SOME OBSERVATIONS ON THE MECHANISM OF SURFACE REACTIONS. WITH SPECIAL REFERENCE TO THE SYNTHESIS AND DECOMPOSITION OF METHANOL.

BY

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ABBREVIATIONS.

A.	Abstract.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Brit. Assoc. Rep.	British Association Reports.
B.P.	British Patent.
Can. Pat.	Canadian Patent.
Chem. Abst.	British Chemical Abstracts.
Chimie et. Ind.	Chimie et Industrie.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Fr. Pat.	French Patent.
Ger. Pat.	German Patent.
J.A.C.S.	Journal of the American Chemical Society.
J.C.S.	Journal of the Chemical Society.
J.I.E.C.	Journal of Industrial and Engineering Chemistry.
J. Phys. Chem.	Journal of Physical Chemistry.
J.R.T.C.	Journal of the Royal Technical College, Glasgow.
J. Russ. Phys. Chem. Soc.	Journal of the Russian Physical Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
Act. Physicochim.	Acta Physicochimica, U.R.S.S.

Naturwiss.	Die Naturwissenschaften.
P. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society.
Physik. Z.	Physikalische Zeitschrift.
P.R.S.	Proceedings of the Royal Society.
U.S. Pat.	United States Patent.
Z. anorg. Chem.	Zeitschrift für anorganische und allegemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische chemie)
Zeitsch. physikal. chem.	Zeitschrift für physikalische chemie, stöchiometric und Verwandtschaftslehre.
Z. physik. chem.	Zeitschrift für physikalische chemie.

INTRODUCTORY SECTION.

INTRODUCTION.

CHAPTER 1.

HISTORICAL.

Catalytic reactions have been recognised since the days of the alchemists, but they were first so-called by Berzelius about 1835 (Jahresberichte für Chemie, 1836, 13, 227.). The first reaction in which the catalytic principle was properly realised was discovered by Mrs. Fulhame ("An Essay on Combustion", London, 1794; Mellor, J. Phys. Chem., 1903, 7, 557.), who found that the oxidation of metals, the reduction of metallic oxides and the combustion of carbon monoxide all required the presence of small quantities of water, which was not altered in the reaction. The fact that dilute acids were unchanged in the hydrolysis of starch to sugars was proved by Kirchhoff (Schweigger's Journal, 1812, 4, 108.).

Sir Humphrey Davy, in a communication to the Royal Society in Jan., 1837, stated that when a piece of platinum foil or wire was warmed and plunged into a mixture of a combustible gas and air or oxygen, it became incandescent and caused the gas to burn, often explosively. He said that a temperature much below that of ignition was necessary (Phil. Trans., 1817, 107, 77.). This type of reaction was further studied by Henry (Phil. Mag., 1825,

65/

65, 269.) in a series of remarkable experiments on the selective combustion of various gases in the presence of platinum. He showed that when a mixture of equal volumes of hydrogen, carbon monoxide and oxygen was exposed to platinum sponge at a high temperature, 80% of the oxygen combined with the carbon monoxide, and 20% with the hydrogen.

These observations by Davy were extended by Faraday (Phil. Trans., 1834, 144, 55.), who developed views on the mechanism of contact action, which even at the present time are not greatly modified. He states that the effects in question are incidental and of a secondary nature; they are dependent upon the natural conditions of gaseous elasticity, combined with the exertion of the attractive force possessed by many bodies, especially solids, in an eminent degree, and probably belonging to all; by which they are drawn into an association more or less close, without undergoing chemical combination at the same time, though often assuming the condition of adhesion; and which occasionally leads, under very favourable conditions, as in the present instance, to the combination of the bodies simultaneously subjected to this attraction.

The general opinion which Faraday expresses is very/

very close to the modern point of view, i.e. that catalytic action is conditioned by a preliminary adsorption or incipient chemical combination between the catalyst and the reactants. When he formulated these conclusions in 1833-4, he had clearly established in his own mind the general causes and effects of what is now termed heterogeneous catalysis.

As already stated, Berzelius was the first to term catalytic changes as such. He studied a number of chemical changes, the mechanism of which appeared difficult to understand by explanations current at that time, and suggested that those which proceeded in many cases in the presence of some specific agent, and not in its absence, were due to the action of what he called a 'catalytic force'. The particular agents which exhibited this force he called 'catalysts', and held that it was in some way a novel form or manifestation of chemical affinity. The consideration and classification of catalysis from an academic standpoint however, was somewhat confused during the nineteenth century, but modern theories such as put forward by Ostwald (Zeit. Electrochem., 1901, 7, 995.), Armstrong (Brit. Assoc. Rep., 1885, 962; P.R.S., 1886, 40, 287.) and many others, help to clarify the position.

These were of two distinct types, namely, those which/

which relied on purely physical factors, and those which assumed the intermediate formation of something very similar to a chemical compound. These rather divergent views have lately been more or less combined to give the present absorption or unstable intermediate compound theory of the mechanism of catalytic reactions.

The most important of a series of 'criteria' of catalysts laid down by Ostwald in 1888 was the definition that catalysts were substances which would change the velocity of a reaction without modifying its energy factors (Physik. Z., 1902, 3, 313.). This, in effect, overwhelmed the theory of Berzelius by the introduction into the problem of the velocity of the reaction, which, by its relationship to a measurable quantity, became the subject of fresh and more detailed enquiry.

From the point of view of a technologist, however, it would seem more useful if a catalyst were defined as a substance which alters the speed of a reaction, including the case of the apparent initiation of the reactio but which remains unchanged in composition after the chemical change is completed. From a chemical point of view, catalytic changes proceed according to the laws of thermodynamics, and so follow the general principles of chemical kinetics and the law of mass action. But the local conditions/

conditions in any catalytic system must be known in order that the specific application of this law may be understood.

There has always been a tendency to divide catalytic actions or systems into two classes, namely, homogeneous and heterogeneous systems, and by far the greatest number of catalysts in use at the present time are solids; and as it is with heterogeneous catalysis that this present work is concerned, reference will be made only to work which concerns it.

CHAPTER II.

THEORETICAL CONSIDERATIONS OF CATALYSIS AT SOLID SURFACES.

Until about ten to fifteen years ago there was a difference of opinion as to the way in which chemical changes were brought about in gases and liquids by a solid catalyst. The two main views were the physical and chemical (or loose intermediate compound) views. The physical theories were first based on the fact that porous materials such as charcoal or platinum, which accelerated such reactions as the union of hydrogen and oxygen, could concentrate the gases in a layer on their surfaces with accompanying thermal effects (similar to those observed in the liquifaction of gases). Van't Hoff (J.H. Van't Hoff, "Physico-Chemical Studies, 1898, 1, 216.) concluded that the gases were brought into a state of compression and abnormal concentration by the catalyst, so that chemical combination was greatly accelerated without any definite chemical reaction with the catalyst. The gaseous concentration or adsorption at this time was regarded as a diffusion layer several molecules thick at the solid surface, the rate of chemical reaction being supposed to be a function of the rate of diffusion in this layer, and not depending on any actual chemical change at the catalyst surface (M. Bodenstein, Z. Physik. Chem., 1899, 29, 665; 1905, 53, 166.).

Sabatier (Sabatier, "La Catalyse en Chemie Organique", 1920, p.48.) has shown by two definite examples that this view does not account for varying chemical action on a single substance by different materials. For example, iso-butyl alcohol over copper at 300°C. yields iso-butyl aldehyde and hydrogen; over alumina, iso-butylene and water; while over uranium oxide, a mixture of all four substances (also at 300°C.). More striking still, formic acid is decomposed by zinc oxide into hydrogen and carbon dioxide, and by titanium oxide into water and carbon monoxide. A more recent example is the reaction between carbon monoxide and hydrogen. With nickel, methane is almost exclusively formed; with zinc oxide or chromate quantitative yields of methyl alcohol are obtained; with iron/alkali catalysts mixtures of higher alcohols, ketones and hydrocarbons are obtained.

Purely physical theories again fail to explain the markedly selective action of many catalysts and their power of producing isomeric and other changes, which is definite proof that chemical inter-relationship of an intimate nature has existed or occurred between the catalyst and the organic molecule (Hilditch and Taylor in "Catalytic Processes in Applied Chemistry", by Hilditch and Hall, 1937, p.19.).

The physical nature of adsorption was defined more clearly by the investigations of the late Lord Rayleigh, (P.R.S., 1890, 47, 364.) Sir W.B. Hardy (P.R.S., A., 1912, 86, 610; 1913, 88, 303.) Langmuir (J.A.C.S., 1916, 38, 2221; 1917, 39, 1848; 1918, 40, 1361.) and others, and it was shown that whilst a 'diffusion layer' of adsorbed molecules may exist in many cases, the primary condition of adsorption of a gas at a solid surface is due to a single layer of molecules which are, according to Langmuir, held at the surface by a force which is indistinguishable from chemical affinity in its effect. Thus the physical or adsorption theory of catalysis, which has been studied closely by a number of workers, approaches in this form very closely to the corresponding development of the older intermediate compound theory.

Sabatier and Mailhe (Ann. Chim. Phys., 1910, viii, 20, 289.) studied the action of a large number of metallic oxides upon ethyl alcohol vapour at 300°C., and showed that certain oxides, for example, manganese or tin, are almost entirely dehydrogenating in character, giving only acetaldehyde and hydrogen, whilst others, especially thoria and alumina, are entirely dehydrating, yielding ethylene and water. Others, for example, uranium oxide, cause both dehydrogenation and dehydration to take place simultaneously/

simultaneously. It is evident, therefore, that the chemical action induced by a catalyst is specific to the chemical nature of that catalyst. Sabatier attributed hydrogenation to the intermediate formation of unstable hydrides, and in this way supported the chemical, or intermediate compound theory of heterogeneous catalysis. But he only considered the possibility of the union of the hydrogen with the metal, abandoning the idea of the formation of complexes between the organic compound and the metal.

Taylor and his co-workers (J.A.C.S., 1921, 43, 1273, 2179; 1923, 45, 887, 900, 920, 1196, 2235; 1924, 46, 43; 1927, 49, 2468, etc.) found that metallic catalysts, for example, nickel and copper, adsorbed much less nitrogen or helium than hydrogen, and that ethylene and carbon monoxide were adsorbed to approximately the same extent as hydrogen. Later they observed that the heat of adsorption of gases such as hydrogen and ethylene was different and greater than that of such gases as nitrogen and helium, which did not take part in chemical reactions which are produced catalytically.

Two distinct types of adsorption have been established and recognised as a result of the work of Taylor and others. The first of these types is the purely physical or 'condensation' type, which is accompanied by

a/

a relatively small heat change, and the second is the 'activated' type, characterised by much greater heat changes. The formation of definite chemical compounds is probably rare in heterogeneous catalytic reactions, but these catalytic reactions are invariably preceded or initiated by activated adsorption of the reactants on the catalyst surface. This activated adsorption is similar to ordinary physical surface adsorption, and can be accompanied by it, but differs in its greater heat of adsorption. This heat is similar to that of a mild chemical reaction, while the forces involved are indistinguishable from those which are called chemical affinity.

CHAPTER III.

THE CATALYST SURFACE.

Many workers have noticed the change in activity produced in a catalyst when it is exposed to high temperatures. Taylor (J.A.C.S., 1921, 43, 1273, 2179; 1923, 45, 887, 900, 920, 1196, 2235; 1924, 46, 43; 1927, 49, 2468, etc.) showed that a catalyst prepared at a low temperature adsorbs less of a reactant after being exposed to a considerably higher temperature than before exposure, and progressively less with increase of temperature. This would seem to suggest that a sintering of the catalyst surface takes place, as a result of which the number of active points or centres on the surface is reduced. Armstrong and Hilditch (P.R.S., A., 1921, 99, 440.) have shown that exposure of unsupported catalysts to high temperatures results in a decrease in their bulk, and that there is a close connection between the 'bulk density' of such catalysts and their activity in catalytic hydrogenations. Taylor (P.R.S., A., 1925, 108, 105; J. Phys, Chem. 1926, 30, 150; J.A.C.S., 1931, 53, 578.) suggested a picture of the atomic structure of an active catalyst. The X-ray examination of metallic hydrogenating catalysts shows that they possess the definite lattice structure of the crystalline material. This of course does not exclude the irregular formation of the crystal surface/

surface itself, and Taylor suggested that the structure of a typical catalyst surface may be characterised by groups of atoms which are thrust irregularly above the normal surface of the crystals. The points at which these isolated, or semi-isolated, atoms are supposed to be situated are, according to Taylor's views, the seats of catalytic activity.

This seems to afford a reasonable explanation of the importance of an irregular surface; the sensitivity of an unsupported metal catalyst to increases in temperature (which would increase inter-atomic vibration, thus making the isolated groups of atoms tend to take up more stable positions in the plane surface); the action of catalyst poisons and possibly the action of promoters; the possibility of interaction with other molecules (due to the affinities of the exposed atoms being less saturated by the neighbouring atoms, thus making these atoms more 'unsaturated', or active, and hence tend to enter into chemical combination with other molecules).

Besides these views of Taylor and his co-workers on the nature of the catalyst surface, there are many others based on the electronic structure of the atom, the arrangement of the lattice of the solid atoms, etc., but the validity of the latter remains to be established in many cases.

The surfaces of metals and metal oxide films on metals/

metals was studied by Constable (Nature, 1927, 120, 769; 1928, 122, 399; P.R.S., A., 1927, 117, 376; 1928, 119, 196, 202; P. Camb. Phil. Soc., 1928, 24, 291, 307.) using a spectrophotometric method. He inferred the presence of specially active areas or patches on the surface of the catalyst, and concluded that the experimental facts of adsorption and catalysis could be explained quantitatively by assuming that strong and specific fields of force emanate from special configurations of the atoms on the catalyst surface. These conclusions do not appear to be very different from those of Taylor, except that Constable does not postulate the existence of atoms which are partly detached from the main surface of the catalyst, but rather attributes the specific fields of force to special atomic configurations at the surface.

Schwab and his co-workers take a more distinct view than does Taylor (Zeitsch. physikal Chem., 1928, B., 1, 385; 1929, 2, 262; 1929, A., 144, 243; 1929, B., 5, 406; 1930, A., 147, 38; 1931, B., 12, 427; 1930, B., 13, 13; 1936, B., 32, 169; Zeitsch. Elektrochem., 1929, 35, 135, 573.), when they suggest that the active centres are not distributed over the whole surface, or at 'active points', except where they are on lines which are phase boundaries. Adsorbed molecules are supposed to be 'adlineated', or collected together on the surface at

phase/

phase boundaries. Microphotographical observations suggested that the phase boundaries were the edges of the micro-crystals on the catalyst surface. This 'topo-chemical' theory of contact action appears to be the most fruitful development of Taylor's theory which has so far taken place.

Schmidt (Naturwiss., 1933, 21, 351; Zeitsch. physikal Chem., 1933, 165, 33, 209; 1936, 176, 237; Ber., 1935, B., 68, 1098.) attributes catalytic hydrogenation entirely to the diffusion of hydrogen into the metal, followed by the subsequent ionisation of the hydrogen. He does not consider the reaction as occurring at the active centres on the crystal surface, but in the cracks or pores within the crystals themselves, the so-called 'Smekal' cavities. He differentiates between adsorbed and absorbed gases, stating that it is the latter which react. These views appear to contradict a great deal of the published work on the subject, and in attributing all hydrogenation effects to the activation of the hydrogen alone, Schmidt's theory takes no account of the effect of the catalyst on molecules of organic reactants. It resembles the older views of Sabatier, which fail to explain selective hydrogenation or concurrent isometric changes in organic molecules, induced by the catalyst.

A 'multiplet' hypothesis of heterogeneous catalysis/

catalysis has been advanced by Balandin (Zeitsch.physikal. Chem., 1929, B., 2, 289; 1929, B., 3, 167; 1932, B., 19, 451; J. Russ. Phys. Chem. Soc., 1929, 61, 909; 1930, 62, 703.). This postulates that the active centres on a catalyst surface do not attract every part of the reacting molecule with the same intensity, but exert a preferential attraction on some aton or groups of it. If all the centres attracted the same part of the molecule, there would be no tendency for the molecule to be broken up, and adsorption would occur without reaction. If, however, various types of centres are present, some attracting one atom or group of the molecule, and some another, decomposition may be possible. But for actual change to take place, the centres must not be too far apart, and be arranged rather in groups or 'multiplets', containing one or more centres of each group. This hypothesis is an attempt to differentiate between several types of active centres or areas on the surface of the catalyst, and is interesting because it is an attempt to account for the highly specific nature of many heterogeneous catalytic actions. It is difficult, however, to envisage suitable experiments to test its validity.

A 'dislocation', or temporary polarity theory of catalytic action was put forward by Boeseken (Chem. Weekblad, 1928, 25, 135.), who suggested that catalysts act/

act by activating the reactants, different catalysts being able to activate the same substance in different ways, producing specific 'dislocations' by a type of induction. According to this view the main factor in catalytic action is that of energy, and that the catalyst would act in spite of, rather than because of, the production of intermediate compounds of the reactants and catalyst.

These are somewhat conflicting views, but whichever be nearer to the truth, it is fairly certain that as a result of the intensive study in the last twenty years of the nature of the surface of solid catalysts, the catalyst must not be regarded as a mass only, but also in respect of certain select atoms in which all the activity displayed is now believed to reside. Recent work, however, helps to emphasise the essential conditions which must be present before any catalytic action can occur.

CHAPTER IV.

PROMOTER ACTION.

The fact that the addition of small amounts of other substances to a catalyst may cause a considerable increase in its activity was emphasised in early patents of the Badische Company (B.P. 19249/1910; B.P. 27963/1913; B.P. 2306/1914, etc.), and has also been described in a large number of patent specifications. Pease and Taylor (J. Phys. Chem., 1920, 24, 241) suggested as a definition of promoter action, "cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present." With certain limitations this definition should serve well.

Rideal and Taylor ("Catalysis in Theory and Practice", 1926, p.102.) suggested that the definition should be restricted to the effects produced by relatively small amounts of a material which was itself inert, or had negligible catalytic effect on the reaction concerned. As a result of his studies on the effect of thoria as a promoter for nickel catalysts in the reduction of carbon monoxide, Taylor (J. Phys. Chem., 1925, 29, 1325.) suggested that it acted in three different ways:-

(i) Supported existing active centres.
(ii) Created additional active surface.
(iii) Altered the proportions in which the reactants and reaction products were absorbed.

These ideas were supported by Wyckoff and Crittenden (J.A.C.S., 1925, 47, 2866.) who showed, using iron catalysts containing alumina and potassium oxide, that the promoters prevented sintering of the catalyst, and that beyond a certain critical concentration the activity was lowered, due to the catalyst surface becoming covered with excess promoter.

Wagner, Schwab and Staeger (Z. Phys. Chem., 1934, 27, B., 439) showed that with copper oxide catalysts promoted with magnesia, zinc oxide, chromium oxide or alumina, and also with copper promoted with nickel, no change in crystal structure occurred corresponding with this increased activity. Frolich (J.I.E.C., 1929, 21, 109.) however, observed an increase in the copper crystal lattice in the case of zinc/copper catalysts employed in the synthesis of methanol, and Frost (Act. Physicochim., 1934, 1, 511.) attributed it to the formation of a brass. This expansion of the lattice was found to coincide closely with catalytic activity. On the other hand, it was found that the addition of promoters to zinc oxide for use as a methanol/

methanol catalyst did not affect the crystal structure. It appears, therefore, that X-ray examination will reveal compound formation, but not true promoter action.

Schenk and Wesslekoch (Z. Anorg. Chem., 1929, 184, 39.) found that there were clear indications of the existence of mixed crystals in the presence of effective oxides such as magnesia or alumina in the case of cobalt and nickel catalysts for the reduction of carbon dioxide, and that the presence of these crystals led to the production of carbon monoxide under conditions where the pure metals alone had no effect. Regarding promoter action in general, they expressed the opinion that "it seems highly improbable that a single explanation of promoter action, applicable to all cases, will ever be found", and the definition of promoter action given by Rideal and Taylor, even if limited in scope, can still be accepted as a working hypothesis.

Griffith (Nature, 1936, 137, 538.) carried out a thorough investigation into the effects of a large number of promoters on molybdenum oxide as a catalyst for the decomposition of hexane, and determined the optimum concentration of oxides of chromium, sodium, cerium, aluminium, barium, boron, silicon and thorium, and also of metallic iron, lead and copper. The very similar nature of the effects showed clearly that they were not due, in this/

this case, to the formation of compounds. It was found on comparing the results, that the ratio of promoter element to molybdenum giving greatest catalytic activity is independent of the particular oxide used, that is , the optimum concentration of the promoter is a function of the catalyst, and not of the promoter. The concentration was also shown to be independent of the hydrocarbon being decomposed. When the promoter is a compound which is capable of being converted to the metal under the conditions of the experiment, the atomic ratio necessary for maximum effect is only half that which is necessary in the case of an oxide promoter. The rate of rise and fall of activity, the maximum value reached, and final value, with excess promotor, are found to depend to some extent on the particular promoter employed.

These facts suggest that the promoter functions by means of valency bonds, and that a metal can be effective with respect to two centres simultaneously. The equivalence of all the oxide promoters suggested that the addition of a second promoter to a catalyst which already contained the maximum amount of the first for optimum activity, would lower the activity. This proved to be so, and it was advanced that in all cases of straightforward promoter action, where no complications due/

due to compound formation can occur, better results should not be obtained by the use of multiple-promoted catalysts than can be obtained with a single promoter.

Cassel (Naturwiss., 1926, 14, 103.) suggested that promoter action took place when the main component adsorbs one reactant, and the promoter the other, but this cannot be reconciled with facts concerning effects of promoters on the decomposition of molecules of a single type, nor does it agree with the observed effects of promoters on the adsorption of such reactants.

CHAPTER V.

THE SYNTHESIS AND DECOMPOSITION OF METHANOL.

When the reduction of carbon monoxide to methane was studied by Fischer and Tropsch (Brennstoff-Chem., 1923, 4, 193-197; Chem. Abst., 1924, 349.), the possibility of the reaction proceeding to an intermediate stage only was considered, with the production of methyl alcohol. In a broad and general way a German patent (Ger.Pat. 293787/1913.) covered a process for the synthesis of oxygenated organic compounds from carbon monoxide and hydrogen. More specific information was given in a patent and paper by Patart (Fr. Pat. 540343/1921; Chimie et Ind., 1925, 13, 179; Compt. rend., 1924, 179, 1336.), who reported the production of pure methyl alcohol, using pure zinc oxide as a catalyst, temperatures of 400-420°C. and pressures of 150-250 atmospheres. This showed conclusively that methanol could be prepared by passing mixtures of hydrogen and carbon monoxide at high temperatures and pressures over suitable catalysts. Patart later stated (Internat. Conference on Bitum. Coal, Nov., 1926.) that zinc oxide promoted with chromium oxide was the most satisfactory catalyst.

Many processes for the production of methanol appear in patent literature, but as far as can be judged, they/

they seem to differ from each other mainly in the catalysts used. These fall into three classes, namely, metallic oxide mixtures, mixtures of metals (including alloys), and mixtures of oxides and metals, or metals with oxides or salts as promoters. Of these, the first type are most generally used as methanol catalysts. The general statement made regarding the mixtures of oxides is that they should be of different groups of the periodic system, and not reducible to metal under the prevailing conditions. More specifically, to be suitable for such mixed catalysts, they should be non-reducible oxides of the second to seventh group (Mittasch, U.S. Pat. 1558559/1925.). Mittasch also specifies in the same patent that the more basic oxide should be in considerable excess. In a later patent he mentions mixed catalysts containing metal and oxide or salt - metals such as copper, lead and zinc, with an oxide or salt derived from a metal of from the fourth to the seventh groups of the periodic system acting as promoter (U.S. Pat. 1569775/1926.). A catalyst of copper and one of the elements titanium, vanadium, chromium, manganese or boron is specified by Schmidt and Ufer (Can. Pat. 251486/1925.) and they state that it must be free from iron and nickel.

One peculiarity of the methanol synthesis is that the catalysts must be free from iron, and also from nickel and/

and cobalt. These metals catalyse other reactions, especially the complete hydrogenation of the carbon monoxide to hydrocarbons. The gases must also be free from carbonyls, and special precautions taken to ensure that the carbon monoxide will not attack the walls of the reaction vessels. No nickel or iron can be used except in the case of special steels, while the apparatus should preferably be lined with copper. Some specifications also exclude alkalis, as they promote the formation of higher alcohols.

The decomposition of primary alcohols, on the other hand, was studied as far back as 1880, when Jahn decomposed methyl alcohol over zinc and zinc oxide catalysts, obtaining about 70% hydrogen and 30% carbon monoxide, together with traces of methane. In 1905, Sabatier obtained similar results with a copper catalyst. He concluded that copper, nickel, iron, platinum, palladium and certain metallic oxides were capable of decomposing methyl alcohol at atmospheric pressure and high temperatures. He later showed by work on zinc oxide/chromium oxide catalysts that zinc oxide decomposed methyl alcohol more readily than chromium oxide, and that it was principally dehydrogenating in character, while chromium oxide was principally dehydrating, and that the specific effect of each depended upon the temperature of calcination/

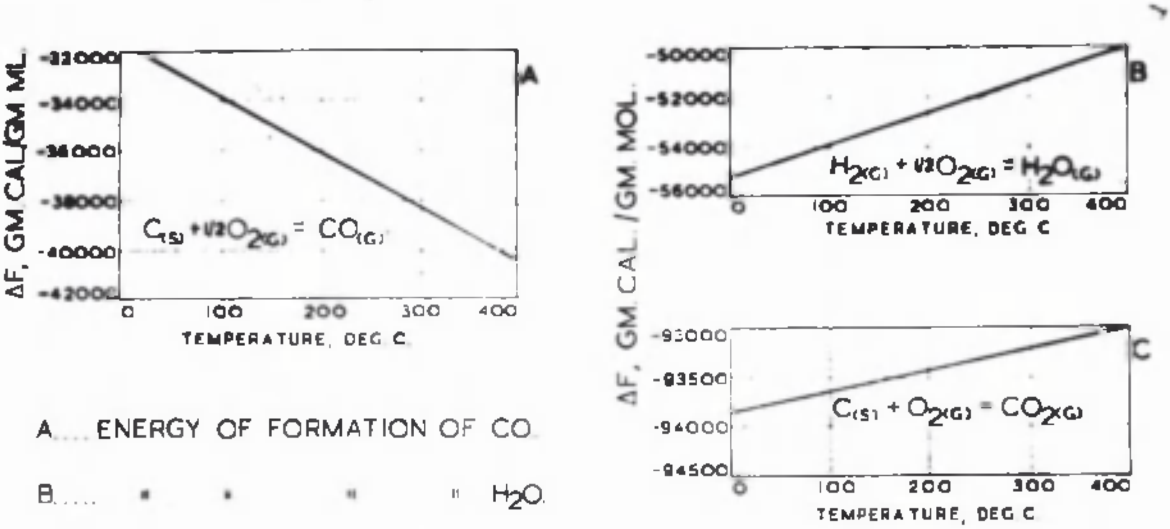
calcination (Sabatier, Catalysis in Org. Chem., 1923, p.674.).

Patart (Lormand, J.I.E.C., 1925, 430.) observed that a combination of the two oxides as chromate gave better results in the decomposition of methanol than either of the two oxides alone. Smith and Hawk (J.Phys. Chem., 32, 414, 1928.) made a study of the decomposition of methanol over a wide range of catalysts. They found that out of 36 different mixtures of oxides, among the best was a mixture of zinc and chromium oxides in the proportion of 4Zn: 1Cr. They showed also by X-ray examination that the zinc and chromium were in actual chemical combination.

Work on the synthesis and decomposition of methanol over copper/zinc oxide catalysts by Frolich, Fenske, Taylor and Southwick (J.I.E.C., 1928, 1327.) led them to conclude that the decomposition and synthesis of methanol were parallel reactions, and that the decomposition method of examination of the reaction was eminently suitable for the study of the activity of catalysts for the synthesis of methanol from water gas at high temperatures and pressures. Audibert and Raineau (J.I.E.C., 1928, 1105.) came to similar conclusions. They add that the method of preparation of the catalysts is most important, it being essential to carry/

carry out the reduction at as low a temperature as possible. They also state that mixed catalysts are more resistant to heat than single component catalysts.

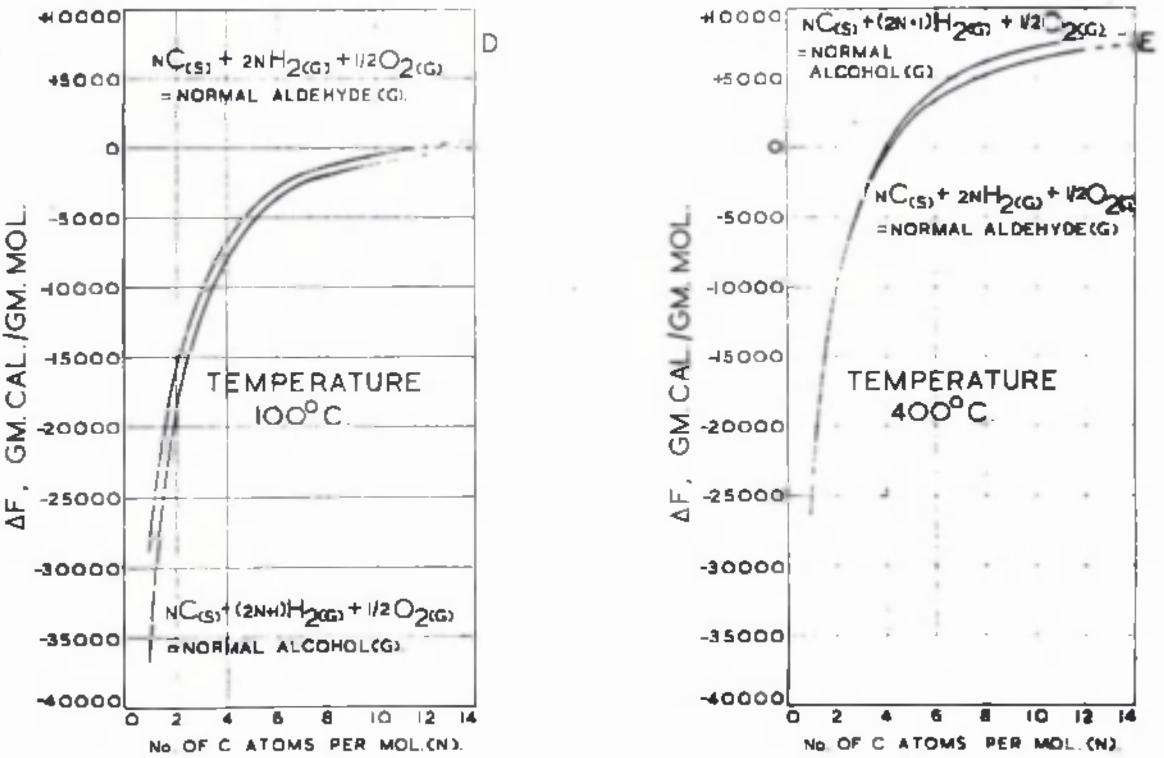
It is apparent, therefore, that the decomposition method of investigating the reaction is particularly useful in that it permits operation at atmospheric pressure, where experimental procedure is greatly simplified.



A.... ENERGY OF FORMATION OF CO

B..... " " " " H_2O

C..... " " " " CO_2



D&E ... ENERGY OF FORMATION OF NORMAL ALCOHOLS AND ALDEHYDES

Fig. 1. Thermodynamical data.

CHAPTER VI.

THEORETICAL ASPECTS OF THE METHANOL DECOMPOSITION AND SYNTHESIS.

As a catalyst affects only the speed of a chemical reaction, having nothing to do with the inherent tendency of that reaction to proceed, it is of paramount importance to know if the reaction is possible under given experimental conditions of temperature and pressure. The problem is one of chemical affinity, and as the free-energy change of a specific chemical reaction is a quantitative measure of such chemical forces, it is desirable to have free-energy data concerning the reactants, if it can be had. If the free-energy data indicate that the reaction is possible under the chosen conditions, experiments can be started to find catalysts which allow the reaction to proceed at a reasonable rate.

It is difficult to obtain accurate free-energy data for a large number of organic compounds, but a reasonable amount of fairly reliable data are now available (Parks and Huffman, "Free Energies of Some Organic Compounds", New York, 1932). Figs. 1a-e opposite give free-energy values of the compounds relating to the methanol reactions. (Groggins, "Unit Processes in Organic synthesis", pp.446, 447, New York, 1938). The values are for the free-energy of formation in the gaseous/

gaseous state at 1 atmos. pressure from the elements. Values are given for 100°C. and 400°C., it being permissible to make linear interpolation between these two temperatures for intermediate temperatures. To show the relationships which exist between the straight-chain aliphatic compounds, the free-energy content per carbon atom is plotted. (To obtain the molal value, the ordinate values must be multiplied by the number of carbon atoms in the straight-chain aliphatic compound in question).

When all the reactants and products are in the gaseous state at a partial pressure of 1 atmos., the well-known relationship exists:-

$$-\Delta F = 4.57 \ T \log. K.$$

ΔF is the free-energy decrease in calories for the reaction as it proceeds from left to right, and represents the difference in free-energy content of all the reactants and products. T is the Absolute temperature in deg. Kelvin, and K the equilibrium constant of the reaction, products being in the numerator and reactants in the denominator, in terms of the individual partial pressures in atmospheres. For calculations this system of units must be strictly adhered to in using the above equation.

On the basis used here for free-energy values, all elements in their normal state of aggregation at 1 atmos./

atmos. pressure and at any temperature T are arbitrarily assigned the value of zero free-energy. In this way the free-energy of any compound will have a plus or minus value, since the free-energy at any temperature T is merely the free-energy of formation from the elements at temperature T.

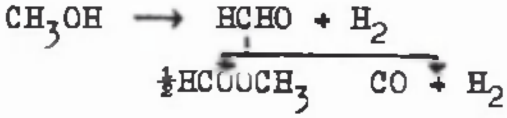
From the equilibrium constant of a chemical reaction it is thus possible to calculate the ultimate yields which may be expected, and also determine quantitatively the effect of pressure on the equilibrium conversion for those reactions affected by pressure, i.e. those involving increase or decrease in the number of gaseous molecules. If the equilibrium constant at another temperature is required, it is necessary only to calculate the free-energy change at that temperature.

All spontaneous reactions, i.e. those proceeding of their own accord, in the absence of any outside influences, e.g. electrical or magnetic, are attended by a free-energy decrease. If a reaction involves only one compound, and an element, e.g. hydrogen, and yields only one compound as product which has the same number of carbon atoms as the original compound, the compound having the lower free-energy under the prevailing experimental conditions is the more stable.

It is interesting to apply these thermodynamical principles/

principles to the analysis of the methanol reactions. For the sake of convenience these will be dealt with separately in the order in which they are investigated experimentally, namely, (1), decomposition, (2), synthesis.

Experiments on the decomposition of methanol over CuO/ZnO catalysts by Fenske, Frolich and Quiggle (J.I.E.C., 1928, 694) led them to put forward a stepwise theory for the decomposition of methanol:-



$$\begin{tikzcd} CH_3OH \arrow[r] & HCHO + H_2 \arrow[d] \arrow[dr] & \\ & \tfrac{1}{2}HCOOCH_3 & CO + H_2 \end{tikzcd}$$

The evidence they put forward in favour of this suggestion is the fairly constant amount of formaldehyde in the decomposition products, there being an appreciable variation in the amount formed only in the case of those catalysts of high Zn and high Cu content. Another point in favour of the intermediate production of formaldehyde, they state, is the high proportion of methyl formate present in the decomposition products when pure ZnO is used as catalyst. This is most readily explained by the following equation:-

$$2\ HCHO = HCOOCH_3.$$

Carbon dioxide and methane are also products of the reaction, due to side reactions. According to the equation:-

$$2\ CH_3OH = CH_4 + CO_2 + 2H_2.$$

they/

they should be present in equivalent amounts, though in many cases the CO_2 is in excess of the CH_4. Cryder and Frolich (J.I.E.C., 1929, 867) support the theory of the intermediate formation of formaldehyde, and suggest that CO_2 and water are formed according to equations (1) and (11) following:-

$$(1)\quad CO + H_2O = CO_2 + H_2,$$

$$(11)\quad 2\ CH_3OH = CH_3OCH_3 + H_2O$$

A reaction such as the latter is highly probable with catalysts containing an excess of chromium oxide, it being principally dehydrating in character as shown by Sabatier. Smith (Smith and Hawk, J. Phys, Chem., 1928, 32, 414) observed that a considerable amount of low-boiling constituent was formed in the decomposition of methanol over a chromium oxide catalyst. This is supposed by Cryder and Frolich to be dimethyl ether, since Brown and Galloway (J.I.E.C., 1929, 310) definitely proved its existence as a bye-product in the synthesis of methanol from carbon monoxide and hydrogen with zinc oxide/chromium oxide catalysts. It seems probable that it is further dehydrated according to the equation:-

$$CH_3OCH_3 = C_2H_4 + H_2O.$$

Frolich, Davidson and Fenske (J.I.E.C., 1929,110)

using/

using Cu/ZnO catalysts, further support the stepwise theory of the decomposition of methanol.

The principal bye-products of the reaction appear, then, to be formaldehyde, methyl formate, unsaturated hydrocarbons, carbon dioxide and methane. Evidence of the occurrence of other side-reactions is obtained from the odour of the reaction products, which is not characteristic of the main constituents. The main reaction, however, is the decomposition of methanol to carbon monoxide and hydrogen in the approximate ratio of 1 : 2 by volume (Fenske, Frolich and Quiggle, J.I.E.C., 1928, 694). These workers also found that with Cu/ZnO catalysts there was maximum activity with 50 mol% copper, and that there was a sharp rise in the production of methyl formate up to 88 mol% Cu., resulting in 80% of the decomposed methanol occurring as such. With zinc oxide/ chromium oxide mixtures, Cryder and Frolich (J.I.E.C., 1929, 867) found that maximum activity was obtained with a catalyst of molecular percentage composition, Zn 78, Cr 22.

The following reactions, therefore, may be taken into account for the decomposition of methanol at atmospheric pressure.

(1) $CH_3OH = CO + 2H_2$

(2) $CH_3OH = HCHO + H_2$.

(3) $HCHO = CO + H_2$.

(4) $2HCOH = HCOOCH_3$.

The following table gives the thermodynamical data for these reactions, calculated from fig.

Table I.

	ΔF.		Kp.	
Reaction.	250^0C	300^0C	250^0C	300^0C.
(1). $CH_3OH = CO + 2H_2$	-6000	-8700	$3.2x10^2$	$2.1x10^3$
(2). $CH_3OH = HCHO + H_2$	+5000	+5000	$8.3x10^{-3}$	$1x10^{-2}$
(3). $HCHO = CO+H_2$	-11000	-13700	$1.5x10^4$	$1.7x10^5$
(4). $2HCHO = HCOOCH_3$	-23400	-30400	$6.6x10^9$	$4x10^{11}$

It will be noticed that the equilibrium constant of each reaction increases with temperature, and that the free-energy value decreases, except in reaction (2).

With regard to the suggested stepwise decomposition of methanol, as represented by reactions (2) and (3) above, it is of interest to note that ΔF for (2) has a positive value, indicating that the reaction is not spontaneous under the above conditions. From the data it is evident that although reactions (1) to (3) are possible, (1) is thermo-dynamically more probable than (2) followed by (3). Furthermore, for a step-reaction of the above type to take place, each of the steps must necessarily be spontaneous. (Lewis and Randal, "Thermodynamics", p.601, New York, 1923). Thus the free-energy data indicate that the/

the decomposition of methanol at atmospheric pressure is more probably direct to CO and H_2 than through formaldehyde.

It will be noticed, however, that the free-energy change of reaction (3) is greater than that of reaction (1), indicating that formaldehyde is more readily decomposed than methanol at atmospheric pressure, and this is found experimentally to be the case. Reaction (3) appears to be offset by reaction (4), the polymerisation of formaldehyde to methyl formate. But experiments on the decomposition of formaldehyde at atmospheric pressure prove that under these conditions reaction (3) and the reverse of reaction (2) predominate (See Part II).

(It is also possible that the following reaction may account for the presence of methyl formate in the decomposition products of methanol at atmospheric pressure:-

$$2CH_3OH = HCOOCH_3 + H_2.$$

$$\Delta F_{250^\circ} = -1410; \ \Delta F_{300^\circ} = -980.$$

On comparison of the free-energy changes of this reaction with those of reaction (4) however, it is evident that the latter is much more probable.)

In other words, although it is possible that methanol can decompose to carbon monoxide and hydrogen through the intermediate formation of formaldehyde, it is/

is thermodynamically much more probable that the decomposition is not stepwise, especially when the thermal data for the first step, i.e. the formation of formaldehyde, are considered.

In the case of the interaction of carbon monoxide and hydrogen there are several courses the reaction may take:-

(1) $CO + H_2 = HCHO + 2000$ calories.

(2) $CO + 2H_2 = CH_3OH + 24685$ "

(3) $CO + 3H_2 = CH_4 + H_2O + 50000$ calories.

(4) $2CO + 2H_2 = CH_4 + CO_2 + 60280$ "

(5) $nCO + mH_2 =$ higher hydrocarbons, alcohols, etc.

(The heats of reaction are given for the reactants and products in the gaseous phase.)

Free-energy data will indicate which of the above reactions will tend to predominate, e.g:-

Reaction (1) $\Delta F_{100^\circ C} = +7000$ cal.; $\Delta F_{400^\circ C} = +16500$ cal.

" (2) $\Delta F_{100^\circ C} = -2500$ " ; $\Delta F_{400^\circ C} + 14300$ "

" (3) $\Delta F_{100^\circ C} = -31000$ " ; $\Delta F_{400^\circ C} = -14000$ "

" (4) $\Delta F_{100^\circ C} = -36600$ " ; $\Delta F_{400^\circ C} = -16500$ "

At 100°C the free-energy decrease indicates that the reduction of carbon monoxide to methanol is possible, but so far no catalyst has been found that will bring about the reaction at this low temperature. At 400°C on the other hand, the reduction to methane is a spontaneous reaction.

The stage at which the reaction stops will be determined/

determined by the catalyst employed, e.g. nickel carries the reduction completely to methane, and oxide catalysts, such as mixtures of oxides of zinc, copper, chromium, manganese, etc., carry it mainly to the methanol stage. Catalysts have yet to be discovered which will stop the reaction at the formaldehyde stage.

From a consideration of the volumes concerned in the above reactions, it can be seen that the synthesis of methanol proceeds with the greatest volume change, and would hence be favoured with increased pressure. Equilibrium data for this synthesis from carbon monoxide and hydrogen are as follows:-

$$Kp = \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

(Newitt, Byrne and Strong, Proc. Roy. Soc., A123, 236, (1929)).

Temp., °C.	Kp.
100	3.0×10
260	1.2×10^{-3}
300	1.6×10^{-4}
340	2.9×10^{-5}
380	6.3×10^{-6}

It is of interest to note that the equilibrium constant of the reaction decreases with temperature. At atmospheric/

atmospheric pressure and room temperature methanol is perfectly stable, whilst at 300°C it exists in equilibrium with the theoretical proportions of hydrogen and carbon monoxide to the extent of less than 2% Even with the best catalysts however, it has apparently been impossible to carry out the synthesis at temperatures much below 300°C, corresponding to practically no methanol production at atmospheric pressure. This clearly shows why attempts to synthesise methanol at atmospheric pressure were bound to fail.

On the other hand, by calculation the equilibrium favours almost 100% methanol at 300°C under a pressure of 1000 lb/in.^{2} With the most sensitive catalysts moreover, it is necessary to use considerably higher pressures to favour the formation of methanol, and reduce the possibility of side reactions. The possibility of side reactions taking place is further reduced by using more than the theoretical proportion of hydrogen.

Lewis and Frolich (J.I.E.C., 1928, 285) found that the conversion of carbon monoxide to methanol increased with temperature up to 330°C, and then fell with further temperature rise, and that the yield increased with rate of gas flow. They found also that the conversion of the carbon monoxide was favoured by increase of pressure, while side reactions increased with temperature.

The/

The data of fig. 1 (p28a) may be applied to the reaction between carbon monoxide and hydrogen which has the greatest tendency to predominate, namely:-

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

$$-40500 + 0 + \Delta F = -4500 \quad -50000$$

$$\Delta F = -14000 \text{ cal. at } 400^{\circ}C$$

The free-energy decrease shows that at this temperature the reduction of carbon monoxide to methane is a very complete reaction as judged by the equilibrium yield which is possible. If the above reaction is considered in the reverse direction, it will be seen that it represents the method of preparation of hydrogen from hydrocarbons by causing them to react with steam at temperatures in the region of 1000°C, where the reverse reaction is possible (methane-steam reaction).

In this connection it might be proposed to carry out a reaction such as the following:-

$$CH_4 + H_2O = CH_3OH + H_2$$

$$-4500 \quad -50000 + \Delta F = -26000 + 0$$

$$\Delta F = +28500 \text{ cals at } 400^{\circ}C$$

While it would be highly desirable to carry out such a reaction, making natural gas into a more valuable product, the magnitude of the free-energy increase indicates the impossibility of doing this at any practical temperature level. It is useless, therefore, to expend any energy in this/

this direction, as the reverse reaction is obviously predominating.

The Fischer-Tropsch process for the synthesis of hydrocarbons higher than methane from water-gas at atmospheric pressure can be analysed in a similar manner from the data of fig. 1 (p.28a). It is found that such reactions are entirely possible, even at atmospheric pressure and temperatures up to 400°C. It must be borne in mind, however, that the higher molecular weight hydrocarbons which result from this synthesis are likely to be further reduced to methane, since methane is the most stable hydrocarbon at temperatures near 400°C. This destructive hydrogenation or hydrogenolysis would be more apt to occur at high temperatures, for here all reaction velocities are increased, and the specific action of a catalyst is in general reduced markedly. The latter is shown to be the case in the experiments on the decomposition of methanol and formaldehyde which follow. Temperature control has therefore been found to be a highly important factor in the Fischer-Tropsch process, and in general for all hydrogenation (catalytic) reactions.

Fig~~s~~.1 show that at 100°C the normal alcohols have lower free-energy values than the corresponding aldehydes. Hydrogenation is therefore possible if catalysts can be found to bring about the reduction with reasonable speed/

speed. At higher temperatures, e.g. 400°C, it is seen that the aldehydes possess lower free-energies than the corresponding alcohols. This means that the normal spontaneous tendency at this temperature is for the alcohols to dehydrogenate to yield aldehydes. Since the reduction proceeds with a decrease in volume, it is possible to carry it out at this temperature under pressure; but without the application of pressure the reduction would not be feasible at 400°C. This reduction of aldehydes to alcohols is apt to be accompanied by side reactions, due to the tendency to complete hydrogenation to methane. This is in fact the case, unless the conditions are carefully chosen.

The mechanism of the higher alcohol synthesis is generally supposed to be as follows:-

$$2\ CH_3OH \longrightarrow C_2H_5OH + H_2O$$

$$CH_3OH + C_2H_5OH = C_3H_7OH + H_2O$$

$$2C_2H_5OH \longrightarrow C_4H_9OH + H_2O, \text{ etc.}$$

This may be typified by:-

$$2CH_3OH \longrightarrow C_2H_5OH + H_2O$$

$$2(-262200) + \Delta F = 2(-8400) + -50000$$

$$\Delta F = -14400 \text{ cals. at } 400^{\circ}C.$$

Thermodynamically this condensation is entirely possible, as the reaction proceeds with a relatively large decrease in free-energy. To carry out this reaction, catalysts possessing/

possessing dehydrating as well as condensing properties would be required. Thus, free-energy data are useful not only in determining whether or not a particular overall reaction is possible, but also in interpreting reaction mechanisms and in aiding in the choice of catalysts for those reactions which seem most feasible.

Reverting to the methanol synthesis, the following reactions can be considered possible at one and the same time:-

Table II.

Reaction.	ΔF.		Kp.	
	250°C	300°C	250°C	300°C
(1) $CO + H_2 = HCHO$	+ 11000	+ 13700	3.5×10^{-5}	5.9×10^{-6}
(2) $HCHO + H_2 = CH_3OH$	-5000	-5000	1.2×10^{2}	9.8×10
(3) $CO + 2H_2 = CH_3OH$	+ 6000	+8700	3.1×10^{-3}	4.8×10^{-4}
(4) $2HCHO = HCOOCH_3$	-23400	-30400	6.6×10^{9}	4×10^{11}

At first sight it would appear from the figures of the above table that the synthesis of methanol is very unlikely, but when it is remembered that the pressure alters the equilibrium, it will be seen that the process becomes feasible. Considering the above data of reactions (1) and (3), the latter is thermodynamically the more probable, though both are possible. Of reactions (2) and (4), the latter is far more probable than the former. This latter is found to be the case experimentally, all efforts/

efforts to hydrogenate formaldehyde under pressure to methanol resulting in polymerisation in preference to hydrogenation (see Part III). It would seem, then, that under the standard conditions (for the definition of Kp and ΔF as used here) it is more probable that methanol is formed by reaction (3) than by reaction (1) followed by reaction (2), remembering that reaction (4) is far more probable than reaction (2). Fig. 2 illustrates graphically the reactions involved in the synthesis of methanol from carbon monoxide and hydrogen.

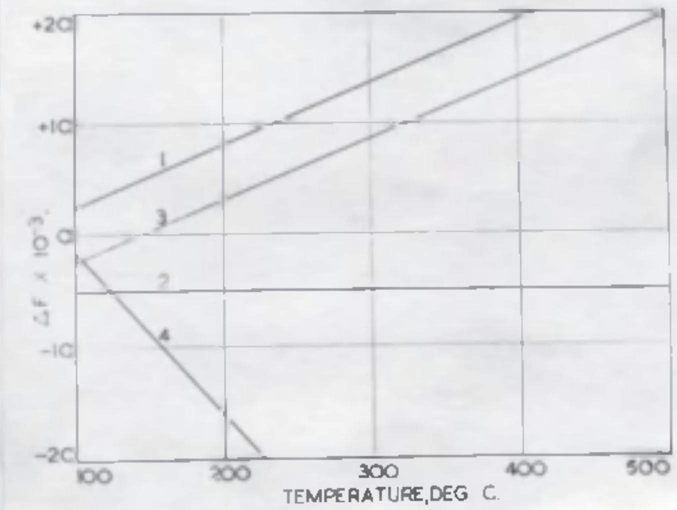


Fig.2. Thermodynamical data of methanol synthesis and allied reactions.

EXPERIMENTAL SECTION.

PART I.

THE DECOMPOSITION OF METHANOL AT ATMOSPHERIC PRESSURE WITH Zn/Cr OXIDE CATALYSTS.

CHAPTER VII.

PREPARATION. ANALYSIS AND REDUCTION OF CATALYSTS.

Preparation.

The method adopted was that of Cryder and Frolich (J.I.E.C., 1929, 867.) which is as follows:-
A concentrated solution of zinc nitrate was prepared by dissolving chemically pure zinc oxide in 50% nitric acid. This solution was heated to about 80°C. and concentrated ammonia solution added with constant stirring till the solution was free from acid. On settling, the clear liquor was decanted off, and the precipitate washed well with water at about 80°C., using 3 washings of 1 litre each. The slurry was analysed for zinc content (see "Analysis"), and about 500 cc. of it weighed out, and the calculated quantity of solid chromic acid added. Where it was in considerable excess, there was still enough water in the zinc hydroxide paste to dissolve the chromic acid. This mixture was evaporated to dryness with continual stirring, the final stages being carried out on a water-bath to prevent overheating. After drying in this manner, the mass was broken up, screened between 10 and 40 mesh (I.M.M.) and finally dried in an air oven at 110°C. for two hours. After cooling, it was stored in a well-stoppered bottle. It was found that catalysts containing a high proportion of chromium were deliquescent, and some difficulty was experienced in handling/

handling them.

Nine samples were prepared in this manner, the estimated range being from about 15 mol.% Zn. to about 75 mol.% Zn.

Analysis of Catalysts.

About 2 gms. of the sample were dissolved in 100 cc. of water and hydrochloric acid. 20 ccs. of the solution were used for the estimation of chromium by the usual iodometric method. A further 20 ccs. were used for the estimation of zinc by the ferrocyanide method, the procedure being as follows:-
The chromic salt was reduced with SO_2, and the excess SO_2 boiled off. To this were added about 5 gms. of solid NH_4Cl, and 5 ccs. of concentrated H_2SO_4, and the solution then diluted to about 200 ccs. with water at a temperature not exceeding 30°C. Three drops of a 5% solution of diphenylamine in concentrated H_2SO_4 were added as indicator. This solution was titrated with standard N/10 potassium ferro-cyanide containing 0.5 gms. potassium ferricyanide per litre. This ferrocyanide solution had been previously standardised against a solution of zinc sulphate of known zinc content, and exposed to light as little as possible.

This was found to be a quick and accurate method of/

of analysis, and the results were obtained on a direct weight : weight basis.

Reduction of Catalysts.

The reduction of zinc oxide/chromium oxide catalysts by methanol is strongly exothermic, the heat evolved in many instances being sufficiently great to cause incandescence of the catalyst mass, with accompanying impaired activity. Audibert and Raineau (J.I.E.C., 1928, 1105.) state that it is essential to carry out the reduction at as low a temperature as possible, and Frolich and Nussbaum (J.I.E.C., 1931, 1386.), using catalysts of the Zn/Cu type, state that the activity of the catalyst depends on its temperature of reduction; generally the higher the reduction temperature, the lower is the resulting activity. They state that a temperature of 240 - 250°C. is best.

It was therefore decided to control the reduction by diluting the reducing methanol vapour with nitrogen.

The catalyst was heated for four hours at a temperature of 220 - 230°C. in a stream of nitrogen (approx. 10 L/hr.) to drive off oxides of nitrogen, water, etc. (Frolich and Nussbaum, J.I.E.C., 1931, 1386.), and then methanol vapour passed in (for method see "Procedure", Ch. VIII). No reduction took place until the temperature was raised to about 250°C. The commencement of reduction was manifested by a sudden, sharp rise in temperature, accompanied/

accompanied by a further evolution of nitrous fumes for a period of about five minutes. This rise in temperature was checked by reducing the supply of methanol to the system. It was found difficult to keep the temperature of reduction below 280 - 290°C. due to the evolution of the heat of reduction, even although the furnace temperature was about 240 - 250°C. This range was therefore fixed as a standard for reduction. The temperature of reduction was maintained by variation of the rate of flow, and more particularly, by variation of the concentration of methanol in the methanol/nitrogen reducing mixture. Increased concentration of methanol resulted in a rise in temperature.

When the temperature started to fall, and was not raised again by increasing the methanol concentration, reduction was judged to be complete, and methanol was passed in for a further 45 minutes at a standard rate of 2.5 gms./hr. in a stream of nitrogen at 4 L/hr. The reduced catalyst was cooled in a stream of nitrogen, and stored in a tightly stoppered bottle. Samples of the reduced catalysts were tested for completeness of reduction by boiling with water for 2 - 3 minutes. Any yellow colour in solution was an indication of incomplete reduction.

As already stated, the activity of both supported and/

and non-supported catalysts is greatly affected by the heat treatment to which they are subjected, and therefore it was important to standardise the reduction conditions of the catalysts if consistent results were to be obtained.

As it was found in the course of experiments that the catalysts lost activity on storing in the reduced state, (see page 82), the required amount of catalyst was reduced immediately before being used in an experiment. The conditions were slightly modified, but in general were the same as described before. Approximately 5.5 ccs. of catalyst were reduced, as the volume diminished during reduction. Reduction was complete (as judged by the temperature fall previously described)in 10 - 20 minutes, depending on the composition of the sample, e.g. those with a high proportion of chromium requiring more time than those high in zinc. After cooling, 5 ccs. of the catalyst were weighed and used for the decompositions.

Fig 3. illustrates the variation in density of the mixed catalysts with composition, and is necessarily approximate.

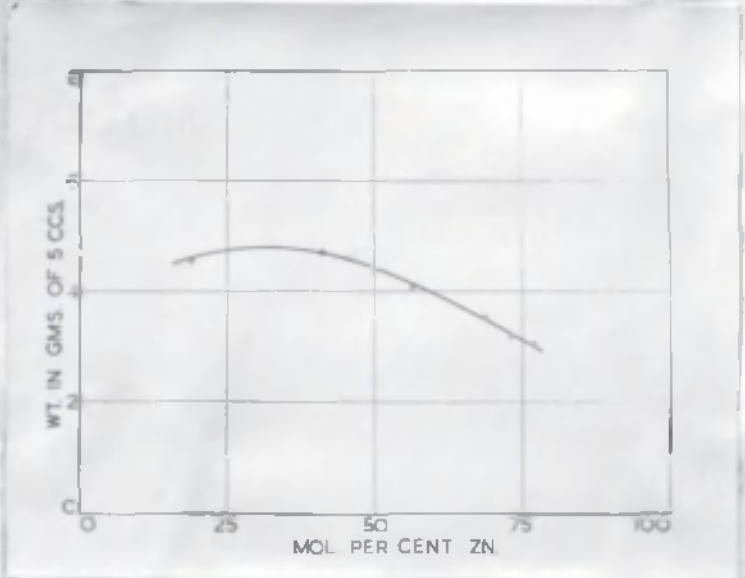


Fig.3. Variation in density of Zn/Cr oxide catalysts with composition.

It was found that the more active catalysts evolved a greater amount of heat during reduction than those less active, and thus had to be reduced with a more dilute mixture of methanol in nitrogen. Generally, the more active the catalyst, the lower was the temperature at which reduction commenced, e.g. with a sample containing 68.8 mol% Zn, reduction started at about 250°C., while one with 18.8 mol% Zn required a temperature of about 280°C. to start reduction.

As a result of work carried out on methanol catalysts, Fenske and Frolich (J.I.E.C., 1929, 1052.) using/

using carbon monoxide and hydrogen, concluded that the catalyst was reduced by carbon monoxide, and not by hydrogen, formed by the decomposition of the methanol. This point was investigated during the reduction of about 5 ccs. of a catalyst of composition 68.8 mol% Zn. The gases issuing during the period of reduction (period of raised temperature) were collected after scrubbing with water to remove nitrous fumes during the initial stages, and analysed. The following is the composition (N_2 free):-H_2 ..46% CO... 8%; CO_2... 46%; CH_4... nil.

When methanol is decomposed, the gas produced consists of 66% H_2 and 33% CO approximately, if no reduction of the catalyst takes place. These values are reduced as follows:-

H_2, from 66% to 46%, a reduction of 3 : 2 approx.
CO, from 33% to 8%, a reduction of 4 : 1 approx.

It would thus seem that reduction is more probably by carbon monoxide than by hydrogen.

The water-gas reaction is as follows:-

$$CO + H_2O = CO_2 + H_2.$$

(water being formed by hydrogen reducing the oxide catalyst. If this reaction occurs, reductions in the proportions of carbon monoxide and hydrogen similar to the above will also be obtained. The results are therefore indeterminate, and can be interpreted either way.

CHAPTER VIII.

APPARATUS AND PROCEDURE.

Apparatus.

The layout of the apparatus is shown in fig. 4.

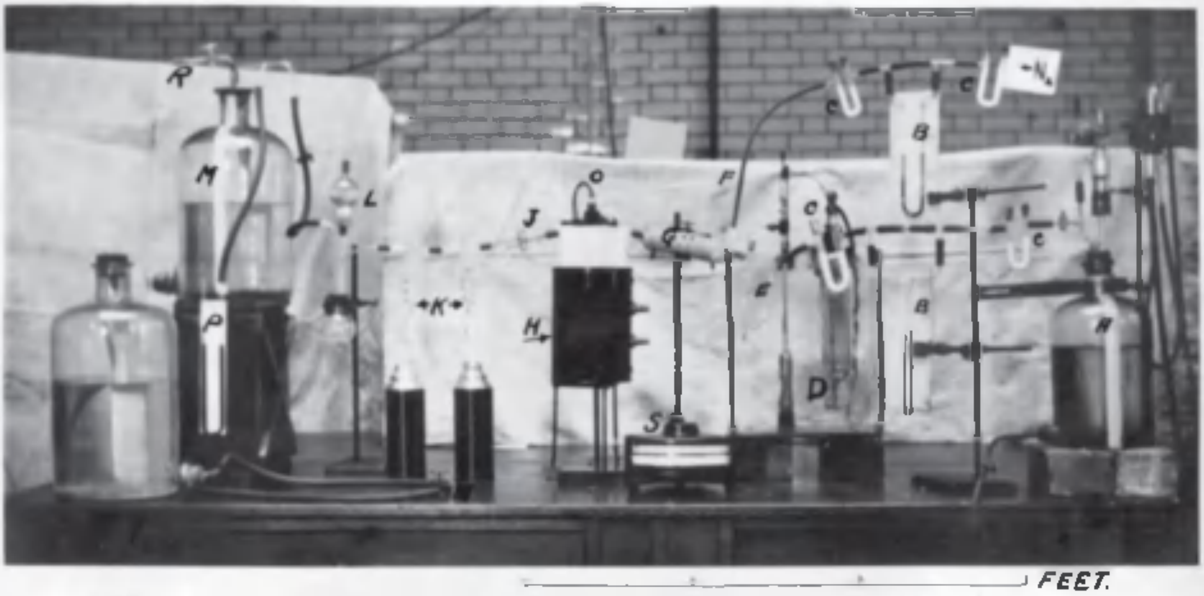


Fig.4. Apparatus for decomposition of methanol at atmospheric pressure.

A. Gray apparatus.

B. Calibrated flow meter.

C. $CaCl_2$ drying tube.

D. Thermostat.

E. Methanol vaporiser.

F. N_2 entry.

G. Preheater.

H. Furnace and reaction vessel.

J. 2-way cock.

K. Immersion condenser.

L. Water scrubber.

M. Gas receiver.

N. Screw-clip regulator.

O. Thermocouple leads to millivoltmeter.

P. Manometer.

R. Venting cock.

S. Millivoltmeter.

The methanol was vaporised by passing a steady stream of nitrogen through it, the methanol being kept at a fixed temperature in a thermostat. The steady stream of nitrogen was obtained from a Gray Constant Pressure Delivery Apparatus (Gray, J.S.C.I., 1928, 47, 187.) which is shown in fig. 5 - the rate being determined by the head of water 'h'.

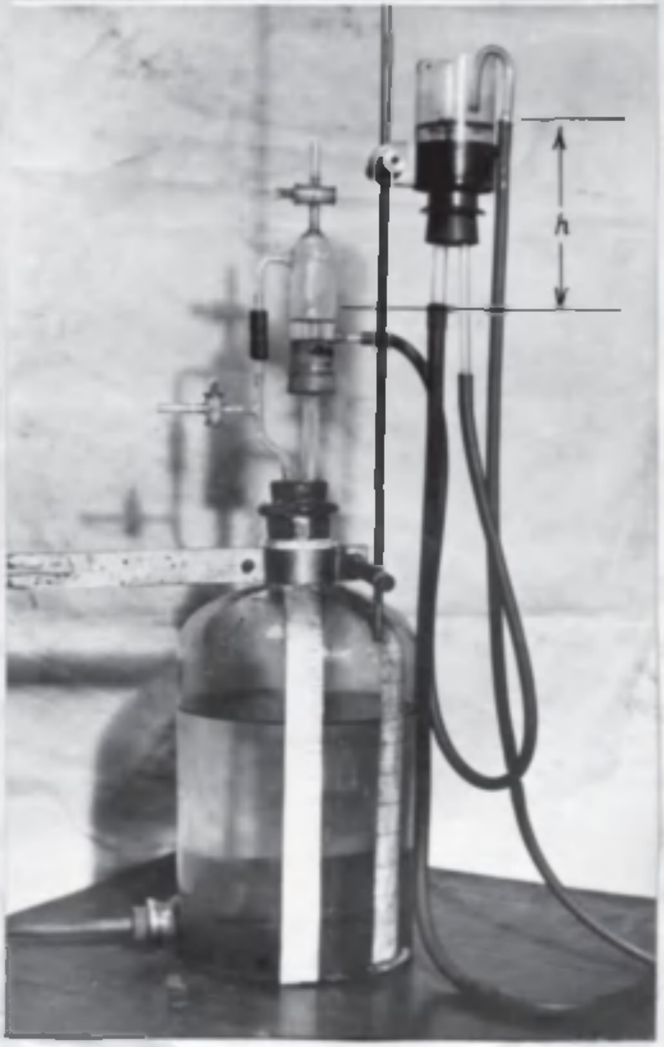


Fig.5. Gray Constant Pressure Delivery Apparatus.

The methanol was contained in a vaporising tube (fig.6)

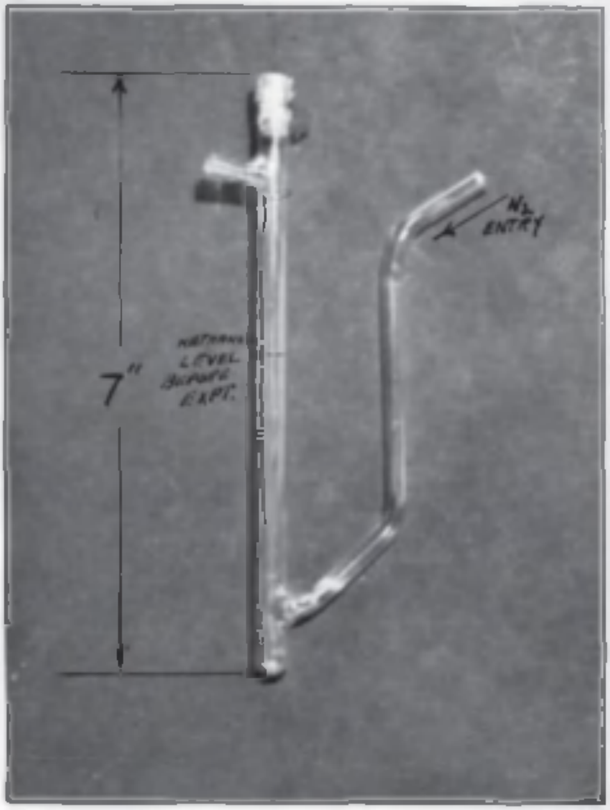


Fig 6. Methanol Vaporiser.

It will be noticed that the outlet of the vaporiser is at an angle to the side of the tube. The reason for this was to drain back any partially condensed methanol from the connection to the preheater into the vaporiser. With the outlet horizontal it was found on removing the vaporiser for weighing after an experiment, that a drop of methanol collected at the junction to the preheater, and was lost, affecting the mass balance.

All the nitrogen entering the apparatus was dried/

dried by means of the $CaCl_2$ tubes, those inserted before the flow-meters preventing condensation of moisture in the orifices.

Preliminary experiments showed that the oxygen-balance was 2 - 3% high, and the cause of this was traced to the nitrogen supply. The cylinder nitrogen was analysed, and was found to contain about 1.3% oxygen. This was removed by bubbling the gas through a solution of the following composition:-

Sodium hydrosulphite	40 gms.
Sodium hydroxide	30 "
Anthraquinone 2-sulphonic acid (sodium salt)	5 "
Water	250 ccs.

This solution was preferred to pyrogallol or phosphorus, as the former tends to liberate carbon monoxide on saturation, and with the latter, difficulty is found in the removal of the P_2O_5 fumes.

Later chromous chloride was used and was found to be even better than the hydrosulphite solution.

The method of vaporisation of the methanol used was preferred to the method of dropping the methanol from a burette into a tube heated to a temperature above the boiling point of methanol, first because a direct gravimetric means of estimation was desired, and secondly, because the drip/

drip method gives rise to an intermittant flow, and hence varied rate, of the methanol vapour over the catalyst. Nitrogen was used as the inert medium for the conveyance of the methanol, as it is not appreciably adsorbed on the catalyst surface (Taylor and his co-workers, J.A.C.S., 1921, 43, 1273, 2179; 1923, 45, 887, 900, 1196, 2235; 1924, 46, 43; etc.).

This method of vaporisation of the methanol was found to be very convenient, as the rate of flow could be varied simply by varying the velocity of the nitrogen through it. Moreover, the amount of volatilisation could be kept almost constant over a large number of experiments.

The mixture of methanol and nitrogen, after being preheated to about 200°C in the preheater, passes into the reaction vessel, shown in fig. 7.

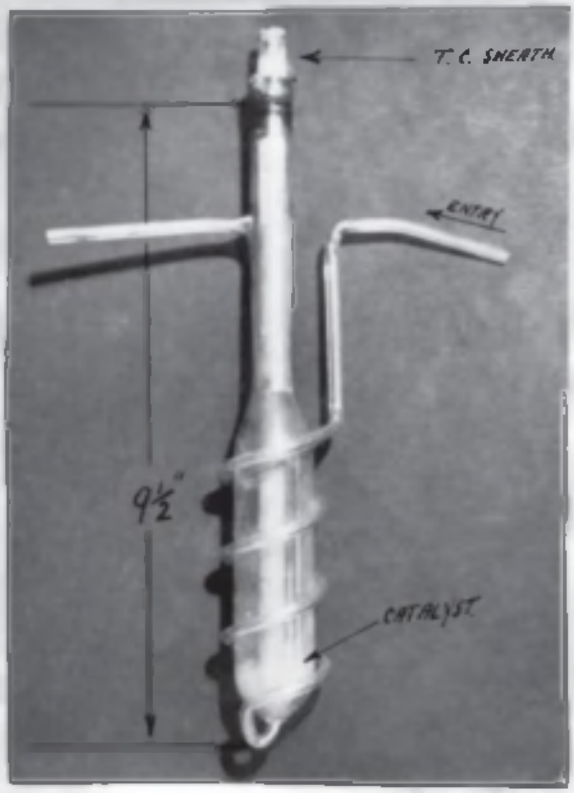


Fig.7. Reaction Vessel.

The gases are further heated by passing through the coil, and pass into the catalyst space at the same temperature as the catalyst itself. The temperature was measured by means of a copper/monel thermocouple, the silica sheath of which was embedded in the mass of the catalyst so that the tip was approximately in the centre of the catalyst.

The products of the reaction were passed through two condensers immersed in a mixture of solid carbon dioxide and ethyl alcohol, with a temperature of approximately - 80°C. Alcohol was preferred to ether as being less volatile. Fig. 8 illustrates the condenser.

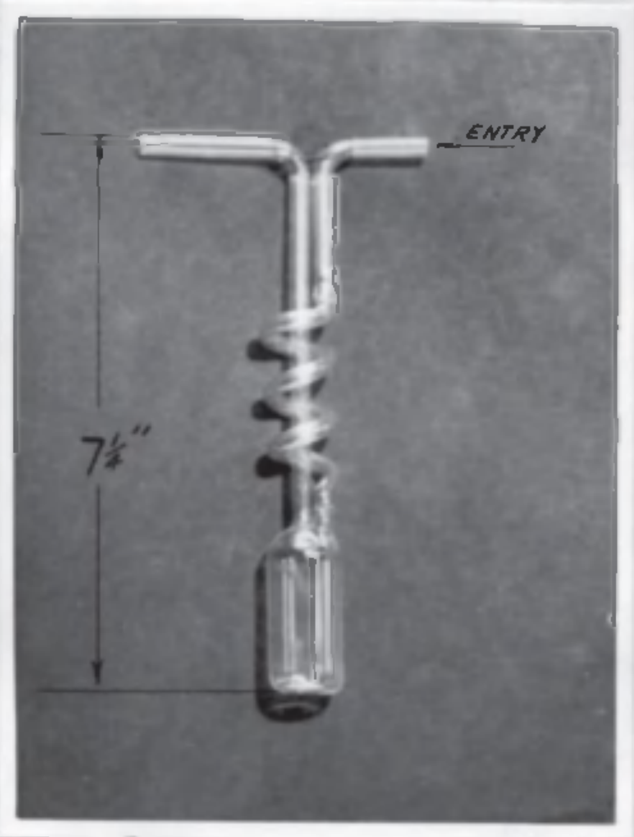


Fig. 8. Immersion Condenser.

A blank experiment without catalyst showed that with a standard rate of 2.5 - 2.6 gms. methanol in 4 litres/hr. of N_2, the amount recovered in the two condensers in series was over 99.5% of the methanol vaporised. This method of recovery of the liquid products (including undecomposed methanol) has the advantage over the usual scrubbing method in that losses due to recovery of the undecomposed methanol by distillation are entirely eliminated, and a direct gravimetric result is obtained for the total condensable products.

The water scrubber (fig. 4 overleaf) serves to remove the last traces of uncondensed material from the gas stream. Only traces of formaldehyde were found in this, and as formaldehyde is more volatile at -80°C. than methanol, it was assumed that all the undecomposed methanol was trapped in the condensers.

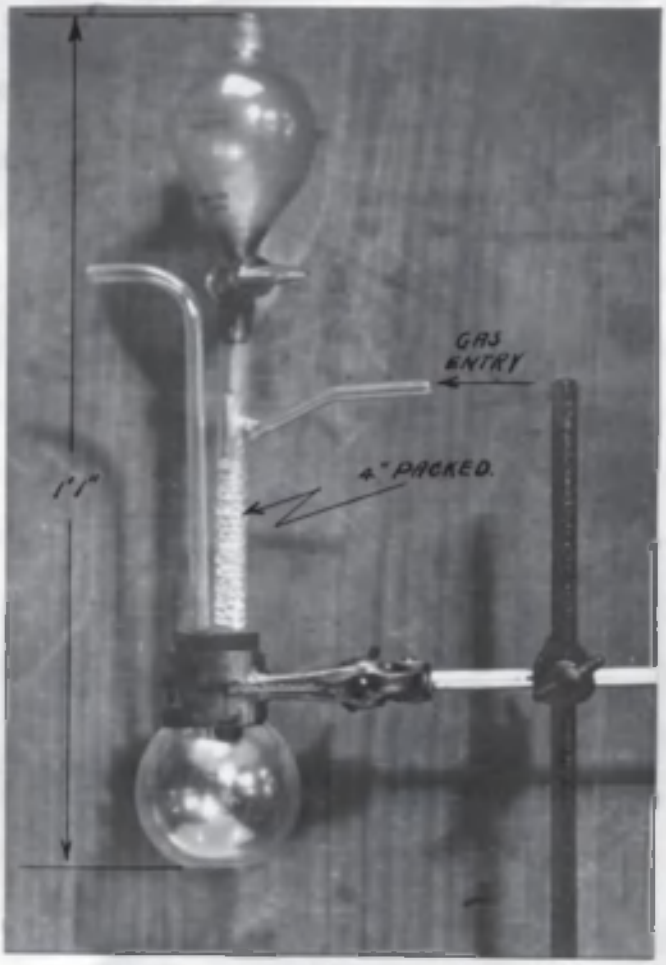


Fig. 9. Water Scrubber.

After scrubbing with cold water (approx. 75 ccs./hr.), the gases were collected in a calibrated aspirator of 10 litres capacity, over a saturated brine solution. The pressure was regulated by means of a screw-clip fitted with a large head for fine adjustment.

Experimental Procedure.

The procedure employed in all the tests was extremely simple. The required quantity of the reduced catalyst was placed in the reaction chamber, the whole system/

system thoroughly flushed with nitrogen and the catalyst heated to the required temperature. The condensers were now immersed in the freezing mixture, and the aspirator filled with the brine, the flushing nitrogen being vented through the tap at the top. When the temperature of the catalyst was steady, the flushing was stopped, and the weighed vaporiser containing methanol attached. About five minutes was allowed for the methanol to reach the temperature of the thermostat, and then the nitrogen from the Gray apparatus was passed into the vaporiser, the tap at the top of the aspirator now being closed. The pressure was kept at atmospheric by means of the screw-clip regulator.

At the end of the test, the nitrogen from the Gray apparatus was shut off, the vaporiser disconnected and cooled with cold water to prevent loss by further evaporisation, and the whole system again flushed with about 0.7 litres of nitrogen from a cylinder in order to carry over the last traces of methanol and the products of decomposition through the condensers. During the flushing operation the vaporiser was weighed. The condensers were removed from the freezing mixture after flushing was complete and weighed. The scrubbing water was kept running while the condensers were warming up to room/

room temperature. The volume of gas collected and its temperature and pressure, were measured.

Purification of Methanol.

The methanol was refluxed for two hours with 5% by weight of solid KOH, and then fractionated with a Dufton column, the fraction distilling over at 64.5°C. (actual thermometer reading) being collected. The methanol was next kept over 20% by weight of freshly burned quicklime for 24 hours, and fractionated as before. It was kept for a further 24 hours over 5% by weight of calcium turnings, fractionated as before, and again twice fractionated over 5% by weight of calcium turnings, and finally stored in a well-stoppered bottle. Once per month the methanol was distilled over 5% by weight of calcium turnings to ensure that it was always perfectly dry. The purified methanol was tested for aldehyde and ketone by the iodoform test, and was found to be free from these compounds.

ANALYSIS OF REACTION PRODUCTS.

Formaldehyde.

This was estimated iodometrically. Some of the condensate was weighed by difference into a flask containing about 25 cc. water. 10 cc. of standard N/10 iodine solution ~~was~~ were added, followed by 20 cc. of 30% NaOH solution (excess). After standing for ten minutes the solution was acidified with dilute HCl, and the liberated excess iodine titrated with standard N/10 thiosulphate solution. The scrubber water was analysed for formaldehyde in the same manner (1 cc. N/10 I_2 soln. = .0015 gm. HCHO).

Methyl Formate.

A portion of the condensate was weighed into a flask containing 10 cc. of standard N/10 NaOH solution, allowed to stand for a few minutes, and the excess NaOH titrated with standard N/10 HCl, (1 cc. N/10 NaOH = .006 gm. $HCOOCH_3$.).

Note: The ester was assumed to be methyl formate and not a higher ester, because in the estimation of formaldehyde by the method described above, there was no trace of iodoform producing products present, which would have been the case if the ester were produced from an alcohol higher/

higher than methyl alcohol. Furthermore, Frolich, Quiggle and Fenske, (J.I.E.C., 1928, 694.) had proved the existence of methyl formate in the products of the decomposition of methanol with catalysts of the Cu/Zn type. Again, formaldehyde is known to polymerise fairly readily, and under the conditions of the experiments it is probable that a certain amount of polymerisation does take place, with the formation of methyl formate.

Undecomposed Methanol.

This was estimated by the difference between the sum of the weights of formaldehyde and methyl formate in the condensate, and the total weight of condensate.

Gaseous Products.

The gaseous decomposition products were analysed for O_2, CO_2, unsaturated compounds, CO, H_2 and CH_4. Fig. 10 shows the Macfarlane Gas Analysis Unit, a modification of the Hempel, which was used. (Macfarlane and Caldwell, J. West of Scotland Iron and Steel Institute No.2, 1, 1892).

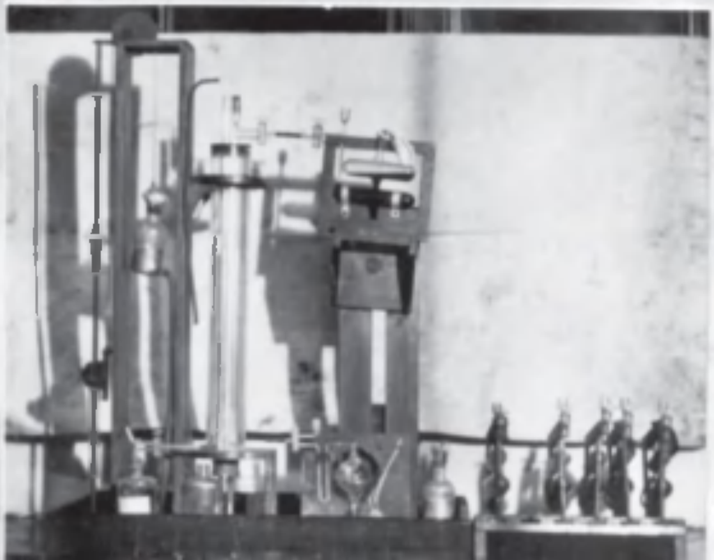


Fig.10. Macfarlane Gas Analysis Unit.

This type of gas analysis unit was largely developed by the South Metropolitan Gas Company, London, and has several advantages over the ordinary Hempel unit:-

(a) The gases are measured and also exploded over mercury.

(b) Constant temperature for measurement of volumes is assured by the water jacket.

(c) The absorption pipettes, being detachable, can be vigorously shaken, ensuring complete removal of even the smallest traces of the component.

(d) A complete analysis can be performed in 20 to 25 minutes.

A disadvantage is that the volume of gas taken for analysis is 50 ccs. instead of 100. The volume is easily read to 0.05 ccs., however, and this limit of accuracy is sufficient for a unit of this type.

The usual absorbents are used. Chromous chloride, prepared by reducing the chromic salt with zinc amalgam was substituted for pyrogallol for absorbing oxygen, and was entirely satisfactory. Concentrated sulphuric acid, activated by 0.6% silver sulphate, was tried as an absorbent for unsaturated compounds, but was found to be none too reliable, as after a few absorptions, the removal of unsaturated compounds gave rise to an increase in volume, and this increase could be reduced again by using the CO_2 absorption pipette.

Oxygen was not found, and unsaturated hydrocarbons/

hydrocarbons were found as traces only, in one instance with a catalyst containing a high proportion of chromium. Accordingly, traces of unsaturated compounds were omitted in the tables of results. The gas analysis was calculated on a nitrogen-free basis, i.e. as formed by the decomposition of methanol. At temperatures where there was very little decomposition, the proportion of gases of decomposition in the nitrogen was very low, and hence the results of the analysis may not be as accurate as could be desired.

Other compounds than those already mentioned are present, as the odour of the gases collected was not that which would be expected of those already mentioned. Compounds such as methylene oxide, dimethyl ether, etc. could be formed, but as methyl formate was found to be less than 1% of the methanol decomposed, and it is, apart from formaldehyde, the most likely bye-product to be formed, any other compounds were assumed to be present only in negligible amounts, and were consequently not analysed or estimated.

CHAPTER IX.

PRACTICAL EXPERIMENTS.

SERIES 1.

VARIATION IN CATALYTIC ACTIVITY WITH CATALYST COMPOSITION.

Conditions:-

Temperature, 360°C.

Rate, approx. 2.6 gm. in 4 litres N_2/hr.

Volume of catalyst, 5 cc.

Duration of test, 1 hour.

Results, Table III

TABLE III Effect of catalyst composition on the decomposition of methanol at 360°C.

Comp., mol % Zn.	Decomp %	HCHO %	Gaseous Prod., % vol.				Mass bal. % error
			H_2	CO	CO_2	CH_4	
77.0	8.0	3.7	60.4	12.3	20.6	6.8	+1
72.8	65.0	1.9	66.3	28.5	3.8	1.4	-2
68.8	80.7	1.0	66.5	28.7	3.3	1.8	-1
56.7	62.0	1.2	66.1	26.9	4.8	2.3	-1
52.1	81.0	0.7	66.0	27.6	3.4	2.9	-2
41.5	28.6	0.7	69.5	13.5	14.5	2.4	-3
18.8	13.3	0.7	65.0	9.8	19.6	5.8	-0.3

The activity of a number of catalysts of varying composition was compared under standard conditions. The change in activity is illustrated by fig. 11.

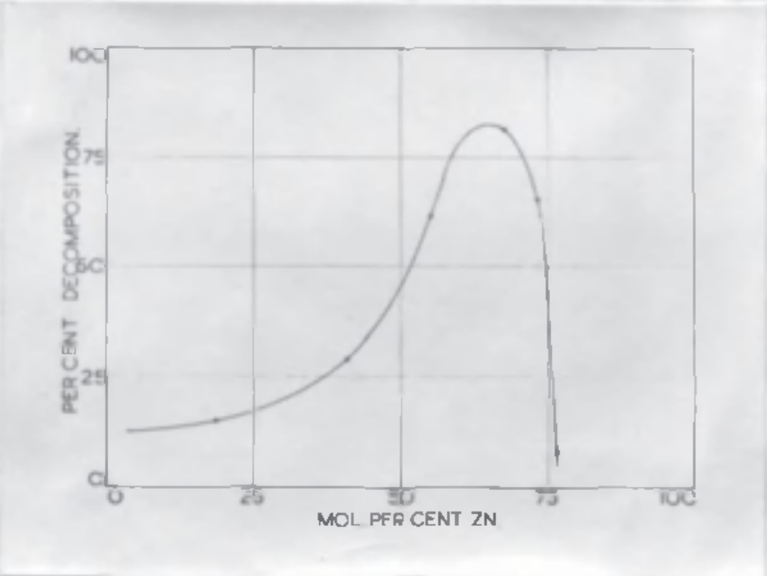


Fig. 11. Variation in catalytic activity with catalyst composition.

From fig. 11 it appears that the addition of small quantities of chromium to zinc oxide rapidly increases the activity (i.e. the % decomposition under standard conditions) up to a maximum of 33 mol% chromium, and further additions of chromium result in a gradual fall in activity. Catalysts containing a high proportion of chromium/

chromium appear to favour the formation of bye-products, as evidenced by the larger amounts of CO_2 and CH_4 in the gaseous products.

The amount of formaldehyde in the products is interesting. It would appear from fig. 12 that its production is governed by the composition of the catalyst. The figure for the formaldehyde is based on the amount of methanol decomposed, and not on the total weight of methanol passing over the catalyst, and throughout the tests the former method of calculation is adopted, as it takes into account the activity of the catalyst.

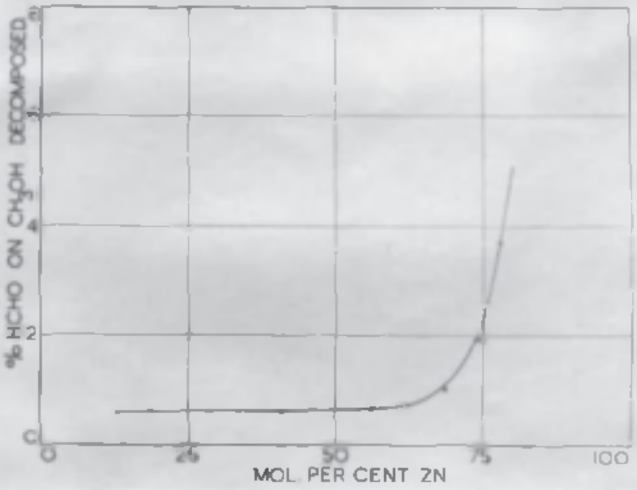


Fig.12. Effect of catalyst composition formaldehyde production.

SERIES 11.

EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF METHANOL.

Conditions:-

Catalyst composition, 68.8 mol% Zn.

Catalyst volume, 5 cc.

Rate, approx. 2.6 gm. methanol in 4 litres N_2/hr.

Temperature range, 200°C. to 400°C.

Duration of test, 1 hour.

Results, Table IV.

Table IV. Effect of temperature on the decomposition of methanol.

Temp., °C.	Decomp.	HCHO %	Gaseous prods., % vol.				Mass bal. % error.
			H_2	CO	CO_2	CH_4	
200	1.5	94	-	-	-	-	-1
230	1.0	94	-	-	-	-	0
260	1.9	94	-	-	-	-	-1
280	2.8	15	-	-	trace	-	-2
300	2.7	3.2	59.5	30.9	-	9.6	-1
300	4.7	1.7	50.9	20.4	20.4	8.4	+0.4
320	7.5	1.3	39.0	13.0	22.0	26.0	-1
320	12.7 *	2.0	39.5	28.5	6.6	25.4	-1
330	19.3 *	4.0	63.0	27.0	6.2	3.8	-2
340	35.5 *	1.4	64.7	28.4	3.2	3.8	+0.5
360	42.4	1.8	64.8	28.3	3.8	3.1	-2
400	97.8	0.5	64.0	29.5	3.2	3.4	-3

The activity of a catalyst was determined at temperatures varying from 200°C. up to 400°C. The sample chosen was one which had exhibited the greatest activity in Series I tests. There appears to be no appreciable decomposition below 300°C., but after this point the rise in activity with temperature is extremely rapid (fig. 13).

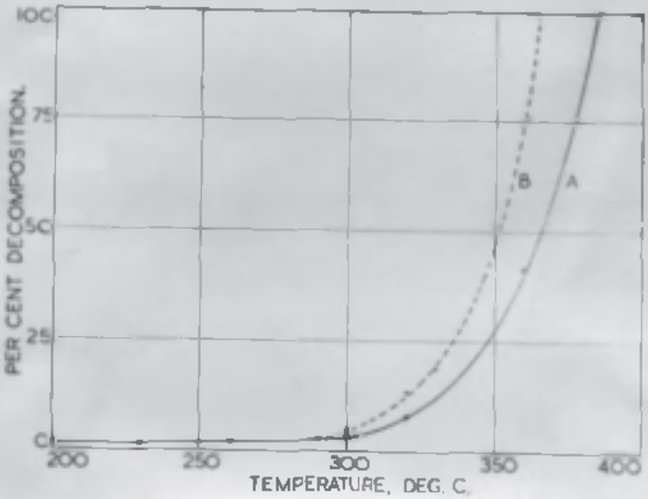


Fig.13. Effect of temperature on catalyst activity.

In/

In Table IV, the figures marked * were obtained after the catalyst had been used at 360°C. It will be noticed that the values are higher than would be expected, and using these higher figures together with that of the activity at 360°C from Series I, the curve 'b' is suggested as representing the true temperature effect were there no ageing of the catalyst. Curve 'a' represents the effect of temperature on the catalyst, but without the overheating. It would appear that after long use, slight overheating will reactivate the catalyst. For each test (in duplicate) the sample of the catalyst had been heated for approximately 8 hours. Hence, after tests at 300°C. it had been heated for approximately 40 hours, and at 360°C., 80 hours, with resulting activity 42%. In Series 1 the activity was 80% after 8 hours use. It seems, therefore, that prolonged use at high temperatures results in a falling off in activity of methanol catalysts.

As far as could be determined, the products of the decomposition below 300°C. are formaldehyde and hydrogen only. Due to the amount of decomposition being so low, the expected gaseous products of the reaction could not be detected. Only formaldehyde could be found in the liquid products; it was therefore assumed that at/

at temperatures below 300°C. the only gaseous product obtained is hydrogen, and is therefore omitted from Table IV . It is suggested that the decomposition at these temperatures is represented by the equation:-

$$CH_3OH \longrightarrow HCHO + H_2,$$

formaldehyde being assumed to be the only other product in Table IV.

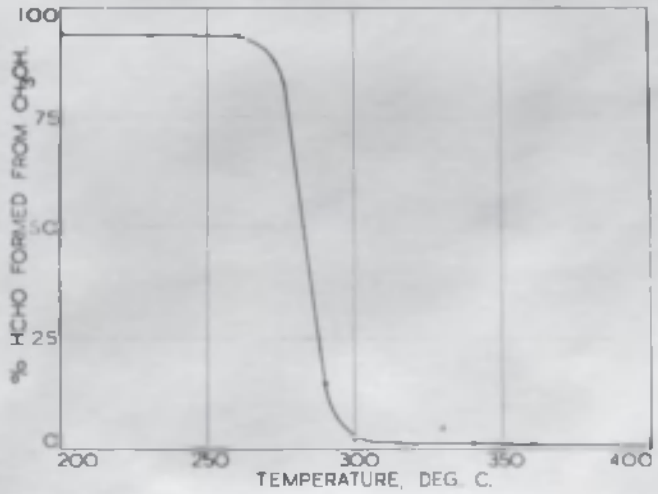


Fig.14. Effect of temperature on formaldehyde formation.

Fig/

Fig. 14 suggests that only formaldehyde and hydrogen are the products of the decomposition of methanol at temperatures below 300°C. Considering curve 'b' in fig. 13 as well, it appears that if the formaldehyde is the intermediate product in the decomposition of methanol to carbon monoxide and hydrogen, then this decomposition cannot proceed further until the formaldehyde is decomposed. This suggestion appears to be supported by the composition of the gaseous products of the reaction. Fig. 15 indicates that no carbon monoxide is formed below 300°C, it being assumed that the only other gaseous product at these temperatures is hydrogen, as indicated previously.

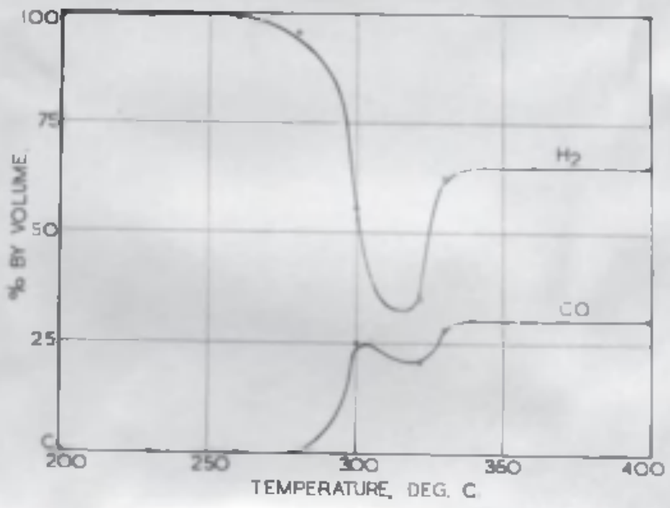


Fig.15. Effect of reaction temperature on decomposition products.

The temperature range 300 - 320°C appears to be a transition stage between the formation of formaldehyde as a main product, and the complete decomposition into hydrogen and carbon monoxide.

During this transition stage very large amounts of methane and carbon dioxide are formed as bye-products. From figs. 13 and 14 ., this stage does not appear to affect the amount of decomposition greatly, but only the composition of the gaseous products. The formation of methane and carbon dioxide appears to be closely related (fig. 16).

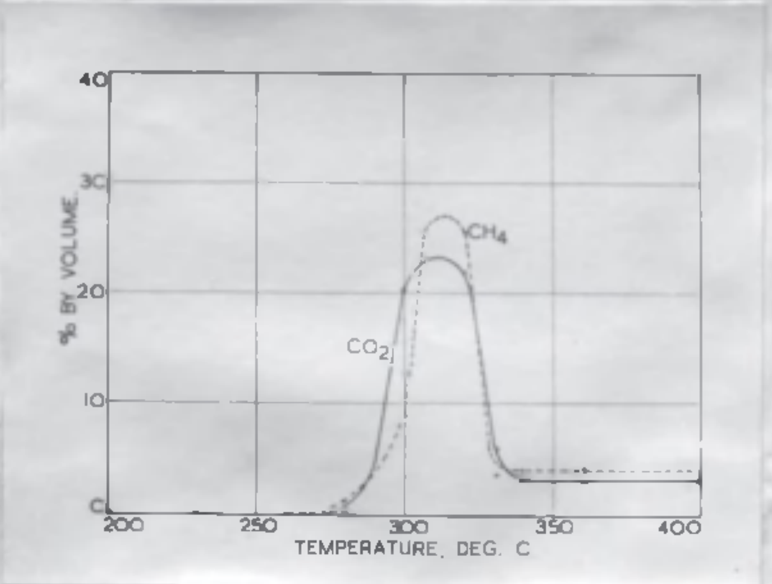


Fig.16. Effect of temperature on reaction products.

This/

This "critical temperature" phenomenon may also be explained by assuming that the methanol is not adsorbed on the catalyst surface below a certain "critical temperature", the lowest at which activated adsorption can take place on the particular catalyst employed. Any slight decomposition taking place below this "critical temperature" might be due to ordinary adsorption or capillary action. The formation of large proportions of bye-products during the transition stage might be due to the change-over from one type of surface action to the other, i.e. at the point where ordinary absorption or capillary action has reached a maximum, immediately before activated adsorption has set in.

SERIES III.

VARIATION IN CATALYTIC ACTIVITY WITH CATALYST COMPOSITION AND TEMPERATURE.

Conditions:-

Temperatures, 300, 360, and 400°C.

Rate, approx. 2.6 gm. CH_3OH in 4 litres N_2/hr.

Volume of catalyst, 5 cc. reduced immediately before use.

Duration of test, 45 minutes.

Results, Tables V to X inclusive.

Table V . Effect of temperature, catalyst composition 18.8 mol% Zn.

Temp. °C.	Decom. %	HCHO %	Meth. frmte %	Gaseous prods., % vol.				Mass bal. % error
				H_2	CO	CO_2	CH_4	
300	4.5	0.6	Nil	47.4	6.0	34.6	12.0	+ 0.6
300	3.3	1.4	"	31.4	21.0	31.4	16.3	+ 0.3
360	11.0	0.8	"	66.7	13.8	19.5	Nil	-2
360	17.7	1.5	0.2	72.2	9.0	16.3	2.2	-3
360	22.8	0.5	Nil	67.4	10.6	19.7	2.3	-2
400	93.3	0.5	-	66.0	20.9	10.6	2.5	-2
400	95.7	0.5	-	66.0	21.5	10.7	1.8	-2

Table VI. Effect of temperature, catalyst composition 41.5 mol% Zn.

Temp. °C.	Dcomp. %	HCHO %	Meth. frmte %	Gaseous prods., % vol.				Mass bal. % error.
				H_2	CO	CO_2	CH_4	
300	4.3	3.8	Nil	63.2	12.5	18.9	5.6	-1
360	36.4	0.6	"	70.7	13.4	15.9	Nil	-1
360	30.8	1.1	-	66.6	17.1	13.6	2.7	-1
360	32.8	1.6	0.3	66.5	20.7	10.3	2.5	-2
400	99.8	trce.	-	66.5	29.6	3.4	1.5	-2
400	99.7	"	-	66.9	29.6	3.0	0.5	-2

Table VII. Effect of temperature, catalyst composition 56.7 mol% Zn.

Temp. °C.	Dcomp. %	HCHO %	Meth frmte %	Gaseous prods., % vol.				Mass bal. % error
				H_2	CO	CO_2	CH_4	
300	4.0	0.8	Nil.	62.4	10.4	27.2	Nil.	-0.7
300	4.5	0.9	"	61.3	13.0	25.5	"	-0.6
360	26.1	2.0	0.3	66.1	23.5	9.0	1.4	-1
360	31.5	1.8	0.6	65.0	28.5	6.0	0.6	+ 1
400	90.4	1.0	-	68.6	26.1	4.6	0.5	-2
400	95.2	0.7	-	67.2	27.8	4.3	0.7	-2

Table VIII. Effect of temperature, catalyst composition 68.8 mol% Zn.

Temp. °C.	Dcomp. %	HCHO. %	Meth. frmte %	Gaseous prods., % vol.				Mass bal. % error.
				H_2	CO	CO_2	CH_4	
300	4.7	3.5	Nil.	32.0	11.0	57.0	Nil.	-0.8
300	4.7	0.6	"	36.0	12.0	52.0	"	-1
360	28.7	1.2	0.1	61.8	23.1	9.4	5.8	-0.7
360	47.5	1.8	0.4	66.6	27.5	4.6	1.5	-2
360	51.3	1.6	0.5	67.2	27.9	4.6	0.5	-0.7
400	97.8	1.0	-	66.5	29.0	4.1	0.5	+0.2
400	99.0	0.3	-	66.0	29.4	3.8	1.0	-1

Table IX. Effect of temperature, catalyst composition 72.9 mol% Zn.

Temp. °C.	Dcomp. %	HCHO. %	Meth. frmte %	Gaseous prods., % vol.				Mass bal. % error.
				H_2	CO	CO_2	CH_4	
300	6.5	3.2	Nil.	59.2	11.2	29.6	Nil.	-1
300	7.5	4.1	"	51.2	16.7	32.1	"	-2
360	27.5	1.2	0.4	Not analysed.				
360	43.6	1.5	0.5	63.4	26.9	7.0	2.7	+ 1
360	52.2	1.5	0.4	66.0	29.1	3.2	1.7	1
400	97.6	0.7	-	65.2	29.6	3.9	1.5	+ 1
400	95.7	0.8	trce.	68.7	27.2	3.1	1.1	-0.5

Table X. Effect of temperature, catalyst composition 77.0 mol% Zn.

Temp. °C.	Dcomp. %	HCHO. %	Meth. frmte %	Gaseous prods., % vol.				Mass bal. % error.
				H_2	CO	CO_2	CH_4	
300	3.6	c35.0	-	-	-	trce.	-	-2
300	3.5	1.0	0.5	-	-	"	-	-2
360	16.6	2.2	0.4	61.6	17.4	15.4	5.9	-1
360	25.7	2.3	0.5	not analysed				
360	32.8	2.3	0.4	63.4	27.0	6.7	3.0	-0.8
400	83.3	1.9	0.3	66.2	27.9	4.5	1.4	-3
400	86.7	1.4	0.5	66.3	28.6	4.5	0.7	-2

This series of tests is a combination of Series I and II . It will be noticed that all the tests at 360°C. show an increase in activity with use, except in Table VI This might at first sight be explained by incomplete reduction of the catalyst, but when it is considered that the catalyst had been used for two decompositions at 300°C., which is considerably above the temperature at which reduction starts, and also when the conditions of reduction are taken into account, it can be assumed that this rise in activity is not due to incomplete reduction of the catalyst before use. This phenomenon of variable activity is more fully investigated in Series VI tests. (p. 101) (See also "Discussion".)

The effect of temperature on the decomposition is best illustrated by fig. 17.

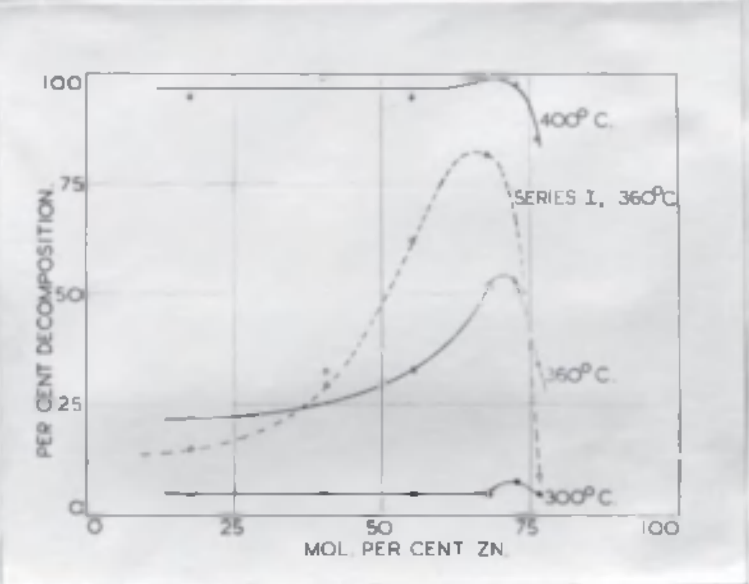


Fig.17. Variation in catalytic activity with temperature and catalyst composition.

This indicates that at 300°C. and 400°C. the effect of the composition of the catalyst is not manifested to any great extent, except in the case of those catalysts containing more than about 72 mol% Zn. It appears that the specific catalytic effect increases to a maximum between these two temperatures and falls to a minimum again/

again as temperature increases.

It will be noticed that the activity of the catalyst samples used in Series 1 are considerably higher than those of this series of tests at 360°C. The tests of this series were carried out approximately 9 months after those of Series 1, and this long period of storage, even in the unreduced condition, may account for the loss in activity.

The formation of formaldehyde is influenced by temperature as shown in fig. 18.

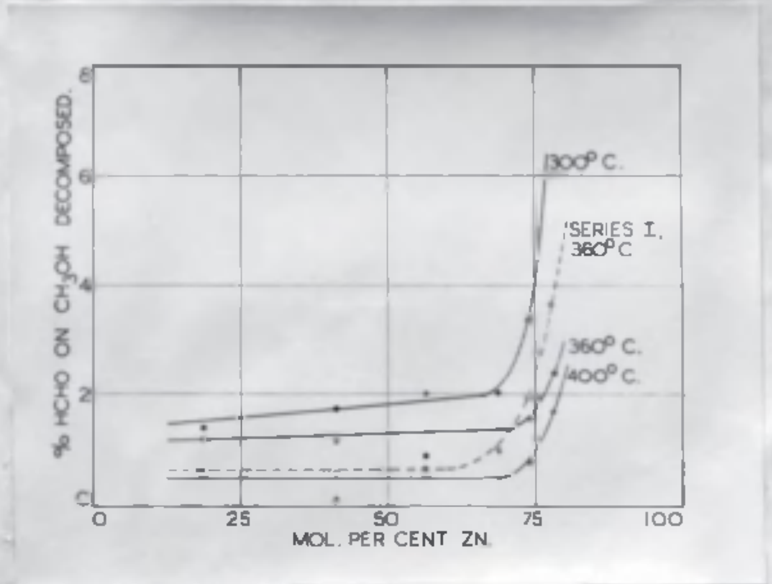


Fig.18. Effect of temperature and catalyst composition on formaldehyde production.

The/

The results are similar to those obtained in Series 1 at 360°C. It will be seen that low temperatures promote the formation of formaldehyde and that with increased temperature the proportion in the products of decomposition decreases. As in Series 1, the composition of the catalyst only makes itself above about 72 mol% Zn., even at 400°C.

At 300°C. there is a large proportion of CO_2 in the gaseous products, suggesting that reduction of the catalyst is not complete. This, however, is not assumed to be the case, bearing in mind the conditions of reduction (see also p. 48.)
The influence of the composition of the catalyst on the formation of CO_2 at the various temperatures is indicated by fig. 19.

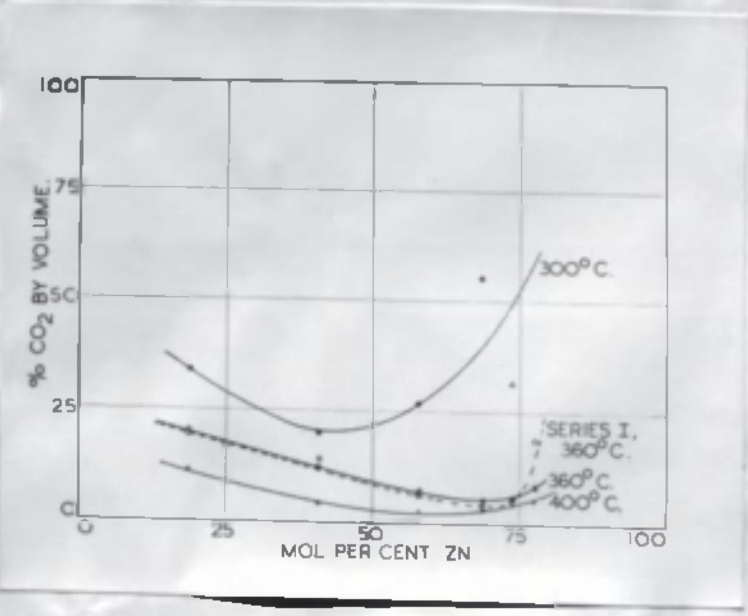


Fig.19. Effect of temperature and catalyst composition on carbon dioxide formation.

It appears that the composition of the catalyst affects the production of CO_2. There appears to be a minimum amount formed by the more active catalysts, and that as the temperature is increased, the proportion in the gaseous decomposition products is decreased.

The amount of CO_2 formed is far in excess of the amount of CH_4, particularly at low temperatures. The effect of temperature and catalyst composition on the formation of methane is illustrated by fig. 20.

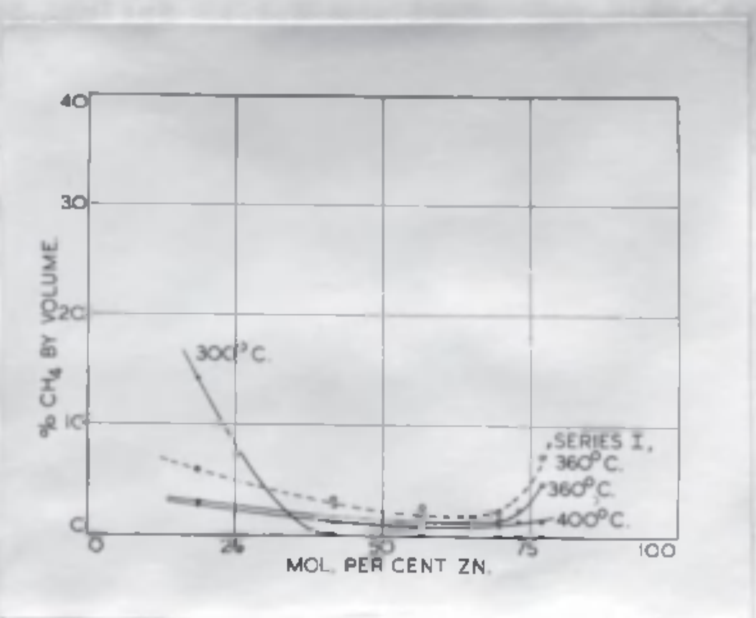


Fig.20. Effect of temperature and catalyst composition on methane formation.

It is apparent, as in the case of the CO_2 formation, that the more active catalysts tend to produce less methane/

methane than do the less active, and that those rich in chromium promote its formation. It can be seen that high temperatures tend to inhibit the formation of methane.

From figs. 19 and 20 it is evident that the formation of side-reactions is promoted by low temperatures and high Zinc content of the catalyst, and that these side-reactions are inhibited by increased temperatures. This is the reverse of the findings of Lewis and Frolich (J.I.E.C., 1928, 285.) for the synthesis of methanol. They state that the amount of CO converted to side reactions increases from about 2% at 300°C to about 6% at 400°C.

SERIES IV.

EFFECT OF RATE OF FLOW OF METHANOL ON THE CONVERSION.

The rate of flow of the methanol over the surface of the catalyst was varied in two ways:-

(a). By increasing the speed of the volatilising nitrogen through the methanol, which was kept at constant temperature.

(b) By increasing the temperature of the methanol, the velocity of the vaporising nitrogen being constant.

In (a) the concentration of the methanol vapour in the gas stream is constant, while in (b) it is varying.

(a) Conditions:-

Catalyst composition, 72.8 mol% Zn.
Catalyst volume, 5 cc., previously reduced.
Temperature, 360°C.
Methanol temperature, 43°C.
N_2 rate varying.
Duration of test, 1 hour.
Results, Table XI.

Table XI. Variable rate, N_2 varying. Catalyst composition 72.8 mol% Zn. (Previously reduced).

CH_3OH in, gm/hr	Dcomp gm/hr	Dcomp. %	HCHO. %	Gaseous prods., % vol.				Spce. vel., cc/cc /mt.	Mass bal. % error
				H_2	CO	CO_2	CH_4		
0.63	0.51	81.1	0.8	65.1	25.2	5.9	3.9	6.0	-1
1.28	0.58	45.0	1.4	59.8	29.3	5.9	5.0	10.7	-1
1.88	0.70	37.2	2.5	62.2	25.7	5.7	6.6	14.8	-1
2.42	0.79	32.4	2.7	64.3	25.2	5.3	5.3	18.5	-2
3.03	0.98	32.3	3.0	63.5	25.6	4.0	6.9	23.1	-2
3.44	1.26	36.7	3.1	64.0	25.8	4.9	5.3	24.8	-3

This method of increasing the flow of methanol over the catalyst surface is, to a certain extent, limited in application, in that the high speed of the gases through the condensers results in incomplete condensation, and hence increased mass balance error. Even with a third condenser in series, condensation is not greatly improved.

(b) Conditions:-

Catalyst composition, 72.8 mol% Zn.

Catalyst volume, 5 cc., reduced immediately before use.

Temperature, 360°C.

Methanol temperature varying.

N_2 rate, 3 litres/hr.

Duration of test, 1 hour.

Results, Table XII.

Table XII. Variable rate, methanol temperature varying. Catalyst composition 72.8 mol% Zn.(freshly reduced).

CH_3OH in. gm/hr	Dcomp gm/hr	Dcomp. %	HCHO. %	Gaseous prods., % vol.				Spce. vel., cc/cc /mt.	Mass bal % error
				H_2	CO	CO_2	CH_4		
2.30	1.25	54.0	1.5	65.6	27.8	5.0	1.8	15.4	-0.3
3.57	1.67	47.0	1.8	65.5	29.8	3.3	1.4	18.0	-1
5.84	1.76	30.0	2.4		not analysed			23.7	
7.08	1.73	24.5	2.4	65.8	28.2	3.9	2.2	26.5	-0.2

It will be noticed that in this case the mass balance error is not so great as in Table XI. Furthermore, the freshly reduced sample of catalyst is more active than the previously reduced sample under similar conditions of entry of the methanol. This is illustrated in fig. 21.

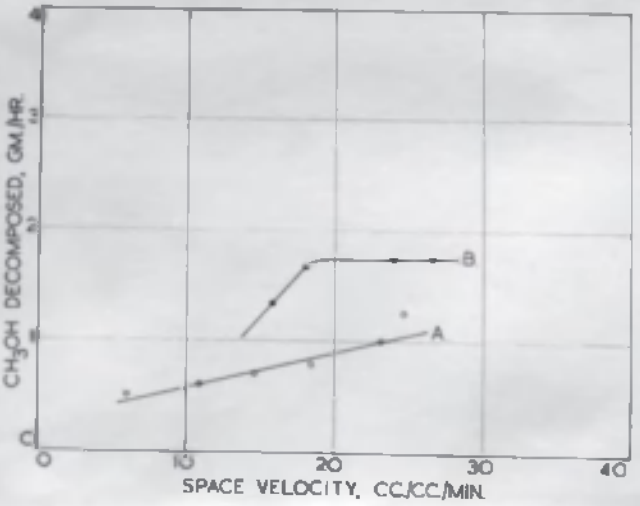


Fig.21. Variation in decomposition rate with space velocity.

It must be remembered, however, that the conditions prevailing in these two tests are different. In (a) the composition of the gas stream over the catalyst is constant, while in (b) the concentration of methanol in the stream is increasing with the gas velocity. Curve (b) indicates that the amount of methanol decomposed increases with the velocity over the surface of the catalyst up to a point, but that further increase in gas velocity does not result in increased decomposition rate, pointing to a change in the mechanism of the decomposition.

When a gas is passing over a catalytically active surface there is a film of the gas adhering to the surface of the catalyst. The thickness of this film determines the rate of transfer of the reactants from the body of the gas to the active surface, and also the transfer of the reaction products from the catalyst surface. As the velocity of the gas is increased, the thickness of the film is diminished, resulting in a higher rate of transfer and hence increased rate of reaction. With increased gas velocity (and hence diminished film thickness), the reaction products are also swept more quickly from the surface of the catalyst.

When the gas velocity is increased to such an extent/

extent that the film thickness becomes so small (approaching a monomolecular layer), as to have no retarding effect, then it is the activity of the catalyst which governs the rate of reaction. Before this the governing factor is the film thickness, and consequently the gas velocity. (Laupichler, J.I.E.C., 1938, 578.).

The results obtained are in agreement with this theory. Curve (a) of fig. 21 indicates that as the gas velocity increases, the rate of reaction increases, while curve (b) indicates that the stage has been reached where the mechanism changes from one governed by film thickness to one governed by catalyst activity. But as in (a) the ratio of reactant to inert gas is constant, and in (b) it is increasing with gas velocity, it appears that the concentration of the reactant in the inert "carrier" also influences the reaction rate. In fig. 21 curve (a) indicates that with a space velocity of about 23 - 24 cc/cc/min. the reaction rate is tending to increase, whilst curve (b) indicates that at this space velocity the reaction rate is not increasing. In the latter case, however, the amount of methanol entering is approximately twice that entering in the former.

This suggests that when one of the constituents of a mixture of gases passing over an active surface is inert,/

inert, the concentration of reactants in the mixture determines the film thickness. In other words, the smaller the concentration of reactants, the greater the gas velocity required to overcome the film thickness.

Fig. 22 indicates that the gas velocity also affects the production of formaldehyde.

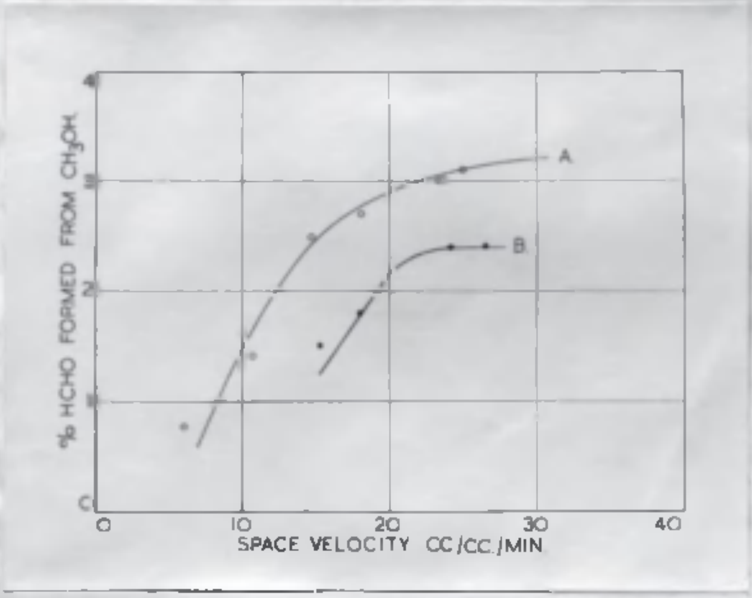


Fig.22. Effect of space velocity on formaldehyde production.

It will be noticed that the more active of the two samples of catalyst yields less formaldehyde than the other. This may be due to the difference in activity, but as can be seen from Table XII the amount of formaldehyde/

formaldehyde in the products of decomposition is constant (within the limits of experimental error) for a variation in activity of over 100%. It is more likely, however, that this difference in the amount of formaldehyde produced is due to the different concentrations of methanol in the gas stream. The difference in the shape of the two curves supports this view. Curve (b) indicates that as the space velocity increases (in this case due to increasing concentration of methanol), the amount of formaldehyde in the decomposition products increases to a limiting value. If formaldehyde were an intermediate product of the methanol decomposition, it would be expected that as the speed of the reacting gas increased, the products would be swept away more quickly and hence would contain more of the intermediate product, i.e. the amount of formaldehyde in the decomposition products would increase with gas velocity.

But it will be noticed that curve (a) is tending to flatten out and approach the shape of curve (b), indicating that the effect of the speed of the gas over the catalyst surface on the production of formaldehyde is diminishing, so that with a sufficiently great space velocity, curve (a) will become similar in form to curve (b).

That formaldehyde is not an intermediate product of/

of the decomposition of methanol to carbon monoxide and hydrogen is further illustrated by fig. 23 which indicates that as the rate of methanol decomposition increases, the amount of formaldehyde in the decomposition products reaches a limiting figure, it being remembered that the rate of decomposition is varied by increase in gas velocity. If an intermediate product, it would be expected that formaldehyde would continue to increase with the rate of decomposition of the methanol.

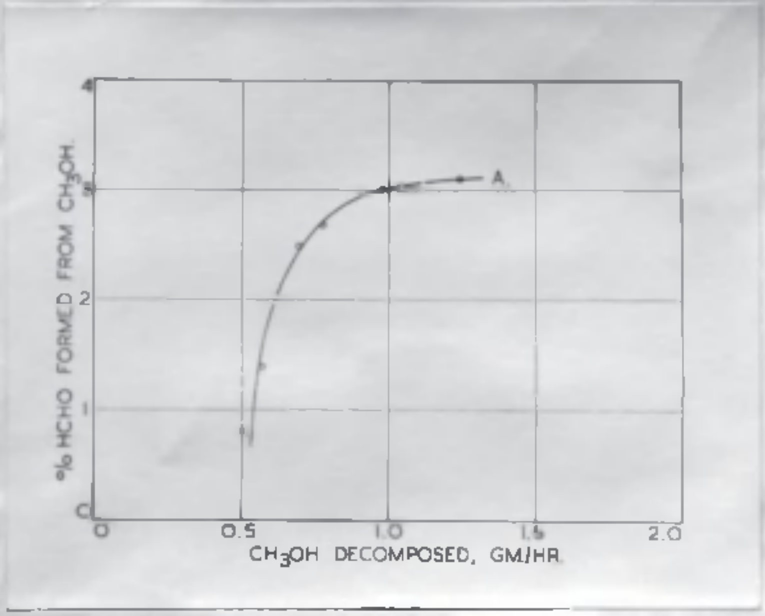


Fig.23. Variation in formaldehyde formation with rate of methanol decomposition.

It/

It will be noticed from Tables XI and XII that the amount of carbon dioxide in the gaseous products decreases with gas velocity, while the methane increases, indicating that they are not formed by the same reaction.

SERIES V.

EFFECT OF VARIED RATE OF FLOW AND CONCENTRATION OF METHANOL IN THE GAS STREAM ON THE DECOMPOSITION.

The concentration of the methanol in the entering gas stream was varied by altering the temperature of the methanol.

Conditions:-

Catalyst composition, 68.8 mol% Zn.

Catalyst volume, 5 ccs. (freshly reduced)

N_2 rate varying.

Methanol concentrations, 32%, 48%, 57%, 75%, by volume in N_2.

Duration of test, 1 hour.

Results, Tables XIII to XVI inclusive.

Table. XIII 32% Methanol by volume.

CH_3OH enter gm/hr.	Dcomp gm/hr	Dcomp %	HCHO. %	Meth. form %	Gas. prods., % vol.				Sp.vl. cc/cc /mt.	Mass bal. % error.
					H_2	CO	CO_2	CH_4		
0.86	0.78	91.4	0.8	nil.	66.3	29.7	3.0	1.0	7.2	-1
1.39	1.06	76.3	1.2	"	66.7	27.8	4.8	0.8	11.2	-1
2.59	1.72	67.2	2.1	0.3	65.4	28.4	3.4	2.9	19.5	-2
3.30	1.87	57.4	2.5	0.4	67.3	27.7	4.2	0.8	24.0	-2
4.31	2.10	49.5	2.7	1.2	66.4	28.3	3.8	1.6	30.0	-3
5.58	2.42	48.6	3.0	1.3	67.7	28.4	3.3	0.8	38.2	-4

Table XIV. 48% Methanol by volume.

CH_3OH enter gm/hr	Dcomp gm/hr	HCHO %	Meth frmte %	Gas. prods., % vol.				Sp.vl. cc/cc /min.	Mass bal.% error.
				H_2	CO	CO_2	CH_4		
1.37	1.06	1.05	0.08	66.5	28.6	3.7	1.1	8.3	nil.
2.78	1.78	1.36	nil	67.3	28.9	3.3	0.6	14.5	-1
5.60	2.30	2.50	2.30	67.5	28.3	3.6	0.6	26.4	-2
7.01	2.33	2.90	1.80	65.2	27.7	6.0	1.0	33.4	-1
8.52	2.80	2.91	1.80	67.5	26.8	4.9	0.8	40.0	-4
11.24	3.30	3.22	3.10	69.4	26.4	4.2	nil	51.5	-4

Table XV. 57% Methanol by volume.

CH_3OH enter gm/hr.	Dcomp gm/hr	HCHO. %	Meth frmte %	Gas. prods., % vol.				Sp.vl cc/cc /min.	Mass bal.% error.
				H_2	CO	CO_2	CH_4		
2.48	1.64	1.10	0.20	67.2	28.5	3.90	0.5	10.8	-1
4.56	2.26	2.10	1.20	67.0	29.0	3.6	0.6	18.7	-2
8.13	3.01	2.70	3.0	68.0	28.1	3.3	0.7	32.5	-1
10.59	3.30	3.2	5.4	69.0	27.0	3.1	0.9	48.2	nil.
16.31	3.31	3.2	4.8	69.0	24.6	5.9	0.8	63.8	-3

Table XVI. 75% Methanol by volume.

CH_3OH enter gm/hr.	Dcomp gm/hr	HCHO. %	Meth frmte %	Gas. prods., % vol.				Sp.vl. cc/cc /min.	Mass. bal.% error
				H_2	CO	CO_2	CH_4		
6.01	2.34	2.40	1.50	67.0	27.8	4.4	0.9	19.7	-1
9.91	2.93	3.10	4.0	68.3	28.7	4.5	0.6	31.2	-2
13.4	3.10	3.21	4.5	69.0	25.0	4.7	1.2	42.0	-2

Fig. 24 below illustrates the effect of this combined change of conditions.

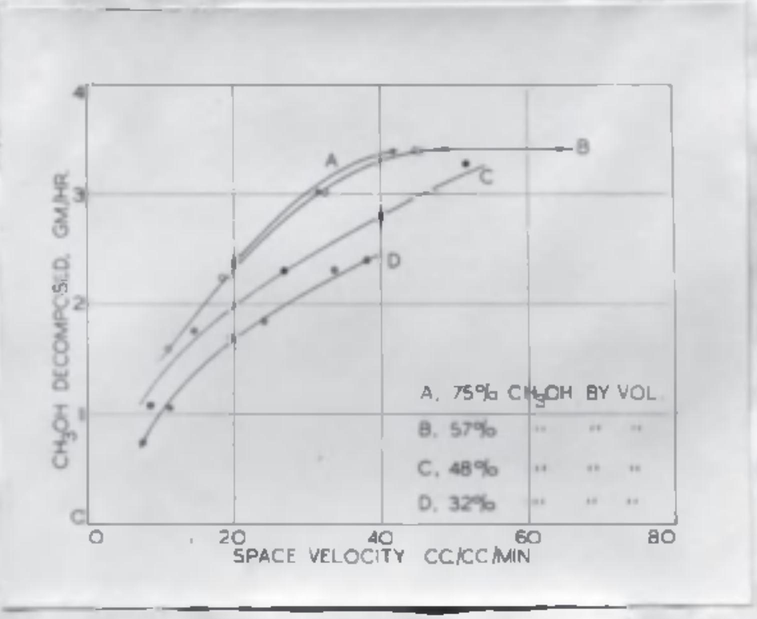


Fig. 24. Effect of varying space velocity and methanol concentration on the reaction.

It will be noticed that as in Series IV. tests, there is a tendency for the rate of reaction to reach a maximum, which remains unaltered with further increase in gas rate. It is to be noted, however, that the whole series of tests was carried out with the same sample/

sample of catalyst, and as will be seen from fig. 24 the ageing becomes more apparent as the time of use increases. It can be seen that the maximum rate of reaction is governed by the weight of methanol passing over the catalyst surface in a certain time, and not the space velocity, e.g. from fig. 24 , with a space velocity of 40 cc/cc/min., the rate of decomposition is 2·46 gms/hr. with 32% methanol by volume; 2·80 gms/hr. with 48% by volume; 3·30 gms/hr. with 57% by volume; and 3·37 gms/hr. with 75% methanol by volume in the vaporising nitrogen.

Thus with a high concentration of methanol in the gas stream, a lower space velocity is required for the maximum decomposition rate than for a low concentration, where a high space velocity is required, in order that the maximum mass-rate may be reached. That is, the minimum space velocity required for maximum decomposition rate is inversely proportional to the concentration/

concentration of methanol in the gas stream.

It will be noticed from fig. 25 that the proportion of methanol decomposed to formaldehyde increases with rate of methanol entry, with a tendency to reach a limiting value as in Series IV tests. The methyl formate production increases with gas rate also, but in a much greater degree than the formaldehyde. The gaseous decomposition products show no particular change; if anything, an increase in side reactions.

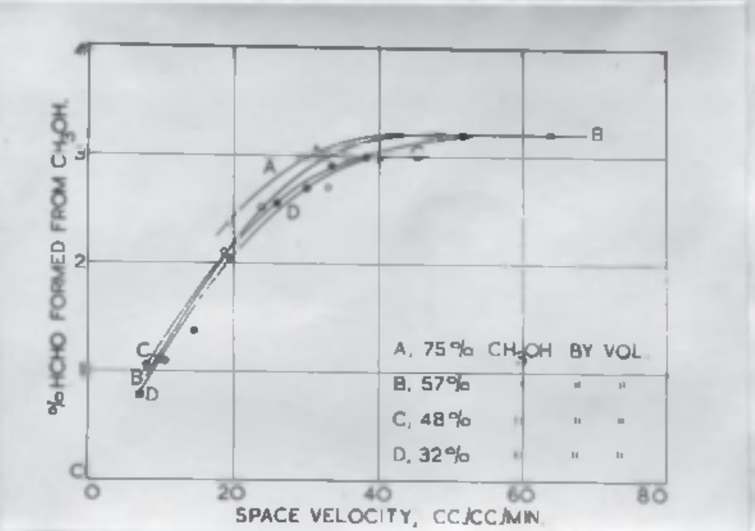


Fig.25. Variation in formaldehyde formation with space velocity and methanol concentration.

The results of this series of experiments

lend/

lend support to the suggestion made in connection with Series IV tests. It is clear that in a mixture of gases, one inert, it is the concentration of the reactant gases or gas in the mixture which determines the rate of reaction. In other words, the gas velocity required to effect the reaction at a certain rate is directly proportional to the amount of inert gas present.

Fig. 26 below is suggested as representing the variation in reaction rate with gas velocity and gas concentration, were the catalyst not subject to diminished activity with time of use.

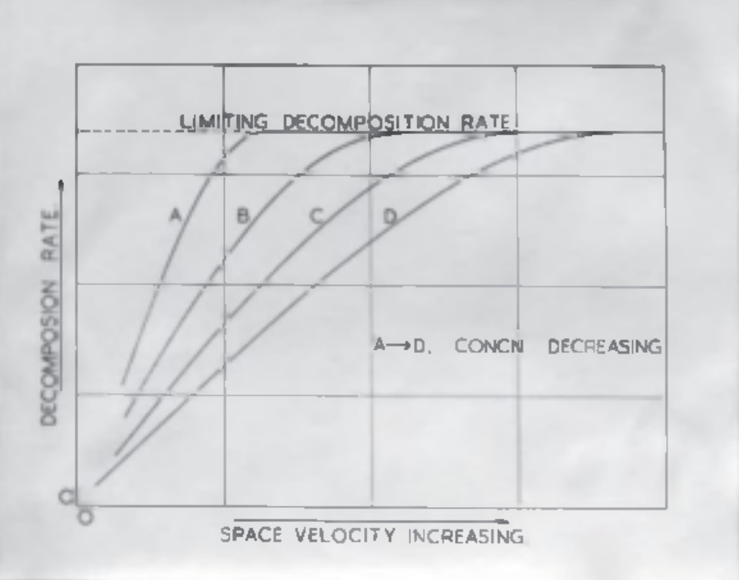


Fig.26. Theoretical effect of space velocity and methanol concentration on the reaction.

SERIES VI.

THE DECOMPOSITION OF METHANOL IN THE PRESENCE OF HYDROGEN.

Three series of tests were carried out, two with previously reduced samples of catalyst, and one with a catalyst sample reduced immediately before use.

(a) Conditions:-

Catalyst composition, 68.8 mol% Zn.

Catalyst volume, 5 cc., used in Series I test.

Temperature, 360°C.

Duration of test, 1 hour.

Proportion of hydrogen in vaporising nitrogen, 0 - 75%

Results, Table XVII.

Table XVII. The effect of hydrogen; catalyst composition 68.8 mol% Zn.

Added H_2, %	Dcomp. %	HCHO %	Gaseous prods., % vol.				Mass bal. error %
			H_2	CO	CO_2	CH_4	
Nil	60.5	1.0	66.5	28.7	3.3	1.8	-1
25	53.3	1.6	64.2	29.5	3.7	2.5	-2
50	59.0	1.5	64.7	29.1	3.5	2.9	-2
75	61.9	1.2	62.2	28.2	4.0	5.6	-2
+ Nil	61.0						
* "	68.1						
§ "	70.8						

(b) Conditions:-

Catalyst composition, 68.8 mol% Zn.

Catalyst volume, 5 cc., previously reduced.

Temperature, 360°C.

Duration of test, 1 hour.

Proportion of hydrogen in vaporising nitrogen, 0 - 15%

Results, Table XVIII.

Table XVIII. The effect of hydrogen; catalyst composition 68.8 mol% Zn.

Added H_2, %	Dcomp. %	HCHO. %	Gaseous products, % vol.				Mass bal. % error.
			H_2	CO	CO_2	CH_4	
Nil	61.0						
2.5	57.6	1.5	64.3	29.8	3.1	2.8	-1
5.0	73.0	1.7	64.0	27.2	4.5	4.3	-2
Nil	66.0						
10.0	62.6	1.2	65.3	26.9	4.2	3.6	-3
15.0	66.7	1.3	65.0	27.8	3.3	4.1	-1

The results of these two sets of experiments indicate that the presence of small proportions of hydrogen in the gas stream tends to increase the activity of the catalyst, and that further addition of hydrogen has little effect. Increase in

excess/

excess hydrogen appears to promote the formation of methane and to a lesser extent, carbon dioxide as bye-products. In Table XVII the result marked † was obtained immediately after those with the hydrogen, that marked * after 4 hours' flushing with N_2, and that marked ∮ after 8 hours. It appears that the treatment with hydrogen has had the effect of partially revivifying the catalyst, the original activity of which was 80% when freshly prepared. It also seems that the hydrogen is removed from the surface of the catalyst with difficulty, and as it is removed the activity progressively increases, tending to the original figure for the fresh sample.

It was decided to investigate more thoroughly the effect of additional hydrogen on the decomposition, particularly with regard to the products formed, and the following series of tests was carried out:-

(c). Conditions:-

Catalyst composition, 72.8 mol% Zn.
Catalyst volume, 5 cc., reduced immediately before use.
Temperature, 360°C.
Proportion of hydrogen in the vaporising nitrogen, 0 - 100%.
Results, Table XIX .

The activity of the catalyst was determined immediately/

immediately before the addition of hydrogen, and it was found that the activity varied with the time the catalyst was in use.

Table XIX. The effect of hydrogen; catalyst composition 72.8 mol% Zn.

Added H_2 %	Dcomp. %	HCHO %	Meth frmte %	Gaseous prods., % vol.				Mass bal. % error	Time mts.
				H_2	CO	CO_2	CH_4		
Nil	23.6	2.7	0.1						80
"	29.8	3.6	0.8	68.3	24.1	6.4	1.2	-0.7	125
"	44.1	2.8	0.1	66.7	27.1	5.3	1.0	-2	170
"	46.9	2.4	-	67.7	25.3	6.2	0.8	-1	215
"	51.8	2.4	0.5	66.5	27.4	5.3	0.8	-1	260
"	56.3	2.1	0.4	67.2	27.0	5.4	0.4	-2	305
"	53.6	2.3	0.5	66.4	28.1	4.5	0.8	-1	350
"	42.0	2.4	0.8	66.5	27.6	5.0	0.9	-0.5	395
5.0	58.6	2.0	0.3	66.7	27.9	3.8	1.7	-2	485
5.0	57.4	2.0	0.6	67.0	29.0	3.5	0.4	-2	530
10.0	53.8	2.5	1.0	66.7	28.6	3.8	0.9	-2	575
10.0	53.2	2.6	0.9	66.6	28.8	3.7	0.9	-2	620
25.0	50.7	2.8	0.9	66.6	28.9	3.5	0.9	-2	665
60.0	49.9	2.5	0.8	64.5	30.6	3.9	1.0	-2	710
100	50.8	2.2	0.6	66.0	28.4	4.5	1.1	-1	755
5.0	59.6	2.1	0.8	Not analysed					800
5.0	56.4	2.2	1.2	"	"				845

The rise in activity of the catalyst with use will be noticed. The increased activity is not maintained, however, and the fall appears to be even more sharp than the rise. The addition of only 5% excess hydrogen is sufficient to check this fall instantly, actually raising the activity to slightly more than the previous maximum. Further additions of hydrogen reduce the activity only slightly, but on adding 5% again the activity is again sharply increased. (Fig. 27.)

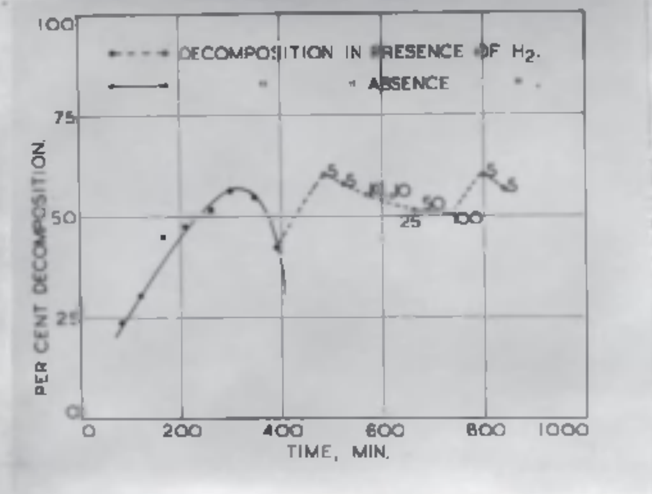


Fig.27. Variation in catalyst activity with time of use, and reactivating effect of small additions of hydrogen.

(The figures on the curve indicate the % hydrogen added to/

to the vaporising nitrogen).

The greatest effect of hydrogen, therefore, is observed when 5% is added to the vaporising nitrogen. This is more clearly illustrated by fig. 28. It is apparent that further addition of hydrogen up to 25% has a slight retarding action, and that above this figure there is no appreciable change in activity of the catalyst.

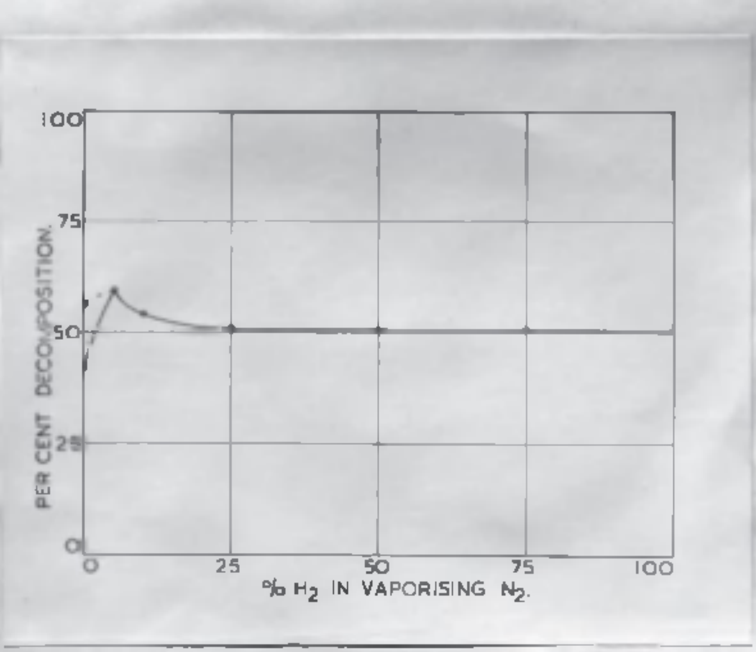


Fig.28. Effect of additional hydrogen on the methanol decomposition.

It can therefore be said that the addition of about 5% of hydrogen to the mixture of nitrogen and methanol vapour passing over the catalyst has an activating effect. This is/

is supported by the results of (b).

Fig. 29 illustrates the effect of the hydrogen on the methane and carbon dioxide in the gaseous products.

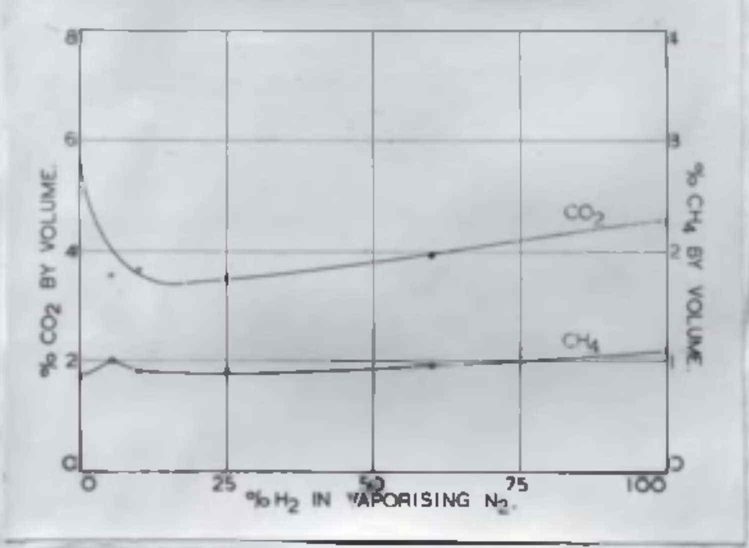


Fig.29. Effect of additional hydrogen on the decomposition products.

On the other hand, the effect of the hydrogen on the formaldehyde and methyl formate in the products is similar, as shown by fig. 30 The values of these substances for pure nitrogen are the averages for all the experiments of this series before hydrogen was added.

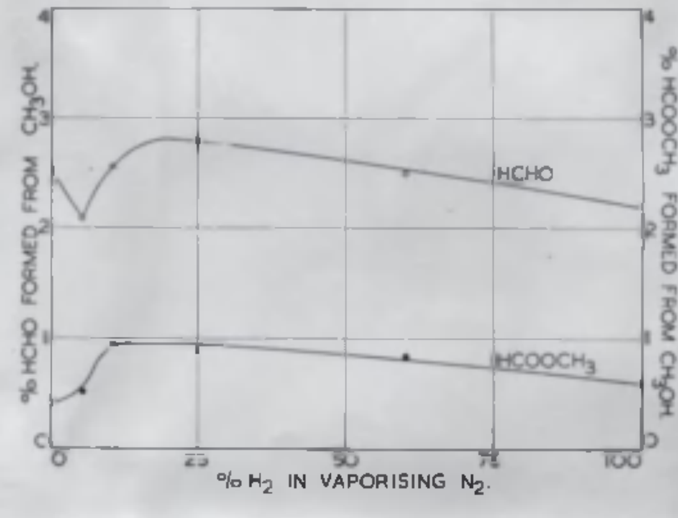


Fig.30. Effect of additional hydrogen on the decomposition products.

These curves follow fairly closely that for the effect of hydrogen on the activity of the catalyst (fig. 28.), except in the early stages (i.e. up to 5%) when the minimum in the latter corresponds to the maximum in the former.

CONTINUED EXPERIMENTS WITH HYDROGEN.

The study of the effect of hydrogen on the reaction was continued over a long period to discover if the addition of small amounts of hydrogen maintained the increased activity of the catalyst . The effect was studied over a further period of about 14 hours, the tests being of 45 minutes each. Fig. 31 following shows the results of the complete series, starting with the freshly reduced sample of catalyst.

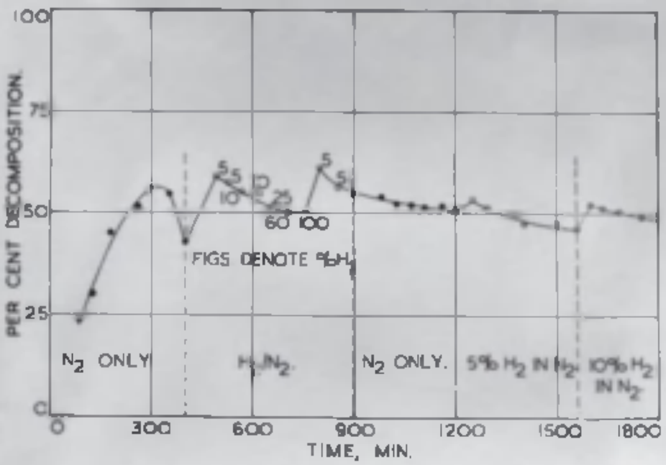


Fig.31. Variation of catalytic activity with time of use, and reactivating effect of small additions of hydrogen.

It will be seen that even the presence of 5% H_2 in the vaporising nitrogen (the concentration giving the greatest rise in activity) does not prevent the activity from/

from falling. But after this period of use, where there is no appreciable check of the falling activity with 5% H_2, there is a slight, though definite rise in activity when this concentration is changed to 10%. The tendency for the activity to fall with further use however, does not appear to be overcome.

SERIES VII.

THE DECOMPOSITION OF METHANOL IN THE PRESENCE OF CARBON MONOXIDE.

Conditions:-

Catalyst composition, 72.8 mol% Zn.

Catalyst volume, 5 cc., freshly reduced.

Temperature, 360°C.

Duration of test, 45 minutes.

Proportion of carbon monoxide in vaporising nitrogen, 0 - 100

Rate, approx. 2.6 gm. CH_3OH in 4 litres vaporising gas/hr.
Results, Table XX.

Table XX. Effect of carbon monoxide; catalyst composition 72.8 mol% Zn.

% CO in N_2	Decomp %	HCHO %	Meth frmte %	Gaseous prods., % by vol.				Mass bal.% error.
				H_2	CO	CO_2	CH_4	
Nil.	64.6	1.8	Nil	65.0	31.2	3.0	1.0	-
5%	76.2	1.3	"	69.2	26.4	3.3	0.7	-2
5%	68.6	2.1	trce	68.0	28.7	3.2	nil	-1
10%	67.4	1.8	nil	67.0	30.0	2.9	"	-1
20%	62.2	1.6	0.1	68.2	27.5	3.5	0.9	-2
40%	57.7	1.9	0.4	66.0	28.8	4.5	0.8	-1
100%	55.6	1.9	0.2	65.5	29.2	4.9	0.5	-
5%	68			Not analysed.				
5%	68			"		"		
Nil	66			"		"		
5%	66			"		"		

These results show that the effect of carbon monoxide on the decomposition is, to all intents and purposes, identically the same as that of hydrogen (Series VIc p. 103). Rumford (Private communication) has demonstrated that with this catalyst, more hydrogen is adsorbed at 360°C than carbon monoxide, and it was expected in consequence that the effect of excess hydrogen on the reaction would be more marked than the effect of excess carbon monoxide (i.e. excess over the quantity produced during the decomposition of methanol) The similarity in effect of the additions of 5% CO and 5% H_2 is interesting.

Theoretically, however, there is a difference in the effect on the equilibrium as is shown by the following:-

In the equation: $\underset{a}{CH_3OH} \rightleftharpoons \underset{b}{2H_2} + \underset{c}{CO}$

$$K_c = \frac{b^2c}{a} \quad \text{(constant volume)}$$

If the reaction be carried out in the presence of excess H_2, suppose x, then the new volume of hydrogen now becomes (b+x). Let a' and c' be the new concentrations of CH_3OH and CO.

$$\text{Therefore } K_c = (b+x)^2 . c'$$

$$= \frac{(b^2+2bx+x^2) . c'}{a'} \quad ....(1)$$

For K_c to be constant, b must be decreased to b' and hence/

hence the reaction will be retarded.

But if there is excess CO, suppose x, then from the foregoing reasoning $K_c = \frac{b'^2(c'+x)}{a'}$, (where b' is the new concentration of CO)

$$= \frac{b'^2c'+b'^2x.}{a'} \quad ....(2)$$

It can be seen from equations (1) and (2) that for K_c to remain constant, the reaction will be retarded to a greater extent by hydrogen than by carbon monoxide, (varying according to the square of the hydrogen concentration, and according to the concentration only of carbon monoxide). Since K_c has such a large value at the temperature of the experiment (5.6×10^6) and since experimental conditions are not necessarily close to equilibrium, it is thought that any difference in the theoretical effect is unlikely to be noticeable under the prevailing experimental conditions.

Fig. 32 following which shows the effect of the addition of carbon monoxide is similar to fig. 28 page 106 which illustrates the effect of the addition of hydrogen.

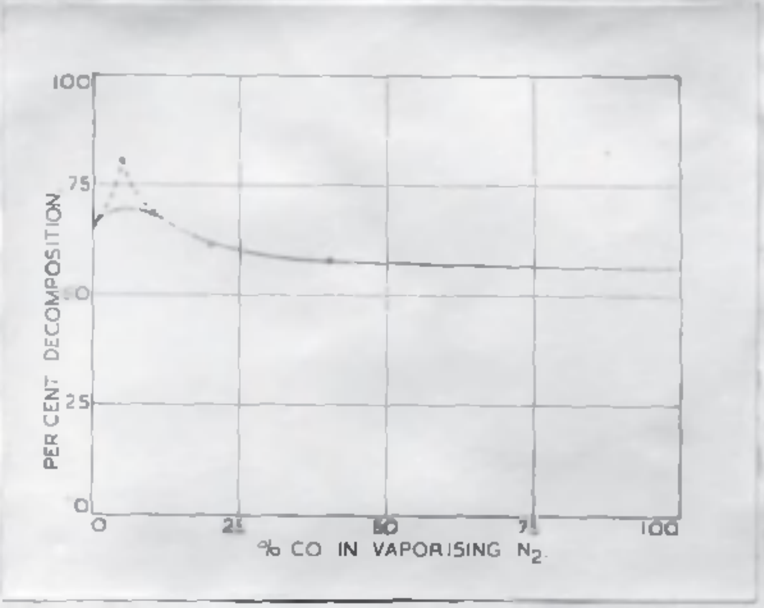


Fig.32. Effect of additional carbon monoxide on the methanol decomposition.

ANOMALOUS TEMPERATURE EFFECTS.

Throughout all the decomposition experiments at 360°C. a sharp rise in temperature was obtained at the beginning of each test. This rise in the first few minutes was followed by a slower fall, generally to below 360°C. This effect was most noticable with catalysts which had been reduced immediately before use. The rise in temperature was at first attributed to reduction of the catalyst taking place, but when it persisted long after reduction was judged to be complete, this theory was abandoned.

Particular attention was paid to this effect in Series VIc . When the methanol was vaporised by nitrogen alone, the rise was about 10°C. in the first minute of the test. This was followed by a slower fall of about 12° during the next two minutes. With the addition of hydrogen to the nitrogen the degree of this temperature change was altered, as shown by the following results:-

N_2 .. 10°C/min; temp. fall to 358°C. in next 2 min.
5 & 10% H_2 " " " " " " " " "
25% H_2 5-6°/min; " " " 355 " " " "
60% H_2 4°/min; " " " 350 " " " "
100% H_2 4°/min; " " " 350 " " " "
5% H_2 10°/min; " " " 360 " " " "

The figures are admittedly approximate, but the/

the difference between the values for pure nitrogen and those for pure hydrogen are sufficiently far apart to exclude experimental error. The temperature was not allowed to remain below 360°C for any length of time, the fall being checked as soon as possible, and hence the drop in temperature is greater than recorded.

It will be noticed that the rise in temperature becomes less with increased hydrogen concentration, and at the same time the fall is increased. After the experiment with 100% H_2 a test was performed with 5% H_2, and the temperature effect in this case was similar to that obtained with the original 5% concentration. It is possible that the greater temperature drop may be due to the greater conductivity for heat of hydrogen. A blank test with hydrogen in the absence of methanol however, produced a definite rise in temperature with practically no subsequant fall.

With pure nitrogen as the vaporising medium this rise in temperature was obtained in tests at 300°C. and also at 400°C. At 300°C. the rise is much more gradual, and of a lower order, e.g. 5° in the first 5 minutes, with a fall again to 300°C in the next 2 or 3. At 400°C. the rise is more rapid, and greater, e.g. 8° in the first 2 - 3 minutes followed by a fall to 390 - 395°C. in the next 3 - 4 minutes.

The/

The figures quoted lead to the suggestion that prior to decomposition, adsorption of the methanol without decomposition takes place on the surface of the catalyst. If the methanol were adsorbed and simultaneously decomposed, it is probable that the heat of adsorption would be partially balanced by the heat of decomposition, resulting in little, if any, temperature change. But the temperature rise points to adsorption without decomposition taking place, followed by decomposition, as evidenced by the fall in temperature. It appears also that the heat required for decomposition is greater than that evolved on adsorption.

The figures for the addition of hydrogen suggest that the hydrogen in excess tends to inhibit the complete adsorption of the methanol molecule. In this case complete adsorption of the methanol molecule may not be possible, and hence the heat of decomposition predominates, and the fall in temperature is greater than the rise.

SERIES VIII.

THE QUALITATIVE MEASUREMENT OF THE ADSORPTION OF METHANOL ON THE CATALYST SURFACE.

It has been suggested previously (p.117) that the peculiar temperature changes observed at the commencement of any experiment on the decomposition of methanol were due to methanol being quantitatively adsorbed on the surface of the catalyst prior to decomposition. The time during which the methanol is held by the catalyst surface is presumed to be sufficiently great to allow the heat of adsorption to manifest itself before decomposition commences, as shown by the fall in temperature subsequently. If decomposition occurred immediately the methanol came in contact with the surface, then the heat of decomposition of the methanol would mask partially, if not completely, the heat of adsorption, it being remembered that activated adsorption is akin to mild chemical action (see p. 7).

It was thought, therefore, that this adsorption might manifest itself in some way which could be measured experimentally, such as a lag in commencement of decomposition after the introduction of the methanol to the catalyst, or by a fall in pressure in a closed system, followed by a rise, due to decomposition.

The/

The experiments following were devised to test, if possible, these assumptions.

(1) A test-tube filled with methanol vapour at 360°C was attached to a manometer. The catalyst was contained in a thin-walled glass bulb placed in the test-tube at the beginning of the experiment. After about an hour to allow constant temperature to be reached, the bulb was broken at the required instant, and the methanol vapour thereby allowed to come in contact with the catalyst (at 360°C). A sensitive thermocouple was placed in the bottom of the test tube, so that when the bulb was broken, the catalyst completely covered the thermocouple junction.

This method proved a failure, as the temperature registered for the catalyst was always slightly lower than that of the atmosphere of the tube. This may be due to insufficient time being allowed for equilibrium temperature conditions to be attained.

(2) Methanol vapour and nitrogen were passed through the apparatus used in (1), a sensitive flowmeter being substituted for the manometer. This method was also a failure, as no lag in gas production could be detected.

(3) This method is similar to (2), except that the catalyst (3 ccs.) was held in a cage which was itself made/

made the thermocouple hot junction. To prevent methanol vapour condensing in the flow-meter orifice, two immersion condensers were placed in series before the flow meter. The results are shown in fig. 33 following:-

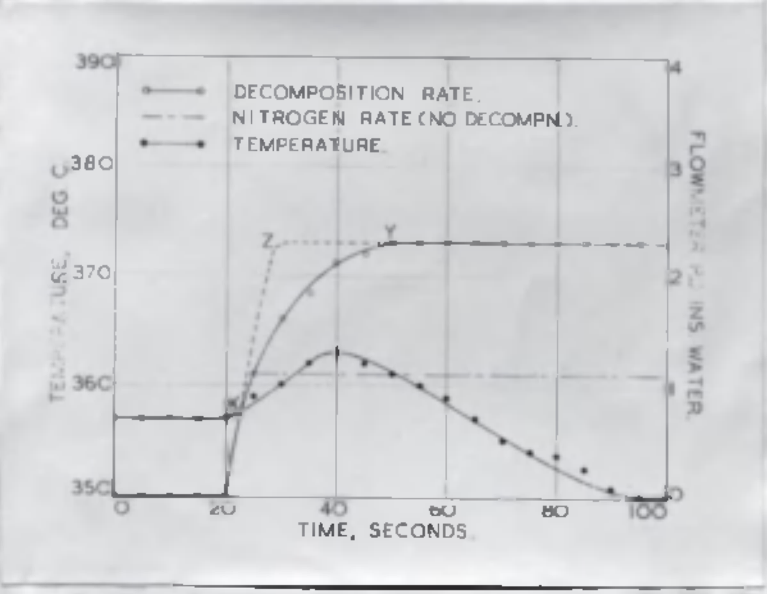


Fig.33. Relation between commencement of reaction and spontaneous temperature variation.

It will be noticed that there is a definite lag (x y) in each case, when it might be expected that the true curve should be x z y. Moreover, the time of contact of the mixture of nitrogen and methanol vapour is approximately one second, and it will be noticed that the lag extends over a period of approximately 20 seconds. The lag in the temperature rise might also be due to the poor conductivity for heat of the catalyst, an appreciable time being required for the temperature to become even throughout the catalyst mass. It is evident, however, that the temperature starts to rise before the maximum outlet gas rate is reached.

(4) In this method a large volume (20 ccs.) of catalyst was employed. A mixture of methanol vapour and nitrogen was passed through the reaction chamber for a short time, the apparatus being cold, to ensure that there was only methanol and nitrogen in the vessel. The vessel was next closed, and a mercury manometer fitted. Slow heating was commenced, and readings of temperature and pressure were taken at minute intervals. Fig. 34 following illustrates the results obtained.

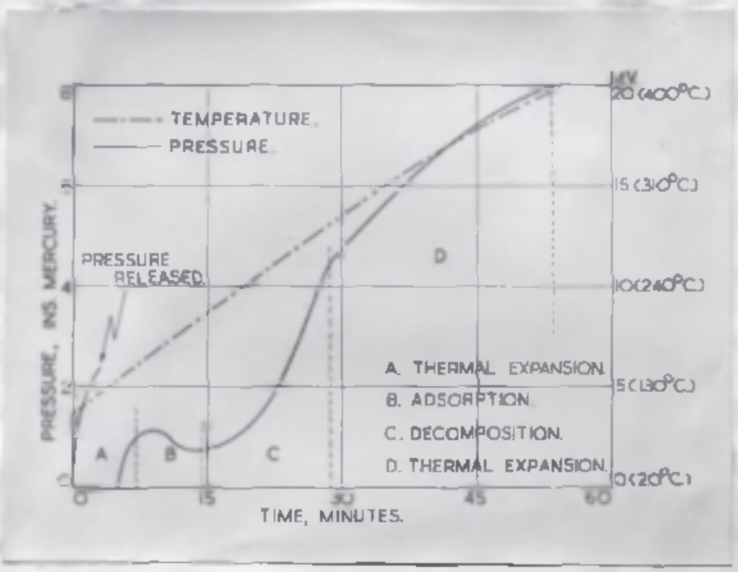


Fig.34. Catalyst phenomena.

This shows fairly conclusively that methanol is first adsorbed without decomposition by the catalyst. As the temperature rises, decomposition sets in, and when it is complete, there is ordinary thermal expansion. The experiment was carried out in duplicate, but in the first attempt a water manomoter was used, and due to the large pressure increase, the pressure had to be released at intervals during the experiment. A fall in pressure similar to that illustrated was obtained in the same temperature range.

The results of the~~se~~ last two ~~four series of~~ experiments, though/

though purely qualitative, suggest that it is possible for methanol to be adsorbed on the catalyst surface without decomposition at low temperatures. It may be assumed that it is also adsorbed temporarily at high temperatures, but that in this case the time of adsorption is extremely short. That there are two steps involved is evident from figs. 33 and 34, the former of which shows a definite lag between the initial contact of the methanol with the catalyst and the final steady decomposition of the methanol.

CHAPTER X.

DISCUSSION OF RESULTS OF THE METHANOL DECOMPOSITION.

The work of Cryder, Frolich, Fenske, and others previously mentioned, on the activity of Zn/Cr catalysts for the decomposition of methanol at atmospheric pressure is borne out by Series I tests. The most active catalysts for the decomposition of methanol appear to lie in the range 55 to 70 mol% Zn. (fig. 11 p. 68)

The catalysts appear to be sensitive to the heat-treatment to which they are subjected. Overheating to incandescence during reduction has been shown by Rumford (J.R.T.C. 427,4, 1939) to impair seriously the activity of such catalysts. As has already been stated ("Reduction of catalysts", p. 48), this overheating on reduction has been overcome. Furthermore, the conditions of reduction were standardised, in order that each sample of catalyst should be subjected to conditions of heating as similar as possible. In spite of this precaution, the activity of the catalysts was found to change on storage, both in the reduced states. The sample of catalyst to be used was therefore reduced under standard conditions immediately before the decomposition experiments.

Contrary to the statement of Cryder and Frolich (J./

(J.I.E.C., 1929, 867.) that the life of an active catalyst was almost indefinite, the activity and the composition of the reaction products hardly changing over a long period of use at 340°C., the results show conclusively that this is not the case especially during the first few hours use of the catalyst (Tables V to X incl.). The activity of the samples used in Series III (which have been kept for approximately 9 months in the unreduced state, and were reduced immediately before use) appeared to rise with time of use. On further investigation of this phenomenon, it was apparent that the activity rose to a maximum and then decreased (Table XIX). The maximum activity obtained is not, however, as great as that obtained in Series 1, where the sample was freshly prepared as well as freshly reduced. It appears, therefore, that the activity of a catalyst of this type depends also on the interval elapsing since its preparation, and hence for maximum activity, the catalyst must be prepared and reduced immediately before use.

At a temperature of about 300°C. the mechanism of the decomposition of methanol appears to undergo a change. Below this temperature there is very little change in the amount of decomposition with change of temperature/

temperature, but as the temperature is increased above 300°C. the rise in decomposition is extremely rapid (fig. 13 p. 71). This temperature effect is further illustrated by fig. 17 p.81 which indicates that at 300°C. and 400°C. the composition of the catalyst (up to about 73 mol% Zn.) has little or no effect on its activity for the decomposition of methanol. Between these two temperatures the effect of catalyst composition is noticeable, increasing from 300°C. to a maximum, and then decreasing again to 400°C. This suggestion of change in mechanism is supported by Rumford (J.R.T.C., 427, 4, 1939) with experiments on the activated adsorption of hydrogen on Zn/Cr catalysts of the type used in these experiments. It was found that a definite type of activated adsorption sets in at, and above, this temperature (300°C.).

The effect of the addition of small proportions of hydrogen to the methanol vapour is interesting. 5% appears to give the maximum effect, when the activity of the catalyst is considerably increased (Tables XVIII and XIX). Further additions have a tendency to reduce the activity. When the surface of the catalyst is swept with nitrogen at 360°C/

360°C., however, the activity is again raised, and to a higher figure than before the addition of hydrogen (Table XIX).

That there is no difference, to all intents and purposes, in results when the reaction is carried out in the presence of excess carbon monoxide is surprising, first, from theoretical reasoning put forward on p. 112 , and secondly, from the difference in amounts of carbon monoxide and hydrogen adsorbable by the catalyst as shown experimentally by Rumford, (private communication). However, as has already been suggested in the discussion of the results of this series of tests, it is highly probable that as the equilibrium constant is so great, any differences between the effects of hydrogen and carbon monoxide on the reaction would not be noticable with the apparatus used under the experimental conditions.

The variation in reaction rate with gas velocity gives rise to speculation. The results of Series IV and V tests point to the concentration of methanol in the gas stream as having as important an effect on the reaction as the gas velocity itself. They show that the gas velocity required to reach the maximum decomposition rate is directly proportional to the/

the concentration of inerts present. In view of these results it is suggested that the definition of the activity of a catalyst at a particular temperature should be based on the maximum reaction rate possible, as this is dependent only on the temperature. The normal definition of catalyst activity is given as a percentage, e.g. percentage change in reactants, and this applies only when conditions of concentration and reaction velocity are specified, at a particular temperature.

The results suggest that formaldehyde is a bye-product of the decomposition, rather than an intermediate product (as indicated by other workers previously mentioned). Support of this view is given by Peytral (Compt. Rend., 1917, 165, 703), with experiments on the decomposition of methanol in a platinum tube at 1150°C. It was found that with increased rates of flow, the ratio CO : HCHO decreases, suggesting that the production of formaldehyde and the decomposition of methanol are not simultaneous reactions.

It was postulated on p. 73 that at temperatures below about 300°C methanol was decomposed to formaldehyde and hydrogen only, and that the decomposition could not proceed further at a temperature below/

below which formaldehyde was itself was not decomposed to carbon monoxide and hydrogen. This infers that formaldehyde can be hydrogenated to form methanol, or that a continual circulation of methanol and the reaction products over the catalyst at these temperatures will result in the complete decomposition of methanol to formaldehyde and hydrogen. There is, so far, no experimental evidence to support these inferences.

With regard to the variation in activity of the catalyst during use, it is possible that the catalyst is still undergoing reduction. Garner and Veal (J.C.S., 1935, 1487) state that adsorption of hydrogen and carbon monoxide on Zn/Cr type catalysts is a slow process, and that in general, the gases diffuse into the fine capillaries in the interior of the catalyst grains, and may continue to do so for many hours before equilibrium between the interior and exterior of the catalyst mass is reached. This reasoning applied to the process of reduction may account for the slow rise in the activity of the catalyst during the first few hours of use. But it does not explain the fall in activity which follows this rise, nor does it account for the effect of the addition of small proportions of hydrogen or carbon monoxide/

monoxide to the methanol vapour in contact with the catalyst. Furthermore, catalytic activity is almost entirely a surface phenomenon, the reactions in the present circumstances taking place in a very short space of time. The variation in catalytic activity experienced in Series VI tests (p.101) appear to be greater than can be accounted for by the slow penetration of hydrogen or carbon monoxide (or both) into the interior of the catalyst mass.

It is possible that the activity of these catalysts is centred on the interface between areas of varying degrees of reduction, say, A and B, A being reduced to B. Note: the reduction referred to is not the reduction from the oxidised state (yellow colour), but a further reduction which proceeds after the latter oxidised state has been reduced by methanol to the standard reduced (green colour) state (see "Reduction of Catalysts", p. 48). As reduction proceeds, A decreases and B increases, the interface between the two increasing from zero until it is maximum when A and B are equal. Reduction still proceeding, A decreases and B increases, until only B remains, the interface falling to zero. The activity, being dependent on this interface, will rise and fall accordingly/

accordingly. This hypothesis, however, takes no account of the effect of small additions of hydrogen or carbon monoxide to the reacting methanol.

Craxford and Rideal (J.C.S., 1939, p.1604) have recently suggested that the Fischer-Tropsch process for the synthesis of hydrocarbons from water-gas, with cobalt/thoria catalysts, involves the following steps:-

(a) Chemi-sorption of carbon monoxide,

$$Co + CO \rightarrow Co\text{-}CO$$

(b) Reduction of chemisorbed carbon monoxide by hydrogen with the formation of water.

$$Co\text{-}CO + H_2 \rightarrow Co\text{-}C + H_2O.$$

(c) Reduction of carbide to chemisorbed methylene groups,

$$Co\text{-}C + H_2 \rightarrow Co\text{-}CH_2.$$

If space is available on the surface for chemisorbed hydrogen, this removes the methylene groups as methane, which occurs in the initial stages of the synthesis (i.e. starting with freshly reduced catalyst). If there is little chemisorbed hydrogen on the catalyst, the methylene groups associate to form macro-molecules, which are then disrupted to form long or short chain hydrocarbons, the length of the chain being determined by/

by the amount of chemisorbed hydrogen present on the surface.

There is thus a tendency for the surface to become covered with carbide, with a corresponding fall in activity. The catalyst is reactivated by reduction with hydrogen at synthesis temperature (195°C.). When this hydrogen is replaced by water-gas, the reaction products for the first few hours are carbon dioxide and methane, followed by normal synthesis products (Herington and Woodward, Trans. Faraday Soc., 1939, 35, 958).

The formation of carbon dioxide suggests that the chemisorbed carbon monoxide is reduced by further carbon monoxide:-

(d) $Co\text{-}CO + CO \longrightarrow Co\text{-}C + CO_2$.

Fischer and Tropsch (Ges. Abh. Kenntn. Kohle, 1930, 10, 313.) have shown that carbide is built up on the catalyst during the synthesis, while during the reactivation at synthesis temperature with hydrogen, large amounts of methane are formed.

It is possible that similar chemisorption of hydrogen and carbon monoxide takes place in the case of Zn/Cr oxide catalysts used for the decomposition of methanol. No evidence was obtained of the formation of hydrocarbons/

hydrocarbons higher than methane, however, showing that a step similar to (c) does not take place. It has been observed throughout the tests that the carbon dioxide formed is always in excess of the methane. Moreover, on the first addition of hydrogen there is a decrease in the amount of carbon dioxide produced, and an increase in the methane. There is a tendency, however, for both these gases to increase with the amount of hydrogen added (see Series V).

In view of the mechanism put forward by Craxford and Rideal (loc. cit.), together with the above observations, it is reasonable to assume that chemisorption of the carbon monoxide takes place on the catalyst, resulting in diminished activity. As the amount of this chemisorption increases, larger proportions of hydrogen require to be added to remove the chemisorbed carbon monoxide, with the continued deposition of carbide, until eventually the entire surface is covered with carbide, and requires reactivation under other conditions.

It has been observed that the amounts of carbon dioxide and methane formed increase with the proportion of hydrogen added. This is possibly due to the following reactions taking place:-

(i) CO/

(i) $CO + 3H_2 = CH_4 + H_2O$

(ii) $CO + H_2O = CO_2 + H_2$

The similar effect of the addition of carbon monoxide on the methanol decomposition is readily explained on the assumption that carbide formation in a manner analogous to reaction (d) takes place on the catalyst.

From the foregoing, therefore, it is possible that the catalyst activity is centred on the interface between areas of chemisorbed carbon monoxide or hydrogen, areas of carbide formation and desorbed areas; but in the light of present knowledge, it is impossible to advance a theory which would explain satisfactorily all the results obtained for this particular case.

It has already been suggested that the anomalous temperature effects experienced were due to complete adsorption of methanol on the catalyst prior to decomposition. The attempts to measure qualitatively this adsorption show that at least two steps are involved in the reaction:-

(a) Delay in appearance of decomposition products, accompanied by temperature rise.

(b) Appearance of decomposition products, followed by temperature/

temperature drop.

The rise in temperature is thought to be due to the heat of adsorption of methanol, and the subsequent fall to be due to the heat of decomposition. If decomposition occurred immediately on contact of the methanol with the catalyst, it is thought that no rise in temperature would be experienced, as activated adsorption is akin to a mild chemical reaction only, and hence the heat of adsorption would be completely masked by the heat of decomposition. Since a rise in temperature is experienced, followed by a fall, it is obvious that there is an interval of time between the contact of the methanol with the catalyst, and its decomposition, i.e. the steps as suggested above. It is therefore suggested that the methanol is completely adsorbed for an appreciable time on the surface of the catalyst prior to decomposition.

It has been shown that the greater the methanol concentration in the gas stream, the smaller is the space-velocity required to obtain maximum decomposition rate. If, as suggested, complete adsorption of methanol occurs on the catalyst surface, then it would be expected that this adsorption would be of a greater order with increased methanol concentration, and hence it is probable that increased reaction rate will result. Thus, for maximum reaction/

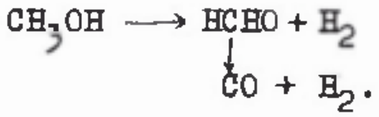
reaction rate, the catalyst surface must be saturated with methanol.

PART II.

DECOMPOSITION OF FORMALDEHYDE AT ATMOSPHERIC PRESSURE.

INTRODUCTORY.

Frolich, Fenske and others (see Introduction) working on the decomposition of methanol by Zn/Cr catalysts of the type used in the following experiments, found that a constant amount of formaldehyde was obtained in the decomposition products, and put forward a 'stepwise' theory to account for it:-



$$\begin{tikzcd}[column sep=small] CH_3OH \arrow[r] & HCHO \arrow[d] + H_2 \\ & CO + H_2. \end{tikzcd}$$

If this be the course of the reaction, then it should be possible to study the mechanism more fully by observing the decomposition of formaldehyde under similar experimental conditions. With this in view, the following experiments on the decomposition of formaldehyde were carried out.

CHAPTER XI.

PRELIMINARY WORK.

Production of Formaldehyde.

Pure, dry formaldehyde cannot be obtained by the fractional distillation of formalin solution, as the vapour pressure of water in an aqueous solution of formaldehyde is lower than that of the formaldehyde. A method of production was attempted in which the mixture of formaldehyde and water vapour was passed through a tube containing activated carbon, and the formaldehyde obtained from this by heating and passing a current of nitrogen through it. This method was a failure as the amount liberated from the charcoal subsequently was negligible. Dropping formalin solution on to anhydrous calcium chloride in a stream of nitrogen was also a failure.

Paraformaldehyde as a source of formaldehyde was more promising, but there was one great drawback, namely, that the paraformaldehyde contains water which cannot be driven off by ordinary methods. Attempts to remove this water by heating with quicklime to about 150°C. in a current of nitrogen were failures. More drastic methods were not employed due to the danger of decomposition, and also to the lack of time available. The water content could/

could not be reduced below about 9% even after prolonged heating at 150°C. This figure is in agreement with a formula of $(CH_2O)_6.H_2O$ for paraformaldehyde. No mention of this composition can be found in the literature.

Formaldehyde was therefore produced by passing a current of nitrogen over heated paraformaldehyde, which has previously been stored over quicklime.

Experimental Conditions.

The conditions of the methanol decomposition were reproduced as far as possible. The catalysts varied in composition from 18.8 mol% Zn. to 77 mol% Zn., this range including those having characteristic properties for the methanol decomposition (p. 68 fig. XI). The samples were of 5 ccs. each, and had been freshly reduced for the decomposition of methanol at 300, 360 and 400°C. (p. 77).

The apparatus was essentially the same, except that the preheater was excluded in order to have as short a passage as possible between the vaporiser and catalyst. The methanol vaporiser was dispensed with, the paraformaldehyde being in powder form. Crushed ice and water replaced alcohol and solid carbon dioxide as the condensing medium.

Analysis of Products.

The liquid reaction products were fractionated

in/

in a specially constructed fractionation unit of approximately 5 ccs. capacity, shown in fig. 35 following.

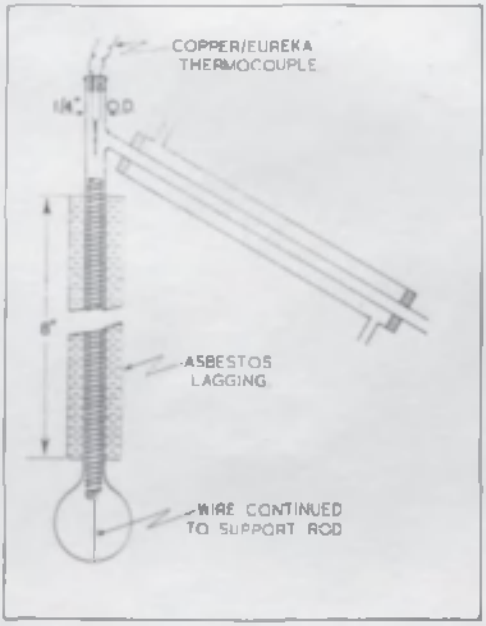


Fig.35. Fractional Distillation Unit.

The column is of the Dufton type, a close spiral of copper wire wound on a glass rod, and lagged with asbestos cord. Temperatures were read by means of a Cu/Eureka thermocouple, previously calibrated. To minimise distillation losses, the condenser was fitted on to the side-arm, while warming the column prior to distillation greatly reduced the tendency to flooding.

This/

This unit worked very satisfactorily, a sharp fractionation being obtained.

Products other than those estimated and analysed are obtained, as judged by the smell of both liquid and gaseous products, but as their production does not constitute the main decomposition reactions, they were consequently neglected. They are present in such small quantity as to make analysis impossible.

Only very small traces of methyl formate were found, and therefore were omitted from the calculations. The liquid products gave no reaction with I_2 and NaOH, showing that iodoform producing substances were absent. No unsaturated compounds were found in the liquid reaction products.

CHAPTER XII.

EXPERIMENTAL.

SERIES I .

EFFECT OF TEMPERATURE AND CATALYST COMPOSITION ON THE REACTION.

Conditions:

Catalysts, composition 18.8 mol% to 77 mol% Zn.

Temperatures, 250, 290 and 360°C.

Rate, approx. 2 gms. in 4 litres N_2/hr. entering.

Results, Table XXI.

Table XXI. Temperature and catalyst composition varying.

Cat. Compn Mol% Zn.	Temp. °C.	Dcomp %	CH_3OH %	Meth. frmte. %	Dcomp gases, % vol.				
					H_2	CO	Unsat.	CO_2	CH_4
18.8	250	26	30	-	-	47	-	33	20
	290	98	37	-	-	74	1	19	5
	360	100	trce.	trce.	45	48	2	5	-
41.5	250	97	24	0.8	-	73	-	23	4
	290	99	32	-	16	68	2	12	-
	360	100	-	-	47	45	1	6	1
58.8	250	18	7	-	-	10	-	43	47
	290	100	28	0.6	21	63	2	12	2
	360	100	-	-	49	40	2	8	1
72.8	250	trce	-	-		traces of CO_2 only			
	290	98	28	0.8	19	64	1	14	2
	360	100	-	-	46	42	2	8	2
77.0	250	trce.	-	-		traces of CO_2 only			
	290	"	-	-		"	" "	"	
	360	95	28	trce.	17	57	1	20	5

It will be seen from fig. 36 that at 360°C. and 290°C. the decomposition is complete, the composition of the catalyst having no effect on the amount of formaldehyde decomposed, except in the case of catalysts of high zinc content.

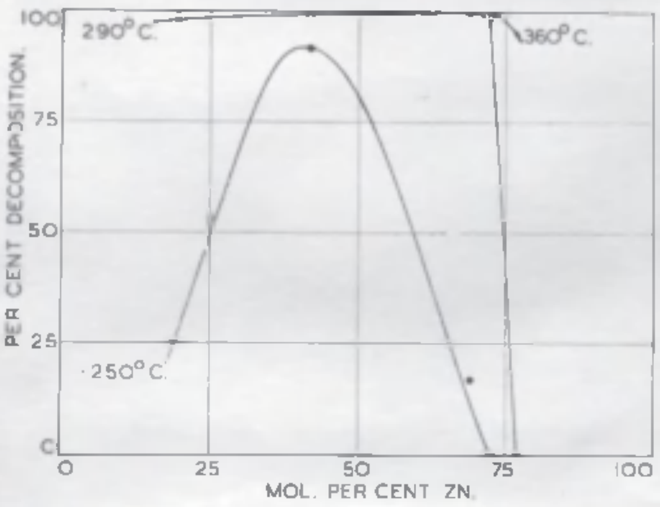


Fig.36. **Effect of temperature and catalyst composition on the formaldehyde decomposition.**

It is interesting to compare this with the decomposition of methanol under similar conditions(see p. 81 fig. 17). At 250°C., however, the effect of catalyst composition is noticeable, the most active in this case containing about 38 to 40 mol% Zn.

Methyl alcohol moreover, is a product of the decomposition/

decomposition of formaldehyde at the lower two temperatures (fig. 37), and that its formation is promoted by chromium.

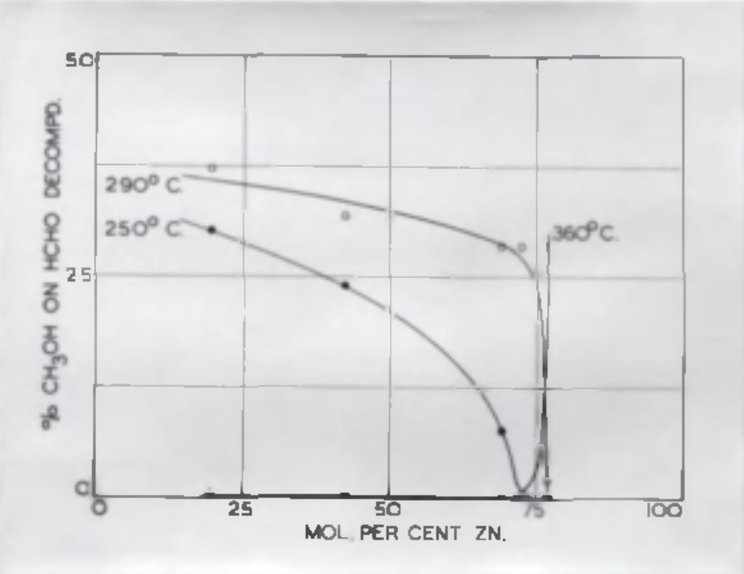


Fig.37. Effect of temperature and catalyst composition on methanol formation.

It is suggested that this compound is formed due to the following reactions taking place:-

(i) $HCHO \longrightarrow CO + H_2$

(ii) $HCHO + H_2 \longrightarrow CH_3OH$.

This theory is supported by the composition of the gaseous products, where there is a large excess of CO, and practically no H_2.

Water also appears to be a product of the reaction/

reaction, as it is present in larger quantities than could possibly be present in the paraformaldehyde used for generating formaldehyde. The amount formed also appears to vary with the temperature of the reaction (fig. 39 p.150).

The large proportion of methanol formed at 360°C. by the catalyst containing 77 mol% Zn. is explained by the fact that the activity of the catalyst is low, and the results are based on the amount of formaldehyde decomposed. It is also explained by supposing that for each catalyst there is a temperature of maximum methanol formation which is dependent on the activity of the catalyst, the greater the activity of the catalyst, the lower the temperature at which maximum methanol formation occurs. Thus the results at 360°C for the catalyst containing 77 mol% Zn. correspond with those of other catalysts (more active) at lower temperatures.

Generally at 360°C., the results indicate that the reaction is a straightforward decomposition into CO and H_2, together with side-reactions. CO_2, CH_4 and gaseous unsaturated compounds are formed to a greater extent than in the methanol decomposition, and are favoured by low temperatures, where the catalytic activity/

activity is low.

It is evident from the results that the mechanism of the formaldehyde decomposition changes between 250 and 360°C., the formation of methanol instead of CO being the main reaction up to about 300°C. (depending on the activity of the catalyst), followed by the decomposition into CO and H_2. as the temperature increases further (fig. 39 p.150)

SERIES II.

EFFECT OF TEMPERATURE ON THE REACTION.

Conditions:

Catalyst, composition 41.5 mol% Zn.

Temperature range, 200 - 360°C.

Rate, approx. 2 gms. in 4 litres N_2/hr. entering.

Results, Table XXII.

Table XXII. Temperature range; Catalyst composition 41.5 mol% Zn.

Temp. °C.	Dcomp %	CH_3OH %	H_2O %	Meth. frmte. %	Decomposition gases, % vol.				
					H_2	CO	Unsat.	CO_2	CH_4
225	-	-	-	-		traces CO and CO_2 only.			
240	23	16	29	-	-	4	-	43	53
260	69	6	36	-	-	63	-	31	6
280	87	38	-	-	16	68	5	9	2
300	99	32	-	-	13	64	14	5	4
330	99	18	-	-	29	47	2	15	6
360	100	-	-	-	44	47	1	6	2

Fig. 38 indicates that below a certain temperature the catalyst is inactive. This is similar to the methanol decomposition (see p. 71 fig. 13), but the minimum "active" temperature is about 70° lower for formaldehyde.

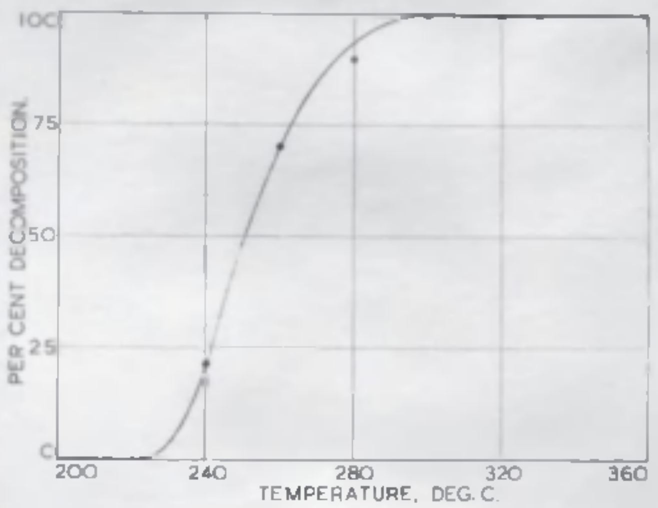


Fig.38. Effect of temperature on the formaldehyde decomposition.

The change in mechanism of the reaction is evident from figs. 39 and 40 methanol production rising with temperature to a maximum at about 280°C.

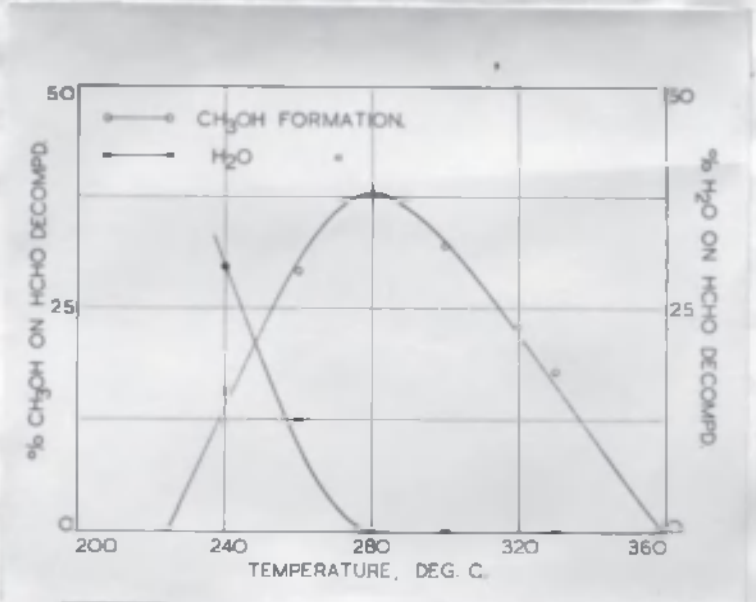


Fig.39. Effect of reaction temperature on decomposition products.

All the catalysts will exhibit this characteristic, but the position of the curve of decomposition temperature will vary with catalytic activity.

As previously stated, water is also a product of the reaction at lower temperatures. It is possible that it is formed either by the hydrogenation of two molecules of formaldehyde by one of hydrogen, with the formation of water, methane and carbon monoxide, or by the dehydration of two or more molecules of formaldehyde, with the formation of gaseous unsaturated hydrocarbons and/

and water. There was no apparent deposition of carbon on the catalyst, and the fall in activity over a long period of use is very much less than would be expected if carbon were deposited on the catalyst surface.

The water appears in the reaction products up to the temperature at which hydrogen appears, i.e. about 280°C (figs. 39 and 40). Thus a reaction such as the following appears to be promoted by low temperature:-

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

At low temperatures, it is seen that carbon dioxide and methane predominate in the gaseous products. Furthermore, the mechanism changes between about 230°C. and 300°C from the production of water to the production of methanol.

Fig. 40 following which illustrates the variation in the gaseous reaction products with reaction temperature, bears out the suggested reaction for the formation of methanol.

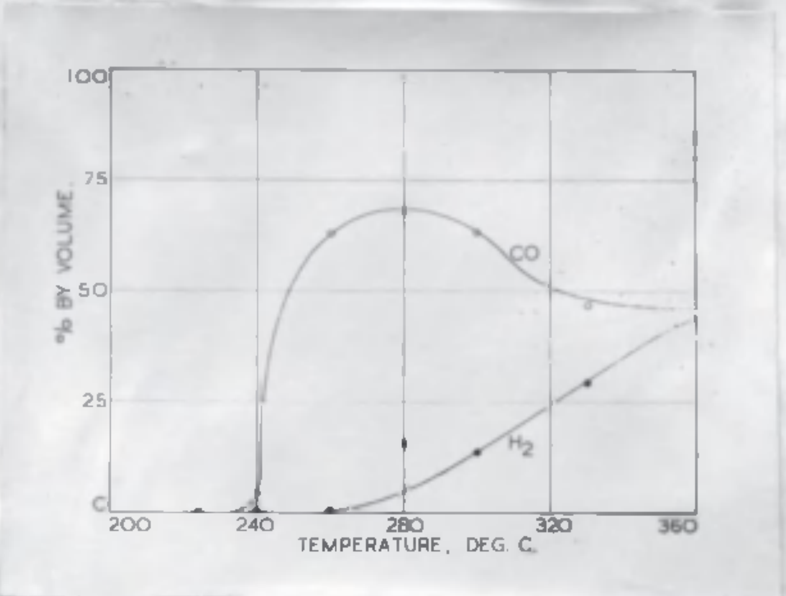


Fig.40. Effect of reaction temperature on decomposition products.

No liquid products other than water, methyl formate and methanol could be identified. The liquid product gives no reaction with iodine and caustic soda, indicating that iodoform-producing compounds are absent. Furthermore, it does not decolorise bromine water, showing that only gaseous unsaturated compounds are formed during the decomposition of formaldehyde. Only traces of methyl formate were found. As previously stated however, compounds other than those already mentioned are present, as evidenced by the odour of the reaction products, both liquid and gaseous. This smell/

smell is very similar to that of the methanol decomposition products (360°C.), and becomes more marked as the reaction temperature is raised.

SERIES III.

EFFECT OF CO AND H_2 ON THE DECOMPOSITION.

Conditions:-

Catalyst, composition 41.5 mol% Zn.

Temperatures, 250, 290 and 360°C.

Rate, approx. 2 gms. in 4 litres/hr. gas N_2 entering.

Results, Tables XXIII and XXIV.

(A) H_2 Effect.

Table XXIII. Effect of hydrogen; Catalyst composition 41.5 mol% Zn.

% H_2 added.	Temp °C.	Dcomp. %	CH_3OH %	Meth frmte %	H_2O %	Dcomp. gases, % vol.				
						H_2	CO	Unsat.	CO_2	CH_4.
Nil.	250	90	23	-	7	12	66	2	20	-
100	250	60	20	-	20	-	65	-	29	6
"	290	99	36	-		9	68	3	15	4
"	360	100	-	-	-	not analysed.				

The results given in the following form show more clearly the effect of hydrogen on the reaction (tables a, b)

Table a. Decomposition.

	250°C.	290°C.	360°C.
No. H_2	90% Dcomp.	99% Dcomp.	100% Dcomp.
100% H_2	60% "	99% "	100% "

Table b. Methanol production.

	250°C.	290°C.	360°C.
No. H_2	23% MeOH	32% CH_3OH	No CH_3OH.
100% H_2	20% "	36% "	" "

In general, the presence of excess hydrogen makes itself felt only in cutting down the decomposition at 250°C, and not at all above this temperature. There is not, however, the anticipated increase in the amount of formaldehyde converted to methanol. This gives rise to the suggestion that the hydrogen liberated from the decomposing formaldehyde is in the nascent or active state, and only by reason of its greater activity can it reduce formaldehyde to methanol under the prevailing experimental conditions. This does not mean, however, that it is impossible to hydrogenate formaldehyde to methanol with hydrogen under other conditions.

(B) CO Effect.

Table XXIV . Effect of Carbon monoxide; Catalyst composition 41.5 mol% Zn.

% CO added	Temp. °C.	Dcomp. %	CH_3OH %	Meth. frmte %	H_2O. %	Decomp. gases % vol.				
						H_2	CO	Unsat.	CO_2	CH_4
Nil	250	90	22	-	10	10	71	3	11	5
100	250	62	22	-		4	8	42	38	8
"	290	100	32	-		15	18	39	26	2
"	360	100	-	-	-	48	33	2	15	2

As tabulated below, the results show more clearly the effect of carbon monoxide.

<u>Table c</u>. Decomposition.

	250°C.	290°C.	260°C.
No CO	90% Dcomp.	99% Dcomp.	100% Dcomp.
100% CO	61% "	99% "	100% "

<u>Table d</u>. Methanol production.

	250°C.	290°C.	360°C.
No CO	23% MeOH	32% CH_3OH	No CH_3OH
100% CO	22% "	32% "	" "

These results show that, for all practical purposes, there is no difference in the effects of hydrogen and carbon monoxide on the reaction. But excess carbon monoxide results in the formation of gaseous unsaturated hydrocarbons, e.g.

100% H_2 ... CO_2 29%, Unsat. nil, CO,65%,H_2 nil,CH_4 6%) }250°C
100% CO ... CO_2 38% " 42%, CO 8% ‡ H_2 4%, CH_4 8%)

100% H_2 ... CO_2 15% Unsat. 3%, CO 69%,H_2 9%, CH_4 4%) }290°C
100% CO ... CO_2 27% " 39%, CO 18%‡H_2 14%, CH_4 2%)

(No/

(No liquid unsats. detectable.)

Note: It is probable that the figures for CO (‡) and those for H_2 (§) are only approximate, as they are obtained by difference. It is claimed, however, that they differ too widely from the normal values at these temperatures to be due to experimental error.

It is probable that for formation of gaseous unsaturated hydrocarbons is due to Fischer-Tropsch reactions taking place, for although the amount of methanol formed is not altered, the amount of CO formed in the decomposition is greatly diminished. As there are no unsaturated compounds present in the liquid products, and these liquid products do not give the iodoform test, it is probable that the formation of gaseous unsaturated compounds is due to a simple type of Fischer-Tropsch reaction taking place.

SERIES IV.

EFFECT OF RATE OF REACTION ON THE DECOMPOSITION.

Conditions:

Catalyst, composition 41.5 mol% Zn.

Temperature, 250°C.

Varying volatilisation temperature of paraformaldehyde.

Results, Table XXV.

Table XXV. . Reaction rate; Temperature 250°C., Catalyst composition 41.5 mol% Zn.

HCHO enter gm/hr.	Dcomp gm/hr	CH_3OH %	CH_3OH gm/hr.	H_2O %	Decomposition gases, % vol.				
					H_2	CO	Unsat.	CO_2	CH_4
0.77	0.54	8	0.04	23	-	67	-	24	9
1.01	0.80	8	0.06	36	-	83	-	6	11
2.12	1.00	14	0.15	42	-	61	-	33	6
2.80	1.66	12	0.20	37	3	62	-	31	4
3.74	2.37	21	0.49	27	9	64	-	25	2
4.73	2.03	6	0.13	49	5	78	-	13	4
6.80	3.25	15	0.48	40	9	65	-	23	3

It was attempted to increase the rate of entry of the formaldehyde to the catalyst by increasing the flow of nitrogen. This method was not successful, as trebling the gas rate resulted in only a 50% increase in the rate of volatilisation. The rate was therefore increased/

increased by raising the temperature of the paraformaldehyde, the gas rate being maintained constant.

Fig. 41 shows that the rate of decomposition increases with the rate of entry of formaldehyde. No limiting rate was found in the range of experiments carried out. This differs from the results in the case of methanol where the amount decomposed, and the amount of formaldehyde formed, reaches a maximum, constant value (see p. 88 fig. 21 & p. 93 fig. 23)

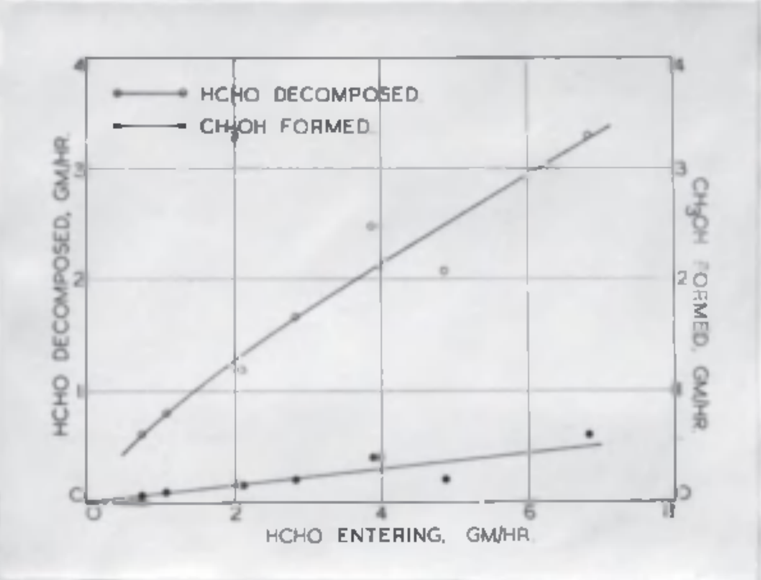


Fig.41. Effect of reaction rate on the formaldehyde decomposition.

Fig. 41 also shows that the rate of methanol formation increases with the rate of formaldehyde entry. This is much more gradual than the rate of decomposition, showing that there is an increasing tendency for formaldehyde/

formaldehyde to decompose to carbon monoxide and hydrogen in preference to undergoing reduction to methanol. This is further supported by fig. 42 which shows that the proportion of formaldehyde converted to methanol does not increase beyond a certain figure.

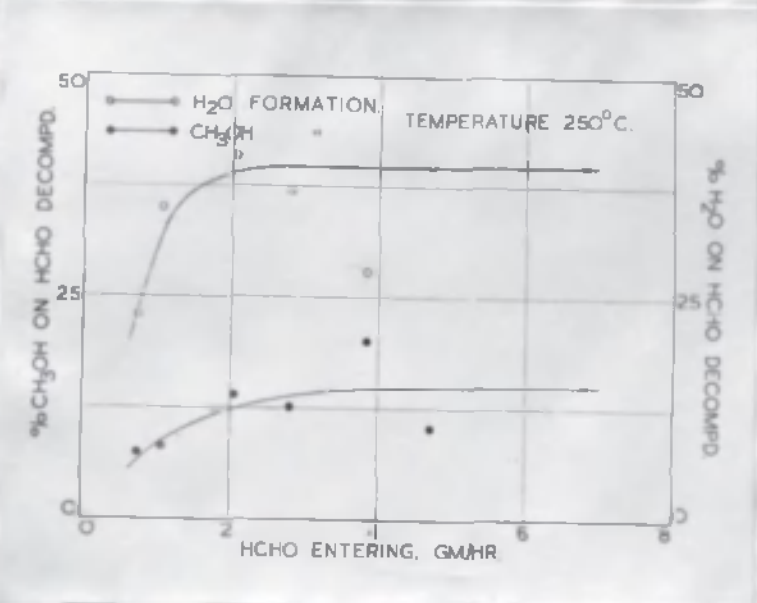


Fig.42. Effect of reaction rate on decomposition products.

(It will be noticed that the water formation is affected in a similar manner to the methanol formation by the rate of entry.) This appears to support the reaction suggested previously for the formation of methanol, i.e. the methanol is formed by a secondary reaction.

CHAPTER XIII

DISCUSSION OF THE RESULTS OF THE DECOMPOSITION OF FORMALDEHYDE.

The results show that over Zn/Cr catalysts of the type used in the foregoing experiments the decomposition of formaldehyde is very much faster than the decomposition of methanol under similar conditions. Indeed, the rate of decomposition of formaldehyde at 250°C is similar to that of methanol at 360°C. As the decomposition rate of the former is so much greater, it is not to be expected that evidence of the course of the methanol decomposition will be forthcoming from this series of tests. In a number of instances, however, the results are interesting.

The most noteworthy is the formation of methanol during the decomposition; its production indicates that secondary reactions take place. Its mode of formation has already been suggested, although it is also possible that it may be formed as follows:-

$$2HCHO = CH_3OH + CO.$$

If it were formed in this manner it would be expected that its formation would increase with the rate of decomposition, but this is not so, the amount of formaldehyde converted to methanol reaching a limiting figure

(see/

(see fig. 42 , p. 160).

The fall in this methanol production as the temperature increases above 300°C lends further support to the theory put forward for its formation, as at this temperature methanol starts to decompose (see fig. 13 p. 71).

The failure to increase the yield of methanol by carrying out the reaction in an atmosphere of hydrogen is interesting. It was expected that as it was formed by a secondary reaction, the excess hydrogen would convert a further amount of formaldehyde to methanol. This apparently does not occur, due, as has been suggested, to conversion proceeding only by the hydrogen which is liberated in an active form during the decomposition. This, coupled with the failure to hydrogenate under pressure (PART III), is fairly conclusive that catalysts of the type used in this work are unsuitable for the hydrogenation of formaldehyde.

In connection with the formation of water during the decomposition of formaldehyde, it is of interest to note that fig.42(p.160) indicates that it is also formed by a secondary reaction.

The similarity of effect of carbon monoxide and hydrogen upon the decomposition is interesting, being noticeable only at 250°C. Above this the rate of reaction appears to be too fast to be affected.

The/

The results of the addition of carbon monoxide during the reaction indicate that this additional carbon monoxide reacts with the decomposition products of formaldehyde to form unsaturated and other compounds, particularly carbon dioxide and methane (See Table XXIV).

It was thought that the catalysts most active for the methanol decomposition would also prove the most active for the formaldehyde decomposition, but at temperatures at which the reaction is slow enough to be affected by the composition of the catalyst, it has been found that this is not so, a catalyst containing more chromium being the most active in the latter case. (Cf.fig.37 p.145and fig.11 p. 68). Catalysts of high chromium content are generally more active in decomposing formaldehyde than those of high zinc content. This might have been expected, as in the experiments of Part I it was found that catalysts of high zinc content promoted its formation. (Fig. 12 p. 69).

PART III.

HIGH PRESSURE EXPERIMENTS.

CHAPTER XIV.

INTRODUCTORY

The experiments are divided into three groups:-

(i) Attempted synthesis of formaldehyde from carbon monoxide and hydrogen.

(ii) Attempted synthesis of methanol from the same gases.

(iii) Attempted hydrogenation of formaldehyde to methyl alcohol.

The American workers (see Introduction) have shown by their experiments that the decomposition of methanol and its synthesis under pressure are parallel reactions, the decomposition method proving a simple means of studying the reaction. The experiments on the decomposition of formaldehyde (PART II) indicated that the catalysts, with one or two exceptions, were very active in decomposing formaldehyde at temperatures much lower than those required for the decomposition of methanol. This, coupled with the findings of the Americans, led to the belief that under modified experimental conditions, it should be possible to synthesise formaldehyde directly from carbon monoxide and hydrogen.

The experiments of PART I indicated that methanol

was/

was decomposed at temperatures in the region of 360°C, and the American workers have shown that with similar temperatures, methanol can be synthesised under high pressures from carbon monoxide and hydrogen. On this basis it was believed that the conditions most suitable for the synthesis of formaldehyde would be high pressures of these gases in theoretical proportions at temperatures not exceeding 300°C, this being the lowest temperature at which methanol starts to decompose at atmospheric pressure, even with the most active of the catalysts used (see fig. 13, p. 71). Furthermore, the reaction $CO + H_2 = HCHO$ proceeds with a smaller volume change than the reaction $CO + 2H_2 = CH_3OH$, and therefore it was assumed that pressures lower than those required for the methanol synthesis were desirable.

As the experiments on the formaldehyde decomposition had indicated that at these temperatures the most active catalyst was one containing about 40 mol% Zn, a catalyst of composition nearest to this (41.5 mol% Zn.) was used at these temperatures.

Description of Apparatus.

The reaction chamber is a piece of alloy steel tubing 9" long x 3/16" i.d. x 11/16" o.d., with lens-ring joints/

joints. The apparatus is shown in fig. 43 following.

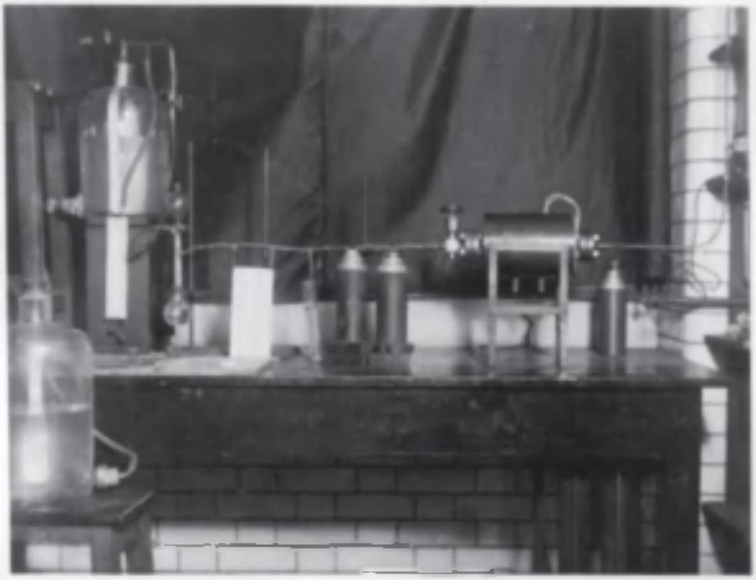


Fig.43. Apparatus used for attempted synthesis of formaldehyde.

The thermocouple hot junction is tied with asbestos string on to the outside of the tube, insulated from the steel by a layer of Miconite. The details are shown in fig. 44 overleaf.

Fig.44. Attachment of thermocouple to reaction chamber.

The gas flow is regulated by means of an I.C.I. type fine-adjustment valve (fig. 68, p. 213), pressure being controlled by another on the inlet side of the apparatus. The reaction products are collected at atmospheric pressure in the receiving side of the usual atmospheric-pressure apparatus (fig. 4 , p. 53). For the storage of the mixed gases, a high pressure autoclave was used, the mixing being effected by means of copper paddles attached to the stirring shaft (fig. 45 overleaf).

Fig.45. Paddles for mixing carbon monoxide and hydrogen under pressure.

Fig. 45a.
attachment of catalyst container

CHAPTER XV.

EXPERIMENTAL TESTS.

SERIES I.

ATTEMPTED SYNTHESIS OF FORMALDEHYDE FROM CARBON MONOXIDE AND HYDROGEN.

The results and conditions of the experiments are given in Tables XXVI and XXVII.

Table XXVI. ; Catalyst composition 41.5 mol% Zn., volume = 4.5 ccs.

Temp. °C.	Press. lb/in^2.	CO:H_2 ratio.	Rate ltr/hr atmos. press.	HCHO. prod.
220	600	1:1	20	trace.
"	900	"	"	"
260	"	"	"	"
300	900	"	"	"
260	"	1:2	"	"
"	600	"	"	"
220	900	"	"	"
300	900	"	"	"
220	1800	"	"	"
300	1800	"	"	"
350	"	"	"	"

Table XXVII. Catalyst composition 77 mol% Zn., volume = 4.5 ccs.

Temp.	Press. lb/in.^{2}	CO:H_2 ratio.	Rate, ltr/hr. atmos. press.	HCHO. prod.
300	1300	1:2	15	trace.
350	"	"	"	"
330	1800	1:4	20	"

Note: The trace of formaldehyde formed in all these experiments is of the order of 1 mg. of formaldehyde per hour.

To all intents and purposes there is no difference in the amount of formaldehyde produced in spite of the widely varying conditions. It is possible that these results are due to (i) the catalyst being much less active for the synthesis than for the decomposition, or, since the apparatus was not copper-lined, (ii) to the inhibiting effect of the steel of the reaction chamber. A decomposition test on formaldehyde showed that the activity of the catalyst for that reaction was unimpaired after the foregoing tests under pressure.

SERIES II.

THE ATTEMPTED SYNTHESIS OF METHANOL FROM CARBON MONOXIDE AND HYDROGEN.

Conditions:-

Catalyst composition, 68.8 mol% Zn.
Catalyst volume, 4.5 ccs.
Operating pressure, 1500 lb/in^2.
Temperature range, 300 to 360°C.
$CO:H_2$ 1:2.
Gas rate, 4 to 10 litres/hr. at atmospheric pressure and room temperature.

In all, four attempts were made to synthesise methanol, and in all cases the results were negative, although the equilibrium under the experimental conditions favours a conversion in the order of 75%, which means that with the amount of catalyst employed, the rate of production should have been about 2 to 3 ccs. of liquid methanol per hour.

One experiment was carried out in a high pressure autoclave of 1½ litres capacity. The conditions were as follows:-

Catalyst composition, 68.8 mol% Zn.
Catalyst volume, 15 ccs.
Pressure, 1200 lb/in^2.
Temperature, 345°C.
Time/

Time, 1 hour at 345°C.

$CO:H_2$ 1:2.

The catalyst was held in a copper gauze basket which was tied to the autoclave stirring shaft. The reacting gases were introduced when the temperature in the autoclave was 250°C, and the agitator started at the same time. Again, no liquid product was obtained, though the equilibrium favours approximately 60% conversion at the temperature and pressure employed. That some reaction had taken place was evident from the residual gas, which, besides carbon monoxide and hydrogen, contained 5% methane, 5% carbon dioxide and 2% unsaturated compounds.

As suggested previously, these negative results may be due either to the metal of the reaction chamber exercising an inhibiting effect on the reaction, or to the catalyst being much less active for the synthesis than for the decomposition.

SERIES III.

THE ATTEMPTED HYDROGENATION OF FORMALDEHYDE TO METHANOL.

Two methods were employed.

(A) Static method in autoclave.

(B) "single passage" method in apparatus shown in fig. 43 (p 167).

(A) Conditions:

Pressure of H_2, 1200 lb/in^2.

Weight of paraformaldehyde in autoclave, 25 gms.

Temperature, 300°C.

Time of test, 1 hour.

Catalyst composition, 41.5 mol% Zn, and 68.8 mol% Zn.

Catalyst volume, 5 ccs. and 15 ccs. respiratory.

Two tests were carried out, the first with a small volume of the catalyst most active for the decomposition of formaldehyde, and the second with a large volume of the catalyst most active for the methanol decomposition. In the first case no liquid product was obtained, the paraformaldehyde becoming completely charred, and in the second a slight amount of liquid was obtained together with a great deal of charred paraformaldehyde. This liquid was found to be approximately 10% methanol and/

and 90% water. (the weight of liquid was 3 gms.) This meant that only about 1% of the formaldehyde had been converted to methanol, while the equilibrium favours complete conversion. The residual gas contained in both cases about 6% carbon dioxide and 2% methane, together with traces of carbon monoxide and unsaturated hydrocarbons. The catalyst was held in a copper gauze basket as described on p. 173

(B) "single passage" flow method.

Conditions:

Catalyst composition, 68.8 mol% Zn.

Catalyst volume, 4.5 ccs.

Temperatures, 300 and 340°C.

Pressure, 1800 lb/in^2.

Gas rate, 8 litres/hr. at atmospheric pressure and room temperature.

Formaldehyde rate, 6 gms/hr.

Results, Table XXVIII.

Table XXVIII Hydrogenation of formaldehyde.

Temp °C.	Press lb/in^2	Vaporising gas.	Cat.	Convert. %	Liquid prod	colour	CO_2% in res. gas.
300	1800	H_2	used.	90	3.7	Lt.brn.	12
"	"	N_2	"	65	2.5	darker	13
340	"	H_2	"	74	3.0	Dk.brn.	10
"	"	H_2	nil.	33	1.8	Lt.brn.	2

The liquid product obtained in the above experiments was approximately of the same composition for each test. The analysis is as follows:-

Methyl formate	...	64%	by	volume.
Methyl alcohol	...	18%	"	"
Water (up to 100°C)	...	6%	"	"
Residue (over 100°C)	...	12%	"	"

The residue was a dark brown, oily liquid, not miscible with water, having a sweet, mustard-like smell, and decomposing on distillation at atmospheric pressure. The issuing gases contain, besides hydrogen, mainly carbon dioxide, with only slight traces of carbon monoxide, methane and unsaturated hydrocarbons.

The results are necessarily approximate, as the apparatus does not lend itself to accurate work, and hence no mass-balance is possible. The method of volatilisation of paraformaldehyde is not completely satisfactory, as there is a tendency for the paraformaldehyde to block up the tube, and also to enter the catalyst space at too great a speed at the beginning of the experiment. The ideal method is to have the gas passing over the paraformaldehyde contained in a pot, so that only gaseous formaldehyde is carried over.

The catalyst appears only to increase the polymerisation, as it is evident that the reaction is one of pyrolysis/

pyrolysis rather than one of hydrogenation. After these experiments the catalyst was found to be thickly covered with a charred, brown deposit.

CHAPTER XVI

DISCUSSION OF THE RESULTS OF THE HIGH PRESSURE EXPERIMENTS.

The results are singularly disappointing in all cases. The failures of Series I and II may, as has been stated, be due to the influence of the constructional material of the apparatus, or to catalytic activity, although the catalysts employed have previously been proved to be active for decomposition experiments. It is difficult to find thermodynamical reasons for these failures, as under the experimental conditions the reactions are thermodynamically possible. (See Chapter VI , p. 28).

With regard to Series III , the results prove that under the conditions employed, formaldehyde tends to polymerise rather than hydrogenate. It has been found that although methyl alcohol can be obtained from formaldehyde, the amount cannot be increased by hydrogenation at atmospheric pressure (Part II). It was expected therefore, that as no appreciable quantity of methyl formate was produced under those conditions, the application of pressures encountered in the usual methanol synthesis would lead to more hydrogenation, but as the results show, this is not so.

A/

A consideration of free-energy data indicates that formaldehyde is much more likely to polymerise than hydrogenate under the experimental conditions.

Reaction	ΔF.		Kp.	
	250°C	300°C	250°C	300°C
(1) $HCHO + H_2 = CH_3OH$	-5000	-5000	1.2×10^2	9.8×10
(2) $2HCHO = HCOOCH_3$	-23400	-30400	6.6×10^9	4×10^{11}

From these figures and the reasoning put forward in Chapter VI, the results of the attempt to hydrogenate formaldehyde are not surprising.

PART IV.

THE DESIGN OF A SMALL EXPERIMENTAL HIGH PRESSURE CIRCULATORY PLANT FOR HIGH TEMPERATURE GAS REACTIONS.

FOREWORD.

Thanks are due to J. Arnott, Esq., F.I.C., of Messrs G. & J. Weir Ltd., Glasgow, for advice on the choice of steel for this plant.

A. R. R.

CHAPTER XVII.

CONSTRUCTIONAL MATERIALS FOR USE AT HIGH PRESSURES AND TEMPERATURES.

The selection of a metal for the construction of plant operating under pressure at normal temperatures is governed chiefly by the mechanical strength in conjunction with corrosion-resisting properties, and as the temperature increases, these properties become more difficult to achieve. Steels are almost the only materials with sufficiently high tensile strength obtainable at reasonable cost to be used in quantity, though occasionally a single piece of equipment may be made of other materials such as nickel or nichrome when conditions of temperature or oxidation are severe, or nichrome if the material must be non-magnetic. As the strength of all metals decreases with increase of temperature, it is vital to know the characteristics of the metal chosen for the conditions to be employed. The following table shows the change in properties of some steels with temperature:-

Table XXIX. Change in properties of steels with temperature

Steel.	Temp. °C.	Yield Pt., tons/in^2.	Ult. tens strength, tons/in^2.
0.24% C.	20	16.0	31.3
"	500	11.6	21.6
0.35% C.	20	20.0	38.6
"	500	7.0	27.7
"18/8" Stainless	20	16.1	42.7
"	500	7.7	25.1

(Firth and Brown, Ltd., "Firth-Brown Forgings").

It will be noticed that high temperatures greatly decrease the elasticity, and creep becomes very marked, even under extremely moderate stresses. With non-ferrous metals the effect is so serious that with few exceptions they cannot be used above 250°C where any stress or strain is applied.

The typical behaviour of a steel under stress is shown in fig. 46 following:-

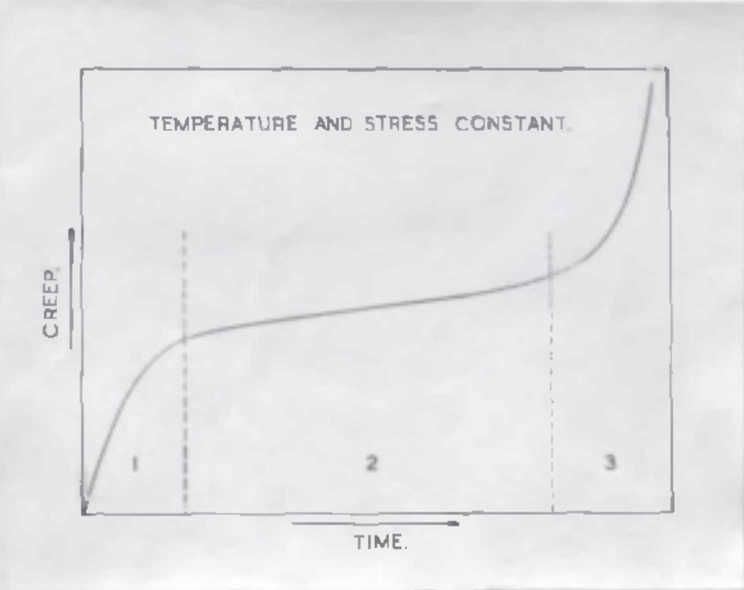


Fig.46. Characteristic behaviour of steel stressed at elevated temperature.

It will be seen that there are three definite stages of stress.

(i) Period of rapid initial elongation.

(ii) Steady period of fairly slow creep.

(iii) Final/

(iii) Final period of rapid creep resulting in destruction of the metal.

For every material there is a limiting temperature above which creep will occur at a given stress. The limiting creep stress is the stress necessary to produce the rate of increase of strain or creep as measured in period (ii) above. The permissible rate of creep being decided, the creep stress, modified by a factor of safety, is adopted as a safe working stress. Tapsell recommends for alloy steels a factor of at least 2, but generally 3, on a limiting creep of 10^{-5} in/in/day. (Tapsell, "The Creep of Metals, 1931). In general, if the working stress is below the elastic limit of the steel, permanent deformation or creep will not result.

For high temperature work special heat-resisting alloys have been developed, and for this there are a number of necessary characteristics:-

(I) Good creep strength.

(2) Absence of structural changes on long exposure to heat.

(3) Freedom from scaling at high temperatures.

(4) Resistance to chemical attack.

(5) Resistance to hydrogen attack and carbonyl formation.

Nickel and chromium, even in quite small proportions/

proportions, enhance non-scaling properties. The addition of 0.05% molybdenum to mild steel doubles the creep strength between 450 and 500°C. Chromium, up to 6%, greatly improves the creep strength of a pearlitic steel up to 500°C, but further chromium increase does not improve it to any marked degree. Nickel has practically no effect upon pearlitic steels, which are generally useless above 600°C. Austenitic steels, which are soft at ordinary temperatures, do not soften much at high temperatures. Such steels are the 18/8 Cr/Ni, or better still, the 18/8/1/1 (Cr/Ni/W/Ti) which possess excellent creep properties, though tending to deteriorate slightly in use. Small additions of a number of alloying elements are better than the same total amount of one element. These 18/8 steels are subject to a form of embrittlement which leads to intercrystalline weakness although 1% of Titanium largely overcomes this defect. (Elliot, Sarjant and Cullen, J.S.C.I., 1932, 51, 502).

The attack by hydrogen on the steel is influenced by the following factors:-

(1) Temperature. The limiting temperature of attack at a pressure of 250 atmospheres may be as low as 200°C for a mild steel, while nickel and chromium steels are generally resistant up to 350°C at this pressure.

(2) Pressure/

(2) Pressure. This generally promotes attack.

(3) Stress. Also promotes attack.

Resistance to hydrogen attack is materially improved by alloying elements, e.g. a 6% Cr. steel is not attacked below 500°C at 250 atmospheres pressure. A fine grain structure further improves the resistance.

There are two stages of attack by hydrogen:-

(a) The steel absorbs hydrogen, becoming embrittled, and this absorption may be surprisingly large. In one case 100 gms. of steel absorbed 180 ccs. of hydrogen (Barber and Taylor, "Experimental Plant for High Pressure Hydrogenation Processes", Inst. Mech. Eng., 1935). The process is reversible, and the condition can be cured by suitable heat-treatment.

(b) Decarburisation sets in, followed by intercrystalline fissuring, leading to disintegration of the steel. Ni/Cr austenitic steels are not prone to this decarburisation. They may be severely embrittled by absorbed hydrogen, but the embrittlement can be removed by suitable heat-treatment.

Non-ferrous metals are liable to very severe attack, e.g. Monel, after exposure to hydrogen at a pressure of 300 atmos. for 630 hours at a temperature of 450°C may be broken easily by hand (Tongue, "Design and Construction of High Pressure Chemical Plant").

CHAPTER XVIII.

THE CALCULATION OF STRESSES IN MATERIALS AT HIGH PRESSURES.

Stresses in Walls of Cylindrical Vessels.

As most high pressure equipment is cylindrical, the conclusions drawn from data of the wall thickness of tubing can also be applied to larger apparatus. In calculating the ratio of the inside to the outside diameter of the vessel for service under high pressure, several methods are available. If

S = Allowable stress, lb/in^2.

P = Internal pressure, " "

$R = r_i / r_o$ = ratio of inner radius to outer radius,

then, assuming a uniform stress distribution across the thickness of the cylinder and neglecting the end pull,

$$\frac{S}{P} = \frac{R}{(1 - R)} \qquad \text{(Thin cylinder)} \qquad (1)$$

A strict adherence to the elastic theory for thick cylinders gives the maximum tangential stress divided by the pressure as

$$\frac{S}{P} = \frac{1 + R^2}{1 - R^2} \qquad \text{(Lamé)} \qquad (2)$$

Assuming the coefficient of lateral contraction, or Poisson's ratio, 0.3 for steel, the following formula gives/

gives the ratio for a cylinder with closed ends that are integral with the walls as

$$\frac{S}{P} = \frac{1.3 + 0.4R^2}{1 - R^2} \qquad \text{(Clavarino)} \qquad (3)$$

For the case of a cylinder with ends which are closed by pistons which are not a part of the walls, the following formula can be used:-

$$\frac{S}{P} = \frac{1.3 + 0.7R^2}{1 - R^2} \qquad \text{(Birnie)} \qquad (4)$$

A simple formula, however, which gives values on the side of safety for all but the thickest cylinders is

$$\frac{S}{P} = \frac{1}{1 - R} \qquad \text{(Barlow)} \qquad (5)$$

With the aid of these formulae the value of R for any given value of $\frac{S}{P}$ may be found.

Screw Thread Stresses.

The stress in screw threads can be estimated safely by considering the screwed part as a bolt in tension, and calculating the stress as a tensile stress across the area at the root of the thread (the core of the bolt), - provided always, of course, that the length of the threaded part is at least equal to the diameter of the screw. (c.f. Dalby, "The Strength and Structure of/

of Steel and other Materials"). This is generally observed, the length of screwed part being given as (d + 1/8"), where d is the outside diameter of the bolt or screwed part.

Other Stresses.

Tightening-up stresses, especially with screws of small diameter, may be greater than the normal working stress. 100% is usually the allowance made for screws less than 1" in diameter. This figure is, of course, purely arbitrary.

Temperature stresses are always encountered, and if the walls of the vessel are particularly thick, these stresses may be serious. Such stresses may be calculated from formulae such as the following:-

$$S_T = \frac{m}{2(m - 1)} aE(\Delta T) \left(\frac{2}{1 - R^2} + \frac{1}{\ln R} \right) \qquad (6)$$

Where S_T = Inside temperature stress,
1/m = Poisson's ratio; m = about 4 for steel,
3.3 for "18/18" at cracking-still temperature,
a = coefficient of expansion,
E = Young's modulus of elasticity,
T = temperature drop through the walls,
R = ratio of inside to outside diameter.

For a more complete discussion of temperature stresses see/

see Luster, "Design of thick-walled Tubes Subjected to Pressure and Heat Input", Trans. Am. Soc. Mech. Eng., Fuel Steam Power, 53-12, 161-172 (1931).

Thermocouple wells or catalyst containers across which there is a large pressure drop resulting from high velocities or the presence of partial plugs, present the reverse of the above conditions, inasmuch as the pressure is applied to the outside of the cylinder. In long cylinders with R = 0.9, the collapsing pressure may be calculated from the following formula:-

$$\frac{S_{y.p.}}{P_c} = \frac{2}{1 - R^2} \qquad (7)$$

in which $S_{y.p.}$ = stress at yield point,

P_c = collapsing pressure.

In thin-walled cylinders the collapsing pressure falls off very rapidly, especially when R has a value between 0.95 and 1.0 (See Jasper and Sullivan, "The Collapsing Strength of Steel Tubes", Trans. Am. Soc. Mech. Eng., Applied Mechanics, 53-17b, 219-245 (1931) for further details). Tubes which are subjected to these conditions should be as nearly round as possible, for variations in wall thickness and 'out-of-roundness' both affect the collapsing pressure.

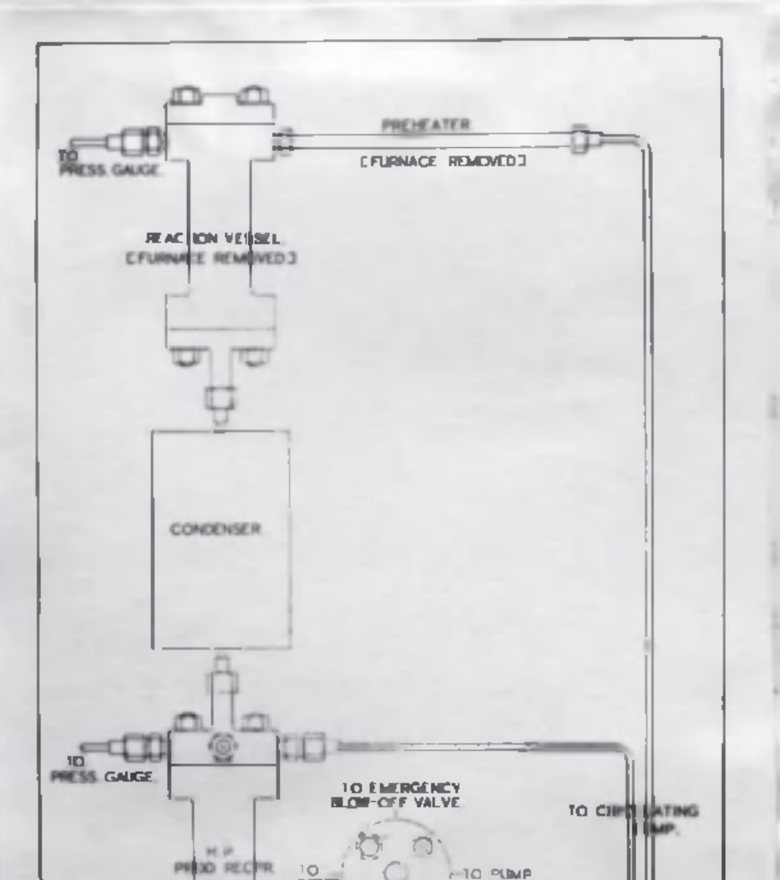


Fig.47. Assembly of Unit.

CHAPTER XIX.

DESCRIPTION OF THE PLANT.

This plant was designed first and foremost as a laboratory unit for the study of the methanol synthesis. As a laboratory unit, therefore, there were certain necessary qualifications:-

(a) Small size.
(b) Simplicity of design.
(c) Safety.
(d) Ease of operation.
(e) Wide limits of operating conditions.
(f) Adaptability to other gaseous phase reactions.

These requirements have been fulfilled as far as possible in this unit, the general assembly of which is shown in fig. 47 opposite:-

(a) The catalyst space is approximately 20 ccs., giving an approximate maximum yield of 40 - 50 ccs. of methanol per hour at 400°C, and 3000 lb/in^2 pressure (i.e. twice its own volume of methanol per hour produced by a good catalyst.)

(b) As the assembly drawing shows, the design is simple and straightforward.

(c) A very large factor of safety is incorporated. For the reaction vessel itself, the minimum value is 8 at

500/

500°C.

(d) Only essential controls have been incorporated, and the number kept to a minimum. The control panel has been designed so that the controls are readily accessible as will be seen from their positioning in fig.57 p.113a which illustrates the control panel.

(e) The limits of operating conditions are indeed wide. The temperature range is up to 500°C; the pressure is up to 3000 lb/in^2; the gas circulation rate is up to 15 litres per hour of high pressure gas, which means that the gas is changed every 5 seconds in the reaction chamber.

(f) With slight modifications in gas connections, etc., the high pressure product receiver, on being heated, say in a similar manner to the reaction vessel, becomes an efficient high pressure liquid vaporiser. A mild steel vessel of the same dimensions can be made to serve as high pressure product receiver in its place. This, however, is only an example of the adaptability of the plant, as it is designed primarily for reactions between gases.

The plant is, however, described part by part in detail.

REACTION CHAMBER.

This was machined from a billet of heat-resisting/

heat-resisting steel, Air Ministry Material Specification No. D.T.D. 306 (April 1937). This is a 60/70 ton Chrome-Molybdenum steel, suitable for nitrogen hardening. The chemical composition is specified as follows:-

Carbon......Not less than 0.15% nor more than 0.35%
Silicon.....Not more than 0.35%.
Manganese... " " " 0.65%
Sulphur....." " " 0.05%.
Phosphorus..." " " 0.05%.
Nickel...... " " " 0.30%
Chromium....Not less than 2.50% nor more than 3.50%.
Molybdenum.. " " " 0.30% " " " 0.70%.

The following elements may be present at the option of the Steelmaker:-

Vanadium.....Not more than 0.25%.
Tungsten..... " " " 1.00%.

The mechanical properties are specified as follows:-

Maximum stress........Not less than 60 nor more than 75 tons per sq.in.
Elongation...........Not less than 17%.
Izod................. " " " 35 ft.lb.
Brinall hardness number. Not less than 269 nor more than 321.

0.1/

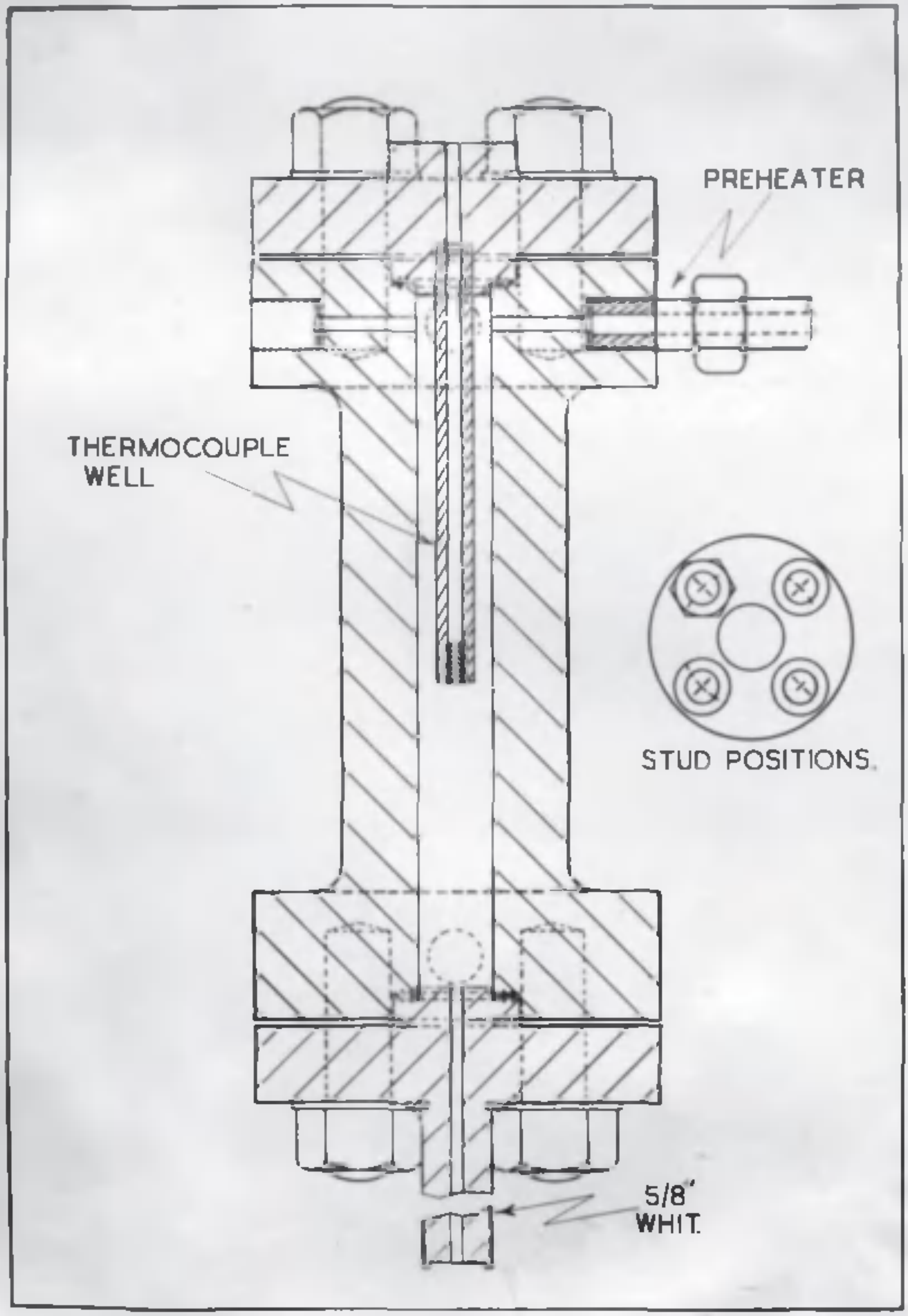


Fig. 48. Reaction Chamber showing attachment of preheater.

0.1 proof stress, if determined.....Not less than 45 tons per sq. in.

Heat Treatment.

It is specified that the steel be hardened by heating to a temperature of 900°C and quenching in oil. It is then tempered by heating to a suitable temperature of not less than 570°C, and cooled in air to give the tensile and Izod values already specified.

The billet of steel was supplied by Messrs The Clyde Alloy Co., Ltd., Motherwell, and machined by Messrs A. & W. Smith, Ltd., Glasgow. Fig.48 opposite illustrates the assembled vessel (Full details are available in fig. 48a in end cover pocket). Fig.49 following is a photograph of the finished part and covers.

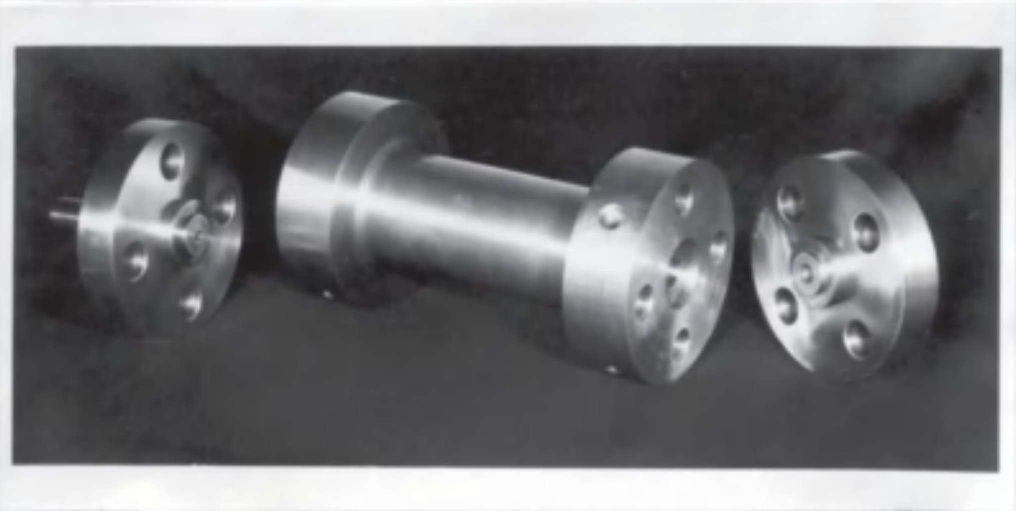


Fig.49. Finished Reaction Chamber and covers.

A ratio of the outside to the inside diameters of 3 : 1 was chosen arbitrarily, for according to Tongue ("The Design and Construction of High Pressure Chemical Plant"), this figure is suitable for solid-drawn tubing for pressures up to 750 atmospheres; the reaction vessel can be considered as a short length of seamless tubing. The calculations which follow will indicate that this assumption errs greatly on the safe side. No special advantage was to be gained by reducing the wall thickness further, as this only meant increased machining costs.

The advantage of such a robust reaction vessel, and plant in general, is that the extremely large factor of safety incorporated in the design enables the plant to withstand fairly rough treatment.

Each cover is fixed by means of four 5/8" B.S.F. studs, these and the nuts being of the same steel as the reaction vessel. The nuts are tightened and loosened by means of a box-spanner, in order that no excessive strain be placed on the supports of the reaction vessel (see later).

The thermocouple well consists of a length of solid-drawn Chrome-Molybdenum steel tubing (approx. 1% Cr., 0.2% Mo), 1/8" i.d. x 3/8" o.d., obtainable from Messrs Accles and Pollock, Birmingham. This is plugged and/

and welded at one end. The other end is screwed 3/8" B.S.F. to fit into the top cover. The joint is of the copper gasket type, the tube being provided with flats for a spanner. The thermocouple well is shown in position in fig. 48 (p. 194a).

It will be seen from the diagram of the reaction vessel (fig. 48, p.194a) that the gas connections are made to the vessel itself, and not to the cover, as is very often the case. This enables the vessel to be opened without disturbing these connections, thus greatly reducing the chances of leaks. The cover joint at either end is of the recessed spigot type with copper gasket-ring. This type of joint is generally considered to be eminently suitable where the joint has frequently to be made and broken.

The method of connecting pipelines to the vessel is by means of an alloy steel nipple and union, illustrated in figure 50 following.

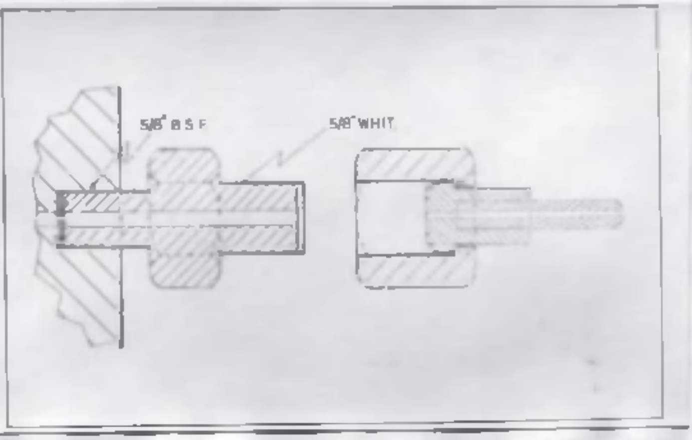


Fig.50. Nipple and Union attachment; alloy steel for hot parts, mild steel for cold.

The reaction vessel is the non-heat-interchange type, a "straight-through" system being preferable for a small plant such as this. The catalyst can either fill the heated volume of the vessel (between the flanges), or it may be held in a wire gauze basket attached to the thermocouple well. To reduce the possibility of chemical attack, the inside of the vessel is reamer-finished to give a very smooth surface. A thin, seamless copper liner is provided which can be fitted (push-fit) into the vessel if required, as a further precaution against attack.

The vessel is bolted to a vertical channel girder and held rigid by means of pipe-collars, the ends of which are shaped to fit the circumference of the flanges. The method is discussed more fully later, however.

LIMITING WORKING CONDITIONS OF TEMPERATURE AND PRESSURE.

Reaction Vessel.

The steel is a heat-resisting steel, and consequently 500°C can be assumed to be the maximum temperature which corresponds with the greatest permissible fall in strength. Above this temperature the strength falls off rapidly. Unfortunately, data of the properties of this/

this steel at 500°C are not at present available, and assumptions must be made. A study of the data of steels of approximately the same composition and properties, indicates that the tensile strength at 500°C is about 75% of that at ordinary temperatures. The creep stress at 500°C can be taken as approximately 25% of the tensile strength at this temperature.

Using the lower limit specified for the tensile strength at ordinary temperatures, the ultimate tensile strength at 500°C is assumed to be 45 tons/in^2, and the creep stress as 11 tons/in^2 (steady creep rate of 10^{-7} in./in./hr.).

Assuming a safety factor of 5, the maximum allowable stress, S, = 9 tons/in^2 at 500°C.

By Lame's formula, maximum pressure, P, = 7.2 tons/in^2.

By Barlow's formula for a thin cylinder, P = 8 tons/in^2.

Average = 7.5 tons/in^2, say.

The normal working pressure will be 1.5 - 2.0 tons/in^2 at a maximum temperature of 500°C.

It will be seen that the creep, if any, under these working conditions will be infinitesimal.

Temperature/

Temperature Stresses in Walls, and Maximum Temperature Difference through Wall Thickness.

For convenience the formula for calculating the temperature stress is given again,

$$S_T = \frac{m}{2(m-1)} .aE(\Delta T). \quad \frac{2}{1-R^2} + \frac{1}{\ln.R}$$

$m = 4$

$a = 1.3$ (say) $\times 10^{-5}$ for range 400 - 500°C.

$E = 25 \times 10^6$ for alloy steels for above range.

$R = 0.333$.

Assuming a temperature stress of 1 ton/in^2, and substituting the above values in the equation,

$$\Delta T = 37^\circ C.$$

As it is improbable that a temperature difference of this magnitude can exist across a 3/4" steel wall, a rapid rate of heating is permissible, even under maximum working pressure. (Actually, to maintain this difference, a heat throughput of about 15000 B.Th.U./ft^2/hr. would be required.)

Maximum Stress in Thermocouple Well.

Assuming a tensile strength of 30 tons/in^2 and a yield point of 9 tons/in^2 at 500°C for the steel, for $R = 0.33$, the collapsing pressure, Pc. = 4 tons/in^2, calculated/

calculated by the formula (7) given on p.190 .

Cover Studs.

The pressure is assumed to act on the area bounded by the outside of the gasket, i.e. on a circle 1.25" in diameter.

Area = 1.227 in^2.

Maximum operating stress under laboratory conditions = 2.0 tons/in^2.

∴ Pull on studs = 2.0 x 1.227, = 2.454 tons.

∴ " " each stud = 0.614 tons.

Tightening up pull on each stud = 0.614 tons.

Studs are 5/8" B.S.F.

Area at bottom of thread = 0.2235 in^2.

Creep stress = 11 tons/in^2

∴ Maximum permissible pull = 11 x 0.2235,

= 2.455 tons per stud.

Total working pull = 1.23 tons per stud.

It will be noticed that the walls of the reaction vessel are capable of taking a very much greater stress than the studs. The reason for this is that the studs are not subjected to the same conditions, i.e. they may be slightly cooler, are not in contact with reactants, and/

and are not subject to the same temperature stresses. Safety factor for ~~streets~~ studs, however, is approximately 8 at the working temperature.

HEATING OF REACTION CHAMBER.

Electrical heating is of course employed, and this is external, as internal heating for a vessel of this size is impracticable. For external heating the flange presented a problem, as an ordinary furnace, to fit over the flange, is too far distant from the body. There are three ways in which this difficulty could be overcome:-

(a) A divided copper block, shaped to the body of the vessel, could be used to conduct the heat from the furnace. The supports of the vessel are not strong enough to support such an additional weight. A similarly shaped aluminium block could be used instead, but the conductivity is not so great as that of copper.

(b) A divided furnace fitting close to the body of the vessel is ideal, as it makes for compactness. Furthermore, it enables the furnace to be opened easily if rapid cooling is desired. The practical difficulties of winding and fabrication of this type of furnace on such a/

a small scale, however, are great, and it is also highly probable that the rate of heating would not be uniform.

(c) The heating element is wound directly on to the body of the vessel, insulated from it by several layers of 'Miconite'. The lagging of asbestos is in two rigid, close-fitting hinged halves, permitting it to be opened for rapid cooling.

The third of these three methods is adopted for heating the reaction vessel. It has the disadvantage that the winding must be removed before hydraulic tests can be made. It is believed, however, that this disadvantage is outweighed by the advantages of rapid cooling, compactness and lightness (the lagging "box" being supported separately from the reaction vessel. The method of lagging is illustrated in fig51following.

Fig.51.
Model of removable furnace lagging.

Current Required.

The current required for heating a vessel of this size rapidly to 500°C and maintaining it at that temperature was arbitrarily fixed at 5 amperes at 250 volts. This figure was decided upon following experience gained with the furnace used for the experiments of Parts I,II and III. In this case the furnace is 2 1/2" int. dia. x 7" dia. over lagging, and 9" in length. The resistance of the element is 83 ohms, controlled by an external variable resistance of 235 ohms max. The furnace was used vertically with both ends open, so that there was a constant current of air passing through it. To maintain a constant temperature of 400°C in the reaction vessel under these conditions, an external resistance of approximately 100 ohms was required, corresponding to approximately 1.4 amperes at 250 volts for the furnace.

The allowance of 5 amperes for heating the reaction vessel would thus appear to be sufficient, even when a large amount of heat is being carried away by the circulating gas. Furthermore, this current will allow of rapid heating, a rate of 200°C per hour being taken as a safe maximum which will not give rise to undue temperature stress in the wall. Moreover, the temperature drop/

drop across the wall will be measured at this rate of heating. The maximum rate of heating obtainable with the full current will also be measured.

Furnace Winding.

The resistance required to pass 5.0 amps. at 250 volts is 50 ohms.

Nichrome V, No. 21 B. & S. Gauge requires a current of approximately 5 amps for a wire temperature of approximately 650°C. This value is for a helical coil heated in the open air; for a lagged coil the temperature may be 50% higher.

Resistance per foot at 800°C = 0.836 ohms.

∴ Length required = 59.8 ft., = 717.6 ins.

Circumference over 'Miconite' insulation = 7.26 ins.

∴ Number of turns = 98.8.

∴ " " " per inch on 4.5 ins. heated length of reaction chamber = 22 turns.

Depth of Asbestos lagging = 2 ins.

The temperature obtainable under these conditions may seem rather high. A lower temperature entailed the use of a heavier wire for 5 amps., or a smaller current for the above wire. A greater length of heavier wire is required/

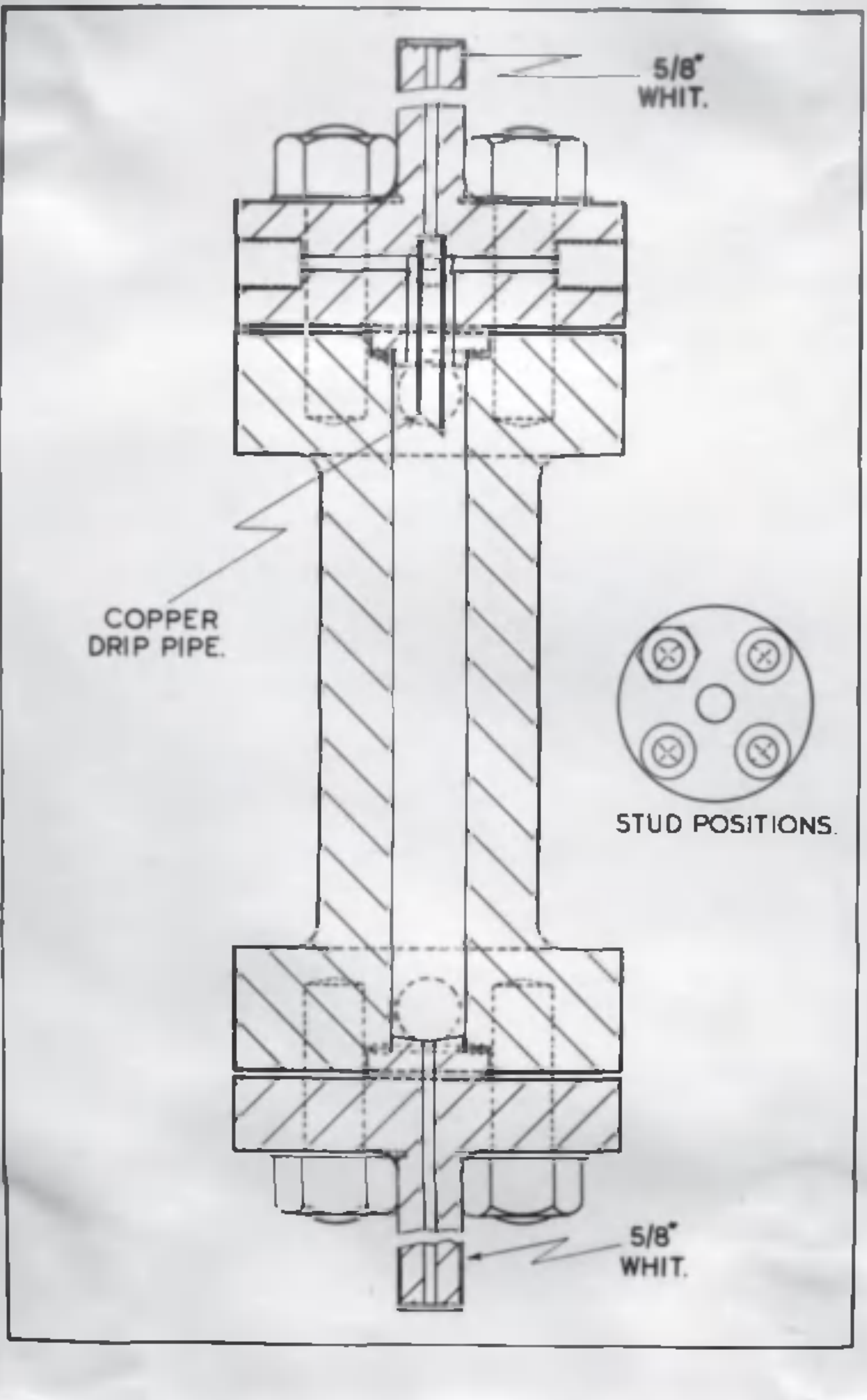


Fig.52. High Pressure Product Receiver.

required, with the result that it cannot all be wound on the vessel in a single layer. It was felt that a lower current would not be sufficient to balance the heat losses.

HIGH PRESSURE PRODUCT RECEIVER.

This is made of the same steel as the reaction vessel, and with a few exceptions, the dimensions are identical. Fig. 52 opposite illustrates the assembly, and fig. 52a in the end cover pocket is a detailed working drawing of the vessel. The gas connections are made by nipple and union to the top cover, enabling the body to be removed if required, without disturbing them. The vessel is supported by bolts and pipe-collars in a manner similar to the reaction vessel, and the methods of closure are identical.

A small copper drip-pipe is fitted into the top cover to carry the liquid products past the gas ports, overcoming the tendency for the liquid to run down the sides and be carried into the pipe lines. The bottom of the vessel is coned 10° to facilitate drainage, while the inside is reamer-finished for smoothness; a thin, seamless copper liner (push-fit) is also provided, and can/

can be fitted if required.

The contents are run off through a fine-adjustment valve to a low-pressure catch-pot on the front of the control panel. The emergency blow-off is taken from the top of the vessel, so that in the event of an emergency the product is retained.

Stresses.

As the vessel is constructed to the same dimensions, except in a few details mentioned above, and of the same material as the reaction chamber, the same calculations apply, and as the vessel is not heated, the allowable stresses are very much greater.

GAS CIRCULATING PUMP.

For a rate of 0 - 15 litres of high pressure gas per hour a very small pump is required. Furthermore, the gas flow should be as continuous as possible over this range. The type of pump most suited to these conditions is a rotary pump.

High pressure gas circulation by rotary pump is a departure from common practice. Provided proper care is taken in the design, however, there is no reason why such a method cannot be made applicable to very small laboratory plants such as the present unit.

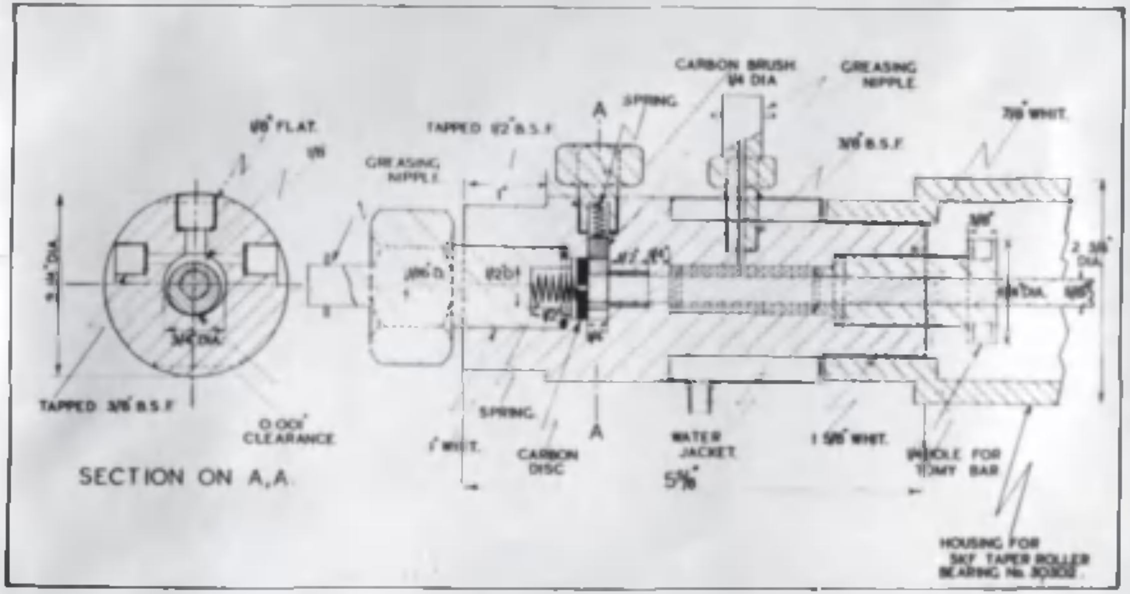


Fig.53. Rotary High Pressure Gas Circulating Pump.

For satisfactory operation, such pumps require to be driven at high speed, and the problem is one of designing a gland which will withstand the pressure at a high shaft speed. Experiments by a colleague (Luckhurst, private communication) on high speed stirring (500 r.p.m) for a high pressure autoclave have shown that with proper support and absolute rigidity of the shaft, high speed stirring, even at elevated temperatures, presents no difficulty. (For full details of autoclave and gland, see "The Design, Construction, and Operation of a High Pressure Chemical Plant", a Thesis presented by John F.C. Gartshore, B.Sc., A.I.C. for the Degree of Ph.D., Glasgow, 1937).

A small rotary pump has been designed for operation under the aforementioned conditions at a speed of up to 1500 r.p.m., and is illustrated in fig. 53 opposite.

The gland is longer than is perhaps necessary, but a long gland does not need to be tightened down as much as a shorter one, and results in less wear. The packing is similar in form to that of the stirring shaft of the high pressure autoclave mentioned above,

consisting of doubly chamfered gunmetal rings, between which are two graphited lead-asbestos packing washers,/

washers, each 1/8" thick (see fig. 54 following).

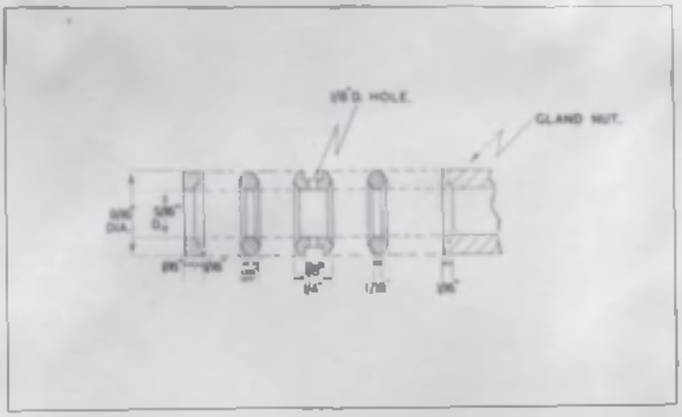


Fig. 54. Details of Gland.

The rings are doubly chamfered to squeeze the washers on to both gland wall and rotor shaft. The gland nut has a right-hand thread, and as it is tightened in the direction of rotation of the shaft, no locking nut is provided. The gland is water-jacketed.

The rotor shaft is of mild steel, and the length in the gland is chromium plated by the "Fescol" process to resist wear. As the rotor is so small an end bearing inside the pump is unnecessary, the shaft bearing being made longer than usual.

The gland and bearing are both lubricated by grease-gun/

grease-gun, and the pump is mounted vertically so that the lubricant will run into the gland rather than into the rotor chamber, thus avoiding the possibility of it being carried into the pipe lines. Furthermore, lubricant rather than gas will tend to leak from the gland. This system of lubrication obviates the need of an oil separator, which would introduce a comparatively large amount of dead-space into the plant.

The valve arrangement is different from the normal type for rotary pumps, the fin being fitted into the side of the chamber and not into the rotor. The fin consists of the carbon brush (self-lubricating) of an electric motor, and can easily be replaced (see fig.53)

The pump is driven by a 1/4 h.p. electric motor mounted at right angles to it on the same baseboard, and is supported vertically by two short lengths of channel iron. The pressure thrust is taken up by a small Skefko SKF taper roller bearing thrust-block. In order to overcome further stress on the gland, the power is transmitted to the pump through a bevel gear which is mounted on a countershaft, the radial thrust of the gear drive being taken up by a single thrust ball bearing. This countershaft is driven by a V-shaped rubber belt from/

from the motor. The arrangement is illustrated in fig. 55 following.

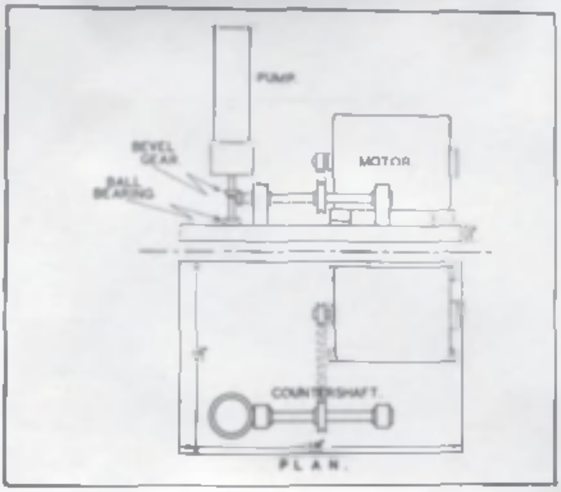


Fig. 55. Drive to Pump.

PREHEATER.

This consists of a piece of solid-drawn heat-resisting steel tubing 12" long, 3/16" i.d. x 1/2" o.d. It is screwed directly on to the reaction vessel, a hexagon nut being welded on at this end to take a spanner. This tubing is standard size, obtainable from Messrs Accles and Pollock, Birmingham. Fig. 48 which illustrates the assembled reaction chamber, also shows the method of attachment of the preheater.

Heating.

Current = 1.5 amps. at 250 volts.

∴ Resistance = 167 ohms.

For/

For a helical coil, open-air temperature 500°C, Nichrome V, B. & S. Gauge No. 27 requires 1.46 amps.

Resistance of this wire at 800°C (lagged temperature) = 3.350 ohms per foot.

∴ Length required = 49.8 ft.

Assuming the external diameter of the furnace former to be 3/4", Circumference = 2.35"

∴ No. of turns = 254.

∴ " " " per in. on a 10 ins. former = 25.

Depth of asbestos lagging = 1 in.

CONDENSER.

This consists of a 15 ft. length of solid-drawn copper tubing, 1/16" i.d. x 1/4" o.d. in the form of a helix of 4 ins. mean diameter and 1/2 in. pitch. The water-jacket is made from galvanised sheet-iron. Details of the condenser are not given in the assembly drawing of the plant on p.191a.

PIPEWORK AND JOINTS.

For flexibility all the pipework is of solid-drawn copper tubing, 1/16" i.d. x 1/4" o.d. This wall thickness may appear excessive, but the factor of safety incorporated is in line with that of the rest of the plant/

plant.

Although excellent for high pressure joints, the I.C.I. type of lens ring joint is too clumsy for such a small plant as this. Accordingly an ordinary union is employed, but more care has to be exercised in making the connections.

The union is made of bronze, the jointing ring being of lead. The end of the pipe is screwed into the union and soft-soldered. As a further precaution the thread is also soldered. Fig. 56 following illustrates the type of union employed.

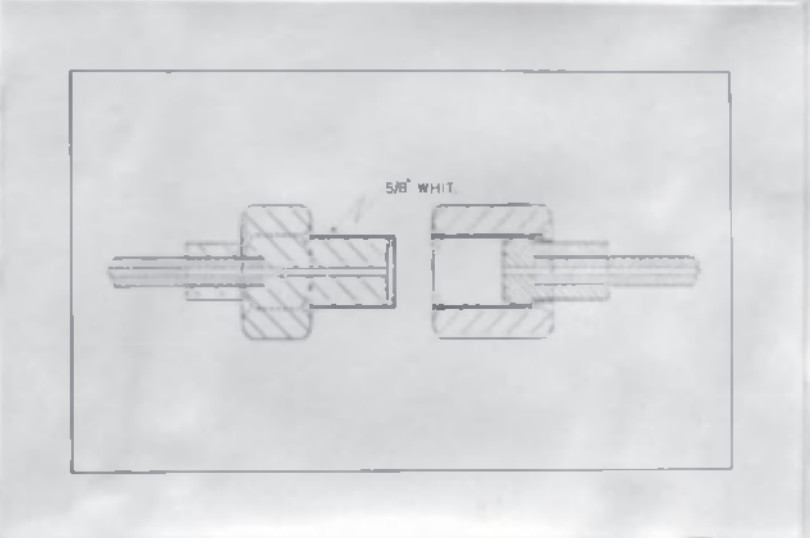


Fig.56. Union in bronze for cold pipework.

CONTROLS.

The lay-out of the control panel is shown in fig./

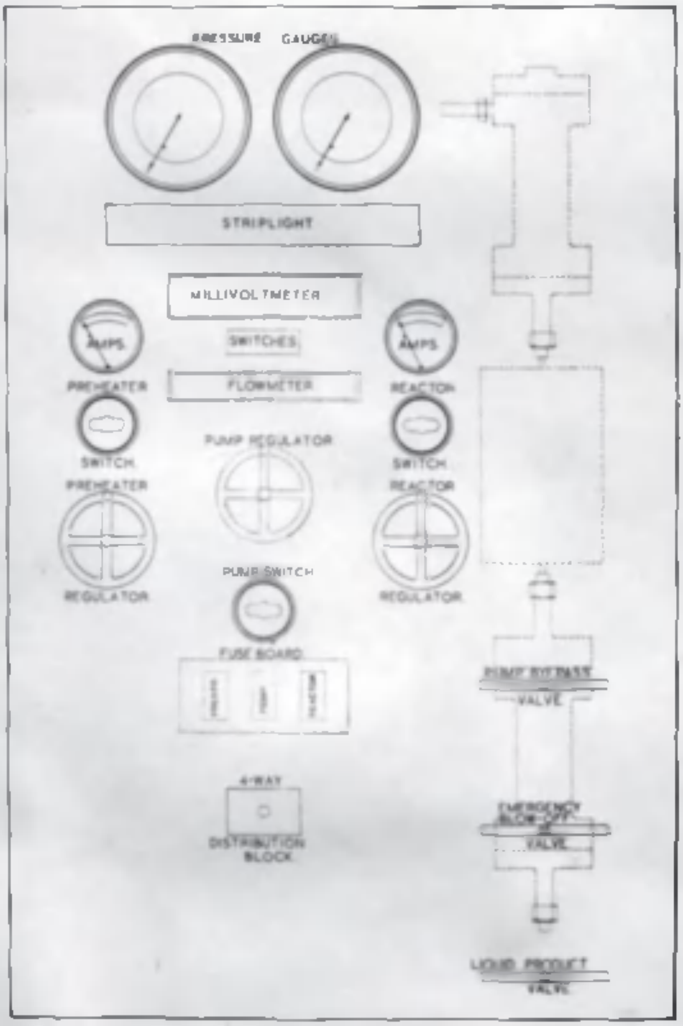


Fig. 57. Control Panel.

fig. 57 opposite. All controls are operated from the front of the panel, and the positions arranged so as to be most readily accessible.

Valves.

The valves used are the I.C.I. type, fine-adjustment, for control and 'stop' for emergency blow-off. (fig. 58). These have been found in practice to be very satisfactory (see Part III)

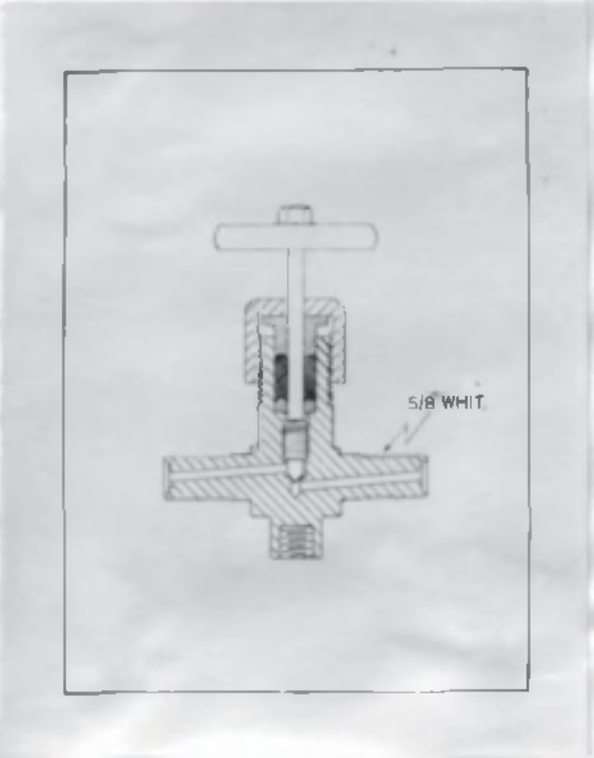


Fig.58. I.C.I. type. Fine adjustment Value.

The gland is sealed by S.E.A. rings. The stems are rather/

rather slender, and the needles must not be screwed down too hard on the seats. For the emergency blow-off valve a short bar grip is provided in place of the usual wheel, so that it can be opened more readily.

Pressure-gauges.

These are Budenberg steel-tube, gas gauges, reading to 6000 lb/in^2 for 3000 lb/in^2 working pressure. The dial is 6" in diameter fitted with safety glass and covered with 1/4" steel wire mesh. The gauges are fitted with pressure-checks, but not with isolating valves, the latter being considered unnecessary for such a small plant. The gauges are designed to blow out through the back in case of failure. They are mounted vertically at eye-level inside the cubicle so that the dials are flush with the front panel, a hole being cut in the panel. The gauges are illuminated by a 'strip-light' mounted on the front of the panel.

Electrical.

All electrical leads are carried in iron pipes behind the panel, and all electrical equipment which is mounted behind the panel is screened.

As can be seen from the illustration of the front/

front panel, the electrical controls are grouped in a convenient manner, e.g. those of the preheater to the left, those of the circulating pump central and those of the reaction chamber to the right. The fuse board is mounted on front of the panel, the fuse-holders being positioned on it corresponding to the controls.

The current to the preheater is controlled by a 100 ohm variable resistance, and indicated by an ammeter reading to 5 amps., graduated to 0.1 amps. The resistance is operated by a hand-wheel from the front of the panel. The on/off switch is the rotary type.

The reaction chamber furnace is controlled similarly to the preheater, except that the controlling resistance is 250 ohms, and the ammeter reads to 10 amps. with divisions of 0.2 amps.

The pump motor speed is controlled by a starter-regulator mounted from the back of the panel, the handle projecting through a slot in the panel.

An opal strip-light illuminates the dials, and is connected in parallel with the power circuit so that it lights when the current to the plant is turned on. This light is mounted on a bracket which raises it 4" from the panel. A reflector is fitted so that the light is/

is shielded from the operator's eyes but illuminates the pressure gauges above it, and the ammeters, millivoltmeter and flowmeter below it.

Temperature.

The temperature is read at only two essential points, the centre of the catalyst, and the centre of the preheater.

For the former, the thermocouple is placed in a well, and for the latter it is fixed to the outside of the preheater tube, at the centre of the furnace.

Copper/Monel thermocouples are employed, and the temperature read on a calibrated millivoltmeter. The switches are the toggle type and are mounted on a bakelite strip placed immediately below the millivoltmeter A range switch and shorting switch are provided. The millivoltmeter (Cambridge) is the straight-dial type, and is mounted on a bracket on the back of the panel, being read through an aperture cut in the panel for it. The cold-junctions are separate, in glass sheaths placed in a vacuum flask containing ice.

Gas Rate.

The gas rate is indicated by a Bosch flow meter. This/

This is of the swinging mercury-filled U-tube type and is illustrated in fig. 59 following.

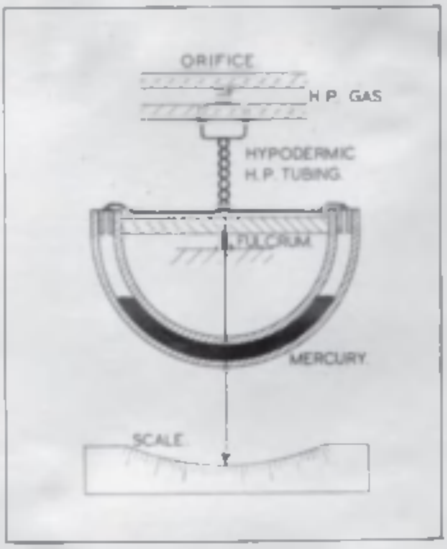


Fig.59. Bosche Flowmeter.

The two ends of the semicircular tube are connected to either side of a standard orifice placed in the inlet side of the reaction chamber. The connections to the U-tube are of capillary high pressure tubing, in order to interfere as little as possible with the free motion of the tube. The ends of the tube are connected by means of a yoke which is supported at its centre by a fulcrum. The tube is partly filled with mercury, and as/

as the flow increases, the mercury rises on the low-pressure side of the U-tube, which swings about the fulcrum to keep the centre of gravity directly below the point of support. This motion is measured by a pointer moving over a scale. The flow meter is mounted from behind the panel, a hole being cut for the dial.

This instrument requires, of course, to be calibrated for the gas or mixture of gases being used, and for different operating pressures. This is most conveniently done by passing gas under pressure through the orifice and measuring the volume at atmospheric pressure passed in a definite time with a steady scale reading of the flow meter. The rate is controlled by a fine-adjustment valve on the outlet side, and the pressure by a similar valve on the inlet side, the system of operation employed for the attempted hydrogenation of carbon monoxide to formaldehyde in Part III. Calibrated graphs are provided for use with varying density of circulating gas, and for different operating pressures.

The rate of flow is varied by altering the speed of the gas circulating pump. It is also further varied by means of a pump bye-pass valve which is an I.C.I. fine adjustment type (fig.58p 213). The reason for the inclusion/

inclusion of the latter is that below a certain speed a rotary pump fails to operate successfully. The maximum variation is possible, therefore, using the bye-pass valve. When low rates of gas flow are required to save wear of the pump gland, the pump is run at the lowest speed compatible with greatest efficiency.

Other Controls.

The main control valves, namely, blow-off, pump bye-pass and liquid product valve, are all situated on the right hand side of the control panel. A four-way distribution block, made of mild steel 3" x 2" x 2", is mounted on the front of the panel, and to it is fitted a valve for gas sampling. Provision is made for the admission of high pressure gas from cylinders to the plant from this distribution block. The fourth lead from the block is to the top cover of the high pressure product receiver. Note; the gas in the plant is blown down to a low pressure gas-holder, but if required can be returned to a high pressure storage cylinder via the distribution block.

SUPPORT OF PLANT.

The reaction chamber, condenser and high pressure product/

product receiver are all bolted top and bottom to a vertical channel girder, 1" x 3" x 1". They are held rigid by pipe-collars 2 1/2" long x ⅞" dia. one end being shaped to fit the circumference of the vessel. The bolt is fitted with a disc waster, and passes through a 2" vertical slot in the supporting girder, allowing the vessel to be raised or lowered for adjustment. The method of support is shown in fig.60 following.

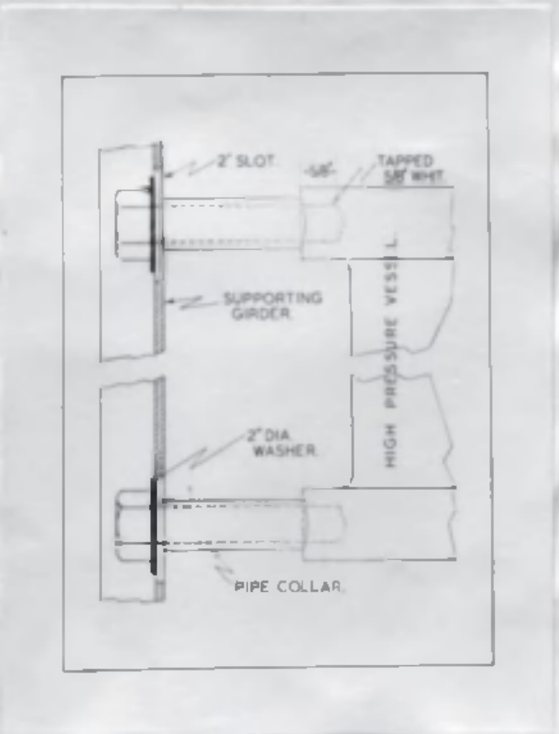


Fig.60. Method of supporting plant.

ERECTION OF PLANT.

The unit is enclosed in a cubicle, 6' high,

3'/

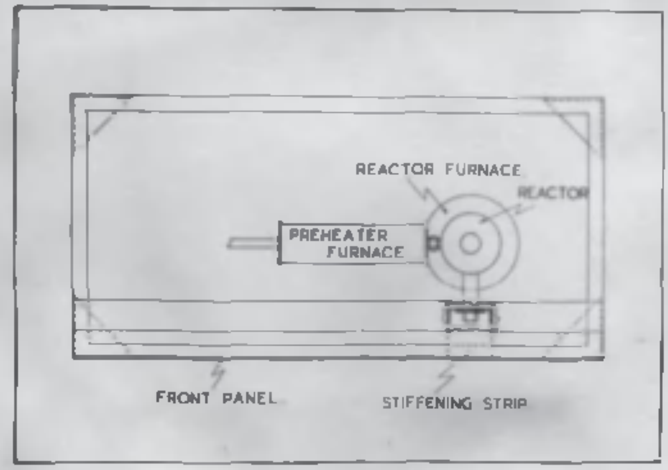


Fig.61. Framework of Plant Cubicle.

3' wide and 18" deep as shown in fig. 61 opposite. The framework of the cubicle is of 1" x 2" x 1" channel iron, bolted together with 1/2" Whitworth bolts. For rigidity 3" fillet pieces are fixed at the angles, as shown in fig. 61 . The supporting girder stands on a piece of 1" x 3" x 1" channel iron running from the back of the framework to the front, and at the top by two distance-pieces of 1" x 1" angle iron to the front of the framework, filletted as before.

The front of the cubicle is formed by a panel of 1/4" mild steel plate, which is bolted by 1/2" Whitworth bolts to the framework. The sides are closed by panels of 1/8" steel sheet, hinged at top, centre and bottom to the front framework. The back of the cubicle consists of two doors of 1/8" steel sheet, hinged similarly to the side panels to the back framework.

Two side-members of 1" x 2" x 1" channel iron run between the side supports at the bottom of the cubicle at the back. The gas circulating pump and motor are mounted on a wooden base, 1" thick, and this base is bolted to these side-members.

The top cover of the cubicle is removable, and consists of a piece of galvanised sheet-iron in a rectangular/

rectangular frame of 1/2" x 1/2" angle-iron.

DRAUGHTING OF THE CUBICLE.

To prevent the escape of inflammable or poisonous gases into the laboratory in the event of a burst or serious leak, the cubicle is draughted by a fan, which exhausts into a flue leading to the roof of the laboratory. Connection to the fan duct is made by a piece of flexible steam-hose, 2" in diameter, which is attached to a 2" "neck" on the top cover by a clip band for easy removal.

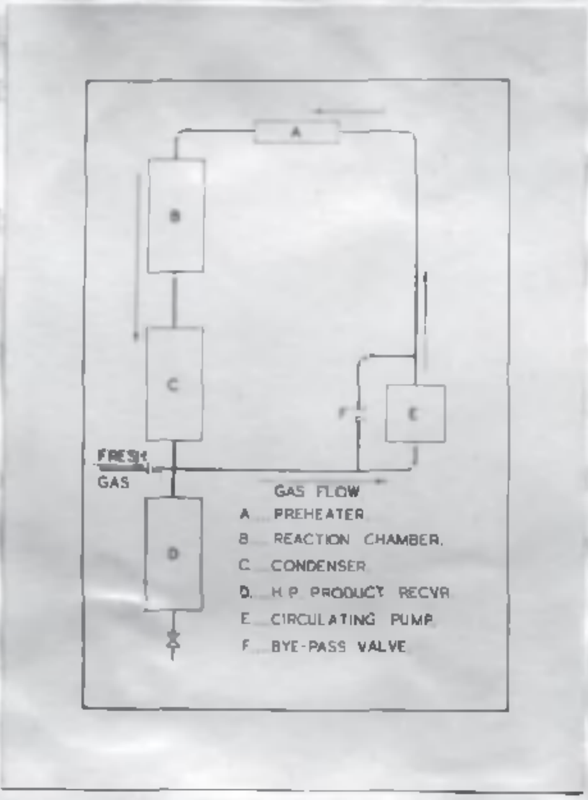


Fig.62. Gas "Circuit".

CHAPTER XX.

DISCUSSION OF DESIGN OF THE PLANT.

It can be seen from a study of the design that the plant has all the qualifications considered necessary for a laboratory unit (p.191). The ease and simplicity of operation and control, together with the extremely large factor of safety which is incorporated, enables the operation of this plant to serve as a means of introduction to high pressure technique.

The plant is designed primarily for the methanol synthesis, but it is equally suitable for the study of other high pressure, high temperature gas reactions. Furthermore, it is easily and simply adapted to suit reactions involving liquids in the vapour phase.

The "circuit" is extremely simple, the flow-diagram being shown in fig.62 opposite, the gas flow being as follows:-

Pump → Preheater → Reaction Chamber → Condenser → H.P. Product Receiver → Pump.

For/

For safety the plant is housed in a draughted steel cubicle, the sides of which are hinged for easy access to the plant. The circulating pump and motor are also situated in the cubicle.

For the circulation of the gas, a departure is made from usual practice, a rotary pump being used in place of a reciprocating pump, for, as already pointed out on p.206, a rotary circulating pump is eminently suitable for this plant. Such a pump has been designed, and it is anticipated that it will operate successfully.

Experience with high pressure plant has shown that the time spent in preparing the plant for an experiment is at least 5 times as great as that of the actual experiment. Most of this time is taken up with the fitting together of the plant, heating to the required temperature, and cooling after the experiment, etc. In the design of this small unit the time-factor has been given careful consideration.

The/

The reaction vessel is opened by undoing only four nuts, the gas connections being left undisturbed. The high pressure product receiver can actually be removed by undoing only the four cover nuts, the two supporting bolts and the union to the drainage valve at the bottom. Rapid heating of the reaction vessel is accomplished by winding the heating element directly on to the body of the vessel, and by having a maximum element temperature very much greater than the maximum working temperature of the plant. Even more rapid cooling is effected by removing the furnace lagging.

The dangerous nature of operations at high pressure and high temperature must never be overlooked by those engaged on such work, and the regulations in respect of the operation of high pressure plant must be strictly adhered to for the wellbeing of all concerned. Such regulations include the following instructions (Technical Chemistry Department, Royal Technical College, Glasgow):-

(1) The rate of pressure rise in vessels must not exceed a maximum figure, which is given for each vessel.

(2) The rate of temperature rise in high pressure vessels must also not exceed a given maximum figure.

(3) No pressure joint, with the exception of gland nuts, may be adjusted under pressure.

(4) When dealing with carbon monoxide or other poisonous gas, two operators must be present, and adequate ventilation ensured.

(5) When dealing with oxygen or oxidising agent, oil or grease must be rigorously excluded from the interior of the plant.

(6) Care must be taken to ensure that the gases in the plant do not at any time form an explosive mixture.

(7) A log book must be kept for each plant for the inclusion of all experimental data, and matters such as repairs, tests, etc.

(8) The extent of individual responsibility must be clearly defined.

Unfortunately, due to the present situation, this plant is only partially completed. As time did not permit of delay in the completion of this work, a simple apparatus constructed from parts of an existing high pressure unit had to be employed for the high pressure experiments of Part III.

CONCLUSION.

GENERAL DISCUSSION AND SUMMARY OF THE RESULTS OF THE INVESTIGATION.

CHAPTER XXI.

DISCUSSION OF EXPERIMENTAL RESULTS.

(1) THE DECOMPOSITION OF METHANOL.

The results of this reaction have been discussed already in detail, and therefore only brief reference to them need be made.

The reduction of the catalysts has shown itself to be strongly exothermic in character, the degree of the latter corresponding to the activity, and not the composition of the catalyst. The amount of reduction, however, depends on the chromium content. The temperature rise has been controlled, so that it was possible for the reduction to proceed with a maximum temperature variation of only 10°C. This control of reduction conditions ensured that discrepancies in the results due to unequal heat treatment of the catalysts before use were eliminated.

The activity of the catalysts for the reaction is in line with the findings of other workers (see Introduction). These workers investigated the problem with a view to finding the most active catalyst possible for the methanol synthesis, and the present investigation deals with the subject in greater detail.

A change in the mechanism of the reaction

has/

has been shown to occur in the region of 300°C, and it has been suggested that this is the temperature at which activated adsorption sets in, as the greater the activity of the catalyst, the lower is this temperature. At 400°C and above the rate of reaction is so fast as to be unaffected by the composition of the catalyst, i.e. all the catalysts are equally active for the decomposition of methanol at this temperature. From 300°C the influence of catalyst composition on the reaction rises to a maximum, and then falls as the temperature approaches 400°C.

The decomposition of methanol has been shown to be a two-stage process:-

(1) Adsorption of the methanol on the catalyst, followed by

(2) Decomposition into carbon monoxide and hydrogen.

At low temperatures this adsorption can be measured quantitatively. It must be borne in mind, however, that the time of contact is great in this case, and the percentage of methanol decomposed increases with the time of contact with the catalyst. Moreover, the problem was investigated under conditions similar to the normal decomposition, i.e. 2.6 gms. methanol in 4 litres N_2/hr. It is probable, therefore, that with a longer/

longer time of contact, the decomposition of methanol will commence at a temperature lower than 300°C.

It has been demonstrated that the percentage of the entering methanol decomposed depends on the concentration of the methanol in the gas stream, and the gas rate over the catalyst. It has been suggested that the activity should be defined as a function of the maximum reaction rate, which is dependent only on temperature.

The effects of excess carbon monoxide and hydrogen on the reaction are similar, although from equilibrium considerations it was expected that there would be a difference. The reactivating effect of small additional concentrations of hydrogen has led to a theory to account for the variation in catalytic activity experienced. There is, however, a more marked degradation of activity with time in the case of carbon monoxide (Table XX).

The conclusions of Craxford and Rideal previously summarised have led to a careful scrutiny of the results of this investigation, giving rise to a theory that the mechanism of the methanol synthesis may be parallel to that of the Fischer-Tropsch synthesis, in that the reaction occurs by means of chemisorbed carbon monoxide and hydrogen, the final stage being methanol/

methanol instead of long-chain hydrocarbons.

It has been postulated that the slow fall in activity of the catalyst is due to the gradual chemisorption of carbon monoxide and the subsequent formation of carbide. After a series of tests with a catalyst, the first addition of hydrogen (5%) brings about a definite rise in activity, together with a sharp fall in the carbon dioxide content and rise in the methane content of the decomposition gases. In a subsequent test with the same amount of hydrogen, however, the methane content drops again (Table XIX , p. 104).

As the hydrogen content is increased until decomposition takes place in an atmosphere of hydrogen, both the carbon dioxide and methane increase Furthermore, when carbon monoxide is substituted for hydrogen, there is a decrease in the methane content, and an increase in the carbon dioxide content ,when a small proportion (5%) is added to the gas stream. As the concentration of this carbon monoxide is increased, however, there is a decrease in the methane formed, and an increase in the carbon dioxide.

It is evident, therefore, that the carbon monoxide/

monoxide is chemisorbed on the catalyst, and possibly forms a carbide, which is removed, though probably not completely, by hydrogen as methane; excess carbon monoxide is apparently converted to carbon dioxide and carbide. As the concentration of hydrogen increases, the amount chemisorbed increases, inhibiting carbide formation by the removal of the chemisorbed carbon monoxide as methane and carbon dioxide according to the following equation:-

$$2CO+2H_2 = CO_2+CH_4$$

It is possible also that the carbon dioxide and the methane are formed by the decomposition of methyl formate:-

$$HCOOCH_3 = CO_2+CH_4,$$

but in the experiments the amounts of carbon dioxide and methane formed were not equal.

On the supposition that the catalyst is represented by X, a possible mechanism of the action of carbon monoxide and hydrogen on the catalyst is as follows:-

(a) Chemisorption of carbon monoxide,

$$X+CO \longrightarrow X-CO$$

(b) Chemisorption of hydrogen,

$$X+H \longrightarrow X-H$$

(c) Reduction of chemisorbed carbon monoxide

by/

by further carbon monoxide, with the formation of carbide and carbon dioxide,

$$X\text{-}CO+CO \rightarrow X\text{-}C+GO_2.$$

(d) Reduction of the carbide by chemisorbed hydrogen, with the production of methane,

$$X\text{-}C + X\text{-}H \rightarrow X+CH_4.$$

As the proportion of carbon dioxide in the products is always greater than the methane, it is evident from the above that its formation is due to reaction (c) above, and that the carbide is probably more stable than the carbon monoxide complex.

When a small excess of hydrogen is present, it is sufficient to reduce the carbide and inhibit its formation. As the concentration of hydrogen increases, the amount chemisorbed may increase, with the result that reaction occurs with the chemisorbed carbon monoxide, producing methane and carbon dioxide:-

(e) $X\text{-}CO + X\text{-}H \rightarrow X+CH_4 + CO_2.$

When the excess hydrogen is replaced by carbon monoxide, a small excess of the latter will tend to inhibit the chemisorption of hydrogen and promote carbide formation. The rise in activity due to this small excess may be explained by the reaction

(f) $X\text{-}CO + X\text{-}CO \rightarrow X+X\text{-}C + CO_2$

taking place, with the formation of further active surface (X). As the excess CO increases, the amount of chemisorption may increase, and carbide formation occur due to reaction (c).

It is to be remembered, however, that the catalyst used by Craxford and Rideal is cobalt promoted by thoria, and cobalt is a metal which forms carbides easily. A mixed oxide catalyst is used in the present work, and though the word carbide is used, it must not be taken to mean a carbide as generally understood e.g. of cobalt, nickel or iron, but rather a complex with the reduced oxide from which the carbon can be liberated in the form of methane or carbon dioxide. The symbol X is used to represent a catalyst, the composition of which in the reduced state is unknown, and for simplicity X-C the carbide or carbon complex.

It has been shown that the activity continues to fall in the presence of slight excess of hydrogen, over a long period, and moreover, that an additional increase in this hydrogen excess reactivates the catalyst. Furthermore, the effect of excess carbon monoxide on the reaction, is, to all intents and purposes, similar to that of hydrogen. It is thought improbable/

improbable, therefore, that the effect of the addition of these gases in excess of the amounts formed in the reaction is to reduce the catalyst further. It is more probable that they form a complexes of the type mentioned above.

The effect of experimental conditions upon the formation of formaldehyde during the decomposition of methanol was different from that expected were the former an intermediate product of the reaction. The discrepancies observed however, together with free-energy data, cast doubt on the theory that it is intermediately formed.

As already stated, methanol is adsorbed on the surface of the catalyst for an appreciable time prior to decomposition. The attachment may be in either of two ways:-

(1) Polar, i.e. through the hydrogen of the hydroxyl group.

(2) Non-polar, i.e. through carbon.

On the evidence put forward for the mechanism of the adsorption of carbon monoxide, it seems more probable that the attachment is non-polar, for as has been shown, carbon monoxide is more readily retained by the catalyst than hydrogen. It is difficult to conceive of the carbon/

carbon monoxide being liberated and then readsorbed, as would be the case for attachment through hydrogen. Rather does it offer that the attachment of the methanol to the catalyst is through carbon. There is, however, no experimental evidence to support this supposition.

(2) THE DECOMPOSITION OF FORMALDEHYDE.

The experiments on the decomposition of methanol have been repeated, as far as possible, under similar conditions with formaldehyde, in order to obtain a basis of comparison.

The most noticeable difference between the decomposition of formaldehyde and the decomposition of methanol is that the speed of the former is of a much greater order than that of the latter. The formaldehyde is decomposed completely at temperatures below which methanol is almost undecomposed, with similar catalysts and rates of entry of formaldehyde and methanol. Furthermore, at temperatures at which the formaldehyde decomposition rate is sufficiently low to be influenced by the composition of the catalyst, the most active catalyst in this case is of different composition to the most active for the methanol decomposition under such/

such conditions.

As in the case of the methanol decomposition, the mechanism of the formaldehyde reaction changes with temperature. The nature of the change in mechanism is, however, more complicated in the latter case. From a study of figs. 39 and 40 , (pp.150 and 152) it is evident that there are three distinct stages involved:-

(1) Formation of water up to 250°C decreasing as temperature increases with the appearance of hydrogen in the products.

(2) Production of methanol, which increases with temperature up to about 300°C.

(3) Formation of carbon monoxide and hydrogen in approximately equal proportions as the temperature rises above the temperature corresponding to maximum methanol production, together with a fall in the latter.

The amount of carbon dioxide present in the decomposition products is very much greater than the amount obtained in the case of the methanol reaction, and the amount decreases as the temperature of the reaction/

reaction is raised, and, in general, as the activity of the catalyst increases. Furthermore, at low temperatures, and where the catalyst activity is low, the amounts of carbon dioxide and methane produced are approximately equal, but as temperature and activity increase, the fall in the methane production is of much greater order than that of carbon dioxide.

It is possible that the production of carbon dioxide and methane is due to decomposition of methyl formate. In this case, however, carbon dioxide and methane would be present in equal amounts, irrespective of the conditions. This, however, is not the case, the methane formation being affected to a greater extent by changes of conditions than the carbon dioxide.

On the reasoning put forward with regard to the chemisorption of carbon monoxide and hydrogen on the catalyst in the case of the methanol decomposition, it is again more probable that the formation of carbon dioxide and methane is due to interaction between chemisorbed carbon monoxide and chemisorbed hydrogen, since in the case of formaldehyde, equal volumes of hydrogen and carbon monoxide are formed, whilst methanol forms twice as much of the former as the latter. When the amounts of these gases on the catalyst are equal reactions/

reactions such as the following are probable:-

$$2CO + 2H_2 = CO_2 + CH_4$$

Methanol and water are formed by secondary reactions, and the former is particularly interesting in that the amount produced is not altered when the reaction is carried out in the presence of hydrogen. On the reasoning of Craxford and Rideal (loc.cit.) this is readily explained by the interaction of the chemisorbed, or active, hydrogen with the adsorbed formaldehyde. If little space remains on the surface for further chemisorption of hydrogen, the presence of excess hydrogen will have little or no effect on the formation of methanol. The effect of carbon monoxide on the decomposition can again be explained by reasoning similar to that advanced for the effect of this gas on the methanol decomposition.

Even at 290°C, the temperature of maximum methanol production, there is practically no change in the production of methanol when either hydrogen or carbon monoxide is added to the reaction. This shows that the surface of the catalyst is always fully saturated with formaldehyde or reaction products.

On the initial introduction of formaldehyde to the catalyst a rise in temperature is experienced, similar to/

to that obtained in the case of methanol. There is no subsequent fall, however, when methanol is the product. This is in agreement with the proposed method of formation, for thermodynamically the reaction

$$HCHO + H_2 = CH_3OH.$$

is exothermic. When the mechanism changes from the production of methanol to the production of carbon monoxide and hydrogen, this temperature increase is followed by a decrease as experienced in the methanol decomposition. It is evident that adsorption takes place prior to decomposition as in the case of methanol.

When the reaction is carried out in an atmosphere of hydrogen, the variations in the production of carbon dioxide and methane are similar to those produced by the decomposition of methanol under similar conditions. The effect of excess carbon monoxide, however, on the reaction appears to be the formation of large quantities of gaseous unsaturated compounds. No such formation of unsaturated compounds results in the case of methanol.

(3) HIGH PRESSURE EXPERIMENTS.

(a) Attempted synthesis of formaldehyde.

It has been demonstrated that under the experimental conditions holding, carbon monoxide and hydrogen cannot be made to combine to form formaldehyde in/

in any appreciable quantity. Even when conditions of temperature and pressure were changed so as to favour methanol production, this was not formed, nor was additional formaldehyde formed (p. 170) At atmospheric pressure the catalysts used were active in the decomposition of both these compounds. The absence of the former compound in particular indicates either:-

(a) The catalyst is much more active for the decomposition of both methanol and formaldehyde than for their synthesis.

or

(b) The constructional material of the high pressure reaction vessel exerts an inhibiting influence on the synthesis.

It is improbable that the metal of the reaction chamber inhibits the reaction to such a degree, and the former is assumed to be the more probable explanation.

Traces of carbon dioxide and methane are found in the gases issuing from the reaction chamber, the former being in slight excess. This supports the theory put forward for the chemisorption of hydrogen and carbon monoxide on the catalyst (p.232).

(b) ATTEMPTED SYNTHESIS OF METHANOL.

As in the case of the attempt to synthesise formaldehyde, the attempted synthesis of methanol was also/

also a failure, although equilibrium data indicate that under the experimental conditions large yields of methanol are to be expected. In this case the catalyst most active in the decomposition of methanol was employed, while in the attempt to synthesise formaldehyde the catalyst most active in the decomposition of formaldehyde was used. Traces of methane and carbon dioxide were also obtained.

(c) ATTEMPTED HYDROGENATION OF FORMALDEHYDE.

Thermodynamically this is a spontaneous reaction, i.e. it should proceed even without the application of pressure. The results of this series of experiments show definitely that under the conditions prevailing polymerisation in preference to hydrogenation of the formaldehyde takes place. Pressure alone is sufficient to bring about this reaction at the temperatures employed, although the presence of hydrogen greatly reduces the charring of the formaldehyde which normally takes place in the absence of hydrogen.

It is evident, therefore, that with catalysts of the type used, formaldehyde can only be hydrogenated to methanol by means of the hydrogen liberated by its own decomposition. This hydrogen is most probably chemisorbed, and/

and thus available in an active form, as the presence of an excess of molecular hydrogen does not increase the hydrogenation of the formaldehyde.

(4) FORMALDEHYDE: INTERMEDIATE COMPOUND OR BYE-PRODUCT?

At 300-400°C. there are two courses which are possible for the decomposition of methanol:-

(1) $$\begin{tikzcd} CH_3OH \arrow[r] & HCHO + H_2. \arrow[d] \\ & CO + H_2. \end{tikzcd}$$

(2) $$CH_3OH \longrightarrow CO + 2H_2.$$

Unfortunately, the decomposition of formaldehyde in this range of temperatures with the methanol catalysts is much more rapid than the decomposition of methanol within this range.

If the reaction is stepwise, it is the preliminary step: $CH_3OH \rightarrow HCHO + H_2$, which determines the rate of decomposition, for the decomposition rate of formaldehyde has been shown to be very much faster than that of methanol. But this step in the reaction involves an increase in free-energy (see p. 34), and is therefore not spontaneous at atmospheric pressure and the temperatures employed. Moreover, for a step-reaction to take place, each of the steps must be spontaneous. Therefore, from thermodynamical considerations (p. 28)

the/

the decomposition of methanol between 300 and 400°C. at atmospheric pressure can-not be through the intermediate production of formaldehyde.

The experimental evidence, though not of itself sufficient proof of the course of the methanol decomposition, when considered in conjunction with the free-energy data of the steps involved, is sufficient to allow of the statement that formaldehyde is not the intermediate product of the decomposition. of methanol at atmospheric pressure, and that the reaction is as represented by the equation:-

$$CH_3OH = CO + 2H_2.$$

It will have been noticed that the chemisorption of hydrogen and carbon monoxide is postulated, and attempts have been made to find a suitable mechanism of reaction between these substances to account for the phenomena noted. It was thought, however, that the experimental evidence put forward could be profitably supplemented, and therefore experiments have recently been carried out with this object in view.

The results (p. 252) have shown that at experimental temperatures (c.360°C.) there is but slight tendency to carbide formation, depending on the activity of the catalyst and not on its chemical composition. Large amounts of carbon monoxide and hydrogen are retained/

retained by the catalyst at these temperatures, however, and can only be removed by heating to mugh higher temperatures. There is still, moreover, no evidence of increased carbide formation with increased temperature. The results, however, are discussed in detail in the Supplement.

CHAPTER XXII.

CONCLUSIONS.

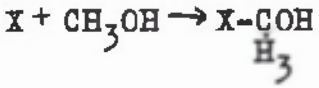
THE MECHANISM OF THE DECOMPOSITION AND SYNTHESIS OF METHANOL.

In view of the evidence put forward, it is possible that the mechanism of the methanol reaction is parallel to that suggested by Craxford and Rideal (loc.cit) for the Fischer-Tropsch reaction:-

METHANOL DECOMPOSITION.

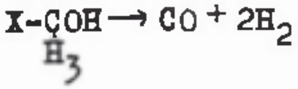
This reaction involves two steps:-

(1) Sorption of the molecule,



$$X + CH_3OH \rightarrow X\text{-}\underset{H_3}{C}OH$$

(2) Desorption with decomposition:-

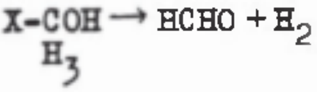


$$X\text{-}\underset{H_3}{C}OH \rightarrow CO + 2H_2$$

(The catalyst is denoted by X for simplicity and the attachments between catalyst and molecule by the usual bond, e.g. X-H.)

Concurrent side-reactions can occur as follows:-

(a) Formation of formaldehyde,



$$X\text{-}\underset{H_3}{C}OH \rightarrow HCHO + H_2 \quad \text{or} \quad X\text{-}CO + X\text{-}H \rightarrow HCHO + X.$$

(b) Formation/

(b) Formation of carbon dioxide,

$X{-}CO + CO \rightarrow X{-}C + CO_2$ (type of carbide formation)

(c) Formation of methane,

$X{-}C + X{-}H \rightarrow X + CH_4$; $X{-}CO + X{-}H \rightarrow X + CO_2 + CH_4$ etc.

As the amount of carbon dioxide produced is always greater than the methane, it is probable that the chemisorption of carbon monoxide is preferential to the chemisorption of hydrogen.

It is preferable at this point to distinguish the various types of sorption to which reference is made.

Sorption. Attachment in general to the catalyst surface.

Adsorption. Attachment of a compound or element to the catalyst, being removable again in the original form.

Chemisorption. Attachment of the substance to the catalyst in the form of a compound, removable in the original form only by extreme measures, e.g. heating to very high temperatures.

Desorption. Removal from the catalyst in the original form or otherwise.

METHANOL SYNTHESIS.

Although the intermediate production of formaldehyde/

formaldehyde in the decomposition of methanol at atmospheric pressure is thermodynamically impossible, its intermediate production in the synthesis is thermodynamically possible. It is suggested that the methanol synthesis involves the following steps, again representing the catalyst by X:-

(a) Chemisorption of carbon monoxide,

$$X + CO \rightarrow X\text{-}CO$$

(b) Chemisorption of hydrogen,

$$X + H \rightarrow X\text{-}H.$$

(c) Reaction between chemisorbed carbon monoxide and molecular hydrogen to form methanol,

$$X\text{-}CO + H_2 \rightarrow X + CH_3OH.$$

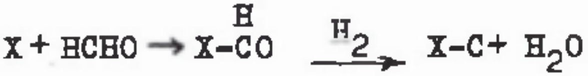
Although it is thermodynamically possible that formaldehyde can be the intermediate product in the methanol synthesis, it is considered unlikely in view of the marked tendency to polymerise under pressure of hydrogen rather than reduce to methanol with the catalysts employed. Furthermore, it is evident that formaldehyde can only be reduced to methanol with chemisorbed hydrogen, and moreover, that carbon monoxide is preferentially chemisorbed to hydrogen. It is therefore considered unlikely that the application of pressure will overcome this preferential sorption to favour/

favour the formation of formaldehyde and its subsequent reduction in preference to its polymerisation to methyl formate.

FORMALDEHYDE DECOMPOSITION.

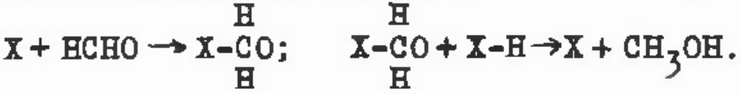
It has been shown that there are three courses which the reaction can take, depending on the temperature. Using the foregoing notation, the reactions involved are as follows:-

(a) Low temperature, water formation,



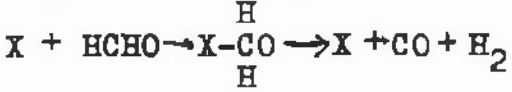
$$X + HCHO \rightarrow X\text{-}\overset{H}{C}O \xrightarrow{H_2} X\text{-}C + H_2O$$

(b) Medium temperature, methanol formation,



$$X + HCHO \rightarrow X\text{-}\overset{H}{\underset{H}{C}}O; \quad X\text{-}\overset{H}{\underset{H}{C}}O + X\text{-}H \rightarrow X + CH_3OH.$$

(c) High temperature, carbon monoxide and hydrogen formation,



$$X + HCHO \rightarrow X\text{-}\overset{H}{\underset{H}{C}}O \rightarrow X + CO + H_2$$

SUPPLEMENT.

Supplementary EXPERIMENTAL WORK.

CHAPTER XXIII.

FURTHER INVESTIGATION OF THE MECHANISM OF SURFACE PHENOMENA.

It has already been postulated that reactions occur between hydrogen and carbon monoxide chemisorbed on the catalyst, and these experiments were carried out in an effort to demonstrate these reactions, and particularly, to determine if carbide formation occurred, and to what extent. The experiments are, of course, only qualitative.

METHOD.

Methanol was passed over 10 ccs. of a freshly reduced catalyst for a period which was judged to be sufficient for the activity to have risen to a maximum (3 hours) (see fig. 27, p.105). The conditions were such that each catalyst had decomposed at least 5 gms. of methanol at 360°C. previous to being examined.

When this quantity of methanol had been decomposed, the catalyst was thoroughly flushed at 360°C. with nitrogen (10 litres in 15 minutes). The nitrogen was now replaced with a slow stream of hydrogen (3 litres per hour) the temperature being maintained at 360°C. The first 300 ccs. of this hydrogen were collected and analysed/

analysed, and also the last 300 ccs. of the flushing nitrogen.

RESULTS.

GAS ANALYSES.

Catalyst Composition 18.8 mol% Zn.

	Flushing Nitrogen.	Flushing Hydrogen.
CO_2.	nil.	1.0%
CO	0.3%	2.6%
H_2	trace	
CH_4	nil.	0.6%

Catalyst Composition 68.8 mol% Zn.

	Flushing Nitrogen.	Flushing Hydrogen.
CO_2	nil.	0.5%
CO	0.4%	2.0%
H_2	nil	
CH_4	nil	2.0%

Catalyst Composition 77 mol% Zn.

	Flushing Nitrogen.	Flushing Hydrogen.
CO_2	Nil.	0.4%
CO	0.2%	1.0%
H_2	nil	
CH_4	nil	0.3%

The catalysts were examined further by overheating to 450°C. and flushing with nitrogen and hydrogen at this temperature. The catalysts already used were caused to decompose a further 2 - 3 gms. of methanol at 360°C., and were then thoroughly flushed with nitrogen at this temperature. The flushing was then stopped, and the temperature raised as quickly as possible to 450°C. At this temperature the nitrogen flow was continued, but at a rate of 3 litres per hour. 300 ccs. were collected at this rate for analysis.

When this sample had been collected, the catalyst was thoroughly flushed as before, and then replaced by a slow stream of hydrogen (3 litres per hour), the first 300 ccs. being collected for analysis. The object of this procedure was to remove any adsorbed gases with nitrogen, leaving carbide, the latter being decomposed by the hydrogen to form methane.

GAS ANALYSES.

Catalyst Composition 18.8 mol% Zn.

	Flushing Nitrogen.	Flushing Hydrogen.
CO_2	11.4%	0.4%
CO	14.0%	0.8%
H_2	36.2%	
CH_4	0.5%	1.0%

Catalyst Composition 68.8 mol% Zn.

	Flushing Nitrogen.	Flushing Hydrogen.
CO_2	0.2%	0.2%
CO	8.4%	1.4%
H_2	16.6%	
CH_4	nil.	2.0%

It was noticed that on flushing the catalyst of low zinc content with nitrogen at 450°C. that some water was evolved, but not with hydrogen. This was the only occasion on which water was observed to be evolved.

The large amount of water and carbon dioxide evolved when the catalyst of high chromium content was flushed with nitrogen at 450°C. cannot be satisfactorily explained except by the further reduction of the chromium oxide by chemisorbed hydrogen and chemisorbed carbon monoxide.

DISCUSSION OF RESULTS.

The results show definitely that there is but little tendency to carbide formation, and that this increases slightly with catalyst activity.

It/

It is improbable that the methane is formed by interaction of hydrogen and carbon monoxide on the catalyst, for according to the equation,

$$2CO + 2H_2 = CO_2 + CH_4,$$

an equal volume of carbon dioxide is also formed.

Note: The above equation is a combination of the two following equations:-

(i) $CO + 3H_2 = CH_4 + H_2O$

(ii) $CO + H_2O = CO_2 + H_2$

It is evident that comparatively large amounts of carbon monoxide and hydrogen can be retained on the catalyst without reacting together at 360°C and that when the temperature is raised to 450°C. these gases are desorbed in preference to reacting together. This is surprising in view of the large free energy decreases of the two methane reactions mentioned above. This means that the X-CO complex mentioned previously is very stable.

It is highly probable that the reactivating effect of overheating the catalyst (see Table IV, p.70) is due to the desorption of carbon monoxide and hydrogen. It is also probable that chemisorption as well as adsorption (see definitions, p. 247) takes place, the amount of chemisorption gradually increasing (i.e. X-CO and/

and X-H increasing) with a corresponding slow fall in catalytic activity.

As the results show that there is little or no tendency for the chemisorbed carbon monoxide to react either with molecular or chemisorbed hydrogen, it is probable that in the synthesis of methanol from carbon monoxide and hydrogen under pressure, chemisorbed carbon monoxide reacts with molecular hydrogen to produce methanol, and with chemisorbed hydrogen to form side reactions (e.g. methane, formaldehyde).

Unfortunately time did not permit of a more detailed examination of the subject. The results are, however, to a certain extent in line with the conclusions already draw, affecting mainly the subsidiary surface phenomena.

The results obtained lend support to the views of Craxford and Rideal already cited in that carbon monoxide is chemisorbed on the catalyst surface. So far as the results go, however, the carbon monoxide complex does not revert to carbide under the experimental conditions. This complex appears to fulfil a similar function to that of the carbide postulated by these workers.

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See p. 3 ¼

University of Glasgow.

HIGHER DEGREES & SPECIAL STUDY & RESEARCH

Session 1939-40

HIGHER DEGREES AND SPECIAL STUDY AND RESEARCH

GENERAL INFORMATION

Higher Degrees

The University awards the higher degrees of Doctor of Letters (D.Litt.) and Doctor of Music (D.Mus.) in the Faculty of Arts, Doctor of Medicine (M.D.) and Master of Surgery (Ch.M.) in the Faculty of Medicine, Doctor of Science (D.Sc.) in the Faculties of Science and Engineering, and Doctor of Philosophy (Ph.D.) in all Faculties.

The regulations governing these degrees are printed below. Candidates for any higher degree are required to submit a thesis embodying original work ; candidates for the degrees of Doctor of Medicine, Master of Surgery and Doctor of Music are also required to submit to examination and candidates for any other higher degree may be required to do so. For the degrees of Doctor of Medicine and Master of Surgery only Bachelors of Medicine of this University, and for the degree of Doctor of Science in Public Health only Bachelors of Science in Public Health of this University, may be candidates, and no residence is required for these degrees. The degrees of Doctor of Letters and Doctor of Science are open both to graduates in Arts or Pure Science or Engineering with Honours of this University, of whom no further residence is required, and to other graduates of this University, or graduates of other Universities, who have spent a prescribed period as Research Students in this University. The degree of Doctor of Music is open both to Bachelors of Music with Honours of this University, of whom no further residence is required, and to Bachelors of Music of other Universities who have spent a prescribed period as Research Students in this University. The degree of Doctor of Philosophy is open to graduates of this University or of other Universities ; all candidates are required to spend a prescribed period as Research Students in this University.

The conditions under which candidates are admitted to the status of Research Student are printed below, p. 375. The fees payable by Research Students, in addition to the normal matriculation fee of £2 12s. 6d. a year, are £5 5s. a year in the Faculties of Arts, Divinity and Law and £10 10s. a year in the Faculties of Medicine, Science and Engineering.

Enquiries regarding admission to the status of Research Student should be addressed to the Clerk of Senate.

Diplomas and Certificates for Post-graduate Study in Arts

Graduates and other advanced students may be candidates for the Diploma and the Certificate of Proficiency awarded for special study in the Faculty of Arts. The Diploma is intended for Honours graduates who have pursued advanced study of a special subject under the direction of a Professor or Lecturer, the Certificate for others who have attended one of the regular advanced courses provided in the Faculty. The minimum period of study required either for the Diploma or for the Certificate is one year ; in addition to the normal matriculation fee, candidates are required to pay a tuition fee of five guineas a year and an examination fee of two guineas. The regulations are printed in the syllabus of the Faculty of Arts (see p. 161).

I. DEGREE OF DOCTOR OF LETTERS

The Degree of Doctor of Letters is awarded under Ordinance XXVI (Glasgow No. 7), which came into force on 26th September, 1908. The following are the relevant provisions of the Ordinance :

VII. Graduates who have obtained any degree in the University of Glasgow, and who have either before or after graduation passed the Examination in an Honours Group for the Degree in Arts, or the Final Science Examination for the degree in Pure Science or in Engineering with Honours may offer themselves for the degree of Doctor of Letters (D.Litt.) after the expiry of five years from the date of their graduation.

VIII. Research Students as aforesaid, who have prosecuted in the University of Glasgow some special study under Ordinance No. 61 (General, No. 23—Regulations for the Encouragement of Special Study and Research, and for the appointment of Research Fellows), may offer themselves for the degree of Doctor of Letters ; provided—

(1) That they have obtained a degree in any Scottish University, or a degree in another University specially recognised by the University Court for the purpose of this section, which the Senatus shall deem to be equivalent to the corresponding degree in the University of Glasgow ; and provided that candidates who have obtained any such degree in a University outside the United Kingdom so recognised may be required if the Senatus think fit, before beginning their course as Research Students with a view to the degree of Doctor of Letters, to pass an examination equivalent to an Honours Examination in a group of subjects cognate to their line of work as Research Students.

(2) That they have spent not less than two terms in each of two academical years, or an equivalent period, as Research Students in the University of Glasgow, and produce to the Senatus evidence of satisfactory progress in the special study undertaken by them during that period.

(3) That a period of not less than five years shall have elapsed from the date of the graduation required in sub-section (1) of this section.

IX. All candidates for the degree of Doctor of Letters shall present a thesis or a published memoir or work, which shall be an original contribution to learning in relation to literature or to philosophy, to be approved by the Senatus on the recommendation of a Special Committee appointed by the Senatus ; provided that, if required by the Senatus, a candidate shall also be bound to pass such an examination, conducted orally or otherwise, on the subjects of his special study, or his thesis, or memoir or work, as may from time to time be determined. The thesis or memoir or work shall be accompanied by a declaration signed by the candidate that it has been composed by himself. If the thesis has not already been published, it shall be published by the candidate in such a manner as the Senatus shall approve, and a copy thereof shall be deposited by the candidate in the University Library.

X. Notwithstanding, and in supplement of the provisions of Ordinance No. 13 (General, No. 8—Regulations as to Examinations), Sections XIV and XV, the Senatus shall appoint such Professors of Lecturers in the University as it may think suitable to examine the theses and to conduct the examination of candidates who may offer themselves under the provisions of Ordinance No. 12 (General, No. 7, Regulations for Degrees in Science) or of Ordinance No. 23, Glasgow No. 2—Regulations for Degrees in Engineering, Science or of this Ordinance, for the degree of Doctor of Letters ... ; and the University Court shall, after consultation with the Senatus, appoint one or more additional Examiners to act along with them in adjudicating on the merits of the candidates. Every such additional Examiner shall be a person of recognised eminence in the subject of the thesis or memoir or work which is to be submitted for approval, and may be a Professor or Lecturer in any Scottish University *other than the University of Glasgow*. The result of the examination and adjudication shall be reported to the appropriate Faculty or Special Committee of Senatus, who shall if they think fit make a recommendation thereon to the Senatus; and no candidate shall be approved for the degree unless the Senatus is satisfied that his work is of distinction as a record of original research undertaken by himself, or of important engineering work designed by himself and actually carried out, or as an original contribution to learning.

SUPPLEMENTARY REGULATIONS

1. The thesis should be presented in the form of a single memoir or writing containing a connected account of the candidate's research or work. Detached papers under various headings will not be regarded as a sufficient substitute, unless they are accompanied by a separate statement, composed by the candidate, giving a full account of the methods, results and conclusions of the research or work on which his candidature is based.

Along with this thesis each candidate must submit a résumé of it, stating what is claimed as original in it, and a bibliography.

2. Only in exceptional circumstances and with the express permission of the Senatus may a thesis not already printed and published be submitted for the degree.

3. Candidates who have been awarded a Certificate of Proficiency in the subjects of an Honours Group will be regarded as having "passed the Examination in an Honours Group" for the purpose of proceeding to the degree of D.Litt.

4. The copies of theses submitted by candidates, whether the theses are approved for the degree or not, shall become the property of the University.

2. DEGREE OF DOCTOR OF MUSIC

The Degree of Doctor of Music was instituted by Ordinance CLXXIII (Glasgow No. 42); the following are the sections of that Ordinance which govern the award of the Degree.

XI. (1) Bachelors of Music of the University of Glasgow, who have taken Honours either before or after graduation, may offer themselves for the degree of Doctor of Music (D.Mus.), after the expiry of five years from the date of their graduation.

(2) Bachelors of Music of other Universities recognised for the purpose by the University Court after consultation with the Senatus may offer themselves for the degree of Doctor of Music, after the expiry of

five years from the date of their graduation, provided they have spent not less than three years as Research Students in the University of Glasgow, under Ordinance No. 61 (General, No. 23), and produce to the Senatus evidence of satisfactory progress in the special study undertaken by them during that period.

XII. The Degree shall be given in three Departments, and candidates may present themselves in one or more of these Departments.

The Departments shall be those of :

(*a*) Composers ;
(*b*) Executants ;
(*c*) Theorists or Historians.

Composers

XIII. (1) Candidates for the Degree of Doctor of Music as Composers shall submit a prescribed number of original works in accordance with regulations to be prescribed by the Senatus.

Compositions must be accompanied by a declaration signed by the candidate that they are his own unaided work, and that no portion has been submitted previously to any University.

(2) Candidates in this department shall also be examined in the following subjects :

(*a*) Eight-part Harmony and Counterpoint ;
(*b*) Canon and Double Counterpoint in four parts, and Fugue in five parts ;
(*c*) Scoring for full Orchestra ;
(*d*) Historical Knowledge.

Executants

XIV. (1) Candidates for the Degree of Doctor of Music as Executants shall be required to pass a test of a wide repertoire of concert works in accordance with regulations to be prescribed by the Senatus.

(2) Candidates in this department must also qualify for the optional subject set forth in VI (8), and may also be required to pass an examination in any or all of the subjects prescribed for candidates for the Degree of Doctor of Music as Composers in accordance with regulations to be prescribed by the Senatus.

Theorists or Historians

XV. (1) Candidates for the Degree of Doctor of Music as Theorists or Historians shall present, in accordance with regulations to be prescribed by the Senatus, one or more treatise on Theoretical or Historical subjects. Such treatises must be the result of original thought and research, not merely abstracts or compilations of existing works.

Each treatise must be accompanied by a declaration signed by the candidate that it is his own unaided work and that it has not been submitted to any other University.

(2) Candidates in this department may also be required to pass an examination in any or all of the subjects prescribed for candidates for the Degree of Doctor of Music as Composers, in accordance with regulations to be prescribed by the Senatus.

SUPPLEMENTARY REGULATIONS

1. **Executants.** Each candidate must submit, not later than six weeks before the examination, an extensive list of works which he professes; if the list is approved, he will be informed, a month before the examination, of not more than four works which he will be required to perform. Violinists and violoncellists must include one or more of the unaccompanied sonatas or suites of J. S. Bach; candidates who profess instruments other than pianoforte, violin, violoncello or organ must include concertos and chamber works; vocalists must include roles in opera and oratorio.

2. **Theorists and Historians.** Before submitting a treatise, candidates must submit a précis indicating its scope and general character; a treatise may not be submitted until the précis has been approved.

3. DEGREE OF DOCTOR OF MEDICINE

The following regulations for the award of the degree of Doctor of Medicine are contained in Ordinance XXXI (Glasgow No. 9).

XXII. (1) Subject to the conditions hereinafter specified, the Degree of Doctor of Medicine may be conferred on any candidate who has obtained the Degrees of Bachelor of Medicine and Bachelor of Surgery of the University of Glasgow, and is of the age of twenty-four years or upwards, and has produced a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Medical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, Colonial, or Public Health Medical Services, or has been engaged for at least two years in Practice other than Practice restricted to Surgery.

(2) Each candidate for the degree of Doctor of Medicine shall be required to pass an examination in Clinical Medicine or in such special department of Medical Science or Practice professed by the candidate as the Senatus, on the recommendation of the Faculty of Medicine, may approve; and he may be admitted to the examination at such time, not sooner than one year after he has received the degrees of Bachelor of Medicine and Bachelor of Surgery, as the Senatus may appoint for the purpose.

(3) Each candidate for the degree of Doctor of Medicine shall submit for the approval of the Faculty of Medicine a thesis on any branch of knowledge, comprised in the several divisions of the Examination for the degrees of Bachelor of Medicine and Bachelor of Surgery, which he may have made a subject of special study, excepting a subject that is exclusively surgical; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus. The faculty may, if it sees fit, before approving the thesis, require the candidate to present himself for oral or other examination on the subject-matter thereof. If the thesis is, in the judgment of the Faculty, of special merit, the Senatus may, on the recommendation of the Faculty, exempt the

candidate from the whole or part of the examination prescribed in sub-section 2 of this Section.

(4) A Bachelor of Medicine and Bachelor of Surgery, who produces to the Senatus satisfactory evidence of his intention of entering within twelve months after obtaining such degrees on the practice of his profession in a British Possession or Colony, or in a Foreign Country, may, under such conditions as the Senatus may from time to time prescribe, be admitted to the examination in Clinical Medicine or in a special department of Medical Science or Practice prescribed in sub-section 2 of this Section at such time after he has received such degrees as the Senatus may appoint for the purpose: provided always that in special circumstances the Senatus may, if it sees fit, on the recommendation of the Faculty of Medicine, exempt him from the whole or part of the Examination; but the degree of Doctor of Medicine shall not be conferred on him unless he shall produce a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Medical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, Colonial or Public Health Medical Services, or for at least two years in Practice other than Practice restricted to Surgery, and unless his thesis, in the judgment of the Faculty of Medicine, is of special merit.

SUPPLEMENTARY REGULATIONS

1. The Examination in Clinical Medicine shall for each candidate consist of a written Report and Commentary, with any oral questions that may be considered desirable, upon at least three medical cases. In the selection of the cases, special regard shall be given to the opportunities they afford for testing the candidate, not only in the ordinary methods of clinical investigation, but also in the more advanced methods requiring practical knowledge in the applications of the ophthalmoscope and laryngoscope, the chemical and microscopical examinations of excreta, the quantitative determination and microscopic characters of the chief constituents of blood possessing clinical importance, the recording by instruments of the condition of the circulation, and the applications of electricity.

A candidate who elects to be examined in a special department of Medical Science or Practice will be expected to show high proficiency in it. The special departments from which the subject of examination may be selected are the following:

Diseases of Women;
Diseases of Children;
Mental Diseases;
Zymotic Diseases;
Diseases of the Eye;
Diseases of the Throat;
Diseases of the Ear;
Diseases of the Skin;
Midwifery;
Tropical Diseases.

The Clinical Examinations will be held twice in each year, about the middle of September and about the middle of March. Candidates are required to enter their names not later than 15th August for the September, and not later than 15th February, for the March Examinations. Entry forms may be obtained from the Registrar.

2. No thesis will be approved unless it gives evidence of original observation, or, if it deals with the researches of others, gives a full statement of the literature of its subject with accurate references and critical investigation of the views or facts cited : mere compilations will in no case be accepted.

A thesis submitted for the degree must be a dissertation written for the purpose, provided that the results of original observations already published in medical or scientific journals or in the transactions of learned societies or otherwise may be accepted in place of such a dissertation.

3. The subject-matter of the thesis submitted by a candidate who *elects to be examined in a special department of Medical Science or* Practice must be cognate to that special department.

4. Three grades of distinction are awarded for the excellence of theses submitted for the degree—Commendation, High Commendation and Honours. A candidate who has been awarded Honours for his thesis will be exempted from the clinical examination prescribed in sub-section 2 above.

5. The copies of theses submitted by candidates, whether the theses are approved for the degree or not, shall become the property of the University.

4. DEGREE OF MASTER OF SURGERY

The following regulations for the award of the degree of Master of Surgery are contained in Ordinance XXXI (Glasgow No. 9).

XXIII. (1) Subject to the conditions hereinafter specified the degree of Master of Surgery may be conferred on any candidate who has obtained the degrees of Bachelor of Medicine and Bachelor of Surgery of the University of Glasgow, and is of the age of twenty-four years or upwards, and has produced a certificate showing that, after having received the degrees of a Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Surgical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, or Colonial Medical Services, or has been engaged for at least two years in Practice other than Practice restricted to Medicine.

(2) Each candidate for the degree of Master of Surgery shall be required to pass an examination in the following subjects: Surgical Anatomy, Operations upon the dead body, and Clinical Surgery or such special department of Surgery professed by the candidate as the Senatus, on the recommendation of the Faculty of Medicine, may approve ; and he may be admitted to the examination at such time, not sooner than one year after he has received the degrees of Bachelor of Medicine and Bachelor of Surgery, as the Senatus may appoint for the purpose.

(3) Each candidate for the degree of Master of Surgery shall submit for the approval of the Faculty of Medicine a *thesis* on any branch of knowledge, comprised in the several divisions of the Examination for

the degrees of Bachelor of Medicine and Bachelor of Surgery, which he may have made a subject of special study, excepting a subject that is exclusively medical; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus. The Faculty may, if it sees fit, before approving the thesis, require the candidate to present himself for oral or other examination on the subject-matter thereof. If the thesis is, in the judgment of the Faculty, of special merit, the Senatus may, on the recommendation of the Faculty, exempt the candidate from the whole or part of the examination prescribed in sub-section 2 of this Section.

(4) A Bachelor of Medicine and Bachelor of Surgery who produces to the Senatus satisfactory evidence of his intention of entering within twelve months after obtaining such degrees on the practice of his profession in a British Possession or Colony, or in a Foreign Country, may, under such conditions as the Senatus may from time to time prescribe, be admitted to the examination in the subjects specified in sub-section 2 of this Section, at such time after he has received such degrees as the Senatus may appoint for the purpose: provided always that in special circumstances the Senatus may, if it sees fit, on the recommendation of the Faculty of Medicine, exempt him from the whole or part of the examination; but the degree of Master of Surgery shall not be conferred on him unless he shall produce a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Surgical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, or Colonial Medical Services, or for at least two years in Practice other than Practice restricted to Medicine, and unless his thesis in the judgment of the Faculty of Medicine is of special merit.

SUPPLEMENTARY REGULATIONS

1. The Examination in Clinical Surgery shall for each candidate consist of a written Report and Commentary, with any oral questions that may be considered desirable on at least three surgical cases.

One of the three surgical cases on which a candidate is examined shall, if the candidate on entering his name for the Examination declares a wish to that effect, be from one of the following departments, namely, Surgical Diseases of Women; Diseases of the Throat, Diseases of the Eye, Diseases of the Ear. Should the candidate specialise in one of these departments he will be expected to show high proficiency in it.

The Clinical Examination will be held twice in each year, about the middle of September and about the middle of March. Candidates must enter their names not later than 15th August for the September, and not later than 15th February for the March Examination. Entry forms may be obtained from the Registrar.

2. Three grades of distinction are awarded for the excellence of theses submitted for the degree—Commendation, High Commendation and Honours. A candidate who has been awarded Honours for his thesis will be exempted from the clinical examination prescribed in sub-section 2 above.

5. DEGREE OF DOCTOR OF SCIENCE

The degree of Doctor of Science is awarded under Ordinance XXVI (Glasgow No. 7), which came into force in September, 1908. The following are the relevant provisions of that Ordinance, with the amendments made in subsequent Ordinances.

I. Graduates who have obtained any degree in the University of Glasgow, and who have either before or after graduation passed the Examination in an Honours Group for the degree in Arts, or the Final Science Examination for the degree in Pure Science or in Engineering with Honours, may offer themselves for the degree of Doctor of Science (D.Sc.) after the expiry of five years from the date of their graduation.

II. Research Students within the meaning of Ordinance No. 61 (General No. 23—Regulations for the Encouragement of Special Study and Research and for the Appointment of Research Fellows), who have prosecuted in the University of Glasgow (or in a College affiliated thereto) some special study or research under that Ordinance, may offer themselves for the degree of Doctor of Science: provided:

(1) That they have obtained a degree in any Scottish University, or a degree in another University specially recognised by the University Court for the purpose of this section which the Senatus shall deem to be equivalent to the corresponding degree in the University of Glasgow; and provided that candidates who have obtained any such degree in a University outside the United Kingdom so recognised may be required, if the Senatus think fit, before beginning their course as Research Students with a view to the degree of Doctor of Science, to pass an examination equivalent to an Honours or to a Final Science Examination in a group of subjects cognate to their line of work as Research Students.

(2) That they have spent not less than two terms in each of two academical years, or an equivalent period, as Research Students in the University of Glasgow (or in a College affiliated thereto), and that they produce to the Senatus evidence of satisfactory progress in the special study or research undertaken by them during that period.

(3) That a period of not less than five years shall have elapsed from the date of the graduation required in subsection (1) of this section.

III. All candidates for the degree of Doctor of Science shall present a thesis or a published memoir or work, to be approved by the Senatus on the recommendation of the Faculty of Science; provided that, if required by the Senatus, the candidate shall also be bound to pass such an examination conducted orally or practically, or by written papers, or by all of these methods, on the subjects of his special study or of his thesis, memoir, or work, as may from time to time be determined. The thesis shall be a record of original research in relation to science undertaken by the candidate, or of some important engineering work designed by the candidate and actually carried out, and shall be accompanied by a declaration signed by him that the work has been done and the thesis composed by himself. If the thesis has not already been published, it shall be published by the candidate in such manner as the Senatus shall approve, and a copy thereof shall be deposited by the candidate in the University Library.

X. Notwithstanding, and in supplement of the provisions of Ordinance No. 13 (General, No. 8—Regulations as to Examinations), Sections XIV and XV, the Senatus shall appoint such Professors or Lecturers in the University as it may think suitable to examine the theses and to conduct the examination of candidates who may offer themselves under the provisions of Ordinance No. 12 (General, No. 7—Regulations for Degrees in Science) or of Ordinance No. 23 (Glasgow, No. 2—Regulations for Degrees in Engineering Science, or of this Ordinance, for the degree of Doctor of Science . . . ; and the University Court shall, after consultation with the Senatus, appoint one or more additional Examiners to act along with them in adjudicating on the merits of the candidates. Every such additional Examiner shall be a person of recognised eminence in the subject of the thesis or memoir or work which is to be submitted for approval, and may be a Professor or Lecturer in any Scottish University other than the University of Glasgow. The result of the examination and adjudication shall be reported to the appropriate Faculty or Special Committee of Senatus, who shall if they think fit make a recommendation thereon to the Senatus ; and no candidate shall be approved for the degree unless the Senatus is satisfied that his work is of distinction as a record of original research undertaken by himself, or of important engineering work designed by himself and actually carried out, or as an original contribution to learning.

SUPPLEMENTARY REGULATIONS

1. The thesis should be presented in the form of a single memoir or writing containing a connected account of the candidate's research or work. Detached papers under various headings will not be regarded as a sufficient substitute, unless they are accompanied by a separate statement, composed by the candidate, giving a full account of the methods, results, and conclusions of the research or work on which his candidature is based.

2. A thesis presented for the degree of Doctor of Science in Engineering must be a record of original research undertaken by the candidate, or of important engineering work designed by himself and actually carried out, and must be accompanied by a declaration signed by him that these conditions have been satisfied. "Important engineering work" has been defined by the Senatus as work involving the application of some new scientific principle, or a new application of known scientific principles, to engineering design and/or construction ; work carried out on more or less standard lines, however large, useful or successful it may be, will not be regarded as falling within this category.

3. Each candidate must submit two copies of his thesis : both copies, whether the thesis is approved for the degree or not, shall become the property of the University.

4. Every candidate whose thesis has been approved for the degree must, before the degree is conferred upon him, furnish the University with a number of copies of his thesis, to be fixed in each case by the Senatus. These copies must be either printed or satisfactorily multiplied from a typewritten copy.

5. It is advisable that a candidate should have published the main original features of his thesis before submitting it for the degree.

6. Candidates who have been awarded a Certificate of Proficiency in the subjects of an Honours Group will be regarded as having " passed the Examination in an Honours Group " for the purpose of preceding to the degree of D.Sc.

6. DEGREE OF DOCTOR OF SCIENCE IN PUBLIC HEALTH

The regulations for the award of the degree of Doctor of Science in Public Health are contained in Ordinance VI (Glasgow No. 2), which came into force in May, 1903. The relevant provisions of the Ordinance are :

X. Graduates who have held the degree of Bachelor of Science in Public Health from the University of Glasgow for a term of five years, may offer themselves for the degree of Doctor of Science in Public Health *in the said University*.

XI. Each candidate for the degree of Doctor of Science in Public Health shall present a thesis or a published memoir or work to be approved by the Senatus, on the recommendation of the Faculty of Science, and shall also be required to pass an examination in Public Health, and in such of its special departments as the Senatus, with the approval of the University Court, by regulations framed from time to time, shall determine.

The thesis, or published memoir or work, shall be a record of original research undertaken by the candidate, and shall be accompanied by a declaration, signed by him, that the work has been done, and the thesis or memoir composed, by himself.

XII. The Senatus Academicus shall appoint such Professors or Lecturers as it may think suitable to conduct the examination of candidates who may offer themselves under the provisions of this Ordinance for the degree of Doctor of Science, and the University Court shall, after consultation with the Senatus Academicus, appoint such additional Examiners as they deem necessary to act along with them. Such additional Examiners shall be persons of recognised eminence in the subject of the thesis, or memoir, or work which is to be submitted for approval, and may be Professors or Lecturers in any Scottish University other than the University of Glasgow.

XIII. The thesis, memoir, or work submitted by a candidate for the degrees of Doctor of Science shall in each case be examined by the additional Examiner to be appointed by the University Court, as well as by the Examiners to be appointed by the Senatus under the provisions of Section XII of this Ordinance.

XIV. The result of the examination of the thesis, memoir, or work submitted by a candidate, as well as the result of the Examination prescribed under Section XI of this Ordinance, shall be reported to the Faculty of Science.

7. DEGREE OF DOCTOR OF PHILOSOPHY

The degree of Doctor of Philosophy was instituted by Ordinance LXXIV (Glasgow No. 21), which came into force in October, 1919. The relevant provisions of the Ordinance are as follows:

II. Research Students within the meaning of Ordinance No. 61 (General No. 23), who have prosecuted in the University of Glasgow, or in a College affiliated thereto, a course of special study or research in accordance with the provisions of that Ordinance, may offer themselves for the degree of Doctor of Philosophy, under the following conditions, namely—

(1) That they have obtained a degree in any Scottish University, or in another University or College specially recognised for the purpose of this Section by the University Court on the recommendation of the Senatus: provided always that a diploma or certificate recognised in like manner as equivalent to a degree may be accepted in place of a degree.

(2) That they have prosecuted a course of special study or research during a period of three academical years as Research Students in the University of Glasgow, or in a College affiliated thereto, and that they produce to the Senatus evidence of satisfactory progress in the special study or research undertaken by them during that period: provided always that the Senatus shall have power, in exceptional cases, to reduce the period to two academical years, and to permit a Research Student during part of the period to prosecute elsewhere his special study or research.

III. All candidates for the degree of Doctor of Philosophy shall present a thesis to be approved by the Senatus on the recommendation of a Special Committee appointed by the Senatus. The thesis shall embody the results of the candidate's special study or research, and shall be accompanied by a declaration signed by the candidate that it has been composed by himself. The Special Committee shall always include the Professor or other Head of a Department who has been appointed by the Senatus to supervise the candidate's work as a Research Student.

The University Court may, on the recommendation of the Senatus, appoint one or more additional Examiners to act along with the Special Committee in adjudicating on the merits of the thesis. The Senatus may, on the recommendation of the Special Committee, require the candidate to present himself for oral or other examination on the subject-matter of his thesis. A copy of the thesis, if approved, shall be deposited by the candidate in the University Library.

SUPPLEMENTARY REGULATIONS

1. The Senatus does not recognise as a Research Student for the purposes of the degree of Ph.D. in the Faculty of Arts any applicant who is prevented by professional or other duties from devoting the major part of his day during term-time to the object of his research.

2. All copies of theses submitted by candidates, whether the theses are approved for the degree or not, shall become the property of the University. Candidates in Science and in Engineering are required to

submit two copies of the thesis: both copies become the property of the *University*.

3. In submitting a thesis a candidate must state, generally in the preface and specifically in the notes, the sources from which his information is derived, the extent to which he has availed himself of the work of others, and the portions of his thesis which he claims as original.

RESEARCH STUDENTS

The following are the provisions of Ordinance No. 61 (General No. 23), by which the admission of Research Students is controlled:

I. It shall be in the power of the Senatus Academicus in each University, with the approval of the University Court, to make regulations under which graduates of Scottish Universities or of other Universities recognised by the University Court for the purposes of this Ordinance, or other persons who have given satisfactory proof of general education and of fitness to engage in some special study or research, may be admitted to prosecute such study or research in the University [or in a College affiliated thereto [1]].

II. It shall be the duty of the Senatus Academicus in each University:

(1) To receive and decide upon all applications for admission to prosecute special study or research;
(2) To prepare a list of all persons so admitted (hereinafter referred to as Research Students);
(3) To make regulations for the supervision of their work;
(4) To satisfy themselves from time to time that the Research Students are carrying on their work in the University in a satisfactory manner;
(5) To suspend or exclude from any course any student whose conduct or progress is unsatisfactory.

III. Every applicant for admission must send in to the Senatus Academicus a written application stating any degree or other distinction which he has already obtained, the line of study or research which he wishes to prosecute, and the probable period of its duration, together with evidence as to his character, capacity, and general qualifications.

IV. Any application for admission shall be in the first instance referred by the Senatus Academicus to the appropriate Faculty, or to a Committee appointed by the Senatus; one member of the Committee shall always be a Professor or Lecturer within whose department the proposed line of study or research falls. No applicant shall be recommended by the Faculty or the Committee who has not satisfied them by examination or otherwise that he is qualified to prosecute the proposed line of study or research, and further:

(*a*) That his proposed line of study or research is a fit and proper one;
(*b*) That he possesses a good general education;
(*c*) That he is of good character;
(*d*) That he proposes to prosecute his studies or research during a period to be approved by the Senatus Academicus.

The Faculty or the Committee shall make a report to the Senatus

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[1] Added by Ordinance XXXIX (Glasgow No. 12).

Academicus upon each application. It shall also be their duty, subject to the regulations of the Senatus Academicus, to provide for the supervision of the Research Student's work, and to report at least once a year to the Senatus as to his progress and conduct. The Senatus shall then determine whether he shall remain a Research Student.

V. Every Research Student shall be required to matriculate each year, paying the ordinary fee.

VI. Research Students shall have access to and the use of the University Laboratories and Museums, under such conditions as to payment and otherwise as the University Court, after consultation with the Senatus Academicus, may determine.

VII. The title of Research Fellow may be conferred by the Senatus Academicus, with the approval of the University Court, on Research Students who have shown special distinction. Such title shall not of itself confer any right to stipend, but it shall be in the power of the University Court to provide a stipend of such amount and for such period as it may think fit to any Research Fellow, under the powers of Section XI, sub-section 8, of Ordinances numbered 25 and 27, Section X, sub-section 8, of Ordinance numbered 26, and Section IV, sub-section 2, of Ordinance numbered 46.

VIII. (1) The Research Fellows shall be appointed as aforesaid after consideration of the report or reports submitted in terms of Section IV hereof.

(2) The title of Research Fellow may be conferred either at the commencement of the Research Student's course of study or research, or at any time during its progress, as the Senatus Academicus may determine.

(3) Research Fellows shall retain their title and stipend, if any, for the period during which they are engaged in special study or research in the University, and no longer.

(4) Research Students who have been appointed Research Fellows shall continue to be subject to the conditions above prescribed as to the supervision of their work, and the reports to be made thereon.

IX. Nothing herein contained shall prejudice the right of Research Students to such Fellowships, Scholarships, or prizes as may be open to them by Ordinance or Deed of Foundation.

X. The University Court may, subject to the provisions of Section XI, sub-section 8, of Ordinances numbered 25 and 27, Section X, sub-section 8, of Ordinance numbered 26, and Section IV, sub-section 2, of Ordinance numbered 46, provide such sums as it may think fit in aid of the expenses of special study or Research.

SUPPLEMENTARY REGULATIONS

1. Application for admission to the status of Research Student must be made to the Clerk of Senate on the prescribed form.

2. A Research Student must in person report his attendance to the supervisor of his research, or to the Clerk of Senate, at least once a week in term-time, except during periods when, with the permission of the Senatus, he is prosecuting his special study or research elsewhere than in the University or in a College affiliated thereto.

3. A Research Student may, with the sanction of his supervisor, attend classes in the University as a Private Student (see p. 84) but he shall not

be eligible for prizes in classes so attended and his attendance shall not qualify for graduation.

4. Each Research Student who is carrying out his work in a laboratory shall make payment of a sum which is estimated by the Professor in charge of the laboratory as sufficient to cover the ordinary expenses incident to the Research Student's work. The cost of apparatus and material beyond what is included in the ordinary operations of the laboratory shall be charged to the Student, unless the Professor judges that such apparatus and material will be a useful addition to the laboratory. But it shall be in the power of each Professor to propose to the University Court in any particular case that these payments be remitted in whole or in part.

5. All papers arising out of work done in a laboratory shall be submitted before publication to the Professor in charge of the laboratory, and in all such papers, when they are published, a due recognition of the laboratory shall be inserted.

CARNEGIE TRUST FOR THE UNIVERSITIES OF SCOTLAND

ENDOWMENT OF POST-GRADUATE STUDY AND RESEARCH

The regulations governing the award by the Trust of Scholarships, Fellowships and Grants in aid of research, and the award by the University of Carnegie Teaching Fellowships to members of its teaching staff, are printed below. Nominations for Scholarships or Fellowships and applications for Grants must be lodged not later than 15th March with the Secretary of the Trust, Merchants' Hall, Hanover Street, Edinburgh, from whom forms may be obtained. All Scholarships, Fellowships and Grants awarded in any year will normally date from 1st October.

A student who has not graduated but expects to take a degree at the summer or autumn graduation may be nominated for a Scholarship or apply for a Research Grant in the preceding March, but will not be eligible to receive either until he has graduated.

I. SCHOLARSHIPS

(a) *In Science and Medicine ;*

(b) In History, Economics and Modern Languages and Literature

I (*a*) A Scholar in Science or Medicine must be a graduate of a Scottish University who desires to devote himself to higher study and research in some department of science or medicine.

(*b*) A Scholar in History, Economics or Modern Languages and Literature must be a graduate of a Scottish University, preferably with Honours in at least one of the groups : History, Economic Science, English, Modern Languages and Literature, who desires, at home or abroad, to devote himself to higher study and investigation within the scope of these groups of study.

II. A Scholarship shall ordinarily be tenable for two years, the extension to a second year being dependent on the receipt of satisfactory reports by the Scholar and from his Supervisor on his work during the first year; but it may be renewed for a third year, if the Executive Committee deem this expedient, in which case the award is termed a Senior Scholarship.

III. A Scholarship shall be of the annual value of £150 for each of the two years for which it is ordinarily tenable. It may be extended to a third year, in which case the value will be £175 per annum. It shall be payable by quarterly instalments in advance, the second and subsequent instalments being payable on the receipt of a satisfactory report by the Scholar and a certificate from the authority under whose supervision the Scholar has been working. The Executive Committee reserve power to suspend or withhold payment, if not satisfied with the progress or conduct of the Scholar.

A Scholarship shall not be held along with any other scholarship or position of emolument, except with the sanction of the Executive Committee.

In the event of a candidate holding or obtaining any other scholarship or position of emolument, the Executive Committee may, in place of granting or continuing to grant a Carnegie Scholarship, supplement the amount of such scholarship or emolument so as to bring the income up to the value of the Carnegie Scholarship at least, the candidate thereby ranking, and coming under the same regulations, as a Carnegie Scholar.

IV. A Scholar shall ordinarily be expected to devote his whole time to the purpose for which the Scholarship is awarded. If he purposes to undertake other work during his tenure of the Scholarship, he must define such work precisely, and obtain the sanction of the Executive Committee.

V. A candidate must be nominated by a Professor or Lecturer in a Scottish University, or by a Teacher in Scotland recognised for the purpose of graduation by a Scottish University, under whose supervision, unless other supervision be approved by the Executive Committee, he shall work during his tenure of the Scholarship.

The Nomination Form, to be signed by the Nominator and the candidate, must contain information on the following points, all of which will be taken into consideration in estimating the relative claims of candidates:

(1) The age of the candidate, his career as a student, and his knowledge of modern languages.

(2) His special fitness for the work proposed.

(3) His programme of study and research during his tenure of the Scholarship; and where and under whose supervision he proposes to work.

(4) Whether the candidate proposes to undertake other work during his tenure of the Scholarship; and, if so, the character of the work proposed, and the demand on his time which it will involve.

(5) Whether the candidate holds, or expects to hold, any other scholarship or position of emolument; and, if so, particulars of the amount and duration of such scholarship or emolument.

(6) The names of two or more authorities other than the Nominator, to whom the Executive Committee may refer as to the qualifications of the candidate.

The Nominator must, if required, satisfy the Executive Committee that the candidate, if appointed to a Scholarship, will be provided with the facilities and supervision necessary for carrying out his programme of study and research, and that such information will be furnished on his progress and conduct as may seem expedient to the Executive Committee.

VI. By accepting a Scholarship a Scholar comes under an obligation to pursue the programme of research which has been approved by the Executive Committee, and to submit such reports on the progress of his work as the Executive Committee may require.

2. FELLOWSHIPS

(a) In Science and Medicine ;
(b) In History, Economics and Modern Languages and Literature

I (*a*) A Fellow in Science or Medicine must be a graduate of a Scottish University who has given evidence, preferably by work already published, of capability to advance science or medicine by original research, and who desires to devote himself further to this work.

(*b*) A Fellow in History, Economics or Modern Languages and Literature must be a graduate of a Scottish University, preferably with Honours in at least one of the groups : History, Economic Science, English, Modern Languages and Literature, who desires to investigate at first-hand, at home or abroad, some historical, social, economic, or educational problem or factor of modern civilisation, and who can give evidence by his previous career and general culture, and also preferably by work already published, of capability to advance knowledge by his proposed investigation.

II. A Fellowship shall ordinarily be tenable for two years, the extension to a second year being dependent on the receipt of a satisfactory report by the Fellow on his work during the first year ; but it may be renewed for a third year, if the Executive Committee deem this expedient.

III. A Fellowship shall be of the annual value of £250, exclusive of such special expenses in connection with his research as the Executive Committee may allow. Payment shall be made by half-yearly instalments in advance ; but the Executive Committee reserve power to suspend or withhold payment, if not satisfied with the progress or conduct of the Fellow.

A Fellowship shall not be held along with any other fellowship or position of emolument, except with the sanction of the Executive Committee.

In the event of a candidate holding or obtaining any other fellowship or position of emolument, the Executive Committee may, in place of granting or continuing to grant a Carnegie Fellowship, supplement the amount of such fellowship or emolument so as to bring the income up to £250 at least, the candidate thereby ranking, and coming under the same regulations, as a Carnegie Fellow.

IV. A Fellow shall ordinarily be expected to devote his whole time to the purpose for which the Fellowship is awarded. If he proposes to undertake other work during his tenure of the Fellowship, he must define such work precisely, and obtain the sanction of the Executive Committee.

V. A candidate must be nominated by a University Professor, or other Head of a University Department.

The Nomination Form, to be signed by the Nominator and the candidate, must contain information on the following points, all of which will be taken into consideration in estimating the relative claims of candidates :

(1) His age, his career as a student, and his knowledge of modern languages.

(2) His special fitness to conduct the research proposed, and his previous experience, along with any published accounts of work already done.

(3) His programme of research during his tenure of the Fellowship ; where he proposes to work ; and his prospective occupation after the Fellowship has expired.

(4) Whether he proposes to undertake other work during his tenure of the Fellowship ; and, if so, the character of the work proposed, and the demand on his time which it will involve.

(5) Whether he holds, or expects to hold, any other fellowship or position of emolument ; and, if so, particulars of the amount and duration of such fellowship or emolument.

(6) The names of two or more authorities, other than the Nominator, to whom the Executive Committee may refer as to his qualifications.

(7) An estimate, as detailed as is possible, of special expenses, if any, required in connection with the research he proposes to undertake.

VI. By accepting a Fellowship a Fellow comes under an obligation to submit such reports on the progress of his work as the Executive Committee may require.

The publication, in some form, of an account of the results of his research will be expected.

3. GRANTS IN AID OF RESEARCH

I. An applicant for a Research Grant must be a Scottish University Graduate resident in Scotland, or an actual member of the staff of one of the Universities or Colleges in Scotland receiving Grants from the Trust.

II. An applicant must furnish the Executive Committee with information on the following points, all of which will be taken into consideration in estimating the relative claims of applicants :

(1) His experience in research, with copies of or references to any published papers, or, if he has no papers to offer, with references to two or more authorities who are acquainted with his qualifications for research.

(2) The nature of the research in which he desires to engage, and the results expected to follow therefrom.

(3) The period over which the proposed research is likely to extend, and the approximate amount of time which he expects to be able to devote to it.

(4) A statement of special requirements for the proposed research, with a detailed estimate of the cost.

(5) Whether he has received, or is receiving, any grant from any other source for the same object; and if so, what results have already ensued from his investigations.

III. A Research Grant is not intended (1) to take the place of such provision as should be made by the University Courts out of the Grants for Permanent Equipment under the Scheme of "Grants for five years to the four Universities of Scotland," or (2) to provide minor apparatus or research materials or instruments which should form part of the equipment of a Laboratory appropriate to the investigation, or (3) to relieve periodicals of the normal charges involved in publishing the results of researches.

IV. Grants are not applicable to the payment of salaries, wages, or honoraria, except in so far as they may be assigned for a specific purpose, as, for example, the cost of preparing necessary illustrations as specified in the application and approved by the Executive Committee. Such illustrations may include drawings, photographs, or maps.

V. Grants in aid of illustration may be applied to defray the cost of the preparation of process blocks or other means of reproduction, and of the actual printing of the illustration, including any special paper necessary for the purpose, but they are not applicable to the cost of printing and publishing the letterpress of the publication unless, in exceptional cases, special tabular matter is required.

VI. Applications for Grants in aid of Laboratory research, or of the adequate publication of its results, must be made by the individual workers concerned, and Grants made for specific purposes to one worker cannot be utilised by another (whether in the same Laboratory or not), *without the express consent of the Executive Committee.*

VII. An application for a Grant to be used by two or more collaborators in the same research must be signed by each; but they shall appoint one of their number who shall be responsible for furnishing the report, for receiving and disbursing the money and in general for the conduct of the research.

VIII. By accepting a Grant an applicant comes under an obligation to pursue the programme of research which has been approved, and to send to the Executive Committee a report containing (*a*) a brief statement (not necessarily for publication) showing the results arrived at, or the stage which the inquiry has reached; (*b*) a statement of the expenditure incurred; and (*c*) copies of or references to any papers in which results of the research have been printed.

The Executive Committee expect that in every case the results of the research will be published in some form. Copies of the published records of all work carried out with the aid of a Grant must be forwarded to the Offices of the Trust without delay.

IX. Instruments of permanent value purchased by means of the Grant shall remain the property of the Trust, but at the conclusion of the research, or at such other time as the Executive Committee may determine, they shall be placed under the care and at the disposal of the institution in which the research has been conducted, provided that the Executive Committee may, if they see fit, request their return.

X. All Grants awarded in any year shall date from 1st October, unless expressly stated otherwise.

4. CARNEGIE TEACHING FELLOWSHIPS

The following are the conditions and regulations under which the Scottish Universities are authorised to award Carnegie Teaching Fellowships to persons appointed University Lecturers or Assistants and possessing certain qualifications as research workers, who undertake to devote not less than half their time to research.

I. *The title shall be " Carnegie Teaching Fellowships ".*

II. The Fellowships shall be awarded only to Research workers whose qualifications are at least equivalent to those of Research Fellows, and who are to hold concurrently with their Fellowships University appointments as Lecturers or Assistants.

III. Appointments shall be annual, and shall not normally be renewed beyond a period of three years, and in any case not beyond five years.

IV. The names of those who hold these appointments in each University shall be entered officially in the University Calendar.

V. Each University shall intimate to the Trust, at as early a date as possible, (1) the name and qualifications of those whom they propose to hold appointments as Carnegie Teaching Fellows, (2) the programme of Research, and (3) the nature and extent of the teaching duties to be undertaken. The appointment of Carnegie Teaching Fellows shall be subject to confirmation by the Carnegie Trust, having due regard to these particulars.

VI. Persons holding these Fellowships shall devote not less than half their time to Research.

VII. Carnegie Teaching Fellows shall pursue the specified programme of Research, and shall submit such reports on the progress of their work as the Executive Committee of the Trust may require. It is expected that an account of the results of the Research will be published in some form.

VIII. The annual Grants to the Universities, out of which the proportion of salary borne by the Trust shall be paid, shall be continued for a period of five years, beginning with 1st October, 1937, and shall be as follows : To Glasgow, £1,500 ; to Edinburgh, £1,500 ; to St. Andrews, £1,200 ; to Aberdeen, £1,200. Any credit balance unexpended by a University, not exceeding £300, and any debit balance not exceeding £300, from one year shall be carried forward to the next until the period of five years has expired.

IX. Each University shall report annually in detail the manner in which the said Grants have been expended.

X. Awards shall not be utilised to make up a small salary for a young graduate entrusted with University teaching of minor importance. The salary for Carnegie Teaching Fellows shall be determined by the University concerned, and shall in no case be less than £350.

XI. The proportion of the salary to be borne by the Trust shall not exceed one-half.

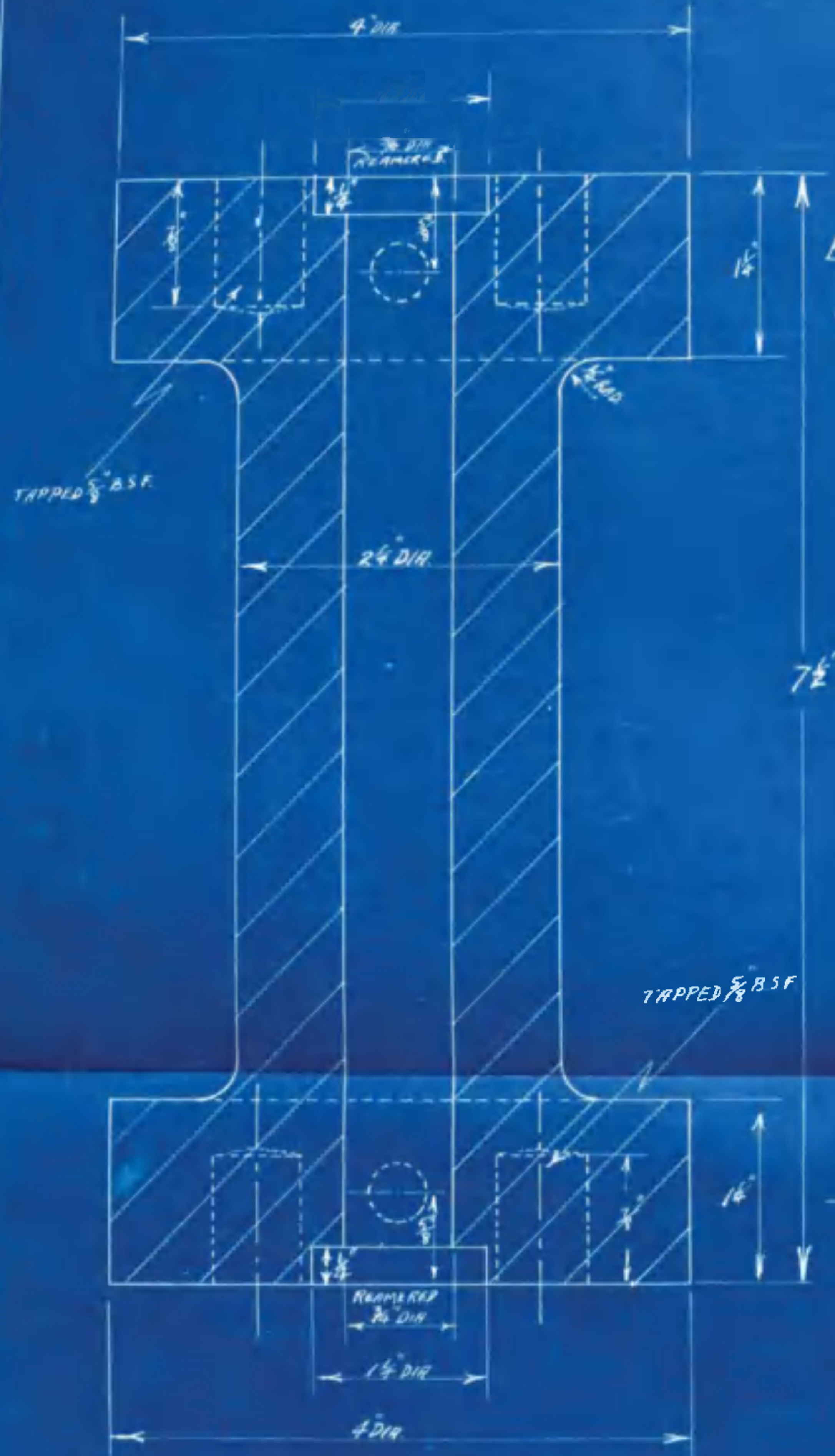
XII. The advantages of the Scheme shall be available in all subjects admitted for Fellowships, Scholarships and Grants.

BURSARIES, SCHOLARSHIPS, FELLOWSHIPS AND PRIZES

FIG. 52A,

H.P. PRODUCT RECEIVER.

H.P. PRODUCT RECEIVER (COVERS REMOVED)

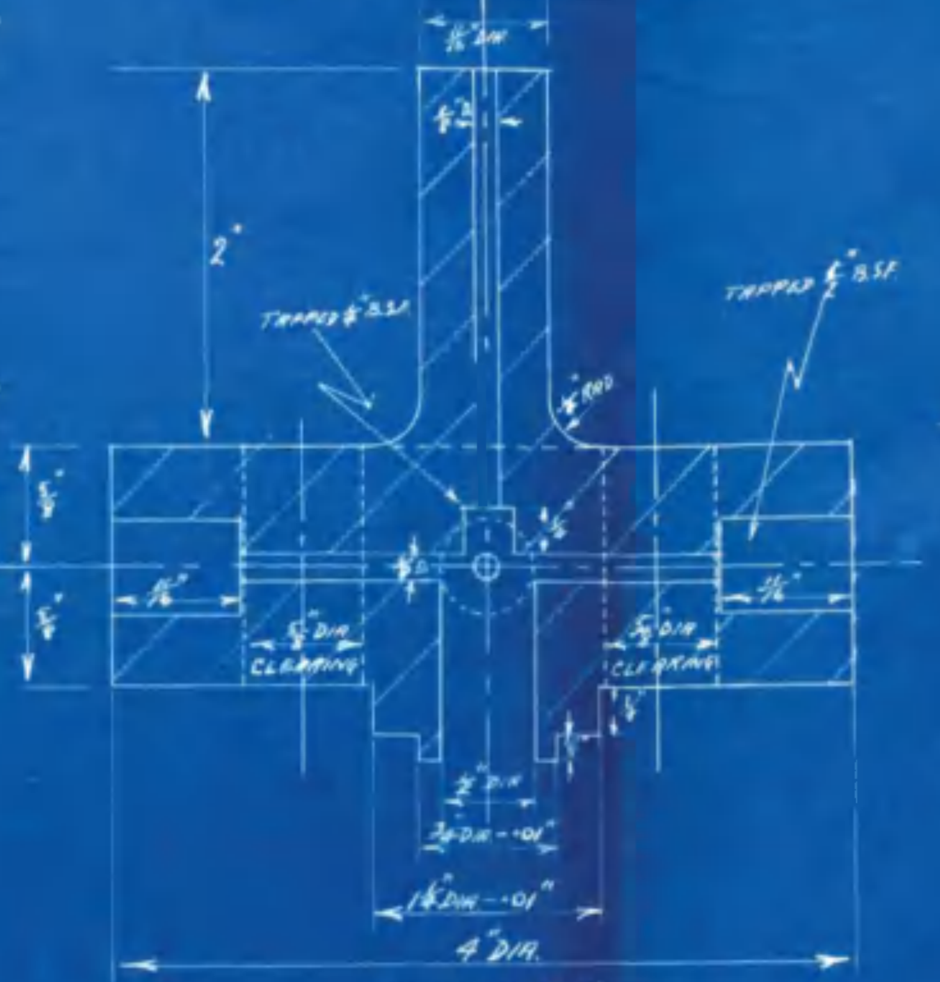


SECTION ON AA′

NOTE ALL JOINTS ARE COPPER-WASHER TYPE.

TOP OF H.P. PRODUCT RECEIVER (COVERS REMOVED)

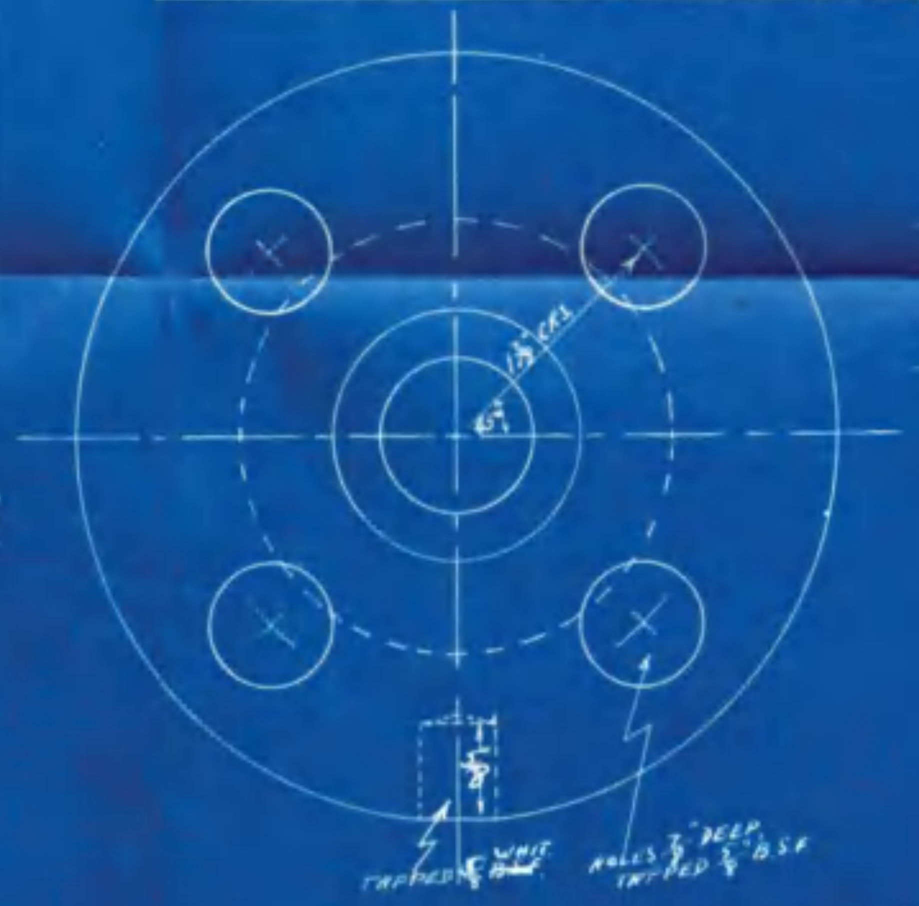
TOP COVER OF H.P. PROD. RECR.



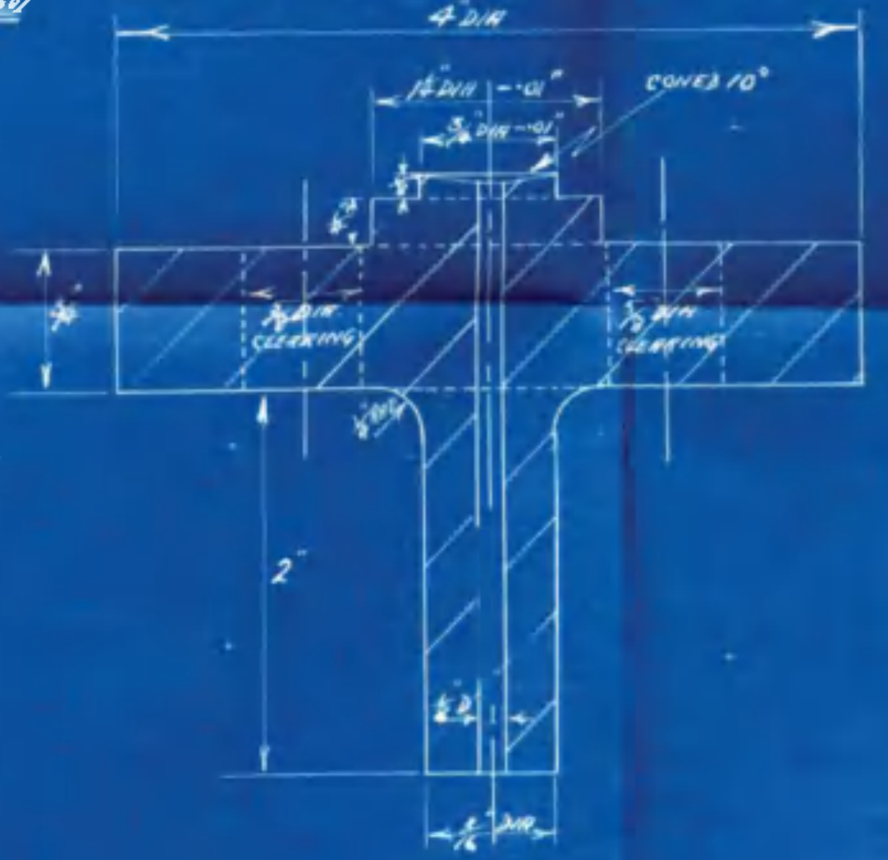
SECTION ON BB′

TOP COVER OF H.P. PROD. RECR.

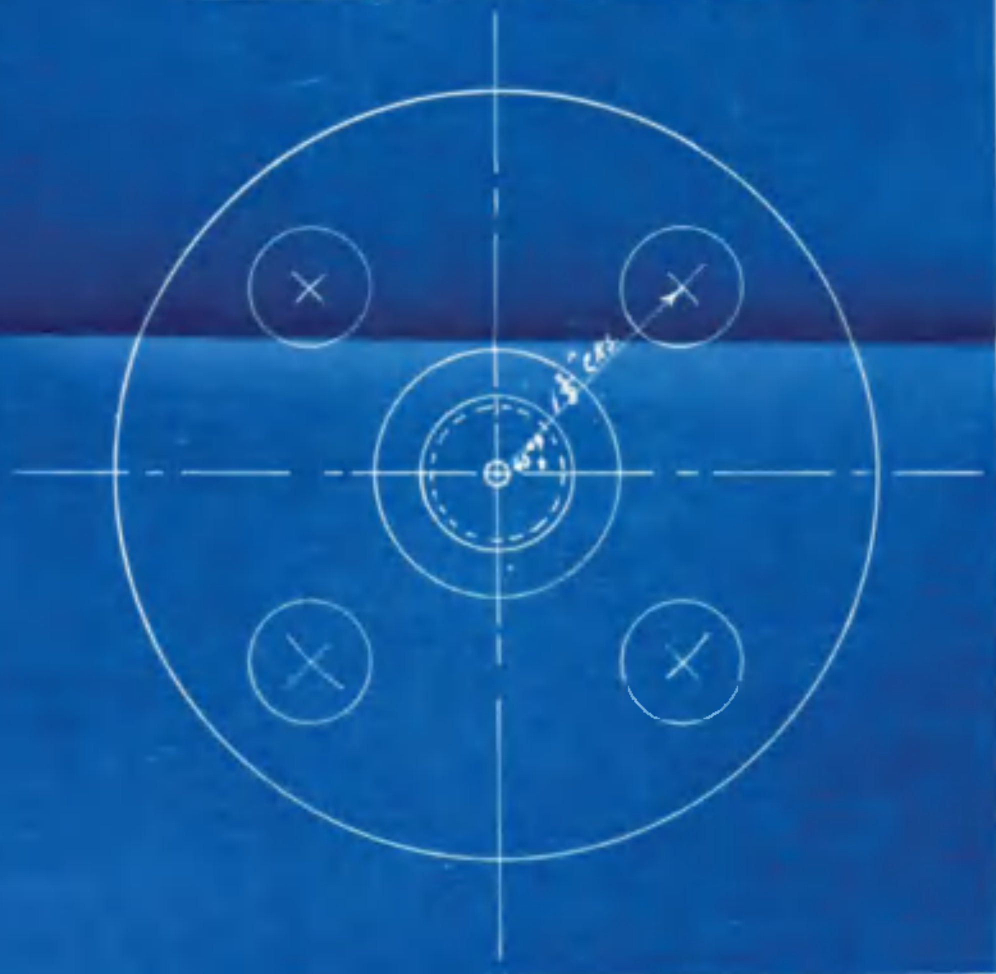
BOTTOM OF H.P. PRODUCT RECEIVER (COVER REMOVED)



BOTTOM COVER OF H.P. PROD. RECR.



BOTTOM COVER OF H.P. PROD. RECR. (PLAN).

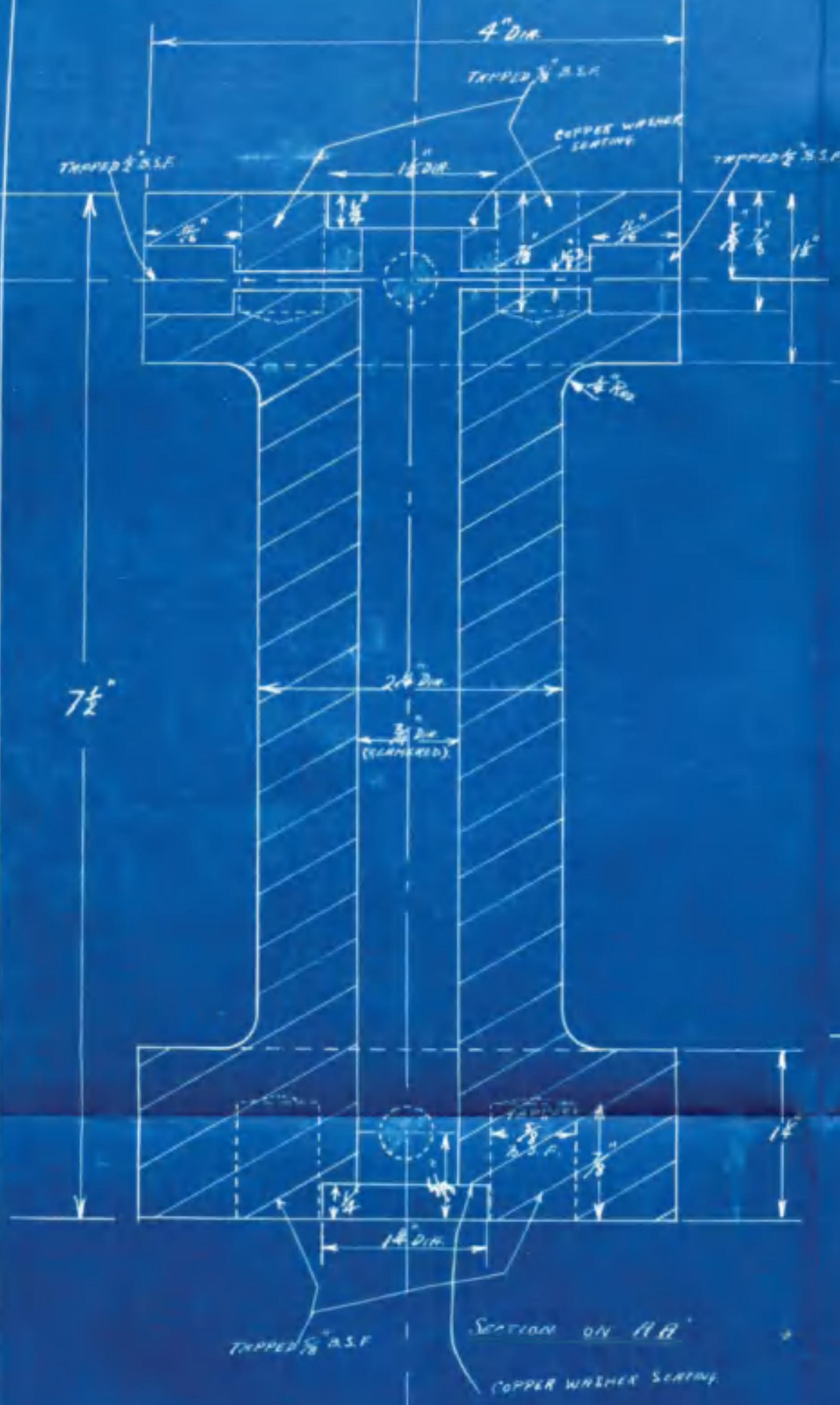


FULL SIZE.

ALEX H. ROY
TECH CHEM DEPT
ROYAL TECHNICAL COLLEGE
GLASGOW
19/6/39.

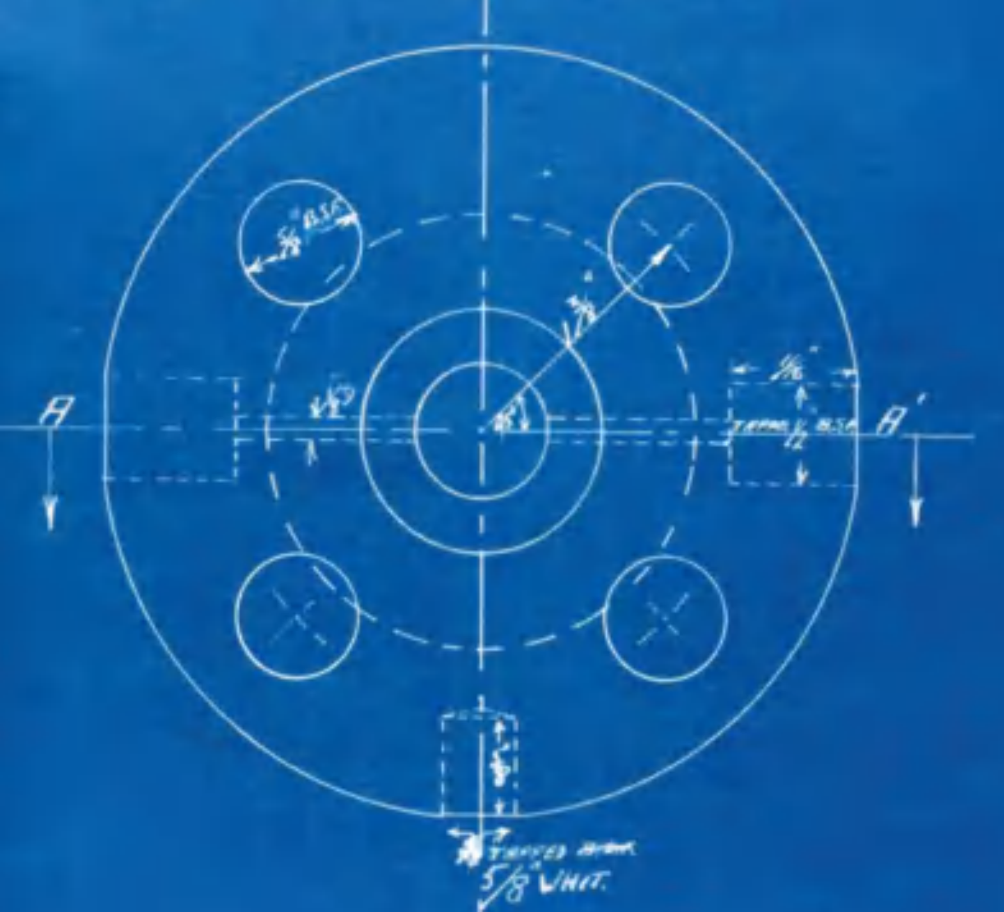
FIG. 48 A,
REACTION VESSEL.

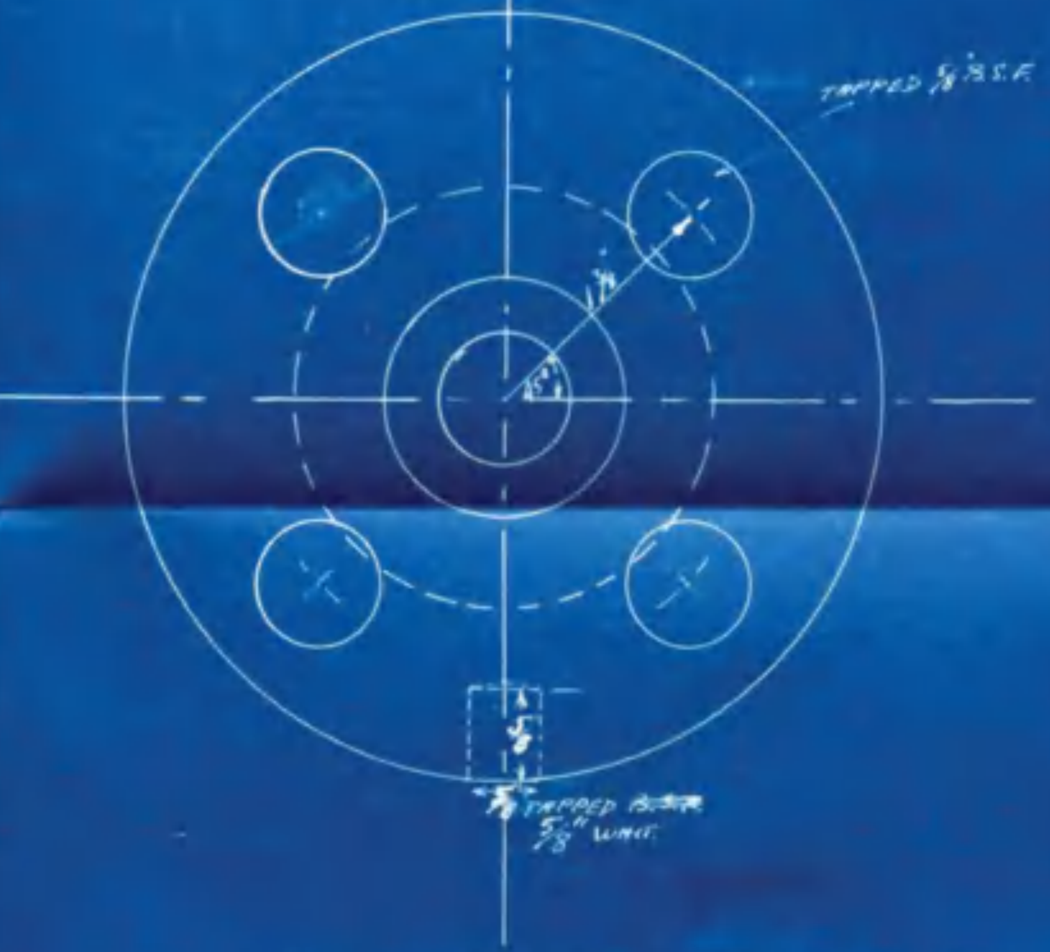
REACTION VESSEL (COVERS REMOVED).



REACTION VESSEL (COVERS REMOVED).

TOP OF REACTION VESSEL (COVER REMOVED)

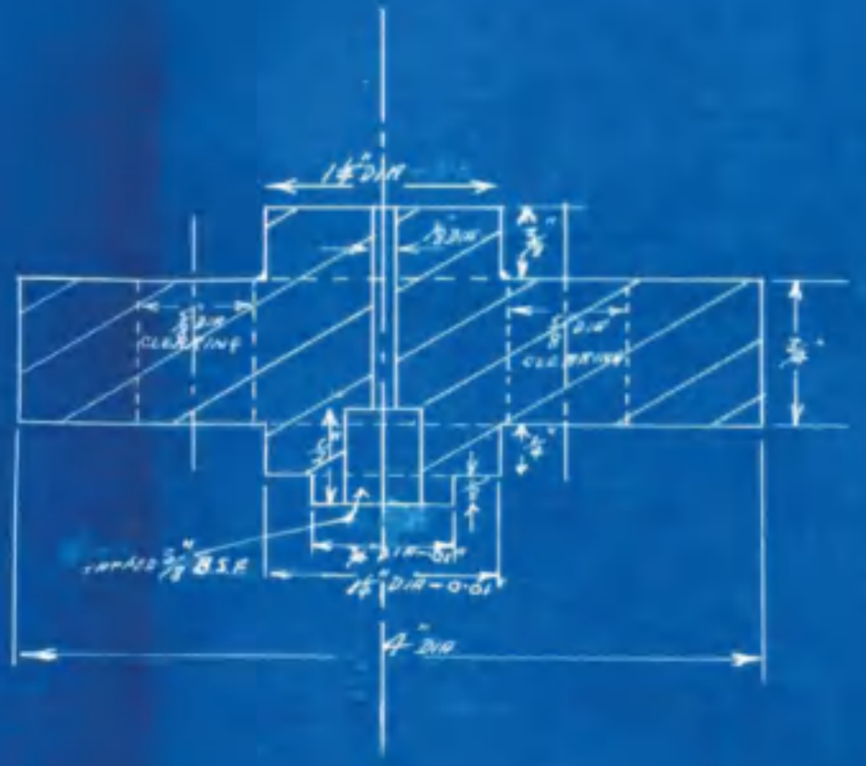




BOTTOM OF REACTION VESSEL (COVER REMOVED)

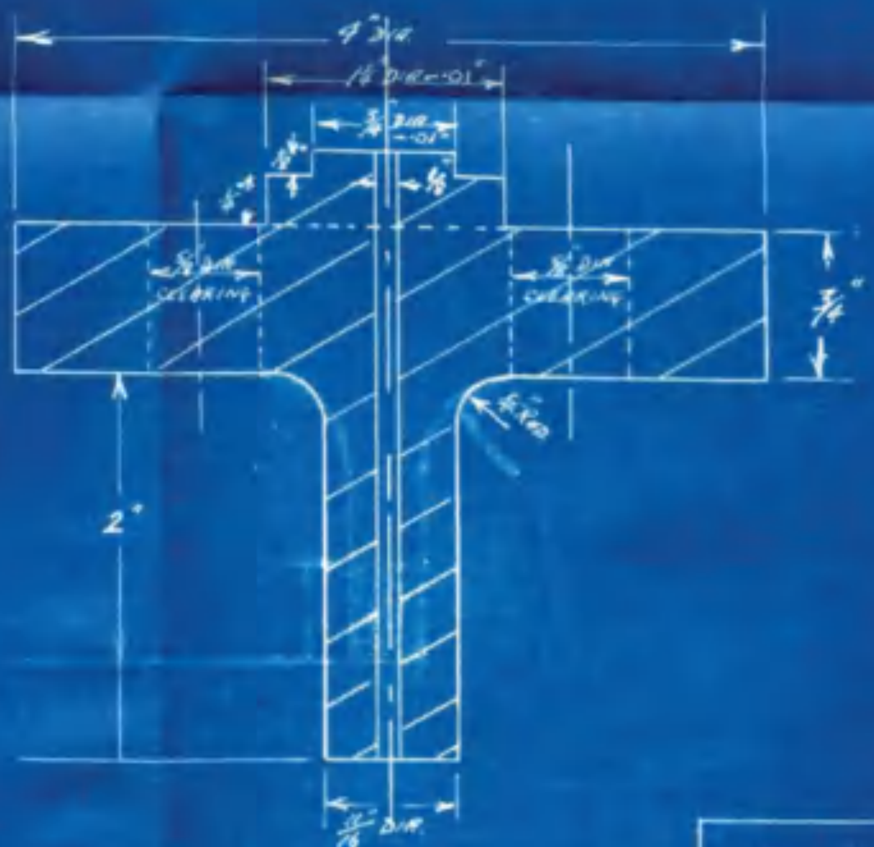
FULL SIZE.

TOP COVER OF REACTION VESSEL.



NOTE ALL JOINTS ARE COPPER WASHER TYPE.

[illegible] REACTION VESSEL



ALEX K ROY
TECH CHEM DEPT
ROYAL TECHNICAL COLLEGE,
10/5/10 GLASGOW