised asbestos used was obtained from stock and had probably been prepared by the ignition of asbestos impregnated with ammonium platinichloride or platinic chloride. 2.9gm. platinised asbestos were used, having in contact with it an available space of 15.8cc., giving an average time of contact of gas and catalyst of 0.32 minutes per circulation.

The results obtained are shown in Table XIX and are grouped in the graph in Fig. 19. The data obtained show that platinised asbestos, as a catalyst, is not so efficient in promoting the oxidation of methane under the conditions of the experiments as palladium black on asbestos. While palladium black causes quite an appreciable oxidation to take place at ordinary temperatures, platinised asbestos does not cause a reaction to take place until a temperature of 430°C. is reached, at which temperature, in presence of palladium black on asbestos, about 25% of the hydrocarbon is converted to carbon dioxide, this being the maximum value possible.

Increase in temperature above 430°C. causes a progressive increase in the amount of carbon monoxide and carbon dioxide formed, the theoretical value of 25% of the hydrocarbon oxidised to the latter oxide being attained at

TABLE

PLATINISED ASBESTOS-

Expt. No.	Temp. °C.	Original Gas				Residual -			
			Methane				Methane		Carbon
		Press. mm.	%	Partial Press. mm.	% O_2	Press. mm.	%	Partial Press. mm.	%
1.	172	482	67.7	326	32.3	482	67.8	327	-
2.	390	482	64.8	312	35.2	481	64.0	308	-
3.	430	520	66.9	348	33.1	521	66.0	343	-
4.	487	517	64.8	334	35.2	448	66.1	297	7.2
5.	547	492	64.8	320	35.2	358	71.0	254	17.8
6.	565	537	66.9	358	33.1	383	71.3	273	19.3
7.	598	537	66.9	358	33.1	361	71.9	259	22.6
8.	627	523	66.5	348	33.5	350	66.6	233	26.1

XIX.

- METHANE -- OXYGEN.

- Gas				% Methane Oxidised				Products Identified in Wash Waters
Dioxide	Carbon Monoxide		% O_2					
Partial Press. mm.	%	Partial Press. mm.		To CO_2	To CO	To Liquid	Total	
-	-	-	32.2	-	-	-	-	-
-	-	-	36.0	-	-	-	-	-
-	-	-	34.0	-	-	-	-	-
32	1.4	6	25.3	9.6	1.8	-	11.4	-
64	1.8	6	9.4	20.0	1.9	-	21.9	-
74	3.7	14	5.7	20.7	3.9	-	24.6	-
82	4.6	17	0.9	22.9	4.8	-	27.7	-
91	5.3	19	2.0	26.0	5.4	Trace	31.4	Trace H.CHO

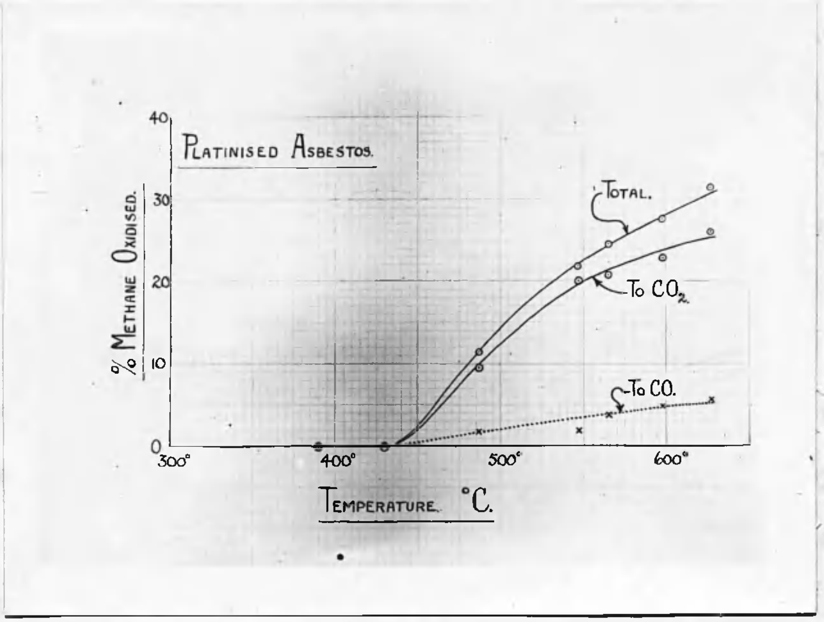

Fig. 19.

625°C.. Neither methyl alcohol, formaldehyde nor formic acid was detected in any of the experiments with the exception of Experiment No. 8, the wash waters from which gave a very faint colour to Wright's rosaniline after 24 hours.

Conclusions.

Platinised asbestos, in that it yields no formaldehyde under the conditions described, may thus be considered a good catalyst for promoting the oxidation of methane by means of oxygen, although, under the same conditions of temperature, it is inferior to palladium black deposited on asbestos.

C. - PLATINUM BLACK on ASBESTOS.

According to Dennstedt (79), palladium is in no way superior to platinum as a combustion catalyst, so that the difference in efficiency of the two catalysts already studied may be explained by the fact that while the palladium used was in the form of black, the platinum was deposited in the spongy state on asbestos. Accordingly it was decided to investigate the influence of platinum black deposited on asbestos on the oxidation of methane.

The general considerations quoted for platinum in the last section hold also for this case but in addition there must be recorded the observation, made by Paal (80) in 1916, that platinum black has no effect on a mixture of carbon monoxide and oxygen.

Preparation of Impregnated Asbestos.

The impregnated asbestos used was prepared by Willstätter and Waldschmidt-Leitz's (81) modification of Loew's (82) method, described in Appendix VI, p 218. In all 3gm. impregnated asbestos, containing 0.027gm. platinum black, were used. The available space in contact with the catalyst was 15.9cc., giving a time of contact of gas and catalyst of 0.32 minute per circulation.

The results obtained, shown in Table XX and collected in the graph in Fig. 20, show that platinum black is a more vigorous oxidation catalyst than spongy platinum.

TABLE

PLATINUM BLACK-

		Original Gas				Residual-			
			Methane				Methane		Carbon
Expt. No.	Temp. °C.	Press. mm.	%	Partial Press. mm.	% O_2	Press. mm.	%	Partial Press. mm.	%
1.	17.5	400	67.8	271	32.2	417*	63.6	265	-
2.	202	442	67.8	299	32.2	432	68.7	297	0.9
3.	274	490	67.8	332	32.2	485	65.7	318	1.2
4.	316	470	67.8	319	32.2	447	68.5	306	1.3
5.	382	487	67.8	330	32.2	461	67.7	312	2.2
6.	411	400	67.8	271	32.2	387	65.3	253	2.9
7.	452	494	67.8	335	32.2	416	69.7	290	8.9
8.	497	513	67.8	348	32.2	396	71.2	283	16.8
9.	528	502	67.8	340	32.2	365	67.6	246	22.2
10.	627	570	67.8	386	32.2	372	70.3	262	26.1

* Increase in pressure due to leakage of air.

XX.

- METHANE -- OXYGEN.

- Gas				% Methane Oxidised				Products Identified in Wash Waters.
Dioxide.	Carbon Monoxide							
Partial Press. mm.	%	Partial Press. mm.	% O_2	To CO_2	To CO	To Liquid	Total	
-	1.9	8	34.5	-	3.0	-	3.0	-
4	2.2	9	28.2	1.3	3.0	-	4.3	-
6	2.0	10	31.1	1.8	3.0	-	4.8	-
6	2.0	9	28.2	1.9	2.8	-	4.7	-
10	1.9	9	28.2	3.0	2.7	-	5.7	-
11	1.8	7	30.0	4.1	2.6	-	6.7	-
37	2.2	9	19.2	11.0	2.7	-	13.7	-
66	0.6	2	11.4	19.0	0.6	-	19.6	-
81	2.6	10	7.6	23.8	3.0	-	26.8	-
97	2.7	10	0.9	25.2	2.6	-	27.8	-

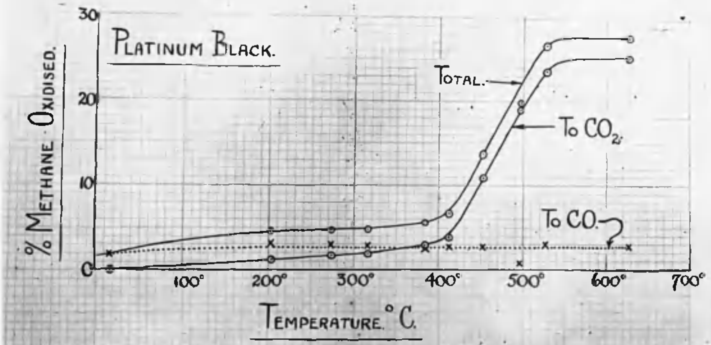

Fig. 20.

Even at ordinary temperatures appreciable oxidation takes place, while the theoretical figure of 25% for the methane oxidised to carbon dioxide is reached, in this case, at 550°C., which, although it is much lower than the corresponding temperature for spongy platinum (625°C.), is still about 100° above that obtained when palladium black was used.

It is noteworthy that, up to about 410°C., the rate of oxidation of the methane is comparatively slow, but immediately above this temperature there is a very rapid increase in the amount of hydrocarbon oxidised, this continuing with increase in temperature until a temperature of 550°C. is reached. With spongy platinum the reaction commences about 430°C. but the oxidation of the hydrocarbon proceeds more slowly, an increase in the amount of carbon dioxide formed continuing until a temperature of 625°C. is reached.

In contrast to the results obtained with palladium black and spongy platinum, the amount of hydrocarbon converted finally to carbon monoxide remains practically constant at 2.8% over the whole range of temperature. As with platinum sponge no intermediate oxidation products were detected in the wash waters.

Conclusions.

As is to be expected from the difference in degrees of sub-division of the catalysts, platinum black is much more efficient catalytically than spongy platinum, although from the point of view of oxidising methane completely to carbon dioxide, platinum black is inferior to palladium black.

D. - COPPER on PUMICE.

In 1922 a method of preparation of methyl alcohol and formaldehyde by the oxidation of methane by means of carbon dioxide was patented (56). The mixed gases were passed through a constricted pipe, made of copper or other metal or alloy, heated to 500° - 700°C. at the constriction and the producrs of the reaction rapidly cooled. The yield of methyl alcohol was favoured by a slower passage of the gases and by the presence of hydrogen in the gases.

Another patent involving the use of copper as a catalyst (83) deals with the preparation of formaldehyde from methane by heating this gas to 150° - 220°C. with a large excess of air or oxygen in presence of copper.

With reference to the catalytic effect of copper in causing the decomposition of intermediate oxidation products of methane, Mannich and Geilmann (84) have shown that at 240° - 260°C. methyl alcohol decomposes primarily into formaldehyde and hydrogen in presence of finely divided copper, but the formaldehyde may be further decomposed into carbon monoxide and hydrogen, this latter decomposition becoming more pronounced with increase of temperature.

Christiansen (85) has shown that when suitable mixtures of methyl alcohol and steam are passed over finely divided copper at 230° - 250°C. carbon dioxide and hydrogen are produced according to the following equation:-

$$CH_3OH + H_2O = CO_2 + 3H_2.$$

Kuznezov (72) has drawn attention to the fact that while copper causes the decomposition of formaldehyde to carbon monoxide and hydrogen, the amount of aldehyde decomposed depends largely on the physical condition of the catalyst, copper turnings causing only 4% decomposition at 600°C. while copper obtained from copper sulphate by reduction with formaldehyde causes 35% of the aldehyde to be decomposed at 200°C.. Copper freshly reduced from the oxide (as used in the following experiment) causes a 9% decomposition at 500°C..

Copper has been classed as a dehydrogenation catalyst in the decomposition of formic acid by Sabatier and Mailhe (73), a result which has been confirmed by Mailhe and de Godon (78).

The results obtained by these investigations point to the production of carbon monoxide and carbon dioxide as the principal products of the reaction between methane and oxygen in presence of copper, with the possibility of a little hydrogen - a decomposition product both of formaldehyde and formic acid - being left unoxidised.

Preparation of Impregnated Pumice.

12gm. 8 - 32 mesh pumice were mixed with 3.8gm. $Cu(NO_3)_2.3H_2O$ and sufficient water to cover the mixture added. The mixture was heated slowly, with constant stirring, and evaporated to dryness. The impregnated pumice was strongly ignited in a current of air in a combustion tube, cooled and the copper oxide reduced by means of hydrogen at 300°C.. This gave 1gm. copper. Immediately before each experiment the catalyst was reduced by means of hydrogen at 300°C..

The available space in contact with the catalyst and its carrier was 15.0cc., corresponding to 0.30 minute contact per passage of the circulating gases.

The results obtained, which are collected in Table XXI and represented in the graph in Fig. 21, show that freshly reduced copper causes methane and oxygen initially to react about 300°C., a temperature more than 100° lower than the initial reaction temperature obtained with platinised asbestos, but the hydrocarbon does not consume all the oxygen until a temperature of over 700°C. is reached.

At temperatures intermediate between 300°C. and

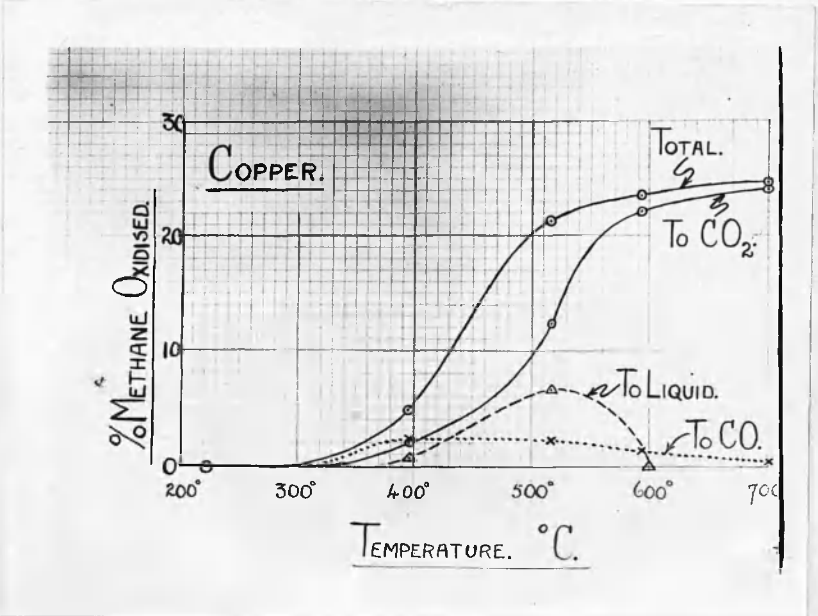

Fig. 21.

700°C. the yields of formaldehyde and carbon monoxide are low

TABLE

COPPER-

		Original Gas				Residual -				
			Methane				Methane		Carbon	
Expt. No.	Temp. °C.	Press. mm.	%	Partial Press. mm.	% O_2	Press. mm.	%	Partial Press. mm.	%	
1.	222	517	65.1	336	34.9	511	65.5	335	-	
2.	397	607	65.1	395	34.9	512	73.1	375	1.6	
3.	517	649	67.4	436	32.6	480	71.4	344	11.4	
4.	592	523	67.4	353	32.6	371	72.5	268	21.0	
5.	700	551	67.4	372	32.6	355	73.5	261	25.0	

XXI.

- METHANE -- OXYGEN.

- Gas				% Methane Oxidised				Products Identified in Wash Waters.
Dioxide	Carbon Monoxide							
Partial Press. mm.	%	Partial Press. mm.	% O_2	To CO_2	To CO	To Liquid	Total	
-	-	-	34.5	-	-	-	-	-
8	1.7	9	23.6	2.0	2.3	0.8	5.1	H.CHO
55	2.0	10	15.2	12.6	2.3	6.2	21.1	H.CHO
78	1.4	5	5.1	22.1	1.4	-	23.5	-
89	0.5	2	1.0	24.1	0.5	-	24.6	-

and these decrease as the temperature increases, until at 700°C. no formaldehyde remains and only a trace of carbon monoxide persists. No hydrogen was detected in any of the experiments.

Conclusions.

In that methane does not absorb all the oxygen until the temperature is raised to above 700°C. in presence of copper, this catalyst is inferior to platinised asbestos in promoting the oxidation of methane in circumstances which include a deficiency of oxygen.

E. - SILVER on PUMICE.

Silver has been suggested as a catalyst in the preparation of methyl alcohol and formaldehyde (56) by the oxidation of methane by means of carbon dioxide and in the preparation of formaldehyde by the oxidation of methane by means of a large excess of air or oxygen (83). In the preparation of formaldehyde from methyl alcohol by means of oxygen in the presence of a catalyst Thomas (86) has found that silver is more active than copper or gold and at the same time produces less decomposition of the aldehyde, thus giving a greater yield.

Preparation of Impregnated Pumice.

12gm. 8-32 mesh pumice were mixed with a solution of 1.58gm. silver nitrate in water in an evaporating basin and the mixture slowly evaporated to dryness with constant stirring. The impregnated pumice was strongly ignited in a stream of air in a combustion tube, cooled and reduced by means of hydrogen at 500°C.. This gave 1gm. silver. Immediately before each experiment the catalyst was reduced by means of a current of hydrogen at 500°C..

The available space in contact with the impregnated pumice was 13.9cc., giving a time of contact of 0.28 minute per passage of the circulating gases.

The results obtained are shown in the table on the following page and in the graph in Fig. 22. These show that

TABLE

SILVER-

		Original Gas				Resulting-			
			Methane				Methane		Carbon
Expt. No.	Temp. °C.	Press. mm.	%	Partial Press. mm.	% O_2	Press. mm.	%	Partial Press. mm.	%
1.	265	551	66.3	366	33.7	552	66.3	367	-
2.	410	577	66.3	383	33.7	486	68.1	331	7.8
3.	468	552	66.3	366	33.7	417	68.1	284	16.2
4.	550	475	67.6	322	32.4	336	69.4	233	22.9
5.	610	405	66.3	269	33.7	367	53.4	196*	18.5

* Residual Gas (nitrogen free) contained 19.9% Hydrogen, equivalent to 36mm. methane or 13.4% of methane supplied.

XXII.

- METHANE -- OXYGEN.

- Gas				% Methane Oxidised				Products Identified in Wash Waters.
Dioxide	Carbon Monoxide							
Partial Press. mm.	%	Partial Press. mm.	% O_2	To CO_2	To CO	To Liquid	Total	
-	-	-	33.7	-	-	-	-	-
38	1.9	9	22.2	9.9	2.4	-	12.3	-
68	2.3	9	13.4	18.5	2.5	-	21.0	-
77	2.4	8	5.3	23.8	2.5	-	26.3	-
68	3.3	12	4.9	25.2	4.5	-	29.7	-

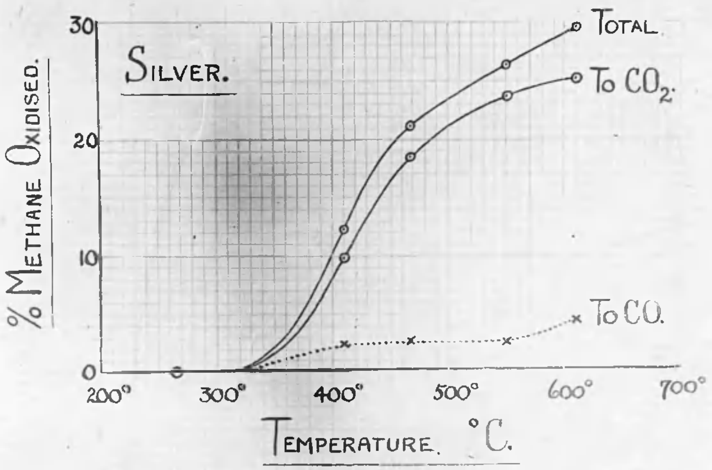

Fig. 22.

silver causes methane and oxygen initially to react somewhere in the neighbourhood of 320°C. and that on increasing the temperature there is a rapid increase in the amount of carbon dioxide formed, the theoretical value being obtained at 610°C.. In this respect, silver is completely comparable with spongy platinum and therefore, as a catalyst, is inferior both to palladium black and platinum black, but is practically equal in efficiency to copper.

Above 400°C. the amount of hydrocarbon oxidised to carbon monoxide remains fairly constant, but rises rapidly from 550°C. to 610°C., where the yield of this oxide is increased almost to double that obtained at 550°C.. Simultaneous with this increased amount of carbon monoxide there appears a large amount of hydrogen in the residual gas. Both of these facts may be explained by assuming that at 610°C. there is initially formed a larger amount of formaldehyde than at lower temperatures and that this intermediate product is immediately decomposed into hydrogen and carbon monoxide, the latter of which is more easily oxidised than the former.

Conclusions.

Finely divided silver is an efficient catalyst in promoting the oxidation of methane by means of oxygen.

Impregnated Pumice.

[illegible] pumice were mixed with an

[illegible] 1.72gm. ammonium vanadate in

F. - VANADIUM OXIDES on PUMICE.

In view of the fact that vanadium oxides have exceptional properties as catalysts in producing intermediate oxidation products (cf. Part I, p. 63) it was decided to investigate the efficiency of a mixture of these oxides in promoting the oxidation of methane by means of a deficiency of oxygen.

According to Sabatier and Mailhe (87) vanadium oxides dehydrogenate methyl alcohol to formaldehyde and its decomposition products, hydrogen and carbon monoxide, while the same authors have shown (73) that the catalytic decomposition of formic acid in presence of vanadium oxides is essentially one of dehydration with a slight formation of formaldehyde.

Thus in the experiments there may be expected, as principal products, carbon dioxide and carbon monoxide, with the possibility of a little formaldehyde.

Preparation of Impregnated Pumice.

12gm. 8-32 mesh pumice were mixed with an aqueous suspension containing 1.28gm. ammonium vanadate in an evaporating basin and water sufficient to cover the pumice added. The mixture was slowly evaporated to dryness with constant stirring. The impregnated pumice was ignited in a combustion tube in a current of air for six hours at 550°C. and 1 litre of a mixture containing approximately 60% methane, 30% oxygen and 10% nitrogen passed over it at 500°C. to cause the catalyst to revert to the oxide or oxides stable under these conditions.

The quantity of ammonium vanadate used was equivalent to 1gm. vanadium pentoxide. The space in contact with the catalyst and its carrier was 14.8cc., corresponding to a time of contact per passage of 0.30 minute.

The results obtained are shown in Table XXIII and are collected in the graph in Fig. 23.

After the experiments had been completed the catalyst was examined under a microscope when it was observed to consist mainly of oxides green and blue in colour. This showed that the oxides stable under the given conditions were vanadous oxide, V_2O_3, and some hypovanadic oxide, VO_2.

In contrast to the other catalysts studied, with which the initial reaction temperatures of methane and oxygen are comparatively ill-defined, vanadium oxides give a very sharply defined value of 480°C. for the temperature at which these two gases commence to interact. At temperatures slightly above this there is indication of appreciable formation of formaldehyde, the decomposition products of which, hydrogen and carbon monoxide, are not completely oxidised and appear in the Residual Gas, while some undecomposed aldehyde is obtained in the wash waters. The yield of formaldehyde increases until the temperature reaches 520°C. above which it gradually decreases, but even at 640°C. some persists.

TABLE

VANADIUM OXIDES-

Expt. No.	Temp. °C.	Original Gas				Resulting-			
		Press. mm.	Methane		% O_2	Press. mm.	Methane		Carbon
			%	Partial Press. mm.			%	Partial Press. mm.	%
1.	380	493	66.3	327	33.7	493	66.4	328	-
2.	459	493	66.3	327	33.7	493	66.0	326	-
3.	476	490	66.3	325	33.7	496	66.1	328	-
4.	491	485	67.6	328	32.4	409	67.0	274	2.3
5.	523	516	67.6	349	32.4	397	54.2	215	11.3
6.	550	563	67.6	382	32.4	373	60.8	227	20.0
7.	642	469	67.6	318	32.4	387	44.8	174	28.2

XXIII.

- METHANE -- OXYGEN.

- Gas					% Methane Oxidised				Products Identified in Wash Waters.
Dioxide	Carbon Monoxide								
Partial Press. mm.	%	Partial Press. mm.	% H_2	% O_2	To CO_2	To CO	To Liquid	Total	
-	-	-	-	33.6	-	-	-	-	-
-	-	-	-	34.0	-	-	-	-	-
-	-	-	-	33.9	-	-	-	-	-
9	3.4	14	16.3	11.0	2.7	4.3	-	7.0	-
45	3.5	14	23.9	7.1	12.9	4.0	14.5	31.4	H.CHO, H.COOH
75	2.9	11	15.4	0.9	19.6	2.9	12.3	34.8	H.CHO
109	2.3	9	22.8	1.9	31.4	2.6	5.5	39.5	H.CHO

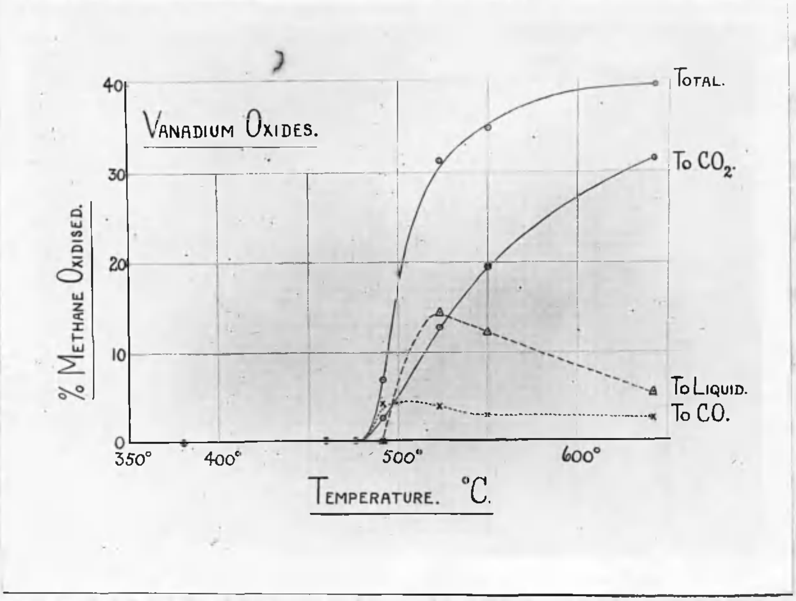

Fig. 23.

The yield of carbon monoxide reaches a maximum at 500°C. and subsequently decreases with increase in temperature, but, as with formaldehyde, this gas persists to a slight extent at 640°C..

As this temperature is increased from 480°C. the amount of methane oxidised to carbon dioxide increases rapidly until at 640°C. over 31% of the hydrocarbon supplied has been completely oxidised. This value, greater than the maximum possible with the other catalysts, is obviously the result of some of the methane being oxidised by the vanadium oxides themselves.

The quantity of hydrogen obtained in the Residual Gas increases rapidly as the temperature increases from 380°C. to 550°C., a maximum amount being formed at this temperature, and then slowly decreases, but even at 640°C. a considerable quantity of this gas remains unoxidised. Since the catalyst used dehydrates formic acid (cf. Sabatier and Mailhe, supra.) it is evident that all the hydrogen obtained must be the result of the catalytic thermal decomposition of methyl alcohol and formaldehyde and since the sum of the amounts of methane oxidised to soluble intermediate products (formaldehyde) and to hydrogen at 523°C. is 23.8%, it is evident that 23.8% of the methane supplied is initially oxidised to formaldehyde at this temperature and is either left unoxidised (appearing in the wash waters as such) or is decomposed into hydrogen and carbon monoxide, the latter gas being oxidised more easily than the former. It would be interesting to ascertain if, by circulating the gases at higher speeds, giving shorter times of contact of gases and catalyst, either under the conditions described or under increased pressure, all this formaldehyde could be obtained in the wash waters. No facilities for dealing with such high speeds or high pressures were available.

Conclusions.

In that the theoretical value of 25% of the methane supplied oxidised to carbon dioxide is reached at 580°C. in presence of the catalysts, vanadium oxides are very efficient catalysts in promoting the oxidation of methane under conditions which include a deficiency of oxygen.

intermediate products of oxidation [illegible]

Impregnated Pumice.

8-20 mesh pumice were mixed with an [illegible]
antimony [illegible] chlorate and [illegible]
[illegible] to dryness with constant stirring
[illegible] it brought with the [illegible]
cc., corresponding to an average [illegible]
and catalyst of [illegible] cc. per [illegible]

Regulator [illegible] in which a gas
[illegible] 66.2% benzene and [illegible] oxygen [illegible]
[illegible] gas) was circulated at 452°C., was

G. - CUPROUS CHLORIDE on PUMICE.

In view of the great success of cuprous chloride as a catalyst in promoting the oxidation of methane by means of copper oxide, it was decided to investigate the influence of this substance as a catalyst in promoting the oxidation of methane by means of a deficiency of oxygen.

No data concerning the influence of this salt in decomposing the intermediate products of oxidation are available.

Preparation of Impregnated Pumice.

12gm. 8-32 mesh pumice were mixed with an aqueous suspension containing 1gm. cuprous chloride and the mass slowly evaporated to dryness with constant stirring.

The available space in contact with the impregnated pumice was 15.0cc., corresponding to an average time of contact of gas and catalyst of 0.30 minute per circulation.

One circulation experiment, in which a gaseous mixture containing 65.2% methane and 34.8% oxygen (calculated to nitrogen free gas) was circulated at 452°C., was carried out. The original pressure of 485mm. finally decreased to 353mm., at least 60% of this contraction taking place during the first hour, showing that the reaction proceeded very rapidly. The Residual Gas was found to contain free hydrogen chloride in spite of the arrangements for the absorption of water soluble products of the reaction, the complete analysis of the nitrogen free gas being as follows:-

32.0%	CO_2 + HCl
1.8%	CO
1.8%	O_2
64.4%	CH_4.

The wash waters gave a very deep magenta colour immediately to Wright's rosaniline reagent.

These data seemed to indicate that in this case there had been considerable oxidation of the methane to formaldehyde, with comparatively little formation of carbon monoxide and possibly carbon dioxide. For this reason and the fact that the reaction proceeded with great rapidity the circulation method was abondoned and direct experiments, in which the gaseous mixture was passed once over the catalyst, carried out.

Direct Experiment.

The apparatus used for these experiments is shown in the sketch in Fig. 24. It consisted of two 3½ litre aspirator bottles, A and B, of which A was graduated, each fitted with a constant pressure supply device and each connected to the three-way stopcock, C, which, in turn was connected to a differential gauge, D. The aspirator, A, contained the methane-oxygen mixture over water, while B contained nitrogen which was used to expel all air from the apparatus from the stopcock, C, to the three-way stopcock connected to the aspirator, H. The pressures of the gases in A and B were maintained at the same value throughout the experiments by a preliminary adjustment of the two constant pressure devices,

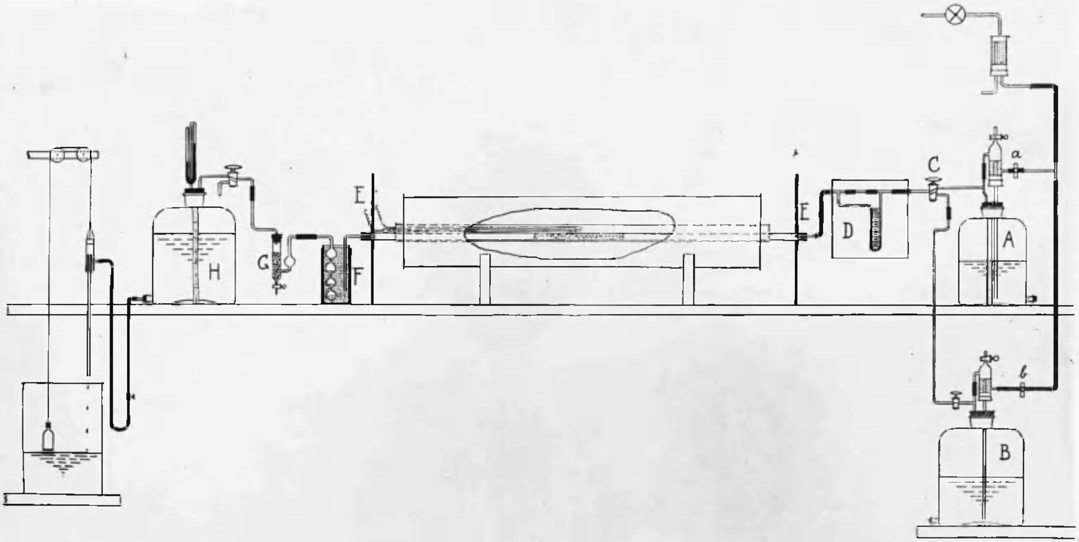

Fig. 24.

so that the nitrogen was driven through the apparatus at the same rate as the methane-oxygen mixture.

The combustion tube containing the catalyst was screened from the other parts of the apparatus by means of asbestos sheets, EE. Connected to the exit from the combustion tube was a series of bulbs, F, containing 10cc. distilled water and immersed in a jacketed vessel containing crushed ice. This was followed by the scrubber, G, containing glass beads covered with 50cc. distilled water, while the receiving aspirator, H, fitted with a constant pressure receiving device, contained a saturated solution of magnesium chloride, over which the gases resulting from the experiment were collected.

Method of Conducting an Experiment.

The aspirator, A, was fitted with a gaseous mixture of known composition, containing approximately two volumes of methane and one volume of oxygen, while the aspirator, B, was charged with pure nitrogen, prepared by the method described in Appendix IV, p. 213. The Combustion tube was charged with 13gm. of the catalytic mixture, containing 1gm. cuprous chloride deposited on 12gm. 8-32 mesh pumice, placed centrally in the tube, occupying 20cm. length of the tube; the absorption system was fitted with the requisity quantities of distilled water and the receiving system arranged in such a manner that the Resulting Gas was collected at a pressure 2" water below atmospheric, the confining liquid filling the connections to the three-way stopcock attached to the aspirator, H. The vessel for receiving the liquid expelled from H was then weighed.

Before the furnace was heated at least 1½ litres of nitrogen were passed through the apparatus and byepassed to the atmosphere through the three-way stopcock connected to H, so that during the preliminary heating the catalyst was raised to the desired temperature in an inert atmosphere, this quantity of nitrogen being sufficient to expel all the air from the apparatus. The furnace was then heated and when the desired temperature was maintained a further 500cc. of nitrogen were passed through the apparatus and the gauge, D, arranged to the required setting by manipulation of the constant level tube shown. During these preliminary arrangements, the clip, a, was kept closed and the clip, b, open and the usual tests for leaks, previously described on p. 21, carried out.

The clip, b, was then closed and a opened and the volume, temperature and pressure of the gas in the aspirator, A, noted. The clip attached to H was turned to allow the Resulting Gas to be collected and at a noted time the stopcock, C, was turned to give communication between A and D.

With the exception of a slight regulation of the temperature of the furnace from time to time the apparatus was then entirely automatic in its action, delivering the gases from the aspirator, A, to the receiver, H, at a perfectly uniform speed. This speed was kept as nearly as possible to 50cc. per minute so that the rate of flow was approximately the same as that in the circulation experiments. The correct value was obtained in the same manner as those for the complete oxidation experiments, detailed in Part I, p. 24. The volume of space in contact with the catalyst and its carrier was taken as 15.0cc., this being the average value from three determinations of this figure made with three different amounts of 13gm. catalyst and pumice. From these figures the time of contact of gas and catalyst was calculated.

When the gas had almost all been expelled from A, the clip, <u>b</u>, was reopened and immediately the water in A rose to the zero graduation mark the stopcock, C, was turned to allow a supply of 1½ - 2 litres of nitrogen, delivered under the same conditions as the methane-oxygen mixture, to pass through the system. This stream of nitrogen served the double purpose of preventing any interruption in the steady flow of the methane-oxygen mixture over the catalyst and of sweeping the products of the reaction through the absorption system to allow of the collection of the whole of the gaseous products in the receiver, H. The time at which the stopcock, C, was turned was noted.

The weight of liquid displaced from H was determined and from it the volume of the Resulting Gas was calculated. By noting the prevailing conditions of temperature and pressure the weight of each constituent was calculated after an analysis had been made. In a similar manner the weights of methane and oxygen supplied were determined from the data obtained at the beginning of each experiment. In this manner it was possible to calculate the weights of methane and oxygen that had been converted to gases obtained in the Resulting Gas.

In order to obtain a balance sheet for the gas supplied and that accounted for in the products of the reaction, provision must be made for the products absorbed or condensed in the absorption system. At first it was proposed to estimate formaldehyde and formic acid in the wash waters volumetrically, but free chlorine and hypochlorous acid were detected in these waters and it was found that one or both of these substances interfered with all methods of estimation of the intermediate products of oxidation. No satisfactory method of eliminating these substances was found, with the result that the intermediate oxidation products could only be determined by difference. Qualitative tests for these products were also rendered invalid. In all cases the wash waters restored the colour to Wright's rosaniline reagent, liberated iodine from potassium iodide and gave a precipitate of silver chloride with silver nitrate.

The first four experiments detailed in Table XXIV were carried out exactly as described, while in Experiments 5 and 6, in an attempt to eliminate chlorine, a silver spiral 10.0cm. long was placed at the exit end of the tube, 10.0cm. from the catalyst.

A fresh charge of catalyst was used for each experiment.

TABLE

CUPROUS CHLORIDE-

Expt. No.	Temp. °C.	Original Gas		Resulting	
		Methane. gm.	Oxygen. gm.	Carbon Dioxide gm.	Carbon Monoxide. gm.
1.	433	0.4523	0.4233	0.1148	0.0414
2.	433	0.3147	0.2945	0.1211	0.0261
3.	363	0.4132	0.3867	0.0329	Nil
4.	363	0.2692	0.2519	0.0199	Nil
5.	433	0.3940	0.3687	0.1129	0.0219
6.	433	0.3843	0.3596	0.1077	0.0314

XXIV.

- METHANE -- OXYGEN.

Gas		Total Methane Accounted for in Residual Gas. gm.	Methane Converted to Intermediate Oxidation Products. gm.	% Methane Oxidised			Time of Contact. min.
Methane. gm.	Hydrogen. gm.			To CO_2	To CO	To Liquid	
0.3911	Nil	0.4565	Nil	9.2	5.2	Nil	0.303
0.2050	Nil	0.2639	0.0508	14.0	4.7	16.1	0.306
0.3505	0.0012	0.3625	0.0507	2.7	Nil	12.3	0.306
0.2555	0.0013	0.2627	0.0065	2.7	Nil	2.4	0.307
0.2890	Nil	0.3426	0.0514	10.4	3.2	12.8	0.301
0.2832	Nil	0.3402	0.0441	10.2	4.7	11.5	0.306

From the results it is seen that the quantities of methane oxidised to the various oxidation products depend on the amount of hydrocarbon supplied, so that cuprous chloride, in that it is destroyed in use, does not really act as a catalyst. The yield of intermediate products is low. The decidedly positive test for formaldehyde obtained in the circulation experiment seems to have been the result of the presence of free chloring in the wash waters, since it was found that a solution of chlorine in water possesses the property of restoring the colour to a reduced magenta solution.

In an attempt to fix the chlorine present in the wash waters these were distilled with excess of finely powdered litharge on a water bath and finally over a naked flame, the distillate being collected under water. This process served to separate any intermediate products of oxidation other than formic acid, which would be retained as the lead salt and possibly formaldehyde, which would be oxidised by means of the chlorine present. Part of the distillate was tested for methyl alcohol and formaldehyde, but these were never detected; the remainder was gently boiled and any odour observed. The distillate from Experiments 3 and 4 possessed a decided odour of methyl formate when gently boiled, this being confirmed by boiling an aqueous solution of this ester. Methyl formate may be formed in one of two ways under the conditions of the experiments, namely, by the direct esterification of formic acid by methyl alcohol, both of which are possible oxidation products of methane, or by the polymerisation of formaldehyde, thus:-

$$2H.CHO = H.COOCH_3;$$

the yield of the ester, however, must have been infinitesimal.

Owing to the impracticability of supplying a constant weight of methane under the same conditions in different experiments, this investigation was abandoned.

Conclusions.

Owing to the danger from the liberation of free chlorine cuprous chloride is not to be recommended as a catalyst in promoting the oxidation of methane by means of gaseous oxygen.

General Conclusions.

The experiments carried out in Part II have been concerned with the influence of various catalysts in promoting the oxidation of methane in a gaseous mixture which contained only 25% of the oxygen necessary to oxidise all the methane to carbon dioxide and water. This gaseous mixture was selected because of its non-explosive character, the limits of inflammability of methane in oxygen being 5.7% - 57.4% (88). It may reasonably be assumed that the catalyst which promotes the oxidation of the hydrocarbon most efficiently to the maximum amount of carbon dioxide possible under the conditions described will be the catalyst which will best effect the complete combustion of the hydrocarbon in cases where an excess of oxygen is present, so that this catalyst will be the best of those studied to use in organic combustion analyses.

In order to facilitate the comparison of the catalysts Table XXV has been prepared from the data obtained in the experiments:-

Table XXV.

Summary of Results.

Catalyst.	Temperature at which Reaction Commences.	Temperature at which 25% Methane is Oxidised to Carbon Dioxide.
Palladium Black	*	450°C.
Platinised Asbestos	430°C.	625°C.
Platinum Black	*	550°C.
Copper	300°C.	700°C.
Silver	320°C.	610°C.
Vanadium Oxides	480°C.	580°C.

* Below ordinary temperatures.

The table shows that the most efficient catalysts are platinum and palladium when these are used in the form of "black" and of these palladium black is more efficient than platinum black, the former causing the methane to consume practically all the oxygen available about 450°C. while the latter requires a temperature 100° higher before this takes place. Both these catalysts induce a reaction between methane and oxygen at ordinary temperatures. Platinised asbestos is not so efficient as platinum black, the reaction between the two gases, when in contact with this catalyst, commencing about 430°C. and reaching completion about 200°

higher or at a temperature 75° above the corresponding temperature given by platinum black. This is in accord with the fact that the more finely divided platinum is the more efficient catalyst.

Copper, which is really the catalyst when copper oxide is used in organic combustion analyses for carbon and hydrogen, is the least efficient of the catalysts detailed in the table. The reaction between methane and oxygen commences at a lower temperature than that obtained with platinised asbestos, but the maximum yield of carbon dioxide is not obtained at 700°C., a temperature considerably in excess of the corresponding temperature for platinised asbestos.

While silver gives an appreciable reaction at much the same temperature as copper the reaction is completed at a much lower temperature than that given by copper, the results, in fact, showing that silver is slightly more efficient than platinised asbestos in causing methane and oxygen to combine to form carbon dioxide.

The table shows that vanadium oxides deposited on pumice form a very efficient catalyst for promoting the oxidation of methane by means of oxygen. They also possess the advantage that in themselves they constitute a source of oxygen available for oxidation. While they require a much higher temperature to give an appreciable reaction between the two gases, a 25% yield of carbon dioxide is obtained at a temperature (580°C.) which is lower than that given by any of the other catalysts except those in the form of "black". From the point of view of comparative cost, vanadium oxides have much to recommend them.

The use of cuprous chloride as a catalyst is not to be recommended.

The final conclusion is that palladium black, platinum black and vanadium oxides are exceptionally efficient catalysts for use in combustion analyses, these catalysts being arranged in the order of their efficiencies.

Viewed in the knowledge of Bone's Hydroxylation Theory of Hydrocarbon Combustion (52), the experiments yield interesting results which are in direct accord with this theory. In the first place it is evident that from the point of view of isolating intermediate products of the oxidation of methane in quantity in presence of catalysts, the conditions of the experiments are entirely unsuitable.

Considering the scheme for the oxidation of methane from the formaldehyde stage onwards

$$\begin{tikzcd}
H.CHO \arrow[r, "1"] \arrow[d, "2"'] & H.COOH \arrow[r] \arrow[d, "3"'] & OC(OH)_2 \arrow[d] \\
H_2 + CO \arrow[r] & H_2O + CO \arrow[r] & H_2O + CO_2.
\end{tikzcd}$$

it is seen that the oxidation can follow one of the two courses indicated by the figures 1 and 2, the formaldehyde either being oxidised to formic acid or decomposing to hydrogen and carbon monoxide, while a similar alternative course is available at the formic acid stage. With all the catalysts studied, with the exception of silver and vanadium oxides, no free hydrogen was obtained in the Residual Gases, so that in the presence of palladium, platinum or copper, the oxidation proceeds from formaldehyde by course 1 rather than by way of the decomposition of formaldehyde. At the formic acid stage, however, decomposition, rather than oxidation, preponderates, the reaction proceeding along course 3 and giving as decomposition products water and carbon monoxide, this latter substance being slowly oxidised to carbon dioxide.

In the experiment in the silver group where free hydrogen was obtained in the Residual Gas, the reaction had probably followed course 2 since, with the first indication of free hydrogen, there was also obtained a sudden increase in the amount of carbon monoxide formed, this gas subsequently being more easily oxidised than the hydrogen. Similarly, owing to the fact that vanadium oxides decompose formaldehyde into hydrogen and carbon monoxide and formic acid into water and carbon monoxide (73,87) it is probable that with this catalyst the reaction mainly followed course 2, but, owing to the fact that in one experiment formic acid was detected, it is probable that at low temperatures there is a tendency for the oxidation to proceed by way of formaldehyde and formic acid.

In general, it may be said that the presence of catalysts in no way affects the scheme of the course of the oxidation of methane proposed by Professor Bone, the only change being that, with catalysts present, the various stages of oxidation or decomposition succeed each other very rapidly, so that intermediate oxidation products are not easily isolated in quantity. The general decrease of the yield of intermediate products with increase of temperature shows that the effect of increasing the temperature is to cause a similar increase in the rapidity with which the various stages follow each other.

PART III.

THE INFLUENCE OF THE TIME OF CONTACT ON THE OXIDATION OF METHANE BY MEANS OF COPPER OXIDE.

Introduction.

The results obtained in the preliminary experiments on the effect of varying the time of contact of methane and copper oxide, carried out in Section A of part I, show that this factor is of prime importance in determining the amount of hydrocarbon oxidised by this oxidising agent. This has been noted previously by Dunstan and Carr (6) and Denham (8), the former showing that in the estimation of nitrogen in aconitine by the Dumas absolute method, where methane was left unoxidised by red-hot copper oxide, an increase in the rate of flow of the gases over the copper oxide resulted in a decrease in the quantity of methane burned. Denham found that on passing a mixture of methane and oxygen, in the proportions necessary for complete combustion, over palladianised asbestos at the rate of 1cc. per $3\frac{1}{2}$ seconds, the initial combustion temperature was 514°- 546°C.; at twice this rate of flow this temperature was about 50° higher.

Quantitative data on this subject are, however, lacking and, in order to repair this deficiency, it was decided to investigate, in an accurate manner, the influence of the time of contact of methane and copper oxide in causing the combustion of the hydrocarbon.

Three main experimental methods were employed, namely,

A. Circulation Method.
B. Single Passage Method.
C. Sealed Tube Method.

A. - CIRCULATION METHOD.

General Method of Procedure.

In this series of experiments a gaseous mixture containing approximately 90% methane and 10% nitrogen was circulated, in a closed system and under reduced pressure, over copper oxide maintained at a constant temperature. The Original and Residual Gases were analysed and the amount of methane oxidised calculated, the pressure of the gas in the system being noted before and after each experiment.

The apparatus designed for these experiments is shown in the sketch in Fig. 25 on page 158. It consisted of a glass bulb reservoir, D, having a capacity of about 750cc. and containing a few ccs. distilled water, so that the gases in the system always entered the combustion tube saturated with water vapour at the temperature indicated by a thermometer immersed in the water jacket which surrounded the bulb. Connected to the bulb was a three-way stopcock, E, which was immersed in a cup of mercury and through which the system was first of all evacuated and finally samples of gas for analyses withdrawn. To the tube leading from the reservoir, D, to the circulation pump were joined an inlet stopcock, C, which was also immersed in mercury and through which the Original Gas was introduced into the system and a manometer, F, by means of which the pressures of the gases in the system could be followed.

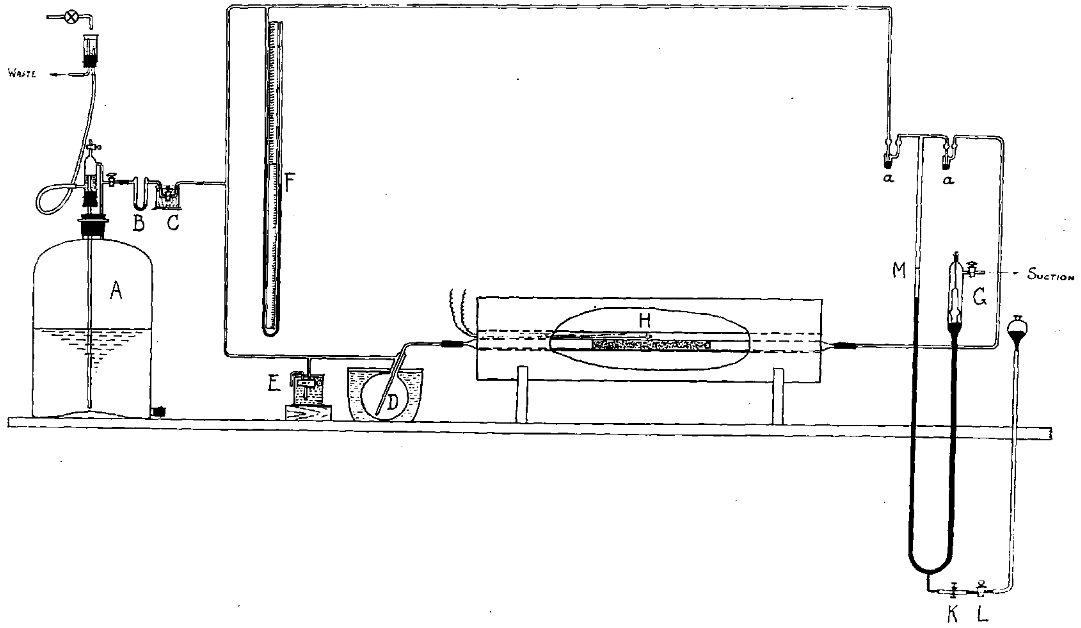

Fig. 25.

The automatic circulation pump, G, used in this case was of the type which functions by means of an oscillating column of mercury and was constructed from details given by Donnelley, Foott, Nielson and Reilly (89); the source of power was an ordinary Bunsen water pump. The levelling bulb was connected to the base of the pump by means of a stopcock, L, and a piece of heavy rubber pressure tubing carrying a screw-clip, K. The outlet valve of the pump was connected to the combustion tube which was contained in an electric furnace, H. The copper oxide used for these experiments occupied 20.0cm. length of the tube and was placed centrally in the furnace tube so that the temperature of the mass was uniform throughout, this temperature being measured by means of a nickel-nichrome thermocouple as before.

The gaseous mixture was stored over water in a 10 litre aspirator bottle, A, which was fitted with a constant pressure supply device and which was connected to the closed system through a mercury valve, B, this valve, in turn, being connected to the stopcock, C.

With the exception of the two rubber tubing connections at the ends of the combustion tube, all joints in the closed system were sealed in a blowpipe flame and, in order to prevent air leakage at the stopcocks, C and E, these were immersed in mercury. In order to test for leakage the system was almost completely evacuated through E and pressure readings taken over a period of six days, with the following results:-

Time in hours	0	24	48	120	144.
Pressure in mm.	16	17	16	16	16.

These figures show that the apparatus was perfectly air tight.

77.8gm. 8 - 32 mesh copper oxide were used, having an available space in contact with it of 18.9cc.. The copper oxide was reoxidised before each experiment.

With such an apparatus as that described it is possible to circulate a gaseous mixture either in a completely closed system, obtained by closing the stopcock, C, or in a closed system at constant pressure, obtained by keeping C open and setting the constant pressure supply device in action. In the experiments carried out the former system was employed.

In such an apparatus at the beginning of an experiment, before the furnace is heated, there is circulating, in a given volume, at known temperature and pressure, a gaseous mixture; at the end of an experiment, after the furnace has cooled, the final gas is circulating at another known temperature and pressure but in a different volume. In order to ensure a strict comparison of the partial pressures of the various gases before and after an experiment it is necessary to compare these pressures at the same temperature and volume. For purposes of comparison, therefore, 0°C. was taken as the standard temperature, while for the standard volume a value of 1139cc., obtained by the method described in Appendix VII, page 220 , was adopted. All pressures were thus reduced to 0°C. and 1139cc.. Further, owing to the use of mercury valves, aa, in the circulation pump, the pressure indicated by the manometer, F, is not the correct pressure throughout the apparatus; allowance was made for this by the method described in Appendix VII. The method of calculating the time of contact of methane and copper oxide is also given in Appendix VII.

Method of Conducting an Experiment.

The apparatus was evacuated through E by means of an electrically driven oil pump until no further diminution in pressure was recorded on the manometer. E was then closed and, the constant pressure supply device having been brought into operation, gas was admitted to the evacuated system, until the pressure recorded by the manometer was approximately half an atmosphere, when C was closed. The gas admitted was circulated for about half an hour and the system again evacuated through E. This served to flush out any traces of air left from a previous reoxidation of the partly reduced copper oxide remaining from the previous experiment.

The sample of gas for the experiment was then admitted in a similar manner and the stopcock, C, closed when the manometer indicated a pressure of approximately half an atmosphere in the closed system. This gas was circulated in the system for about half an hour when the pump was stopped and the mercury in the closed limb raised to the mark, M, to which mark the mercury was always raised before a pressure reading was made (Cf. Appendix VII.). The mercury was raised accurately to the mark by raising the levelling bulb, with K and L full open, until the mercury was a few millimetres below M. L was then closed and the mercury finally raised to the required position by compressing the screw-clip, K.

The pressure indicated by the manometer was then determined and from this reading and the barometric pressure the uncorrected pressure of the gas in the system was obtained. This was corrected for

(a) Vapour pressure of water
(b) Back pressure of mercury valves.
(c) Reduction to Standard Temperature, 0°C.
(d) Reduction to Standard Volume, 1139cc.

The pressures reported in the results have been corrected in this manner.

The Initial Pressure thus having been determined, the furnace was heated until the temperature, as indicated by the galvanometer, was maintained at the required value. At a noted time the circulation pump was started and the experiment allowed to proceed for the required period of time, the temperature being periodically checked.

At a noted instant the pump was stopped and the furnace current switched off simultaneously and the furnace allowed to cool. The apparatus was allowed to assume a uniform temperature over night and the Residual Gas circulated for one hour in order to ensure homogeneity before the Final Pressure was determined in the same manner as the Initial Pressure.

A sample of the Residual Gas was withdrawn from the system and analysed in Bone and Wheeler's apparatus over mercury. The composition of the Original Gas previously having been determined, it was possible to calculate the percentage of methane that had undergone oxidation during the experiment.

Method of Calculation.

The Original Gas contained 87.7% methane and 12.3% nitrogen.

In Experiment 1 the Residual Gas contained

42.2% CO_2 44.9% CH_4 12.9% N_2.

Assuming that methane, under the conditions described, is oxidised only to carbon dioxide and possibly carbon monoxide, it is evident that the sum of the percentages of the gaseous products containing carbon should be equal to the percentage of methane in the Original Gas and the percentage of methane oxidised to carbon dioxide will be

$$\frac{100.C}{87.7}\%$$

where C is the percantage of carbon dioxide in the Residual Gas. Thus in Experiment 1 the quantity of methane completely oxidised is

$$\frac{100 \times 42.2}{87.7}\% \quad \text{or} \quad 64.9\%.$$

The value for carbon monoxide (if formed) can be calculated in a similar manner, but no carbon monoxide was detected in any of the experiments.

Further, if any water soluble or condensable intermediate oxidation product were formed and persisted at the end of an experiment, there would be a difference in the pressures of the gases before and after an experiment. Failing the persistence of any such product it is obvious that the nitrogen contant of the gaseous mixture should remain constant throughout.

Results.

The results obtained are given in Table XXVI and arranged in the order in which the experiments were carried out.

Conclusions.

In the first place, since the Initial and Final Pressures are in close agreement, it is evident that the yield of intermediate oxidation products, if any, is negligible. No carbon monoxide was detected in any of the Residual Gases and the water in the reservoir, D, contained no formaldehyde, the most stable of the intermediate oxidation products containing hydrogen. It may thus be concluded that at 547°C. the sole products of the reaction between methane and copper oxide are carbon dioxide and water.

The results also show that the copper oxide used, which was obtained freshly from stock, becomes at first more active as the process of alternate reduction and oxidation takes place, but in the later experiments a stable condition seems to have been attained.

For the following reasons the method failed to give concordant results and therefore was abandoned:-

TABLE

CIRCULATION

Expt. No.	Temp. °C.	Original Gas.		Initial Pressure. mm.	Final Pressure. mm.
		% CH_4	% N_2		
1.	547	87.7	12.3	383.2	381.9
2.	547	87.7	12.3	349.5	350.9
3.	547	87.7	12.3	373.3	373.0
4.	547	87.7	12.3	364.9	361.9
5.	547	87.7	12.3	366.2	363.5
6.	547	87.7	12.3	377.4	376.1
7.	547	87.7	12.3	378.3	373.0
8.	547	87.7	12.3	372.9	368.3
9.	547	87.7	12.3	367.6	374.0

XXVI.

EXPERIMENTS.

Residual Gas.			Time of Contact.	Methane Oxidised to CO_2.
% CO_2	% CH_4	% N_2	min.	%
42.2	44.9	12.9	9.85	48.1
57.9	29.4	12.7	5.91	66.0
52.3	34.8	12.9	3.94	59.6
48.0	39.7	12.3	3.94	54.8
54.7	33.4	11.9	3.94	62.3
56.8	30.1	13.1	3.94	64.9
57.2	30.4	12.4	3.94	65.4
52.4	35.5	12.1	3.94	59.8
52.7	35.2	12.1	3.94	60.1

(a) In each experiment the time required to heat the furnace to the required temperature varied and consequently the gas in contact with the copper oxide during this preliminary heating was subjected to the action of the copper oxide for a different period of time in each case. The times of cooling were approximately the same in each experiment.

(b) Although the total time of contact of gas and copper oxide was the same for each of Experiments 3 - 9, the time of contact per passage varied, depending on the rate at which the pump was circulating (Cf. Appendix VII, page 222).

B. - SINGLE PASSAGE METHOD.

Owing to the failure of the circulation method recours was made to the Single Passage Method which eliminates all the faults of the former method.

The apparatus designed for this series of experiments is shown in Fig. 26, page168 . It consisted of a 10 litre aspirator bottle, A, fitted with a constant pressure supply device, BC, and connected to one limb of a differential gauge, E, by means of a stopcock, C. The other limb of the gauge was connected, through a three-way stopcock, F, to the combustion tube. The free limb of the stopcock, F, was attached to an air purification system, similar to that described in Part I, page 9, and which was connected to a compressed air main.

The combustion tube was of the usual hard glass type and contained the same copper oxide as was used for the series of circulation experiments, this layer of oxide being placed centrally in the furnace as before and its temperature measured by means of the thermocouple shown. The volume of space in contact with the copper oxide was again 18.9cc. and the length of the column, 20.0cm..

The exit end of the combustion tube was connected by means of capillary glass tubing to the three-way stopcock, G, attached to a 500cc. aspirator bottle, H, fitted with a constant pressure receiving device. The confining liquid in this aspirator was at first mercury, but a few experiments which were conducted at very slow rates of flow, indicated

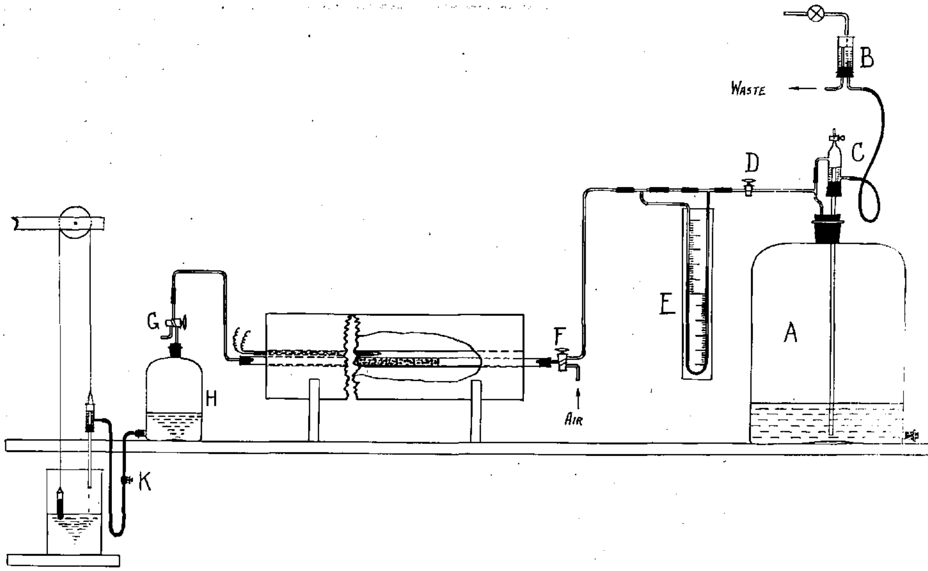

Fig. 26.

that this liquid was quite unsuitable for these low speeds owing to its high surface tension causing a very uneven flow from the levelling tube. For this reason the liquid used in the later experiments was a saturated aqueous solution of magnesium chloride. In order to ensure a perfectly uniform rate of flow of gas throughout an experiment, the experiment was commenced with sufficient air in the aspirator, H, to keep the confining liquid clear of the "shoulders" of the bottle, so that during an experiment the liquid in H fell in a bottle whose cross-sectional area remained constant. In order to prevent the back-diffusion of air from the receiving aspirator during an experiment, the connection from the reaction tube to this receiver was made of narrow bore capillary tubing, through which, even at the lowest rates of flow of gas used, the gaseous products travelled with considerable speed.

Method of Conducting an Experiment.

During the preliminary heating of the furnace air was passed over the copper oxide, in order to oxidise any material left unoxidised from the previous experiment, and bye-passed to the atmosphere through the stopcock, G. The levelling tube attached to the aspirator, H, was arranged so that the Resulting Gas was collected at atmospheric pressure and the clip, K, left open in order to allow liquid to be expelled from H as the air in this aspirator became heated by radiation from the furnace.

When the desired temperature had nearly been attained by the furnace the current of air was cut off and a current of methane from the Original Gas storage bottle, A, passed through the tube, the rate of flow being adjusted by arranging B to give the required fall in pressure across the jet in the differential gauge, E. (Cf. Appendix I, page 203). This current of methane was continued until the temperature of the furnace remained constant, when the clip, K, was closed and the receiving vessel weighed. This vessel was then replaced and the apparatus tested for leaks in a manner similar to that described in Part I, page 21.

When sufficient methane had passed from A to ensure that all the air had been expelled from the apparatus (at least 500cc. being used for each experiment) the stopcock, G, was turned to allow the Residual Gas to be collected and a stop-watch started. The apparatus was then entirely automatic in action and the temperature remained quite constant.

The experiment was allowed to proceed until 300 - 400cc. gas had passed over the copper oxide when, simultaneous with the stopping of the watch, the stopcock, G, was turned to bye-pass the gases coming from the combustion tube. The pressure of the gas in the receiving aspirator was adjusted to atmospheric pressure in the manner described in Part I, the receiving vessel reweighed and the volume of gas passed over in the noted time calculated. The time of contact of gas and copper oxide was obtained from this volume in the usual manner.

The Resulting Gas was allowed to stand for at least one hour to ensure thorough mixing and a sample withdrawn for analysis. The Original and Resulting Gases were analysed, either in Bone and Wheeler's apparatus or in Haldane's apparatus; their composition being known it was possible to calculate the quantities of methane oxidised to carbon dioxide.

Method of Calculation.

The results of the circulation experiments showed that the only oxidation product obtained in these experiments were carbon dioxide and water, so that in the present series of experiments the Resulting Gas contained only methane, carbon dioxide, oxygen and nitrogen, all the carbon compounds present having been derived from the methane in the Original Gas. Thus in order to calculate the amount of methane oxidised it was only necessary to know the ratio of carbon dioxide to methane in the gas issuing from the combustion tube. This gas being diluted with the air initially in the receiving aspirator, the ratio of carbon dioxide to methane was the same in the Resulting Gas as that in the gas issuing from the combustion tube, so that this ratio, obtained from an analysis of the Resulting Gas could be used to determine the amount of hydrocarbon oxidised, no reference to the Original Gas being necessary. Owing to this dilution with air, however, it was impossible to check the results by adding the percentages of the two carbon compounds in the Resulting Gas and comparing the sum with the percentage of methane in the Original Gas in the same manner as in the circulation experiments.

The following figures, taken from Experiment 1 of the series of experiments carried out at 547°C. illustrate the method adopted:-

Volume of gas collected = 453.0cc..

Time = 24.4min..

Rate of Flow = 18.5cc. per min..

Time of Contact = $\frac{18.9}{18.5}$min. = 1.02min..

Resulting Gas contained 7.6% CO_2 and 63.6% CH_4.

$$\text{Ratio } \frac{CO_2}{CH_4} = \frac{7.6}{63.6}$$

$$\therefore \text{Ratio } \frac{CO_2}{CO_2\ CH_4} = \frac{7.6}{71.2}$$

Thus for every 71.2cc. of methane supplied 7.6cc. have been converted to carbon dioxide, so that the percentage of methane converted to carbon dioxide is

$$\frac{7.6}{71.2} \times 100\%, \quad \text{or} \quad \underline{\underline{10.7\%.}}$$

Results and Conclusions.

The results obtained are tabulated in Table XXVII and the curves obtained by plotting the quantities of methane oxidised against the times of contact are shown in the graph in Fig. 27, page 174.

The curves show that for low temperatures (i.e. below 547°C.) the quantity of methane oxidised is almost proportional to the time of contact of hydrocarbon and copper oxide, but the greater the increase of temperature above this the greater

TABLE

SINGLE PASSAGE

Temp. °C.	Expt. No.	Original Gas. % CH_4	Resulting Gas.		Volume of Gas. cc.
			%CO_2	%CH_4	
328	1.	88.4	0.00	-	322.4
390	1.	88.4	0.25	50.1	300.5
528	1.	88.4	2.92	54.2	307.0
547	1.	90.3	7.61	63.6	453.0
	2.	90.3	10.0	63.0	362.2
	3.	90.3	11.6	56.3	280.5
	4.	90.3	16.8	54.9	269.0
	5.	90.3	19.8	65.7	227.1
	6.	90.3	14.4	36.5	192.2
	7.	90.3	21.5	41.0	239.3
560	1.	85.1	12.0	42.5	364.4
	2.	85.1	21.8	41.8	258.2
	3.	85.1	25.4	41.9	324.4
	4.	85.1	33.3	33.5	325.5
	5.	85.1	27.0	26.1	283.2
	6.	85.1	35.9	26.0	263.1
579	1.	83.4	26.2	40.8	357.1
	2.	83.4	32.5	37.2	343.1
	3.	83.4	35.5	25.8	260.5
	4.	83.4	43.6	17.2	284.0
	5.	83.4	42.3	15.5	238.7
	6.	83.4	40.0	11.7	252.2
612	1.	83.4	31.7	25.4	257.1
	2.	83.4	44.4	23.1	326.9
	3.	83.4	50.8	20.1	319.2
	4.	83.4	53.1	12.9	329.7
	5.	83.4	56.1	8.22	308.2
	6.	83.4	54.7	8.10	294.8
658	1.	85.1	59.0	5.87	337.0
	2.	85.1	58.2	4.44	356.9
	3.	85.1	65.0	2.01	339.6
	4.	85.1	61.8	1.47	306.5
	5.	85.1	65.0	1.36	318.7
700	1.	87.0	75.3	1.20	321.5
	2.	87.0	75.6	1.05	351.7
	3.	87.0	67.6	0.23	253.7
741	1.	88.4	55.0	0.00	326.6

XXVII.

EXPERIMENTS.

Time. min.	Rate of Flow. cc./min.	Time of Contact. min.	CH_4 Oxidised to CO_2. %	Av. Rate of Oxidation. %CH_4 Oxidised/min.
119.0	2.71	6.98	0.00	0.00
111.5	2.70	7.00	0.49	0.07
113.7	2.70	7.00	5.1	0.73
24.4	18.5	1.02	10.7	10.5
29.6	12.2	1.55	13.7	8.8
34.0	8.25	2.29	17.1	7.5
44.0	6.11	3.09	23.4	7.6
44.3	5.13	3.69	23.2	6.3
52.0	3.70	5.11	28.3	5.5
92.5	2.59	7.31	34.4	4.7
15.4	23.6	0.80	22.0	27.5
22.0	11.7	1.61	34.3	21.3
34.3	9.45	2.00	37.7	18.9
68.9	4.73	4.00	49.9	12.5
69.1	4.10	4.61	50.8	11.0
97.3	2.70	7.00	58.0	8.3
14.0	25.5	0.74	39.1	52.8
21.4	16.0	1.18	46.6	39.5
35.6	7.32	2.58	57.9	22.4
58.0	4.90	3.86	71.7	18.6
65.3	3.66	5.17	73.2	14.2
93.5	2.70	7.00	77.4	11.1
10.6	24.3	0.78	55.6	75.2
17.3	18.9	1.00	64.2	64.2
27.0	11.8	1.60	71.7	44.8
60.0	5.50	3.44	80.5	23.4
88.1	3.50	5.40	87.2	16.2
105.0	2.81	6.73	87.1	12.9
13.4	25.2	0.75	91.0	121.4
15.6	22.9	0.83	92.9	111.9
38.3	8.87	2.13	97.0	44.5
65.5	4.68	4.04	97.7	24.2
115.5	2.76	6.85	98.0	14.3
15.3	21.0	0.90	98.4	109.3
26.7	13.2	1.43	98.6	69.0
98.0	2.59	7.30	99.7	13.7
17.3	18.9	1.00	100.0	100.0

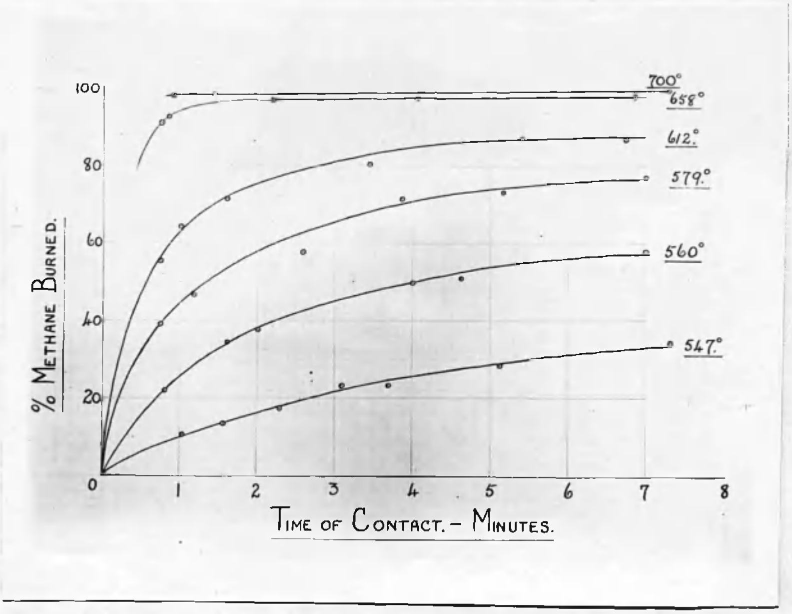

Fig. 27.

is the deviation from this approximation. Even at 560°C. the curve obtained is markedly bent towards the origin. At higher temperatures the amount of methane oxidised at first increases very rapidly with increase in time of contact, but subsequently the curve becomes gradually less steep and a tendency to a maximum value for the amount of methane burned is indicated, this being most pronounced in the curves for 658°C. and 700°C.

Perhaps a better method of showing the effect of varying the time of contact of methane and copper oxide is to plot curves for each whole minute instead of for each temperature, the axes being suitably changed. This has been

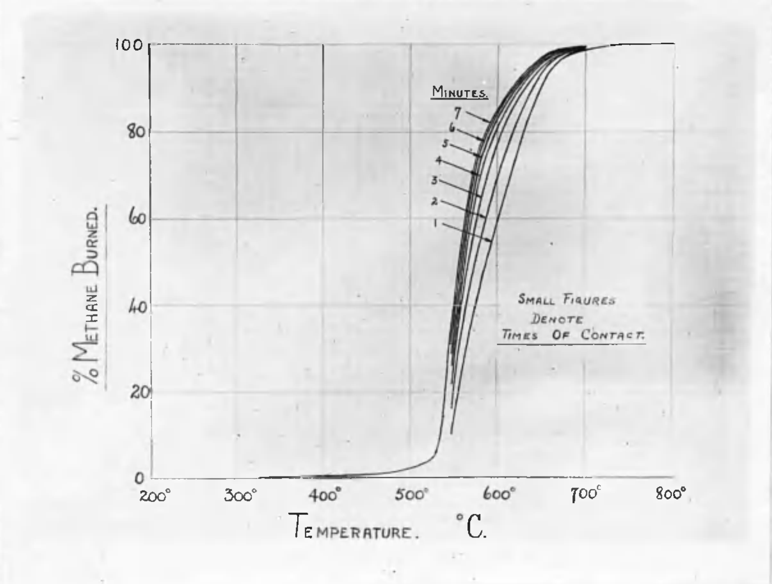

Fig. 28.

done in the graph in Fig. 28, the data for which have been obtained from the graph in Fig. 27 and for the isolated cases (i.e. those below 547°C. and above 700°C.) from Table XXVII.

These curves indicate that at very low temperatures, with a sufficiently long time of contact, methane and copper oxide interact to give an appreciable amount of carbon dioxide. The amount of methane oxidised after 7 minutes' contact at any temperature up to about 525°C. is very small indeed, showing that the reaction proceeds very slowly. Above 525°C. the time of contact has a very great influence on the amount of methane oxidised, this influence becoming most pronounced at 580°C., but with a subsequent increase in temperature the curves again tend to coincide, showing that at high temperatures the time of contact has a less pronounced influence in determining the quantity of hydrocarbon oxidised.

As is to be expected, at any temperature in the range studied the quantities of methane oxidised with the larger times of contact tend to one value for one particular temperature, for example, at 580°C. the difference between the amounts of methane oxidised with 6 and 7 minutes' contact is very small, so that an infinite time of contact is theoretically necessary to ensure complete combustion.

In the last column in Table XXVII are given figures which are proportional to the average rate at which the methane and copper oxide have interacted during the experiments. These figures have been obtained by dividing the total percentage of methane oxidised by the time of contact, thus giving the average amount of methane oxidised per minute during the experiment and thus a measure of the average rate of the oxidation. (Obviously, in some cases where the time of contact has been less than one minute, the figure obtained must be more than 100%, but in all cases the figures are proportional to the required rate.) A series of curves, one for each temperature investigated has been constructed from these date and is shown in the graph in Fig. 29. These curves show that as the time of contact is increased

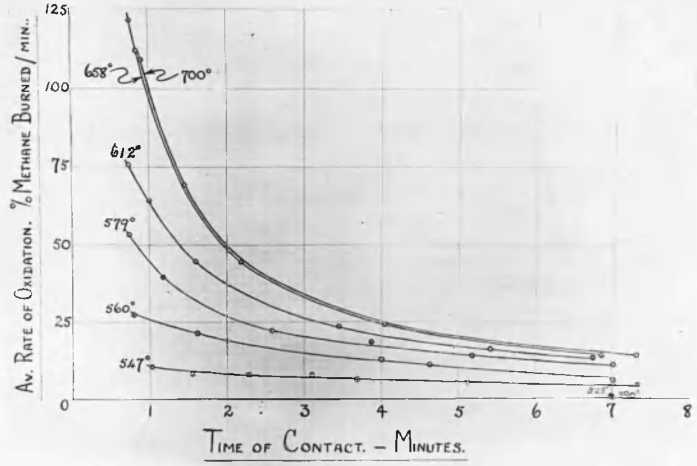

Fig. 29.

the average rate of oxidation decreases, very rapidly at first and then more slowly. The only factor which can cause this and which must be dependent on the time of contact, is the variation of the concentration of methane. With long periods of contact more methane is oxidised than with shorter periods, so that in the former case the concentration of methane in the gases in contact with the copper oxide is continually decreasing and this has the effect of causing the rate of oxidation to decrease, with the result that, while the actual quantity of methane oxidised with a long period of contact is greater than that resulting from a shorter period of contact, the average rate of oxidation is less in the former than in the latter. In other words, the rate at which the oxidation of methane by means of copper oxide proceeds is a function of the concentration of the methane in the gas over the copper oxide. With large times of contact the average rate is low owing to the accumulation of carbon dioxide and the consequent decrease in concentration of methane, while with short periods of contact the resulting carbon dioxide is comparatively quickly removed from the reaction zone and the concentration of methane is kept at a high value, the result being that the average rate of oxidation is considerably increased.

C. - SEALED TUBE METHOD.

The two methods already described were primarily intended for use with short periods of contact at comparatively high temperatures, but were entirely unsuited for periods of contact longer than a few minutes. For this reason the Sealed Tube Method was adopted for use with long periods of contact at low temperatures.

I. Experiments with Manometer in Apparatus.

The original apparatus designed for this purpose is shown in the sketch in Fig. 30, page 180 . It consisted of a tube, B, 34.0cm. long and 2.0cm. internal diameter, with a ridge at C, 26.0cm. from the closed end, of sufficient height to retain all the copper oxide (77.8gm. 8 - 32 mesh copper oxide) within the 26.0cm. length of the tube. This ridge ensured that the copper oxide, throughout its whole length, was maintained at a uniform temperature when placed in the furnace, A, the central 30cm. of which gave a uniform temperature. Connected to the open end of the tube, by means of a piece of heavy rubber tubing, was a mercury manometer, E, and a three-way stopcock, F, through which the system could be evacuated or charged.

The volume of that part of the tube retaining the copper oxide was 81.7cc.. The volume of 77.8gm. copper oxide is 12.3cc., so that the volume of gas actually over the copper oxide is (81.7 - 12.3)cc., or 69.4cc.. The standard volume of the apparatus, obtained by the same method as before and

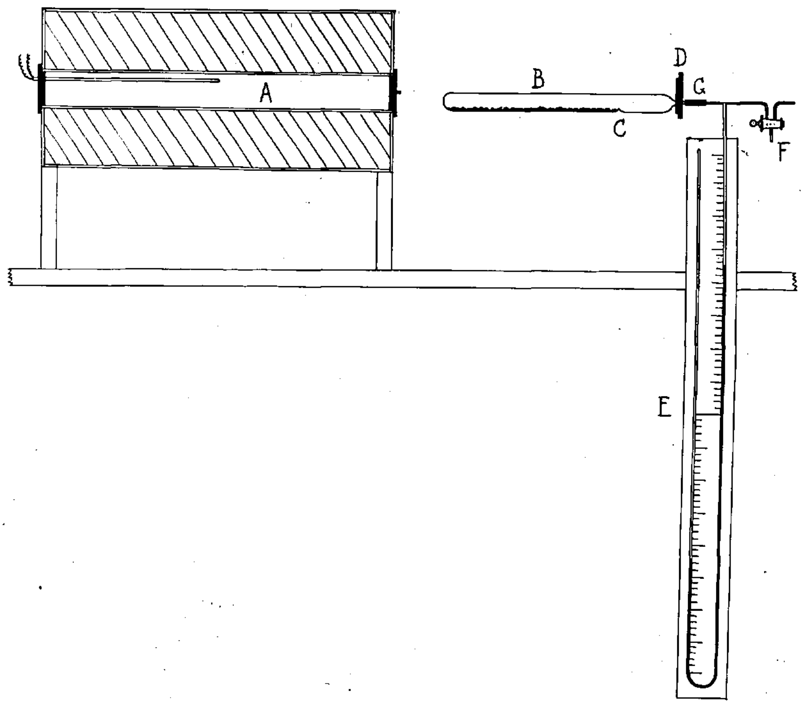

Fig. 30.

detailed in Appendix VII, page 222, was found to be 92.6cc., so that the gas in the immediate vicinity of the copper oxide was 75.0% of the standard volume.

Method of Conducting an Experiment.

The apparatus was evacuated through the stopcock, F, traces of air being removed in a manner similar to that described in the circulation experiments and the Original Gas, of known composition, fed in through F until the pressure recorded by the manometer was such that, when the contents of the tube were heated to the required temperature, the pressure of gas in the system was approximately atmospheric. The Initial Pressure was then determined by applying the necessary corrections detailed in the circulation experiments.

The furnace was heated with both ends plugged with asbestos discs until the required temperature, measured by means of the thermocouple shown, was maintained. At a noted time the moveable plug was withdrawn and the furnace pushed over the tube until the plug, D, fitted into the end of the furnace tube. The experiment was allowed to proceed until the necessary period of contact had elapsed, the temperature being periodically noted to ensure that it remained constant within limits of ±5°C..

At a noted instant the furnace was withdrawn from around the tube and the tube and its contents allowed to cool overnight before the Final Pressure, corrected as before, was determined. A sample of gas was then withdrawn through F and analysed in Bone and Wheeler's apparatus.

Owing to the fact that at the beginning of the period of contact, under these conditions, the tube and its contents did not immediately reach the temperature of the furnace, this method of procedure was slightly modified after the first two experiments had been carried out. In these two experiments the Initial and Final Pressures were in sufficiently close agreement to enable the pressure of the gas in the system to be determined from one observation only, so that in the subsequant experiments no Initial Pressure was determined.

In the modified method the tube was evacuated at ordinary temperature in the furnace, the furnace heated until the required temperature was maintained and, at a noted time, the Original Gas introduced through F until the pressure in the system was atmospheric, so that the gas almost immediately reached the required temperature. The experiment was allowed to proceed until the required interval had elapsed, the furnace withdrawn from around the tube and the tube allowed to cool overnight. When completely cold, the pressure of the Residual Gas was determined in the usual way and a sample of gas withdrawn for analysis.

The composition of the Original and Residual Gases being known the quantity of methane oxidised to carbon dioxide was calculated by the method used in the circulation experiments.

Results and Conclusions.

The results are given in Table XXVIII and the results

TABLE XXVIII.

PRELIMINARY SEALED TUBE EXPERIMENTS.

Expt. No.	Temp. °C.	Original Gas. % CH_4	Initial Pressure. mm.	Final Pressure. mm.	Residual Gas.		Time of Contact. min.	Methane Oxidised to CO_2. %
					% CO_2	% CH_4		
1a.	520	86.5	238.9	237.1	42.2	45.8	300	48.8
2a.	520	86.5	309.7	310.0	34.0	53.0	240	39.3
1.	520	86.5	-	325.1	7.5	79.8	30	8.7
2.	520	86.5	-	340.8	10.3	76.1	60	11.9
3.	520	86.5	-	375.2	11.2	75.4	90	13.0
4.	520	86.5	-	331.6	14.2	73.2	120	16.4
5.	520	86.5	-	336.8	21.9	64.3	150	25.3
6.	520	86.5	-	327.0	29.3	56.2	180	33.8
7.	520	86.5	-	332.4	33.6	52.8	240	38.8
8.	520	86.5	-	324.7	37.9	48.7	300	43.7
9.	520	86.5	-	334.7	41.5	44.3	360	48.0

of Experiments 1 - 9 are grouped in the graph in Fig. 31.

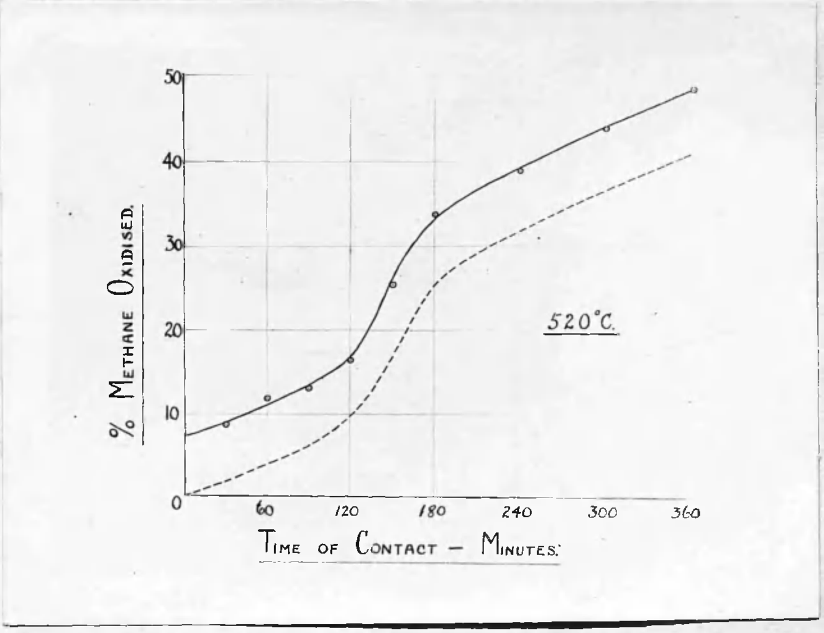

Fig. 31.

Experiments 1a and 2a indicate that in these experiments no intermediate oxidation products were formed, the sole products of the combustion being carbon dioxide and water.

When the graph drawn from the results of Experiments 1 - 9 is produced to zero time of contact a value of 7.3% of the methane supplied burned to carbon dioxide is obtained. This is obviously the result of the fact that the time required for cooling is comparatively great and an appreciable oxidation takes place during this period. The broken line curve in the graph has been drawn from the complete line by subtracting 7.3% from each ordinate of this latter curve and gives a first approximation to the variation in the quantities of methane oxidised resulting from the variation of the time of contact of gas and copper oxide in these experiments.

Owing to there being only 75% of the original methane in immediate contact with the copper oxide and to the fact that a reaction took place during the period of cooling, a new apparatus was constructed, in which practically all the Original Gas was in the immediate vicinity of the copper oxide and from which samples of gas for analyses were taken under conditions which precluded any oxidation during cooling.

II. - Experiments without Manometer.

Owing to the fact that no intermediate oxidation products have been detected in the experiments in this section, it was decided to dispense with the manometer so that the apparatus finally used consisted of a simple sealed tube, A, as shown in Fig. 32, page 187, of such a length that the layer of copper oxide, distributed evenly over the whole length of the tube, was heated to a uniform temperature over its whole length when placed in the furnace. The tube was closed by means of a capillary three-way stopcock, B, one limb of which extended to the point where the tube, A, commenced; this limb was kept as short as possible. The apparatus for instantaneous sampling consisted of a strong flask, D, carrying a three-way capillary stopcock, C, and having a volume at least twice that of the tube, A, the method of operation of which will be explained later.

Method of Conducting an Experiment.

The tube, A, was evacuated by means of the oil pump, all air being expelled as in the previous experiments, until a vacuum manometer in series with the tube and pump showed no further decrease in pressure. B was then closed and the furnace heated to the required temperature; when this temperature was maintained by the furnace the Original Gas, of known composition, was admitted through B at a noted time and the levelling bottle attached to the Original Gas storage bottle arranged so that the tube, A, was filled at atmospheric

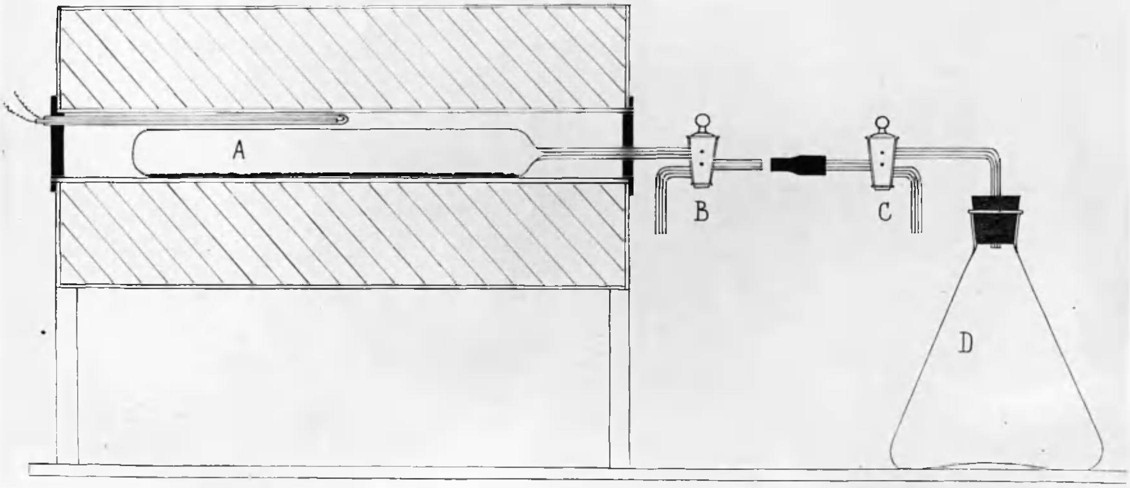

Fig. 32.

pressure. B was then closed and the experiment allowed to proceed for the necessary period of time, the temperature of the furnace being periodically checked.

Towards the end of the experiment the flask, D, was completely evacuated by means of the oil pump, the arrangement, CD, attached to the stopcock, B, by means of the piece of rubber tubing shown and the air contained in the limbs between B and C displaced by means of mercury. B was opened to the tube, A, a few minutes before the period of contact had expired and at the required instant C was opened so that a large volume of the Residual Gas was immediately sucked into the flask. C and B were then closed and the sampling arrangement disconnected from B. By this means the flask contained a sample of Residual Gas formed under conditions which precluded any preliminary heating or final cooling in contact with the copper oxide. A sample of this gas was withdrawn from the flask and analysed in Bone and Wheeler's apparatus or in Haldane's apparatus, over mercury.

The method of calculation was the same as in the last series of experiments.

The copper oxide used was the same as in the last experiments and was reoxidised between the experiments. Owing to unavoidable breakages, three tubes were used in the course of the investigation, their characteristics being as follows:-

Tube .	A.	B.	C.
Length of Furnace.	48.0cm.	48.0cm.	48.0cm.
Length of Layer of CuO.	24.5cm.	25.0cm.	28.0cm.
Length of Tube.	27.0cm.	27.5cm.	28.5cm.
Internal Diameter of Tube.	3.7cm.	5.1cm.	5.1cm.
Volume of Tube alone.*	274.2cc.	516.1cc.	530.0cc.
Volume of Capillary to Stopcock.	0.4cc.	0.6cc.	0.6cc.
Volume of Tube + Capillary.	274.6cc.	516.7cc.	530.6cc.
Volume of Copper Oxide.	12.3cc.	12.3cc.	61.7cc.
Net Volume in Tube + Capillary.	262.3cc.	504.4cc.	468.9cc.
Volume of Gas actually in contact with Copper Oxide.	261.9cc. or 99.85%.	503.8cc. or 99.88%.	468.3cc. or 99.87%.

(* Determined by estimating the weight of water tube contained.)

Results and Conclusions.

The results are tabulated in Table XXIX and the curves obtained by plotting the quantities of methane burned against the times of contact for each temperature are shown in the graph in Fig. 33, page 191. These curves show that for temperatures of 520°C. and below the quantity of methane oxidised by copper oxide is almost directly proportional to the time of contact of hydrocarbon and copper oxide, but even at 389°C. the graph is slightly curved towards the origin, indicating that this is only approximately correct.

As in the case of the single passage experiments, increase of temperature above 520°C. causes a progressive

TABLE

FINAL SEALED

Temp. °C.	Expt. No.	Original Gas. % CH_4	Residual Gas. % CO_2	% CH_4	Pressure of Dry Gas. mm.
*	1.	87.1	0.26	-	754
279	1.	94.4	0.79	-	745
319	1.	94.4	1.20	-	742
389	1.	94.4	0.50	-	745
	2.	94.4	0.95	-	745
	3.	94.4	1.43	-	745
	4.	94.4	1.69	-	748
	5.	94.4	1.80	-	729
	6.	94.4	1.82	-	736
465	1.	94.4	4.21	90.8	737
	2.	94.4	4.47	-	745
	3.	94.4	6.82	-	740
	4.	94.4	6.93	87.6	742
	5.	94.4	8.80	85.8	746
	6.	94.4	9.59	85.1	741
	7.	94.4	11.9	82.7	743
520	1.	86.5	8.01	77.3	718
	2.	86.5	10.5	75.9	732
	3.	86.5	12.9	74.4	718
	4.	86.5	17.3	69.1	741
	5.	86.5	21.7	64.0	730
	6.	86.5	26.7	58.7	718
	7.	86.5	30.7	56.0	731
	8.	86.5	36.9	50.6	734
	9.	86.5	45.4	41.4	743
	10.	86.5	50.2	36.6	733
561	1.	94.4	53.8	40.7	731
	2.	94.4	67.0	28.0	738
	3.	94.4	73.7	20.2	738
	4.	94.4	81.8	12.9	739
	5.	94.4	90.0	5.3	743

* Tube left for 2,784 hours at atmospheric temperatures.

XXIX.

TUBE EXPERIMENTS.

Time of Contact. min.	Methane Oxidised to CO_2. %	Average Rate of Oxidation. $\%CH_4$ Oxidised per hour.	Tube.
*	0.30	0.0001	-
360	0.83	0.14	B
360	1.27	0.21	B
30	0.53	1.06	B
60	1.01	1.01	B
120	1.51	0.76	B
180	1.79	0.60	B
240	1.91	0.48	B
360	1.93	0.32	B
60	4.46	4.46	B
120	4.74	2.37	B
150	7.22	2.89	B
180	7.34	2.45	B
240	9.32	2.33	B
300	10.2	2.04	B
360	12.6	2.10	B
35	9.26	15.9	A
50	12.2	14.6	A
60	14.9	14.9	A
90	20.0	13.3	A
120	25.1	12.6	A
150	30.8	12.3	A
180	35.5	11.8	A
240	42.7	10.7	A
300	52.5	10.5	A
360	58.0	9.67	A
120	57.0	28.5	B
180	71.0	23.7	B
240	78.1	19.5	B
300	86.6	17.3	B
360	95.3	15.9	B

deviation from this approximation, the graph at 561°C. having a well defined curve towards the origin. This indicates that at temperatures above 561°C. there is at first a rapid increase in the amount of methane oxidised, but as the time of contact is increased the rate of oxidation decreases considerably.

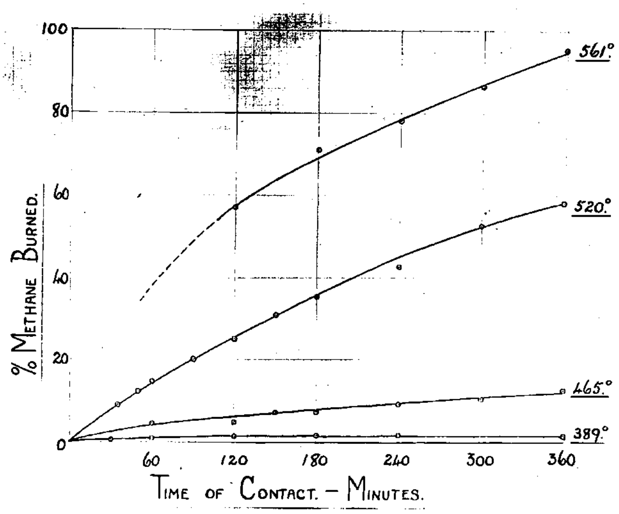

Fig. 33.

The curves for each whole hour for Tube B, plotted on axes of Temperature - Amount of Methane Burned, are shown in Fig. 34. These curves indicate that at temperatures as low as 279°C. methane and copper oxide interact to give a quantity of carbon dioxide which becomes appreciable if the deviation from this approximation, the graph at 561°C. having a well defined curve towards the origin. This indicates that at temperatures above 561°C. there is at first a rapid increase in the amount of methane oxidised, but as the time of contact is increased the rate of oxidation decreases considerably.

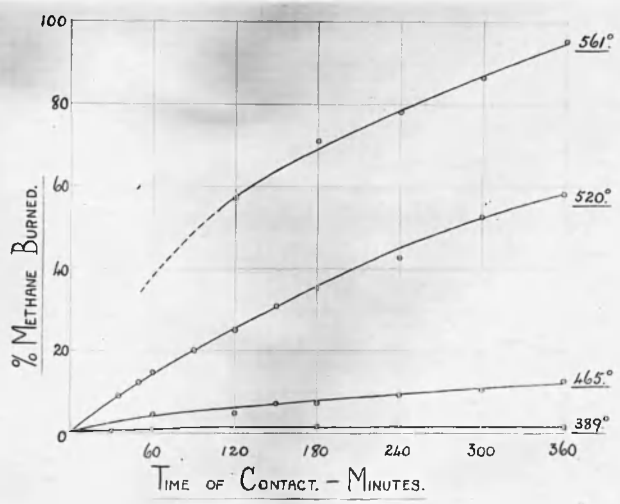

Fig. 33.

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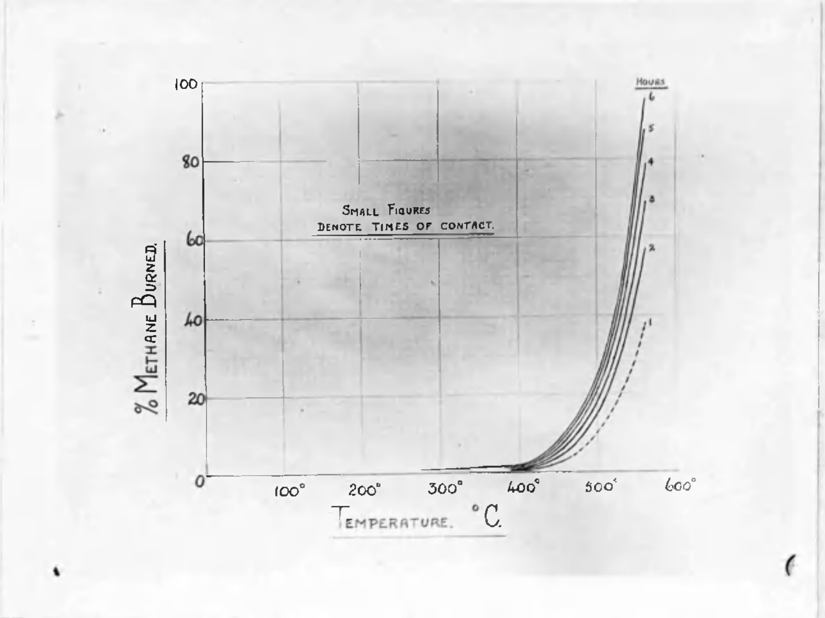

Fig. 34.

time of contact is sufficiently long, but up to 400°C. the reaction proceeds very slowly indeed. The results of the experiment carried out at ordinary temperatures for 116 days show that even at atmospheric temperatures the reaction between methane and copper oxide does take place to a very small extent.

As the temperature is increased above 440°C. the time of contact becomes an important factor in determining the amount of oxidation taking place, the effect becoming more pronounced as the temperature is increased. Unfortunately, owing to the difficulty of sealing a tube to withstand a vacuum at high temperatures (Tube B collapsed before the curve for 561°C. was completed) these curves could not be extended to higher temperatures, but the probability is that at higher temperatures the curves will approach each other again in the same way as those obtained in the single passage experiments.

In this case also it is seen that in the range studied, the curves for the longer periods of contact are more closely grouped together than those for the shorter periods, so that for any temperature between the limits of an combustion and complete combustion, an infinite period of contact is theoretically necessary to ensure complete combustion.

The curves for the average rate at which the oxidation took place, shown in Fig. 35, bear out the conclusions drawn in the single passage experiments with respect to the effect of the progressive decrease in the concentration of methane during an experiment.

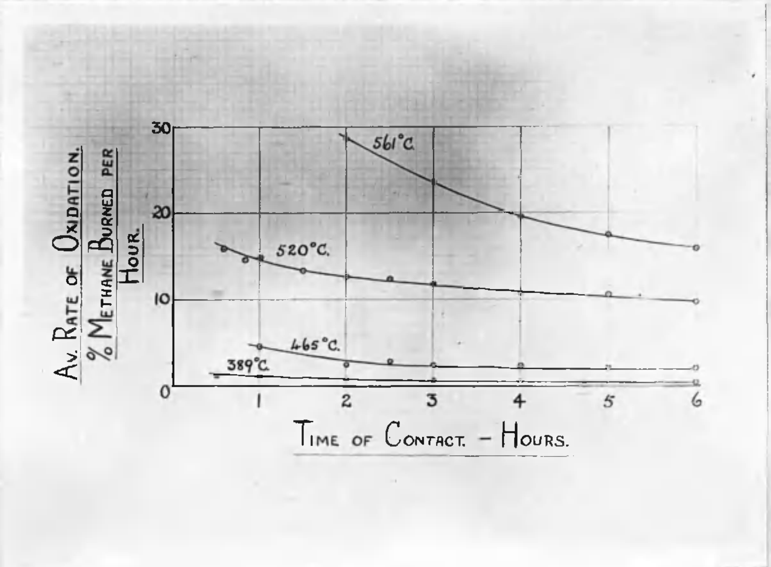

Fig. 35.

THE INFLUENCE OF THE CONCENTRATION OF METHANE IN DETERMINING THE QUANTITY OXIDISED BY COPPER OXIDE.

In order to confirm the conclusions drawn in the single passage experiments and in the sealed tube experiments with respect to the rate of oxidation of methane by means of copper oxide being dependent on the concentration of methane in the gas in contact with the copper oxide, the following experiments were carried out in Tube B with different concentrations of methane. The dilutions were made by diluting 94.4% methane (the remainder being nitrogen) with pure nitrogen, prepared by the method described in Appendix IV, page 213, and the experiments carried out in the manner described for the sealed tube method. The experiments were conducted for 3 hours at 528°C..

Results and Conclusions.

The results obtained are shown in Table XXX and are represented graphically in Fig. 36.

These show that while the percentage of methane oxidised decreases with increase of concentration, the actual volume of hydrocarbon oxidised increases, or, that the amount of hydrocarbon oxidised is a function of its concentration in the gas in contact with the copper oxide.

TABLE XXX.

INFLUENCE OF CONCENTRATION OF METHANE.

Expt. No.	Original Gas.	Residual Gas.		Pressure of Dry Gas.	Volume of Methane Supplied.	Methane Oxidised to CO_2.	
	% CH_4	% CO_2	% CH_4	mm.	cc.	%	cc.
1.	3.12	1.07	-	738	15.8	34.3	5.4
2.	5.35	1.81	3.62	730	27.0	33.8	9.1
3.	10.6	3.18	7.49	728	53.8	30.0	16.1
4.	19.9	5.80	14.2	729	101	29.1	29.3
5.	30.4	8.43	22.0	738	154	27.7	42.6
6.	45.0	11.7	33.3	747	227	26.0	59.0
7.	59.4	15.5	43.4	744	300	26.2	78.3
8.	78.1	17.7	60.6	738	395	22.7	89.5
9.	94.4	19.4	74.9	750	477	20.5	97.9

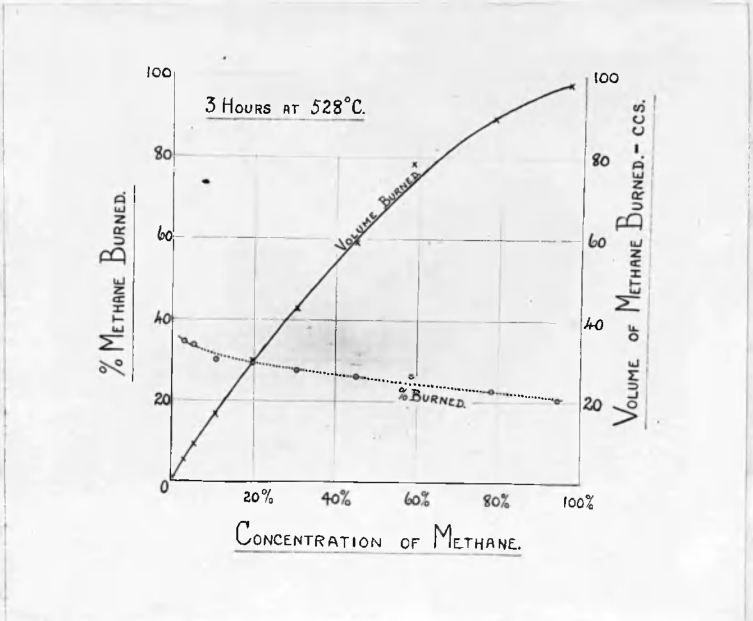
3 Hours at 528°C.
% Methane Burned.
Volume of Methane Burned. - ccs.
Volume Burned
% Burned.
Concentration of Methane.
0
20
40
60
80
100
20%
40%
60%
80%
100%

Fig. 36.

THE INFLUENCE OF INCREASING THE SURFACE OF COPPER OXIDE IN DETERMINING THE QUANTITY OF METHANE OXIDISED.

Tube C, which contained 389.0gm. copper oxide (sifted to 8 - 32 mesh as in the preceding experiments), or five times the amount used in the sealed tube experiments, was used to ascertain if an increase in the surface of the copper oxide exposed to the gas had any great influence in determining the quantity of methane oxidised.

While the copper oxide used was five times the amount previously used in these experiments, it is obvious that any great change in the amount of methane oxidised will be the result of an increased surface rather than an increased weight of copper oxide.

One experiment was conducted for 3 hours at 528°C. and the results are shown below together with those from Experiment 9 of the series on page 195.

Units of Copper Oxide used		5.	1.
CH_4 in Original Gas.		95.7%.	94.4%.
Residual Gas.	CO_2	53.8%	19.4%.
	CH_4	41.9%	74.9%.
Pressure of Dry Gas		741mm.	750mm.
Volume of Methane Supplied.		448cc.	477cc.
Methane Oxidised to CO_2	Volume	252cc.	92.7cc.
	%	56.3%	20.5%

Conclusions.

It is seen that the effect of increasing the surface of copper oxide is to increase the quantity of methane oxidised, but the quantity oxidised is not directly proportional to the area of surface exposed to the gas, owing to the effect of the fall in concentration of the methane during the experiment becoming more pronounced the greater the volume of hydrocarbon oxidised.

General Conclusions.

In summing up, only the single passage experiments and those carried out in the sealed tubes without the manometer need be considered. Both series of experiments yielded similar results so that the general conclusions may be made to include both sets of conditions.

The results of experiments carried out at low temperatures indicate that methane and copper oxide interact at temperatures below 279°C. but the amounts of carbon dioxide formed with moderate periods of contact are very small indeed. From 279°C. up to 400°C. the rate of oxidation is very small and in these cases it is reasonably accurate to assume that the quantity of carbon dioxide formed is directly proportional to the time of contact of methane and copper oxide.

At temperatures above 400°C. the rate of oxidation gradually increases and the amount of carbon dioxide formed, although increasing with increase in the time of contact is not directly proportional to this factor, but is less than the amount demanded by this approximation, the curve obtained being hyperbolic in shape. The experiments carried out with various concentrations of methane indicate that this hyperbolic curve is the result of the progressive decrease in the speed of the reaction as the concentration of methane falls with progressive accumulation of carbon dioxide.

As the temperature is further increased there is still a further deviation from the above approximation, the amounts of methane oxidised tending to a maximum value for any one particular temperature and being almost independent of the time of contact, provided this is not small.

The rate of oxidation in these experiments in large at first, but gradually decreases owing to the fall in concentration of the methane in the gas in contact with the copper oxide, so that in oxidising methane by passing it over copper oxide it is better to use a high temperature, which gives a high rate of oxidation, and a short period of contact, which does not allow the concentration of methane materially to decrease, owing to the fact that the carbon dioxide formed is almost immediately swept away from the reaction zone by the stream of methane, than to use a low temperature and a long period of contact, both of which tend to give a very low rate of oxidation.

The rate of oxidation of methane by means of copper oxide is accelerated by using copper oxide which presents a large surface to the gas.

The conclusions drawn in this section do not invalidate the conclusions formed in Part I with respect to the initial combustion temperatures of methane, in a 5% methane mixture, over copper oxide alone and copper oxide impregnated with various catalysts. With methane in such low concentration the rate of oxidation will be so very small at the initial combustion temperatures quoted in Part I that the carbon dioxide formed in the comparatively small periods of contact in these experiments will be negligible.

Viewed in the light of the fractional combustion method of gas analyses, the results obtained in this section point to the necessity of oxidising hydrogen and carbon monoxide by means of copper oxide at temperatures not exceeding 300°C. if methane is the only other combustible gas present. This is the maximum permissible temperature for hydrogen and carbon monoxide recommended by Burrell and Oberfell (20).

APPENDICES.

APPENDIX I.

CALIBRATION OF DIFFERENTIAL GAUGES.

For the purpose of calibrating the jets fitted in the differential gauges used in Part I and Part III the apparatus shown in the sketch in Fig. 37 was used. The gauge, A, was connected to a graduated aspirator bottle filled with water and fitted with the constant pressure receiving device, BCE, (21).

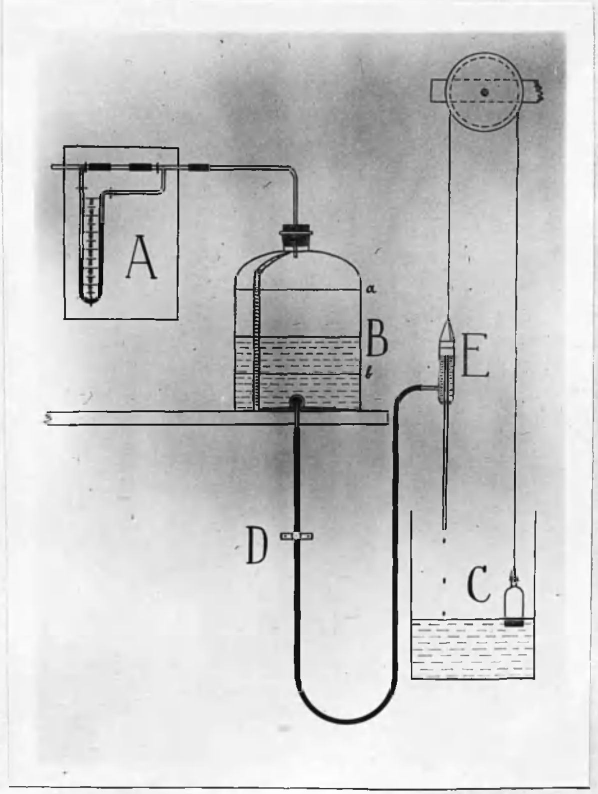

Fig. 37.

A mark, a, on the aspirator at a point exactly on a scale division was noted and taken as the zero reading. With the difference in levels of the water in B and E equal to 2 inches the clip, D, was opened sufficiently to give a reading of 0.10" on the gauge and the time taken for the jet to deliver the volume of air contained between the marks, a and b, noted by means of a stopwatch. The mark, b, was an arbitrarily chosen scale division which varied throughout the determination. This was repeated for various settings of the clip, D. The results are shown in Tables XXXI and XXXII and are collected in the graphs in Figs. 38 and 39, from which the gauge reading for any required rate of flow was obtained during the experiments.

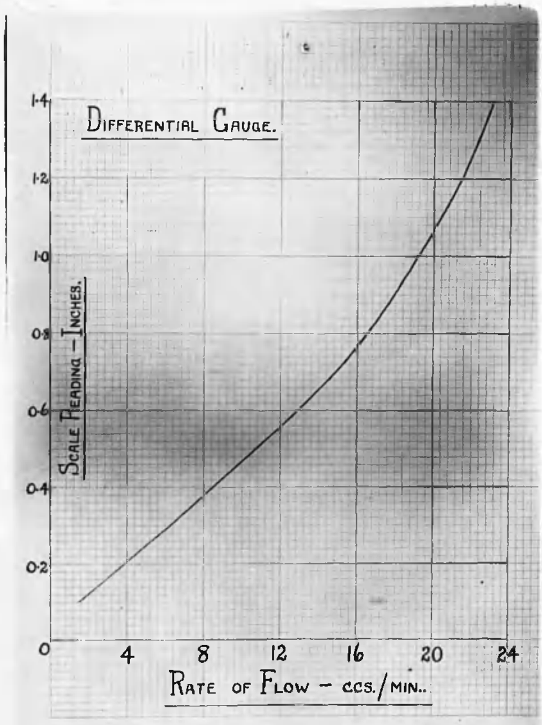

Fig. 38.

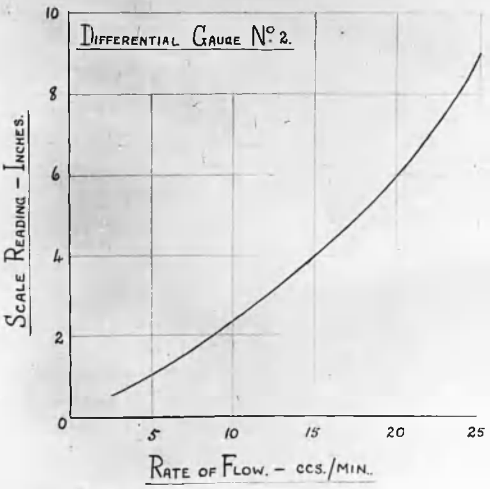

Fig. 39.

TABLE XXXI.

CALIBRATION OF No.1 GAUGE.

Scale Reading. Inches.	Volume. cc.	Time. min.	Rate of Flow. cc. per min.
0.10	200	140.8	1.42
0.20	500	130.2	3.84
0.30	1000	160.3	6.24
0.40	1000	118.0	8.48
0.50	1000	93.0	10.7
0.60	1000	77.0	13.0
0.70	1000	67.0	14.9
0.80	1000	61.0	16.5
0.90	2000	111.0	18.0
1.00	2000	104.0	19.2
1.10	2000	98.0	20.4
1.20	2000	94.0	21.3
1.30	2000	89.0	22.4
1.40	2000	87.0	23.0

TABLE XXXII.

CALIBRATION OF No.2 GAUGE.

Scale Reading. Inches.	Volume. cc.	Time. min.	Rate of Flow. cc. per min.
0.50	300	115.0	2.61
1.00	300	60.0	5.00
1.50	300	43.0	6.98
2.00	400	45,5	8.79
2.50	420	40.0	10.5
3.00	400	33.3	12.0
3.50	400	29.7	13.5
4.00	400	26.7	15.0
4.50	400	24.0	16.7
5.00	520	29.3	17.7
6.00	500	25.0	20.0
7.00	500	22.7	22.0
8.00	500	21.2	23.6
9.00	1000	40.0	25.0

APPENDIX II.

(a). - STANDARDISATION OF THERMOCOUPLE.

The temperatures measured in the experiments were estimated by means of a nickel-nichrome thermocouple. This couple was standardised against a standard platinum - platinum:rhodium thermocouple by having both enclosed in an electric furnace, a comparison of the respective e.m.f's being obtained by allowing the furnace to cool. As a result of this determination the graph shown in Fig. 40 was constructed and used during the experiment.

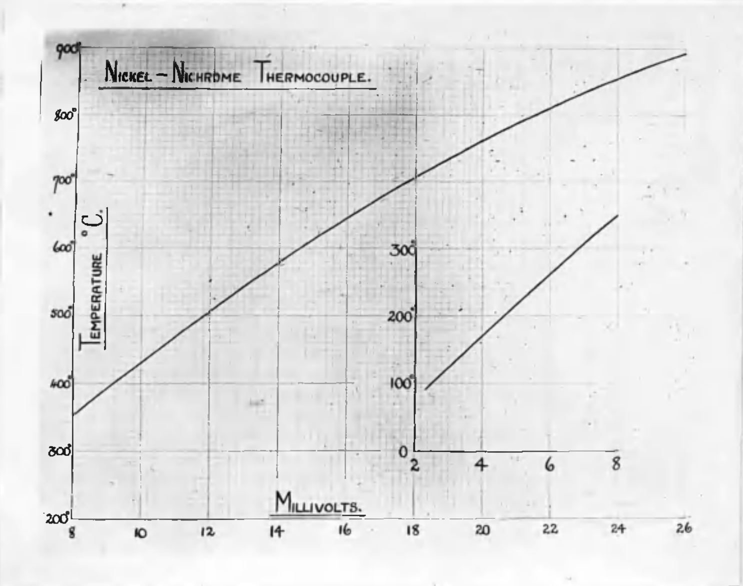

Fig. 40.

As a further check on the accuracy of the relationship obtained between the temperature and the e.m.f. developed by the couple, the couple was used to determine two fixed temperatures, the first the melting point of pure (Merck) sodium chloride and the second the boiling point of sulphur.

In the first case the melting point apparatus shown in Fig. 41 was used. The salt was kept in a well superfused condition for 15 minutes and the flame withdrawn. The couple was then inserted into the superfused salt and half-minute readings of the e.m.f. developed noted. This method gave 797°C. for the required melting point, the correct value being 801°C..

For the determination of the boiling point of sulphur the jacketted apparatus shown in the sketch was used. The estimation, carried out in the usual manner, gave 448°C. for the required boiling point, the correct value under the prevailing conditions being 445°C..

These values checked the accuracy of the standardisation of the couple and it was concluded that the temperatures given in the experiments are correct to ± 5°C..

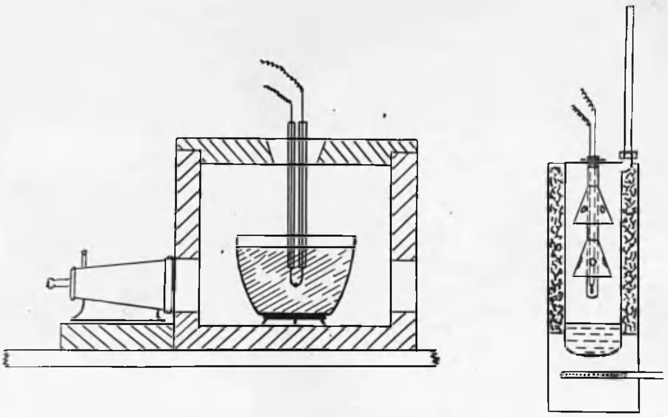

Fig. 41.

(b). - EQUALISATION OF INTERIOR AND EXTERIOR TEMPERATURES.

The temperatures given were measured between the furnace wall and the combustion tube, but the following results of an experiment in which the values of the temperature inside the tube, i.e. the temperature of the oxidising agent, are compared with those outside the combustion tube, show that the exterior temperature, as measured in the actual experiments, is equal to the actual temperature of the oxidising material, when equilibrium is established.

Table XXXIII.

Comparison of Interior and Exterior Temperatures.

External Temperature °C.	Internal Temperature °C.
720	720
660	660
600	600
535	535
460	460
385	385
340	340
305	300
260	260

(e). - EXPLORATION OF FURNACE TEMPERATURES.

After the experiments in Part I had been completed the variation in temperature along the furnace was investigated; the results are shown in the graph in Fig. 42. The uneven curves obtained do not interfere with the actual conclusions made in the experiments in so much that each series of experiments was carried out under the same conditions and the results obtained are, therefore, directly comparable.

Before commencing the experiments in Part II, however, it was decided to re-lag the furnace in order to obtain a central portion which would give a uniform temperature. The graphs in Fig. 43 show the variation in temperature after this

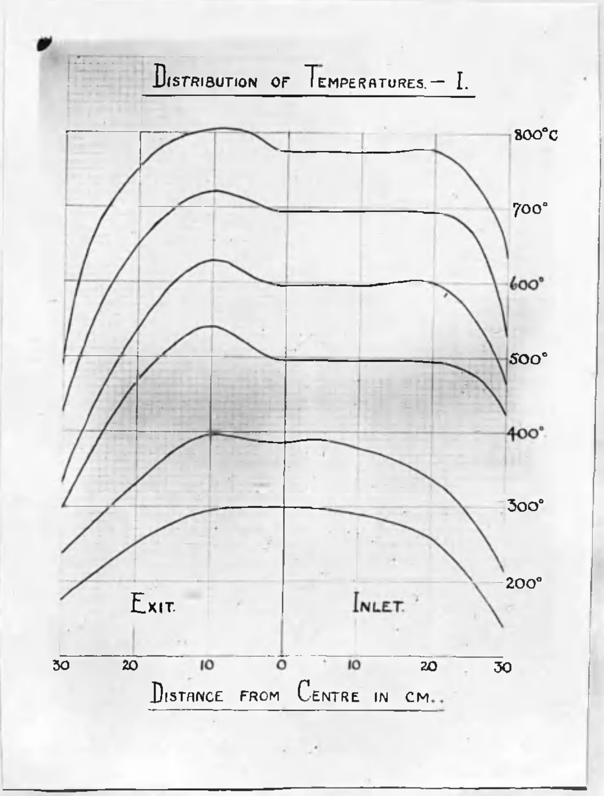

Fig. 42.

had been done. The central 20cm. of the furnace now gave practically a uniform temperature, so that in the experiments in Parts II and III in which this furnace was used, only the central 20cm. of the combustion tube were filled.

The furnace used for the sealed tube experiments in Part III gave a uniform temperature over the central 30cm..

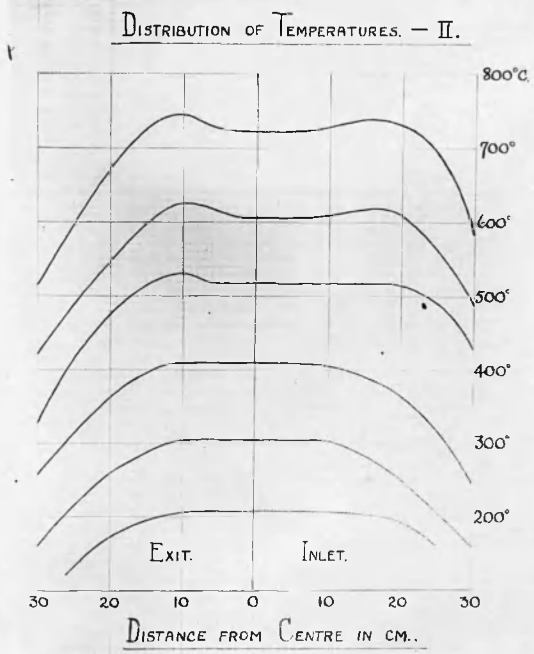

Fig. 43.

APPENDIX III.

VOLUME OF GAS SAMPLING TUBE.

The volume of gas contained by the gas sampling tube from the top of the stopcock, A, to the mark, M, was determined as follows.

The sampling tube, Fig. 2, page 18, having been carefully cleaned and dried, was filled with clean mercury from the levelling tube, C, until the mercury had risen above the stopcock, A, into the top capillary tube. A and B were then closed and the excess mercury run off from the upper capillary tube through the side capillary tube. A similar procedure was carried out with the mercury in the lower capillary of B after the levelling tube had been removed.. Having ascertained the gas sampling tube to be free from air bubbles, the mercury was allowed to run slowly through B into a tared bottle, the stopcock, B, being closed when the mercury meniscus stood at M. The mercury retained by the lower capillary tube of B was allowed to flow into the bottle by turning this stopcock to allow of communication between the upper side capillary and the lower one.

The tared bottle and its contents were reweighed and by noting the temperature during the calibration the required volume was deduced from the weight of mercury found. The volume for the density of mercury at the given temperature was obtained from tables (90).

The following are the results:-

Temperature.	14.5°C.	14.5°C.
Weight of Mercury	3187.00gm.	3187.60gm.
Density of Mercury	13.5597gm. / cc.	
Required Volume	202.07cc.	202.08cc.
Volume used in Experiment	**202.1cc.**	

[illegible]

[illegible] e gas was periodically tested for [illegible] caustic potash solution, for oxygen [illegible] gases by means of Haldane's gas analy[illegible]

[illegible]ION OF METHANE BY GRIGNARD'S METHOD

[illegible] In all the exp[illegible] of those on the complete combustion [illegible] ydrogen was mixed with ethylene, the [illegible] Grignard's method (24).

[illegible] gm. magnesium turnings, 50gm. methyl i[illegible] re refluxed until no more magnesium [illegible] compound was hydrolysed with distill[illegible] fied by slow passage through two wash [illegible] containing concentrated sulphuric [illegible] and immersed in a freezing mixture, to trap ether vapour and two wash bottles, containing alkaline pyrogallol solution, to absorb oxygen.

APPENDIX IV.

(a) - PREPARATION OF NITROGEN.

The nitrogen used throughout the course of the experiments was prepared by the method described by von Knorre (91). A solution containing 1 part of sodium nitrite, 1-2 parts of ammonium sulphate and 1 part of potassium dichromate was gently warmed and the evolved gas washed by passage through two wash bottles containing a mixture of 5 volumes of saturated potassium dichromate and 1 volume of concentrated sulphuric acid.

The gas was periodically tested for constituents absorbable by caustic potash solution, for oxygen and for combustible gases by means of Haldane's gas analysis apparatus.

(b) - PREPARATION OF METHANE BY GRIGNARD'S METHOD.

In all the experiments, with the exception of those on the complete combustion of methane mixed with hydrogen and mixed with ethylene, the methane was prepared by Grignard's method (24).

5gm. magnesium turnings, 28gm. methyl iodide and 100cc. dry ether were refluxed until no more magnesium would dissolve. The Grignard compound was hydrolysed with distilled water and the gas purified by slow passage through two wash bottles, containing concentrated sulphuric acid and immersed in a freezing mixture, to trap ether vapour and two wash bottles, containing alkaline pyrogallol solution, to absorb oxygen.

The gas was collected and stored over water and the analyses carried out in Bone and Wheeler's apparatus over mercury.

The methane obtained was rejected if the explosion analyses proved the following ratios,

$$\frac{\text{Contraction after explosion}}{CO_2 \text{ formed}} \ \& \ \frac{\text{Oxygen consumed in explosion}}{CO_2 \text{ formed}}$$

to lie outwith the limits of 1.98 and 2.02, the theoretical values being 2.00.

(c) - PREPARATION OF METHANE FROM ALUMINIUM CARBIDE.

In the experiments carried out on the combustion of methane in the presence of hydrogen, the methane was prepared by the hydrolysis of aluminium carbide, carried out by Campbell and Parker's method (92). The gas evolved was passed through bromine to remove unsaturated hydrocarbons, caustic soda solution to remove bromine vapour and carbon dioxide, alkaline pyrogallol to remove oxygen and ammoniacal cuprous chloride solution followed by sulphuric acid to remove carbon monoxide. This gave a gas containing only methane, hydrogen and nitrogen.

In the case of the methane - ethylene mixtures, the gas from the hydrolysis was collected without any washing and was found to consist of

52.7% CH_4	2.4% C_mH_n
18.2% H_2	4.2% O_2
2.1% CO_2	20.4% N_2.

This gas was passed over copper oxide at 450 C. and the carbon dioxide formed absorbed in 50% caustic potash solution. The resulting gas contained

$$52.7\%\ CH_4$$

$$47.3\%\ N_2.$$

To this the amount of ethylene necessary to give the required proportions of methane and ethylene was added.

APPENDIX V.

ESTIMATION OF VOLUME OF SPACE IN CONTACT WITH THE OXIDISING AGENT.

In order to estimate the volume of the space over the oxidising agent the following procedure was adopted.

To one end of the tube containing the oxidising agent was attached a delivery tube leading to a eudiometer tube standing over 50% caustic soda solution and filled with this reagent, while to the other was attached a Kipp apparatus generating carbon dioxide from air-free hydrochloric acid and marble chips which had been immersed in boiling water for several hours. The carbon dioxide evolved expelled all the air from the tube and delivered it into the eudiometer, where the carbon dioxide was absorbed by the caustic soda solution. When no further increase in volume was obtained in the eudiometer tube, the gas was subjected to atmospheric pressure in the usual way and the volume noted.

This volume was made up of

(a) - The air from the connections,
(b) - The air contained by the free spaces in the combustion tube
and (c) - The air over the oxidising agent.

Of these three volumes, the first two can be calculated from direct measurements and, knowing the sum of all three, the third can be found.

An example will make this clear; the figures given below were obtained from the copper oxide used in the complete combustion of methane.

Volume of space at posterior end of tube	17.8cc.
Volume of space at anterior end of tube	18.2cc.
Volume of connections	7.0cc.
Total volume obtained by measurement	43.0cc.
Volume of air in eudiometer (98.0, 98.2)	98.1cc.
Volume of space over copper oxide	<u>55.1cc.</u>

In the case of a gas travelling at a speed of 15.4cc. per minute over this copper oxide it will be in contact with this oxidising agent for (55.1)/(15.4)min., or 3.58 minutes.

APPENDIX VI.

PREPARATION OF PLATINUM BLACK DEPOSITED ON ASBESTOS.

(Willstatter and Waldschmidt-Leitz's (81) modification of Loew's (82) Method.)

3gm. asbestos were soaked with a solution containing 0.047gm. platinic chloride in about 20cc. water and 30cc. formalin and 20cc. of a 50% aqueous solution of potassium hydroxide added slowly, the mixture being stirred and kept cool. After standing for 24 hours the impregnated asbestos was drained in a Buchner funnel and washed with water until a deep black liquid began to pass through. At this point washing was suspended for 24 hours and then resumed and continued until the washings were free from chloride. The impregnated asbestos was then dried in a steam oven.

The quantity of platinic chloride used gives 0.027gm. platinum.

APPENDIX VII.

CIRCULATION APPARATUS IN PART III.

The methods of correction described below are those used by T. S. Wheeler and Blair (59).

(a) - CORRECTION FOR BACK PRESSURE OF PUMP VALVES.

After evacuation of the apparatus, with the mercury in the pump at the mark, M, Fig. 25, page 158, the gauge, F, corrected for the thermal expansion of mercury, read, at 12.5°C., 729.5mm.. The barometer, also corrected for the thermal expansion of mercury, read 743.0mm.. At 12.5°C. the vapour pressure of water is 10.8mm., so that the pressure exerted by the gas retained by the pump valves is

$$(743.0 - 729.5 - 10.8)\text{mm., or } 2.7\text{mm..}$$

A rouhg measurement of the volume of the apparatus gave the value 1110cc. and a similar rough estimation of the volume between the pump valves gave the value 4.5cc.. Thus, if the gas retained by the valves were dispersed throughout the whole apparatus it would exert a pressure of

$$\frac{4.5 \times 2.7}{1110} \text{ mm., or } 0.01\text{mm..}$$

Thus the correction for the back pressure exerted by the gas retained by the pump valves is negligible.

(b) - CORRECTION FOR CHANGE IN VOLUME OF THE APPARATUS.

The Standard Volume of the apparatus, S, was taken as the volume of the apparatus with the mercury standing at 341.5mm. in the closed limb of the manometer and that in the pump at the mark, M.

Pressure in apparatus after evacuation (corrected for back pressure exerted by pump valves) = 0.0mm..

690.0cc. gas at 743.0mm. and 13.0°C. were introduced. This is equivalent to 634.3cc. dry gas at N.T.P..

Pressure exerted by gas in apparatus = 445.9mm. at 13.0°C.

= 434.8mm. (dry gas).

At 0°C., this pressure would be (434.8 x 273)/286mm..

or 415.0mm..

The increase in volume in the apparatus is due to the mercury falling in the manometer and pump tubes.

Sum of radii of manometer and pump tubes = 0.55cm..

Increase in volume $= \pi(0.55)^2 \times$ difference in manometer readings.

$= \pi(0.303)(34.15 - 13.75)$cc..

= 19.4cc..

Thus the gas introduced exerts a pressure of 415.0mm. in a volume (S + 19.4)cc. at 0°C.. If in a volume S at 0°C. it would exert a pressure of

$$\frac{S + 19.4}{S} \times 415.0\text{mm..}$$

This pressure is also equal to

$$\frac{634.3}{S} \times 760\text{mm.,}$$

so that

$$\frac{S + 19.4}{S} \times 415.0 = \frac{634.3}{S} \times 760,$$

whence

$$S = 1142\text{cc.}.$$

A duplicate gave the result $S = 1136$cc., so that the value adopted was $S = 1139$cc..

In order to eliminate the change in volume caused in the pump barrel it was decided to raise the mercury in the pump to the mark, M, before taking a pressure reading, but the original mark was found to be too high up the barrel, since, with a gas in the apparatus, bringing the mercury up to the mark, M, entailed the risk of breaking the float in the other limb of the pump. Accordingly, for Experiments 2-9 in this series, the mark, M, was placed at a point 24.80cm. below its original position. This meant that S had been increased by

$$\pi \times (0.25)^2 \times 24.80\text{cc., or } 5\text{cc.},$$

0.25cm. being the radius of the pump barrel, to $\underline{S = 1144\text{cc.}}$.
The change in volume of the apparatus was now solely due to the change in volume caused by the variation of the mercury in the manometer tube and was given by

$$\pi(0.3^2)(\underline{w})\text{cc.},$$

0.3cm. being the radius of the manometer tube and $\underline{w}$ the difference in mercury levels (in cm.) in the closed limb of the manometer before and after an experiment.

(c) - STANDARD VOLUME OF SEALED TUBE.

In the sealed tube apparatus with the manometer attached the standard volume was taken as the volume of the apparatus when the mercury in the closed limb of the manometer stood at 30.00cm.. This volume was found, by the method described above, to be 92.6cc.. The radius of the manometer tube being 0.23cm., the correction for change in volume in this case was given by

$$\pi(0.23^2)(\underline{w})\text{cc..}$$

(d) - CALCULATION OF TIME OF CONTACT.

The following reasoning shows that the time of contact of gas and copper oxide is a function of

(i) - The volume of space over the copper oxide, (18.9cc.)
(ii) - The volume of the apparatus,
and (iii) - The duration of the experiment.

Let n = Number of oscillations of mercury in pump per hour.
a = Amplitude of oscillations in cm..
r = Radius of pump barrel in cm..

Then

Volume per oscillation $= \pi ar^2$.

Volume per hour $= \pi ar^2 n$.

Time of contact per passage $= \dfrac{18.9}{\pi ar^2 n}$.

Time for one circulation * $= \dfrac{1150}{\pi ar^2 n}$.

Total circulations per hour $= \dfrac{\pi ar^2 n}{1150}$.

Time of contact per hour's circulation = T =

$$\frac{18.9}{\pi ar^2 n} \times \frac{\pi ar^2 n}{1150} \times \frac{60}{1} \text{ minutes.}$$

$$= \underline{0.985 \text{ min..}}$$

(*This calculation is based on a total volume of gas in circulation of 1150cc., an average value for the experiments.)

During the experiments this value of 0.985min. was checked by measuring n, a and r. The following indicate the type of results obtained:-

Expt. No.	1.	2.	3.	4.	5.	6.
n	51	50	50	50	49	50
a	19.0	17.7	18.8	16.6	16.7	16.2
r			0.25cm..			
T	.985	.985	.985	.985	.985	.985

(e) - METHOD OF APPLYING CORRECTIONS.

As an example of the method of applying the various corrections the results of Expt. 1 of the circulation experiments may be quoted.

	Original Gas.	Residual Gas.
Barometer	744.9	758.8mm.
Corrected for Mercury Expansion	743.3	757.4mm.
Manometer	333.4	352.3mm.
Uncorrected pressure	409.9	405.1mm.
Temperature	13.2°	10.8°C.
Pressure of Water Vapour	11.3	9.7mm.
Pressure of Dry Gas	398.6	395.4mm.
Pressure at 0°C.	381.5	380.3mm.
Increase over S	5.0	5.0cc.
Fully Corrected Pressure (i.e. at 0°C. and in S)	$\frac{381.5 \times 1144}{1139}$	$\frac{380.3 \times 1144}{1139}$ mm.
	= 383.2	381.9mm.

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The contractions adopted are those in general use in scientific literature.

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