INTERACTION BETWEEN CARBON-DIOXIDE AND HYDROGEN WITH PROMOTED METALLIC SURFACES

by

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RESUME.

The interaction between carbon dioxide and hydrogen was studied in presence of nickel and nickel thoria catalysts at atmospheric pressure and at elevated pressures of the order of 150 lbs. per sq.inch. In part I, the reaction is studied at atmospheric pressure with nickel thoria catalyst. The preparation of the catalyst is described in detail in Chapter I. The description of apparatus employed, reduction of the catalyst, and experimental procedure are dealt with in the following chapters. In chapter V, the results and discussion of the results are given. Here, the method of calculation for a run is shown. Experiments were carried out by varying the partial pressure of both the components. Equations from kinetics of heterogeneous reactions are applied to interpret the results and it is found that both the gases are adsorbed on the catalyst surface. The trend of results obtained by keeping the partial pressure of one component constant and varying that of the other suggests that reaction takes place by the interaction between adsorbed molecules of carbon dioxide and hydrogen. Results when plotted on log log graph showed that diffusion of neither reactants nor products through a gaseous film seem to exert any great influence on the rate of reaction.

In part II, nickel catalyst was employed. The apparatus employed, experimental procedure, and method of calculation are all the same as that in nickel thoria section. The reaction is studied first by keeping the partial pressure of hydrogen constant/

constant and varying that of carbon dioxide and then by keeping partial pressure of CO_2 constant and varying that of H_2. The results suggest the same sort of mechanism as in nickel thoria catalyst.

In section B, part II, a method is presented to determine the most plausible mechanism out of a number of postulated mechanisms. The complete derivation of the equation for one of the mechanisms is shown and the method of analysis using experimental results also is illustrated. A final equation is recommended for the hydrogenation of carbon-dioxide at atmospheric pressure in presence of nickel catalyst.

In part III, the reaction is studied at elevated pressures using nickel and nickel thoria catalysts. The general layout of the plant and a detailed description of the parts are given in Chapter I. In the next chapter is described the operation of the plant. The results are discussed in chapter III. The calculations for a run are shown. The effect of pressure on yield through its effect on the density etc. is discussed. The trend of results point out to the same conclusion as that arrived at under reaction at atmospheric pressure.

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Introductory Section.

Part I.

Part II.

Part III.

Elevated Pressure Reactions.

GENERAL INTRODUCTION.

An ordinary chemical equation gives only the final result of change in composition suffered by two or more elements or compounds when they react with each other to produce the change. Thus the equation:-

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

suggest that four molecules of hydrogen react with one molecule of carbon dioxide to form one molecule of methane and two molecules of water. The effect of pressure or temperature changes on the system can be predicted, but the equation does not show what exactly is the mechanism involved in the transformation of carbon dioxide to methane. A knowledge of mechanism is of paramount importance in the full understanding of a reaction. Only in this way is it possible to suggest modifications of an accepted method which may be of great industrial importance.

In the present work an attempt is made to study the mechanism of reaction between carbon dioxide and hydrogen using nickel and nickel thoria catalysts.

CATALYSIS: GENERAL SURVEY.

The potentialities of the application of catalytic methods in industry were foreseen by Ostwald when he prophesied that a scientific knowledge of control of catalytic phenomena would lead to great industrial development. This prophesy has been fulfilled and to-day problems associated with catalysis are of far reaching and fundamental importance.

The fact that chemical action between two or more given compounds may be influenced by the presence of a relatively small quantity of an extraneous substance was recognised very early in the development of chemical theory. Berzelius in 1836 first termed it "Catalytic force". A catalyst was defined as a substance which in minimal amounts will bring about the transformation of large quantities of the reacting substances and will be found unchanged in chemical composition at the end of the reaction. This does not imply that the physical state of the catalyst remains unaltered, for it is known for example that platinum wire actually does change during catalytic oxidation and becomes pitted or spongy.

A catalyst is generally supposed to modify the velocity of two inverse reactions to the same degree and, therefore, does/

does not affect the final stage of equilibrium in any given chemical system. The normal mode of action of a catalyst is the acceleration of a reaction "positive catalysis". Sometimes the reaction itself develops substances which themselves accelerate the reaction and then the process is called "auto catalysis". The terms "negative catalysis" (or retardation) and "auto-retardation" may be readily understood as the reverse of the processes. "Promoters" are substances which by admixture with the catalysts enhance its positive catalytic effect. "Catalytic poisons" are substances which reduce the activity of solid catalysts. "Carriers" are porous materials like pumice etc. which when impregnated with the catalyst afford it a greater surface per unit of bulk.

The functions which a catalyst may perform depend upon the nature and complexity of the reactions involved. These functions may be grouped under two broad headings: (1) increasing the rate of a given reaction or, as is usually the case, a lowering of the temperature at which a reaction will occur at a desirable rate, and (2) direction of reaction along a particular path when several are possible. The distinction between the two functions is not sharp since a catalyst may perform both functions: such a catalyst is called a "selective catalyst".

The/

The energy contribution of a catalyst to a reacting chemical system is zero, since the catalyst emerges from the system without loss or chemical change and is capable of inducing changes in an indefinite quantity of reactants. Therefore a catalyst influences the rate of both forward and reverse reactions in a balanced system equally. This has been proved experimentally and has been used in the selection of proper catalysts for a given reaction. Lemoine (1) for example, showed that in the system

$$H_2 + I_2 = 2HI$$

the same equilibrium was reached from both directions for all temperatures in presence of platinum catalyst. Catalysts for the synthesis of methyl alcohol can be chosen on the basis of activity in its decomposition(2).

With regard to the second function, Sabatier and Mailhe (3) showed that the route over which a reaction travelled depended upon the presence of a certain catalyst. Thus ethanol decomposes in two ways.

$$C_2H_5OH = C_2H_4 + H_2O$$
$$C_2H_5OH = CH_3CHO + H_2$$

Thoria catalyses the first reaction almost exclusively; while with/

with silver or copper the second occurs practically alone. This ability of a catalyst to direct a reaction over a certain route is due to selective influence in accelerating the rate of a single reaction out of a number of competing types. This does not mean that the final equilibria in the system are in any way affected but that relative rates of reactions are preferentially altered.

HETEROGENEOUS CATALYSIS.

The great majority of catalytic reactions that are in use in industrial processes are those where gaseous or liquid materials react on solid catalysts. This is one type of heterogeneous catalysis. In these cases theoretical considerations based on Laws of Mass action do not apply in the same way as in homogeneous catalysis. In homogeneous catalysis the catalyst tends to act by its mass, and in many cases the velocity coefficient varies directly as the catalyst concentraction; values for velocity coefficient may be obtained and these provide an accurate basis for estimating the relative activity of the catalyst in question.

However, in heterogeneous catalysis where the catalyst cannot be in a true admixture with the reactants, it is impossible to apply reaction velocity formula. It is known that other factors than the law of mass action control velocity of/

of reaction. Bone and Wheeler for example (4) have proved this by carrying out experiments on the system $2H_2 + O_2 = 2H_2O$. The operation of the law of mass action is completely masked since it is impossible to determine the concentration of the reactants and products at the actual zone of interaction on the catalytic surface.

The kinetics of heterogeneous catalytic reactions are complicated by the composite nature of the total process involved. There are many factors which contribute to the continuity of the change. Firstly, it is dependent on an adequate supply of reactants at the catalytic surface and on the removal of the resultants. Secondly, it depends on the rate at which the product can disengage and diffuse from the catalyst surface. This factor is very important since, if the products were not removed from the active surface, it would become poisoned and further reaction would stop due to the impossibility of any reactants reaching the surface. Thirdly, if reaction is to take place, the adsorbed molecule must possess at least a certain minimum energy, and be adsorbed at an area which possesses sufficient free energy - together with that possessed by the molecule - to cause activation, (4).

With a given reaction mixture and catalyst, the rate of heterogeneous reaction will be directly proportional to area of active catalyst surface exposed, whereas the rate of homogeneous reaction by its very nature will be independent of surface area (5). In heterogeneous reactions the character of the surface of the material used as the catalyst is a very critical factor in determining the activity. Because of this sensitivity, it is very difficult to prepare two batches of same catalysts of the same activity. The method of preparation and treatment prior to use go a long way in determining activity.

First attempts to understand the mechanism of contact catalysis (gas-solid interphase) were concerned with adsorption. At the surface of a solid, forces exist of the same order of magnitude and variety as those which are responsible for holding the atoms together in a compact mass. These factors are responsible for the adsorption of gases and vapours at the catalytic surface. Therefore, as a consequence of adsorption of the gases by the catalyst, a layer is formed in which the reactants are at a higher concentration than in the bulk of the gas. There were at first doubts as to the thickness of the layer, but a much clearer outlook has been obtained as the result of Langmuir's work. He suggested (6) that the adsorption on a solid surface involves forces similar to those concerned in chemical valency and that since such forces are exerted over distances of/

of the order of 2 - 3 x 10^{-8} cms. only a unimolecular layer of adsorbed gas will form. This view is now widely accepted for adsorption at low pressures or at moderately high temperatures. However, the adsorbed molecules can hold other gas molecules by Van der Waals forces, so that multimolecular layers are possible; this seems to occur only at relatively low temperatures and at pressures approaching the saturation value.

Adsorption takes place in different ways and these are classified into three main divisions (1) purely physical or Van der Waals adsorption (2) physical-chemical or activated adsorption and (3) purely chemical or chemisorption.

(1) Van der Waals adsorption.

This is a term applied to the fully reversible adsorption of a gas or vapour due to weak physical forces which attains equilibrium very soon. It does not bring about the dissociation of the adsorbed molecule. It occurs at relatively low temperatures and decreases with temperature rise.

Adsorption in these cases is regarded simply as an accumulation of the gas at the surface of the catalyst and increase in activity is assumed to be due to an increase in velocity of reaction arising from an increase in concentration of one or more of the reactants at the surface and hence a greater probability of collision. If this is true, catalytic activity/

activity should vary directly with adsorption. Exhaustive investigations on this aspect of the subject were made.

(a) The results of McBain (7) and other investigators on the amount of different gases adsorbed by one gm. of activated charcoal when compared with their respective critical temperatures suggest that the most easily liquefiable gases are the most readily adsorbed. When dealing with gases that are most easily liquefiable, the adsorbed layer may be more than one molecule thick (8) for at this stage there are attractive forces between the molecules of the gas themselves, which will enable thicker layers to be built up. Therefore in dealing with gases that are readily liquefiable one should expect greater adsorption and hence greater catalytic activity. The results however show that this is true only in certain cases.

(b) An adsorbent should not show specific adsorption for different gases and so the catalytic activity should remain the same. Here the exact opposite had been noted so frequently that selective adsorption seems to be a rule rather than an exception so that the catalytic activity varies for different gases.

(c) The affinity of the adsorbent for the adsorbed would be of the nature of mass for mass and so would be unaffected by the presence of minute quantities of foreign substances/

substances, and thus the catalytic activity should also be unaffected by their presence. This too is not in accordance with actual facts of experiments. Other deductions are also equally untenable and therefore it is reasonable to conclude that the mechanism of catalysis cannot be fully accounted for on the basis of purely physical adsorption.

(2) Activated adsorption.

Without wholly discarding the above conceptions, a second group of scientists like Taylor and others proceed to explain adsorption on a physical chemical basis. They suppose that the surface attraction of the catalyst on one or more of the reactants is not merely a mass for mass attraction, but that some sort of loose chemical reaction is also involved.

Activated adsorption takes place at a higher temperature than the Van der Waals; reaches equilibrium much more slowly, and has a velocity characterised by a temperature coefficient from which an apparent energy of activation can be calculated. It is reversible only by the combined effects of pressure and temperature changes.

The difference in catalytic activity due to different conditions of physical aggregation of the surface of a catalyst is generally conceded by this school of thought to be due to difference/

difference in the number and degree of unsaturated fields of force. This fact is supported by experimental evidence on certain lines. Palmer and Constable (9) consider that the solution of the problem lies in the orientation of the surface atoms and in this way attempt to explain the difference in activity due to different methods of preparation. Another theory explains the difference in activation as due to differences in the actual distances which exist between active atoms, which would depend on the size of molecular pores. This theory is supported by a large number of experimental results. For example Adkins (10) studied the catalytic effect of alumina prepared by different methods on the reaction:-

$$2CH_3COOC_2H_5 \xrightarrow{Al_2O_3} (CH_3)_2CO + 2C_2H_4 + CO_2 + H_2O$$

He used eleven varieties of alumina and showed that the velocity varied, being greatest in case of alumina (particle size 4^{-7}cms) prepared by heating hydrated alumina obtained from water and aluminum amalgam, and least in case of alumina (particle size 8^{-6}cms) prepared from the branched chain isopropyl alkoxides. Frolich (11) attributed the difference in catalytic activity to the internal crystalline structure of the catalyst.

A/

A gradually increasing weight of evidence as to the lack of uniformity of the catalytic surface led Taylor (12) to put forward the idea of active centres, that is to say, specific limited parts of the surface which have a very high activity. The distribution of such centres is pictured in terms of peaks and valleys. The atoms in these parts were imagined to be very loosely attached to the bulk of the catalyst so that their valency bonds were not completely satisfied. In support of such views he cited the following facts:

(1) The catalyst surface is sensitive to heat, so sintres and loses activity at temperatures below normal melting point of the compound. Schwab and Martin (13) found ammonia is unchanged by contact with zinc, antimony, or cadmium at their melting points.

(2) The surface is often poisoned by very small concentrations of an impurity.

(3) The adsorption of different gases is affected to varying degrees by the same poison.

(4) Chemical combination takes place between the catalyst and a gas under conditions where the massive component would not react.

(5) The heat of adsorption of a gas on the catalyst is not uniform. Garner and Kingman (14) found that the heats of/

of adsorption of hydrogen and carbon monoxide in contact with zinc oxide, or chromium oxide are not uniform.

(6) The heat of activation of adsorption on the surface is not uniform. The results of Taylor and Sickman (15) for the adsorption of hydrogen on zinc oxide serve as an example of this phenomenon.

(7) Different parts of the surface are involved in specific reactions as emphasised by Hoover and Rideal (25).

(8) Saturation capacity of certain metals for hydrogen varies with temperature indicating that the number of spaces that could be occupied by gas molecules are less at high temperatures than at low temperatures.

A modified view concerning the location of activity in the catalyst has been expressed by Schwab and Pietsch (16-18) in which the active centres of Taylor's theory are replaced by phase boundaries. That is to say, reaction will take place mainly on a series of lines in the catalyst and this is known as "Adlineation Theory". The following facts are cited in support of this theory:-

(1) There is ample experimental evidence for the preferential adsorption of ions on crystal edges.

(2) Pietsch (19) and others have demonstrated the fact that reaction on crystal surfaces occurs at linear discontinuities of the solid. These two examples may not be strictly/

strictly comparable with gas-solid system, but illustrate the point in a qualitative manner.

(3) Extensive calculations as to the results to be expected on the assumption of this theory have shown the equations derived therefrom are in good agreement with experimental data.

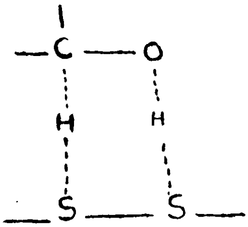
(4) The examination of the behaviour of zinc oxide - ferric oxide mixtures by Hüttig, Tschakert, and Kittel (20) lends support to this theory. They heated equimolecular amounts of the two oxides to different temperatures and determined the activity of the products for the decomposition of nitrous oxide. Increased catalytic activity was observed and was shown to coincide with incipient appearance of a new phase.

(5) Maxted's observations (21) on the linear effect of poisons on catalyst activity are compatible with Schwab's adlineation theory.

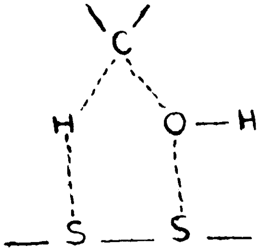
A further development of the concept of active centres is the "Multiple adsorption" theory suggested by R.E. Burk in 1926 (22) and in 1929 by A.A. Balandin (23) and by others. According to this theory; it is supposed that the molecule is activated only when it is adsorbed at two or more of the active centres, so that a direct strain is produced in a particular bond or bonds. This hypothesis provides an interpretation/

interpretation of the alternative modes of decomposition of substances such as alcohols and formic acid vapour according to the spacing of the active centres, and other properties, of the catalytic surface. Two simple types of attachments can be postulated, namely,

(a)



(b)



where S represents the active centres, which are not necessarily identical. In case (a) which would represent the behaviour on a dehydrogenation catalyst, it is evident that removal of two atoms of hydrogen would be favoured; in case (b) the reaction would clearly be dehydration. Evidence for the theory that a particular part of an alcohol molecule must be attached to the surface for it to be activated, is provided by the work of W.G. Palmer and F.H. Constable (24) on the dehydrogenation of alcohols on a copper catalyst. They found that the rate of decomposition of the primary alcohol on a given catalyst at a definite temperature is independent of the hydrocarbon chain length. The activation energy of the reaction is also the same for the different alcohols.

(3)/

(3) Chemisorption.

In the preceding discussions it will be noted that while the idea of chemical attraction has been introduced to explain selective adsorption, no attempt has been made to define the chemical character of any of the combinations that result from the union of the catalyst and the reactants. So another school of thought attempts to define the nature of addition products by the so called chemisorption. This takes place at high velocities when a gas reacts with a solid to form a surface compound which has a very considerable stability. The bonds formed between the material of the surface and the adsorbed gas are thus almost as strong as those existing in stable stoichiometric compounds. "Chemisorption" may thus be defined as a process involving the greater part of the surface of a solid by which a new solid surface is formed at a very high velocity with a very high collision efficiency, this new substance having considerable stability at temperatures higher than those at which it is formed and under low pressures. Chemisorption will not produce a higher catalytic activity except when a second component in the gas phase reacts with the chemisorbed component easily and without itself being adsorbed. Thus chemisorption frequently accounts for catalyst poisoning.

A falling off in catalytic activity during use was observed/

observed by the earliest investigators and has led to the recognition of catalyst "poisons". Poisoning may be due to the presence of impurities in the catalyst which gradually impair its properties, or to impurities in the reactants, or to secondary, or side reactions which produce substances depositing on, or reacting with the catalyst. In any case, the effect may be permanent or transitory. The specific nature of poisoning was emphasised by Hoover and Rideal (25). Small amounts of chloroform check dehydrogenation of ethyl alcohol to aldehyde, but accelerate the dehydration to ethylene over a thoria catalyst. This suggests that different parts of the catalyst surface are concerned with the alternative reactions.

The mechanism of poisoning is obscure and probably varies with the catalyst as well as the poisons. It has long been appreciated that very small concentrations of poisons had a marked effect on the surface of the catalyst. Vavon and Husson (26) showed that there could be progressive poisoning resulting finally in complete supression of activity. Later investigations by Maxted (27-30) showed that the effect of the first additions of the poison was considerably larger than that of the final amounts. The activity first decreases at a rate which is a linear function of poison concentration, but addition beyond a certain amount gave much smaller effects and complete suppression of activity is seldom attained. The activity of any particular poison may be expressed as a poisoning coefficient α which is given by the relation

$$K_c = K_o(1 - \alpha C)$$

where K_c = reaction velocity constant in presence of a concentration C of poison and

where K_o = reaction velocity constant in absence of poison.

An interpretation of Maxted's results by Herington and Rideal (31) shows that the character of the poisoning curve (relative activity plotted against milligrams of poison) for a set of completely uniform sites of catalytic activity would be expected to change from a simple straight line when the reactant is a small molecule occupying a single site on the surface, to a curve for reactants of larger molecules that would occupy more than one active site. A surface saturated with large "poison" molecules will still contain gaps large enough to adsorb small reactant molecules so that certain types of reaction would still go on. This reasoning suggests that catalytic activity resides in the presence of a number of active centres on the catalyst surface.

Retardation is the suppression of catalytic activity by means of either reactants or reaction products and should not be/

be confused with poisoning. It has been suggested that poisoning may be regarded as due to chemisorption on the catalyst, while retardation is due to activated adsorption. Chemisorption leads to the formation of a surface completely lacking the catalytic properties, while activated adsorption prevents adsorption of one or more reactants by covering in a physical sense all or part of the effective surface.

A promoter is a compound which can increase the activity of a given catalyst which by itself is inert or of negligible activity in the reaction concerned. When the activity - promoter concentration curve rises to a sharp maximum very sharply and then falls steeply again; graph (a), unlike graph (b), the case is supposed to be one of true promoter action.

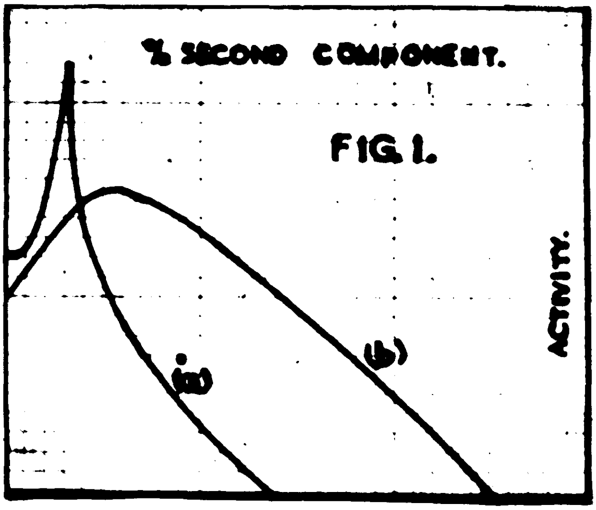


FIG. 1.

It is possible that the first action of a promoter may be a lowering of the activity when a process involving two reactants/

reactants is in question. If the first additions of promoter increase the adsorption of one reactant so strongly that it causes retardation of reaction, then the mixed catalyst will be at first less effective than that of the catalyst itself. The further addition of promoter, however, may then restore the balance of adsorption of both reactants and lead to a pronounced increase in activity of the catalyst.

For the decomposition of hexane, Griffith (32) found that in case of an oxide promoter, the optimum promoter concentration is a function of the catalyst and not of the promoter. Although the atomic ratio of promoter to catalyst was constant for maximum effect, actual rate at this maximum varied with the promoter. Another fact of importance revealed during this investigation is that the addition of a second promoter to a mixture already containing the optimum amount of a first promoter, would lead to a lowering of activity. The decomposition of hexane concerns a reaction involving a single type of molecule. In cases where there are two types of molecules, the results are different. Under these conditions the optimum concentration varies with change in promoter. Again the concentration required is different from the previous values on the similar catalysts.

It is not possible to give the mechanism of promoter action in a single explanation. H.S. Taylor (33) as a result of/

of his studies on nickel thoria catalysts in the reduction of carbon monoxide suggested that a promoter acted in three different ways (1) by supporting existing active centres (2) by creating additional active surface and (3) by altering the proportions in which the reactants and reaction products were adsorbed.

A promoter does not generally affect crystal structure of catalyst. After detailed X-ray work, Wagner and Staeger (34) showed that no change in crystal structure occurred when an increase in catalytic activity was observed. In certain cases there is a striking relation between crystal structure and catalytic activity, but this is due to compound formation.

In certain cases the promoter prevents the decay of the catalyst. This was shown by Appleby (35) studying the promoter action of the oxides, especially alumina, in iron catalysts used for ammonia synthesis. It was found that iron by itself is an active catalyst but rapidly loses its efficiency, and that the promoter prevents this decay.

The effect of promoters may be considered in the light of the two alternative theories of catalysis, the "active centre" theory and the "adlineation" theory. In the case of active centres the promoter may be expected to function either by increasing the number of these or by preventing their coalescence. The former possibility is excluded by results obtained/

obtained in carrier action. There are three alternative functions in carrier action. Curve A (Figure 2) shows the simplest function in which straight dilution occurs. The activity of the catalyst may, however, remain unaltered by the addition of quite large amounts of carrier, until it eventually falls as indicated in curve B; this may be termed delayed dilution. Sometimes addition of a carrier leads to a rise in activity, as represented by Curve C, and is due to prevention of physical or chemical changes which would otherwise lead to a lowering of the catalytic activity.

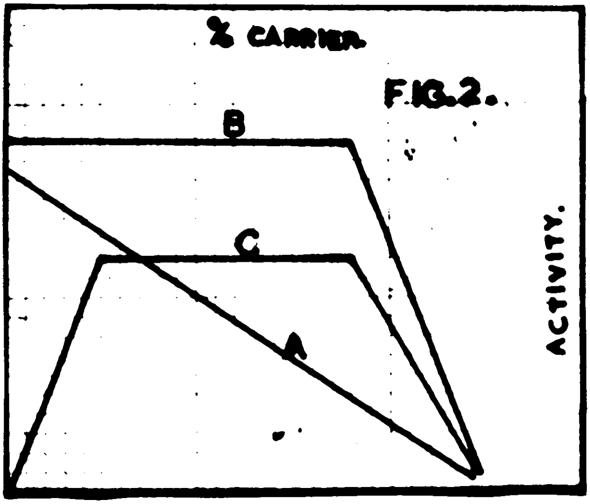


FIG.2.

The difference between delayed dilution and instant dilution must lie in the fact that some catalysts contain very large numbers of active centres while others have relatively few. Therefore, if a promoter increased the number of active centres it/

it would be expected that the dilution effect, on addition of an inert carrier, would occur at a smaller catalyst concentration with the promoted catalyst than it did with one component catalyst. This was investigated with chromium oxide-silica catalysts and magnesia as carrier using dehydrogenation of dekalin as the reaction. The results showed that the promoter has not increased the number of active centres (36-38). Hence, two types of promoter action must exist if active centres are responsible for catalytic effects. In one, the promoter functions by creating a new type of active centre where the energy of activation is materially lower than is the case with simple catalyst. In the other, the promoter merely preserves an existing point of high activity.

The action of promoters on the basis of adlineation would be due to an increase in interphase boundaries on the addition of the second component; this is equal to an increase in the active area of the surface, which has been already shown not to occur. If, on the other hand, the optimum quantity of promoter is determined by its solubility (the capacity for actual entry into the crystal lattice) in the main catalyst, there might be a decrease in the number of active centres simultaneously with a change in their quality.

Thus the promoter activity may be due to three distinct causes/

causes (1) Interaction between the two components leads to the separation of a new phase with a higher activity (2) The growth of crystals of the active catalyst is prevented by admixture of an inert material (3) The creation of a new type of active centre but by a mechanism quite different from compound formation.

Conclusion.

The precise nature of activation is not fully understood, yet all recent experimental work on catalysis leads back to ideas closely approaching the old intermediate compound theory and gives stronger support to the view that valency forces are involved in activated adsorption. There appears to be no reason to abandon the concepts of active parts of the catalyst having specific adsorptive effects. Application of existing methods of study of kinetics and of energy relations might clear up the various points that are still obscure.

FUNCTION OF CATALYST IN PRESENT WORK.

For the study of the reaction between carbon dioxide and hydrogen to form methane, the catalysts used here are nickel and nickel thoria. It is known that nickel catalyses hydrogenation and dehydrogenation and adsorbs hydrogen strongly. So the possible mechanism may be, that hydrogn is adsorbed on the catalyst by activated adsorption, and the carbon dioxide then diffuses through a stagnant film of the reacting gases and reacts with the adsorbed hydrogen to form methane. This methane is then desorbed leaving the active spots to adsorb fresh hydrogen and the cycle is repeated. The desorption of methane might be the controlling step. Or the mechanism could be that both carbon dioxide and hydrogen are adsorbed on the catalyst surface. Interaction of the adjacently adsorbed carbon dioxide and hydrogen molecules may then proceed resulting in the formation of methane. In this case surface reaction might be the rate controlling step. Chemisorption of carbondioxide could play a part. Oxygen of a carbon dioxide molecule might be removed by hydrogen molecules and result in surface carbide formation. This carbide when reacts with hydrogen will give rise to methylene radicals which by combination with excess hydrogen produce methane. Here the oxygen removal could be the rate controlling factor. Or, an intermediate compound like methanol is formed, which on/

on dehydration gives methylene radicals and then methane as before.

From the equation: $CO_2 + 4H_2 = CH_4 + 2H_2O$, it is seen that water is one of the products of the reaction. According to Le Chatelier's principle, the effective removal of water would shift the equilibrium and more methane would be formed. Nickel has very poor dehydrating property and the addition of thoria which adsorbs moisture very strongly at temperature of reaction should increase the catalytic activity of nickel. Thoria is known to act as a promoter in a nickel thoria catalyst.

A considerable amount of work has been carried out on the mechanism of the promoter action in the nickel thoria catalyst mentioned above. Medsforth (47) considered that promoters like thoria increase the catalytic activity of nickel by effectively adsorbing the water, one of the products of the reaction due to dehydration. To prove this dehydration theory, he classified the functions of the promoters thus:-

(1) The promoter decomposes the intermediate compound formed by the catalyst.

(2) The promoter combines with one of the reacting substances producing a high concentration of the latter upon the surface of the catalyst.

Contrary to Medsforth, Armstrong and Hilditch (39) attribute the accelerating effect of the promoters to the increase/

increase in the active surface of the catalyst and not to the dehydration effect. They illustrate this theory by the increase in the catalytic activity of the nickel promoted by metallic copper. Baxter (40) showed that a small addition of the promoter increases the surface of the catalyst to an appreciable extent. According to Baxter, certain oxides penetrate the interstices of the metallic particles resulting in a less compact surface. This increases the surface and consequently the catalytic activity.

W.W. Russell and H.S. Taylor (41) worked on nickel and nickel thoria catalysts. The conclusions drawn from their results are that, the greater the irregularity of the metal atoms (i.e. the further they are removed from their regular crystal lattice) the greater is the force by which they can hold molecules by adsorption due to the greater valency forces available and hence the greater catalytic activity. The lower the temperature of reduction the more unsaturated are the metal atoms. Molecules of thoria which are more or less electrically neutral act as insulators between the changed metal atoms and prevent coalescence of unsaturated nickel atoms on the surface. This has been confirmed by Wyckoff and Crittenden (42) by X-ray examination. Taylor and Russel also observed that thoria has a specific action of adsorbing CO_2 and this shows the influence which promoter may exert on ratio/

ratio in which reacting gases are adsorbed. Adsorption of hydrogen on either catalyst shows comparatively little change with temperature. Amount of CO_2 adsorbed decreases with temperature rise, but gains by the presence of promoters. Nitrogen is adsorbed to a small extent at 285°C on nickel catalyst and to still smaller amounts on nickel thoria catalyst.

A falling off of the activity of the nickel catalysts has been noted. This could be due to impurities introduced in the preparation of the catalyst, like alkaline impurities which make itself felt gradually. Or there could be sulphur containing vapours or gases in reaction mixture which would poison the catalyst. Water vapour is supposed to have a poisoning effect on nickel catalysts. But the reaction is reversible and so the catalyst could be easily reactivated. Finally, there may be poisoning from side reactions, as in deposition of carbon on nickel. This carbon could come from the decomposition of carbon dioxide thus:

$$CO_2 = CO + C.$$

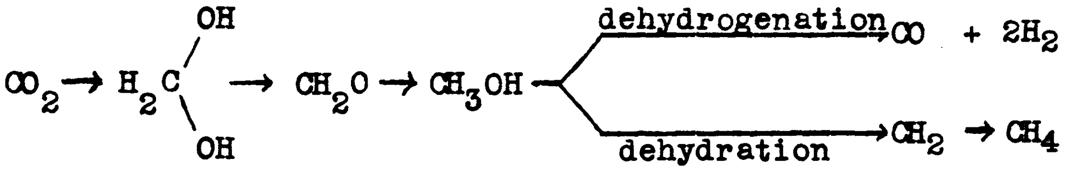
INTERACTION OF CO_2 AND H_2 AND ALLIED CATALYTIC REACTIONS.

A considerable amount of work has been carried out on the mechanism of reaction between carbon monoxide and hydrogen, but relatively little has been done on the mechanism of carbon dioxide and hydrogen reaction. Probably this is because of the waste of hydrogen involved in the hydrogenation of carbon dioxide compared with that of carbon monoxide from an economic view-point.

Perhaps the pioneers in this field are Jahn (43) and Bach (44). They studied the accelerating effect of palladium in the reaction between carbon dioxide and hydrogen. Later Sabatier and Senderens (45) investigated the reaction in presence of finely divided nickel catalyst. They noted that hydrogenation begins at 230°C and is complete at 300°C. Sabatier (46) showed that when hydrogen was present in slight excess (80%) of carbon dioxide excellent yields of methane were obtained.

Medsforth (47) did work on the reduction reaction of both carbon monoxide and carbon dioxide by hydrogen in presence of nickel catalyst accelerated by promoters like cerium, thoria, etc. According to him, an intermediate compound of the methyl alcohol type is formed which is dehydrated/

dehydrated to give methylene radical which is immediately hydrogenated to methane



$$CO_2 \rightarrow H_2C(OH)_2 \rightarrow CH_2O \rightarrow CH_3OH \begin{cases} \xrightarrow{\text{dehydrogenation}} CO + 2H_2 \\ \xrightarrow[\text{dehydration}]{} CH_2 \rightarrow CH_4 \end{cases}$$

This representation also explains the presence of carbon monoxide found in product in small amounts. Probably a simpler step might be:

(a) $Ni + CO_2 + H_2 \rightarrow Ni(HCO.OH) \rightarrow Ni + CO + H_2O$

(b) $CO + 2H_2 \longrightarrow H_2CHOH \longrightarrow >CH_2 \longrightarrow CH_4$

Here, the catalyst takes part in an extra hydrogenation and the promoter in an extra dehydration. This would account for the higher temperature required in case of carbon dioxide, and also for the lower accelerating effect obtained by the use of promoters in the CO_2 reaction compared to the CO reaction.

Ipatieff (48) worked on CO_2 and H_2 reaction on nickel catalyst at atmospheric as well as at high pressures and came to the following conclusions:-

At ordinary pressure,

(a) In presence of excess of carbon dioxide (150%) there was complete removal of hydrogen.

(b) With theoretical amounts of CO_2 and H_2, a considerable amount/

amount of H_2 remained unreacted.

At high pressures,

(a) Hydrogen in excess with respect to CO_2 does not reduce CO_2 completely.

(b) Nickel oxide and nickel are both equally active.

Ipatieff (49) suggests a mechanism which differs from that of Medsforth. He points out that an intermediate compound of the type methyl alcohol is formed from carbon dioxide and hydrogen. This on dehydration cannot give methylene radical, but dimethyl ether.

$$2CH_3OH \longrightarrow CH_3 - O - CH_3 + H_2O.$$

In support of this he shows that this ether is very stable and even at 520°C very little decomposition takes place. He used alumina as promoter; if under its influence methyl alcohol is dehydrated to methylene radical, some ethane and ethylene would be expected in the product. Ipatieff agrees that methyl alcohol is first formed, but he differs from Medsforth in that he considers that methyl alcohol forms an ester with alumina hydrate which under the influence of the strong hydrogenating catalyst gives methane.

$$AlO(OH) + CH_3OH \longrightarrow AlO(OCH_3) + H_2O.$$
$$AlO(OCH_3) + H_2 \longrightarrow AlO(OH) + CH_4.$$

J. Nicolai, M.D'Hont, and J.C. Jungers (50) studied the synthesis/

synthesis of methane from oxides of carbon and hydrogen on nickel catalyst. They found that in case of CO_2 and H_2 mixture the surface of the catalyst is equally shared between the reactants, whereas carbon monoxide seemed to be notably much better adsorbed than carbon dioxide. The reduction of CO by deuterium D_2 was effected more rapidly than with hydrogen. This is explained by the fact that D_2 in view of its higher mass is bound up more strongly to the catalyst than hydrogen and presents stronger opposition than hydrogen to being displaced by carbon monoxide. In case of CO_2, due to its less coefficient of adsorption, the difference between D_2 and H_2 is less marked.

The products of reaction affect the reduction of CO very feebly while they wholly retard the reduction of CO_2. This could be attributed to the stronger resistance of CO in virtue of its higher coefficient of adsorption, to displacement by the reaction products. In regions of low temperatures the reduction of CO is much less than CO_2 (since CO occupies more of the catalyst surface), but as the temperature rises the difference diminishes and the two reactions tend to become equal. The energy of activation was found to be much higher for CO than CO_2.

These observations by Jungers and others make it possible to predict the mode of reaction that would take place in the hydrogenation of a mixture of carbon monoxide and carbon dioxide/

dioxide. As the CO is adsorbed more readily than CO_2, the latter will be able to react only when the first would have disappeared in a major quantity. This was confirmed by experimental results.

F. Fischer and H. Pichler (51) studied the simultaneous reaction of CO and CO_2 during hydrogenation. Experiments with nickel, cobalt and iron catalysts indicated that the presence of CO in a CO_2 and H_2 mixture retards the catalytic hydrogenation while the presence of CO_2 in a CO and H_2 mixture exerts no influence. This could be explained in the light of Junger's results and explanation.

A number of investigators have studied the water gas equilibrium:-

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + 10.1 \text{ K cals.}$$

A number of papers concern themselves with the reaction conditions and constants of this equilibrium. In 1912, Wieland (52) suggested that the change from $CO + H_2O$ $CO_2 + H_2$ takes place by way of intermediate formation of formic acid. Sabatier and Mailhe (53) showed that formic acid can be decomposed according to the catalyst used, either to form CO and H_2O or CO_2 and H_2. Armstrong and Hilditch (54) observed traces of formic acid in the condensate from the water gas shift reaction. Fischer and Prziza (55) obtained formic acid from CO_2 and H_2 at high pressures by electrochemical/

chemical methods. Later, Fischer and Schrader (56) were able to get 0.1N. HCOOH, starting from CO and H_2 at 135 atmospheres pressure and 300-400°C. These above observations go to prove Wieland's suggestion that $CO + H_2O \quad CO_2 + H_2$ takes place by way of formic acid.

The components CO, H_2O, CO_2, and H_2 at equilibrium may give different products by way of intermediates, which do not appear in the water gas equilibrium, according to the type of catalyst employed (57). These could be the starting point for the synthesis of organic compounds containing high oxygen contents. In connection with these changes we can differentiate between three groups of catalysts, (57). First are those with whose help the left hand side of the equation,

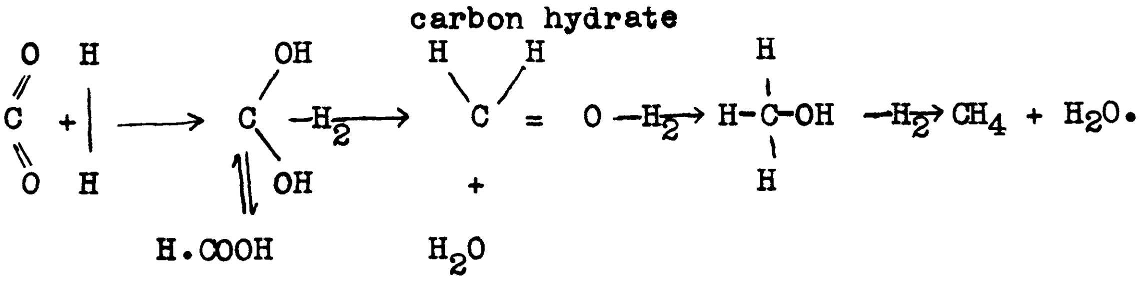
$$CO + H_2O \rightleftharpoons HCOOH \rightleftharpoons CO_2 + H_2$$

could be catalysed. Secondly, those which catalyse the right hand side and thirdly, those whose action lies between these two groups. Sulphuric acid and phosphoric acid etc. belong to the first group. The second group comprises hydrogenating catalysts like nickel, cobalt, ruthenium etc. The third group of catalysts are oxides whose hydrogenation activity is not so great as the metals of group 2, while their ability to act as dehydrator is not so great as the acids of group 1. These are generally used for the hydrogenation of CO to/

to alcohols and other oxygen containing compounds.

Starting from CO_2 and H_2 the catalysts of group 2, give only methane (57). If the CO_2 is first reduced to CO using a catalyst of lesser hydrogenation activity like copper, then higher hydrocarbons are formed. Thus it is found by the use of proper catalysts higher hydrocarbons, higher alcohols, fatty acids, etc., could be produced from CO and H_2; whereas starting from CO_2 and H_2 only the first member of the homologous series could be produced, that is of the hydrocarbons methane, of alcohols methanol, and of fatty acids formic acid. This shows that the formation of methane etc. from CO_2 and H_2 proceeds according to a basically different mechanism than of the higher hydro-carbons from CO and H_2.

The direct hydrogenation of CO_2 to methane may take place by way of formic acid, giving methanol and then methane (58). The course could be shown thus:



Fischer and Tropsch (59) explained the difference in the mechanism of the reaction between CO_2 and H_2; and CO and H_2. They said that the formation of higher hydro-carbons from CO and/

and H_2 takes place with the help of carbides, while the methane formation from CO_2 and H_2 takes place by changes in the chemisorbed hydrogen.

Fischer and Pichler (58) observed that CO_2 does not react in the presence of CO in the Fischer-Tropsch synthesis and that higher hydro-carbons are synthesised when the cobalt in the catalyst surface is in the form of carbide. They also noted that during the formation of higher hydro-carbons very little chemisorbed hydrogen is present on the surface of the catalyst. They supposed that, for the hydrogenation of CO_2, atomic hydrogen is necessary.

S.R. Craxford (60) investigated the hydrogenation of CO using a Fischer-Tropsch catalyst and his results fit in with and confirm the above observations of Fischer. He showed, by observing the ortho-para hydrogen conversion, the intermediate formation of atomic hydrogen in those cases where the reaction took place with the formation of methane. If higher hydro-carbons are formed, little atomic hydrogen is noticed. The carbide formed under these conditions reacts with molecular hydrogen to form higher hydro-carbons.

S.R. Craxford and E.K. Rideal (61) envisaged the formation and utilisation of the carbide in the Fischer-Tropsch synthesis as follows:-

(1) $Co + CO \longrightarrow Co\text{-}CO$ (chemisorption)

(2) $CoCO + CO \longrightarrow Co\text{-}C$ (surface carbide) + CO_2

(3) $CoCO + H_2 \longrightarrow CoC$ (") + H_2O

(4) $CoC + H_2 \longrightarrow CH_2 \longrightarrow$ higher HCs.

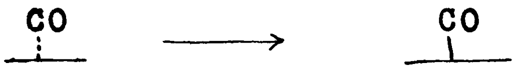
The fact that the oxygenated product of the Fischer synthesis is water and not CO_2 suggests that (3) proceeds more rapidly than (2). It is impossible that the water could have been produced by the water gas reaction, for at 200°C the equilibrium concentration of water vapour would be extremely small. This point was confirmed by a series of experiments, the catalyst used being Fischer catalyst containing cobalt, thoria and kieselguhr in the proportion 100:18:100. Carbide formation was rapid at first, showing surface carbide formation and this was followed by a second slow stage which is the formation of the carbide in the bulk of the metal.

The next stage of the Fischer synthesis is the reduction of the carbide so formed to give higher hydrocarbons or to give methane. This can be distinguished through ortho-para hydrogen conversion. It was noticed that when the Fischer synthesis is proceeding at about 200°C the ortho-para conversion does not occur to any marked extent, but that it does occur where there is no reaction or else methane is being formed. Thus synthesis of higher hydro-carbons proceeds by way of molecular hydrogen, while methane/

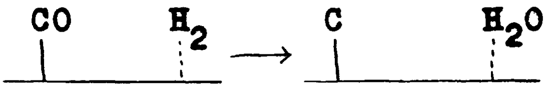
methane synthesis by way of chemisorbed hydrogen.

According to Craxford and Rideal (61) the above results along with other experimental results indicate that the mechanism of Fischer reaction involves the following steps, where - X represents chemisorbed radical and---Y represents a molecule Y adsorbed by Van der Waal's forces:-

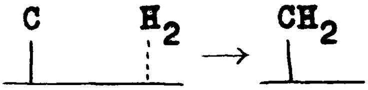
(1) Chemisorption of CO



(2) Reduction of Chemisorbed CO by H_2 to give carbide

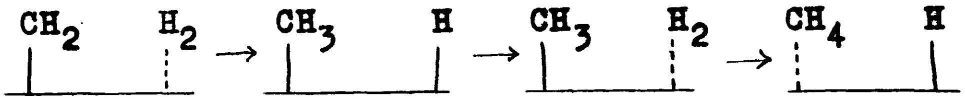


(3) Reduction of the carbide to chemisorbed methylene groups



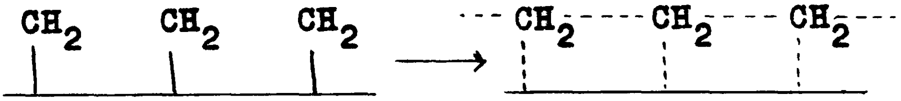
If at this stage there is a large amount of chemisorbed H_2 on the catalyst surface, the next step is

(a)

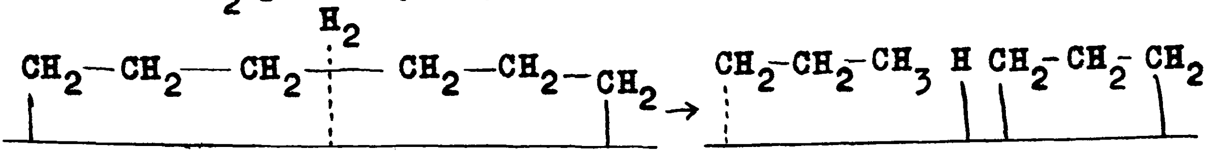


and methane is the product; but if on the other hand only a little chemisorbed H_2 can be present, association of the methylene groups occur to give mono molecules.

(b)



(4) These mono molecules are then disrupted by interaction with H_2 probably as,



and/

and the chain length of the products will depend on the amount of H_2 available for the process which is given by the amount of chemisorbed H_2 present on the surface.

The inhibition of the conversion during the synthesis may be due to either the surface being completely covered with carbide, or to the presence of chemisorbed hydro-carbons. The saturated hydro-carbons do not inhibit the conversion, but Farkas, Farkas, and Rideal (62) found that ethylene, which is very strongly chemisorbed, does so act.

S. Weller (63) carried out work on kinetics of carbiding and hydro-carbon synthesis with Fischer-Tropsch catalyst. He agrees with Craxford and Rideal and points out that at present the possibility that oxygen removal may be a rate limiting step cannot be ruled out.

J.E. Hofer and W.C. Peebles (64) carried out X-ray diffraction studies on the action of CO on Co-ThO_2-Kieselguhr catalyst. Reduction of catalyst at 400°C leaves cobalt atoms in the face centred cubic (β) from which they do not convert readily to the hexagonal close packed (α) form. On carbonisation of the reduced catalyst, cobalt carbide is formed; the rate of carbonisation of α and β cobalt proceeds at nearly the same rate and results in the same crystalline carbide. Hydrogenation of this carbide forms methane and the stable α cobalt. This cycle of reduction and carbiding and hydrogenating the carbide can be repeated indefinitely at 210°C.

J./

J.T. Kummer, T.W. Dewitt and P.H. Emmett (65) by using C^{14} as a tracer in the study of Fischer Tropsch synthesis came to the conclusion that only about 10% of the hydrocarbon products appear to come through the carbide using CO at 200°C. They consider that it is possible that an incipient surface carbide formed on the surface during synthesis may be an intermediate. Such carbon atoms formed may be bound to the metallic phase by the same type of chemical bond involved in the formation of metal carbides and may react with hydrogen to form CH_2 groups which then polymerise.

Elvin and Nash (66) suggested that certain oxygenated compounds could be an intermediate because of their presence in small quantities along with the hydro-carbons even at low pressures. Smith (67) suggested the possibility of acetone as an intermediate. In 1942 Ya.T.Edins and N.D. Zelinsku (68) declared that cobalt carbide is neither an intermediate product, nor a catalyst in the synthesis of gasoline from CO and H_2 in presence of Fischer catalyst. However, intermediate formation of methylene radicals during the synthesis had been confirmed. In 1943, Ya.T.Edins (69) postulated intermediate formation of methylene radical without assuming intermediate formation of carbide by the help of Balandin's multiple theory of adsorption in catalysis. According to Warner, Denig, and Montgomery (70) ketene could be the source of methylene radicals. Rice and Glazebrook (71) have shown that methylene and/

and carbon monoxide can combine to form ketene in detectable quantities.

Though it had not been possible to reduce CO_2 to higher hydro-carbons than methane, Fischer, Bahr, and Mensel (72 & 73) found that this can be done with a ruthenium catalyst to which small amounts of strong alkali are added. Gaseous and liquid hydro-carbons are obtained. At first a colourless low boiling oil, later a high boiling oil, and finally paraffin like products are formed. The most favourable temperature range seemed to be 200-25°C. Above 300°C only methane was formed. The formation of higher hydro-carbons by alkalised Ru is believed to proceed through CO, to which the catalyst first reduces the CO_2. From anology with the metals of the iron group it would seem possible that the catalyst is a carbide, although no ruthenium carbide is as yet known.

H. Pichler and H. Buffleb (74) said that the activity of the Ru catalyst was the same whether reduced by hydrogen or synthesis gas under pressure. Addition of alkali (K_2CO_3) to the catalyst, had little influence on its activity or on the ratio of liquid to solid hydro-carbons in the product. They (75) also observed that only methane and water are produced by passing CO_2 and H_2 over unalkalised Ru catalyst.

Kyowa (76) prepared a catalyst consisting of one mole each of Mn, Zn, and Cu hydroxides (or oxides or carbonates) - Cr/

Cr may be substituted for Cu- 0.2M Fe_2O_3 (or oxides or carbonates) and 0.125 M KOH (or oxide or carbonate) and kiesel guhr. In presence of this mixed catalyst a 25% CO_2-75% H_2 mixture at 400°C and 150 atmospheres pressure gives 39.5% ethyl alcohol, 35.5% propyl alcohol, 8.3% iso-butyl alcohol, and 18.7% methyl alcohol.

C.R. Prichard and C.N. Hinshelwood (77) as a result of many experiments on the interaction of CO_2 and H_2 on the surface of tungsten came to the conclusion that the adsorption of each gas is independent of the other. This shows that the whole surface is not active. Only certain parts are able to adsorb hydrogen and carbon dioxide and cause them to react. The parts that adsorb hydrogen in this way are different from those that adsorb carbon dioxide. Interaction takes place when molecules of the two gases are adsorbed on adjacent centres of the appropriate kind. They found that platinum also adsorbs both CO_2 and H_2.

Fryling (78) has shown that in case of a promoted nickel catalyst the first portions of hydrogen added are dissociated into atomic hydrogen before adsorption, after which more hydrogen is adsorbed to saturation in the same manner as the unpromoted nickel catalyst. S. Roginskü (79) by photoelectric studies of nickel and tungsten surfaces showed that the adsorption of atomic hydrogen from 180° to 150° is very strong while that of molecular hydrogen is very weak.

Kistiakowsky/

Kistiakowsky (80) confirmed Wolfenden's (81) assumption that adsorbed hydrogen on the surface of nickel is present partly in the atomic state. He showed that nitrogen is also adsorbed.

Kimio Kawakita (82) has observed remarkable chemisorption of carbon dioxide by reduced iron at 300° - 400°C. From experimental evidence he showed that (83) adsorbed carbon dioxide molecules after their diffusion into inner surface of a catalyst through minute cracks or grain boundaries of small dimensions, acted upon the iron atoms according to a heterogeneous chain reaction as:

(1) $Fe + (CO_2)_{adsorbed} \rightleftharpoons Fe_XO_Y + CO$

(2) $2CO_{ads.} \rightleftharpoons C + (CO_2)_{ads.}$

Reaction (1) takes place only in strong active centres as minute cracks and (2) even in weak active centres on the surface of the catalyst.

A number of investigators have studied the poisoning of the hydrogenation catalysts. W.B. Binford and J.C.W. Frazer (84) found that even a small amount of water vapour is a poison for nickel hydrogenating catalyst. The reaction is reversible and so the catalyst could be reactivated by heating in a current of hydrogen.

Another reason for falling off of the catalytic activity may be the deposition of graphitic carbon on the catalyst.

M./

M. Randall and F. Gerard (85) have found that a possible reaction may be between carbon dioxide and methane to form graphitic carbon and water vapour.

$$CO_2 + CH_4 \longrightarrow 2C + 2H_2O$$

They showed that the free energy of methane calculated from experiments on:-

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

reaction is in agreement with the value found from the direct synthesis from graphite and hydrogen in the same temperature range. The negative values of the unaccounted for carbon are used by the synthesis of methane from the hydrogen and graphite previously deposited.

J.A. Tebboth (86) worked with promoted and unpromoted nickel catalyst supported and unsupported. He suggested that the conditions of CO and H_2 reaction were very favourable for elementary carbon formation as follows:-

$$3Ni + 2CO \longrightarrow Ni_3C + CO_2 \quad \text{(carbiding reaction)}$$

$$Ni_3C \longrightarrow C + 3Ni \quad \text{(elementary carbon)}$$

G.L. Clerc and H.Lefebore (87) studied loss of catalytic activity in reduced nickel catalyst when a mixture of CO and H_2 is passing. They observed that the loss of activity is accompanied by transformation of nickel from the ferromagnetic cubic to the nonmagnetic hexagonal form.

K./

K.M. Chakravarty and P.B. Chakravarty (88) found the Fischer Tropsch catalysts and other catalysts containing traces of K_2CO_3 were found to lose their activity after passage of small volumes of CO and H_2 mixture. The presence of K_2CO_3 favours the formation of C, CO_2, and water rather than hydro-carbons.

SIMPLE KINETICS OF HETEROGENEOUS REACTIONS

Two Reacting Gases:-

In a system consisting of a solid surface and a single reacting gas, the gas molecules will strike the surface and as a general rule will "condense", that is, adhere for an appreciable period. As a result of thermal agitation the gas molecules will evaporate, that is, leave the surface from time to time, and eventually an equilibrium is reached when the rates of condensation and evaporation are equal. When a reaction involves two or more gases a number of possibilities may arise according as one or the other of the reactants or products are adsorbed. Let it be assumed in the first place, that the products are not adsorbed and the surface is sparsely covered with both reactants. Suppose the reaction is:-

$$aA + bB \longrightarrow \text{products}$$

The mass of a given gas, and hence the number of molecules (μ), striking one sq. cm. of catalyst surface per second is proportional to the pressure (p) of the gas. If α is the fraction of the molecules striking the surface which adhere, then $\alpha\mu$ molecules condense on each sq. cm. of available surface per second. If θ is the fraction of the total surface covered with gas molecules at any instant, then $1 - \theta$ is the fraction of the surface which is bare; assuming that/

that only a single layer of gas molecules can form on the solid, the actual rate of condensation will be $(1-\theta)\alpha\mu$ molecules per sq. cm. per sec. The rate of evaporation will be proportional to the number of molecules on the surface, that is to the area covered, θ , and so may be represented by $v\theta$, where v is a constant for the given gas and surface. At equilibrium the rates of condensation and evaporation will be equal, so that

$$(1-\theta)\alpha\mu = v\theta \qquad \text{------------------1.}$$

Since in the reaction aA + bB ⟶ products, it is assumed that the products are not adsorbed and that the surface is sparsely covered with both reactants, it may be assumed that $1-\theta$ to be unity. Thus according to equation 1

$$\alpha_A \mu_A = v_A \theta_A \quad \text{and} \quad \alpha_B \mu_B = v_B \theta_B \qquad \text{---2.}$$

for the gases A and B respectively, θ_A and θ_B being the fractions of the surface covered by these molecules. The rate of reaction on the surface is given by

$$\frac{dx}{dt} = k\,\theta_A^a\,\theta_B^b \qquad \text{--------------------------3.}$$

and substituting the values of θ_A and θ_B in equation 3 from equation 2, we get that:-

$$\frac{dx}{dt} = k\left(\frac{\alpha_A}{v_A}\right)^a \mu_A^a \left(\frac{\alpha_B}{v_B}\right)^b \mu_B^b$$

$$= k\,k_2\,\mu_A^a\,k_3\,\mu_B^b$$

$$\therefore\ \frac{dx}{dt} = k_1\,p_A^a\,p_B^b \qquad \text{-------------------------4.}$$

On the other hand, if one of the reacting gases is firmly held on the surface it may have the surprising effect of retarding the reaction as its pressure is increased. Consider a reaction in which one molecule of A and one molecule of B take part. Suppose the gas A is strongly adsorbed and θ the fraction of the surface covered by it where θ is nearly unity; then the fraction covered by B is negligible. When equilibrium is reached:-

$$(1 - \theta)\alpha_A \mu_A = v_A \quad \text{---------------}5.$$

the θ on the right hand side is taken as unity. The rate of reaction is taken to be equal to the rate of condensation of B on the free surface, since there is always sufficient A available to combine with B; hence:

$$\begin{aligned} \frac{dx}{dt} &= k(1 - \theta)\alpha_B \mu_B \\ &= k\frac{\alpha_B v_A}{\alpha_A} \times \frac{\mu_B}{\mu_A} \end{aligned}$$

$$\therefore \quad \frac{dx}{dt} = k_1 \frac{p_B}{p_A} \quad \text{---------------}6.$$

where p_A and p_B are the partial pressures of A and B. The rate of reaction is thus inversely proportional to the pressure of the gas strongly adsorbed.

In some cases the products are capable of retarding the reaction. This results from the products being preferentially adsorbed/

adsorbed on the surface. On a similar reasoning as in the retardation by the reactant, it could be seen that whichever reactant is present in excess probably occupies most of the surface not covered by the products, and reaction may occur when molecules of the second reactant meet those of the first already on the surface, the rate of reaction thus being proportional to the pressure of the second reacting gas, but inversely proportional to the pressure of the strongly adsorbed product.

PART I.

Interaction of Carbon dioxide and Hydrogen in presence of Nickel Thoria Catalyst.

CHAPTER I.

PREPARATION OF CATALYST.

General conditions for preparation of catalysts:-

The catalysts employed were nickel and nickel thoria supported on pumice. A detailed account of preparation of catalysts is of great importance from its practical consequences. The preparation of catalysts falls into three stages: (1) selection of starting material for the catalyst in suitable form, (2) formation of this material into particles, grains, or deposition, (3) activation by conversion into the element or compound which is actually the catalyst.

It is preferable to select as the starting material a compound that will undergo some sort of chemical change before it is actually converted into the form that acts as the catalyst. So nickel nitrate was selected as the starting material, for it is first oxidised to nickel oxide before it is reduced to nickel which acts as the catalyst in the reduction of carbon dioxide. Preliminary reactions have to be carried out under very carefully controlled conditions in order to get reproducible results, particularly in cases where the catalyst consists of more than one component. For example, Boswell and Iler (89) showed that the particle size of nickel oxide obtained by heating the hydroxide in nitrogen, increased/

increased with temperature according to the equation,

$$\log D = KT + C$$

where, D = crystal diameter.
T = temperature.
K & C = constants.

A catalyst with a high specific surface like nickel adsorbs various impurities easily and as such, strict precautions have to be observed in its preparation. Further, the composition of the catalyst is known to be influenced by the conditions of its preparation. Great care is necessary in the preparation of promoted catalysts, for it is very important to obtain a uniform distribution of the promoter. This condition is very difficult to fulfil when the promoter is present in very small amounts as compared with the main catalyst. The general methods of preparation of the promoted catalysts are (1) co-precipitation from mixed solutions and (2) evaporation of mixed solutions.

The main defect in preparing catalysts by co-precipitation is the possibility of incomplete precipitation because it is very rare for both components to be precipitated simultaneously and in a steady ratio. The second method of precipitation suffers from the same defects, but to a lesser extent. The evaporation of a mixed solution leads to a preferential deposition of the major component and this results in a larger concentration/

concentration of the lesser component in the remaining liquid towards the final stages of evaporation and in the solid deposited from it.

Carriers are used to economise in the consumption of expensive materials; further, they enable the catalyst to be obtained in a form that would stand mechanical shock. The ideal carrier must be cheap, abundant, mechanically strong, porous enough to be light and give a high concentration of catalyst on surface, and be inert to chemical attack by the catalyst, reactants and products. It should not contain any material that would be a poison to the catalyst. Pumice possesses most of these properties and so was selected as a carrier for the nickel catalysts.

The temperature of reduction of the catalyst is also of importance as the catalytic activity varies with temperature. Thomas (90) obtained catalysts by reduction of nickel hydroxide deposited on kieselguhr and determined their efficiencies for the hydrogenation of olive oil with results shown below:-

Reduction temperature	Relative activity of Ni catalyst
250	1.00
350	1.18
500	1.25
650	0.23
750	0.00

Preparation/

Preparation: The details.

The pumice was crushed and sieved between 5-8 B.S.S. sieves to give uniformly sized particles. The pumice was found to contain many foreign visible bodies. These were separated by a panning motion in a basin placed under a tap of running water. The pumice being lighter were carried off by the stream of water into another basin kept below the first. This eluted pumice was boiled with 1:1 HCl acid to remove alkalies and other soluble impurities; the pumice was washed free of the first acid, and boiled twice more with fresh lots of acid. Finally, it was washed free of HCl with distilled water, filtered, dried and weighed.

A solution of nickel nitrate was prepared containing approximately 140gms. in one litre. The nickel nitrate was not taken to be pure and so the nickel content was estimated by the dimethyl glyoxime method and was found to be 0.0259 gms. per c.c. of the solution. Then the calculated amount of solution was added to a known weight of pumice in a beaker so as to give 10% by weight of nickel on the weight of pumice. Meanwhile, 100% pure thorium nitrate was taken and weighed accurately so as to give 3% by weight of thoria on the weight of pumice. A solution of the weighed thorium nitrate was made and added to the beaker containing the pumice and nickel nitrate solution. The whole mixture was evaporated over a bunsen/

bunsen flame with frequent stirring. Towards the last stages it was evaporated to dryness over a water bath with constant stirring to ensure a uniform coating of the nitrates on the carrier.

The next stage in the preparation is the decomposition of the nitrates into their respective oxides. The decomposition temperature of nickel nitrate is 230°C and that of thorium nitrate is 500°C. Therefore, to ensure complete decomposition the second stage of the catalyst preparation was carried out at 500°C. The catalyst was placed in a china dish and the decomposition was carried out in a muffle furnace in presence of air. The temperature was raised very slowly and reached 500° in three hours, the temperature being recorde by a standardised thermocouple. The catalyst was kept at this temperature for one and a half hours, then cooled and bottled.

The third stage is the reduction of the catalyst. The nickel oxide is reduced to nickel which is the actual catalyst. A constant volume of the catalyst was taken every time, weighed and reduced in a stream of hydrogen in the reaction vessel itself.

Nickel thoria catalyst was prepared in two batches; IA and IB. Nickel catalyst was also prepared in two batches; IIA and IIB. In case of nickel catalyst, the decomposition was/

was carried out at 300°C, the temperature being gradually raised in two hours. Other conditions remained the same as in promoted catalyst.

Catalyst IA.

Mesh size	----------	5 to 8 B.S.S.

10% Ni by weight on weight of pumice.

3.06% ThO_2 by weight on weight of pumice.

Catalyst IB.

Mesh size	----------	10 to 14 B.S.S.

10% Ni by weight on weight of pumice.

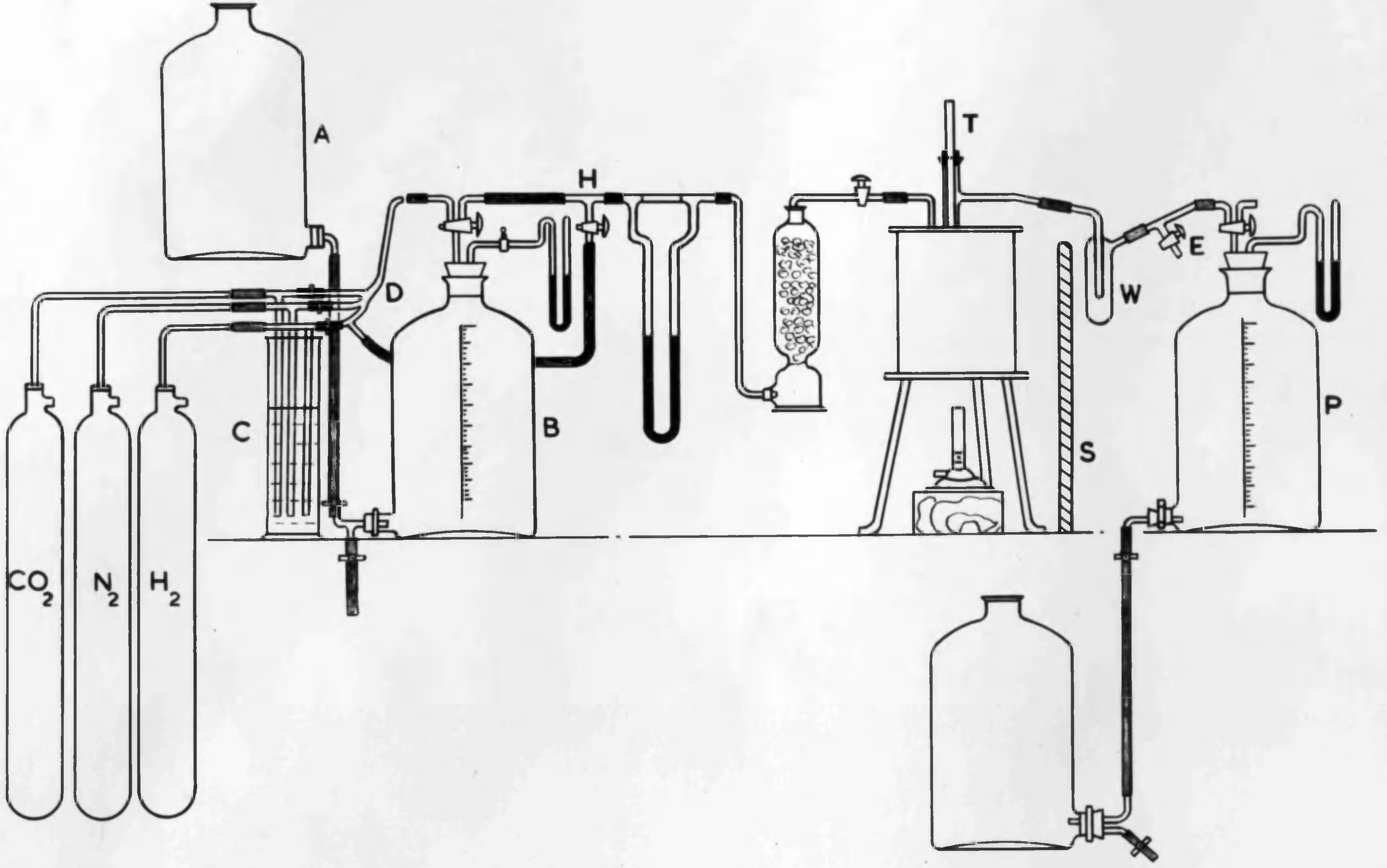
3.4% ThO_2 by weight on weight of pumice.

Catalyst IIA and IIB

Mesh size	----------	5 to 8 B.S.S.

10% Ni by weight on weight of pumice.

REACTION UNIT.



CHAPTER II.

THE DESCRIPTION OF THE APPARATUS.

The general layout of the apparatus is shown in fig. 3 on page 56A. The main parts consist of a reservoir for the synthesis gas, a reaction vessel containing the catalyst, a flow meter, and a product receiver. There is a gas analysis unit for the gases to be analysed.

The synthesis gas reservoir.

This consists of two aspirators 'A' and 'B'. Aspirator 'B' is of 12 litres capacity and is calibrated. It is closed air tight by means of a rubber bong carrying a two way stop cock and a mercury manometer. Through one limb of the two way cock, the gases hydrogen, nitrogen and carbon dioxide are introduced straight from gas cylinders in the required proportion. There is a water seal 'C' for each cylinder, in between the aspirator 'B' and the cylinder. The water seal enables the feeding of the aspirator approximately at constant pressure and if the pressure exceeds, the seal is blown off and the gas escapes to the atmosphere. The mercury manometer helps to adjust conditions so as to make the pressure inside the aspirator equal to that of the atmosphere, before reading the volume of the gas. Through the other limb of the stop cock/

cock the gases could be fed into the reaction system.

The hydrogen from the cylinder after passing the water seal follows two paths, one to the aspirator and the other directly to the reaction system at 'H' in between the aspirator and the flow meter. This arrangement is to pass hydrogen through the system during reduction and reactivation of the catalyst. Similarly there is a by-pass E between the condenser W and the aspirator P for letting out the gases to the atmosphere during reduction and reactivation of the catalyst and also just before collecting the gases in the product receiver during the run.

The flow meter.

This is of the orifice flow meter type, the orifice being provided by a drawn capillary tube. It was calibrated for air. Two flow meters were calibrated, one for small rates of flow and the other for higher rates of flow.

The reaction vessel.

This is illustrated in figure 4 shown on the next page. It is about 10 ins. long and stands vertically in an oil bath 'F'. The gases entering are preheated by passing through the coiled glass tube surrounding the catalyst chamber proper and pass up through the catalyst mass supported on asbestos wool at the bottom of the vessel. The thermometer T (360°C) is kept in a glass tube embedded in the catalyst mass/

mass. A little oil is kept in the glass tube to ensure proper contact of the thermometer bulb. The reaction products pass up and leave the reaction chamber at the top to a condenser W.

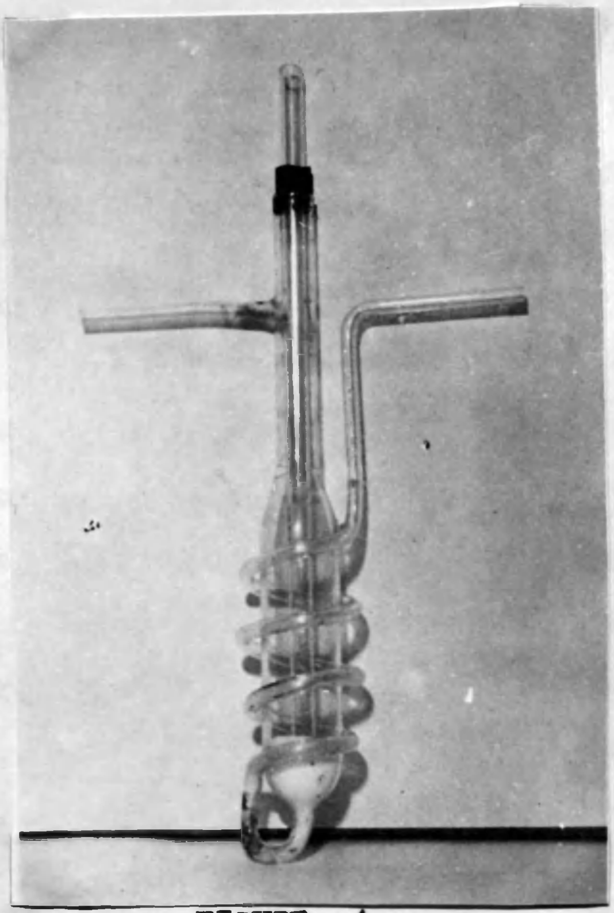


FIGURE 4.

<u>The Condenser</u>.

This is a simple arrangement and consists of a long bulb carrying a central tube almost to the bottom. The products from the reaction vessel pass down the central tube to the bottom of the bulb, then up along the annular space and/

and leave the condenser at the top through a side tube. The bulb is kept immersed in water.

The product receiver.

This consists of two aspirators of 8 litres capacity each. Aspirator P is calibrated and closed with a rubber bong carrying a two way stop cock and a manometer. The reaction products when desired can be drawn into it through one arm of the two way cock. Through the other arm of the stop cock samples are drawn out when required.

The synthesis gas from aspirator B pass first through a flow meter,up a calcium chloride tower to remove moisture, then through the preheater which is the coiled tube around the reaction vessel, and then into the catalyst chamber. Reaction products then pass into the condenser to remove the water formed during the reaction and finally into product receiver. 'S' is an asbestos screen which cuts off the heat from the burners to the gas in the product receiver.

The gas analysis unit.

Both the synthesis and the product gases were analysed in the "Macfarlane Gas Analysis" unit, a modification of the Hempel apparatus. Here, the gases are measured and exploded over mercury. The burette is kept at constant temperature by a water jacket. The absorption pipettes can be removed and shaken, thus increasing the rate of absorption. For complete/

complete liquid seal between the burette and the pipettes, these have three way cocks one of which leads to a small cup kept filled with dilute sulphuric acid. Then the acid is blown from one cup to the other thus removing all air from the capillaries. The following gases were estimated:-

	Gas estimated.	Absorbent used.
1.	Carbon dioxide	30% KOH.
2.	Oxygen	40% alkaline pyrogallol.
3.	Carbon monoxide	ammoniacal cuprous chloride.
4.	Methane and Hydrogen	By explosion with oxygen and measuring contraction and also estimating CO_2 formed by absorption in KOH.

CHAPTER III.

THE REDUCTION OF CATALYST.

A known volume of the catalyst was weighed. To maintain a constant volume every time, the catalyst was filled up to a certain mark on the weighing bottle and weighed. Meanwhile, the reaction vessel was cleaned well, dried and loosely packed at the bottom to a certain mark with hot asbestos wool. This asbestos wool had been previously boiled with 1:1 HCl, washed free of the acid and dried for it was found that the untreated asbestos contained some alkali which is a poison to the catalyst. Then the weighed catalyst was dropped carefully into the reaction vessel on to the asbestos support. The thermometer pocket was introduced centrally through a one holed air tight rubber bong. The reaction vessel was then clamped vertically in the oil bath and connected to the reaction system. To ensure that the system was leak proof all the joints were coated with collodin and the whole unit was tested for leaks.

The air in the system was swept out by a slow current of hydrogen direct from the cylinder through the by-pass H. When all the air had been displaced the by-pass exit cock E was closed and the oil bath was heated, the catalyst being kept in an atmosphere of hydrogen under slight pressure.

When the catalyst temperature was about 290°C, the by-pass exit cock was opened and adjusted so as to give a rate of about 2 litres of hydrogen per hour through the system. The reduction was carried out for 12 hrs., and often the temperature rose to 300°C.

CHAPTER IV.

THE EXPERIMENTAL PROCEDURE.

For filling in the synthesis gas, the aspirator B was completely filled with 20% NaCl slightly acidified with sulphuric acid. The air in the single common tube connecting all the three gas cylinders was displaced by opening the cylinders in turn. With the last cylinder open and the hydrogen gas still passing through, the tube was connected to the limb of the two way stop cock by means of a short rubber tube. Then the aspirator was filled with the required volume of hydrogen, the volume being read at atmospheric pressure; then with nitrogen (if required) and finally with carbon dioxide in the required proportions. After this, it was allowed to stand for two hours with occasional shaking for thorough mixing of the gases. The mixing is enhanced through diffusion by filling in the lighter gas first and the heavier gas last.

Meanwhile, the catalyst was heated to 280°C in an atmosphere of hydrogen. Due to the probability of carbon dioxide dissolving even in acidified brine, the synthesis gas was sampled just before the experiment and analysed in Macfarlane unit. Then the hydrogen was cut off and the synthesis/

synthesis gas passed at the required rate of flow. Heat supply to the oil bath was reduced and the exothermic nature of the reaction kept up the temperature. About two litres of the synthesis gas was passed to obtain steady conditions. During this time the reaction products were by-passed to the atmosphere through E.

When steady conditions were reached, the brine into the synthesis gas aspirator was cut off and the gas was allowed to flow till the pressure inside was atmospheric, and then the by-pass exit valve was closed and the volume of the gas was noted. The synthesis gas was again passed through the system, the reaction products were turned on to the product receiver and a stop clock was started simultaneously. The exothermic nature of the reaction makes the temperature control difficult and it often shoots up by 3 to 5 degrees C. in spite of the two litres of the gas passed to obtain steady conditions. The rate of flow was controlled by adjusting the screw clips both at the synthesis gas aspirator end as well as at the product receiver end. When about four litres of gas had been passed: the brine into the synthesis aspirator was stopped, the gas still passing due to the slight pressure inside. When the pressure inside equalled the atmospheric pressure, the stop cocks of the aspirators were closed and the stop clock was stopped. The products were allowed/

allowed to cool, brine was levelled for atmospheric pressure, volume noted, sampled and analysed. The volume of synthesis gas passed was also noted down.

Since the flow meter was calibrated for air, its readings become unreliable with a mixture of gases of various proportions. So, the flow meter was used only as an indicator for steady rate of flow and to give an approximate idea of the rate. The real rate of flow is obtained by dividing the volume of the synthesis gas passed by the time taken.

CHAPTER V.

RESULTS AND DISCUSSION ON NICKEL THORIA CATALYST.

The apparatus employed and the experimental procedure are described in Chapters II and IV of this section. The results of the experiments are given in Tables 1; 2,2-A; 5, 5-A; and 6,6-A. The method of calculation for a run is shown below:-

Run No. 11.

Weight of catalyst	5.32 gms.
Volume of catalyst	8.2 c cs.
Time of Run	32 mints.
Temperature	280° C.
Gas passed	4 litres
Gas collected	2.195 litres

Synthesis gas.

CO_2	14.2%
O_2	0.1%
H_2	85.0%

Product/

Product gas.

CO_2	4.6%
O_2	0.1%
CO	0.5%
CH_4	21.4%
H_2	73.5%

CO_2 Balance:-

In gas passed the CO_2 is $14.2 \text{ X } 40 = 568$ c.cs.

In gas collected,

$$\left.\begin{array}{l} \text{As } CO_2 \text{ ------------ } 21.95 \text{ X } 4.6 = 101 \\ \text{As } CH_4 \text{ ------------ } 21.95 \text{ X } 21.4 = 470 \end{array}\right\} = 571 \text{ c.cs.}$$

$\therefore$ % Recovery $= \frac{571}{568} =$ 100% nearly.

C.Cs. converted / C.C. Catalyst / Minute $\frac{470}{32 \text{ X } 8.2} = 1.82$

Rate $= \frac{4000}{32} =$ 125 c.cs/min.

The first few experiments were carried out to get familiar with the experimental technique. It would be noted from the tables, that there is some oxygen in both the synthesis gas and product gas. This could come from (1) oxygen present in the cylinder gases, (2) the dissolved air in the confining liquid namely 20% NaCl, and (3) leaks in the apparatus.

In/

TABLE 1.

Catalyst ——————— Ni-ThO_2 ––– IA.

Vol. of cat. ———— 18 c.cs.

Wt. of cat. ————— 11.07 gms.

Expt. No.	Time of run.	Synth. of gas %			Product gas %.					Temp.	Rate. c.cs. per min.	Yield.
	Mins.	CO_2	H_2	O_2	CO_2	O_2	CO	CH_4	H_2	°C		
4.	31	14.8	84.5	0.5	3.8	0.3	0.6	28.0	67.0	278	132	0.96
5.	13	14.5	84.6	0.2	5.3	0.0	0.1	17.9	76.4	275–8	308	1.91
6.	7.5	14.7	84.6	0.2	11.3	0.3	0.1	8.9	78.1	275	546	2.14
7.	10	14.4	84.3	0.4	8.3	0.0	0.5	13	76.3	275–8	400	1.95
8.	10	14.8	84.6	0.4	10.1	0.2	0.2	11	77.1	278	400	1.73
9.	29	14.0	84.2	0.6	5.3	0.2	0.4	20.0	72.4	275–8	138	0.87
10.	29	14.0	85.0	0.4	6.2	0.0	0.2	17.8	74.7	275–8	136	0.82

In the analysis of the product gas, carbon-monoxide was detected to the extent of 0.1 to 0.6%. The significance of this was already pointed out in the introduction while referring to Medsforth's work (47). As the determination of such small amounts of CO cannot be accurately made by ordinary methods of gas analysis, its determination was given up in the later experiments.

As pointed out before, the temperature control was difficult and the temperature recorded is the average of a number of readings.

In any flow system, the yield is expressed as lb. mols converted/unit weight of catalyst/unit time and the yield increases with rate up to a maximum and then begins to fall while the conversion falls with rate due to the less time of contact. For a common basis of comparison, the yield is expressed here as c.cs. CO_2 converted/c.c.Catalyst/minute.

Table 1 gives the results of experiments carried out with 18.2 c.cs. of catalyst on a mixture of 14% CO_2 and 84% H_2 at various rates. To see whether the catalytic activity remained the same, some of the experiments were repeated and from the last column in table 1 it would be seen that the activity was falling steadily as the number of experiments carried out on the same catalyst increased. This falling off in catalytic activity might be due to (1) poisoning impurities in/

TABLE 2A.

Expt. No.	Carbon dioxide balance.				Recovery %
	In gas collected.			In gas	
	As CH_4 c.cs.	As CO_2 c.cs.	Total c.cs.	passed. c.cs.	
11.	470	101	571	568	100
12.	196	~~101~~ 409	~~571~~ 605	590	98
14.	184	384	568	568	100
15.	146	444	590	578	102
16.	157	671	828	788	105
17.	164	534	698	679	102
18.	155	626	781	787	99
19.	121	835	956	987	97
20.	176	703	879	960	92
21.	112	945	1057	1017	104
22.	108	1720	1828	1960	93
24.	168	1763	1931	1955	99

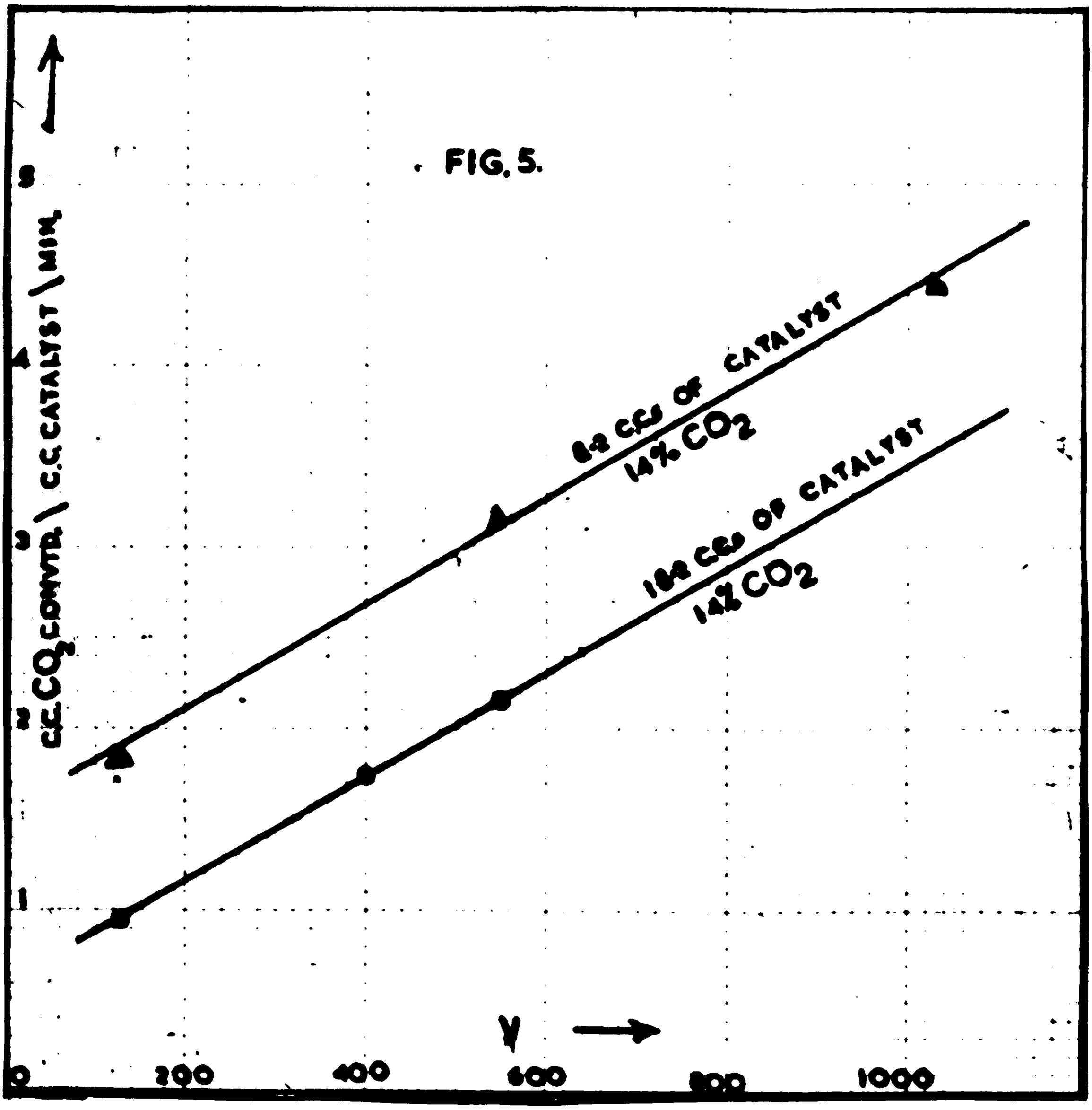
TABLE 2.

Catalyst ——— Ni-ThO$_2$

Vol. of cat. ——— 8.2 c.cs.

Expt. No.	Time. Mins.	Synth. gas %			Product gas %				Wt. of cat. Gms.	Temp. °C.	Rate c.cs per min.	YIELD.
		CO$_2$	H$_2$	O$_2$	CO$_2$	H$_2$	CH$_4$	O$_2$				
11.	32	14.2	85.0	0.1	4.6	73.5	21.4	0.1	5.32	280	125	1.82
12.	7.5	14.4	85.0	0;3	11.7	79.8	5.6	0.2	5.32	275-8	546	3.19
14.	3.75	13.6	86.0	0.2	12.3	74.8	5.9	0.5	5.19	289	1118	5.98
15.	4.0	14.1	85.0	0.2	12.0	82.0	3.9	0.4	5.19	275	1025	4.46
16.	4.75	18.3	80.8	0.5	17.5	73.1	4.1	0.1	5.26	280	910	4.03
17.	8.5	17.0	82.0	0.4	15.9	73.2	4.9	0.4	5.26	275-8	470	2.35
18.	6.0	19.2	80.0	0.5	17.0	76.8	4.2	0.2	5.22	275-8	683	3.14
19.	6.0	24.7	74.0	0.5	24.6	67.5	3.6	0.3	5.22	275	666	2.46
20.	9.5	24.0	73.0	0.2	26.5	65.6	6.6	0.2	5.29	278	422	2.25
21.	5 .0	25.4	73.5	0.4	25.3	65.2	3.0	0.2	5.20	278	800	2.73
22.	10.0	49.0	49.0	0.3	54.0	41.0	3.4	0.7	5.20	275	400	1.31
23.	7.75	49.6	49.6	0.2	55.5	39.0	4.7	0.3	5.30	275	516	2.17
24.	5.75	48.9	50.0	0.3	51.4	40.3	4.9	0.2	5.30	280	695	3.56

FIG. 5.


C.C. CO_2 CONVTD / C.C. CATALYST / MIN.
1
2
3
4
5
V
0
200
400
600
800
1000
82 C.Cs OF CATALYST
14% CO_2
182 C.Cs OF CATALYST
14% CO_2

in the gases passed, (2) impurities in the asbestos support (On testing, this was found to contain alkali and so in later tests was boiled with dilute HCl, washed free of the acid, and dried before use), (3) carbon deposition on the catalyst. To ensure full activity and hence facilitate comparison in subsequent experiments, small amounts of the catalyst were taken (8.2 c.cs. of catalyst weighing about 5 gms.) and not more than four runs were made on each batch. The conditions of reduction were also standardized as far as possible. Though the procedure might not have been sufficient to ensure the same extent of reduction every time, it may be noted that nickel and nickel oxide have the same catalytic activity, as pointed out by Ipatieff (48) and Medsforth (47).

I. Partial Pressures of Both Components Varying.

Tables 2 and 2A give the results of experiments from 11 to 24 in which the partial pressures of both the components are varied. The synthesis gases employed were of 14, 18, 25, and 50% CO_2. From a comparison of yields on a 14% CO_2 synthesis gas mixture with 18.2 c.cs of catalyst (table 1) and 8.2 c.cs. catalyst (table 2), it was found that the yield in the latter case was much higher than in the former and this is seen clearly in figure 5 where yield is plotted against rate V. This might mean that with a thick bed of catalyst, the gases coming in contact with the lower portions of the catalytic bed may soon get some of the carbon-dioxide converted to methane/

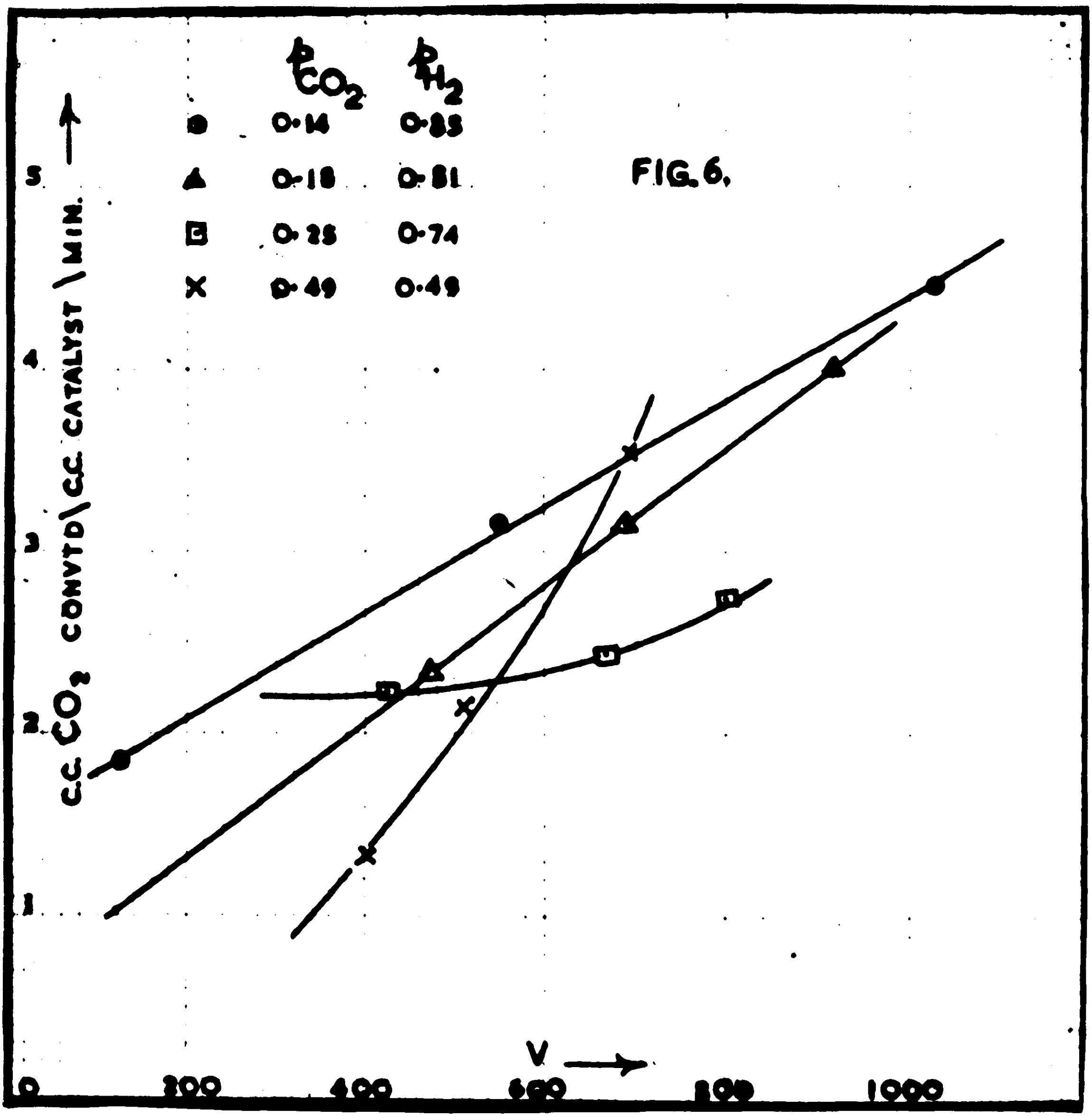

p_{CO_2} p_{H_2}
● 0·14 0·85
▲ 0·18 0·81
□ 0·25 0·74
× 0·49 0·49
C.C. CO_2 CONVTD \ C.C. CATALYST \ MIN. ↑
1
2
3
4
5
V ⟶
0
200
400
600
800
1000

FIG. 6.

methane and passing up the rest of the bed results in very little conversion. That is to say, in a thick bed, the upper layers of catalyst practically does not perform any function.

The results of experiments with the partial pressures of both the components varying are plotted with yield against rate in figure 6. The lines for 14, 18 and 50 per cent CO_2 are progressively steeper, but the behaviour of 25 per cent CO_2 is peculiar in the sense that its slope is even less than that of 14 per cent CO_2.

The results when plotted on a log-log graph gave the following slopes for the different lines:-

14% CO_2 ------------ slope = 0.418

18% CO_2 ------------ slope = 0.716

50% CO_2 ------------ slope = 1.75

If the lines were parallel to each other and all had a slope of the order of 0.7 to 0.8, then one could have expected the diffusion of gases through a stagnant gaseous film to be the rate controlling step in the reaction; for, according to the principle of heat transfer it is known that when a fluid passes through a pipe, the heat transfer to and from the fluid depends upon the thickness of a stagnant film which is a function of the velocity of the fluid raised to power 0.8. But gas passing up a catalyst bed may resemble more/

more the case of gases flowing at right angles to a bank of staggered tubes where the heat transfer is a function of velocity raised to power 0.66 (91). However, it should be noted that the physical characteristics of the catalyst mass may exert a great effect on the thickness of gaseous film. However, the lines should be parallel if diffusion through a film is the controlling step in a reaction. Since the lines in this case were not parallel it would be justifiable to conclude that there is no film controlling the reaction. That is, in case of interaction between CO_2 and H_2, diffusion of neither the reactants nor the products through a gaseous film seem to be a rate controlling step.

Instead of plotting the yield against a function of velocity, it could also be plotted against a function of Reynolds number $Re = \frac{D V \rho}{\mu}$ where

D = linear function of system.
V = Velocity of flow
ρ = density of fluid
and μ = viscosity of fluid.

In this case D is constant and V, ρ, μ are varying. In actual practice, the Reynolds number is calculated by taking each factor in consistent system of units. Here, comparative rather than absolute values of the number were desired and the units were therefore chosen arbitrarily. The/

The values for density of the gases were taken from the International Critical tables and are at 0°C. These were not corrected to the reaction temperature because the temperature coefficient of the individual gases do not vary much in relation to each other. The values are:

Density of Hydrogen = 0.8987×10^{-4} gms/c.c.
Density of Carbon dioxide = 19.7600×10^{-4} gms/c.c.

Values for viscosities were also taken from the International Critical tables. These values had to be corrected to the reaction temperature, 285°c or 558°K by using Sutherland's relationship.

$$\mu_t = \mu_o \times \frac{To + C}{T + C} \times \left(\frac{T}{To}\right)^{3/2}$$

where $_t$ = viscosity at temp. T °K.
and C = Sutherland's Constant.

Values of C varies for each gas. C for hydrogen = 72 and C for carbon dioxide = 274.

Thus for H_2:-

$$\mu_{558} = 88.7 \times \frac{293 + 72}{558 + 72} \left(\frac{558}{293}\right)^{3/2} \times 10^{-6} \text{ poises.}$$

$$= 135 \times 10^{-6} \text{ poises.}$$

Similarly for CO_2 $\mu_{558} = 260.8 \times 10^{-6}$ poises.

The/

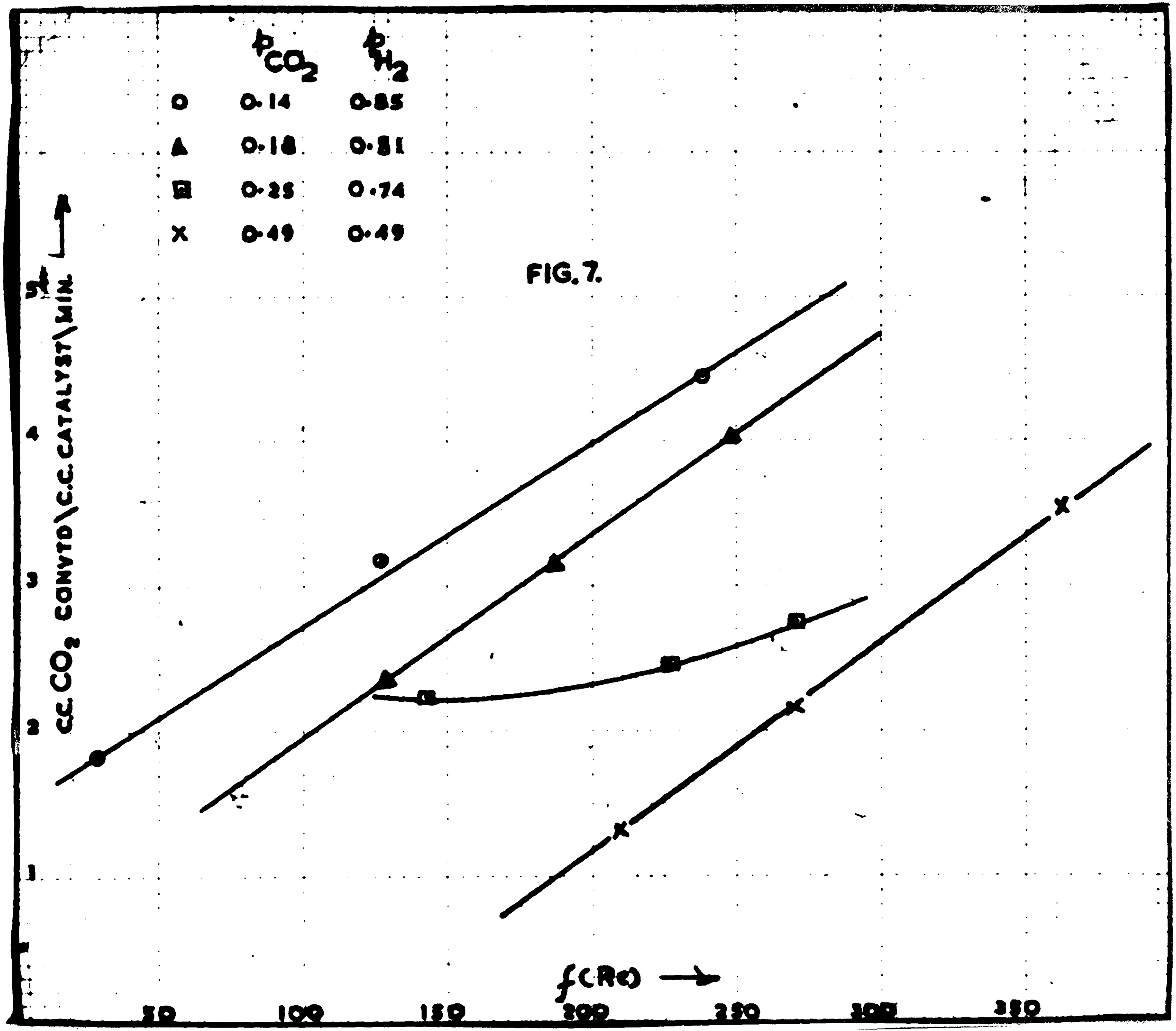

p_{CO_2} p_{H_2}
○ 0·14 0·85
▲ 0·18 0·81
▨ 0·25 0·74
× 0·49 0·49
C.C. CO₂ CONV'TD\C.C. CATALYST\MIN. →
1
2
3
4
5
f(Re) →
50
100
150
200
250
300
350

FIG. 7.

The net viscosity and density values were calculated from the percentage composition of the mixture.

A plot of the yield against Reynolds number is shown in figure 7. The lines for 14, 18 and 50 per cent CO_2 seem to fall more or less parallel to each other. To understand the significance of figure 7 more fully, table 3 has been drawn up:

TABLE 3.

Expt. Nos.	p_{H_2} atms.	p_{CO_2} atms.	$\frac{p_{CO_2}}{p^4_{H_2}}$	$\frac{p^4_{H_2}}{p_{CO_2}}$	CCs. Conotd./c.c. Cot./Min at (Re)			
					150	200	250	300
11-15	0.86	0.14	0.25	3.90	3.4	4.02	4.62	5.25
16-18	0.81	0.18	0.42	2.39	2.64	3.33	4.02	4.70
19-21	0.74	0.25	0.83	1.20	2.24	2.38	2.60	3.02
22-24	0.49	0.49	8.5	0.12	0.5	1.20	1.92	2.62

the values being taken from the figure for various values of (Re). From kinetics of reaction (see introductory section) the rate of a reaction when one molecule of A reacts with a strongly adsorbed molecule of B is given by:-

$$\frac{dx}{dt} = k_1 \times \frac{p_A}{p_B}$$

On/

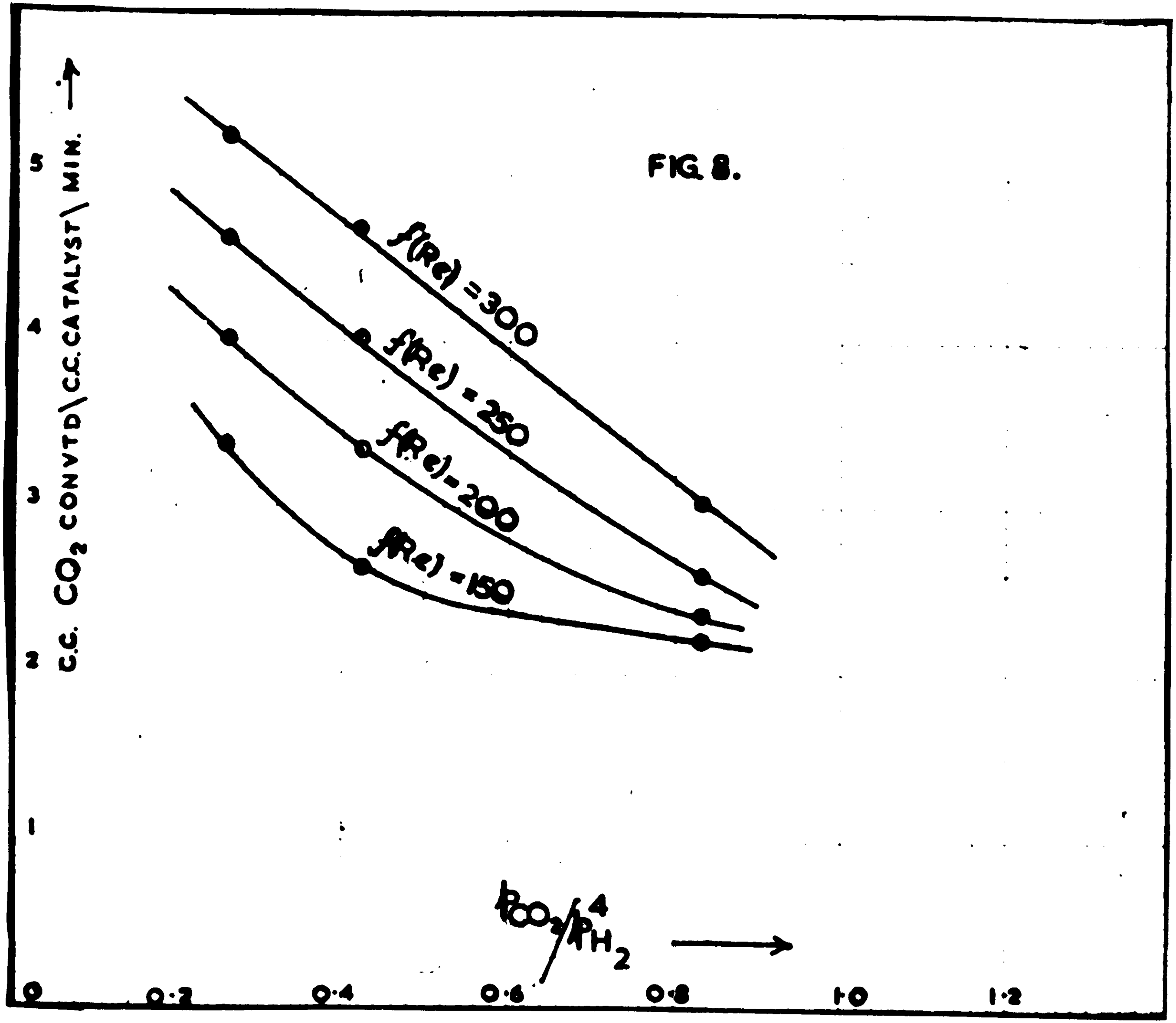
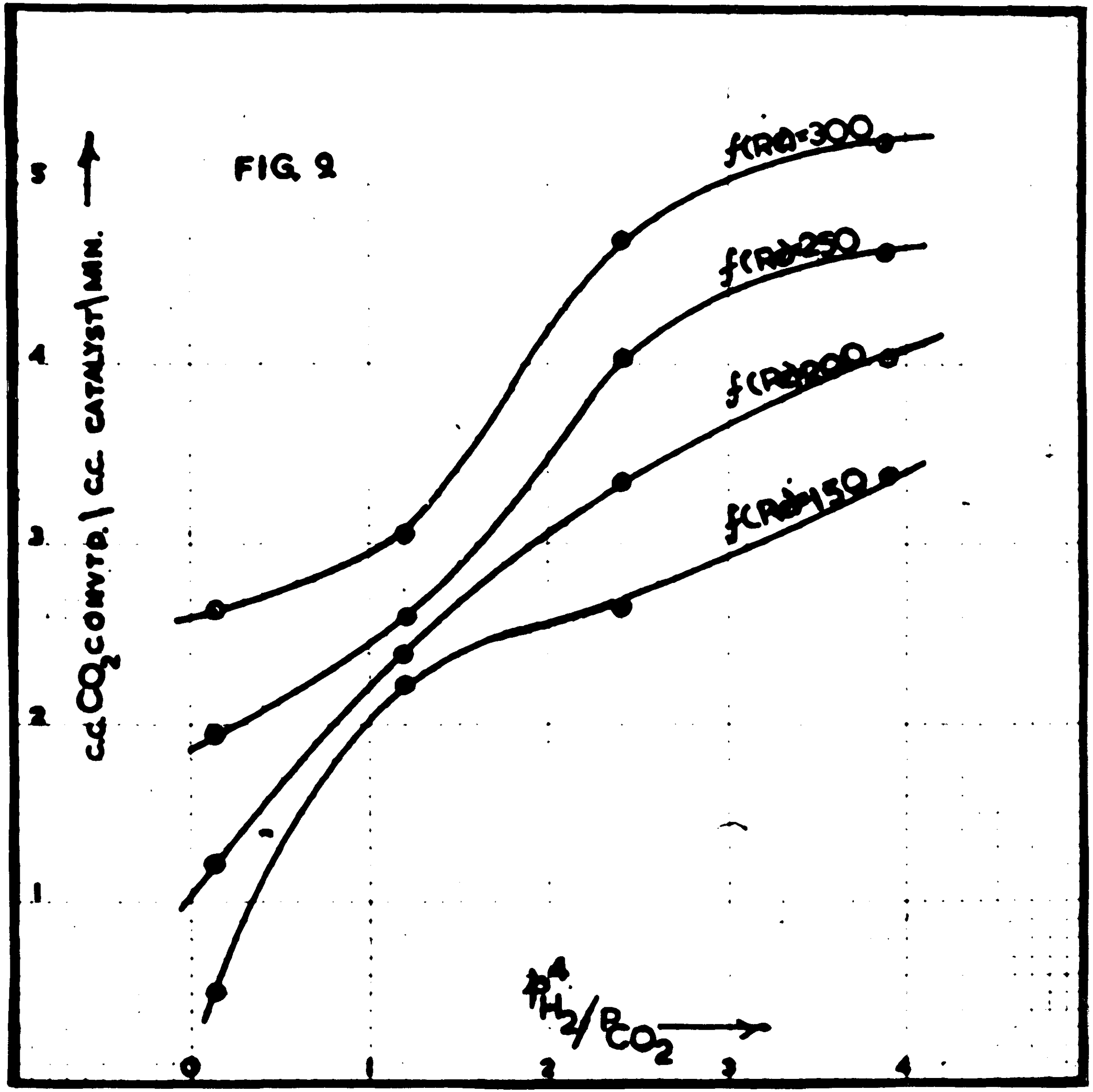


FIG. 8.

C.C. CO_2 CONVTD\C.C. CATALYST\ MIN. →
5
4
3
2
1
0
0·2
0·4
0·6
0·8
1·0
1·2
$P_{CO_2}/P_{H_2}^{4}$ →
f(Re) = 300
f(Re) = 250
f(Re) = 200
f(Re) = 150

FIG. 9


c.c. CO_2 CONVTD. / c.c. CATALYST/MIN.
5
4
3
2
1
0
1
2
3
4
$P^4_{H_2}/P_{CO_2}$
f(R)=300
f(R)=250
f(R)=200
f(R)=150

On the other hand, if one molecule of A reacts with four molecules of B, then $\frac{d\,x}{d\,t} = k_1 \times \frac{p_A}{{p_B}^4}$. Therefore, as hydrogen is known to be far strongly adsorbed than carbon-dioxide by nickel, the equation becomes:-

$$\frac{d\,x}{d\,t} = k_1 \times \frac{p_{CO_2}}{p^4_{H_2}}$$

Thus figure 8 is plotted with yield against $p_{CO_2}/p^4_{H_2}$ The lines obtained are contrary to expectation, because if hydrogen is strongly adsorbed then the yield should increase with the increase in the partial pressure of CO_2 compared to that of hydrogen. On the other hand, the lines in figure 8 fall steadily up to $p_{CO_2}/p^4_{H_2} = 0.8$ and then the slope becomes gradual. This shows that though hydrogen is adsorbed it is not strongly adsorbed. If, on the other hand, CO_2 is the strongly adsorbed gas of the two, then the equation becomes $\frac{d\,x}{d\,t} = k_1 \times \frac{p^4_{H_2}}{p_{CO_2}}$. Thus, in figure 9, yield is plotted against $\frac{p^4_{H_2}}{p_{CO_2}}$. Here the yield rise steadily with increase in partial pressure of H_2. This shows that not only CO_2 is adsorbed by nickel thoria catalyst, but it is the strongly adsorbed of the two gases. Somewhat similar results were noticed when the values were plotted for different values of

rate/

rate instead of f (Re). The same shape of curves were obtained for values of V below 500 c.cs/min. For values more than V = 500, the curves first fall and then rise. These also suggest that both the gases are adsorbed and CO_2 is more strongly adsorbed than hydrogen. Thus, the controlling step in the reaction between carbon dioxide and hydrogen in presence of Ni-ThO_2 catalyst may be the surface reaction between adsorbed CO_2 and adsorbed H_2. In support of this suggestion, the conclusions of W. Aker and R.R. White (96) on a similar problem could be pointed out. They showed that in the reaction between carbon monoxide and hydrogen to form methane, the rate controlling step is the reaction between adsorbed molecules of carbon monoxide and hydrogen.

The calculations along with the Reynolds number for the different sets of experiments are shown in Table 4.

TABLE/

TABLE 4.

Expt. No.	CO_2 %	H_2 %	$f(\rho)$	$f(\mu)$	$f\left(\frac{\rho}{\mu}\right)$	f (V)	f(Re)	Yield.
11	14	86	3.54	152.5	2.33	12.5	29.1	1.82
12	14	86	3.54	152.5	2.33	54.6	127.2	3.19
15	14	86	3.54	152.5	2.33	102.5	238.5	4.46
16	18	81	4.29	157.4	2.72	91.0	247	4.03
17	18	81	4.29	157.4	2.72	47.0	128	2.35
18	18	81	4.29	157.4	2.72	68.3	185.5	3.14
19	25	74	5.62	166.0	3.38	66.6	225.5	2.46
20	25	74	5.62	166.0	3.38	42.2	143.0	2.25
21	25	74	5.62	166.0	3.38	80.0	270.0	2.73
22	50	50	10.32	198.0	5.22	40.0	209	1.31
23	50	50	10.32	198.0	5.22	51.6	270	2.17
24	50	50	10.32	198.0	5.22	69.5	363	3.56

The yield plotted against Reynolds number on log-log graph paper gave the following slopes for the lines.

14% CO_2 ------------ slope = 0.427
18% CO_2 ------------ slope = 0.80
50% CO_2 ------------ slope = 1.87
25% CO_2 ------------ slope = 0.29

A comparison of the slopes with that obtained by plotting yield/

TABLE 5A.

Expt. No.	Carbon dioxide balance.				Recovery.
	In gas collected.			In gas passed. c.cs.	%
	As CH_4. c.cs.	As CO_2. c.cs.	Total c.cs.		
25.	120	301	421	464	91.0
26.	101	377	478	477	100.0
27.	174	258	442	460	96.2
28.	213	685	898	935	96.2
29.	158	749	907	939	97.0
30.	170	850	1020	1000	102.0
31.	118	1214	1332	1446	92.0
32.	335	1082	1417	1437	98.6
33.	218	1063	1281	1400	92.0
34.	123	1382	1505	1460	103.0
35.	165	1300	1465	1444	103.0
36.	162	1275	1438	1440	100.0

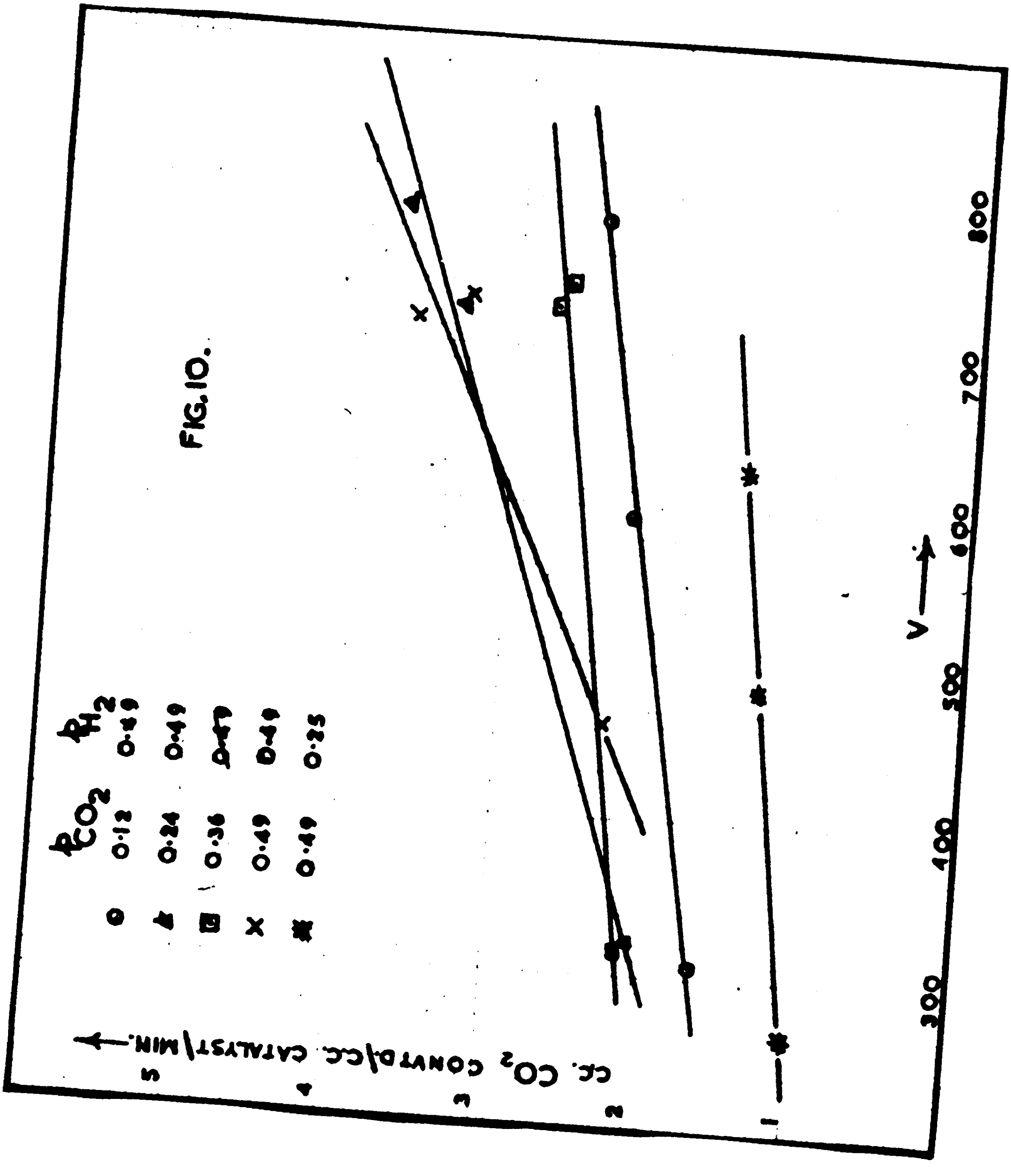
TABLE 5.

Catalyst------- Ni-ThO_2 -- I-B.

Cat. vol. ----- 8.2 c.cs.

Expt.	Time.	Synth. gas compn. %				Product gas compn. %					Wt. of cat	Temp.	Rate.	YIELD.
No.	Mins.	CO_2	H_2	O_2	N_2	CO_2	H_2	CH_4	O_2	N_2	gms.	°C.	c.cs per min.	
25.	6.6	12	48.3	0.3	39.4	10.6	39.4	4.2	0.4	45.4	5.62	280	593	2.17
26.	5.1	11.9	48.4	0.3	39.4	11.1	43.4	2.96	0.2	42.3	5.62	280	784	2.41
27.	12.6	11.8	48.4	0.3	39.5	9.7	35.3	6.6	0.2	49.2	5.62	282	308	1.63
28.	12.2	24.0	49.6	0.4	26.0	23.6	37.2	7.4	0.3	31.5	5.62	280	320	2.08
29.	5.1	24.0	49.6	0.6	25,8	23.7	39.6	5.0	0.6	31.1	5.62	285	784	3.78
30.	5.5	25.0	49.0	0.5	25.5	23.5	40.3	4.7	0.3	31.2	5.28	285	721	3.34
31.	5.4	36.2	49.7	0.6	13.5	37.3	44.8	3.6	0.3	14.0	5.62	285	740	2.67
32.	6.75	35.9	50.6	0.4	13.1	39.7	25.7	12.3	0.2	22.1	5.52	300	592	6.04
33.	12.6	36.0	49.7	0.6	13.7	39.3	34.6	8;1	0.2	17.8	5.52	285	318	2.11
34.	5.5	36.5	49.6	0.7	13.2	37.5	43.0	3.3	0.2	16.0	5.28	285	727	2.74
35.	5.7	36.1	49.0	0.5	14.4	36.0	40.9	4.6	0.3	18.2	5.28	288	702	3.54
36.	8.25	36.0	49.2	0.6	14.2	38.4	39.8	4.8	0.8	16.2	5.28	285	485	2.40

FIG. 10.


p_{CO_2}
p_{H_2}
○ 0·12 0·49
▲ 0·24 0·49
⊡ 0·36 0·49
× 0·49 0·49
✱ 0·49 0·25
C.C. CO_2 CONVTD/C.C. CATALYST/MIN. →
1
2
3
4
5
300
400
500
600
700
800
V →

yield against rate on log-log graph shows that to get a correlation between function of velocity and function of Reynolds is difficult.

Partial Pressure of One Component Varying:-

It was then decided to study the reaction keeping the partial pressure of one of the components constant and varying the partial pressure of the other by introducing a third inert gas, nitrogen. This is not so desirable a method as reaction carried under pressure or vacuum. Nitrogen might exert some effect on this reaction. Tables 5 and 5-A give the results of experiments in which H_2 is constant and CO_2 varied. These are plotted in figure 10. It would be noted from this figure that the lines for $p_{CO_2} = 0.12$, $p_{H_2} = 0.49$ and $p_{CO_2} = 0.24$, $p_{H_2} = 0.49$ are in order. Some difficulty was encountered for $p_{CO_2} = 0.36$, $p_{H_2} = 0.49$. Experiment 32 gave a very high yield and the temperature in this case went beyond 300°C. To confirm the result it was repeated thrice. The yield for experiment 35 is far below and is only about 3.5. Experiments 31 and 34 seem to give almost concordant results. So, taking these to be correct, the line for $p_{CO_2} = 0.36$, $p_{H_2} = .49$ is drawn.

The experiments with partial pressure of CO_2 constant and varying that of H_2 are tabulated in tables 6 and 6-A. These values are plotted in figure 10, along with the values for keeping/

TABLE 6A.

Carbon dioxide balance.

Expt. No.	In gas collected.			In gas passed c.cs.	Recovery %
	As CH_4 c.cs.	AS CO_2 c.cs.	Total c.cs.		
37.	161	1813	1974	1948	101
38.	169	1827	1996	1984	99.4
39.	150	1820	1970	1941	101.5
40.	162	1800	1962	1980	99.0
41.	76	1889	1965	1936	101.5
42.	129	1810	1939	1952	99.3
43.	93	1855	1948	1960	99.5
44.	120	1884	1896	1905	99.5
45.	118	1885	2003	2016	99.4
46.	73	2866	2939	2958	99.4

TABLE 6.

Catalyst ---------- Ni-ThO_2 -- IB.
Catalyst volume -- 8.2 c. cs.

Expt. No.	Time. Mins.	Synthesis gas %. CO_2	H_2	O_2	N_2	Product gas % CO_2	H_2	O_2	CH_4	N_2	Wt. of cat Gms.	Temp. °C.	Rate. c.cs. per min.	Yield
37.	6.1	49.0	50.3	0.2	0.5	52.1	41.7	0.2	4.6	1.4	5.39	290	658	5.0
38.	5.6	49.6	49.0	0.2	1.2	50.9	40.6	0.5	4.72	3.2	5.28	288	714	3.68
39.	5.5	48.5	49.8	0.7	1.0	53.5	40.2	0.5	4.4	1.3	5.28	288	727	3.33
40.	8.7	49.5	49.3	0.2	1.0	54.1	39.0	0.3	4.86	1.7	5.28	285	460	2.30
41.	6.4	~~6.4~~ 48.5	48.5	0.6	25.9	50.3	19.1	0.2	2.04	28.4	5.39	283	625	1.45
42.	15.1	49.0	24.0	0.4	26.6	51.0	14.2	0.4	3.6	30.8	5.39	284	265	1.04
43.	8.3	49.0	25.0	0.5	25.5	51.8	17.5	0.6	2.6	27.5	5.30	285	482	1.30
44.	6.5	48.0	18.7	0.6	32.7	49.6	16.3	0.6	0.33	33.2	5.30	283	615	0.24
45.	6.4	50.4	40.4	0.6	8.6	53.8	32.5	0.5	3.28	9.9	5.39	288	721	2.25
46.	6.4	73.0	25.0	0.6	1.4	75.4	20.2	0.4	1.9	2.0	5.39	283	625	1.40

keeping p_{H_2} constant and varying p_{CO_2}. Experiments 37, 38, 39 and 40 are all with $p_{CO_2} = 0.5$, $p_{H_2} = 0.5$. The yield for experiment 37 was too high as in experiment 32. So, to confirm it, experiments 38 and 39 were done and their values are far below that of 37, but agreement between the two is satisfactory. They just fall on both sides of line for $p_{CO_2} = .24$, $p_{H_2} = 0.49$.

To understand figure 10 better, the following table is drawn up for a value of V = 700.

TABLE 7.

p_{H_2}	0.49	0.49	0.49	0.49
p_{CO_2}	0.12	0.24	0.36	0.49
Yield	2.3	3.4	2.7	3.45

also Table 8 is drawn up for a value of V = 650 where most of the points for keeping p_{CO_2} constant and p_{H_2} varying seem to fall.

TABLE 8.

p_{CO_2}	0.49	0.49	0.49	0.49
p_{H_2}	0.18	0.25	0.40	0.49
Yield	0.24	1.5	2.2	3.2

The/

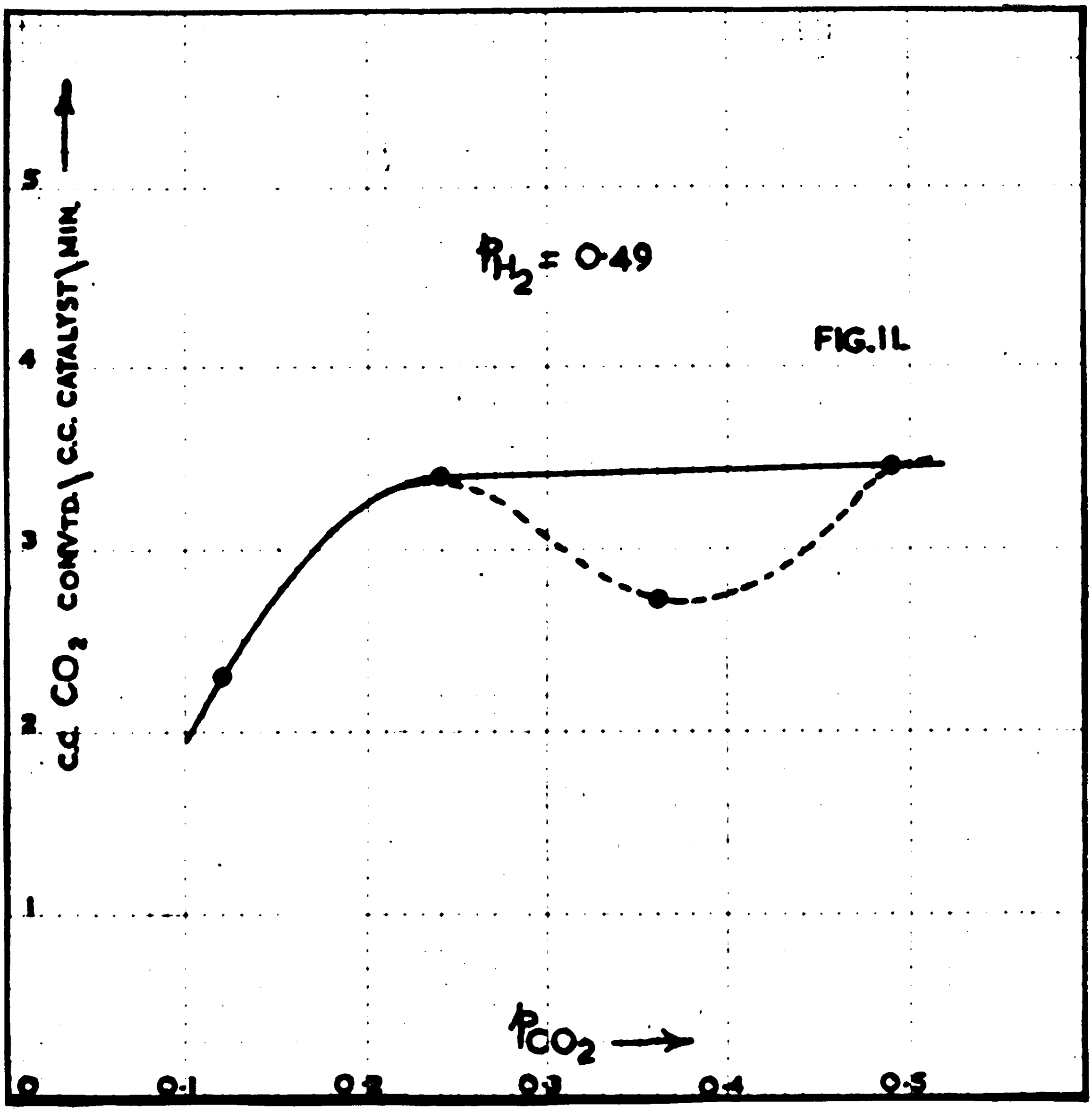

C.C. CO₂ CONV'TD.\ C.C. CATALYST\ MIN.
5
4
3
2
1
0
0·1
0·2
0·3
0·4
0·5
P_{H_2} = 0·49
P_{CO_2} →

FIG. 1L

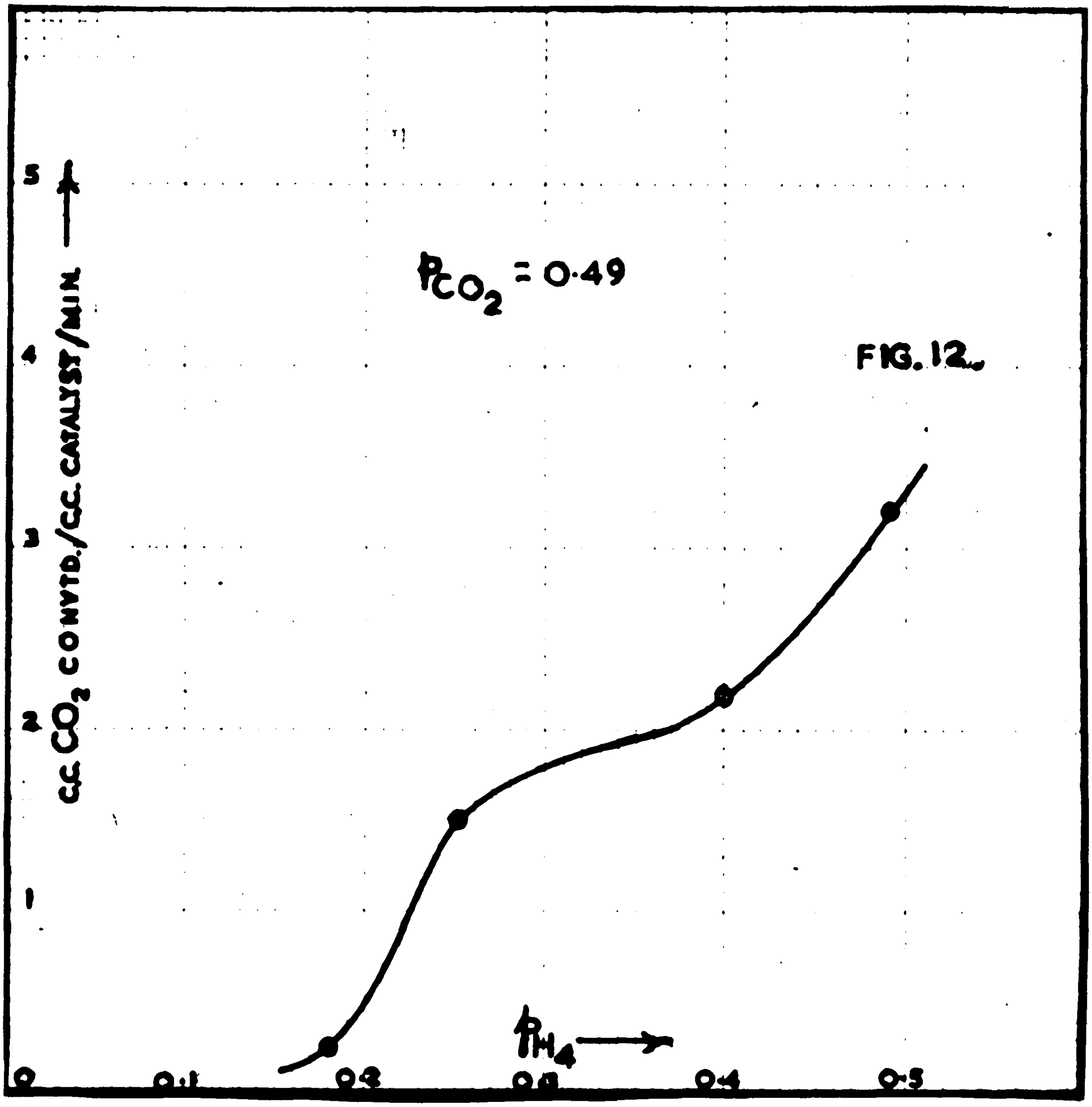


FIG. 12.

READ p_{H_2} FOR p_{H_4}

The results of table 7 are plotted in figure 11, and it is seen that as the partial pressure of CO_2 is increased there is a rise in yield at first and then it remains steady up to $p_{CO_2} = 0.49$, $p_{H_2} = 0.49$. Taking the point for $p_{CO_2} = 0.36$ into account there is a fall and rise in the yield between $p_{CO_2} = 0.24$ and $p_{CO_2} = 0.49$ as shown by the dotted line. If this is correct, the behaviour is unusual. In the first case, as the partial pressure of CO_2 is increased it displaces more of hydrogen from the catalyst surface so that yield increases due to increase in CO_2 on the surface for reaction. Beyond a value of p_{CO_2} = about 0.24 the increase in pressure of CO_2 has little effect on yield. This suggests that the rate at which CO_2 displaces H_2 from catalyst surface is very rapid at first, then slows down, and finally the rate of displacement falls to zero up to a certain limit of about $p_{CO_2} = 0.49$. Further increase in p_{CO_2} may, however, displace more of H_2 so that enough H_2 is not present on surface for reaction. This is seen from result of experiment 46 (table 6) where $p_{CO_2} = 0.73$, $p_{H_2} = 0.25$ and the yield is only 1.4 for a rate of 625 c.cs/min.

The results of table 8 are plotted in figure 12, and it is seen that as the partial pressure of H_2 is increased the yield increases suggesting that the H_2 progressively displaces CO_2 so that more and more of the H_2 is available for reaction on/

on the surface of the catalyst. At low partial pressures of H_2 of the order of 0.18, it is seen that there is very little reaction. This may be due to the fact that the H_2 may not be sufficient to displace the CO_2, which has been shown to be more strongly adsorbed.

The general trend of experimental results seems to show that both CO_2 and H_2 are adsorbed on the catalyst surface and reaction results from the interaction of the adsorbed molecules. The diffusion of the reactants and products through a gaseous film existing at the surface of the catalyst seems not to have any considerable effect on the reaction rate.

PART II.

Interaction of Carbon dioxide and Hydrogen in presence of Nickel Catalyst.

INTRODUCTION.

The reaction between carbon dioxide and hydrogen was studied in presence of unpromoted nickel catalyst. The apparatus employed and the experimental technique were the same as used in the study of the reaction in presence of promoted nickel catalyst. The experimental results are given in Tables 1, 1a and 4, 4a.

SECTION A.

THE DISCUSSION OF THE RESULTS.

1. The partial pressure of CO_2 varying.

The experiments 1 to 21 were carried out keeping the partial pressure of hydrogen constant at about 0.49 atmosphere and varying that of Carbon dioxide. The results are tabulated in table 1, where the experiments 1 to 5 are with $p_{CO_2} = 0.12$; from 6 to 12 are with $p_{CO_2} = 0.24$; from 13 to 16 are with $p_{CO_2} = 0.35$ and those from 17 to 21 are with

p/

TABLE IA.

Catalyst — Ni IIA.

Cat. vol. ––– 8.2 c.cs.

Carbon dioxide balance.

Expt. No.	In gas collected.			In gas passed.	Recovery.
	AS CO_2 c.cs.	AS CH_4 c.cs.	Total c.cs.	c.cs.	%
1.	368	132	500	468	106
2.	433	127	560	530	105
3.	369	131	500	460	108
4.	352	148	500	461	108
5.	400	151	551	534	
6.	954	136	1090	1075	101
7.	826	134	960	948	101
8.	875	111	986	988	100
9.	1155	125	1280	1200	106
10.	885	98	982	964	101
11.	874	96	970	964	100.5
12.	885	115	1000	988	101
13.	1131	149	1280	1240	103
14.	1223	177	1400	1380	101
15.	1594	226	1820	1800	101
16.	1270	180	1450	1390	104
17.	1798	162	1960	1910	102
18.	1819	161	1980	1940	102
19.	1732	158	1890	1960	97
20.	1739	161	1900	1880	101
21.	1778	162	1940	1930	100.5

TABLE 1.

TABLE 1.

Catalyst ---- Ni IIA.

Cat. vol. --- 8.2 c.cs.

Expt. No.	Temp. °C.	Time. Mins.	Synthesis gas %				Product gas %					Weight of cat. gms.	Rate. c.cs. per min.	Yield.	f(Re)
			CO_2	O_2	H_2	N_2	CO_2	O_2	CH_4	H_2	N_2				
1.	285	14	11.7	0.6	49.0	38.7	10.2	0.1	3.49	43.5	42.7	5.46	285	1.15	10.5
2.	284	7.5	13.2	0.2	49.2	37.4	11.9	0.1	3.28	41.5	43.2	5.46	534	2.08	19.8
3.	282	5.75	11.5	0.3	49.8	38.4	10.7	0.2	3.44	44.0	41.8	5.46	695	2.78	25.7
4.	285	4.75	11.3	0.4	49.6	38.7	10.3	0.1	3.80	42.0	43.8	5.46	863	3.71	32.0
5.	285	4.15	13.3	0.3	49.0	37.4	10.3	0.1	3.88	41.0	44.7	5.88	996	4.57	36.9
6.	285	15.25	23.9	0.6	49.8	25.7	22.6	0.3	3,43	43.0	30.7	5.88	295	1.09	12.2
7.	285	13.5	23.7	0.6	49.2	26.5	22.6	0.1	3.62	43.1	30.6	5.88	338	1.21	14.0
8.	285	9.5	24.7	0.7	50.3	24.3	23.9	0.3	2.95	45.0	27.9	5.88	421	1.43	17.4
9.	282	8.3	23.4	0.6	49.4	26.6	24.6	0.2	2.61	43.6	29.0	5.38	615	1.84	25.4
10.	285	5.25	24.1	0.6	50.8	24.5	23.1	0.5	2.55	45.0	28.8	5.38	763	2.27	31.6
11.	282	4.5	24.1	0.6	48.9	26.4	22.9	0.3	2.51	44.5	29.8	5.38	889	2.67	37.2
12.	285	4.0	24,7	0.4	49.9	24.2	23.2	0.3	2.86	45.2	29.5	5.56	1000	3.42	41.4
13.	284	8.0	35.3	0.4	49.9	14.4	34.7	0.2	4.46	41.3	19.4	5.56	448	2.32	20.5
14.	286	6.0	34.4	0.6	48.8	16.2	33.4	0.2	4.60	41.6	20.2	5.56	666	3.60	30.4
15.	285	7.0	35.5	0.4	50.4	13.7	33.6	0.2	3.88	42,5	19.8	5.92	722	3.90	35.0
16.	286	4.5	34.7	0.6	50.2	14.5	34.0	0.1	4.68	41.8	19.4	5.92	889	4.88	41.0
17.	285	11.5	47.8	0.4	49.6	2.2	47.7	0.1	4.26	43.1	4.8	5.92	348	1.72	17.7
18.	285	8.0	48.5	0.6	48.6	2.3	48.4	0.2	4.21	41.0	6.2	5.92	500	2.46	25.5
19.	282	6.5	49.0	0.6	49.3	1.1	48.2	0.2	4.08	42.5	5.0	5.92	615	2.96	31.4
20.	286	5.5	47.0	0.6	50.4	2.0	46.1	0.2	4.17	44.2	5.3	5.28	728	3.58	37.2
21.	282	4.5	48.1	0.4	49.8	1.7	47.5	0.1	4.17	42.0	6.2	5.28	889	4.35	45.8

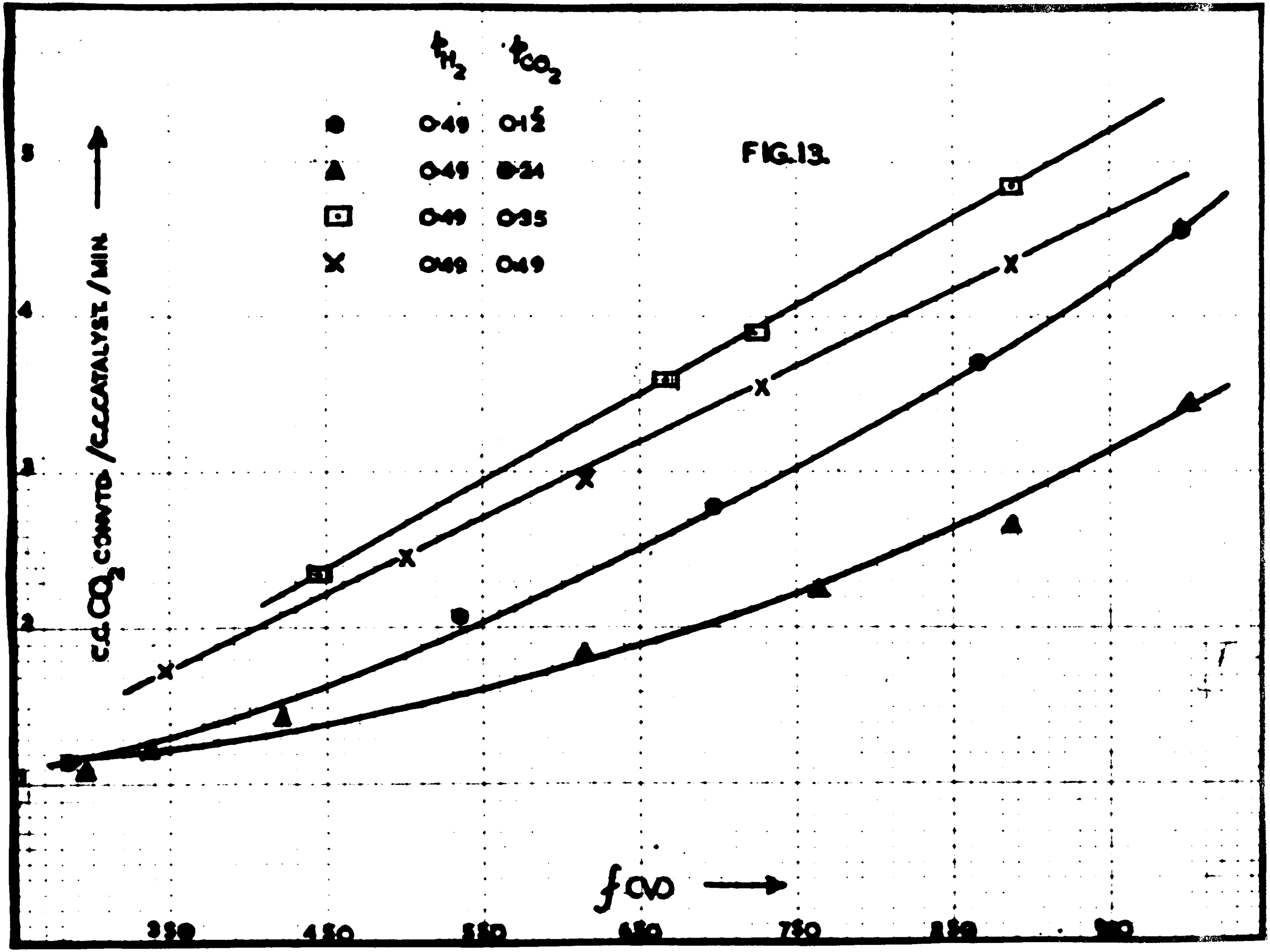

p_{H_2} p_{CO_2}
● 0·49 0·12
▲ 0·49 0·24
⊡ 0·49 0·35
× 0·49 0·49
c.c. CO_2 CONVTD /c.c.CATALYST /MIN
1
2
3
4
5
f CVD
350
450
550
650
750
850
950

FIG.13.

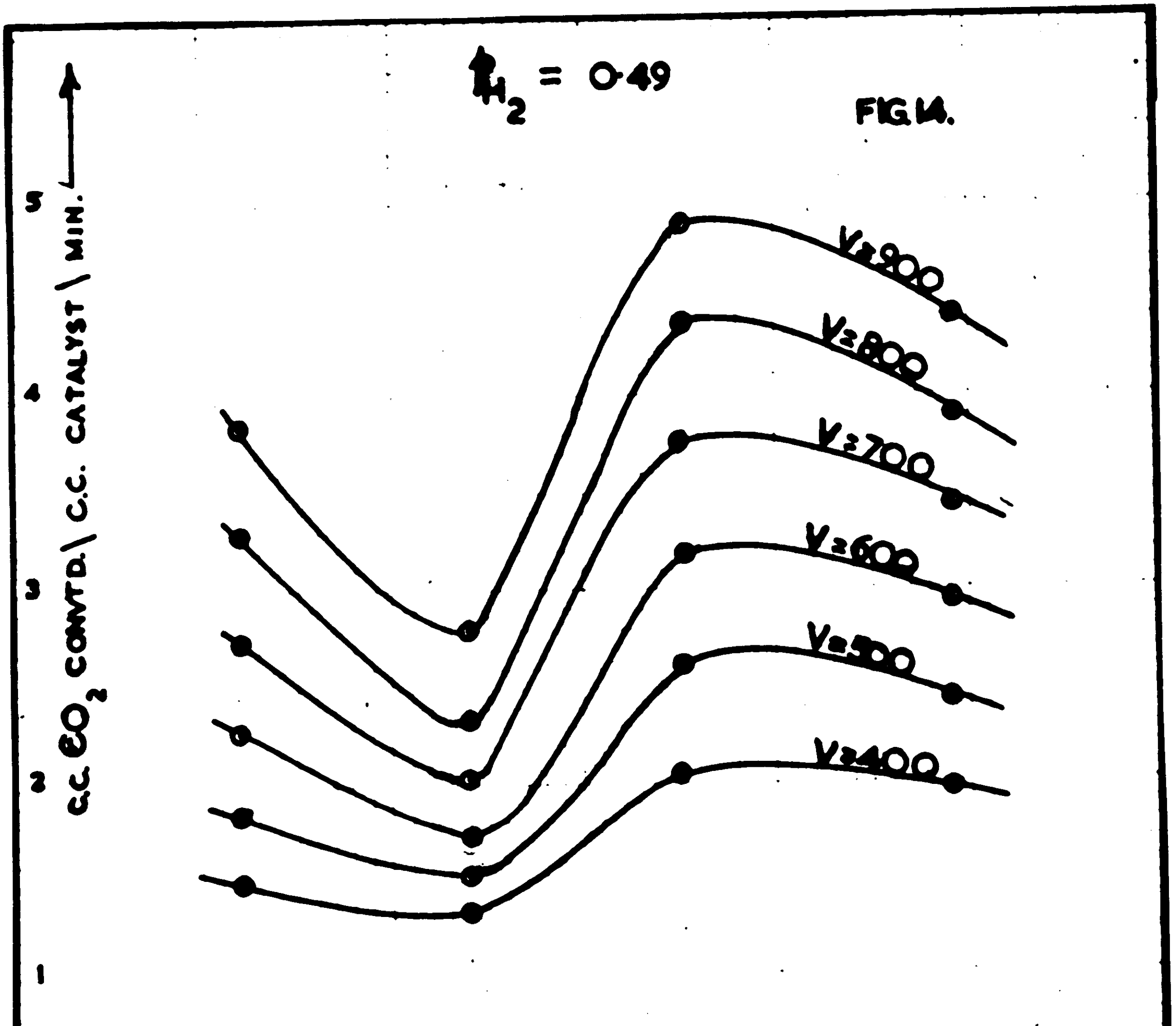
$p_{CO_2} = 0.49$. Considering the exothermic nature of the reaction, the temperature control was more or less satisfactory and was kept within the limits 282° to 286° and mostly at 285°. Only three or at most four runs were performed on each batch of freshly reduced catalyst so that full activity of the catalyst is ensured for each run. However, it should be pointed out that complete reduction of the catalyst was not tested for, and reduction conditions might not always be identical. Table 1A shows the carbon dioxide balance. As seen from experiments 1 to 5, it is difficult to obtain a good balance when the concentration of carbon dioxide is small of the order of 12%.

In Figure 13, the yield (c.cs. of CO_2 converted per c.c. of catalyst per minute) is plotted against rate, V. (c.cs. of gas per minute). From Figure 13, it is seen that the yield rises for a given rate in the order of $p_{CO_2} = 0.24$, $p_{CO_2} = 0.12$; $p_{CO_2} = 0.49$; and $p_{CO_2} = 0.36$, the value of p_{H_2} being 0.49 in all the cases. The yield for $p_{CO_2} = 0.24$ is far below that of the yield for $p_{CO_2} = 0.12$ and is very peculiar. This somewhat resembles results obtained in case of Ni-ThO_2 catalyst where the figures for the yield with a 25% CO_2 75% H_2 mixture were below those with a 14% CO_2 86% H_2 mixture.

So as to picture the experimental results in a better way, Table 2 is drawn up from Figure 13.

TABLE/

FIG. 14.



$p_{H_2} = 0{\cdot}49$
C.C. CO_2 CONVTD. \ C.C. CATALYST \ MIN.
5
4
3
2
1
V=900
V=800
V=700
V=600
V=500
V=400
p_{CO_2}
0
0·1
0·2
0·3
0·4
0·5

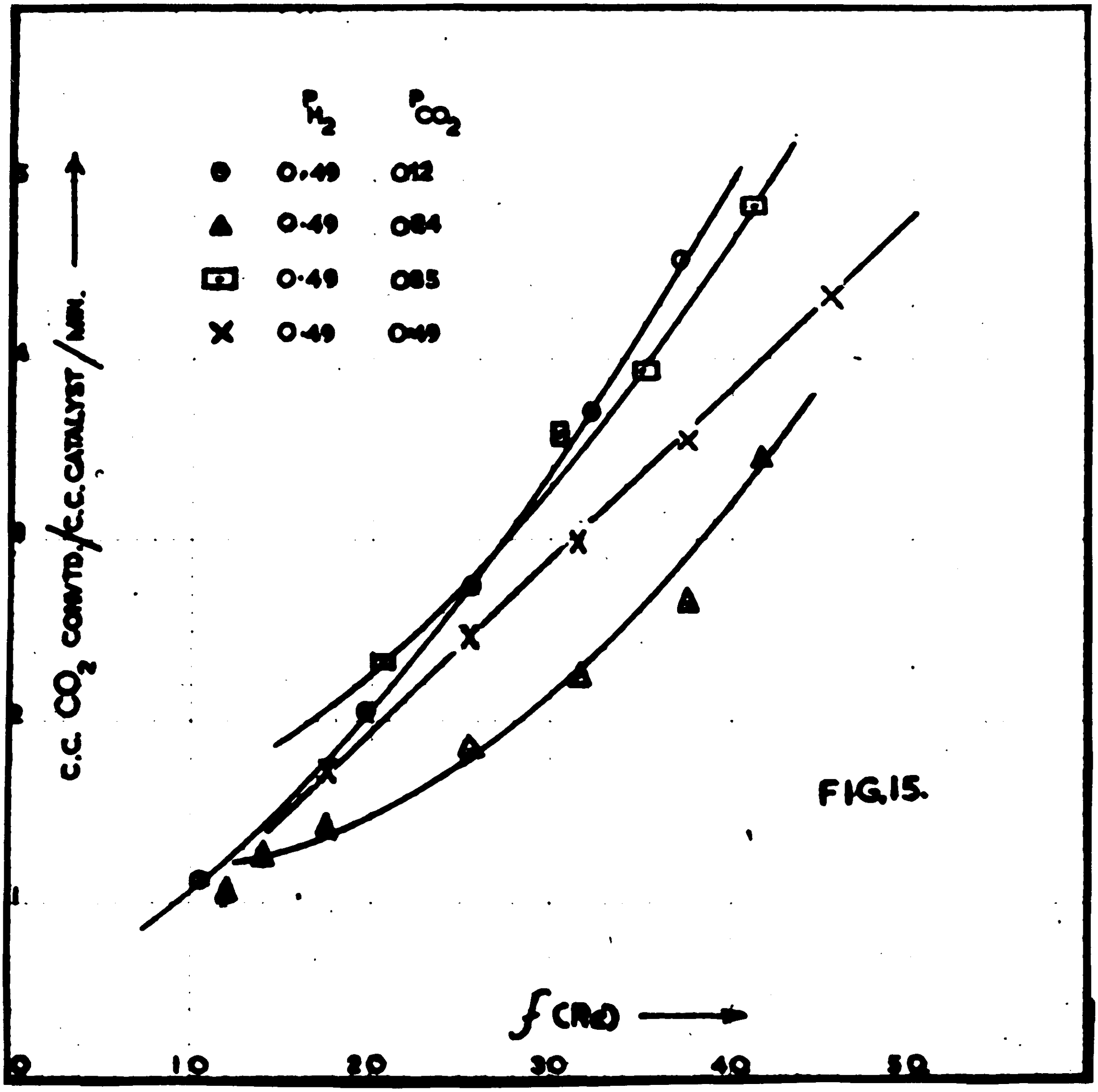

P_{H_2}
P_{CO_2}
● 0·49 012
▲ 0·49 084
⊡ 0·49 085
× 0·49 0·49
C.C. CO_2 CONV'TD./C.C. CATALYST/MIN.
1
ƒ(RE)
0
10
20
30
40
50

FIG.15.

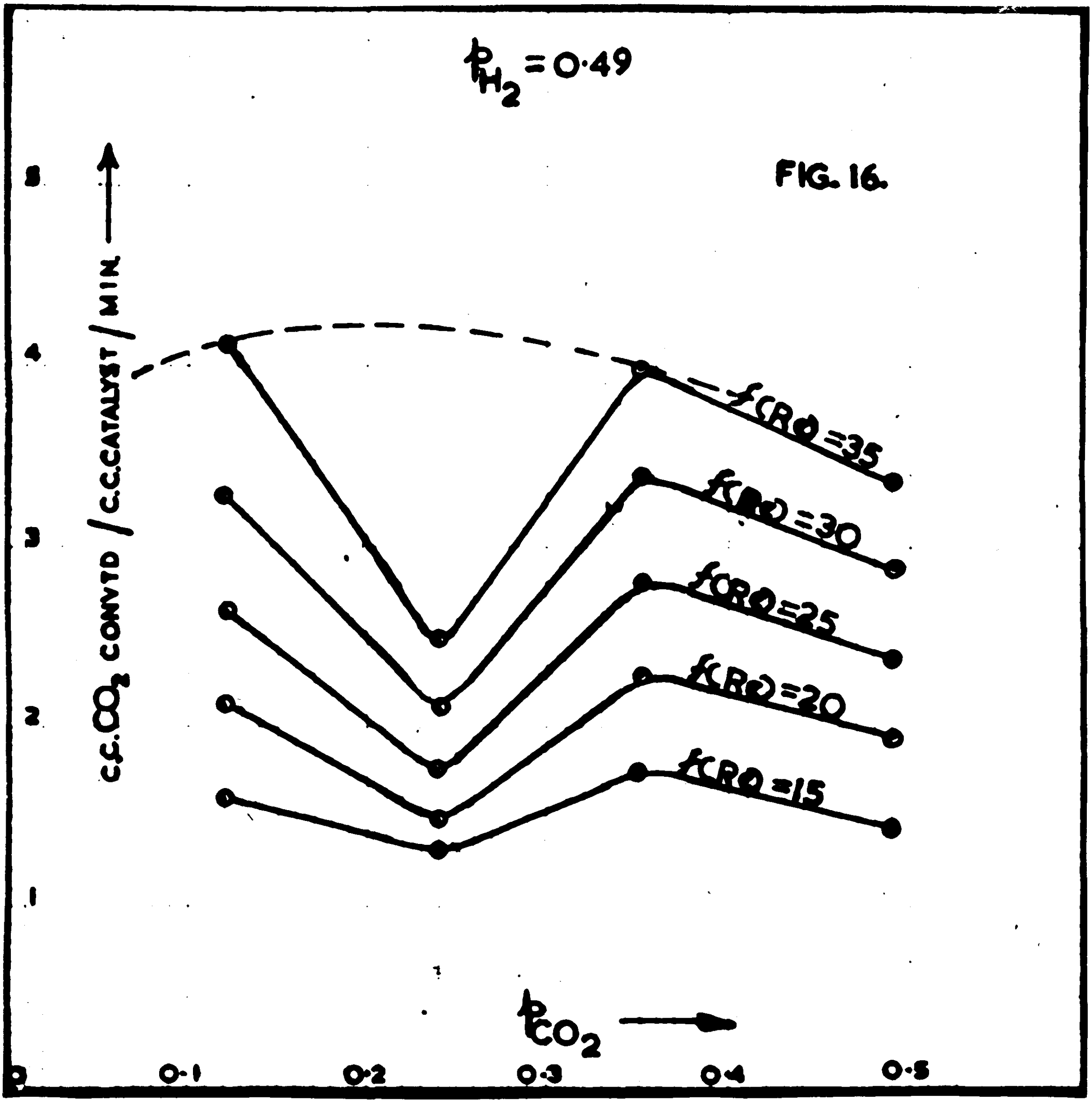
TABLE 2.

Expt. Nos.	p_{H_2}	p_{CO_2}	C.Cs. CO_2 convtd./c.c. cat./min. at velocities:-					
			400	500	600	700	800	900
1-5	0.49	0.12	1.50	1.85	2.30	2.75	3.30	3.85
6-12	0.49	0.24	1.32	1.51	1.75	2.02	2.35	2.80
13-16	0.49	0.35	2.05	2.62	3.20	3.78	4.35	4.90
17-21	0.49	0.49	1.98	2.45	2.95	3.42	3.90	4.40

showing the partial pressures of hydrogen and carbon dioxide and the corresponding yields at rates equal to 400, 500, 600, 700, 800 and 900 c.cs. per minute. The values, yield Vs p_{CO_2} are plotted in Figure 14 for the various rates. The shape of these curves indicates that as p_{CO_2} is slowly raised from 0 to 0.5 keeping p_{H_2} at 0.49, the yield rises at first, then falls, rises again, and finally falls. The first fall in the shape of the curves is very difficult to understand.

The yield is plotted against a function of Reynold's Number f (Re) in Figure 15. The values for f (Re) were calculated only for the inflowing synthesis mixture, because it was found that it is not very different from the average of f (Re) initial, and f (Re) final, taking into consideration the presence of water vapour as well, in the product. In Figure 15 the lines are more closer and compact than in Figure 13, but results are confused and indeterminate.

To/



$p_{H_2} = 0{\cdot}49$
C.C. CO₂ CONVTD / C.C. CATALYST / MIN.
5
4
3
2
1
f(Re) = 35
f(Re) = 30
f(Re) = 25
f(Re) = 20
f(Re) = 15
p_{CO_2}
0
0·1
0·2
0·3
0·4
0·5

FIG. 16.

To understand the significance of Figure 15, the partial pressures of carbon dioxide and the corresponding yields at f (Re) = 15, 20, 25, and 30 are tabulated in Table 3.

TABLE 3.

Expt. Nos.	p_{H_2}	p_{CO_2}	C.Cs.CO_2 convtd/C.C. Cat/min. at f(Re)=				
			15	20	25	30	35
1-5	0.49	0.12	1.60	2.12	2.68	3.3	4.15
6-12	0.49	0.24	1.32	1.50	1.78	2.1	2.50
13-16	0.49	0.35	1.78	2.30	2.80	3.4	4.0
17-21	0.49	0.49	1.45	1.95	2.40	2.9	3.35

Figure 16 gives these values plotted, yield against p_{CO_2} for the various values of f(Re). The nature of the curves in Figure 16 is the same as that in Figure 14, except for the difference that the yield for $p_{CO_2} = 0.12$ is higher than for $p_{CO_2} = 0.36$ at values of f(Re) beyond 32. Thus the introduction of the factor f(Re) has not helped to explain the behaviour of $p_{CO_2} = 0.24$, $p_{H_2} = 0.49$, synthesis mixture, but has made an even plot of yield Vs p_{CO_2}.

If, at present, the existence of the $p_{CO_2} = 0.24$ line is overlooked, then the nature of curves would be as shown by/

by the dotted lines in Figure 14 and 16. That is to say, keeping p_{H_2} at 0.49, the rate of reaction rises rapidly at first as p_{CO_2} is pushed up from 0 to 0.12, then the rate remains almost steady till p_{CO_2} reaches the value of 0.36 (Figure 16), and then falls with further increase of p_{CO_2}. This could be explained by assuming from the nature of reaction of CO_2 and H_2 on the promoted nickel catalyst, that both the gases are adsorbed on the catalyst and reaction takes place between the adsorbed molecules of CO_2 and H_2. Thus, in the initial stages, addition of carbon dioxide displaces some of the adsorbed hydrogen, so that more adsorbed CO_2 is available on the catalyst surface for the adsorbed H_2 to react with. This process is carried on till an optimum stage is reached when further additions of CO_2 cause no appreciable difference in the ratio in which CO_2 and H_2 are adsorbed on the catalyst. This remains so up to a certain point beyond which further increase in the partial pressure of CO_2 displaces more of the adsorbed hydrogen to disadvantage so that there is not enough hydrogen on the catalyst surface to react with the adsorbed CO_2 molecules.

II. THE PARTIAL PRESSURE OF H_2 VARYING.

Experiments were carried out keeping the partial pressure of CO_2 constant at about 0.49 and varying the partial pressure of/

TABLE 4-A.

Catalyst -- Ni IIA.

Cat. vol. --- 8.2 c.cs.

Carbon dioxide balance.

Expt. No.	In gas collected. AS CO_2 c.cs.	As CH_4 c.cs.	Total c.cs.	In gas passed c.cs.	Recovery %
17.	1798	162	1960	1910	102
18.	1819	161	1980	1940	102
19.	1732	158	1890	1960	97
20.	1739	161	1900	1880	101
21.	1778	162	1940	1930	100.5
22.	1840	137	1977	1980	99.9
23.	1851	129	1980	1952	101.5
24.	1825	125	1950	1920	101.5
25.	1800	140	1940	1900	102
26.	2118	142	2260	2210	102
27.	1848	122	1970	1940	101
28.	1857	113	1970	1956	100.5
29.	1870	107	1977	1980	99.9
30.	1840	100	1950	1960	99.8
31.	1820	98	1918	1930	99.8

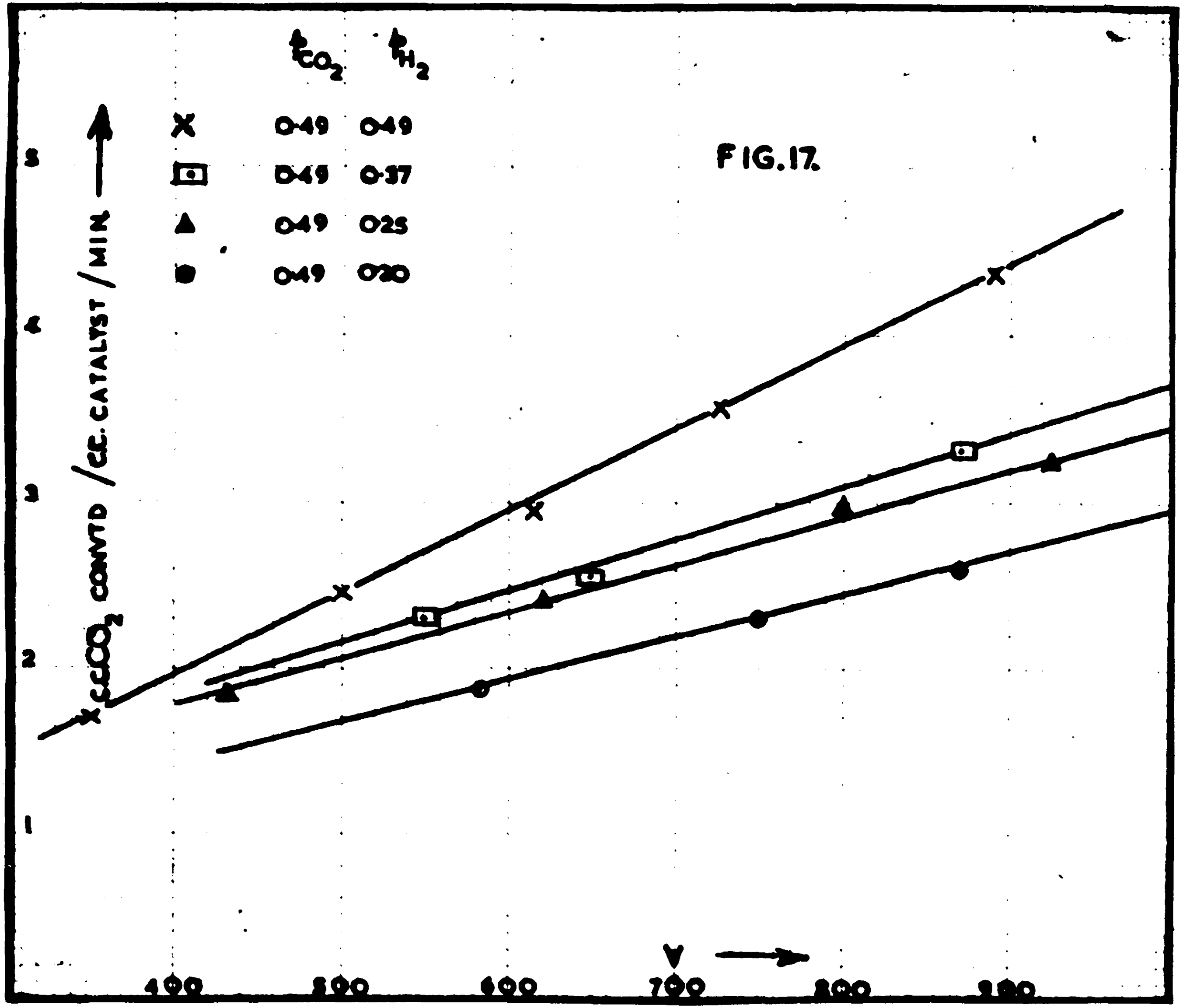
TABLE 4.

TABLE 4.

Catalyst ------ Ni IIA

Cat. vol. -------- 8.2 c.cs.

Expt. No.	Temp. °C.	Time. Mins.	Synthesis gas %				Product gas %					Weight of cat. gms.	Rate. c.cs. per min.	Yield.	f(Re)
			CO_2	O_2	H_2	N_2	CO_2	O_2	CH_4	H_2	N_2				
17.	285	11.5	47.8	0.4	49.6	2.2	47.7	0.1	4.26	43.1	4.8	5.92	348	1.72	17.7
18.	285	8	48.5	0.6	48,6	2.3	48.4	0.2	4.21	41.0	6.2	5.92	500	2.46	25.5
19.	282	6.5	49.0	0.6	49.3	1.1	48.2	0.2	4.08	42.5	5.0	5.92	615	2.96	31.4
20.	286	5.5	47.0	0.6	50.4	2.0	46.1	0.2	4.17	44.2	5.3	5.28	728	3.58	37.2
21.	282	4.5	48.1	0.4	49.8	1.7	47.5	0.1	4.17	42.0	6.2	5.28	889	4.35	45.8
22.	284	7.25	49.5	0.6	37.5	12.4	53.1	0.3	4.04	27.0	15.6	5.28	550	2.30	29.5
23.	282	6.15	48.8	0.8	37,2	13.2	48.2	0.2	3.30	31.2	17.1	5.28	650	2.56	34.9
24.	282	4.6	48.0	0.6	37.7	13.7	47.2	0.1	3.20	31.0	18.5	5.28	870	3.30	46.7
25.	286	9.15	47.5	0.4	25.2	28.9	47.5	0.1	3.63	16.3	32.5	5.99	433	1.84	23.8
26.	286	7.25	49.0	0.6	24.0	26.4	50.1	0.2	3.28	13.8	32.6	5.99	620	2.40	34.1
27.	285	5.0	48.5	0.6	25.5	25.4	48.0	0.1	3.12	17.0	31.8	5.99	800	2.98	44.0
28.	285	4.33	48.4	0.4	25.8	25.4	47.6	0.1	2.92	18.8	30.6	5.99	924	3.25	50.8
29.	284	6.85	49.5	0.6	19.1	30.8	52.5	0.2	3.02	9.5	34.8	5.49	585	1.90	33.2
30.	282	5.33	48.9	0.4	19.9	30.8	51.5	0.1	2.80	11.2	34.4	5.49	750	2.29	42.5
31.	286	4.6	48.1	0.3	20.2	31.4	47.1	0.1	2.54	18.2	32.2	5.49	870	2.62	49.3



c.c.CO_2 CONVTD /CC. CATALYST /MIN
5
4
3
2
1
400
500
600
700
800
900
V
p_{CO_2} p_{H_2}
× 0·49 0·49
⊡ 0·49 0·37
▲ 0·49 0·25
● 0·49 0·20

FIG.17.

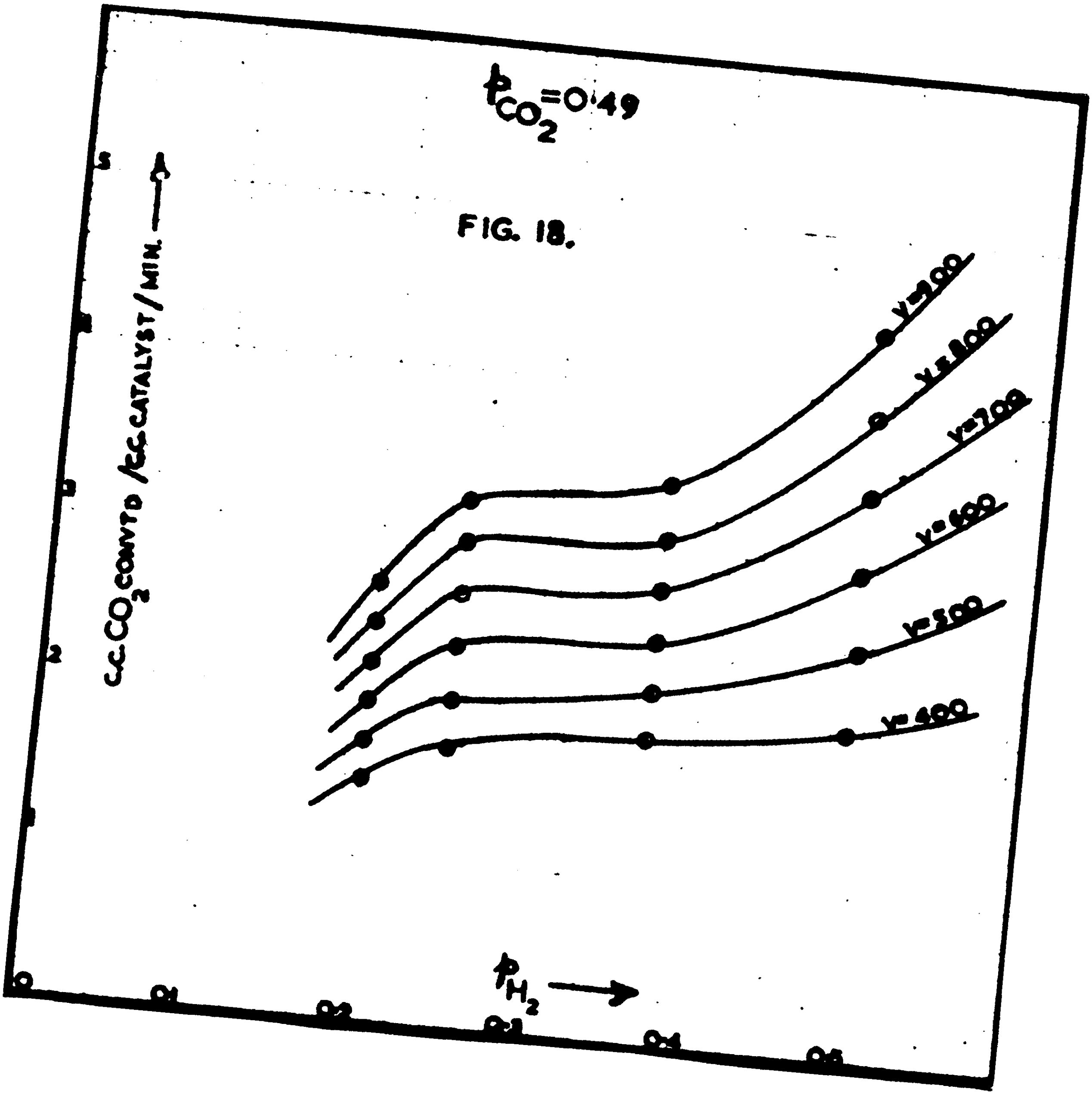


FIG. 18.

$p_{CO_2} = 0{\cdot}49$
C.C. CO_2 CONVTD /C.C. CATALYST/MIN. →
p_{H_2} →
v=900
v=800
v=700
v=600
v=500
v=400
0
0·1
0·2
0·3
0·4
0·5
5
2

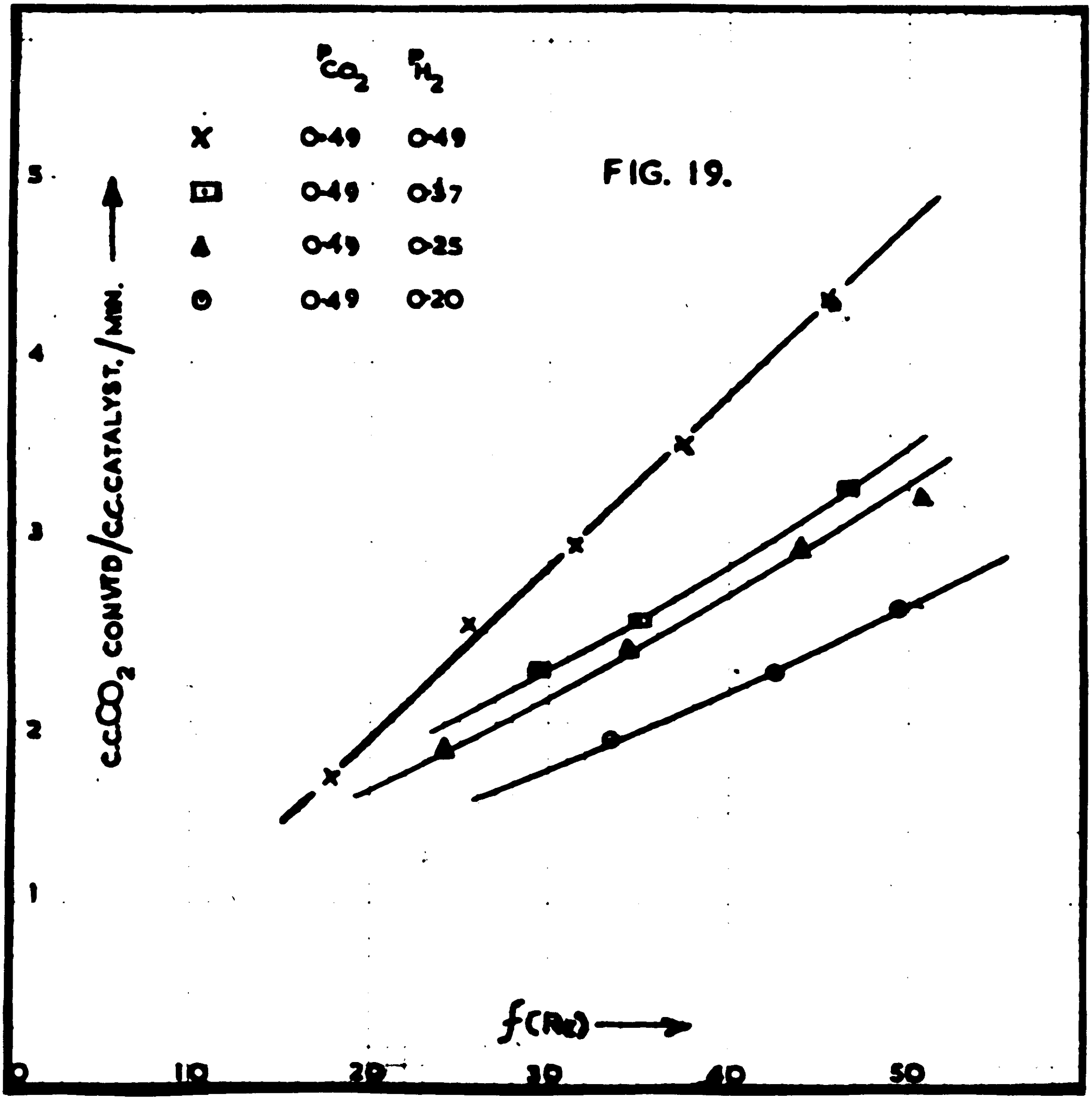


FIG. 19.

p_{CO_2}
p_{H_2}
× 0·49 0·49
⊡ 0·49 0·37
▲ 0·49 0·25
⊙ 0·49 0·20
C.C. CO_2 CONV'D/C.C. CATALYST./MIN. →
$f(p_{H_2})$ →
1
2
3
4
5
0
10
20
30
40
50

of H_2. The results are given in Table 4. Experiments 17 to 21 are with p_{H_2} = 0.49, experiments 22 to 24 are with p_{H_2} = 0.37, 25 to 28 with p_{H_2} = 0.25 and from 29 to 31 with p_{H_2} = 0.20, keeping p_{CO_2} at about 0.49 throughout. The carbon dioxide balance for these experiments is given in Table 4A.

The results are plotted in Figure 17. To understand the significance, Table 5 is drawn up from Figure 17.

TABLE 5.

Expt. Nos.	p_{H_2}	p_{CO_2}	C.Cs. CO_2 convtd/C.C. Cat/min. at velocities =					
			400	500	600	700	800	900
17-21	0.49	0.49	1.98	2.45	2.95	3.42	3.90	4.40
22-24	0.37	0.49	1.84	2.15	2.46	2.78	3.08	3.40
25-28	0.25	0.49	1.70	2.00	2.32	2.64	2.95	3.20
29-31	0.20	0.49	1.48	1.70	1.95	2.18	2.42	2.65

showing the various partial pressures and the corresponding yields for values of rates = 400, 500, 600, 700, 800 and 900. These are plotted as shown in Figure 18. From the curves obtained, it is seen that the yield continuously rises as the partial pressure of CO_2 is kept at 0.49 and varied p_{H_2} from 0 to 0.49. Figure 19 is drawn by plotting yield against f(Re). By comparing both Figures 17 and 19 it is found that/

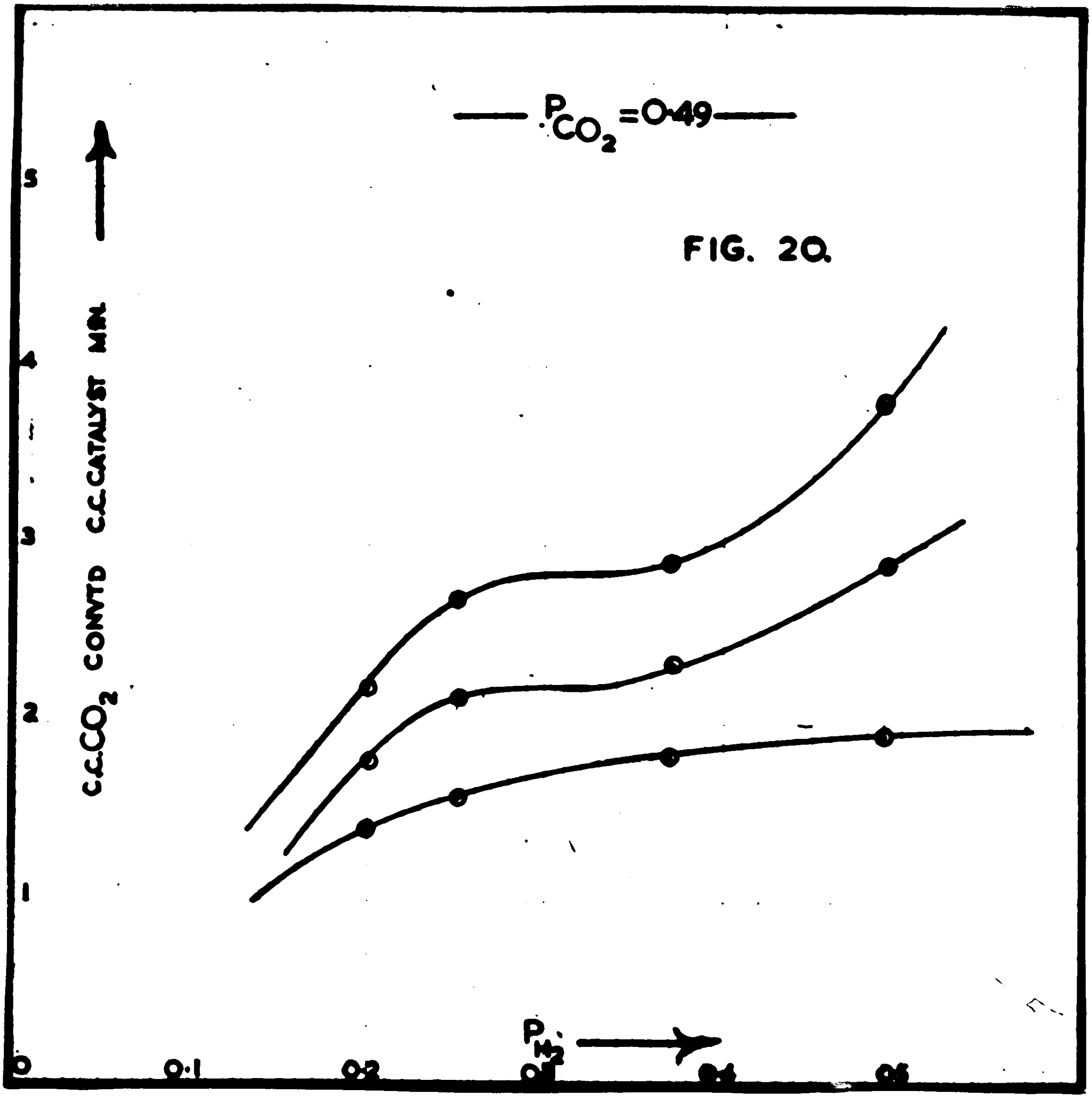

— P_{CO_2} = 0·49 —
C.C. CO_2 CONVTD C.C. CATALYST MIN.
5
4
3
2
1
0
0·1
0·2
0·3
0·4
0·5
P_{H_2}

FIG. 20.

that the shape of the lines and their relative positions are not changed in the two figures, only there is a difference in the slope of the lines. As before, Table 6 is drawn up from Figure 19.

TABLE 6.

Expt. Nos.	p_{H_2}	p_{CO_2}	Yield at f (Re) = 20	30	40
17 - 21	0.49	0.49	1.95	2.90	3.80
22 - 24	0.37	0.49	1.80	2.32	2.90
25 - 28	0.25	0.49	1.60	2.15	2.72
29 - 31	0.20	0.49	1.40	1.76	2.20

tabulating partial pressures and the corresponding yields for values of f(Re) - 20, 30 and 40. These values are plotted as shown in Figure 20. By comparing Figures 18 and 20, it is seen that there is no difference in the shape of the curves.

These results show that as the p_{H_2} is raised from 0 to 0.49, keeping p_{CO_2} = 0.49, the yield rises. This could be explained in the light of the mechanism postulated in Section B.

As p_{H_2} is pushed up from 0 to 0.49, keeping p_{CO_2} at 0.49/

0.49, the hydrogen progressively displaces adsorbed molecules of CO_2 from the catalytic surface so that more adsorbed H_2 is available on the surface to react with adsorbed CO_2.

Finally in conclusion it may be said that when surface reaction takes place between adsorbed molecules on adjacently situated active centres the reaction proceeds at rates proportional to the concentrations of adjacently adsorbed reactants. Thus, if an adsorbed molecule or atom A reacts with an adsorbed molecule or atom B, the rate of reaction is proportional to the number of pairs of adjacently adsorbed A and B molecules or atoms per unit area of surface. Similarly in reactions involving simultaneous interaction of several molecules the rates should be proportional to the concentration of groups of the required number of molecules adsorbed on adjacent active centres. Naturally, it should be expected that the reaction rate is low because of the low concentration of properly adsorbed groups. But in the reaction:

$$\underset{(A)}{CO_2} + 4\ \underset{(B)}{H_2} \quad = \quad CH_4 + 2\ H_2O$$

though it involves five molecules for interaction is of a different nature because it is a case of one reactant molecule CO_2 (A) reacting with several other molecules or atoms/

atoms of another reactant H_2 (B). In such cases high rates are obtained with a catalyst which strongly adsorbs reactant B, so that the majority of surface is covered with adsorbed B molecules or atoms and most of the A molecules which are adsorbed are surrounded by the requisite number of B units on adjacent centres. Since H_2 is very strongly adsorbed by nickel, fairly high rates could be expected for the methane synthesis from CO_2 and H_2 in presence of nickel or promoted nickel catalysts. If the geometrical pattern of distribution of active centres on the catalytic surface is such that the active centres occupy the corner of a rectangle or equilateral triangle we would have $S = 4$ or $S = 6$. In other words, for such a geometrical pattern a CO_2 molecule would be surrounded by four or six H_2 molecules or atoms which would react to form methane.

SECTION B.

MATHEMATICAL ANALYSIS OF THE RESULTS.

R. B. Beckmann (92) studied the reaction of hydrogenating iso-octene to iso-octane in vapour phase in presence of Ni catalysts and showed that the rate determining step is the surface reaction between adsorbed hydrogen and adsorbed iso-octene.

John L. Tschernity and R. B. Beckmann (93) recently worked on the hydrogenation of mixed iso-octenes and have suggested a method for determining the most plausible mechanism in a reaction catalysed by a solid surface from among the many mechanisms which might be postulated. A similar method is adopted in the following pages to determine the mechanism of reaction between CO_2 and H_2 on Ni catalyst.

In order that a reactant in the main gas phase may be converted catalytically to a product in the main gas phase it is necessary that the reactant is taken from the main gas phase to the catalyst, is activatedly adsorbed on the surface and then undergo reaction to form adsorbed product. This product then must be desorbed and finally transferred from catalytic/

catalytic surface to the main gas phase. The rate of each one of these steps influences the distribution of concentrations in the system and plays a part in determining the overall rate. It is very convenient to classify these steps as follows:-

1. The mass transfer of reactants and products to and from the catalytic surface and the main body of the gaseous phase.

2. The diffusional and flow transfer of reactants and products in and out of the pores of the catalyst if reaction takes place at interior interfaces.

3. The activated adsorption of reactants and desorption of products at the catalytic surface.

4. The surface reaction of adsorbed reactants to form activated adsorbed products.

The rates of the above four operations are dependent on different factors. Type I is determined by flow characteristics of the system like the mass velocity of the fluid stream, size of particles, diffusional properties of the system, etc. Type 2 is determined by the porosity of catalyst, size of pores, their distances apart, etc. Type 3 is determined by the characteristics of the catalytic surface and by the activation energies required for the adsorption and desorption of each of the components of the system/

system. Type 4 is determined by the nature of catalytic surface and the activation energies required for the reaction on the surface.

Type 1 is important only in the case of rapid reactions. Type 2 is negligible for catalysts of low activity and porosity. Types 3 and 4 are chemical phenomena usually involving large activation energies and hence are sensitive to temperatures. The actual chemical transformation is often proceeded by many successive stages and since chemical rates vary over wide ranges, it is not very possible that the rates of any two steps of types 3 and 4 will be of equal order in any given system. Hence the slowest single step is considered and it is assumed that equilibrium is maintained in all other steps. Under these conditions the slowest activated step may be termed "the rate-controlling step".

For the hydrogenation of CO_2 in presence of Ni catalyst seventeen different mechanisms can be postulated besides the independent steps of diffusion of reactants to the catalyst surface and of product away from the surface. As an example of the derivation of these equations, the case of surface reaction between molecularly adsorbed CO_2 and molecularly adsorbed H_2 as the rate controlling step is illustrated below:-

Activated/

Activated adsorption is a highly specific reaction between the adsorbate and the surface and possesses the characteristics of a reversible chemical reaction. This concept introduced by Taylor in 1930 has been recently summarized by Taylor (94), Emmett (94) and Glasstone, Laidler, and Eyring (95).

It may be assumed that a unit area of catalytic surface contains L' active centres and that all of these centres behave similarly. The rate of adsorption of a component A in contact with the surface is then proportional to its activity a_{Ai} at the interface and to the concentration C'_1 of vacant active centres per unit area of surface. A surface concentration of C'_A adsorbed 'A' molecules per unit area will result. It is convenient to express surface concentrations in moles per unit mass of catalyst. Thus, if A is the catalytic area per unit mass,

$L = \frac{AL'}{N_o}$ = maximum molal adsorption capacity per unit mass of catalyst (gm) with one molecule per active centre.

$C_A = \frac{AC'_A}{N_o}$ = moles of adsorbed A per unit mass of catalyst.

$C_1 = \frac{AC'_1}{N_o}$ = molal adsorption sites unoccupied per unit mass of catalyst.

N_o = Avogadro number.

Expressing the rate of adsorption r in moles per unit time per unit mass of catalyst we get:-

$$r = k_A \; a_{Ai} \; C_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where k_A = adsorption velocity constant of compound A.

Since activated adsorption is reversible, component A is also desorbed from the surface at a rate proportional to the concentration of adsorbed molecules on the surface. Thus, the rate of desorption is expressed by

$$r = k'_A \; C_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where k'_A = desorption velocity constant of component A.

When adsorption equilibrium is reached the two rates become equal and so equating 1 and 2

$$k_A \; a_{Ai} \; C_1 = k'_A \; C_A$$

or $$\frac{C_A}{a_{Ai} C_1} = \frac{k_A}{k'_A} = K_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where K_A = adsorption equilibrium constant of component A.

If component A is in admixture with other components B,R,S, etc., which are also adsorbed on active centres of the same type, rate and equilibrium equations similar to 1, 2 and 3 may be written for each component.

Thus:-

$$C_1 = L - (C_A + C_B + C_R + C_S + \qquad) \quad \ldots\ldots\ldots\ldots (4)$$

At/

At equilibrium conditions each of the adsorbate concentration terms in equation 4 may be replaced by an expression similar to that obtained by solving equation 3 for C_A.

Therefore, from equation 3, $C_A = K_A \ a_{Ai} \ C_1$ and similarly $C_B = K_B \ a_{Bi} \ C_1$ and so on. Substituting these values for C_A, C_B, etc., in equation 4 we get

$$C_1 = L - C_1(a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + \quad)$$

$$\text{or } C_1 + C_1(a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + \quad) = L$$

$$\text{or } C_1(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + \quad) = L$$

$$\text{or } C_1 = \frac{L}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + \quad)} \text{.....(6)}$$

An expression for the equilibrium surface concentration of A in terms of interfacial fluid activities is obtained by combining equations 6 and 3.

From equation 3, $C_1 = \frac{C_A}{K_A a_{Ai}}$ and substituting this in 6:-

$$C_A = \frac{a_{Ai}K_A L}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + \quad)} \text{......(7)}$$

Similar equations may be written for the equilibrium surface concentration of the other components of the mixture.

Now/

Now a surface reaction may be assumed to take place either between an adsorbed reactant molecule and a molecule in the fluid phase or between adsorbed molecules on adjacently situated active centres. It is assumed that the active centres of the surface are distributed in a regular geometrical pattern such that each individual active centre is surrounded by 'S' other centres equi-distant from it. Thus, if the pattern is a rectangle with active centres forming the corners of squares, $S = 4$. If the pattern is such that the centres form the corners of equilateral triangles $S = 6$.

Suppose a molecule of A is adsorbed on an active centre, then adjacent to it there would be $s\theta_1$ vacant centres where θ_1 is the fraction of the total centres which is vacant. Similarly, $S\theta_B$ molecules of B are adjacent to each adsorbed A molecule, where θ_B is the fraction of the total centres which is occupied by adsorbed B molecules. Then the concentration of A molecules and B molecules adsorbed in adjacent positions becomes $\frac{1}{2}\, sC'_A\theta_B$. The factor $\frac{1}{2}$ results from the fact that in multiplying the concentration and fractional adsorption terms, each pair of adjacent molecules and centres is counted twice.

Now/

Now from definition $\theta_B = \frac{C'_B}{L'}$ and therefore:-

$$C'_{AB} = \frac{S}{2L'} \; C'_A \, C'_B \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where C'_{AB} = surface concentration of pairs of adsorbed A and B molecules in adjacent positions.

Equation 8 written with concentrations in moles per unit mass of catalyst would be

$$C_{AB} = \frac{S}{2L} \; C_A \, C_B \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Therefore, taking the adsorption to be equal to the forward rate of a monomolecular surface reaction between adsorbed A and adsorbed B molecules we have:-

$$r = kC_{AB} \; = \; \frac{Ks}{2L} \; C_A \, C_B$$

where k = forward reaction velocity constant.

Taking reactions of the type:-

$$A + B \quad = \quad R + S$$

the net rate of forward reaction is the difference between the forward and reverse reactions and can be expressed, for reaction between adsorbed molecules of A and B as the rate controlling step, thus:-

$$r = \frac{S}{2L} \left(kC_A C_B \; - \; k'C_R C_S\right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where k' = reverse reaction velocity constant.

Now/

Now substituting in equation 10 the values for C_A, C_B, C_R, and C_S from equation 7 we have:-

$$r = \frac{S}{2L} \left\{ kx \frac{a_{Ai} \quad K_A \quad L}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S)} \; x \; \frac{a_{Bi}K_BL}{(1 + a_{Ai}K_A + \ldots\ldots\ldots a_{Si}K_S)} \right.$$

$$\left. - k' \; x \frac{a_{Ri} \quad K_R \quad L}{(1 + a_{Ai}K_A + \ldots\ldots\ldots + a_{Si}K_S)} \; x \; \frac{a_{Si}K_SL}{(1+a_{Ai}K_A + \ldots\ldots + a_{Si}K_S)} \right\}$$

Now $\frac{k}{K'}$ = K'' = surface equilibrium constant

.'. $k' = \frac{k}{K''}$ and substituting this value of k' in the above equation we get:-

$$r = \frac{SkL}{2(1+a_{Ai}K_A+\ldots a_{Si}K_S)^2} \left\{ K_A a_{Ai} K_B a_{Bi} - \frac{K_R a_{Ri} K_S a_{Si}}{K''} \right\}$$

At equilibrium this net rate becomes zero and so

$\frac{a_{Ri}a_{Si}}{a_{Ai}a_{Bi}} = \frac{K_AK_B}{K_SK_R} \; x \; K'' = K$, the overall equilibrium constant of the reaction.

Therefore, $\frac{K_RK_S}{K''} = \frac{K_AK_B}{K}$ and substituting this in the above equation we get:-

r/

$$r = \frac{skL \quad K_A K_B}{2(1+a_{Ai}K_A+a_{Bi}K_B+a_{Ri}K_R+a_{Si}K_S)^2} \times \left\{ a_{Ai}a_{Bi} - \frac{a_{Ri}\ a_{Si}}{K} \right\} \qquad (11)$$

Equation 11 gives the final equation for a reaction of the type A + B = R + S where surface reaction between adsorbed molecules of A and B is the rate controlling step. However, if they are admixed with an inert gas such as Nitrogen, then its effect should not be overlooked in case the inert gas also is adsorbed by the catalytic surface.

In the reaction:-

$$CO_2 + 4H_2 \quad = \quad CH_4 + 2H_2O$$

the equation 11 has to be slightly modified for one molecule of CO_2 reacts with four molecules of hydrogen. Taking that the activity of these gases to be proportional to their partial pressures at the interface of the catalyst we get the modified form of equation 11 for the CO_2, H_2 reaction, thus:-

$$r = \frac{Skl}{2(1+K_{CO_2}p_{CO_2}+K_{H_2}p_{H_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O})^5} \times$$

$$\left\{ K_{CO_2}p_{CO_2}(K_{H_2}p_{H_2})^4 - \frac{K_{CO_2}K_{H_2}p_{CH_4}p_{H_2O}}{K} \right\}$$

Where I stands for inerts like N_2.

Now since K is very large compared with others, the term $\frac{K_{CO_2}K_{H_2}p_{CH_4}p_{H_2O}}{K}$ could be taken to be constant.

Thus/

Thus $$r = \frac{S\ k\ L\ K_{CO_2}\ p_{CO_2}\ (K_{H_2}\ p_{H_2})^4}{2(1 + K_{CO_2}p_{CO_2} + \ldots\ldots + K_1p_1)^5}$$

$$\therefore\quad R = \sqrt[5]{\frac{p_{CO_2}\ p_{H_2}^4}{r}} = \frac{2}{\sqrt[5]{s\ k\ L\ K_{CO_2}K_{H_2}^4}}\ (1+K_{CO_2}p_{CO_2}+\ldots K_1p_1)$$

$$\therefore\quad R = \sqrt[5]{\frac{p_{CO_2}p_{H_2}^4}{r}} = a + bp_{CO_2} + cp_{H_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}. \qquad \ldots\ldots(12)$$

Where R = gas law constant.

Equation 12 is the final simplified form in which the surface reaction between molecularly adsorbed CO_2 and molecularly adsorbed H_2 is taken to be the rate controlling step in the reaction between the two gases to form methane.

In a similar manner a few equations were derived and the rest by inspection. These possible chemical steps together with their corresponding rate equations are expressed in convenient forms as in equation 12 for comparison and are tabulated in Table 7.

Since the rate equations are based on the kinetic theory, it is required that the constants a,b,c,d,e, and f must all have positive or zero values according as they appear or disappear in the equations. These constants for all the seventeen postulated mechanisms are evaluated using the/

TABLE 7.

I. Reaction between molecularly adsorbed H_2 and molecularly adsorbed CO_2:

(1). Adsorption of H_2 controlling:-

$$R = \frac{p_{H_2}^4}{r} = \frac{1}{\alpha}\left(1 + K_{CO_2}\, p_{CO_2} + K_{CH_4}\, p_{CH_4} + K_{H_2O}\, p_{H_2O} + K_{N_2} p_{N_2} \right)$$

$$= a + bp_{CO_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

(2). Adsorption of CO_2 controlling:-

$$R = \frac{p_{CO_2}}{r} = \frac{1}{\alpha}\left(1 + K_{H_2}p_{H_2} + K_{N_2}p_{N_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O} \right)$$

$$= a + cp_{H_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

(3). Desorption of CH_4 controlling.

$$R = \frac{p_{CO_2}p_{H_2}^4}{rp_{H2O}} = \frac{K_{H_2O}}{\alpha K_{H_2}K_{CO_2}}\left(1 + K_{H_2}p_{H_2} + K_{CO_2}p_{CO_2} + K_{H_2O}p_{H_2O} + K_{N_2}p_{N_2} \right)$$

$$= a + bp_{CO_2} + cp_{H_2} + dp_{N_2} + fp_{H_2O}.$$

(4). Surface reaction controlling.

$$R = \sqrt[5]{\frac{p_{CO_2}p_{H_2}^4}{r}} = \sqrt[5]{\frac{1}{\alpha K_{CO_2}K_{H_2}^4}}\left(1 + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2} + K_{N_2}p_{N_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}\right)$$

$$= a + bp_{CO_2} + cp_{H_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

TABLE 7 CONTINUED.

II. Reaction between atomically adsorbed H_2 and molecularly adsorbed CO_2.

(5). Adsorption of H_2 controlling:-

$$R = \sqrt{\frac{p_{H_2}^4}{r}} = \frac{1}{\sqrt{\alpha}} \left(1 + K_{CO_2}p_{CO_2} + K_{N_2}p_{N_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O} \right)$$

$$= a + bp_{CO_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

(6). Adsorption of CO_2 controlling.

$$R = \frac{p_{CO_2}}{r} = \frac{1}{\alpha} (1 + \sqrt{K_{H_2}p_{H_2}} + K_{N_2}p_{N_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O})$$

$$= a + c\sqrt{p_{H_2}} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

(7). Desorption of CH_4 controlling:-

$$R = \frac{p_{CO_2}p_{H_2}^4}{rp_{H_2O}} = \frac{K_{H_2O}}{\alpha K_{H_2}K_{CO_2}} (1 + \sqrt{K_{H_2}p_{H_2}} + K_{CO_2}p_{CO_2} + K_{N_2}p_{N_2} + K_{H_2O}p_{H_2O})$$

$$= a + bp_{CO_2} + c\sqrt{p_{H_2}} + dp_{N_2} + fp_{H_2O}.$$

(8). Surface reaction controlling:-

$$R = \sqrt[5]{\frac{p_{CO_2}(\sqrt{p_{H_2}})^4}{r}} = \sqrt[5]{\frac{1}{\alpha K_{CO_2}(\sqrt{K_{H_2}})^4}} (1 + K_{CO_2}p_{CO_2} + \sqrt{K_{H_2}p_{H_2}} + K_{N_2}p_{N_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O})$$

$$= a + bp_{CO_2} + c\sqrt{p_{H_2}} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

TABLE 7 (CONTINUED.)

III. Reaction between CO_2 in gas phase and molecularly adsorbed H_2.

(9). Adsorption of H_2 controlling:-

$$R = \Bigg/ \frac{p_{H_2}^4}{r} = \frac{1}{\alpha} (1 + K_{N_2} p_{N_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O})$$

$$= a + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

(10). Desorption of CH_4 controlling:-

$$R = \frac{p_{CO_2} p_{H_2}^4}{r p_{H_2O}} = \frac{K_{H_2O}}{\alpha K_{H_2}} (1 + K_{H_2} p_{H_2} + K_{N_2} p_{N_2} + K_{H_2O} p_{H_2O})$$

$$= a + cp_{H_2} + dp_{N_2} + \cancel{ep_{CH_4}} + fp_{H_2O}.$$

(11). Surface reaction controlling:-

$$R = \frac{p_{CO_2} p_{H_2}^4}{r} = \frac{1}{\alpha K_{H_2}} (1 + K_{H_2} p_{H_2} + K_{N_2} p_{N_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O})$$

$$= a + cp_{H_2} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

IV. Reaction between CO_2 in gas phase and at adsorbed H_2.

(12). Adsorption of H_2 controlling:-

$$R = \sqrt{\frac{p_{H_2}^4}{r}} = \sqrt{\frac{1}{\alpha}} (1 + K_{N_2} p_{N_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O})$$

$$= a + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

TABLE 7 CONTINUED.

(13). Desorption of methane controlling:-

$$R = \frac{p_{CO_2}p_{H_2}^4}{rp_{H_2O}} = \frac{K_{H_2O}}{\alpha K_{H_2}}(1+\sqrt{K_{H_2}p_{H_2}}+K_{N_2}p_{N_2}+K_{H_2O}p_{H_2O})$$

$$= a + c\sqrt{p_{H_2}} + dp_{N_2} + fp_{H_2O}$$

(14). Surface reaction controlling:-

$$R = \sqrt[5]{\frac{p_{CO_2}p_{H_2}^4}{r}} = \sqrt[5]{\frac{1}{\alpha K_{H_2}}}(1+\sqrt{K_{H_2}p_{H_2}}+K_{N_2}p_{N_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O})$$

$$= a + c\sqrt{p_{H_2}} + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

V. Reaction between H_2 in gas phase and adsorbed CO_2:-

(15). Impact of H_2 upon adsorbed CO_2 controlling:-

$$R = \frac{p_{CO2}p_{H_2}^4}{r} = \frac{1}{\alpha K_{H_2}}(1+K_{CO_2}p_{CO_2}+K_{N_2}p_{N_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O})$$

$$= a + bp_{CO_2} + dp_{N_2} + ep_{H_2} + fp_{H_2O}.$$

(16). Desorption of CH_4 controlling:-

$$R = \frac{p_{CO_2}p_{H_2}^4}{rp_{H_2O}} = \frac{K_{H_2O}}{\alpha K_{CO_2}}(1+K_{CO_2}p_{CO_2}+K_{N_2}p_{N_2}+K_{H_2O}p_{H_2O})$$

$$= a + bp_{CO_2} + dp_{N_2} + fp_{H_2O}.$$

TABLE 7 CONTINUED.

(17). Adsorption of CO_2 controlling:-

$$R = \frac{p_{CO_2}}{r} = \frac{1}{\alpha}\left(1+K_{N_2}p_{N_2}+K_{CH_4}p_{CH_4}+K_{H2O}p_{H_2O}\right)$$

$$= a + dp_{N_2} + ep_{CH_4} + fp_{H_2O}.$$

---

the experimental data by the method of least squares and are tabulated in Table 10.

METHOD OF CALCULATING REACTION RATE.

Experiment No. 1.

Synthesis gas:-

CO_2 - 11.7%
O_2 - 0.6%
H_2 - 49.0%
N_2 - 38.7%

Product gas:-

CO_2 - 10.2%
O_2 - 0.1%
CH_4 - 3.49%
H_2 - 43.5%
N_2 - 42.7%

Time of run = 14 min.
Temp. of react. = 285°C.
Gas passed = 4 litres
Gas collected = 3.8 litres
Temp. of gas = 60°F.
Bar. Pr. = 755 cm.Hg.
Volume of Cat. = 8.2 C.Cs.
Wt. of Cat. = 5.46 gms.

C.Cs. CO_2 converted to CH_4 = 3.49 x 38 = 132.

∴ C.Cs. CO_2 converted per minute = $\frac{132}{14}$

∴ C.Cs. CO_2 converted at N.T.P. = $\frac{132}{14} \times \frac{755 \times 460}{520 \times 760}$ per min.

∴ C.Cs. CO_2 converted at N.T.P/hr. = $60 \times \frac{132}{14} \times \frac{755 \times 460}{520 \times 760}$

∴Gm/

EXPERIMENTS 1 TO 21 ON Ni CATALYST.

Expt. No.	ENTERING. p_{CO_2}	p_{H_2}	p_{N_2}	LEAVING. p_{CO_2}	p_{H_2}	p_{N_2}	p_{CH_4}	p_{H_2O}	AVERAGE. p_{CO_2}	p_{H_2}	p_{N_2}	p_{CH_4}	p_{H_2O}	r	$R=5/\frac{p_{CO_2}p_{H_2}^4}{r}$
1.	11.7	49	39.3	9.54	40.7	40.1	3.49	6.98	2	0.4485	0.3970	0.0349	0.0698	.004062	1.0110
2.	13.2	49.2	37.6	11.1	38.9	40.6	3.28	6.56	215	0.4405	0.3910	0.0328	0.0656	0.007092	0.9160
3.	11.48	49.8	38.7	10.02	41.2	39.3	3.44	6.88	075	0.4550	0.3900	0.0344	0.0688	0.009819	0.8596
4.	11.25	49.6	39.15	9.57	39.04	40.08	3.8	7.60	041	0.4432	0.3977	0.0380	0.0760	0.013110	0.7893
								TOTAL-	393	1.7872	1.5757	0.1401	0.2802		3.5759
								AVERAGE	098	0.4468	0.3939	0.0350	0.0700		0.8939
6.	23.9	49.8	26.3	21.56	40.5	28.9	3.43	6.86	253	0.4505	0.2760	0.0343	0.0686	0.003850	1.1920
7.	23.7	49.2	27.1	21.06	40.2	28.6	3.62	7.24	238	0.4470	0.2785	0.0362	0.0724	0.004275	1.1418
8.	24.7	50.3	25.0	22.56	42.5	26.5	2.95	5.90	363	0.4640	0.2575	0.0295	0.0590	0.005034	1.1670
9.	23.4	49.4	27.2	23.40	41.4	27.7	2.61	5.22	340	0.4540	0.2745	0.0261	0.0522	0.006500	1.0880
10.	24.1	50.8	25.1	21.98	42.8	27.87	2.55	5.10	304	0.4680	0.2648	0.0255	0.0510	0.008019	1.0660
11.	24.1	48.9	27.0	21.80	42.35	28.66	2.51	5.02	295	0.4563	0.2783	0.0251	0.0502	0.009432	1.0110
								TOTAL-	793	2.7398	1.6296	0.1767	0.3534		6.6720
								AVERAGE	299	0.4566	0.2716	0.0294	0.0589		1.1120
13.	35.3	49.9	14.8	31.86	37.95	18.0	4.46	8.92	358	0.4392	0.1640	0.0446	0.0892	0.008196	1.0870
14.	34.4	48.8	16.8	30.58	38.10	18.7	4.60	9.20	249	0.4345	0.1775	0.0460	0.0920	0.012720	0.9813
15.	35.5	50.4	14.1	31.20	39.50	18.6	3.88	7.76	335	0.4495	0.1635	0.0388	0.0776	0.013780	0.9974
16.	34.7	50.2	15.1	31.08	38.20	17.8	4.68	9.36	289	0.4420	0.1645	0.0468	0.0936	0.017240	0.9385
								TOTAL-	231	1.7652	0.6695	0.1762	0.3524		4.0042
								AVERAGE	308	0.4418	0.1674	0.0440	0.0881		1.0010
17.	47.75	49.6	2.6	44.00	39.70	4.5	4.26	8.52	587	0.4465	0.0355	0.0426	0.0852	0.006064	1.2470
18.	48.50	48.6	2.9	44.60	37.80	5.9	4.21	8.42	655	0.4320	0.0440	0.0421	0.0842	0.008690	1.1330
19.	49.00	49.3	1.7	44.50	39.30	4.8	4.08	8.16	675	0.4430	0.0325	0.0408	0.0816	0.010460	1.1150
20.	47.00	50.4	2.6	42.50	44.70	5.08	4.17	8.34	475	0.4755	0.0384	0.0417	0.0834	0.012620	1.1270
21.	48.10	49.8	2.1	43.80	38.70	5.8	4.17	8.34	595	0.4425	0.0395	0.0417	0.0834	0.015370	1.0280
								TOTAL-	987	2.2395	0.1899	0.2089	0.4178		5.6500
								AVERAGE	597	0.4479	0.0379	0.0418	0.0835		1.1300

.˙. Gm. mole CO_2 converted/hr. $= 60 \times \frac{132}{14} \times \frac{755 \times 460}{520 \times 760} \times \frac{1}{22400}$

.˙. lb. mole CO_2 converted/hr. $= 60 \times \frac{132}{14} \times \frac{755 \times 460}{520 \times 760} \times \frac{1}{22400}$
$\times \frac{1}{454}$

.˙. lb. mole CO_2 converted/hr/lb. of cat. =

$$\frac{60 \times \frac{132}{14} \times \frac{755 \times 460}{520 \times 760} \times \frac{1}{22400} \times \frac{1}{454}}{\frac{5.46}{454}}$$

$= .004062$

.˙. $r = .004062$ lb. mole CO_2 converted/hr/lb. of catalyst.

METHOD FOR EVALUATING THE CONSTANTS OF THE EQUATIONS

The experimental results of runs 1 to 21 keeping $p_{H_2} = .49$ and varying p_{CO_2} from .12 to .49 are given in Table 8. The composition of the product gas given here is that given by calculation to include the presence of water vapour formed during the reaction. The partial pressure of the reactants and products at the surface of the catalyst are taken to be the average of the partial pressures of the components in the entering and leaving gas mixtures. The calculated reaction rate 'r' is also given. The value R is/

is included here to show the method of evaluation of the constants in the postulated mechanism equations.

As an illustration of the method of evaluating the constants, the calculations for mechanism I(4) are shown. According to the theory of least squares the following Summation equations apply to I(4):-

$$a\,n+b\Sigma p_{CO_2}+c\Sigma p_{H_2}+d\Sigma p_{N_2}+e\Sigma p_{CH_4}+f\Sigma p_{H_2O} = R \text{ ....A}$$

$$a\Sigma p_{CO_2}+b\Sigma p^2_{CO_2}+c\Sigma p_{H_2}p_{CO_2}+d\Sigma p_{N_2}p_{CO_2}+e\Sigma p_{CH_4}p_{CO_2}+f\Sigma p_{H_2O}p_{CO_2}$$
$$= R\Sigma p_{CO_2} \text{......B}$$

$$a\Sigma p_{H_2}+b\Sigma p_{CO_2}p_{H_2}+c\Sigma p^2_{H_2}+d\Sigma p_{N_2}p_{H_2}+e\Sigma p_{CH_4}p_{H_2}+f\Sigma p_{H_2O}p_{H_2}$$
$$= R\Sigma p_{H_2} \text{......C}$$

$$a\Sigma p_{N_2}+b\Sigma p_{CO_2}p_{N_2}+c\Sigma p_{H_2}p_{N_2}+d\Sigma p^2_{N_2}+e\Sigma p_{CH_4}p_{N_2}+f\Sigma p_{H_2O}p_{N_2}$$
$$= R\Sigma p_{N_2} \text{......D}$$

$$a\Sigma p_{CH_4}+b\Sigma p_{CO_2}p_{CH_4}+c\Sigma p_{H_2}p_{CH_4}+d\Sigma p_{N_2}p_{CH_4}+e\Sigma p^2_{CH_4}+f\Sigma p_{H_2O}p_{CH_4}$$
$$= R\Sigma p_{CH_4} \text{.....E}$$

$$a\Sigma p_{H_2O}+b\Sigma p_{CO_2}p_{H_2O}+c\Sigma p_{H_2O}p_{H_2O}+d\Sigma p_{N_2}p_{H_2O}+e\Sigma p_{CH_4}p_{H_2O}+f\Sigma p^2_{H_2O}$$
$$= R\Sigma p_{H_2O} \text{.....F}$$

where/

TABLE No.9.

Expt. set;-	p_{CO_2}	p_{H_2}	p_{N_2}	p_{CH_4}	p_{H_2O}	$p^2_{CO_2}$	$p^2_{H_2}$	$p^2_{N_2}$	$p^2_{CH_4}$	$p^2_{H_2O}$	$p_{CO_2}p_{H_2}$	$p_{CO_2}p_{N_2}$	$p_{CO_2}p_{CH_4}$	$p_{CO_2}p_{H_2O}$
I	.1098	.4468	.3939	.0175	.0350	.01206	.1995	.1550	.000306	.001225	.04906	.04324	.001921	.003842
ll.	.2299	.4566	.2716	.0147	.0294	.05284	.2084	.0737	.000216	.000864	.10490	.06241	.003378	.006756
lll.	.3308	.4418	.1674	.0220	.0440	.10940	.1951	.02805	.000484	.001936	.14610	.05540	.007278	.014556
lV.	.4597	.4479	.0379	.0209	.0418	.21120	.2004	.00143	.000437	.001747	.20580	.01742	.009602	.019204
Σ	1.1302	1.7931	.8708	.0751	.1502	.38550	.8034	.25818	.001443	.005772	.50586	.17847	.022179	.044358

	$p_{H_2}p_{N_2}$	$p_{H_2}p_{CH_4}$	$p_{H_2}p_{H_2O}$	$p_{N_2}p_{CH_4}$	$p_{N_2}p_{H_2O}$	$p_{CH_4}p_{H_2O}$	R	Rp_{CO_2}	$R\ p_{H_2}$	$R\ p_{N_2}$	$R\ p_{CH_4}$	$R\ p_{H_2O}$
	.1759	.007816	.01563	.00689	.01378	.00061	.8939	.0981	.3992	.3520	.01563	.03126
	.1240	.006711	.01342	.00399	.00798	.00043	1.1120	.2558	.5080	.3021	.01636	.03272
	.07394	.009718	.01944	.00368 ~~.00737~~	.00737	.00097	1.0010	.3311	.4422	.1676	.02202	.04404
	.01698	.009359	.01872	.00079	.00158	.00087	1.1300	.5195	.5060	.0428	.02361	.04722
Σ	.39082	.033604	.06721	.01536	.03071	.00289	4.1369	1.2045	1.8554	.8645	.07762	.15524

where n (in equation A) = number of experiments and R =

$$\sqrt[5]{\frac{p_{CO_2}\, p_{H_2}^4}{r}}$$

By substituting the summation terms from Table 9 into equations A to F, the following equations are got:-

$$4a+1.1302b+1.7931c+.8708d+0751e+.1502f = 4.1369$$

$$1.1302a+.3855b+.5058c+.1785d+.02218e+.04436f = 1.2045$$

$$1.7931a+.5058b+.8034c+.3908d+.03360e+.06721f = 1.8554$$

$$.8708a+.1785b+.3908c+.2582d+.01536e+.03071f = .8645$$

$$.0751a+.02218b+.0336c+.01536d+.001443e+.002886f = .07762$$

$$.1502a+.04436b+.0672c+.03072d+.002886e+.00577f = .15524$$

The above quotations are, however, complicated simultaneous equations and so had to be solved by trial and error method. The following values were obtained:-

$a = 26$

$b = 15.5$

$c = -90$

$d = 14.4$

$e = 80$

$f = 160$

Similar calculations were made for all the seventeen mechanisms and the values of the empirical constants are tabulated in Table 10. From a study of this Table it would be seen that all the mechanisms except II (8) are rejected because certain constants are either negative or not/

TABLE 10.

Mechanism No.	a	b	c	d	e	f	Reason for rejection.
I (1).	2.87	-42	51	-39	-1.07	-2.14	b,d,e,and f should + ve. c should be zero.
(2).	197	-254	116	-370	660	1320	b should be zero. d should be + ve.
(3).	718	-920	-480	-770	-610	-1220	e sholud be zero. b,c,d,&fshould be + ve.
(4).	26	15.5	-90	14.4	80	160	c should be + ve.
II (5).	14.6	-56	37	-54	-15	-30	c should be zero. b,d,e,&f should be + ve.
(6).	380	-346	6.6	-23	-2625	-5250	b should be zero. d,e,&f should be + ve.
(7).	0.26	0.15	-52	17	478	956	e should be zero. c should be + ve.
(8).	0.25	0.50	1.0	0.8	0.2	4	Acceptable.
III (9).	2.87	-42	51	-39	-1.07	-2.14	b and c should be zero. d,e,andf should be + ve.
(10).	718	-920	-480	-770	-610	-1220	b & e should be zero. c,d,& f should be + ve.

TABLE 10 CONTINUED.

Mechanism No.	a	b	c	d	e	f	Reason for rejection.
(11).	5.7	5.9	-6.7	0.66	-34	-68	b should be zero. c,e,& f should be + ve.
IV (12).	14.6	-56	37	-54	-15	-30	b, and c should be zero. d,e& f should be + ve.
(13).	0.26	0.15	-52	17	478	956	b& e should be zero c should be + ve.
(14).	-3.36	2.3	-0.11	4.15	31	62	b should be zero. a, & c should be +ve
V (15).	5.7	5.9	-6.7	0.66	-34	-68	c should be zero. e & f should be +ve
(16).	718	-920	-480	-770	-610	-1220	c & e should be zero. b,d, & f should be + ve.
(17).	197	-254	116	-370	660	1320	b & c should be zero. d should be + ve.

not equal to zero when otherwise demanded. The possibility of mechanism I(4) occurring along with mechanism II(8) is very great because of the six constants, only 'c' is negative which should have been positive. That is to say five conditions out of six are satisfied. However, if both the mechanisms do occur side by side, II(8) might be the predominant of the two.

It has been already pointed out that the slowest activated step may be termed "the rate-controlling step". Hence, we could say at a glance at the seventeen postulated mechanisms that I(1), II(5), III(9), IV(12), V(15),(16) and (17) could not be the rate controlling mechanisms, since it is known that hydrogen is strongly adsorbed by nickel. The results tabulated in Table 10 agree with this reasoning. So the possible mechanism as pointed out is II(8) and perhaps I(4). That is to say, since mechanism II(8) has been derived for the case where the surface reaction between molecularly adsorbed CO_2 and atomically adsorbed H_2 is the rate controlling step, and since the constants of the equation on being evaluated from experimental results satisfy the required conditions, it would be justifiable to assume that in the reaction between CO_2 and H_2 in presence of nickel catalyst, the above mechanism is the rate controlling step.

Similarly, perhaps to a great extent, the reaction between molecularly adsorbed molecules of CO_2 and H_2 might exert a great influence on the rate of the reaction. Next to these two mechanisms, the one that would exert some influence as seen from Table 10 is II(7) - that is the desorption of methane. Thus, the final recommended equation for the hydrogenation of CO_2 in presence of Ni catalyst is:-

$$r = \frac{s\ k\ l \left(K_{CO_2} p_{CO_2} \left(\sqrt{K_{H_2}\ p_{H_2}} \right)^4 - \frac{K_{CO_2} \sqrt{K_{H_2}}\ p_{CH_4}\ p_{H_2O}}{K} \right)}{2(1+K_{CO_2} p_{CO_2} + \sqrt{K_{H_2}\ p_{H_2}} + K_{CH_4}\ p_{CH_4} + K_{H_2O}\ p_{H_2O})^5}$$

$$\text{i.e. } r = \frac{skl\ K_{CO_2} \sqrt{K_{H_2}} \left(\sqrt{K_{H_2}^3}\ p_{CO_2}\ p_{H_2}^2 - \frac{p_{CH_4}\ p_{H_2O}}{K} \right)}{2(1+K_{CO_2} p_{CO_2} + \sqrt{K_{H_2}\ p_{H_2}} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O})^5}$$

where S L = E = effectiveness factor.

k = forward reaction velocity constant.

$K_{CO_2} K_{H_2}$, etc. = adsorption equilibrium constants for CO_2, H_2, etc.

K = overall equilibrium constant of the reaction;

p_{CO_2}, p_{H_2}, etc. = partial pressure of CO_2, H_2, etc.

In conclusion it should be said that the seventeen equations derived are ideal forms based on several assumptions and/

and the correct mechanism cannot be selected by consideration of storchiometric equations alone, but further must be supported by comparison of the trends of experimental data. It is reasonable to say that the mechanism of reaction between CO_2 and H_2 is a surface reaction between adsorbed CO_2 and adsorbed H_2 as the equations were solved using experimental data, and since the same conclusion was arrived at in Part I about Ni-THO_2 catalyst by consideration of the shapes of graphs obtained by plotting $p_{CO_2}/p^4_{H_2}$ and $p^4_{H_2}/p_{CO_2}$ against yields using experimental results got by varying the partial pressures of both the components. As pointed out in Section A, Part II, the experimental results on Ni catalyst seem to indicate the same trend. Thus, from these considerations it is justifiable to assume that the controlling mechanism of reaction between the two gases CO_2 and H_2 is the surface reaction between molecularly adsorbed CO_2 and atomically adsorbed H_2. In support of this view two facts could be cited (1) Taylor and Russel (41) showed that CO_2 is adsorbed on nickel catalyst and (2) S.R. Craxford (60) showed that the formation of methane either through CO or CO_2 and hydrogen is accompanied by O - p H_2 change and under these conditions an appreciable amount of atomic hydrogen is noticed on the catalytic surface.

Though/

Though the above postulated mechanism is the rate controlling step in the hydrogenation of CO_2 as shown by the above results, it should be pointed out that the other reactions like rate of methane adsorption, rate of diffusion of reactants through gaseous film, nature of catalyst, etc., also have an influence to varying degree on the overall rate.

PART III.

Interaction of Carbon dioxide and Hydrogen at elevated pressures.

CHAPTER I.

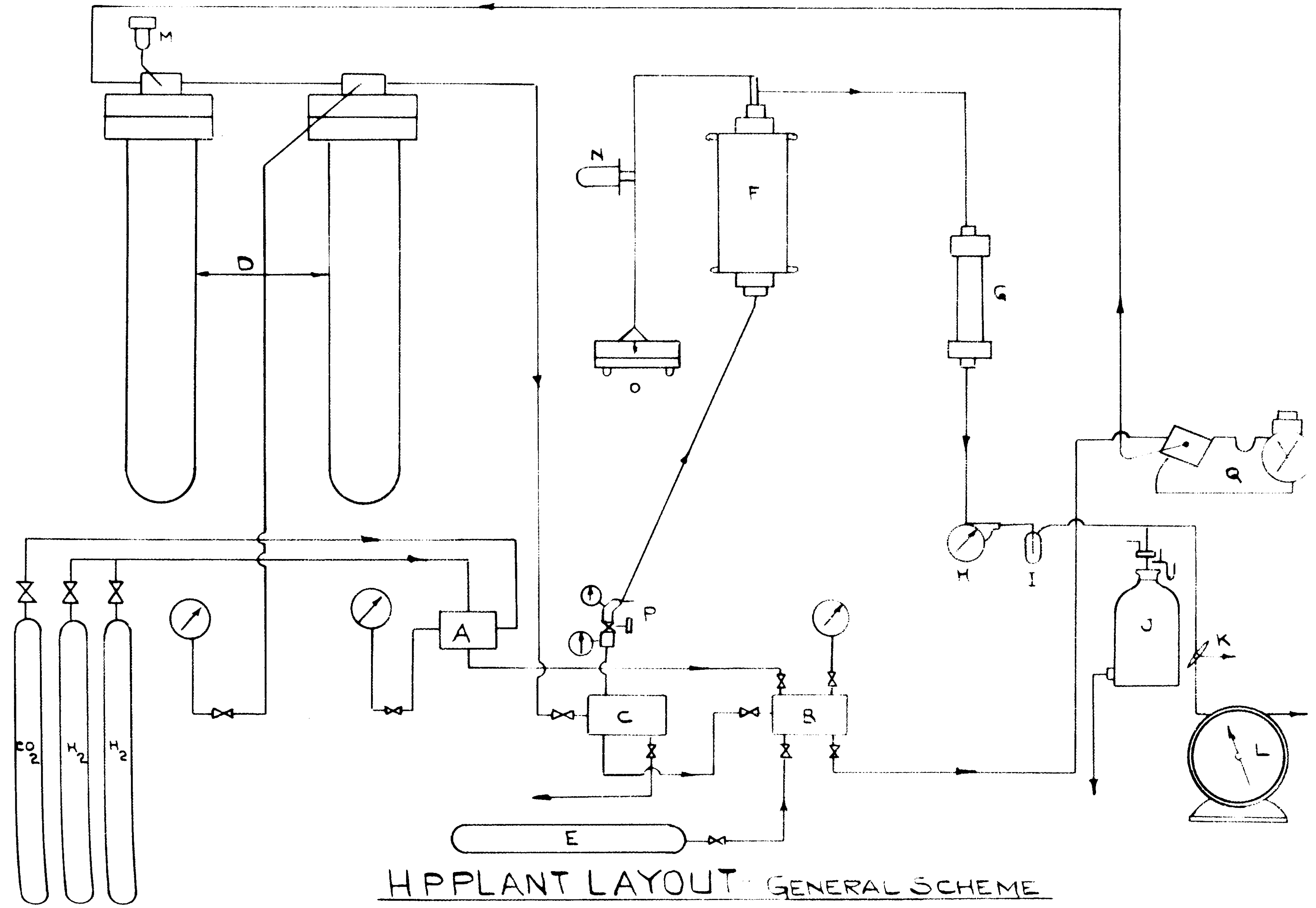
INTRODUCTION.

The majority of the parts used in the plant assembled in 1946 for the study of methanol synthesis were taken from a circulatory system installed at the Royal Technical College in 1935 for the study of gas reactions at high temperature and pressure. In the plant assembled for the present work, most of the parts belonging to the methanol synthesis plant were used. The parts that were used external to the components available were a pressure regulator, a reaction chamber, a drier, a pressure reducing valve, a sampler and a gas meter. The reaction between CO_2 and H_2 was studied under elevated pressure in presence of nickel, nickel thoria, and Fischer's catalysts. A considerable amount of time had to be spent in dismantling and overhauling the plant, reassembling with the necessary changes in design, and in overcoming the many difficulties encountered during the operation of the plant.

GENERAL DESCRIPTION OF PLANT.

The general scheme of the plant layout is shown in figure/

FIG. 21.



HP PLANT LAYOUT: GENERAL SCHEME

figure 21 on page 158 . The main parts of the plant consist of two storage cylinders 'D' of enough capacity to handle large volumes of gas, a pressure regulator P to enable the reaction to be carried out at a predetermined pressure, a reaction chamber and a furnace F, a drier G to remove the water formed during reaction so that it does not choke the system, a reducing valve H to let out the reaction products at atmospheric pressure, a sampler J, a gas meter L, and a circulating pump Q.

The gases CO_2 and H_2 are led into the system from the gas cylinders through a four-way distribution chest A. There is a pressure gauge connected to this chest to read directly the pressure of the gas in the supply cylinder. The gases from A enter the storage cylinders D through the low pressure block B and the pump Q. When the required amounts of CO_2 and H_2 have been introduced into the storage cylinders, the four-way distribution chest is cut off from the L.P. Block. The high pressure block C is then put in communication with the L.P. Block and the gases circulated for mixing. The path of the gases in this case would be from storage cylinders through the H.P. Block, the L.P. Block, and the pump back to the cylinders. A safety valve 'M' is connected to one of the storage cylinders and a pressure gauge to the other.

When/

When the gases have been mixed properly as shown by the analysis of the mixture sampled through a by-pass from the low pressure block; they are passed to the reaction chamber via the pressure regulator P. The reaction products from the reaction chamber pass to a drier G and then to the reducing valve H. The bulb I is a bubbler containing dilute H_2SO_4 acid to enable one to see the passing of the gases. Finally, the gases are let out into the atmosphere through the three way stop cock K. Just before starting to take readings, the gases are turned on to the gas meter and at the same time connecting a sampling arrangement to the gas stream.

The reaction chamber is heated by an electric furnace F. The temperature of the catalyst is measured by means of a calibrated copper-constantan thermocouple, the leads of which are brought out to a millivoltmeter O mounted on the control panel and the cold junction of the thermocouple is kept in a flask N containing ice.

For testing leaks, the system is divided into separate units of H.P. Block, L.P. Block and the pump, storage cylinders, and the reaction system. Nitrogen from cylinder E is introduced into the system through the L.P. Block when testing for leaks.

The storage cylinders, the reaction chamber, the drier, and/

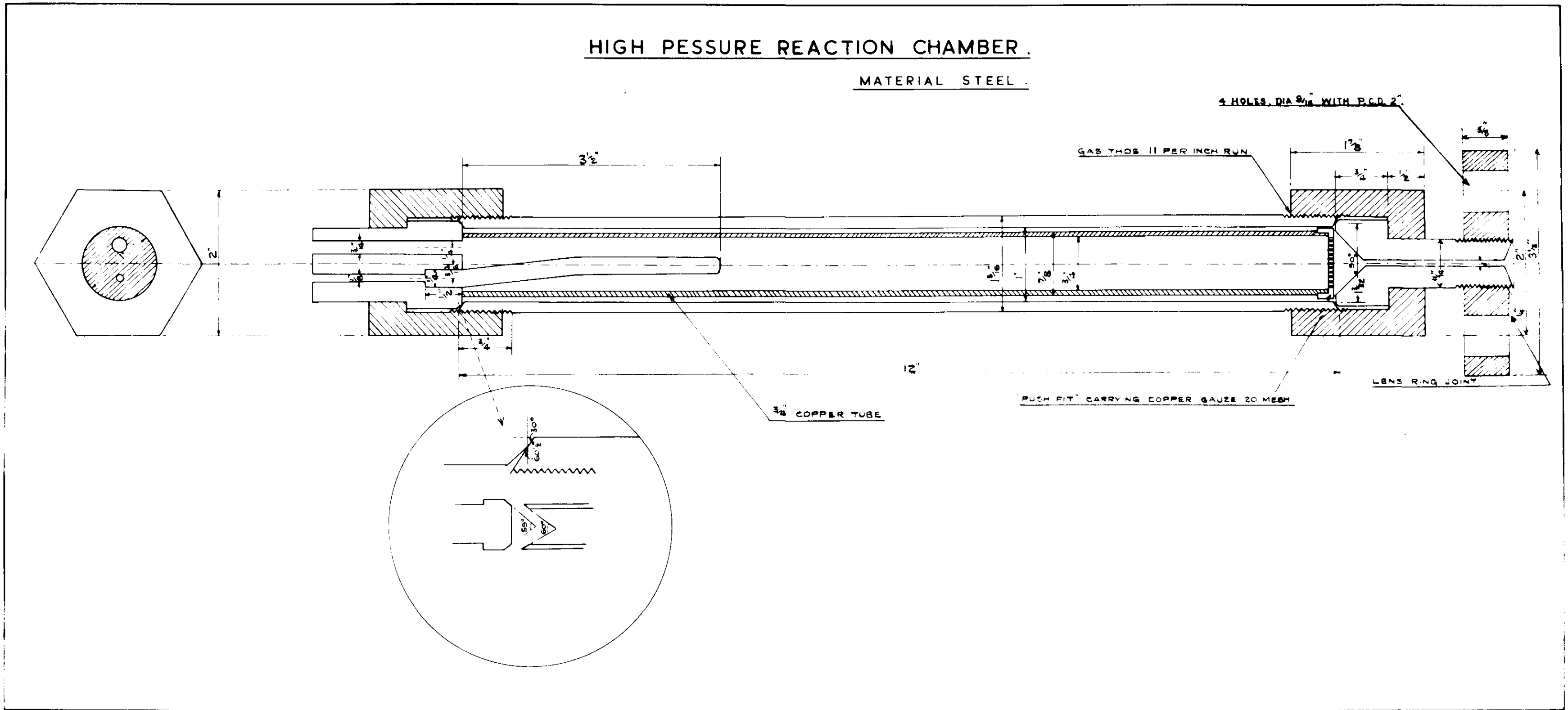
and the four-way distribution chest are housed in a steel cubicle. The L.P. and H.P. Blocks, the millivoltmeter, the pressure regulator, the reducing valve, all the pressure gauges, the control valves, electrical switches for pump furnace, and lights, and the rheostat for the furnace are mounted conveniently in front of the cubicle and constitutes as the control panel.

DETAILED DESCRIPTION OF THE PLANT.

Reaction Chamber:

A drawing of the reaction chamber is shown in fig. 22 on page 162. This consists of a steel pipe 1 inch bore, 5/32 inch thick with gas threads cut at either end to carry union nuts. The nipple of the union coupling at the right hand end of the steel pipe carries a 3 1/8 inches diameter screwed flange with four 9/16 inch holes drilled along a P. C.D. of 2 inches to facilitate the connection at this end by lens ring joint to the pressure regulator through a steel tube. The left hand end of the steel pipe is made gas tight by means of a union coupling. The nipple of this union has two holes 3/16 inch and 1/8 inch bore drilled diametrically opposite to each other. The 1/8 inch hole is widened/

Fig. 22.


HIGH PESSURE REACTION CHAMBER.
MATERIAL STEEL.
4 HOLES, DIA 9/16" WITH P.C.D. 2".
GAS THDS 11 PER INCH RUN
3½"
1⅞"
¾"
½"
5/8"
2"
3⅛"
¼"
1 5/16"
1"
7/8"
3/4"
90°
1/32"
11/16"
2"
3/16"
1/8"
½"
12"
¾" COPPER TUBE
"PUSH FIT" CARRYING COPPER GAUZE 20 MESH
LENS RING JOINT
30°
60°
59°
60°

widened at the inside end of the nipple to 1/4 inch and to a depth of ½ inch and threaded. A thermocouple pocket is screwed to this and gas welded to ensure gas tightness. This thermocouple pocket is offset so as to be at the centre of the reaction chamber, in order that the thermocouple registers the temperature at the centre of the catalyst mass. The 3/16" hole is threaded at the outside end of the nipple and to this a 0.25 inch outside diameter steel tube is screwed and gas welded, the other end of the tube being connected to the drier by means of a union coupling.

A copper tube of 3/4 inch bore is placed co-axially with the outer steel tube and is held in position by a circular recess corresponding to the outer diameter of the copper tube and cut in the inside end of the nipple carrying the thermocouple pocket. The other end of the copper tube is closed with a perforated copper cap (20 mesh), the fit between the two being a push fit. This copper tube has been incorporated in the reaction chamber so that the catalyst could be introduced without having to dismantle the entire connections of the reaction chamber thus enabling simplicity of operation.

DRIER.

The drier consists of a steel pipe 8 inches long, ½ inch/

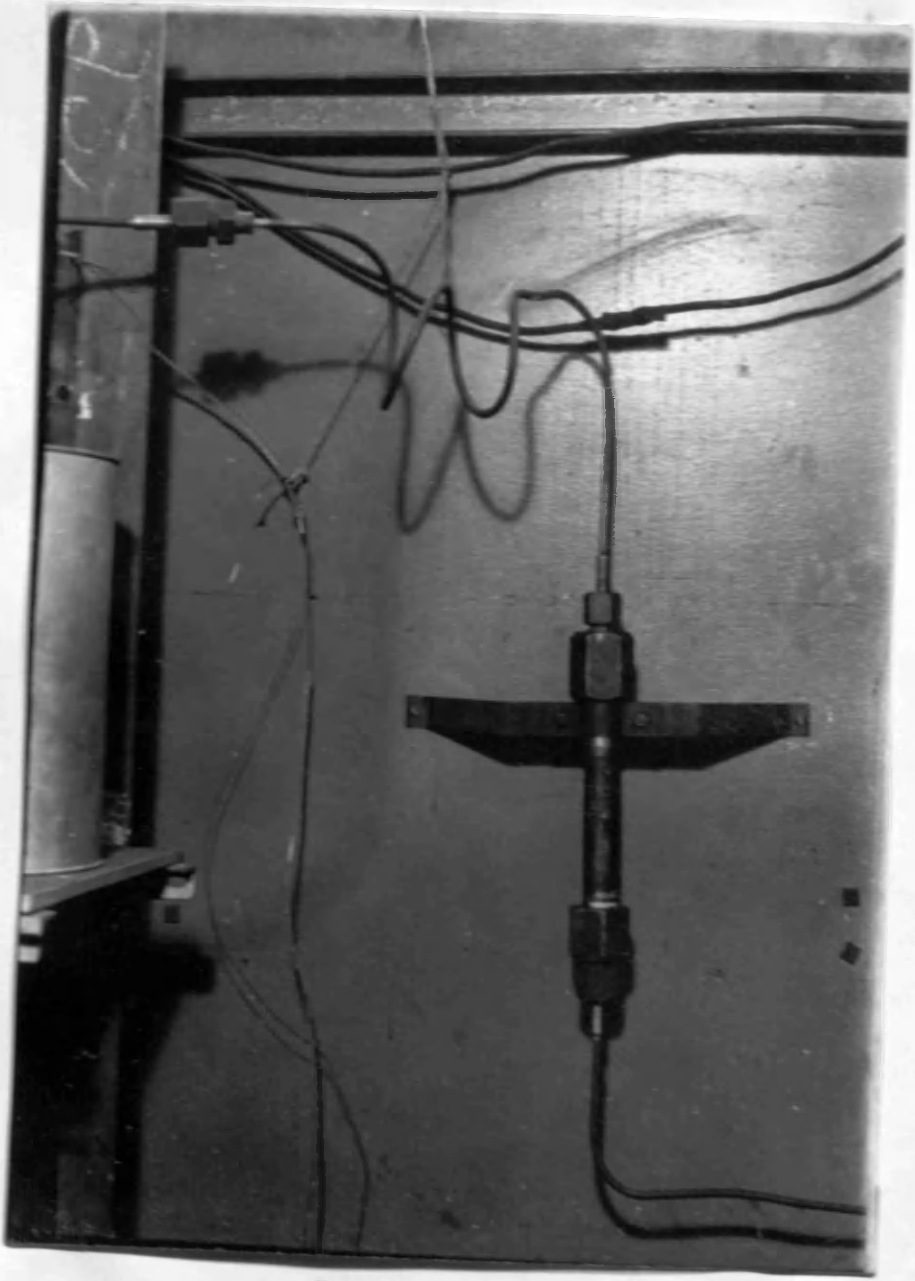


FIG. 23.

FIG. 24.

FIG. 25.

inch bore and 1/4 inch thick. It is connected to the outlet from the reaction chamber by a union and nipple coupling having copper gaskets. The other end of the drier is connected to the reducing valve by means of another union coupling. The drier is filled with activated silica gel.

A photograph of the drier with its connections is illustrated in figure 23 on page 164.

PRESSURE REGULATOR:

The pressure regulator is a standard oxygen regulator carrying two pressure gauges, and is connected to the high pressure block through an adaptor and a lens ring joint. A photograph of the adaptor is shown in figure 24 on page 165

The outlet from the regulator is connected to the bottom of the reaction chamber by a steel tubing. The connection at the regulator end of the steel tube is made by **H.P.** union coupling.

REDUCING VALVE:

For the pressure reducing valve, a suitable needle type of valve was not readily available. So use had to be made of an old R.A.F. valve of the type shown in figure 25 on page 165 , and it is welded all round so that its actual mechanism is not understood.

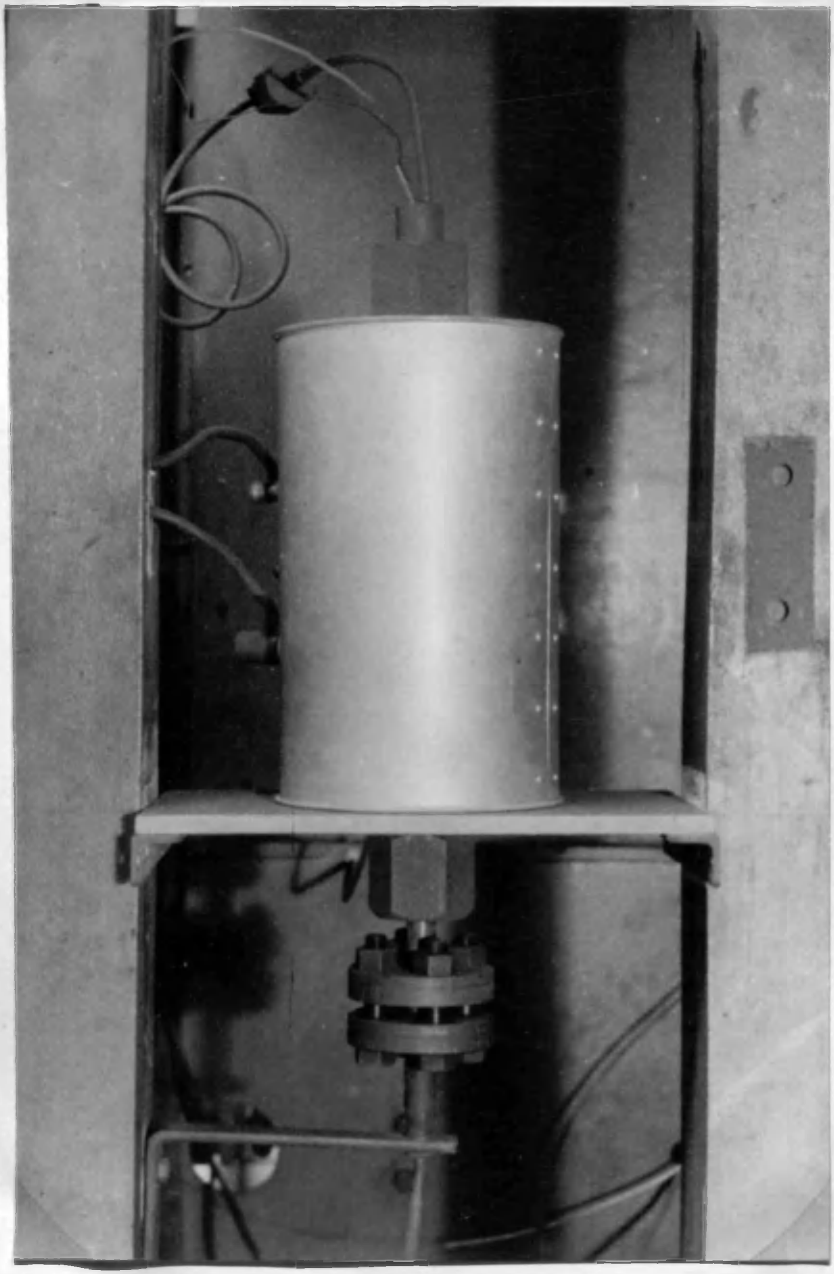
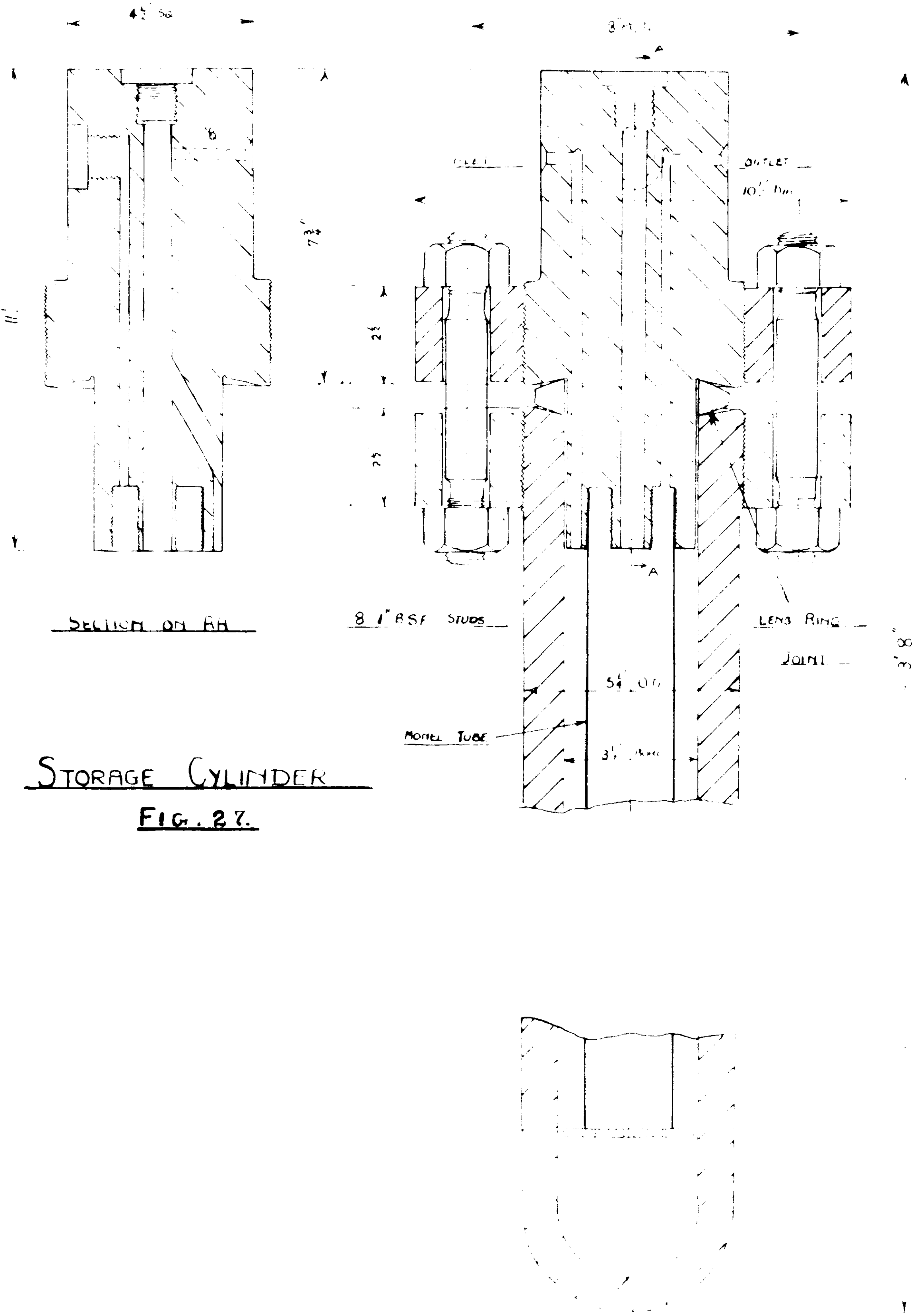


Fig. 26.



STORAGE CYLINDER

FIG. 27.

FURNACE:

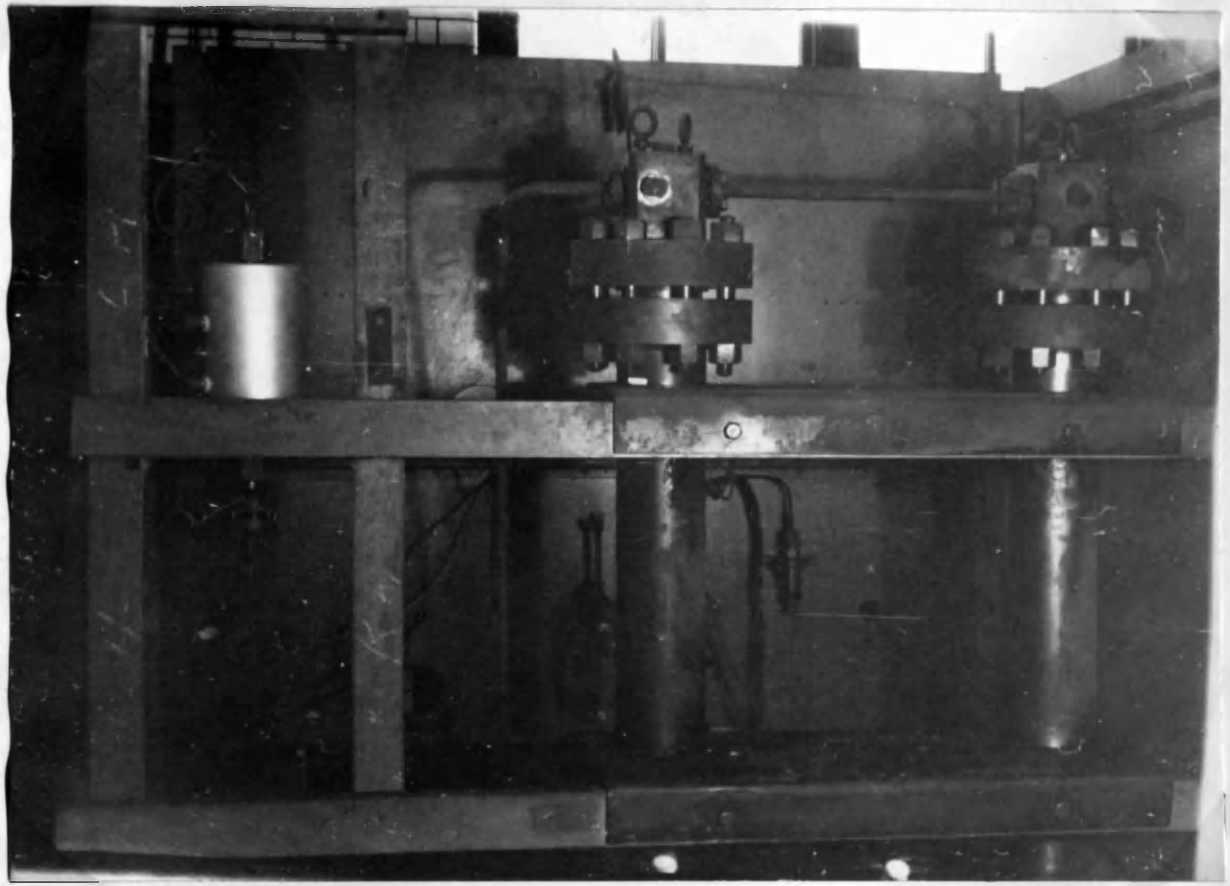
The reaction chamber is heated by an electric furnace. The furnace proper consists of a silica tube wound with Nichrome wire and is insulated with asbestos lagging. The furnace with its seating arrangement and the reaction chamber fixed in position is photographed and is illustrated in figure 26 on page 167 .

STORAGE CYLINDERS:

A drawing of one of the cylinders is shown in figure 27 on page 168 . The main dimensions of both the cylinders are the same and are made of a 6% chrome steel alloy. They consist of a cover block and a main body. The main body seats a large lens ring on which the cover block rests. The main body and the cover block are threaded to take a loose flange of 10½ ins. diameter. There are eight holes on these flanges on a P.C.D. of 8 inches, through which pass large studs secured at top and bottom by large nuts. In this way the cover block is held firmly on to the main body and makes a gas tight joint by means of the lens ring. The advantage of the lens ring type of joint is that it is self aligning within wide limits of variation in the adjusting studs and nuts.

The/

FIG. 28.



The bottom of the cover block carries a screwed Monel tube which extends almost to the bottom of the cylinder. The gas passages are drilled in the cover block and it is obvious from the drawing that the gas entering should pass to the bottom of the cylinder, through the annular space between the cylinder and the Monel tube before it passes up the Monel tube to the outlet. This arrangement helps complete circulation and mixing of the gas and is further assured by projecting spiral grooves on the outside of the Monel tube.

A sectional view of the cover block along AA is shown alongside separately. The hole shown in this view by the dotted lines at B is directly linked with central channel as indicated. In one cylinder the pressure gauge is connected to the hole and in the other to a Hopkinson safety valve. The two big holes shown in the sectional view were not required and so were sealed by means of steel plug seatings on an annealed copper ring.

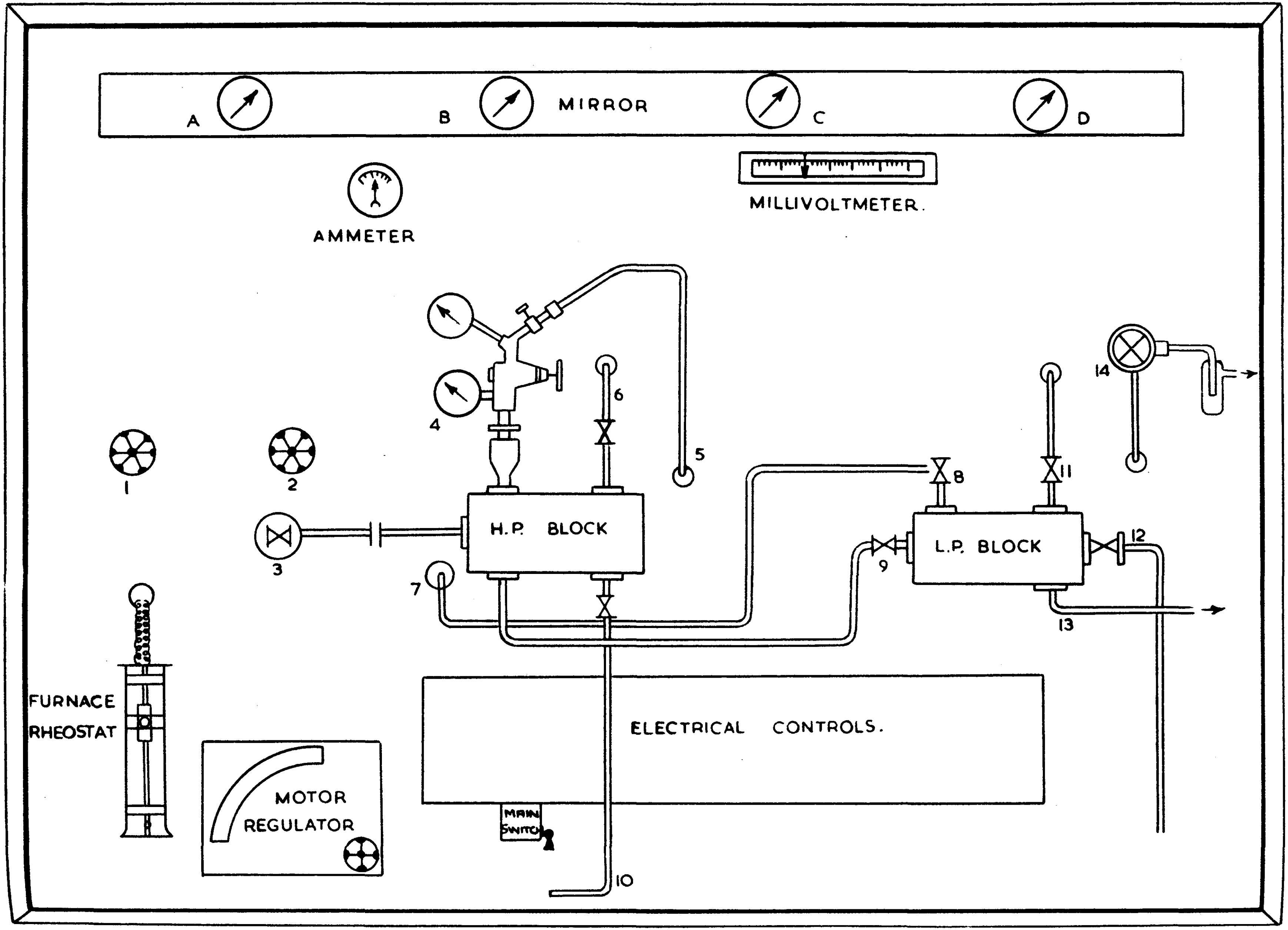
A photograph showing the storage cylinders in position is illustrated in figure 28 on page 170.

PUMP:

The circulating pump together with its motor is mounted on a wooden stand. It is a reciprocating pump and is capable of handling 60 litres of gas per hour at a speed of 330 r.p.m.

CONTROL PANEL

Fig. 29.



CONTROL PANEL:

A drawing of the control panel is shown in figure 29 on page 172 . Key to the diagram is as follows:-

(1) Valve to gauge A.
(2) Valve to gauge B.
(3) From storage cylinders.
(4) Pressure regulator.
(5) To reaction chamber.
(6) To gauge C.
(7) Gas supply line.
(8) Valve in gas supply line.
(9) Valve connecting H.P. and L.P. Blocks.
(10) To L.P. gas holder.
(11) To gauge D.
(12) From nitrogen cylinder.
(13) To pump.
(14) Reducing valve.

The electric controls consist of switches for the furnace, the thermocouple, the electric motor, and for illuminating the pressure gauges by means of "striplite" lighting.

A photograph of the control panel is shown in fig. 30 on page 174 .

CUBICLE/

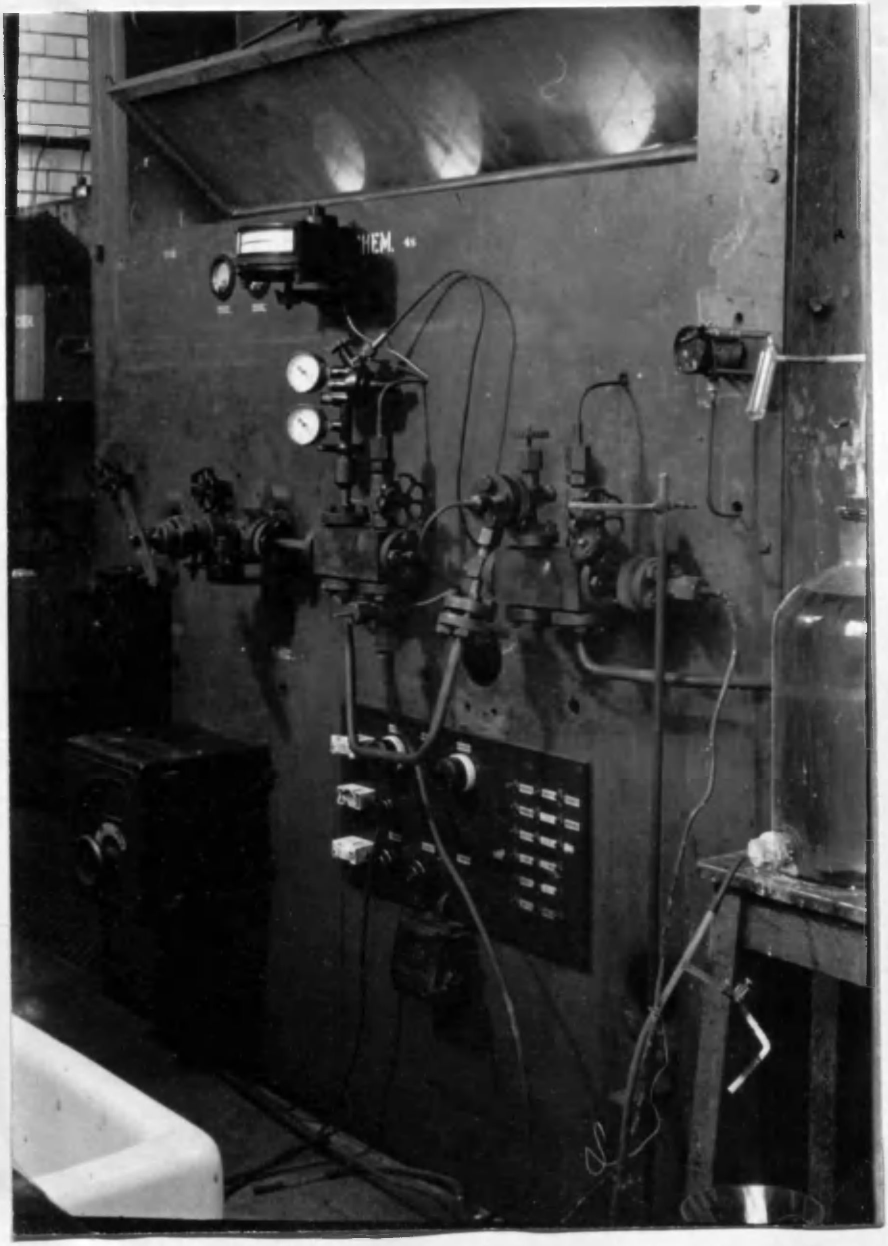


FIG. 30.

FIG. 31.

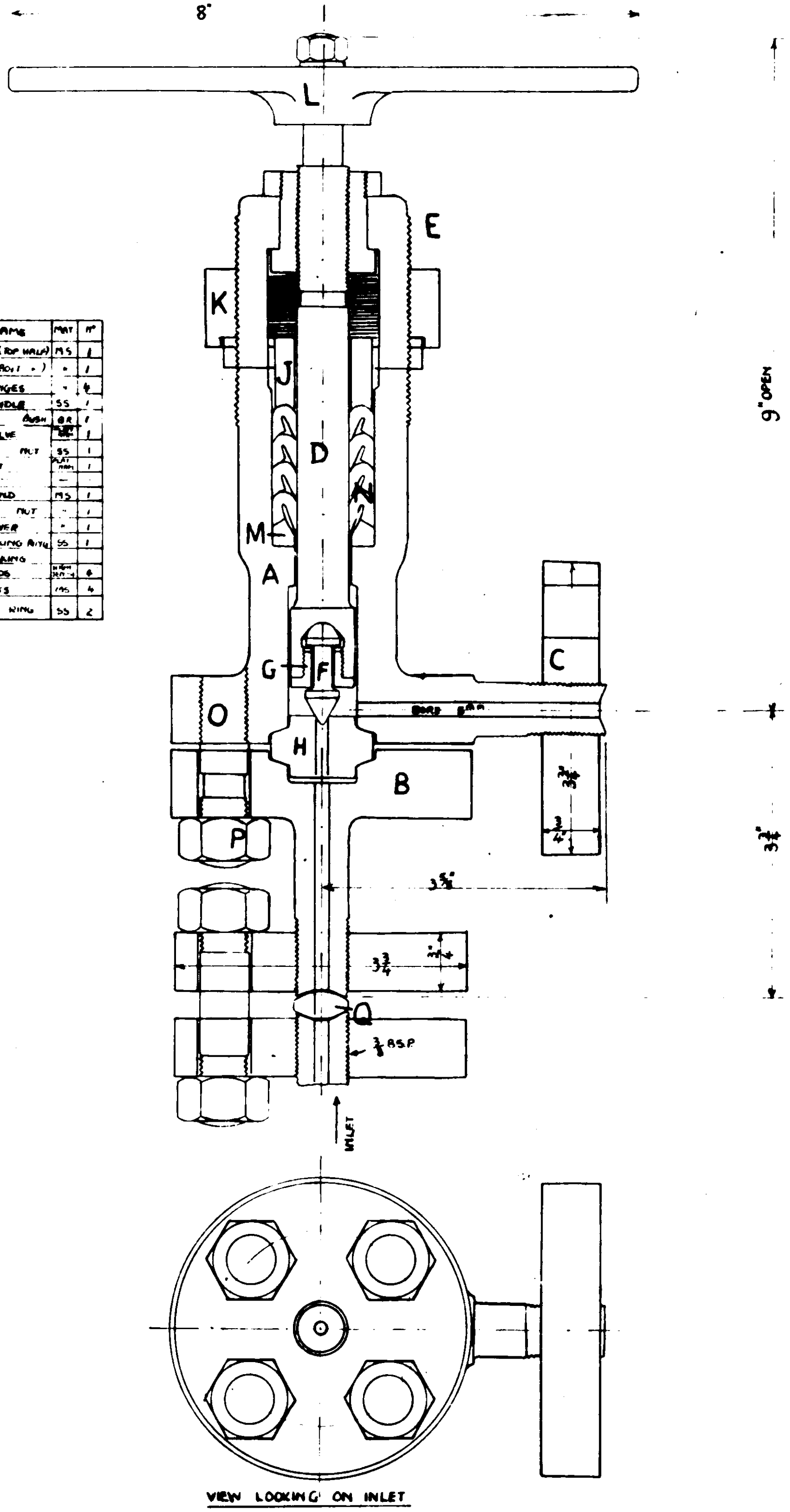
CUBICLE:

The components, namely, the reaction chamber, drier, and storage cylinders are housed in a steel cubicle. At the back of the cubicle there is a horizontal girder on which are supported the two storage cylinders steadied by two horizontal plates bolted to girders at the back of the cubicle (see figure 28 on page 170). There are also two vertical channel iron girders at the back left hand corner of the cubicle on which are fixed horizontally two small angle irons. These carry a horizontal support for the furnace. The reaction vessel passes through the furnace and is secured at the bottom to one of the girders (see fig. 26 on page 167).

ASSEMBLY OF GAS CYLINDERS:

A photograph illustrating the assembly of the gas cylinders is shown in figure 31 on page 175. A CO_2 cylinder and two H_2 cylinders are used and held in position on one side of the cubicle by a metal frame screwed on to the side steel sheet of the cubicle. The hydrogen cylinders are used in parallel by means of a two cylinder coiled type coupler adaptors. This enables the complete charge of gas into the system without any replacement of cylinders and full use of cylinders is obtained by using low pressure hydrogen in/

FIG. 32.



REF	NAME	MAT	Nº
A	BODY (TOP HALF)	MS	1
B	" (BOT ")	"	1
C	FLANGES	"	4
D	SPINDLE	SS	1
E	" BUSH	BR	1
F	VALVE	[illegible]	1
G	" NUT	SS	1
H	SEAT	PLAT NAM	1
I		—	
J	GLAND	MS	1
K	" NUT	"	1
L	LEVER	"	1
M	PACKING RING	SS	1
N	SPACING		
O	STUDS	HIGH TEN-S	4
P	NUTS	MS	4
Q	LENS RING	SS	2

VIEW LOOKING ON INLET

HOPKINSONS HIGH PRESSURE

STOP VALVE

in a used cylinder for the initial stages of the charge. The H_2 line passes through a hole in the steel sheet to the four way distribution chest within the cubicle. The CO_2 line is connected to the cylinder by means of H.P. union coupling having a copper gasket. It passes from cylinder to the distribution chest through the expanded metal screen at the lower part of the cubicle.

VALVES, PIPELINES, AND JOINTS:

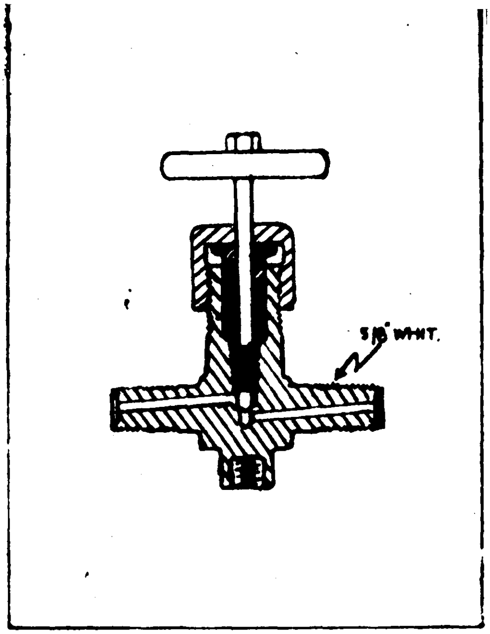
There are three types of valves used in the plant apart from the pressure regulator and the reducing valve.

(1) Hopkinson H.P. stop valve shown in figure 32 on page 177. This is incorporated in the line between the storage cylinders and the H.P. Block. It is made of mild steel for use at high temperatures up to 500°C. The valve seat and needle are made of platnum alloy.

(2) Four needle type valves are employed in the gauge lines.

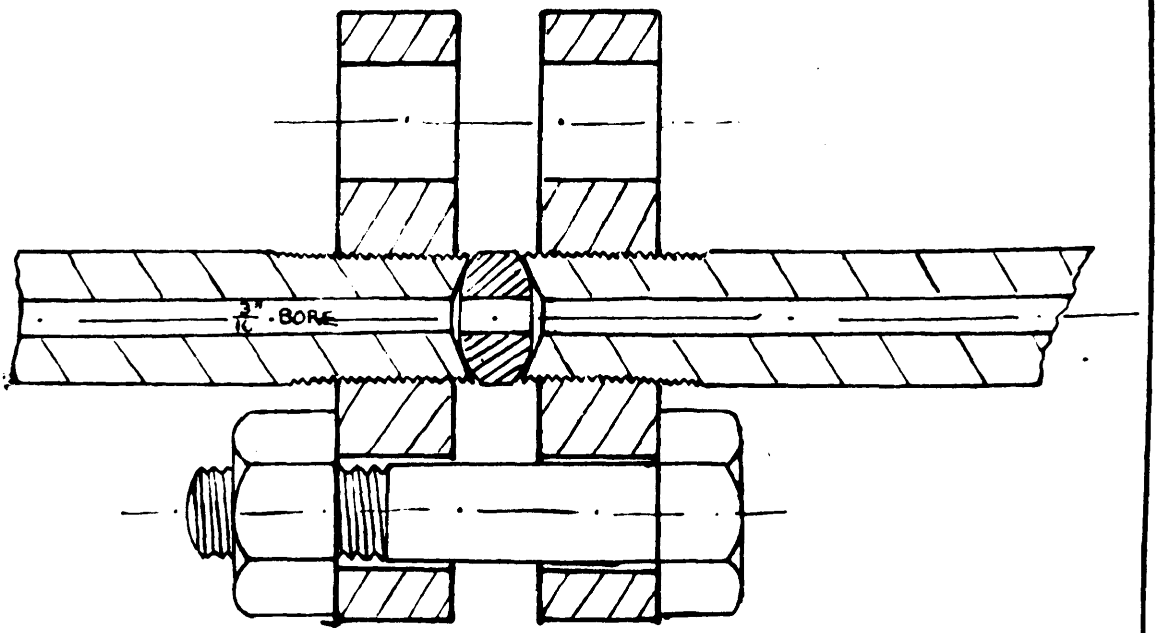
(3) The remainder of the valves employed are of the I.C.I. fine adjustment type shown in figure 33 on page 179. The gland packing consists of soft lead washers.

The pipe lines used in gauge lines, gas cylinder lines, and the lines in the reaction system consist of 6% Cr; 6% Ni; high pressure steel tubing of 1/16" bore and 0.25 inch external diameter. These are joined by bronze unions, or may/



FINE-ADJUSTMENT VALVE
[I.C.I. TYPE]

FIG. 33.



LENS RING JOINT

FIG. 34.

may be screwed into a short length of pipe suitable for I.C.I. type of lens ring joint, shown in figure 34 on page 179. All the other pipe lines are of high pressure steel tubing of the same alloy and $^3/16$" bore and $^{11}/16$ inch external diameter. The ends of these pipes are coned and threaded so that they could be joined by lens ring joints.

PRESSURE GAUGES:

These are Budenberg pressure gauges calibrated for pressures up to 6,000 lbs. per $in.^2$ and mounted in a steel box fitted with a chromium plated mirror. The gauges are made of special steel tubes, triplex glass, solid fronts and loose backs. The gauges are viewed in the mirror and thus providing protection in case any of the gauges blow out.

CHAPTER II.

OPERATION OF THE PLANT.

The catalyst was often renewed so that not more than four to five runs were carried out on each batch of the catalyst. For renewing the catalyst, the union coupling at the top of the reaction chamber was unscrewed and lifted out bodily so that the union coupling and the nipple carried along with them the copper tube which serves as the catalyst basket. First, an asbestos sheath was placed centrally along the recess cut in the nipple and the sheath was then packed with asbestos wool. The copper tube was then fitted on to the recess tightly and held upright. 20 c.cs. of the catalyst was introduced into the copper tube on to the packed asbestos sheath which was of such length that the tip of the thermocouple pocket would be halfway up the catalyst bed. Some asbestos wool was then put on top of the catalyst followed by purified pumice to fill the rest of the tube. Finally, a little asbestos wool was packed on. The whole assembly was then lowered into the reaction chamber and fitted. The reaction system was then flushed out with hydrogen/

hydrogen and the catalyst was reduced. In the first few instances the reduction was carried out under a pressure of 50 lbs/sq.in. Later on it was carried out under atmospheric pressure so that there could be a free flow of the gas and the reduction time could be cut down to 6 hours from 12 hours.

The experimental procedure for a run was as follows: The storage vessels first were filled with CO_2 up to the required pressure, followed by H_2 till the total pressure reached a predetermined value. The gases were then circulated by the pump for satisfactory mixing. When the gases were mixed, an analysis was made. The synthesis gas was passed through the reaction chamber (kept at 280°C) at the calculated reaction pressure by means of the regulator. The gases after reaction were metered, sampled and analysed. By back calculation the rate of flow was determined and the synthesis gas composition checked with the analysis results.

The circulating pump at 200 r.p.m. is supposed to circulate 40 litres/hr. Now, as the whole volume of storage cylinders and pipe connections is not more than about 6 litres at the most, about 3 hours circulation should mix the gases thoroughly. But analysis of the gases at regular intervals show this assumption to be at fault. The following/

following is a typical analysis result of the synthesis gas:-

Gases filled in at 10 a.m.

CO_2 filled	11 atms.
H_2 "	22 atms.
Total	33 atms.

	Time	CO_2%
	11.30 a.m.	1.3
	1 p.m.	2.2
	2 p.m.	4.88
	5 p.m.	11.95
next day	11 a.m.	37.0

It seemed that circulation did not help in mixing the gases in this case. So it was decided to fill in the gas and keep it over night so that mixing might take place by diffusion, but it was noted that there were some minute leaks in the storage cylinder and the H_2 being a lighter gas escaped more rapidly than CO_2, thus the percentage of CO_2 constantly increased with time. Therefore, after a few runs the storage cylinders were dispensed with and one of the hydrogen gas cylinders was used for filling in the gases. It was found that if CO_2 was filled in first, followed by H_2, the mixing was not complete even after three to four days; whereas/

whereas, if the cylinder was filled in first with H_2 followed by the heavier gas CO_2 mixing was complete in about 24 hours.

During the first few runs, it was found that at the reducing valve, due to sudden expansion of the gases and hence cooling, the water of reaction condensed inside the valve and consequently choked it. Therefore, it was decided to put in a $CaCl_2$ or activated Silica gel tube just after the reaction chamber. The reducing valve gave a considerable amount of difficulty throughout the course of investigation of the problem of interaction of CO_2 and H_2 at elevated pressures. The narrow steel tubes, used to get choked giving low values of yields and these experiments were naturally rejected. The plant was not completely leak proof, for there were a few minute leaks which were difficult to trace. On the whole, the plant worked satisfactorily.

T A B L E 1.

Catalyst ____________ Ni-ThO$_2$ – 1-B
Catalyst volume ---- 20c.cs.

Expt. No.	Temp. °C	Time mins.	Flow (under press.) c.cs./min.	Press. ~~(under press.)~~ atms.	Synthesis gas %		Product gas %			Yield
					CO_2	H_2	CO_2	H_2	CH_4	
1.	300	20	107	10	5.5	90.5	1.4	87.0	5.25	2.34
2.	290	30	80	~~30~~10	57.0	39.5	67.5	18.6	8.5	2.64
3.	270	30	107	10	64.0	32.0	70.0	20.5	4.1	1.89
4.	282	20	40.8	10	43.2	53.0	55.1	21.6	16.5	2.0
5.	293	20	41.7	10	58.1	37.4	75.4	3.3	13.5	1.83
6.	298	20	89.0	10	55.0	40.0	62.0	23.8	8.7	3.01
7.	280	18	28.2	10	13.0	81.5	10.5	77.6	5.6	3.58
8.	300	18	29.2	2.5	22.7	73.4	21.8	64.0	9.0	5.36

CHAPTER III.

RESULTS AND DISCUSSION.

In all fifty experiments were carried out, 1 to 37 with Ni-ThO_2 catalyst and 38 to 50 with Ni catalyst. The experimental results are tabulated in tables 1; 2,2a; 3,3a; 6,6a; and 9,9a. Experiments 1 to 8 (table 1) were carried out to get used to high pressure experimental technique.

In all the experiments, it would be noted that there is some oxygen in the synthesis and product gases and this might be due to some oxygen present in cylinder gas. In the analysis of product gas, carbon monoxide was detected to an appreciable extent; sometimes as high as 2.5%. The presence of this CO in light of Medsforth's work (47) could come from the dehydrogenation of an intermediate compound of the methyl alcohol type. In this connection it should be mentioned that the used silica gel from the drier always possessed a sweet smell. The condensate from distillation of/

TABLE 2A.

Catalyst---- $NiThO_2$- IB.
Cat. vol. -- 20 c.cs.

Expt. No.	Temp. °C.	f(V)	Synth. Gas % CO_2	Synth. Gas % H_2	Product Gas % CO_2	Product Gas % O_2	Product Gas % CO	Product Gas % CH_4	Product Gas % H_2	Yield
9.	290	2873	28.3	71.0	28.5	0.4	1.4	12.2	56.6	11.4
10.	290	79	29.0	71.0	28.3	0.4	0.4	7.3	62.8	2.22
11.	285	159	27.4	71.2	27.6	0.5	0.4	3.0	67.6	3.60
12.	290	239	36.0	62.0	37.2	0.3	0.7	2.6	58.5	3.10
13.	285	114.5	35.7	62.8	37,3	0.9	0.8	3.5	57.8	1.32
14.	290	221	34.9	64.2	38,2	0.5	0.7	8.4	52.5	2.84
15.	290	396.5	51.2	48.8	55.6	0.3	2.5	6.3	36.0	5.58
16.	290	151	49.6	50.0	54.2	0.4	0.8	5.7	38.6	1.96
17.	290	200	50.7	49.0	51.7	0.4	1.2	1.8	45.4	2.60
18.	290	181.5	50.5	49.6	54.2	0.6	1.5	5.9	37.1	4.36
19.	290	205	28.3	71.3	28.3	0.4	0.8	6.34	63.7	5.18

(check run)

TABLE 2.

Catalyst -------- Ni-ThO_2--IB
Catalyst vol. ----20 c.cs.

Expt. No.	Temp. °C.	Time. Mins.	Product Gas @ 1 atm. Litres.	Equivt. Synth. Gas. Litres.	f(V).	Reaction Press. Atm.	Synth. gas. Partial Press.		Yield.	f(Re)
							CO_2 atm.	H_2 atm.		
9.	290	10	18.6	27.7	277	10.0	2.8	7.1	11.40	99.8
10.	290	12	7.34	9.5	79.0	10.0	2.9	7.1	2.22	28.4
11.	285	12	17.0	19.1	159.0	10.0	2.8	7.2	3.60	57;2
12.	290	10	16.4	18.1	239.0	10.0	2.8	4.77	3.10	76.5
13.	285	16	12.25	14.0	114.5	7.57	2.8	4.77	1.32	36.6
14.	290	12	13.90	18.6	221.0	7.57	2.9	4.67	2.84	70.8
15.	290	10	17.9	22.2	396.5	5.60	2.8	2.8	5.58	105.0
16.	290	16	11.1	13.5	151.0	5.60	2.8	2.8	1.96	40.0
17.	290	10	15.3	16.5	200.0	5.60	2.8	2.8	2.60	53.0
18.	290	12	17.9	21.8	181.0	10.0	5.0	5.0	4.36	86.0
19.	290	15	24.4	30.75	205.0	10.0	2.82	7.1	5.18	73.6

(check run)

TABLE 3A.

Catalyst--- Ni-ThO$_2$-- IB.
Cat. vol. --- 20 c.cs.

Expt. No.	Temp. °C.	f(V)	Synth. gas %		Product gas %					Yield.
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
20.	290	95.7	30.8	68.4	32.2	0.4	0.2	6.1	60.8	2.06
21.	290	93.8	31.4	68.6	32.4	0.3	0.2	5.52	60.3	1.91
22.	290	182.0	31.0	68.1	32.0	0.4	0.1	3.75	63.5	2.62
23.	285	248.0	31.2	68.3	32.0	0.4	0.2	3.14	64.1	3.05
24.	290	76.0	20.4	79.5	19.8	0.0	0.2	4.0	76.4	1.88
25.	290	152.0	19.4	80.3	18.7	0.2	0.2	3.15	77.2	3.08
26.	290	250.0	20.1	79.4	19.4	0.3	0.1	2.65	77.3	4.30
27.	290 (check run)	200	35.5	63.0	37.1	0.6	0.2	3.90	57.2	2.59

TABLE 3.

Catalyst---- Ni-ThO$_2$-- IB.
Cat. vol. ---- 20 c.cs.

Expt. No.	Temp.	Time.	Product	Equivt.	f(V)	Reaction	Synth. gas Partial Press		Yield.	$f(R_e)$
	°C.	Mins.	gas Litres.	synth. gas. Litres.		Press. Atm.	CO$_2$ Atm.	H$_2$ Atm.		
20.	290	14	9.48	11.8	95.7	8.8	2.7	6.1	2.06	32.2
21.	290	20	13.83	16.6	93.8	8.84	2.77	6.06	1.91	31.9
22.	290	15	20.96	24.15	182.0	8.84	2.74	6.02	2.62	61.8
23.	285	15	29.14	32,85	248.0	8.83	2.77	6.06	3.05	84.4
24.	290	20	18.8	21.92	76.0	14.6	2.90	11.60	1.88	31.9
25.	290	15	29.34	33.02	152.0	14.6	2.83	11.70	3.08	63.5
26.	290	15	48.6	54.0	250.0	14.4	2.90	11.50	4.30	105.0
27. (check run)	290	25	33.15	38.3	200	7.62	2.70	4.8	2.59	64.0

of the used silica gel had also a similar sweet smell. This might have been due to the formation of some ester, but unfortunately, the condensate was extremely dilute and of insufficient quantity to attempt an analysis of the supposed ester. The presence of nitrogen in the gases is from the pressure nitrogen introduced often, to test for leaks in the system and due to the difficulty of flushing out the nitrogen completely and effectively.

NICKEL THORIA CATALYST.

Partial Pressure of H_2 Varying.

Experiments were carried out with a view to study the effect of keeping the partial pressure of one of the components, CO_2, constant and varying that of the other H_2. Accordingly, several runs were made keeping p_{CO_2} at 2.8 atmos. and varying p_{H_2} from 2.8 to 11.6 atmospheres. The results are given in tables 2,2a and 3,3a. Experiments 9 to 11 are with $p_{H_2} = 7.1$ atmos.; from 12 to 14 are with $p_{H_2} = 4.7$ atmos.; from 15 to 17 with $p_{H_2} = 2.8$ atmos.; from 20-23 with $p_{H_2} = 6.1$ atmos.; and from 24 to 26 with $p_{H_2} = 11.6$ atmos. Method of calculation in each of the experiments was the same. As an example, the calculation for experiment 9 is shown below:-

Analysis of Synthesis gas:-

CO_2 - 28.3%
H_2 - 71.0%
O_2 - 0.6%
N_2 - 0.1%
100.0

Analysis of Product Gas.

CO_2 - 28.5%
O_2 - 0.4%
CO - 1.4%
CH_4 - 12.2%
H_2 - 56.6%
N_2 - 0.9%
100.0

Synthesis gas back calculation

CO_2 - 28.5%
CO - 1.4
CH_4 - 12.2
42.1

H_2 = 56.6
H_2 used up to form CH_4 $\Big\}$ = 12.2 x 4 = 48.8
105.4

O_2 - .4
N_2 - .9
Inerts 1.3

$$\therefore \%\ CO_2 = \frac{42.1}{10.54+42.1+1.3} = \frac{42.1}{148.8} = 28.3\%$$

$$\%\ H_2 = \frac{105.4}{148.8} = 71\%$$

%/

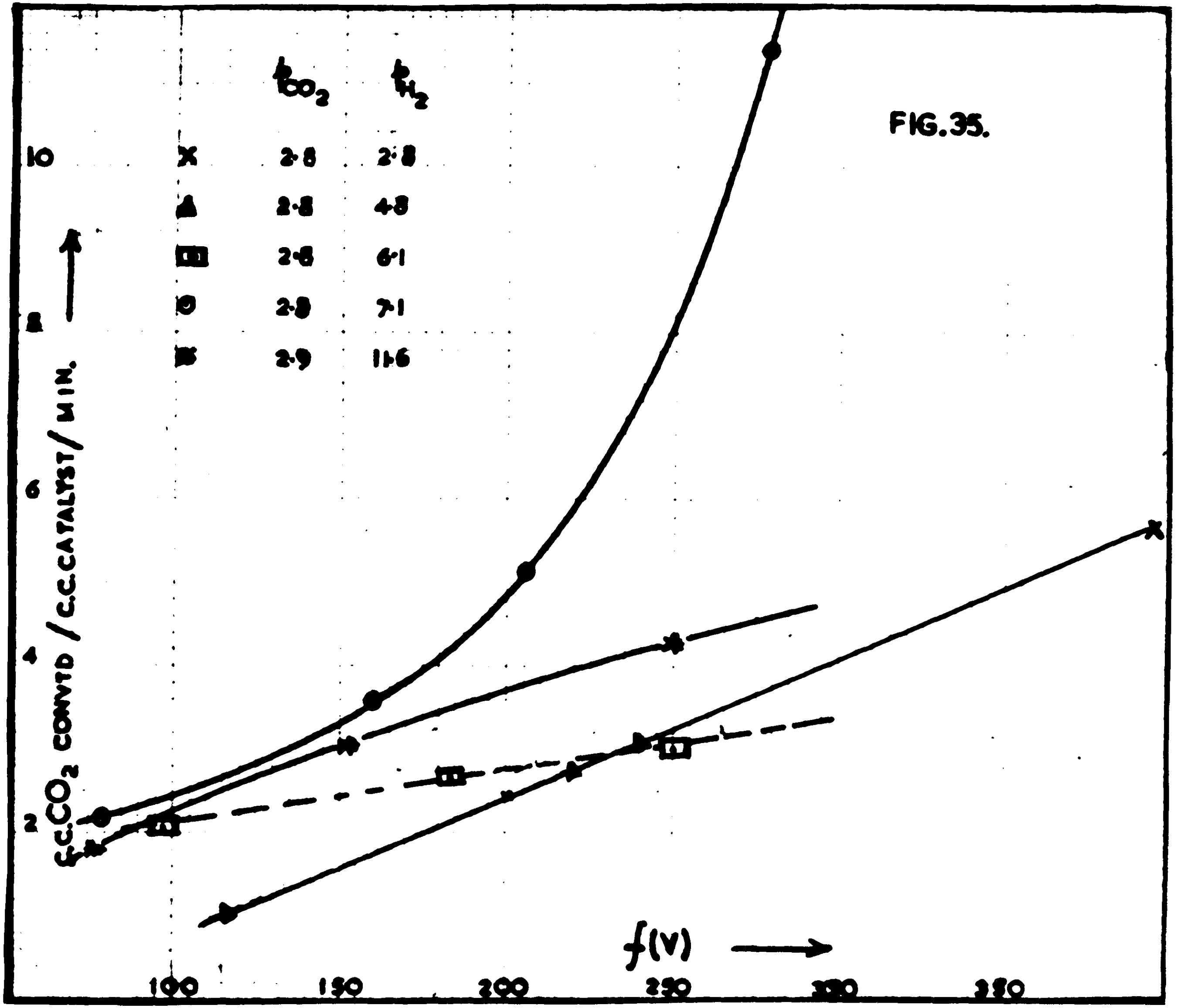


FIG.35.

p_{CO_2} p_{H_2}
× 2·8 2·8
▲ 2·8 4·8
⊞ 2·8 6·1
⊙ 2·8 7·1
✱ 2·9 11·6
C.C.CO_2 CONV'TD / C.C.CATALYST / MIN.
2
4
6
8
10
$f(V)$
100
150
200
250
300
350

$$\% \text{ inert i.e. } O_2 + N_2 = \frac{1.3}{148.8} = .8\%$$

Time of run - 10 mints.

Gas passed registered by wet gas meter - 16.3 litres

Gas collected by sampler - 2.3 litres

Temperature of reaction - 290°C.

Reaction pressure 150 lbs/sq.in. = 10 atmos. (approximately).

$\therefore$ Total gas passed = 16.3 + 2.3 = 18.6 litres.

$\therefore$ Equivalent volume of synthesis gas passed = 18.6 x 1.488 = 27.7 litres.

$\therefore$ Synthesis gas passed under pressure $= \frac{27.7}{10} = 2.77$ litres.

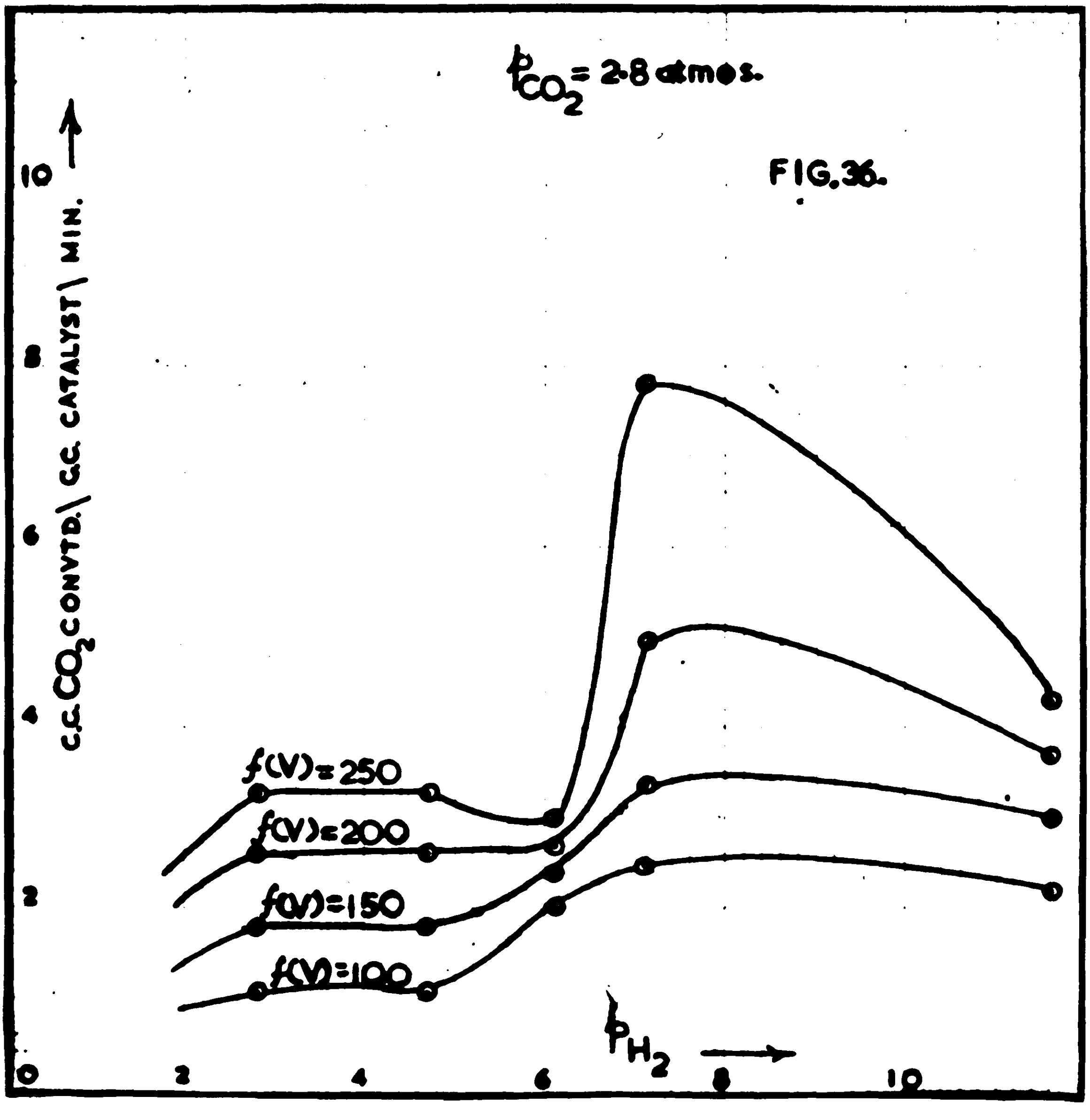
$\therefore$ Rate of flow under pressure $f(V) = \frac{2.77}{10} \times 1000 = 277$ c.cs/min.

Total methane formed = 12.2 x 18.6 = 2270 c.cs.

$\therefore$ CH_4 formed/cc cat./min. $= \frac{2270}{20 \times 10} = 11.35 = 11.4$ nearly.

The results of experiments 9 to 28 keeping p_{CO_2} constant and varying p_{H_2} are plotted in figure 35 with yield against f(V). Experiments 12 to 24 with $p_{CO_2} = 2.8$, $p_{H_2} = 4.7$ and experiments 15 to 17 with $p_{CO_2} = 2.8$, $p_{H_2} = 2.8$ seem to fall on the same straight line. In figure 35 values for yield for different values of f(V) are taken from the figure and tabulated in Table 4,

TABLE/



p_{CO_2} = 2·8 atmos.
C.C. CO_2 CONVTD.\ C.C. CATALYST\ MIN.
10
8
6
4
2
0
2
4
6
8
10
p_{H_2}
f(V)=250
f(V)=200
f(V)=150
f(V)=100

FIG. 36.

TABLE 4.

Expt. Nos.	p_{CO_2} atm.	p_{H_2} atm.	Yield at values of f(V) =			
			100	150	200	250
15-17	2.8	2.8	1.1	1.8	2.6	3.3
12-14	2.8	4.7	1.1	1.8	2.6	3.3
20-23	2.8	6.1	2.1	2.4	2.7	3.0
9-11	2.8	7.1	2.5	3.4	5.0	7.8
24-26	2.9	11.6	2.2	3.0	3.7	4.3

these are plotted in figure 36 for the various values of f(V) with yield against p_{H_2} for p_{CO_2} = 2.8 atmos., and it is seen that the yield increases with the increase in partial pressure of hydrogen from 0 to 2.8 atmos., then remains constant till $p_{H_2} = 4.7$, then again rises with increase in partial pressure of H_2 up to $p_{H_2} = 7.1$ beyond which it begins to fall. This suggests that as the partial pressure of H_2 is increased slowly from 0 to 2.8 atmos., more adsorbed H_2 is present on the surface for reaction and naturally the yield increases. When the partial pressure of H_2 is further increased up to 4.7 atmos., more of H_2 is adsorbed no doubt, but perhaps on odd active centres of the catalyst surface, so/

so that the number of suitably oriented adsorbed CO_2 and H_2 is not increased by any means, so the yield remains the same in spite of the increase in H_2 content. Further addition of hydrogen, however, seem to increase the yield. Beyond a value of p_{H_2} = about 7.1 atmos. the yield starts to fall because the hydrogen may displace the adsorbed CO_2 to such an extent that enough CO_2 may not be available on the surface to react with the adsorbed hydrogen.

Experiment 18 was performed with the same synthesis mixture as of experiments 15 to 17, but at the higher reaction pressure of 10 atmospheres so as to give $p_{H_2} = 5$ and $p_{CO_2} =$ 5 atmos. The yield was found to be raised by a considerable amount with the increase of pressure and if plotted in figure 35, the point falls far above the line for experiments 15 to 17. This shows that the influence of pressure is marked and so the comparison of results becomes very difficult as the reaction pressure (see tables 2 and 3) are different in each sets of experiments. This point is further illustrated from figure 35, in that the experiments 12 to 14 (reaction pressure = 7.57 atmos.) fall on the same straight line as that of experiments 15 to 17 (reaction pressure = 5.6 atmos.) but in each case with different values of p_{H_2} - in the first set of experiments p_{H_2} = 4.7 atmos., and in the second p_{H_2} = 2.8 atmos. Therefore, it is important to take/

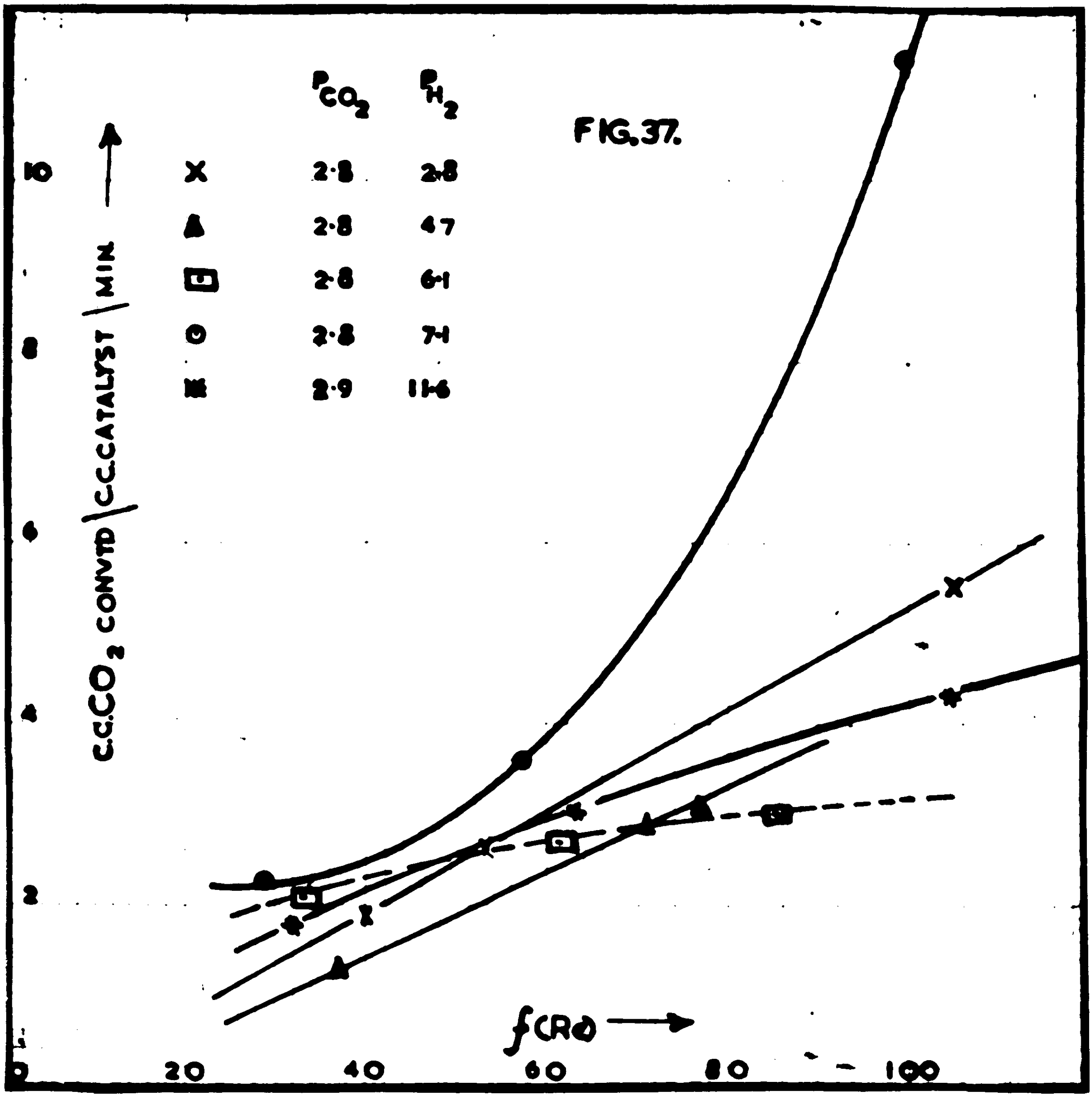


FIG.37.

P_{CO_2}
P_{H_2}
× 2·8 2·8
▲ 2·8 4·7
⊡ 2·8 6·1
⊙ 2·8 7·1
✱ 2·9 11·6
C.C.CO_2 CONVTD / C.C.CATALYST / MIN. →
10
8
6
4
2
0
20
40
60
80
100
f(R) →

take into consideration the effect of pressure on the physical properties of the gas mixture. Unfortunately, insufficient data is available on the viscosities and heat transfer properties of gases under pressure. However, the effect of pressure on the density of a gas is simple and is made use of in calculating a function of Reynold's number $f(Re) = \frac{V\rho^*}{\mu}$ where ρ^* = the density of synthesis mixture at reaction pressure, V = velocity of gas under that pressure; and μ = viscosity of the gaseous mixture and is assumed to be independent of pressure.

The yield is replotted against calculated values of f(Re) in figure 37. Here the experiments 12 to 14 and experiments 15-17 are separated and fall on different lines. Also, the yield of experiment 18, carried out at 10 atmos. reaction pressure, falls on the same line for $p_{CO_2} = 2.8$ and $p_{H_2} = 2.8$ atmos. (expts. 15 to 17). Thus, it seems that the effect of pressure is taken into account to some extent by the use of f(Re). To understand figure 37 better, table 5 is drawn up:

TABLE/

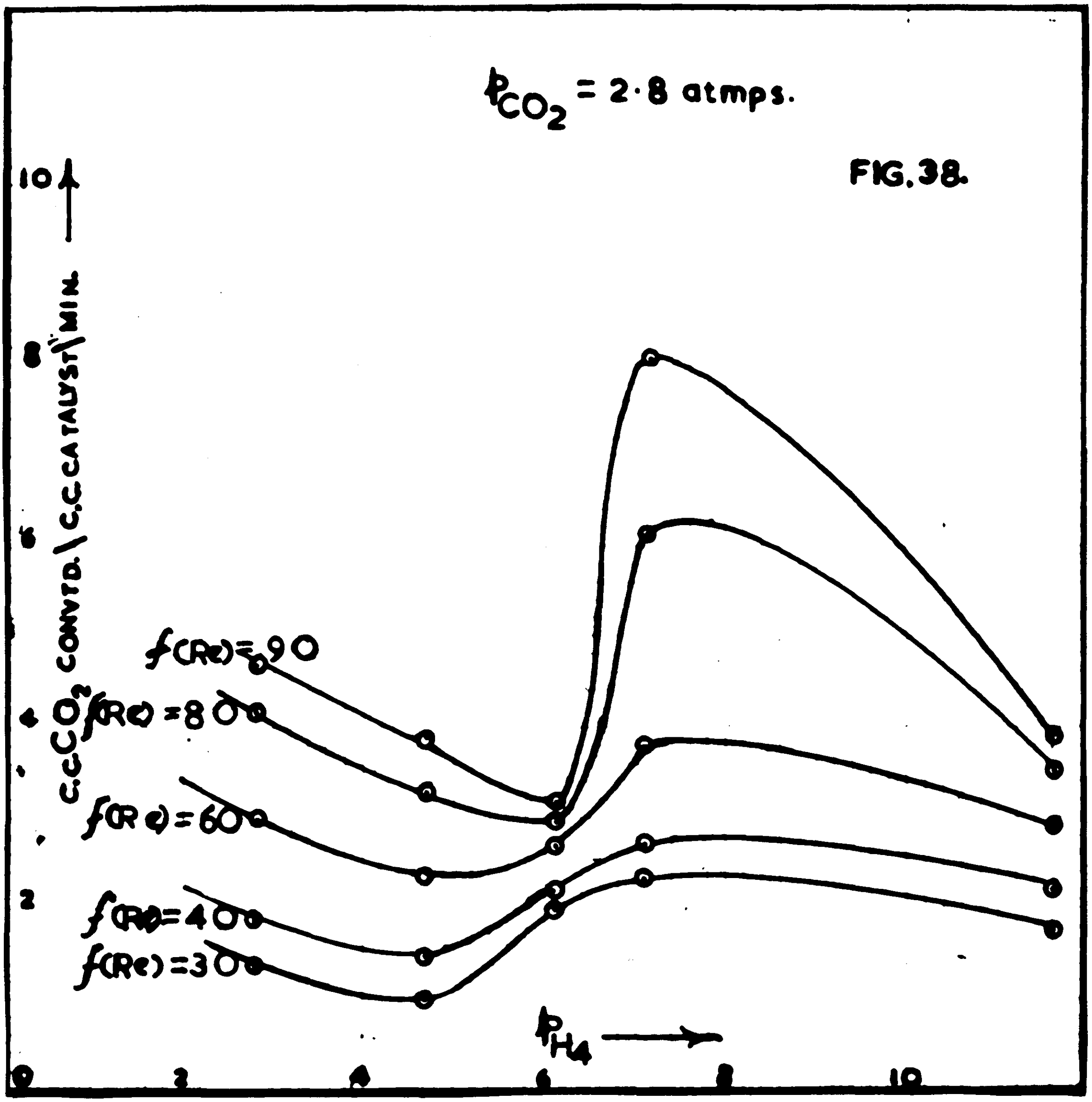


FIG. 38.

READ p_{H_2} FOR p_{H4}

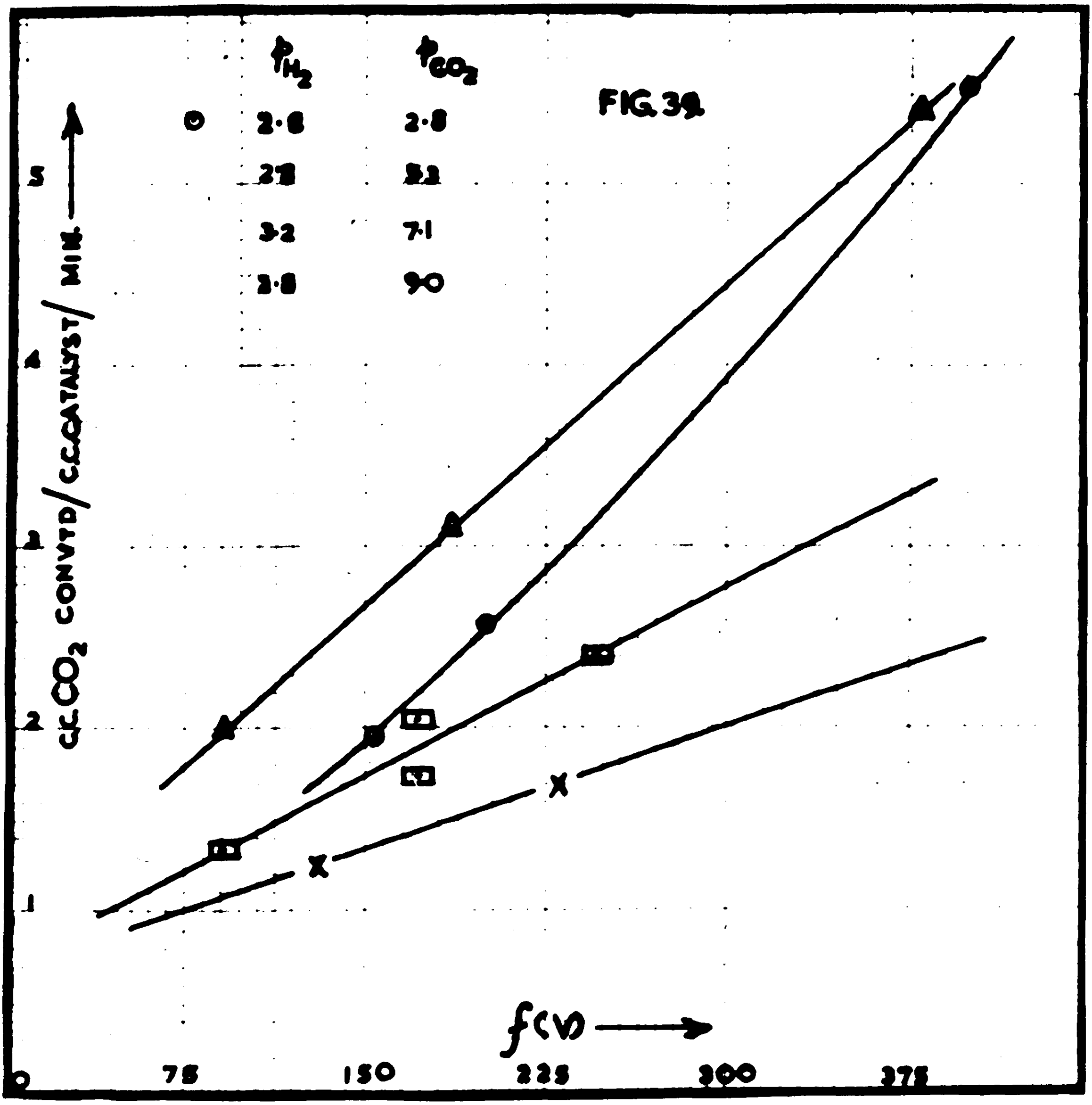


FIG. 39

p_{H_2}
p_{CO_2}
○ 2·8 2·8
2·8 5·2
3·2 7·1
2·8 9·0
C.C. CO_2 CONVTD/C.C. CATALYST/MIN. →
1
2
3
4
5
$f(V)$ →
0
75
150
225
300
375

TABLE 5.

Expt. Nos.	p_{CO_2} atm.	p_{H_2} atm.	Yield at values of f(Re) =				
			30	40	60	80	90
15-17	2.8	2.8	1.4	1.9	3.0	4.2	4.7
12-14	2.8	4.7	1.0	1.45	2.4	3.3	3.9
20-23	2.8	6.1	2.0	2.2	2.7	3.0	3.1
9-11	2.8	7.1	2.3	2.7	3.8	6.1	8.1
24-26	2.8	11.6	1.8	2.2	2.9	3.6	3.9

taking the yields for the different partial pressures of H_2 from figure 37, for various values of f(Re). These results are plotted with yield against p_{H_2} for the different values of f(Re) in figure 38. The form of curves suggests that the yield fluctuates with pressure of hydrogen in an irregular manner, but for all pressures is a definite function of Re. The fall and rise in the shape of the curves before the final falling off in yield makes it difficult to explain and perhaps might have been clearer if the effect of pressure on all the properties of the gases were taken into account. Thus, for example, in f(Re) the effect/

TABLE 6A.

Catalyst ---- Ni-ThO_2

Cat. vol. --- 20 c.cs.

Expt. No.	Temp. °C.	f(V)	Synth. Gas %		Product Gas %					Yield.
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
28.	285	90	65.7	34.2	77.6	0.3	0.2	7.1	15.8	2.0
29.	290	186	65.2	33.8	72.3	0.3	0.8	4.95	20.6	3.12
30.	290	376	64.6	34.3	70.4	0.3	0.9	4.15	23.5	5.4
31.	285	165	64.8	34.0	69.0	0.6	0.2	2.8	26.6	2.11
32.	290	88	68.2	30.8	73.6	0.5	0.2	3.36	21.4	1.34
33.	290	164	68.5	31.0	72.5	0.4	0.2	2.68	23.4	2.06
34.	290	168	68.4	30.3	72.0	0.5	0.2	2.18	24.3	1.74
35.	290	244	68.5	30.8	72.3	0.5	0.3	2.10	24.8	2.4
36.	290	127	76.7	23.2	79.8	0.1	0.3	1.7	18.0	1.21
37.	285	230	76.7	23.1	79.1	0.3	0.2	1.32	19.1	1.70

TABLE 6.

Catalyst---- Ni-ThO_2-- IB.
Cat. vol. ---- 20 c.cs.

Expt. No.	Temp. °C.	Time. Mins.	Product gas @ 1 atm. Litres.	Equivt Synth. Gas @ 1 atm; Litres.	f(V)	Reaction Press. Atm.	Synth. gas Partial Press.		Yield	f(Re)
							CO_2 Atm.	H_2 Atm.		
28.	285	23	13	16.8	90.0	8.1	5.32	2.77	2.0	44
29.	290	21	26.4	31.6	186.0	8.1	5.28	2.74	3.12	91
30.	290	19	49.7	58.1	376.0	8.1	5.23	2.78	5.4	184
31.	285	15	22.6	25.2	165.0	10.3	6.68	3.5	2.11	102
32.	290	22	17.57	19.85	88.0	10.3	7.05	3.2	1.34	56
33.	290	14	21.5	23.8	164.0	10.3	7.05	3.2	2.06	104
34.	290	20	31.92	34.7	168.0	10.3	7.05	3.1	1.74	107
35.	290	15	34.5	37.5	244.0	10.3	7.05	3.1	2.40	155
36.	290	15	21.36	22.8	127.0	12.0	9.0	2.8	1.21	100
37.	285	15	36.68	40.72	230.0	12.0	9.0	2.8	1.70	181

effect of pressure on viscosity if taken into account might have simplified to some extent the shape of the curves.

There is an annular space in the reaction chamber between the copper tube containing the catalyst bed and the outer steel tube of the reaction chamber. This space is free and as such could offer no resistance to gas flow compared to the packed copper tube. It was thought that there is a possibility of some gas passing through this space without actually coming into contact with the catalyst. Therefore, an artificial resistance was introduced by winding asbestos rope round the outside of the copper tube at the bottom and top. Experiment 19 (Table 2) and experiment 27 (Table 3) were carried out to test the difference in the yield. When the results were plotted on figures 35 and 37 no appreciable difference was noted. Hence, there is no necessity to correct the previous results.

II. PARTIAL PRESSURE OF CO_2 VARYING.

After studying the effect of keeping p_{CO_2} at 2.8 atmos. and varying p_{H_2} from 2.8 to 11.6 atmos., it was decided to study the effect of varying p_{CO_2} keeping p_{H_2} at about 2.8 atmos. The results of these experiments, 28 to 37, are tabulated in tables 6 and 6a.

The/

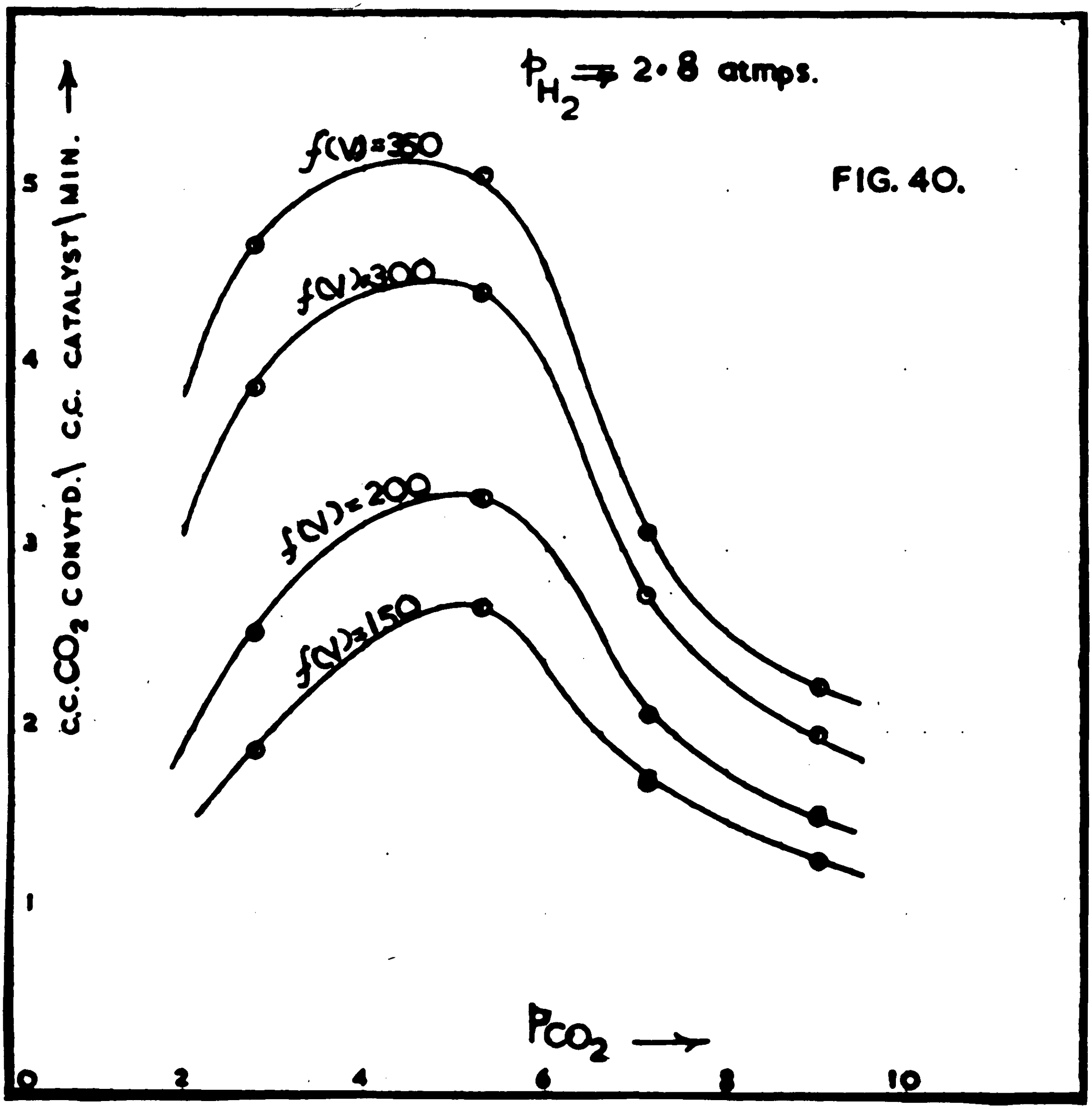


FIG. 40.

$p_{H_2} = 2\cdot8$ atmps.
f(V)=350
f(V)=300
f(V)=200
f(V)=150
C.C. CO₂ CONVTD.\ C.C. CATALYST \ MIN.
1
2
3
4
5
P_{CO_2} →
0
2
4
6
8
10

The experimental results are plotted in figure 39, with yield against f(V). The line for p_{H_2} = 2.8, p_{CO_2} = 2.8 lies across between the lines for p_{H_2} = 2.8, p_{CO_2} = 5.3 and for p_{H_2} = 3.2, p_{CO_2} = 7.1. To understand figure 39 fully, the yield for various values of f(V) is taken from the figure and tabulated in Table 7.

TABLE 7.

Expt. Nos.	p_{H_2} atms.	p_{CO_2} atms.	Yield for values of f(V) =			
			150	200	300	350
15-17	2.8	2.8	1.9	2.55	3.9	4.7
28-30	2.8	5.3	2.7	3.28	4.45	5.06
32-35	3.2	7.1	1.75	2.08	2.75	3.1
36-37	2.8	9.0	1.3	1.55	2.0	2.25

These results are plotted in figure 40, with yield against p_{CO_2} for the various values of f(V).

From figure 40, it is seen that the yield increases at first when the partial pressure of CO_2 is raised from 0 to 5.3 and then the yield falls off with further increase in the partial pressure of CO_2. The simple explanation for this is, that as the CO_2 partial pressure is increased from 0 to 5.3 atmos. the adsorption of CO_2 by the catalyst surface/

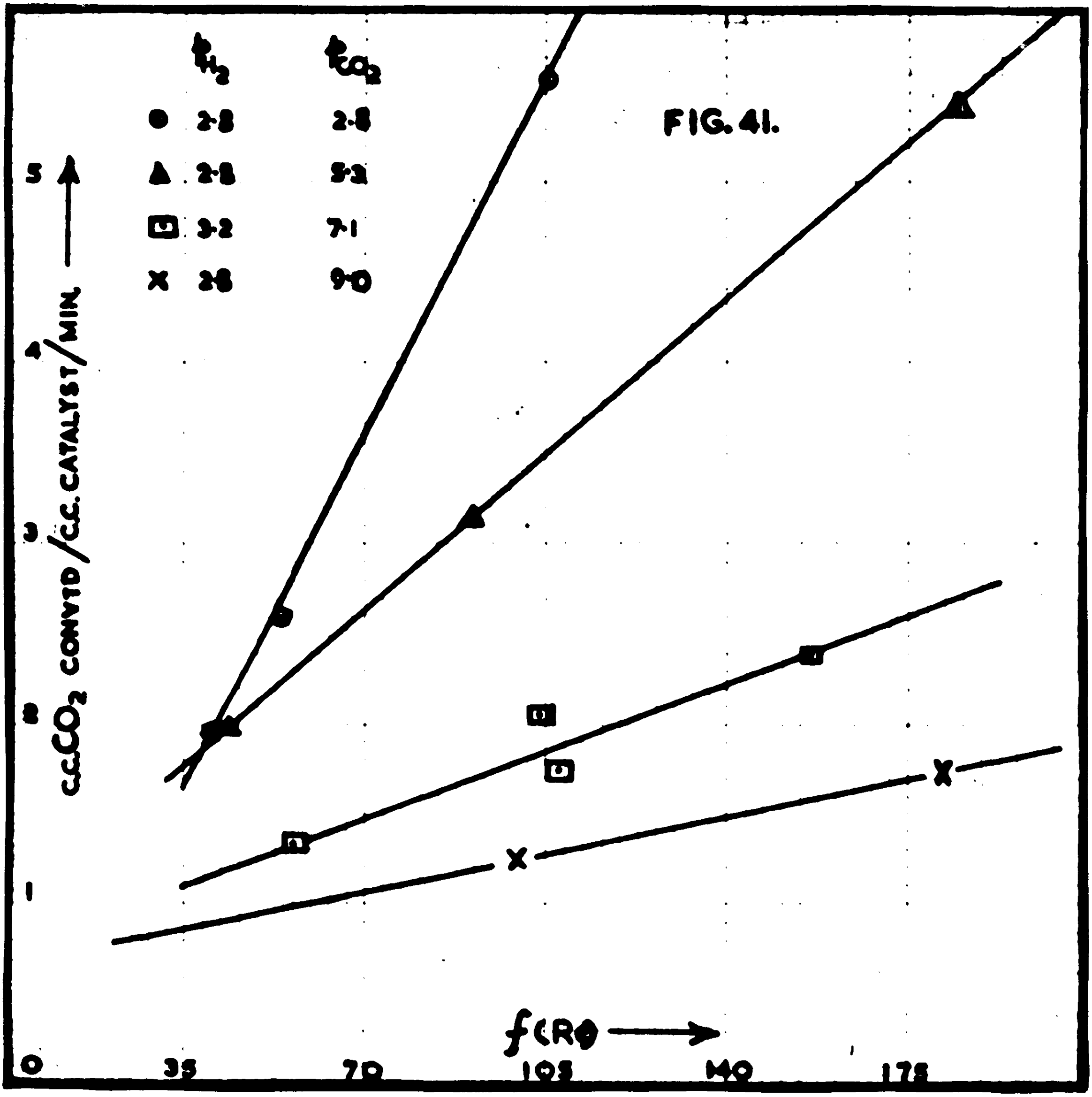

p_{H_2} p_{CO_2}
● 2·8 2·8
▲ 2·8 5·2
⊡ 3·2 7·1
× 2·8 9·0
c.c. CO₂ CONVTD/C.C. CATALYST/MIN.
f(Rθ)
0
35
70
105
140
175
1
2
3
4
5

FIG. 41.

surface progressively increases so that enough CO_2 and H_2 are present on the surface for interaction and thus the yield increases. But as the partial pressure of CO_2 is increased further, the CO_2 molecule displaces more adsorbed H_2 from the surface so that enough H_2 is not present for the reaction of all the adsorbed CO_2 molecules. This lowers the yield.

To take into consideration the effect of pressure, figure 41, is drawn in which yield is plotted against f(Re). Here, it is of interest to note that the line for $p_{H_2} = 2.8$, $p_{CO_2} = 2.8$, has been shifted and occupies the topmost place. To picture the figure better the values of yield corresponding to the different values of p_{CO_2} are taken at values of f(Re) = 50, 60, 80 and 90, and tabulated in Table 8.

TABLE 8.

Expt. Nos.	p_{H_2} atms.	p_{CO_2} atms.	Yield for Values of f(Re) =			
			50	60	80	90
15-17	2.8	2.8	2.45	2.92	4.0	4.6
28-30	2.8	5.3	2.15	2.38	2.85	3.1
32-35	2.8	7.1	1.28	1.38	1.6	1.7
36-37	2.8	9.0	0.95	1.02	1.12	1.18

The/

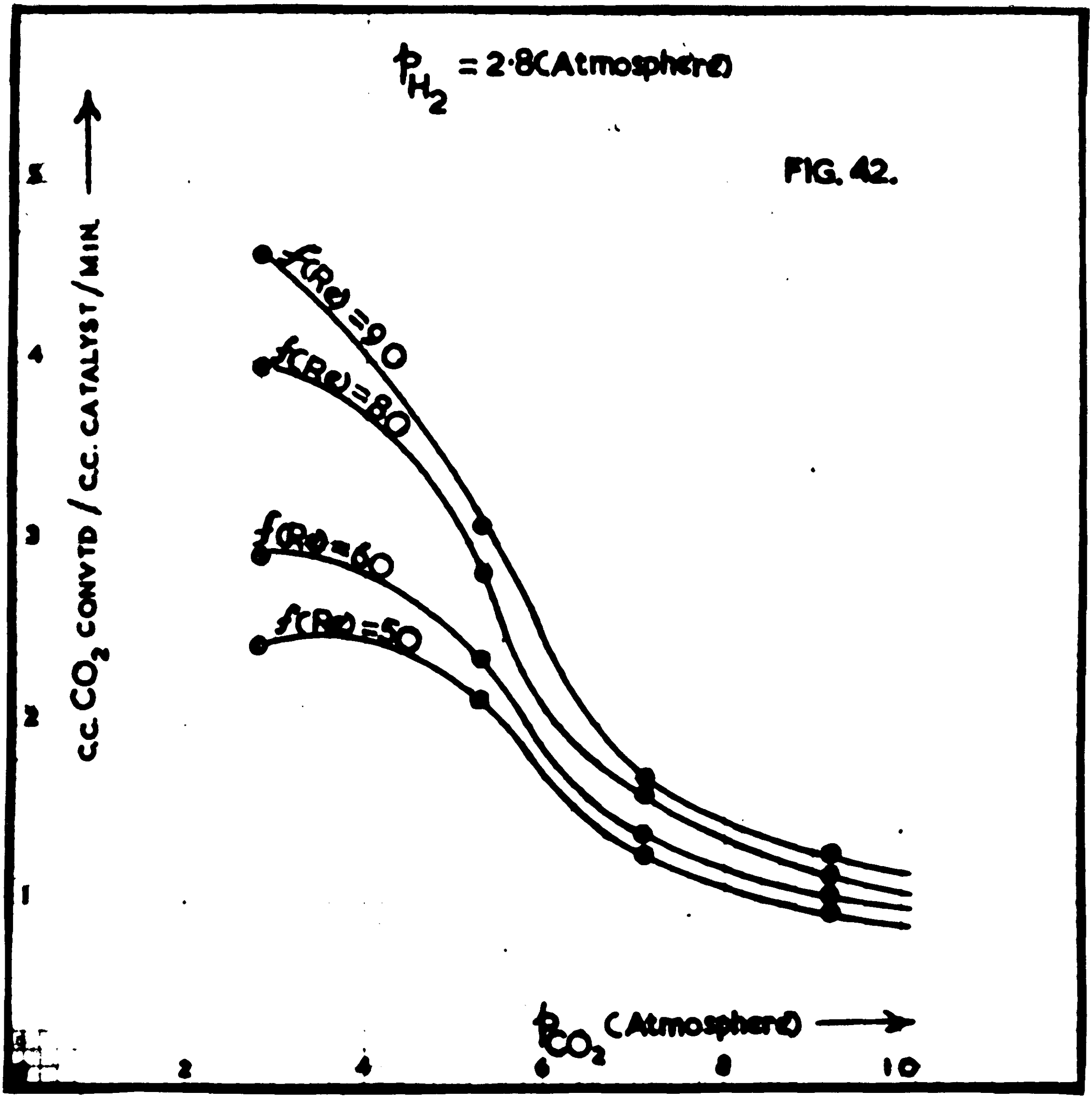


FIG. 42.

p_{H_2} = 2·8 (Atmosphere)
C.C. CO$_2$ CONVTD / C.C. CATALYST / MIN.
5
4
3
2
1
f(Re) = 90
f(Re) = 80
f(Re) = 60
f(Re) = 50
p_{CO_2} (Atmosphere)
2
4
6
8
10

The values are plotted in figure 42 with yield against p_{CO_2} for various values of f(Re). The curves show that at first the yield may increase rapidly as the partial pressure of CO_2 is pushed up from 0 to 2.8 atmos. Further increase in value of p_{CO_2} makes the yield fall rapidly at first and then slowly. At $p_{CO_2} = 9$ atmos. the difference in yield for various values of f(Re) seems to be very small. In other words the yield seems to be practically independent of rate of flow of gas at high values of p_{CO_2}.

According to the kinetics of gas reactions, if the two gases are adsorbed on the surface of a catalyst, the rate equation is of the form:-

$$r = K \frac{p_{CO_2} \times b_{CO_2}}{1+p_{CO_2} b_{CO_2}+p_{H_2} b_{H_2}} \times \frac{p_{H_2} \times b_{H_2}}{1+p_{CO_2} b_{CO_2}+p_{H_2} b_{H_2}}$$

An analysis of the equation keeping either p_{CO_2} or p_{H_2} constant suggests that the shape of the curves should somewhat be similar to that of the curves of figures 40 and 42 - that is to say, a rapid rise followed by a somewhat gradual fall. The shape of the curves in figure 36 (page 195) for p_{CO_2} constant and varying p_{H_2} is of a similar shape for f(V) - 100, 150 and 200. In figure 38 (page 200) the shape of the curve is more complicated and as pointed out previously/

TABLE 9-A.

Ni catalyst.

Cat. vol. ---- 20 c.cs.

Expt. No.	Temp. °C.	f(V)	Synth. Gas % CO_2	H_2	Product Gas % CO_2	O_2	CO	CH_4	H_2	Yield
38.	285	144	48.7	49.2	55.0	0.6	0.5	7.1	34.8	2.22
39.	285	248	49.0	49.2	51.3	0.4	0.4	2.8	43.6	1.77
40.	285	384	47.7	49.0	50.5	0.7	0.5	3,66	41.5	3.43
41.	285	113	48.7	49.2	50.8	0.5	0.5	2.70	43.7	1.37
42.	285	155	48.2	49.3	51.2	0.2	0.2	3.50	42.4	2.35
43.	285	179	48.2	49.3	50.2	0.5	0.4	2.60	44.1	2.10
44.	290	135	35.8	62.4	37.0	0.8	0.2	3.30	57.4	1.46
45.	285	190	35.2	64.8	36.5	0.7	0.4	3.70	59.7	2.40
46.	285	337	35.2	63.1	35.8	0.8	0.2	1.80	60.5	2.20
47.	285	115	28.7	69.5	28.9	0.7	0.2	2.86	65.9	1.48
48.	285	254	30.1	68.5	30.4	0.8	0.1	2.00	65.9	2.36
49.	285	759	31.1	67.7	31.0	0.1	0.5	1.37	65.9	4.92
50.	290	346	29.6	69.0	29.6	0.4	0.5	2.70	65.5	2.30

TABLE 9.

Ni catalyst.

Cat. vol. ---- 20 c.cs.

Expt. No.	Temp. ^{o}C.	Time. Mins.	Product Gas. Litres.	Equivlt. Synth. Gas. Litres.	f(V)	Reaction Press. atm.	Synth. Gas Partial Press.		Yield
							CO_2 atm.	H_2 atm.	
38.		28	17.6	22.5	144	5.6	2.8	2.8	2.22
39.	285	18	22.6	25.1	248	5.6	2.8	2.8	1.77
40.	285	30	56.4	64.4	384	5.6	2.8	2.8	3.43
41.	285	30	30.6	33.8	113	10.0	5.0	5.0	1.37
42.	285	28	38.3	43.5	155	10.0	5.0	5.0	2.35
43.	285	15	24.4	26.8	179	10.0	5.0	5.0	2.10
44.	290	20	17.8	20.1	135	7.62	2.7	4.8	1.46
45.	285	15	18.9	21.8	190	7.62	2.7	4.9	2.40
46.	285	12	28.8	30.9	337	7.62	2.7	4.8	2.20
47.	285	15	15.5	17.3	115	10.0	2.9	7.0	1.48
48.	285	15	35.3	38.2	254	10.0	3.0	6.9	2.36
49.	285	9	64.7	68.3	759	10.0	3.1	6.8	4.92
50.	290	15	26.2	28.5	346	5.6	1.7	3.9	2.30

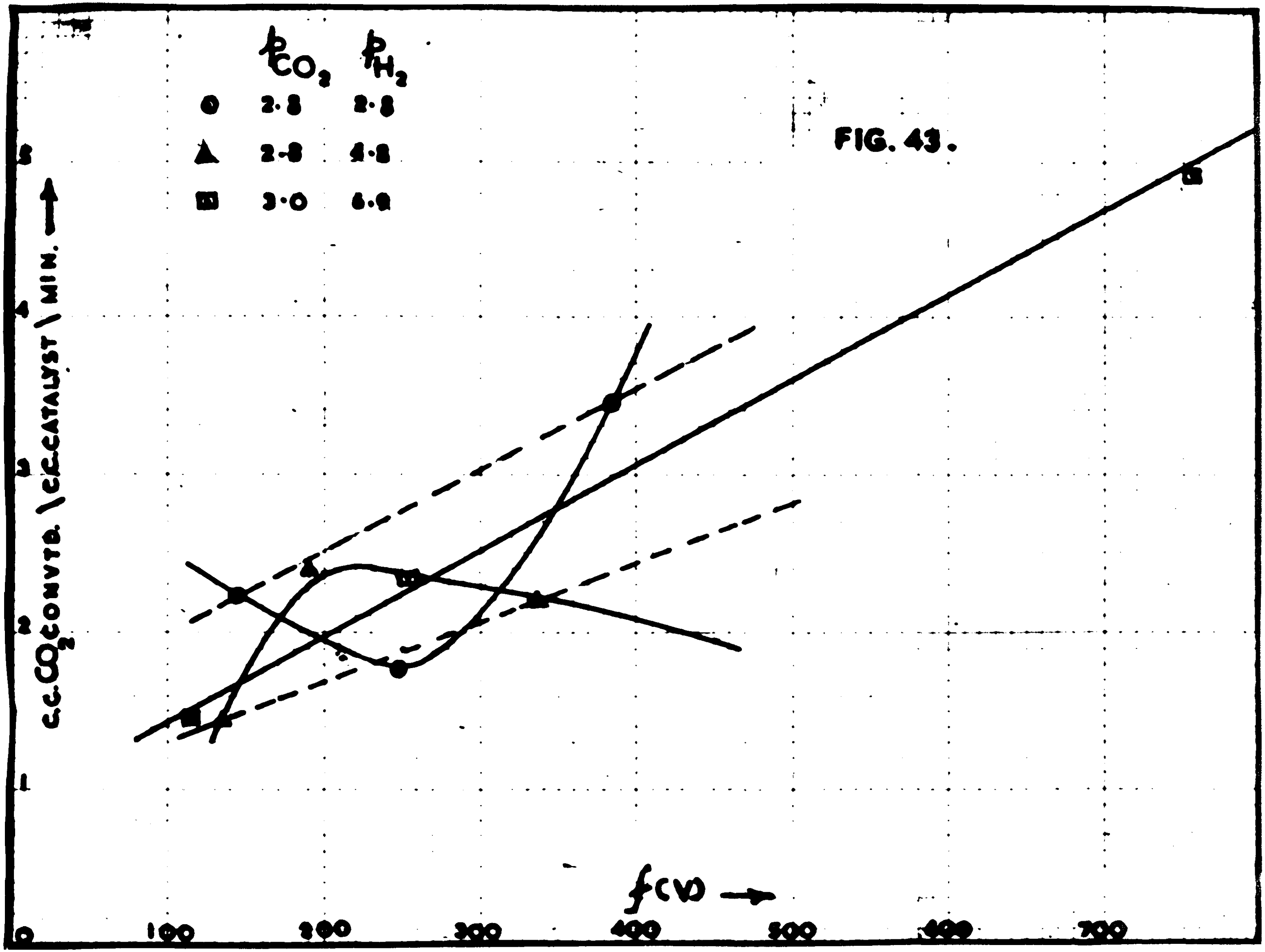

p_{CO_2} p_{H_2}
● 2·8 2·8
▲ 2·8 4·8
▣ 3·0 6·8
C.C. CO_2 CONVTD. \ C.C. CATALYST \ MIN. →
f(V) →
0
100
200
300
400
500
600
700
1
2
3
4
5

FIG. 43.

previously, the results of the experiments where p_{H_2} = 4.7 atmos. and p_{H_2} = 6.1 atmos. are difficult to explain. If these points were not there, the shape of the curve would have been of the form shown by the dotted line in the figure. So, it is thus reasonable to assume that the trend of results show that both gases CO_2 and H_2 are adsorbed on the catalyst surface and it is a necessary condition for the interaction of these gases in presence of Ni-Thoria catalyst.

Experiments were then carried out in presence of the Ni catalyst and the results are tabulated in tables 9 and 9a. The results are not sufficient to draw any definite conclusions, but the general trend is as shown in figure 43. The line for p_{CO_2} = 3.0 atmos., p_{H_2} = 6.9 atmos., is in order. The results of p_{CO_2} = 2.8 atmos., p_{H_2} = 4.8 atmos., and p_{CO_2} = 2.8., p_{H_2} = 2.8 atmos., seem to be erroneous. Unfortunately, there was not enough time to repeat these runs and check the results.

Two runs, one at atmospheric pressure and the other at elevated pressure, were carried out with Fischer Tropsch catalyst (CO, ThO_2, MgO, Kieselguhr in the proportion 100:6:12:200) to see whether any higher hydrocarbons other than methane would be produced. At atmospheric pressure a continuous run of 45½ hrs. was carried out. Total synthesis gas/

gas passed was 84 litres. Gases were sampled at 6 hrs., 20 hrs., 30 hrs., and 45 hrs., after starting the experiment. The analysis figures of these samples are:-

	6 Hrs.	20 Hrs.	30 Hrs.	45 Hrs.
CO_2	33.15	34.2	33.7	36.6
O_2	0.41	0.4	0.2	0.7
CO	0.41	0.2	0.0	0.3
CH_4	2.82	4.3	2.66	9.8
H_2	62.4	60.2	62.5	51.55
Total	99.2	99.3	99.06	99.02

The above analysis show that no higher hydrocarbon has been formed. The experiment carried out at elevated pressure also did not produce any higher hydrocarbon.

FINAL CONCLUSION.

The interaction between carbon dioxide and hydrogen in presence of nickel and nickel thoria catalysts was studied under atmospheric pressure and elevated pressures of the order of 150 lbs. per sq.inch. Throughout the course of this investigation, carbon monoxide was detected to the extent of 0.1 to 0.6 percent. Medsforth (47) explained the presence of carbon monoxide by assuming that an intermediate compound of the methyl alcohol type is formed which on dehydration gives methylene radical which is immediately hydrogenated to methane, but that some of the methyl alcohol may be dehydrogenated to give carbon monoxide and hydrogen. In any flow system, the yield (c.cs.CO_2 converted/c.c.catalyst/minute) increases with rate up to a maximum and then begins to fall and accordingly the experimental results when plotted yield against rate gave straight lines. So it was thought that diffusion of either reactants or products through a stagnant gaseous film existing at the surface of the catalyst could be a rate controlling step in the reaction. However, plotting the results on a log log graph showed that this is not the case (page 76).

In order to understand the results better, the Reynolds Number was introduced. This has simplified the shape of some graphs, but not all. An attempt to get a correlation between/

between function of velocity and function of Reynolds Number was difficult (page 87-8).

The results of experiments carried out with nickel thoria catalyst varying the partial pressure of both the gases are plotted against $p_{CO_2}/p^4_{H_2}$ and $p^4_{H_2}/p_{CO_2}$ in figures 8 and 9. An interpretation of the figures, according to the kinetics of heterogeneous reactions, show that both the gases are adsorbed and of the two gases carbon dioxide and hydrogen, the former is adsorbed more strongly than the latter (page 82-3). W.W. Russell and H.S. Taylor (41) working on nickel and nickel thoria catalysts showed that the catalysts adsorb carbon dioxide and hydrogen. The general trend of experimental results keeping the partial pressure of one component constant and varying that of the other suggests that both gases are adsorbed on the catalyst surface and reaction takes place by the interaction of the adsorbed molecules of the gases. W. Aker and R.R. White(96) working on the interaction of carbon monoxide and hydrogen in presence of nickel catalyst to form methane showed that the rate controlling step is the reaction between adsorbed molecules of carbon monoxide and hydrogen.

It was found that the catalytic activity was falling steadily as the number of experiments carried out on the same batch of catalyst increased. This falling off in catalytic activity/

activity might be due to impurities in gases passed, impurities in the asbestos support and carbon deposition on the catalyst. The first two sources were eliminated by taking proper precautions and so the poisoning is probably due to the carbon deposition (page 69 & 73). Another point revealed during this investigation is that small amounts of catalyst gave a better yield than that given by large amounts.

The results of experiments carried out to study the reaction in presence of nickel catalyst at atmospheric pressure, keeping the partial pressure of hydrogen constant and varying that of carbon dioxide suggest the same, namely that both the gases are adsorbed on the catalyst and reaction takes place between the adsorbed molecules of the gases. However, the behaviour of the mixture of $p_{H_2} = 0.49$, $p_{CO_2} = 0.24$ is peculiar in that its yield is below that of $p_{H_2} - 0.49$, $p_{CO_2} = 0.12$ (page 111). The results of experiments keeping partial pressure of carbon dioxide constant and varying that of hydrogen when plotted give figures that are easier to understand than those given by the previous set of experiments varying the partial pressure of carbon dioxide. The yield seems to rise continuously as the partial pressure of hydrogen is increased from 0 to 0.49 (figures 18 and 20). That is to say, the hydrogen progressively displaces adsorbed molecules of carbon dioxide from the catalytic surface so that/

that more adsorbed hydrogen is available on the surface to react with adsorbed molecules of carbon dioxide, and naturally the rate of reaction increases because it is proportional to the concentration of adjacently adsorbed groups of reactants.

In section B, part II, an attempt is made to interpret the experimental results by mathematical analysis. The actual chemical transformation is often proceeded by many successive stages and since chemical rates vary over wide ranges it is not very possible that the rates of any two steps will be of equal order in any given system. Hence, the slowest single step is considered and it is assumed that equilibrium is maintained in all other steps. Under these conditions the slowest activated step may be termed the "rate-controlling step". Accordingly, seventeen different mechanisms were postulated and were analysed mathematically using the experimental results. It was seen that only one mechanism was generally acceptable, namely the surface reaction between molecularly adsorbed carbon dioxide and atomically adsorbed hydrogen to be the rate controlling step. The possibility of surface reaction between molecularly adsorbed carbon dioxide and molecularly adsorbed hydrogen to be a rate controlling step is also present (page 150-153). However, if both the steps do occur side by side, the former mechanism might be the predominant of the two. A final equation/

equation has been suggested (page 154) for the hydrogenation of carbon dioxide and is:-

$$r = \frac{SkLK_{CO_2}\sqrt{K_{H_2}}\left(\sqrt{K^3_{H_2}}\,p^2_{H_2}\,p_{CO_2} - \frac{p_{CH_4}\,p_{H_2O}}{K}\right)}{2(1+K_{CO_2}p_{CO_2}+\sqrt{K_{H_2}p_{H_2}} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O})^5}$$

where SL = E = effectiveness factor.

k = forward reaction velocity constant.

K = overall equilibrium constant of the reaction.

K_{CO_2}, K_{H_2}, etc. = adsorption equilibrium constants for CO_2, H_2, etc.

p_{CO_2}, p_{H_2}, etc. = partial pressure of CO_2, H_2, etc.

S.R. Craxford (60) studied the hydrogenation of carbon monoxide using Fischer-Tropsch catalyst. He showed, by observing the ortho-para hydrogen conversion, the intermediate formation of atomic hydrogen in those cases where the reaction took place with the formation of methane and that if higher hydrocarbons are formed little atomic hydrogen is noticed.

The reaction was then studied under elevated pressures. The results showed that the effect of pressure on the physical characteristics like the density, viscosity, etc., of the gaseous mixture should not be overlooked. For example, experiments carried out on the same gaseous mixture of composition 50% CO_2, 50% H_2, but at two different reaction pressures of 5.6 atmospheres and 10 atmospheres gave different yields/

yields, the yield increasing with the reaction pressure. The effect of pressure on density was taken into account by making use of Reynolds Number and when the results were replotted it was found that the points belonging to the same synthesis mixture fell on the same straight line irrespective of the reaction pressure. So for comparison of results the effect of pressure on the density of gaseous mixtures was taken into account (page 199).

Activated Silica gel was employed to dry the reaction products and the used Silica gel always had a sweet smell suggesting that some sort of ester might have been formed as an intermediate during the reaction. Unfortunately the condensate from distilling the used Silica gel was extremely dilute and of insufficient quantity to attempt an analysis of the supposed ester. The trend of experimental results suggests the same mechanism as under atmospheric pressure reactions, namely that it is surface reaction between adsorbed carbon dioxide and adsorbed hydrogen.

Finally, according to the kinetics of gas reactions in presence of solid catalysts, if the two gases are adsorbed on the catalyst surface, the general rate equation is of the form:-

$$r = K \frac{p_{CO_2}\, b_{CO_2}}{1+p_{CO_2}b_{CO_2}+p_{H_2}b_{H_2}} \times \frac{p_{H_2}\, b_{H_2}}{1+p_{CO_2}b_{CO_2}+p_{H_2}b_{H_2}}$$

and/

and an analysis of the above equation keeping either p_{CO_2} or p_{H_2} constant suggests that the shape of the curves should somewhat be similar to that of most of the curves obtained throughout - that is to say a rapid rise followed by a somewhat gradual fall.

In summarising, it could be said that the interaction of carbon dioxide and hydrogen in presence of nickel catalysts takes place through the surface reaction between molecularly adsorbed carbon dioxide and molecularly or atomically adsorbed hydrogen. The diffusion of neither the reactants nor the products through a gaseous film surrounding the catalyst is a rate controlling step.

ABBREVIATIONS

used in bibliography to original papers.

ABBREVIATED TITLE.	JOURNAL.
Abh. Kenntnis Kohle	Gesammelte Abhandlungen zür Kenntnis der Kohle.
Ann. Chim. Phys.	Annales de chimie et de physique.
Ber.	Berichte der deutschen Chemischen Gesellschaft.
Brenn. Chemie.	Brennstoff-Chemie.
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique.
Chem. Eng. Prog.	Chemical Engineering Progress.
Compt. Rend.	Comptes rendus hebdomadaires des Séances de l'Académic des Sciences.
C.R.Acad.Sci.U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
J.A.C.S.	Journal of the American Chemical Society.
J.C.S.	Journal of the Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J.S.C.I. Japan.	Journal of the Society of Chemical Industry, Japan.
P.R.S.	Proceedings of the Royal Society.
T. Farad. Soc.	Transactions of the Faraday Society.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. phys. Chem.	Zeitschrift für physikalische Chemie.

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