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Studies in the oxidation of methane and in the thermal decomposition of formaldehyde.

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PART I.

STUDIES IN THE OXIDATION OF METHANE.

A. INTRODUCTION AND SUMMARY OF PREVIOUS WORK.

The process of oxidation of methane by means of oxygen has been studied by many investigatiors from the beginning of this century. The first researches intended to explain the mechanism of this process were interpreted on the basis that the slow oxidation of methane occured in a number of successive stages, but the isolation of the postulated products of each stage met with difficulties which seemed to be insurmontable. In spite of these difficulties a general theory about the slow oxidation of aliphatic hydrocarbons, saturated as well as unsaturated, was worked out, - the so-called hydroxylation theory. This theory was held for about thirty years, but was afterwards attacked by many investigators who obtained results, which the theory could not directly explain. They put forward a new theory based on so-called chain reactions and they worked out new explanation of the slow oxidation of hydrocarbons. Although new investigations appear to support the theory of chain reactions, the question still seems to be undecided.

Besides this discussion as to the real mechanism of the slow oxidation of methane and other hydrocarbons, investigations into the combustion of methane

took a practical direction and sought to obtain from methane just as from natural gases - which are cheap and widely distributed row materials - the products most needed in industry, namely, methyl alcohol and particularly formaldehyde. Even though the problem of producing methyl alcohol from natural gases on a scale helpful to industry appears to have been solved, the problem of large-scale transformation of methane into formaldehyde still seems to be awaiting solution.

In the following research work it was attempted to interrupt the oxidation of methane at an intermediate stage, i.e. at the oxidation of methane to formaldehyde, inquiring at the same time to which mechanism of reaction the oxidation was due.

It was moreover interesting to discover the influence exerted by the steam of the reaction of the slow oxidation of methane, a problem about which there are contradictory data in the literature on the subject.

Finally, as the temperatures of methane oxidation are relatively high and, on the other hand, as formaldehyde decomposes very easily at these high temperatures, it was important to determine the course of the thermal decomposition of formaldehyde for the experimental conditions in question.

(1) FIRST RESEARCHES.

The first accounts of the slow oxidation of methane in its mixture with oxygen were published by Bone and Wheeler (1). The authors heated pure methane in sealed glass tubes with the aim of studying its behaviour at hight temperatures. It appeared that it started to decompose only at 650°-700°C and that this decomposition was very slow. Then the authors heated the mixture of methane and oxygen in the volume ratio 2:1 in sealed glass tubes in a furnace for many days and weeks at temperatures varying from 300°-400°C and subsequently they made a number of analyses of the gases formed by the reaction. They determined CO_2, CO and residual O_2 and they calculated the amount of methane from the difference and of hydrogen from the contraction after an explosion of the mixture $CH_4+H_2+nO_2$. As the analyses did not show the presence of hydrogen, the authors came to the conclusion that the reactions

$$2CH_4 + O_2 = 2CO + 4H_2 \quad \text{or}$$

$$CH_4 + O_2 = CO_2 + 2H_2$$

did not occur but that probably there took place reactions of simultaneous oxidation of methane and hydrogen, namely

$$2CH_4 + 3O_2 = 2CO + 4H_2O \text{ and}$$

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

At 300°-325°C 3-6 % CO was formed and a corresponding amount of oxygen disappeared. At 350°C

16 % CO was produced and almost all the oxygen was used. In further experiments carried out at the same temperature 16·2 % CO and 10 % CO_2 were formed. At 400°C the production of 18-19 % CO and of 10-12 % CO_2 was much quicker, occuring after one day's heating and remaining unaltered on the following eleven days. In none of the experiments were traces of formaldehyde or formic acid found.

In later research the same authors (2) passed the same mixture of gases ($CH_4:O_2$ = 2:1) for several days and nights by means of a Sprengel's authomatic pump through a glass tube heated on one occasion to 450°C and on another to 500°C. Behind the furnace were placed wash-bottles with distilled water to absorb the products of the oxidation of methane and then the gases were conducted back so as to form a close cycle. The authors describe two of their experiments. In the first the gases were passed for 24 days and nights, the temperature of the furnace was 450°-455°C, 4·46 % CO and 9·84 % CO_2 were formed, 13 % CH_4 was oxidized to formaldehyde.and hydrogen was not detected. In the second, the velocity of the passage of the gas mixture was twice as great as in the first, the temperature of the furnace being 497°-500°C, 0·50 % CO and 19·85 % CO_2 were formed and 22 % of CH_4 was oxidized to formaldehyde. In the former and latter cycles the gas mixture was during single passage in contact with the furnace for 6 minutes and 3 minutes respectively.

In the second experiment considerable amounts of formic acid were detected. Hydrogen and methyl alcohol were not found in any of these experiments.

In the same manner Bone and his co-workers investigated first the slow oxidation of three other aliphatic hydrocarbons, ethane (3), ethylene (4) and acetylene (5), - and second the explosive oxidation of hydrocarbons by means of an electric spark (6). Finally, the influence of steam on the slow oxidation of ethylene and acetylene was investigated (7) and the investigators came to the conclusion that the moisture had little if any influence of the rate of oxidation of hydrocarbons.

During the slow as well as the explosive oxidations of hydrocarbons a certain amount of simultaneously formed aldehydes was formed, particularly in the case of saturated hydrocarbons. The aldehydes appeared also during the combustion of hydrocarbons in a flame in an atmosphere of oxygen or of oxygen mixed with neutral gases, such as N_2 and CO_2. The investigators noticed the difference between gas products formed in the case of unsaturated and saturated hydrocarbons, the former giving in the oxidation process mostly CO and H_2 in accordance with the equation

$$C_nH_{2n} + {}^{n}/_{2}\ O_2 = nCO + nH_2,$$

and the latter, mixed with oxygen in a stechiometric amount, producing fairly large amounts of CO_2 and

certain amounts of lower unsaturated hydrocarbons, methane etc.

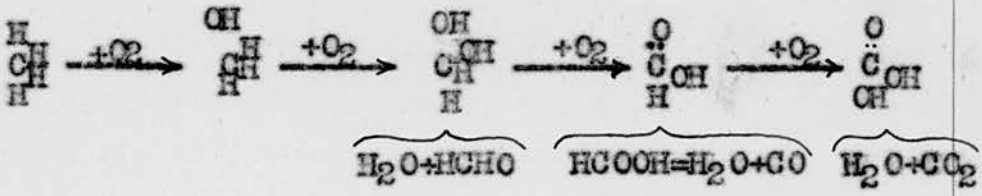
Attempts were also made to assist the oxidation of hydrocarbons by mixing a suitable amount of ozone with oxygen. These latter experiments (8) were conducted at 15°C and 100°C, and although formaldehyde and formic acid were found in "appreciable" quantities, they were not determined quantitatively. Methyl alcohol and hydrogen were not detected and the investigator stated that, the oxidation of methane to methyl alcohol being very slow, each amount of alcohol formed is immediately oxidized to aldehyde. On the other hand he considered that the unsaturated hydrocarbons are oxidized in such a manner that the double bound breaks down and products, mostly aldehydes, are formed which possess less carbon atoms than the previous compounds.

The amount of formaldehyde obtained by the above mentioned investigators was small, coming to less than 0·5 % of the methane involved in a single passage of the gaseous mixture through the furnace. This was also found to be the case in experiments which took the form of the combustion of methane in a flame or by means of an electric spare.

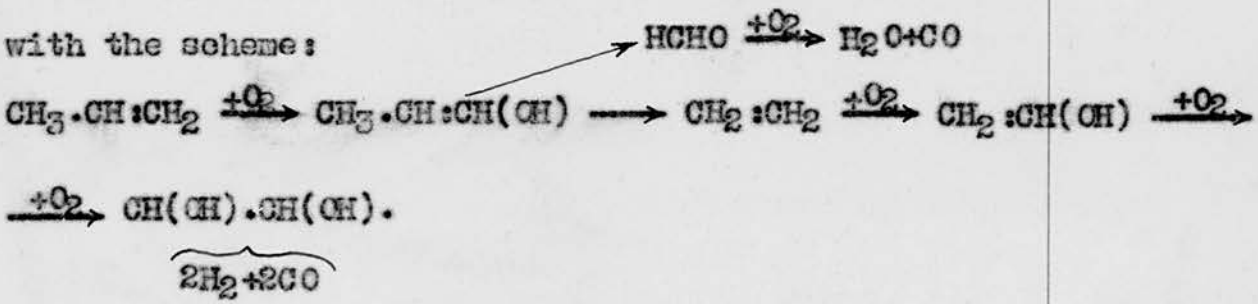
On the basis of the foregoing experiments Bone and his co-workers put forward the so-called "hydroxylation theory" of the oxidation of hydrocarbons (loc. cit. - 6 page 678). According to this theory

the oxidation of hydrocarbons occurs in many stages, during which the successive atoms of hydrogen attached to carbon atoms are replaced by an hydroxyl group, thus forming a product with one or more hydroxyl groups attached to one atom of carbon, and during which steam is seperated and corresponding alcohols, aldehydes etc. formed.

Thus in the case of methane oxidation was assumed to take place in the following manner:



and propylene, for instance, is oxidized in accordance with the scheme:



This theory clearly explained the fact that by the oxidation of saturated hydrocarbons large amounts of carbon oxide and steam are formed together with small amounts of carbon dioxide and aldehydes, and that by the oxidation of unsaturated hydrocarbon a relatively large amount of hydrogen is created - a phenomenon which was not observed by the analysis of gases after the oxidation of saturated hydrocarbons. On the other hand, this theory did not explain why, by the oxidation of, say, methane in atmospheric or near-atmospheric

pressure methyl alcohol could not be detected as the first stage of oxidation. Various investigators tried to explain this fact in different ways. Thus it was said by some (8) that the conversion of methane into methyl alcohol occurs very slowly but that the oxidation of methyl alcohol to formaldehyde is very quick, therefore each amount of methyl alcohol formed is converted immediately into formaldehyde. Others (13), after calculating the heat effect of each seperate stage in the oxidation of methane, deducted the constants of the equilibrium of this convertion on the basis of Nernst's heat theorem, and assuming that of the reactions which occur simultaneously or successively, those which have the highest constants of equilibrium have the greatest chance of occurrance, these investigators came to the conclusion that the reaction of the oxidation of methane to methyl alcohol is the most unlikely of all.

As mostly CO, CO_2, H_2 and H_2O were formed in the combustion of hydrocarbons in an explosive-pipette, C.W. Andrew (9) investigated the rate of the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ using gas mixtures of different composition. His experiments were carried out in such a way that the mixtures of hydrocarbons with oxygen were sealed in glass tubes provided with platinum wires, heated for 30 minutes at 130°C, cooled down, and afterwards brought to quick combustion by means of an electric spark. The shapes of the tubes were chosen so as to avoid detonation. After cooling the

change of gas pressure was measured and the composition of gases determined. The experiments were carried out with the following mixtures: CH_4+O_2, $2CH_4+3O_2$, $C_2H_6+O_2$, $2C_2H_6+3O_2$, $2C_2H_6+5O_2$, $C_2H_4+2O_2$, $3C_2H_4+5O_2$ and $2C_2H_2+O_2$. From the value of the constant $K_t=\frac{[CO][H_2O]}{[CO_2][H_2]}$ it followed that this constant is independent of the nature of hydrocarbon and of the original ratio between the amount of hydrocarbon and oxygen used, and that it is approximately equal to 4. After the combustion of unsaturated hydrocarbons methane was usually found and a large amount soot was deposited, but this latter fact was not observed after the combustion of methane.

(2) RESEARCHES INTO THE LARGE-SCALE PRODUCTION OF FORMALDEHYDE FROM METHANE.

Further researches were connected with the investigation of the slow oxidation of methane and natural gases with special regard to the large-scale production of formaldehyde. If the oxidation could be carried out in such a way that the successive stages

$$CH_4 \longrightarrow CH_3(OH) \longrightarrow HCHO$$

could be isolated, the economic value of such a method would be considerable, as methane is a cheap and widely distributed raw material. The petroleum industry produces methane in large quantities. Natural gases indeed vary greatly in composition, but in most cases they contain 85-95 % of lower aliphatic hydrocarbons, 9/10-th of which are methane. Cracking gas contains from 40 % (gas phase) to 80 % (liquid phase) of methane and methane is provided in appreciable amounts by the coal industry. Gas from coke-factories contains on the average 25 % of methane and gases from blast furnaces are a very cheap source of methane.

The problem of oxidizing methane to formaldehyde if not completely, yet to a high degree, was very difficult to solve. Although the thermal decomposition of methane starts only at 850°C (10), methane starts to oxidize appreciably at about 600°C. Pure formaldehyde, on the other hand, starts to decompose

at about 310°C and at 600-650°C 90 % of formaldehyde is already decomposed (127).

The first researches for the purpose of producing formaldehyde by the slow oxidation of methane were carried out by Wheeler and Blair (11). They applied a flow-method using a circulating apparatus already employed in the oxidation of ethylene (12). The temperatures of the furnace fluctuated between 600°C and 760°C and the times of contact of the gas mixtures with the furnace were 0·8-1·9 seconds. The investigators obtained the best results at temperatures between 700° and 720°C and when the time of contact of the gas mixture ($CH_4:O_2=1:1$) was 0·8-1·0 seconds. The amount of methane which was oxidized into formaldehyde in a single passage through the furnace was 0·40-0·43% of the methane used. By repeated passage and by the absorption each time of small amounts of formaldehyde in water beside the furnace, the investigators succeeded in oxidizing to formaldehyde 65 % of the methane used. In the gases after the reaction hydrogen was never detected but only carbon oxide, water and small amounts of carbon dioxide. On the basis of their previous experiments with ethylene (loc. cit. - 4) and acetylene (loc. cit. - 5) they came to the conclusion that the presence of catalysts and the influence of larger surface do not help the oxidation of hydrocarbons and methane. They only provoke a quick

decomposition of formaldehyde, because in the conditions of Wheeler and Blair's experiments the gases formed by the reaction contain more formaldehyde than corresponds to the equilibrium $HCHO + \frac{1}{2}O_2 \rightleftharpoons CO + H_2O$. In the presence of catalysts this equilibrium establishes itself immediately and almost the whole amount of the formaldehyde decomposes. In their summary the investigators come to the conclusion that the yield of formaldehyde from methane is inversely proportional to the temperature and to the time of contact of the gas mixture with the furnace, and if the time of contact is short an equimolecular mixture of CH_4 and O_2 gives better results, while if the time of contact is longer and the temperatures (in a suitable range) are lower, better results are obtained from a mixture with a proponderance of methane.

The experiments of Blair and Wheeler which were carried out for the purpose of discovering how formaldehyde must be produced by the slow oxidation of methane were not at all encouraging. If we represent the particular stages of the oxidation of methane according to Bone's hydroxylation theory, by the scheme:

$$CH_4 \xrightarrow{(a)} CH_3(OH) \xrightarrow{(b)} HCHO \xrightarrow{(c)} HCOOH \xrightarrow{(d)} CO+H_2O \xrightarrow{(e)} CO_2+H_2O$$

$$HCHO \xrightarrow{(b^1)} CO+H_2 \xrightarrow{(c^1)} CO+H_2O$$

the problem lies in stopping the oxidation at the

desized stage, i.e. after the reaction (b). The experiments showed however that methane shows much greater resistance to the action of oxygen than formaldehyde. The first starts to oxidize only at temperatures higher than 600°C, while the second decomposes at 310°C.

It follows, therefore, that if one wishes to obtain a suitable yield of formaldehyde, one must heat the mixture of methane and oxygen to a high temperature (higher than 600°C) in a very short period. In these conditions, however, a small amount of methane undergoes oxidation and the concentration of the formaldehyde formed is very low (about 0·25 mg./ L); hence the reactions (c), (d), (e), (b^1) and (c^1) have no practical value. It is clear that the investigators decided to carry out their experiments in closed circles, i.e. to pass the gas mixture many times through the hot zone and to cool it after each passage, recovering at the same time from the gas mixture the formaldehyde formed. Only in this way they succeeded in transforming into formaldehyde 65 % of the methane used. Although these investigations have had great theoretical value they have not led to a practical method of transforming methane into formaldehyde, because the small yields of formaldehyde formed by each passage of the gas mixture through the hot zone caused a great waste of thermal energy.

The practical conclusions which can be drawn from the experiments of Blair and Wheeler show that the production of formaldehyde by the oxidation of methane could have an economic value only if a catalyst could be found, which had the property of accelerating the rate of reactions (a) and (b) and at the same time diminishing (or at any rate not increasing) the rate of reactions (c) and (b^1).

Similar experiments with a flow-method were carried out by Berl and Fischer (13) who tried to establish an optimum for the yield of formaldehyde using the following parameters: a) temperature, b) time of contact of the gaseous mixture with the furnace, c) composition of the gaseous mixture. The authors' best result was a yield of formaldehyde of 0·48 % of the methane used at a temperature of 375°C and with the composition of gases $N_2:O_2:CH_4$ = 39·5:10·5:50. The investigators stated that on the addition to the gaseous mixture of small amounts of NO_2, (about 1-2 %), the methane started to oxidize at 350°C, but on account of the presence of HNO_2, HNO_3 and their salts they could not determine in the absorption wash-bottles the amount of formaldehyde absorbed. The efforts of the investigators to obtain better yields of formaldehyde by oxidizing methane with the help of sulphur dioxide and trioxide and by converting the small amounts of formaldehyde formed

into hexa-methyl-tetramine by adding ammonia to the gaseous mixture did not succeed.

At the end of their work the investigators express the opinion that if anyone can find a catalyst which could cause the oxidation of methane to formaldehyde at a temperature of about 450°C he could solve the problem of producing formaldehyde from methane on a large scale.

Further researches have been carried out in this direction. SS. Medvedev (14) tried as catalysts: Au, Pt, Mn_2O_3, NiO, Al_2O_3, CuO, Ag_2O, PbO and CeO, all of them on the foundation of asbestos. These catalysts did not give any satisfactory results at temperatures 350°C and 500°C, as the investigator obtained only CO and CO_2 without any traces of formaldehyde. The best results were obtained with lead phosphate and borate, as at 600°C the yield of formaldehyde was 5·04 % of the methane used.

Similarly T.E. Laying and Roy Soukup (15) oxized methane, ethane and natural gas with oxygen in the presence of catalysts. As small amounts of nitrogen oxide were added to the gas-mixtures, the absorption waters became acid, they were neutralised, the formaldehyde was destilled and its quantity determined in the receptor. The catalysts used were: Cu, Ag, CuO, Ag_2O, BaO_2, Pt and activated coal at temperatures 400-610°C. The only effect of the

catalysts was to cause a quick combustion of methane into CO, CO_2 and H_2O. By the addition of nitrogen oxides the yield of carbon oxides and water increased 30- fold in comparison with the yields without nitrogen oxides under more or less the same conditions of experiment. The addition of small amounts of hydrogen chloride had no influence at all on the composition of gases after the reaction.

From these researches one can draw the conclusion that the usual catalysts which increase the rate of oxidation, cause the oxidation of formaldehyde rather than the oxidation of methane and that they lead to the complete conversion of methane into carbon oxide, carbon dioxide and water.

Further attempts were made to choose such catalysts as, on the one hand could diminish the temperature of the oxidation of methane and, on the other hand, could slow down the oxidation of formaldehyde. For this purpose complex catalysts were tried. These were a mixture of oxidizing and reducing substances, the latter being intended to restrain the oxidation of formaldehyde. Thus Selden and Co. (16) proposed the use of phosphor pentoxide alone; C.P. Bryner (17) put forward complex mixtures, such as $MnO_2 \cdot Mn_2O_3$, $CoO \cdot MnO_2$ etc. and I.G. Farbenindustrie (18) recommends a mixture of phosphates and borates of metals formed by the precipitation of nitrates of cerium, cadmium and aluminium by disodium hydrogen phosphate.

Considering the successive stages of oxidation of methane on the basis of the hydroxylation theory, we observe that the first stages of oxidation, namely reactions (a), (b) and (c), are bound up with a decrease in volume, while the final reactions, namely (b^1), (d) and (e) occur with an increase in volume. Owing to this fact, the Doherty Research Co (19) recommends that after heating the mixture of methane and oxygen it should be passed through a tube with a smaller diameter, where reactions (a) and (b) may occur, and after that through a tube with a still smaller diameter for the purpose of preventing further oxidation of formaldehyde. This patent, however, although interesting from the theoretical point of view, seems never to have been adopted for practical work.

The fact that the addition of small amounts of nitric oxide to the mixture of methane and oxygen dimishes the temperature of the oxidation of methane gave rise to much research with the purpose of producing the greatest possible amounts of formaldehyde from methane and to numerous patents. This phenomenon was first obseved by A. Reis and O. Waldbauer (20). The investigators stated that by burning methane in air in a specially constructed burner not even traces of formaldehyde were formed, while by adding to the air certain amounts of nitrogen oxides they obtained

considerable ("beträchtliche") amounts of formaldehyde, which, however, they did not determine.

C.H. Bibb and H.J. Lucas (21) in their flow--experiments passed a mixture of natural gas and air (in the ratio 1:4·5) through a wash-bottle containing concentrated nitric acid at room-temperature and they stated that the amount of nitrogen oxides drawn off (1·65 mg./L) was sufficient to produce a "catalytic" effect. The authors obtained their best results at 730–745°C and when the time of contact of the gas mixture with the furnace was 0·06–0·18 seconds. In these conditions the yield of formaldehyde formed in relation to the methane passed was 3·6–4·3 %. The investigators state that the "catalytic" action of nitrogen oxides is more advantageous than the effect of solid catalysts, as the formaldehyde formed is more strongly adsorbed on the surface of the catalyst than the methane, and this is the cause of its being subjected to oxidation more quickly, even if the amount of oxygen is limited. A gaseous catalyst on the other hand allows intermidiate products of the oxidation, - one of which is formaldehyde, - to pass very quickly with the stream of gases and to leave the reaction zone before the oxidation is completed.

D.F. Smith and R.T. Milner (22) explain the catalytic action of nitrogen oxides differently. They tried to determine the optimum amount of nitrogen

oxides, which, added to the mixture of methane and oxygen, would produce better yields of formaldehyde and they added nitrogen oxides to cold, heated, and hot gases. As they obtained their best results by adding nitrogen oxides to cold gases, they expressed the opinion that a loose combination of methane and nitric oxide is formed which breaks in the reaction-chamber and thus allows formaldehyde and suitable lower oxides of nitrogen to form. By the addition of nitric oxide the investigators obtained yields of formaldehyde amounting to 0·6-3·4 % but without the addition of nitrogen oxides the yield fell to 0.0-0·2 % of formaldehyde in relation to the methane passed. The investigators used different nitrogen oxides (NO, NO_2, N_2O_3, N_2O_5), but the results of the experiments remained constant which ever gas was used. Finally, the investigators state that the presence of steam in the gaseous mixtures has no influence on the rate of oxidation of methane.

K. Frölich, P.J. Harrington and A.H. Waitt (23) tried to oxidize methane by using a flow-method with pure nitrogen peroxide (8-55 %) without either oxygen or air. The experiments were made with a reaction tube which was first empty and afterwards filled in turn with pumice, platinised asbestos, vanadium pentoxide, nickel wire and hopcalite. It was proved that the lowest temperature of oxidation of methane by nitrogen pentoxide was 430°C in an empty tube. The presence of pumice or catalysts raised

the temperature due to the hot spots formed. The yield of formaldehyde was 0·9-3·4 % in relation to the methane passed.

C.H. Bibb (24) repeated his previous experiments (21) with nitric oxide on a larger scale. He passed a mixture of natural gas and air (ratio 0·4:1) through 66 % nitric acid and afterwards through a tube of chrom-nickel steel heated to 735°C. He made his experiments with three modifications: (1) he passed the gas mixture only once through the reaction tube; (2) he passed the mixture succesively through four identical reaction-tubes, while beside each tube he placed a wash-bottle with water to absorb the aldehyde formed; (3) he passed the gases through a closed circulation circuit, adding suitable amounts of air and nitrogen oxides from time to time. In the first case the yield of formaldehyde in relation to the methane passed was 4·13 %, in the second case, 12·33 %, and in the third case, where the mixture circulated for a long time, he succeeded in transforming 40 % methane into formaldehyde. The ratio of nitric oxide used to the formaldehyde formed was 1: 2·36-2·97.

On the basis of all these experiments many patents were worked out. Bailey (25) suggests passing through a hot tube 1 volume of methane with 2 volumes of nitric oxide and with a sufficient amount of air to tranform the nitric oxide into nitrogen peroxide. But he adds that the purification of the product is a

troublesome matter.

Further patents were taken out by C.H. Bibb (26) and Gutehoffnungshütte Oberhausen A.G. (27). The latter firm uses a method of oxidizing hydrocarbons by air with the addition of nitrogen oxides, which has been employed for several years in the Sterkrade mine near Oberhausen; as the raw product gases from blast furnaces are used.

But the methods of oxidizing methane or natural gases respectively by means of pure oxygen or air--oxygen with the addition of nitrogen oxides were not adopted in industry, as is shown by the new American patents.

The firm Cities Service Oil Co. has developed an industrial process (28), by means of which it produces from natural gases considerable amounts of formaldehyde together with smaller quantities of acetaldehyde, acetone and other products without the addition of nitrogen oxides. The patents recommend the use of mixed catalysts which contain aluminium phosphate and metal oxides, provided the pressures are 7-20 atmospheres and the temperatures 430-480°C. The absorption wash-bottles may contain on the average 34-36 % metanol, 20-23 % formaldehyde, 5-6 % acetaldehyde and variable quantities of higher alcohols, ketones, aldehydes and water. The first factory devoted to this type of oxidation process was built

at Tallant, Oklahoma.

Studying these patents, however, one does not get the impression that the problem of the oxidation of methane or natural gases into formaldehyde, methanol, and other products needed by industry, is solved, as from the patents one cannot deduce what percentage of methane can be oxidized into these products. Rather one has the impression that the natural gases before consumption (i.e. before burning in the furnaces) are passed through installations which oxidize only a part of them into formaldehyde, metanol and other products, the rest of the methane being burnt unchanged.

This impression is all the better founded as in the newest process, patented by the Celanese Corporation (29), the favourite raw material is butane, which is after all much more expensive than natural gas. In the typical example which the patent cites, 1 volume (one part by weight) of butane is mixed with 110 volumes (34 parts by weight) of steam and 10 volumes (5 parts by weight) of air at a temperature of about 400°C and under a pressure of 300-400 lbs., and the reaction is quenched by water after one second. From 100 lbs of butane; 15·2 lbs. of formaldehyde, 19·6 lbs. of acetaldehyde, 7 lbs. of acetone, 19 lbs. of methanol, 1 lbs. of propane, 0·5 lbs. of butanol and 11·4 lbs. of organic acids are obtained. The formaldehyde and the organic acids remain in the absorption wash-bottles,

while the pure formaldehyde is obtained by refining this solution.

(3) THE THEORY OF CHAIN-REACTIONS AND THE OPPOSTION TO THE HYDROXYLATION THEORY.

The hydroxylation theory, which was worked out by W.A. Bone and his co-workers, was held for about thirty years, but afterwards new experimental facts were collected which could not be directly explained by this theory.

The observed data relating to slow oxidation reactions of hydrocarbons showed that they are proceeded by an "induction period" of several minutes duration, in the course of which only an exceedingly small measure of reaction can be detected by analytical methods. This induction period is then followed by a period in which the pressure increases, till finally the reaction is complete. At pressures around atmospheric, the first products detected by chemical means are methane, formaldehyde, ethylene, acetaldehyde and ethane.

This induction period was first observed by H.W. Thompson and C.N. Hinshelwood (30) on investigation of the slow oxidation of ethylene. The investigators used a static method and observed at a temperature of between 400°C and 500°C the increase of pressure resulting from the reaction: $C_2H_4+O_2 = 2CO+2H_2O$. They proved that, in the slow oxidation of ethylene, the rate of reaction depends much more on the concentration of ethylene than that of oxygen. The induction period

took several minutes and was shortened by the presence of nitrogen or argon. To explain this phenomenon the authors supposed that the induction period may depend upon the initial production of some kind of peroxide, probably the unstable $C_2H_4:O_2$, due to a collision between ethylene and oxygen molecules. The effect of argon in shortening the induction period seemed to depend upon the order in which the various gases were admitted to the reaction bulb, being greatest when oxygen was admitted last. It is conceivable that the varying conditions of concentration or even the varying degrees of adiabatic compression associated with different orders of admission of the gases might influence the initial concentration of the unstable substance. It should be noted that in the absence of argon or nitrogen the order of admission of ethylene and oxygen had no influence.

Similar results were obtained by R. Fort and C.N. Hinshelwood (31) on investigation of the slow oxidation of gaseous benzene. Using a static method they observed that when the benzene and oxygen were admitted to the reaction vessel the pressure changed only very slowly at first, but that after an apparent period of induction (about 3·5 to 5 minutes), it rose rapidly. Their explanation of this behaviour was that the existence of the induction period is not so much due to an initial inhibition of the oxidation, as to the

fact that the first oxygenated products, which had a phenolic smell, were formed without any pressure increase, and that only the subsequent stages of the reaction were shown on the manometer. The investigators assumed that hydroxylation of the double bond occurred, followed by rapid further oxidation of the open chain unsaturated compounds so produced to a substance like glyoxal. Since, however, the practical pressure of this intermediate substance was estimated not to exceed about 5 mm. at normal temperature, investigation of its nature was not carried out. In other words, there occurred a primary oxidation to a product which was possible phenolic but which did not accumulate, being rapidly oxidized further by a mechanism resembling the oxidation of ethylene. When a silica bulb was used, filled with cylindrical silica with a surface several times greater, the induction period was somewhat shortened by the packing.

The influence of foreign gases on the rate of combination of hydrogen and oxygen was very marked indeed. In the reaction of ethylene and oxygen their influence was very much smaller. With benzene and oxygen the addition of an equal volume of nitrogen or argon caused an acceleration of about 20 % only.

The rate of reaction varied according to the high power of the benzene concentration; and a high ratio of benzene to oxygen favoured rapid oxidation. Over

a certain range, increase in the oxygen concentration may retard the reaction, though in another range the rate increases with the oxygen concentration.

In their later experiments carried out with a static method, R. Fort and C.N. Hinshelwood (32) investigated the slow oxidation of methane, methyl alcohol and formaldehyde. It was observed that the initial concentration of methane, and in a smaller degree of methyl alcohol and formaldehyde, exerts a great influence on the rate of oxidation, while the initial concentration of oxygen has a much smaller influence. In the oxidation of methyl alcohol, and in particular of methane, an induction period was observed, which lasted in the case of methyl alcohol about 100 seconds and in the case of methane more than two minutes and during which the pressure remained constant. The authors, explanation of this behaviour was that unknown intermediate products accumulate until the velocity of their formation is equal of their decomposition and that only when this point is reached conditions become stationary and the proper reaction of oxidation can start. The oxidation of formaldehyde did not show any induction period at all and the investigators explained that this was due to the formation of formic acid, a very stable compound, as an intermediate product.

The second phenomen~~on~~ which could not be explained

by the hydroxylation theory was the large influence of the surface of the experimental vessels on the rate of slow oxidation of hydrogen and hydrocarbons.

This fact was stated first by C.N. Hinshelwood and H.W. Thompson (33). The authors investigated the velocity of the contraction of oxygen and hydrogen at temperatures a) below or not much above 500°C and b) in the region of 550°-650°C. In the first series of experiments it was shown that the reaction was very much accelerated by the presence of powdered silica in the experimental bulb. The second series proved that the rate of the reaction was greatly diminished if the bulb was packed with powdered silica. In their latter experiments two special bulbs were made and completely packed with spherical silica beads. In each of these bulbs the reaction proceeded extremly slowly at temperatures far above that at which explosion would have occurred in an empty vessel.

Similar observations were made by the investigators who examined the induction period during the slow oxidation of hydrocarbons and who have already been cited above. Thus H.W. Thompson and C.N. Hinshelwood (loc. cit. - 30), when observing the rate of the slow oxidation of ethylene, showed that when ethylene was introduced to the packed vessel at 460°C a rapid though small increase in pressure was observed, which continued for a short time after the admittance of

oxygen and, as gas analysis showed, was due to the decomposition of ethylene on the hot surface ("hot spot") of the silica spheres. This decomposition, although occuring to some extent in all experiments, was hardly measurable in an empty vessel. When 300 mm. ethylene were allowed to remain at 450°C for 30 minutes, - longer than would be required for complete oxidation in the ordinary way - analysis showed that less than 2 % had been decomposed. In another experiment the reaction velocity - as measured by the percentage of the total pressure increase occurring in a given time - was far less than in an empty bulb. It was clear that the oxidation of ethylene was considerably retarded, for analysis always showed considerable amounts of unchanged ethylene and oxygen after long periods, Thus in an empty bulb at 450°C 100 mm. ethylene and 200 mm. oxygen would have combined completely in 10 minutes, whereas in the sphere packed bulb there was 53·5 % of unchanged ethylene after 30 minutes.

During the examination of the slow oxidation of gaseous benzene, when F. Fort and C.N. Hinshelwood (loc. cit. - 31) used a silica bulb which was completely filled with small spheres of silica possessing a very large surface indeed, an abnormal reaction predominated. The results were erratic; there was a decomposition of the benzene, the proportion of CO_2 was increased,

and the total rate of reaction was decreased, temperatures about 40°C higher having to be employed to obtain rates comparable with those found in the other bulbs.

Almost the same behaviour was observed in the case of the slow oxidation of methyl alcohol. Two series of experiments were made by R. Fort and C.N. Hinshelwood (loc. cit. - 32). In the first series and empty vesse A of silica was used, and in the second series - a vessel B of almost the same size but entirely filled with silica tubing. The half life of the methyl alcohol (i.e. the time required for oxidation of 50 % alcohol passed initially into the vessel) was observed. The results were as follows: half life in vessel A (minutes): 3·5 3·5 3·5 3·9 half life in vessel B (minutes): 17·8 14·2 16·6 17·6. As the silica of the vessels was of different origin the investigators made several bulbs from the same silica, the length of the bulbs being equal, but the diameter varying from 7·5 cm. to 1·8 cm. The results showed that the surface of the bulbs exerted a very marked influence on the rate of the reaction.

Temperature	Time required for reaction between 20 % and 80 % (minutes)			
	7·5 cm. diameter	4·9 cm. diameter	3·2 cm. diameter	1·8 cm. diameter
427°C	6·6	25·5	59	Too long to measure
447	1·7	13·0	25·4	No experiment
463	0·80	4·8	14·6	Anomalous - 3·3.

It may be noted that the actual nature and condition of the walls of the reaction vessels have a considerable influence. In the case of methyl alcohol, for instance, the rate of the reactions depended upon the layer of oxygen adsorbed by the walls of the bulbs; and the probability that surface adsorption relations play a part would account for the considerable divergences in the behaviour of different substances.

The observed data relating to slow oxidation reactions of hydrocarbons and some alcohols show that their velocities are reduced by an increase in surface and that their ouset is proceeded by an induction period of several minutes duration in the course of which only an exceedingly small measure of reaction can be detected by analytical methods. The hydroxylation theory, while adequately accounting for the analytical data, does not, however, take account of the induction period nor does it explain the remarkable inhibition of the slow combustion produced by an increase in surface. Then again it is remarkable that it has consistently been proved difficult to demonstrate analytically the primary formation of an alcohol in hydrocarbon combustion at low pressures as required by the hydroxylation theory. Other facts which are not explained by the hydroxylation theory are the sharp kinetic limit of explosion (34) and the effect of the variation of the diameter of the

reaction vessel on the ignition temperature (35).

The above mentioned facts, together with some observations of photochemical reactions (examination of molecules transformed for each quantum, investigation of the sensitivity of the reactions to inhibitors) inspired the creation of a new theory, the theory of chain reactions. This theory is based on the following considerations:

Concerning the nature of a gaseous state, it is known that molecules of a gas are in rapid motion (thermally agitated) and collide frequently with each other. Thus in air under ordinary conditions an oxygen molecule collides with nitrogen molecules some billion times per second, but escapes from every collision without having reacted to form an oxide of nitrogen. This must be expected on the ground of thermodynamics, because molecules of nitrogen and oxygen are more stable than their compounds; but the stability of a mixture of hydrogen and chlorine molecules, for instance, is less so. The reaction product, HCl, is more stable than the mixture of hydrogen and chlorine molecules. Such a mixture, however, may be stored for a very long time without changing its characteristics; in other words, a molecule of hydrogen undergoes untold billions of collisions with molecules of chlorine without ever breaking up to form HCl. If, however, a number of

atoms of chlorine or hydrogen are introduced into the mixture as, for instance, by illumination with light of determined wave-length which can dissociate chlorine molecules, a reaction sets in which may assume even an explosive rate, being completed in a time to short to be measured. The sequence of reactions is then:

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$

$$Cl + H_2 \longrightarrow HCl + H$$

$$H + Cl_2 \longrightarrow HCl + Cl \text{ etc.}$$

The quantum efficiency of HCl formation may under suitable conditions run to 10^6 molecules of HCl formed per quantum of light energy absorbed.

This type of reaction is referred to as chain reaction. One single atom would thus seem to be able to bring about in a definite time the reaction of the whole contents of a vessel filled with molecules of hydrogen and chlorine, but this is not the case, because the chain may be broken by removal of the atom, notably at surfaces like the walls of the vessel or objects present in it, where atoms can be rendered ineffective by adsorption, and because sometimes two atoms combine to form a neutral molecule.

Under certain circumstances, when enough energy is available and possibly other more specific conditions are satisfied, each elementary reaction may induce more than one new reaction (36 and 37). Thus the number of active centres present at any

moment tends to increase, and would increase indefinitely unless the rate of deactivating processes, such as molecular collisions or adsorption by the walls of the vessels, balanced the rate of production. If the number of fresh chains starting in unit time is greater than the number which can be broken, then explosion results; if, on the other hand, the two rates become equal, then a stationary state is established and the reaction proceeds with a measurable velocity depending on the length of the chains. The balance between the rate of production of fresh centres and the rate of deactivation depends upon the concentration. In thermal reactions the operation of a chain mechanism is revealed by retardation of the transformation by an increase in surface of the containing vessel, acceleration by inert gases which hinder the active centres from reaching the walls but which hinder at the same time collisions of the activated bodies, and an abnormally great influence of pressure or temperature on the reaction rate.

Sometimes a chain can be branched. If, for instance, the other component of the hydrogen mixture is not chlorine but oxygen, a significant difference at once becomes apparent. For, unlike the chlorine atom, the atom of oxygen released in the reaction: $H + O_2 = OH + O$ possesses not one but two free valencies and the product of the reaction, OH, is not

a neutral molecule like HCl, but a free radical possessing one free valence. Hence by the subsequent reactions:

$$1) \quad H + O_2 = OH + O$$

$$2) \quad O + H_2 = OH + H$$

$$3) \quad OH + H_2 = H_2O + H$$

the original hydrogen atom entering into reaction with an oxygen molecule is not only regained, but two more hydrogen atoms are formed, capable of starting two new chains. The chain, therefore, is branched and even though atoms of hydrogen and molecules of oxygen etc., as is known, often collide ineffectively, it almost envelops the whole gas-mixture in explosive reactions, unless by sufficiently rapid chain-breaking process all the branches and also the original chain are suppressed.

A high temperature greatly increases the fraction of effective collisions of atoms (or radicals) and they, as chain carriers, are not adsorbed by the vessel wall as rapidly as is required to prevent the chains from continuing and branching. When the pressure is low (i.e. when relatively few molecules are in the vessel) there occur relatively few collisions of the chain carriers with molecules of gas inside the vessel compared to collisions with the wall, particularly if a small or narrow vessel is used in which chains may be broken more frequently than they are continued and branched. By packing a vessel with

fragments of some otherwise inert materials, the branches could be suppressed altogether. The existence of chains in the gas-phase also depends on the nature of the vessel's surface, because a chain is broken only when at the zone of contact with the chain carrier, the wall has sufficient adsorptive power. Surfaces of even the same materials differ greatly from each other in this respect and may also undergo obscure changes, which make systematic observation of the processes in the gas-phase difficult. This was especially proved by G. von Elbe and B. Lewis (38) by study of the slow combustion of hydrogen in an atmosphere of oxygen.

Some surfaces (notably clean quartz, various clean glasses and boric acid) do not retain the activated molecules and atoms (or free radicals) readily and allow a substantial fraction of them to return to the gas-phase, where they have again a chance of reacting with molecules of gases present in the vessel. This effect is characteristic of surfaces which have a chainbreaking efficiency ε, defined as the inverse of the number of times a chain carried must on the average contact the surface before being destroyed, smaller than the ratio λ/d (where λ is the mean free path of the molecule between two collisions, and d is the diameter of the vessel). Such surfaces permit a substantial fraction of chain carriers in their vicinity to escape in the gas-phase to a greater

extent the smaller ε is, while only a negligible fraction escapes from surfaces if ε is large compared to λ/d. Surfaces of the latter type may adsorb much poison without noticeable increase of the reaction rate, because, λ/d being usually of the order of 10^{-3} to 10^{-5}, ε may decrease from unity to 10^{-3} or less without appreciable effect on the chain-breaking rate. Such surfaces are obtained by coating quartz or glass which is resistant to high temperature and is unaffected by the molecules present in the vessel, but whose chemical nature seems to be otherwise unimportant, since KCl, $K_2B_2O_4$, $K_2B_4O_7$, $BaCl_2$ and Na_2WO_4 have been found equally effective. The reaction rates in such salt-coated vessels do not increase the course of reaction and are much smaller than rates in vessels of clean quartz, glass etc. They are reasonably identical for various salt coatings under otherwise identical conditions, differences being attributed to varying catalytic efficiencies in the surface decomposition of activated molecules and to a lesser degree in the reaction forming these activated molecules. The two latter reactions are of consequence only when the chains are short; therefore under conditions of slow reaction the rate differs somewhat more, when certain other coatings are used. In clean or boric acid coated vessels the rates are not only large and self-accelerating but also erratic, varying usually from experiment to experiment, due to obscure and hardly controllable

surface changes. Such erractic results were obtained by C.N. Hinshelwood and H.W. Thompson (loc. cit. - 33), G. von Elbe and B. Lewis (loc. cit. - 38), R.N. Pease (39), M. Prettre (40), S.K. Chirkov (41) and others.

Further development of the chain reactions theory was due to J.A. Christiansen (42). He pointed out that the molecules of the reaction products just after the reaction possess an available energy greatly in excess of the average energy at the temperature considered. Not only do they contain the energy necessary for the reaction to occur, but also, as is well known, they very often cause the reaction to be accompanied by an evolution of heat, which must appear in the molecules resulting from the reaction as kinetic energy, or potential energy easily transformable into kinetic. Now these very "hot" molecules have sufficient energy to activate molecules of the reactants at the first encounter, and when these react, the resultants in their turn are again able to act as activators and so on. Consequently, it is possible that the occurrence of one elementary reaction will give rise to a whole series of reactions. Christiansen assumes that negative catalysts are substances that have the power of breaking the reaction chains thus set up by capturing energy from the "hot" molecules of the reaction products, or by reacting with them in some way or another. As negative catalyst produce the same characteristic effects in photochemical, as well

as in thermal reactions, Christiansen put forward the view that some thermal reactions are also chain reactions.

To justify this view, H.L.J. Bäckström (43) studied the rates of oxidation of benzaldehyde, enanthaldehyde and solutions of sodium sulphite both in monochromatic light and in the dark. In every case it appeared that the photochemical reaction was a chain reaction. Both the photochemical and the thermal reactions showed negative catalysis and there was a marked parallelism between them as regards the action of different inhibitors. Bäckström concludes that the mechanism of the thermal reactions is similar to that of the photochemical reactions and, consequently, that these reactions are examples of thermal chain reactions.

Parallel with the theory of chain reaction a new theory has been developed, the so called peroxidation theory.

In 1927 H.L. Callender (44) on the basis of his experiments on the oxidation of hexane and higher hydrocarbons, came to the conclusion that the initial stage of oxidation involves, contrary to Bone's hydroxylation theory, the formation of an alkyl peroxide rather than of an alcohol, by the direct incorporation of oxygen molecules in the hydrocarbon molecule and that after direct collisions such peroxide splits, subsequently giving rise to the

formation of aldehydes and water as decomposition products.

A.C. Egerton and W. Gates (45) studied the combustion of hydrocarbons below their ignition temperature and showed that the effect of inhibitors (such as phenol or aniline) on the gaseous oxidation process appears to be similar to their effect on the oxidation of benzaldehyde observed by J.L.J. Bäckström (loc. cit. - 43 , see note on the previous page). They conclude, therefore, that the mechanism of oxidation in both cases is the same, and that "in the combustion of hydrocarbons, bodies of a peroxide character are formed and these act as centres from which chains are propagated."

A general explanation of gaseous combustion was deduced by A.C. Egerton (46) as follows: reaction will commence when a sufficiently energetic molecule of hydrocarbon combines momentarily with an energetic oxygen molecule. A temporary peroxide in a highly energetic state is thereby formed. Among the several possible changes which may result, a breakdown into an aldehyde and a water molecule is quite a likely one. These molecules would possess not only the initial energy of activation but also the reaction energy and on their next encounter with other hydrocarbon molecules or oxygen molecules could communicate sufficient energy to enable combination to occur and so start a reaction chain. Such a mechanism would

explain why the initial stages of combustion are so influenced by concentration.

In 1929 H.W. Thompson and C.N. Hinshelwood (loc. cit. - 30) proposed a modification of the Egerton's peroxydation theory. By studying the slow oxidation of ethylene they concluded that the initial act in the oxidation is a collision between ethylene and oxygen giving the unstable peroxide C_2H_4OO, thus providing active centres from which reaction chains proceed. If this peroxide collides with another ethylene molecule, the oxygen is shared and two active hydroxylated molecules, e.g. $\overset{CHOH}{\underset{CH_2}{\ddots}}$, are produced, and so continues the chain. If, however, the peroxide collides with oxygen it may either be decomposed or oxidized completely to stable products which break the continuity of the chain. In such a way Thompson and Hinshelwood tried on a basis of chain reactions theory to build a bridge between Bone's hydroxylation theory and Egerton's peroxidation theory.

A further modification of Egerton's peroxidation theory was put forward by M. Bodenstein (47). The experiments of his co-workers, von der Hellen, Paetsch, Titschack and Lange, which were started as early as 1919, showed that the acetaldehyde did not oxidize to acetic acid but to peracetic acid, CH_3COOOH, which only in the further stages of the reaction was decomposed into aldehyde.

Such a general scheme is in a good agreement with

the experiments of the slow oxidation of acetylene (48), of ethylene (loc. cit. - 30), of benzene, methane and formaldehyde (loc. cit. - 31) and acetylene (49).

W.A. Bone and his co-workers then studied in a detailed manner the nature of the induction period and of the reaction period in a large range of temperatures and pressures. W.A. Bone and R.E. Allum (50) observed the slow oxidation of methane at atmospheric pressure by the stationary method using the same apparatus as on the investigation of ethane (51). Using experimental mixtures $3CH_4 + O_2$, $2CH_4 + O_2$, $CH_4 + 1{\cdot}86\ O_2$ at temperatures 423°-447°C they unvariably observed a marked induction period during which little or no perceptible pressure or other change occured in the system. No sign of any peroxidation could be detected either during induction period or at any subsequent stage of the oxidation, although the most delicate means for its detection were employed. Both the induction and reaction periods were considerably retarded by packing the reaction vessel with fragments of silica, but both were accelerated by introducing a small percentage of water vapour into the dry system, and the induction period was entirely obliterated and the reaction accelerated by the introduction of 2 % either methyl alcohol, formaldehyde, iodine or nitrogen peroxide

vapour.

The $2CH_4 + O_2$ mixture, and not the $CH_4 + O_2$, was found to be the most reactive of all methane-oxygen mixtures.

The next work of Bone and his co-workers was represented by D.M. Newitt and A.E. Haffner (52). Considering the stoichiometric and thermal aspects of the formation of methyl alcohol, formaldehyde and formic acid:

$$2CH_4 + O_2 = 2CH_3OH + 2 \times 29730 \text{ cal.}$$

$$2CH_3OH + O_2 = 2HCHO + H_2O + 2 \times 20640 \text{ cal. and}$$

$$2HCHO + O_2 = 2HCOOH + 2 \times 81540 \text{ cal.},$$

they observed that while methyl alcohol and formic acid are formed with a contraction in volume, formaldehyde involves an expansion. Consequently the effect of increasing the pressure in a reacting system of methane and oxygen would be to favour the survival of alcohol and acid at the expence of formaldehyde. As an increase of temperature would accelerate all three reactions and tend to promote the complete oxidation of methane, a combination of high pressure with as low a temperature as possible would probably favour the survival of the alcohol. The effect of increasing pressure would be to speed up the reaction and an additional advantage is thereby gained since it becomes possible to work at much lower temperature than would otherwise be possible. Precautions were

taken to dissipate the heat evolved during the reaction so that no considerable rise in temperature occurs; this was done by diluting the initial methane--oxygen mixture with a large excess of methane, nitrogen or carbon dioxide, and the initial mixture employed have had the composition $2CH_4 + O_2 + 6\text{-}6{\cdot}5X$, where X was one of the diluents.

The investigatiors worked with a stationery method at temperature between 340° and 375°C and at pressures ranging from 10 atm. to 150 atm. The reaction vessel was connected to an expansion chamber of a capacity of 2 litres which contained wash water. When it was desired to stop the reaction the content of the reaction vessel was expanded into the expansion chamber; the gases and vapours remaining in the reaction vessel were passed through two cooling coils surrounded by ice and through a scrubber containing distilled water; gas samples for analysis were taken between the cooling coils; the contents of the cooling coils, scrubber and expansion chamber were mixed and aliquot parts used for the determination of methyl alcohol, formaldehyde and other products. The quantitative estimation of methyl alcohol was carried out by the method of Fischer and Schmidt which consisted in converting the alcohol to methyl nitrite, hydrolysing the ester in presence of acid potassium iodide and estimating the iodine liberated by means of

standard sodium thiosulphate.

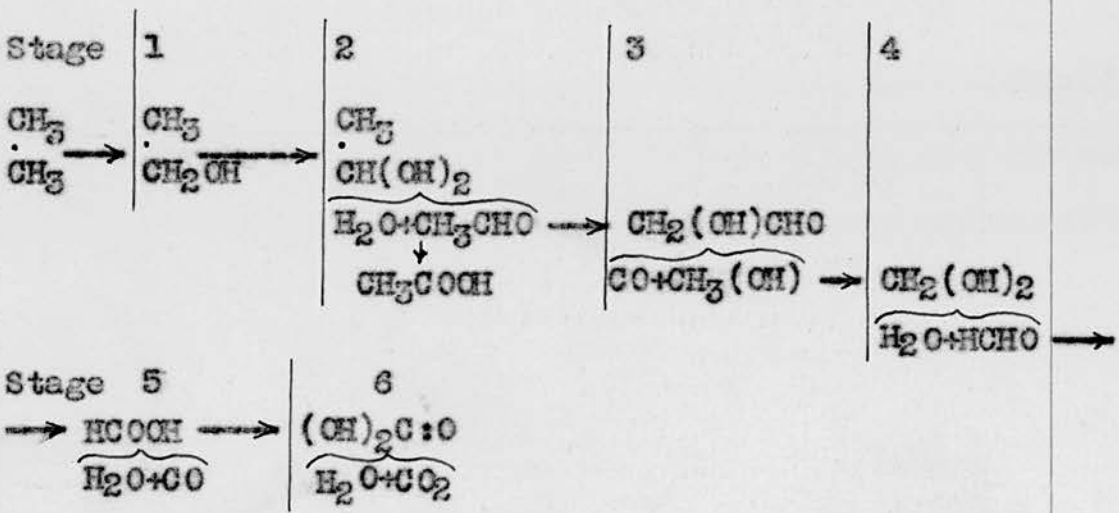
In one of the series of experiments the amount of methyl alcohol isolated and determined was 13 % and 22 % at pressure of 48 atm. and 106 atm. respectively of the methane burnt (corresponding to the 1·75 % and 1·4 % respectively of the methane initially introduced in the reaction vessel). The formation of methyl alcohol was accompanied by small amounts of formaldehyde and the ratio of $CH_3OH/HCHO$ was 13·0, 31·5 and 41·6 at pressures 48·2 atm., 106·4 atm. and 150·4 atm. respectively.

The diluents, irrespective of whether they were inert gases or the non-combustible products of combustion, slowed down the rate of reaction to such an extent that in order to obtain times of reaction comparable with those for the $2CH_4 + O_2$ mixture it was necessary to employ temperatures nearly 20°C higher.

Prof. W.A. Bone summarised the results of the above described experiments stating that there was a direct hydrocarbon oxidation entirely uncomplicated by any sign of peroxidation, in which 1) the most reactive mixture corresponded with the alcohol-forming proportion, 2) substantial quantities of the alcohol have been isolated at high pressure favouring its stability and survival and 3) all other happening fulfilled the prediction of the hydroxylation theory.

With the same apparatus D.M. Newitt and A.M.

Bloch (53) carried out their experiments on the slow oxidation of ethane at high pressures. The composition of ethane-oxygen mixtures varied in different experiments between the limits $(85\text{-}90)C_2H_6:(15\text{-}10)O_2$, the temperatures being 260°-315°C and the pressure varying from 10 atm. to 100 atm. In one of the experiments not less than 36·5 % of the total carbon of the ethane burnt was found in the products as ethyl alcohol, another 20 % as methyl alcohol, 8 % more as acetaldehyde, 6·5 % as acetic acid, besides smaller proportions as formaldehyde and formic acid. These products illustrated the six stages in the oxidation of ethane according to the hydroxylation theory:



The general influence of an increase in the reaction pressure was favourable to the survival of such products, as ethyl alcohol, acetaldehyde and acetic acid, which did not involve any disruption of the bond between the two carbon atoms of the ethane burnt;

conversely a lowering of the pressure tended to promote such disruption and to favour the formation or survival of methyl alcohol, formaldehyde and formic acid. No trace of peroxide was ever detected and these experiments very strongly support the hydroxylation theory and are against the peroxidation theory.

In addition to the experiments of Bone and his co-workers on the Egerton's peroxidation theory, other investigators showed that the mechanism of a slow oxidation of hydrocarbons does not agree with this theory. Thus, R.N. Pease (54), who studied the slow oxidation of propane and butane in various conditions, showed that in these reactions which give every indication of being a chain reaction molecules of oxygen do not directly react with molecules of hydrocarbons. If these reactions are suppressed by a broken-glass packing, especially when this is coated with potassium chloride or when the diameter of the reaction vessel is very small, propane or butane do not react with oxygen appreciably until the temperature is raised to such a point that cracking of the hydrocarbon occurs. A similar result has been obtained with benzaldehyde and formaldehyde by P.J. Askey (55). From the work which has been done by Pease (loc. cit. - 54), by F. Gill, E.W.J. Mardles and H.C. Tett (56) and by J.C. Pope, F.J. Dykstra and G. Edgar (57) it appears not only that aldehydes are

intermediate products of the oxidation of various hydrocarbons, but also that they exhibit, when oxidized themselves, characteristics such as luminescence and sensitiveness to inhibitors which are typical chain reactions. Pease (loc. cit. - 54), therefore, concludes that the aldehyde oxidation is the basis of a chain mechanism for the oxidation of hydrocarbons. It should, however, be pointed out that whereas Gill, Mardles and Tett (loc. cit. - 56) in studying the oxidation of hexane came to the conclusion that the luminescence was due not to the intermediate formation of aldehydes but to the formation of primary peroxides of hexane, Pope, Dykstra and Edgar (loc. cit. - 57) in studying the oxidation of octane, heptaldehyde and butyraldehyde stated that the existence of luminiscent chain reactions corresponds apparently to the oxidation of the aldehydes, carbon monoxide and water.

Various schemes have been suggested for the thermal oxidation of hydrocarbons at higher temperatures. The first stage was suggested to be the dissociation of hydrocarbon molecules in free radicals and atoms of hydrogen (a dehydrogenisation). These free radicals could form unsaturated hydrocarbons. The second stage was the combination of the latter with oxygen to produce unstable peroxide and the third stage consisted in the decomposition of the peroxides to aldehydes, which were farther oxidized to water and

oxides of carbon if the mixtures were rich in oxygen (58).

F.O. Rice (59) made an attempt to describe the mechanism of the decomposition of paraffin hydrocarbons based on the primary formation of free radicals. For example, a methyl group formed in the primary decomposition is assumed to take a hydrogen atom from one of surrounding hydrocarbon molecules to form methane; if the hydrocarbon has several carbon atoms, the free radical thus formed will be unstable and will break down into a olefin and a smaller free radical, which then in turn will take a hydrogen atom from the surrounding hydrocarbon; in this way the chain is continued. L. Belchetz (60) showed that methane decomposes at 1000°C into CH_2 radicals and hydrogen molecules, the radicals being detected by their subsequent reaction with iodine to give methylene iodide.

On the basis of these experimental Data R.G.W. Norrish (61) advanced a new hypothesis, which he called "atomic chain hypothesis," concerning the slow oxidation of hydrocarbons. He modified the hydroxylation theory asserting that the hydrocarbon is supposed to react with atomic oxygen to form initially a complex $[RCH_3O]$ which could stabilise to alcohol at the surface or on other suitable conditions, but which normally break down to the radical RCH and water, so that for methane the process was visualised as follows:

$$O + CH_4 = [CH_4O] = CH_2 + H_2O$$

$$CH_2 + O_2 = HCHO + O,$$

and the chain was carried along alteratively by the radicals CH_2 and the oxygen atoms. The chain is terminated by formation of methyl alcohol and oxygen molecules:

$$O + CH_4 + X = CH_3\,OH + X \quad \text{and}$$

$$O + \text{Surface} = \tfrac{1}{2}O_2.$$

The oxygen atoms were supposed to be formed initially at the surface by oxidation of aldehyde to an unstable peroxide, which then decomposed into acid and atomic oxygen:

$$RCHO + O_2 = \left[RCOOOH\right] = RCOOH + O.$$

Norrish stated that there is a little difference between Bone's hydroxylation theory and his new hypothesis, because the reaction according to the first can be written

$$CH_4 + \tfrac{1}{2}\,O_2 = CH_3OH \xrightarrow{+O_2} HCHO,$$

and to the second in the form:

$$CH_4 + O \longrightarrow \begin{cases} CH_2 \xrightarrow{+O_2} HCHO + O, \\ H_2O \end{cases}$$

all the more so as Bone and Davies (62) in their experiments on the decomposition of methyl alcohol came to the conclusion that at low temperature methyl alcohol decomposes in CH_2+H_2O. The two schemes are then mutually consistent, assuming that a collision between an oxygen atom and methane molecule produces a complex CH_4O which may either split to CH_2+H_2O, giving rise to reaction chains, or become stabilized to alcohol by a ternary colision, i.e.,

$$CH_4+O = (CH_4O) \longrightarrow \begin{cases} CH_2+O_2 \longrightarrow \underline{\text{chain process}} \\ H_2O \end{cases} \quad \underline{HCHO+O}$$

$$(CH_4O) \xrightarrow[\text{colision}]{\text{Ternary}} CH_3OH \xrightarrow{+O2} HCHO+H_2O.$$

A new hypothesis was suggested by A.R. Ubbelohde (63). The scheme commences from the aldehyde oxidation mechanism propsed by L.J. Bäckström (64) in the following form:

$$RC(=O)H \xrightarrow{\text{activation}} RC(-O)H$$

This activated molecule becomes able to rob a hydrogen atom from a neighbouring aldehyde molecule:

$$RC(-O)H + RC(=O)H \longrightarrow RC(-OH) + RC(=O).$$

This acyl-radical annexes an oxygen molecule and so created peroxide-radical dehydrates in an analogous way a molecule of aldehyde:

$$RC(=O) + O_2 \longrightarrow RC(=O)(O-O-)$$

$$RC(=O)(O-O-) + RC(=O)H \longrightarrow RC(=O)(O-OH) + RC(=O)$$

and the chain is propagated by the radical RC=O. Ubbelohde developes a number of rather complicated chain mechanisms for hydrocarbon oxidation, the chain being propagated by the radical RCH_2 and the peroxidic body RCH_2OO:

1) $$RC(=O)(O-O-) + RCH_3 \longrightarrow RC(=O)(O-OH) + RCH_2\cdot$$

2) $$RCH_2 + O_2 \longrightarrow RCH_2(O-O-)$$

3) $RCH_2{<}^{O-O-}$ + $RCH_3 \longrightarrow RCH_2{<}^{O-OH}$ + RCH_2.

The change: $RCH_2{<}^{O-O-}$ + X $\longrightarrow$ X + $RC{<}^{=O}$ + H_2O

may also take place to continue the change, following by either $RCH_2{<}^{O-OH} \longrightarrow RC{<}^{=O}_{H} + H_2O$

or $RCH_2{<}^{O-OH} \longrightarrow RCH_2{<}^{O-}$ + OH

with $RCH_2{<}^{O-}$ + $O_2 \rightarrow$ R-O-O- + $HC{<}^{=O}_{H}$.

In the meantime some observations have been collected which threw new light on the slow oxidation of hydrocarbons. Many hydrocarbons and related compounds react slowly with oxygen at temperatures far below the ignition temperature corresponding to the production of normal flames. In some cases (65) this slow combustion is accompanied by the emission of light in the form of either a faint glow of the reacting gases or a "cool flame" which slowly traverses the mixture. Chemical sampling of the products of the slow oxidation of hydrocarbons at various stages during the oxidation shows that a variety of compounds are produced, among which are alcohols, peroxides, aldehydes, acids, unsaturated hydrocarbons etc. (66). In all cases there appears to be an induction period before appreciable reaction, or a passage of the cool flame, occurs. Cool flames have been observed in oxidation of the higher hydrocarbons, aldehydes and ethers, but not of methane and formaldehyde. V. Kondratiev (67) suggested that the bands obtained

spectroscopically from the cool flames might be due to formaldehyde and A. Egerton and J.N. Pidgeon (68), who worked on the absorbtion spectra of burning hydrocarbons, investigated the absorption and slow combustion of alcohols up to amyl alcohols, aldehydes up to valeraldehyde, acids up to butyric, amylene, ethylene, ethyl acetate, ethyl hydroperoxide, diethyl peroxide and compared the results with the slow combustion of the normal hydrocarbons up to pentane in the same apparatus, showed that the only intermediates which could be demonstrated spectroscopically in the slow combustion of hydrocarbons were formaldehyde and acids.

Emeléus (69) also examined the spectra of the cool flames of acetaldehyde, propaldehyde and hexane, and found that all these are identical with the cool flame of ether. Thus all the cool flame spectra of this type are due to the same emitter, formaldehyde.

The cool flames occur at quite low temperatures, usually below 400°C, so that the excitation of formaldehyde molecules cannot occur thermally, but must be a chemiluminescent phenomenon. The combustion processes during the low-temperature reaction probably differ from those in ordinary flames and explosions, and the presence of activated formaldehyde molecules in the cool flame has naturally been taken into account in discussing the mechanism of the combustion.

Thus G. von Elbe and B. Lewis (70) have discussed the probable chain mechanism in the low temperature oxidation of hydrocarbons and aldehydes on a modified peroxidation theory. The considerations, on which this theory is based, are as follows:

When an organic molecule has lost a hydrogen atom and thus become a radical with a free valence, an oxygen molecule may associate itself with the free valence. If the free radical is small, an unstable association may occure which breaks up after the re-arrangement of the atoms. Thus from studies of the photodissociation of methyl iodide (where free radicals CH_3 are formed) in the presence of oxygen Bates and Spence (71) concluded that CH_3OO exists and it breaks up to form formaldehyde HCHO and OH. If, however, the free radical is large, no third body is required to stabilize the association, because the reaction energy may distribute itself over the various chemical groups comprising the radical. This is illustrated, for instance, by the photochemical oxidation of acetaldehyde (72). Molecules of acetaldehyde may split into free radicals on absorbing ultra-violet light of suitable wave length:

$$CH_3CHO + h\nu \longrightarrow CH_3 + HCO$$

In the absence of oxygen this would be followed by

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO.$$

In the presence of oxygen it plausible that O_2 adds directly to the CH_3CO forming a peroxidic radical:

$$CH_3CO + O_2 \longrightarrow CH_3CO(OO).$$

Since the only radicals regenerated are CH_3CO and $CH_3CO(OO)$ the chain would then be carried on essentially by the reactions:

$$CH_3CO(OO) + CH_3CHO \longrightarrow CH_3CO(OOH) + CH_3CO \text{ and}$$

$$CH_3CO + O_2 \longrightarrow CH_3CO(OO),$$

so that the acetyl radical CH_3CO alternates with the peracetic acid radical $CH_3CO(OO)$. The acetyl radical, therefore, appears to be sufficiently large to permit association of O_2 without the aid of a third body. Some of the CH_3CO radicals are removed by the reaction:

$$CH_3CO + O_2 \longrightarrow HCHO^* + CO + OH,$$

the reactions being accompanied by the evolution of about 110 K. cal., which is available for the formation of the activated formaldehyde molecules, $HCHO^*$, which give the observed luminescense or cool flame. This hypothesis appears satisfactory in that it explains the chemiluminescent excitation of the formaldehyde molecules in the slow combustion of higher aldehydes and hydrocarbons, although formaldehyde is produced in the high temperature combustion, according to von Elbe and Lewis, by the reaction:

$$CH_3 + O_2 \longrightarrow HCHO + OH,$$

the formaldehyde molecules so produced will not be excited and so do not give the formaldehyde emission spectrum, which is only given by the cool flame.

For the chain reaction between methane and oxygen the following scheme was suggested:

a) Chain initiation:

$$HCHO + O_2 \xrightarrow{surface} HCO(OOH) \xrightarrow{surface} HCOO + OH$$

b) Methane oxidation chain:

$$OH + CH_4 \longrightarrow H_2O + CH_3 \xrightarrow{+O_2} HCHO + OH$$

c) Aldehyde oxidation chain:

$$OH + HCHO \longrightarrow H_2O + HCO \xrightarrow{+O_2} CO + HO_2 \xrightarrow{+HCHO} HCOOH + OH + CO$$

$$H_2O + 2CO + OH.$$

d) Chain breaking:

$$OH \xrightarrow{surface} \text{destruction.}$$

Von Elbe and Lewis stated that this scheme conforms to the results of experiments on methane-oxygen mixtures at pressures below or not greatly exceeding atmospheric and at temperatures range of 420°-700°C. The oxidation products under such conditions are in the main CO, H_2O and HCHO, and the small amounts of CO_2 are perhaps due to catalitic oxidation of HCHO at the surface and have been neglected in the above scheme. No CH_3OH and H_2O_2 is formed and no peroxide or peracid in the oxidation process of formaldehyde (73).

If, however, chains are generated by photochemical means in a mixture of formaldehyde and oxygen at room temperature, formic acid, HCOOH, becomes the principal product besides CO and H_2O, suggesting the corresponding reaction step above. At high temperature formic acid is known to decopose into CO and H_2O, as shown. Formaldehyde accumulates until the two reactin paths of the chain carrier OH have become equally frequent; the formaldehyde concentration then remains stationary (loc. cit. - 50) in relation to the methane concentration,

while CO and H_2O continually accumulate.

As to the reactions between methane and oxygen at high pressures carried out, for example, by Newitt and Haffner (loc. cit. - 52), von Elbe and Lewis stated that it is not clear what role is played by surface catalysis under these conditions but the partial chain character of the reaction is suggested by its gradual acceleration, which is generally noted in the slow combustion of hydrocarbons and interpreted as an increase of the number of chains with time. Considerable amounts of methylalcohol have been formed and the data show that the ratio of the yields of methyl alcohol to form aldehyde is proportional to the pressure of the mixture. This suggests that, while formaldehyde is formed in binary collision of CH_3 and O_2 ($CH_3+O_2=$ $=HCHO+OH$), methyl alcohol results from ternary collision of CH_3, O_2 and a third molecule such as methane, since the ratio of the number of ternary collisions to the number of binary collisions is proportional to the total pressure. The immediate result of a ternary collision of $CH_3+O_2+CH_4$ appears to be the formation of a methyl peroxide radical, CH_3OO. From this radical methyl alcohol, CH_3OH, could be formed by the subsequent reactions:

$$CH_3OO + CH_4 \longrightarrow CH_3OH + CH_3O$$

$$CH_3O + CH_4 \longrightarrow CH_3OH + CH_3,$$

but it seems quite possible that the sequence of the reactions is more complex. It is, for example, pos-

sible that by the reaction: $CH_3OO+CH_4 = CH_3OOH + CH_3$, the methyl peroxide, CH_3OOH, is formed, which decomposes easily: $3CH_3OOH = 2CH_3OH + CO_2 + 2H_2O$ producing methyl alcohol and only this product of decomposition can be isolated, because the peroxide is a very unstable compound.

Turning now to higher hydrocarbons of the paraffin series, von Elbe and Lewis explain the oxidation-reactions so that the alkyl radical RCH_2 takes the place of the methyl radical CH_3 in the previous scheme. This radical may add a molecule of O_2 but, alkyl peroxides being very unstable, may decompose to OH and the aldehyde RCHO analogous to CH_3 and O_2 in the methane scheme:

$$RCH_3 + OH \longrightarrow RCH_2 + H_2O.$$

$$RCH_2 + O_2 \longrightarrow RCH_2OO \longrightarrow RCHO + OH.$$

Aldehydes being destroyed by a chain reaction, viz.:

$$RCH_2CH_2CHO+O_2 \longrightarrow RCH_2CHO+CO+H_2O$$

$$RCH_2CHO+ \quad O_2 \longrightarrow RCHO+ \quad CO+H_2O,$$

there are again two parallel chain reactions, one producing aldehydes and the other destroying them. If, however, the various per-acid and HO_2 radicals, which are formed in the latter chain, frequently react with hydrocarbon to form radicals RCH_2 which in turn form aldehydes, a destroyed aldehyde molecule is frequently replaced by a freshly formed one, so that the aldehyde concentration may reach a steady state. This corresponds, for example, to the results

obtained with mixture of propane and oxygen in the ratio 1:1 (74).

W.A. Bone and his co-workers were still in opposition to the chain and peroxidation theories. Thus W.A. Bone and J.B. Gardner (75) in their study of the induction period of the slow oxidation of methane reasoned as follows: if the duration of the induction period depends upon the activation of the reactants, this duration will be diminished if each reactant will be activated immediately before the reaction. The experiments were carried out at 400°C by the usual stationary method and both methane and oxygen in the ratio $CH_4:O_2=2:1$ were preheated at the same temperature just before passing them into the experimental vessel. The results did not show any shortening of the induction period. In the second series of experiments the investigators exposed the same gas mixture to ultra-violet radiation immediately after passing the gases into the experimental vessel. The results of these experiments did not show any shortening of the induction period either. The induction period and the subsequent reaction period were both much longer by increasing the surface/volume ratio of the reaction vessel although the kind of the surface had a great influence on the duration of both periods. The introduction of silica rods which increased the surface/volume ratio from 0·8 to 1·6

lenghtened the induction period from 14·5 sec. to 62·5 sec., while introduction of fragments of porous porcelain in one series of experiments had little or no effect upon the induction period and in another shortened the induction period considerably. An increase of temperature shortened the induction period considerably and the determinations of amount of formaldehyde vapour showed that in the first 1/3 of the duration of the induction period no formaldehyde was formed. It appeared only at the 2/3 of the duration and at the end of the induction period in amounts 0·01–0·05 % and 0·18–0·25 % respectively. It was further shown that the addition of various substances to the medium immediately after passing the reactants into the experimental vessel gave very different results. Thus, water vapour (up to 2 %) had very little effect on the shortening both the induction and the reaction periods. Methyl alcohol, ethyl alcohol, acetaldehyde and especially formaldehyde and formic acid shortened both periods appreciably. No peroxide could be detected during the induction period, the end of which synchronized with the accumulation of about 0·2 % of formaldehyde in the medium.

In the further series of experiments on the slow oxidation of methyl alcohol the investigators stated that mixture $2CH_3OH+O_2$ was the most reactive medium. The

oxidation was marked by the intermediate successive formation of formaldehyde and formic acid, the former being always present in much greater quantities than at any stage of a corresponding methane oxidation. They discovered traces of peroxide which were transiently formed when the intermediate formation of formaldehyde reached its maximum.

In addition the authors investigated the slow oxidation of formaldehyde and formic acid, They stated that during the slow oxidation of formaldehyde formic acid was always intermediately formed as well as, incidentally, both performic acid and formaldehyde peroxide and that the last named was evidently consequential upon the prior formation of performic acid. In the slow oxidation of formic acid there was never any sign of the intermediate formation of either peracid or any peroxide.

The results of their experiments the authors sumarized stating that all reactions show typical features of the hydroxylation theory. About Norrish's supposition (loc. cit. - 61) that both CH_2: radicals and oxygen atoms may be concerned in the initial stage of the methane oxidation, the authors had a somewhat different opinion. They suggested that the initial stage in the oxidation of methane is a slow reaction at the surface of the reaction vessel but afterwards

involving the formation of meta-stable methyl alcohol which in part is rapidly oxidized and in part decomposed into CH_2 radical and H_2O:

$$2CH_4+O_2 \longrightarrow 2CH_3OH \longrightarrow 2HCHO$$
$$\searrow 2H_2O+2CH_2$$

The formed CH_2 radicals react with O_2 and set up the following sequence:

$$CH_2+O_2 = HCHO+O.$$
$$CH_4+O = CH_3OH$$
$$CH_3CH = CH_2+H_2O.$$

The formation of very small amounts of performic acid and formaldehyde peroxide the investigators explained by the oxidation of nascent formic acid which rapidly decomposes into $CO+H_2O$ but part of it undergoes further oxidation:

$$2\begin{matrix}OH\\H\end{matrix}\!\!>C:O+O_2 = \begin{cases} a)\ 2\begin{matrix}OH\\OH\end{matrix}\!\!>C:O = 2CO_2+2H_2O \\ b)\ 2\begin{matrix}HOO\\H\end{matrix}\!\!>C:O = 2CO+2H_2O_2 \end{cases}$$

This H_2O_2 (produced in b)) reacts with formaldehyde producing the peroxide $(CH_2OH)_2O_2$, which then decomposes yielding hydrogen:

$$2HCHO+H_2O_2 = (CH_2OH)_2O_2 = 2CO+2H_2O+H_2.$$

In the oxydation of methane the equilibrium concentration of formaldehyde is so small (0·2-0·25 %) that it is insufficient to allow of a peroxidation to any appreciable extent and no hydrogen is formed, but in a methyl alcohol oxidation, where the formaldehyde concentration is about 1 %, such peroxidation just

becomes perceptible and in a formaldehyde oxidation (at 275°C) it becomes prominent. The authors had no explanation for not finding any peroxides or peracids in the slow oxidation of formic acid.

In their next work D.M. Newitt and J.B. Gardener (76) passing the mixture of methane - oxygen and ethane-oxygen respectively at atmospheric pressure through a furnace at temperatures 440°-450°C. and 315°-345°C respectively and choosing the time of contact of the gas mixtures with the furnace in such a way that this time was equal to the duration of the corresponding induction periods - succeeded in isolating measurable quantities of methyl alcohol and ethyl alcohol respectively and thus proving that the formation of alcohols in the initial stage of oxidation preceedes that of the corresponding aldehydes.

D.M. Newitt (77) studying the oxidation of methane, ethane, propane, benzene and toluene at high pressure, explained the reactions ocurring in terms of the hydroxylation theory; no traces of any peroxides or peracids being found at any stage of either induction or the reaction periods.

R.G.W. Norrish and S.G. Foord (78) according to the observations of Fort and Hinshelwood (loc. cit. - 32) upon pressure-time curves of the oxidation of methane, methyl alcohol and formaldehyde, - which

suggest that the main reaction is developing from some intermediate substances, the concentration of which is tending towards an equilibrium value and showing the equal rates of production and removal, - and according to the theory of Semenoff (79 - page 68) that the development of the maximum velocity from zero in the space of minutes could be interpreted in terms of a chain mechanism with degenerate branching,- concluded on the basis of their experiments that methane is oxidized by a straight chain with the production of comparatively stable intermediate products,which by its subsequent oxidation is capable from time to time of starting fresh methane chains. The reaction starts very slowly from certain adventitious centres,but after the induction period,during which the intermediate product is growing in concentration,the reaction proceeds more rapidly and reaches a maximum value if an equilibrium concentration of the intermediate product is reached,i.e. when its rate of oxidation is equal to its rate of production, and this only occurs if the Semenoff's effective branching factor ϕ is reduced to zero during the progress of the reaction. In view of these ideas the authors decided to modify the Norrish's "atom chain hypothesis" (loc.cit. 61) in such a way that the first oxygen atoms are produced from traces of formaldehyde formed on the surface by reactions such as:

$$CH_4 + O_2 = HCHO + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$HCHO + O_2 = HCOOH + O \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\searrow H_2O + CO$$

and once they are formed, formaldehyde may be assumed steadily to increase in concentration by the operation of a straight chain, according to the "atom chain hypothesis":

$$O + CH_4 = CH_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

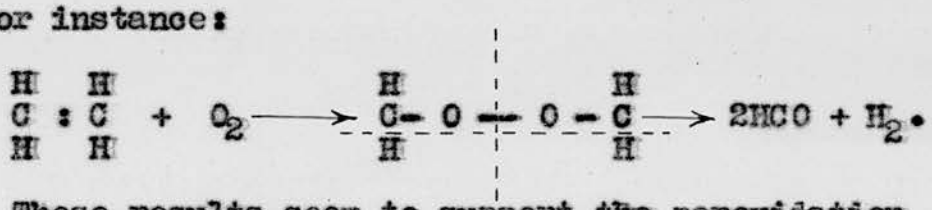
$$CH_2 + O_2 = HCHO + O. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4),$$

while from the formaldehyde fresh chains may occasionally start by the reation (2) above. Alternatively the formaldehyde may be removed by oxidation without forming a chain:

$$HCHO \xrightarrow{\text{oxidation}} CO + H_2O.$$

In order to find the initial oxidation products in the combustion of hydrocarbons many spectroscopical investigations have been made. Thus W.M. Vaidya (80) studied the conal flame spectra of ethylene and in addition to the OH-bands (at 2608Å, 2811Å and 3064Å), CH - bands (at 3143 Å, 3900 Å and 4300 Å) and C_2 - bands (at 4737 Å, 5165 Å and 5635 Å) he found a band system (extending from 4100 Å to 2500 Å) which he designated as the "ethylene flame" and ascribed it to the CHO radical. In support of this suggestion he found that molecules having the same number of external electrons show certain similarities in their spectra as expressed in Mecke's principle of isosterism (81).

The spectrum of CHO would show some similarity to that of NO, since each of these molecules has 15 external electrons and the substitution of CH for N in NO involves only a small change of mass. It is found indeed that the vibrational constants of CHO-bands are not very different from those of the β-bands of NO. Furthermore, if according to the peroxidation theory it is assumed that O_2 molecules are directly incorporated in the hydrocarbon molecules and the oxygenated molecules decompose, CHO molecules could be produced; in the case of ethylene, for instance:



These results seem to support the peroxidation theory and oppose the Bone's hydroxylation theory.

J.Bell (82) observed the explosion spectra of the methane-oxygen mixtures and the spectra of the steady flames of methane, methyl alcohol and formaldehyde mixed with various amounts of oxygen and nitrogen. The explosion spectra obtained at an initial pressure of 1 atm. showed that over the composition range CH_4+O_2 to $4CH_4+3O_2$ the CH radiation was emitted in considerable quantity and that its intensity was diminished by the progressive addition of methane to the explosive mixture until with $4CH_4+3O_2$ mixture it could be not detected. CH-bands, C_2-bands and "ethylene flame"-bands were not visible. Moreover, with any given mixture the intensity of the CH-radiation was rapidly diminished by increasing

the initial explosion pressure. In explosions of media containing more oxygen than the equimolecular proportion, the combustion of the carbonic oxyde and hydrogen initially formed came into play. In such cases a corresponding increase in the initial pressure resulted in a much smaller diminution in the intensities of the OH--bands. This was also the case in H_2+O_2 and $CO+H_2+O_2$ explosions ,which under comparable conditions emitted OH radiationb much more strongly than the equimolecular CH_4+O_2 explosions. As in equimolecular CH_4+O_2 explosions either a decrease in the flame temperature or an increase in the pressure eventually surpressed the formation of the OH radicals, the investigator assumed that in such cases these radicals were mainly produced by the thermal decomposition of some intermediate oxidation products, although to a minor extent by the thermal decomposition of water. It was further observed that the proportion of the original oxygen appearing as water in the explosion products was greatest at the lowest initial pressure, decreasing as the pressure was increased and reached a minimum at some higher pressure. In the second series of experiments Bell constructed an arrangement whereby in the first stage of explosion the gases could be suddenly cooled and the explosions stopped altogether. The analysis of these gases showed the presence of methyl alcohol and formaldehyde and the amount of these intermediate pro-

ducts increased with pressure. This experimental evidence, - the investigator concludes, - indicates that the initial oxidation product in the explosive combustion of methane is methyl alcohol and that this primary reaction is rapidly succeeded by further hydroxylation stages and by thermal decomposition. In the spectra of the continous flames of methane and methyl alcohol CH - bands, C_2 - bands and "ethylene flame" - bands were found; the formaldehyde flames showed only the "ethylene flames" - bands. Bell doubts if these bands can be attributed to the CHO radicals and considers that they can be reasonably ascribed to the CH_2 group, particularly as they are always associated with a strong CH emission. Since, however, the analytical data indicate that there must be an appreciable concentration of methyl alcohol in the methane flame, Bell assumed that these "ethylene flame" - bands are produced by the low temperature decomposition of methyl alcohol:

$$CH_3OH \longrightarrow CH_2 + H_2O \longrightarrow C + H_2 + H_2O,$$

and came to the conclusion that the explosive combustion of methane may be represented by a hydroxylation scheme which, apart from the thermal decomposition, is identical with that representing the course of slow combustion.

Some interesting studies by L. Slotin and D.W.G. Style (83) on methane and oxygen and by F.F. Snowdon

and D.W.G. Style (84) on formaldehyde and oxygen should be mentioned. In the first work the authors used a spectrometric method investigating the intencity of the "D" band of formaldehyde (λ = 2800 - 3200 Å) by means of a recording micro - photometer during an oxidation process of methane at 430° ± 5°C. The rate of the pressure change, i.e. the rate of oxidation of formaldehyde to carbon monoxide they represented by the equation $\frac{dP}{dt} = K \frac{\Delta P_{max}}{\Delta P} [CH_2O] \{[CH_2O] - C\}$ where K and C were constants. The concentration of formaldehyde increased in the first 10 minutes of the oxidation process very rapidly, passed through a maximum after which it decreased considerably.

In the second work the investigators studied the oxidation of gaseous formaldehyde by stationary and spectro-photometric methods at temperature 344°C. Except for a short initial period the rate of reaction could be expressed by the equation:

$$\frac{dF}{dt} = KF\ (F-C),$$

where K and C were constants for a given run and F was the formaldehyde concentration. This expression and their experimental results were in agreement with Spence's (85) data also, but the "constants" of this expression showed a tendency to vary erratically. This was particularly true of C which represented probably a surface reaction. Although traces of peroxides were

found amongst the condensible products their amounts were inconsiderable and could not be determined. Out of the numerous possibilities for an oxidising agent which could produce the reaction the authors have chosen the peroxidic substances of Spence's (loc. cit. 85) mechanism, namely, CH_2O_2 and CH_2O_3, and the selected scheme was:

$$CH_2O_3 + CH_2O \longrightarrow 2CH_2O_2 \quad \ldots\ldots\ldots\ldots \quad k_1$$

$$CH_2O_2 + CH_2O \longrightarrow CO + H_2O + CH_2O_3 \quad \ldots \quad k_2$$

$$2CH_2O_2 \longrightarrow 2CO + 2H_2O \quad \ldots\ldots\ldots \quad k_3$$

$$CH_2O_2 + \ldots\ldots \longrightarrow CO_2 + \ldots \quad \ldots\ldots\ldots \quad k_4,$$

which led to the equation:

$$\frac{dF}{dt} = \frac{k_2}{k_3}\frac{2}{-} F\left(F - \frac{k_4}{k_2}\right) = KF(F-C).$$

This equation the authors explained by a branching chain in which the carriers are removed by both bimolecular and monomolecular reactions.

The oxidation reactions of the hydrocarbons have been shown by Semenoff (loc. cit.-79) to take place by a process of branching chains termed degenerate, which he proposed in explanation of the much greater induction periods shown by these reactions than by those of the simpler branching reactions, such as the oxidation of hydrogen and carbon monoxide. According to his theory the induction period τ gives a measure of the net branching factor ϕ ($\phi\tau$= constant approximately) which controls the development of the reaction and which for a self - accelerating reaction, characteri-

zed by the equation $\omega = Ae^{\phi t}$, must be greater than zero. The hydrocarbon oxidations, which are controlled by much smaller values of ϕ than those of simple branching reactions, require a special mechanism to explain this slower development of the reaction. This mechanism postulated the formation of comparatively stable intermediate by oxidation of the hydrocarbon through a straight chain reaction, while this intermediate is subsequently oxidized to final products, occasionally in an alternative reaction giving rise to additional chain centres long after the parent chain has been destroyed. The stable intermediate in the oxidation of hydrocarbons is almost certainly the derived aldehyde, which has been isolated in most cases of oxidation of hydrocarbons. Semenoff has demonstrated that, in chain reactions exhibiting degenerate branching, the net branching factor ϕ can be expressed in the form:

$$\phi = k_2(v - 1) - k_1 = k_2\left(\frac{bd^2}{gd^2 + \pi^2 D} - 1\right) - k_1$$

where the constants k_1 and k_2 represent the oxidation of intermediate product into final products by alterative reactions, k_2 alone representing the reaction in which additional chain centres are formed and where v is the length of the unbranched primary chain; g is the factor of chain breaking in the gas - phase, d - the diameter of the experimental vessel, D - the coefficient

of diffusion, b being a constant. It is apparent that for sufficiently large values of diameter, v becomes constant and ϕ consequently achieves a constant value dependent on the factors which influence the oxidation of the intermediate substance. As the diameter d decreases, the chain length v becomes increasingly dependend on the diameter and for sufficiently small values of d will approximate the form $v = cd^2$, where c is a constant. In this case ϕ tends to the form:

$\phi = k_2(v-1)-k_1 = k_2(cd^2-1)-k_1 = C_1d^2-C_2$.

It may be seen from the above equation that any change in the factors controlling the destruction of the intermediate product which would cause either an increase in C_2 or a decrease in C_1, or both, could bring the net branching factor ϕ to zero while the diameter still remains at finite size.

In connection with this theory R.G.W. Norrish and J.D. Reagh (86) made a study of the effect of surface on the slow oxidation of methane, ethane, propane acetylene, ethylene and propylene. They used special reaction vessels constructed from sections of tubing of any desired diameter joined together in parallel, by means of which vessels of approximately constant volume although varying widely in diameter (3 - 40 mm.) were obtained. All reactions were found to be of the degenerate branching type and principally homogenous in character. When the diameter of the reaction vessel was sufficiently reduced (to about 5 mm.), the reaction

rate was observed to drop abruptly to zero, while the corresponding induction period increased towards infinity. Data so obtained have demonstrated that in narrow vessels surface deactivation predominated over other processes of deactivation, while in wider vessels surface and gas - phase deactivation occurred to a comparable extent so that the rate of reaction was nearly constant over a considerable range of pressure. When the vessel's diameter was decreased to a critical value, the surface deactivation almost alone could suppress the factor ϕ leading to chain branching, and from the reactions investigated the existence of such a critical diameter appeared to be a general property of hydrocarbon oxidation in conformity with the theory of degenerate branching.

Gaydon's experiments (87) indicated that high - -temperature flames of hydrogen burning with pure oxygen were blue and that in the presence of nitrogen there occurred a pale yellowish-green coloration, which is due to emission of the vibration - rotation bands of N_2O(88). Flames of hydrogen burning with nitrous oxide under suitable conditions showed the yellow-green colour strongly. It was shown that the oxy-hydrogen blow-pipe in air always smelt of oxides of nitrogen, when the yellow-green coloration was well developed, and that this luminosity (89) is due to a reaction between nitric oxide and atomic oxygen; and this explanation

agrees with the earlier observations of Rayleigh (90). The assignment, then, of the yellow-green continuum to a reaction between nitric oxide and atomic oxygen gives a simple quantitative test for the presence of atomic oxygen in a flame by introducing a little amount of nitric oxide and observing whether or not the yellow--green continuous emission is obtained. In this way Gaydon studied the continous emission of carbon monoxide, hydrogen, methane, ethylene and butane burning in air and in oxygen when small amounts of nitric oxide were added.

The spectrum of the inner cone of the methane flame before the introduction of nitric oxide showed the usual C_2 Swan and CH - bands. When nitric oxide was present the CN Violet system came up strongly (this accounting for the violet colour) and the C_2 Swan bands were partly suppressed, but the CH-bands did not appear to be affected. With a steadily burning flame there was no trace of the yellow-green continous emission in the inner cone, whereas the outer cone showed a strong yellow-green coloration. The results with ethylene and butane were similar to those with methane.

These experiments show clearly that in the outer cone, corresponding to the later stages of the combustion of these hydrocarbons when hydrogen and carbon

monoxide are the principal combustibles, there was a high concentration of atomic oxygen, but that in the inner cone, corresponding to the early stages of the combustion of hydrocarbons, atomic oxygen is not present in sufficient quantity to give the slightest coloration with the nitric oxide test. These experiments, showing a negligible amount of atomic oxygen in the inner cone, appear to provide evidence against Norrish's (loc. cit. - 61) modification of the hydroxylation theory, - which requires atomic oxygen for the chain reactions, - and give some support for the peroxidation rather than the hydroxylation theory.

The synthesis of formaldehyde by the controlled oxidation of methane was studied by M. Ratry and P. Monceaux (91). The investigators passed a mixture of air and methane in the ratio: 90:10, 80:20, 70:30 and 30:70 through an empty tube of transparent quartz heated to temperatures from 500° to 900°C and analysed the exit gases. The time of contact of the gas mixture with the furnace was 0·5 - 4·0 seconds. From their experiments they arrived at the following conclusions: (1) The yield of formaldehyde was always low; the percentage of carbon from the methane transformed hardly exceeded 1 % and the concentration of formaldehyde in the exit gases was 0·20 % at the maximum. (2) All

the curves (when the time of contact was plotted against the percentage of carbon from the methane transformed) between 600° and 900°C passed through a maximum. The concentration of formaldehyde increased at first with time of contact then decreased. (3) All other conditions being the same, the maximum yield increased with temperature at least below 800° and decreased sharply in the vicinity of 900°C. Below 600°C the yields of formaldehyde were very small. (4) In experiments carried out below 700°C the composition of the gaseous mixture had little importance. The most favourable proportions corresponded to 20 % of methane, i.e. almost the theoretical reaction mixture for the production of formaldehyde. At higher temperatures the highest yields were obtained with mixtures poorer in methane.

In their final experiments the authors studied the influence of carbon black and of the wall effect on the rate of oxidation of methane. It was found that the carbon black coating vessels' walls had a considerable catalytic action which persisted during a time of contact which was greater as the temperature of the reaction was reduced. When the contact was prolonged the reverse phenomena occurred, the carbon causing the acceleration of the oxidation of methane to carbon monoxide and water. The wall effect caused

more rapid decomposition of formaldehyde as well as the oxidation of methane. The experiments showed that the increase in the surface of contact in the experimental vessel caused an important diminution in the yield of formaldehyde and an increase of carbon monoxide and water formed.

Summing up the above described experimental works on the slow oxidation of methane and other hydrocarbons one must conclude that the real mechanism of these reactions has not yet been elucidated. The problem of the hydroxylation, peroxidation and chain reactions theories is not yet solved and each has its strong and weak points. The hydroxylation theory, although simple and clear, posulates the existence of the methyl alcohol as the first stage of the oxidation of methane; unfortunately this substance has never been isolated when the oxidation was carried out at pressures varying not greatly from the atmospheric. The fact that methyl alcohol was isolated in abundant quantities when the oxidation of methane was carried out at high pressures (loc.cit.-50,52) does not confirm this theory but only indicates that the mechanism of oxidation at high pressures is different to that at atmospheric pressure. The peroxidation theory which elucidates very clearly the induction period has the disadvantage that the peroxides and peracidic substances have a very short life and consequently the isolation of such substances is exceptionally difficult if not impossible. The chain reactions theory, as developed recently by G.von

Elbe and B.Lewis (loc.cit.-70) postulates a quick sequence of complicated reactions which conforms to experimental evidence in describing the formation of the various reaction products and the dependence of their yields on the experimental variables. It must be pointed out that this last theory is the most satisfactory in relation to the experimental data but it still appeares of a hypothetical character, as the existence of chain carriers OH and HO_2 are not confirmed and so the real existence of chain reactions is yet to be proved.

As regards the influence exerted by steam on the rate of the slow oxidation of methane and other hydrocarbons there are contradictory data in the literature on the subject.

Thus W.A.Bone and G.W.Andrew (loc.cit.-7) studying the slow oxidation of ethylene and acetylene stated that "from the results of these experiments we have arrived at the conclusion that the rigid exclusion of moisture by means of the best known method of dissication has little if any influence on the rate of oxidation of a hydrocarbon." T.S.Wheeler and E.W.Blair (loc.cit.-11) came to the conclusion that the presence of steam in the gas-mixture (methane plus oxygen) has no influence on the rate of oxidation of methane, and C.H.Gibson and C.N. Hinshelwood (92) proved that the combination of hydrogen and oxygen at temperature range of 500°-600°C is accelerated by the presence of steam as well as by the influence of neutral gases and that the ratio of reaction rates in these media were: $He:N_2:A:H_2O = 1:3:4:5$.

D.F.Smith and R.T.Milner (loc.cit.-22) on the basis of their experiments concluded that the presence of steam in the gas-mixture containing methane, oxygen and nitrogen oxides had no effect on the rate of methane oxidation. W.A.Bone and R.E.Allum (loc.cit.-50) by the investigation of the slow oxidation of methane at the temperature range of 423°-427°C stated that "both the induction and reaction periods were accelerated by introducing a small percentage of water vapour into the dry system" of gases, and by studying the slow combustion of ethane W.A.Bone and S.G.Hill (loc.cit.-51) found that the introduction of 1 % of moisture in a dry mixture of $C_2H_6+O_2$ at 316°C shortened the induction period from 30 minutes to 10 minutes and the reaction period from 70 minutes to 25 minutes, whereas according to experimental results of W.A.Bone, A.E.Haffner and H.F.Rance (93) the slow oxidation of the medium $C_2H_4+O_2$ at 300°C "does not depend upon the presence of water vapour, neither the induction nor the reaction periods being materially affected thereby." W.A.Bone and J.B.Gardner (loc.cit.-75) write: "Small additions, up to 2 % of water vapour to a dry $2CH_4+O_2$ medium always curtailed somewhat the induction period, though rather irregular; the subsequent reaction period was sometimes (but noy always) slightly accelerated." R.G.W.Norrish and S.G.Foord (loc.cit.-78) studied the kinetics of the combustion of methane and measured the rate of reaction at 530°C with and without addition of carbon monoxide, carbon dioxide and water vapour. Using 200 mm. of the methane-oxygen mixture

($CH_4:O_2=1:1$), addition up to 150 mm. of either carbon dioxide or water vapour had no other effect on the velocity of the reaction than the normal increase approximately proportional to the total pressure obtained by addition of an innert gas. Finally, G. von Elbe and B. Lewis (94) studying the explosion limits of hydrogen and oxygen combination stated: "We have found that water vapour effects a marked lowering of the upper explosion limit of hydrogen and oxygen. This is illustrated by the following typical results for a 2:1 mixture at 530°C, H_2O being admitted to the reaction vessel from the reservoir:

% H_2O	0	3·35	6·37	11·03
Upper limit, mm. Hg	85·6	54·9	41·8	29·4

These results demonstrate that the water effect is no different in kind than the influence of other gases as described by explosion conditions." In their next work on the same subject the investigators (95) wrote: "Water is an inhibitor in a restricted sense, as it inhibits branching through reaction: $H_2+O_2+M=HO_2+M$. It also may accelerate the reaction as an innert gas impeding diffusion and by poisoning the surface for chain-carrier destruction." It must be remembered that G. von Elbe and B. Lewis in their work on slow oxidation of hydrocarbons (loc. cit. - 70) stated that the aldehyde oxidation chain is propagated also by the HO_2 ra-

dical, then the water vapour may (1) inhibit this chain slowing down the oxidation reaction and on the other hand (2) accelerate the reaction impeding diffusion and poisoning the surface of experimental vessels for chain-carriers destruction.

B. EXPERIMETAL RESULTS.

In the experimeta now to be described an attempt was made to interrupt the slow oxidation of methane at an intermediate stage, i.e. at the oxidation to formaldehyde. It was thought that - if the mixture of methane, oxygen and nitrogen were passed in a very quick stream through a furnace heated to a high temperature and cooled immediately afterwards - a large part of methane would not be oxidized to carbon oxides but to formaldehyde or to intermediate products only. It was hoped that by a suitable adjustment 1) of time of contact of the gas mixture with the furnace, 2) of the composition of the gas mixture and 3) of the temperature it would be possible to achieve this result.

The experiments were carried out by a flow method so that the mixture of methane, nitrogen and oxygen first in the ratio $N_2:O_2:CH_4 = 2:1:1$ and afterwards in the ratio $N_2:O_2:CH_4 = 2:0{\cdot}1:1$ was passed in a quick flowing stream through an electrically heated furnace made of Pyrex-glass. (In war time conditions it was impossible to obtain quartz tubes of a suitable size). In order to cool the gases immediately after their passage through the hot zone of the furnace a cooler was inserted deep into the inside of the latter; through the cooler a quick stream of water was passed. The products of the reaction were passed through two

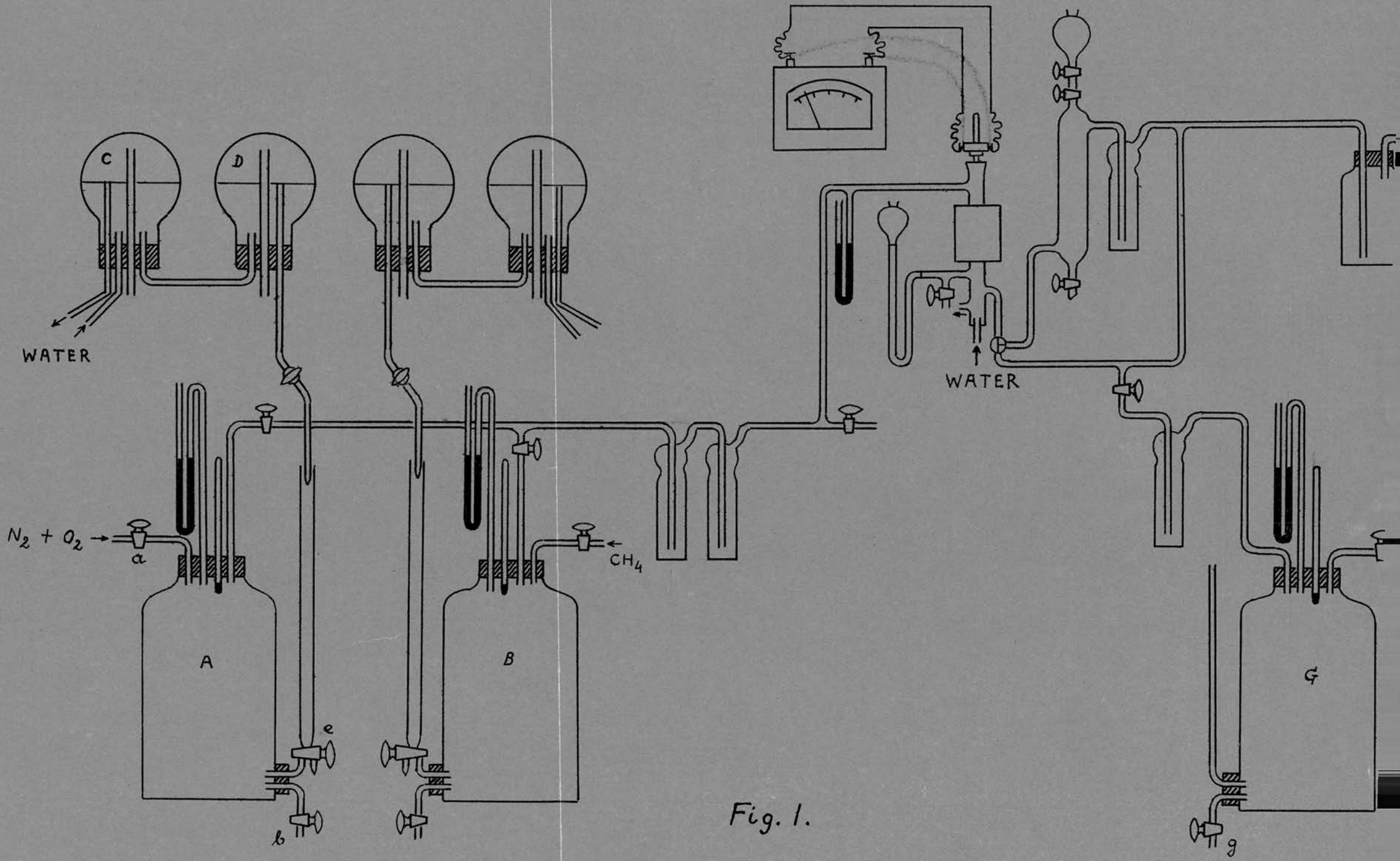


Fig. 1.

successive wash-bottles filled with water, after which they escaped.

The sketch of the apparatus is given in Fig. 1. In the 10-litre volume bottle A a mixture of nitrogen and oxygen in the ratio $N_2:O_2 = 2:1$ or $2:0{\cdot}1$ was collected by the following method. After filling the bottle with water taps a and b were opened and after a calculated amount of water had poured out through tap b, the remaining volume of the bottle was filled up with oxygen from cylinder (which contained in the average 98·3 % of pure oxygen and 1·7 % of nitrogen). In a similar manner the 5-litre bottle B was filled with cylinder methane.

In order to measure the gases which passed through the furnace the following instalation was made: over the bottle A containing nitrogen and oxygen were placed two inverted flasks C and D which were connected with each other by a glass tube. Into each of these bottles two tubes were inserted at different levels for introducing and drawing off water. After a certain time the levels of water in both flasks established themselves and remained constant throughout the period of the experiment. From bottle D the water ran through a nozzle, which was specially made for each experiment, into the burette which had a double-way tap e at the bottom, by means of which the water could enter the

bottle A or could ran away. The volume of water which in the unit of time ran from the burette gave the volume of gas which was displaced from the bottle to the furnace. The same installation was made for displacing methane from the bottle B to the furnace. In order to check the exact volume of gases passed through the furnace from bottle A or B the gases were allowed to displace water from the bottle G after passing the furnace, while tap g was adjusted so that the pressure inside bottle G was equal to the atmospheric pressure. The volume of the water poured out over a longer period of time gave the average volume of gases passed through the installation. In the same manner the volume of methane displaced from bottle B was checked.

The mixture of gases from the two bottles was passed through wash-bottles filled with water or, in some of the experiments, through drying towers into the furnace. After passing the furnace the gases were immediately cooled and passed through wash-bottles filled with water, in which the formaldehyde produced was absorbed, after which they were allowed to escape .

As shown by analyses and by the equations of the oxidation of methane, the product gases contained steam formaldehyde, carbon monoxide, carbon dioxide, hydrogen and oxygen. The condensation of steam and the absorption of formaldehyde in water would thus give a contraction

in volume as compared with the origianal volume of gases entering the reaction chamber. Carbon dioxide, however, is not completely absorbed by water and accordingly a 50 % KOH aqueous solution was inserted in the gas stream before it entered the bottle G. The total contraction, measured here by volume of water expelled through tap g, while the pressure remined atmospheric as indicated by the U-type manometer attached to G, was corrected to the true contraction, due to reaction, by means of gas-analysis as applied to the issuing gases.

Of the other gases remaining after the reaction only oxygen dissolves in appreciable quantities in water. As the gases, however, contained about 21-23 % of oxygen and the water in bottle G was for a long period of time in contact with the air, it was very unlikely that appreciable quantities of oxygen would be further dissolved in the water. Moreover, the bottle G was filled with water only to $\frac{3}{4}$ of its volume to minimise the diffusion of the product gases to the water.

A sketch of the furnace is given in Fig. 2. In order to cool quickly the gases produced after the reaction a cooler was inserted deep into the furnace, so that the upper part of the cooler was only a few milimeters away from the bottom of the furnace itself. Through the cooler a quick stream of the cold water

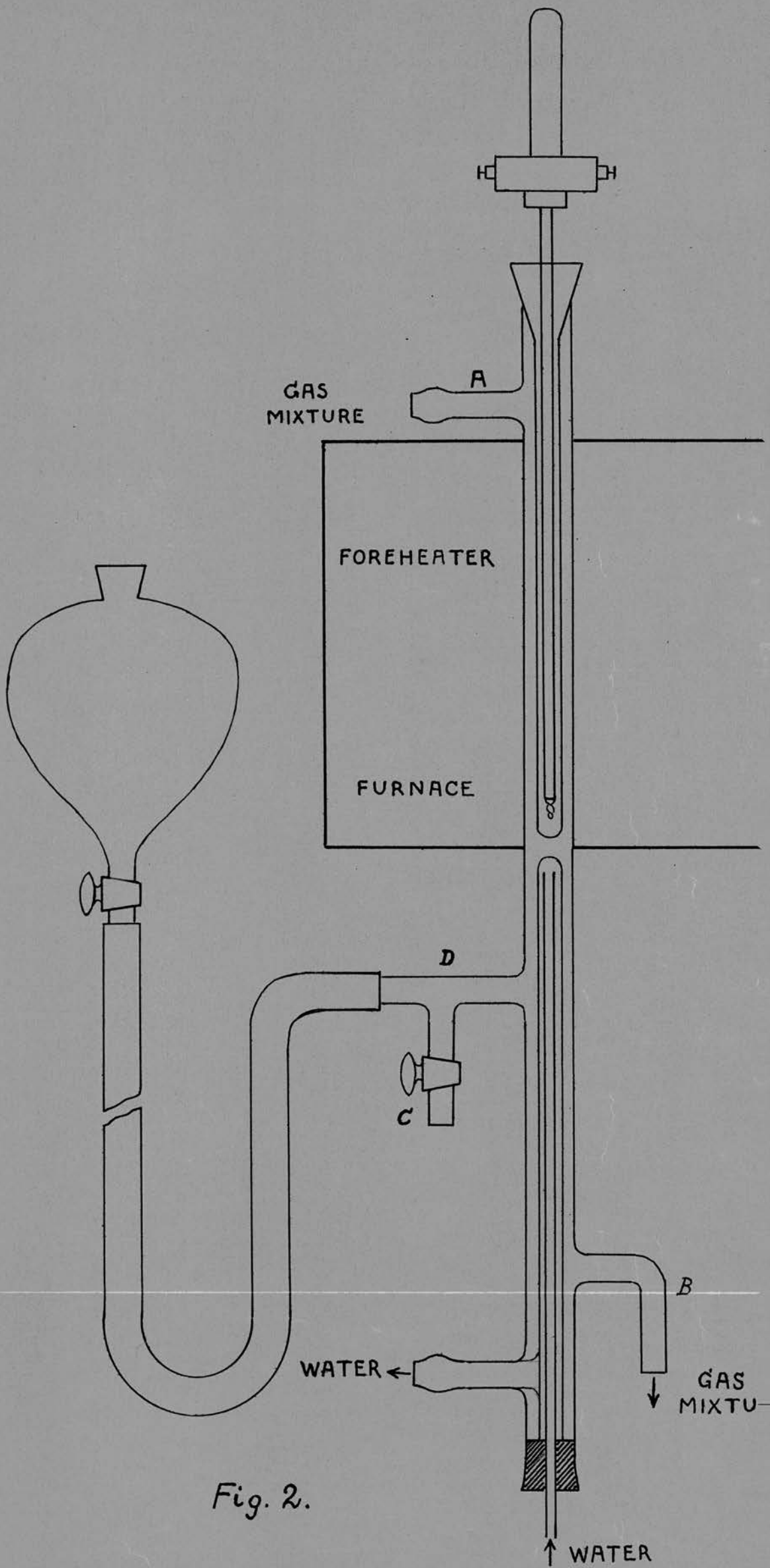


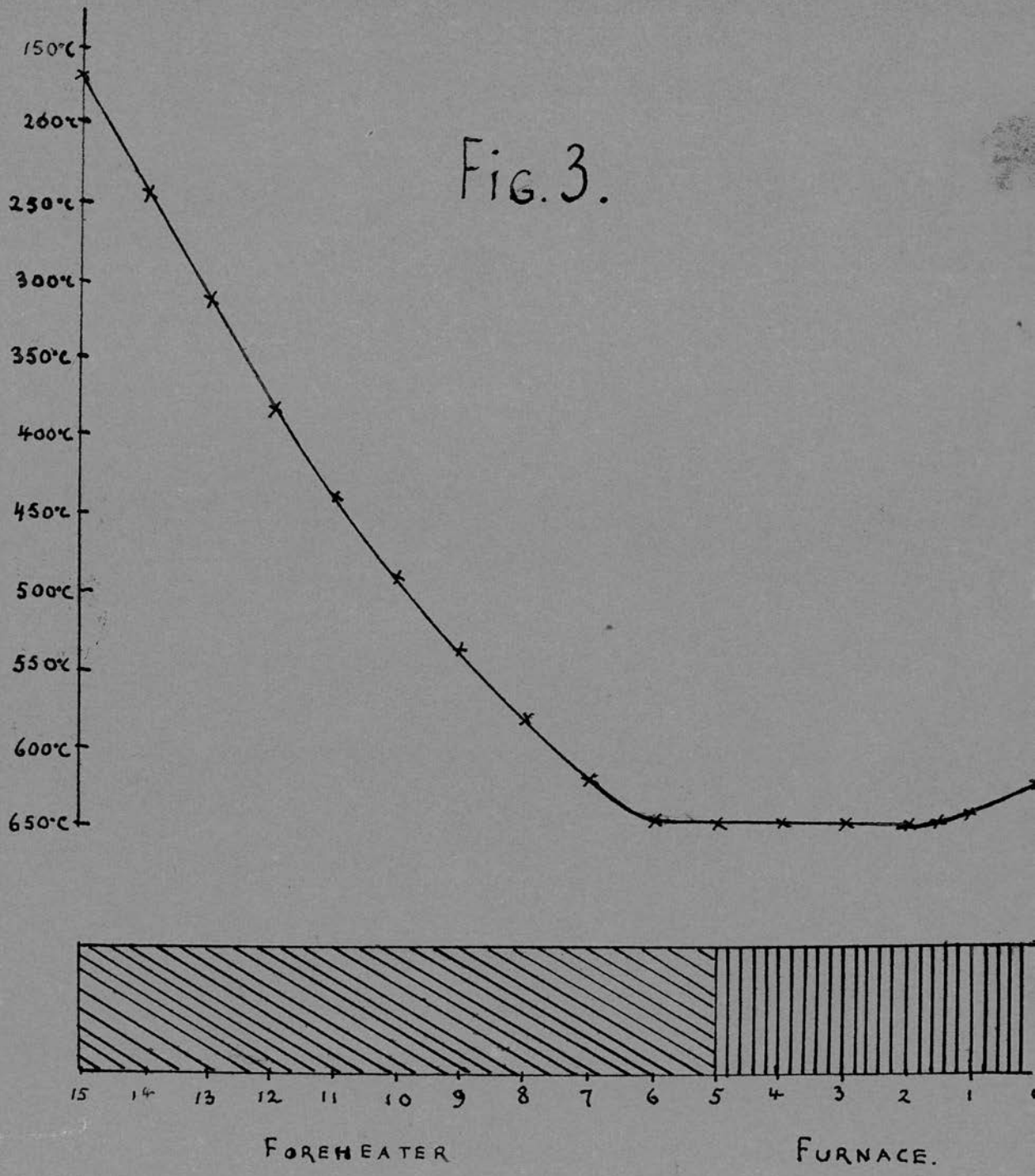
Fig. 2.

was passed. The furnace was made of Pyrex-glass. The inside diameter of the furnace-tube was 15·8 mm.; the outside diameter of the thermocouple-tube was 11·5 mm. The mixture of gases entered through side tube A, passed through the foreheater 100 mm. in lenght and then through the furnace 50 mm. in lenght. After leaving the furnace the gases impacted on the surface of the cooler and then passed through the cooling space which was 110 mm. long. Finally the mixture passed through tube B to the wash-bottles filled with distilled water where the formaldehyde was completely absorbed.

The furnace was wound round with a Cr - Ni wire which had a resistance of 36·7 ohms/meter. The furnace and the foreheater was wound round seperately the former with 40-50 coils, the latter with 25-30 coils. The ends of the wires were carried outside the furnace so that two independent circuits were formed which could be regulated at will by means of resistances.

The temperature of any part of the foreheater or furnace could be measured during the experiments by lifting the thermocouple in the tube situated inside the furnace. The couple had previously been calibrated using the melting points of pure metals: antimony (630°C), zinc (419°C), lead (327·5°C) and the boiling points of mercury (357°C) and water. For the temperature 650°C, for example, the individual places of the

Fig. 3.


150°C
200°C
250°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
650°C
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
FOREHEATER
FURNACE.

foreheater and of the furnace had the following temperatures (Fig. 3.):

Furnace

0 cm.	1	1·5	2·0	2·5	3·0	3·5	4·0	5·0
540°C	605	650	650	650	650	650	650	650

Foreheater

6 cm.	7	8	9	10	11	12	13	14	15
650°C	622	578	530	478	430	385	322	250	170

It follows, therefore, that for the space of 45 mm. in the middle of the furnace the temperature was constant. The experiment was not started until it was certain that the temperature inside the furnace was constant in this space.

During the experiment samples of the gases were taken through tube C in such a way that simultaneously one part of the gases was passed through the furnace and wash-bottles and another at the same time collected in sample tubes for analysis.

The whole furnace was well insulated and its outer cover almost cold.

The furnace was insufficiently strong to stand the strain of long periods of experiments and after a time it broke down and it was necessary to construct, wind and insulate it again. On occasions some explosions of the methane-oxygen mixtures occurred which shattered

the furnace.

The furnace and the foreheater were filled with pumice which was powdered and grains collected which remained between sieves Nos. 10 and 20 (10 meshes and 20 meshes per inch). The time of contact of the gas--mixture with the furnace is the number of seconds in which a molecule of the gas traverses the lenght of 50 mm., i.e. from the beginning to the end of the furnace.

As the oxidation of methane and of the intermediate products of this oxidation takes place with an appreciable evolution of heat, the mixture of methane and oxygen was diluted with nitrogen in order to avoid a local rise in the temperature. The same reason was given by Newitt and Haffner (loc. cit. - 52) in their stationary experiments, where the ratio of gases used was $CH_4:O_2:X = 2:1:6\cdot0-6\cdot5$, where X represented nitrogen, methane, or carbon dioxide. On the other hand, as the time of contact of the gas-mixtures with the furnace was very short and as it was feared that it would be shorter than the induction period it was decided to accelerate the reaction by means of a neutral gas which impeded the diffusion to the walls of the furnace and poisoned the surface for chain-carrier destruction (loc. cit. - 95). As the experiments were carried out at high temperatures it was feared

that explosions might occur; the components of the gas mixtures were, therefore, selected to ensure that the mixtures were beyond the explosion limits though very near these limits. The limiting mixtures according to W. Payman (96) are as follows:

Lower Limit			Upper Limit		
CH_4 %	O_2 %	N_2 %	CH_4 %	O_2 %	N_2 %
6·4	12·8	80·8	6·9	12·7	80·4
6·1	16·0	77·9	8·9	15·5	75·6
5·8	19·8	74·4	13·3	18·2	68·5
5·8	31·4	62·8	25·1	25·0	49·9
5·8	47·1	47·1	38·8	30·6	30·6
5·8	62·8	31·4	47·5	35·0	17·5
5·7	94·2	-	59·2	40·8	-

From these limiting mixtures a mixture which corresponded to the ratio $N_2:O_2:CH_4 = 2:1:1 = 50:25:25$ was selected. In the second series of experiments a mixture $N_2:O_2:CH_4 = 2:0{\cdot}1:1 = 64{\cdot}52:3{\cdot}23:32{\cdot}25$ was used.

As the Bone-Wheeler apparatus (97) for gas analyses was not available an apparatus was built to the design of A.C. Fieldner, G.W. Jones and W.P. Holbrook (98). This apparatus is a precise one because owing to atmospheric pressure compensator the "readings" of gas volumes always are made at atmospheric pressure,

which is not possible with the normal Orsat's apparatus. There were four pipettes filled with (1) 50 % KOH for absorption of carbon dioxyde; (2) concentrated sulphuric acid activated with 0·6 % (by weight) of silver sulphate (99) for the absorption of unsaturated hydrocarbons; (3) alkaline solution of pyrogallic acid for the absorption of oxygen; and (4) a solution of β-naphtol cuprous oxyde for checking the amount of carbon monoxide. After the absorption of carbon dioxide, unsaturated hydrocarbons and oxygen the gases were passed in a slow stream (about 5 cm.^{3}/min.) through a glass tube filled with copper oxide at a temperature of 300-310°C. During the latter process hydrogen was oxidized to water and carbon monoxide to carbon dioxide; the saturated hydrocarbons, viz. methane, ethane and higher bydrocarbons were not affected by this process. The volume of hydrogen present was determined by the contraction of the gases and the volume of carbon monoxide by the absorption of carbon dioxide formed. In the second analysis of the same gas-mixture the carbon mohoxide was first absorbed into the β-naphtol cuprous oxide solution. For the determination of methane, ethane, etc. the gases mixed with a suitable amount of oxygen were passed several times in a very slow stream through an explosion pipette in which a platinum wire heated red-hot was present.

In this pipette one can determine simultaneously two saturated hydrocarbons; it is easy to show that by burning v_1 cm.^{3} of a hydrocarbon C_nH_{2n+2} and v_2 cm.^{3} of a hydrocarbon C_mH_{2m+2}.

$$v_1 = \frac{2m(T.C.) - (m+3)CO_2}{3(m-n)} \text{ cm.}^3 \text{ and}$$

$$v_2 = \frac{(n+3)CO_2 - 2n(T.C.)}{3(m-n)} \text{ cm.}^3$$

where T.C. represents the total contraction and CO_2 is the volume of the carbon dioxide formed. In order to find the experimental error of the analyses, several analyses of coal gas and methane from cilinders were carried out. The coal gas was passed in the 10-litre bottle A and collected over water; after 96 hours samples of 100 cm.^{3} each were withdrawn and analysed. The maximum difference in the respective determinations was $\pm$ 0·2 %, and a similar difference was obtained by the analyses of methane though each cylinder of methane contained a different composition of gases. A typical analysis of the cylinder methane was as follows: CH_4-97·52 %, CO-0·06 %, N_2-2·42 %.

As the inside diameter of the furnace tube was 15·8 mm. and the outside diameter of the thermocouple tube was 11·5 mm., the volume of the furnace and the foreheater was 13·83 cm.^{3}. After filling the furnace and the foreheater with pumice the free space in the

furnace and the foreheater was measured; this space was at 15°C - 8·96 cm.^{3}. The free space in the furnace was therefore 8·96/3 = 2·99 cm.^{3} The volume of the gases which passed in one second through the furnace heated to 600°C at a speed of, say, 400 cm.^{3}/min. was $400(1+\frac{600-20}{273})\cdot\frac{1}{60}$ = 21·00 cm.^{3}, and the time of contact with the furnace was 2·99/21·00 = 0·14 sec. Tables were thus establised which embodied times of contact of gases with the furnace at various flows and various at temperatures.

The various methods employed for the determination of small amounts of formaldehyde in aqueous solutions were tested for the purpose of choosing the simplest and the most accurate one.

1) Particularly suitable is the iodometric method devised by G. Romijn (100). This procedure is dependent on the oxidation of formaldehyde by hypoiodite formed when potassium hydroxide is added to a solution of formaldehyde, to which a known amount of a standard iodine solution has been added. The iodine consumed is measured by back-titration of the iodine liberated when the reaction mixture is acidified. The reaction involve:

$$6KOH + 3J_2 = 3KJ + 3KJO + 3H_2O,$$

$$HCHO + KJO + KOH = HCOOK + KJ + H_2O,$$

$$3KJO = 3J_2 + 6KCl + 3H_2O,$$

$$J_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaJ.$$

1 cm.^{3} of N/10 iodine is equivalent to 0·001501 gr. of formaldehyde. According to P. Borgström (101) methyl alcohol and formic acid present in formaldehyde solution have no effect on the iodometic determination.

2) Because of its rapidity the sodium sulphite method first developed by G. Lemme (102) and afterwards improved by A. Seyewetz and S. Gibello (103) and S.S. Sadtler (104), is a reliable procedure for determination of small amounts of formaldehyde. The method is based on the quantitative liberation of sodium hydroxyde when formaldehyde reacts with sodium sulphite to form the formaldehyde-bisulphite addition product.

$$HCHO+Na_2SO_3+H_2O = NaOH+CH_2(NaSO_3)OH$$

$$NaOH+HCl = NaCl+H_2O.$$

3) The Ripper's method with sodium bisulphite (105) consists in the formation of formaldehyde-bisulphite compound according to equation:

$$HCHO+NaHSO_3 = HO.CH_2.SO_3Na.$$

This salt dissolves readily in water and in methanol but only a small quantity dissolves in ethanol (106). The structure of this salt was studied by many investigators (107, 108).

4) The alkaline peroxide method which was developed by O. Blank and H. Finkelbeiner (109) and corrected by J.K. Heywood and B.H. Smith (110) is prescribed in the United States Pharmacopeia (111). It is based on the oxidation of formaldehyde by hydrogen peroxide

in the presence of a measured excess of alkali according to the equation:

$$2HCHO+2NaOH+H_2O_2 = 2HCOONa+2H_2O+H_2.$$

The amount of sodium hydroxide consumed is determined by the back-titration of the unreacted alkali with bromothymol-blue solution as indicator.

5) L. Legler (112) and B.H. Smith (113) are the originators of the ammonium chloride method. It was modified later by J. Bücki (114). It consists of the formation of hexa-methylene-tetramine from formaldehyde and ammonia, according to the equation:

$$6HCHO+4NH_3 = (CH_2)_6N_4+6H_2O.$$

The ammonia consumed is measured by the back-titration with normal hydrochloric acid.

6) The mercurimetric method was worked out by G. Romijn (115) and is based on the action of potassium mercuri iodide (Nessler's reagent) in an alkaline solution on formaldehyde, according to the equation:

$$K_2HgJ_4+HCHO+3NaOH = Hg+HCOONa+2KJ+2NaJ+2H_2O.$$

This method was later modified by W. Stüve (116), R. Gross (117) and J. Bücki (118). The excess of iodine is measured by back-titration with sodium thiosulphate.

7) Potassium cyanide method suggested by G. Romijn (119) and worked out by E. Elvove (120) and A. Mutschin (121) consists of a quantitative formation of cyanohydrin

When formaldehyde is treated with a solution containing an known excess of potassium cyanide:

$$HCHO+KCN+H_2O = CN.CH_2.OH+KOH.$$

When a mixture obtained after the above reaction is treated with a measured quantity of standard silver nitrate solution in the presence of nitric acid, the unreacted cyanide is converted in silver cyanide and the excess of silver nitrate measured by back-titration with potassium thiocyanate and ferric alum as indicator.

8) The hydroxylamine hydrochloride method worked out by A. Brochet and R. Cambier (122) consists in the liberation of hydrochloric acid when hydroxylamine hydrochloride reacts with formaldehyde to form formaldoxime:

$$HCHO+NH_2OH.HCl = CH_2:NOH+H_2O+HCl.$$

The hydrochloric acid formed is titrated with a normal solution of potassium hydroxide using bromo-phenol blue as indicator.

All the above mentioned methods have been tested in turn, but because of its accuracy and simplicity it was considered desirable to use finally the iodometric method described in paragraph 1).

In order to compare the final products of the slow oxidation of methane in the presence of water vapour and in the dry medium respectively two experiments were carried out in quick sequence. In the first the gas

mixture was passed before reaching the furnace through two wash-bottles filled with distilled water and kept at room temperature. When this experiment ended the wash-bottles were removed and three towers filled with granular dehydrated calicium chloride, silica gel and phosphorus pentoxide pespectively were placed in order to dry the gas mixture. The calcium chloride was heated before use for 2-3 hours at 120°C and left for 2 hours in a vacuum desiccator above conc. sulphuric acid. The silica gel was heated before the experiment to a high temperature (by means of a Teclu burner) and afterwards left to cool in a vacuum desiccator above conc. sulphuric acid. The phosphorus pentoxide was purfied by distillation in an iron tube in a stream of oxygen. The conc. sulphuric acid as a drying agent was not applied, because it was feared that the SO_2 and SO_3 vapours would obscure the results and create another difficulty. According to J.H. Bower (123) the under mentioned drying agents leave amounts of water in gases passed through them (in mg./L.) as follows: $CuSO_4$(anh.) - 2·8; $ZnCl_2$ -0·98; $Ba(ClO_4)_2$ - 0·82; NaOH(sticks) -0·80; $CaCl_2$(granular, dehydrated)-0·36; $Mg(ClO_4)_2.3H_2O$-0·031; Silica gel -0·030; KOH (sticks) -0·014; Al_2O_3-0·005; $CaSO_4$(anh.)-0·005; CaO-0·003; $Mg(ClO_4)_2$- 0·002; BaO-0·00065.

The most efficient drying agent, however, is phos-

phorus pentoxide. In his experiments E.W. Morley (124) passed a stream of wet gases through a tube filled with 25 gr. P_2O_5 at a speed of 2 litres per hour and found only 1 mg. of water in 40.000 litres of gases.

The results of the first experiments were very encoureging. When the gas-mixture containing nitrogen, oxygen and methane in a ratio $N_2:O_2:CH_4 = 2:1:1$ was passed through the furnace with a temperature of 670--690°C at a rate where the time of contact of the gas-mixture with the furnace was 0·18 sec., there was found in the wash-bottles an abundant amount of absorbed formaldehyde ranging from 15 % to 36 % of the methane passed. Subsequent gas analyses, however, did not correspond to the reaction which apparently thus occurred, and the amount of methane and oxygen found in the gas analyses was always much too high. Further, two experiments carried out in similar conditions of temperature, speed of gas stream, composition of gases etc. gave different results so that the amount of formaldehyde produced flactuated from 0·2 % to 37 % of the methane used.

The capricious behaviour of the oxidation of hydrocarbons in clean quartz or Pyrex vessels has often been noted previously (see loc. cit.: 33, 39, 40, 41, 95).

In order to ascertain the cause of these difficulties each part of the apparatus was carefully examined, a

series of gas analyses was carried out with known composition of gases, the part of the apparatus for determination of contraction was changed, the Romijn's iodometric method for determination of small amounts of formaldehyde was again tested. The whole apparatus proved to be in complete order, the methods used showed a satisfactory accuracy, but the results of experiments differed to a very large degree. It was thought that by the oxidation of methane to formaldehyde

$$CH_4 + O_2 = HCHO + H_2O$$

the formaldehyde produced dissolves in the water vapour formed and remains in the form of small drops on the walls of the lower cold part of the furnace. It was decided to cool the furnace to the room temperature after each experiment by passing through a stream of nitrogen and to rinse the lower part of the furnace with water through the tube D adding this rinsing water to the wash-bottles. This arrangement prolonged the time of the experiments but did not remove the erratic results. Finally, the walls of the furnace were "cleaned" before or after each experiment by a stream of methane or oxygen at the highest temperature possible in present conditions, i.e. at 750°C.

After each experiment the temperature of the furnace rose to 750°C, the stream of oxygen (as it is cheaper than methane) was passed through, the current was cut off and the stream of oxygen continued to pass until

the furnace was cooled to the room temperature. This procedure proved satisfactory as the results of experiments showed much less variation, but the production of formaldehyde was always very low.

The experiments were carried out in two series: first with dry gases and secondly with wet gases. It was observed that the oxidation of methane in a wet medium produced more heat than when the gases were carefully dried. Before starting each experiment the furnace was heated to a suitable temperature and only when the temperature remained constant for 30 minutes the stream of gases commenced to pass through the furnace. In the experiments with dry gase the temperature of the furnace remained constant during the time of the experiment, but when the gases were wet the temperature showed a tendency to rise. In the case of wet gases therefore the outside resistances should be augmanted in order to keep the temperature at an even level.

In each experiment a "chemical balance" of the reaction was calculated, i.e. the average gas analysis ought to be in accordance with the contraction of the gases shown after passing through the furnace and with the equation of the oxidation. Each experiment was repeated frequently until all the results were in a reasonable conformity with each other. In order to show,

how a "chemical balance" was established, the calculation of one of the experiments (Run No. 84A) is quoted.

Run No. 84A.

Conditions of experiments:

Temperature of the furnace: 750°± 1·5°C. Atmospheric pressure: 746·2 mm. Hg.; room temperature 20·3°C; pressure of the gases 67 mm. H_2O. Flow of the gases:

N_2+O_2 (ratio 2:1)	36·6 cm.^{3}/min.
CH_4	12·0 cm.^{3}/min.
Together	48·6 cm.^{3}/min.

As the average analysis of the methane used was: CH_4 - 97·52 %; CO - 0·06 %; N_2 - 2·42 %, the composition of gas-mixture was: $N_2:O_2:CH_4$ = = 50·21:25·10:24·69.

The experiment lasted for 60 minutes. The gas-mixture was wet.

	Gas analysis I	Gas analysis II	Average gas analysis
CO_2+HCHO	0·85 %	0·79 %	0·82 %
O_2	22·40	22·52	22·46
H_2	0·24	0·32	0·28
CO	1·05	0·97	1·01
CH_4	23·05	22·95	23·00
N_2	52·41	52·45	52·43
	100·00 %	100·00 %	100·00 %

Contraction.

The time of passage of gases in the contraction bottle G: 60·15 min. The amount of the displaced and collected water: 2772 cm.^{3}

The volume of the gas-mixture passed at N.T.P. per minute: $\frac{48\cdot6(746\cdot2+\frac{67}{13\cdot6}).273}{760.293\cdot3} = 44\cdot707$ cm.^{3}/min.

The volume of the gas-mixture which displaced the water in the contraction bottle at N.T.P. per minute:

$$\frac{2772}{60\cdot15} \cdot \frac{293\cdot3}{273} = 42\cdot999 \text{ cm.}^3/\text{min.}$$

The apparent contraction: (44·707–42·999).100/44·707 = = 3·82 %.

Before reaching the contraction bottle G the gases passed through a wash-bottle, filled with 50 % KOH which dissolved the CO_2 and HCHO, the real contraction therefore was: 3·82 % - 0·82 % = 3·00 %.

Calculation of the amount of formaldehyde.

The volume of the methane passed at N.T.P.:

$$\frac{12\cdot0.60.0\cdot9752(746\cdot2+\frac{67}{13\cdot6}-17\cdot87).273}{760.293\cdot3} = 630\cdot55 \text{ cm.}^3$$

If all the methane passed were oxidized to formaldehyde the amount of the latter would be:

630·55.30·016/22414=0·84 gr.

The water of the wash bottles with the dissolved formaldehyde was made up to 1000 cm.^{3}. For each analysis

there was used 250 cm.^{3} solution and 10 cm.^{3} N/100 J_2 to which a suitable volume of N/100 $Na_2S_2O_3$ (F=0·99881) was added.

Blank test (dist. water) -9·95 cm.^{3} N/100 $Na_2S_2O_3$;

a) -9·35 cm.^{3} - " -

b) -9·30 cm.^{3} - " -

Average: 9·95-9·325 = 0·625 cm.^{3}.

The percentage of methane which was oxidized to formaldehyde was:

$$0{\cdot}625.0{\cdot}99881.0{\cdot}001501.4.100/0{\cdot}84 = 0{\cdot}044\ \%.$$

"Chemical blance" calculation:

The composition of gases before the reaction	Gas analysis	The composition of gases after the reaction
CH_4 - 24·08 %	23·00 %	22·33 %
N_2 - 50·80	52·43	50·80
O_2 - 25·10	22·46	21·81
CO_2 - - -	0·82	0·80
HCHO - - -		0·01
CO - 0·02	1·01	0·98
H_2 - - -	0·28	0·27
100·00 %	100·00 %	97·00 %.

The gas analysis was carried out with 100 cm.^{3} gas mixture but each 100 cm.^{3} of the gas before reaction was later contracted to 97 cm.^{3}, showing a contraction of 3 %.

The equations of the reaction are as follows:

$$\overset{0.80}{\overbrace{CH_4}} + \overset{1.60}{\overbrace{2O_2}} = \overset{0.80}{\overbrace{CO_2}} + 2H_2O$$

$$\overset{0.09}{\overbrace{CH_4}} + H_2O = \overset{0.09}{\overbrace{CO}} + \overset{0.27}{\overbrace{3H_2}}$$

$$\overset{0.87}{\overbrace{CH_4}} + \overset{1.74}{\overbrace{1.5\,O_2}} = \overset{0.87}{\overbrace{CO}} + 2H_2O$$

$$\overset{0.01}{\overbrace{CH_4}} + \overset{0.01}{\overbrace{O_2}} = \overset{0.01}{\overbrace{HCHO}} + H_2O\,.$$

The contraction showed by these equations is:

$-(0{\cdot}80+1{\cdot}60+0{\cdot}09+0{\cdot}87+1{\cdot}74+0{\cdot}01+0{\cdot}01)+(0{\cdot}80+0{\cdot}09+$ $+0{\cdot}27+0{\cdot}87+0{\cdot}01) = 3{\cdot}08\ \%$, which is in a very good agreement with experiment.

The percentage of methane oxidized to CO_2, CO, H_2 and HCHO is:

CO_2	-	0·80.100/24·08	= 3·32 %
H_2	-	0·09.100/24·08	= 0·37
CO	-	0·87.100/24·08	= 3·61
HCHO			= 0·04
		Together	7·34 %.

All experiments were carried out in this way and the "Chemical balance" calculated. The results are illustrated by means of Tables I, II, III, and IV. The Tables were represented also in diagrams, where the percentage of methane oxidized to CO_2, CO etc. is plotted against times of contact with the furnace (Fig. 4, 5, 6 and 7). The decomposition in a wet medium being represented by continuous lines, and in a dry medium by broken lines.

Fig. 4.

750°C.

$N_2 : O_2 : CH_4 = 2 : 1 : 1.$

WET.

DRY.

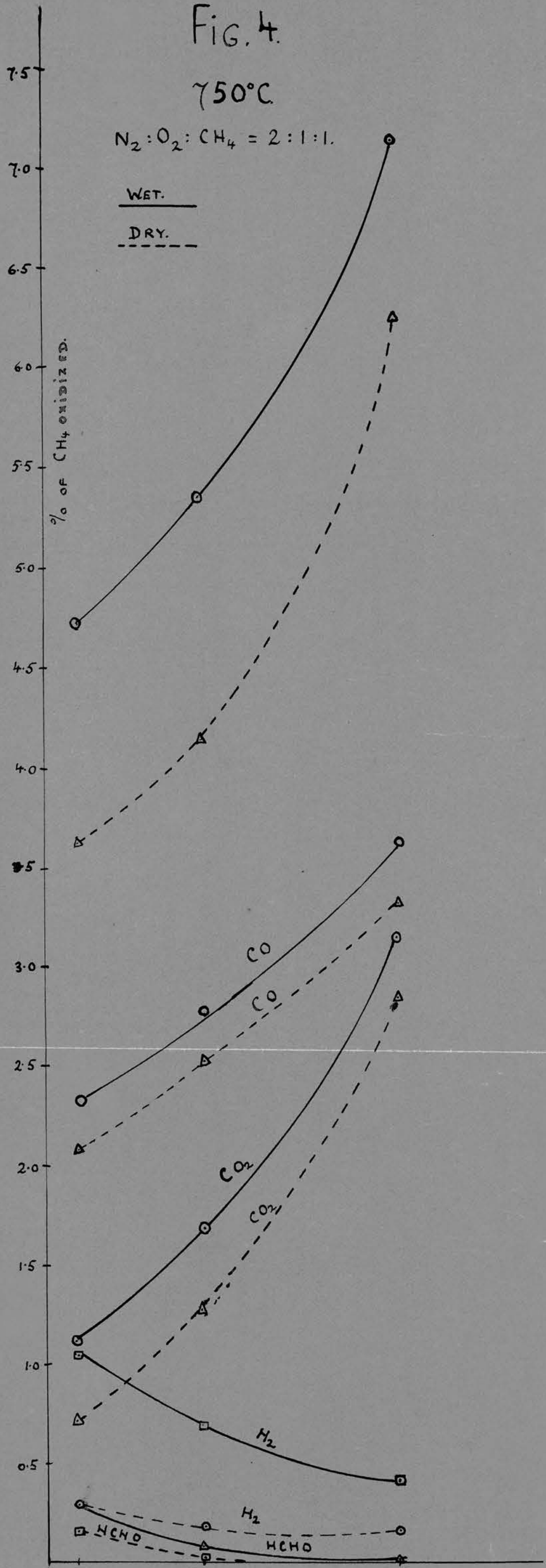


TABLE I.

Temperature 750°C.

Composition of the gas-mixture: $N_2:O_2:CH_4 = 2:1:1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·50 second		1·0 second	
	Runs No 80A & 81A		Runs No 82A & 83A		Runs No 84A & 85A	
to CO_2	1·12 1·12	1·12 *	1·67 1·71	1·69 *	3·32 3·01	3·17 *
to H_2	1·04 1·08	1·06 *	0·70 0·67	0·69 *	0·37 0·45	0·41 *
to CO	2·25 2·32	2·29 *	2·82 2·98	2·90 *	3·61 3·52	3.66*
to HCHO	0·26 0·27	0·27 *	0·09 0·08	0·09 *	0·04 0·04	0·04 *
Together	4·67 4·79	4·73	5·28 5·44	5·36	7·34 7·02	7·18

Dry gases.

	Runs No 80B & 81B		Runs No 82B & 83B		Runs No 84B & 85B	
to CO_2	0·72 0·73	0·73 *	1·22 1·34	1·28 *	2·92 2·71	2·82 *
to H_2	0·25 0·32	0·29 *	0·16 0·23	0·20 *	0·15 0·16	0·16 *
to CO	2·09 2·04	2·07 *	2·69 2·46	2·58 *	3·32 3·28	3·30 *
to HCHO	0·13 0·14	0·13 *	0·08 0·09	0·09 *	- -	-
Together	3·19 4·12	3·63	4·12 4·15	4·14	6·39 6·15	6·27

*) This figures represent the average of at least four gas analyses.

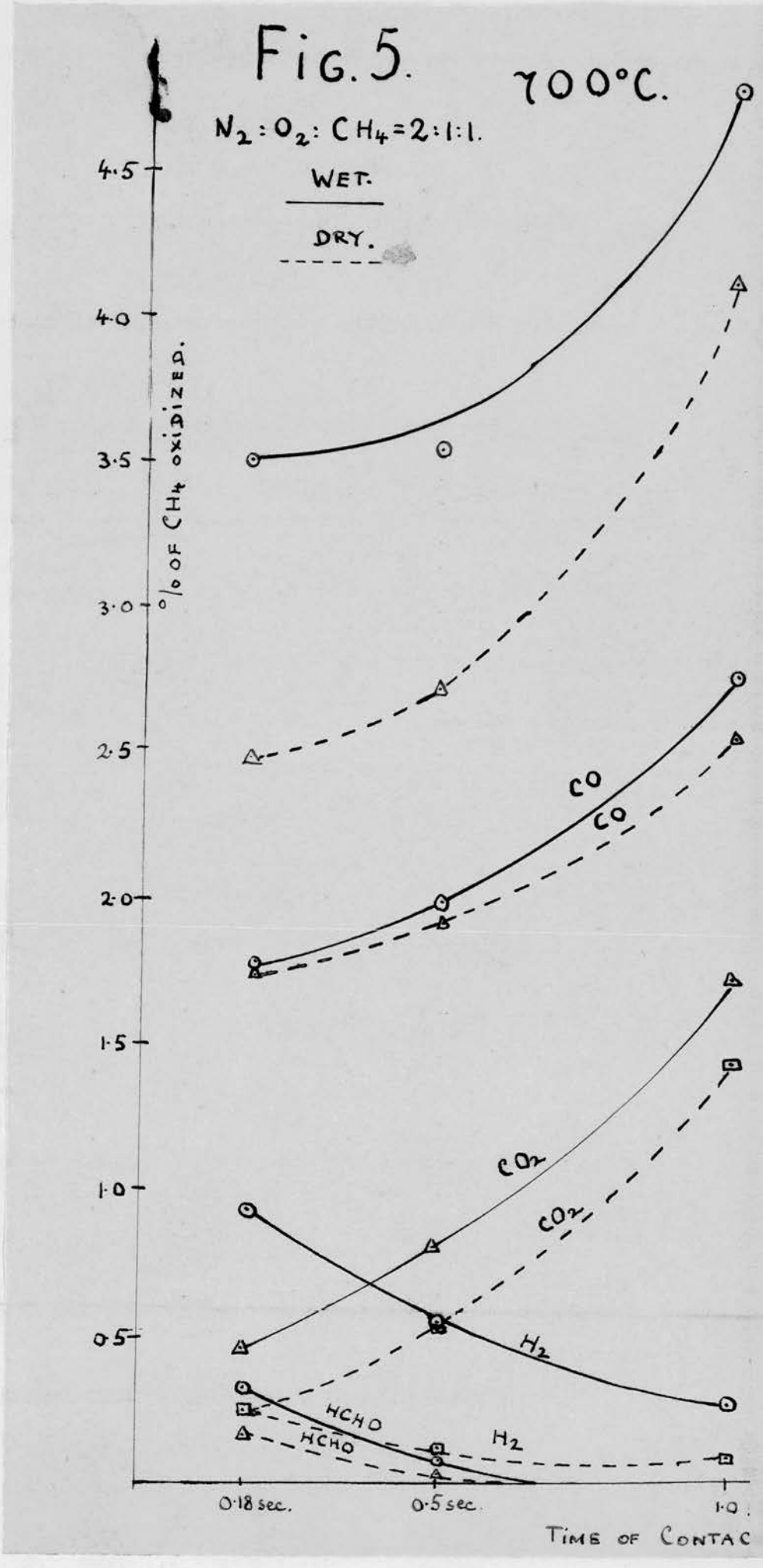


Fig. 5.
700°C.
$N_2 : O_2 : CH_4 = 2 : 1 : 1.$
WET.
DRY.
% OF CH_4 OXIDIZED.
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
CO
CO
CO_2
CO_2
H_2
H_2
HCHO
HCHO
0·18 sec.
0·5 sec.
1·0
TIME OF CONTAC

TABLE II.

Temperature 700°C.

Composition of the gas-mixture: $N_2 : O_2 : CH_4 = 2 : 1 : 1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 86A & 87A		Runs No 88A & 89A		Runs No 90A & 91A	
to CO_2	0·49 0·45	0·47 *	0·81 0·82	0·82 *	1·73 1·73	1·73 *
to H_2	0·98 0·90	0·94 *	0·65 0·49	0·57 *	0·28 0·28	0·28 *
to CO	1·87 1·63	1·75 *	2·15 1·80	1·98 *	2·86 2·70	2·78 *
to HCHO	0·32 0·35	0·34 *	0·08 0·08	0·08 *	- -	-
Together	3·66 3·33	3·50	3·69 3·19	3·45	4·87 4·71	4·79

Dry gases.

	Runs No 86B & 87B		Runs No 88B & 89B		Runs No 90B & 91B	
to CO_2	0·25 0·25	0·25 *	0·49 0·56	0·53 *	1·41 1·48	1·44 *
to H_2	0·21 0·25	0·23 *	0·16 0·12	0·14 *	0·12 0·12	0·12 *
to CO	1·73 1·93	1·83 *	2·03 1·83	1·93 *	2·69 2·45	2·57 *
to HCHO	0·17 0·16	0·17 *	0·12 0·12	0·12 *	- -	-
Together	2·36 2·59	2·48	2·80 2·63	2·72	4·22 4·05	4·14

*) These figures represent the average of at least four gas analyses.

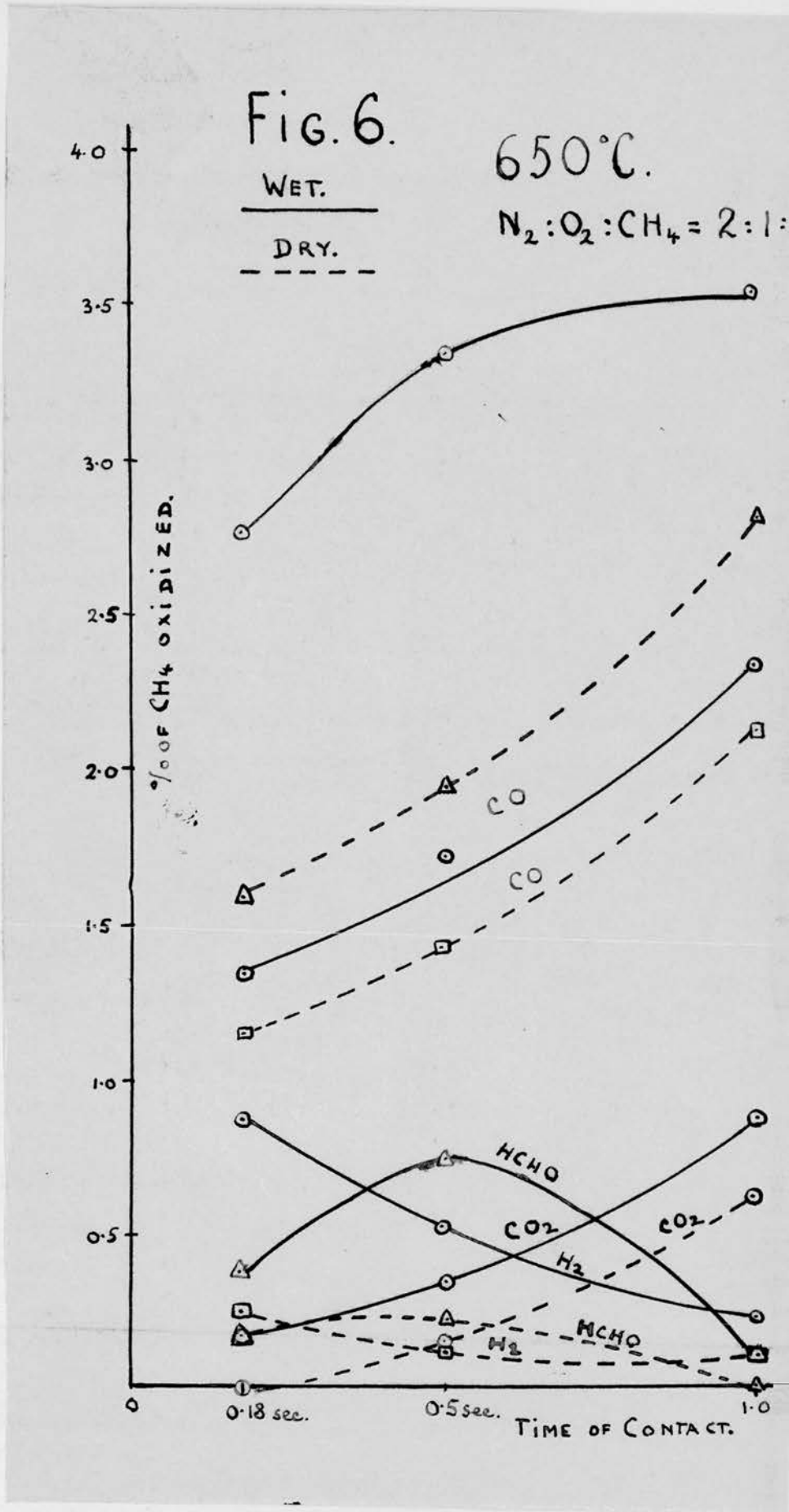


Fig. 6.
650°C.
WET.
DRY.
$N_2 : O_2 : CH_4 = 2 : 1 :$
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
% of CH_4 oxidized.
CO
CO
HCHO
CO_2
H_2
CO_2
HCHO
H_2
0·18 sec.
0·5 sec.
1·0
Time of Contact.

TABLE III.

Temperature 650°C.

Composition of the gas-mixture: $N_2:O_2:CH_4 = 2:1:1$.

Wet gases.

% CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 92A & 93A		Runs No 94A & 95A		Runs No 96A & 97A	
to CO_2	0·25 0·08	0·17 *	0·41 0·33	0·38 *	0·79 0·95	0·87 *
to H_2	0·80 0·92	0·86 *	0·57 0·49	0·53 *	0·27 0·19	0·23 *
to CO	1·59 1·13	1·36 *	1·80 1·64	1·72 *	2·41 2·25	2·33 *
to HCHO	0·38 0·39	0·39 *	0·75 0·77	0·76 *	0·11 0·11	0·11 *
Together	2·68 2·86	2·77	3·53 3·23	3·38	3·58 3·50	3·54

Dry gases.

	Runs No 92B & 93B		Runs No 94B & 95B		Runs No 96B & 97B	
to CO_2	- -	-	0·16 0·16	0·16 *	0·55 0·70	0·63 *
to H_2	0·28 0·22	0·25 *	0·12 0·12	0·12 *	0·12 0·08	0·10 *
to CO	1·27 1·01	1·14 *	1·55 1·31	1·43 *	2·26 1·98	2·12 *
to HCHO	0·21 0·21	0·21 *	0·23 0·23	0·23 *	- -	-
Together	1·76 1·44	1·60	2·08 1·82	1·94	2·93 2·76	2·85

*) These figures represent the average of at least four gas analyses.

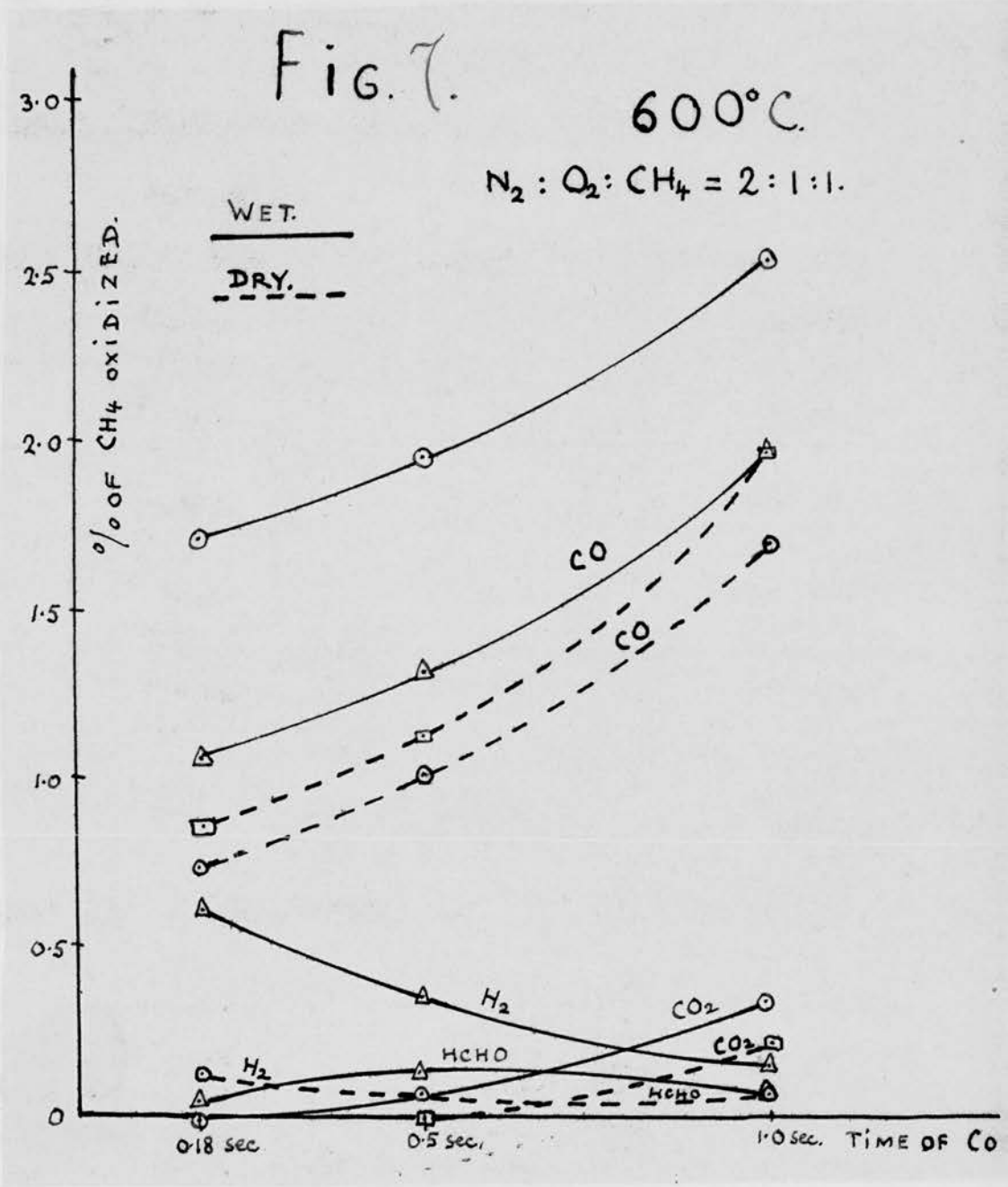


Fig. 7.
600°C.
$N_2 : O_2 : CH_4 = 2 : 1 : 1.$
WET.
DRY.
% of CH_4 oxidized.
3·0
2·5
2·0
1·5
1·0
0·5
0
CO
CO
H_2
CO_2
CO_2
HCHO
H_2
HCHO
0·18 sec.
0·5 sec.
1·0 sec.
Time of Co

TABLE IV.

Temperature 600°C.

Composition of the gas-mixture: $N_2:O_2:CH_4 = 2:1:1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

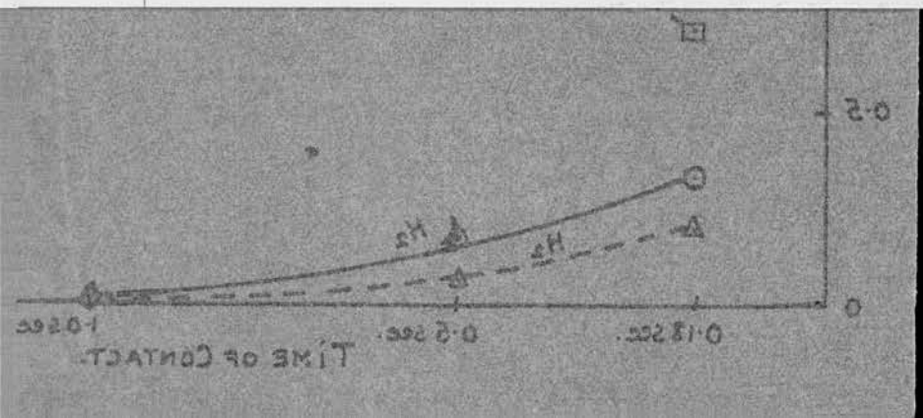
	0·18 second		0·5 second		1·0 second	
	Runs No 98A & 99A		Runs No 100A & 101A		Runs No 102A & 103A	
to CO_2	- -	-	0·28 -	0·14 *	0·35 0·33	0·33 *
to H_2	0·65 0·57	0·61 *	0·32 0·40	0·36 *	0·21 0·13	0·17 *
to CO	1·14 0·98	1·06 *	1·21 1·45	1·33 *	2·04 1·88	1·96 *
to HCHO	0·04 0·04	0·04 *	0·12 0·13	0·13 *	0·07 0·07	0·07 *
Together	1·83 1·59	1·71	1·93 1·98	1·96	2·65 2·41	2·53

Dry gases.

	Runs No 98B & 99B		Runs No 100B & 101B		Runs No 102B & 103 B	
to CO_2	- -	-	- -	-	0·37 -	0·19 *
to H_2	0·12 0·12	0·12 *	- 0·12	0·06 *	0·12 -	0·06 *
to CO	0·85 0·65	0·75 *	1·01 0·96	0·99 *	1·92 1·44	1·68 *
to HCHO	- -	-	0·05 0·05	0·05 *	0·05 0·05	0·05 *
Together	0· 97 0·77	0·87	1·06 1·13	1·10	2·46 1·48	1·97

*) These figures represent the average of at least four gas analyses.

The next series of experiments were carried out with a gas-mixture of different composition, i.e. where the ratio of nitrogen, oxygen and methane was $N_2 : O_2 : CH_4 = 2 : 0{\cdot}1 : 1$. These experiments are represented in TABLES V, VI, VII and VIII and in Fig. 8, 9, 10 and 11.



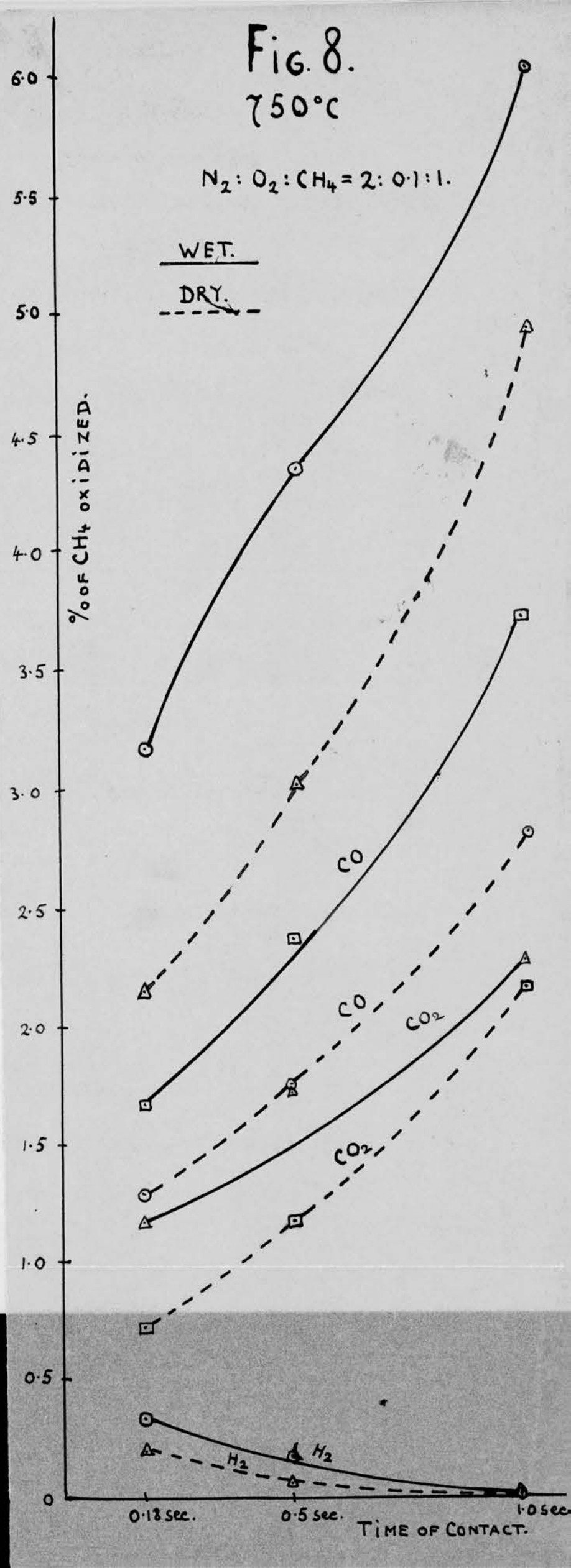


Fig. 8.
750°C
$N_2 : O_2 : CH_4 = 2 : 0.1 : 1.$
WET.
DRY.
% of CH_4 oxidized.
6·0
5·5
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
CO
CO
CO_2
CO_2
H_2
H_2
0·18 sec.
0·5 sec.
1·0 sec.
Time of Contact.

TABLE V.

Temperature 750°C.

Composition of the gas-mixture: $N_2:O_2:CH_4 = 2:0{\cdot}1:1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 104A & 105A		Runs Nc 106A & 107A		Runs No 108A & 109B	
to CO_2	1·08 1·27	1·18 *	1·66 1·92	1·79 *	2·38 2·23	2·30 *
to H_2	0·31 0·34	0·33 *	0·25 0·16	0·20 *	- -	-
to CO	1·84 1·50	1·67 *	2·44 2·34	2·39 *	3·66 3·81	3·73 *
to HCHO	- -	-	- -	-	- -	-
Together	3·23 3·11	3·17	4·35 4·42	4·38	6·04 6·04	6·04

Dry Gases.

	Runs No 104B & 105B		Runs No 106B &107B		Runs No 108B & 109B	
to CO_2	0·79 0·60	0·70 *	1·29 1·09	1·19 *	2·36 1·99	2·18 *
to H_2	0·22 0·16	0·19 *	0·06 0·06	0·06 *	- -	-
to CO	1·14 1·39	1·27 *	1·61 1·96	1·78 *	2·61 2·93	2·77 *
to HCHO	- -	-	- -	-	- -	-
Together	2·15 2·15	2·15	2·96 3·11	3·04	4·97 4·92	4·95

*) These figures represent the average of at least four gas analyses.

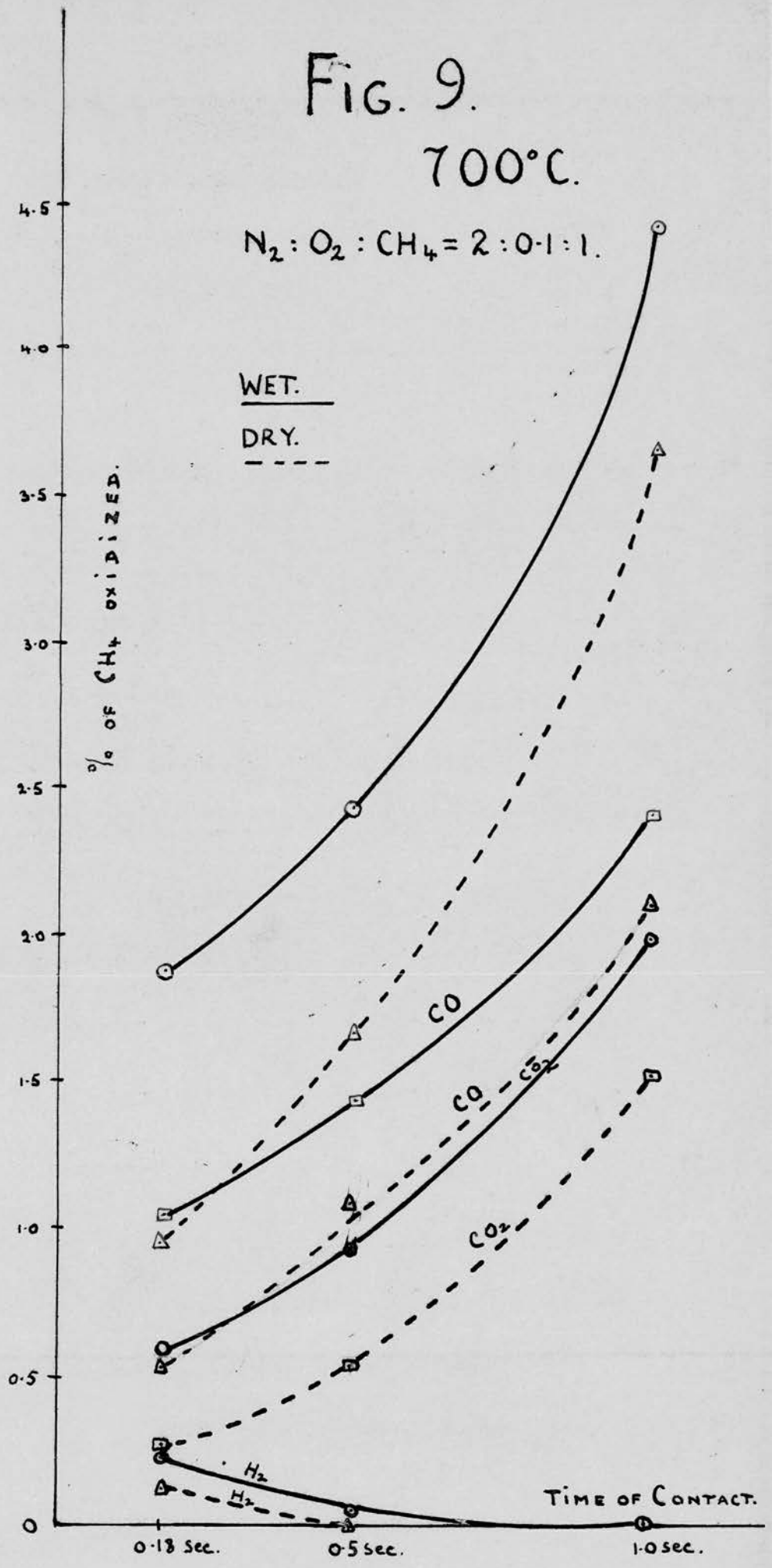


FIG. 9.
700°C.
$N_2 : O_2 : CH_4 = 2 : 0{\cdot}1 : 1$.
WET.
DRY.
% OF CH_4 OXIDIZED.
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
CO
CO_2
H_2
H_2
TIME OF CONTACT.
0·18 sec.
0·5 sec.
1·0 sec.

TABLE VI.

Temperature 700°C.

Composition of the gas-mixture: $N_2 : O_2 : CH_4 = 2 : 0{\cdot}1 : 1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 116A & 117A		Runs No 118A & 119A		Runs No 120A & 121A	
to CO_2	0·80 0·41	0·61 *	0·80 1·05	0·93 *	1·87 2·13	2·00 *
to H_2	0·26 0·16	0·21 *	0·06 0·06	0·06 *	- -	-
to CO	0·80 1·27	1·04 *	1·17 1·67	1·42 *	2·54 2·28	2·41 *
to HCHO	- -	-	0·03 0·03	0·03 *	- -	-
Together	1·86 1·84	1·85	2·06 2·81	2·44	4·41 4·41	4·41

Dry gases.

	Runs No 116B & 117B		Runs No 118B & 119B		Runs No 120B & 121B	
to CO_2	0·16 0·32	0·24 *	0·76 0·38	0·57 *	1·65 1·40	1·53 *
to H_2	0·09 0·16	0·13 *	- -	-	- -	-
to CO	0·79 0·35	0·57 *	0·89 1·34	1·13 *	1·93 2·31	2·12 *
to HCHO	- -	-	- -	-	- -	-
Together	1·04 0·83	0·94	1·65 1·72	1·69	3·58 3·71	3·65

*) These figures represent the average of at least four gas analyses.

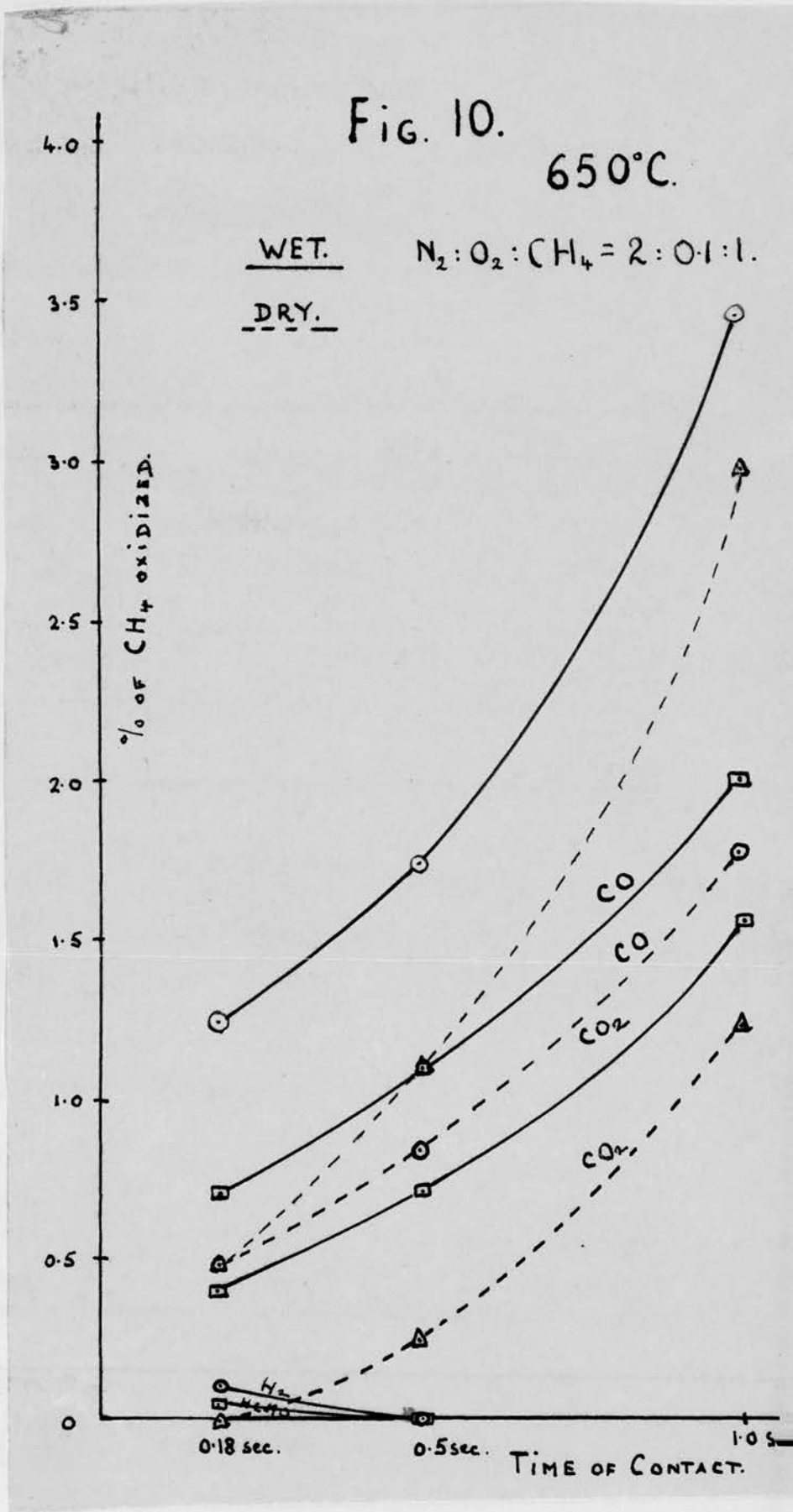


Fig. 10.
650°C.
WET.
DRY.
$N_2 : O_2 : CH_4 = 2 : 0.1 : 1.$
% of CH_4 oxidized.
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
CO
CO
CO_2
CO_2
H_2
0.18 sec.
0.5 sec.
1.0 s
Time of Contact.

TABLE VII.

Temperature 650°C.

Composition of the gas-mixture: $N_2 : O_2 : CH_4 = 2 : 0{\cdot}1 : 1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 110A & 111A		Runs No 112A & 113A		Runs No 114A & 115A	
to CO_2	0·32 0·44	0·38 *	0·80 0·48	0·74 *	1·56 1·37	1·47 *
to H_2	0·22 -	0·11 *	- -	-	- -	-
to CO	0·48 0·96	0·72 *	0·89 1·15	1·02 *	1·84 2·15	2·00 *
to HCHO	0·06 0·06	0·06 *	0·06 0·06	0·06 *	- -	-
Together	1·08 1·46	1·27	1·75 1·69	1·72	3·40 3·52	3·46

Dry gases.

	Runs No 110B & 111B		Runs No 112B & 113B		Runs No 114B & 115B	
to CO_2	- -	-	0·25 0·25	0·25 *	1·11 1·30	1·21 *
to H_2	- -	-	- -	-	- -	-
to CO	0·59 0·41	0·50 *	0·72 0·91	0·82 *	1·89 1·64	1·77 *
to HCHO	- -	-	0·06 0·06	0·06 *	- -	-
Together	0·59 0·41	0·50	1·03 1·22	1·13	3·00 2·94	2·97

*) These figures represent the average of at least four gas analyses.

Fig. 11.

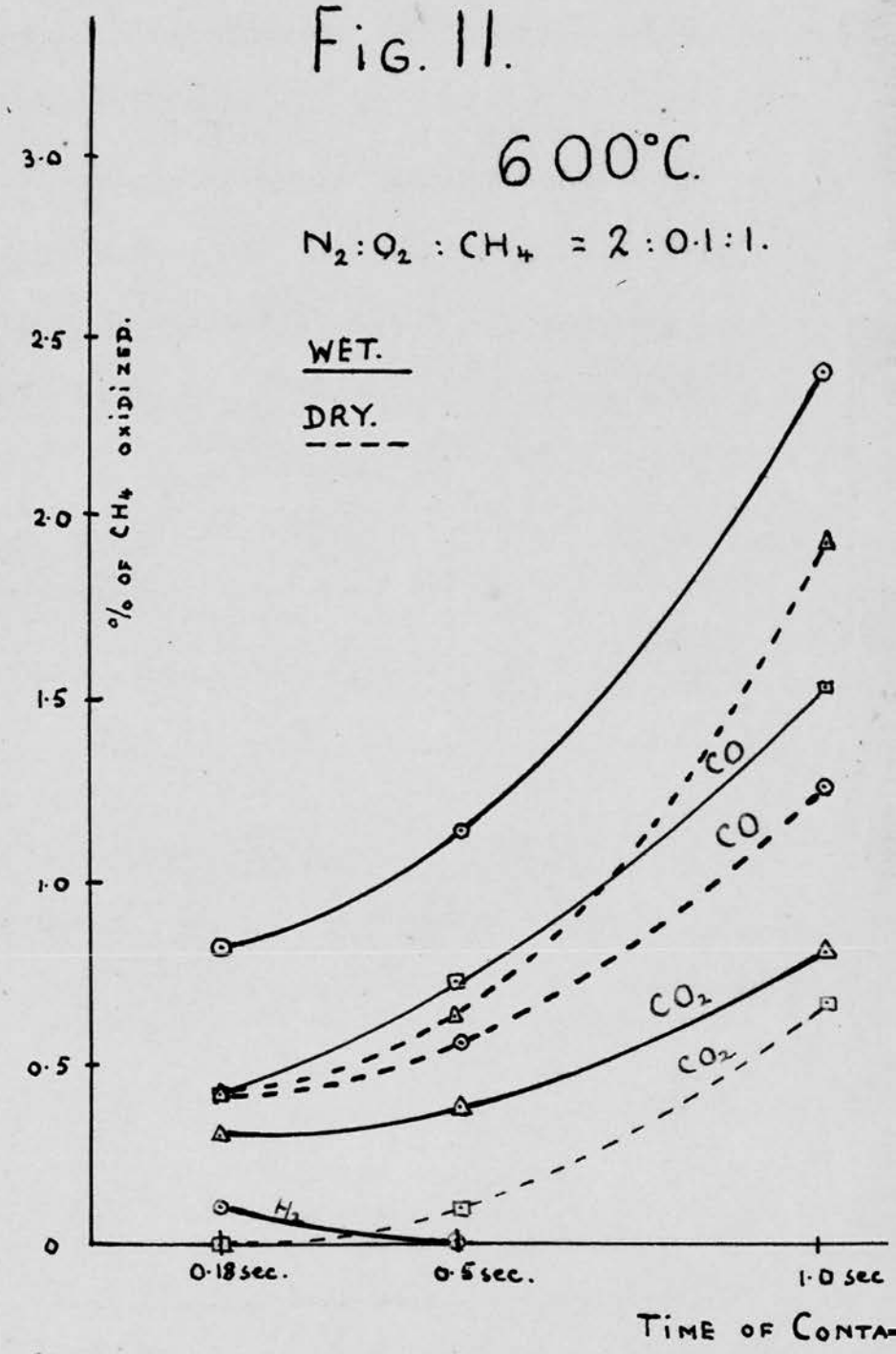

600°C.
$N_2 : O_2 : CH_4 = 2 : 0.1 : 1.$
WET.
DRY.
% of CH_4 oxidized.
3·0
2·5
2·0
1·5
1·0
0·5
0
CO
CO
CO_2
CO_2
H_2
0·18 sec.
0·5 sec.
1·0 sec
Time of Conta-

TABLE VIII.

Temperature 600°C.

Composition of the gas-mixture: $N_2 : O_2 : CH_4 = 2 : 0{\cdot}1 : 1$.

Wet gases.

% of CH_4 oxidized during contact with the furnace of:

	0·18 second		0·5 second		1·0 second	
	Runs No 122A & 123A		Runs No 124A & 125A		Runs No 126A & 127A	
to CO_2	0·41 0·16	0·29 *	0·44 0·32	0·38 *	0·79 0·91	0·85 *
to H_2	0·13 0·07	0·10 *	- -	-	- -	-
to CO	0·29 0·54	0·42 *	0·64 0·89	0·77 *	1·64 1·45	1·54 *
to HCHO	- -	-	- -	-	- -	-
Together	0·83 0·77	0·80	1·08 1·21	1·15	2·43 2·36	2·39

Dry gases.

	Runs No 122B &123B		Runs No 124B & 125B		Runs No 126B & 127B	
to CO_2	- -	-	0·09 0·09	0·09 *	0·79 0·54	0·67 *
to H_2	- -	-	- -	-	- -	-
to CO	0·57 0·38	0·45 *	0·69 0·38	0·54 *	1·18 1·37	1·27 *
to HCHO	- -	-	- -	-	- -	-
Together	0·57 0·38	0·45	0·78 0·47	0·63	1·97 1·91	1·94

*) These figures represent the average of at least four gas analyses.

C. DISCUSSION.

1) As the experiments show, the production of formaldehyde in abundant quantities by the slow oxidation of methane was not at all successful, although the gas-mixture containing methane was heated for a very short time, ranging from 0·18 second to 1·0 second, and was cooled immediately afterwards. The yield of formaldehyde was low and did not exceed 0·8 % of the methane used. The best results were obtained when using the gas-mixture $N_2 : O_2 : CH_4$ = 2:1:1 at temperature 650°C and when the contact with the furnace was 0·5 second. The yield of formaldehyde was low either because methane heated for a short time at this temperature oxidizes very slowly, or because formaldehyde produced in larger amount decomposes at high temperatures so quickly that only a small fraction remains undecomposed, or because these two factors take place simultaneously. At any rate, though it was hoped during the first experiments, where the yield of formaldehyde was sometimes nearly 36 % of the methane used, that good results would be obtained, deeper investigations proved the hope to be completely unjustified.

2) The difficulties which were encountered in the first experiments, - namely, that experiments carried out in identical conditions gave completely

results, - indicate the oxidation of methane carried out in the experimental conditions described above to be a surface reaction. As may be seen from the cited literature on the subject, many investigators considered this reaction to be a chain reaction; on the basis of the experiments it is difficult to confirm whether there is actually a chain reaction, but the fact that results were better and were comparable with each other after the pumice, which filled the furnace, and its walls had been rinsed with a stream of clean oxygen or methane at a high temperature, seems to indicate that a chain reaction really takes place or that initiation of reaction takes place mainly on such surfaces.

3) The experiments which were carried out indicate without doubt that the water vapour added before the reaction has a large influence on the slow oxidation of methane. From all the diagrams, which show the oxidation of methane in a wet and in a dry medium, it is apparent that the oxidation of methane in a wet medium is more complete and the reaction is quicker even disregarding the time of contact with the furnace. It must be kept in mind that the reaction does not occur in a medium ideally dry, because the oxidation of methane either to formaldehyde or to carbon monoxide or dioxide is accompanied by the production of

water vapour. But it can be stated that an excess of water vapour causes in the condition of the experiments a quicker oxidation of methane.

4) An interesting problem is the derivation of hydrogen, which is present in samll amounts in the gas--mixtures after passing through the furnace. The hydrogen can result from different reactions. It is known that at temperatures near ignition point a molecule of methane decomposes into CH_3 or CH_2 radicals and into hydrogen or the following reaction takes place (loc. cit. - 113):

$$CH_4+O_2 = CO+H_2+H_2O.$$

A part of hydrogen liberated combines with oxygen forming water. Against this assumption, however, is the fact that hydrogen was found in a gas-mixture which passed through the furnace heated to temperatures far below the ignition temperature of methane and even to temperature 600°C (TABLE IV and VIII). It seems that at this temperature the breaking up of the isolated methane molecule into CH_3 or CH_2 radicals and hydrogen would not occur.

Other reaction which could produce hydrogen are as follows:

$$CH_4+CO_2 = 2CO+2H_2 \text{ and}$$

$$CH_4+H_2O = CO+3H_2.$$

The occurence of both of these reactions is possible but the first is less probable than the second, because

one must remember the work by W.A. Bone and R.V. Wheeler (loc. cit. - 1) in which the investigators heated for a long time inclosed vessels a mixture containing methane and oxygen at high temperatures and they never found any trace of hydrogen but only certain amounts of carbon dioxide and some larger amounts of carbon monoxide.

As mentioned above, each of the experiments carried out was completed by a "chemical balance." In each case, when hydrogen was found in the gas-mixture passed through the furnace, it was attempted to discover which of these two possible reaction above corresponded to the experimental data obtained. In all cases it was found that the second reaction was more likely in such an experiment. The objection that in the case of dried gas-mixture no hydrogen ought to be found is not correct, as the oxidation of methane to formaldehyde and carbon oxides is bound up with the production of water which reacts at these high temperatures on methane molecules present.

As the diagrams show, the amount of hydrogen determined in gas-mixtures after their passage through the furnace becomes larger as the time of contact with the furnace becomes shorter. The curves, therefore, showing the percentage of methane used which was transformed into hydrogen, decrease as the time of contact with the furnace of the gas-mixture increases. It is

caused probably by the fact that at high temperatures hydrogen combines easily with oxygen and that time is an important factor in this reaction. Comparison of the numbers in TABLES I and V, - which differ one from another in this that in the first the composition of the gas-mixture was $N_2:O_2:CH_4 = 2:1:1$ and in the second $N_2:O_2:CH_4 = 2:0{\cdot}1:1$, - shows that when the amount of oxygen present in the gases is smaller the quantity of the hydrogen found (after the passage through the furnace) is also smaller. This is probably due to the fact that a smaller amount of methane was oxidized and therefore, a correspondingly smaller amount of water vapour was produced which decompcsed methane molecules into hydrogen and carbon monoxide.

5) Comparision of the oxidation process of the gas-mixture $N_2:O_2:CH_4 = 2:1:1$ (TABLES I, II, III and IV) and of that of the gas-mixture $N_2:O_2:CH_4 = 2:0{\cdot}1:1$. (TABLES V, VI, VII and VIII) does not show large differences. In the latter the numbers showing the percentage of methane oxidation are smaller, but the general character of the oxidation process is much the same. This result is in agreement with the investigations by Bone and Allum (loc. cit. - 64) where methane--oxygen mixtures of the composition $O_2:CH_4 = 0{\cdot}33:1$, $0{\cdot}50:1$, $1:1$, $1{\cdot}86:1$ were tried by the stationary method at atmospheric pressure. They proved that although the course

of the oxidation process is in all these cases similar, the most reactive of all mixtures is the $O_2:CH_4$ = = 0·5:1.

The interesting problem, how the oxidation process of methane to formaldehyde proceeds (namely, whether large amounts of formaldehyde are formed which decompose immediately, or whether only a small fraction of the methane present is oxidized to formaldehyde) led to the study of the thermal decomposition of formaldehyde. It was intended to carry out experiments in conditions similar to the proceding ones, namely, when the time of contact of formaldehyde with the furnace was 0·5 and 1·0 second and at temperatures of the furnace from 750°C downwards.

PART II.

STUDIES IN THE THERMAL DECOMPOSITION OF FORMALDEHYDE.

A. GENERAL.

Apart from its tendency to form reversible polymers, formaldehyde possesses a surprising degree of chemical stability. Measurable thermal decomposition of gaseous formaldehyde is practically negligible at temperatures below 300°C although at higher temperatures it decomposes almost exclusively to carbon monoxide and hydrogen with no seperation of carbon, as indicated by the equation:

$$HCHO = CO + H_2 .$$

The first investigations on thermal decomposition of formaldehyde were carried out by W.A. Bone and H.L. Smith (125), who worked with the usual stationary method. The gaseous formaldehyde was introduced in a vacuous glazed porcelain tube (capacity 34 $cm.^3$) and the difference in the pressure exerted by decomposition products was measured by means of a manometer. No difference in pressure was observed at temperatures above 700°C and no seperation of carbon. After the experiment the gases were withdrawn from the tube and analysed. The obtained almost equal amounts of carbon monoxide and hydrogen with traces of carbon dioxide and methane and they illustrated the results by means of the following table:

Temperature		1125°C	900°C	700°C	500°C	400°C
Duration of heating		1 min.	2 min.	2 min.	2 min.	2 min.
% Composition of products	CO	49·8	49·4	50·20	50·75	52·7
	H_2	48·9	49·1	48·75	47·00	45·2
	CO_2	0·4	0·5	0·40	0·25	trace
	CH_4	0·9	1·0	0·65	2·00	2·1

R.H. Newton and B.F. Dodge (126) determined the equilibrium constant for the reaction

$$CO + H_2 \rightleftharpoons HCHO$$

and according to their findings

$$K_p = \frac{P_{HCHO}}{P_{CO} \cdot P_{H_2}} = \log_{10}^{-1} \left\{ \frac{324}{T} - 5{\cdot}431 \right\}.$$

Although these studies have shown that the equilibrium involved in this reaction favours the decomposition to such an extent that it may be regarded as almost irreversible under ordinary circumstances, reaction rates are very slow below 300°C.

Some idea of the rates at higher temperatures may be gained by the data of S.S. Medvedev and E.A. Robinson (127). These investigators report that when a gaseous mixture containing 40 % formaldehye and 60 % carbon dioxide is passed through a refractory glass tube (30 cm. long) heated to various temperatures and under conditions such that the exposure time is 29 seconds in each case, the percentage decomposition is as follows:

Temperature	700°C	650°C	600°C	550°C	500°C	450°C
% decomposition	97·6	94·9	87·5	44·7	38·6	10·2

According to C.J.M. Fletsher (128), who studied formaldehyde decomposition between 510°C and 607°C at a pressure range of 30 to 400 mm., the decomposition of formaldehyde to carbon monoxide and hydrogen, although unquestionably the principal reaction, is also accompanied by condensation reactions, which exert a disturbing influence on the rate of decomposition even though they eventually lead in part to carbon monoxide formation. An immediate pressure rise due to simple splitting in carbon monoxide and hydrogen is followed by a subsidiary rise which extends over several hours.

M. Patry and P. Monceaux (loc. cit.-91) studied the thermal decomposition of formaldehyde independently in air-formaldehyde and nitrogen-formaldehyde mixtures, in which the formaldehyde concentrations were 0·1-0·2 %. It was ascertained that under otherwise uniform conditions the decomposition was approximately the same in air-formaldehyde mixtures as in the nitrogen-formaldehyde mixtures. Removal by oxidation was therefore negligible in comparison with the thermal decomposition and the investigation could therefore be limited to the study of this latter phenomenon. Below 600°C the reaction was slow. At 700°C, however, the reaction was very rapid, since for a time of contact of 0·5 sec. and without a catalyst about 90 % of the

formaldehyde in the furnace was decomposed.

Catalysts have considerable influence on both the rate and nature of formaldehyde decomposition. In presence of finely divided platinum, decomposition is stated to occur at 150°C (129), whereas copper shavings are reported to have no effect below 500°C (130). Various inorganic compounds, such as sodium carbonate, chromic oxide, alumina etc., are stated to modify the decomposition with formation of small quantities of methanol, formic acid, carbon dioxide, methane and complex organic products (131).

Ultraviolet light causes decomposition of formaldehyde to carbon monoxide and hydrogen at ordinary temperatures (132). In the presence of water vapour these products are accompanied by methane and carbon dioxide (133). G. Bredig and A. Goldberger (134) showed that, when formaldehyde is irradiated with light absorbed by the carbonyl group, it gives carbon monoxide and hydrogen with only a very small quantity (if any) of carbon dioxide and methane.

F.W. Kirkbridge and R.G.W. Norrish (135) studied the photochemical decomposition of carbonyl compounds and they came to the conclusion that for formaldehyde and benzaldehyde the photolysis occurs in one primary act and it is represented by the equation:

$$\begin{matrix} R \\ H \end{matrix}\!\!>\!CO = CO+RH,$$

in which a molecule of CO is eliminated bodily from

the molecule of the aldehyde and the remaining parts, a radical and a hydrogen atom, combine together. Since this net reaction involves practically no energy change the photoactive quantum should correspond to the heat of dissociation of the product RH in R and H and should lead to a quantum efficiency of unity. The investigators have obtained values between 1 and 2 for formaldehyde but accurate results were difficult to obtain owing to errors due to polymerisation.

Theoretical calculations of the thermal decomposition of formaldehyde (and other compounds) on the basis of thermodynamical considerations were given by B.C. Vickery (136). His argumentations are as follows:

The equilibrium constant of the gaseous reaction

$$HCHO \rightleftharpoons CO + H_2$$

is given by the experssion: $K_p = \frac{P_{CO} \cdot P_{H_2}}{P_{HCHO}}$.

The changes of free energy for the gases in their standard states (P = 1 atm.) and at a particular temperature T is defined by the expression:

$\Delta F_T^o = \Delta E_o^o + (F_T^o - E_o^o)_{CO} + (F_T^o - E_o^o)_{H_2} - (F_T^o - E_o^o)_{HCHO}$, where

$\Delta E_o^o = (E_o^o)_{CO} + (E_o^o)_{H_2} - (E_o^o)_{HCHO}$. E_o^o is the internal energy of each gas in its standard state at absolute zero. The relation between the changes of the free energy state and the equilibrium constant K_p at a normal pressure is given by the expression: $-\Delta F_T^o = RT \cdot \ln K_p$.

$\triangle F_T^o$ can be calculated by means of free energies of the gases involved on the basis of statistical mechanics, the only other quantity needed being the value of $\triangle H_T^o$ (the heat of the reaction at the temperature T), where $\triangle H_T^o = \triangle E_o^o + (H_T^o - E_o^o)_{CO} + (H_T^o - E_o^o)_{H_2} - (H_T^o - E_o^o)_{HCHO}$. The quantities $(F_T^o - E_o^o)$ and $(H_T^o - E_o^o)$ are energy differences which can be derived by a consideration of the energy levels of the substance based on a knowledge of the energy levels of a molecule, which are theoretically deduced from a quantum mechanical treatment or experimentally from spectroscopical data. From these values the author calculates the value of $\triangle E_o^o$ (internal energy change) $\triangle E_o^o = +0{\cdot}196$ Kg.cal. and $\triangle F_{300}^o = -5{\cdot}9792$ Kg. cal. The equilibrium constant for the reaction at 300°K is calculated from the equation:

$$\ln K_p = \frac{-\triangle F_{300}^o}{RT}; \quad \log K_p = \frac{1}{2{\cdot}303} \cdot \frac{5{\cdot}9792}{0{\cdot}0019865 \cdot 300} = 4{\cdot}357,$$

or $K_p = 2{\cdot}275 \cdot 10^4$. If this procedure is repeated for a series of temperatures, a series of values of K_p is obtained. The numbers calculated by some authors differ somewhat one from another. Thus, Newton and Dodge (loc. cit. - 126) and Natta (137) claim for the reaction $HCHO \rightleftharpoons CO + H_2$ the following values:

	log K_p at temperatures °C							
	100	200	300	400	500	600	700	800
Vickery	4·65	4·95	5·18	5·38	5·52	5·63	5·72	5·79
Newton & Dodge	4·4	4·63	4·8	4·9	4·96	4·96	5·05	-
Natta	-	-	6·85	7·1	7·28	7·28	7·58	-

On the basis of these figures formaldehyde would be a very unstable compound and at 100°C would be almost entirely decomposed.

B. EXPERIMENTAL RESULTS.

For the comparison with the previous work on methane oxidation it was decided to use in these experiments the same furnace which had been employed and the same arrangement fort the measuring and the displacement of the original gas-mixtures.

Difficulties, were, however, encountered in the first experiments. It was hoped that when a stream of nitrogen was passed through a formaldehyde solution (the solution used contained 38·1 % of formaldehyde) an abundant amount of formaldehyde would be found in the gas-mixture. The experiments, however, showed that when a very slow stream of nitrogen was passed through this solution the formaldehyde could not be detected even by the modified Schiff's reagent (138). After passing a slow stream of nitrogen through formaldehyde solution for 60 minutes and after absorption of the formaldehyde in water it was found that the stream contained only 0·036 % of formaldehyde. It was then decided to pass air through 300 cm.^{3} of the formaldehyde solution for several hours and to determine the percentage of formaldehyde in the solution after this operation. The original percentage of formaldehyde solution was 37·107 %; after 6 hours it appeared to be 37·088 % and after 21 hours - 36·850 %.

These difficulties were caused by the extremely low partial pressure of formaldehyde over its aqueous

solution, because of the presence of polymers in this solution. In 1905 F. Auerbach and H. Barschall (139) determined the average molecular weight of dissolved formaldehyde at room temperature (approx. 20°C) in aqueous solutions of various concentrations up to approximately 38 %. All measurements were made in dilute solutions by the cryoscopic method. The concentrated solutions studied were deluted with ice--water for freezing point measurement. The success of this method lay in the fact that depolymerisation on dilution was slow at ice-water temperature. Only in the case of the most concentrated solutions was difficulty encountered. With such solutions series of molecular weight measurements were made at various time intervals after dilution. By plotting these values against time and extrapolating to zero time, the molecular weights value for the instant of dilution was estimated. These data are as follows:

Formaldehyde Concentration (%)	Apparent Molecular Weight Determined.
2·4	30·0
5·9	32·5
11·2	36·2
14·7	38·5
21·1	43·0
22·6	44·6
24·0	44·9
28·2	48·5
33·8	53·5

Auerbach found that these cryoscopic data were consistent with a chemical equilibrium between formaldehyde monohydrate (methylene glycol) and a trimeric hydrate (trioxymethylene glycol) as shown in the equation:

$$3HO.CH_2O.H \rightleftharpoons HO.(CH_2O)_3.H + 2H_2O$$

and he concluded that polymeric hydrates other than the trimeric hydrate $HO.(CH_2O)_3.H$ are not present in appreciable proportions in solutions containing up to 30 % formaldehyde. Deviations encountered when more concentrated solutions were used were attributed to the presence of substantial concentrations of higher polymers.

Compound formation in solution is similarly manifested by a pronounced negative deviation from Raoult's law. A deviation from Henry's law, which becomes apparent at a 4 % concentration and increases with increasing formaldehyde content, bears witness to the steadily growing proportion of polymeric hydrates. J.F. Walker (140) has found that this deviation is in quantitative agreement with Auerbach's data in that the partial pressure of formaldehyde is almost directly proportional to the apparent mol fraction of methylene glycol as calculated from the cryoscopic measurements.

The partial pressure of formaldehyde over its aqueous solutions was studied by Auerbach and Barschall (loc. cit.-139), Ledbury and Blair (141) and Korzev and Rossinskaya (142). The partial-pressure data of Ledbury and Blair cover solutions containing up to 37 % formaldehyde at temperatures of 0° to 45°C. These data for room temperature (20°C) are as follows:

HCHO Concentration in % by weight.	Partial Pressure of HCHO (mm. Hg).	Mg. HCHO per Litre saturated air
9·25	0·340	0·59
18·6	0·575	1·01
27·2	0·780	1·39
28·6	0·795	1·40
36·2	1·025	1·75

These data were determined by measuring the formaldehyde content of air which had been passed through scrabbers containing solutions of definite temperature and concentration at equilibrium conditions.

Partial-pressure measurements for boiling formaldehyde solutions were determined by Auerbach and Barschall (loc. cit. - 139) and Korzev and Rosinskaya (loc. cit. - 142) from distillation data. These latter data for higher concentrations of formaldehyde are as follows:

HCHO Conc. in % by weight.	Total Pressure in mm. Hg.	Temp. (°C)	P_{HCHO} in mm. Hg.
17·50	753	98·5	85·1
19·51	753	98·5	88·9
19·54	735	97·5	87·2
25·90	735	97·5	109·5
25·90	753	98·5	114·5

An abundant concentration of formaldehyde vapours in air can be obtained by distillation. Thus, A. Zimmerli (143) reported that concentrated distillates containing up to 55 % formaldehyde could be obtained by distilling comparatively dilute formaldehyde solutions at atmospheric pressure. This was accomplished by the use of a five-foot distilling column surmounted by an efficient reflux condenser. His results are as follows:

Conc. of HCHO solution %	Pressure (mm. Hg.)	Boiling Temp. (°C)	Conc. of HCHO in vapours %
6·82	740	98·0	6·95
17·34	742	98·1	14·96
27·67	751	98·5	22·79

Another source of production of an abundant concentration of formaldehyde in air is paraformaldehyde. Commercial paraformaldehyde contains 95-97 % lower polyoxymethylene glycols corresponding to the formula $HO.(CH_2O)_n.H$, where n = 8-50, and melting at 120°-160°C.

At ordinary temperatures paraformaldehyde gradually vaporizes and on long exposure to the atmosphere it volatilizes completely. G. Nordgren (144) has demonstrated that the vapour obtained under these conditions consists principally of monomeric formaldehyde gas, accompanied by water vapour. This depolymerisation is greatly accelerated by heat. Auerbach and Baschall (145) have shown that when 93 % paraformaldehyde is completely vaporized at 224°C the gas obtained has a vapour density of 29·3, which is in fair agreement with the value 28·7 calculated for a mixture of 93 % formaldehyde and 7 % water vapour.

Paraformaldehyde dissolves slowly in cold water and more rapidly in hot water, hydrolyzing and depolymeryzing as it dissolves. Formaldehyde solutions obtained in this way are identical with those obtained by dissolving gaseous formaldehyde in water (loc. cit. - - 186).

On the basis of these experimental results and in order to produce a stream of gas-mixture containing an abundant percentage of gaseous formaldehyde, it was decided to use 1) paraformaldehyde and 2) a concentrated solution of formaldehyde in water at temperatures near boiling point.

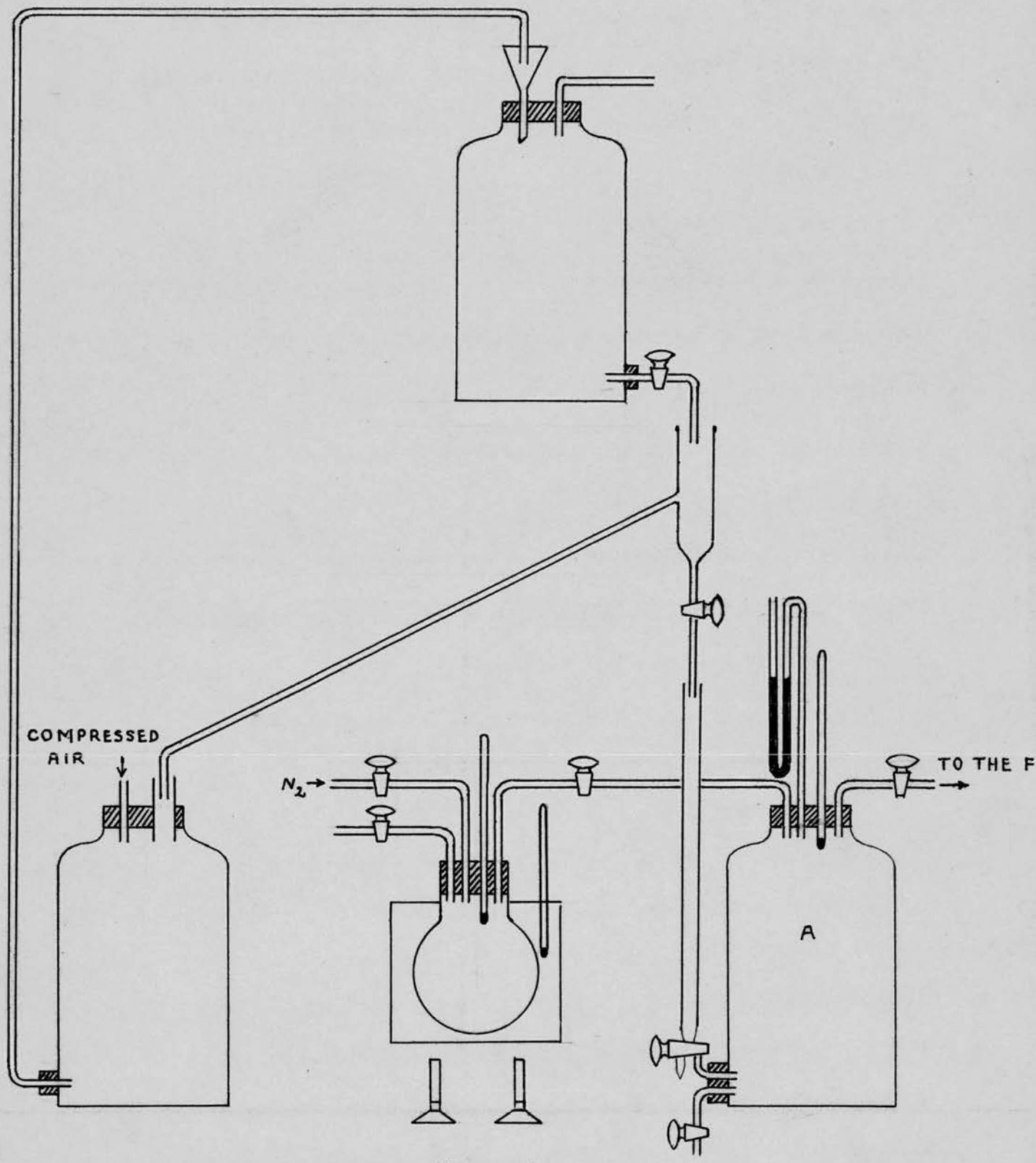


Fig. 12.

Paraformaldehyde obtained from the Lothian Chemical Company, Ltd., contained 96·65 % formaldehyde and had not an exact melting point. The melting process started at 118°C and at 137°C all the paraformaldehyde had liquified.

In the first experiments the paraformaldehyde was heated in a round-bottom flask on an oil-bath to 100°C, 120°C and 150°C and the gases were collected in a 5-litre bottle over a 38 % formaldehyde solution. When gases started to pass from the flask to the bottle, the formaldehyde solution was simultaneously removed in order to suck the gases into the bottle. These experiments were not successful because, as soon as the formaldehyde left the flask and came into contact with the cold walls of the glass tubing connected to the flask, it polymerized and obstructed the tubes.

In the second series of experiments a round-bottomed flask was filled with paraformaldehyde and a stream of nitrogen was passed over the surface of the heated powder. The gas-mixture was collected in a 5-litre bottle over 38 % formaldehyde solution, and (as in previous experiments) it was displaced by the solution and sent to the furnace (Fig. 12). These experiments were also a failure, because again part of the gaseous formaldehyde polymerized on the cold walls of the connecting tubes and the remainder dissolved in

the formaldehyde solution in bottle A, so that the gas mixture contained only 0·06 % formaldehyde the rest being nitrogen.

It was originally intended to use in the bottle A, instead of a strong formaldehyde solution, a liquid which does not dissolve formaldehyde (benzene, toluene etc.) but it was later decided not to do so for the fear that the vapours of this liquid would be carried by the stream to the furnace and would obscure results. Besides, the tendency towards polymerization shown by the formaldehyde produced by the passage of nitrogen over the surface of heated paraformaldehyde was so marked, that all the tubing after each experiment was white from paraformaldehyde deposition. It was, therefore, never certain how much of the formaldehyde collected in a bottle and sent afterwards to the furnace would really pass through the furnace and how much would be deposited on the walls of the connecting tubings. In such conditions it was decided that an exact investigation of the formaldehyde decomposed by the heat of the furnace would be very difficult if not impossible.

Turning to the experiments with a boiling solution of formaldehyde, the arrangement was such that a slow stream of nitrogen was bubbled through a solution containing 37·1 % formaldehyde heated on a water-bath to 98·0°C. As it was feared that too much water vapour

would be carried by the stream, wash-bottles with conc. sulphuric acid were placed between the formaldehyde solution and the furnace, but the sulphuric acid turned brown, and the stream had a poor formaldehyde content (0·1 %), a sign that formaldehyde combined with conc. sulphuric acid. A tower filled with granulated calcium chloride absorbed not only water but also formaldehyde, because it appeared that calcium chloride is a strong polymerizing agent, and the stream contained only 0·88 % formaldehyde. The use of water trap immersed in a cool-mixture containing ice and common salt and producing a temperature of -12°C was not successful, as part of the formaldehyde polymerized and closed the tubings; water with pieces of ice floating on its surface gave better results.

When a slow stream (approx. 50 cm.^{3}/min.) of nitrogen was bubbled through a solution of 37·1 % formaldehyde in water at 98°C the gas-mixture contained about 18 % formaldehyde. But after three hours' time the concentration of formaldehyde in the solution fell to 36·8 % and the percentage in the gas-mixture was only 17·2 %. It was clear that the nitrogen blew away considerable quantities of formaldehyde from the solution. To avoid this some experiments were carried out with a 37·1 % solution of formaldehyde, in which a large excess of paraformaldehyde was present. The cold solution before the experiments contained 37·1 %

formaldehyde; when it was heated to 98°C and a slow stream of nitrogen was passed through it, the concentrations of formaldehyde in the solution after three hours time were 41·43 %, 41·67 % and 41·73 %, and the gas-mixture, contained 18·005 %, 18·403 % and 18·536 % formaldehyde respectively.

In further experiments the gas-mixture was passed through the furnace heated to 750°C, 700°C, 650° etc. In order to ascertain whether the composition of the gas-mixtures remained constant during all the time of the experiment. Samples of formaldehyde absorbed in water were taken every 15 minutes and analysed by the iodometric method (loc. cit. - 100).

The results were as follows:

Temperature	% of formaldehyde in gas-mixtures		
750°C	0·790 %,	0·763 %,	0·725 %
700°C	2·22	2·12	2·18
650°C	4·65	4·71	4·61
500°C	6·08	6·22	6·18
450°C	7·36	7·15	7·20

The rates of flow of nitrogen were different in every experiment.

In order to check the results of the determination by the iodometric method (loc. cit. - 100) of formaldehyde passed through the furnace and absorbed in the wash-bottles, a volumetric method for determination of formaldehyde decomposition was worked out. When a

stream of nitrogen-formaldehyde mixture is passed through wash-bottles and afterwards allowed to enter into a graduated flask of 1 litre volume, the time required for filling the flask corresponds to the volume of nitrogen only, as all the formaldehyde is absorbed in the wash-bottles. When the same gas-mixture under the same pressure is passed first through a heated furnace, then through the wash-bottles and is finally let into the same graduated flask, the time required for filling the flask is shorter, because part of the formaldehyde decomposes in the furnace to H_2 and CO. If the composition of the original gas-mixture is known it is easy to calculate the percentage of formaldehyde decomposed, but the figures obtained by this method were always lower than those gained by the iodometric method. The results of the volumetric method were satisfactorily near one another. Thus, by passing the same gas-mixture into the flask, the following results were obtained:

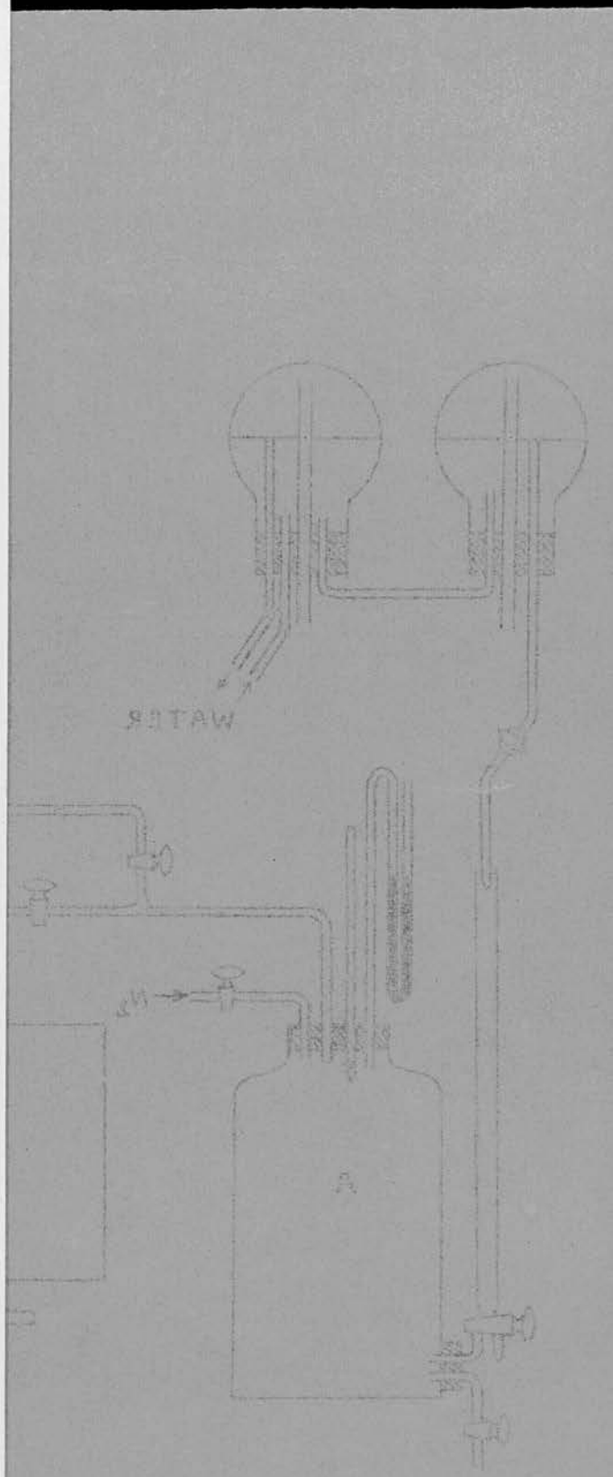
$$\frac{1001}{19'29\cdot4''} = \frac{1001}{19\cdot49'} = 51\cdot36 \text{ cm.}^3/\text{min.}$$

$$\frac{1012}{19'43\cdot2''} = \frac{1012}{19\cdot72'} = 51\cdot21 \text{ cm.}^3/\text{min.}$$

$$\frac{1005}{19'34\cdot4''} = \frac{1005}{19\cdot59'} = 51\cdot44 \text{ cm.}^3/\text{min.}$$

$$\frac{996}{19'27''} = \frac{996}{19\cdot45'} = 51\cdot29 \text{ cm.}^3/\text{min.}$$

In the light of knowledge gained from these preliminary experiments the following apparatus (Fig. 13)



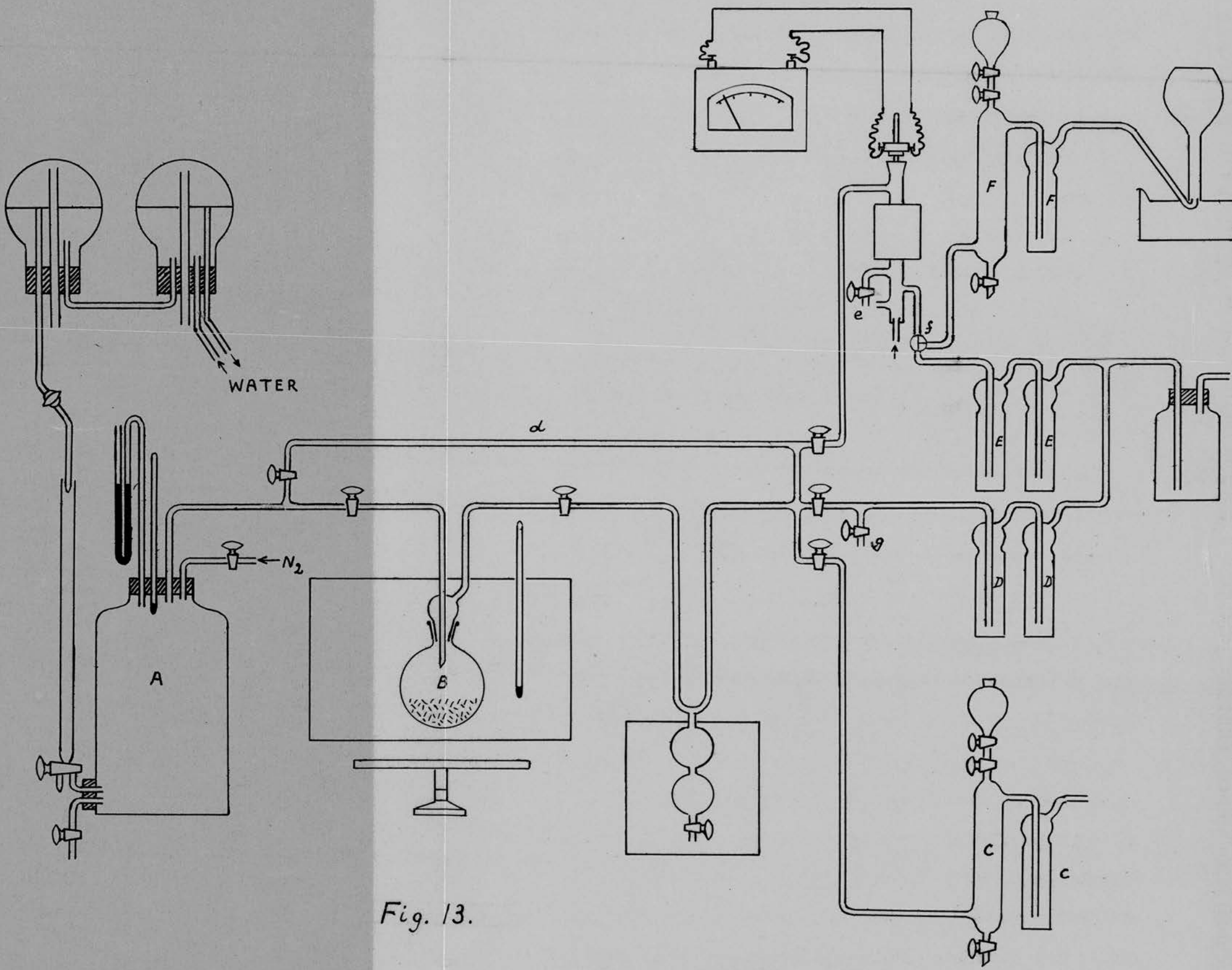


Fig. 13.

was built for the investigations proper. Nitrogen was collected in the 10-litre bottle A, and its flow was measured by displacement with water as in the previous experiments. The stream of nitrogen was passed into a 1-litre round-bottomed bottle made from Pyrex-glass (with a head ground in the same way as an ordinary wash-bottle), which was immersed in a thermostat filled with water at 98°C. On the bottom of this flask was a large excess of paraformaldehyde and the flask was filled almost entirely with 38 % solution of formaldehyde. The stream of nitrogen which bubbled through this solution then passed through a water--trap immersed in cold water and ice. After passing through the trap the stream could pass either (1) into the wash-tube and a wash-bottle C where the amount of absorbed formaldehyde was measured, or (2) into the wash-bottle D and outside, or (3) through the furnace and through the 3-way tap f into the wash-tube and wash-bottle F where the amount of absorbed formaldehyde was measured, or finally (4) through the furnace, then through the 3-way tap f into the wash-bottles E which conducted the gases outside. For the volumetric measurement of formaldehyde decomposed, the graduated flask immersed in a vessel and filled with water was attached either to the wash-bottle C or to the wash-bottle F. For cleaning the furnace with nitrogen the bottle A was connected with the furnace

by means of the tube d.

The experiments were conducted in the following way: The bottle A was filled with nitrogen and this gas was displaced by water running in a burette through a glass tube, which was stretched out and ground to allow calculated amounts of water to pass through. A manometer on the bottle A showed the pressure in mm. water of the gas displaced. The nitrogen stream bubbled throguh the formaldehyde solution in flask B, which was immersed in a thermostat filled with water at 98°C. After passing through the water-trap the stream of nitrogen-formaldehyde mixture was conducted either through trap c in the wash-tube C where the formaldehyde was absorbed by water, or through the furnace and the wash-tube F where the formaldehyde undecomposed in the furnace was absorbed. Before every experiment the wash-tubes C and F were filled with such amounts of water that the gases passed through the tubes under the same pressure (shown on the manometer on the bottle A) and that after passing through these wash-tubes the gases did not react with Schiff's reagent. The determination of formaldehyde content in the water which filled the wash-tube C showed the amount of formaldehyde in gases before decomposition; the same determination in the water which filled the wash-tube F showed the amount of formaldehyde after

decomposition. Samples of gases for gas-analysis before decomposition were withdrawn through the tap g and after decomposition through the tap e.

The results of these experiments are illustrated by the Tables IX and X.

TABLE IX.

Thermal decomposition of formaldehyde.

Furnace and foreheater filled with punice.

Run No.	Temperature °C	Time of contact sec.	Initial % of HCHO in gas-mixtures	Percentage Decomposition of formaldehyde		
				Iodometric method	Volumetric method	Gas-analysis method.
1	750°	1 sec.	18·21	99·21	99·13	98·08
1A	750	"	18·46	99·35	99·19	-
2	700	"	15·95	97·86	97·48	96·46
2A	700	"	15·96	97·61	97·33	-
3	650	"	14·15	95·46	94·92	92·01
3A	650	"	14·72	95·28	94·86	-
4	600	"	12·45	91·21	88·87	86·74
4A	600	"	12·32	89·70	87·54	-
5	550	"	9·99	91·39	80·05	78·27
5A	550	"	9·99	79·21	77·58	-
6	500	"	8·10	60·95	58·46	56·81
6A	500	"	8·01	59·58	58·05	-
7	450	"	6·50	18·70	16·63	-
7A	450	"	6·11	16·88	16·85	-
8	400	"	4·50	5·02	-	-
8A	400	"	4·15	4·35	-	-
9	350	"	2·49	0·49	-	-
9A	350	"	2·21	0·30	-	-
10	310	"	1·61	0·00	-	-
10A	310	"	1·83	0·00	-	-

TABLE X.

Thermal decomposition of formaldehyde.

Furnace and foreheater were filled with pumice.

Run No.	Temperature °C.	Time of contact in sec.	Initial % HCHO in gas-mixtures	Percentage Decomposition of formaldehyde
				Iodometric method
11	700°	0·5	1·50	84 55
11A	700	"	1·50	85·02
12	650	"	1·45	78·01
12A	650	"	1·43	78·68
13	600	"	1·30	72·06
13A	600	"	1·40	73·28
14	550	"	1·25	54·40
14A	550	"	1·30	53·87
15	500	"	1·20	37·42
15A	500	"	1·22	36·77
16	450	"	1·10	7·76
16A	450	"	1·11	8·03
17	400	"	0·99	1·74
17A	400	"	0·81	1·87
18	350	"	0·90	0·00
18A	350	"	0·91	0·39

It can be seen from Tables IX and X that the initial percentage of formaldehyde contained in the gas-mixtures decreases with the fall of temperature to which the furnace was heated. This is due to the expansion of gases. The volume of a definite amount of molecules is larger at 750°C, than at, say, 350°C and if the time of contact of each molecule with the furnace is to be kept equal, the rate of flow of the gas-mixture at 750°C must accordingly be quicker than at 350°C (48·54 cm.^{3}/min. and 80·48 cm.^{3}/min. respectively when

the time of contact is 1 second). Consequently, also, the volume of nitrogen bubbled through the formaldehyde solution must be accordingly larger. A quick stream of nitrogen carries off smaller amounts of formaldehyde vapour.

The volumetric and gas-analysis methods for the determination of formaldehyde decomposed gave satisfactory results only when the amounts of formaldehyde decomposed were large, i.e. when the volumes of hydrogen and carbon monoxide in the gas-mixtures were large enough in comparison with the experimental error. When the percentage of formaldehyde in the gas-mixture was smaller than 8 % or 6 %, the amount of formaldehyde decomposed could be not determined satisfactorily.

The results of gas-analyses carried out when the contact of gas-mixture with the furnace was 1 second are shown in the following table:

into	Percentage decomposition of formaldehyde at temperatures					
	750°C	700°C	650°C	600°C	550°C	500°C
CO	49·37	51·30	51·31	52·04	53·77	52·39
H_2	48·39	47·14	48·69	47·96	46·23	47·61
CO_2	1·29	1·56	-	-	-	-
CH_4	0·95	-	-	-	-	-
	100·00%	100·00%	100·00%	100·00%	100·00%	100·00%

The same difficulties as had occured in previous experiments were encountered in the first of the new. Determinations carried out in the same experimental

conditions gave results which differed greatly one from another. These difficulties were removed by cleaning before or after each experiment the walls of the furnace and the pumice that filled it by passing a stream of nitrogen through the furnace heated to 700°C or 750°C. It seemed, therefore, that the decomposition of formaldehyde which occured in the conditions of these experiments was a reaction in which the surface of pumice and of the walls of the furnace played an important part. In order to ascertain whether this assumption were correct, a series of experiments was carried out with an empty foreheater and furnace. The results of these experiments are shown in Tables XI and XII.

TABLE XI.

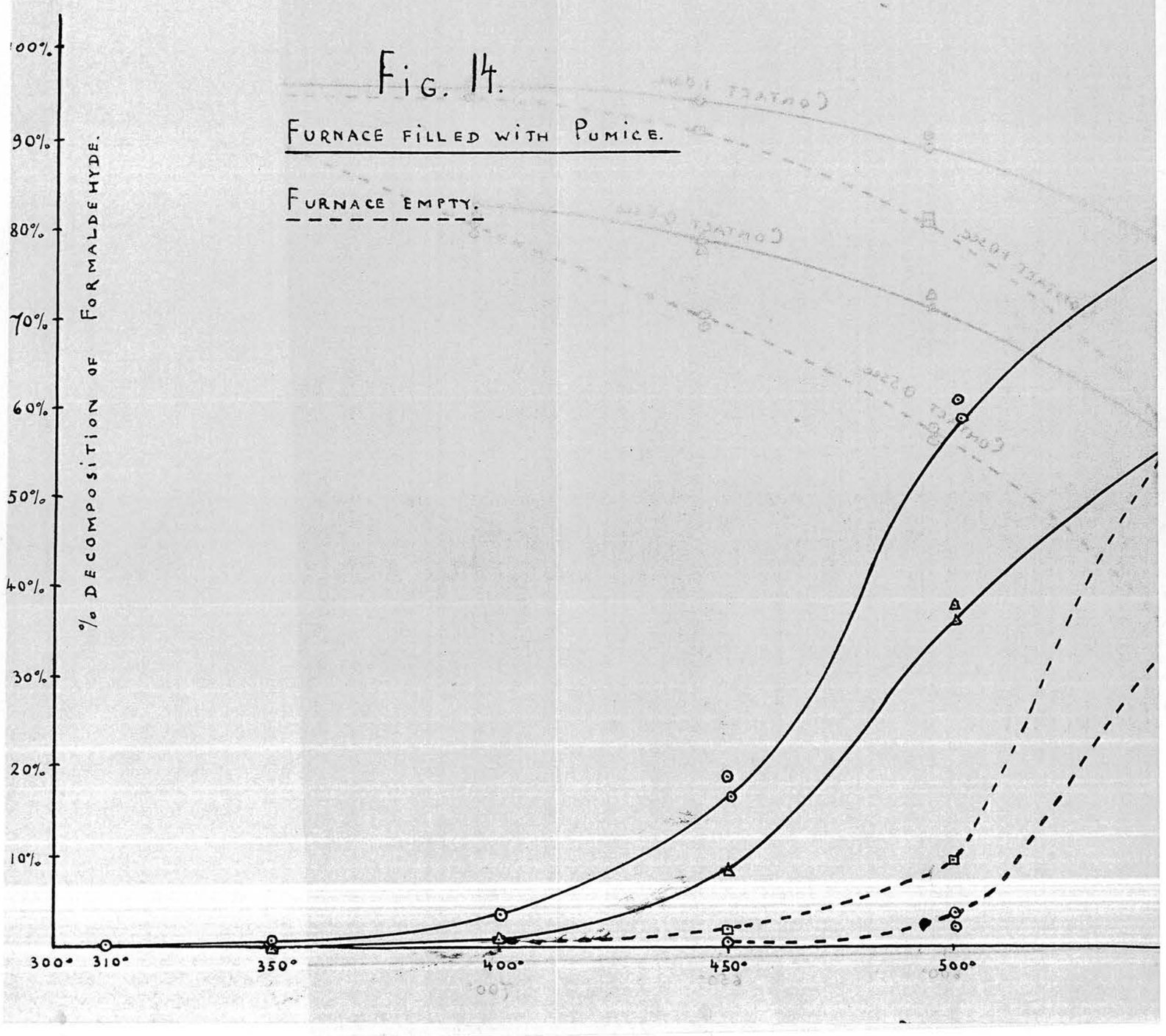
Thermal decomposition of formaldehyde.
Furnace and foreheater empty.

Run No.	Temperature °C.	Time of contact	Initial % of HCHO in gas-mixtures	Percentage Decomposition of HCHO by the iodometric method
19	750	1 sec.	4·20	99·07
19A	750	"	3·80	98·73
20	700	"	2·30	96·55
20A	700	"	2·12	96·82
21	650	"	1·82	91·79
21A	650	"	2·00	91·87
22	600	"	1·50	81·72
22A	600	"	1·70	81·47
23	550	"	1·33	59·30
23A	550	"	1·41	59·12
24	500	"	1·35	9·82
24A	500	"	1·26	9·65
25	450	"	1·30	2·61
25A	450	"	1·20	2·01
26	400	"	1·24	1·01
26A	400	"	1·10	0·66

Fig. 14.

FURNACE FILLED WITH PUMICE.

FURNACE EMPTY.



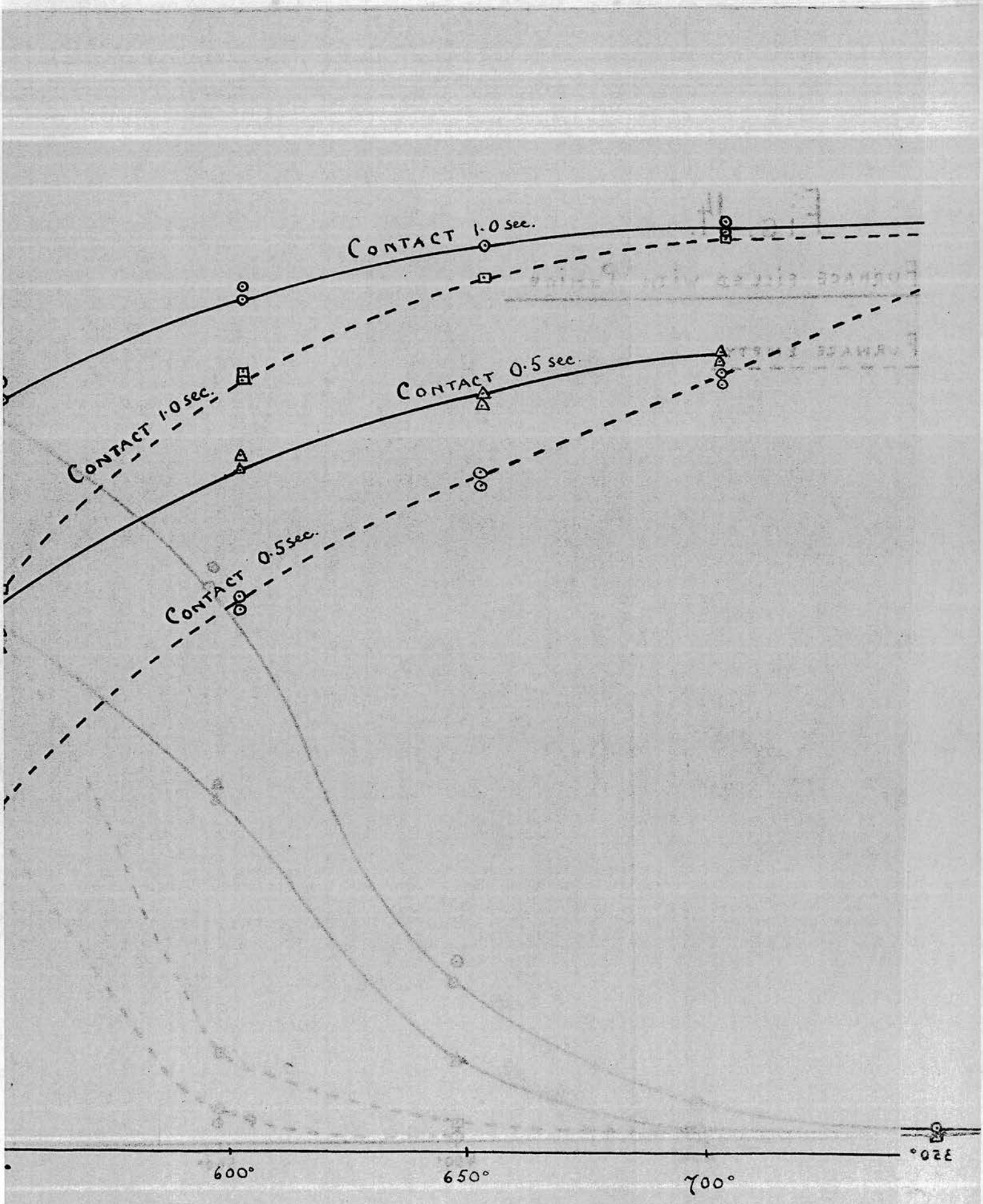

CONTACT 1.0 sec.
CONTACT 1.0 sec.
CONTACT 0.5 sec.
CONTACT 0.5 sec.
600°
650°
700°
320°

TABLE XII.

Thermal decomposition of formaldehyde.

Furnace and the foreheater empty.

Run No.	Tempera-ture °C	Time of contact	Initial % of HCHO in gas--mixtures	Percentage Decomposition of HCHO by iodometric method
27	750	0·5 sec.	0·99	93·53
27A	750	"	0·97	92·91
28	700	"	0·80	81·39
28A	700	"	0·86	82·32
29	650	"	0·80	71·45
29A	650	"	0·74	71·12
30	600	"	0·67	57·24
30A	600	"	0·62	57·67
31	550	"	0·60	36·26
31A	550	"	0·56	35·82
32	500	"	0·51	3·87
32A	500	"	0·52	3·15
33	450	"	0·47	1·23
33A	450	"	0·45	0·84

The thermald decomposition of formaldehyde is illustrated also by diagrams (Fig. 14) where the percentage decomposition of formaldehyde is plotted against the temperature. The decomposition - when the foreheater and the furnace were filled with pumice - is represented by continuous lines and when both were empty - by broken lines.

C. DISCUSSION.

The Tables IX, X, XI and XII and the diagrams (Fig. 14) show that the rate of decomposition of formaldehyde when the furnace was filled with pumice was greater than when the furnace was empty. Many investigators, who have studied the slow oxidation of hydrocarbons, have found that the packing of experimental vessels with fragments of glass silica, pumice etc. suppresses the reaction and that this behaviour is one of the characteristics of chain reactions. - It must therefore be concluded that the thermal decomposition of formaldehyde - carried out in the conditions of the experiments described above - does not show this characteristic. The greater rate of formaldehyde decomposition in the furnace packed with grains of pumice is probably due to the fact that the molecules of formaldehyde when meeting the hot surfaces of pumice grains decompose on these surfaces more easily and more quickly than in the gas-phase.

In order to ascertain whether the decomposition of formaldehyde is a reaction of the first order the usual equation $K = \frac{2{\cdot}303}{\theta} \cdot \log \frac{a}{a-x}$, was applied, where θ, a and a-x represent the time of contact with the furnace, expressed in seconds and the initial and the final concentration of the formaldehyde respectively. K is the velocity constant for the decomposition of formaldehyde.

Tables XIII and XIV show the results of these calculations. Table XIII relates to the experiments in which the foreheater and the furnace were filled with pumice, and Table XIV to that at which both the foreheater and the furnace were empty.

TABLE XIII.

Run No.	Temperature °C	Time of contact	Mole fractions x 10^3 in litre of gases			K
			a	a-x	lg $\frac{a}{a-x}$	
1	750	1 sec.	8·124	0·00064	3·103	7·15
1A	750	1	8·236	0·00054	3·183	7·33
2	700	1	7·116	0·152	1·669	3·84
2A	700	1	1·720	0·170	1·622	3·74
11	700	0·5	0·669	0·103	0·811	3·74
11A	700	0·5	0·669	0·100	0·824	3·80
3	650	1	6·313	0·287	1·342	3·09
3A	650	1	6·563	0·310	1·326	3·05
12	650	0·5	0·646	0·142	0·658	3·03
12A	650	0·5	0·638	0·136	0·671	3·09
4	600	1	5·555	0·488	1·056	2·43
4A	600	1	5·497	0·566	0·987	2·27
13	600	0·5	0·580	0·162	0·555	2·55
13A	600	0·5	0·625	0·164	0·581	2·67
5	550	1	4·457	0·829	0·730	1·68
5A	550	1	4·457	0·927	0·682	1·57
14	550	0·5	0·558	0·254	0·341	1·57
14A	550	0·5	0·580	0·268	0·336	1·55
6	500	1	3·613	1·411	0·408	0·94
6A	500	1	3·574	1·445	0·393	0·91
15	500	0.5	0·535	0·335	0·203	0·93
15A	500	0·5	0·544	0·344	0·199	0·92
7	450	1	2·900	2·357	0·090	0·21
7A	450	1	2·726	2·256	0·082	0·19
16	450	0·5	0·491	0·453	0·065	0·16
16A	450	0·5	0·496	0·457	0·036	0·17
8	400	1	2·012	1·912	0·021	0·049
8A	400	1	1·852	1·771	0·019	0·044
17	400	0·5	0·442	0·434	0·008	0·035
17A	400	0·5	0·361	0·355	0·008	0·038

TABLE XIV.

Run No.	Temperature °C	Time of contact (sec.)	Mole fractions x 10^3 in 1 litre of gases			K_1
			a	a-x	lg $\frac{a}{a-x}$	
19	750°C	1 sec.	1·874	0·0056	2·513	5·79
19A	750	1	1·546	0·0196	1·896	4·36
27	750	0·5	0·442	0·029	1·189	5·48
27A	750	0·5	0·433	0·031	1·149	5·29
20	700	1	1·026	0·035	1·462	3·37
20A	700	1	0·946	0·030	1·497	3·45
28	700	0·5	0·357	0·066	0·730	3·36
28A	700	0·5	0·384	0·068	0·752	3·46
21	650	1	0·812	0·067	1·088	2·50
21A	650	1	0·892	0·072	1·094	2·52
29	650	0·5	0·357	0·100	0·552	2·54
29A	650	0·5	0·330	0·095	0·538	2·48
22	600	1	0·669	0·122	0·738	1·70
22A	600	1	0·758	0·141	0·732	1·69
30	600	0·5	0·299	0·128	0·369	1·70
30A	600	0·5	0·278	0·117	0·373	1·72
23	550	1	0·593	0·242	0·390	0·90
23A	550	1	0·629	0·257	0·388	0·90
31	550	0·5	0·268	0·171	0·196	0·90
31A	550	0·5	0·250	0·160	0·193	0·89
24	500	1	0·602	0·543	0·0449	0·104
24A	500	1	0·562	0·508	0·0441	0·102
32	500	0·5	0·228	0·219	0·0171	0·079
32A	500	0·5	0·232	0·225	0·0139	0·064
25	450	1	0·580	0·565	0·0115	0·026
25A	450	1	0·535	0·525	0·0088	0·020
33	450	0·5	0·210	0·207	0·0054	0·025
33A	450	0·5	0·201	0·200	0·0036	0·018

In Fig. 15 the different values of the velocity constant for the decomposition of formaldehyde have been plotted against the temperature. The straight lines represent the effect of temperature on the average value of constants obtained. The continuous line represents this effect, when the foreheater and

the furnace were filled with pumice, the broken line - when the foreheater and the furnace were empty.

This diagram shows that between 750°C and 700°C the decomposition of formaldehyde is so swift that it can hardly be measured. At temperatures below 450°C - and for an empty furnace below 500°C - this decomposition is very slow.

From these graphs equations may be derived representing the effect of temperature on the velocity constant for the decomposition of formaldehyde, and thus

$$K = 0{\cdot}01439t - 6{\cdot}294 \quad \text{and}$$

$$K_1 = 0{\cdot}016622t - 8{\cdot}224.$$

for temperatures between 700°C and 450°C, and 700°C and 400°C respectively, where the velocity constant K relates to the experiments with the furnace filled with pumice and the constant K_1 to that with an empty furnace.

These results provide at least a partial explanation of the low yields of formaldehyde recorded in the methane oxidation previously described. This effect will be the more pronounced at the higher temperatures and it is thus not surprising that little or no formaldehyde could be detected at 750°C or 700°C. At the lower temperatures apart from the condition of formation of formaldehyde from methane the time of contact will have a pronounced effect in the formaldehyde decomposition.

It is perhaps significant that in Fig. 6 and 7 a maximum formaldehyde concentration is to be observed for an intermediate time of contact. The decrease at the shorter time of contact is to be escribed to the smaller initial production from methane.

Consideration of the velocity coefficient results as a whole leades to the conclusion that the yield of formaldehyde from methane under such conditions could not even in the absence of formaldehyde decomposition itself be raised by a factor of more than two or three in the lower temperature region.

GENERAL CONSIDERATIONS.

On the basis of the above observations some general suggestions may be tentatively put forward for discussion.

It would appear that the initiation of reaction between methane and oxygen may be visualized as taking place in two alternative ways, either by the preliminary decomposition of methane itself with one or more of the products of such decomposition reacting with oxygen in seperate reactions, or by direct reaction between oxygen and methane as such.

In the first instance, experiment has been quoted to show that methane itself is, in the absence of oxygen, relatively very stable in the temperature ranges which can reasonably be investigated. Some small decomposition is indeed to be recorded at very high temperatures. It is therefore possible that such products of decomposition react further with oxygen, but at the lower temperatures, which suffice for rapid methane oxidation, it is obviously necessary to introduce a chain reaction by which the initial small decomposition may be augmanted to a considerable degree.

On the other hand, modern reaction kinetics generally may be examined on the basis of the initial production of an intermediate activated complex, in the present instance of the form $[CH_4O_2]$. This of course may have only a transient existence with a very short

life period, but its formation would seem to be the more probable when it is remembered that hydrocarbon peroxide formation has been experimentally demonstrated in other connections.

In attempting to distinguish between these two main possibilities, the effect of surface may be considered. The fact that a surface alters the rate of a chemical reaction is in itself no difinite criterion of a chain reaction. When the rate is decreased by surface action or increased when such surface action is minimised by, say, the introduction of otherwise inert gas preventing diffusion of reactive intermediates to the walls, then the possibility of chain reaction is certainly enhanced. When, however, increased surface--to-volume ratio increases the rate of reaction, it is more likely that reaction is initiated by the surface in a catalytic manner, and indeed reactions have been quoted in which both initiation and rapture of chains are brought about by the same vessel walls. In the present case, the thermal decomposition of methane itself appears to be little affected by silica of pyrex surfaces; on the other hand, the oxidation of methane is, as the present experiments show, increased by an increased surface-to-volume ratio or by increased time of contact with the surface. This may then be taken to support the "peroxide" complex theory, on the basis

that such action is due to the production of an activated complex facilitated by the lower activation energy of a surface catalysed reaction. This is the more likely when it is remembered that the erractic results recorded previously were rendered more reproducible by pretreatment of the surface walls by both the reactant partners, methane and oxygen. The fact that peroxide formation cannot be analytically confirmed in the present case is not a direct negation of this hypothesis, because obviously such surface formation will be small in extent and will represent a transient species rapidly transformed into other products in the main reaction which follows. The recorded observations on induction periods etc. are not in disagreement with this conception.

We have now to enquire as to the fate of such a complex. It is easier to remove the first hydrogen atom from methane, energetically, than it is to remove, singly, the other three. At the same time there is evidence from other reactions that the radical HO_2 has a definite existence. Accordingly, a possible second step is the break up of the $[CH_4O_2]$ complex into the radical CH_3 and HO_2, this being represented in the general case of the saturated hydrocarbons as

$$[RH:O_2] \longrightarrow R + HO_2$$

In the case of HO_2 it is difficult to visualize further reaction with oxygen or methane, but mutual destruction of such radicals is possible in the following ways:

$$HO_2 + HO_2 \longrightarrow H_2 + 2O_2$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \longrightarrow H_2O + O \quad \text{or}$$

$$H_2O_2 \longrightarrow 2OH.$$

The mechanism of the thermal decomposition of H_2O_2 does not appear to be definitely established, except that it will be very rapid for the present high temperature surface conditions. In the methane oxidation attempts to prove the existence of atomic oxygen have not been successful. The first reaction does offer an explanation of the production of hydrogen in such oxidation. It is true that such a scheme would suggest that enhanced oxidation would produce a greater amount of hydrogen; but at the temperatures concerned hydrogen and oxygen unite to form water vapour and the final percentage of hydrogen in the products will then depend on the relative rates of production and disappearance. The present results indicate less final hydrogen at longer times of contact and at higher temperatures.

In the case of the CH_3 radical, the other postulated product of the initial stage, immediate reaction with oxygen is to be regarded as highly probable. Unpublished results (by. W.I.H. Winning and M. Ritchie)

show that the photochlorination of methane, which almost certainly proceeds by a chain reaction involving CH_3 radicals and Cl atoms, is remarkably sensative to traces of oxygen, the retarding effect of which is much greater that the corresponding retarding effect on the hydrogen-chlorine reaction. When a large amount of oxygen is present, as in the methane oxidation, the concentration of CH_3 will never rise above a very low value; while mutual recombination with the formation of C_2H_6 is possible, it is extremely improbable that such will be detected in the reaction products even if it were to survive further oxidation. This is in agreement with experiment. It would appear then that the products of the methane oxidation are largely determined by the oxidation of the CH_3 radical.

A possible chain reaction involving the production of formaldehyde is then:

$$CH_3 + O_2 \longrightarrow [CH_3O_2] \longrightarrow HCHO + OH$$

$$OH + CH_4 \longrightarrow H_2O + CH_3.$$

An overall mechanism might then be written as follows:

(a) Initiation:

(1) $CH_4 + O_2 \longrightarrow [CH_4O_2] \longrightarrow CH_3 + HO_2.$

(b) Chain:

(2) $CH_3 + O_2 \longrightarrow [CH_3O_2] \longrightarrow HCHO + OH$

(3) $OH + CH_4 \longrightarrow H_2O + CH_3.$

(c) Chain endings:

(4) $CH + HO_2 \longrightarrow H_2O + O_2$

(5) $CH + CH_3 \longrightarrow CH_3CH$.

(d) Subsequent reactions:

(6) $HCHO \longrightarrow H_2 + CO$

(7) $2HO_2 \longrightarrow H_2 + 2O_2$

(8) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

(9) $CO + \frac{1}{2}O_2 \rightarrow CO_2$

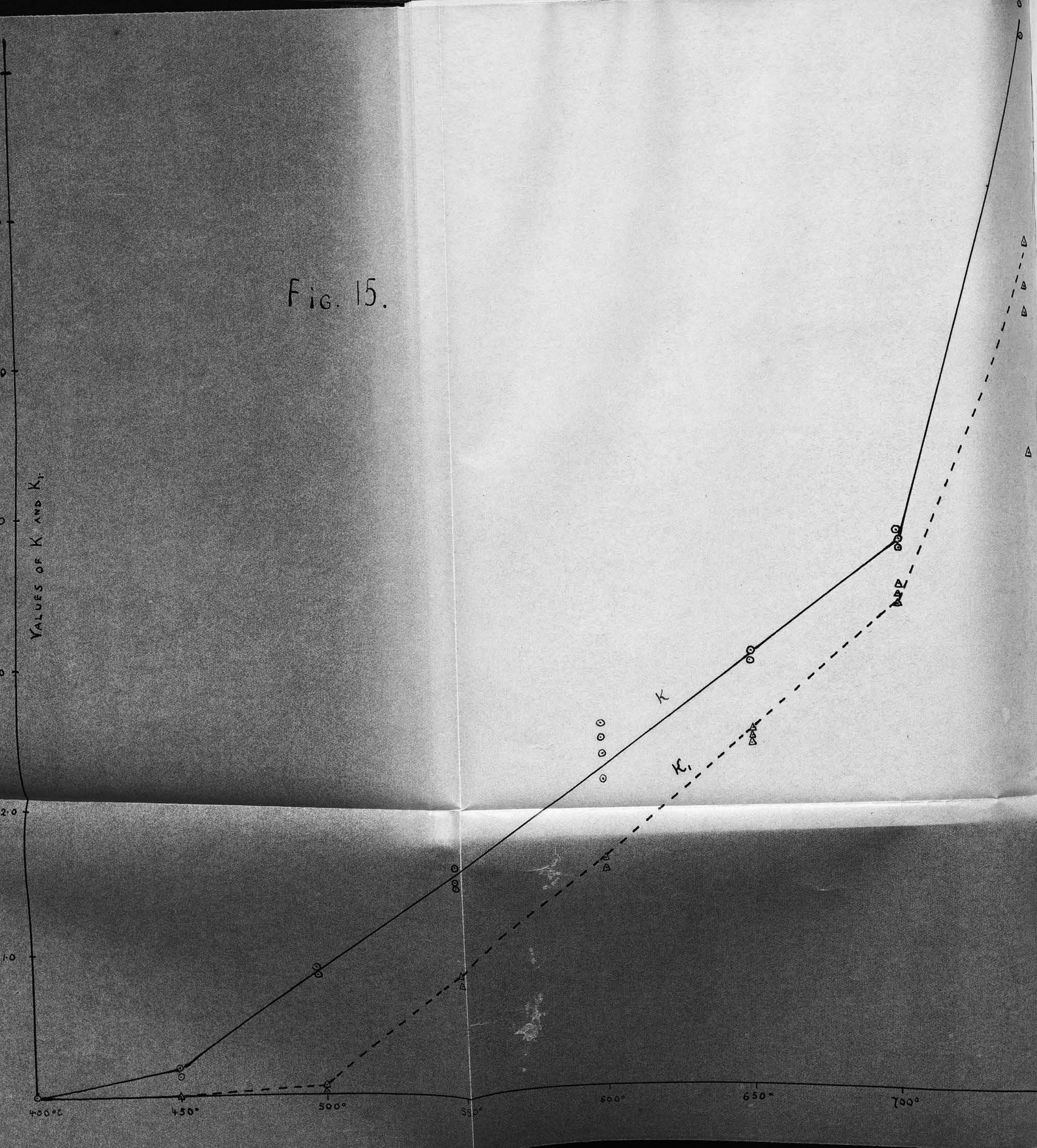
(10) $CH_3CH + O_2 \longrightarrow CO_2 + 2H_2O$.

The introduction of equation 5 would suggest the possibility of small amounts of CH_3CH rendered even smaller by subsequent oxidation. As visualized in the scheme the amount of HO_2 will be not large, but it is possible that the oxygen atom produced by its decomposition via H_2O_2 as above ($2HO_2 \rightarrow H_2O_2 + O_2 \longrightarrow H_2O +$ $+ O_2 + O$) would lead to branching chain formation at higher temperatures.

It was unfortunate that in the present work time was not available for the examination of the oxidation of hydrogen and carbon monoxide under the same conditions as applied in the slow oxidation of methane and decomposition of formaldehyde. It may also be suggested that investigation of the amount of formaldehyde and water might profitably be made in the photochlorination of methane in the presence of oxygen at room temperature; the second stage (3) of the mechanism above will not

be appreciate in such a temperature and the possible quantum efficiency of formaldehyde and water formation would then be of the order of unity.

Fig. 15.



SUMMARY.

1) The slow oxidation of methane was studied by a flow method in the range of temperatures between 500°C and 750°C.

2) The hope that by subjecting methane mixed with nitrogen and oxygen to a high temperature for a very short time and by cooling the products of oxidation immediately the greater part of the methane would be transformed into formaldehyde was not followed by success. The yields of formaldehyde were very low and did not exceed 0·8 % of the methane passed through the furnace.

3) Many of the experimental results were erratic. The passing of methane or oxygen through the heated furnace removed this difficulty.

4) Methane was oxidized in a mixture with nitrogen and oxygen in the ratio $N_2:O_2:CH_4$ = 2:1:1 and 2:0·1:1 respectively. The decreasing of oxygen in these mixtures had only a small effect on the oxidation products.

5) Water vapour added to the gas mixtures before the reaction, increased markedly the rate of oxidation.

6) The presence of hydrogen in the final products is probably due to the decomposition of methane by steam.

7) The thermal decomposition of formaldehyde was also studied by the same flow method and by means of the

furnace used in previous experiments.

8) The experiments were carried out both when the furnace was empty and when it was filled with pumice grains. The rate of decomposition was greater when the furnace was filled with pumice.

9) Formaldehyde decomposes very quickly at temperatures between 750° and 700°C and relatively slowly below 450° or 500°C. Between 700°C and 450°C the effect of temperature on the velocity constant for decomposition of formaldehyde in the furnace filled with pumice can be represented by the simple equation

$$K = 0{\cdot}01439t - 6{\cdot}294$$

while that in the empty furnace and in the range of temperature between 700°C and 500°C can be expressed by the equation

$$K_1 = 0{\cdot}016622t - 8{\cdot}224.$$

10) In the lower temperature region the thermal decomposition of formaldehyde itself is not mainly responsible of the low yield of formaldehyde in the methane oxidation.

11) General considerations on the mechanism of the slow oxidation of methane have been given.

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REFERENCES.

(1) W.A. Bone and R.V. Wheeler, J. Chem. Soc., 81, 535, 1902.

(2) W.A. Bone and R.V. Wheeler, J. Chem. Soc., 83, 1074, 1903.

(3) W.A. Bone and Stochings, J. Chem. Soc., 85, 693, 1904.

(4) W.A. Bone and R.V. Wheeler, J. Chem. Soc., 85, 1637, 1904.

(5) W.A. Bone and G.W. Andrew, J. Chem. Soc., 87, 1232, 1905.

(6) W.A. Bone and J. Drugman, J. Chem. Soc., 89, 660, 1906; ibid, 89, 1614, 1906.

(7) W.A. Bone and G.W. Andrew, J. Chem. Soc., 89, 652, 1906.

(8) J. Drugman, J.Chem. Soc., 89, 939, 1906.

(9) G.W. Andrew, J. Chem. Soc., 95, 444, 1914.

(10) H.F. Coward and S.P. Wilson, J. Chem. Soc., 115, 1380, 1919.

(11) T.S. Wheeler and E.W. Blair, J. Soc.Chem. Ind., 42, 81T, 1923.

(12) E.W. Blair and T.S. Wheeler, J. Soc. Chem. Ind., 41, 307T, 1922.

(13) E. Berl and H. Fischer, Z. f. ang. Chem., 36, 297, 1923.

(14) S.S. Medvedev, Trans. Karpov Inst. Chem., No.3, 54-65, 1924; Am. Chem. Abstr., 20, 2273, 1926.

(15) T.E. Laying and Roy Soukup, Ind. and. Ing. Chem., 20, 1052, 1928.

(16) Selden & Co, B.P. 170.022, 1920.

(17) C.P. Brynes, U.S.P. 1.941.010, 1924.

(18) I.G. Farbenindustrie, D.R.P. 542.487, 1928; U.S.P. 1.813.478, 1929; U.S.P. 1.882.712, 1931.

(19) Doherty Research Co, U.S.P. 1.978.621, 1930.

(20) A.Reis and O. Waldbauer, Z. f. physik. Chem., 85, 85, 1913.

(21) C.H. Bibb and H.J. Lucas, Ind. Eng. Chem., 21, 633, 1929.

(22) D.F. Smith and R.T. Milner, Ind. Eng. Chem., 23, 357, 1931.

(23) K. Froelich, P.J. Harrington and A.H. Waitt, J. Am.Chem. Soc., 50, 3216, 1928.

(24) C.H. Bibb, Ind. Eng. Chem., 24, 10, 1932.

(25) Bailey, U.S.P. 1.319.784, 1919.

(26) C.H. Bibb, U.S.P. 1.392.886, 1922; 15.789, 1924; 1.547.725, 1925; Canadian Patent 302.672, 1930.

(27) Gutehoffnungshütte Oberhausen A.G., Br. Fr. 694.330, 1930; 709.823, 1931; 770.179, 1934; 788.538, 1935.

(28) U.S.P.: 2.007.115-6, 1935; 2.042.134, 1936; 2.153.526, 1939; 2.186.688, 1940.

(29) U.S.P.: 2.128.908, 1938.

(30) H.W. Thompson and C.N. Hinshelwood, Proc. Roy.Soc., A125, 277, 1929.

(31) R. Fort and C.N. Hinshelwood, Proc. Roy. Soc., A127, 218, 1930.

(32) R. Fort and C.N. Hinshelwood, Proc. Roy. Soc., A129, 284, 1930.

(33) C.N. Hinshelwood and H.W. Thompson, Proc.Roy.Soc., A118, 170, 1928.

(34) M. Neumann and A. Serbinoff, Nature,128, 1040, 1931.

(35) R.G.W. Norrish and J.Wallace, Proc. Roy. Soc., A145, 307, 1934.

(36) J.A. Christiansen and H.A. Kramers, Z.f. Physik. Chem., 104, 451, 1923.

(37) N.N. Semenov, Z. Pysik., 46, 109, 1927; ibid, 48, 571, 1928.

(38) G. von Elbe and B. Lewis, J. Chem. Phys., 10, 366, 1942.

(39) R.N. Pease, J.Am. Chem. Soc., 52, 5106, 1930.

(40) M. Prettre, J. de Chem. Phys., 33, 189, 1936.

(41) S.K. Chirkov, Acta Phys. Chim. (U.S.S.R.), 6, 915, 1937.

(42) J.A. Christiansen, J. Phys. Chem., 28, 145, 1924.

(43) H.L.J. Bäckström, J. Am. Chem. Soc., 49, 1460, 1927.

(44) H.L. Callender, Engineering, 123, 147-8, 182-4, 210-12, 1927.

(45) A.C. Egerton and W. Gates, J. Inst. Petroleum Technol., 13, 281, 1927.

(46) A.C. Egerton, Nature, 121, 10, 1928.

(47) M. Bodenstein, Z. f. physik. Chem., B12, 151, 1931.

(48) G.B. Kistiakowsky and S. Lehner, J.Am. Chem. Soc., 52, 3785, 1930.

(49) R. Spence and G.B. Kistiakowsky, J. Am. Chem. Soc., 52, 4837, 1930.

(50) W.A. Bone and R.E. Allum, Proc. Roy. Soc., A134, 578, 1931.

(51) W.A. Bone and S.G. Hill, Proc. Roy. Soc., A129, 434, 1930.

(52) D.M. Newitt and A.E. Haffner, Proc. Roy. Soc., A134, 591, 1931.

(53) D.M. Newitt and A.M. Bloch, Proc. Roy. Soc., A140, 426, 1932.

(54) R.N. Pease, J. Am. Chem. Soc., 51, 1839, 1929.

(55) P.J. Askey, J.Am. Chem. Soc., 52, 974, 1930.

(56) F. Gill, E.W.J. Mardles and H.C. Tett, Trans. Faraday Soc., 24, 574, 1928.

(57) J.C. Pope, F.J. Dykstra and G. Edgar, J. Am. Chem. Soc., 51, 1875, 1929.

(58) J.S. Lewis, J. Chem. Soc., Part I, 58, 1930.

(59) F.O. Rice, J.Am. Chem. Soc., 53, 1959, 1931.

(60) L. Belchetz, Trans. Faraday Soc., 30, 170, 1934.

(61) R.G.W. Norrish, Proc. Roy. Soc., A150, 36, 1935.

(62) W.A. Bone and H. Davies, J. Chem. Soc., 105, 1691, 1914.

(63) A.R. Ubbelohde, Proc. Roy. Soc., A152, 354, 1935.

(64) L.J. Bäckström, Z. physik. Chem., B25, 99, 1934.

(65) K.F. Bahnhoeffer and P. Harteck, Z. physik. Chem., A139, 64, 1928.

(66) R.N. Pease and W.P. Munro, J. Am. Chem. Soc., 56, 2034, 1936.

(67) V. Kondratiev, Z. Phys., 63, 322, 1930.

(68) A.C. Egerton and J.M. Pidgeon, Proc. Roy. Soc., A142, 26, 1933.

(69) H.J.Emeleus, J. Chem. Soc., Part II, 1733, 1929.

(70) G. von Elbe and B. Lewis, J.Am. Chem. Soc., 59, 976, 1937.

(71) J.R. Bates and R. Spence, J. Am. Chem. Soc., 53, 1689, 1931.

(72) J.A. Leermakers, J. Am. Chem. Soc., 56, 1537, 1934.

(73) J.E. Carruthers and R.G.W. Norrish, J. Chem. Soc., Part II, 1036, 1936.

(74) E.J. Harrish and A. Egerton, Chem. Rev., 21, 287, 1937.

(75) W.A. Bone and J.B. Gardner, Proc. Roy. Soc., A154, 297, 1936.

(76) D.M. Newitt and J.B. Gardner, Proc. Roy. Soc., A154, 329, 1936.

(77) D.M. Newitt, Chem. Rev., 21, 299, 1937.

(78) R.G. Norrish and S.G. Foord, Proc. Roy. Soc., A157, 503, 1936.

(79) N. Semenoff, Chemical Kinetics and Chain Reactions, Oxford, 1935

(80) W.M. Vaidya, Proc. Roy. Soc., A147, 513, 1934.

(81) R. Mecke, Trans. Faraday Soc., 30, 200, 1934.

(82) J. Bell, Proc. Roy. Soc., A158, 429, 1937.

(83) L. Slotin and D.G.W. Style, Trans. Faraday Soc., 35, 420, 1939.

(84) F.F. Snowdown and D.G.W. Style, Trans. Faraday Soc., 35, 426, 1939.

(85) R. Spence, J. Chem. Soc., Part I, 649, 1936.

(86) R.G.W. Norrish and J.D. Reagh, Proc. Roy. Soc., A176, 429, 1940.

(87) A.G. Gaydon, Proc. Roy. Soc., A183, 111, 1944.

(88) A.G. Gaydon, Proc. Roy. Soc., A181, 197, 1942.

(89) M.L. Spealman and W.H. Rodebush, J. Am. Chem. Soc., 57, 1474, 1935.

(90) Lord Rayleigh (R.J. Strutt), Proc. Roy. Soc., A86, 56, 1911.

(91) M. Patry and P. Mocaux, Trans. Faraday Soc., 43, 341, 1946.

(92) C.H. Gibson and C.N. Hinshelwood, Proc. Roy. Soc., A119, 591, 1928.

(93) W.A. Bone, A.E. Haffner and H.F. Rance, Proc. Roy. Soc., A143, 16, 1934.

(94) G. von Elbe and B. Lewis, J. Chem. Phys., 9, 194, 1941.

(95) G. von Elbe and B. Lewis, J. Chem. Phys., 10, 366, 1942.

(96) W. Payman, J. Chem. Soc., Part II, 115, 1436, 1919.

(97) W.A. Bone and R.V. Wheeler, J. Soc. Chem. Ind., 27, 10, 1908;
E.W. Blair and T.S. Wheeler, J. Soc. Chem. Ind., 41, 187T, 1922;

W.J. Goodeham, J. Soc. Chem. Ind., 56, 33T, 1937.

(98) A.C. Fieldner, G.W. Jones and W.F. Holbrook, Department of Commerce, Bureau of Mines, Washington, 1925.

(99) W.J. Goodeham, J. Soc., Chem. Ind., 57, 388, 1938.

(100) G. Romijn, Z. anal. Chem., 36, 19, 1897.

(101) P. Borgström, J. Am. Chem. Soc., 45, 2150, 1922.

(102) G. Lemme, Chem. Ztg., 27, 896, 1903; Chem. Zentr., 1903, II, 911.

(103) A. Seyewetz and S. Gibello, Bull. Soc. Chem., 31, 691, 1904.

(104) S.S. Sadtler, Ann. J. Pharm., 76, 84, 1904; Chem. Zentr., 1904, I, 1176.

(105) M. Ripper, Monatsh. Chem., 21, 1079, 1900.

(106) K. Kraut, Ann., 258, 105, 1890.

(107) F. Raschig, Ber. Ber., 59, 2025, 1926; ibid, 61, 179, 1928; Ann., 448, 265, 1926.

(108) W.M. Laues and C.M. Langkammer, J. Am. Chem. Soc., 57, 2360, 1935.

(109) O. Blank and H. Finkelbeiner, Ber. Ber., 31, 2979, 1898; ibid, 32, 2141, 1899.

(110) J.K. Heywood and B.H. Smith, J. Am. Chem. Soc., 27, 1183, 1905.

(111) Pharmacopoeia of the United States of America, U.S.P. XII, page 267, Easton Pa., Mack Printing Co., 1942.

(112) L. Legler, Ber. Ber., 16, 1333, 1883.

(113) B.H. Smith, J.Am. Chem. Soc., 25, 1028, 1903.

(114) J. Bücki, Pharm. Acta Helv., 13, 1, 1931.

(115) G. Romijn, Pharm. Weeblad., 40, 149, 1903.

(116) W. Stüve, Arch. Pharm., 244, 540, 1906.

(117) R. Gros, J. Pharm. Chem., 26, 415, 1922; Chem. Abstr., 17, 1402, 1923.

(118) J. Bücki, Pharm. Acta Helv., 13, 132, 1938; Chem. Abstr., 33, 9550, 1939.

(119) G. Romijn, Z. anal. Chem., 36, 19, 1877.

(120) E. Elvove, Am. Journ. Pharm., 83, 455, 1910; Chem. Zentr., 1911, II, 1658.

(121) A. Mutschin, Z. anal. Chem., 99, 346, 1934.

(122) A. Brochet and R. Cambier, Compt. Rend., 120, 449, 1895; Z. anal. Chem., 34, 623, 1895.

(123) J.H. Bower, Bur. Standards J. Research., 12, 241, 1934; Chem. Abstr., 28, 3283, 1934.

(124) E.W. Morley, J. Am. Chem. Soc., 26, 1171, 1904.

(125) W.A. Bone and H.L. Smith, J. Chem. Soc., 55, 4747, 1933.

(127) S.S. Medvedev and E.A. Robinson, Trans. Karpov. Inst. Chem. (U.S.S.R.), No. 4, 117, 1925; Chem. Abstr., 20, 2273, 1926.

(128) C.J.N. Fletcher, Proc. Roy. Soc., A146, 357, 1934.

(129) M.J. Marshall and D.F. Stedman, Trans. Roy. Soc. Canada, 17, Sect. III, 53, 1923; Chem. Abstr., 18, 968, 1924.

(130) M.I.J. Kuznetzov, J. Russ. Phys.-Chem. Soc., 45, 557, 1913; Chem. Abstr., 7, 3126, 1913.

(131) H. Tropsch and O. Roelen, Abhandl. Kenntnis Kohle, 7, 15, 1925; Chem. Zentr., 1926, I, 3258; Chem., Abstr., 21, 3530, 1927.

(132) D. Berthelot and H. Gaudechon, Compt. Rend., 150, 1690, 1910; Chem. Abstr., 4, 2408, 1910.

(133) R. Pribram and A. Franke, Monatsh., 33, 415, 1912; Chem. Abstr., 6, 2074, 1912.

(134) G. Bredig and A. Goldberg, Z. phys. Chem., 110, 532, 1924; Chem. Abstr., 18, 3144, 1924.

(135) F.W. Kirkbridge and R.G.W. Norrish, Trans. Faraday Soc., 27, 404, 1931.

(136) B.C. Vickery, The Ind. Chem., 23, 141, 1947.

(137) Natta, Giorm. Chim. Ind. Appl., 14, 545, 1932.

(138) E. Elvove, Ind. Eng. Chem., 9, 295, 1917; F.R. Georgia and R. Morales, Ind. Eng. Chem., 18, 305, 1926.

(139) F. Auerbach and H. Barschall, Studien über Formaldehyd, Part I. Formaldehyd in wässeriger Lösung, Jul. Springer, Berlin, 1905.

(140) J.F. Walker, J. Phys. Chem., 35, 1104, 1931.

(141) W. Ledbury and E.W. Blair, J. Chem. Soc., 127, 33, 1925; ibid, 127, 2834, 1925.

(142) P.P. Korzev and I.M. Rossinskaya, J. Chem. Ind. (U.S.S.R.), 12, 610, 1935.

(143) A. Zimmerli, Ind. Eng. Chem., 19, 524, 1927.

(144) G. Nordgren, Acta Path. Microbiol. Scand., 40, 21, 1939.

(145) F. Auerbach and H. Barschall, Studien über Formaldehyd. Die festen Polymeren des Formaldehyds, Jul. Springer, Berlin, 1907.