METHANOL REACTIONS ON COPPER

THESIS

Submitted for the degree of

DOCTOR OF PHILOSOPHY

of the University of Glasgow

by

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AUGUST, 1962.

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ACKNOWLEDGEMENTS.

I wish to express my very sincere thanks to my Supervisor Dr. S.J. Thomson, who, by his sustained interest and sound advice has provided a constant source of inspiration and encouragement during the preparation of this thesis.

I also wish to express my gratitude to Dr. R. Reed and Mr. Hilson C. Hill of the Mass Spectrometer Group, to Dr. J. Eglinton and members of the Infra Red Spectroscopy Group, and to the Gas Chromatography Group of Messrs British Hydrocarbon Chemicals Limited., for their aid with analytical problems.

In addition, I would also like to thank Mr. J. McAllister and Mr. R. Smith for their invaluable aid with technical problems.

Finally I am also very grateful to Mr. R. Lawson and to Mr. B. Riach for stencilling and photographing services, and to Mrs. R.W. Veitch for typewriting services.

This work will be prepared for publication in collaboration with Dr. S.J. Thomson.

ALEXANDER LAWSON.

SUMMARY.

The catalytic dehydrogenation of methyl alcohol to formaldehyde, carbon monoxide and hydrogen has been studied on various copper foil and wire catalysts. Pure copper foil and wire were found to be inactive towards the decomposition of methanol, and yet many authors have reported decomposition occurring on reduced copper powder activated by oxidation/reduction techniques. The present author has found that once copper foil or wire is oxidised to predetermined extents, then a pure dehydrogenation reaction occurs. No dehydration of the alcohol has been observed. The activity of the catalyst has been ascribed to the presence of a p-type semi-conducting cuprous oxide defect structure in the catalyst. This is contrary to present opinion which suggests that dehydrogenation is facilitated by n-type oxide catalysts. It is therefore proposed that the activity imparted to copper powder catalysts by oxidation/reduction techniques is due to the presence of unreduced copper oxide in the powder, and it is suggested that careful interpretation of results obtained on reduced powder catalysts is necessary.

The course of the dehydrogenation reaction, and the secondary reactions produced by interaction of the products of decomposition with the catalyst oxide, was found to depend critically upon the

degree and type of oxidation of the catalyst. Thus, two secondary reaction mechanisms have been proposed as occurring on catalysts corresponding to low and high p-typeness respectively. Oxygen-18 studies have indicated that the production of carbon dioxide from catalysts corresponding to high p-typeness probably proceeds via. the formation of a carbonate surface complex. Such a complex has already been tentatively suggested by several authors. In the case of catalysts exhibiting high p-typeness, a partial poisoning of the dehydrogenation reaction was observed to occur, with consequent increase in the yield of formaldehyde. The yield of formaldehyde was also increased by work hardening the copper wire prior to oxidation. This result may be of considerable interest to those workers intent on preparing formaldehyde by dehydrogenation of methanol.

In addition, the decomposition of formic acid has been studied on work hardened and annealed copper wires. The rate of decomposition was found to be less on work hardened wires, and the reason for this, based on vacancy diffusion, is suggested.

INTRODUCTION

INTRODUCTION.

The first experimental work on the catalytic decomposition of alcohols dates from 1878, when Hofmann (1) decomposed methanol into formaldehyde by passing an air-alcohol mixture through a red hot platinum tube. Later, in 1886, Berthelot (2) showed that the decomposition of alcohols could proceed along two paths; that of dehydrogenation, and dehydration. The proportion of each reaction depended upon the type of catalyst used, and one of the first examples of selectivity in catalysis was thereby discovered. A great deal of work has since been undertaken on this subject, and Sabatier and Mailhe (3) were among the first to publish a list of catalysts sub-divided into those showing dehydrogenation, those showing dehydration and those giving a mixture of both reactions. Thus, metals, and a few oxides such as those of manganese and magnesium, were shown to be dehydrogenation catalysts; oxides, such as thoria and alumina, were said to be dehydration catalysts and a variety of other oxides were classified as giving mixed reactions. Both of these major reactions however, were found to give side reactions. Thus, dehydrogenation, under certain conditions, could continue beyond the aldehyde stage to give more hydrogen and oxides of carbon, and dehydration could produce either an olefine or an ether. Again the catalyst used determined which reaction would predominate. Thus, thoria e.g., was found to catalyse predominately the olefine reaction and exclude ether formation entirely (4). However, not only does the type of catalyst used determine the selectivity, but so does the mode of preparation and temperature of reaction. In 1923, Adkins (5) found that alumina at high temperatures gave a mixture of dehydrogenation and dehydration reactions, whereas, at lower temperatures, dehydration was predominant. Schwab (6) concluded from his experiments that such a change in selectivity with temperature was due to a change in surface texture. On flat surfaces, dehydrogenation occurred, but in the pores of molecular dimensions, extensive polarisation of the molecule induced dehydration. This, therefore, was an example of the geometric effect in catalyses. Pradel and Imelik (7), however, rejected this view and concluded that the selectivity was a surface property.

In the case of methanol, the dehydration reaction is simplified in that only dimethyl ether can result, as the olefine reaction would produce the highly unstable methylene. Dehydration to dimethyl ether is normally catalysed by oxides at 200 - 300°C, but at higher temperatures a mixed reaction can occur (8). On metals, such as copper, dehydrogenation is the normal reaction observed.

Thus Rideal and Taylor (9) have stated that, with freshly reduced copper oxide at 200°C, dehydrogenation of methanol proceeds according to the equation:

$$CH_3OH = HCHO + H_2,$$

with only 5% loss of formaldehyde from the secondary decomposition. At 250°C, however, the secondary reaction becomes important. Further decomposition takes place according to the equation:

$$HCHO \rightarrow H_2 + CO,$$

and at 300°C is practically complete.

Sabatier and Reid (10),however, indicate that the temperature at which the secondary reaction becomes important, depends largely on the method of preparation of the reduced copper; in particular the temperature used in the reduction stage from copper oxide. The classic work on alcohol decompostion came in the 1920's with the papers of Palmer and Constable (11) → (16). They studied the rates of decomposition of various alcohols, including methanol, on supported, reduced, copper powders, and again concluded that the rate of reaction depended upon the temperature of reduction of the oxide. Other information at this time came from the work of Ghosh and Chakravarty (17), and Ghosh and Bakshi (18) (19) who studied methanol dehydrogenation on reduced copper supported on pumice.

Frolich, Fenske and Quiggle found that the rate of decomposition of methanol on reduced copper, prepared by precipitation with ammonia, varied with the precipitation temperature (20) and with the precipitation agent (21). Thus sodium hydroxide was found to produce a more active catalyst than ammonia. More recently Kawamoto (22) studied the rates of dehydrogenation of isopropyl and sec-butyl alcohol as a function of precipitating agent, and found that precipitation with potassium carbonate produced a dehydrogenation catalyst, but sodium hydroxide produced a catalyst which initiated side reactions in addition to dehydrogenation. In 1961, Balandin and Teteni (23), studied the decomposition of alcohols, again on reduced copper powders, and concluded that hydrogen was chemisorbed on the surface of the copper during dehydrogenation. This conclusion is surprising for Beeck (24) found that hydrogen would not chemisorb on pure copper.

In every case, in all the studies described in these papers, it was found necessary to "activate" the copper surface, or to prepare the copper by reduction of the oxide for varying lengths of time, and at varying temperatures.

This was also the case in industrial use of copper as a catalyst. The industrial preparation of formaldehyde and acetaldehyde is largely a catalytic process and The United States Industrial Alcohol Co.·(30) have suggested a method of activation of copper gauze involving deposition of finely divided cupric hydroxide on to the gauze followed by ignition to cupric oxide, and reduction in situ. with hydrogen at 300°C. The copper gauze is, in this case however, probably acting as a support for the reduced copper powder, the active part of the catalyst.

It appears therefore, that if pure bulk copper metal is used, reaction will not take place. In fact, Palmer (11), in his early work, found that pure electrolytic copper would not catalyse the decomposition of methanol, and was obliged to activate his copper surfaces by alternate oxidation and reduction. More recently, Schwab in 1946 (25), studied the decomposition of methanol on copper foil and copper chips with a geometrical surface area of 50 cm^2, and contrary to Sabatier's observation that decomposition took place at 200°C, found that no appreciable reaction took place at 500°C. He concluded that "Reaction took place on active centres which exist in abundance only on topochemically prepared metals, but meagrely on compact ones".

When we consider the classic demonstration of the now well established electronic factor in catalysis, by Dowden and Reynolds (26), we see that as the atom percentage of copper increases in the series of copper-nickel alloy foils, then the activation energy for the decomposition of methanol rises to a high value at 100% copper. Thus according to the "d-band" theory, copper, having no d-band vacancies, would provide no sites for electron transfer during adsorption of the methanol, the chemisorption bond formed would be weak, and the activation energy for the decomposition reaction accordingly high. This result was again confirmed recently by Taylor and Quinn in a paper presented at a colloquium in Edinburgh in March, 1962. Again they found that the decomposition rate of methanol over a series of copper nickel alloys became neglible at high copper content.

The primary aim of this thesis is therefore to study factors which bring about the activation of copper. Why, for example, should pure copper foil be inactive for methanol decomposition, but reduced copper powder be so efficient? It seems improbable that surface areas alone would account for so large a difference in behaviour. Palmer (12), has found that the activity of his catalyst increased to a maximum after five alternate oxidations and reductions, and he attributed this to a difference in particle size, while Constable maintains that a compensation effect is operating. In all cases however, the activity of the catalyst was not maintained, and some self-poisoning mechanism soon began to operate. Rideal and Taylor (9) were the first to observe this, and Palmer and Constable (11) likewise found it necessary to reactivate their copper after a variable period of time by further oxidation and reduction. Ghosh and Chakravarty (17) again found that the activity of their copper catalyst diminished rapidly with time, and Ghosh and Bakshi (18) found that the activity was maintained, provided that thoria or ceria was present to act as a promoter. More recently some Russian workers (27) found that self-poisoning of copper catalyst was avoided when 12% Manganese was present. Taylor (28) in 1926 suggested that the self-poisoning effect was due to a geometric factor. He concluded that the active centres were peaks on the surface of the copper, where the metal atoms were only slightly bound to the lattice, thus providing a high degree of bond unsaturation. The heat of the catalytic reaction was therefore supposed to reduce the height of these peaks, and consequently the activity of the surface. Pease and Purdom (29) likewise considered that the roughness of the surface was the important factor, and showed that by lowering the temperature of reduction of copper oxide, and supposedly increasing the roughness factor, then a surface could be produced which would hydrogenate benzene, whereas high temperature reduction produced a surface inactive to benzene hydrogenation.

The aim of the research described in this thesis was to study the activation of copper, and to study the "poisoning" of the reaction for methanol decomposition. In addition, should the reaction be secured on the bulk metal, then investigation would proceed to the effect of work hardening of the metal on the catalytic activity of the surface.

The Thesis has accordingly been divided into the following sections:

CHAPTER I: which describes the various catalysts used, and the reactions obtained thereon.

CHAPTER II: which deals with the development of the analytical technique used to determine the nature and quantity of the products obtained from the reactions, and to elucidate the reaction mechanism.

CHAPTER III: The discussion of the work conducted in Chapters I & II.

CHAPTER IV: An account of the experiments conducted on the relationship between the work hardening of copper catalysts and their catalytic activity, with respect to:
(a) Dehydrogenation of Methanol.
(b) Decomposition of Formic Acid.
A discussion is included.

CHAPTER V: Full experimental details subdivided into the various sections of the Chapters I to IV.

In general, Graphs and Figures have been included on the page following their first mention in the text. In addition, the Graphs and Figures and their corresponding page numbers have been included in the Table of Contents for convenience.

CHAPTER I

The Catalysts

CHAPTER I - THE CATALYSTS.

Part I - Preliminary Experiments.

I) Clean Copper Surfaces.

In the first experiment an attempt was made to decompose methanol vapour directly on a piece of copper foil without pre-treatment other than a rinse in very dilute nitric acid followed by a thorough wash with distilled water. The foil used was $\frac{1}{4}$ mm. thick and had a geometrical area of 24 cm^2. This was placed in a simple vacuum system, incorporating a catalyst vessel, methanol reservoir, circulating system and mercury manometer. The apparatus was connected through a gold trap, for removal of mercury vapour, to two mercury diffusion pumps and a backing oil pump. The mercury manometer was connected to the circulating system via a long length of capillary tubing, to prevent back diffusion of mercury vapour. Thus mercury vapour, reported as being a poison to the reaction (19) was excluded from the reaction system. The reaction vessel was then "baked out" at 500°C. for several hours under a vacuum of 10^{-5}mm. and allowed to cool. Methanol vapour was then admitted to the reaction system until the pressure was several cm. below the methanol saturation vapour pressure, to avoid any possibility of condensation of the vapour in the colder parts of the circulating system. The catalyst vessel was then heated to 300°C, the temperature at which decomposition of the gas to hydrogen and carbon monoxide should be complete (10), and any reaction followed by the increase in pressure due to formation of the products. The pressure increased slowly with temperature until 300°C. was reached, after which the pressure remained steady, i.e. the only increase in pressure appeared to be due to expansion of the gas. This was confirmed by a blank run without catalyst, when the same increase in pressure was observed. Thus, copper foil prepared in this way would not catalyse the decomposition of methanol. As was indicated in the introduction, this result was not entirely unexpected, but it was decided to investigate other methods of surface preparation. Dilute nitric acid, for instance, might have produced a protective coating of copper nitrate on the surface of the foil, a barrier which would not be removed during the "Baking out" process.

It is known that hot alcohol will clean copper surfaces quite effectively, and so pieces of copper foil were suspended in the hot vapour of refluxing methanol for several days. At the end of this period the copper developed a beautiful clean metallic lustre. They were then quickly transferred to the catalyst vessel, while still wet with alcohol, and this was evacuated and "baked out". In this fashion it was felt that contamination of the surface would be reduced to a minimum, since the methanol would protect the surface during the transfer, and would be readily desorbed on "baking out".Again, however, an inactive catalyst was the result.

This experiment was then repeated, this time with the copper immersed in boiling methanol, but again an inactive catalyst was produced.

Yet another cleaning method was tried using a mixture, details of which are given in the experimental section, which is used in this laboratory to clean copper cathodes for use in Geiger-Müller counting tubes. After treatment with this mixture, the foil was rinsed thoroughly in distilled water and methanol, and immediately placed in the apparatus as before. Again however, a negative result was obtained even when the temperature was raised as high as 500°C. The same results were obtained with copper wires.

2) Reduced Copper Surfaces.

It is obvious then, that clean copper foil or wire will not catalyse the decomposition of the alcohol. On the other hand activated copper powders, that is powders which have been oxidised and reduced several times do catalyse this reaction, and so it was decided to try to activate the foil and wire by this means.

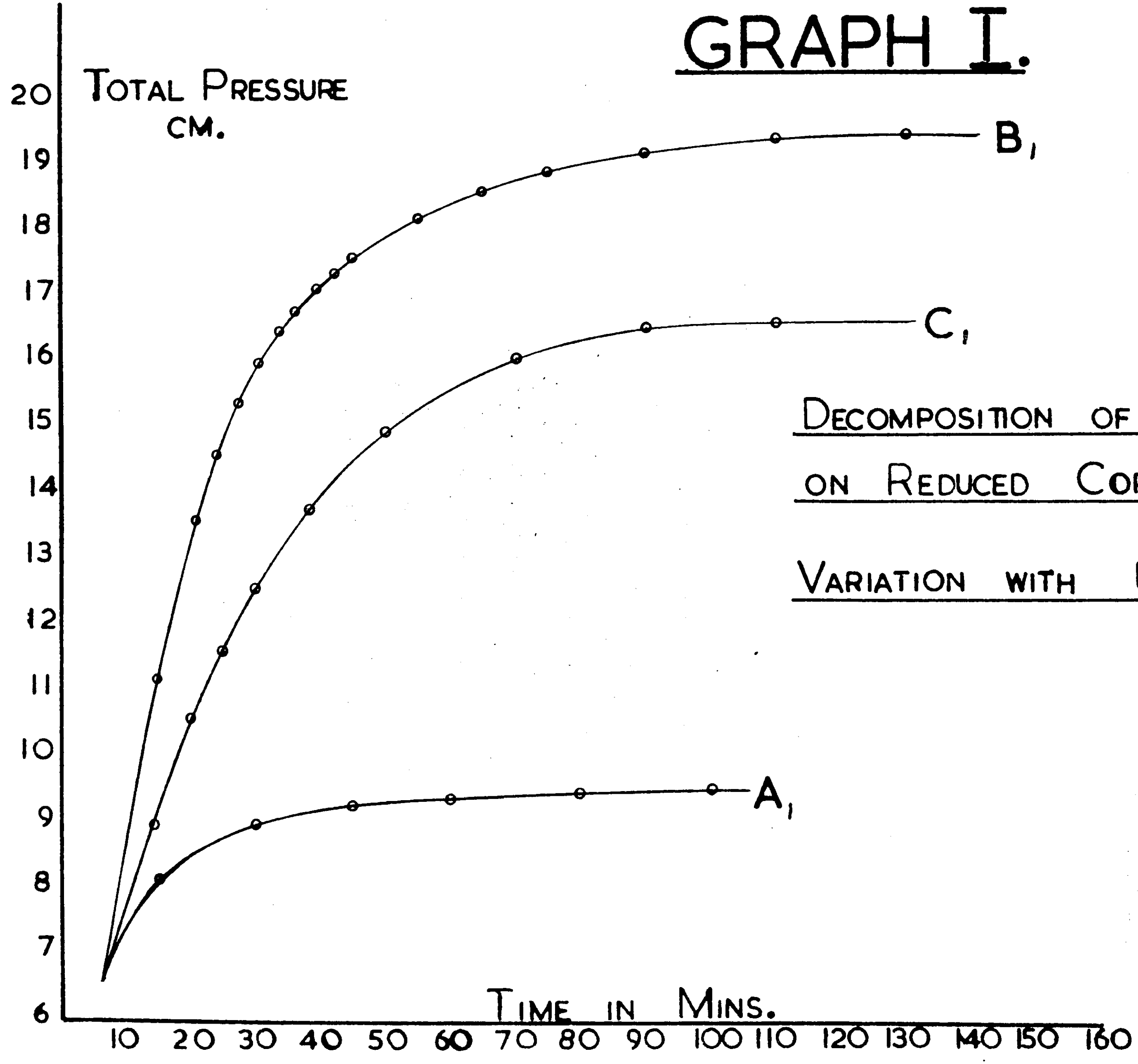
The foil, of area 24 cm^2, was accordingly cleaned as in the second experiment, that is it was refluxed in methanol, and placed in the apparatus. Initially some purified oxygen was admitted to the apparatus up to a few cm. in pressure. The reaction vessel was heated for a short time to chemisorb some oxygen on the surface, which it was hoped might initiate the reaction. The result was again negative. More drastic action was then taken and the copper was oxidised in a stream of purified oxygen for several hours, and reduced in a stream of purified hydrogen for a similar time. This process was repeated five times. At the end of this treatment the catalyst was "baked out" to a vacuum of 10^{-5}mm. This should have activated the foil in the same way in which previous workers activated their powders, but in fact the foil was again found to be completely inactive. The other cleaning methods were then applied followed by the oxidation/reduction technique but activation of copper foil or wire could not be attained by these methods.

It was then decided to try one of the Industrial Patents methods (30) for activating copper foil or gauze, suitable for preparing aldehydes from alcohols. As has been pointed out in the introduction however, the copper foil or gauze is, in this case, probably acting as a support for reduced copper powder, the active part of the catalyst. By undertaking this experiment, an example of the reaction on reduced powders will be obtained.

The method used was to immerse the foil in a solution of copper nitrate or nitric acid, and precipitate copper hydroxide on to the metal. This was then dried and ignited to copper oxide, which was reduced in the apparatus under a slow stream of hydrogen for several hours, to produce a surface coating on the foil of reduced copper powder. This was then "baked out" in the usual manner. Methanol vapour was then admitted to the reaction system to a pressure of 6 cm., and on being heated to 300°C, a reaction commenced.

The result is shown in Graph I, plot A_1. An initial, fairly rapid, increase in pressure was followed by a period of slower increase, and the reaction stopped at a pressure corresponding to the decomposition of only 13% of the methanol. Accompanying this decomposition was the production, in the cold parts of the circulating system, of a small amount of condensation. This could not be methanol, as the initial pressure of the latter was several cm. below saturated vapour pressure, and it was assumed that in all probability the condensate was water. Now if all the oxide originally present in the catalyst had not been reduced during the catalyst preparation, then hydrogen from methanol dehydrogenation would react with the oxide to produce water. This, in turn, may poison the surface of the catalyst. In fact there is evidence in the literature that water is a poison in the dehydrogenation of

GRAPH I.



Decomposition of Methanol on Reduced Copper Powders.

Variation with Usage.

ethanol (31). It is realised that a great many more factors may be influencing the rate of this catalytic reaction, but for dehydrogenation according to:

$$\mathrm{MeOH} \rightarrow 2H_2 + CO,$$

the final pressure should eventually reach three times the starting pressure of undecomposed methanol and this we shall take as our definition of an unpoisoned reaction. What we shall call a "partial" or poisoned reaction is thus one in which this total rise in pressure is inhibited.

It would seem therefore that it is more difficult to remove all the oxygen from the powder catalyst than might be supposed. Accordingly the catalyst was further reduced in a stream of hydrogen at 300°C. for 24 hours, cooled, evacuated, and "baked out" to 10^{-5}mm. More methanol was admitted to the reaction system to the same pressure as before, and this time a vigorous decomposition of methanol ensued, as will be seen from Plot B_1 of Graph I. This time also no condensation was observed in any part of the system. This, therefore, was an unpoisoned reaction, the final pressure being three times the starting pressure. The activity of this catalyst was not maintained, however, and after several more runs, the total decomposition pressure of the methanol fell off from a value approaching 20 cm. to slightly less than 17 cm.

(Plot C_1 on same graph). A self-poisoning,or inhibiting, mechanism had thus set in.

It should be pointed out, at this stage, that in all the catalytic decompositions in this thesis, the initial time was taken as from the instant of switching on the furnace, and since the latter took some minutes to warm up to the reaction temperature, graphs have been plotted as starting from the point at which the change in pressure due to the reaction took over from that due to expansion of the gas. This is to avoid any confusion in thinking that an induction period exists.

The above results seem to follow the literature as expected; even foil or wire, which has been pre-treated by the oxidation/reduction method is completely inactive compared with a similar technique applied to copper powder. It was at this stage of the work then, that a method of pre-treating copper foil and wire was found which produced an extremely active catalyst, and these catalysts will be called "FLAME QUENCHED" catalysts.

Part II - Flame Quenched Catalysts.

We have seen that cleaning a copper surface with hot methanol will not activate it for methanol decomposition: perhaps more drastic treatment is required. As early as 1925 Schotz (32) had observed that copper surfaces may be reactivated for ethanol dehydrogenation by oxidising the surface with hot air followed by reduction of the metal oxide with alcohol. If we were to heat the copper to a high temperature, about 900°C., and treat it with methanol, the high temperature may be sufficient to bring about dehydrogenation. Thus the reaction might be initiated , and the surface may then become active at lower temperatures. The influence of the crystal face in catalysis is well known (33), and it is possible that this process may expose the correct faces on the surface of the copper so that the reaction will take place. It was for these reasons that the following simple experiment was carried out. A piece of copper foil was exposed to the flame of coal gas/compressed air mixture, thereby being heated to a bright red-heat within about 30 seconds. It was then immediately transferred to methanol at room temperature, in which it was quenched: the oxide formed during the heating process was quickly reduced to copper, and the whole foil took on a gleaming copper colour. As before, it was then quickly transferred to the vacuum

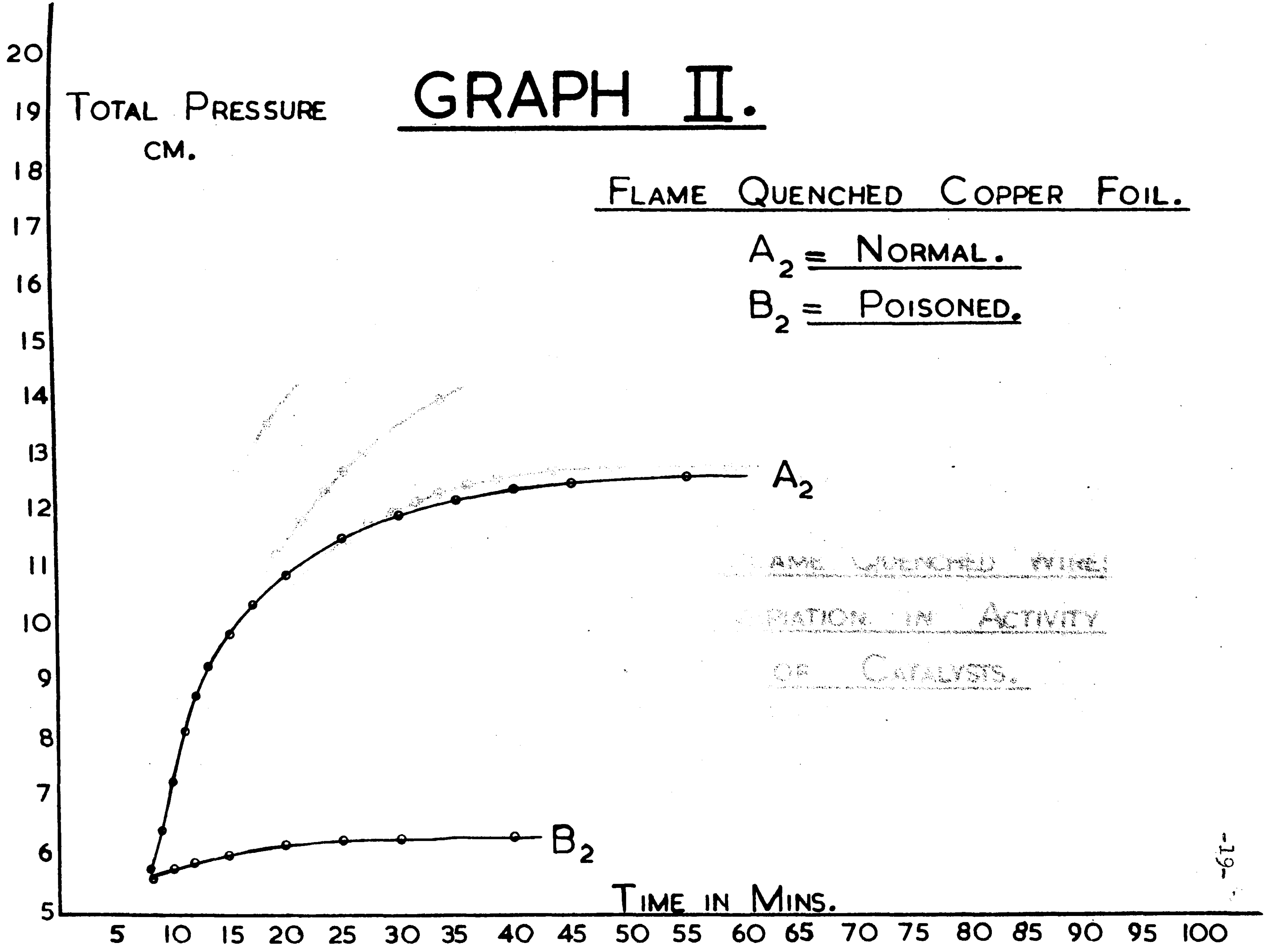
apparatus, and "baked out" to a high vacuum. As before, several cm. pressure methanol vapour was admitted to the reaction vessel, which was heated to 300°C. This time a vigorous reaction ensued, similar to that previously obtained on copper powder. No condensation was observable in the apparatus. The results are shown in Graph II Plot A_2. This activity, however, was not maintained, and on evacuating and "baking out" the same piece of copper,to remove adsorbed products, a repeat reaction gave a negative result. In other words the reaction would again appear to be self-poisoning, or self inhibiting, in some manner.
Plot B_2 on the same graph shows the difference between active A and poisoned B reactions on the same catalyst. The activity, however, could be regenerated by further flame treatment followed by quenching in methanol.

Copper wires produced similar results, as shown in Graph III, for various wire catalysts prepared in the same manner, exactly the same lengths of wire being used in each case, that is:

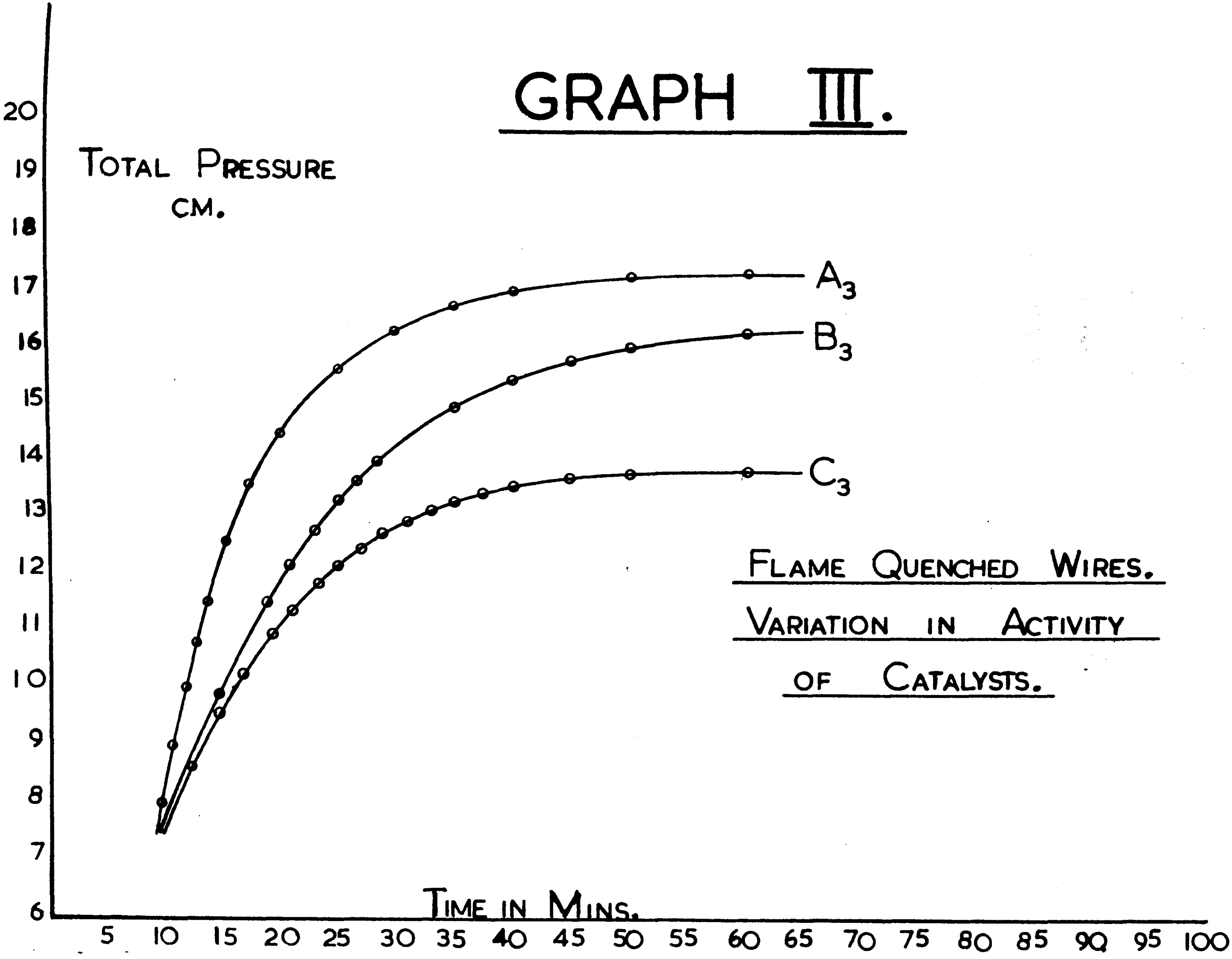
1 metre of 18 s.w.g. wire shaped in the form of a spiral coil.

It is to be noted that the ability of each catalyst to decompose methanol, measured by the increase in pressure due to decomposition products, varies considerably, even though the same lengths of wire were prepared in exactly the same manner. Some wires are activated

GRAPH II.


Total Pressure
cm.
Flame Quenched Copper Foil.
A_2 = Normal.
B_2 = Poisoned.
A_2
B_2
Time in Mins.
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

GRAPH III.



Total Pressure
cm.
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
A$_3$
B$_3$
C$_3$
Flame Quenched Wires.
Variation in Activity
of Catalysts.
Time in Mins.
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

to a greater extent than others, and the reaction at this stage is not at all reproducible. The same variation was obtained with copper foil and there was no reason to distinguish between the two as far as efficiency went.

There was therefore some unknown activating agent present in the wire, and foil, and the questions to be answered now, were as to whether the actual process of quenching was important in activating the catalyst, or whether it was some factor involved during the heating of the catalyst in the flame. Accordingly, an experiment was conducted in which a wire catalyst was flame treated as usual, but instead of being quenched, it was allowed to cool in air, the resulting oxide layer being reduced in the vacuum apparatus under a stream of hydrogen. This catalyst was completely inactive and the result was the same as in previous oxidation/reduction experiments. Thus, Flame treatment alone does not activate the surface. Is the drastic methanol reduction therefore the important factor? At this stage it was decided to avoid flame treatment altogether,and the next section deals with these sets of experiments.

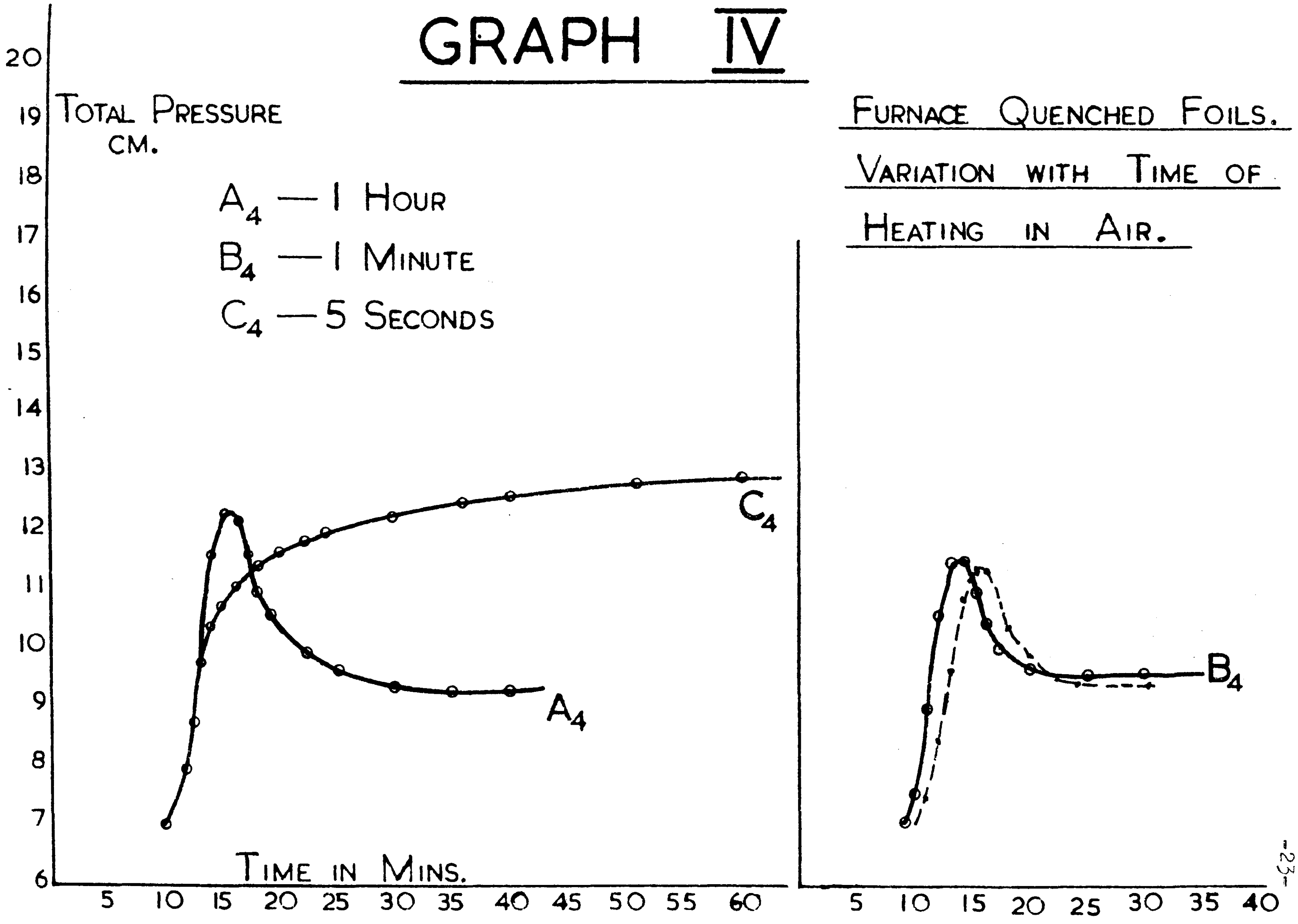
Part III - Furnace Quenched Catalysts.

First attempts at these experiments involved heating the copper wire electrically to a high temperature in vacuum,in a vessel designed to rotate about a quick-fit joint so that the vessel could be up-ended and methanol poured on to the hot wire to quench it. These experiments proved dangerous however, and it was decided to resort to heating 24 cm^2 foil in a silica apparatus, by means of a Kanthal high temperature furnace. Full experimental details are given later ; it is sufficient to say at present that the apparatus was designed so that the foil could be heated in any given atmosphere for a given time, and then released so that it would drop into a reservoir of methanol. It could then be transferred to the reaction vessel as usual. First experiments involved heating the foil in an air atmosphere for:

A - 1 hour
B - 1 min.
C - 5 secs.

The variation in results are shown in Graph IV. When the foil was heated for one hour at 900°C in an air atmosphere and then quenched it was found on removal of the foil, that although it still retained its appearance of being copper foil, the whole interior had been oxidised to copper oxide making the foil very brittle in nature,

GRAPH IV



Total Pressure
cm.
A_4 — 1 Hour
B_4 — 1 Minute
C_4 — 5 Seconds
Time in Mins.
Furnace Quenched Foils.
Variation with Time of
Heating in Air.
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
10
15
20
25
30
35
40
45
50
55
60
A_4
C_4
B_4
5
10
15
20
25
30
35
40

and only the top surface coating had been reduced to copper. When a reaction was attempted on this unusual foil the results appeared as in Plot A_4 on graph IV. The reaction was accompanied by a large amount of condensation. When the time of heating in air was reduced to one minute, Plot B_4 resulted showing a decrease in peak height, but when time of heating was further reduced to five seconds, Plot C_4 on the same graph resulted. Condensation again accompanied this reaction and although the time of heating had not been sufficient to oxidise the wire to any great depth, it was observed that some oxide still lay beneath the surface coating of copper after quenching. The behaviour of the system in this run in fact resembled to a great extent the behaviour of the system with reduced copper powder when it was suspected that oxide still remained in the catalyst, and that hydrogen produced in the dehydrogenation process was attacking the oxide to form water which then gradually poisoned the reaction. This would also explain the results obtained as on Plot A_4, namely the rise followed by a fall in pressure. In this case it would seem that since a large excess of oxide was present, water production was rapid, the dehydrogenation was completely poisoned, and the remaining hydrogen then continued to react with the excess oxide to produce water. Since the saturated vapour pressure of water at 20°C is 1.25 cm. it soon condenses in the cold parts of the apparatus, is effectively removed from the reaction system, and thus the pressure falls until all the hydrogen is consumed.

Thus, as with the reduced powder experiments, we want to avoid this excess oxygen being present which produces water vapour to poison the reaction. It was therefore decided to exclude oxygen from the activation process completely, and the next experiment involved heating the foil to a high temperature in an atmosphere of nitrogen for several minutes followed by the usual quenching process in cold methanol. The catalyst thus produced was completely inactive, and it was deduced that the quenching process was unimportant in the activation process.

Now when the above experiments were repeated using copper wires, similar results were obtained, and since there is no reason to suppose that any basic difference exists between foil and wire, all future work from this stage has been devoted to wire catalysts, because of their ease of cleaning and with a mind to possible future experiments on work hardening.

To summarise the study so far, three main classes of catalyst and their associated reactions have emerged:-

1)	<u>Flame Quenched Wires</u>:	gives vigorous, mostly unpoisoned reaction with no water.
2)	Furnace Quenched Wires: Five second oxidation -type C.	partially poisoned reaction, water produced.
3)	Furnace Quenched Wires: One min. oxidation - type B. One hour oxidation - type A.	completely poisoned reaction large amount of water.produced.

It was then decided to attempt to prepare one type of catalyst and convert it into another: from this study it was hoped that the controlling factor in the catalyst preparation might emerge.

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Part IV - Interconversion of Catalysts.

It was decided to attempt a conversion of flame quenched to furnace quenched catalysts to determine conclusively whether the difference between them was due to oxide present in the latter. This was done by preparing flame quenched catalysts as usual and re-heating them in the high temperature furnace in an air atmosphere, followed by further quenching. The results were completely successful. When a reaction was attempted on a flame quenched wire which had been re-heated in the furnace for one minute followed by further quenching, a graph was obtained typical of Plot B_4 on Graph IV rather than the characteristic plot of a flame quenched wire such as A_3 on graph III. Condensation also accompanied this reaction, again typical of Graph IV catalysts rather than Graph III. Again, when the above experiment was repeated, this time reducing the time of heating in the furnace to five seconds, then a graph resulted typical of Plot C_4 on Graph IV, with its accompanying condensation. Thus, flame quenched catalysts can be converted to furnace quenched catalysts by this process, and the difference between them must be due to oxide present in the furnace quenched types.

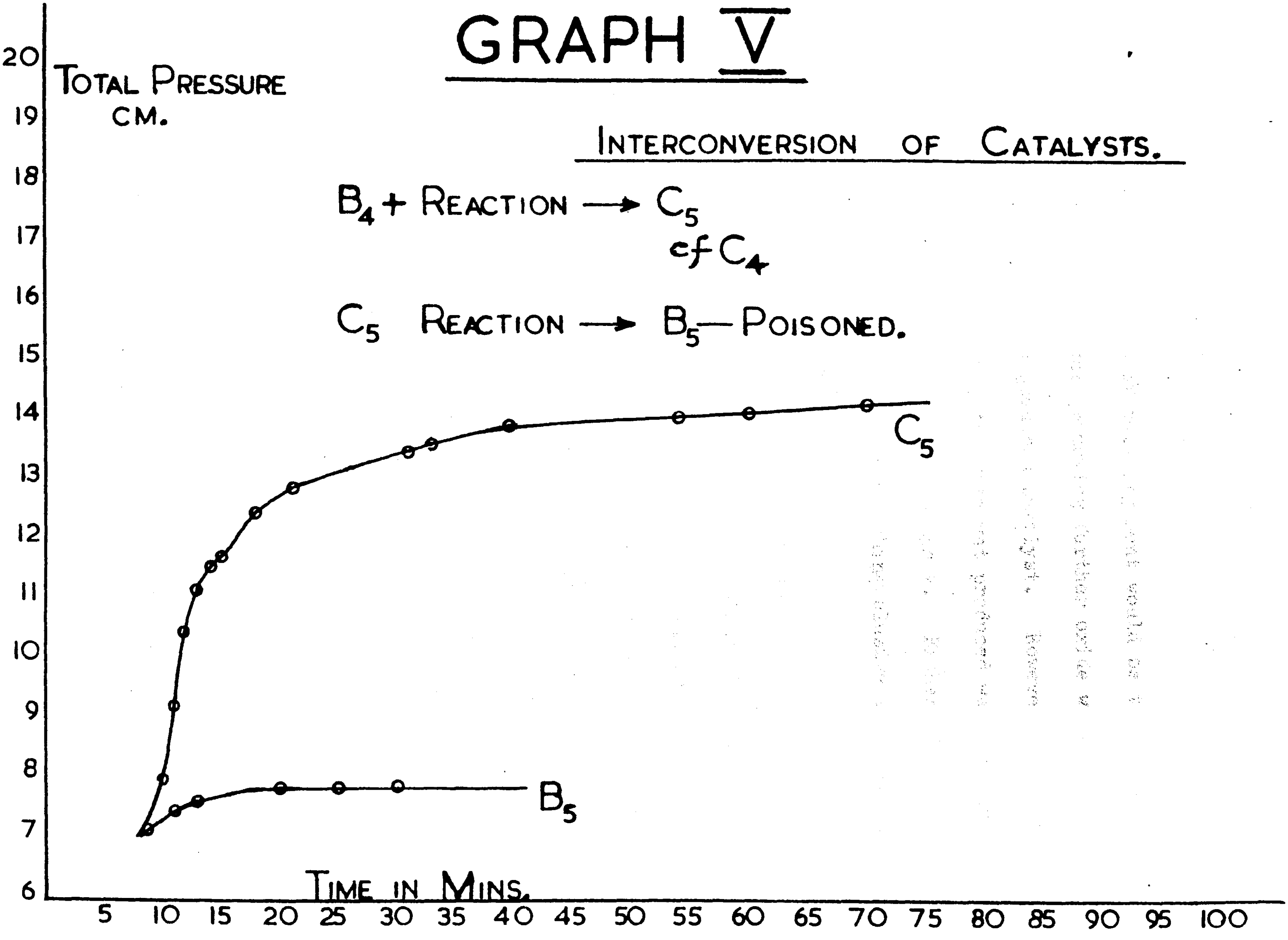
Interconversion of furnace quenched catalysts was also obtained in the following manner.

Using the nomenclature as in Graph IV, i.e.

Type A - Furnace - 1 hour - quenched.
Type B - Furnace - 1 minute - quenched.
Type C - Furnace - 5 seconds - quenched.

it was found that after a reaction as on type A catalyst, if the wire was "baked out" to remove adsorbed products of the previous reaction, particularly water, then a repeat run on the same catalyst showed that short of being poisoned, as was the case with the flame quenched catalysts, a similar reaction was obtained with a smaller peak height shown in Graph IV as the dotted line alongside Plot "B", the similarity between Plot B and the dotted line is obvious, and it would seem that as succeeding runs are done on these types of catalysts,the peak height is gradually reduced until type C catalyst results, i.e. Type A catalyst is converted towards type B, and type B is converted towards type C. This was confirmed by a repeat run on a type B catalyst, and the result is shown plotted in Graph V labelled C_5. The peak has now entirely disappeared, although there is still a suggestion of it occurring at about 15 min., and a type C catalyst results. Thus the difference in reaction between these furnace quenched catalysts and the flame quenched catalysts is due to the excess oxide of the former which is gradually reduced by the hydrogen produced in each reaction causing

GRAPH V



INTERCONVERSION OF CATALYSTS.

B_4 + REACTION → C_5
cf C_4

C_5 REACTION → B_5 — POISONED.

the variations described on previous page.

The logical conclusion of this argument would be that repeat reaction on a type C catalyst, removing further oxide would give a reaction similar to a flame quenched catalyst. However when such an experiment was carried out, the catalyst produced was inactive or poisoned as is shown in Plot B_5 of Graph V. Either all the oxide had been removed,or there was something elusive about the activity produced in flame quenched wires.

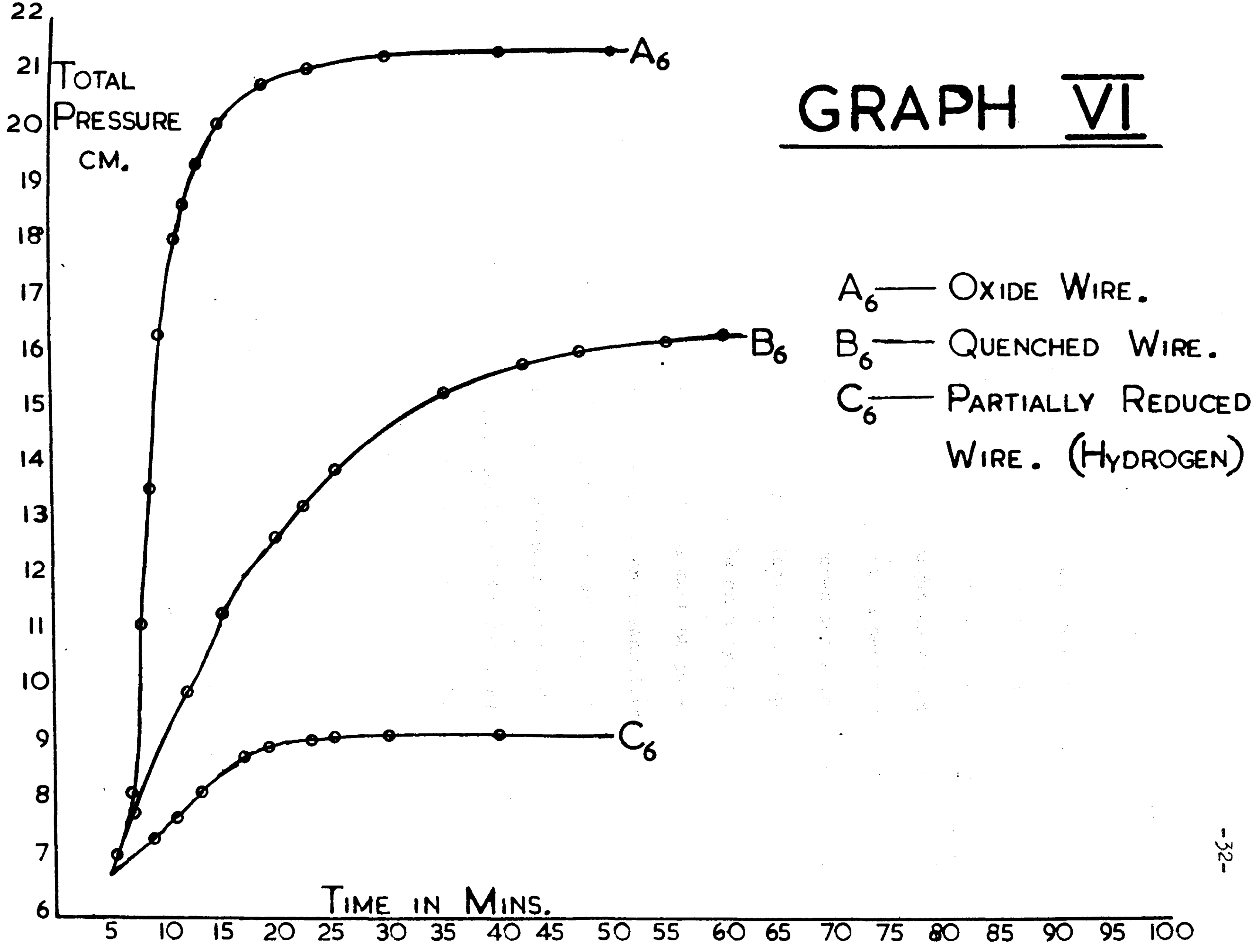
However since the presence of oxide in the catalysts was obviously so important, it was decided to find out what the effect of a reaction on a pure oxide surface would be without the intervention of a quenching stage. Accordingly, a wire catalyst was flame treated as usual, but this time allowed to cool in air without being quenched. A similar experiment had already been performed in Part II, but there it had been reduced with hydrogen prior to reaction with methanol, and all activity had been lost. When this oxide wire was "baked out" in the reaction vessel, and a reaction attempted, it was found to give a result similar to a flame quenched wire but with higher activity. At the end of the reaction, and on removal of the furnace, the wire was found to have been reduced to a bright copper colour, and succeeding reactions on this wire showed that it had lost its activity.

Also when such an oxide wire was again prepared and this time only partially reduced with hydrogen then the reaction was again secured but to a much smaller extent. The results are shown in Graph VI.

It is now obvious that quenching of the wire was unimportant in activating it for methanol decomposition, except in that the process of quenching was such that a little oxide was left in the wire: this was sufficient to promote the dehydrogenation reaction. Oxide, up to a critical amount, would therefore appear to activate the wire, and beyond this, a poisoning or inhibiting mechanism of some description sets in. At this stage therefore it would be wise to re-define our concept of poisoning in this reaction.

There are now two "Poisons". Our original inhibition at the end of each reaction, for example poisoned run B_5, was simply due to removal of oxygen from the catalyst, and provided that this oxygen was maintained to a limited extent, then the activity of the catalyst remains. Our second poison is water, which, if it appears during a reaction, tends to inhibit the total decomposition of the methanol. Such a reaction will now be called a poisoned reaction.

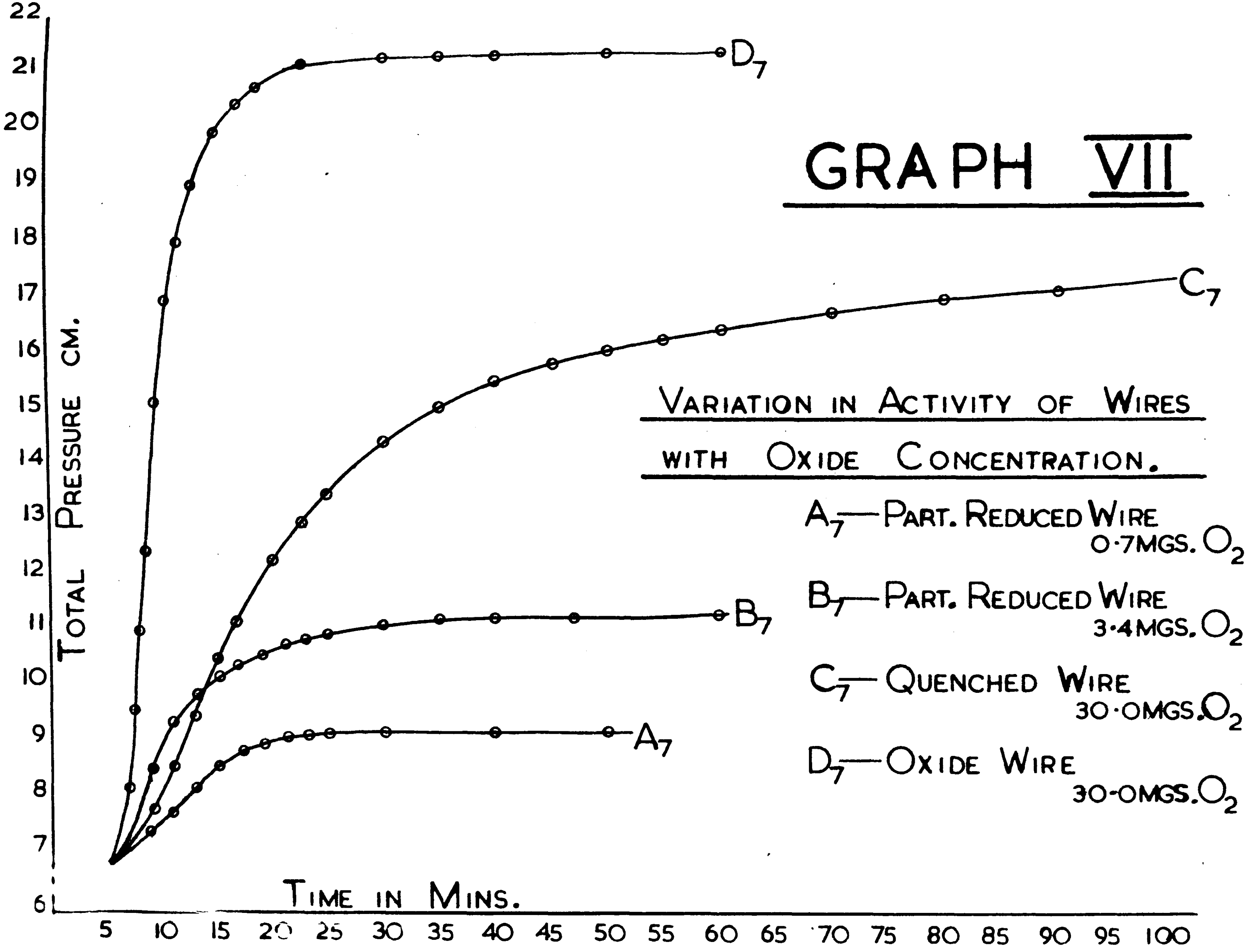
GRAPH VI


Total Pressure cm.
Time in Mins.
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
A_6
B_6
C_6
A_6 — Oxide Wire.
B_6 — Quenched Wire.
C_6 — Partially Reduced Wire. (Hydrogen)

Part V. - Gravimetric Experiments.

In order to confirm the postulate of oxide activation of the wire, it was decided to attempt a series of gravimetric experiments, in which the wire was weighed before and after activation, and also at the completion of an experiment. It might be thought that the difference in weight would be too slight to permit accurate analysis, but in fact these experiments proved quite feasible. Other workers (34) studying rates of oxidation of copper specimens have done likewise. For example on a typical wire catalyst weighing 10 g., there might be as much as 30 - 40 mg. oxygen present, a weight quite detectable on a sensitive balance. A series of wires were therefore weighed accurately and subjected to the usual catalyst preparation techniques, followed by re-weighing. In all cases an increase in weight resulted due to uptake of oxygen to a greater or lesser extent. Methanol reactions were then performed on these catalysts, namely an oxide wire, partially reduced oxide wires by both hydrogen and methanol, and a flame quenched wire. The results are shown in Graph VII together with the various oxide concentrations found on the wires. At the end of each experiment, the wires were re-weighed and in all cases the wire was found to have returned to its original weight. The oxide had therefore been completely removed during the methanol

GRAPH VII



VARIATION IN ACTIVITY OF WIRES WITH OXIDE CONCENTRATION.
A_7 — PART. REDUCED WIRE 0·7MGS. O_2
B_7 — PART. REDUCED WIRE 3·4MGS. O_2
C_7 — QUENCHED WIRE 30·0MGS. O_2
D_7 — OXIDE WIRE 30·0MGS. O_2
TOTAL PRESSURE CM.
TIME IN MINS.
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
D_7
C_7
B_7
A_7

reaction on the wire. Examining Graph VII, we see that for wires A_7, B_7, and C_7, the reaction rate goes up, as does the oxide concentration on the wire, and assuming excess methanol is present, when all the oxide has been used up, the reaction then stops. However, when we compare oxide and quenched wires it is seen that both wires have 30 mg. oxygen present but the oxide wire has the higher reaction rate, and is therefore a more efficient catalyst. This difference will be discussed later.

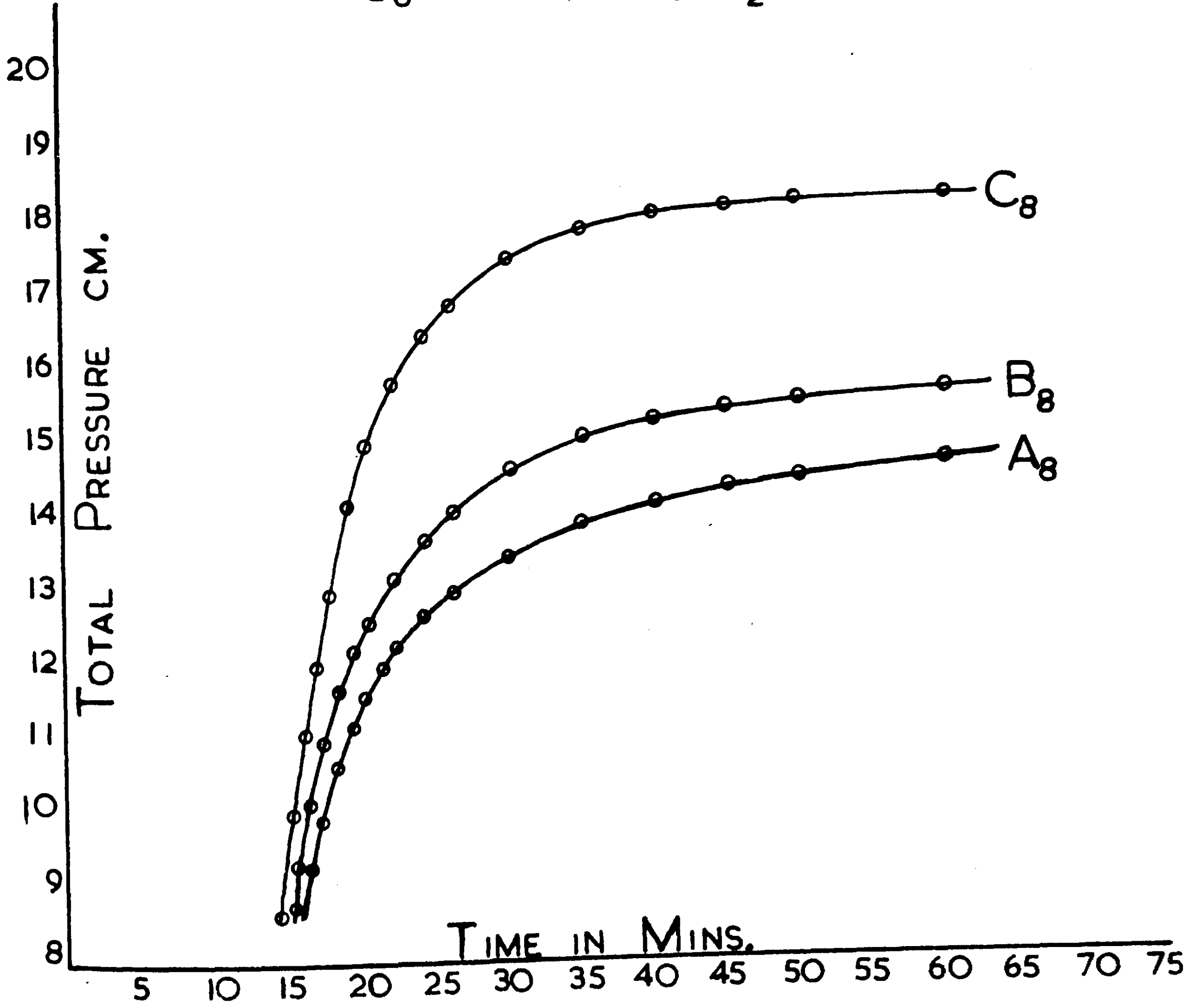
Flame quenched wires are thus shown to contain a layer of oxide beneath the surface coating of copper. In other words, when the hot wire is plunged into the cold methanol, initially a hot vapour jacket of methanol surrounds the wire,but as it cools, the liquid phase quenches the wire and terminates the methanol reduction of the oxide before it is completely removed. Assuming that the wire be heated to the same temperature by the flame on each occasion, then quenching in the same volume of methanol will remove the same amount of oxide from the surface. Therefore,by heating the wire in the flame for various times, following this quenching, varied and known amounts of oxide can be introduced into the wire and the activity of a series of quenched wires compared with oxide concentration. The result is shown in Graph VIII, and /-

GRAPH VIII

FLAME QUENCHED CATALYSTS.

EFFECT OF OXIDE CONCENTRATION ON ACTIVITY.

A_8 — 7·4 mgs. O_2
B_8 — 10·4 mgs. O_2
C_8 — 16·5 mgs. O_2



it is seen that the activity of the catalyst is a function of the oxide concentration. Quenched wires having the same amount of oxide give an identical reaction, and the latter is therefore reproducible to this extent.

It might be argued at this stage, that these results were not indicative of a catalytic reaction at all. They might indicate a simple combustion of methanol and copper oxide, the extent of reaction increasing as does the oxide concentration, assuming excess of methanol to be present; but this idea must be discarded; firstly, because with flame quenched type catalysts, water was not in evidence, despite the large increase in pressure during a reaction, and a simple combustion of methanol and copper oxide would be expected to form carbon dioxide and water as its chief products. Secondly, although water appeared with high oxide concentrations in the catalysts, it would be difficult on the basis of a simple combustion to explain the type of reaction characterised by Plot A.4. There was obviously a more complicated set or sequence of reactions occurring on these catalysts.

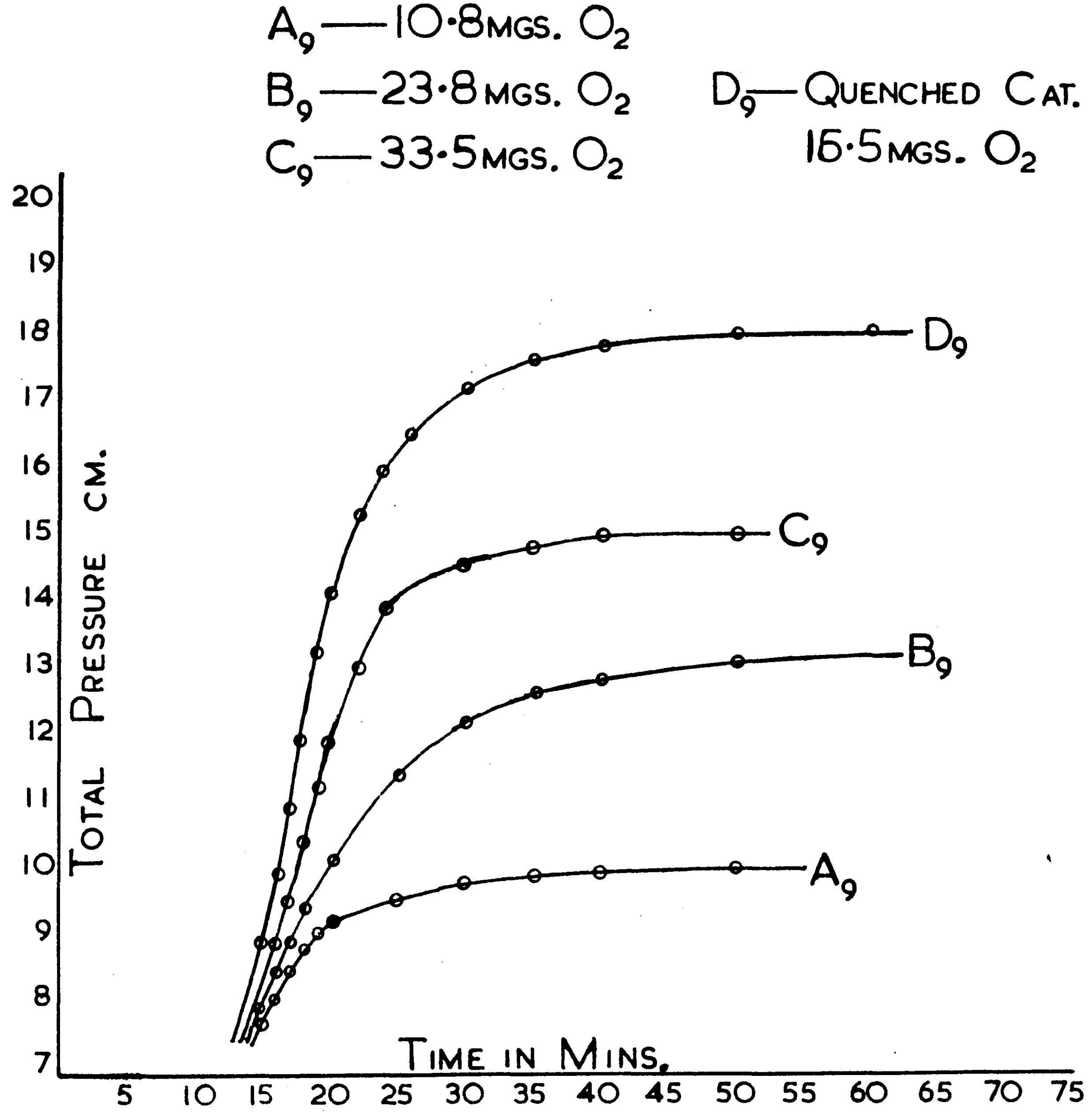
Part VI - Low Temperature Oxidation Experiments.

Since "Flame-quenched" wires showed reproducibility of behaviour once the oxide concentration was known, it was to be expected that pure oxide wires, shown to have a higher activity as above, would behave likewise. A more convenient and precise method of preparation of these oxide catalysts was therefore devised. The vacuum system was reconstructed to accommodate a more convenient catalyst vessel, which could also be used in the experiments detailed in the next part of this chapter. In this new apparatus was incorporated a highly efficient circulating pump, working on a moving diaphragm principle, and suitable for circulation of low pressure gases, which was designed and constructed by the author. Efficient circulation of the gases over the catalyst was found to be important in this static system. Also included at this stage, was a section of apparatus suitable for isolation of the reaction products preparatory to analysis: This analysis will be detailed in the next chapter. The previous mercury manometer was replaced by another giving greater accuracy in measurement and covering a wider range of pressures. Provision was also made for admission of various gases to storage bulbs included in the system. Full details are given later.

In this apparatus it was possible to oxidise wires in the catalyst vessel, in an atmosphere of oxygen, and to measure the extent of oxidation of the wire by following the decrease in pressure in the circulating system. From the volumes of the various sections in the apparatus, it was calculated that for an uptake of 30 mg. of oxygen, a decrease in pressure in the system of about 4 cm. would be observed. With a view to later experiments on the work hardening of copper wires, it was decided to keep the temperature of the oxidation as low as practically possible. A few experiments served to show that, using an oxygen pressure of 60 cm. and a temperature of 300°C., the rate of oxidation was such that 30 mg. oxygen would be taken up in four hours. A length of copper wire, 3 metres long, was selected and surface dirt removed by sanding lightly with fine emery paper. The wire was then formed into a spiral, immersed in boiling methanol for a short time to remove any loose particles adhering to the wire, and "baked out" in the catalyst vessel, before oxidation at 300°C. as above for one hour. Two other catalyst wires were prepared in an identical manner but given two and four hour oxidations respectively. Thus, catalyst wires containing approximately 10, 20 and 30 mg. of oxygen were prepared. Methanol decomposition at 300°C. was then attempted on each of these wires and the results are shown in Graph IX. They may be compared with a typical result from a flame-quenched wire

GRAPH IX

LOW TEMPERATURE OXIDATION CATALYSTS.
VARIATION IN ACTIVITY WITH O_2 CONC.



shown on the same graph. The oxide wires thus prepared, instead of being more active than the quenched wire, as was the case in Graph VII, were much less active. In fact the flame quenched wire which had absorbed 165mg. oxygen showed greater activity than wires oxidised at low temperatures with twice as much oxide present. Admittedly, the geometrical surface area of the quenched wire was slightly greater than that of the wires oxidised at low temperatures, but this did not account for such a large difference.

Another feature of methanol decomposition observed with wires oxidised at low temperatures was the appearance of water to a greater or lesser extent: that is, these reactions appeared to be changed or poisoned to some extent. The reactions of methanol on these wires prepared by low temperature oxidation were once again found to be reproducible: the extent of the poisoned reaction depending again upon the concentration of oxide in the wire. Thus, the decomposition products of methanol depended on the method of preparation of the catalysts.

-ooOoo-

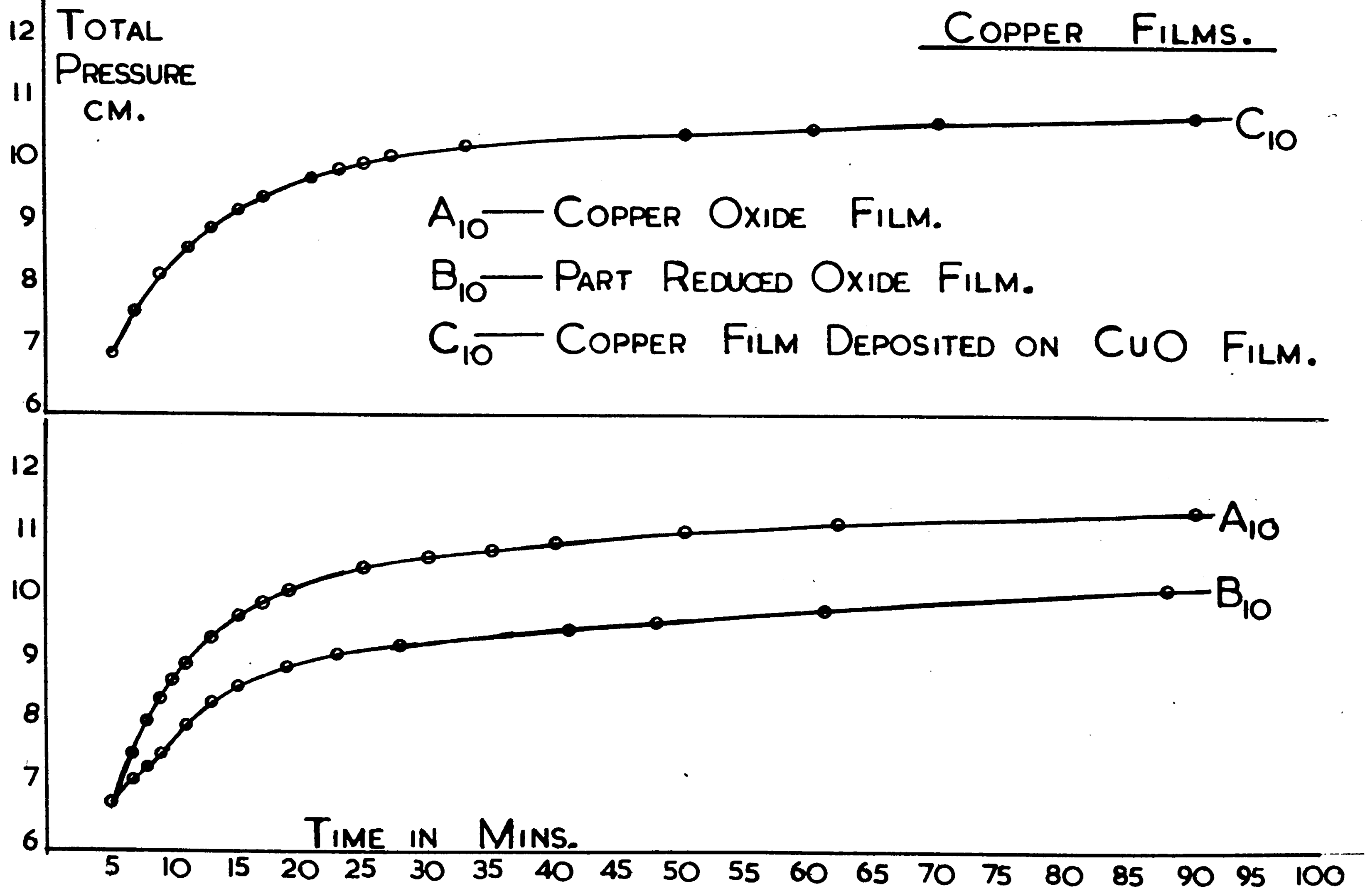
Part VII - Copper Films.

This chapter will be concluded with a description of experiments on methanol decomposition on copper films. One important advantage in using copper films to study this reaction was that by using the usual "baking out", gettering and cleaning techniques, clean and uncontaminated copper metal could be employed as the starting material: whereas there was always some doubt about the nature of the surface of copper foil or wire. Films were prepared by evaporation of copper from a glowing filament of wire on to the walls of a catalyst vessel which was immersed in liquid air. There is evidence (24) that at this temperature porous films are obtained, and although it is probable that on warming the catalyst during reaction, complete sintering occurs, it was thought that the surface area would be great enough to bring about reaction.

Again, just as with pure copper wires, it was found that these films were completely inactive in methanol decomposition. When this film was "baked out" however, and oxidised with pure oxygen at 300°C and 60 cm. pressure followed by further evacuation, then it was found that activity had been imparted to the catalyst, and a reaction with methanol was obtained similar to that of wires oxidised at low temperatures. The reaction rates were not directly comparable with previous values because of the large discrepancy in surface areas. Again when such an oxide film was partially reduced with hydrogen, a decrease in activity resulted, compared with the pure oxide film. These results are shown in Graph X, A_{10} and B_{10}.

The problem still exists at this stage as to whether the reaction is taking place on copper metal or on copper oxide. It is known that both dehydrogenation and dehydration can occur on oxide surfaces (3), although it is generally assumed that dehydrogenation usually takes place on the metal. An interesting experiment was conducted at this stage with this in mind. The aim was to find out whether a copper film deposited on top of a previously oxidised film would still catalyse the decomposition reaction. This was done using a double filament technique as explained in the experimental section. The first copper film prepared was oxidised at 300°C and 60 cms oxygen pressure for several hours to ensure complete oxidation, and on removal of the furnace, this was observed to have taken place by the black colouration imparted to the film. After the deposit of oxide had been removed from the copper filaments, a second copper film was then deposited on top of the first oxide film.

GRAPH X


COPPER FILMS.
TOTAL PRESSURE CM.
12
11
10
9
8
7
6
C_{10}
A_{10} — COPPER OXIDE FILM.
B_{10} — PART REDUCED OXIDE FILM.
C_{10} — COPPER FILM DEPOSITED ON CuO FILM.
12
11
10
9
8
7
6
A_{10}
B_{10}
TIME IN MINS.
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

Although this deposition occurred at liquid air temperature, the film was thereafter allowed to reach room temperature, complete sintering should then occur, and the oxide film should thus be protected from direct reaction with methanol. When such a reaction was attempted, a result was obtained similar to that of an oxide film, as shown in Graph X, C_{10}. It was also noted at the conclusion of the experiment that the oxide present had been reduced to copper, but this may have been as a result of penetration of the film by hydrogen, being of small molecular diameter. It would seem therefore, that methanol reaction can take place on a copper metal surface activated by oxide situated within the metal lattice. The possibility that copper films are still porous at 300°C, however, must not be neglected.

<u>CONCLUSION</u>: THERE HAS BEEN PRESENTED IN THIS CHAPTER AN ACCOUNT OF THE PREPARATION OF VARIOUS CATALYSTS, SHOWING THE DIVERSITY OF THEIR ACTIVITIES AND REACTIONS THEREON. BEFORE THESE RESULTS CAN BE DISCUSSED, MORE INFORMATION ON THE PRODUCTS OF THE REACTION IS NECESSARY.

CHAPTER II

The Analysis

CHAPTER II - PART I.

1) It has been seen in Chapter I that the reaction products obtained from certain catalysts are condensible, and first attempts at analysis were therefore directed towards the determination of these condensible products. It was essential to find out, for example, if the condensation appearing in the apparatus was caused by water. Infra-red analysis was selected as a possible "analytical tool". Accordingly, synthetic mixtures were prepared comprising of the possible condensible products at -195°C., that is methanol, water and formaldehyde. Two such mixtures were prepared in the ratio of methanol: formaldehyde: water as 4 : 2 : 1 and $\frac{1}{2}$: 2 : 4, that is, one with high methanol content and low water, and the other of low methanol content and high water. These samples were analysed in the infra-red Unicam S.P.100 Mk.I. Prism Grating Monochromotor, by enclosing a small drop of the sample between two quartz plates. In the case of the low water ratio sample, the spectrum produced showed peaks for all three compounds; although the water peak was rather broad in nature. In the case of the high water ratio sample, however, the water peak was so broad that is swamped all other peaks, and only the first trace of the methanol peak was observed before

the water band appeared. Such an analysis would therefore be suitable only for samples of low water content, and it would indicate the presence of water in the condensation products.

Accordingly, methanol reactions were conducted on three different catalyst types: a flame-quenched wire, a furnace - quenched wire; time of heating - 1 minute, and a furnace-quenched wire; time of heating - 5 seconds. These latter two catalysts were the types producing condensation in the apparatus. After each reaction, the catalyst vessel was allowed to cool and tap 5 (Fig.1.) closed, when it was possible to condense products in the "by-pass" tubing shown, by cooling it in a Dewar of Liquid Air. The tubing was then sealed off, removed from the apparatus, and examined in the Unicam S.P.100 Mk.I. In the case of the flame-quenched catalyst, no condensible product was found. With both furnace quenched catalysts however, the infra-red spectrum indicated the presence of fairly large quantities of water which masked the presence of any other peaks. The condensation noted during these reactions was therefore due,at least in part, to water.

2) Detailed Analysis - Infra-red.

At this stage it was deemed wise to consider all the possible products of methanol decomposition which had been found by previous workers . From a dehydrogenation reaction, the products expected are hydrogen, formaldehyde and carbon monoxide (3), (9), (18), according to the equations;

$$CH_3OH \rightarrow H_2 + HCHO.$$

$$HCHO \rightarrow H_2 + CO.$$

In addition, Ghosh and Chakravarty (17) found methane and carbon dioxide, apparently according to the Armstrong-Hilditch reaction (35).

$$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4$$

As copper oxide was present in our catalysts, dehydration may also have been possible (3), according to the equation;

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O.$$

Thus dimethyl ether and water are possible products.

A combustion reaction may be partly operative, giving rise to carbon dioxide and water according to the equation;

$$CH_3OH + 3CuO \rightarrow CO_2 + 2H_2O + Cu.$$

This type of reaction was suggested by Kemball (36), who studied the desorption products of ethanol on Analar cupric oxide. The only products found were carbon dioxide and water, and he showed that such a combustion reaction was thermodynomically possible.

It was necessary therefore to search for the following 8 products:

H_2, CO, CO_2, HCHO, H_2O, MeOH, CH_4, $(CH_3)_2O$.

It should be pointed out at this stage, that although two Gas Chromatographic apparatuses were available in this Department, neither was suitable for complete analysis of the above products. The Pye Argon apparatus with its β- ionisation detector could not detect the permanent gases, and the Griffin and George apparatus Mk.2 with it's thermal conductivity cell, was inaccurate for quantitative work.

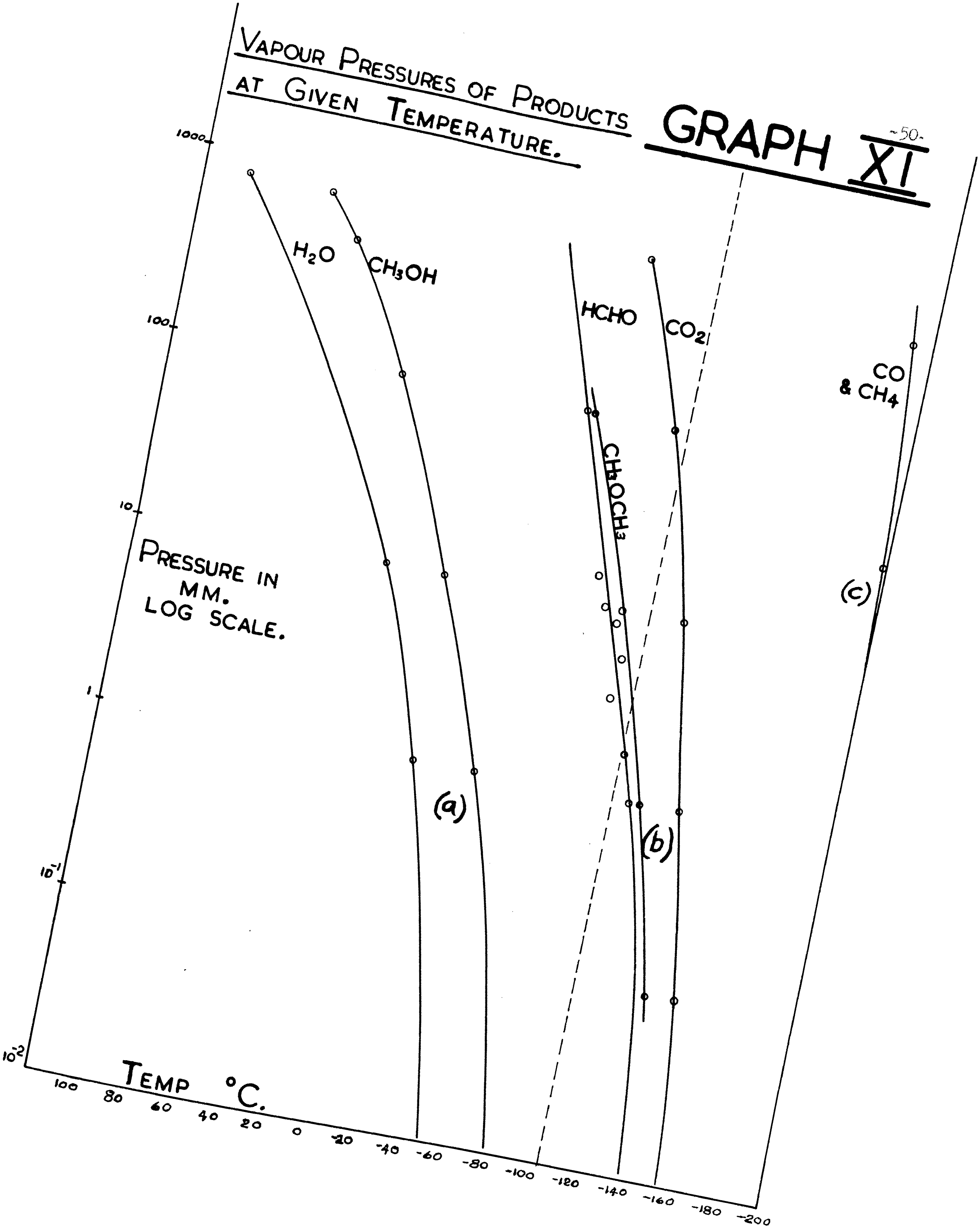
It was therefore decided to investigate the possibility of analysing the majority of the products on a Perkin-Elmer 13, Double Beam Infra-red spectrophotometer, made available to the author. It was essential to remove water from the product gas mixture;

(a) because as has been seen in the previous preliminary experiments, water in any appreciable amount masks all other peaks present.

(b) the Infra-red Gas Cell had, of necessity, quartz windows, susceptible to attack by water vapour.

The vapour pressures of the above compounds were then examined in detail. Graph XI shows a plot of the logarithm of the vapour pressure versus temperature for the various compounds. It is seen that they fall into three distinct regions:

GRAPH XI



VAPOUR PRESSURES OF PRODUCTS AT GIVEN TEMPERATURE.

(a) Water and Methanol.

(b) Formaldehyde, Dimethyl ether and Carbon Dioxide.

(c) Carbon Monoxide, hydrogen and methane, having much larger values.

At this stage, an interesting method of analysis devised by Le Roy (37) was investigated. This method involved the low temperature fractionation of the polycomponent sample. If the ratio of the vapour pressure of two components was greater that 10^{-3}mm., then complete separation could be effected in the following way. If the mixture was cooled to such a temperature that the vapour pressure of the lowest boiling fraction was 10^{-3}mm., then using a "Take-off" pressure of 1 mm., the higher boiling fraction could be pumped off quantitatively with a Toepler pump until the vapour pressure of the original mixture was 10^{-3}mm. The higher boiling fraction was not contaminated to any appreciable extent with the lower boiling fraction, and the separated gas could then be measured at a fixed volume with a McLeod Gauge.

Examination of Graph XI, however, shows that although separation of fractions (a), (b) and (c) is possible by this method, individual separation of the components of each fraction would be impossible, and the method, although interesting, was rejected. It is obvious however, that methanol and water may be easily separated from the other products by cooling to a temperature of -60°C. The apparatus used to accomplish this will be described, but suffice to say at present that the gaseous products of a reaction could be expanded into a section of apparatus containing a cold trap and a Toepler pump. The gases could be circulated through the cold trap at any desired temperature until constant pressure was reached. It was then possible to Toepler the non-condensing gases into an Infra-Red Gas Cell or other receptacle suitable for their analysis. Methanol solvent could then be admitted to the cold trap which was raised to atmospheric pressure with dry nitrogen. The trap was then brought to room temperature and removed from the apparatus. This condensible fraction could then be analysed.

A synthetic gas sample mixture was then prepared containing hydrogen, carbon monoxide, carbon dioxide and methane. Formaldehyde was not included in this mixture due to the ease with which it polymerised in the apparatus to paraformaldehyde. This mixture was then admitted to the Infra-Red Gas Cell at a definite pressure, and the spectrum determined. Absorption was obtained at wave numbers 2290, 2100, 2980 cm.$^{-1}$ and commencing at 1264 cm.$^{-1}$, a series of peaks were obtained corresponding to silicone grease in the apparatus. These corresponded to carbon dioxide, carbon monoxide and methane respectively. No absorption with hydrogen was obtained. Various pressures of the synthetic gas mixture were then admitted to the Gas Cell to determine the accuracy of the analysis with respect to quantitative results. Reasonable agreement was found.

It was then necessary to find a method of analysis for the condensible fraction, namely water. A search of the literature revealed that, of the various methods described for analysing water (38), the Karl Fischer Reaction (39), (40), remains the most popular. Electrometric end-points are necessary for very accurate results, but visual end-points have also been used successfully. Jones (41) suggests a colour standard of 0.003 N Iodine in water, but Mitchel (42) suggests that a colour standard of 0.01 N Iodine in methanol is closer to the true end-point, and claims an accuracy of ± 0.5 mg. water. This latter method was therefore adopted and found to be satisfactory.

The synthetic gas mixture together with a little water was then admitted to the circulating system of the vacuum apparatus, and the condensible and non-condensible fractions at -60°C. separated. The efficiency of the analytical system of the apparatus was thereby tested, particularly towards the entry of spurious water.

Several flame-quenched catalysts were then prepared by the usual technique, containing approximately 10 mg. Oxygen. These are the conditions for avoiding the appearance of water condensation during a reaction. Methanol reactions were then effected upon them. At the end of a reaction, the catalyst vessel was cooled and any water separated from the product mixture by the method described previously. The remaining gases were Toeplered into the Infra-Red Gas Cell, and their spectrum determined. Absorption was obtained at 2290, 2100 and 1760 $cm.^{-1}$ wave numbers. These corresponded to carbon dioxide, carbon monoxide and formaldehyde. The remaining gas undetermined was assumed to be due to hydrogen. In addition, the silicone grease peaks commenced at 1264 $cm.^{-1}$, but superimposed on this band was a series of peaks which lay in the ether region of absorption. However, investigation of the literature (43), (44), (45), showed that the spectrum of formaldehyde also appeared at this point and there was therefore little evidence to suppose that dimethyl ether was present. Methane was quite definitely absent.

Titration of the condensible fraction with Karl Fischer Reagent showed that water was present to an extent of less than 1%.

When quantitative analysis was attempted on the non-condensible fraction however, the height of the calibration peaks was found to vary erratically and no satisfactory result could be obtained. The previous analysis of synthetic mixtures in this respect therefore proved to be the exception rather than the rule. This method of quantitative analysis was therefore abandoned for the following reasons.

(a) The apparatus tended to be erratic in the presentation of quantitative data.

(b) The carbon monoxide absorption was small and insensitive to quantitative measurement.

(c) Formaldehyde could not be estimated due to the difficulty of preparing a calibration sample of formaldehyde gas.

The results did show however, that for flame-quenched catalysts of low oxygen content:

(a) Formaldehyde and carbon dioxide were present.

(b) Carbon monoxide was present to a small but undetermined extent.

(c) Water was present to an extent less than 1% by volume.

-ooOoo-

PART II - IMPORTANCE OF WATER-GAS REACTION.

Considering the results obtained in Part I of this Chapter, we see for that type of flame-quenched catalyst, carbon dioxide was formed in appreciable quantities, but both carbon monoxide and water formed only a small percentage of the total decomposition production. Yet oxide disappeared from the catalyst during a reaction. This signifies that :-

(a) Water was never formed in any appreciable quantity and that the copper oxide was removed completely probably by reaction with carbon monoxide to give carbon dioxide.

(b) Water was formed by reduction of the oxide with hydrogen but was probably removed by the water-gas shift to give carbon dioxide and more hydrogen.

Values for the water-gas equilibrium obtained by various authors (46),(47),(48), indicate that,at the reaction temperature used, namely 300°C., the equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

will lie largely towards the right-hand side of the equation. $CO/_{CO_2}$ ratios reported vary from 0.05 to 0.1

To test this postulated mechanism, the following experiments were carried out. A flame-quenched catalyst was prepared containing

24 mg. oxygen, and placed in the catalyst vessel. Water was admitted to the reaction system until it condensed in the tubing, and then a limited quantity of carbon monoxide added; less than the theoretical amount required to react with all of the oxide according to the equation;

$$2\ CO + O_2 \rightarrow 2CO_2$$

There was therefore excess of oxide and water present, but only a limited amount of carbon monoxide. This mixture was then circulated over the catalyst which was heated to 300°C. for one hour, the normal time for the completion of a dehydrogenation reaction. The catalyst vessel was then cooled and the products analysed in the analytical section of the vacuum apparatus by freezing out the water and carbon dioxide produced in the cold trap, and observing the decrease in pressure. This process indicated that 95% of the carbon monoxide had been converted to carbon dioxide. Further gravimetric experiments confirmed that most of the oxide had reacted, but that there was still an appreciable quantity left (20%). It is realised that such an experiment does not prove the existence of the water-gas shift, but it does show that carbon monoxide can be removed under such conditions. The fact that all of the carbon monoxide was not oxidised to carbon dioxide would seem to indicate however, that $CO/_{CO_2}$ equilibrium ratio of 0.05 had been established.

The above experiment was then conducted with no catalyst present and it was found that after one hour, only 15% of the carbon monoxide had been converted to carbon dioxide. Even this value was surprisingly high.

The same experiment was then conducted on a pure copper catalyst, again with excess water present. After one hour, analysis by freezing showed that only 6% of the carbon monoxide had been converted; that is, copper alone would not catalyse the water-gas shift.

Yet another experiment was conducted, this time using excess of carbon monoxide on a flame-quenched catalyst and only a small quantity of water, sufficient to initiate the water-gas reaction, if present. The pressure of water present in the apparatus was less than its saturated vapour pressure, and was therefore a known quantity. Any change in the quantity of water after the reaction could therefore be noted. The carbon monoxide and water was heated,in presence of the catalyst,to 300°C. for one hour. The products were then cooled and analysed as described previously. The results of this experiment are given on the following page.

H_2O before reaction = 2.1 mg.

CO before reaction = 41.9 mg.

O_2 on catalyst = 12 mg.

H_2O after reaction = 0.85 mg.

CO after reaction = 18.7 mg.

CO_2 produced = 35.5 mg.

$\therefore$ CO reacted = 41.9 - 18.7 = 23.2 mg.

Now 23.2 mg. CO should react stoichiometrically with 13.25 mg.O_2; but there were only 12 mg.(O) available from the catalyst.

$\therefore$ 1.25 mg. (O) had to be accounted for.

1.25 mg. H_2O had reacted, which provided a source of 1.1 mg. O_2.

THUS ALL THE OXYGEN WAS ACCOUNTED FOR.

Again

Assuming complete reduction of the copper oxide with hydrogen;

12 mg. O_2 $\equiv$ 13.5 mg. H_2O

$\therefore$ The total water possible in the system:

= 13.5 mg. + 2.1 mg. originally present.

= 15.6 mg. H_2O

Now assuming 95% water-gas equilibrium as found in the first water-gas experiment:

then H_2O left after equilibrium = 5% 15.6 mg.

= <u>0.8 mg. H_2O</u>

The experimental result showed 0.85 mg. H_2O after reaction. The water originally present had been reduced to the water-gas equilibrium value, within the time normally taken for a dehydrogenation reaction to reach completion. The conclusion was therefore reached that the water-gas shift could take place, but the possibility of carbon monoxide reducing the oxide on the catalyst directly, was not excluded.

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PART III - QUANTITATIVE DATA:

INITIAL GAS CHROMATOGRAPHY EXPERIMENTS.

Further investigation was now made as to the possibility of analysing the products quantitatively by gas chromatographic techniques. Discussion with the members of gas chromatography group of British Hydrocarbon Chemicals Ltd., at Grangemouth, revealed that if separation could be accomplished into the fractions:

(a) H_2, CO, CO_2.
(b) MeOH, H_2O, HCHO.

then they would be willing to undertake the chromatography of the non condensible fraction (a), on a Perkin Elmer chromatography unit which had an accurate thermal conductivity detector. Ionisation detectors as used in the Pye-Argon unit could not detect the permanent gases, as their ionisation potentials were similar to the carrier gas Argon. The condensible fraction (b) could not be analysed by gas-chromatography, as the retention time of formaldehyde is similar to that of methanol and no separation is obtained (49).

Examination of Graph XI, reveals that at a temperature of -105°C., the vapour pressure of formaldehyde is only 1 mm., whereas that of carbon dioxide is almost 10 cm. It was possible therefore to effect a separation of fractions (a) and (b) above, at this temperature, assuming that the carbon dioxide pressure never rose higher than 10 cm. This in fact proved to be the case.

The condensible fraction could be analysed for water using Karl Fischer Reagent as described previously, but a method of analysis for formaldehyde remained to be found. This was realised in the method of Bricker and Johnson (50), who developed an accurate colourimetric method of analysis using chromotropic acid. This acid, in the presence of concentrated sulphuric acid, develops a deep violet colour with formaldehyde absorbing in the ultra violet region at 570 m/u.

Also considered at this stage was an interesting method of analysis for methanol (51), which involved mild oxidation of the methanol to formaldehyde followed by colourimetric analysis using chromotropic acid. The solvent used in the preparation of the condensible fraction was, of course, methanol, but if another suitable solvent could be found, then a valuable estimation of the methanol remaining at the end of each reaction would be obtained by this method. However, investigation of the literature (41) revealed that the other obvious solvents apart from methanol, such as ethanol, or acetone, interfered with the Karl Fischer titration. The ethanol, for example, would be oxidised to acetaldehyde, and it was found that carbonyl compounds can react with the methanol in the Karl Fischer reagent, to produce ketals and water.

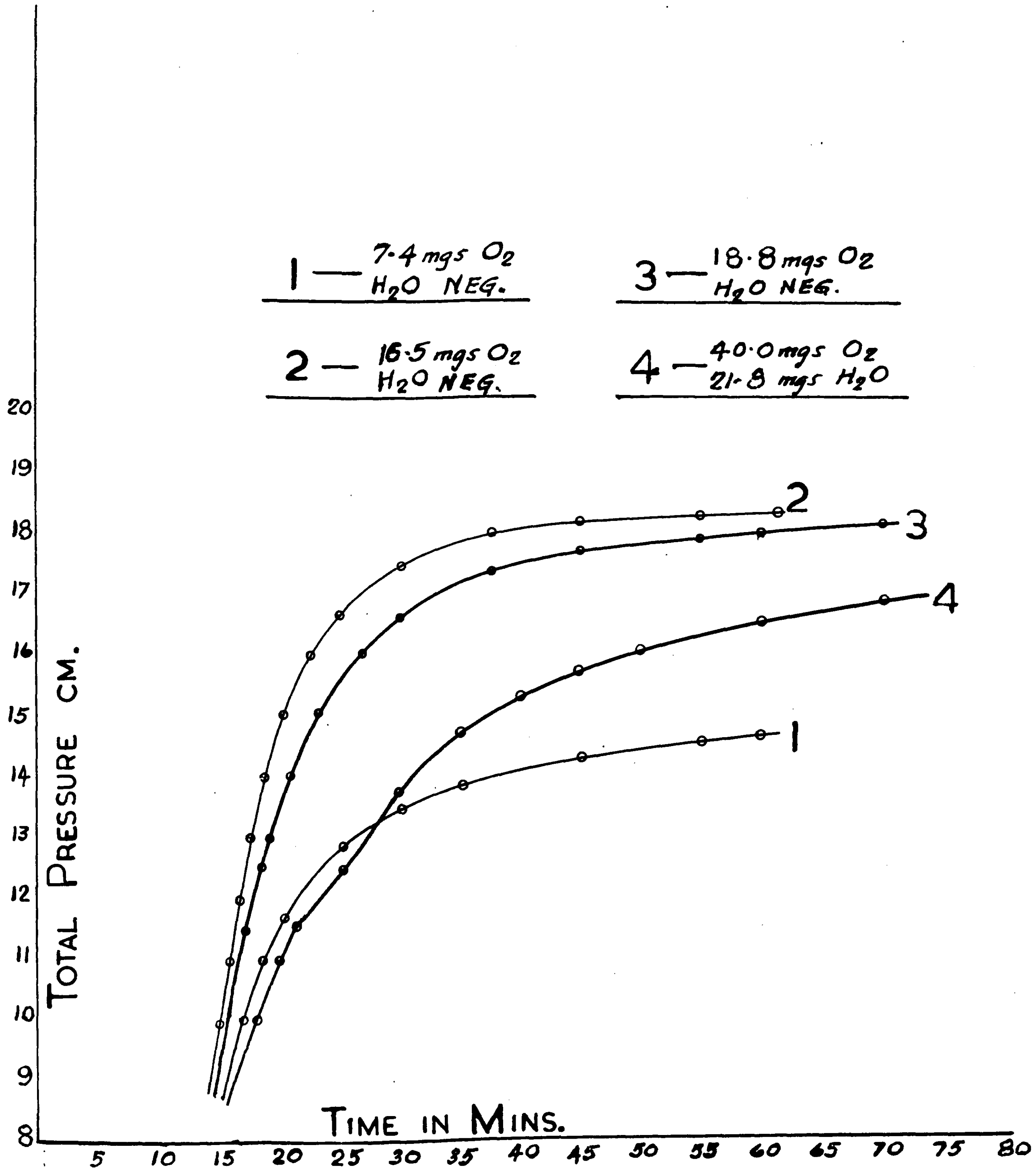
$$RCHO + 2MeOH \rightarrow RCH(OMe)_2 + H_2O$$

Formaldehyde, fortunately, was an exception to this reaction. Dioxane was also tried as an inert solvent, but this was found to affect the colour development with the chromotropic acid. The method for methanol analysis was not pursued further.

Flame-Quenched catalysts were now prepared, by the usual technique, containing varying amounts of oxide present, namely 7.4, 16.5, 18.8 and 40.4 mg. oxygen. The geometrical surface area of these wires was 180 cm^2. Assuming that the oxidised layer was spread evenly over the surface and that it was Cu_2O, then the number of $mg./cm^2$. could be converted into the thickness of the layer by the conversion factor 1 $mg./cm^2 \equiv 145.9A^o$ (52). The thickness of the "sandwich" layer of oxide therefore varied from 6×10^{-5}cm. to 3×10^{-4} cm. Methanol reaction was then conducted on each of these wires at 300^oC. and the results plotted in Graph XII. It is interesting to note that a maximum occurs at 16.5 mg. oxygen. At higher oxide concentrations, for example, 40.4 mg. oxygen, the partial poisoning mechanism develops. At higher oxide concentrations still, the completely poisoned reaction such as was seen with the furnace-quenched catalysts types A_{IV} or B_{IV}, page 23, would result. The wires were weighed at the completion of

GRAPH XII

FLAME QUENCHED CATALYSTS.



each experiment, and in every case the copper oxide was found to have been reduced to copper.

After the reaction was complete, the catalyst vessel was cooled, and the products expanded into the analytical section of the apparatus. The pressure was noted, the cold trap cooled to -105°C. to condense methanol, water and formaldehyde, and the pressure again noted. The cold trap was now cooled to -195°C., to condense carbon dioxide and the pressure noted. The Trap was then warmed to -105°C. again, before Toeplering the carbon monoxide, carbon dioxide and hydrogen into a sample vessel for analysis at British Hydrocarbon Chemicals Ltd. In this way, a check could be made on the carbon dioxide content of the sample. 0.25 ml. of the condensible fraction containing methanol, water and formaldehyde was extracted for colourimetric analysis of the formaldehyde, and the remainder was titrated with Karl Fischer reagent to estimate the water present. The results are shown in Tables I and II compared with a set of results based on the carbon dioxide values obtained in the freezing experiments. The carbon monoxide here was assumed to be negligible because of the water-gas shift, and the pressure of the product mixture at -195°C. was assumed to be due to hydrogen. The B.H.C. results are bracketed. The amount of

Table I.

Flame Quenched Catalysts.

Weights of Products from given Weight of Methanol.

Experiment No.	I.	2.	3.	4.
Weight of O_2 on Catalyst.	7.4 mg.	I6.5 mg.	I8.8 mg.	40.4 mg.
Initial Weight of Methanol.	44.6mg.	43.8mg.	42.8mg.	44.4mg.
Products. mg.				
H_2	3.42(3.45)	3.94 [No B.H.C. Values]	3.87(2.88)	2.95(3.I)
CO_2	2I.8(I6.4)	4I.4	4I.2(33.4)	56.4(49.5)
CO(B.H.C.)	NIL(3.I)	NIL	NIL(I8.8)	NIL(2.3)
H_2O	NIL.	0.6	0.6	I5.8
HCHO	0.II	0.37	0.I8	0.04
Methanol Unreacted.	I4.5	6.7	6.6	7.65

Table 2.

Flame Quenched Catalysts.

Pressure in cm. of Products at Constant Volume (420 ml.)

Experiment No.	I.	2.	3.	4.
Starting Press. Methanol	6.06	5.95	5.8I	6.03
H_2	7.39(7.44)	8.5 (No	5.35(6.22)	6.38(6.70)
CO_2	2.I6(I.62)	4.I B.H.C.	4.I(3.3)	5.57(4.90)
CO(B.H.C.)	NIL(0.50)	NIL Values)	NIL(2.92)	NIL(0.36)
H_2O	NIL	0.I5	0.I5	3.8
HCHO	0.02	0.05	0.02	0.005
Methanol Unreacted	I.95	0.90	0.90	I.05
Total press.	II.55	I3.70	I3.50	I3.40
Weight of O_2 On Catalyst	7.4 mg.	I6.5 mg.	I8.8 mg.	40.4 mg.

unreacted methanol was calculated by difference.

It was immediately obvious that the carbon dioxide results obtained from the freezing experiment did not agree with those obtained by gas chromatography. Calculation, however, showed that the carbon:hydrogen ratios based on methanol as the starting material were correct for the freezing values, but wrong in the case of the gas chromatography samples. The latter set of results were therefore rejected. Sample II was broken in transit to Grangemouth for analysis and no gas chromatography results were obtained in this case.

The major products from flame-quenched catalysts were therefore carbon dioxide and hydrogen. At higher oxidation values, water became important with a corresponding decrease in hydrogen and increase in carbon dioxide. Assuming Kemball's combustion reaction (36), and dehydrogenation were both occurring, the following argument could then be advanced:

Considering the results from experiment 2:

Oxygen on Catalyst = 16.5 mg.

CO_2 produced = 41.4 mg.

This must have been produced from 30 mg. CH_3OH.

The following convenient stoichiometric reactions can then be considered: (They are not suggested mechanistically)

$CH_3OH \rightarrow 2H_2 + CO$............(1)

$CH_3OH + 3CuO \rightarrow CO_2 + 2H_2O + Cu$.....(2)

it was seen that if no water was to be produced during a reaction, as was the case in this experiment, then the extent of reaction (1) could be no less than twice reaction (2).

Thus:

20 mg.$CH_3OH \rightarrow$ 2.5 mg.H_2 + 17.5 mg.CO............ (1)

10mg.CH_3OH+15mg.$O_2 \rightarrow$ 13.8mg.CO_2 + 11.25mg.H_2O........ (2)

Finally.

17.5 mg.CO + 11.25 mg.H_2O $\rightarrow$ 27.5 mg.CO_2 + 1.25 mg. H_2

Total H_2 produced = 3.75 mg.

Total CO_2 " = 41.3 mg.

The hydrogen calculated therefore compared favourably with the hydrogen determined experimentally, and showed that the carbon:hydrogen ratios were correct for this analysis. In addition it was seen that the calculated amount of oxygen was removed from the catalyst by this mechanism.

DEHYDROGENATION WAS THEREFORE THE MAJOR REACTION.

In the case of Experiment 4, where copper oxidation was more extensive, and water was produced, a similar argument could be applied:

Oxygen on catalyst = 40 mg.

CO_2 produced = 56 mg. $\equiv$ 41 mg. CH_3OH.

15.8 mg. H_2O produced.

Assuming this water to be produced exclusively by the combustion reaction, then:

15.8 mg. H_2O $\equiv$ 14 mg. CH_3OH

$\therefore$ 41 - 14 = 27 mg. CH_3OH must have reacted under conditions such that no water was formed; i.e. 2:1 ratio of dehydrogenation to combustion.

$\therefore$ 14 + 8.5 = 22.5 mg. CH_3OH had been used in the combustion reaction.

$\therefore$ 17.5 mg. $CH_3OH \rightarrow$ 2.15 mg. H_2 + 15 mg. CO...............(1)

22.5mg.CH_3OH + 34mg.$O_2 \rightarrow$ 31mg.CO_2 + 25.5mg.H_2O.........(2)

<u>and</u> 15 CO + 9.5 H_2O $\rightarrow$ 1.05 H_2 + 23.5 CO_2

Thus there were 16 mg. H_2O more than could be removed by the water-gas reaction.

Only 50% of the methanol was decomposing by dehydrogenation according to this mechanism.

It was realised however, that other mechanisms were possible giving rise to the same quantities of products. For example, in Experiment 2, it was equally possible that all of the oxygen on the catalyst was being removed by reduction with carbon monoxide, and the total reaction was 100% dehydrogenation. Again, in Experiment 4, it might be argued that 100% dehydrogenation was taking place and that both carbon monoxide and hydrogen were reducing the oxide on the catalyst producing carbon dioxide and water, and that the water-gas reaction then became unimportant.

At this stage it was realised that greater insight as to the mechanism of this reaction could be obtained by the use of an oxygen tracer technique, as it was not known to what extent the methanol oxygen was involved in the reaction.

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PART IV - TRACER EXPERIMENTS USING OXYGEN-18

The tracer selected was the oxygen-18 isotope, which was supplied in the form of water by 20th Century Electronics Ltd. A decision had to be taken whether to label the catalyst oxygen or the methanol oxygen, and it was decided, on the grounds of experimental convenience, to label the former. The water enriched with oxygen-18 to the extent of 6 atom % was therefore electrolysed in a specifically designed electrolys's cell, to prepare labelled oxygen-18 gas. This was stored in a 2 L. bulb connected to the main vacuum system.

Low temperature oxidations of catalyst wires could then be accomplished in an atmosphere of 0^{18}, by admitting the gas to the circulating system of the apparatus to the desired pressure. The apparatus was arranged so that the labelled gas remaining after the oxidation, could be Toeplered back into the storage bulb again, thus preserving it for future experiments, Labelled flame-quenched or high temperature oxidation catalysts could obviously not be prepared in the normal manner, and a new method of preparation was developed. This involved the use of finer gauge copper wire (24 s.w.g.), which was formed into the shape of a spiral filament held in the catalyst vessel by fine glass supports. The ends of the wire were connected to two standard B.7. metal cones, which acted as terminals. The wire could then be heated electrically to a high and constant temperature in an atmosphere of labelled oxygen. The extent of oxidation, as in the case of the low temperature oxidations, could be measured by the decrease in pressure of the oxygen gas in the circulating system during the oxidation.

In order to analyse the permanent gases from this set of experiments, it was decided,on the grounds of convenience and accuracy,to construct a gas chromatography unit. This was done using a radioactive ionisation detector in combination with an ethylene/argon system. It was found that if ethylene was adsorbed on to the column prior to analysis, then the carrier gas leaving the column became permanently contaminated with ethylene, causing a steady ionisation current to flow in the detector. Permanent gases, on reaching the detector, therefore quenched this ionisation, giving rise to negative peaks. It was found necessary to analyse the gases in two stages. Hydrogen and carbon monoxide were estimated on a 5' molecular sieve type 5A, column, while a 12" charcoal column was used in the estimation of carbon dioxide. Thus all of those permanent gases, if present, could be positively and quantitatively determined.

It was also necessary however, to analyse two of the products for O^{18} enrichment; that is the carbon dioxide and water. Herein lay the first difficulty, because water could not be examined directly on the mass spectrometer because of interference from the high background of water normally present in the instrument. It was necessary therefore to convert the water into a suitable compound which had no background on the blank spectrum. Acetic acid was selected as such a compound for it may be prepared by water hydrolysis of acetic anhydride giving rise to the labelled acid. The enrichment of the acid thus prepared, would, ofcourse, be halved compared with the original enrichment of the water, but this latter quantity was great enough to allow for such dilution and still be well within the limit of detection of the mass spectrometer (0.1 atom %). However, the problem was not yet solved. The difficulty now lay in the fact that the water samples normally prepared were present in methanol solution, which can also react with acetic anhydride to give the methyl ester and acetic acid. The enriched acetic acid would therefore be diluted by an amount equivalent to half of the methanol solvent present, a dilution larger than was desirable in the mass-spectrometry. This problem was overcome by chromatographing a small quantity of each liquid sample on a carbowax column at

78°C. Thus, methanol and any formaldehyde came off the column, followed a few minutes later by the water. As soon as the water peak appeared, the carrier gas flow was deflected into a trap containing acetic anhydride cooled to -78°C. In this fashion all of the acetic acid produced in the acetic anhydride would be due to hydrolysis with the enriched water. At the same time chromatographing the condensible fractions on such a column should show the presence of any ether, if present, and settle any doubts as to whether any dehydration was taking place. Mass spectrometric analysis of the enriched carbon dioxide presented no difficulties however, and the analysis was conducted directly on part of the permanent gas mixture.

For the mass-spectrometry, calibration samples had to be prepared. This was carried out by oxidising copper with the enriched oxygen and preparing water and hence acetic acid, and carbon dioxide from this enriched copper oxide. It should be noted therefore that, as the carbon dioxide was prepared by oxidising un-enriched carbon monoxide, and the acetic acid was prepared by reaction of pure enriched water with un-enriched acetic anhydride, then both the carbon dioxide and acetic acid calibration samples were diluted by half from the original O^{18} enrichment.

Accordingly, five experiments were therefore conducted on the following catalysts enriched with O^{18}.

CATALYST A - High Temperature Oxidation.

The preparation involved the oxidation of 24 s.w.g. copper wire, (total geometrical surface area = 16.1 cm^2) at a high temperature in the presence of a few cm. pressure, of normal un-enriched oxygen. The time of oxidation was 15 minutes. This experiment provided a comparison for catalyst B prepared under the same conditions but in an enriched oxygen atmosphere. The calculated weight of oxygen present was 33.5 mg., although probably less than that amount of oxygen took part in the ensuing catalytic reaction owing to scaling of the oxide produced on the wire; some of the scale fell from the reaction zone contained by the furnace. The thickness of the oxide layer, assuming Cu_2O was spread evenly over the surface, was therefore calculated to be 3×10^{-3} cm.

CATALYST B - High Temperature Oxidation.

This was identical to Catalyst A except that oxidation was conducted in a few cm. pressure of the O^{18} enriched oxygen. The calculated weight of oxide present was again 33.5 mg.

CATALYST C - High Temperature Oxidation.

This was again prepared by high temperature oxidation of the

24 s.w.g. copper wire in the presence of a few cm. pressure of oxygen-18. The time of oxidation was however longer (45 minutes), and consequently there was a larger uptake of oxygen. The calculated weight of oxygen present on the catalyst was 82 mg. The thickness of the oxide layer in this case was 7×10^{-3} cm.

CATALYST D - Low Temperature Oxidation.

This catalyst was prepared in a similar manner to those prepared in Part VI of Chapter I. The wire used was 18 s.w.g. (total geometrical surface area = 105 cm^2) oxidised in the presence of 60 cm. pressure of O^{18} enriched oxygen, at 300°C., for two hours. The weight of oxygen on the catalyst was 13.5 mg. ≡ thickness of 2×10^{-4} cm.

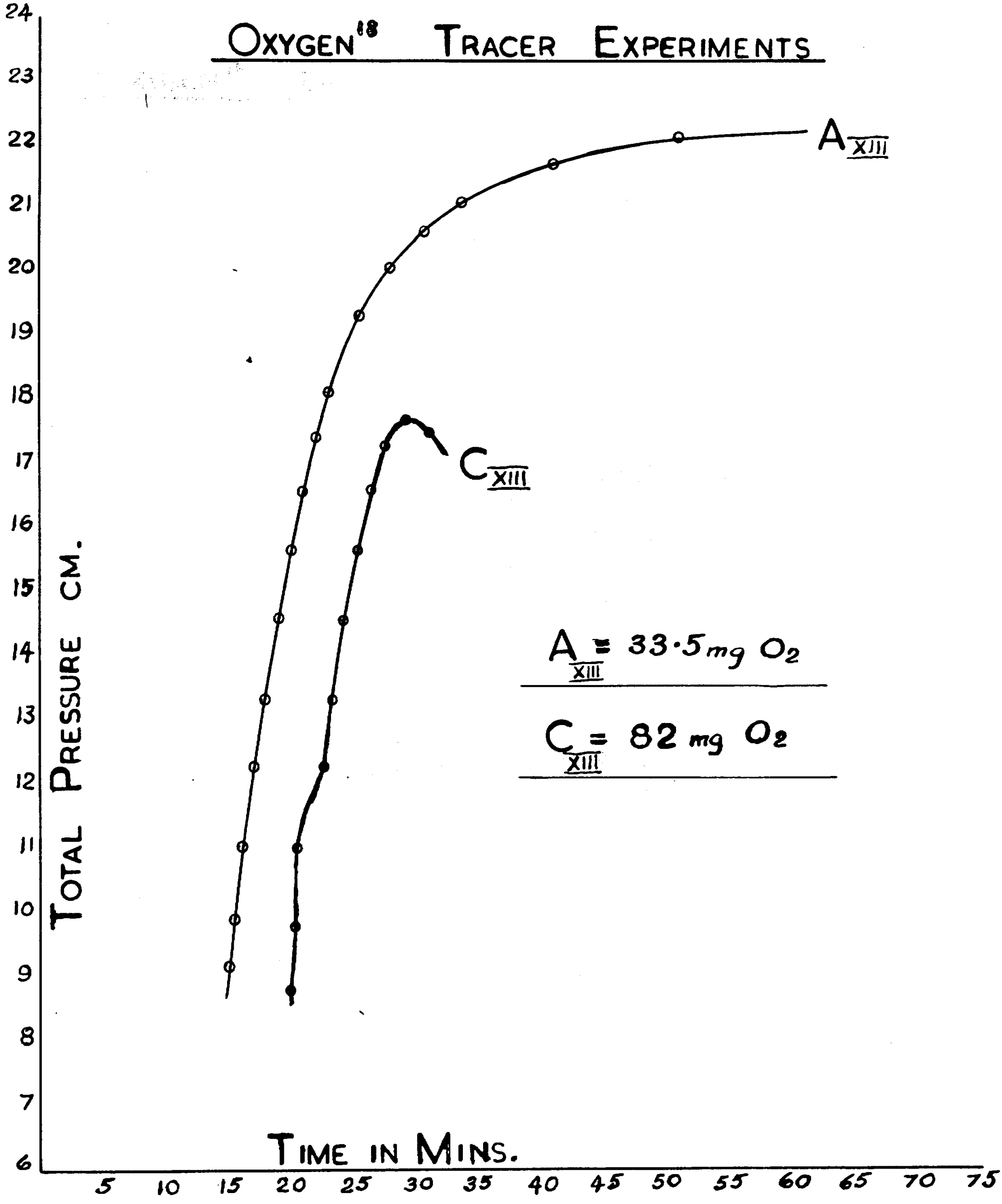
CATALYST E

This catalyst was again 18 s.w.g. copper wire of surface area 105 cm^2., and it was intended to oxidise it again at low temperature,but for a longer period, to obtain a high state of oxidation. Erroneously however, the temperature was raised to 500°C. for approximately one hour. The remainder of the oxidation was however carried out at 300°C. and 60 cm. pressure of O^{18} enriched oxygen. The total time of oxidation was 6 hours, and the weight of oxygen absorbed was 21 mg. ≡ thickness of 3×10^{-4} cm.

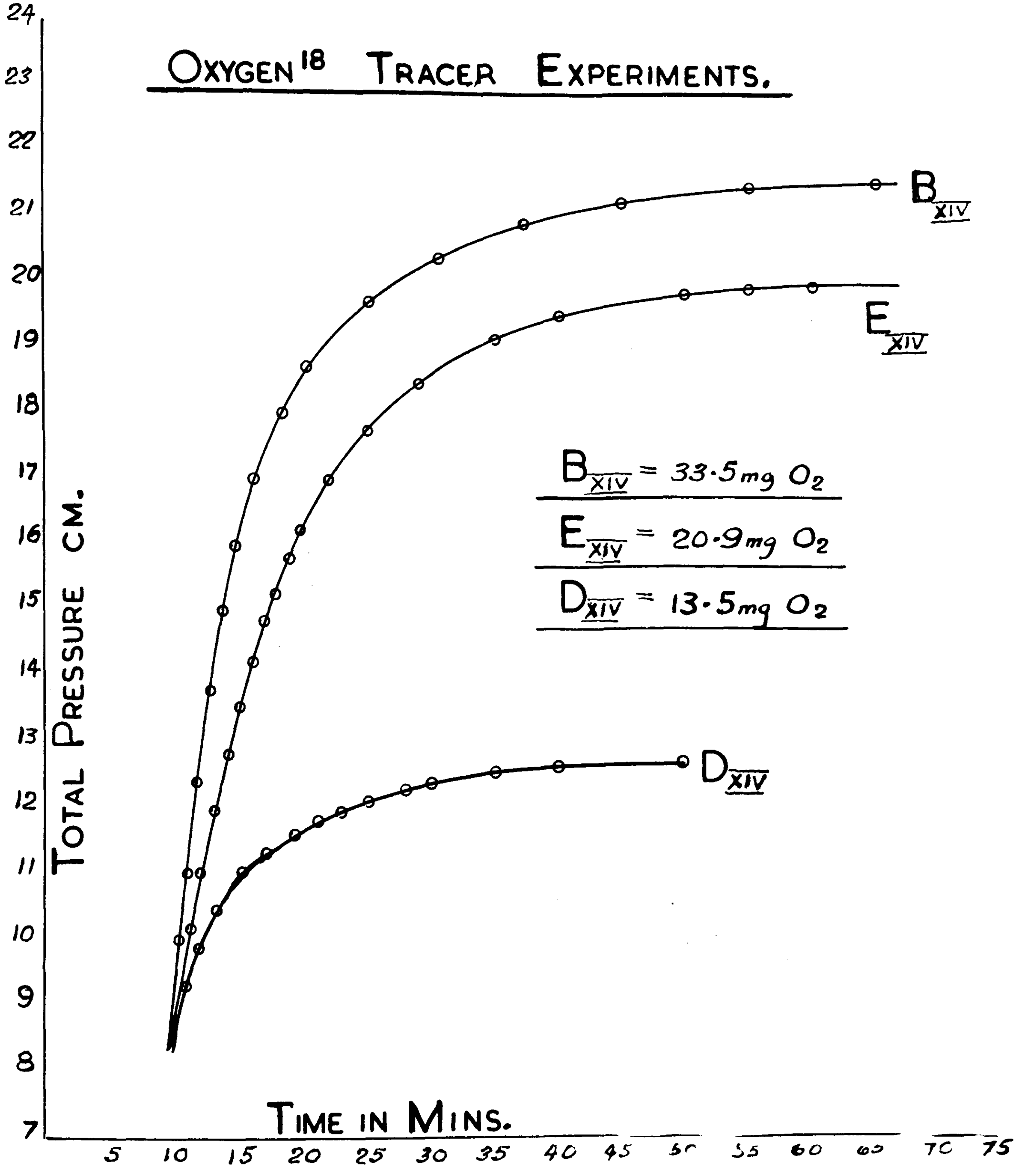
Methanol reactions at 300°C. were then conducted on each of these catalysts in turn and the results are plotted in Graphs XIII $_{\text{Exps.A, C.}}$ and XIV $_{\text{Exps.B, D, E.}}$ Experiments A and B showed the high activity reaction normally given by flame-quenched catalysts, while C was the completely poisoned reaction normally shown by furnace-quenched catalysts Type A_{IV} or B_{IV}. The reaction was terminated soon after the maximum had been reached, by cooling the reaction vessel. This was to avoid excessive conversion of hydrogen to water, thus providing a water sample excessively rich in Oxygen-18 with possible masking of a more useful value. Experiment D was again as expected, the partially poisoned reaction of lower activity normally associated with low temperature oxidation catalysts. Experiment E was the exception, in that it showed activity comparable to experiments A and B and yet was oxidised at low temperature. This anomally was attributed to the rise in temperature to 500°C. during the oxidation.

At the conclusion of each reaction, the catalyst vessel was cooled and the gaseous products separated as described previously into two fractions. A gaseous fraction containing H_2, CO, CO_2. A liquid fraction containing CH_3OH, H_2O, HCHO in methanol solvent.

GRAPH XIII


OXYGEN^{18} TRACER EXPERIMENTS
TOTAL PRESSURE CM.
TIME IN MINS.
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
A_{XIII}
C_{XIII}
A_{XIII} = 33·5 mg O_2
C_{XIII} = 82 mg O_2

GRAPH XIV


OXYGEN 18 TRACER EXPERIMENTS.
TOTAL PRESSURE CM.
TIME IN MINS.
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
B XIV
E XIV
D XIV
B XIV = 33·5mg O2
E XIV = 20·9mg O2
D XIV = 13·5mg O2

Again, during the separation, a value was obtained for the carbon dioxide present by freezing it out at - 195°C., and observing the decrease in pressure.

A portion of the gaseous fraction was then analysed on the Mass Spectrometer for Oxygen-18 enrichment in the carbon dioxide, and the remainder of the sample was chromatographed on the molecular sieve and charcoal column to determine the $H_2 : CO : CO_2$ ratio.

0.25 ml. of the liquid fraction was extracted and chromatographed on a carbowax column to separate the water and prepare it in a suitable form for mass spectrometric determination. No dimethyl ether was observed at this stage in any samples, but the result was inconclusive as a synthetic sample of dimethyl ether in methanol likewise only showed the methanol and water peaks. However, at the separation stage of condensible and gaseous fractions described previously, no appreciable decrease in pressure of the gases in the circulating system was obtained by cooling the cold trap successively to -78°C and -105°C, i.e. the region in which the vapour pressure of dimethyl ether decreases from 6 cm. to 1 mm. It was concluded that dimethyl ether could not be present in the reaction mixture to any appreciable extent. A further 0.25 ml.

was extracted for colorimetric determination of formaldehyde, and the remainder of the sample was titrated with Karl Fischer reagent to determine the water present. Unreacted methanol was calculated by difference. The analytical results are shown in Tables III and IV. Table V overleaf shows the results of the mass spectrometric determinations.

TABLE V

CO_2^{18}: CO_2^{16} ratios expressed as % CO_2^{18}.	
Calibration for samples A,B,C.	2.33%
Original undiluted O_2^{18}: O_2^{16} used for A,B,C.	4.66%
Sample B.	2.56%
Sample C.	3.45%
Calibration for Samples D,E.	1.60%
Original undiluted O_2^{18}: O_2^{16} used for D,E.	3.20%
Sample D.	2.15%
Sample E.	1.80%

Table 3.

Catalysts Oxidised with Oxygen-18

Pressure in cm. of Products at Constant Volume (485ml.)

Experiment No.	A. High Temp. Oxidation	B. High Temp. Oxidation	C. High Temp. Oxidation	D. Low Temp. Oxidation.	E. 500 C Oxidation.
Weight of O_2 on Catalyst.	33.5	33.5	82	13.5	20.9
Starting Press. of Methanol.	6.14	5.96	6.26	6.04	6.09
H_2	10.8	10.85	4.34	3.15	8.91
CO_2	5.45	5.25	5.86	1.90	4.29
CO	Nil	Nil	Nil	Nil	Nil
H_2O	0.19	Nil	7.0	1.0	0.2
HCHO	Nil	Nil	Nil	0.15	0.05
Methanol Unreacted	0.16	0.22	1.36	3.43	1.25
Total Press.	16.6	16.33	12.06	9.13	14.70

Table 4.

Catalysts Oxidised with Oxygen - 18

Weight of Products from given Weight of Methanol.

Experiment No.	A. High Temp. Oxidation	B. High Temp. Oxidation	C. High Temp. Oxidation	D. Low Temp. Oxidation	E. 500°C Oxidation
Weight of O_2 on Catalyst.	33.5 mg.	33.5 mg.	82 mg.	I3.5 mg.	20.9 mg.
Initial Weight of Methanol	52.Img.	50.6 mg.	53.2mg.	5I.3 mg.	5I.8 mg.
Products. mg.					
H_2	5.8	5.84	2.34	I.7	4.8
CO_2	63.2	6I.0	68.0	22.0	49.8
CO	NIL	NIL	NIL	NIL	NIL
H_2O	I.0	NIL	28.0	4.8	I.0
HCHO	0.002	0.002	0.002	I.I9	0.35
Methanol Unreacted	I.4	I.9	II.05	28.5	I0.5

Unfortunately, the mass spectrometer ceased to function before all of the acetic acid samples could be determined, and only one result was obtained. (We still await the remaining results.) This was for a sample F, which will be described in Chapter IV. The acetic acid enrichment obtained with sample F was the same as the carbon dioxide enrichment however, and it was assumed that the other acetic acid values would likewise be the same as the carbon dioxide values. This was in fact an indication that the water-gas shift is operative on oxidised copper catalysts.

Considering the results of the product analyses; the first important fact to be noted is that carbon monoxide is never formed to any appreciable extent. A and B are as expected from the previous analysis of flame-quenched catalysts. It should be noted that they are identical in every respect. Water and formaldehyde are negligible, the major products being carbon dioxide and hydrogen. In experiment C, as expected from a poisoned reaction, water is produced in large quantities. With experiment D there is a change in that both formaldehyde and water are formed in appreciable quantities. This is the partially poisoned reaction. Reaction E is now seen to resemble reactions A and B, with negligible water and little formaldehyde.

The mass spectrometer results are however very enlightening, and will be discussed fuller in the discussion. If a pure dehydrogenation is taking place according to:

$$CH_3OH \rightarrow 2H_2 + CO,$$

and the carbon dioxide is formed by intervention of carbon monoxide and one atom of enriched oxygen from the catalyst surface then the expected enrichment of the carbon dioxide would be exactly one half of the value of the original enrichment of the O^{18} enriched oxygen; that is equivalent to the calibration sample enrichment. In all cases however, the carbon dioxide samples were enriched over this value. This would seem to indicate that Kemball's combustion mechanism was taking place, i.e.

$$CH_3OH + 3O \rightarrow CO_2 + 2H_2O$$

Such a reaction involving three enriched oxygen atoms from the catalyst would provide a maximum enrichment of $\frac{3}{4}$ initial enrichment of oxygen-18 gas ≡ 3.5% for sample B.

100% dehydrogenation for sample B would provide carbon dioxide enrichment equal to the calibration sample, i.e. 2.33%

The experimental value of 2.56% obtained would therefore seem to indicate 80% dehydrogenation, and 20% combustion.

Consideration of sample D however indicated the inadequacy of the above argument.

CO_2 calibration ≡ 1.6% enrichment.

∴ 100% combustion mechanism ≡ 2.4% enrichment.

100% dehydrogenation mechanism ≡ 1.6% enrichment.

Sample D however was 2.15% enriched.

and this was equivalent to 70% combustion and 30% dehydrogenation. Such a system of reactions however would produce 9.6 mg. of water, twice as much as actually determined experimentally. A more complex mechanism is thereby operating, which will be discussed in the next chapter.

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CHAPTER III

Discussion.

CHAPTER III - DISCUSSION.

At this stage it would be wise to summarise briefly the various types of catalysts and their associated reactions. On pure copper, no decomposition of methanol was observed. Once the copper had been oxidised, however, a reaction was observed, the nature of which depended on the conditions of oxidation. Copper oxidised at a high temperature (ca. 900° C.) to a limited extent produced a catalyst which exhibited a methanol reaction, the products of which were carbon dioxide and hydrogen. No water was observed as a product, and yet oxygen disappeared from the catalyst. Excessive oxidation of copper at 900°C., however, produced a catalyst which changed the methanol reaction mechanism in some manner, to produce water, in addition to carbon dioxide and hydrogen. Formaldehyde was not observed to any appreciable extent, but more will be said about this later. This type of reaction often exhibited characteristic behaviour of a sharp rise in pressure to a maximum followed by a decrease in pressure and production of water. Some of the methanol was left intact and the reaction had been poisoned in some manner. Finally, low temperature oxidation of copper produced a catalyst which exhibited a partially poisoned reaction in that formaldehyde was produced to an appreciable extent, the decomposition of which had been inhibited in some manner. In addition, water was formed to an appreciable extent, and the carbon dioxide: hydrogen ratio was consequently higher. Carbon monoxide was never found to be present in any appreciable quantity.

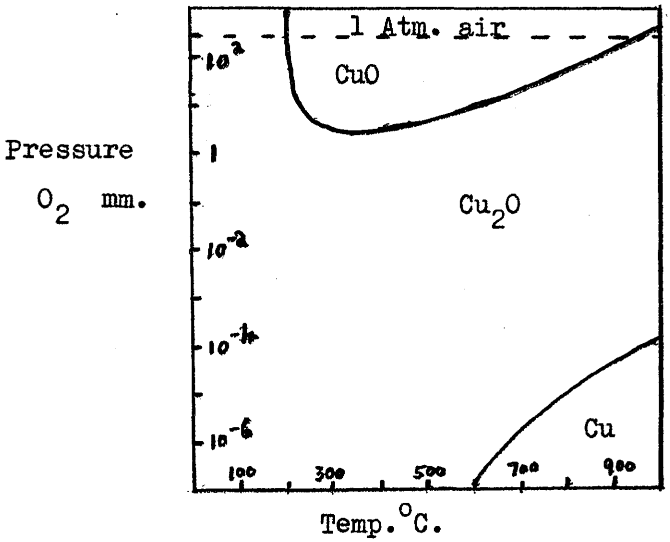
It is now necessary to consider the nature of the catalyst surface, upon which the reactions are taking place. A great deal of relevant research on the oxidation of copper has been conducted by Tylecote who has for example, studied the oxidation of copper between 300°C and 900°C. in air (34). More recently, a review published by Rönnquist and Fischmeister (52), on the oxidation of copper, has provided much useful information. It is now generally accepted that the oxidation of copper takes place by a diffusion mechanism; copper ions, together with an equivalent number of electrons, diffuse across an oxide layer to build up oxide on the surface (53). Copper can form two oxides, corresponding to compositions CuO and Cu_2O. Tylecote (54) found that the CuO content of the oxidised layer increased with time at 270°C., close to the temperature used in the preparation of the low temperature oxidation catalysts described in this thesis. At higher temperatures however, the opposite trend was observed. Tylecote explained this by assuming that oxidation commenced with the formation of Cu_2O nuclei, which were oxidised to CuO before a coherent oxide layer was formed. Thus an increase in CuO content is observed as the nuclei grow until they touch, and a coherent oxide layer is formed. Access of oxygen is then limited, and the CuO is reduced to Cu_2O by copper ions diffusing out to the surface. At low temperatures, where the diffusion rate is slow, this stage is never reached, and only an increase in CuO is observed. At high temperatures only the second fast diffusion stage is observed.

On the other hand, Gwathmey has observed (55) that both at 150°C and 500°C. no CuO was observed until a coherent layer had been formed. Then diffusion would commence either to dilute the CuO formed with copper, giving rise to an oxide largely corresponding to Cu_2O, or, if diffusion was slow, to build up an oxide largely corresponding to CuO.

There does however seem to be a limiting thickness below which CuO cannot be formed (56). The values for this critical thickness vary considerably from, for example, 600 Å at 240°C. (56), to 2600 Å at 247°C. (57). Gwathmey (58) found that the critical thickness depended upon the crystal face exposed, and found a maximum initial thickness of 3000 Å on the (001) face. This value is still considerably less than the thicknesses calculated to exist on the catalysts described in this thesis, and so the formation of CuO was possible in all of the catalysts described.

Honjo (59) has constructed an interesting diagram, reproduced below, showing the temperature/pressure region of formation of Cu_2O and CuO, after a fixed oxidation time of "A few minutes".

Diagram I.



It is readily seen from this diagram that, at 900°C, the approximate temperature of oxidation of the flame-quenched, furnace-quenched, and electrically heated oxidised catalysts, in the pressure range used, Cu_2O would be the stable oxide formed. Under the conditions of preparation of the low temperature oxidised catalysts, however, namely 300°C and 60 cm. pressure of oxygen, then CuO will be the stable oxide.

More work on this has recently been conducted by Wieder and

and Czanderna (60), who showed, by using diffraction, optical microgravimetric techniques, that the oxidation of copper at low temperatures produced an oxide with the composition corresponding to $CuO_{0.67}$, that is, a gross defect structure of Cu_2O.

From the information here presented, it is now possible to make suggestions about the surface of the various catalysts, described in this thesis. It is proposed that limited high temperature oxidations, such as was the case with catalysts A and B, (Chapter II) and flame-quenched catalysts, would produce a defect structure of Cu_2O. Further oxidation at high temperature, for example, catalyst C (Chapter II), or the preparation of furnace quenched catalysts, would cause a further uptake of oxygen, such that the outer layer of oxide close to the surface becomes oxygen rich beyond the Cu_2O stage with Cu:O ratio = 2:1, tending perhaps towards the $CuO_{0.67}$, i.e. $Cu_{1.5}O$ stage. Thus a gross defect structure of Cu_2O would be produced which grades towards the initial defect structure within the interior of the catalyst. This situation thus explains the interconversion of catalysts described in Part IV of Chapter I. A first methanol reaction on a heavily oxidised catalyst will reduce the oxide towards Cu_2O, and a second reaction will then be characteristic of the new degree of oxidation on the catalyst. In the case of the low temperature oxidation catalysts e.g. Catalyst D (Chapter II), this gross defect structure, tending towards the composition CuO, the thermodynamically stable form under the present conditions, will exist throughout the whole oxidised film. Catalyst E, (Chapter II), which had been oxidised at a slightly higher temperature (500°C) for a short period could therefore have formed a Cu_2O defect structure similar to Catalysts A and B, due to the increased diffusion rate of the copper ions at 500°C. diminishing the gross defect structure.

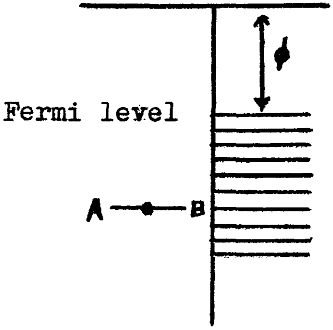
The important observation must now be made that <u>all</u> the catalysts described above were in fact <u>p-type semi-conductors</u>, showing increasing numbers of cation vacancies and associated Cu^{2+} ions, the greater was the extent of pre-oxidation. This supposition stems from the work of Stone (61) and Smith (62), who studied the conductivity of oxidised copper films. The latter, for example, concluded that in every case, independent of the state of oxidation, the oxidised films showed p-type hole conduction, even when the film was oxidised almost to CuO.

Several aspects of the catalytic decomposition of methanol can now be examined.

(a) It is known that hydrogen will not chemisorb on pure copper (24). This fact is probably due to the absence of vacant d-orbitals, which, in the case of nickel metal for example, normally provides the necessary bonding strength. Such an argument was in fact the basis of the classic work on alloy systems conducted by many authors, e.g. Dowden and Reynolds (26). In the case of copper however, only weak $d^{2.56}$ $sp^{2.22}$ metal hybrid bonds are available, most of which are involved in the bonding of the metal, so that only weak bonding with hydrogen will be possible. It is therefore suggested by the present author that this is one of the reasons why pure copper will not dehydrogenate methyl alcohol.

(b) It is now necessary to consider what effect the semiconductor might have on the metal substrate, or any reduced copper formed during the reaction. Here we consider what may, or may not be a likely hypothesis: that is, that catalytic reaction takes place on the metal. Chemisorption of hydrogen when it does occur, is generally considered to be covalent chemisorption. If we consider the diagram, chemisorption might be described in the following way.

Diagram II.



Elevation of a metal electron to the Fermi surface from a filled level at about the height A.B. would be the first hypothetical step.

The adsorbate electron in level A.B. can now interact with the unfilled metal level to form a homopolar bond. The process thus concerns the promotion of an electron, and its accommodation at the Fermi surface. Covalent chemisorption will therefore be facilitated if the Fermi level of the metal is lowered and this is what probably happens in the case of p-type semi-conductors, such as the Cu_2O defect structure described above. The Fermi level of the copper metal is lowered due to the acceptor surface states formed, and covalent chemisorption of the hydrogen atoms in the methanol can then occur with consequent dehydrogenation of the molecule.

Although Methanol decomposition may be an interface process between Cu/Cu_2O, there are two objections.

(a) The extent of alteration of the Fermi level is probably small.

(b) Diffusion of methanol to an interface could be a slow process, unless reaction took place at a growing interface near the surface.

For example, during a methanol reaction, it was observed that the copper oxide was reduced to metal. This reduction could be accounted for by hydrogen and/or carbon monoxide produced in the reaction. Reduction of the oxide may be considered to be the reverse of the process of copper oxidation, that is,removal of oxygen from the surface of the oxide sets free electrons, which, together with their associated copper ions, can then diffuse across the oxide layer to build up the metallic phase. If the reduction is fast enough, then the surface concentration of electrons becomes great enough to form nuclei of metallic copper on the surface, which can then build up as the metallic phase: this new metal phase is closer to the site of the surface reaction than the original underlying phase. Such a condition has in fact been observed by Pease and Taylor (68) for hydrogen reduction, and by Jones and Taylor (69) for carbon monoxide reduction. In fact, the latter authors found that oxygen present in the carbon monoxide inhibited the reduction by oxidising the copper nuclei as fast as they were formed. If, however, oxygen was admitted to the reducing gas after the nuclei had been formed and well established, then carbon monoxide reacted with oxygen by contact catalysis.

It is proposed therefore that dehydrogenation of methyl alcohol may occur at the metal/semi-conductor interface, which moves into the interior of the catalyst as the dehydrogenation reaction and consequent reduction of the oxide takes place.

Chemisorption on a p-type semi-conductor could make a reduction of positive hole conductivity, by electron donation to the oxide. This has in fact been observed by Bielanski (63) who found a decrease in conductivity of p-type oxides on adsorption of methanol. Thus, methanol evidently acts, during adsorption, as an electron donor to the substrate, and it would therefore be reasonable to suppose that the desorption of the products will in turn require electron donation from the catalyst. Thus, Bielanski (63),has found that both hydrogen and acetaldehyde act as electron donors when chemisorbed on copper oxide. Stone (64) likewise has found that carbon monoxide is adsorbed on Cu_2O as a positive species.

It is surprising then that several authors (65), (66), (67), have maintained that the tendency towards dehydrogenation of alcohols will be increased as the n-typeness of the oxide is increased. This is difficult to understand on the basis of the results obtained in this thesis, where the p-typeness of the catalyst is suggested as being the activating factor in producing dehydrogenation of methanol; a speculation supported by conductivity measurements.

It is now necessary to comment on the different methanol reactions obtained as the p-typemess of the copper oxide is increased. For example, water and formaldehyde were produced with heavily oxidised catalysts, and the reaction could be completely poisoned in some manner. Also it is necessary to explain why the carbon dioxide obtained was always enriched in O^{18}, and why the enrichment increased concomitantly with the quantity of water produced. Kemball's combustion mechanism (36) seems unlikely and has been shown to be untenable in Chapter II.

A pattern of the true interpretation only is offered for the true nature of surface processes must await further theoretical development for chemisorption and catalytic processes.

To begin with, a simple reaction mechanism given below may be considered. The enriched oxygen on the catalyst is designated thus: Θ

Mechanism I $CH_3OH \rightarrow CO + 2\,H_2$ .... (1)

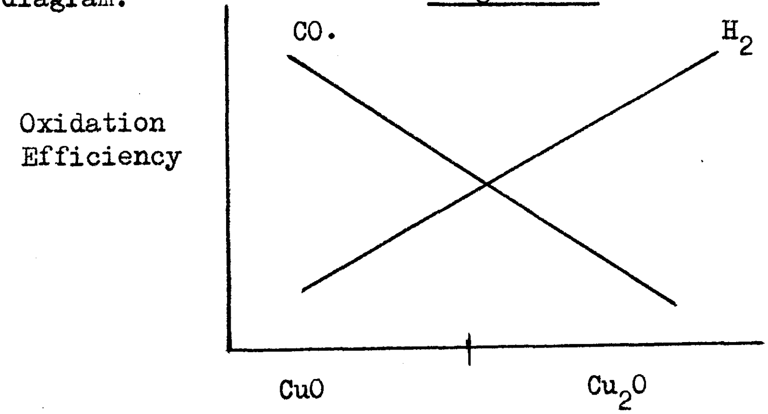
$CO + \Theta \rightarrow CO\Theta$ .... (2)

$2H_2 + 2\Theta \rightarrow 2H_2\Theta$ .... (3)

$CO + H_2\Theta \rightarrow CO\Theta + H_2$ .... (4)

In the case of lightly oxidised catalysts where no water was produced, then reaction (2) alone, or a combination of reactions (3) and (4) could take place. In either case, the enrichment of the carbon dioxide would be by a half of the enrichment in the Cu_2O, that is equivalent to the calibration sample. In fact the enrichment of carbon dioxide was greater than this (Table V,P.83) and hence mechanism I is inadequate to explain our results. Greater insight into the problem is obtained by consideration of the relative efficiencies with which hydrogen and carbon monoxide reduce cupric and cuprous oxides. Information on this subject was obtained from a paper by Tatierskaya et al (70) which has been summarised (and extended) in the following diagram:

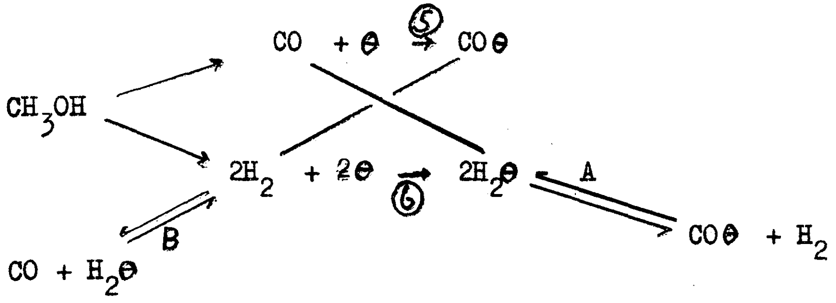
Diagram III



If the present catalysts approximate to Cu_2O and CuO, lightly oxidised catalysts, prepared at high temperatures, will be reduced readily with hydrogen, whereas heavily oxidised catalysts prepared at high temperatures, and catalysts prepared at low temperatures i.e. those approximating to CuO, will tend to be reduced by carbon monoxide.

The following speculative mechanism can now be proposed.

Mechanism II



Consideration of diagram 3 for lightly oxidised catalysts, e.g. B of Chapter II, Part IV, then shows that reaction (5) might be slow, and reaction (6) might be relatively fast. There would therefore be large quantities of carbon monoxide and water produced, and the water-gas shift could then operate to remove water from the system. There are two reaction paths for the water-gas shift, A and B. B will not alter the enrichment of the carbon dioxide produced by reaction (5) and may be neglected. A, however, will enrich the carbon monoxide, which by reaction (5) will further enrich the carbon dioxide beyond the 2.33 atom% value already mentioned. Reaction (5) is slow in this case, and hence the enrichment of carbon dioxide will not be greatly in excess of the 2.33 atom% value. Table V P. 83 indicates that this was in fact the case for sample B - 2.56 atom% compared with the calibration sample of 2.33 atom%.

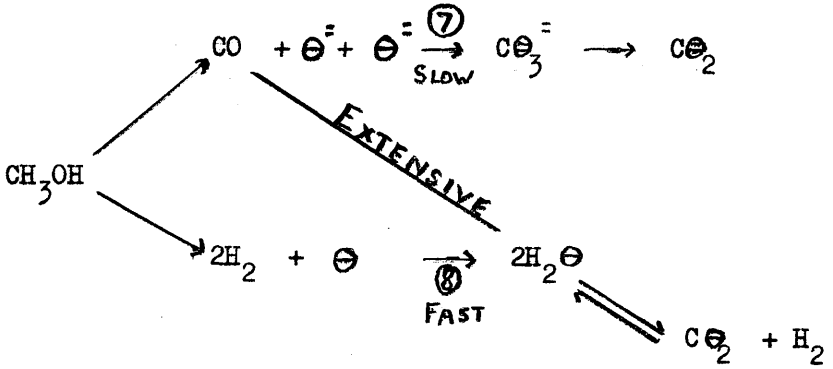
When we consider the heavily oxidised catalysts, i.e. as the p-typeness of the oxide increases, (we quote sample D, Chapter II, as an example), Mechanism II becomes inadequate to explain the degree of enrichment of the carbon dioxide samples. In this case reaction (5) should be fast and reaction (6) should be relatively slow. Thus carbon monoxide will be removed rapidly by oxidation from the catalyst surface, and the water produced by reaction (6) can therefore not be removed by the water-gas shift. This would explain the production of water as the p-typeness of the oxide is increased, but such a reaction scheme would produce carbon dioxide enriched only to the 2.33 atom% value, as the water gas path A will be relatively slight. Consideration of Table V however, shows that the enrichment of sample D is considerably more than the 2.33 atom% value indicated by the calibration sample.

We are therefore forced to the conclusion that the carbon monoxide must interact with two surface atoms of enriched oxygen; this could be so if the oxidation of carbon monoxide to carbon dioxide by the catalyst oxygen proceeds through a carbonate surface-complex stage. It is interesting that we should have arrived at such a conclusion, because several authors, notably Garner (71), Stone (64) and Hauffe (72) have postulated the existence of a carbonate ion during the reduction of transition metal oxides by carbon monoxide, and during the oxidation of carbon monoxide with oxygen on a Cu_2O catalyst. Kwan (98) in a study of the chemisorption of carbon dioxide on zinc oxide catalysts, has likewise considered the existance of an intermediate carbonate complex. We feel that our oxygen-18 studies are strong evidence in favour of the formation of such a carbonate complex.

It should be pointed out at this stage that mechanism II, and ensuing mechanisms in this thesis, explain the apparent difference in reaction rates observed in Graph IX between the quenched catalyst D, containing 16.5 mg.oxygen and the catalyst oxidised at low temperature, e.g. C_9 containing 33.5 mg. oxygen. The low rate observed in the case of C_9 is due simply to the production of water, rather than hydrogen, which condenses in the apparatus, and fails to contribute substantially to the total rise in pressure. If water had a high vapour pressure, then the rate observed in the cases of B_9 and C_9 would in fact have been greater than D_9, maintaining the regularity of increased methanol decomposition with increased oxygen content.

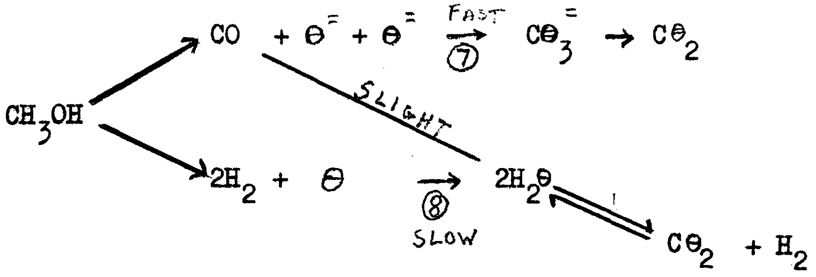
We now propose two mechanisms which explain the results obtained.

Mechanism III   Low p-typeness - e.g. most flame-quenched catalysts. Catalysts A and B, Chapter II, part IV.



The carbon dioxide is produced mainly by the water-gas shift as 50% enriched, compared with the O^{18} in the catalyst, and is enriched slightly above this value by reaction (7) taking place to a small extent. We see that no water would be formed, and that there would be only slight enrichment of the carbon dioxide. This was observed experimentally; e.g. sample B quoted previously.

Mechanism IV   Enhanced p-typeness - e.g. furnace-quenched catalysts, low temperature oxidation catalysts.D, Chapter II, Part IV.



The carbon dioxide in this mechanism is now mainly produced in reaction (7) through the carbonate complex, and will consequently be enriched in oxygen-18 to a greater extent than was found for low-p-type catalysts. According to this mechanism, the carbon dioxide and water should increase as the p-typeness of the catalyst is increased. This was observed experimentally.

Considering again the O^{18} enrichments in Table V:-

Calibration value ≡ 50% dilution = 1.6 atom%

∴ Original undiluted O^{18} enrichment = 3.2 atom%

∴ Theoretical maximum enrichment due to CO_3 = 2.15 atom%

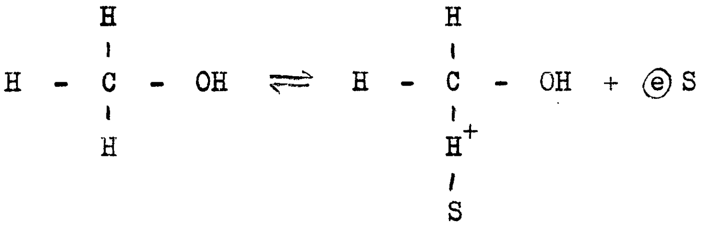
From Table V, Sample D = 2.15 atom%

Thus in the case of Sample D, where the p-typeness had been increased relative to Sample B, for example, so also was there oxygen-18 enrichment. In fact the value obtained for Sample D indicates reaction (7) taking place exclusively.

We also predict on the basis of mechanism IV, that the more enriched the carbon dioxide becomes, the more water should be produced during a reaction. Consideration of Tables V and IV show this to be the case. In the case of sample C, table V, we see that the degree of enrichment is now greater than can be accounted for on the basis of the carbonate complex formation.

This reaction however, was a completely "poisoned" one, in that the pressure rose to a maximum and then decreased to a steady value. This has been explained earlier in this thesis, on the assumption that the methanol decomposition was poisoned completely, and the hydrogen produced during the initial decomposition then reduced the remaining oxide on the catalyst to water. This postulate would therefore also explain the extra enrichment of carbon dioxide. Once the methanol decomposition was poisoned, no further unlabelled carbon monoxide would be produced, but fully enriched water will continue to appear due to hydrogen reduction of the oxide, and this would then exchange by the water-gas shift in the presence of the copper oxide still present on the catalyst, to enrich the carbon dioxide to a considerable degree.

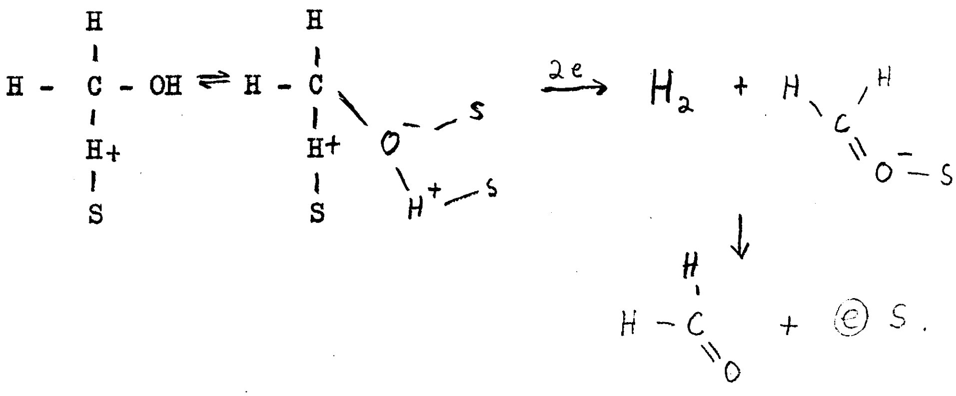
The true nature and mechanism of the poisoning mechanism however remains obscure. Poisoned reactions are always associated with the production of formaldehyde. The reason why formaldehyde was not observed in the case of experiment C in Chapter II, was possibly due to its polymerisation after the partial pressure had reached a high enough value. Such a poisoned reaction is in fact the basis of an industrial preparation of formaldehyde, where a mixture of alcohol and air is passed over a copper catalyst heated to 200-300°C. (97) In the latter case, constant regeneration of the catalyst is being obtained by oxidation with the air, and a high yield of formaldehyde is produced. We know however, that methanol is adsorbed on p-type semi-conductors, such that the semi-conductivity is reduced. We therefore propose a first reversible step thus:



$$H - \underset{H}{\overset{H}{C}} - OH \rightleftharpoons H - \underset{\underset{S}{H^{+}}}{\overset{H}{C}} - OH + \textcircled{e}S$$

where S = substrate.

This stage will be favoured by p-type semi-conductors. In the second stage the formaldehyde can therefore decompose either to hydrogen and carbon monoxide from whence it could follow either of the mechanisms III and IV described above, or it could follow a reaction path similar to that proposed by Hauffe (72) for n-type semi-conductors.



This latter step is perhaps encouraged by increasing the p-typeness of the semi-conductor, and formaldehyde then tends to appear in the gas phase; but this explanation is inadequate in that the p-typeness affects all the other steps.

The p-typeness and position of the Fermi level is probably the critical factor in determining the nature of the ensuing reaction. This may explain the discrepancy shown in Graph VII, where an oxide wire catalyst was found to give a different reaction from a quenched wire catalyst containing the same quantity of oxygen. The states of oxidation or p-typeness of both catalysts were probably not exactly equal, and close to the critical value which would change the reaction.

We conclude this discussion by pointing out that the reduced copper powder catalysts used by a great many authors, e.g. Constable (14), Palmer (12), Ghosh and Bakshi (18) etc., must in fact have contained residual oxides of copper which was imparting activity to their catalysts. This would explain why the activity of their catalysts was not maintained with use. Again, the activation of copper surfaces by alternate oxidation/reduction techniques, generally considered to be due to surface roughening (64), (99), (73), must in fact be due to the electronic properties associated with residual oxide, rather than to a pure geometric factor. We would therefore suggest that care is necessary in the interpretation of results obtained from reduced powder catalysts.

---ooOoo---

FUTURE WORK.

Future work will therefore be designed:

(a) To classify the various catalysts according to semiconductivity measurements, coupled with close control of the experimental conditions of oxidation.

(b) To study adsorption of methanol, hydrogen, carbon monoxide, carbon dioxide, water, etc., on oxidised copper catalysts.

(c) To study the water-gas reaction as a method of examination of the proposed reaction scheme.

(d) To undertake catalyst studies in a flow system, where the efficiency is not obscured by carbon monoxide and hydrogen reduction of the catalyst.

CHAPTER IV

Work Hardening Experiments.

CHAPTER IV - WORK HARDENING EXPERIMENTS.

INTRODUCTION

Crystal defects have long been considered as possible sites for catalytic decomposition, and several workers have in fact obtained some kind of relationship between the number of defects present and the catalytic activity. Thus, Sosnovsky (74) found an increased rate of decomposition of formic acid on silver crystals, into which dislocations had been introduced by bombardment with argon ions. Eckell (75) likewise found an increased rate of hydrogenation of ethylene over cold worked nickel foil. Woodcock and Farnsworth (76) however, considered that their catalysts' activity was associated with vacancies in the crystal rather than dislocations. They showed that resistivity and catalytic activity were complementary whereas hardness, associated with dislocations, bore no direct relationship with catalytic activity. Recently, however, Uhara (77) conducted several experiments on the catalytic decomposition of diazonium salts on deformed copper wires. (Gattermann Reaction). His method of work hardening of the copper wires was interesting. He found that copper wires could be twisted about an axis parallel to the length of the wire L up to a stage $\frac{nd}{L} = 1$ without fracture of the wire.

(n = the number of turns of twist, and d = diameter of the wire). Such a wire was found to enhance the heterogeneous decomposition reaction considerably, and the catalytic activity was related to the hardness of the wire.

Curiosity prompted the author to prepare such a work hardened wire, and it was found that up to 500 turns of twist could be imparted to a 50 cm. length of 18 s.w.g. copper wire without fracture recurring. This wire was then found to have unusual physical properties, in that it lost all ductility normally associated with copper wire, and bending it at an angle of 90^o caused complete fracture in some cases. It was therefore decided to find out whether such a wire would enhance the catalytic activity of a gas phase heterogeneous reaction in a similar manner to that obtained in the liquid phase by Uhara.

Two gas phase reactions were investigated.

(1) Dehydrogenation of Methanol.

(2) Decomposition of Formic Acid.

(1) Dehydrogenation of Methyl Alcohol.

Preliminary experiments involved attempts to dehydrogenate methanol on pure copper wires, work hardened according to the method described above, and on work hardened copper wires which had been etched in various specific etching solutions. Further details of these experiments are given in Appendix III, but it is sufficient to say at this point that they met with no success. A few experiments served to show however that a length of wire work hardened to $\frac{nd}{L} = 1$ still showed considerable hardness after a two hour oxidation at 300°C. The rate of annealing at this temperature was slow.

Accordingly, during the course of the oxygen-18 experiments conducted in Part IV of Chapter II, a further experiment, F, was performed on a work hardened wire, oxidised at low temperature. For comparison purposes, the same geometric surface area (105 cm^2) was used, and the wire in experiment D was selected as the standard annealed wire. Experiment F was therefore an exact replica of Experiment D, that is oxidation for two hours at 60 cm.oxygen-18 pressure and 300°C, except that wire F had been work hardened to an extent just short of $\frac{nd}{L} = 1$. After the oxidation, the wire was "baked out" for a short time (30 minutes at 350°C) to remove some of the adsorbed oxygen, and provide better comparison between this surface, and the fully deoxygenated surface of sample D. "Baking out" could not be prolonged because of likelihood of annealing of the work hardened wire. Methanol reaction was then conducted on this wire at 300°C and the result is shown in Graph XV., compared with experiment D, F has been displaced along the time axis slightly, to aid clarity. It is immediately obvious that although the uptake of oxygen in both cases was comparable, under comparable conditions, experiment F showed a "poisoned" reaction compared with experiment D. Analysis of the products was carried out by the usual technique, and the results obtained are tabulated in Table 6 on the following page.

GRAPH XV

EFFECT OF WORK HARDENING OF OXIDISED COPPER WIRES ON THERMAL DECOMPOSITION OF METHANOL.

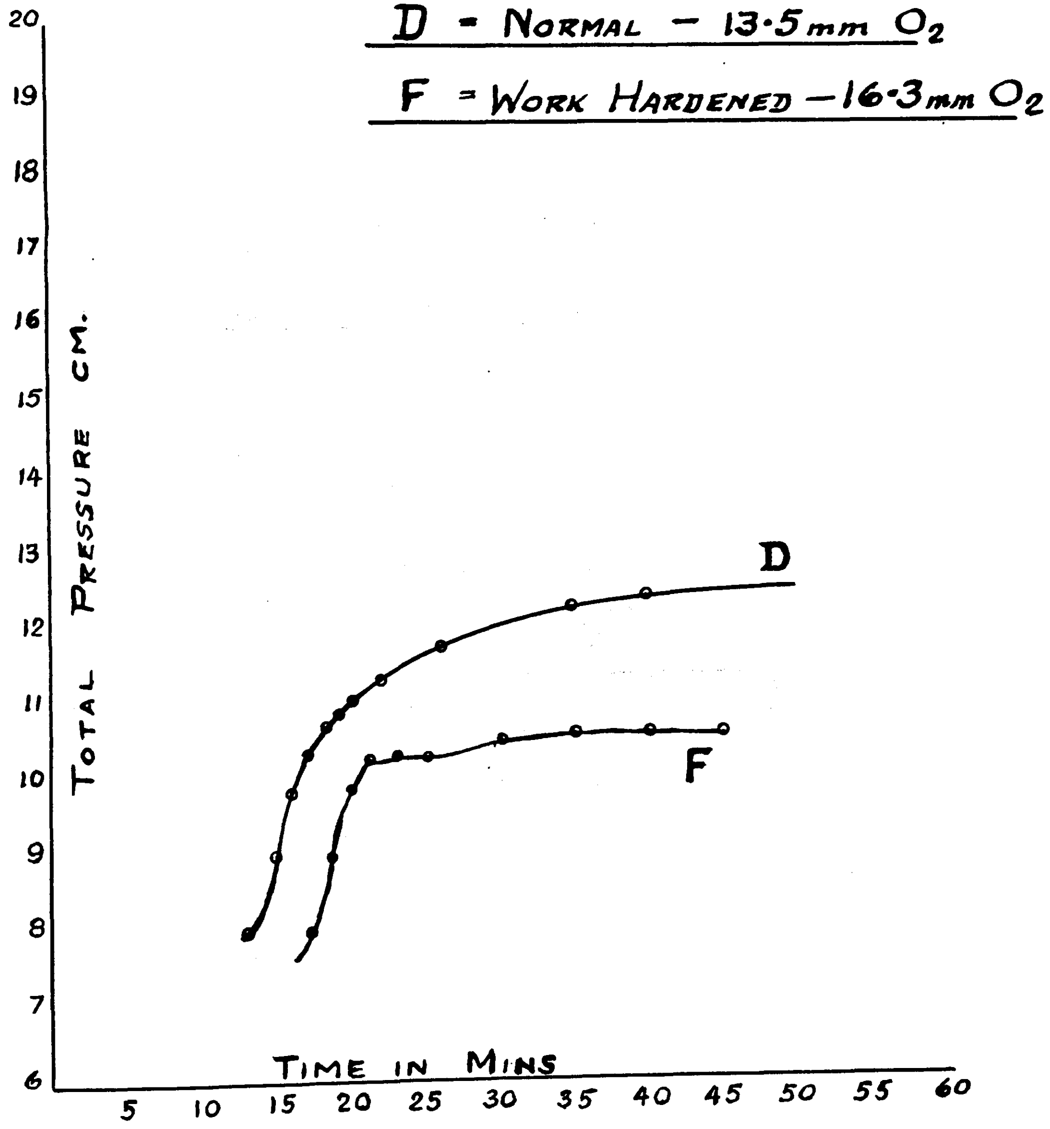


TABLE 6

	D.	F.
O_2	13.5 mg.	16.3 mg.
MeOH Initial.	51.3	50.6
H_2	1.7	1.15
CO	Nil	Nil
CO_2	22.0	21.8
H_2O	4.8	9.7
HCHO	1.19	2.7
MeOH Unreacted.	28.5	24.

Oxygen-18 Analysis.

$CO_2^{18}:CO_2^{16}$ expressed as % CO_2^{18}

Calibration	1.6 atom%
Sample D	2.15 atom%
Sample F	2.85 atom%

It is seen that the analytical results indicate, as expected, that the reaction is a poisoned one, characteristic of a catalyst of increased p-typeness. Thus, the formaldehyde produced is more than doubled, the water formed is increased, and the oxygen-18 enrichment of carbon dioxide rises to a high value. An oxygen-18 result for water was also obtained with this sample, and the enrichment ratio of the acetic acid produced during the preparation of the sample showed a value of 2.85 atom%, that is exactly the same as the carbon dioxide enrichment ratio. No great emphasis can be placed on this result, however, as a calibration sample was not obtained at the same time. The result does show however, positive enrichment of the water produced in the reaction, and this again, must exclude any possibility of a dehydration reaction occurring to produce dimethyl ether and un-enriched water.

The increase in p-typness of a work hardened, oxidised catalyst is in fact to be expected when we consider that the dislocations produced will serve to trap out vacancies in the crystal, thereby reducing the diffusion of copper ions to the surface into the surface oxide. This result may therefore be of considerable interest to those workers intent on preparing formaldehyde by dehydrogenating methanol, that is, poisoning the reaction at the formaldehyde stage. It would be interesting to find out whether in fact a mixture of methanol and air passed over work hardened copper wires heated to 200-300°C. would increase the yield of formaldehyde produced. A device could be arranged to regenerate the work hardening of the wires, just as the catalyst is constantly being regenerated by oxidation with the air.

(2) Decomposition of Formic Acid Vapour.

This reaction was chosen as one known to take place on pure copper metal without pre-treatment or pre-oxidation being required. It has often been used as a "Yardstick" for measuring relative catalytic activities, and a great deal of work has been done on attempting to evaluate the reaction mechanism. Valuable reviews on the reaction have been written by Bond (78), DeBoer (79), Hirota (80) and Sachtler (81).

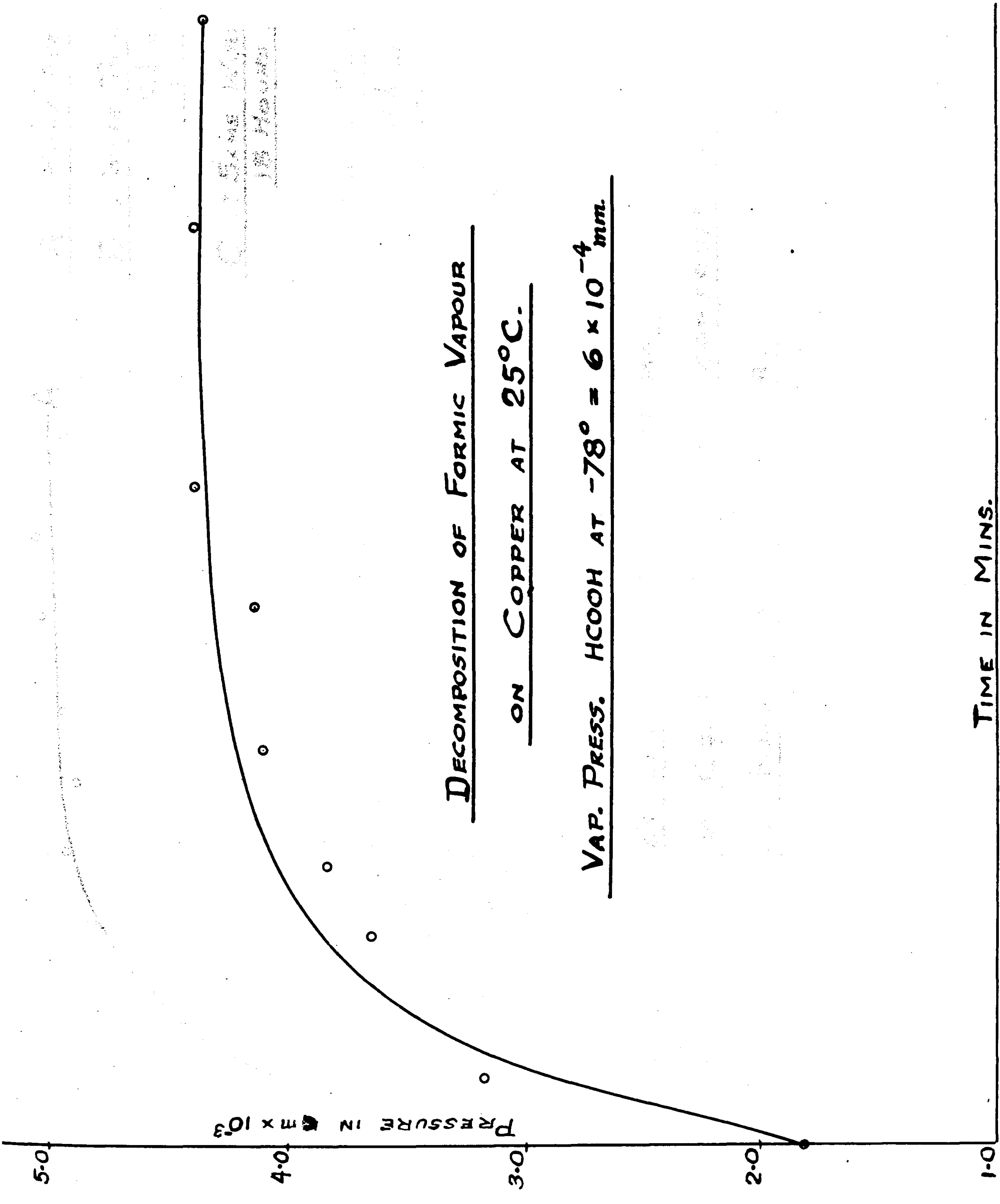
The apparatus used for these studies is shown in Fig.13. A similar apparatus was in fact used by Eley and Leutic (82) in the study of the decomposition of the acid on Pd/Au alloy wires. A sample of pure high conductivity 20 s.w.g. copper wire was obtained from P. Ormiston & Sons Ltd. This diameter of wire was chosen as a compromise between facility of electrical heating of a narrow gauge wire and facility of work hardening of a heavy gauge wire. The wire, 15 cm. long, was sealed into the catalyst vessel as shown, so that by rotating the B.7. copper cone, the wire could be deformed to any extent within the apparatus. The temperature of the wire could be measured accurately with a thermocouple and Doran thermocouple Potentiometer. The procedure adopted was to "bake out" the catalyst vessel and trap to 10^{-5}mm. at 300-400°C., the wire being heated to similar temperature electrically. The trap was then cooled to -195°C. to protect the copper wire from tap grease and mercury vapour, and the wire cleaned with purified atomic hydrogen according to the method of Couper and Eley (83). Finally the trap was warmed to -78°C and the wire heated electrically to 300°C under constant evacuation for several days to remove dissolved hydrogen. The cleaned wire was now ready for formic acid decomposition.

The mercury cut-off was lowered to distill a quantity of formic acid into the cold trap at -78°C, which served as a reservoir for solid formic acid. The apparatus was thereby filled to a constant pressure of 6×10^{-4}mm. formic acid vapour ((Eley and Leutic (82))). It should be pointed out at this stage that calculation showed that at the pressures of formic acid used, no condensation was possible in the stem of the McLeod Gauge.
A preliminary experiment served to show however that reaction on the wire was taking place at room temperature, and the pressure due to decomposition products rose quite rapidly without recourse being made to heating the wire. Future experiments were therefore conducted with the catalyst vessel thermostated at 25°C.

A kinetic experiment was therefore commenced by noting the time at the instant of lowering the mercury cut-off and the zero reading was taken at the time of the first McLeod Gauge pressure measurement, one minute later. Successive pressure measurements were repeated at intervals of three minutes. The result of such an experiment on a clean wire is shown in Graph XVI. It should be noted that the initial pressure reading was as high as 2×10^{-3}cm. and that after rising to 4.5×10^{-3}cm., the reaction stopped. This was surprising as sufficient formic acid was present in the cold trap to provide a constant supply of formic acid vapour to the wire. Eley and Leutic, for example, found that the limiting rate due to the diffusion of formic acid vapour from the trap to the wire was 12×10^{-4}mm/minute. When the vessel and wire were "baked out" again at 300°C for a short time, and more formic acid distilled into the cold trap, then an almost identical plot to Graph XVI was obtained, but is not reproduced here to avoid confusion.

A fresh wire was then placed in the apparatus and cleaned by the method described previously, preparatory to reaction. Formic acid decomposition was then conducted on this wire and the result, similar to that of Graph XVI is shown as plot A on Graph XVII. The wire and vessel and trap were "baked out" for several hours to 10^{-5}mm pressure. After the "baking out" procedure was complete the vessel and wire were cooled, the

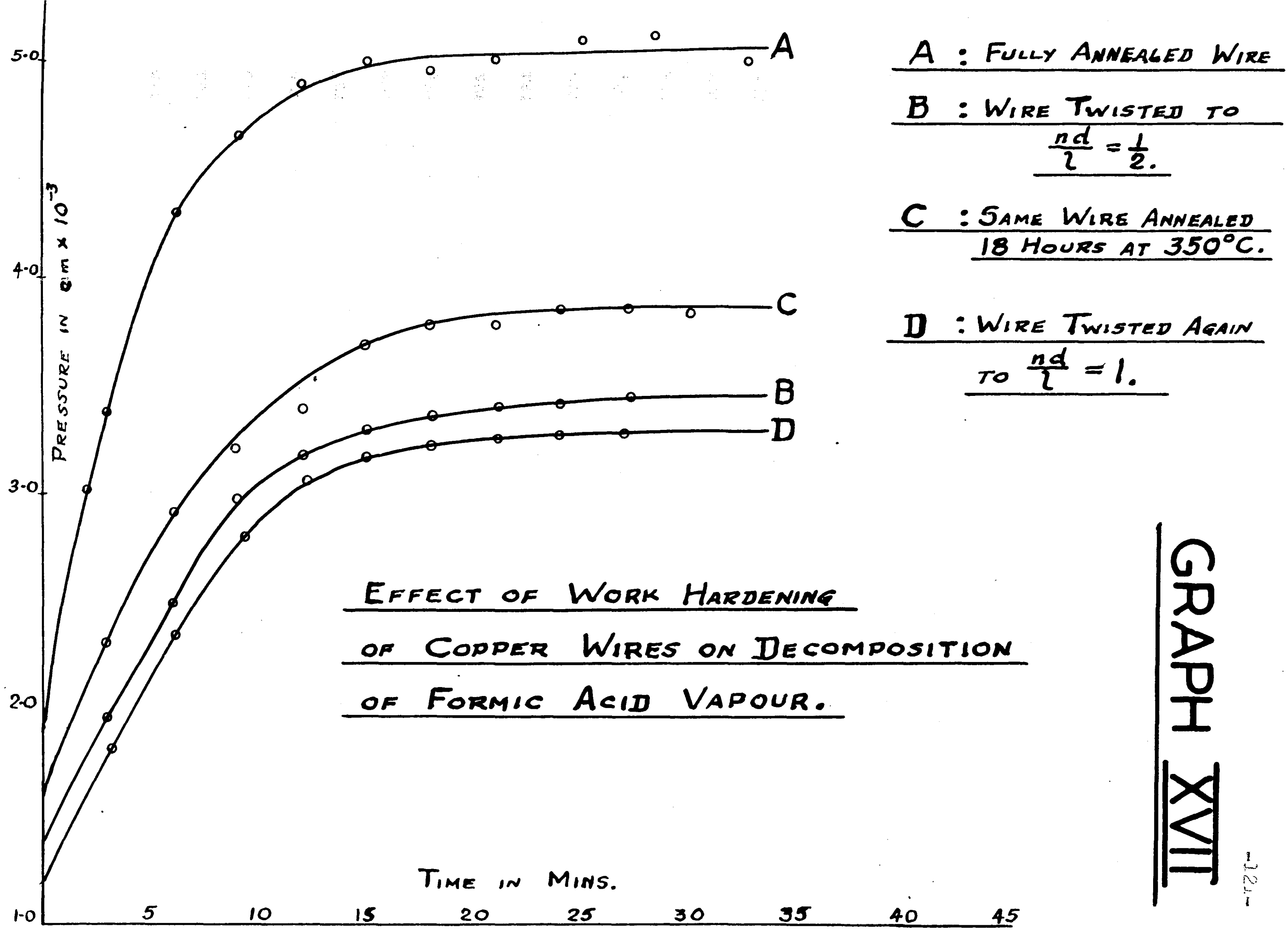
GRAPH XVI



DECOMPOSITION OF FORMIC VAPOUR ON COPPER AT 25°C.

VAP. PRESS. HCOOH AT $-78^{\circ} = 6 \times 10^{-4}$ mm.

GRAPH XVII



EFFECT OF WORK HARDENING OF COPPER WIRES ON DECOMPOSITION OF FORMIC ACID VAPOUR.

trap immersed in Drikold/Acetone mixture, and purified nitrogen admitted to the apparatus up to atmospheric pressure. This was done so that the Apiezon wax joint on the B.7 copper cone could be warmed to allow free rotation of the latter in its socket. This avoided contaminating the catalyst wire with air, leaking past the cone during the warming process. Nitrogen was selected as a suitable atmosphere in which to conduct the work hardening process, as it would be readily desorbed from the wire on evacuation. Recourse to heating the wire was unnecessary and consequently the wire was not annealed. The catalyst wire was then deformed in the catalyst vessel up to a point corresponding to $\frac{nd}{L} = \frac{1}{2}$. The vessel was then evacuated to 10^{-5}mm. pressure, and formic acid decomposition attempted on the wire. The result of this experiment is shown as Plot B, Graph XVII. After the completion of this experiment, the wire, vessel and trap were again "baked out" to a high vacuum, and the wire was thereby annealed at 350°C. for 18 hours. In order to provide a complete parallel to experiment B, after cooling the catalyst vessel and wire, and protecting them from contamination by cooling the trap to -78°C. nitrogen was again admitted up to atmospheric pressure and then removed prior to formic acid decomposition being attempted on the wire. This precaution was also taken prior to reaction A being attempted. The result of this experiment is shown plotted as Plot C, Graph XVII. Finally, the work hardening process in nitrogen was repeated as described previously, but this time to a state of deformation corresponding to $\frac{nd}{L}$ = Unity. The result of this experiment is shown as Plot D in Graph XVII.

DISCUSSION

Formic acid decomposition on metals is generally held to take place through the intermediate formation of a formate ion, or radical, on the surface, which can then react intermolecularly perhaps with another ion, or radical, to form hydrogen and carbon dioxide thus:

$$2HCOOH \rightarrow 2HCOO + H_2$$

$$2HCOO \rightarrow H_2 + CO_2$$

Many other mechanisns of a similar nature have also been suggested. Copper however, seems to be exceptional, in that evidence for the formation of a formate ion on the surface is slight, and claims to the recognition of formate ion on reduced copper powders (84) must, as we have indicated in Chapter III, be treated with caution. Copper is also exceptional in that it exhibits a relatively high activity towards formic acid decomposition compared with other transition metals, a situation which is reversed in the case of other dehydrogenation reactions. Exceptional activity of copper was recently demonstrated by Duell and Robertson (85) who found that copper wires which had been annealed at a high temperature and then cooled rapidly, showed exceptionally high reactivity towards formic acid decomposition at 600°C. The "Superactivity" lasted only a few minutes and was thought to be due to "Quenched in" vacancies diffusing to the surface, and providing the necessary sites for adsorption and decomposition of the acid. A parallel may thus exist between the results obtained by the aforementioned authors and the results shown in Graph XVII. The vapour pressure of formic acid vapour at -78°C. as measured by Eley and Leutic (82), is 6×10^{-4} mm., and yet one minute after the commencement of reaction A described above, the pressure had risen to 2×10^{-3}cm. A very fast initial reaction must have taken place which gradually slowed, and was eventually poisoned after the pressure had risen to 5×10^{-3}cm. Duell and Robertson explained this on the basis that the reaction brought about mobility of the surface and anihilated the active sites, and time was then needed for more vacancies to diffuse from the bulk of the wire when heated. It has been reported (78) that the products of the decomposition reaction on copper do not inhibit the reaction rate, and so poisoning of the wire by this means may be disregarded.

If the activity of the metal is due to the presence and diffusion of crystal vacancies, then a high dislocation density should serve to trap out these vacancies and hence reduce the activity of the metal. The surface coverage will in effect be much smaller. This is in fact what is observed in experiment B; the reaction is "Poisoned" much more quickly. Conversely, when dislocations are annealed, a large number of vacancies will be injected into the crystal lattice, and if they are the activating agents, then the reaction rate should again rise. Experiment C does in fact show this to be the case although the original activity was not regained. Again, when the wire was work hardened, as in experiment D, the reaction rate again decreased.

We conclude by suggesting tentatively that these experiments serve to lend support to the work of Duell and Robertson, and may in fact indicate that crystal vacancies are more liable to be sources of catalytic activity than are dislocations.

We realise, however, that the rate of vacancy diffusion to the surface at the reaction temperature of 25°C. will probably be slow, but on the other hand this may be compensated by the lower activation energy for vacancy movement reported by Duell and Robertson.

-ooOoo-

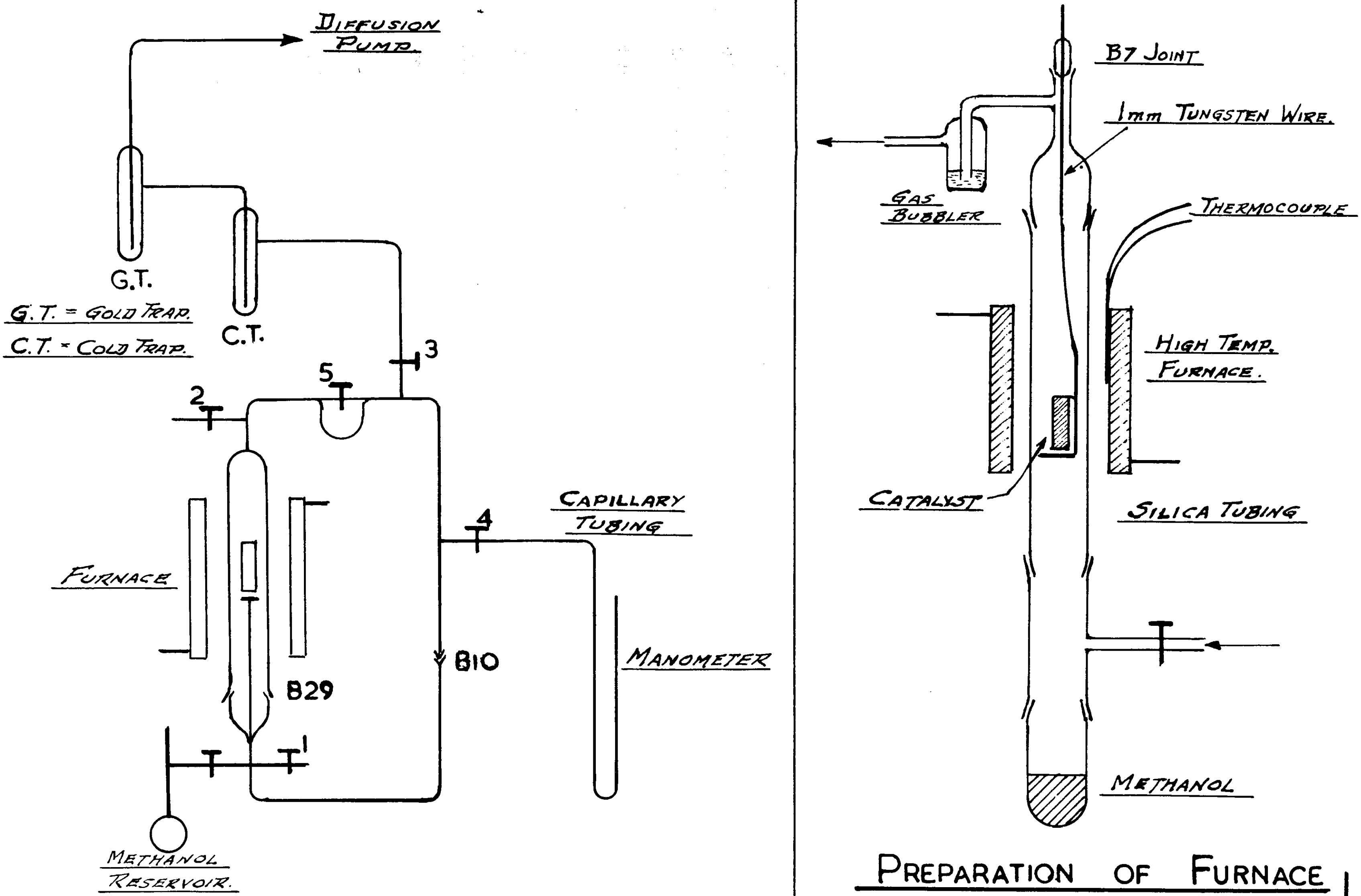
CHAPTER V

Experimental Details.

CHAPTER V - EXPERIMENTAL DETAILS.

Experimental for Chapter I - Parts I to VII

An apparatus was constructed to study the decomposition of methanol on various copper catalysts, and is shown in Fig.1. The catalyst vessel was constructed from a 12" - B.29 Quick-fit socket, and arranged vertically in the apparatus, so that when surrounded by a Nichrome-tape wound furnace, gases present in the catalyst vessel would be circulated by convection over the catalyst and around the simple circulating system. The lower half of this circulating system could be disconnected at the Quick-fit joints, to allow both furnace and catalyst to be removed and replaced. The catalyst was supported in the vertical catalyst vessel by two lengths of glass rod, joined together and thickened at one end, and resting on the base of the B.29 cone. To load the catalyst vessel, therefore, the catalyst, held between two pieces of tissue, was placed at the entrance of the B.29 socket, the glass rod engaged with the bottom of the foil or wire, and the whole pushed home and fitted together at the Quick-fit joints. At either end of the catalyst vessel, two taps were provided to allow ingress and egress



PRELIMINARY VACUUM APPARATUS.

PREPARATION OF FURNACE QUENCHED CATALYSTS.

FIG. 1.

of gases at atmospheric pressure. At the bottom of the catalyst vessel was the methanol reservoir, from which methanol vapour could be admitted to the circulating system to any desired pressure, below saturation vapour pressure. Tap 5 was always open during an experiment. This pressure, and any change in pressure during the reaction, was measured by a 30 cm. mercury manometer, connected to the circulating system by a 30 cm. length of 2 mm. capillary tubing and a tap, which was closed when the manometer was not in use. Diffusion of mercury vapour through the capillary into the circulating system would be negligible and was thus excluded from the reaction system as a possible poison. The whole system could be evacuated through tap 3, and a gold trap, and cold trap, again to remove mercury vapour, this time from the McLeod gauge used to measure the ultimate vacuum in the system.

The methanol used was B.D.H., A.R. grade, which had been distilled several times over A.R. anhydrous sodium sulphate, to remove water. Approximately 5 ml. were then placed in the reservoir, which was cooled, to -195°C., and evacuated to a high vacuum. The apparatus was now ready to receive the first catalyst.

COPPER FOIL:- Cleaned with Nitric Acid.

First experiments were attempts to decompose methanol on pure copper metal, and accordingly the first catalyst was a section of copper foil $\frac{1}{4}^{th}$ mm. thick and 24 cm^2. in area, which was immersed in 2 N. Nitric acid for five minutes, and washed thoroughly with distilled water. This was then placed in the catalyst vessel, and the latter evacuated to a pressure of 10^{-3}mm. The furnace surrounding the catalyst vessel was then heated to 500°C. and the vessel and catalyst thereby "baked out" to an ultimate vacuum of 10^{-5}mm. The furnace was then cooled, and methanol vapour allowed to flow into the system from the reservoir, until the pressure was 6 cm. The furnace was again heated, this time to 300°C., and the pressure was noted to increase slowly to 7.5 cm. at which pressure it remained constant until the furnace was cooled when it dropped again to 6 cm. No reaction had taken place.

COPPER FOIL:- Cleaned in Alcohol.

A 250 ml. round bottom flask containing A.R. methanol, was fitted with a Quick-fit condenser. Several pieces of copper foil, 24 cm^2. in area, were suspended in the lower part of the condenser by means of a length of copper wire. The flask was heated with a heating mantle to boil the methanol and the foils arranged so that they lay in the region of the hot methanol vapour. The methanol was refluxed over the copper in this fashion for several days, at the end of which period the copper was quickly transferred to the catalyst vessel and "baked out" as before. 6 cm. of methanol were then admitted to the reaction system and the temperature of the furnace raised to 300°C. No reaction was observed and the pressure again reached only 7.5 cm.

COPPER FOIL:- Cleaning Mixture.

This mixture is used to clean copper cathodes prior to assembly in Geiger-Müller counting tubes. The composition of the mixture is as follows:

Solution A:

Ammonium Chloride	:	300 g.	make up to I l. with water.
Conc. hydrochloric acid	:	90 ml.	
Gelatin/0.2% Acetic acid	:	50 ml.	

Solution B:

Chromic acid	:	250 g.	make up to I l. with water.
Conc. Sulphuric acid	:	75 ml.	
Solution A	:	35 ml.	
Gelatin	:	50 ml.	

Solution C:

Chromic acid	:	250 g.	make up to I l. with water.
Conc. Sulphuric acid	:	75 ml.	

The procedure was to immerse the 24 cm^2. copper foil in solution B for 2 minutes, wash it well with water, and immerse it in solution C for 5 secs. followed by immediate and thorough washing in distilled water. It was then transferred to the catalyst, "baked out" to 10^{-5} mm., 6 cm. pressure methanol admitted, after cooling, and the furnace re-heated. No reaction was observed even when the temperature was raised to the maximum of 500°C., and on cooling, the pressure again dropped to the original 6 cm. admitted.

Reduced Copper Surfaces:

Since pure copper foil was found to be inactive to methanol decomposition, it was decided to attempt to activate the surface by alternate oxidation/reduction techniques. The oxygen and hydrogen gases used in these experiments were purified by being passed through activated charcoal of high surface area, in a trap cooled to liquid air temperature. 24 cm^2. copper foil was cleaned, by being refluxed in methanol as before, and placed in the catalyst vessel. Through the taps I and 2, above and below the catalyst vessel (Fig.I), a slow stream of oxygen gas was allowed to flow over the catalyst, while the latter was heated to 300°C. for 3 hours. The vessel was then cooled and the oxygen flushed out with purified hydrogen. After 5 minutes, the hydrogen flow rate was reduced, and the furnace again heated to 200°C. for 2 hours, to reduce the copper oxide. The furnace was then cooled and the hydrogen flushed out with more oxygen prior to re-oxidation. This cycle was repeated five times, at the end of which period the catalyst was "baked out" to an ultimate vacuum of 10^{-5}mm. 6 cm. methanol were admitted to the cooled catalyst vessel and the furnace heated to 300°C. Maximum pressure rise was only 1.5 cm.

Reduced Copper Powder.

The procedure used was based on the method of activation of copper surfaces used by the United States Industrial Alcohol Co.Ltd., (30) in the preparation of aldehydes from alcohols. 24 cm^2. copper foil was again chosen as the substrate. It was immersed in 100 ml., 0.5 m. solution of cupric nitrate, prepared from A.R. cupric nitrate and distilled water. Excess of dilute ammonia was then added to precipitate copper hydroxide on to the surface of the metal support. The solution was then evaporated to dryness, leaving a deposit of cupric hydroxide and ammonium nitrate on the copper foil. This was then ignited strongly in a porcelain. crucible to volatilise the ammonium nitrate, and leave a black deposit of cupric oxide supported on the copper foil. This catalyst was then transferred to the catalyst vessel, and reduced in a stream of purified hydrogen at 300°C., for 4 hours. The system was then evacuated, and the catalyst "baked out" at 500°C for some days until a vacuum of 10^{-5}mm. was reached. Methanol was then admitted to the reaction system, to a pressure of 6 cm., and the furnace heated to 300°C. The pressure rose to 10 cm. as seen in Graph A_I. Condensation was observed, and on cooling the furnace, the pressure dropped to 8.5 cm. $\therefore$ pressure increment = 2.5 cm.

Assuming, for the moment, that methanol decomposes to products having three times the original volume of the methanol, then this pressure increment must be due to the decomposition of 0.8 cm. pressure of methanol. That was 13% decomposition.

Repeat Experiment on same Catalyst:

After the last decomposition, the products of the reaction were evacuated from the system, the catalyst further reduced by hydrogen at 300°c for 24 hours, cooled, evacuated and ~~and the catalyst again~~ "baked out" to 10^{-5}mm. pressure. 6 cm. methanol were again admitted to the cooled catalyst vessel, and the furnace re-heated to 300°C. The pressure then rose rapidly to 19.4 cm. (Graph B_I). This corresponded to almost complete decomposition of the methanol, assuming a theoretical maximum of a threefold increment in pressure.

The above sequence was repeated several times, but after four such reactions, the pressure rise changed from 6 cm. → 19 cm., to 6 cm. → 16.5 cm. (Graph C_I).

PART II - FLAME QUENCHED CATALYSTS.

Preparation of Foils:

24 cm^2 copper foil was rolled into the form of a cylinder,

and held by a pair of laboratory tongs, in the flame of a coal gas/compressed air mixture for approximately 30 seconds. The copper was thus heated to approximately 900°C. At the end of this period it was quickly plunged into a glass measuring cylinder containing 200 ml. of methanol at 20°C. The foil was thereby quenched, and oxide formed during the heating process reduced to bright metallic copper. The foil was then transferred to the catalyst vessel prior to a reaction being attempted.

Preparation of Wires:

A 1 metre length of 18 s.w.g. copper wire (1.2 mm. diameter), Geometrical surface area 38 cm^2., was wound around a piece of glass tubing 12 mm. in diameter, thereby forming it into the shape of a spiral, approximately 6 cm. in length. This was heated in the gas/air Flame as before, and when uniformly red-hot, plunged into the measuring cylinder containing 200 ml. methanol. Again oxide formed on the wire during the flame treatment, was reduced by the methanol to copper. The wire was then placed in the vacuum system.

The results of methanol reactions on these catalysts are shown in Graphs II and III.

Graph B_{II} shows the results of a repeat reaction on the catalyst which had given rise to Graph A_{II} after the latter had been "baked out" to remove previous reaction products.

Graphs A_{III}, B_{III}, and C_{III} are the results from different wires activated by the method stated previously.

All the wire catalysts used in Chapter I, Parts II, III and IV, were of the same area, namely 38 cm^2.

PART III - FURNACE QUENCHED CATALYSTS.

As it was suspected that flame treatment of copper wires and foils might be a source of their catalytic activation, it was decided to heat copper foil to a high temperature in a Furnace, and follow this by quenching in methanol. Any difference in activity between such furnace quenched catalysts and the flame quenched catalysts prepared in Part II, could then be noted. The apparatus used to activate the foils in this manner is again shown in Fig.I. A length of silica tubing, 25 mm. internal diameter, was fitted at the top with the pyrex glass apparatus shown, and made gas tight with an asbestos paper gasket. The length of the 1 mm. tungsten wire was arranged so that the lower extremity, bent at right angles, was situated within the silica tubing, and just over half-way down its total length. This was the catalyst support. At the lower end of the silica tube was the reservoir containing 100 ml. methanol. The procedure was to support the catalyst foil or wire with the end of the tungsten wire, and lower it carefully into the silica tubing, until the apparatus was fitted together. In the case of the experiments involving heating the catalyst in air, the bubbler was removed, and the tap at the bottom of the apparatus left open to permit free convection to take place. The silica tube was surrounded with a furnace wound from 0.5 cm. diameter Kanthal wire. By passing a current of 50 amp. through this wire, the temperature of the furnace could be raised to 900°C. The circuit diagram showing the method of supply of this high current is shown in Fig.4.

In the first experiment, when the time of heating in air was great, the copper foil 24 cm^2. in area, was supported in the apparatus, as indicated above, and the furnace slowly heated to a temperature of 900°C. This temperature was measured using a Platinum/Rhodium thermocouple connected, via. a cold junction in ice, to a millivoltmeter. The calibration of the latter was made at lower temperatures, and the higher temperatures estimated by extrapolation of the calibration graph. This temperature was maintained for one hour, at the end of which period, the B.7 joint at the top of the apparatus was rotated through 90°, thus turning the 1 mm. tungsten wire and allowing the catalyst to fall into the reservoir of methanol, where it was quenched. By removing the bottom test tube end, the catalyst could be recovered and immediately placed in the vacuum apparatus, The result of methanol decomposition on this catalyst is shown in Graph A_{IV}. The specimen thus prepared was found to be completely oxidised in this treatment prior to quenching.

For shorter times of heating, a slightly different procedure was adopted. The furnace was first heated to 900°C., then the catalyst foil was engaged with the bottom of the tungsten support and lowered quickly into the region heated by the furnace. At the end of the required time period, the B.7 joint was rotated through 90° and the catalyst allowed to fall into the reservoir of methanol. Graphs B_{IV} & C_{IV} show the results of decomposing methanol on catalysts of 24 cm^2. area, which had been heated for times of 1 minute and 5 seconds in air.

When it was desirable to prepare catalysts by heating copper in nitrogen, the gas bubbler was replaced and a source of nitrogen connected to the bottom tap in the apparatus. The flow of nitrogen was gauged by observation of the gas bubbler, and, after a rapid flushing out period with the catalyst foil in position within the furnace, the flow rate was reduced, and the furnace heated to 900°C. within 30 minutes. The catalyst was maintained at that temperature for 10 minutes, before being released to fall into the reservoir of methanol. The catalyst thus prepared was inactive.

The above set of experiments were also conducted with 38 cm^2. copper wire catalysts mentioned previously, and a similar set of results were obtained. There was therefore no basic reason to distinguish between copper foil and copper wire.

PART V - GRAVIMETRIC EXPERIMENTS.

These experiments were conducted to find out if oxide was in fact present in the wire catalysts, and if it disappeared during a reaction.

Preparation of Partially Reduced Wires.

Hydrogen Reduction: A spiral wound wire, 38 cm^2. in area was weighed in a weighing bottle prior to the usual flame treatment technique. The wire was not quenched but allowed to cool in air, and then re-weighed to determine the extent of oxidation. The wire was then placed in the apparatus which was flushed out with hydrogen. The wire was reduced by being heated to 200°C.,for a short time, followed by immediate evacuation of the system to terminate the reduction. The wire was then removed from the apparatus and re-weighed to determine the amount of oxide left on the wire. It was then replaced in the apparatus, and "baked out" to a high vacuum prior to attempted reaction with methanol. After the reaction, the wire was again re-weighed.

As it was difficult to control the partial reduction using hydrogen, the following technique was developed.

Methanol Reduction: The wire was weighed, flame treated, and re-weighed. It was then placed in the apparatus which was evacuated to a reasonable vacuum (10^{-3}mm.). The catalyst vessel was then heated to 300°C. and the tap to the methanol reservoir opened for a short time to allow methanol to flow into the hot catalyst vessel : this partially reduced the oxide. The apparatus was then evacuated to terminate the reduction and the furnace cooled. The wire was then removed from the apparatus, weighed to determine the amount of oxide present, and replaced in the apparatus prior to attempted reaction with more methanol. After the reaction, the wire was again weighed.

Preparation of Oxide Wires.

The wire was weighed, flame treated and allowed to cool in air. It was then re-weighed to determine the amount of oxide present and placed in the apparatus prior to evacuation, "baking out" and methanol reaction on it. After the reaction, the wire was again weighed.

Preparation of Quenched Wires.

The wire was weighed, flame treated and quenched in methanol. It was then re-weighed to determine the amount of oxide present and placed in the apparatus prior to methanol reaction on it. After the reaction, the wire was again weighed.

IN ALL THESE CASES, THE WEIGHT OF THE WIRE AFTER A METHANOL REACTION ON IT, WAS FOUND TO HAVE RETURNED TO ITS ORIGINAL VALUE BEFORE ACTIVATION.

Typical results are given below:

Partially Reduced Wire (Graph B_{VII}).

Wt. of Copper before oxidation = 10.7475 g.

Wt. of Copper after oxidation = 10.7645 g.

Wt. of copper after partial reduction = 10.7507 g.

Wt. of copper after reaction = 10.7473 g.

Wt. of oxygen used in reaction = 3.4 mg.

Flame-Quenched Wire (Graph C_{VIII}).

Wt. of Copper before oxidation	=	49.6458 g.
Wt. of Copper after flame-quenching	=	49.6623 g.
Wt. of Copper after reaction	=	49.6455 g.

Wt. of oxygen used in reaction = 16.5 mg.

The surface areas of the flame-quenched wires shown in Graph VIII are longer than those previously used, being 180 cm^2. The reason for this difference was the fact that, as is described in Part VI of this Chapter, a catalyst of larger surface area was necessary to obtain measurable oxidation at low temperatures. The flame-quenched wires of similar surface area thus served as a useful comparison.

PART VI - LOW TEMPERATURE OXIDATION EXPERIMENTS.

The purpose of the following experiments was to prepare oxidised wire catalysts "in situ.", in the vacuum apparatus. In order to accomplish this at low temperatures, it was found necessary, firstly to use a larger surface area of wire, so that a measurable oxidation would be obtained, and secondly to oxidise the specimens at a reasonably high pressure of oxygen. In all the experiments described above, the apparatus used was found to be completely efficient; but it was now found necessary to re-design the apparatus:

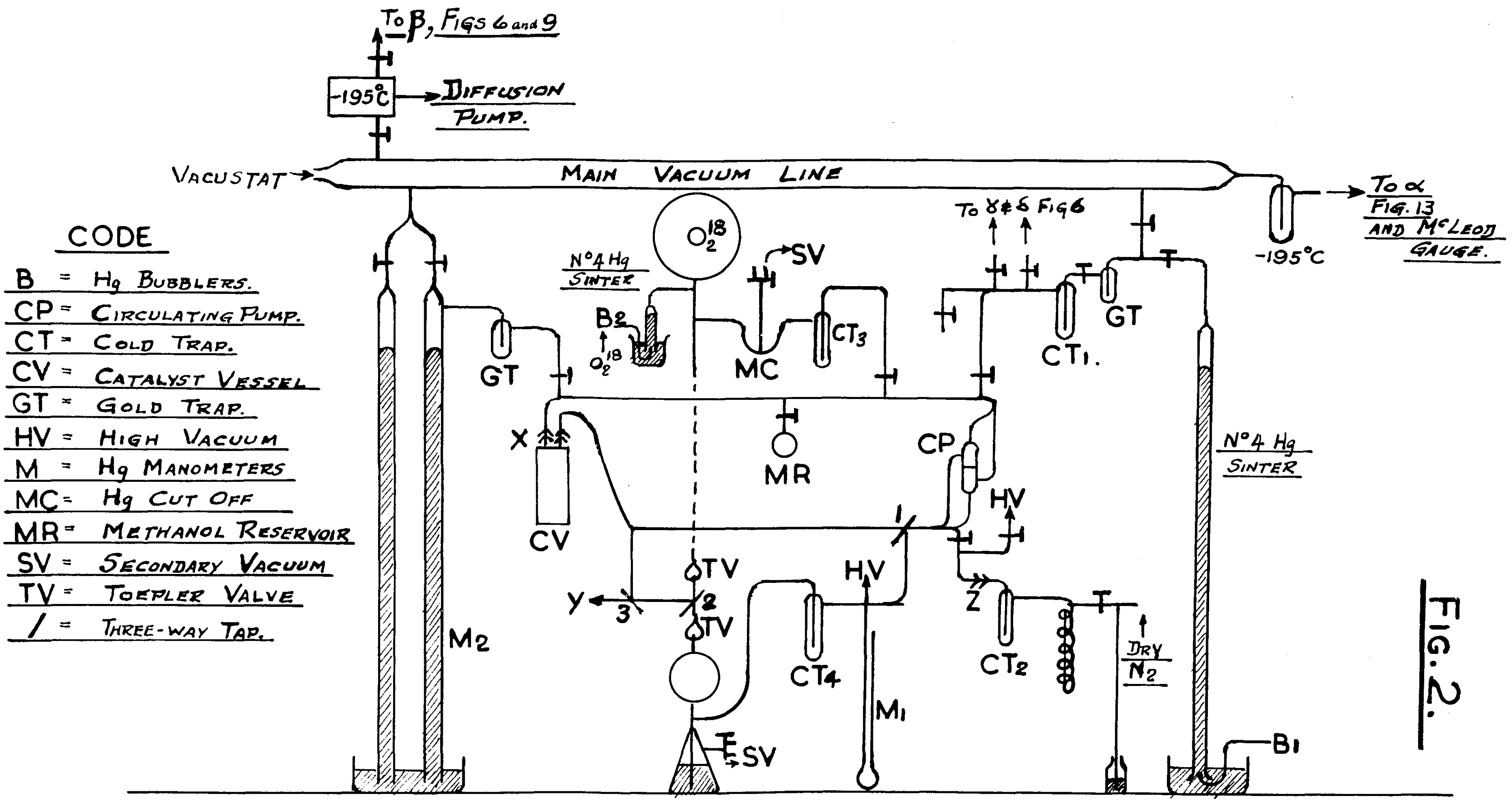
(a) To accommodate a manometer capable of covering a wider range of pressure.

(b) To accommodate a more convenient catalyst vessel.

(c) To include a section of apparatus suitable for isolating the products of the reaction in a form suitable for analysis. This latter apparatus will be described under the analytical section.

The apparatus constructed is shown in Fig.2. The main circulating system, comprising of the circulating pump and catalyst vessel is shown in the centre of the apparatus.

The design of the catalyst vessel was altered, and is shown in Fig.5, 1: having both entry and exit of the vessel at the same level simplified the removal and replacement of catalysts, and also allowed simple interchange of catalyst vessels for differently designed experiments. Loading of the catalyst vessel was accomplished by removing it from the circulating system, and releasing the B.29 sealed joint. The catalyst could then be placed within the vessel, and supported by a glass rod, and the whole fitted together, prior to evacuation.



CODE

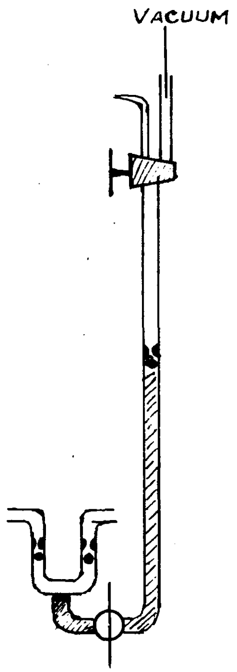
B = Hg Bubblers.
CP = Circulating Pump.
CT = Cold Trap.
CV = Catalyst Vessel
GT = Gold Trap.
HV = High Vacuum
M = Hg Manometers
MC = Hg Cut Off
MR = Methanol Reservoir
SV = Secondary Vacuum
TV = Toepler Valve
/ = Three-way Tap.

FIG. 2.

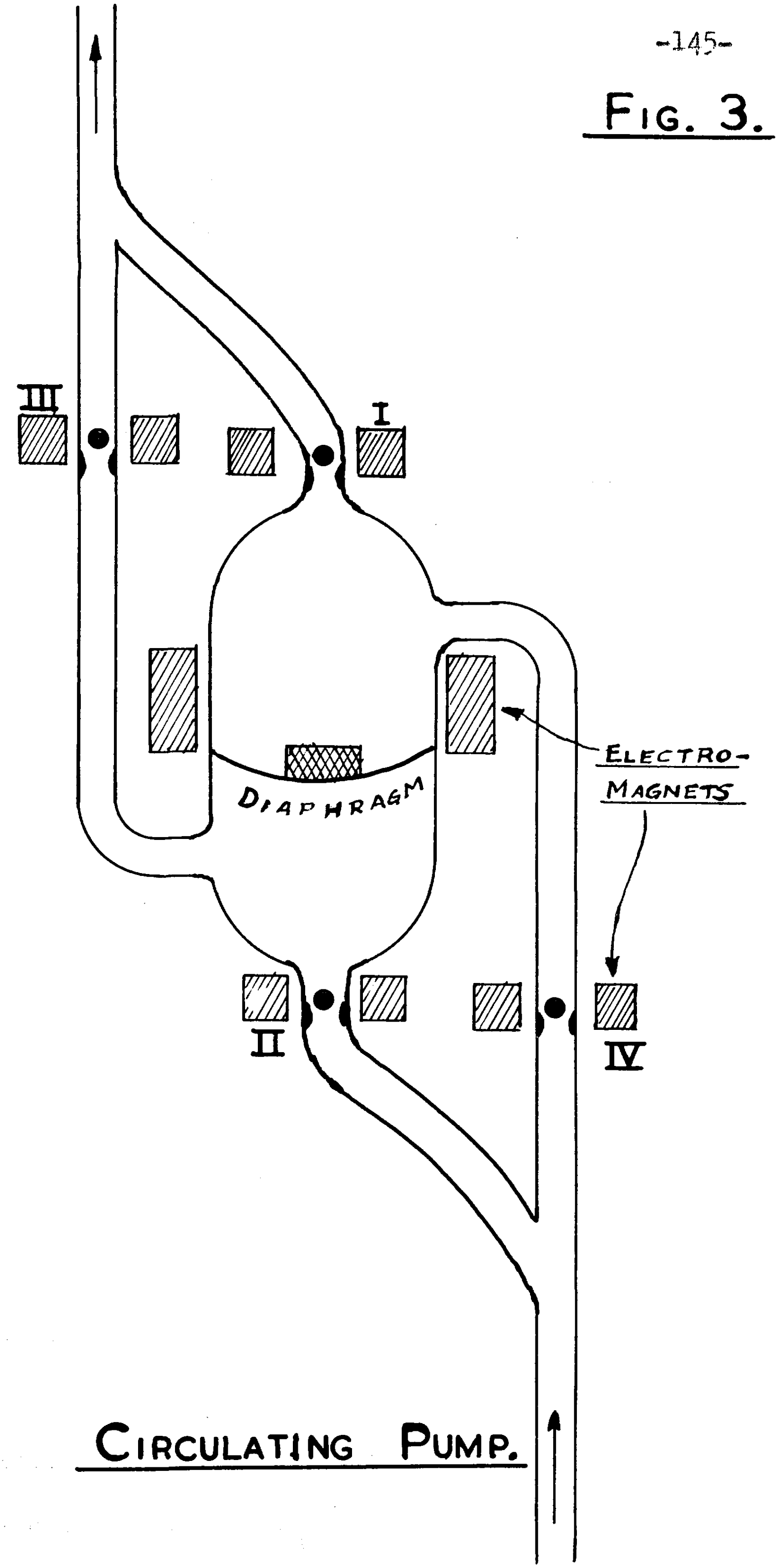
MAIN APPARATUS.

With this arrangement of catalyst vessel, circulation of the gases by convection would be restricted, and accordingly a circulating pump was constructed as shown in Fig.3. The moving diaphragm was constructed from a piece of Visqueen plastic 0.012" thick, and sealed with Apiezon wax between two glass flanges. At the centre of this diaphragm a small hole was punched sufficiently large to accommodate a small brass screw and nut. Leakage through this hole was prevented by two small rubber gaskets on either side of the diaphragm. On to the head of this screw was affixed, with Araldite, a short length of glass tubing (3-4 cm.), in the upper extremity of which was sealed 2 cm. length of silver steel rod, so that it lay within the field of the main electromagnet shown in the figure. A calculation was made to find out approximately what strength of electromagnet would be required to move the silver steel into the centre of the solenoid, thus moving the diaphragm. This calculation is given in Appendix I; it shows that 1000 turns of wire carrying 4 amp. gives the necessary strength. To avoid a large bulk of wire, 26 s.w.g. cotton covered copper wire was chosen, although the current rating for this wire is much less than 4 amp. It was found, however, that the rise in temperature due to overloading never exceeded 40-50°C. and so its use was quite permissable. The covered wire was quickly wound on to the glass tubing of the pump by means of a lathe, and it was found that after

FIG. 3.



MERCURY
CUT-OFF.



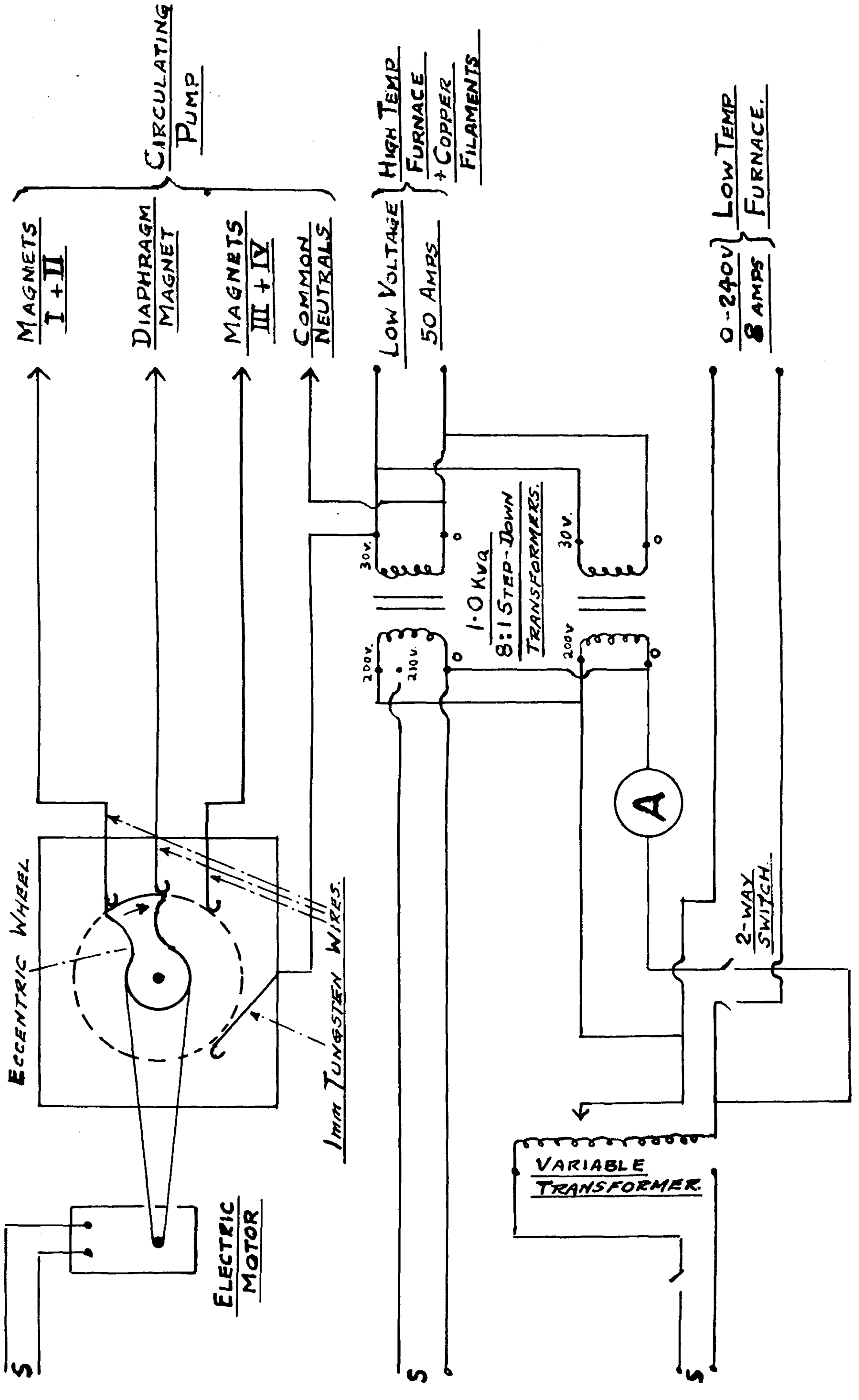
CIRCULATING PUMP.

700 turns had been wound on, the magnet had sufficient strength to move the diaphragm. On switching off the electromagnet, the diaphragm would fall back into its original position under the force of gravity. Four ball-valves were then glass-blown on to the pump,as shown in the figure, and surrounded by small commercial electromagnets. These are numbered I, II, III and IV.

The pumping cycle is thus as follows. Magnets I and II are energised, thus lifting balls I and II out of their seating. The main electromagnet is then energised, and the diaphragm lifts, pumping gas out through I, and drawing gas into the body of the pump through II. Magnets I and II were then de-energised and the balls fell back into their seating. Magnets III and IV were then energised, lifting balls III and IV, and then the main electromagnet was de-energised, the diaphragm fell back under gravity to its original position. This pumped gas out through III, and drew more gas into the body of the pump through IV, in preparation for the next pumping cycle. The last phase in the cycle was the de-energising of magnets III and IV. The pump was therefore "double acting", each movement of the diaphragm corresponding to a positive pumping stroke.

It might be thought that the electric circuitry for such an operational cycle would be exceedingly complicated, but this is not the case. The circuit diagram is shown in Fig. 4 A voltage of 30 volt. supplied sufficient current to the magnets to raise the diaphragm and ball valves. This was supplied from the 8:1 step-down transformer shown. A small support was arranged to carry an eccentric wheel (Fig.4), which was rotated by means of an electric motor. This wheel was raised to an electric potential of 30 volt. via. its shaft and another wheel on the same shaft (dotted circle, Fig. 4), which was in moving contact with a length of tungsten wire connected to the transformer. On the same horizontal level as the eccentric, three tungsten wires were positioned so that as the eccentric rotated it came into moving contact with each one in turn. The length of arc of the eccentric was arranged so that it was slightly greater than the arc between successive tungsten wires. Thus as the eccentric rotates, in turn magnets I and II are energised, followed by the diaphragm magnet. Contact is then broken with I and II, and is shortly engaged with III and IV. Contact is then broken with the diaphragm magnet, followed shortly by III and IV: thereby completing a cycle. The pump may therefore be run at any desired speed, controlled by the electric motor, and since the ball-valves are raised and lowered electrically, pumping of both low and high pressure gas may be achieved. This pump has been found to work

FIG. 4.



CIRCUIT DIAGRAM — MAIN APPARATUS

efficiently over a period of two years without attention.

Referring again to Fig.2: a different design of manometer was constructed, covering a wider range in pressure. This consisted of two vertical glass tubes 15 mm. in diameter, with their lower extremities immersed in mercury. The upper extremities were connected to the main vacuum line via. two taps, and one was provided with a side arm leading to the circulating system. This latter therefore measured the pressure in the circulating system, to be compared with the level of mercury in the other limb. Any change in volume in the mercury reservoir was therefore compensated by a corresponding change in the other limb. The manometer was connected to the reaction vessel via. a length of capillary tubing and a gold trap to remove mercury vapour.

On the right hand side of the apparatus is a mercury inlet with a No.4 sinter allowing any gas to be admitted to the evacuated system. The mercury sinter was placed 76 cm. above the reservoir so that as gas entered into the system, the column of mercury acted as its own pressure measuring device. The remainder of this apparatus will be described later.

LOW TEMPERATURE OXIDATION EXPERIMENTS.

3 metres of 18 s.w.g. copper wire was lightly abraded with fine emery paper, and loose particles removed with cotton wool soaked in

methanol. It was then bent into the form of three spirals fitting inside each other so that the total length of each spiral was approximately 5 cm. The total geometrical surface area was 115 cm^2. Final cleaning was effected by immersion of the wire in boiling methanol for a short time; it was then transferred to the catalyst vessel and "baked out" to a high vacuum. The furnace was cooled and purified oxygen (purified by passing through an activated charcoal trap at -78°C.) admitted through the inlet bubbler into the circulating system until the pressure was 60 cm. The furnace was then heated to 300°C., and after an initial expansion due to rise in temperature, the pressure fell steadily as the oxidation took place. After the required degree of oxidation, the furnace was removed, and catalyst vessel cooled quickly, by blowing cold air on to it. The decrease in oxygen pressure was then noted, and, from the total volume of the system, the weight of oxygen taken upon the copper could be calculated. Volume calibration of the system is given in Appendix II.

Typical Calculation - Graph B_{IX}

Initial Oxygen Pressure = 59.41 cm.

Final Oxygen Pressure = 56.39 cm.

∴ Oxygen taken up = 3.02 cm./452 ml.

∴ weight of oxygen $= \frac{3.02 \times 452 \times 273 \times 32}{76 \times 293 \times 22.4}$ mg.

= 23.8 mg.

Volume of Circulating system = 361 ml.

Volume of Manometer at 59.41 cm.pressure=91 ml.

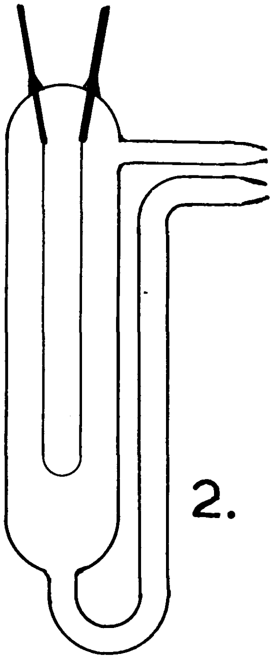
∴ Total Volume = 452 ml.

After the oxidation, the catalyst was evacuated to 10^{-5} mm., 7 cm. of methanol were admitted to the reaction system, and the catalyst vessel heated to 300°C., when reaction was observed to take place. Catalysts containing 10.8, 23.8 and 33.5 mg. oxygen were prepared after oxidation times of 1, 2 and 4 hours respectively. Methanol, initially at 7 cm. pressure, when decomposed on these wires gave rise to pressures of 10.1, 13.3 and 15.1 cm. respectively at 300°C.

PART VII - COPPER FILMS.

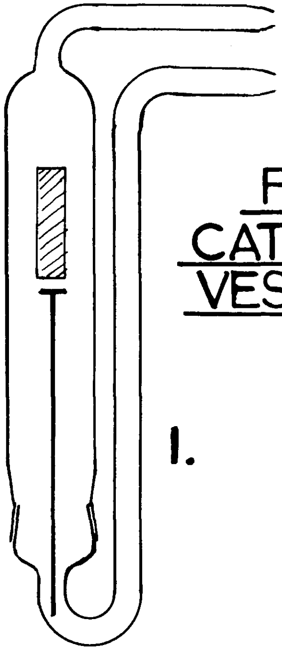
The catalyst vessel used is shown in Fig.5, 2. 24 s.w.g. copper wire, approximately 20 cm. in length, was bent into the form of a loop, and the ends wrapped around two 1 mm. diameter tungsten leads. These leads were then glass-blown on to the catalyst vessel through tungsten/glass seals. The catalyst vessel was placed on the apparatus, evacuated and "baked out" at 500°C. The copper wire was also heated electrically to a dull red heat to free the wire from any oxide, This process was continued usually for 8 - 12 hours. The final vacuum attained was 10^{-5}mm. The electrical circuit used to heat the wire is shown in Fig.4. Two 1 Kva 8:1 step down transformers were connected in parallel to carry the high current. The primary circuit contained a 0 - 14 ammeter, and a variable transformer. The leads in the secondary circuit were $\frac{1}{4}$" copper strip, which would carry 50 amp. of current without appreciable heating. This circuit was also used to heat the high temperature Kanthal furnace used in Part III experiments. The two-way switch enabled the variable transformer to be used also to control the low temperature furnace during methanol reactions.

FIG. 5.
CATALYST VESSELS.



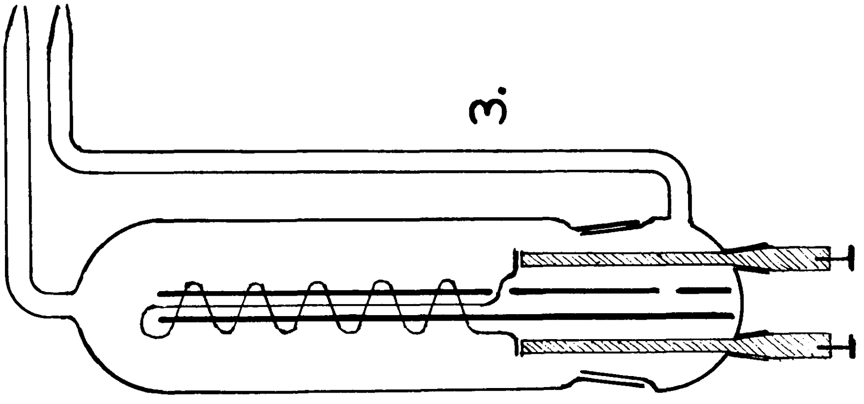
2.

COPPER FILMS.



1.

COPPER WIRES
LOW TEMP. OXIDATION.



3.

COPPER WIRES
HIGH TEMP. OXIDATION.

After the "baking out" process was complete, the catalyst vessel was immersed in liquid air, and the current passing through the copper filament increased to 7 amp.in the primary circuit, which corresponded to approximately 40 amp. in the secondary. The filament was evaporated in this way for four hours, after which it burnt out. A copper film had been formed on the walls of the catalyst vessel, and this was now brought to room temperature prior to methanol introduction to a pressure of 7 cm. It was heated to 300°C.,but there was no increase in pressure, and the film was an inactive catalyst.

Oxidation of this film was brought about using the same technique as with the low temperature oxidation of wires; that was treatment with 60 cm. pressure of oxygen at 300°C; the time of heating was 3 hours, after which the film was found to be completely black in colour. This catalyst proved to be active, 6 cm. pressure of methanol rising to 11.3 cm. at 300°C. within 1 hour. (Graph A_X). Partial reduction of oxide films was secured as before, in the case of the wire experiments. In Graph B_X is shown the result of methanol decomposition on the oxidised film, partially reduced with hydrogen.

At the conclusion of these experiments, the catalyst vessel was detached from the apparatus. The top of the vessel and the filaments were removed and 5 ml. of concentrated nitric acid was then added to the vessel, which was gently shaken, to dissolve the copper film. 5 ml. of distilled water was then added to increase the volume of the liquid in the vessel, and this was then washed into a 350 ml. conical flask with more distilled water. The solution was then diluted to approximately 40 ml., boiled briskly for a few minutes, and 0.5 g. urea added to destroy any nitrous acid present. Ammonia (0.88 s.g. diluted 50/50 by volume) was then added to remove excess nitric acid, until a precipitate formed, or the deep blue colouration due to the cuprammonium ion appeared; and the precipitate redissolved in dilute acetic acid. The solution was then cooled, 2 g. potassium iodide were added, and the liberated iodine titrated with 0.0256 N sodium thiosulphate solution using soluble starch as indicator. A few experiments with known amounts of copper showed this method to be satisfactory.

Titration indicated that the total weight of the copper film was 10.6 mg. The theoretical amount of cupric oxide which could have formed would have required only 0.25 mg. oxygen, and this would therefore explain why no appreciable decrease in pressure of oxygen was noted after the oxidation in the apparatus.

At the conclusion to Chapter I, an experiment was described wherein a copper film was deposited on top of a previously oxidised film. The technique used was as follows. Three tungsten leads were sealed into the catalyst vessel, containing two filaments of copper wire, joined so that one of the tungsten leads was common to both filaments. By using two of the three filaments, a copper film was prepared as above, from one of the copper filaments which again burnt out during the process. The time of evaporation, amperage, diameter of wire, geometry and temperature of substrate were as before, and it was assumed that a similar weight of film was deposited. Oxygen, to a pressure of 60 cm. was then admitted, and the film oxidised at 300°C. for 3 hours. Again the appearance of the film indicated complete oxidation. The oxidised film was cooled to room temperature. The second filament was then heated by passing 7 amp. through it, but due to the coating of oxide on the wire, it could not be brought to the red-heat required to decompose the oxide. Accordingly, methanol to a few cm. pressure, was admitted to the apparatus to react with the oxide on the hot wire. It soon commenced to glow brightly as oxide was removed. The oxidised film was not affected. The residual gases were then evacuated, and the oxidised film "baked out" at 500°C. with the filament glowing to remove final traces of oxygen. Finally the oxidised film was cooled to liquid air temperature and temperature of the filament increased to deposit a copper film on top of the oxidised film; after 3 hours the filament

"Burnt out" /-

6 cm. of methanol were then admitted to the reaction system, and reaction attempted at 300°C. After one hour the pressure increased to 10.5 cm. (Graph C_X).

Titration indicated that the total combined weight of both films was 31 mg.

EXPERIMENTAL FOR PART I OF CHAPTER II

Preparation of Synthetic Gas Mixtures:

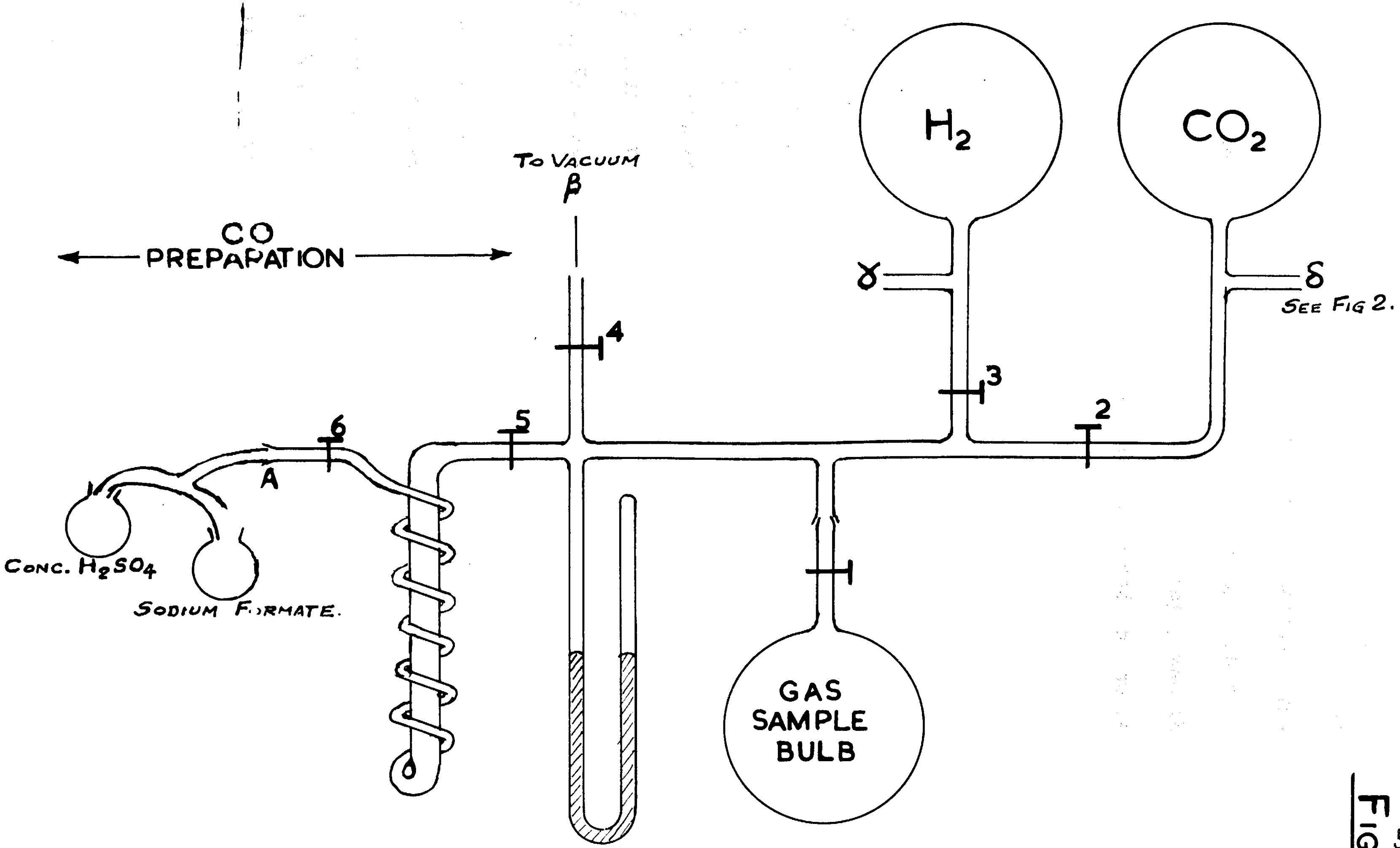
In order to analyse the products obtained from the various reactions described in Chapter I, it was necessary to prepare a series of synthetic gas mixtures of similar composition to that expected from the reactions. The mixtures prepared contained H_2, CO, CO_2 and CH_4. The apparatus used to prepare the individual gases and the gas mixtures is shown in Fig. 6.

Preparation of Individual gases:

HYDROGEN: Cylinder hydrogen was used, and was passed through a liquid air trap to remove moisture prior to admission to the storage bulb (Fig.6.) via.B_1 (Fig.2.) and tubing γ (Fig.6.)

CARBON DIOXIDE: This was prepared from Drikold, which was placed in a 250 ml. round bottomed flask fitted with an outlet and Bunsen safety valve. The rate of evolution of the carbon dioxide was controlled by altering the external temperature of the flask, and by a screw clip attached to rubber tubing on the outlet. The carbon dioxide evolved was passed through a cold trap at -78°C. to remove moisture and admitted to the storage bulb (Fig.6.) via.B_1 (Fig.2.), and tubing δ (Fig.6.).

FIG. 6.



GAS SAMPLE PREPARATION APPARATUS.

CARBON MONOXIDE: This was prepared as shown in Fig.6., by the reaction of concentrated sulphuric acid on sodium formate. The CO preparation apparatus was evacuated through tap 5, with the sulphuric acid cooled to -195°C. Tap 5 was then closed and a dewar of liquid air placed round the spiral trap. The sulphuric acid was then warmed to room temperature and poured on to the sodium formate in the other flask, by rotating both flasks about the Quick-fit joint A. Carbon monoxide could then be admitted to the major section of the apparatus through tap 5. The spiral trap served to dry the gas and act as a reservoir for liquid carbon monoxide should the pressure of the gas produced rise above 30 cm. (the saturated vapour pressure at -195°C.)

METHANE: This gas was prepared in the same apparatus as above except that only one flask was used, which contained a mixture of sodium acetate and soda lime. The flask was evacuated again through tap 5, and the spiral trap was cooled to -195°C. Methane was liberated when required by heating the flask, and admitting the gas to the major section of the apparatus.

Synthetic formaldehyde was not prepared owing to the readiness with which it polymarises.

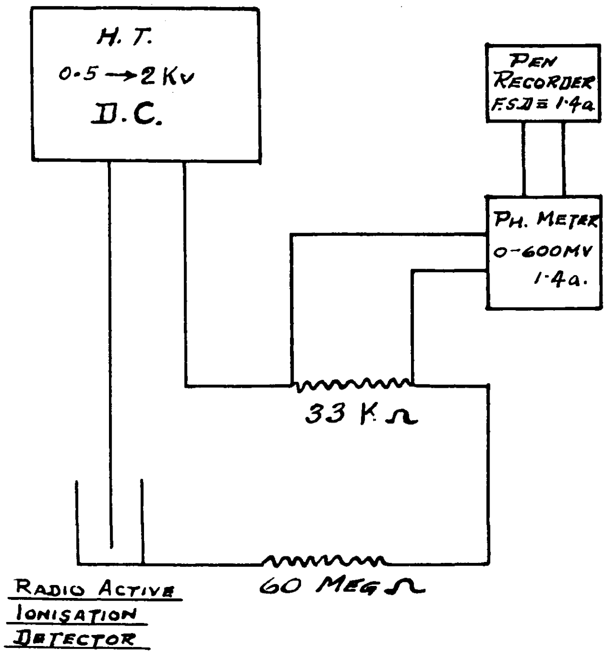
Preparation of Gas Mixtures.

EXAMPLE.

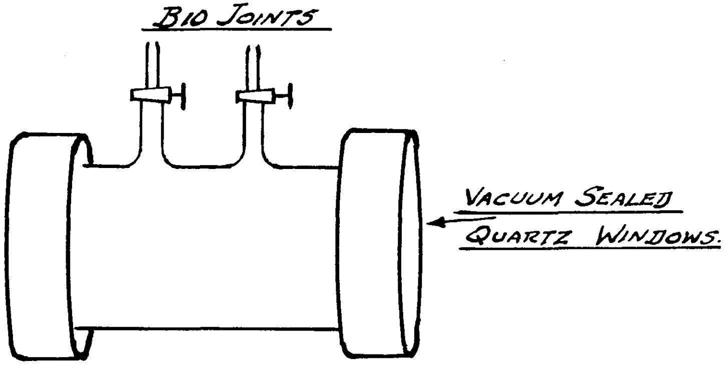
If an equimolar gas mixture of CO_2, CO and H_2 were required, amounting to a total pressure of 15 cm. the following procedure was adopted. The gas sample bulb was evacuated through tap 4, which was then closed. CO was then admitted to the sample bulb through tap 5 until the pressure reached 5 cm. The tap to the sample bulb was then closed, and the manometer section of the apparatus evacuated. CO_2 was then admitted to the manometer section through tap 2, until the pressure was greater than 5 cm., and the tap to the gas sample bulb then opened to allow entry of the CO_2. As soon as the pressure in the system was equalised, the tap to the gas sample bulb was closed. By manipulation of both taps in this fashion, the total pressure in the gas sample bulb was raised to 10 cm. Using a similar procedure with hydrogen, the total pressure within the sample bulb could be raised to 15 cm. An equimolar mixture containing 5 cm. pressure CO. 5 cm. CO_2 and 5 cm. H_2 was thus prepared. The sample bulbs, usually of 500 ml. or 1000 ml. capacity were normally allowed to stand for a minimum of several hours before usage to ensure complete mixing of the gases by diffusion.

Calibration of Infra-Red absorption measurements.

The Infra-Red gas cell used in the measurements is shown in Fig.7. It was fitted with two taps and Quick-fit joints so that it could be evacuated through one tap whilst the gas sample bulb fitted over the other. Evacuation was accomplished by attaching it to the gas sample preparation apparatus (Fig.6). By making use of the manometric section of this apparatus, gas mixtures of varied but known ratios, could be admitted to the cell to a known pressure. The Infra-Red absorption spectrum was then determined on the Perkin Elmer, double beam, direct ratio, Infra-Red Spectrophotometer. By undertaking a series of experiments such as is described above, a calibration graph was determined for carbon dioxide and carbon monoxide by plotting the optical density against the gas pressure of each component admitted to the cell. These calibration plots are shown in Graph XVIII, being the results of a series of experiments conducted at different times. Examination of the graph indicates that the results will be reasonably quantitative if a fresh calibration is conducted prior to each unknown measurement.



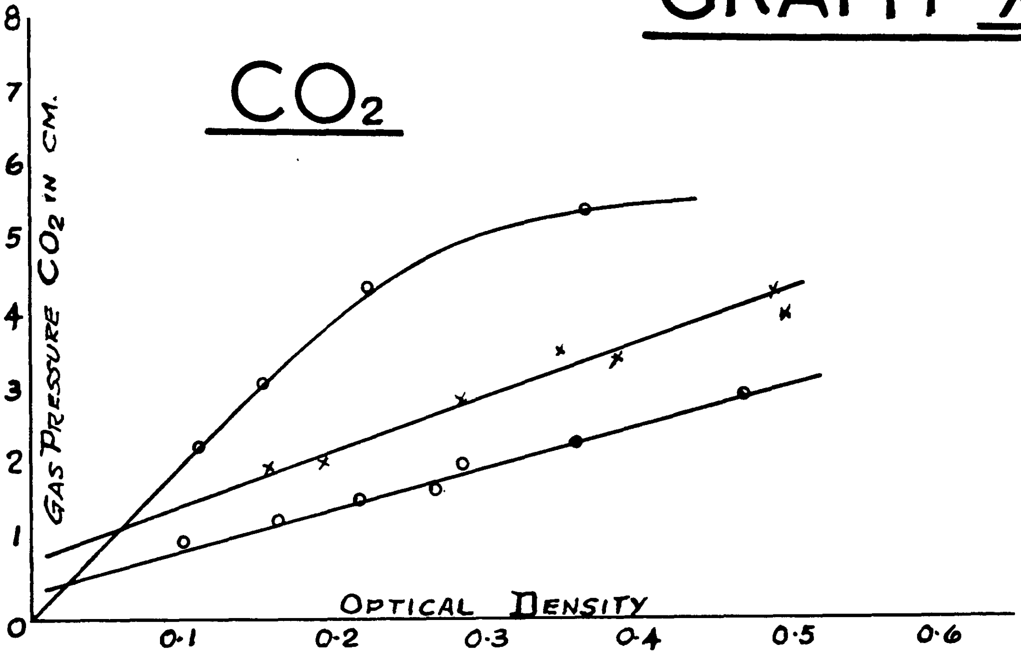
Circuit Diagram for Gas-Chromatography Apparatus.



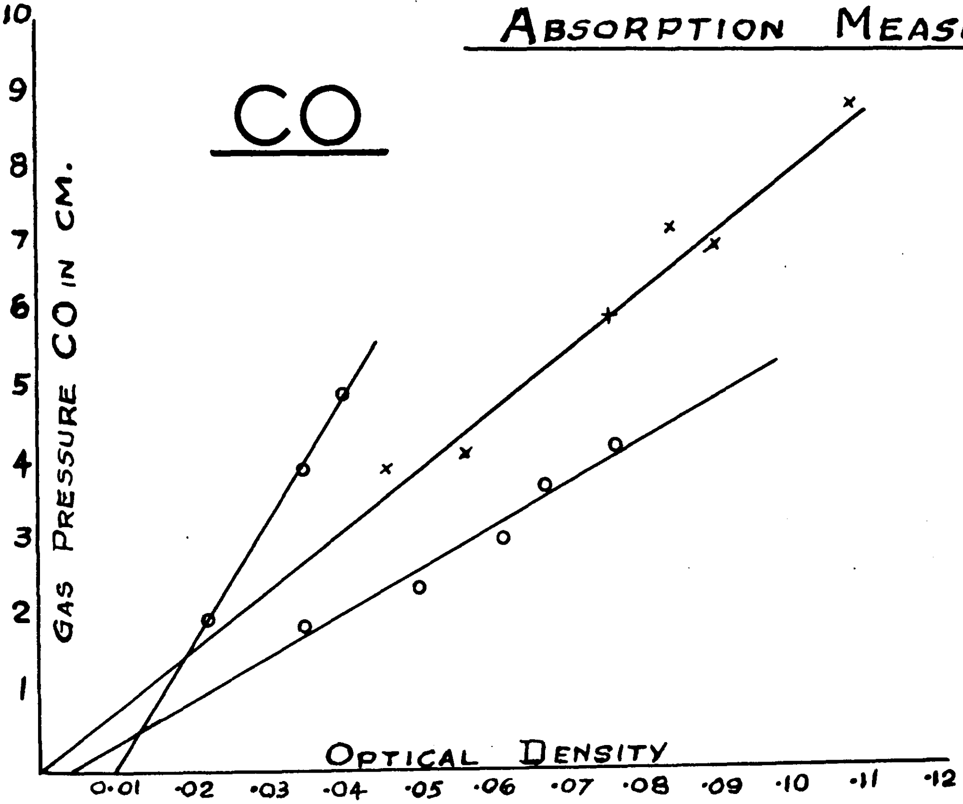
Infra-Red Gas Cell.

Fig. 7.

GRAPH XVIII



CALIBRATION OF INFRA-RED ABSORPTION MEASUREMENTS.



Analysis of Non Condensible Fraction:

In the case of the Infra-Red series of experiments, it was decided to separate the product mixture into two fractions, one condensible at -60°C. i.e. water and methanol, and the other gaseous at -60°C. i.e. H_2, CO, CO_2, HCHO. This was accomplished using the analytical section of apparatus attached to the main apparatus, shown in Fig.2. It consisted of a three-way, tap 1, within the circulating system, a manometer M_1, a cold trap CT_4, a Toepler pump, and two further three-way taps 2 amd 3, leading back into the circulating system. To analyse the product mixture at the completion of an experiment, the first step was to isolate the manometer section M_2 to allow complete circulation of the gases. The gas mixture was then expanded from the circulating system into the analytical section via. the three-way taps 1, 2 and 3. The mercury in the Toepler pump was then raised to the position of the seat of the lower Toepler valve. This was taken as the standard volume position used in all the ensuing pressure measurements. The total pressure of the expanded gas was then read on M_1 using a cathetometer.

A constant temperature bath of -60°C. was conveniently prepared using a chloroform "Slush bath" (86), and this was placed around the cold trap CT_4. With the aid of the Toepler pump, the gas mixture could now be circulated through the cold trap. The pressure in the system was measured at intervals of four strokes of the Toepler pump, until no change in pressure due to condensation of products was observed. This normally occurred after three or four such cycles described above. When this stage was reached, the three-way tap 3 was turned so that the non-condensible gases could be Toeplered through 3 and out at point y into a suitable receptacle, such as an Infra-Red cell or sample storage bulb.

In the case of the Infra-Red experiments, the volume ratio of the gases present in a sample Toeplered into the Infra-Red gas cell was determined. Knowing the original total pressure of non-condensible products at a given volume, the absolute amounts of each gas present could now be calculated.

Analysis of Condensible Fraction - Karl Fischer Titration.

An analytical method was now required to analyse the condensible fraction. After residual permanent gases had been removed from the circulating system the first step was to provide a small quantity of solvent into which the condensible fraction would dissolve. Accordingly, the temperature of the cold trap was lowered to -195°C, and the three-way tap 1 was closed. The mercury in the Toepler pump was raised, so that the cold trap was isolated. Methanol vapour was then expanded into the circulating system to an approximate pressure of 7 cm. Tap 1 was then opened and the vapour allowed to condense in the cold trap. The changes in pressure observed were followed using manometer M2. This process was repeated ten times, and finally, calculation showed that approximately 1 ml. of methanol solvent had been condensed in CT_4. The procedure above was adopted so that a controlled amount of solvent could be added to the trap. The next step was to admit dry nitrogen to the apparatus up to atmospheric pressure. This was done slowly via. the cold traps CT_2, cooled to -195°C. The cold trap CT_4 was then warmed to room temperature, lowering the cold trap slowly so that the liquid present distilled to the bottom of the trap. Finally, when room temperature was reached, the trap was removed at the Quick-fit joint and the stem of the trap rinsed with 1 ml. of the reservoir methanol. The liquid sample thus prepared was now ready for water determination by Karl Fischer method. In addition, dry nitrogen had also been admitted to the methanol reservoir M.R., so that the latter could be removed and a sample used to rinse the stem as above. A 2 ml. sample was also extracted from the reservoir for a blank determination of the water present in the methanol used as solvent.

The Karl Fischer Determination of Water.

The Karl Fischer reagent and a standard solution of Water (5 mg. H_2O/ml.solution) were obtained from BDH. The Karl Fischer reagent had a strength corresponding to 5 mg. water per ml. reagent. Standardisation of the reagent was accomplished by titrating against the standard Solution of Water. The reagent consists of a pyridine/methanol solution of sulphur dioxide and iodine. Reaction with water may be considered to take place according to the simplified equation:

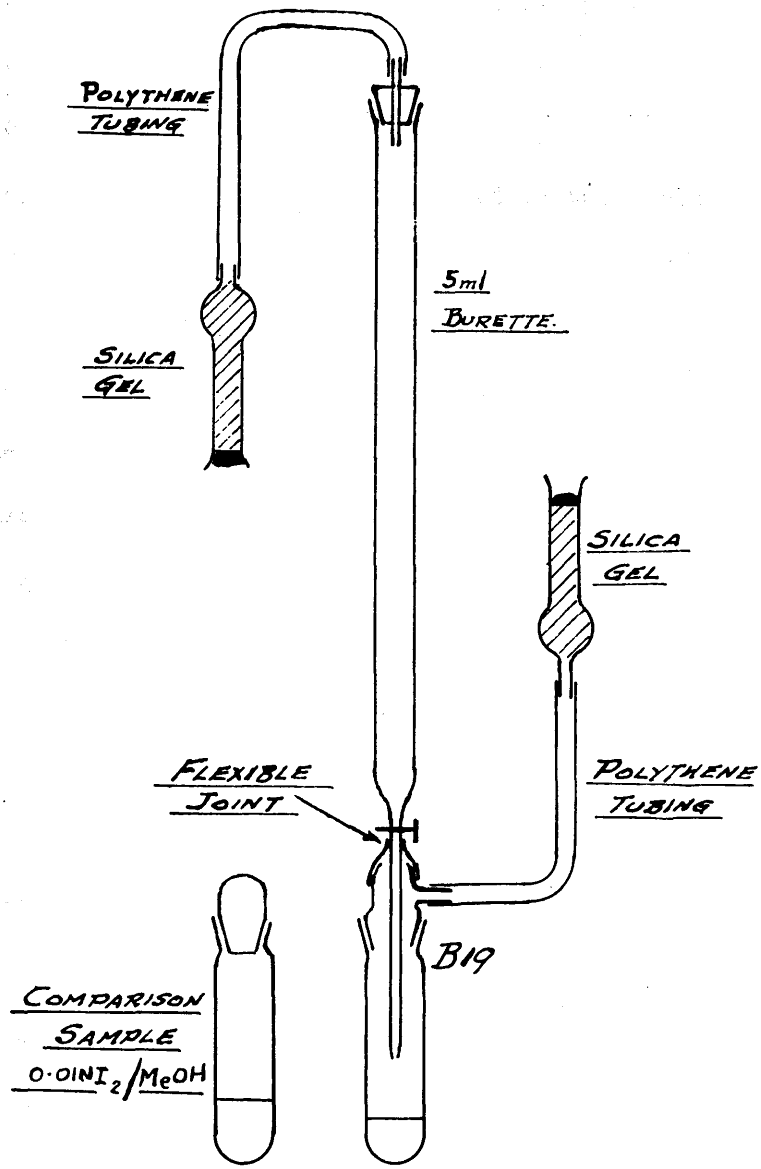
$$H_2O + SO_2 + I_2 \rightarrow SO_3 + 2HI$$

Iodine is therefore removed from the reaction mixture during titration. The visual end-point was therefore recognised by the appearance of excess iodine in the solution. This was compared against a synthetic sample of 0.01 N. Iodine in methanol solution, as suggested by Mitchell (42). The apparatus used is shown in Fig.8. The Karl Fischer reagent was placed in a 5 or 10 ml. burette, which was fitted with an extended delivery tube below the tap. This was acheived by breaking off the tip, and glass blowing a suitable length of soda glass tubing between the tip and the tap of the burette. The tip of the burette therefore extended well inside the test tube containing the solution for titration. This latter test tube was fixed to the burette by a flexible piece of polythene tubing to allow agitation of the solution during titration. The whole apparatus was protected from atmospheric moisture with Silica Gel drying tubes. The comparison sample of 0.01 N I_2/MeOH was mounted alongside the unknown sample in front of a white background. A piece of cobalt glass was found to facilitate observation of the end-point. Successive titrations of the standard Solution of Water showed differences of only 0.1 ml; that is, an accuracy of 0.5 mg. water.

Efficience Test of Apparatus.

The method used to isolate the various condensible and non-condensible fractions of the products of reaction, in a form suitable for analysis, has been described. It was now essential to test the method using synthetic gas mixtures, particularly towards inadvertent admission of water to the liquid fraction. Accordingly, the one

FIG. 8.



KARL FISCHER TITRATION APPARATUS.

litre gas sample bulb (Fig.6) was filled with a mixture of carbon dioxide and carbon monoxide in the approximate ratio of 1:2.

Pressure of CO_2 = 8.8 cm. i.e. 33% Mole.

Pressure of CO = 17.9 cm. 67% Mole.

Considering now Fig.2; water was admitted to the circulating system from the reservoir M.R. to a pressure of 15.cm. Methanol was also admitted to the system to a pressure of 1.65 cm. Finally, 10.20 cm of the gas mixture described above was admitted to the system via. the point Z.

The circulating system now contained a synthetic gas mixture similar to the reaction product mixture.

i.e.

$$\left.\begin{array}{lcl} H_2O & = & 1.5\ \text{cm.} \\ \text{MeOH} & = & 1.65\text{cm.} \\ \text{Mixture} & = & 10.21\text{cm.} \\ \text{Total Pressure} & = & 13.35\text{cm.} \end{array}\right\} \text{408 ml.volume.}$$

Pressure on expansion into analytical section = 11.50 cm./460 ml.volume. Cold Trap then cooled to -78°C, and Gas mixture Toeplered through trap, until constant pressure was reached.

Pressure now = 8.50 cm./460 ml.volume.

A portion of this sample was now Toeplered into the Infra-Red gas cell.

Decrease of Pressure in circulating system = 2.65 cm./460 ml.volume

≡ 10.40 cm/126 ml.volume (= volume of section from Toepler valve to gas cell)

∴ Pressure of mixture in gas cell = 10.40 cm.

$$\left.\begin{array}{r}\text{i.e. } 3.4 \text{ cm. } CO_2 \\ 7.0 \text{ cm. } CO.\end{array}\right\}$$

Absorption spectrum of this mixture on Perkin Elmer I.R.Spectrophotometer was now determined and by referring to Graph XVIII, the following values were obtained:

$$\left.\begin{array}{l}CO_2 - \text{ Optical density} = 0.384 \equiv 3.6 \text{ cm.} \\ CO - \text{ Optical density} = 0.089 \equiv 7.1 \text{ cm.}\end{array}\right)$$

Comparison of the two bracketed values show that the results are quite acceptable quantitatively.

The liquid fraction containing the water was then prepared as described previously. Before the water estimation was attempted however, the total volume of liquid present in the tube was found as follows. The tube was clamped in a vertical position, and the difference in height between the meniscus of the liquid and the bottom of the tube measured with a cathetometer. Two readings were taken at the top and bottom of the meniscus and the average value taken as the upper limit of the level of the liquid. The tube had been calibrated previously with known volumes of water, and the results plotted on a graph. This method was found to be experimentally simple, and accurate to within 0.1 ml.

The solution was then titrated with standard Karl Fischer reagent.

Titration of solution = 2.96 ml. K.F.R./ 2 ml.total solution

Blank titration of methanol solvent = 1.08 ml.K.F.R./ 2ml.total solution.

∴ Water estimated ≡ 1.88 ml. K.F.R. (K.F.R. = Karl Fischer Reagent)

Standardisation of K.F.R. with Solution of Water (5 mg./ml.)

2.55 ml. K.F.R. ≡ 10 mg. water.

∴ 1.88 ml. K.F.R. ≡ 7.3 mg. water.

Amount of water admitted to circulating system = 1.50 cm./460 ml.volume.

≡ 6.6 mg. water.

Thus there was a quite acceptable error of approximately 1 mg.water,

CONCLUSION: The apparatus used to separate the required fractions in a form suitable for analysis was efficient, and foolproof against inadvertent admission of water. Although the results of the Infra-Red gas analysis described appear to be quantitative; in practice this was found to be the exception rather than the rule. When such an analysis was attempted on the products obtained from a methanol reaction, it was found that there was a variation in calibration even during the time required to obtain an absorption spectrum. Qualitative results alone were therefore obtained by this method.

EXPERIMENTAL FOR PART II OF CHAPTER II

Water Gas Experiments.

These experiments were undertaken to determine whether carbon monoxide and water could be converted to carbon dioxide in the presence of flame-quenched catalysts.

They were conducted using the circulating system and catalyst vessel of Fig.2. Water was admitted to the circulating system from the reservoir M.R. and carbon monoxide was then admitted through z. to the required pressure measured by the manometer M_2.

1st Experiment.

A flame-quenched catalyst (180 cm^2 geometrical surface area) was prepared containing 24.2 mg. oxygen. This was placed in the apparatus and "baked out" prior to admission of water and carbon monoxide as described above. These gases were circulated over the catalyst, heated to 300°C. for one hour, the normal time involved in a dehydrogenation reaction. At the end of this period the catalyst vessel was cooled, and the products expanded through Taps 1 and 3, into the analytical section of the apparatus. The pressure was noted, and the cold trap CT_4 cooled to -195°C. The gases were then circulated through this trap until no further decrease in pressure due to condensation of water and carbon dioxide, was noted.

Initial pressure of CO admitted to circulating system = 7.12 cm./ 357 ml.volume

= 6.03 cm/ 421 ml. (= total volume of circulation system + analytical section).

Residual pressure after freezing to -195°C. = 0.25 cm./421 ml./-195°C.

= 0.275cm./421 ml./20°C.

$$\therefore \frac{0.275}{6.03} = 4.5\% \text{ carbon monoxide remaining.}$$

i.e. 95.5% conversion to carbon dioxide.

At the completion of the reaction, the catalyst was removed and re-weighed. From the gravimetric experiments, it was found that 18.7 mg. out of the total 24.2 mg. oxygen present on the catalyst had been removed during the reaction.

Experiments 2 and 3.

These were conducted in an identical manner except that no catalyst was present in experiment 2, and a pure copper catalyst was used in experiment 3.

Effecting a calculation similar to that used in experiment 1, showed 15% conversion to CO_2 in the case of experiment 2, and only 6% conversion to CO_2 in the case of experiment 3.

Details of experiment 4 have already been supplied.

In all these cases the same geometrical surface area of wire was used, namely 180 cm^2.

It was concluded that carbon monoxide could be converted to carbon dioxide in the presence of water and a flame-quenched catalyst, within the time normally taken to complete a dehydrogenation reaction. The water gas reaction probably took place, but the extent of the reaction was not determined.

EXPERIMENTAL FOR PART III OF CHAPTER II

This section will be concerned with preliminary attempts to obtain quantitative analysis of the reaction products using gas chromatographic techniques. Gas chromatography of the gases CO, CO_2, H_2 was offered to be undertaken by British Hydrocarbon Chemicals Ltd., at Grangemouth using a Perkin Elmer Thermal Conductivity Unit. Formaldehyde could not be estimated by gas chromatography for reasons described earlier, and hence this gas had to be separated from the CO, CO_2, H_2 mixture. This was acheived by separating the fractions MeOH, H_2O, HCHO, and H_2, CO, CO_2, as described in Part 1, at a temperature of -105°C. This temperature was conveniently maintained using a methanol "Slush bath", prepared by cooling a Drikold/MeOH mixture with liquid air until solid methanol appeared in equilibrium with the liquid phase. The H_2, CO, CO_2, was Toeplered into a suitable sample vessel for despatch to British Hydrogen Chemicals Ltd., and the MeOH, H_2O, HCHO, collected in methanolic solvent as described in Part I.

It was now necessary to estimate the formaldehyde present in the above solution, and this was accomplished colorimetrically by determination with chromotropic acid.

Estimation of Formaldehyde : Method of Bricker & Johnson (50)

A methanolic solution of formaldehyde may be detemmined colorimetrically by making use of the violet coloration obtained by reaction with chromotropic acid solution in the presence of concentrated sulphuric acid. (Disodium salt of 4,5 - dihydroxy - 2,7 - naphthalene disulphonic acid). The sensitivity of the method is such that the sample must be diluted until not more than 150 mcg formaldehyde are present in the solution. The temperature at which the colour is developed is not too critical but 100°C is usually selected,being convenient. 30 minutes, a 500:1 ratio of reagent:formaldehyde, and at least 5 ml. conc.sulphuric acid is necessary to obtain full colour development.

Calibration solutions were of course essential, and were prepared as follows. The starting material was 40% Formalin solution the strength of which was estimated by oxidation to formic acid with excess of sodium iodate. Iodine was then liberated from the excess iodate and titrated with standard sodium thiosulphate using soluble starch as indicator (87). 25 ml. of the 40% Formalin was diluted to 100 ml. with water in a graduated flask. 10 ml. of this solution was then diluted to 100 ml.with water. 1 ml. of this solution was finally diluted to 100 ml. with methanol to provide a solution containing 100 mcg formaldehyde/

ml.methanol solution. By diluting 10, 20, 30 and 40 ml. of this solution to 50 ml. with methanol then a series of 5 calibration solutions were prepared containing 20, 40, 60, 80 and 100 mcg formaldehyde/ml. methanol solution respectively.

Chromotropic Acid Solution.

10% aquerus solution was prepared by dissolving 1.0 g. chromotropic acid in 10 ml. of water and filtering the solution. The solution was stored in a brown bottle and was discarded after a week, when fresh solution was made up.

1 ml. of each of the calibration solutions prepared, was then placed in a test tube and 0.5 ml. chromotropic acid solution added. 5 ml. conc. sulphuric acid was then poured in carefully, and the test tubes were then stood in a beaker of boiling water for 30 minutes. At the same time a reagent blank was prepared containing 1 ml. methanol, 0.5 ml. chromotropic acid solution and 5 ml. of conc. sulphuric acid. At the end of the 30 minutes, each of the solutions were diluted with water to 50 ml. in a graduated flask. The extinction of each solution was then determined against the reagent blank on a Unicam S.P. 500.
at 570 m/u. The extinction, read on a logarithmic scale, was then plotted against the weight of formaldehyde in mcg. to give the required calibration graph. Provided that a fresh reagent blank was prepared before each unknown determination, then this calibration

graph remained constant.

In the case of the liquid fraction to be determined, 0.25 ml. of the solution was extracted by means of a 1 ml. Hamilton syringe, fitted with a glass capillary delivery tube, and injected into 0.5 ml. chromotropic acid solution. 5 ml. conc. sulphuric acid were then added, and the procedure repeated as described above. Only in rare cases was it found necessary to dilute the final solution to obtain an extinction value within the calibration graph.

Preparation of Samples for analysis at B.H.C.

The following method was therefore adopted. Four flame-quenched catalysts (180 cm^2. geometric surface area) were prepared containing 7.4 mg., 16.5 mg., 18.8 mg. and 40. 4 mg. oxygen. Methanol reactions at 300°C. were then conducted on each of these catalysts in the customary manner. The products were then expanded into the analytical section of the apparatus and the methanol, water and formaldehyde separated by cooling the cold trap CT_4 to -105°C. and circulating the gases through the trap until constant pressure was reached. The cold trap was then cooled to -195°C., and the remaining gases again circulated through the trap until constant pressure was reached. The difference in pressure noted was due to condensation of carbon dioxide. Finally, the trap was warmed again to -105°C and the gases again circulated until the original pressure reading obtained at -105°C was regained. The residual gases CO, CO_2, H_2, were then Toeplered into a sample bulb, and compressed with mercury to atmospheric pressure. The gas samples thus obtained were despatched to British Hydrocarbon Chemicals Ltd., at Grangemouth. The remaining liquid sample was isolated as usual in methanol solvent. The total volume of the solution was determined using a cathetometer as described previously, and 0.25 ml. solution was then extracted for formaldehyde analysis. The volume of the solution remaining was again determined, and then titrated with Karl Fischer reagent to estimate the water present.

The results have been tabulated earlier. A sample calculation of the results is not included at this stage, as an exactly similar calculation will be given in Part IV of this experimental chapter, where the final analytical technique is developed.

EXPERIMENTAL FOR PART IV OF CHAPTER II.

This part will be concerned with the final analytical techniques used to solve the reaction mechanism occurring on the various catalysts. The results of the permanent gas analysis performed on the Perkin-Elmer thermal conductivity unit were shown to be unsatisfactory, due to incorrect carbon:hydrogen ratios. For example, consideration of Experiment 3 (Table I) shows the B.H.C results to be:

CO_2 = 33.4 mg. $\therefore$ C = 9.1 mg.
CO = 18.8 mg. $\therefore$ C = 8.1 mg.
$\therefore$ total C = 17.2 mg.
also total H = 2.88 mg.

$\therefore$ C:H = 17.2 : 2.88 ≈ 6 : 1
But C : H ratio for methanol = 3 : 1

$\therefore$ a large discrepancy exists.

However, consideration of results obtained on the basis of the CO_2 freezing experiments show correct C : H ratios.

We quote Sample 1:

CO_2 = 56.4 mg. $\therefore$ C = 15.4 mg.
H_2O = 15.8 mg. $\therefore$ H = 1.75 mg.
Hydrogen = 2.95 mg. $\therefore$ H = 2.95 mg.
Total H = 4.7 mg.

$\therefore$ C : H ratio = 15.4 : 4.7 3 : 1

On the basis of convenience and accuracy it was therefore decided to design and construct a gas chromatography unit suitable for analysing the products immediately at the completion of a reaction. In addition it was found necessary to oxidise the catalysts with oxygen labelled with the oxygen-18 isotope, to distinguish between this oxygen and the methanol oxygen. It was therefore necessary to develop an experimental technique to accomplish this, and to prepare the products in a suitable form for mass spectrometric analysis.

The Gas Chromatography Unit.

As stated previously, normal ionisation detectors cannot be used for permanent gas detection as their ionisation potentials are similar to, or higher than the usual carrier gases. Willis (88), however, in an article in Nature has described a suitable ionisation detector for permanent gases. This involves the use of an ethylene bleed into the carrier gas to give a steady ionisation current. Introduction of a permanent gas into the system causes a depression in the ionisation current and permanent gases are therefore observed as negative peaks.

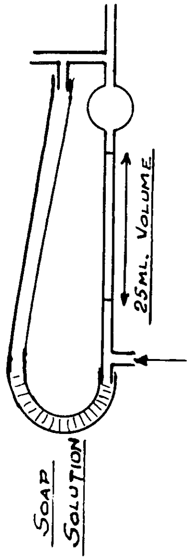
For choice of column a variety of suggestions were available. Messrs. British Hydrocarbon Chemicals Ltd., suggested a 8' charcoal column for H_2, CO and CO_2 using N_2 carrier gas. Members of the research group at Thornton Research Centre (89), suggested that H_2, CO, CO_2, should be separable in two experiments on an activated molecular sieve column (5A., 50-60 mesh). A first experiment using the H_2 carrier should give separation of CO, CO_2 while a second experiment using N_2 carrier should give the hydrogen peak. Kyryacos and Boord (90) separated H_2 and CO again on a 16' molecular sieve type 5A column at 100°C, while Darby and Kemball (36) used a 6' charcoal column (40-60 mesh) for H_2 and CO, but an 8" charcoal for CO_2.

Kyryacos and Boord (91) however separated CO_2 on a 30-60 mesh silica gel column at 80°C. Gunning (92) however, used a silica gel column with N_2 carrier to separate H_2 and CO.

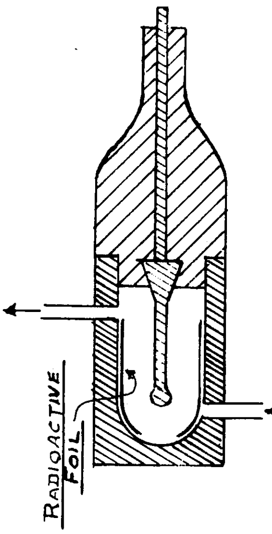
For gas sample admission, a method by Littmann (93) was rejected on the grounds of complexity and a simpler tap system used.

The final design is shown in Fig.9. The complete apparatus was built on an Angle-Iron framework supported by four trolley wheels, and was provided with a vacuum lead, which could be connected to any part of a vacuum apparatus by means of a flexible ball and socket joint. The carrier gas was admitted to the system via. an Edwards High Vacuum Needle Valve, and drying tube packed

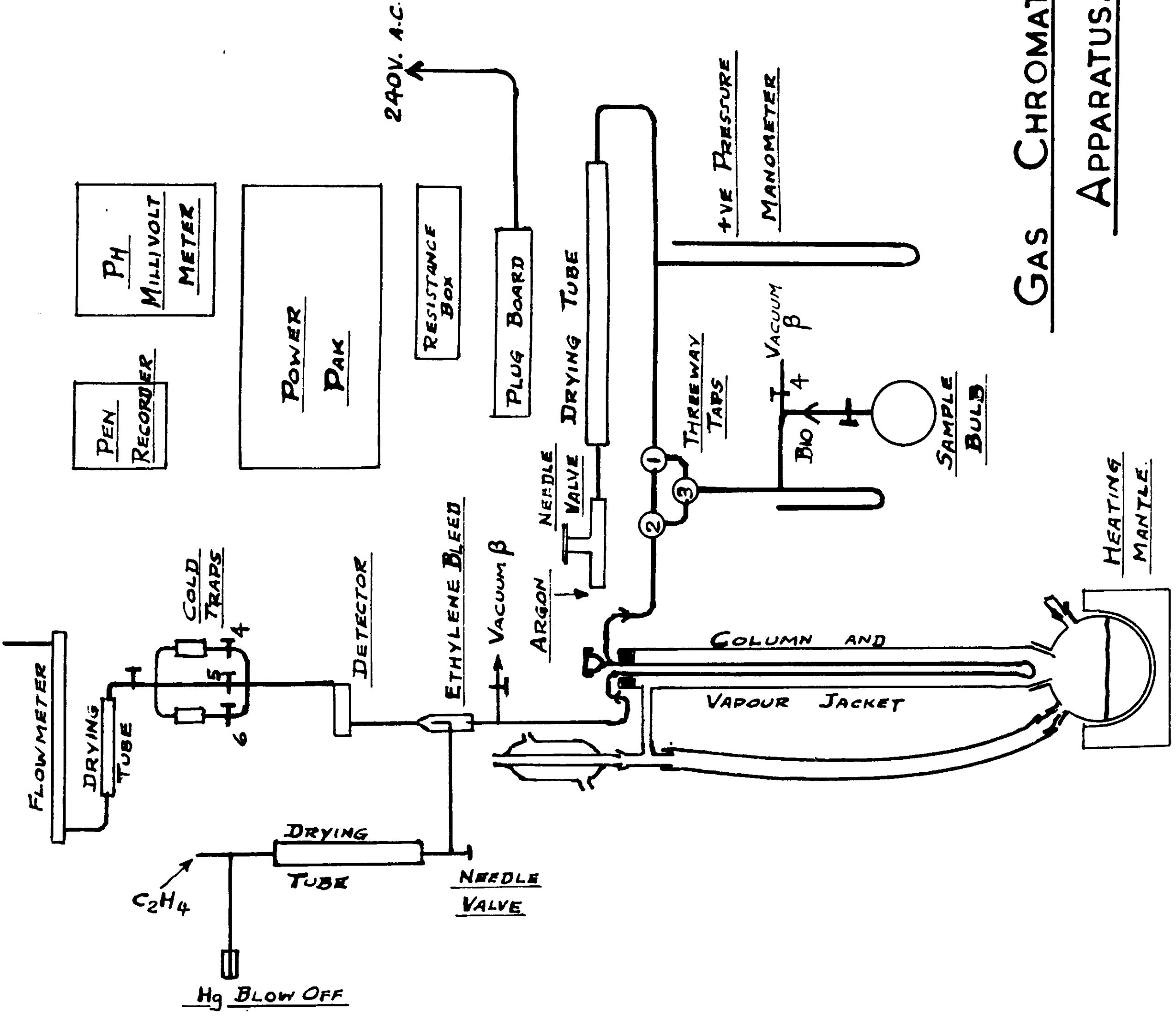
FIG. 9.



FLOWMETER.



IONISATION DETECTOR.



GAS CHROMATOGRAPHIC APPARATUS.

with activated molecular sieve type 5 A(1/16" pellets). The pressure of the carrier gas admitted to the column was measured on an 80 cm. length mercury manometer which was therefore capable of measuring pressures from 1 cm. up to 2 atm. The end not connected to the flow system was open to the atmosphere.

Gas Sample Admission.

This was accomplished by means of the three, three-way taps shown. Taps 1 and 2 were normally open so that the carrier gas flowed directly through 1 and 2. The sample bulb containing the gas sample at low pressure (several cm.) was fitted at the B.10 Quick-fit joint shown, and the sample system was evacuated through tap 4 and three-way tap 3 up to the three-way taps 1 and 2 which were carrying the flow of carrier gas. Tap 4 was then shut to isolate the system from the vacuum pump, and the gas sample then admitted to the system to a pressure indicated on the capillary mercury manometer. The three-way tap 3 was turned through 180° so that the known pressure of sample was trapped in the volume between taps 1, 3 and 2. Three-way taps 1 and 2 were then turned through 90° to deflect the carrier gas through 1, 3 and 2, thus flushing the sample into the carrier stream. The distance between tap 2 and the column was as small as was practically possible to obtain as near as possible "Plug" admission of the sample. This system on trial was found to be convenient and satisfactory.

The Column.

The column selected was molecular sieve type 5 A ground to 30-60 mesh and packed into a 5' column of 5 mm.internal diameter according to the method of James and Martin (94). This involved holding the column against the rotating shaft of an electric motor containing a curved piece of rubber tubing. The column vibrated at high frequency and packed the material efficiently. The material was held in place by means of small plugs of glass wool. The ends of the column were fitted with side arms containing B7 Quick-fit joints, ensuring simple removal and replacement of columns. One of the ends of the column was fitted with a serum cap for admission of gas or liquid syringe samples. The other end was sealed after admission of the packing material. The design of column used by Kyryacos and Boord (90) whereby the column lengths were connected at the bottom with capillary tubing was tried and rejected on the grounds that excessively high inlet pressures were required to ensure a reasonable flow rate. The 5 mm. internal diameter tubing was therefore employed throughout the column length, the packing material filling the whole column.

The vapour jacket was constructed from a 5 litre B.34 3-necked flask, supported by a heating mantle. Into the B.34 neck of the flask was fitted a 4' length of 4 cm. diameter tubing connected to a B.34 cone. The upper end of this tube was sealed to the column with rubber tubing and copper wire. Any desired liquid could be placed in the flask and boiled, the vapours of which would then pass up the column, be condensed in the condenser and return to the flask again. The condenser was placed in the position shown so that the condensate would not cool any part of the column in returning to the flask.

For efficient evacuation of the column at any time, vacuum "Take-offs" were provided on both sides of the column packing as shown.

Choice of Columns.

Gaseous Fraction: H_2, CO, CO_2.

Using Argon carrier, a 5' Molecular sieve type 5 A column at 100°C, was found to give good resolution of H_2 and CO, but CO_2 would not come off the column. Helium was then used as the carrier gas but CO_2 still would not desorb from the column and the sensitivity of the H_2 and CO peaks became poor.

When an 8' charcoal column was used at 100°C, the CO_2 retention time was 7 minutes, but by this time the peak had broadened into a band and quantitative measurement would be poor. Also the retention times for H_2 and CO were within 15 seconds of one another; an inadequate separation.

Accordingly, a 12" charcoal column was tried and although no resolution was obtained between the H_2 and CO, the CO_2 retention time was reduced to 2½ minutes, and a good peak was obtained. Therefore it was decided to carry out the analysis in two experiments:

(1) <u>H_2 and CO.</u>

Argon Carrier; 5' Molecular sieve Type 5 A column, 30-60 mesh;

Retention time H_2 = 55 seconds

Retention time CO = 2½ minutes.

Temperature of column = 100°C.

Flow rate = 75 ml./minute; Positive Pressure = 580 mm.

Voltage applied to detector = 1700 volts.

N.B. The Molecular sieve column was "baked out" at 350°C under vacuum for several hours before using.

(2) <u>CO_2</u>

Argon Carrier; 12" Activated Charcoal column 30-60 mesh;

Retention time H_2 + CO = 1 minute.

Retention time CO_2 = 2½ minutes

Temperature of column = 100°C.

Flow rate = 150 ml./minute: Positive Pressure = 230 mm.

Voltage on detector = 1800 volts.

Liquid Fraction.

It was necessary to separate the water from the methanolic solution so that it could be trapped out in acetic anhydride solution and the acetic acid produced analysed on the mass spectrometer. The column chosen was 5' 25% Carbowax on celite 80 - 100 mesh, using Argon carrier. At 100°C the retention time MeOH = 1½ minutes - 2 minutes : Retention time H_2O = 2 minutes. If more than 20 μ-litres solution were admitted to the column by the Agla syringe, then the separation was poor, as the retention times were close.

However at 78°C Retention time MeOH = 1 - 2½ minutes.

Retention time H_2O = 4½- 5 minutes.

50 μ-Litres solution could be injected on to the column and good separation was obtained between the methanol and the water.

The Ionisation Detector.

Details of the detector are shown inset.

It consisted of a brass body with a smooth hollow chamber and two outlets. The top of the body was threaded to fit a standard automobile sparking plug. The internal terminal of this sparking plug was re-designed so that wires or brass rods of varying diameter could be soldered to it.

After several trial experiments, the best background was obtained using a smooth brass rod 0.2 mm. in diameter, and having present inside the detector 4 cm^2 of silver foil coated with α and β emitting Radium D, with a specific activity of 37.5 c/cm^2. This was obtained from the Radiochemical centre at Amersham, Code No. RBM.3.

A high voltage was supplied to the terminal of the sparking plug, and a terminal on the brass body of the detector was provided. The circuit diagram for operating the detector is shown in Fig.7. This was the result of many experiments to determine the most stable background consistent with good sensitivity of detection. A Power Pak unit supplied a variable high d.c. voltage to the terminal of the sparking plug. Any tendency for spurious discharge to occur with consequent increase in background instability was reduced by raising the potential of the body of the detector by means of the 60 megohm resistor shown. The current flowing was indicated by measuring the drop in potential across the 33,000 ohm resistor, with an E.I.L Model 23 A Direct Reading PH Meter incorporating a millivoltmeter scale. Any change in the ionisation current was therefore detected by the PH meter and coupled pen recorder (Everett Edgcumbe "Inkwell" Dwarf Recorder).

Ethylene Bleed.

In order to provide a steady background current which would be depressed by admission of permanent gases, it was necessary to bleed ethylene into the system, after the column but before the detector. Initially this was done by careful manipulation of the ethylene needle valve, but considerable time and skill of the operator was necessary to accomplish a steady background by this method, and the following procedure was therefore adopted. The column heated in its vapour jacket, was evacuated up to the ethylene needle valve, which was then opened and ethylene drawn through the column and into the vacuum pump. After a few minutes the ethylene flow was stopped at the needle valve and the column was continued to be evacuated for approximately 5-10 minutes. Evacuation was then terminated and Argon allowed to flow into the apparatus until atmospheric pressure was reached. The various taps were then opened and the Argon pressure to the inlet of the column allowed to build up until a reasonable flow rate was obtained. Ethylene had, in this manner, become adsorbed on the column. High voltage was then applied to the detector, and after approximately 10 - 15 minutes, the background current due to the ionisation of ethylene commenced to rise as ethylene was desorbed from the column by the carrier gas. The current soon reached a steady value and remained thus indefinitely. Even when a column was removed from the apparatus and replaced some time later, the same steady background could be obtained once the carrier gas commenced to flow through the column. The ethylene would be removed completely from the column by evacuation at 100°C.

THE COLD TRAPS: The cold traps were used to separate the water from the methanolic solution prior to mass spectrometric determination.

THE FLOWMETER: The flowmeter was of the simple soap film type shown inset, Fig.9. By raising the polythene tubing containing the soap solution a bubble could be formed at the entrance of the gas flow, and its rate of travel timed between the two calibration marks corresponding to 25 ml.

FINAL ANALYTICAL TECHNIQUE.

Experiments A → F using oxygen-18 tracer.

In the following experiments, the copper wire catalysts were oxidised under varying conditions with oxygen-18 labelled oxygen.

As flame-quenched or furnace-quenched catalysts could not be oxidised with oxygen-18 during their normal mode of preparation, a new method of preparation was developed. The catalyst vessel used is shown in Fig.5. A length of 24 s.w.g. Copper Wire, one yard in length, was selected (geometrical surface area = 16 cm^2) and surface dirt cleaned from it by light abrasive action with fine emery paper, followed by washing it in methanol. This was then formed round the centre piece of glass tubing shown in Fig.5, and supported by fine glass hooks fixed to the outer edge of the tubing. The ends of the wire were attached to two lengths of 16 s.w.g. gold wire which in turn were connected to the two silver steel terminals shown. As the furnace could not be placed in such a position that the steel terminals were being heated during a methanol reaction, then such a precaution prevented oxidised copper wire adjacent to the terminals being situated outside the reaction zone.

Catalysts A, B, C, were therefore prepared by heating such a copper wire electrically to 800-900°C. in the presence of 5-6 cm. pressure of oxygen-18, which was admitted to the apparatus from the 2 litre storage bulb shown in Fig.2. The reaction was followed by observing the decrease in pressure due to uptake of oxygen. When sufficient oxidation had taken place, the copper filament was cooled, the decrease in pressure of oxygen-18 noted, and the remainder Toeplered back into the storage reservoir via. three-way taps 1, 2, and the upper of the two Toepler valves. Catalyst C was oxidised for a greater length of time than A and B.

Catalyst D, E, F were prepared by low temperature oxidation, as has been described previously, using 115 cm^2. 18 s.w.g. copper wire. The catalyst vessel used is again shown in Fig.5. In order to obtain the necessary pressure of O^{18} within the circulating system, the tap to O^{18} reservoir was opened to allow O^{18} to flow into the circulating system and through the three-way tap 3, to a cold finger at -195°C. placed on Y. (Fig.2). After sufficient O^{18} had condensed, the tap to O^{18} reservoir was shut and the cold finger was warmed and the O^{18} pressure allowed to build up within the circulating system to the required value (60 cm. pressure). Excess O^{18} was returned to the reservoir through the tap connected to circulating system and CT_3. CT_3 was always cooled to -78°C. to reduce the partial vapour pressure of mercury present in the oxygen.. The catalysts were then oxidised at 60 cm. pressure and 300°C. until the required uptake of oxygen had been observed. After the oxidation, CT_3 was cooled to -195°C. to reduce the vapour pressure of oxygen to 30 cm., and the O^{18} in the circulating system Toeplered back into the reservoir as described previously. Catalyst F was a work hardened wire described in Chapter IV, but the experimental conditions of oxidation and methanol reaction were identical with Catalyst D, and it is therefore included in the description. Catalyst E was exceptional in that the temperature of oxidation was inadvertently raised to 500°C. for one hour out of the total six hours of its oxidation.

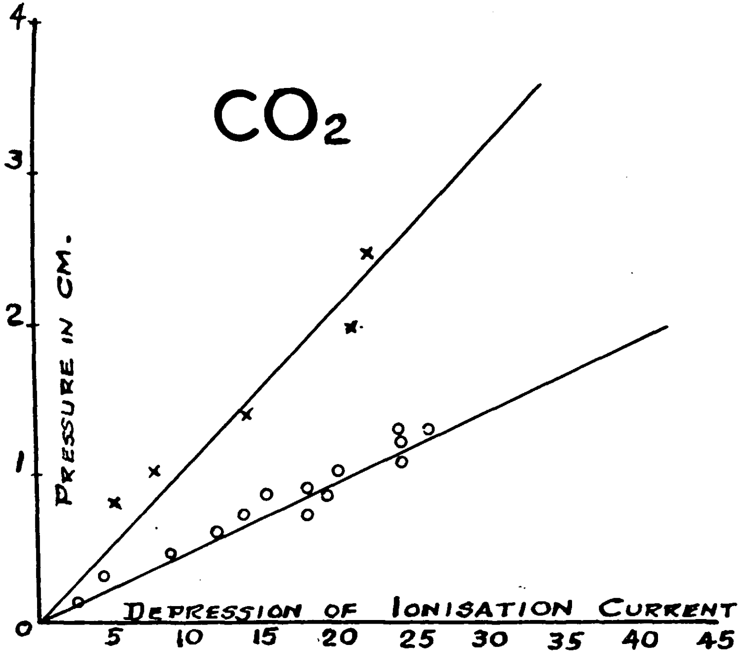
Methanol reactions were then conducted on each of these catalysts at 300°C. After the reaction was complete, the catalyst vessel was cooled and the final pressure noted. The gases were then expanded into the analytical section of the apparatus and after noting the pressure, CT_4 was cooled to -78°C., -105°C, and - 195°C in turn; circulating the gases through the trap until a constant pressure reading was obtained on M_1. Finally CT_4 was warmed to -105°C. and the gases H_2, CO, CO_2 Toeplered into a 500 ml. sample bulb for gas chromatographic analysis.

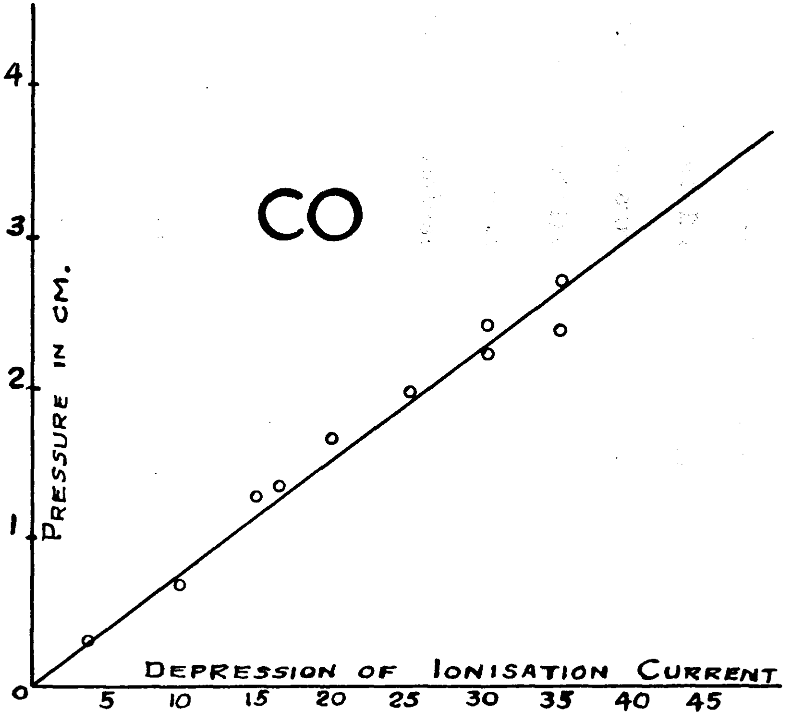
The liquid sample: was isolated as described previously in methanol solvent. The total volume of the sample was found using the cathetometer technique (Part I), and 0.25 ml. solution was extracted for formaldehyde analysis (Part II) A Further 0.25 ml. solution was extracted in 50μ-litre portions using a 100μ-litre Agla syringe, and chromatographed on the carbowax column, described earlier, at 78°C. The cold trap shown in Fig.9. was cooled to -78°C., with tap 6 shut and the gas flowing through Tap 5. The methanol leaving the column passed through tap 5, but as soon as the water was detected, tap 5 was shut, tap 6 was opened and the water was condensed in the cold trap containing acetic anhydride solution. It should be noted that the whole chromatography apparatus was protected from atmospheric moisture by the various molecular sieve type 5A drying tubes shown. Previous to a separation experiment these had been "baked out" under vacuum at 350°C. After five portions of water had been condensed in the acetic anhydride, the tube was removed, refluxed for a few minutes to ensure hydrolysis and the resultant acid/acetic anhydride solution was ready for mass spectrometric determination.

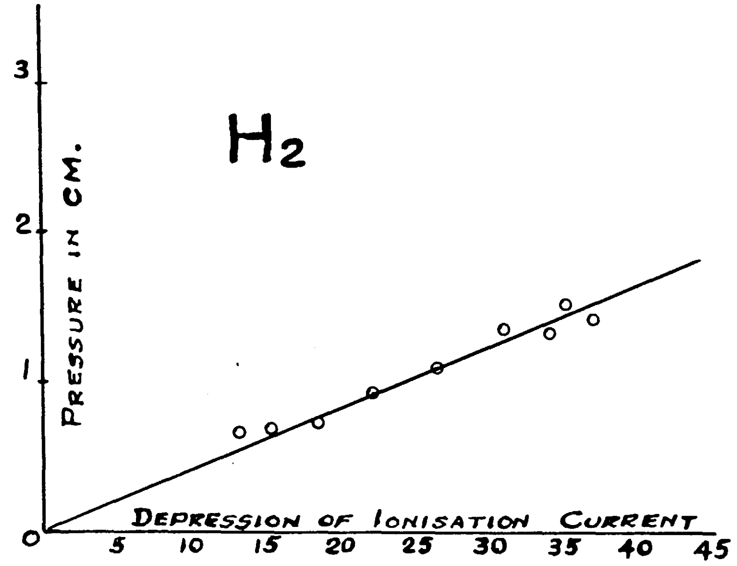
The volume of the remainder of the liquid sample was again determined using the cathetometer technique of Part I, and finally the whole was titrated with Karl Fischer reagent to determine the water present (Description Part I).

The Gaseous Sample was chromatographed as described earlier in this section on 5' Molecular sieve and 12" charcoal columns to estimate H_2, CO, CO_2. At the same time a series of synthetic gas mixtures containing H_2, CO, CO_2 in known proportions were prepared (Description, Part I), and chromatographed similarly to provide the necessary calibration graphs. These graphs are shown plotted in Graph XIX. The difference between the two

GRAPH XIX







CALIBRATION OF GAS CHROMATOGRAPHY IONISATION DETECTOR.

calibrations shown for CO_2 is due to the fact that the detector took several hours to warm up. The top calibration was used for samples D and F, the bottom for samples A, B, C, E. The ionisation current is measured in arbitrary units. Typical results obtained for samples A, B, C, D, E, are given in Table 7, overleaf. Carbon Monoxide was found to be negligible in all samples.

TABLE 7

H_2

	Total pressure admitted	Depression of ion current	Pressure H_2(graph)	Mole.% H_2
A.	1.8	31.5	1.3	72%
	0.65	12.5	0.5	77%
B.	1.0	17	0.7	70%
	1.95	34	1.4	72%
C.	4.45	35.5	1.45	32%
	1.70	20.5	0.85	50%
	1.90	20.5	0.85	44%
D.	2.60	36.5	1.5	57.5%
	1.80	27	1.11	61.5%
	1.65	26	1.10	65%
E.	1.8	31	1.3	72.3%
	1.6	27.5	1.15	72%
	1.4	24.5	1.00	71.5%

Continued overleaf /-

It was found that, while approximately correct $CO_2 : H_2$ ratios could be obtained, a discrepancy existed in that the total CO_2 and H_2 observed amounted to more than 100% in every case. The reason for this may be that peak areas may have to be measured rather than peak heights. The peak area could not be determined graphically due to its small value. The remainder of the CO_2, H_2 gaseous samples were then analysed mass spectrometrically. However, since it was now known that no carbon monoxide was present in any of the samples, then the freezing values of carbon dioxide obtained could be used as a basis of accurate estimation, as the only gas left uncondensed at -195°C. would be Hydrogen. A typical calculation is therefore given below for sample D, as it contains appreciable quantities of all the products. The calculations for all other samples including the earlier B.H.C. samples of Part III, and Sample F of Chapter IV were calculated in an identical manner.

TYPICAL CALCULATION : SAMPLE D.

Diminution of oxygen pressure during oxidation = 1.54 cm.

$\equiv$ 13.5 mg.oxygen.

Reaction: 7.14 cm.MeOH $\xrightarrow[\text{1 hour}]{300^\circ\text{C.}}$ 10.68 cm. at 410 ml.= volume of circulating system.

On expansion into Analytical section (volume=75 ml.) pressure= 9.13cm./485 ml.

Cooling to - 78°C. pressure = 4.95 cm./485 ml./-78°C.

Cooling to -105°C. pressure = 4.80 cm./485 ml./-105°C.

Cooling to -195°C. pressure = 2.88 cm./485 ml./-195°C.

= 3.00 cm./485 ml./-105°C.

∴ pressure H_2 + CO at -105°C = 4.80 cm./485 ml./-105°C.

pressure H_2 at -105°C = 3.00 cm./485 ml./-105°C.

∴ By difference pressure CO_2 at -105°C = 1.80 cm./485 ml./-105°C.

∴ Mole.% H_2 = 62.5%

Mole.% CO_2 = 37.5%

This compares favourably with the gas chromatography results.

Pressure of H_2 + CO_2 in system = 4.80 cm./485 ml./-100°C.

= 5.05 cm./485 ml./ 20°C.

∴ Hydrogen: 3.15 cm./485 ml./ 20°C ≡ 1.7 mg. H_2

Carbon Dioxide: 1.90 cm./485 ml./ 20°C ≡ 22 mg. CO_2

Liquid Fraction: Total volume = 2.05 ml.

Water: Vol.of solution prior to titration = 1.45 ml.

Blank titration = 3.02 ml.K.F.R./2 ml. methanol solution.

= 2.22 ml.K.F.R./1.45 ml. methanol solution.

Unknown titration = 4.05 ml.K.F.R./1.45 ml. solution.

∴ actual titration less blank = 1.83 ml.K.F.R./1.45 ml.solution.

≡ 3.44 mg.H_2O/1.45 ml.solution.

≡ 4.80 mg.H_2O/2.05 ml.solution.

∴ Water = 4.80 mg.

Formaldehyde: 0.25 ml. solution extracted for analysis.

Colorimetric analysis indicated 145 mcg/0.25 ml. solution.

∴ Total HCHO = 1185 mcg./2.05 ml. solution.

∴ Formaldehyde = 1.19 mg.

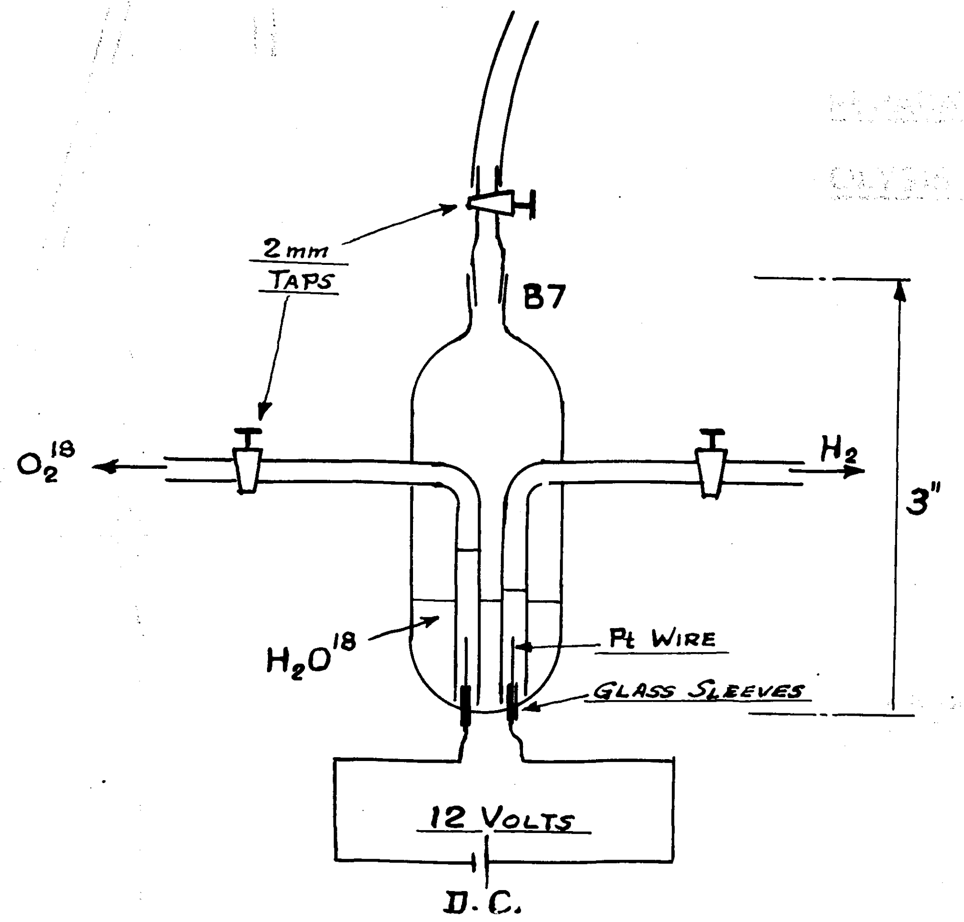
From the above information, the results were tabulated as shown in Tables III and IV. Unreacted methanol was calculated by difference.

The mass spectrometric results for carbon dioxide have been given earlier in Table V. The method of calibrating these results and the preparation of the oxygen-18 gas will now be described.

Preparation of Oxygen-18.

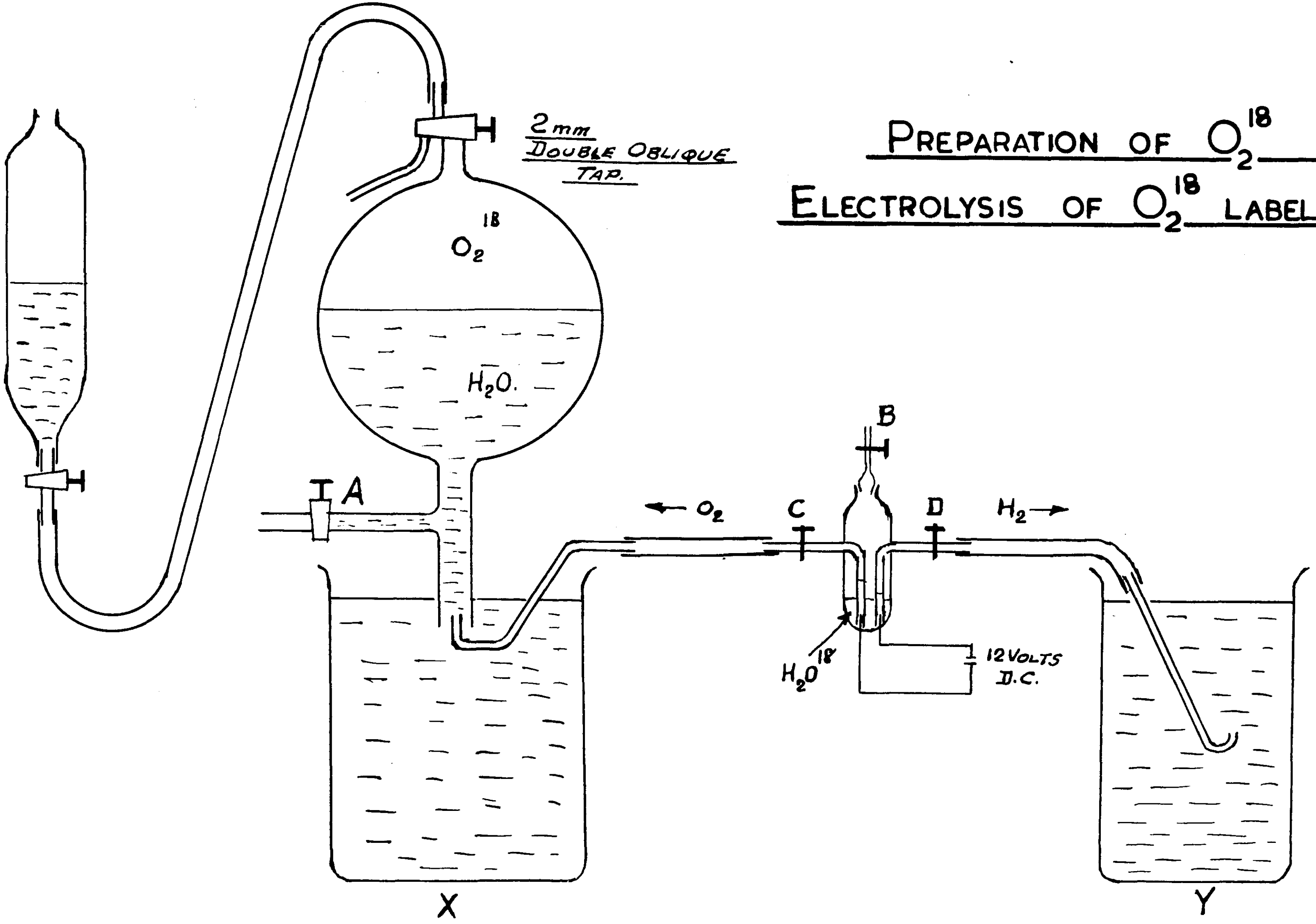
Oxygen-18 was supplied by 20th Century Electronics Ltd., in the form of water enriched to the extent of 6 atom% with oxygen-18. The enriched water was converted into oxygen by electrolysis in the specifically designed cell shown in Fig.10. This allowed the collection of pure Oxygen-18 without fear of contamination by hydrogen. The design was such that the water could be electrolysed, and the oxygen collected even when the volume involved was very small. The complete apparatus is shown in Fig.11. Direct admission of the O^{18} into the vacuum system via. the normal mercury bubbler device was not possible since too high a pressure was required to force the gas through the mercury. Accordingly, it

FIG. 10.



ELECTROLYSIS CELL $H_2O^{18} \rightarrow O_2^{18}$

PREPARATION OF O_2^{18} BY ELECTROLYSIS OF O_2^{18} LABELLED WATER.



HYDROSTATIC PRESSURE BALANCE FOR X.

FIG. 11.

was decided to collect the gas by the time honoured method of water displacement. The one litre reservoir bulb was filled with water through the 2 mm. double oblique tap, and inverted over a beaker of water as shown. It was found that no construction or tap could be placed between the end of 0^{18} delivery tube and the bulb, as otherwise the oxygen tended to form a "lock" at the constriction, thereby preventing the gas reaching the main reservoir. The electrolysis was started by connecting the terminals to a 12 volt D.C. supply. As the electrolysis proceeded, the oxygen pressure built up in the 0^{18} delivery tube thus causing a fall in level of the H_20^{18},in 0^{18} collection tube within the cell. Electrolysis would soon stop when the H_20^{18} level reached the bottom of the platinum wire, but this was prevented by building up the hydrogen pressure within the cell, controlled by the position of the hydrogen delivery tube in Y. A small outlet was provided in hydrogen collection tube within the cell so that this could be achieved. Thus, before the H_20^{18} level could drop below the platinum terminal, the pressure within the cell had become such that 0^{18} was forced out of the 0^{18} delivery tube and into the reservoir. The H_20^{18} level then rose within the 0^{18} collection tube and the cycle of events again commenced. The hydrostatic balance was initiated by blowing gently through B and immediately shutting the tap B. Once initiated, the process continued smoothly until the O^{18} reservoir was full, (about 7-8 hours.) The bottom of the reservoir was then plugged with a rubber stopper, the bulb inverted and the O^{18} gas then forced out through tap A, by admitting water to the bulb through the double oblique tap. A was connected to a trap immersed in Drikold/Acetone mixture to remove moisture, which,in turn, was connected to the mercury bubbler B_2 shown in Fig. 2. O^{18} was thus stored in the reservoir as shown in Fig.2 and was protected from air leakage by mercury cut-offs. By designing the cut-off so that the ball valve and tap were in the position shown in Fig. 3., the cut-off could be used to protect the O^{18} when not in use even when the O^{18} was nearly at atmospheric pressure. The amount of mercury in the cut-off was regulated so that when the top ball-valve was closed by the mercury, the bottom level of mercury was just sufficient to allow the passage of O^{18} through the cut-off.

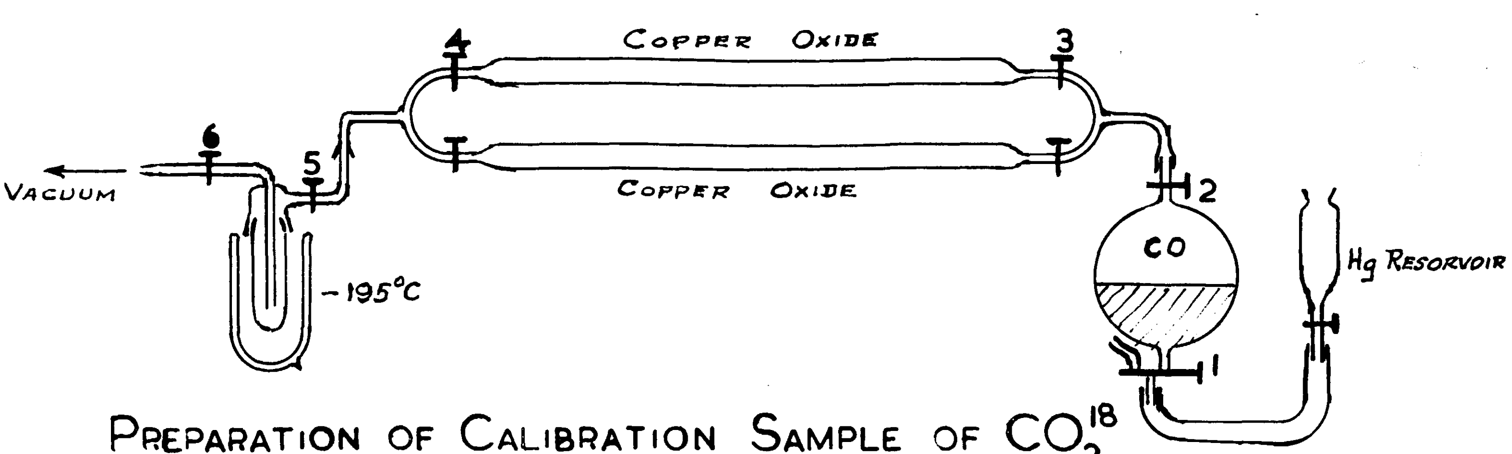
Preparation of Calibration Samples.

The enrichment of the O^{18} gas was determined by preparing H_2O^{18} and $CO^{16}O^{18}$ in the following way. At the completion of the oxidation of a copper catalyst, two pyrex tubes filled with copper powder were attached to the main vacuum apparatus at the point z. (Fig.2). The copper powder had previously been reduced with hydrogen at 350°C for several hours. The tubes were then evacuated and "baked out" to remove adsorbed hydrogen and water. O^{18} was then admitted to both tubes, which were then heated to 350°C. for 30 minutes to oxidise the copper powder. The tubes were then cooled, evacuated and "baked out" again at 300-400°C. for two hours. The tubes were then fitted to the apparatus shown in Fig.12.

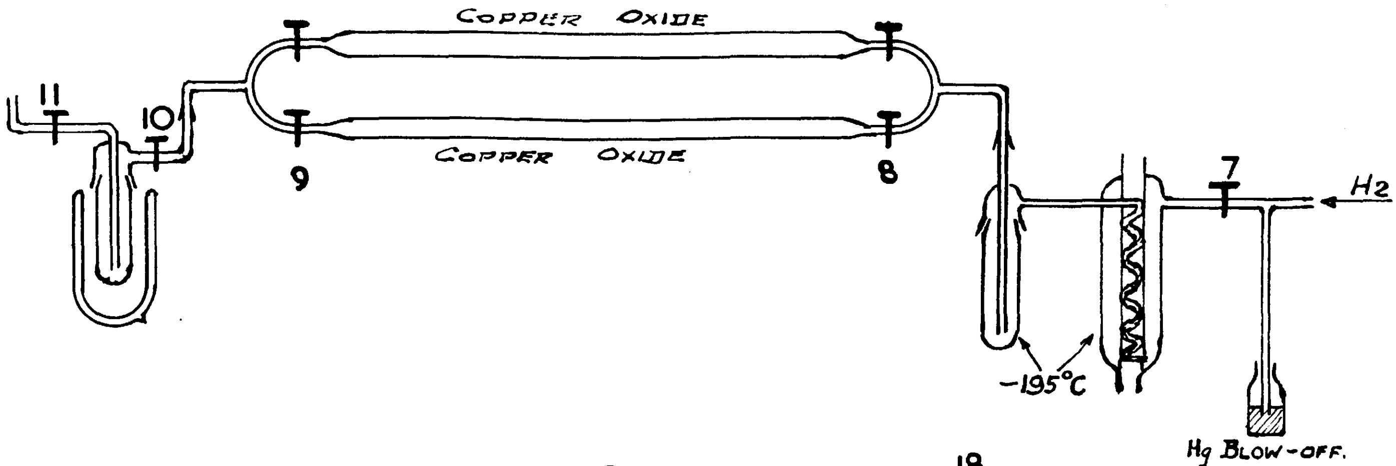
Preparation of Calibration Sample of $CO^{16}O^{18}$

A reservoir of carbon monoxide was prepared,as described previously, using the apparatus shown in Fig.6. This was attached to the copper oxide tube as shown. The other end of the tube was attached to a trap cooled to -195°C. Carbon monoxide was admitted to the copper oxide tube and the mercury level in the reservoir adjusted until the pressure was atmospheric. The tube was then heated to approximately 300°C for one hour. The tube was then cooled and the carbon monoxide pressure in the reservoir was reduced to 30 cm. Taps 4 and 5 were then opened to admit the carbon monoxide/carbon dioxide mixture to the cold trap. At the pressure of 30 cm., no carbon monoxide condensed. Tap 6 was then opened slowly and the gases pumped out through the cold trap. The enriched carbon dioxide was collected in the trap while the carbon monoxide was "Pumped-off".

FIG. 12.



PREPARATION OF CALIBRATION SAMPLE OF CO_2^{18}



PREPARATION OF CALIBRATION SAMPLE OF H_2O^{18}

Taps 5 and 6 were then shut, the trap removed and warmed to room temperature, and excess CO_2 pressure released by opening one of the taps. The amount of oxide present in the tube was arranged so that this excess of pressure in the cold trap would be obtained. The enriched $CO^{16}O^{18}$ was then analysed on the Mass Spectrometer.

Preparation of Calibration Sample of H_2O^{18}.

This preparation was simpler in that hydrogen would not condense at -195°C at a pressure of one atmosphere, as carbon monoxide does. Accordingly, cylinder hydrogen, dried by passing through the cold traps shown in Fig.12, was allowed to flow through the copper oxide tube via. taps 8 and 9, heated to 300°C for one hour. The water produced was collected in the cold trap shown, containing acetic anhydride cooled to -195°C. At the end of the hour, the trap was warmed by slowly lowering the Dewar of liquid air to condense the water in the acetic anhydride. The trap was then removed, and the liquid refluxed for a short time to ensure complete hydrolysis of the acetic anhydride. The sample was now ready for mass spectrometric determination.

EXPERIMENTAL FOR CHAPTER IV.

(1) Dehydrogenation of Methyl Alcohol - Work Hardening Experiments.

The purpose of the experiments now undertaken was to study the effect of oxidised work hardened wires on the catalytic dehydrogenation of methanol compared with oxidised annealed wires.

Work hardening of copper wires was accomplished using the method of Uhara (77). Surface dirt was cleaned from six pieces of copper wire 50 cm. in length, and 0.122 cm. in diameter (18 s.w.g.), by lightly abrading with fine emery paper, followed by thorough washing in methanol. Each length was then work hardened individually by clamping one end to a firm support and attaching the other end to a geared down electric motor (eccentric wheel of Fig.4.), which, when rotated, twisted the wire about its lengthwise axis. The work hardening of a wire, according to Uhara, varies directly as the number of turns and length of wire, and inversely as the diameter. For a work hardening value of $\frac{nd}{L}$ = unity, $\frac{50}{0.1}$ = 500 turns of twist were therefore required. This was quickly accomplished using the electric motor and a small revolution counter. The total length of work hardened wire thus prepared had a geometrical surface area of 105 cm^2

which compared favourably with previous catalysts oxidised at low temperatures in Part VI of Chapter I. The work hardened wires were then formed into three spirals fitting inside one another and final grease and dirt was removed by immersing in boiling methanol for 15 minutes. They were quickly transferred to the catalyst vessel (Fig 5.1.), which was evacuated to 10^{-5}mm. without any "baking out" procedure to avoid annealing the wire. Oxygen-18 was then admitted to the apparatus, (Fig 2) as described in the experimental section of Part IV of Chapter II., to a pressure of 60 cm. and the wire was then oxidised by heating the catalyst vessel to 300°C. until the uptake of oxygen, as measured by the decrease of pressure in the system, was similar to that of experiment D in Chapter II. The catalyst vessel was then cooled, the oxygen-18 Toeplered back into the storage reservoir, and the vessel finally evacuated to 10^{-5} mm. The vessel and wire were also "baked out" for 30 minutes at 350°C. to remove most of the adsorbed oxygen from the surface of the oxidised wire. The vessel was then cooled and 7 cm.pressure of methanol admitted to the reaction system. The circulating pump was started, the catalyst vessel was heated to 300°C. and the methanol decomposition observed by the change in pressure in the apparatus. After the reaction was complete, the catalyst vessel was cooled, and the products isolated and analysed by gas chromatographic and mass spectrometric techniques as described in the experimental section of Part IV of Chapter II. The results have been shown earlier. The amount of carbon dioxide was again estimated by cooling the cold trap CT_4 (Fig.2) to -195°C., and circulating the gases through this trap by means of the Toepler pump, until constant pressure was indicated on Manometer M_1. The decrease in pressure in the system was taken as a measure of the carbon dioxide present. In addition a similar freezing experiment was carried out cooling CT_4 initially to -78°C. and Toeplering to constant pressure. CT_4 was then cooled to -105°C. and again Toeplering was carried out until constant pressure was reached. This was the temperature range in which the vapour pressure of dimethyl ether decreased from 5 or 6 cm. to 1 mm. The pressure change actually observed was less than 0.5 cm., due mainly to contraction, and to the small amount of formaldehyde present. The conclusion was that no dimethyl ether was present.

(2) Decomposition of Formic Acid Vapour.

The purpose of this series of experiments was to examine any difference in the rate of formic acid decomposition on annealed and work hardened copper wires prepared "in situ." in the vacuum apparatus.

The method of work hardening has been explained in Part (1) of this section. The wire was 15 cm., i.e. approximately 6 in. in length. The diameter of the 20 s.w.g. wire was 0.036".

$\therefore$ No.of turns to work harden to $\frac{nd}{L} = \frac{1}{2}$ 85 turns.

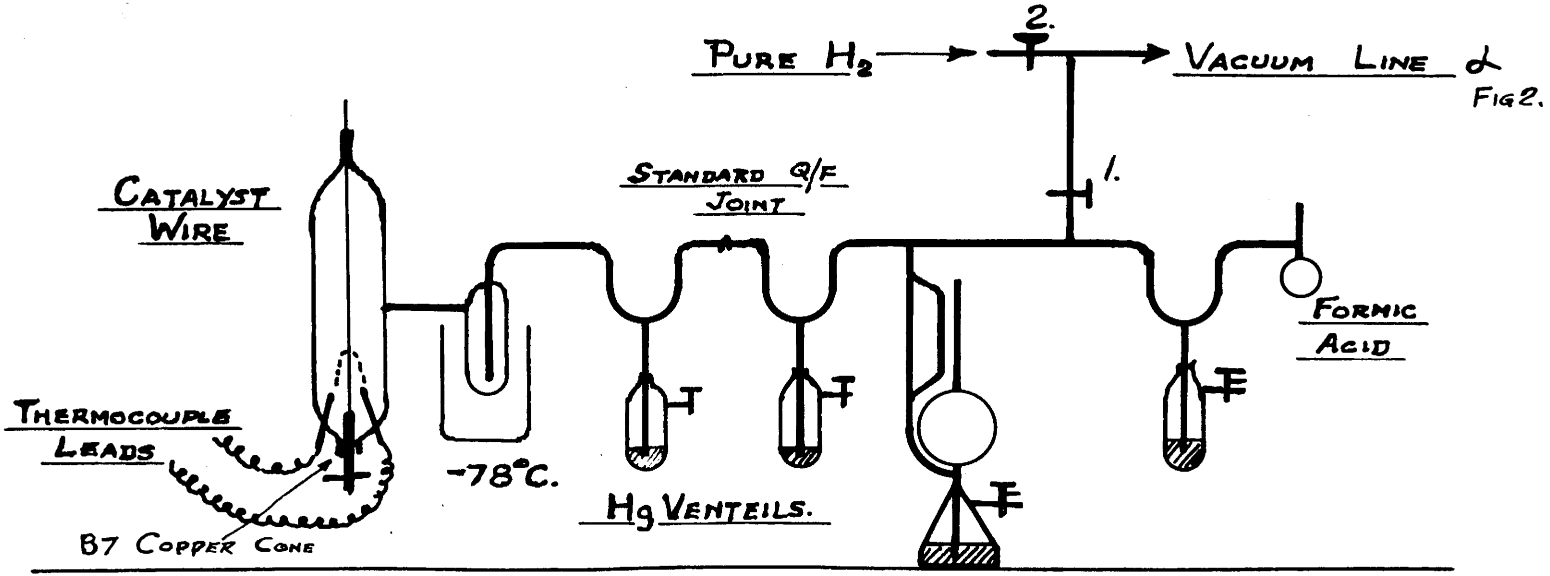
No.of turns to work harden to $\frac{nd}{L} = 1$ 170 turns.

The apparatus used in these studies is shown in Fig.13. It consists of a formic acid reservoir, mercury cut-off, McLeod Gauge, cold trap and catalyst vessel, in that order. The mercury venteils shown in the centre of the apparatus were included for another purpose, and are irrelevant to the present work.

The Catalyst Vessel.

The catalyst vessel was prepared from 3.5 cm. diameter Pyrex tubing drawn down at one end to accommodate a tungsten glass seal. The other end was drawn down to a B.7. Quick-fit socket, on either side of which was sealed two 1 mm. diameter tungsten wires silver soldered on to an iron/constantin thermocouple. The end of the spot-welded thermocouple was silver soldered to a small 24 s.w.g.

FIG. 13.



APPARATUS FOR FORMIC ACID STUDIES.

copper wire spiral just wide enough to accommodate the 20 s.w.g. copper catalyst wire. The copper spiral was in fact prepared by winding it round 20 s.w.g. copper wire. The thermocouple had been previously calibrated in an oil bath. The potential difference between the ends of the thermocouple, with the reference junction in ice, was measured with a Doran Thermocouple Potentiometer. To load the catalyst vessel, the pure copper catalyst wire (99.99%, soft copper, high conductivity, 20 s.w.g) 15 cm. in length was silver soldered at one end to a tungsten/glass seal. The other end was then pushed into the catalyst vessel through the small copper spiral connected to the thermocouple, and out through the B.7. Quick-fit socket. This end was then connected to a specifically machined standard B.7. copper cone, through a small hole drilled in its end. The cone was then sealed into the B.7. socket with Apiezon wax and the other end of the catalyst wire could now be glass blown on to the end of the vessel.

The vessel was connected to the cold trap via a short length of 10 mm. diameter glass tubing to allow free access of the formic acid vapour to the wire.

The McLeod Gauge.

This was constructed from a length of 1.5 mm. diamter precision bore capillary tubing and a bulb of approximately 100 ml.volume.

The base of the bulb was fitted with a cut-off so that a precise volume of gas was compressed during each pressure measurement. The total volume of the bulb and stem was calibrated by filling both full of water at a known temperature, and weighing the quantity of water present.

The total volume of bulb and stem = 144.5 ml.

The pressure readings were calculated as follows:

Volume of stem V_s at $\Delta hp = \pi r^2 \times \Delta hv$

$= \underline{1.765 \times 10^{-2} \times \Delta hv}$.

where $\underline{\Delta hp}$ = difference between Hg levels in the two limbs of the gauge.

$\underline{\Delta hv}$ = difference between Hg level and top of stem.

$\underline{r}$ = radius of precision bore capillary tubing.

$\therefore$ Pressure in cm.= $\frac{V_s \times \Delta hp}{144.5}$.

Calculation of Pressure of Formic Acid Vapour present in the stem of the McLeod Gauge after compression from 6 x 10^{-4}mm. pressure

Vapour pressure of formic acid at -78°C. = 6 x 10^{-4} mm.

$\therefore$ Maximum pressure of formic acid vapour in apparatus = 6 x 10^{-4}mm.

During a pressure measurement, this will be compressed from

144.5 ml to 0.04 ml.

$$\therefore \text{ Pressure in stem of McLeod at 0.04 ml. volume} = \frac{144.5 \times 6 \times 10^{-4}}{0.04} \text{ mm.}$$

$$= \underline{2.17 \text{ mm.}}$$

The vapour pressure of formic acid at room temperature, is approximately 4 cm., i.e. greatly in excess of 2 mm.

The conclusion was that no formic acid should condense in the stem of the McLeod Gauge during pressure measurements.

Purification of Materials.

Formic Acid Formic Acid 98-100% B.D.H.reagent was distilled four times in a Quick-fit apparatus, collecting the middle fraction boiling at 100.5°C, on each occasion. The final fraction was dried over A.R. anhydrous sodium sulphate and placed in the reservoir of the vacuum apparatus. The reservoir was then evacuated at room temperature and the liquid formic acid allowed to boil for a few seconds to remove any dissolved permanent gases. It was then cooled to - 195°C. and the evacuation was continued until a vacuum of 10^{-5}mm. pressure was obtained. The mercury cut-off could then be raised and the reservoir allowed to reach room temperature.

Hydrogen Hydrogen gas was admitted to the apparatus via. a palladium leak and tap 2 (Fig.13).

Nitrogen Nitrogen was purified by passing it slowly through an activated charcoal trap cooled to -195°C. The gas was then admitted directly to the apparatus via. tap 2.

Method used to clean the copper wire.

The catalyst vessel, connecting tubing and cold trap were all wrapped in "Heat by the Yard" heating tape, to "bake out" at 350°C. This temperature was measured with a 500°C thermometer enclosed within the tape surrounding the catalyst vessel. For this design of catalyst vessel, such a procedure was found more convenient than the usual type of furnace. Higher temperatures than 350°C. could not be attained due to danger of local overheating of the tape, and consequent shorting. The wire was heated electrically by means of the circuit shown in Fig.4, to 300°C, or higher if it was found necessary to remove visible oxide produced during the glass blowing of the tungsten seal. After the baking out process was complete, usually several days at 10^{-5}mm. pressure, the cold trap was cooled to -195°C. to protect the wire from contamination by mercury and tap grease vapour. The wire was now ready to be cleaned with atomic hydrogen according to the method of Cooper and Eley (83).

Purified hydrogen was first admitted to the apparatus to a pressure of 10^{-1}mm. The catalyst vessel could not be immersed in liquid air due to the danger of cracking the sealing Apiezon wax on the B.7. cone, with consequent leakage of air into the apparatus; instead the vessel was wrapped in several absorbent tissues and liquid air poured over them. This procedure cooled the catalyst vessel to -195°C. for the necessary length of time. In addition the catalyst vessel was also surrounded with several turns of 18 s.w.g. copper wire. A high frequency discharge passed through this wire has been claimed (83) to remove oxide by reaction with "Atomic Hydrogen" produced during the discharge. This discharge was maintained for at least five minutes, at the end of which period the vessel was warmed to room temperature, the cold trap was warmed to -78°C, and the whole system evacuated to 10^{-5}mm pressure. The wire was then heated electrically to 300-400°C. in this vacuum for at least 24 hours to remove dissolved hydrogen. At the end of this period, the wire was cooled, and the vessel thermostated at 25°C. The wire was now considered to be clean, and ready for attempted formic acid decomposition.

Details of the experimental procedure as from this point have already been described.

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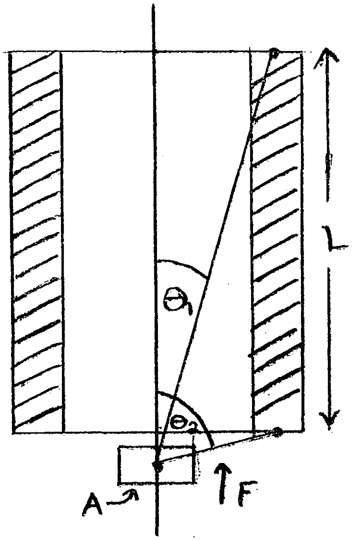
APPENDIX I.

CALCULATION OF STRENGTH OF ELECTROMAGNET NECESSARY TO MOVE DIAPHRAGM OF CIRCULATING PUMP.



Consider a solenoid of length L metres and having T turns of wire round it, carrying a current I amp.

The Field strength $H = \frac{I\ T}{2L} (\cos\theta_1 - \cos\theta_2)$

where θ_1 and θ_2 are the angles subtended by the axis of the solenoid and lines joining the centre of the weight m, at the entrance to the soleniod, and the mid-points of the coil of wire at either ends of the soleniod.

The force F required to move this weight into the soleniod =

$\frac{B^2\ A}{2\mu_o}$ Newtons. where A = Area in metres^2 of top surface of weight exposed to the field force.

$$\mu_o = 4\pi \times 10^{-7}$$

$$B = \mu_o H \ Wb/m^2$$

9.81 Newtons = 1 kg.

Total weight of object = 7.5 g. $\doteqdot$ 0.08 newtons.

Radius of steel = 0.25 cm. = 0.0025 metres.

$\therefore$ Area $= \pi r^2 = 3.14 \times (0.0025)^2$ metres^2.

$$B^2 = \frac{2F\mu_o}{A} = \frac{2 \times 0.08 \times 4\pi \times 10^{-7}}{\pi \times (0.0025)^2}$$

$$\therefore B = \sqrt{\frac{0.64 \times 10^{-7}}{(0.0025)^2}} \quad Wb/m^2$$

$$\therefore H = \sqrt{\frac{\frac{0.64 \times 10^{-7}}{(0.0025)^2}}{4\pi \times 10^{-7}}} \approx 50{,}000 \text{ gauss.}$$

Now for a solenoid of length 5 cm., 0.05 metre, and assuming the weight to be at the entrance to the solenoid, in which case $\theta_2 = 90^\circ$ and $\theta_1 \approx 20^\circ$, then if a current of 4 amp is passed through the wire :-

$$\text{No. of turns } T = \frac{2 \times L \times H}{I \times \cos\theta_1} \qquad (\cos\theta_2 = \cos 90^\circ = 0)$$

$$\approx \underline{1000 \text{ turns}}.$$

$\therefore$ 1000 turns of wire carrying 4 amp will give necessary strength of solenoid.

APPENDIX II.

VOLUME CALIBRATION OF APPARATUS.

During the volume calibration of the apparatus, and in estimating the amounts of various gases, for example oxygen, present in the circulating system by pressure measurement, error will result due to the change in volume of the manometric system with variation in mercury level. The total volume of the manometer tube M_1 (Fig.2), was approximately 100 ml. i.e. $\frac{1}{4}$ of the volume of the circulating system, so that the error involved was appreciable. Correction was therefore applied in the following manner.

The volume of a 100 ml. round bottom flask fitted with a tap was determined accurately by weighing evacuated, and full, of water. The volume of the bulb was 129 ml. This bulb was then attached to the manometric system, between the gold trap and M_2, and evacuated. Air was then admitted to the bulb to a pressure read on M_1, the tap on the bulb was closed, and the manometer system evacuated. The air in the bulb was then expanded into the manometer system and the new pressure noted. This procedure was repeated several times with varied pressures of air.

Let V_1 = volume of standard bulb.

V_o = volume (manometer system when mercury level is 76 cm. above the reservoir.)

V_m = volume of manometer tube from the position of V_o to the position of the mercury level at pressure P_2.

V_2 = Total volume of manometric system after expansion from bulb.

P_1 = Pressure of air at volume V_2.

A_m = Cross section area of manometer tubing.

Then:

$$P_1V_1 = P_2V_2$$

$$\therefore P_1V_1 = P_2(V_1 + V_o + V_m)$$

$$= P_2(V_1 + V_o + P_2A_m)$$

$$\therefore \frac{P_1V_1}{P_2} = V_1 + V_o + P_2A_m.$$

$$\therefore \frac{P_1}{P_2} = \frac{A_m}{V_1} \cdot P_2 + \frac{V_1 + V_o}{V_1}$$

A plot of $\frac{P_1}{P_2}$ versus P_2 will therefore give as its slope $\frac{A_m}{V_1}$

and intercept $\frac{V_1 + V_o}{V_1}$

Such a graph was plotted from the values obtained in the experiment described on the previous page.

From the graph: intercept = 1.212

$$\text{Gradient} = \frac{0.23}{28.2} = \frac{A_m}{V_1}$$

$$\therefore A_m = 1.05 \text{ cm}^2$$

$$\therefore \text{Diameter} = 1.16 \text{ cm.}$$

V_o = 27.3 ml. at 76.92 cm. Atmospheric Pressure.

A graph was now plotted of the pressure reading on the manometer scale versus the volume of the manometric system at the pressure indicated. This graph is shown in Graph XX.

Thus the volume of the manometric system could be conveniently read from this graph at the existing pressure in the apparatus.

The remainder of the apparatus could now be calibrated by expansion from the manometer system into the various sections of the apparatus.

The volume of the various parts of apparatus are as follows:

Volume of Circulating system (Infra-Red Experiments) = 410 ml.

Volume of Circulating System (B.H.C.Experiments) = 360 ml.

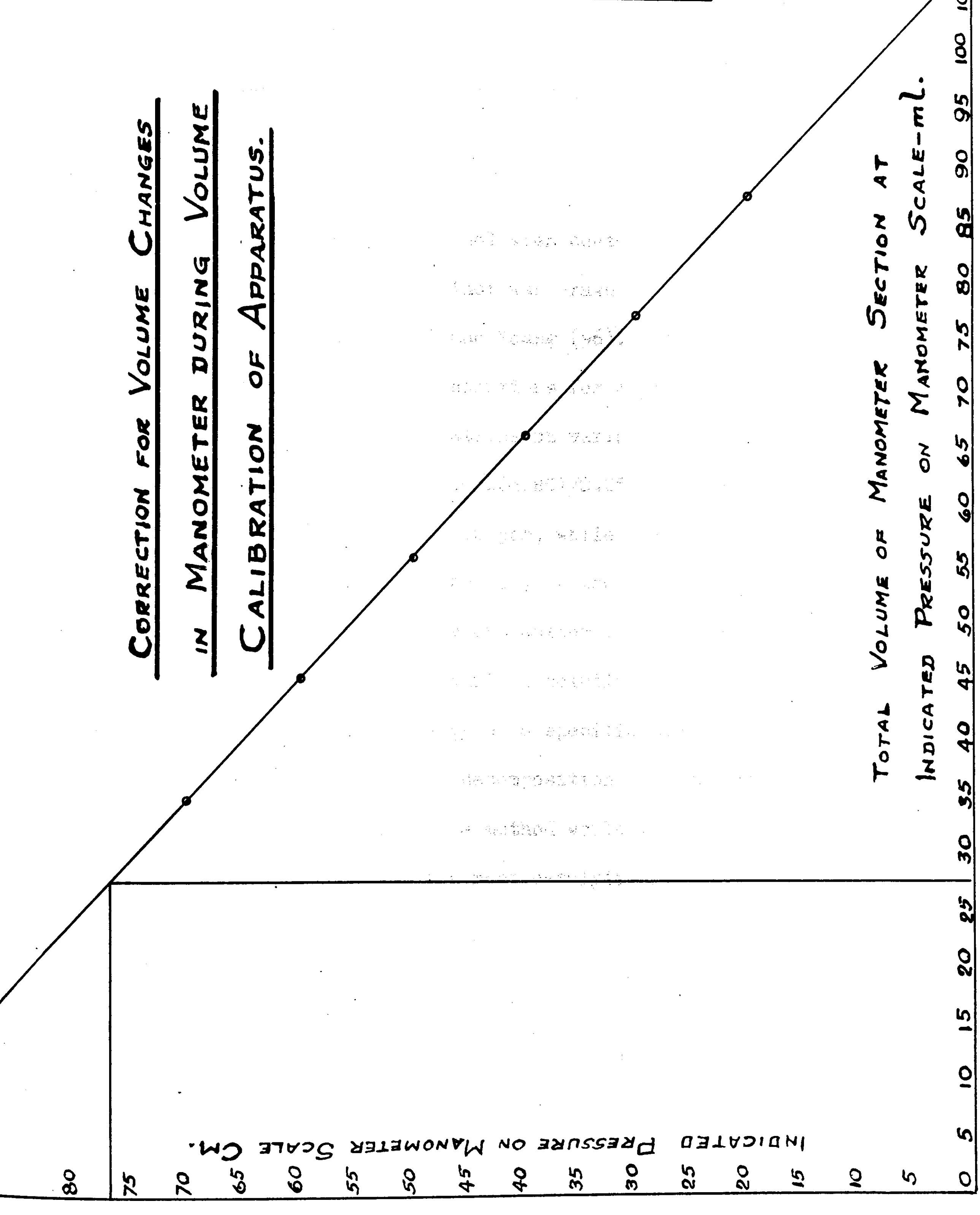
Volume of Circulating System (Oxygen-18 Experiments) = 410 ml.

Total Volume of Analytical Section of Apparatus = 70 ml.

Volume of Analytical Section up to ball valve in Toepler Pump= 50 ml.

Volume of Infra-Red Gas Cell = 110 ml.

GRAPH XX



CORRECTION FOR VOLUME CHANGES IN MANOMETER DURING VOLUME CALIBRATION OF APPARATUS.

APPENDIX III.

SPECIFIC ETCHING SOLUTIONS FOR WORK HARDENED WIRES.

It has been found in this thesis that pure copper wire will not catalyst the decomposition of methanol. Work hardened wires, prepared according to the method of Uhara (77)(Chapter IV) likewise had no effect on methanol when heated to 300°C. However, the interest of the present author was drawn to a series of papers published by Livingstone (95) and Young (96). These authors developed a series of etching solutions for copper, which specifically etched out dislocations on various crystal faces. Thus for example a $IM.FeCl_3.6H_2O/12M.HCl/0.25$ MHBr. solution was specific for the (111) face of copper, while a $2MFeCl_3.6H_2O/7.8$ MHBr. solution etched out dislocations only on the (100) face. It was therefore considered by the present author that if a work hardened copper wire was etched in the various solutions described by these authors, then the surface energy of a specific portion of the surface would be increased and decomposition of methanol may be initiated; in particular such a method would indicate which of the crystal faces on copper was the most catalytically efficient. It was found however, that no decomposition of methanol could be obtained on any of the work hardened wires etched in the various solutions.

It was concluded that the decomposition of methanol on copper could not be initiated by a surface roughening process. Thus, more evidence has been found against the postulate that the activation of copper surfaces by alternate oxidation/reduction techniques is due to surface roughening.

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