THE MECHANISM OF REACTION BETWEEN HYDROGEN AND OXY COMPOUNDS OF CARBON AT SOLID SURFACES.

by

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3.) Experimental.

ABBREVIATIONS

Bull.Inst.Phys.Chem.Res.Tokyo - Bulletin of the Institute for Physical and Chemical Research, Tokyo.

"Griffith"-Catalysis - "The Mechanism of Contact Catalysis " by Griffith .

"Hinshelwood" - "Kinetics of Chemical Change in Gaseous Systems" by Hinshelwood.

Ges.Abh.Kenn.Kohle - Gesammelte Abhandlungen zur Kenntniss der Kohle.

Gazz.Chim.Ital. - Gazzetta Chimica Italie.

J.Am.C.S. - Journal of the American Chemical Society.

J.C.S. - Journal of the Chemical Society.

J.I.E.C. - Journal of Industrial and Engineering Chemistry.

J.Phys.Chem. - Journal of Physical Chemistry.

J.Phys.Chem.U.S.S.R. - Journal of the Physical and Chemical Society of the U.S.S.R..

J.S.C.I. - Journal of the Society of Chemical Industry.

Proc.Roy.Soc. - Proceedings of the Royal Society.

Rept. Gas Engs. - Report of the Proceedings of the Institution of Gas Engineers.

Rev. Phys. Chem. Japan - Physical Chemistry Review of Japan

Trans. Farad.Soc. - Transactions of the Faraday Society.

Ukraine Khem.Zhur.- Ukrainian Chemical Journal.

ABBREVIATIONS. (Cont.)

Z.Elec.Chem. - Zeitschrift für Electrochemie.

Z.Phys.Chem. - Zeitschrift für Physikalische Chemie,etc,.

Sitz. Ber. Preuss. Akad. Wiss. – Sitzungsberichte der Kgl. Preussischen Akademie der Wissenschaft zu Berlin.

GENERAL INTRODUCTION.

The actual mechanism by which chemical change occurs presents one of the most fundamental problems in chemistry. As a typical and simple illustration, the union of hydrogen and oxygen to form water may be considered. It is known that these gases, in the free state, consist normally of diatomic molecules, which may react to form water. At ordinary temperatures the two gases react very slowly indeed, and may be kept together indefinitely without any measurable amount of reaction. At high temperatures reaction is very rapid, while slow formation of water can go on at intermediate temperature ranges. It might be supposed that reaction occurs when two molecules of hydrogen come into contact with one molecule of oxygen and produce a certain energy of impact. There exists, however, a very similar gaseous reaction, that between nitric oxide and oxygen to form nitrogen peroxide; the speed of this reaction is very great in temperature ranges in which the union of hydrogen and oxygen is immeasurably slow. This suggests that the occurrence of normal molecular encounters is by no means the only condition which has to be fulfilled, but that these encounters must be between molecules in an energised or active form. Active molecules may be brought into being by an increase in the total energy of the molecule, or by a re-arrangement of the existing energy. This latter change is brought about most readily by the introduction into the gaseous system of a solid or liquid surface.

It has long been the fashion to class as "Surface Reactions" a very large number of chemical actions which proceed at the interface between two phases. The great majority of catalytically influenced reactions are of this type, and their mechanism remains very obscure, despite the large amount of work which has been done on the problem. It is common practice to write such equations as

$$CO_2 + 4H_2 \xrightarrow{\text{Ni at } 200^\circ C} CH_4 + 2H_2O$$

without any consideration of the actual reaction mechanism involved. Taking the equation above at its face value, it will be seen that a simultaneous reaction between five molecules is suggested. This is unlikely, and it is usual to suppose that the equation above merely represents the end stages of a series of simple bimolecular reactions, in which the carbon dioxide is reduced first to carbon monoxide, then to formaldehyde, and so on. Such step reactions are possible under the conditions of experiment, but no experimental evidence of their occurrence is to be found. If it is desired to produce measurable quantities of such intermediate products as carbon monoxide, then different catalysts and/or conditions must be chosen.

Were the reaction of a type which is taking place in an homogeneous medium, it would be easier to determine the order, and hence suggest the mechanism of the reaction. Where a second phase is present, evidence of the order of reaction will be distorted by several causes, to be discussed later. Other physical constants of reaction, such as the Heat of Activation, may also be affected by the introduction of a surface, and so rendered useless as a guide to reaction mechanism.

There is no doubt that the surface on which a reaction occurs exercises a profound influence over the course of the change. It appears that the active surface prepares the molecule in some specific way for reaction, either by an increase in energy, or by some particular orientation which facilitates specific chemical change. If it were possible to measure this molecular change in some way, a guide to reaction mechanism might be obtained. The measurement of adsorption at an active surface has always seemed to be of particular interest in this connection, but until recently has been restricted to comparatively low temperatures, far removed from actual reaction ranges, and the results have been of little value. With the recognition of the so-called Activated Adsorption occurring at much higher temperatures, the range of these measurements has been considerably widened, and work on these lines will be described in the following pages. Whatever the mechanism by which the molecules are activated by the surface, or the manner in which they are held in its proximity, it is certain that reaction is determined by the nature of the adsorption layer. Conceptions of the nature and thickness of the adsorption layer have been changing, following the work of Langmuir and others. In the present work attempts will be made to correlate experimental results with these various hypotheses.

It appears, then, from this brief review, that information as to the mechanism of a surface reaction may be gained from consideration of the order of the reaction, its physical constants, and the phenomenon of adsorption. It must be remembered that all these factors can vary very widely in heterogeneous systems, and for this reason experimental conditions should be varied as widely as possible. The writer has for some time been interested in the mechanism of reduction of the oxides of carbon, and the work with which this thesis is concerned deals with this reduction, as it occurs at catalytic surfaces.

THEORETICAL DISCUSSION.

When considering the mechanism of any chemical change, it is necessary to classify it, if possible, as a simple or as a composite reaction. Composite reactions are those which may be resolved into simpler steps, representing intermediate stages in the complete reaction. The formation of ether from alcohol by means of sulphuric acid may be taken as an example. The chemical change represented by the equation

$$2\,C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

may be written as the two successive simple reactions

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$
$$C_2H_5HSO_4 + C_2H_5OH \rightarrow (C_2H_5)_2O + H_2SO_4$$

These simple reactions have been shown to make up the first composite reaction.

Those reactions which cannot be resolved into simpler components are simple or elementary reactions. They are generally of a bimolecular order, and are either additions or substitutions. These simple reactions are not so numerous as has been supposed in the past. For instance, the reaction between hydrogen and chlorine, being almost entirely inhibited by intensive drying, is probably not a simple substitution. This conclusion would hold even if the doubts cast upon the mechanism of the inhibition by Bernreuther (Sitz. Ber. Preuss. Akad. Wiss. 1933. VI) are justified. This worker has suggested that traces of volatile drying agents were acting as inhibitors. These could only be attached to certain energised molecules, which must have abnormal properties.

It is probable that all reactions require some definite state of energy in the molecules undergoing change, and that no reaction can occur until a definite energy level is reached. On this basis, it may be argued that no simple reaction can occur, and that even the simplest reaction is of the type

$$A + \lambda \rightarrow A\lambda ; A\lambda + B \rightarrow AB + \lambda ; A + \lambda \rightarrow A\lambda \cdots$$

and so on, certain quanta of energy being handed on in chain fashion. If, in the reaction above, the energised molecule is taken up by an inhibiting molecule, then no reaction will occur. The problem is not simplified by the fact that many reactions can occur in two or more ways. As an example, the union of hydrogen and iodine, or its reverse, the decomposition of hydrogen iodide, can both be simple reactions. Bodenstein (Zeit. Phys. Chem.

1899. 29. 295), as far back as 1899, showed that both were simple bimolecular types under the experimental conditions employed. Later, however, Taylor (J. Phys. Chem. 1924. 28. 984) investigated the course of the reaction over a wider range of conditions, and found abundant proof that interaction could occur on a surface, and in these circumstances did not exhibit the characteristics of a bimolecular reaction.

Consider the ordinary uni-molecular reaction. Let a be the concentration of the reactant at the beginning of the reaction, and let $(a-x)$ be the concentration after a time t.

Then $\frac{dx}{dt} = k(a-x)$ whence $kt = \log \frac{a}{a-x}$.

For a bi-molecular reaction, with equivalent quantities of both reactants initially present

$\frac{dx}{dt} = k(a-x)^2$, whence $kt = \frac{x}{a(a-x)}$.

If the time of half change is T, then for the uni-molecular reaction $T = \frac{1}{k} \log 2$, and for the bi-molecular type $T = \frac{1}{k} \cdot \frac{1}{a}$.

Thus, for the first type, the time of half change is independent of the initial concentration, while for the second type, the time of half change is inversely proportional to this concentration. In general it may be shown that, in a reaction of the order N, the time of half change is inversely proportional to the $N-1$th power of the initial concentration. For example, the thermal decomposition of nitrous oxide is bi-molecular, while that of phosphine follows the uni-molecular law, as will be seen from the following figures (Hinshelwood, p. 42).

Decomposition of Nitrous Oxide.

Initial Pressure. (m.m.)	Half Change Time. (secs.)
296	255
139	470
53	860

Decomposition of Phosphine.

Initial Pressure. (m.m.)	Half Change Time. (secs.)
707	84
79	84
38	83

It will be realised from the above considerations that investigation of the rate of change at any one particular temperature may lead to a correct formulation of the mode of reaction. The velocity of chemical change, however, changes very markedly with temperature. It has been found empirically that the variation of velocity with temperature can be expressed by the equation $\frac{d(\log K)}{dT} = \frac{E}{RT^2}$ or, integrating $\log K = C - \frac{E}{RT}$. If now, for any reaction, the logarithm of the velocity constant, which may be taken as proportional to the time of half change, is plotted against the reciprocal of the temperature of reaction, a straight line should be obtained. The slope of this line gives a measure of the value of E , the Activation Energy, which can be measured in calories per gram molecule if R is given its corresponding value of 1.98 calories.

This equation has been interpreted as indicating an equilibrium between normal and activated molecules. Only the latter can enter into reaction, and the rapid increase in velocity with temperature is due to a shift in this equilibrium. As the velocity constant K is proportional to the number of active molecules, then the equation above will formulate this shift, and E becomes a measure of the heat required to activate a normal molecule. No suggestion need be made that this activation involves tautomeric change in the molecule.

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Figures 1 & 2.

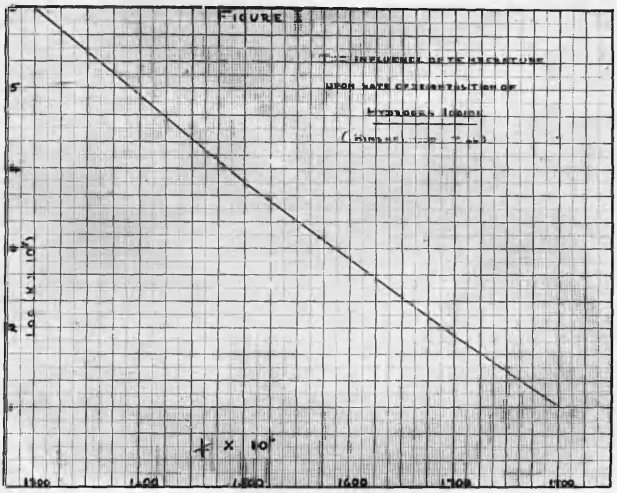

FIGURE 1

THE INFLUENCE OF TEMPERATURE
UPON RATE OF DECOMPOSITION OF
HYDROGEN IODIDE
(HINSHELWOOD, P. [illegible])

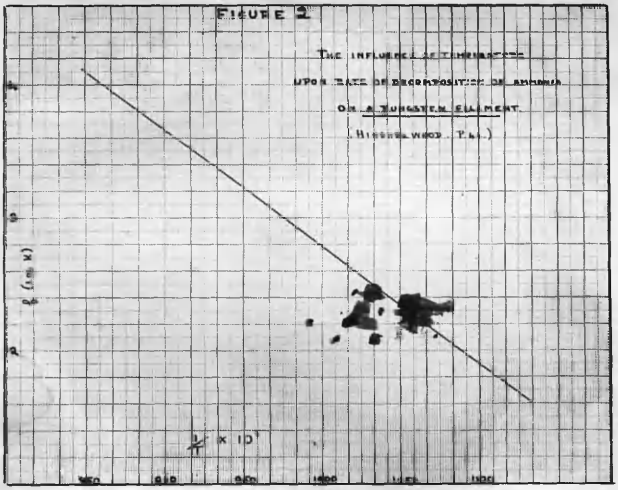

FIGURE 2

THE INFLUENCE OF TEMPERATURE
UPON RATE OF DECOMPOSITION OF AMMONIA
ON A TUNGSTEN FILAMENT.
(HINSHELWOOD, P. [illegible])

It is clear that, the lower the heat of activation, the greater will be the temperature change for units ~~coefficient of~~ increase in velocity.

In the case of a simple reaction, in which E is fixed, a straight line will be obtained by plotting log. K against the reciprocal of the absolute temperature, even though the reaction is occurring on a surface. This is illustrated by Figures 1 and 2. The second case is of particular interest, in that E is a function of the catalytical surface as well as of the reaction between the molecules. Nevertheless, the straight line indicative of a simple reaction is obtained.

If, for any reaction, a markedly broken or curved line is obtained for the graph of the function above, then this indicates that the reaction is a composite one, made up of two or more simple reactions differently influenced by temperature. It should be noted that for any arbitrary temperature range, one or other of these reactions may so [illegible]dominate rate that the slope of the curve will conform to the value of E for the dominant reaction. At a further temperature range, another portion of the composite reaction will dominate in the same way. Figure 3 shows the type of curve

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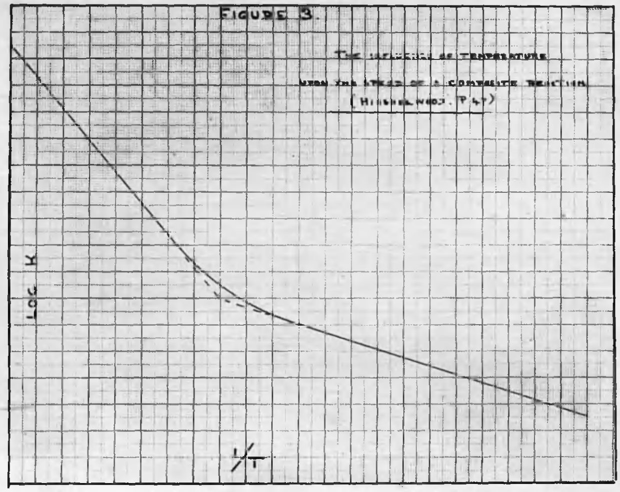
Figure 3.

FIGURE 3.



THE INFLUENCE OF TEMPERATURE UPON THE SPEED OF A COMPOSITE REACTION. (HINSHELWOOD, P.47) which will then be obtained. An interesting example of this delineation between reactions was investigated by Norrish and Rideal (J. Chem. Soc. 1923 123 696). They showed that hydrogen and sulphur could react either in an homogeneous gas phase, or at the interface between gas and liquid sulphur. The two reactions had widely different temperature coefficients, and the curve obtained by plotting log. K against $\frac{1}{T}$ closely resembled Figure 3.

This gives, then, another method whereby a reaction may be investigated and a composite form detected. Instead of graphing, as suggested above, it may be found simpler, in practice, to determine E from the change in K between different temperatures, and to note whether E remains constant over a further range. This is the method which has been employed later in this thesis.

These considerations of the nature of a reaction will hold whether the change takes place at a surface or not, but the surface may substantially modify both reaction order and activating energy. In fact the introduction of an active surface seems primarily to effect a change in the activation energy of a given reaction. This must be due to the way in which the reacting molecule associates itself with the surface. Many years ago it was suggested by Faraday that the films of reactant understood to be adsorbed by surfaces were the seat of chemical change, and that increased concentration in the condensed film brought about increased velocity of reaction by a simple mass effect. This theory is now felt to be quite inadequate to explain the highly specific action of different surfaces, and mere increase in the number of molecular impacts cannot be the determining factor. As an example of this specific action, even with similar reactants, consider the reduction of carbon monoxide to methane over nickel, and to methyl alcohol over zinc-chromium oxide mixtures.

These specific influences have been attributed to the formation of intermediate compounds or unstable complex associations between the catalytic surface and the reactants. It is now generally supposed that these associations are in the form of molecules held at the surface by ordinary valency forces, probably of a non-polar type. The atoms of the surface remain firmly associated with each other, but form compounds of a definite structure with the reactants. It is quite clear that this association cannot be differentiated from adsorption, but the theory demands an adsorption layer which is limited in thickness, probably to one molecule. Langmuir (J.Am.Chem.Soc. 1918, 40, 1361), who first propounded the unimolecular theory, based his conclusions upon adsorption measurements at very low pressures. Paneth (Zeit. Phys. Chem. 1922, 101, 445) measured a surface accurately by a radioactive method and then adsorbed dyestuffs upon it, his results confirming those of Langmuir. Rupp (Zeit. Electro. Chem. 1929, 35, 586) showed by adsorption spectra that a nickel catalyst adsorbed hydrogen to form a lattice spaced evenly between the nickel atoms of the surface. At the same time, Palmer (Proc. Roy. Soc. 1926,A. 110, 138) and others have published results which are not in accord with this unimolecular layer theory.

It must be recognised that measurement of adsorption is complicated by the following factors:-

(a) Actual solution of the adsorbed material in the solid can occur.

(b) The adsorbing surface may not be homogeneous. In fact, this is always the case, except with perfect crystalline surfaces. It has been suggested by Taylor (Proc. Roy. Soc. 1925 A, 108, 105) and others that catalyst activity is partially due to a marked irregularity of surface, ranging from a perfect crystal face down to the system presented by a single atom attached at one point only. Adsorption at such a surface would vary widely from point to point.

(c) There may be more than one type of adsorption. A distinction can clearly be drawn between vapours condensing on such inert materials as charcoal, and gases being adsorbed on metals. In the first case, the amount of adsorption appears to depend mainly upon the ease with which the vapour may be liquefied. This suggests adsorption of a more purely physical kind than in the second case, and may well be due entirely to the action of capillary condensation, although some selective action may occur. The adsorption of benzene and water vapour on active charcoal illustrates this point. Although both are adsorbed, the benzene is taken up to a much greater degree and will actually displace previously adsorbed water. Silica gel, another industrial adsorbent, gives exactly the reverse action, water displacing benzene. The adsorption of gases of a more permanent nature by active surfaces is highly specific, and no relation to ease of liquefaction can be traced. While this second adsorption is more intimately bound up with catalytic activity than the first, measurement of its extent will be complicated by the first type of adsorption, should such occur. It is also recognised that even the specific adsorption of the second type can occur in more than one way, according to the temperature range at which the phenomenon is observed.

Were these disturbing features to be absent, it would be easier to establish, or to disprove, the theory of the monomolecular layer. Assuming the theory to be correct at a fixed temperature there should be a definite saturation limit to adsorption. If not, then as concentration in the gaseous phase of the adsorbate increases, there will be a steady increase in the amount adsorbed, according to the well known Freundlich Adsorption Isotherm

$$X = a.p^n$$

Figures 4 and 5 show the type of adsorption which may be obtained experimentally. In the former, curve 1 shows a type of adsorption in which the isotherm equation

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Figures 4 & 5.

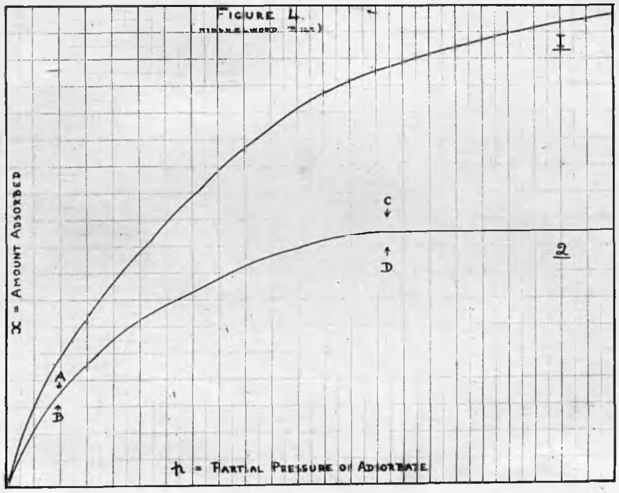

FIGURE 4.

(HINSHELWOOD, P. [illegible])

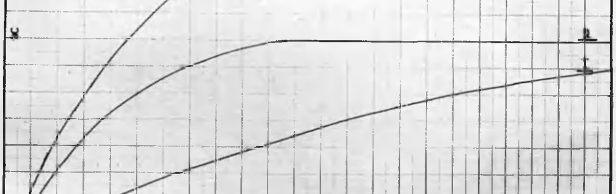

FIGURE 5.

(HINSHELWOOD, P. [illegible])

is followed, while curve 2 shows adsorption to a definite limit, and suggests the formation of a layer of definite and unchangeable thickness. It should be noted that, if only the region to the left of the line A - B is considered, then both lines will appear to be examples of the isotherm equation. Again, if the surface is not uniform, but possesses areas of varying adsorptive capacity, then it will probably be impossible to distinguish between the different adsorptive effects, and two curves will combine to give one of a different form to either, as in Figure 5. Here a curve of the form of 3 is made up by a combination of the adsorptions shown by curves 1 and 2. Even the most careful measurements, therefore, may fail to determine the nature of the adsorption.

For many catalytic surfaces, the behaviour of the reacting molecules seems to indicate that some definite saturation limit exists, and the unimolecular layer theory can, therefore, be used to predict certain phenomena which are capable of experimental verification.

Adopting the suggestions of Langmuir (J. Am. C. S. 1916, 38, 2221) let it be supposed that a gas at pressure P is in equilibrium with unit area of a surface at a given temperature. Let X be the fraction of the surface covered by the adsorbed gas, when $1-X$ will be the fraction left uncovered. Equilibrium with the surface will be established when the rate of evaporation from the covered surface is equal to the rate of condensation on the uncovered portion. This latter will be proportional to the pressure, and the adsorption relation may be expressed mathematically by the equation

$K_1P(1-X) = K_2X$ (where K_1 and K_2 are constants).

When the surface is only sparsely covered by the adsorbed molecules, $(1-X)$ approximates to unity, and the adsorption equation reduces to

$$K_1P = K_2X, \text{ or } X = \frac{K_1}{K_2} \cdot P \text{ .... } (1)$$

Again, when the surface is nearly saturated, the fraction covered (X) approximates to unity, and the equation becomes

$$K_1P(1-X) = K_2, \text{ or } (1-X) = \frac{K_2}{K_1} \cdot \frac{1}{P} \text{ .... } (2)$$

It will be seen from these considerations that, when adsorption is small, the total amount is proportional to the pressure - (1).

When the adsorption is large, the amount of free surface remaining is inversely proportional to the pressure of the gas - (2).

In the case of a surface reaction, if it be assumed that all reaction is on the surface and does not occur in the gaseous phase, the active mass is actually the amount of the gas adsorbed. Where the reaction is monomolecular, and the adsorption is small, then the active mass, from (1) above, is directly proportional to the pressure. As the change will involve only one molecule, the rate of change will be proportional to the gas pressure. The ordinary unimolecular law of reaction rate will be observed, and many examples of this type of reaction are known. The decomposition of nitrous oxide on gold at 900°C., studied by Hinshelwood (Proc. Roy. Soc. 1925 A, 108, 211), gives very good agreement with theory. With an initial pressure of 200 mm., the time of half change was 52 minutes, while with initial pressures of 400 mm., this time was 53 minutes, i.e. the same within the limits of experimental error. Unimolecular reactions of this type seem, on the whole, to be associated with the less active catalytic surfaces, which seems to relate amount of adsorption to catalytic activity. This point will be returned to later.

At the other extreme of the adsorption system, the surface is practically saturated, and considerable amounts may be removed by chemical change without the concentration in the adsorbed layer being appreciably changed. Thus there is a constant rate of reaction in spite of diminishing concentration in the gaseous phase, and the reaction appears to be of zero order. In the case of the decomposition of ammonia on a tungsten filament, some 30% is decomposed in 500 seconds, and 56% in 1000 seconds - a very slight falling off from a linear relationship (Hinshelwood and Burk J.C.S., 1925, 127, 1116). Practically all hydrogenations in solution show this apparent zero order, although, of course, these are not unimolecular reactions (Schwab. Zeit. Phys. Chem., 1931 B, 12, 427). With this type of reaction, it is clear that if the pressure is reduced, a point will finally be reached when the surface is no longer saturated, and the zero order reaction changes to one of a higher order. This can be illustrated from the adsorption isotherm (2) shown in Figure 4 (p.16). Here reaction at pressures in the region to the left of A - B will be unimolecular, or nearly so, while to the right of C - D, it will appear to be of zero order. Over the middle range of pressure, reaction rate varies in proportion to the fraction of the surface covered. This is given by the expression (p.17)

$$X = \frac{K_1 P}{K_2 + K_1 P}$$

It may, therefore, be said that the rate of reaction varies as some fractional power of the pressure, or, for a monomolecular reaction

$$\frac{dP}{dr} = K.P^n$$

where n and K are appropriate constants. An equation of this type was used successfully by Stock and Bodenstein (Ber. 1907, 40, 570) to express the rate of decomposition of antimony hydride on metallic antimony.

If any of the products of the reaction are themselves adsorbed strongly enough to occupy an appreciable fraction of the surface, less space becomes available for the reacting molecules, and the rate of change is correspondingly decreased. Using the same nomenclature as before, and assuming that X' is the fraction of the surface covered by the adsorbed product when the pressure of this is P' the fraction left free is $1 - X - X'$

By equating for equilibrium as before, the following equations are obtained:-

$$K_1 P(1-X-X') = K_2 X \quad \text{and}$$
$$K_1'(1-X-X') = K_2' X'$$

Writing b for $\frac{K_1}{K_2}$ and b' for $\frac{K_1'}{K_2'}$,

$$X = \frac{bP}{1+bP+b'P'} \text{ and } X' = \frac{b'P'}{1+bP+b'P'}$$

In the special case where X approximates to 0

$$X' = \frac{b'P'}{1+b'P'}$$

$$\text{and } 1-X' = \frac{1}{1+b'P'} \quad \text{.....................(3)}$$

As this last represents the free space available the amount of reactant adsorbed on it will be proportional to the pressure, or

$$X = \frac{bP}{1+b'P'} \quad \text{...............(4)}$$

Then the rate of reaction will be proportional to

$$X, \text{ or } \frac{dP}{dr} = \frac{bP}{1+b'P'} \quad \text{..........(5)}$$

Reactions governed by an equation of this type are the decomposition of nitrous oxide on cadmium oxide (Schwab. Zeit. Phys. Chem. 1933, B, 21, 65), and also upon platinum at certain pressures (Steacie. J. Phys. Chem. 1934, 585).

When the adsorption of molecules causing retardation is so marked that the free space available for reaction becomes inversely proportional to the pressure P', then equation (5) above will reduce to

$$\frac{dP}{dt} = \frac{bP}{b'P'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

In general, the reaction rate will be inversely proportional to some fractional power of P'. It has been found experimentally that in several cases the retarding effect of a gas is proportional to the square root of its pressure. For instance, Bodenstein and Fink (Zeit. Phys. Chem. 1907, 60, 1), in an investigation of the formation of sulphur trioxide on platinum, showed that the rate was inversely proportional to the square root of the sulphur trioxide pressure.

Returning to the general case of strong adsorption of products in which the rate may be expressed as in equation (6) above, if a, proportional to P, is the initial concentration of the reactant, and $(a-x)$ the amount left unchanged at the end of a time t, then the equation of rate may be written in the form

$$\frac{dx}{dt} = \frac{k(a-x)}{x} \text{ .... from (6) above.}$$

This may be integrated to the following form

$$kt = a(\log a) - a(\log \overline{a-x}) - x$$

If T is the time of half change, when $x = \frac{a}{2}$ then

$$T = \frac{1}{k}\left(a \log 2 - \frac{a}{2}\right)$$

or the time of half change is in direct proportion to the initial pressure. The first order reaction thus appears to be of zero order. Similarly, it may be shown that a reaction of the second order, under similar conditions, will appear as one of the first order, and that in general, the apparent order of the reaction will be one rank lower than the true order.

In the case of two or more reactants, the same effects will appear as in the simpler monomolecular reactions. Where strong adsorption occurs, either of reactants or of products, there will be an apparent lowering of the order of reaction; where the adsorption effects are slight, the true order of the reaction will be manifest. As examples of the latter the cases of hydrogen - oxygen combination on porcelain, and ethylene bromination on glass may be cited. In the first

(Bodenstein, Zeit. Phys. Chem. 1899, 29, 665) the rate of reaction is proportional to the product of the square of the hydrogen pressure and the pressure of the oxygen. This indicates a trimolecular reaction, so

$$2H_2 + O_2 \rightarrow 2H_2O$$

A reaction involving so many molecules suggests that a special arrangement on the surface of the catalyst precedes reaction. In the case of the bromination (Stewart et al, J. Am. Chem. Soc., 1923, 45, 1914), the reaction is found to be bimolecular, and proportional to the product of the pressures of the reactants.

The author, in the course of some work on the gasification of carbon carried out several years ago, came upon a typical instance of the case of strong adsorption and of a zero reaction order. It was found necessary to investigate the variation in rate of the action of steam on carbon with variations in the steam pressure. According to Cobb (Rept. Inst. Gas. Eng. 1924) the reaction rate was independent of this pressure (i.e. of zero order), but this had been denied by Haslam (J.I.E.C., 1923, 15, 115) and his co-workers. The author's own results, which are set out in some

detail in an appendix to this thesis, confirmed the results obtained by Cobb, although the whole experimental technique was totally different.
As one of the reactants was solid, the reaction might be considered as monomolecular, but it could not be of zero order, and it was clear that strong adsorption of some type had occurred.

Where the reactants are adsorbed in varying amounts, it may well be found that the reaction will actually be retarded by an excess of one or other of the various molecules involved in the reaction. Reverting to the two equations (3)and(4) on p.21, and considering two adsorbed molecules (a) and (a'), the formulae for fractions of space covered may be rewritten as

$$X_a = \frac{bP_a}{1+b'P_{a'}} \text{ and } X_{a'} = \frac{b'P_{a'}}{1+b'P_{a'}}$$

where (a') is the more strongly adsorbed molecule. Then for the rate of the whole reaction

$$\frac{dx}{dt} = k.X_a.X_{a'} = \frac{K.P_a.P_{a'}}{(1+b'P_{a'})^2} \quad \text{........}(7)$$

This last expression, which gives the reaction rate in terms of the partial pressures of the reactants, has the interesting feature that it passes through a maximum when $P_{a'} = \frac{1}{b'}$

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Figure 6 .

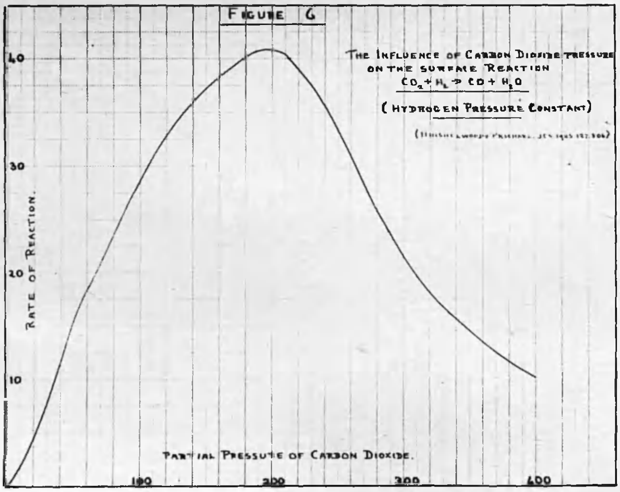

FIGURE 6

THE INFLUENCE OF CARBON DIOXIDE PRESSURE ON THE SURFACE REACTION

$CO_2 + H_2 \rightarrow CO + H_2O$

(HYDROGEN PRESSURE CONSTANT)

provided that p_a is constant. An example of a reaction governed by an equation on these lines is the interaction of carbon dioxide and hydrogen on platinum. This was investigated by Hinshelwood and Prichard (J. Chem. Soc., 1925, 127, 806), and their findings are illustrated by Figure 6. In this case, the carbon dioxide was much more strongly adsorbed than the hydrogen. A similar mechanism is suggested by the work of Rideal (J.C.S., 1922, 121, 309) on the hydrogenation of ethylene.

When the equation maximum is very near to zero - one reactant very strongly adsorbed - the form of the expression (7) approaches to

$$\frac{dx}{dt} = K.\frac{p_a}{p_a'}$$

In this limiting case, the rate of reaction becomes inversely proportional to the partial pressure of one reactant. Several instances of this type of reaction have been discovered. In one case, the interaction of carbon monoxide and hydrogen on platinum, Langmuir (Trans. Farad. Soc., 1922, 17, 621) showed that the rate of reaction is inversely proportional to the pressure of the carbon monoxide, and directly proportional to the pressure of the hydrogen, provided that the temperature is below 700°C. At higher temperatures the carbon monoxide appears to be less strongly adsorbed and conditions revert to the system studied before - an optimum pressure for each reactant when the pressure of the other remains constant.

The products of a reaction may retard the reaction markedly, as in the already quoted case of sulphur trioxide formation on platinum (Bodenstein, Zeit. Phys. Chem. 1907, 60, 1). The sulphur trioxide retards the reaction to an extent which is rather difficult to measure in practice. The rate of reaction can be represented by the expressions below:-

$$\frac{dx}{dt} = K\frac{[O_2]}{[SO_3]^{\frac{1}{2}}}\,(SO_2 \text{ in excess}) = \frac{[SO_2]}{[SO_3]^{\frac{1}{2}}}\,(O_2 \text{ in excess})$$

This was a case in which explanation by the multimolecular layer theory of adsorption was comparatively simple. The whole surface could be considered as covered with sulphur trioxide in a thickness proportional to the square root of the partial pressure. The process determining reaction velocity then became the diffusion rate of either oxygen or sulphur dioxide through this layer. This explanation agrees well with the fact that the ratio controlling change over from one governing concentration to another could be predicted successfully from the actual diffusion rates. On the basis of a unimolecular layer hypothesis, this explanation becomes untenable, and it is not easy to see how simple displacement in a single layer of adsorbed molecules can explain the facts. It has been suggested by Bodenstein (Zeit. Phys. Chem., 1929,B, 2, 345) that the diffusion process occurs not to the surface, but on the surface, to the active atoms or centres of activity. This may be so, but it is difficult to visualise a process of diffusion in two-dimensional space with all paths to some extent obstructed. There is also the possibility that the surface is a layer some molecules in depth, in which a limited degree of freedom of movement can be obtained.

It would appear that the amount of any gas adsorbed on a surface is proportional to the partial pressure of the gas in the vapour space, provided that a sufficiently low pressure range is chosen. If this be so, then either the surface is irregular in its adsorptive capacity, or else layers of more than one molecule in thickness must be formed. The instance quoted above suggests that more than one layer of molecules can form on the surface of a catalyst, and be sufficiently attached to the surface to be capable of playing some part in the reaction. Another case of similar nature is given by Dohse (Zeit. Phys. Chem., 1929 B, 5, 131) who showed that the decomposition of alcohols into olefine and water over aluminium oxide slowed down steadily as the percentage of alcohol decomposed increased. This slowing down was found to be due to retardation by the water formed. When this water was removed from the vapour space by a dehydrating agent the velocity became independent of the degree of conversion, i.e. became of an apparent zero order - a reaction on a fully saturated surface. By reducing the initial pressure to a sufficiently low level, the reaction became one of the first order, as might be expected. The gradual nature of the changes again seemed to indicate different degrees of adsorption.

It is perhaps unnecessary to assume that all reactants must be adsorbed before reaction can occur. If one reactant is adsorbed, and thus activated in some way, reaction may occur ~~of~~ by the collision of the other reactant with the adsorbed molecule. In this case, whatever the state at the surface, the rate of reaction would be proportional to the pressure of the unabsorbed reactant. The rate might be independent of the partial pressure of the other reactant if this pressure were sufficiently great to keep the surface fully saturated. Farkas and Rideal (Proc. Roy. Soc., 1934, 146 A, 630) showed that the reduction of ethylene on platinum occurred equally rapidly with either hydrogen or deuterium at low temperatures. At higher temperatures, where activated adsorption of both hydrogen and deuterium is known to occur, the rates of reduction were different. This has been held to indicate that reaction occurs between adsorbed ethylene and the bombarding hydrogen or deuterium. Again, the reaction between sulphur dioxide and carbon bisulphide has been found to set in rapidly at a temperature just above 200°C. over a titanium sulphide catalyst (Griffith - Contact Catalysis , p. 158). It has been shown that activated adsorption of sulphur dioxide is first noticeable at the same temperature, while the adsorption of carbon bisulphide remains immeasurably small. This certainly indicates that reaction is occurring between gaseous bisulphide and adsorbed sulphur dioxide.

There is no theoretical objection to the activation of only one of the reactants in a polymolecular reaction. It should be noted at this point that the activation energy in an heterogeneous reaction as deduced from the change in velocity with temperature (p.9), may be in error. The calculation is necessarily based upon the total number of molecules in the system, and not upon the number actually adsorbed Hinshelwood (Kinetics of Chemical Change, p.176 et soq) has shown that for unretarded reactions the true heat of activation E is equal to the apparent heat Q, less a quantity equal to the heat of desorption of the molecule (unimolecular reaction) or

$$E = Q - q$$

Where a second molecule exercises a retarding effect, and has a heat of desorption equal to q', then the true heat of activation is given by the expression

$$E = Q - q - q'$$

At present, however, actual measurement of these quantities has seldom been attempted, and experimental evidence is both scanty and inconclusive. Dohse (Zeit. Phys. Chem., 1929 B, 5, 131) measured the apparent activation energy of decomposition of alcohols, both retarded by water vapour and unretarded. The difference represented the heat of desorption of water vapour, and was found to be in fair agreement with independently determined values. This supposed, however, that water was preferentially adsorbed on the catalyst surface, and would therefore be expected to have a much greater heat of desorption than the alcohols tested. Actually, the reverse was found to be the case, and it is perhaps justifiable to assume that all the necessary data for these reactions are not yet available.

Very similar fortune attended the efforts of Hinshelwood (Kinetics of Chemical Change, p.181) to correlate heat of activation with the decomposition of formic acid to carbon dioxide and hydrogen. Over a wide range of catalysts the reaction velocity varied ten thousandfold, while the apparent heat of activation remained the same. Here it must be pointed out that the heat of adsorption was not measured, and it may be that the potentially active surface, and hence the amount of adsorption, varied in as wide a degree as the reaction velocity.

In connection with this decomposition of formic acid, an interesting development follows from the fact that the reaction can proceed in two ways, as follows:-

(i) $H.COOH \rightarrow CO + H_2O$ (ii) $H.COOH \rightarrow CO_2 + H_2$

On a glass surface, at about 280°C., the two reactions go on at much the same speed, but the heat of activation for decomposition (1) is 16000 calories, while for course (2) the corresponding value is 28000 calories. From these values, the first reaction should greatly predominate over the second, whereas, as stated above, the speed of both reactions is the same. This shows that the supply of heat for activation is not the only factor determining reaction, but that some other factor must be playing a part. No satisfactory explanation has so far been supplied as to the nature of this other factor, although many speculations have been made. It may be that a special orientation as well as an energy increment is required in order that a molecule shall react in a particular way. It is known that in many, heterogeneous catalytic reactions, the activation energy is considerably lower than that of the same reaction in the absence of a catalyst which would support the orientation hypothesis. For instance, in the homogeneous reaction for the decomposition of hydrogen iodide, the heat of activation is found to be 44000 calories, while for the same decomposition on a gold surface, the value of this constant is lowered to 25000 calories (Hinshelwood - Kinetics - p.187). If some modification has been introduced into the activation energy in this way, it need not be manifested by a change in the total amount. The values usually

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Figure 7.

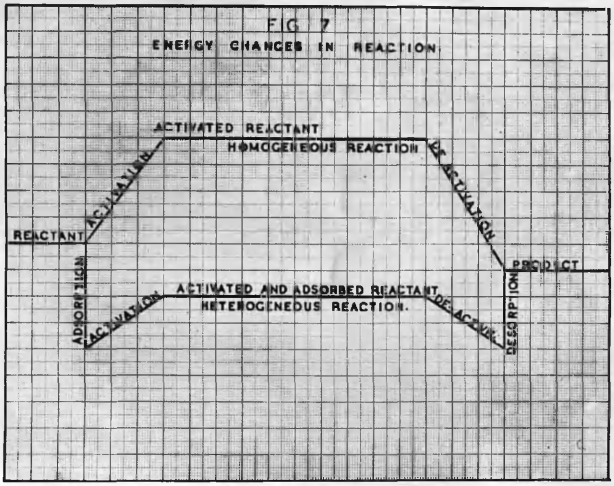


FIG 7

ENERGY CHANGES IN REACTION.

given are the apparent heats of activation, which may be misleading, but there is no doubt that a substantial lowering of the heat of activation does occur in catalysis. The enormous changes in reaction velocity brought about by an active surface cannot be explained by such alterations as the change in concentration of reactants due to adsorption at a surface. For instance, the speed of reaction between hydrogen and oxygen on a porcelain surface is 10^7 times that of the homogeneous reaction, whilst the number of collisions due to adsorption is only 10^3 times the normal number (Bodenstein, Zeit. Phys. Chem., 1899, 29,665). This discrepancy is much more marked with more active catalysts.

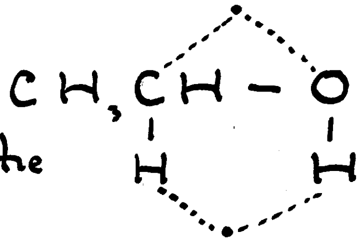
It might be suggested that the energy changes in a reacting molecule could be represented as in Figure 7. Here the activation energy on the catalyst surface is shown as considerably smaller than in the corresponding homogeneous reaction. This is in accordance with the theory embodied in a treatment, by the aid of wave mechanics, of the mechanism of atomic activation (Bawn & Ogden ~~(~~Trans. Farad. Soc., 1934, 30, 432). It has been shown that the energy necessary to enable an atom to climb over a barrier of high electric potential may be diminished by the making of a tunnel through the wall.

~~No~~ Very little experimental evidence has been brought forward in support of this theory.

Other suggestions as to the mechanism of activation energy changes, based upon theoretical reasoning, have been made but are not of direct interest in the practical aspects of reaction under review here. Sherman and Eyring (J. Am. Chem. Soc., 1932, 54, 2661) however, were able to show that the activation energy for the reaction between hydrogen and carbon varied markedly with the distance between the carbon atoms of the surface. This relationship between atom distance and activation energy may well have great importance in the study of the mixed zinc-chromium oxide catalysts used in the course of the practical work described herein.

In this connection, the hypotheses of Balandin (Zeit. Phys. Chem., 1929 B, 3, 167) should be mentioned. He postulates that the links between atoms are broken if they are attracted by different catalyst atoms, while, if attracted by the same atom, links are formed or strengthened. Thus, for the dehydrogenation and dehydration of alcohols, which occur simultaneously on various catalyst surfaces, the following schemes are propounded.

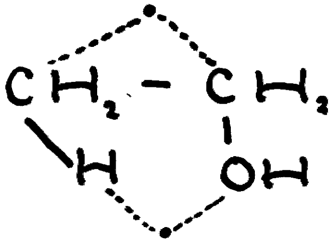
1. Adsorption to



where • represents the catalyst.

This is followed by scission to acetaldehyde and hydrogen.

2. Adsorption to



This is followed by scission to ethylene and water. The alcohol is adsorbed in form (1) and/or (2) and breaks down to the appropriate scission products. Further developments of this theory, however, have not met with practical support (Lazier, J. Am. Chem. Soc. 1932, 54, 3080).

Whatever the method of association, or activation of the reactant, it must be associated with the catalyst surface during the reaction, and it does not seem of much value to discuss the formation of so-called intermediate compounds. All catalytic reactions must involve the formation of these compounds in some form or another, and it is, to the author's mind, quite beside the point to demonstrate that in some cases intermediate compounds can be isolated in which the reactants are chemically associated with the surface. In this connection, it should be noted that the heats of adsorption of gases on catalyst surfaces are of the same order of magnitude as the chemical heats of reaction, indicating that there is no real difference in the manner of compound formation (Dew & Taylor, J. Phys. Chem., 1937, 31, 297).

It has been shown by several workers (Fryling, J. Phys. Chem., 1927, 30, 818) that the first portions of gas admitted to a previously cleaned surface exhibit an higher heat of adsorption than the subsequent additions. Certain discrepancies, notably the appearance of a maximum in the measured heats of adsorption, have now been shown to be due to experimental error. (Beebe, J. Am. Chem. Soc., 1936, 58, 1703). This again indicates that the surface of a catalyst is very far from uniform, and possesses areas of varying adsorptive capacity (probably also of varying catalytic activity). There exists the alternative hypothesis that adsorption takes place in layers of more than one molecule in thickness. It might be suggested that thick layers of this type will necessarily be formed if any adsorption at all occurs, inasmuch as the first layer of adsorbed material will create a fresh and different surface with some force of attraction, even if the attractive force of the original surface is completely saturated. There is no reason why a surface of unequal activity, adsorbing layers of more than one molecule in thickness, should not satisfy simultaneously both hypotheses.

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Figure 8.

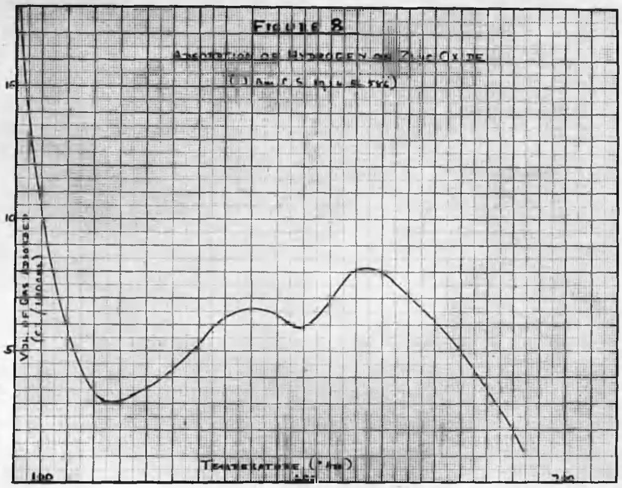

FIGURE 8

ADSORPTION OF HYDROGEN ON ZINC OXIDE

(1 Atm. C.S. [illegible])

Much of the earlier work on adsorption was carried out with active surfaces at temperatures much below those at which reaction occurred, and little or no connection could be traced between the two phenomena. Benton and White (J. Am. C.S. 1930, 52, 2325), and later Taylor and his co-workers (J. Am. C.S., 1931, 53, 578) threw a fresh light on the subject by a demonstration of another type of adsorption at much higher temperatures. This type of adsorption was termed activated, and various levels of activation seemed to exist, as shown in Figure 8. It should be noted, in connection with this example, that zinc oxide is only active as an hydrogenating catalyst at temperatures above about 550° Abs. The absence of this type of adsorption at lower temperatures can be explained by assuming that the rate at which the adsorption occurs is too slow for the effects to be noticeable. It has been shown experimentally that activated adsorption is fairly slow, and that the rate falls off markedly with fall in temperature (Griffith and Hill, P.R.S., 1935, 148 A, 194). Practical work described later in this thesis illustrates this point.

The extent to which normal adsorption, generally known as "van der Waals" adsorption, can be disentangled from the activated type depends upon the values of the heats of adsorption and the activation energies relative to one another. These are more sharply differentiated in oxide than in metal surfaces, and, following this, oxide catalysts are generally used at higher temperatures than the pure metal. In consequence, most of the measurements of activated adsorption have been carried out with active oxide surfaces. It has been shown that the heat of adsorption in the activated range is about ten times as great as in the range of the van der Waals type as would be expected. (Taylor & Williamson, J.Am.C.S., 1931, 53, 813). The heat of activation varies greatly showing lowest energy levels with the first few molecules adsorbed. (Taylor, J.Am.C.S., 1931, 53, 2168). It must be pointed out that these values have been calculated, as a rule, from the velocities of adsorption and the amounts adsorbed at various temperatures. These calculated values are subject to experimental error, as will be indicated in the course of descriptions of practical work later. (See p.90).

Attempts were made to differentiate between various types of adsorption by the use of ortho and para hydrogen (Taylor, Trans. Farad. Soc., 1932, 28, 247). It was soon found that many factors, such as the influence of molecular magnetic dipoles, played a part in the transformation of one form to the other, and the indications as to adsorption were vague. (Bonhoffer, Zeit. Phys. Chem., 1933 B, 21, 225). The use of deuterium to investigate the differences of adsorption was somewhat more successful, but the work is still in its early stages (Taylor, J.Am.C.S., 1935, 57, 660).

There is considerable doubt as to whether the activated adsorption process is reversible, as experimental evidence is in conflict on this point. Garner and Kingham (Trans. Farad. Soc., 1931, 27, 322) declared that the activated adsorption of hydrogen on a zinc oxide surface was irreversible, the hydrogen being removable only as water. This type of adsorption is generally known as chemisorption. On the other hand, Flosdorf (J. Phys. Chem., 1930, 34, 1908) stated that a catalyst surface of this type gave truly reversible adsorption after a long series of reducing adsorptions and evacuations. Further work by Garner (J.C.S., 1935, 1487) supported this, and it appears that the difference between reversible and irreversible adsorption is not very marked, and the two types merge into one another without any marked change in characteristics.

The reduction of a mixed zinc-chromium catalyst of the type used in these tests is very slow, and during the reduction period the surface seems quite capable of exerting a catalytic effect in, for instance, the decomposition of methanol (A.R. Roy, Ph.D. Thesis, 1940). The dividing line between chemisorption and reversible adsorption appears to be very faint, and it is perhaps better to refer to the two types as reversible and irreversible to stress this point of similarity.

This raises an interesting point in the mechanism of activated adsorption vis-a-vis catalytic action. Several workers have established the close resemblance between synthesis and decomposition of methanol on zinc-chromium catalysts. (J.I.E.C., 1929, 867). Presumably, therefore, a partly reduced catalyst can produce synthesis of methanol under suitable conditions. If the initial stage of the synthesis is assumed to be an activated adsorption of both reactants, then the adsorption of the carbon monoxide must exercise some effect on the adsorption of the hydrogen. Were this not the case, then the release of the hydrogen in the course of reaction would remove some of the oxygen from the surface. Reduction to a metal surface, or at least to some form of stable sub-oxide, would necessarily occur, which does not appear to be the case in practice. In the reverse case, where decomposition is occurring, hydrogen and carbon monoxide are liberated at the surface without any associated oxygen. In these circumstances it appears that the reactants cannot be associated with the surface in the same way for reaction and for activated adsorption.

It may be that the activated adsorption shown by many catalytic surfaces is merely an indication of a more or less active surface, rather than an actual precursor to catalytic reaction. This conclusion has long since been reached with respect to ordinary adsorption of the van der Waals type (Taylor & Burns, J.Am.Chem.Soc., 1921, 43, 1273). A very close connection between activated adsorption of hydrocarbons and their decomposition by the same surfaces has been demonstrated by Griffith and Hill (Proc. Roy. Soc., 1935, 148A, 194), but this connection does not mean an identity in mechanism. In fact, further work on a wider range of catalysts by the same workers (Nature 1934, 129, 834) was held to show that the extent of activated adsorption does not necessarily measure catalytic activity, or even indicate a material likely to bring about reaction. The results were masked by chemical reaction in some cases.

It is possible that the quality of the adsorption may be more important than the amount. The speed of adsorption, for instance, may be critical. Taylor and Howard (J.Am.C.S., 1934, 56, 2259) in an investigation of ethylene hydrogenation suggested that the rate of ethylene adsorption determined the rate of reaction, as the hydrogen was much more rapidly adsorbed, and therefore always available. These results were supported by the work of Insley (J. Phys. Chem., 1935, 39, 623).

An interesting case where two maxima are obtained in a curve relating promoter concentration to catalyst activity was met with in the high pressure hydrogenation of tar oils. (Hollings & others. Proc. Roy. Soc., 1935, 148A, 186). It was at first suggested that the two maxima corresponded with the best conditions for the adsorption of the two reactants. Later work, however, showed that the depression in the curve of activity between the two peaks corresponds with the point of maximum adsorption of hydrocarbons, and actually represented a composition of maximum activity in the low pressure decomposition of hexane. Here, then, the determining factor appears to be the relative amount of the reactants present in the adsorbed layer, a case which could be represented by an equation of the type of equation (7) on p.25.

This introduction represents the basis upon which the practical work of this thesis was commenced in 1936-37. A note upon other developments in the last three years will be found included in the final section. There appeared to be a fruitful field for investigation in the relationship between activated adsorption and chemical reaction at a surface, and the bulk of the following work has been directed to this end.

EXPERIMENTAL.

Section 1.

The Synthesis and Decomposition of Methyl Alcohol.

The predominant reaction between carbon monoxide and hydrogen over a mixed zinc-chromium catalyst is the formation of methyl alcohol -

$$CO + 2H_2 \rightleftarrows CH_3OH.$$

This reaction is reversible, and the value of the equilibrium constant is as follows (Newitt et al. Proc. Roy. Soc., 1929, 123, 236).

TABLE I.

Temperature (°C.)	100	260	300	340	380
K	30	1.2×10^{-3}	1.6×10^{-4}	2.9×10^{-5}	6.3×10^{-6}

From this the amount of methyl alcohol existing in the equilibrium mixture at 340°C. will be of the order of 0.001% at a pressure of 1 atmosphere, and ~~8%~~ c. 20 % at a pressure of 200 atmospheres, provided that the value of K is not altered by changes in pressure. As the minimum temperature at which reaction velocity becomes rapid enough for industrial working is about 300°, synthesis is carried out at a pressure of 200 atmospheres and a temperature of about 350°. The catalyst is usually made up from zinc and chromium oxides in the proportion of four atoms of zinc to one of chromium. This mixture has been found to be the most active of the whole range from pure zinc oxide to pure chromium oxide, and the curve for activity against atomic percentage of zinc shows a very marked maximum around this composition. (Frolich & Cryder, J.I.E.C., 1929, 21, 867, 1056). It has been demonstrated by the same workers and others that this activity for synthesis is very closely paralleled by activity for the decomposition of methyl alcohol at the same temperature but at atmospheric pressure. There exists, therefore, a very close connection in this reaction between decomposition and synthesis, which enables the mechanism of reaction to be investigated without having recourse to high pressures.

It was decided, in the first place, to attempt to trace a connection between activated adsorption of the reactants on the surface of the catalyst, and the activity of the surface in promotion of reaction. While some workers had shown previously (Garner & Kingman, Trans. Farad. Soc., 1931, 27, 322) that activated adsorption does occur on mixed zinc-chromium catalysts, no complete range of composition had been investigated.

The first stage in the work was the preparation of a range of zinc-chromium catalysts, and the measurement of their catalytic activity. The catalysts were made up in the manner recommended by Frolich & Cryder (Loc. cit.). An aqueous solution of zinc nitrate is prepared by dissolving zinc oxide (A.R. standard) in 30% nitric acid. The zinc oxide is then reprecipitated at 80 - 90°C. by the addition of 20% ammonia solution, the ammonia being added till no further precipitation occurs, but not in excess. The precipitate is allowed to settle, and then washed three times with hot water by decantation. The residual suspension is used as a stock solution for catalyst manufacture, after determination of the zinc content by titration with potassium ferrocyanide, using uranium nitrate as an external indicator.
A stock solution of chromium trioxide is also prepared, the chromium content being determined iodometrically. The required amounts for any proportion of zinc to chromium are weighed or measured, and the chromium solution added to the zinc suspension, with stirring, at a temperature of 80 - 90°C. The mixture is then evaporated to dryness, with continuous stirring, at a temperature not in excess of 100°C. The friable mass is heated in an oven at 110° for one hour, and

then broken to pass a 10 mesh sieve (I.M.M.). The portion retained on a 40 mesh sieve is then used as the catalyst mass.

The above procedure was carried out with a zinc oxide suspension containing 86.4% of water, while the chromium trioxide solution contained 25% of the oxide (both by weight). All samples were very friable, and had to be handled carefully to avoid further breakage and powdering. A portion of each catalyst was analysed for zinc and chromium content. The chromium, as chromate, interfered with the titration of the zinc, but could be reduced to a chromous salt with sodium bisulphite, when titration of the zinc with ferrocyanide was again possible. The chromium was estimated as chromate by the liberation of iodine as before, after any reducing effect during drying had been eliminated by the addition of sodium peroxide. There was no interference effect from the zinc.

The results of a typical analysis are shown below.

Catalyst 1.

Sample (3.5810 gms.) was dissolved in dilute hydrochloric acid and made up to 250 ml.

Determination of Zinc.

25 ml. of solution were boiled with 1 gm. of sodium bisulphite until free from sulphur dioxide, making up with water when necessary. The hot solution was then titrated with standard ferrocyanide solution (1 ml.= 0.0122 gms. of zinc oxide). The 25 ml. of solution were equivalent to 10.7 ml. of ferrocyanide solution, and therefore contained 0.1305 gm. of zinc oxide.

Determination of Chromium

10 ml. of original solution were boiled with 0.1 gm. of sodium peroxide, and evaporated nearly to dryness. 2 ml. of conc. hydrochloric and 10 ml. of 20% potassium iodide were added, and after five minutes' keeping the sample was titrated with sodium thiosulphate (starch indicator). The 10 ml. of solution were equivalent to 16.1 ml. of N/10 sodium thiosulphate, or contained 0.054 gm. of chromium trioxide.

The original sample of catalyst contained water which was estimated by heating a weighed sample in a current of dry oxygen-free nitrogen at 150°C., until constant in weight. The loss in weight was found to be 25.0%.

From these figures, the composition of the catalyst is as follows:-

Zinc Oxide	36.4%
Chromium Trioxide	37.7%
Water	25.0%

The unexplained residue is almost certainly water, the last traces of which are very tenaciously held. The molecular ratio of zinc oxide to chromic oxide is 1 to 0.85, or an atomic percentage of zinc of 54.1.

The complete range of catalysts made up and analysed in this way is shown in the table below.

TABLE 2.

Catalyst.	Molecular Ratio. (ZnO - CrO_3)	Atomic Percentage of zinc.
1	1.18 : 1	54.1
2	2.24 : 1	69.2
3	3.54 : 1	78.2
4	4.31 : 1	81.2
5	5.7 : 1	85.1
6	1.1 : 2	35.5
7	Pure ZnO.	100.0

The sized catalysts were reduced with methyl alcohol vapour after a preliminary drying in a current of dry oxygen-free nitrogen. The operation was carried out in actual catalyst chamber (figure 9) the whole

p.53.

arrangement being the same, up to the catalyst tube, for both the reduction and the activity tests. In the reduction, the catalyst tube was three quarters filled with the oxide mixture, and then heated to 220° for four hours, while nitrogen from a cylinder passed through the apparatus. The nitrogen had previously been scrubbed with pyrogallol solution and dried with calcium chloride to remove oxygen and moisture. During this initial drying period, a darkening of the bright yellow oxide mixtures in some instances suggested that a slight reduction was going on. The nitrogen rate was 2 cubic feet per hour.

The nitrogen was then replaced by a slow current of methyl alcohol vapour. This methyl alcohol, which was used throughout the work, had been purified by the following method. (Organic Chemistry - Cumming, Hopper and Wheeler). The alcohol is refluxed for an hour with 5% by weight of solid caustic potash, and then distilled from any residue boiling above 68°C. on a water bath. The distillate is allowed to stand for 24 hours over 40% by weight of quicklime, and then redistilled. The final product is freed from water by three distillations from metallic calcium. This method of purification is rather costly, losses of up to 50% of the commercial alcohol being sustained, but the amount of material required for this investigation was small and rigorous purification was considered desirable.

The effect of replacing nitrogen by alcohol vapour was to cause a strongly exothermic reduction of the catalyst accompanied by a colour change from yellow to dark green. This exothermic reaction was so marked in the case of catalyst 4 that visible incandescence was observed, indicating local temperatures well in excess of the thermo-couple reading, of about 350°, registered some minutes after the admission of the alcohol. The temperature of 220° had been chosen by observation as being the lowest at which this reaction set in, but was still too high to prevent marked rise in temperature with catalyst 4 and slight rise with the other samples. If the methyl alcohol were admitted at a lower temperature, and the temperature gradually raised, then at about 220° the characteristic reaction would occur with even greater violence. It was clear from this work that reduction conditions were unsuitable, and would have to be revised, but for the first series of catalysts the method was adhered to, with, as will be seen, some interesting results in the case of catalyst 4.

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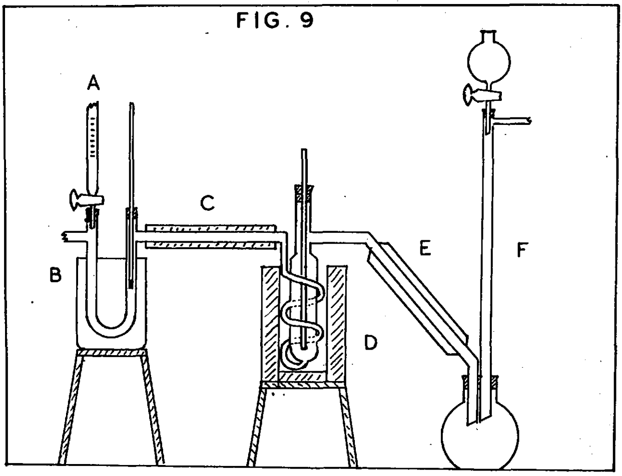
Figure 9

FIG. 9



The sharp rise of temperature brought about by the first stages of reduction was of the order of 20-30°, except in the case of catalyst 4, and when the heat had been dissipated, the temperature of the catalyst mass was raised slowly, over three hours, to 360°C.; during this period the methyl alcohol vapour was passed at a rate of a cubic foot per hour. The catalyst was then cooled in a stream of purified nitrogen, removed from the tube when cold, and kept in a tightly stoppered bottle till required.

The reduced catalysts were used, in turn, for the decomposition of methyl alcohol vapour at 360°C. This temperature had been chosen as that at which synthesis of methyl alcohol was carried out in industry. The apparatus is shown in the diagram of figure 9. Burette A, graduated in twentieths of a ml. measured the methyl alcohol added to the system via the vapouriser B. This was a glass U tube, carrying the burette and a thermometer for checking temperatures, and immersed in a boiling water bath. The methyl alcohol was kept from condensing by the heater C, which was heated electrically to a temperature of 200°C. The preheating was completed in the coiled tube round the centre catalyst container of the tube D. This tube, of pyrex glass, was heated in an air bath, the temperature of the catalyst being measured by a thermo-couple, in a thin silica sheath at the centre of the catalyst bed. The cross sectional area of the central section of the catalyst tube, allowing for the space occupied by the thermocouple tube, was approximately 2.5 sq.cms., and a depth of 2 cms. was thus obtained with 5 ml. of the graded and reduced catalyst. This volume of catalyst was used in each test, but each sample was weighed, and it will be seen from Table 3 below that the weight of catalyst varied rather widely, owing to the change in apparent bulk density with composition.

TABLE 3.

Catalyst.	Weight of 5 ml.	Atomic Percentage of zinc.
1	3.70 gms.	54.1
2	2.60 gms.	69.2
3	2.50 gms.	78.2
4	2.40 gms.	81.2
5	2.50 gms.	85.1
6	3.80 gms.	35.5
7	2.95 gms.	100.0

The catalyst grains were supported on a level bed of ignited asbestos wool, which was previously found to be inert towards methyl alcohol under the conditions of test.

The products of reaction passed through a Liebig condenser E to a scrubbing tower F, twelve inches long and just under an inch in diameter, filled with glass beads. These beads were kept wet by a steady flow of distilled water from a tap funnel. A weighed amount of water was used in each test, and the hold up in the tower kept constant by a fixed draining time under similar conditions. The gaseous products remaining were collected in an aspirator over brine solution (20 gms. NaCl + 1 gm. H_2SO_4 per 100 ml.). The aspirator run off was adjusted to regulate the pressure in the whole system to as nearly atmospheric pressure as possible.

The experimental procedure was as follows:- After assembly of the apparatus, and test for gas tightness, the water bath of the vapouriser was heated to boiling, the preheater to 200°C., and the catalyst to 360°C. The methyl alcohol was set to drip into the vapouriser at a rate of 8 ml. per hour, and the whole of the products passed to waste at the outlet of the condenser. After an hours run to establish equilibrium in the system, a fresh weighed receiver was put on to the condenser outlet, the whole system coupled to the aspirator, and the pressure regulated to atmospheric level. At the same time, flow of 40 ml. of water was started through the scrubber, which had previously been drained for ten minutes after being washed with water at a rate of 40 ml. per hour. The initial reading of methyl alcohol in the burette was noted, and the experiment continued for one hour, during which about 8 ml. of alcohol (accurately measured to 1/20 ml.) entered the system, and the 40 ml. of water flowed through the scrubber. At the end of the hour, the flow of alcohol was stopped, and the scrubber flushed out with a further 10 ml. of water before allowing to drain for ten minutes, as before the test. The total hold up in the column had been found by experiment to be 3.1 gms. of water, so that it was considered that all the condensed products of reaction were removed from the column by the experimental procedure.

The liquid in the receiver was weighed, and one half distilled direct from the flask through a special 15 inch Dufton column 3/8 of an inch in diameter (Dufton, J.S.C.I., 1919, 38, 45). The vapours were condensed in a small Liebig condenser, 4 inches long, fitted direct on to the side arm at the column head. By leaving the top two inches of the column unlagged, and distilling at a rate of only 0.1 ml. per minute, a high reflux ratio was obtained and the separation of methyl alcohol and water made very sharp. It was found, by a series of tests upon mixtures of known composition, that the amount of fraction boiling between 66 and 67°C. was between 97 and 103% of the methyl alcohol present, and this accuracy was considered sufficient. The remaining half of the liquid was then analysed for formaldehyde by the method given in Sherman's Organic Analysis, p.44, using potassium cyanide. In view of the small quantities present, it was decided that the method was sufficiently accurate for the purpose. The main bulk of the products were in the form of either unchanged alcohol or gas. The gas collecting in the aspirator was analysed in a modified Hempel apparatus by standard methods for which the gas composition was eminently suitable.

A typical example of the results obtained, and of the methods of calculation employed, is given below.

Catalyst No.5. Weight of Catalyst used 2.52 gm

Methyl alcohol added 8.0 ml. = 6.33 gm.

Weight of liquid in receiver = 53.27 gm.

Gas volume 2400 ml. at 17°C. and 758 mm.

Analysis of Liquor

Taken for distillation, 26.64 gm.

Weight of methyl alcohol fraction = 2.60 gm.

Weight of unchanged methyl alcohol = 5.20 gm.

Weight of formaldehyde in residual 26.63 gm. = 0.06 gm.

Analysis of Gas.

CO_2	1.4%	H_2	56.0%
O_2	3.2%	CH_4	0.0%
CO	27.6%	N_2	11.8%

From these figures, volume of $CO + CO_2$ = 648 ml.

at N.T.P.

Therefore, weight of methanol decomposed to gas is

0.93 gm.

Mass Balance.

Methanol added 6.33 gm.	Recovered unchanged	5.20 gm.
	Recovered as formaldehyde	0.06 gm.
	Recovered as gas	0.93 gm.
	Loss (2%)	0.14 gm.

Percentage of methanol decomposed 16.0%.

A check upon this test gave a mass recovery of 103%, with a percentage decomposition of 16.1%.

Similar tests carried out on the whole range of catalysts gave the results set out in an abbreviated form in Table 4 below.

TABLE 4.

Catalyst.	% of Methanol decomposed.	Mass Recovery. %
1	27.3 (37.0)	98.3
2	24.3 (46.7)	98.0
3	20.2 (40.4)	98.2
4	8.4 (17.5)	100.0
5	16.0 (32.0)	100.5
6	21.0 (27.6)	98.0
7	10.3 (17.6)	99.5

The figures in brackets after the middle column show the amounts that would be decomposed by 5 gm. of each catalyst were a true weight ratio obtained.

In the determination of catalyst activity by means of a flow system, it is necessary to ensure that, as far as is possible, the concentration of reactants remains the same for catalysts of varying activity. In these tests, therefore, the amount of methyl alcohol passing was always considerably in excess of the amount that might be decomposed. Again, the catalysts

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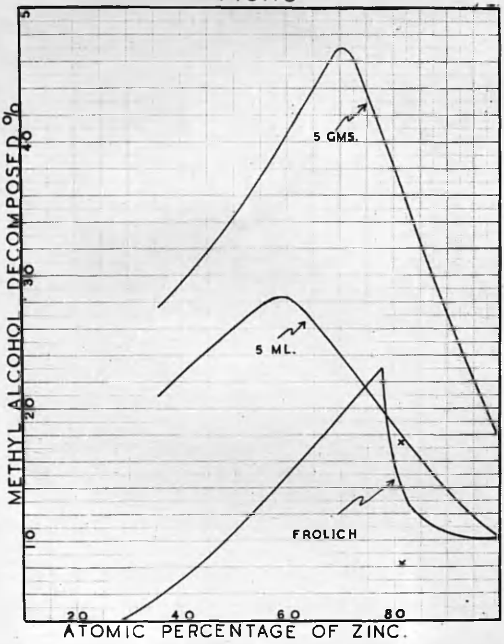
Figure 10

FIG. 10


METHYL ALCOHOL DECOMPOSED %
50
40
30
20
10
5 GMS.
5 ML.
FROLICH
20
40
60
80
ATOMIC PERCENTAGE OF ZINC.

varied markedly in density - a point that will be referred to later. Equal weights of each catalyst would have varied the actual time of contact, given by the apparent volume of the catalyst divided into the volume of vapour passing per second. As equal volumes of catalyst were chosen, the time of contact was the same in each test, although some allowance must be made for the change in volume due to decomposition. Actual volume measurement of a powdered solid is not a very easy matter, as the apparent density varies with the nature of the packing. The results for packing density given in Table 3 (p.54) were obtained by weighing a fixed volume of the powder in a weighing bottle of known volume, after filling to a mark with constant gentle tapping. As the catalysts were all rather fragile, this packing density tended to vary, and was not considered an ideal basis for activity measurements.

It was thought desirable to calculate the values for decomposition given by 5 gm. of the catalyst from the values actually determined for equal volumes, and curves showing the variation of both values with catalyst composition are shown in Figure 10. The results obtained by Frohlich and his co-workers (J.I.E.C., 1929, 21, 867) are included for comparison.

It may be noted that a determination of the amount of methyl alcohol decomposed by 5 gm. of catalyst No.2 was found to be 48%.

It will be seen that the results are in very fair agreement with those of the earlier workers, with the exception of the activity of catalyst 4, which seems completely abnormal. This was the catalyst which had exhibited in so marked a degree the phenomenon of incandescence on reduction (p.52). This marked exothermic reaction might well have produced sintering of the active surface, with diminution of catalytic activity. There was no evidence of any notable side reaction, as this would have been detected by a variation in the mass balance. The only product of decomposition, apart from the gaseous oxides of carbon and hydrogen, was a small and almost constant quantity of formaldehyde.

These tests of catalytic activity were neither very comprehensive nor very exact. They had, however, served to show that a series of catalysts had been prepared with properties similar to those already established by other workers, There seemed no purpose, as far as the present work was concerned, in going further into the matter, either with a view to adjusting reduction conditions, or with the intention of making more exact measurement. Further work carried out by Dr. A.R. Roy (Ph.D. Thesis, Glasgow, 1940) substantiated the general form of the curves. In addition, the reduction method was modified and violent initial stages avoided by the use of mixtures of methyl alcohol and nitrogen. This change restored a catalyst of composition 4 to its normal place in the table of activity.

The next step in the investigation was to determine amounts of carbon monoxide and hydrogen adsorbed on this series of catalysts.

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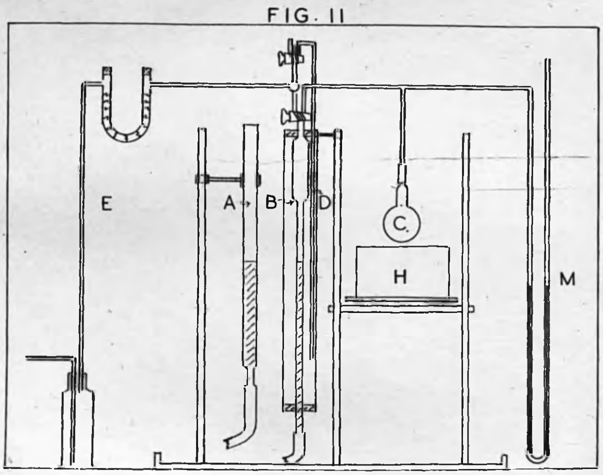
Figure 11

FIG. 11



Section 2.

Adsorption on Methanol Catalysts.

The first apparatus set up for the measurement of adsorption is shown in Figure 11. A gas burette (B) graduated in hundredths of a ml., which could be read by a travelling microscope to the nearest 0.001 of a ml., was used for measuring the gases supplied to the catalyst bulb (C). This burette was water jacketed, and, together with the reservoir (A), was used for evacuating the adsorption system by creating a Torricellian vacuum. At first the pressure obtained by this means was only 15 mm. Hg., but this was found to be due to traces of moisture. After heating to 60 - 70°C., and sweeping out repeatedly with dry nitrogen, it was found that the pressure could be reduced to 7 mm. of Hg. In view of later work, it was probable that the apparatus still contained moisture but the evacuation was accepted as satisfactory for preliminary tests.

The gas evacuated from the catalyst system could either be exhausted to the air, or passed into a small subsidiary burette (D). Communication to the main burette was also made, by means of a three-way stopcock, with the supply of gases, which came through a final purifying train (E). This train, containing a wash bottle with alkaline pyrogallol solution and a calcium chloride tube, was only intended to remove adventitious traces of oxygen and water, as the gases had previously been purified and stored over concentrated brine.

The catalyst bulb (C) in hard glass, was heated by means of a fused salt bath (potassium-sodium nitrates) with an external electric heater. The bath temperature was measured with a mercury thermometer and assumed to be the same as the catalyst. It was necessary to remove bulb and thermometer from the fused salt before cooling, as contraction on solidification generally broke the glass. Apart from this the bath gave no trouble, and was retained throughout the whole of subsequent work, although a gas heating system replaced the electrical as being more robust. All leads from the bulb to the burette and gauge were made from 1 mm. bore capillary tube to reduce the dead space of the apparatus. The pressures in the unit were read by means of a mercury manometer (M), reading to 0.5 mm. The various sections of the apparatus were joined with rubber pressure tubing, held firmly by copper wire, and painted over with cellulose acetate solution.

This gave a completely gas-tight unit, holding a vacuum of 750 mm. with no apparent change for 24 hours. It was found necessary in the later course of this work to replace most of these rubber joints by fused glass work. Picien Wax in benzene gave a more durable film than cellulose acetate, and was slightly better in checking leakage.

The catalyst to be tested was measured into the previously weighed catalyst bulb, 5 ml. of the selected material being used in each case. The weight was then determined by weighing the filled bulb. The catalyst had already been reduced by methyl alcohol vapour at 360°C. but it was thought advisable to treat with hydrogen at 500°C. to bring the surface of the catalyst to a uniform state. This final reduction was carried out in situ, after assembling the apparatus and testing for leaks. The whole system was exhausted as compldtely as possible, then filled with hydrogen to atmospheric pressure while the catalyst was maintained at a temperature of 300°. The temperature of the heating bath was then raised to 500° over 30 minutes, and maintained at that level for a further 60 minutes. Some adsorption or decrease in volume was observed at first, and after 15 minutes the apparatus was re-exhausted and refilled with hydrogen. No appreciable change in pressure was noticeable thereafter.

At the end of the reduction period, the catalyst was cooled to the temperature at which measurements were to be taken, and then the hydrogen was removed from the system as completely as possible, determining the actual pressure by comparison with barometric. As has been stated, the evacuation process gave a pressure of the order of 7 mm. Hg. Purified nitrogen was then measured in the burette, and admitted to the evacuated adsorption system in portions of about 1 ml. at a time, measuring the manometer pressure after each addition. This nitrogen addition was continued until a pressure of 760 mm. was reached in the unit. A graph was then constructed showing the pressure produced by the addition of known volumes of nitrogen, corrected of course for temperature and pressure. These volumes were taken as a measure of the dead space of the apparatus, it being assumed that the nitrogen was not adsorbed on the surface of the catalyst. This assumption was considered to be justified by the fact that no change in pressure could be detected when the nitrogen had once been admitted and given time (about 20 seconds) to assume the temperature of the catalyst and catalyst space. The manometer level, after the initial changes, was maintained indefinitely, in contrast

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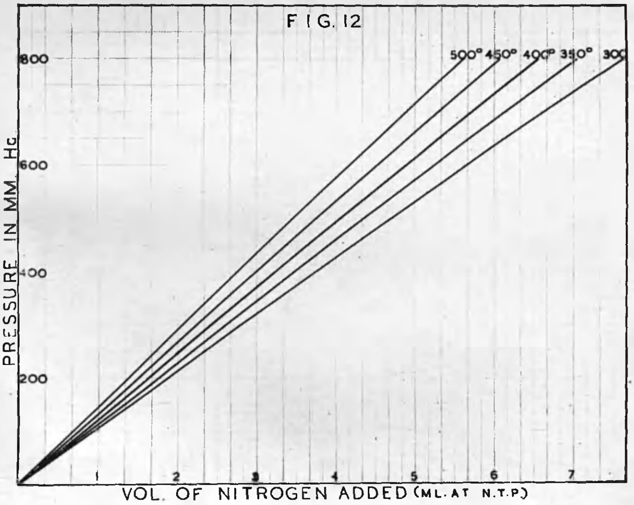
Figure 12.

FIG. 12



500°
450°
400°
350°
300
800
600
400
200
PRESSURE IN MM. Hg
1
2
3
4
5
6
7
VOL. OF NITROGEN ADDED (ML. AT N.T.P)

to behaviour with hydrogen and carbon monoxide. It might have been preferable to use one of the inert gases, such as argon, for measurement of dead space, as was actually done by some other workers, see for instance Taylor & Strother, (J.Am.C.S., 1934, 56, 586) but no evidence whatever existed in this series of experiments of any adsorption of nitrogen.

A dead space chart for a typical catalyst, showing the various temperature lines, has been drawn in Figure 12,. In actual practice, these lines were drawn on such a scale that the volume could be read easily to 0.01 ml. and the pressure to 1 mm. Hg. Provided that such details as the depth of immersion of the catalyst bulb in the salt bath were carefully controlled, these dead space measurements could be repeated with very small discrepancies. The maximum variation in readings was about 0.05 ml., and the average error was less than 0.02 ml.

After establishing the dead space measurement for any one temperature, the nitrogen was re-evacuated, and hydrogen admitted in measured volume. A certain pressure was obtained, falling steadily over a considerable period of time due to adsorption. At any specific time and pressure, the volume corresponding to the pressure could be read from the graph, and hence, by difference, the amount of hydrogen adsorbed. Divergencies from the ideal Gas Laws were too small to be considered in the circumstances of the experiment.

The hydrogen was admitted in three portions, giving pressures of approximately 250, 500, and 760 mm. Hg. in the catalyst bulb. In the first test attempted, the adsorption was carried out at a temperature of 350°, immediately after dead space measurement, as stated above. An attempt at repetition after evacuation to 7 mm. pressure gave a very different result, as shown in Table 5.

TABLE 5.

Catalyst.	Volume of hydrogen adsorbed. (ml. per 100 gm.)		
	At 250 mm.	500 mm.	760 mm.
Test 1.	10	16.5	24.0
Test 2.	3	4.0	6.0

These, with similar results for another sample of the catalyst, suggested that simple evacuation at the working temperature was insufficient. The tests were, therefore, repeated, but between the two adsorptions the temperature was raised to 500°C. during the evacuation, and maintained at this level for an hour, at the lowest obtainable pressure. After this the temperature was again reduced to 350°, and the second adsorption measured. It will be seen from the table below that much more consistent results were obtained.

TABLE 6.

Catalyst.	Volume of hydrogen adsorbed. (ml. per 100 gms.) At 250 mm.	500 mm.	760 mm.
Test 1	8	19	25
Test 2	9	20.5	26.5

These results made it clear that a more efficient system of evacuation was necessary, as pressures of the order of 7 mm. were not low. Arrangements were, therefore, made to instal a rotary vacuum pump, but experiments were continued with the first method of evacuation in the meantime.

The results above are expressed in ml. of gas adsorbed per 100 gm. of the catalyst. This reduction to a common weight basis was obviously necessary in view of the varying densities of the catalysts. The results could be expressed on a common volume basis, but it was found in practice that an exact determination of 5 ml. or so of a granular solid was difficult, whilst the weight was much easier to determine (p. 60.). The actual weight involved in these determinations was 2-4 gm., and the volume of gas adsorbed was of the

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Figure 13.

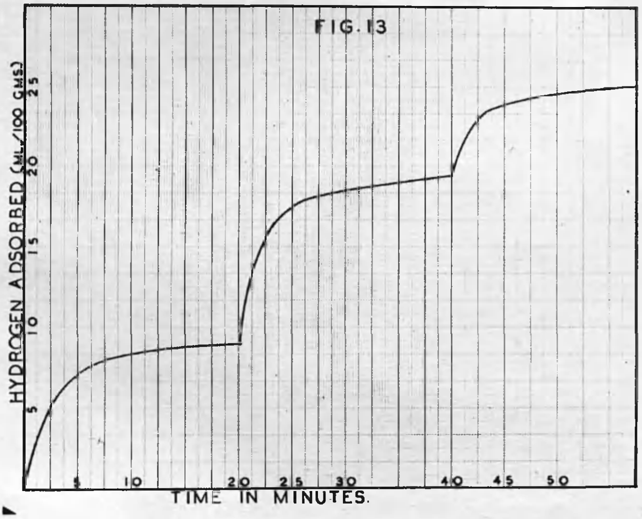
HYDROGEN ADSORBED (ML./100 GMS)
5
10
15
20
25
5
10
20
25
30
40
45
50
TIME IN MINUTES.

FIG. 13

order of 1 - 2 ml. As the error of measurement was not greater than ± 0.05 ml. (p. 67) and probably of the order of ± 0.02 ml., the adsorptions, as given, are correct to about 0.2 ml. (for the 100 gm. unit). As will be seen, all figures are given to the nearest 0.5 ml., which is well within the limit of accuracy of the observations. The figures given in the pages to follow have all been stated in this form.

The adsorption was found to proceed at a measurable velocity, which fell off rapidly and ultimately became very slow. Table 7 shows the readings taken in a typical test, and curves showing volume adsorbed plotted against time are shown in Figure 13. It will be seen from these that an arbitrary period was allowed for adsorption at any one pressure before proceeding to the next pressure level by the admission of more hydrogen.

The bulk of catalytic reactions, and in particular the synthesis or decomposition of methyl alcohol, are completed in a few seconds, and it is very improbable that the later stages of adsorption play any part in such reactions. It is obvious that the reaction is largely determined in the early stages, and this made necessary the fixing of some arbitrary period for measurement of this stage of

TABLE 7.

Adsorption at 350°C.   2.35 gms.   Catalyst No.3.

Time in mins.	Burette reading.	Difference.	Total volume at N.T.P. (ml)	Manometer A.	Manometer B.	Difference.	Pressure in mm. Hg.	N_2 equivalent in ml.	H_2 adsorbed in ml.	H_2 in ml./100 gms.
0.00	20.22			879.5	61	758.5	0.02			
15 secs.	17.64	2.58	2.42	675	196.5	478.5	280			
30 secs.				682	189	493	265.5	2.25	0.17	≡ 12.8
1.0				685	186	499	259.5	2.19	0.23	
2.0				687	184.5	502.5	256.0	2.15	0.27	
5.0				689	183	506	252.5	2.12	0.30	
20.0				695	177	518	240.5	2.02	0.40	
15 secs.	15.20	2.44		574	288	286	472.5	4.19	0.52	0·25 ≡ 10.6
30 secs.			4.71	577	286	291	467.5n	4.13	0.58	
21.0				578	284	294	464.5	4.11	0.60	
22				579	283	296	462.5	4.08	0.63	
25				580	282	298	460.5	4.08	0.65	
40	19.88			585	277.5	307.5	451.0	3.97	0.74	
15 secs.	16.18	3.70		424	425.5	+1.5	760	7.36	0.83	0·27 ≡ 11.1
30 secs.			8.19	425	424	1	757.5	7.33	0.80	
1.0				426	423	3	755.5	7.31	0.88	
2				427.5	421	6.5	752	7.27	0.92	
5				431	417	14.0	744.5	7.18	1.01	
20				435	413.5	21.5	733	7.10	1.09	

Total (to 733 mm.) = 34.5

adsorption. The period was taken to be the first five minutes after admitting the gas (See figure 13), while a further period of fifteen minutes was allowed for saturation before admitting the next portion of gas. The second five minute adsorption was measured from the point reached just before the fresh addition of gas. The method of computation is made clear by inspection of Table 7.

The actual adsorption proceeds at a much reduced rate, for a long time. In one case, hydrogen was still being adsorbed after 24 hours. The curves of Figure 13, p.70 have been selected as typical of most results, and show that after twenty minutes, the rate of adsorption is very slow, while the bulk of the gas is adsorbed over the first five minutes. Quite apart from any question of activity in reaction, it would have been impossible to carry out investigations in a reasonable time had the adsorptions been carried to completion. The rate of adsorption may also indicate the nature of the catalyst surface, and an active catalyst will probably give a greater velocity of adsorption than a comparatively inert surface.
The choice of a five minute adsorption period was therefore, considered to be fully justified, and all adsorptions throughout this work are based on this.

The fifteen minute period following sufficed to saturate the surface of all but the less active adsorbing agents. The characteristic adsorption for the next pressure level was then obtained with the further addition of gas.

Attempts were made to remove the hydrogen after adsorption by evacuation. The following table shows the results obtained from four such attempts:-

TABLE 8.

Test.	Hydrogen added. ml.	Adsorbed. ml.	Evacuated. ml.	Dead Space. ml. (Fig. 12).
1	12.45	0.80	11.80	11.65
2	12.50	0.80	11.55	11.70
3	11.10	1.45	9.65	9.65
4	12.15	1.30	10.60	10.80

It is clear from these figures that the amount of permanent gas which could be removed was only equivalent to the volume of the dead space. These figures were for evacuation at adsorption temperature, but on heating the catalyst up to 500°, no more gas was obtained. As this treatment was sufficient to remove adsorbed molecules from the surface, it was clear that a condensible vapour, which, in the circumstances, could only be water, had been removed from the catalyst. This water would migrate to cooler parts of the adsorption system and there condense wholly or in part. The system of evacuation, by reducing only to 7 mm. pressure, would be inadequate to remove these traces of water. It would be necessary to introduce a scouring gas, such as dry nitrogen, in order to complete removal. After these tests, therefore, scouring with nitrogen gas was combined with the evacuation at 500°C., although it was hoped that a better system of evacuation would render this unnecessary.

The non-reversibility of the adsorption is in accordance with the work of Garner and Kingham (Trans. Farad. Soc., 1931, 27, 322), while the effect of water in checking adsorption on a zinc oxide surface was also demonstrated by Burwell and Taylor (J.Am.C.S., 1936, 58, 1753). These adsorptions are therefore of the type generally styled Chemi-sorptions, although, as pointed out in the general introduction (p.41) the dividing line between these and the reversible adsorption is difficult to discern. As a result, the surface of the catalyst during a series of adsorptions is gradually changing, and in all probability the amount adsorbed will gradually change also. The catalysts used in the formation of methanol would not appear to be of a fully reduced type (Roy, Ph.D Thesis.) and the first few adsorptions are, therefore, of greater interest from this point of view. It was clear, however, that the number of adsorptions measured on any one sample of catalyst must be limited in order to ensure comparable results.

Using the same system of evacuation, a series of experiments were carried out with a sample of catalyst 6, measuring adsorptions at 350, 400, and 450°C. These adsorptions were measured in turn, evacuating at 500° and sweeping with nitrogen between each test. As stated above, all figures are given for the five minute period following the admission of hydrogen gas. The results obtained are shown in Table 9 below.

TABLE 9.

Temperature. °C.	Adsorption in ml. per 100gms. Catalyst. at 250 mm.	500mm.	760 mm.	Total.
350	10	5.5	4.0	19.5
400	15.0	6.5	3.0	24.0
450	16.5	4.5	9.0	30.0

These results were somewhat surprising, as they indicate at first glance an adsorption with a negative temperature coefficient. Were these

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Figure 14.

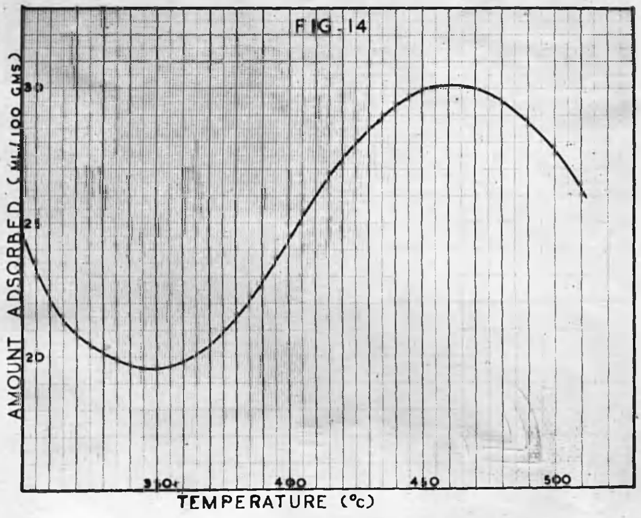

FIG. 14

AMOUNT ADSORBED (ML/100 GMS)
30
25
20
350
400
450
500
TEMPERATURE (°c)

figures the expression of a single type of adsorption, then the heat of this adsorption would be negative, from the relation

$$\log \frac{V_1}{V_2} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(Where V_1 and V_2 are the volumes adsorbed at T_1 and T_2 while λ is the heat of adsorption).

Taylor and Struther (J.Am.C.S., 1934, 56, 586) had noted a similar phenomenon with zinc oxide, and attributed the effect to another type of adsorption, manifested only at higher temperatures. It can therefore be supposed that a second type of adsorption is manifested on Catalyst 6 with a measurable velocity at a temperature range between 300 and 350°C. This, provided that the catalyst is not perfectly homogeneous, would give a curve of the type shown in Figure 14.

To investigate this hypothesis further, another catalyst, No.2, was tested under the same conditions. The temperature range was extended to 300°C., an adsorption at this lowest temperature being carried out after the other three, for comparison with Catalyst No.6. The results are shown in Table 10.

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Figure 15.

FIG 15

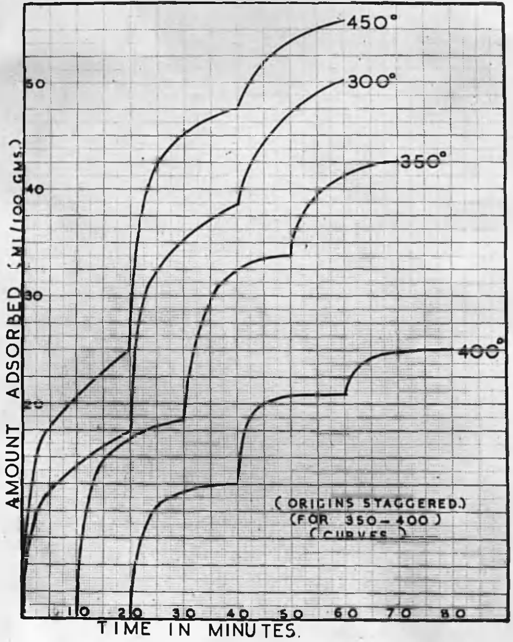
450°
300°
350°
400°
(ORIGINS STAGGERED.)
(FOR 350-400)
(CURVES.)
AMOUNT ADSORBED (ML/100 GMS.)
50
40
30
20
10
20
30
40
50
60
70
80
TIME IN MINUTES.

TABLE 10.

Temperature °C.	Adsorption in ml. per 100 gms. catalyst. at 250 mm.	500 mm.	760 mm.	Total.
300	12.0	15.0	6.0	33.0
350	14.5	11.0	6.0	31.5
400	10.5	7.5	3.5	21.5
450	18.0	17.5	4.5	40.0

From these figures it will be seen that a second type of adsorption is again suggested, but that with Catalyst 2, it does not occur with measurable velocity until a temperature above 400°C. has been reached. A normal fall in adsorption from 300° to 400° is therefore followed by a rapid increase to a much higher value at 450°C. The form of the time volume curves for these tests is also interesting (Figure 15). It will be seen that the rate of adsorption increases steadily from 300° to 400°, and is followed by a decrease as the temperature rises further. This would suggest that the second type of adsorption is still slow, compared with the first, as might have been expected. It has been supposed by previous workers that the velocity of activated adsorption is too slow for measurement at ordinary temperature, and this adsorption appears only when a measurable velocity is reached by elevation of temperature. The gases, once adsorbed, are held at a lower temperature, and may interfere with the normal "van der Waals" adsorption (Howard, Trans. Farad. Soc., 1934, 30, 278). Curves of the form shown in these tests are to be expected on the basis of this hypothesis, which they appear to confirm. It must be remembered that the catalysts are in the form of a granular solid, and it is unlikely that the surface is of uniform activity throughout.

In the next stages of the work, the evacuation was carried out by a rotary oil pump, and the apparatus was suitably modified to work at lower pressures and over a wider temperature range.

This preliminary work has demonstrated that more than one type of adsorption occurs in the temperature range of catalytic activity. It has shown that the mode of preparation of the catalyst surface is an essential part of the measurement, while the nature of the ~~forces~~ force binding adsorbed hydrogen is such that it cannot be removed except as water.

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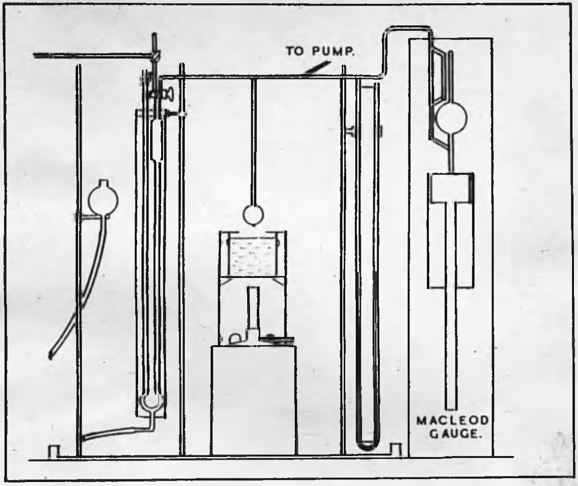
Figure 16

FIG. 16



EXPERIMENTAL.

Section 2.

Hydrogen Adsorption on Methanol Catalysts.

The adsorption system for this series of tests was modified as shown in Figure 16. As it was not proposed to collect gases evacuated from the system, the subsidiary burette shown in Figure 11 was discarded, while a somewhat larger water jacket for the main burette made possible the mounting of a levelling arm immediately adjacent to the measuring tube. The electric heating first adopted for the fused salt bath had given some trouble, as the fused nitrates were found to creep over the edge of the iron container, and into the insulating system of the heater. This was especially marked at temperatures above 450°C., and the work ahead was planned to include tests at 500°C. For this reason, the heater was replaced by a simple iron stand of cylindrical form with a ring to carry the salt bath and the heating was supplied by a Meker burner. It was found difficult to localise the heating with this arrangement, and gas taps in the vicinity were found to lose vacuum tightness due to heat unless constantly greased. The freedom from anxiety over the heating during a long test more than compensated

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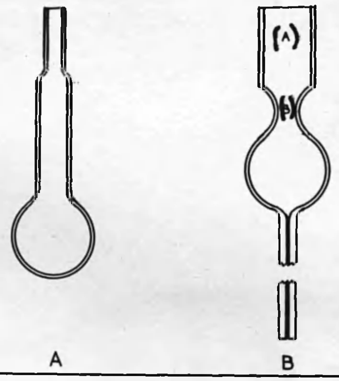
Figure 17.

FIG. 17



for this difficulty, and gas heating was used for the rest of the work. A pressure gauge on the burner inlet and a screw clip sufficed to control the temperature to within five degrees of the desired level.

The catalyst bulb, of hard glass, had originally been of the form shown in Figure 17a. This shape had the disadvantage that a large proportion of the total volume was just out of the salt bath, but closely adjacent to it, and therefore at an uncertain temperature. A silica bulb of similar form was tried and found to suffer from the same defect. The final form adopted is shown in Figure 17b, and was made up in Pyrex glass. The bulb was weighed, 5 ml. of the chosen catalyst introduced by means of the wide neck (A), tube and catalyst reweighed, and then sealed at the constriction (B) by means of a small flame, The bulb section was large enough to keep the catalyst out of the heated section while this sealing was done. When the sealed bulb was inverted and fixed in position, it could be immersed in the bath up to the capillary n neck, and the available free space was almost entirely in the salt bath.

The evacuation was carried out with a rotary Hyvac pump, claimed to give 0.001 mm. Hg. on a closed suction. Actually the degree of exhaustion, as measured by a Macleod gauge fixed at a point adjacent to the manometer was of the order of 0.02 - 0.03 mm. It will be realised that there were factors to be considered other than simple reduction of the pressure at the surface of the catalyst. The total free space of the system was necessarily as small as possible, to reduce errors in measurement. This meant the use of capillary glass leads, offering considerable resistance to the flow of gas at these low pressures. The temperature difference between bulb and leads also resulted in a difference in pressure between that indicated by an outside gauge and that existing in the bulb. It is not known what the actual pressure at the surface of the catalyst was during any evacuation; all that could be done was to reduce the external pressure to the same level for each test, and maintain a constant temperature for the final evacuation. Some attempts to determine the effect of varying degrees of evacuation are described later in this thesis (p. 81).

The temperature of the catalyst was taken, as before, to be the same as that of the fused salt bath. As no glass thermometer of the nitrogen filled type will stand prolonged immersion in a salt bath at a

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Figure 18.

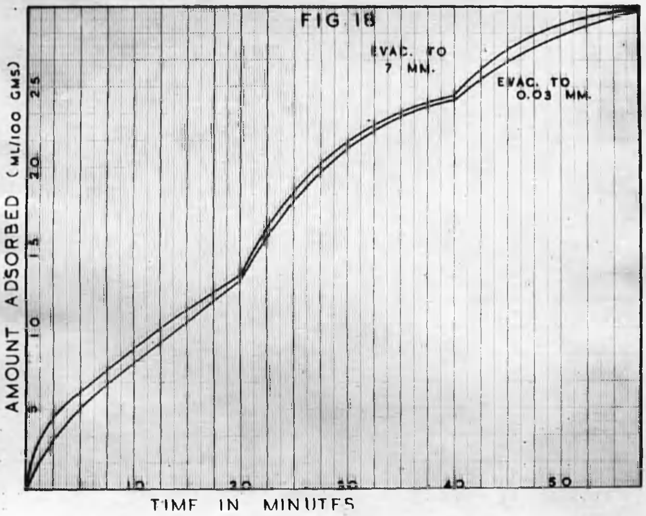
FIG. 18

EVAC. TO
7 MM.
EVAC. TO
0.03 MM.
AMOUNT ADSORBED (ML/100 GMS)
5
10
15
20
25
10
20
30
40
50
TIME IN MINUTES

tamperature of 500°, the temperature was measured by a copper constantan thermocouple contained in a thin hard glass sheath. Measurements in various parts of the bath showed even temperature distribution after a steady state had been reached.

The catalyst first tested in the new apparatus was a sample of No.4, which had shown abnormally low activity in the decomposition of methanol. The procedure of reduction was carried out as described on p. 65 , and the dead space was measured, using at first the old system, and reducing the pressure only to 7 mm. before measurement. The adsorption at 350° for hydrogen was then determined, starting with a pressure of 7 mm. and pre-evacuation at 500°, as in previous tests. The whole test was then repeated, but for evacuation the rotary pump was used, and the system pressure reduced to 0.03 mm. before both dead space measurements, and in the evacuation at 500° before test. The results obtained are shown in Figure 18, and were so much alike that it was concluded that the evacuation pressure was not important provided that it was reduced to 7 mm. or below. Later, however, it was found that the use of nitrogen before each adsorption measurement had aided the surface scouring very considerably (p. 84).

The volumes recorded, although in good agreement, were very much lower than the amounts of hydrogen adsorbed by either of the two other catalysts tested. This difference was most marked when only the five minute periods of adsorption were considered, as the adsorption was much slower than in the two other cases. Catalyst 4, after reduction, was a mixture of hard lumps and friable powder and seemed markedly heterogeneous in character.. Another sample was tested, and in order to give a wider range, adsorptions at 400° and 450°C., using the lower evacuation pressure, were also measured. The results are set out in Table 11.

TABLE 11.

Temperature °C.	Adsorption in ml./100 gm. catalyst. at 250 mm.	500 mm.	760 mm.	Total.
350	3.5	4.0	3.0	10.5
400	3.0	2.5	3.0	8.5
450	5.0	2.5	2.5	10.0

The amounts of gas adsorbed are much lower than in the case of the catalysts previously tested, and at all three temperatures the adsorption was much

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Figures 19 & 20

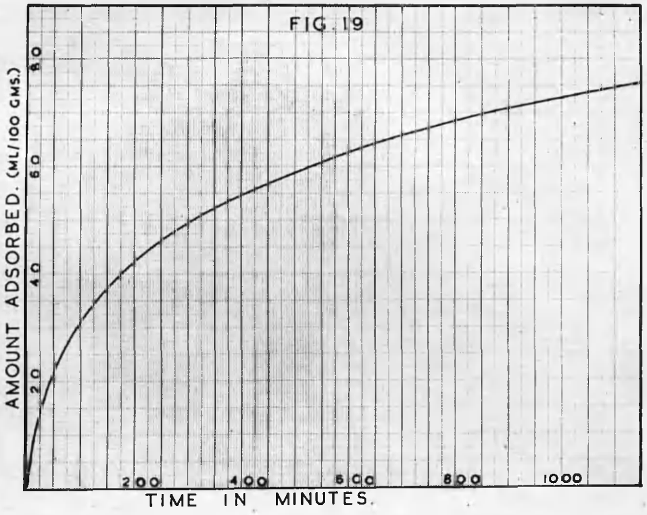
AMOUNT ADSORBED. (ML/100 GMS.)
8.0
6.0
4.0
2.0
200
400
600
800
1000
TIME IN MINUTES.

FIG. 19

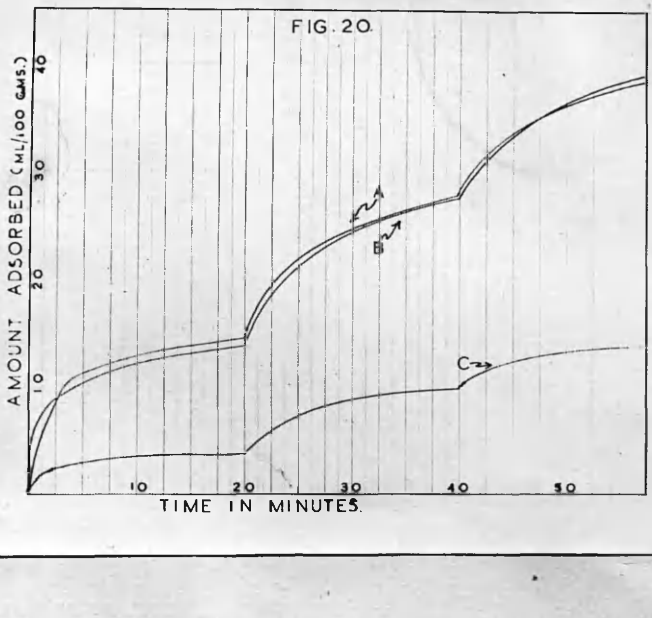
AMOUNT ADSORBED (ML/100 GMS.)
40
30
20
10
A
B
C
10
20
30
40
50
TIME IN MINUTES.

FIG. 20.

slower than had previously been observed. The low catalytic activity of this particular mixture has already been referred to, and it seems that there may be some connection between this and the low adsorption. It was in the course of the test at 350°C. that the adsorption was allowed to continue for a period of 20 hours. The results obtained are shown in Figure 19, and demonstrate the possibility of slow adsorptions of considerable final magnitude. As already pointed out, this fact made the fixing of an arbitrary adsorption period a necessity.

The temperature range would have been extended, but an accidental breaking of the catalyst bulb made it necessary to introduce a fresh catalyst. As the low adsorptive capacity of No.4 had been demonstrated, it was decided to make tests on catalyst 3, and a 5 ml. sample was duly inserted and weighed.

In an attempt to cut down the time taken for the tests, dead space determinations for the entire range 300° to 500°C. were made one after the other, and these were followed by a measurement of the hydrogen adsorption at 350°. This gave the results which are shown by curve A, Figure 20.

The catalyst was then re-evacuated to 0.03 mm. while heating to 500°, and maintained at this level for 30 minutes. After cooling to 350°, the adsorption test was repeated, with the results shown in curve C. The only departure from previous practice had been that nitrogen had not been used for sweeping at 500°. This operation was carried out, and a third adsorption test made. This gave the results shown in curve B, which agree very closely with those of the first test. This showed that the adsorbed gas on the surface could not be removed by simple evacuation, even to a much higher degree than had been used in the previous tests. The gas had to be removed by means of a scouring agent - nitrogen.

It is suggested that the mechanism of this scouring is as follows:- The nitrogen, present in large excess, saturates the surface of the catalyst completely, and prevents the more strongly adsorbed water molecules from returning when they, in the normal course of equilibrium evaporation, leave the active surface. The mixed water and nitrogen gases are then evacuated as a whole in the early stages of the pressure reduction. As the external pressure is reduced the weakly held nitrogen molecules distil off, and leave a clean surface for subsequent adsorption. It is necessary to suppose that in no case is the pressure at the surface of the catalyst low enough for the water molecules to be removed by evacuation alone. In view of the fact that the reduction of pressure in the outside system from 7 mm. to less than 0.05 mm. made no difference in the cleaning of the surface, it is suggested that the level of pressure at the catalyst surface was much higher than in the outside system. This was caused by the difference in temperature, and by the long capillary leads, as already indicated.

If the above suppositions are correct, then the mechansim of adsorption of the nitrogen is fundamentally different from the mechanism of adsorption of the hydrogen, and the dead space measurements are not quite accurate. Perhaps different parts of the surface are concerned in the two adsorptions, and the nitrogen molecules prevent the return of hydrogen or water molecules. In this case the nitrogen so held would rightly be included in the dead space measurements, as indicating space that another gas must fill. The amount must be small, as no difference could be detected in the volumes of dead space measured after evacuation at adsorption temperatures of 350°., and 500°C.

An interesting point arises when the adsorbed gas is released in combination with a component of the surface. This compound may then condense at ordinary temperatures. Then compound molecules, distilling slowly from the surface in accordance with Langmuir's hypothesis, will migrate in part to the cooler parts of the measuring system and condense there. Further molecules of the originally adsorbed gas will then be adsorbed on the vacated spaces, and not the compound molecules, pro rata to their concentration, as would have been the case had they remained in the neighbourhood in a gaseous state. From this there would be a fairly rapid attainment of equilibrium with the surface, followed by a slowly changing condition as the surface altered and the original gas was converted into the compound. This would appear as a slow adsorption of the gas, and such a phenomenon reinforces the arguments for the choice of a short adsorption period.

The two tests shown as A and C in figure 20 had established adsorption at 350°C. for catalyst 3. In order to confirm these, and to obtain results comparable with other tests, another sample of the same catalyst was measured and weighed into the unit,

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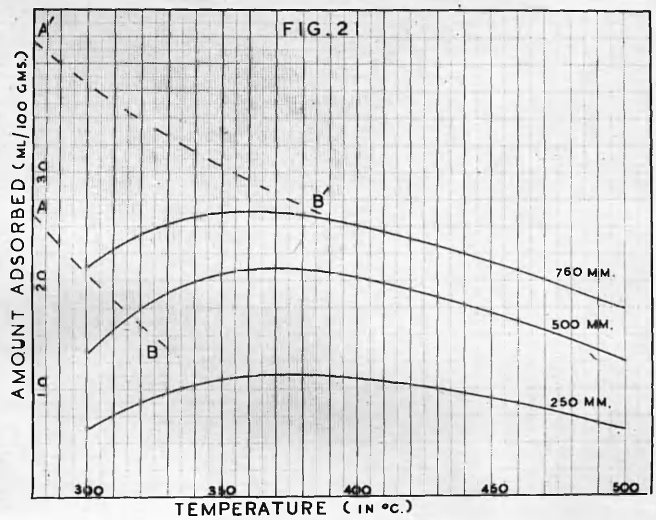
Figure 21

FIG. 2


A
A
B
B
AMOUNT ADSORBED (ML/100 GMS.)
30
20
10
760 MM.
500 MM.
250 MM.
300
350
400
450
500
TEMPERATURE (IN °C.)

and adsorptions over the whole range from 300 to 500°C. were measured, working from 350 to 500°C. and back to 300°. All adsorption measurements were preceded by a dead space measurement, and by nitrogen sweeping at 500°, followed by evacuation to a pressure of 0.03 mm. After maintaining at this pressure and temperature for 30 minutes, the catalyst was cooled to adsorption temperature, and the measurements commenced when the temperature was steady. In the test at 500° no cooling was necessary, and the experiment was started immediately after the evacuation period. It was not thought desirable to heat to higher temperatures, on account of the risk of sintering. The results obtained are set out in the following table:-

TABLE 12.

Temperature °C.	Adsorption (in ml. per 100 gms.) at 250 mm.	500 mm.	760 mm.	Total.
300	6.5	7.0	7.5	21.0
350	11.0	10.0	5.5	26.5
400	11.0	8.5	4.5	24.0
450	10.5	8.0	4.5	23.0
500	6.5	5.0	6.0	17.5

These figures are again represented in Figure 21, in which the adsorptions are plotted against temperature.

It will be seen that the volume adsorbed passes through a well marked maximum at 350°, indicating two types of activated adsorption. This change was not due to the order of the tests, as a check adsorption at 350°, after the 300° test, gave an adsorption of 27.5 ml.

Using these date, calculations were made of the heat of adsorption using the equation

$$\log \frac{V_1}{V_2} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where V_1 and V_2 are the volumes adsorbed at the temperatures T_1 and T_2 (in ° Abs.), R is the gas constant, and λ is the heat of adsorption.

Thus, for adsorption at 350°C. (623° Abs.) and 400°C. (673° Abs.), equation can be re-arranged to the following:-

$$\lambda = 2 \log \frac{26\cdot5}{24\cdot0}\left(\frac{1}{\frac{1}{623} - \frac{1}{673}}\right)$$

$$= 1650 \text{ gm. cals. per gm. mol.}$$

Similarly for adsorptions at 400° and 450°

$$\lambda = 850 \text{ gm. cals per gm. mol.}$$

and for adsorptions at 450° and 500°

$$\lambda = 5920 \text{ gm cals per gm. mol.}$$

These figures are far from consistent, but may be explained by the fact that what is being measured as a single adsorption was really two, or even more, types of adsorption superimposed one on the other. Reverting to Figure 21, a dotted line A - B might well be supposed to represent the form of the first adsorption measured at 300°, while on this the activated adsorption, first setting in with measurable velocity at 350°, can be represented by the line A′ - B.′ At the same time, sufficient remains of the first type of adsorption to give inconsistent results at the higher temperatures. Alternatively, it may be supposed that some parts of the catalyst surface are more active than others in bringing about the second type of adsorption. This again would make it difficult to measure accurately any definite value for the heat of adsorption.

The same factors will influence the determination of the apparent heat of activation. The calculation of this is based upon the equation

$$\log \frac{K_1}{K_2} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_1 and K_2 are the velocities of adsorption at the temperatures T_1 and T_2, E the heat of activation and R the gas constant. To obtain a

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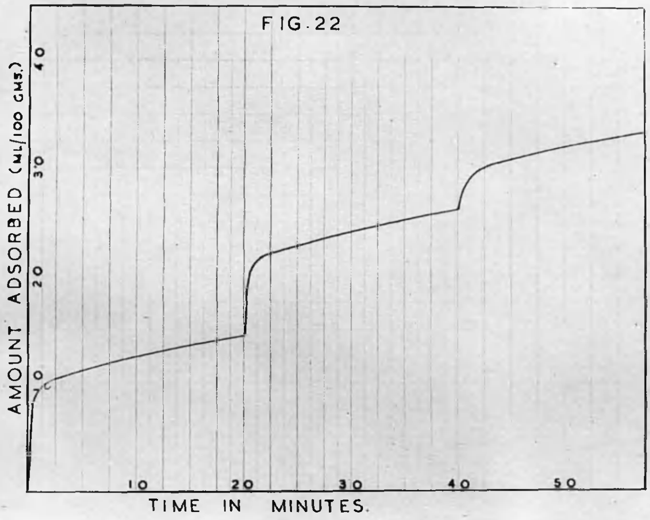
Figure 22

FIG. 22


AMOUNT ADSORBED (ML/100 GMS.)
10
20
30
40
10
20
30
40
50
TIME IN MINUTES.

value for the velocity of adsorption, curves were drawn for volume adsorbed against time, and an estimate made of the period required to reach half of the total adsorption during the first five minutes after admitting gas. These estimates were not very satisfactory, especially at the higher temperatures. The curves were necessarily extrapolated from the readings taken at 15, 30, and 60 seconds after admission of the gas. The actual time taken to admit a quantity of hydrogen was approximately 5 seconds, and readings before 15 seconds were almost impossible owing to oscillations of the mercury gauge. In Figure 22 the curve obtained for the adsorption at 450° is shown, and inspection of this shows the difficulty of estimating the half adsorption time. The actual figures are given in the table below.

TABLE 13.

Temperature. °C.	Half adsorption time (in seconds) at 250 mm.	500 mm.	760 mm.
300	27	15	35
350	25	25	35
400	17	20	27
450	5	9	25
500	2	3	4

It will be seen from the table above that the figures for the adsorption from 350° to 500° are fairly regular, and show a steady increase in rate of adsorption with temperature. The figures for the adsorption at 300° are abnormal, and are those which might be expected if another type of adsorption manifests itself at a temperature somewhere between 300 and 350°. The values for the heat of activation, calculated from the consistent range above, are as follows:-

TABLE 14.

Range. °C.	Heat of activation (g. c./g. m.) 250 mm.	500 mm.	760 mm.
350 - 400	6400	3720	4300
400 - 450	22000	14360	1400
450 - 500	20400	24400	40500

It would appear from these figures that the heats of activation for the adsorption at 350 - 400° are lower than at the higher temperature ranges. In view of the uncertainty of the basic values, however, it was felt that any speculation on this point would be of little value. The only real observation that could be made was that a marked change in the type of adsorption had occurred between 300 and 350°.

More experimental data were required, utilising other catalysts.

In one ortwo of the tests on this last catalyst, some difficulty was experience in reducing the pressure to 0.03 mm. Hg. with the rotary oil pump alone. The system was, therefore, altered to include a mercury vapour diffusion pump as a final stage, using a rotary oil pump as a backing unit only. The services were also altered to eliminate all but two rubber joints, replacing the others with blown glass connections. With these alterations, it was found possible to obtain an end pressure of 0.02 - 0.03 mm. This might have been still further improved by wider pipe connections, but in view of the conditions existing at the surface of the catalyst (p.85) a lower pressure was not considered necessary.

Some little time had elapsed since the work had commenced, and the catalysts might have been changing slowly, so it was decided to carry out a complete series of tests, using the whole range of catalysts, and the experimental technique settled on the lines of the last series of tests described. The catalysts had actually been made up at the beginning of 1937. These tests were carried out about one year later.

The results obtained for hydrogen adsorption are given in Table No.15. All figures are, as before, expressed as ml. per 100 gms. of catalyst and are obtained over the first five minutes after admitting the three portions of gas. As the only change made from the last tests was the adoption of a slightly more efficient evacuation system, the results for Catalyst 3, as set out on page 87 - Table 12, were accpeted as satisfactory. The figures of the complete table are represented graphically in Figures 23 and 24.

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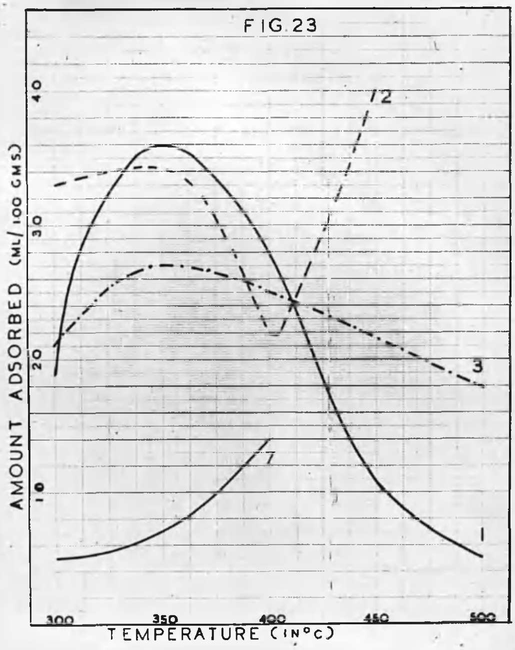
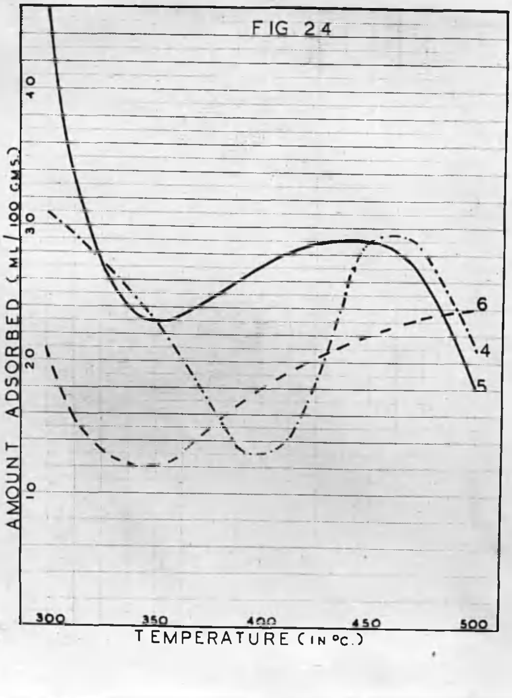
Figures 23 & 24

FIG. 23



40
30
20
10
AMOUNT ADSORBED (ML/100 GMS.)
300
350
400
450
500
TEMPERATURE (IN °C)
1
2
3

FIG. 24



40
30
20
10
AMOUNT ADSORBED (ML/100 GMS.)
300
350
400
450
500
TEMPERATURE (IN °C.)
4
5
6

Table 15.

Catalyst No.		Adsorption (ml. per 100 gm. catalyst)									
		300		350		400		450		500	
1.	250 mm	5	19	12	36	11	28	5	11	1	5
	500 mm	9		16		8		3		2	
	760 mm	5		8		9		3		2	
2.		6	33	15	34	4	22	4	40		
		15		12		7		17			
		12		7		11		19			
3.		7	21	11	27	11	24	10	23	7	18
		7		10		9		9		5	
		7		6		4		4		6	
4.		14	31	10	23	7	13	9	29	7	21
		9		6		5		10		10	
		8		7		1		10		4	
5.		12	46	5	23	10	27	11	29	9	18
		18		10		10		8		9	
		16		8		7		10		0	
6.		6	21	5	12	6	18	7	22	8	24
		7		5		5		9		11	
		8		2		7		6		5	
7.		3	5	6	7	10	14				
		2		1		4					
		0		0		0					

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Figures 25 and 26.

FIG 25

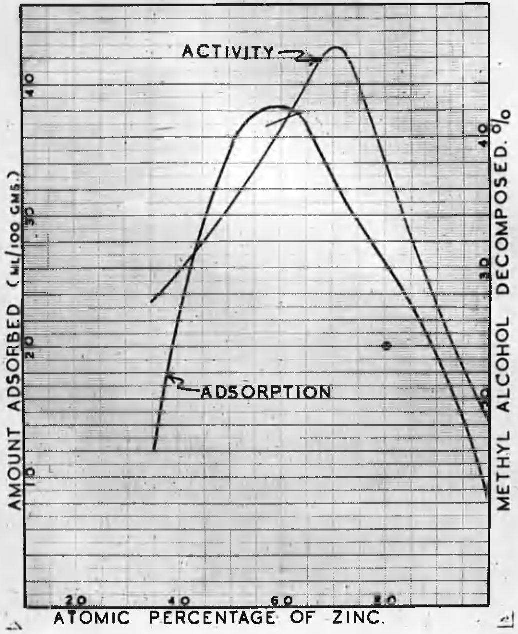
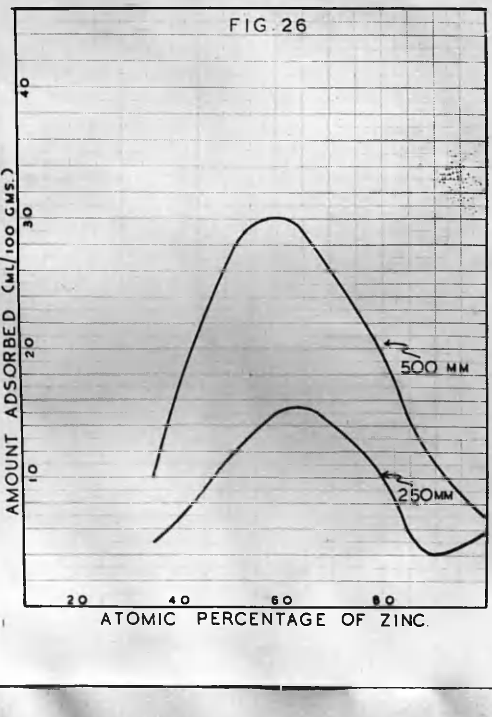

ACTIVITY
ADSORPTION
AMOUNT ADSORBED (ML/100 GMS.)
10
20
30
40
METHYL ALCOHOL DECOMPOSED. %
20
30
40
20
40
60
80
ATOMIC PERCENTAGE OF ZINC.

FIG 26


AMOUNT ADSORBED (ML/100 GMS.)
10
20
30
40
500 MM
250MM
20
40
60
80
ATOMIC PERCENTAGE OF ZINC.

These results were unconvincing, and their interpretation obscure. The sample of catalyst 4 had shown results much more in agreement with those of other catalysts, but this was not so surprising when the nature of this catalyst was considered. As already stated, the reduced material had contained hard lumps and a friable powder, and it was probable that errors in sampling had played some part in this discrepancy. An attempt might be made to group the catalysts in the two sections shown in Figures 23 and 24 respectively. In the first of these, portrayed in Figure 23, an activated adsorption is manifested at about 350°C., while in the second (Figure 24), this adsorption does not appear till about 450°C.. Such a grouping is, however, a little artificial.

In view of the very vague nature of these indications, it was rather surprising to find that when the amount of hydrogen adsorbed at 360° was plotted against molecular percentage of zinc in the catalyst, a curve closely resembling the corresponding activity ratio (Figure 19, h.co) was obtained. This result is set out in Figure 25, in which the activity curve is also drawn for comparison. The adsorptions are given as totals for the pressure of 760 mm., but the adsorptions for the two lower pressure levels, shown in Figure 26, form

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Figures 27 and 28.

FIG. 27

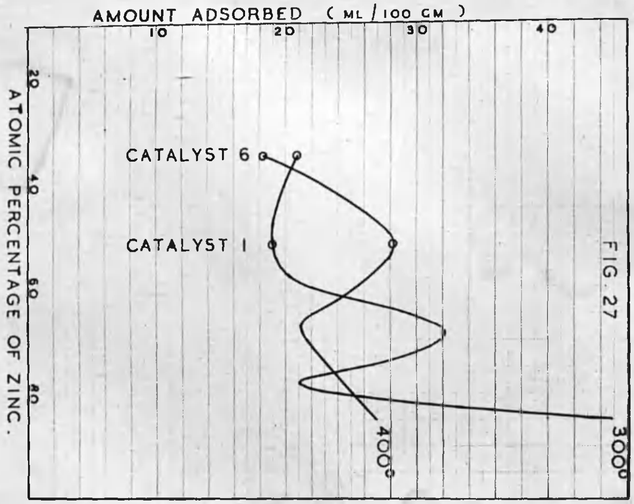
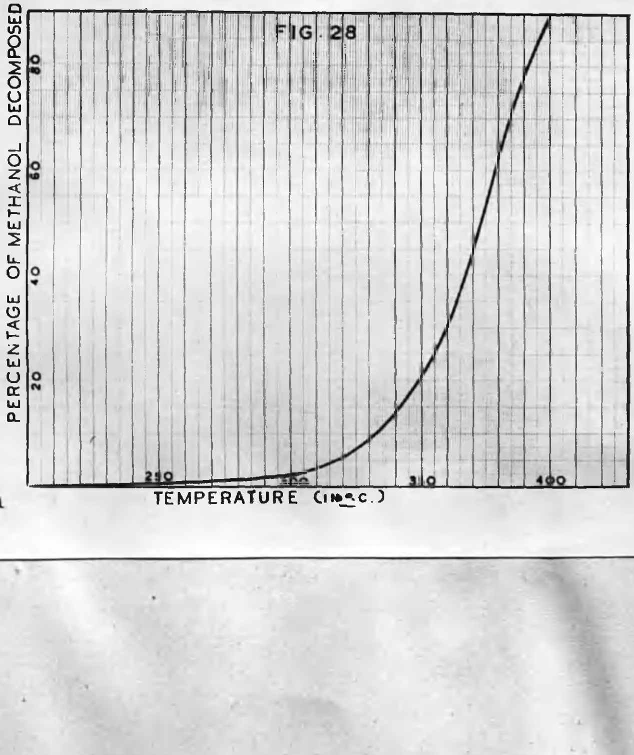

AMOUNT ADSORBED (ML / 100 GM)
10
20
30
40
ATOMIC PERCENTAGE OF ZINC.
20
40
60
80
CATALYST 6
CATALYST 1
400°
300°

FIG. 28


PERCENTAGE OF METHANOL DECOMPOSED
20
40
60
80
TEMPERATURE (IN °C.)
250
300
350
400

curves of practically the same form. The maxima of adsorption and activity occur at very much the same catalyst compositions, while catalyst 4, even with the newer figures, is still abnormal in both properties.

The unique feature of these curves at 360° is shown by the corresponding data for the adsorptions at 300 and 400°C. (Figure 27) Here there is no clearly marked maximum, and correlation with activity is impossible unless the relative activities of the catalysts change rapidly over a narrow temperature range. An attempt was made to determine activity at 300 and 400° in order to clarify this position. It was found that the decomposition of methyl alcohol was very slow at 300, while at the higher temperature the decomposition had become extremely rapid.

Another worker (A.R.Roy, Ph.D.thesis, 1940) had carried out tests on this point with the results shown in Figure 28. These decompositions were made with a different range of catalysts, and in a somewhat different manner. The tests were, however, comparable and illustrate one of the failings of a dynamic test. In order to obtain measurable decomposition at 300°, it was necessary to choose a time of contact which gave almost complete~~x~~ decomposition at 400°. Then in this second case, the rate of decomposition tends to become a measure of the rate at which the reacting molecules can diffuse through the layers of inert gas on the surface rather than a measure of activity at that surface. This is an inevitable fault of a dynamic system in which true equilibrium is never established. Bearing these facts in mind, it is doubtful if very reliable indications of the relative activities can be obtained at the two ends of the temperature scale.

Two catalysts, nos. 1 and 6, were chosen, and their activities measured at 300, 360, and 400°C. The apparatus used has already been described (P.53) The results obtained are shown in Table 16.

Table 16.

Catalyst No.	Percentage of methanol decomposed At 300°	360°	400°C.
1	7	38	68
6	6	27	54
	Adsorptive capacities (ml/100gm)		
1	19	36	28
6	20	12	18

(The adsorptions shown are from the Figures 23, 27, and 24, and the position of the catalysts chosen is indicated in the~~se~~ figure~~s~~ 27.)

The two catalysts show the greatest difference between each other, for both reaction and adsorption, at 360°C., but there seems to be little connection between amount of adsorption and decomposition. Had the amount of methanol decomposed by catalyst 1 at 400° been higher, something might have been made of the figures. It is therefore proper to recall the arguments of the two previous pages, and to note that the amount decomposed may be too small. These comparatively inert catalysts are better than those prepared by Roy (loc.cit.) from the point of view of measurement of activity. Even so, the amount decomposed was only 68%, and it is doubtful whether the arguments mentioned above are fully applicable.

In the circumstances it was felt desirable to investigate the adsorption of the other component of the reaction - carbon monoxide. The moment was thought opportune for the introduction of a new adsorption unit, which had been built up while the earlier work was in progress.

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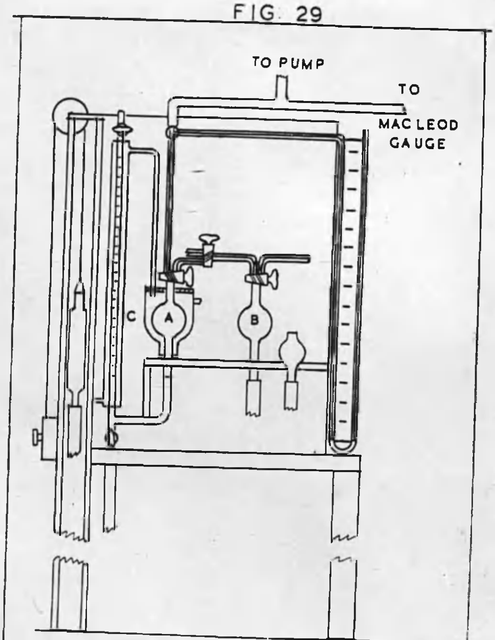
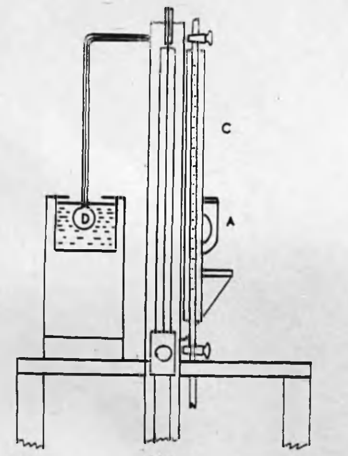
Figures 29 and 30

FIG. 29



FRONT ELEVATION

FIG. 30



SIDE ELEVATION

EXPERIMENTAL.

Section 3.

The Adsorption of Carbon Monoxide on Methanol Catalysts.

The adsorption apparatus described and used in the first section of this work suffered from various disabilities. Experience showed that the measuring device, which had been improvised from a disused Haldane apparatus, could be improved with advantage. The evacuation of gases for measurement was slow and inaccurate. The largest amount of gas which could be admitted to the catalyst bulb at any one time was only 5 ml., and this was measured by difference from a larger volume of about 25 ml. A change in the nature of the gas used made it necessary, with this type of measuring vessel, to employ five times as much gas as was actually required. While this was not a serious matter when only cylinders of hydrogen and nitrogen were being used, the introduction of carbon monoxide, which had at first to be made in the laboratory, necessitated a more economical usage.

The adsorption unit which was designed to overcome these difficulties is shown in Figures 29 and 30. The individual pieces of glassware were made by a local glassblower (Messrs. McCulloch Bros.), and the wooden framework was constructed in the Royal Technical College Workshops. The apparatus consists of a fixed volume bulb A, enclosed in a water jacket, and connected with a water jacketed measuring scale C. This scale was divided into 1000 divisions of equal length, over a total graduated portion of 20 inches. The gas pressure in the bulb A could thus be measured to an accuracy of 0.1%. By varying the size of this bulb, the apparatus could be modified to give gas measurements over a wide range of volume, while retaining the same proportionate accuracy of measurement. As will be seen from the figures, the scale was so arranged that the gas pressure in the bulb was always less than atmospheric, and, in consequence, variations from the Gas Laws could be disregarded, and the pressure taken to be directly proportional to the volume of gas in A.

The total volume of the bulb A, from stopcock at the top to a mercury meniscus on the measuring mark at the base, was determined by filling with distilled water at known temperature, discharging slowly, and weighing. The error due to drainage was estimated by discharging at rates varying from 2 minutes up to one hour, and assessing weight for infinitely slow discharge. The method of weighing the amount of mercury required for filling would have given an inverted meniscus at the base of the bulb, and this water method was deemed preferable. With the bulb of 27.65 ml. capacity (at 15°C.) used in the carbon monoxide experiments, the maximum variation due to drainage was only 0.2 ml.

The gas contained in this bulb was measured at a mercury pressure indicated by 1000 divisions of the scale C, or less. The total height of these 1000 divisions above the zero mark on the base of the bulb A, which was set exactly level with the zero of the scale, was 50.8 cm. The maximum volume of gas which could be measured was, therefore, $27.65 \times \frac{50.8}{760}$ or 18.48 ml. As previously stated, the scale C could be read to one thousandth part, and the accuracy of measurement was therefore equal to ± 0.018 ml., or slightly greater than in the first part of this work.

The temperature of the gas being measured was taken to be the same as that of the water in the jacket, and all gas volumes were corrected to N.T.P. As a steady stream of tap water flowed through the water jacket, all readings were taken at a temperature not far from 15°C., and variations in the volume of the bulb could therefore, be ignored.

Gas was admitted into the system through the bulb B, which also served as a receiver for the gas which could be evacuated, by the use of a Torricellean Vacuum, with the bulb A and the attached mercury reservoir. When evacuation was complete, the gas was re-transferred to the bulb A and measured. The analysis of this evacuated gas could then be undertaken by introducing reagents into the bulb B, as in normal gas analysis technique on units of the well-known Bone and Wheeler type. Analyses were carried out in two or three tests, but it was found that the wetting of the glass bulbs and leads during analysis gave so much trouble in re-drying that it was easier to pass the gas to a separate gas analysis apparatus.

The catalyst was contained in a hard glass bulb in the same way as before, and heated in a fused salt bath arranged at the back of the apparatus, as shown at D. Evacuation was by means of a mercury vapour diffusion pump of the all metal Kaye type, backed by a rotary oil pump as before. Only in the actual adsorption section of the unit was capillary tubing used, and all leads to and from the pumps were of at least 1 cm. bore. On the entire low pressure side there were only two rubber joints, which were painted with P~~u~~icien Wax, and all the remaining connections were fused together in situ.

As a result of these precautions, the pressure could be reduced to a level of 0.007 mm. at the Macleod gauge. It must be remembered that the actual pressure at the surface of the catalyst may have been much higher. The experimental practice of sweeping the catalyst surface with nitrogen at a temperature of 500°C. before each adsorption measurement was continued.

The carbon monoxide used in the tests was, in the first place, made in the laboratory by the decomposition of formic acid with syrupy phosphoric acid. The formic acid had previously been heated to boiling point to remove dissolved gases. The products of decomposition were cooled and then passed through a scrubbing tower against a current of caustic potash solution. The residual gas was over 99% soluble in acid cuprous chloride solution. It was stored over brine till required, and immediately before use was passed through alkaline pyrogallol solution to remove any traces of oxygen or carbon dioxide. Final drying, as before, was by means of freshly heated calcium chloride.

When the tests were commenced in the Spring of 1938, no other source of carbon monoxide was available, but in 1939 the British Oxygen Company started to market the gas in cylinders at a pressure of 100 atmospheres. This convenient source was made use of in one or two of the last tests. The gas was free from carbon dioxide, oxygen and nitrogen, and would have been an ideal material for all the work. The danger of such a quantity of very poisonous gas was guarded against by the use of a special cylinder key, and by storage outside the laboratory.

The first catalysts to be tested were those which had previously been used for the measurement of hydrogen adsorption. These had been prepared and reduced in the Spring of 1937, and stored subsequently in tightly stoppered bottles. Unfortunately, the stock of catalyst 1 was too small for tests to be made, so that the measurements were confined to catalysts 2 - 7.

As already stated, all the sample of catalyst had been reduced with methyl alcohol vapour at 360°C., and then stored in tightly stoppered bottles. After weighing a 5 ml. sample into the adsorption tube, and connecting up the apparatus, the catalyst tube was first evacuated, and then heated up in an atmosphere of hydrogen, raising the temperature to 500°C. in 60 minutes.

After maintaining at this temperature for a further 30 minutes, the catalyst tube was again evacuated to a pressure of 0.007 mm. The temperature was then lowered to the required levels and dead space measurements with nitrogen carried out. The surface was then scoured with nitrogen at 500°, and measurements of carbon monoxide adsorption at 300, 360, and 400°C. were made. Between each measurement, the catalyst surface was scoured with nitrogen at 500°, as already specified for comparable conditions. Although it was now possible to add in a single operation the amount of gas required to give a pressure of 760 mm., it was decided to adhere to the previous method. The carbon monoxide was therefore admitted in three stages, at the end of 20 minute periods, in amounts calculated to give pressures of 250, 500, and 760 mm., at the end of each period. The adsorptions given in the table below were measured, as before, over the first five minutes after admitting the carbon monoxide. The results recorded in Table 17 are also given graphically in figures 31, 32, and 33.

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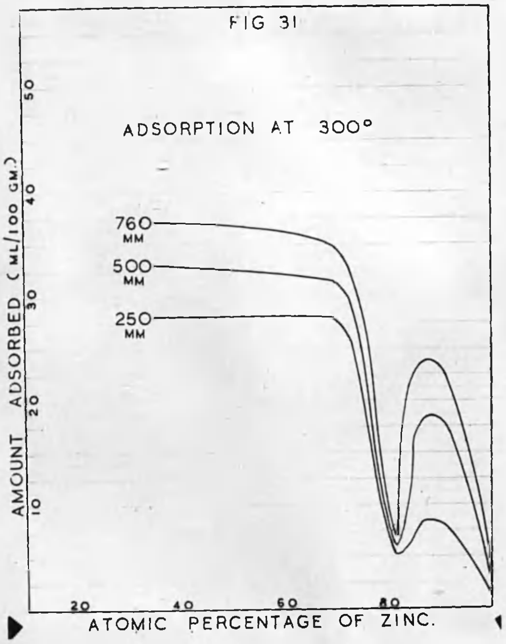
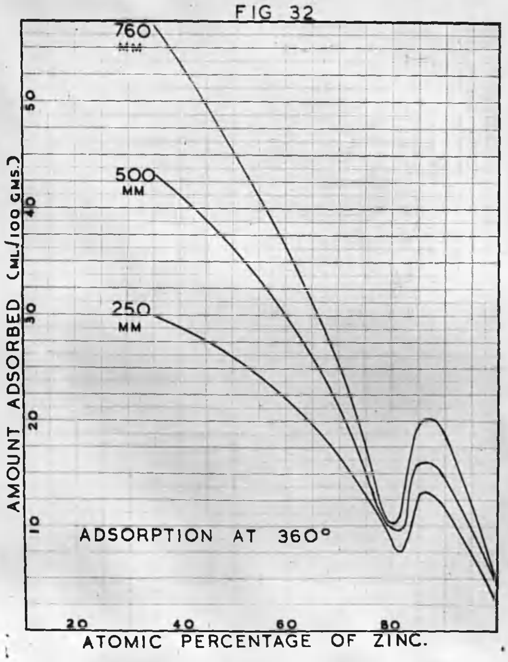
Figures 31 and 32.

FIG 31



ADSORPTION AT 300°

FIG 32



ADSORPTION AT 360°

Table 17.

Catalyst	Adsorption (ml./100 gm. Catalyst)					
	300°		360°		400°C.	
2	28	35	17.5	27	21.5	27.5
	3.5		5.5		4.5	
	3.5		4.0		1.5	
3	13	15	10.0	10.5	16.0	18.5
	2		0.5		2.5	
	0		0.0		0.0	
4	5	7	7.5	10.5	7.0	9.5
	1		2.0		2.0	
	1		1.0		0.5	
5	7	23	13	20	14.0	18.5
	10		3		2.0	
	6		4		2.5	
6	28	37	30	57	18	36
	5		13		4	
	4		14		14	
7	1.0	3	2.5	4	7.0	10
	1.5		1.5		1.5	
	0.5		0.0		1.5	

These figures show, in the first place, a high adsorptive capacity for carbon monoxide with catalysts containing a high proportion of

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Figures 33 and 34.

FIG 33

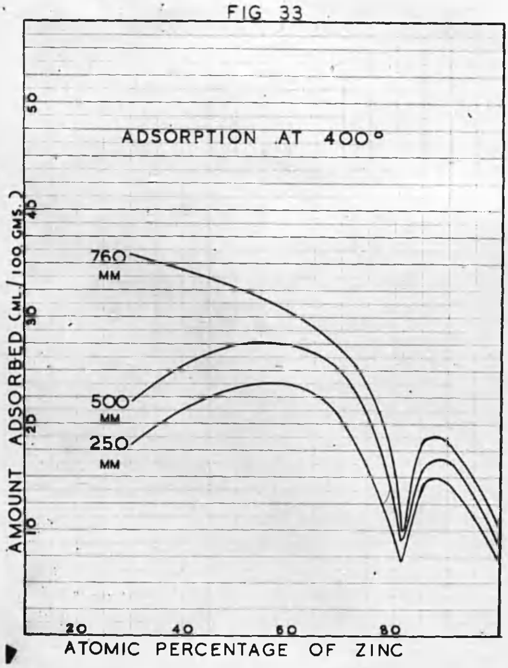
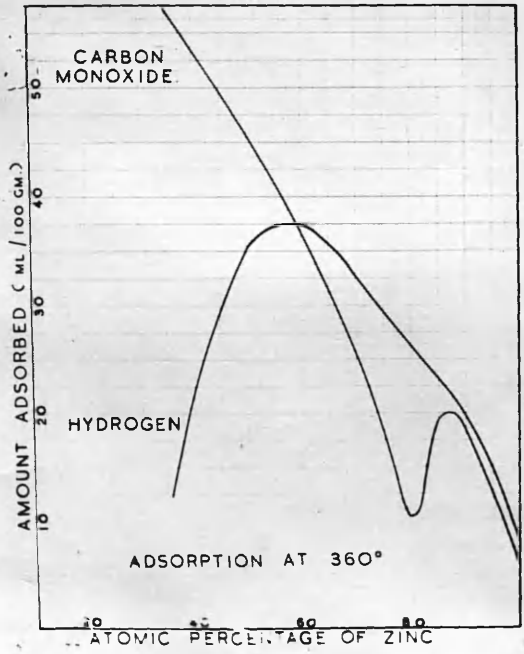

ADSORPTION AT 400°
AMOUNT ADSORBED (ML./100 GMS.)
50
40
30
20
10
760 MM
500 MM
250 MM
20
40
60
80
ATOMIC PERCENTAGE OF ZINC

FIG 34


CARBON MONOXIDE
HYDROGEN
ADSORPTION AT 360°
AMOUNT ADSORBED (ML/100 GM.)
50
40
30
20
10
20
40
60
80
ATOMIC PERCENTAGE OF ZINC

chromium. This is in sharp contrast to the adsorptive capacity of these catalysts for hydrogen, as will be seen from the Figures 25, 26, and 27. The adsorptive capacity appears to fall to a minimum with a catalyst containing 80% (atomic) of zinc, although this minimum was reached with catalyst 4, which had previously given such anomalous results with hydrogen. The general shape of the adsorption curve is well established, however, and the minimum adsorptive capacity is exhibited at about the same point if the results for catalyst 4 are ignored. As the zinc content of the catalyst increases beyond this 80% value, the adsorptive capacity appears to increase again to a maximum value with a zinc content of 87%. There follows another fall to the low capacity exhibited by the pure zinc oxide.

As the activity tests were carried out at 360°, adsorptions for this temperature for both hydrogen and carbon monoxide are shown side by side in Figure 34. The curves show total adsorption plotted against catalyst composition. The peak of catalytic activity, it will be remembered, occurs with a catalyst composition of about 67%

of zinc, or nearly in the same place as the adsorption peak for hydrogen. There is no such correlation between carbon monoxide adsorption and activity, for at this particular composition the adsorption is falling steadily towards a minimum capacity, but has not nearly reached this point. The only interesting feature of the carbon monoxide adsorption at this maximum activity point is that it shows nearly the same value as the hydrogen curve. The catalyst composition for maximum activity, therefore, is one which gives approximately equal adsorptive capacities for both hydrogen and carbon monoxide.

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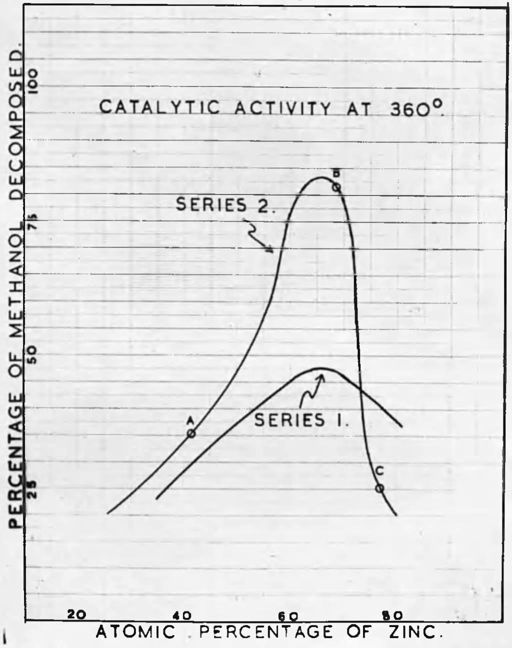
Figure 35.

FIG 35


CATALYTIC ACTIVITY AT 360°
SERIES 2.
SERIES 1.
A
B
C
PERCENTAGE OF METHANOL DECOMPOSED.
100
75
50
25
20
40
60
80
ATOMIC PERCENTAGE OF ZINC.

EXPERIMENTAL

Section 4.

Adsorption on More Active Catalysts.

Another series of catalysts of the same nature as those tested were available in the College. They had been prepared by A.R.Roy in the course of his work on the synthesis of methanol (Roy - Ph.D. Thesis, 1940). The method of manufacture was the same as that already described in the course of this thesis (P.47), but the reduction process was so modified as to eliminate the overheating phenomenon.

In place of methanol vapour alone, a mixture of methanol and nitrogen was used, and the concentration of methanol kept so low that no temperature change could be detected during the reduction. As a result of these precautions, not only was the abnormality shown by catalyst 4 avoided, but the whole range of catalysts showed a greatly increased activity in the decomposition of methanol. Figure 35 shows the relative activity of the two series of catalysts, Curve 1 showing the range of catalysts studied in the previous sections of the work, while Curve 2 shows the catalysts prepared by Roy. The method of assessing activity was not quite the same, as a diluting gas was used in the tests for Series 2. This change, however, could only tend to diminish the apparent activity slightly, and the position of maximum activity set by the general form of the curve will be unchanged.

Three typical catalysts were chosen from this second series, having compositions as shown in the table below. Their places in the graph of activity are indicated in Figure 35.

Table 18.

Catalyst A	41.5% Zinc	(Atomic)
Catalyst B	68.8% Zinc	(")
Catalyst C	77.0% Zinc	(")

These catalysts were now tested for adsorptive capacity with both hydrogen and carbon monoxide, at the single temperature of 360°C..

It was found that the adsorptive capacity of all three was much greater than that of any other catalyst previously tested. The volumes of gas adsorbed were sufficient to reduce practically the whole of the catalyst sample to the metal, and the problem of change of surface during measurement became much more important. It was therefore

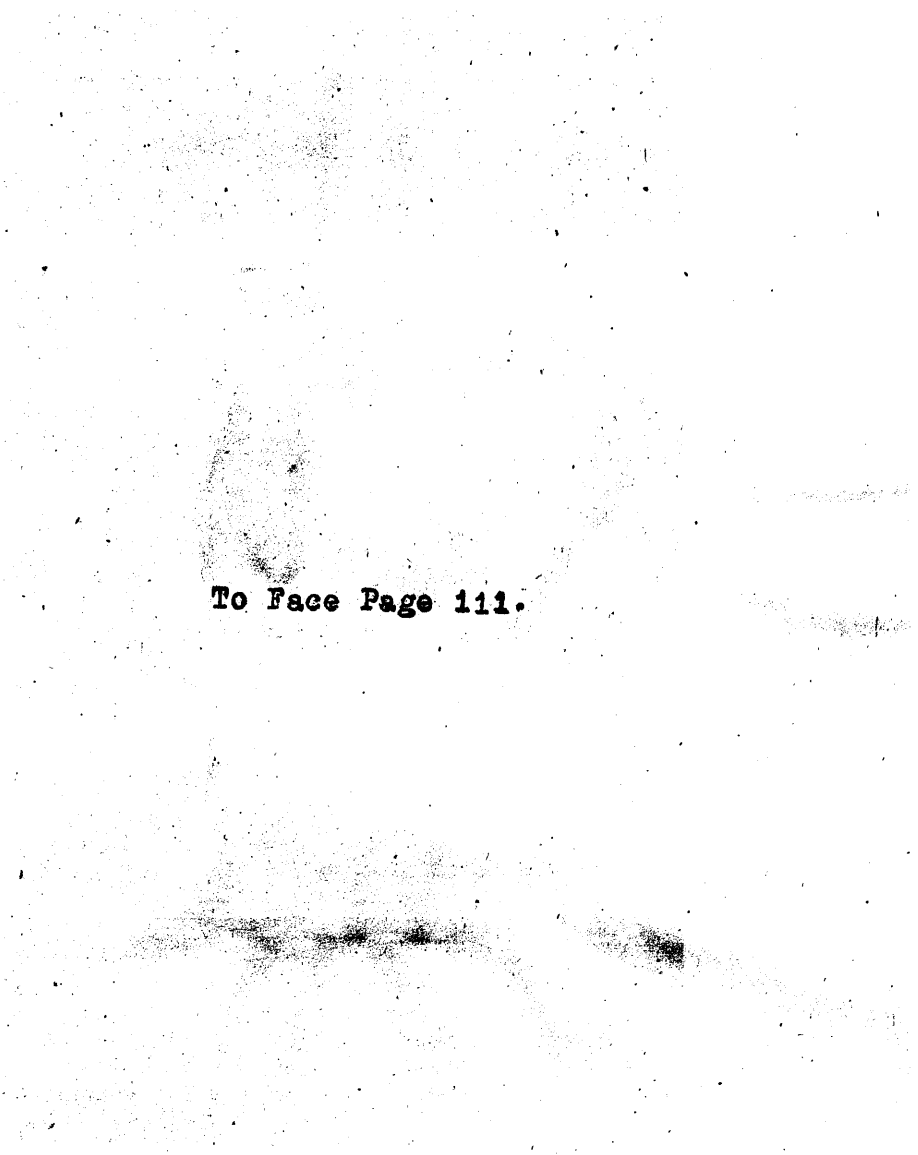


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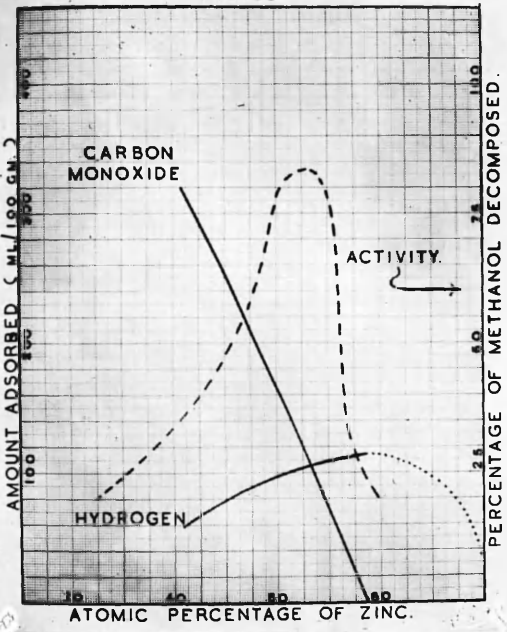
Figure 36.

FIG 36


AMOUNT ADSORBED (ML/100 GM.)
100
200
300
400
PERCENTAGE OF METHANOL DECOMPOSED.
25
50
75
100
CARBON MONOXIDE
ACTIVITY.
HYDROGEN
20
40
60
80
ATOMIC PERCENTAGE OF ZINC.

decided to carry out the adsorptions in definite order after one treatment with hydrogen at 500°C. The first was an adsorption of hydrogen, the second of carbon monoxide, and these were followed by checking adsorptions in the same order. Table 19 sets out the results obtained, and they are represented graphically in Figure 36.

Table 19

Catalyst	Volumes adsorbed (ml/100 gm.catalyst)					
	Hydrogen			Carbon Monoxide		
	1	2	Average	1	2	Average
A	60	55	57.5	330	310	320
B	115	103	109	90	78	84
C	116	114	115	Nil	Nil	Nil

These large adsorptions appeared to be partly reversible for both gases, as will be seen from the following typical cases.

Catalyst A (4.66 gm.)

Hydrogen adsorbed	2.89 ml.
Removed by evacuation to 5 mm	1.42 ml
Carbon Monoxide adsorbed	15.49 ml.
Removed by evacuation to 5 mm	8.50 ml.

Catalyst B (1.83 gm.)

Hydrogen adsorbed	2.23 ml.
Removed by evacuation to 5 mm	1.42 ml.
Carbon monoxide adsorbed	1.67 ml.

Removed by evacuation to 5 mm 0.95 ml.

It is probable that a still greater proportion of the adsorbed gas could have been removed had the evacuation been carried to lower pressure levels, or been more prolonged. After reaching pressure levels below 10 mm Hg., the evacuation by means of a Torricellean vacuum began to be very slow, and gas was obviously being released slowly from the surface. The Hydrogen could only have been liberated as the unchanged gas, but some of the carbon monoxide might have been released as the dioxide, a point which was not investigated.

Some reduction obviously occurred, as the three catalysts, after testing, were left in a state which spontaneously oxidised, with considerable evolution of heat, when exposed to air. It was also found necessary to prevent the access of air to the catalyst at any stage during the tests. One complete series of measurements was spoiled in this way by the entry of air through a faulty vacuum pump.

Comparing the figures 34 and 36, which set out the adsorptive capacities of the two series of catalysts at 360°C., it will be seen that the same high value for carbon monoxide adsorption is obtained in each when the proportion of zinc is below 50%. The complete absence of any adsorption of carbon monoxide in the case of catalyst C was at first set down to some error, but two other samples of the catalyst gave similar results, while exhibiting the same relatively high adsorbtive capacity for hydrogen.

The actual form of the adsorption curve for carbon monoxide is the same in both series of catalsyst, although in the second case the range of compositions is restricted. In the curves for the hydrogen adsorption, however, little liekness can be traced, and the curve for the second series shows no marked maximum, as was the case with the first. The pure zinc oxide has, of course, very little adsorptive capacity, and the curve for the second series of catalysts, if more fully investigated, would probably take the form suggested by the dotted prolongation in Figure 36. A fuller discussion of this and other points will be found later in this work.

This work on adsorption would clearly be limited if confined to the catalysts for one reaction and it had been planned originally to include all stages in the reduction of carbon dioxide to methane. This was ~~clearly~~ too ambitious a programme for the time available. It was clear, however, that some other type of reaction than the single methanol synthesis and decomposition should be studied, and a very convenient one, from all points of view, was the reduction of carbon dioxide to methane over a nickel catalyst. It might have been better to use carbon monoxide as a starting product rather than the dioxide, but the comparative ease with which supplies of the latter gas could be obtained and handled decided the choice made.

EXPERIMENTAL.

Part 5.

The Preparation and Testing of Nickel Catalysts.

The nickel catalysts to be used were supported on pumice. This pumice was sized to 16 - 20 mesh, and then washed vigorously with dilute aqua regia to remove traces of soluble material. The acid was afterwards removed by prolonged extraction in a soxhlet system, using several fresh quantities of water, and the purified pumice dried at 100°C.

The nickel was used in the form of a solution of the nitrate, which had been found by analysis to contain over 98% of the hydrated salt. The solution was made up to contain 20 gm. of metallic nickel per litre, the final concentration being checked by analysis. As it was desired to obtain catalysts of varying activity, a solution of thorium nitrate was used to provide the promoter. This thorium salt ($Th(NO_3)_4.6\ H_2O$) was taken as pure, and a solution made up to contain 2.2 gm. of thorium oxide per litre. These two solutions in equal amounts gave a concentration of thoria in the nickel catalyst of about 11%. This had been shown by Medsforth (J.C.S. 1923. 123. 1452.) to be the best concentration for activation.

The catalysts were prepared by adding to the nickel or nickel-thoria solutions sufficient pumice to give 10% by weight of the nickel metal, or nickel thoria mixture, in the dried and reduced catalyst. The mixture, which contained sufficient water to ensure the even wetting of the pumice, was then dried as far as possible on a steam bath and stored in a tightly closed bottle till required. Samples of this air dried material were taken for each test and reduced in situ immediately before use.

It was at first intended to supply the gases for reaction from two separate aspirators, and to regulate the respective rates by means of flow meters. This arrangement was difficult to work, and the mixture of gas obtained varied in composition even when the utmost attention was paid to the flow meters. The gases (always hydrogen and carbon dioxide) were therefore mixed beforehand in one ten litre aspirator, with acid brine as the containing fluid. The solubility of the carbon dioxide made this method a trifle unreliable when widely varying concentrations of carbon dioxide were used in two successive experiments. So long as this was avoided tests showed that the carbon dioxide concentration did not alter over the period of a test within the limits of experimental error.

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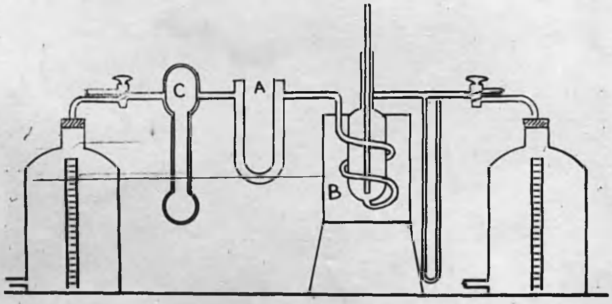
Figure 37.

FIG. 37



The apparatus as used finally took the form shown in Figure 37. The gas mixture passed through a flow meter (C) to the drying tube A filled with calcium chloride, and then to the reaction tube B, which was of the same form as that used for a similar test on the methanol catalysts (p. 53). This tube was heated in an oil bath. The products of reaction passed straight into a collecting aspirator, without any attempt being made to condense liquid products of any type. The collecting aspirator was filled with acid brine, and a lower reservoir manipulated so as to maintain an even pressure in the whole system. This simple arrangement was used in preliminary tests, and showed that so little of the reaction mixture remained unaccounted for (see Table 21) that no more complicated system was called for. A two-way tap allowed the passage of a stream of dry hydrogen for reducing or sweeping out purposes.

In each experiment, 10 ml. of the supported catalyst was tipped into the catalyst tube, and arranged evenly round the central thermometer tube by tapping. A stream of dry hydrogen flowing ata rate of 300 ml. per minute was then passed over the catalyst, the temperature of which was raised to 280°C.

over 60 minutes, and maintained at that level for a similar period. Without cooling the catalyst, or allowing any air to enter the system, the reaction mixture was then set to flow through the catalyst tube at a specific reaction rate (this varied from test to test). The gases issuing from the reaction chamber had passed to waste during the reduction period, and this was continued for another ten minutes, during which time the temperature could be adjusted and maintained at 280° and the various pressure levels adjusted.

The collecting aspirator was then connected to the system, and a standard experimental period of ten minutes followed. At the end of that time the gas supply was cut off and the collecting aspirator closed. The volume of gas mixture passed in, and the volume of product collected over, the experimental period were measured. The gas mixture for test was analysed immediately before each experiment, and the products as soon as possible afterwards. A fresh sample of catalyst was used for each test to eliminate errors due to gradual changes in the catalsyt with prolonged use.

The following data for a typical experiment show how the results were obtained and interpreted.

TABLE 20.

Experiment 3, Series 3.

Volume of gas mixture passed	5700 ml.	Both at N.T.P.
Volume of gases collected	4950 ml.	

Analysis of gas.

	Initial gas Mixture.	Gas produced.
CO_2	15.0%	13.0%
O_2	-	-
CO	-	-
CH_4	-	4.2
H_2	85.0	82.3
N_2	-	0.5

Mass Balance.

	IN.		OUT.
CO_2	1.600 gm.	CO_2	1.270 gm.
H_2	0.435	H_2	0.363
		CH_4	1.146
		H_2O	0.275 (Calc. on O_2).
Total	2.035	Total	2.054

Mass Recovery 102%.

Rate of production of methane 20.8 ml. per minute.

It will be realised that the reaction causes volume change, and that the composition and volume of the gas can only be kept constant in the initial stages. A basis of comparison between catalysts of varying activity is not easy to obtain, as both the gas velocity and the gas composition in the later stages of reaction vary with different catalysts. Any result must, therefore, be carefully scrutinised, and attempts made to ensure that conditions vary as little as possible. This is most easily effected by passing the gas mixture so rapidly that there is always a large excess of unreacted gas. The figure which then seemed the most logical basis for comparison was the volume of methane produced per minute.

Unfortunately, the reaction is so rapid with an active catalyst that such gas velocities would be difficult to obtain, while the exothermic nature of the reaction would, at the same time, cause considerable temperature disturbance. In view of previous experience with the methanol catalysts, it was not expected that very close correlation between adsorption and activity would be obtained, so that an exact determination of relative activity was hardly necessary at this stage. The figures given below, showing the results obtained with the nickel and nickel-thoria catalysts at two temperatures, were considered sufficiently indicative of the activities of the two catalysts.

TABLE 21.

Series 1. Inlet gas rate 170 ml. per minute.

Catalyst.	Temp. °C.	Gas Analyses. Inlet Gas. CO_2	H_2.	Outlet Gas. CO_2	H_2	CH_4.	CH_4 ml/min.	Mass Balance
Ni-ThO_2	300	14.8	85.2	0.8	64.0	35.2	26	100.3
	280	14.7	85.3	3.6	67.3	29.1	22	99.1
Ni	300	14.8	85.2	9.8	76.8	13.4	15.8	100.6
	280	16.4	83.6	14.0	78.4	7.6	10.3	100.5

The results above show that the thoria activated catalyst is twice as active as the simple nickel type. The figures for the test at 300° for the more active catalyst illustrate the point above concerning the inaccuracy of such dynamic tests. The carbon dioxide had nearly disappeared, and no doubt the reaction rate was falling off owing to this cause. Had this not been the case, the relative activities at 300° might well have been the same as at 280°. However, there is no doubt as to the superior activity of the thoria type and without further measurement, the next stage of the work, viz. the measurement of adsorptive capacity, was attempted.

At a later stage in this work, these activities were re-determined on a much wider basis, in an attempt to obtain some insight into the mechanism of the reaction.

A full account of these tests will be found on p.131

EXPERIMENTAL.

Part 6.

The Adsorption of Carbon Dioxide and Hydrogen on Nickel Catalysts.

The apparatus used for measurement of adsorption has already been described on p. 99, and was the same as that for carbon monoxide adsorptions on methanol catalysts. The reduction of the nickel catalysts was carried out in the bulb of the adsorption unit. After weighing 5 ml. of the catalyst into the bulb and connecting up the apparatus, the bath temperature was raised to 400° in 60 minutes, while the air over the catalyst was replaced by hydrogen. During the heating period this hydrogen was twice removed by evacuation and replaced with a fresh supply. The catalyst was then maintained at a temperature of 400° for another hour, changing the hydrogen three times during this period. Finally, the hydrogen was removed by evacuation to a pressure of 0.007 mm., still keeping the temperature steady. The catalyst was then ready for dead space measurements with nitrogen, as previously described. Final evacuation before each test was from an atmosphere of nitrogen at a temperature of 400°.

It will be noted that both the final reduction and the desorption temperatures were lower than was the case with the methanol catalysts. This change was made because the reaction and adsorption temperatures were also, to about the same degree, lower than those for the methanol synthesis.

It was necessary in the first place to measure the adsorptive capacity of the pumice used as a base for the catalysts. Two samples were tested, both being treated in exactly the same way as the catalyst-bearing pumice. It was found that, both at 250° and 300°C. there was no measureable amount of adsorption of either carbon dioxide or hydrogen. The amounts of these gases required to fill the apparatus to atmospheric pressure were practically identical with the dead space nitrogen measurements. Neither with nitrogen nor with the two other gases was there any gradual change of pressure indicating gradual adsorption.

The pumice was then replaced by the nickel impregnated material, and hydrogen adsorption measured at 250, 300, and 350°C., using the same sample for all tests. Marked adsorptions were observed at all three temperatures. A characteristic feature of

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Figure 38.

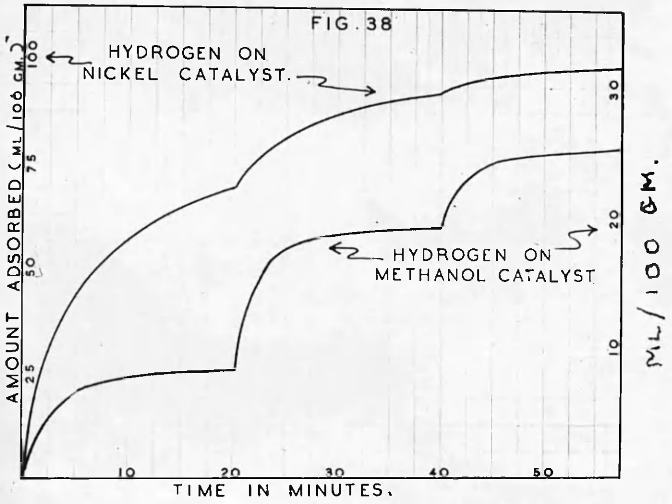

FIG. 38

HYDROGEN ON NICKEL CATALYST.
HYDROGEN ON METHANOL CATALYST
AMOUNT ADSORBED (ML/100 GM.)
25
50
75
100
ML/100 GM.
10
20
30
TIME IN MINUTES.
10
20
30
40
50

all these was that the adsorption was spread over a much longer period than was the case with those measured on methanol catalysts. This point is illustrated in Fig. 38., in which the graph of amount adsorbed against time is compared with a typical case in the earlier work. This made the fixing of a proper time interval over which to measure adsorption much more difficult than before. In order to avoid confusion, the same system was adopted as in the earlier work. Adsorption at each pressure level continued for twenty minutes, but only the amount adsorbed over the first five minutes was reckoned in the final calculations.

It is obvious, from a study of Fig.38, that this recognition of periods of adsorption is quite arbitrary, and for the nickel catalysts alone, unjustifiable. The manner of manufacture of the nickel catalysts is probably responsible for the difference in rate of adsorption. The following table shows the results obtained for hydrogen adsorption on the sample tested. The volumes are those adsorbed in the first five minutes after admitting the gas for the three pressure levels.

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Figures 39 and 40.

FIG. 39

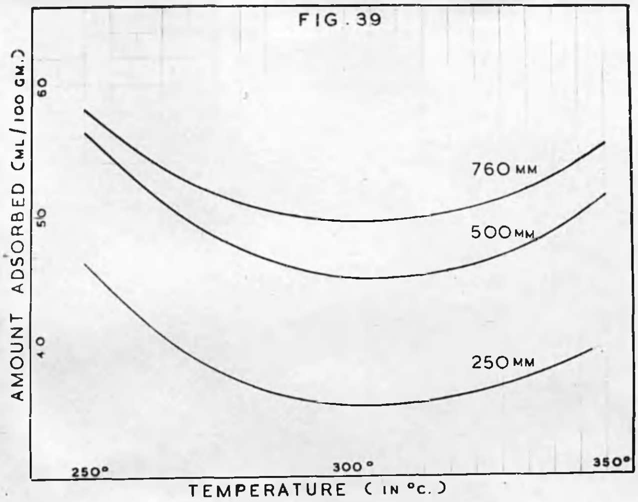
AMOUNT ADSORBED (ML/100 GM.)
60
50
40
760 MM
500 MM
250 MM
250°
300°
350°
TEMPERATURE (IN °C.)

FIG. 40

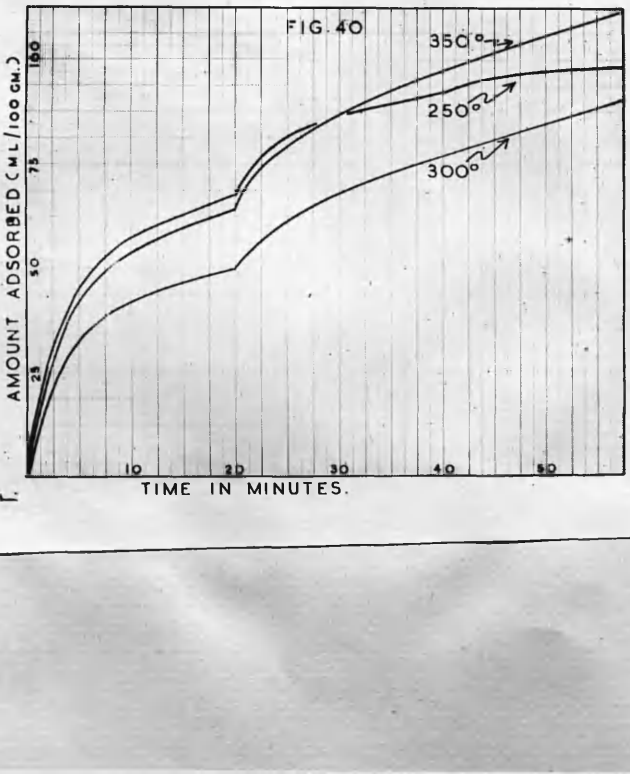
AMOUNT ADSORBED (ML/100 GM.)
100
75
50
25
350°
250°
300°
10
20
30
40
50
TIME IN MINUTES.

TABLE 22.

Temperature. °C.	Adsorption in ml./100 gm. at 250	500	760 mm.	Total.
250	46.5	10.0	1.5	58.0
300	35.5	9.5	4.5	49.5
350	40.0	11.5	3.5	55.0

These figures are also set out in Fig.39.

The first noticeable point with these figures is the large amount of gas adsorbed by a catalyst mass which contains only ten per cent of nickel. On the basis of nickel weight these amounts are much higher than those adsorbed by the most active methanol catalysts. The bulk of this adsorption is at lower pressure levels, and the shape of the adsorption curves, volume against time, suggests that the total pressure in the system has very little effect upon the amount adsorbed once a certain pressure level has been reached. This is common to adsorptions at all three temperature, as will be seen from a study of Fig. 40. From the change in the characteristics of the adsorption, it was hoped that calculation of the heats of activation and adsorption might give figures of more definite meaning than had been obtained with the methanol catalysts. The method of calculation has already been given on p. 88

and the results obtained in this case were as follows:-

TABLE 23.

Heat of Adsorption.

(a) 250 - 300°C. 1990 gm. cals./gm. mol.

(b) 300 - 350°C. -1330 gm. cals./gm. mol.

Heat of Activation (for first (250 mm.) adsorption only).

(a) 250 - 300°C. -2380 gm. cals/gm. mol.

(b) 300 - 350°C. 3490 gm. cals/gm. mol.

Consideration of the volumes adsorbed suggests that a second type of adsorption manifests itself at temperatures of above 300°. As it is probable that some indications of this would appear in the adsorption at 300°C., both the heats of activation and adsorption would be calculated on false premises, and the discordant results probably arise from this factor. It will be noted that only the first adsorption was used in the calculation of activation heat, as the much smaller quantities adsorbed at higher pressure levels made these measurements relatively unimportant.

Another sample of the nickel catalyst was introduced and treated with hydrogen for reduction exactly as stated on p. 123. After dead space

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Figures 41 and 42.

FIG. 41

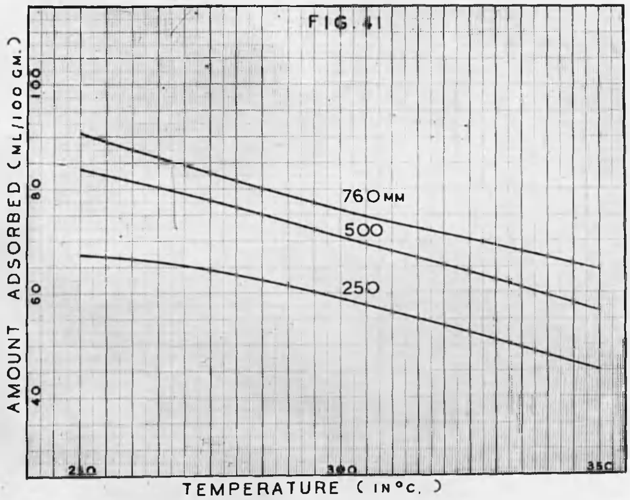
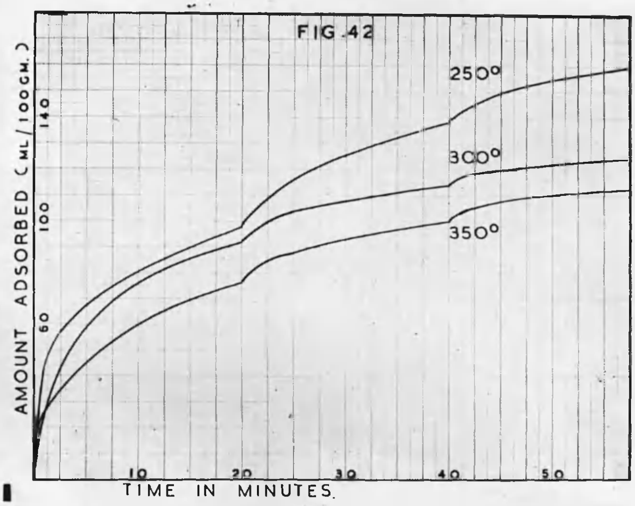

AMOUNT ADSORBED (ML/100 GM.)
40
60
80
100
760MM
500
250
250
300
350
TEMPERATURE (IN°C.)

FIG. 42


AMOUNT ADSORBED (ML/100GM.)
60
100
140
250°
300°
350°
10
20
30
40
50
TIME IN MINUTES.

measurement with nitrogen, an attempt was made to determine adsorption ofcarbon dioxide at 250°C. The adsorptive capacity was found to be negligible, and similar results were found with tests at 300° and 350°. A measurement of hydrogen adsorption at 300° gave a result (73 ml./100) very close to that obtained with the first sample. These figures were confirmed with a third sample of the catalyst.

The nickel-thoria catalyst was now used for adsorption measurements. In the case of hydrogen, large adsorptions were again observed,, as will be seen from the following table:-

TABLE 24.

Temperature °C.	Adsorption in ml./100 gm. at			Total.
	250	500	760 mm.	
250	67.5	16.5	6.5	90.5
300	59.0	12.0	5.0	76.0
350	45.0	12.0	7.5	64.5

Fig. 41 sets out these results in graphical form, while in Fig. 42 the volume of adsorption is plotted against time.

The shape of the time-volume curves are similar to those obtained with nickel catalysts, and the same criticism of a five minute period for adsorption can be made. There is no evidence, in the total volumes adsorbed, of the existence of a second form of adsorption, as the amount falls steadily with increasing temperature. The effects of pressure are similar to those observed with the nickel catalysts, and the bulk of adsorption is at the lower pressure levels. The heats of adsorption and activation were calculated in the same way as for the nickel catalysts, with the following results:-

TABLE 25.

Heat of Adsorption.

(a) 250 - 300°C. 2190 gm. cals./gm. mol.

(b) 300 - 350°C. 2210 gm. cals./gm. mol.

Heat of Activation.

(a) 250 - 300°C. -3630 gm. cals./gm. mol.

(b) 300 - 350°C. 2970 gm. cals./gm. mol.

It is interesting to note that the discrepancy in heats of activation is similar to that noted in the case of the nickel catalyst. This may be a coincidence, due to the difficulty of measuring very rapid initial adsorptions, but the shape of the time volume curves for the nickel-thoria catalyst suggests some change in the nature of the adsorption around 300°.

Comparison of the tables 22 + 24 shows that the nickel-thoria catalyst adsorbs about 50% more hydrogen than the unactivated nickel catalyst, and an approximate parallel can be drawn between this capacity and the relative catalytic activity of the two types of catalyst.

A fresh sample of the thoria activated catalyst was now used for measurement of carbon dioxide adsorption, and again it was found that the adsorptive capacity, over the range 250 - 300°C., was immeasurably small. A test with hydrogen showed the sample to be normal. The nickel-thoria catalyst was, therefore, very similar to the ordinary nickel specimen, and in particular showed the phenomenon of adsorption of only one reactant.

Experimental.

Section 7. The Conditions of Reaction between Carbon Dioxide and Hydrogen on Nickel Catalysts.

Before discussing these results for adsorption it was thought best to investigate more closely the conditions of reaction for the reduction of carbon dioxide. The apparatus for this work was already in existence (p.117), and the general experimental proceedure follows that already described. In this new investigation the gas rate was varied from 100 ml. up to 500 ml. per minute, while working with various mixtures of carbon dioxide and hydrogen. The results which were obtained are set out in the tables which follow.

TABLE 26.

Reaction Mixture 4% CO_2 96% H_2.

Experiment.	Gas Rate. In. ml/min.	Gas Rate. Out.	Analysis of Exit Gas. CO_2 %	Analysis of Exit Gas. CH_4 %	Analysis of Exit Gas. H_2.%	Methane ml/min.	Mass Balance.
1	150	135	0.4	7.0	90.5	9.4	102.5
2	300	250	1.0	4.2	91.0	12.0	101.5
3	600	560	1.8	4.0	93.0	22.6	97.5

TABLE 27.

Reaction Mixture 7.5% CO_2 92.5% H_2.

Experiment.	Gas Rate. In. ml/min.	Gas Rate. Out. ml/min.	Analysis of Exit Gas. CO_2 %	Analysis of Exit Gas. CH_4 %	Analysis of Exit Gas. H_2 %	Methane. ml./min.	Mass Balance.
1	220	160	4.2	8.8	80.0	15.4	97.5
2	220	160	3.6	10.2	83.5	16.3	97.5
3	300	250	3.4	9.5	83.0	23.4	103.0
4	300	250	3.4	8.2	86.0	22.4	101.5
5	570	500	7.0	5.8	80.0	30.2	93.5
6	570	500	6.8	5.8	83.0	30.2	98.5

TABLE 28.

Reaction Mixture 15% CO_2 85% H_2.

Experiment.	Gas Rate. In. ml./min.	Gas Rate. Out.	Analysis of Exit Gas. CO_2 %	CH_4 %	H_2 %	Methane. ml./min.	Mass Balance.
1	160	125	13.0	15.0	66.0	18.9	97.0
2	160	125	12.0	16.1	68.0	20.1	103.0
3	307	300	9.2	5.6	77.0	19.4	97.6
4	307	300	9.0	6.1	76.5	18.7	98.5
5	570	500	13.0	4.2	82.0	20.8	101.5
6	570	500	13.0	4.2	78.5	20.8	98.5

TABLE 29.

Reaction Mixture 30% CO_2 70% H_2.

Experiment.	Gas Rate.		Analysis of Exit Gas.			Methane.	Mass Balance.
	In.	Out.	CO_2 %	CH_4 %	H_2 %	Ml./min.	
	ml./min.						
1	160	120	22.4	12.4	64.0	14.9	97.5
2	280	240	26.0	6.8	62.0	16.4	101.1
3	570	520	27.0	3.5	66.0	18.4	98.1

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Figures 43 and 44.

FIG. 43

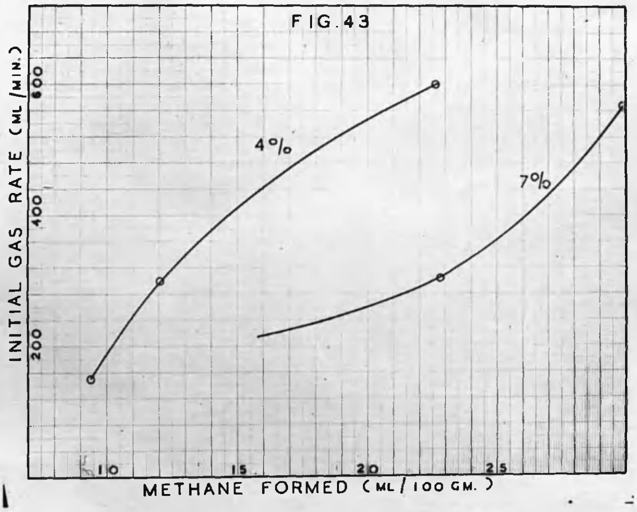
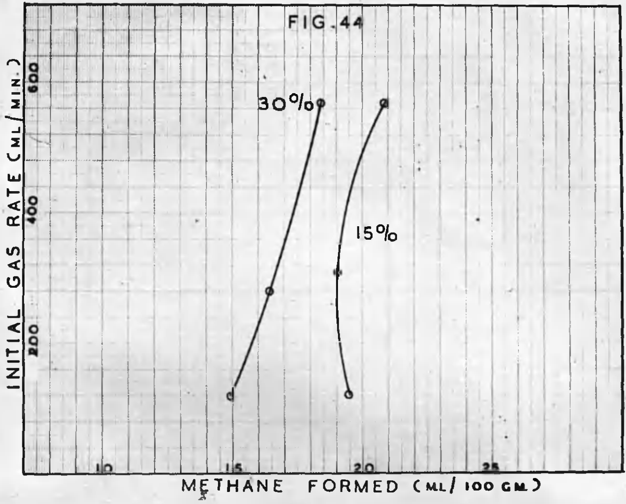

INITIAL GAS RATE (ML/MIN.)
600
400
200
4%
7%
10
15
20
25
METHANE FORMED (ML/100 GM.)

FIG. 44


INITIAL GAS RATE (ML/MIN.)
600
400
200
30%
15%
10
15
20
25
METHANE FORMED (ML/100 GM.)

These results suggest, in the first place, that with low initial concentrations of carbon dioxide in the reaction mixture the reaction rate is governed by diffusion through a surface film. This film diminishes in thickness as the gas velocity increases, and the rate of reaction therefore appears to be proportional to some power of the gas velocity. This point is illustrated in Figure 43.

When the initial concentration of the carbon dioxide is increased beyond a critical value, around 10 % by volume, the nature of the controlling factor changes. The rate of diffusion no longer governs the rate of reaction and reaction velocity becomes independent of gas velocity or nearly so, as will be seen from Figure 44.

The reaction rate is greater at low gas velocities than that attained by mixtures poorere in carbon dioxide. At high gas rates, however, the reverse is the case, and the poorer mixtures exhibit the greater reaction velocity. Comparison of Figures 43 and 44 makes this point clear.

A more detailed discussion of these results and their implications will be given later in this thesis.

REVIEW OF RECENT LITERATURE.

In Section 1 of this work, a general review was made of the subject of surface reactions, covering matter published up to 1936. A brief account of subsequent work, and some further comments on previous publications which seem to deal intimately with practical work described in the preceding pages, is given below.

The action of a surface in promoting chemical reaction is now generally believed to be through formation of intermediate compounds. For instance, Adkins (J.I.E.C.,1940.32.1189) laid down the following criteria for hydrogenation catalysts.

(1) They must adsorb and activate hydrogen.
(2) They must adsorb and activate the hydrogen acceptor.
(3) They must hold these two reactants in the proper ratio and space relationship.
(4) They must desorb the desired product.

The work of Craxford and Rideal (J.C.S..1939.1604.) illustrates these points. Their research on the Fischer-Tropsch synthesis led them to suggest that carbon monoxide is first chemi-sorbed on the surface of the catalyst. This complex is then reduced by adsorbed hydrogen to a carbide. The carbide is then further reduced, in the first place to an adsorbed methylene nucleus. If the surface is fully saturated with hydrogen, then the methylene nucleus is completely reduced to methane. When less hydrogen is present, the methylene nuclei tend to condense to complex hydrocarbons. It is known that carbide tends to accumulate on the surface of a catalyst during this reaction, and can be removed by substituting at intervals pure hydrogen for the carbon monoxide-hydrogen mixture. (Fischer and Tropsch. Ges. Abh. Kenn. Kohle 1930.10.313) As the reduction of the carbon monoxide proceeds smoothly throughout the period of deposition of the carbide, it is at least possible that this deposition is the product of a side reaction. The change in character of the products from methane to more complex hydrocarbons during the same period, however, bears out the theory of a step reaction through a carbide.

Farkas and Farkas (J.Am.C.S. 1939.61.3396), in a similar connection, showed that the hydrogenation of acetylene on platinum was retarded by increasing the partial pressure of acetylene. An increase in the partial pressure of hydrogen had the opposite effect, although the variation in relative amounts might with advantage have been wider. The idea of adsorption in the correct amounts ~~was~~ or volume proportions was extended by Adkins (loc.cit.) to hydrogenation catalysts which only function at high hydrogen pressures. Only at these pressures is sufficient hydrogen taken up for the adsorption to be active in reaction. Ivanov and Kobozov (J.Phys.Chem..U.S.S.R. 1937.10.1) studied the oxidation of carbon monoxide to dioxide over an iron catalyst and postulated reaction through a complex adsorption product of the monoxide on the iron oxide.

Solid surfaces are recognised to be markedly uneven, active centres for adsorption, and presumably reaction, being scattered over the main area of the surface. All solid substances are probably composed of small crystalline aggregates held together by a variety of cohesive forces, and in such aggregates the centres of activity may be small in relation to the surface area of the catalyst as a whole. Almquist and Black (J.Am.C.S. 1936.48.2814) suggested that only one atom in two thousand was active in the formation of ammonia on an iron surface. The position of these active centres with regard to other atoms of the surface seems to be of importance, as shown by the work of Adkins and Millington (J.Am.C.S. 1929.51.2449). Two titania catalysts were prepared in an identical fashion, but one was made from tetra ethyl and the other from tetra butyl titanate. These two were used in the decomposition of ethyl~~e~~ alcohol, and found to give widely different results. This supported the evidence from other pairs of catalysts, of similar composition but different surface characteristics, that the configuration of the surface atoms determined the course of the reaction. From this it would appear that the active atom is not an isolated peak, as visualised by several other workers (See, for instance, Taylor. Proc.Roy.Soc.1925.108.105.)

The relative rate of adsorption and desorption of the various molecules may be very important. In a notable piece of work by Reid (J.Am.C.S. 1931.53 4553) yields of over 80% of ethyl acetate were obtained by passing equi-molecular amounts of alcohol and acid over silica gel. The equilibrium concentration of ethyl acetate in such a system could not be more than 67 %, and the results were criticised on this account. They were, however, substantiated by further work, and it was suggested that the explanation lay in the rate of adsorption and desorption. If alcohol and acid were irreversibly adsorbed and water and acetate rapidly desorbed, then the yield of ester would be 100%, and their seems no doubt that such a mechanism was responsible for the apparent shift in equilibrium. Another instance of the relative importance of desorption is found in the oxidation of methanol over iron catalysts. With pure iron oxide the reaction goes to completion, and only carbon dioxide is formed. When molybdenum oxide is incorporated, the first product of reaction, formaldehyde, is rapidly desorbed, and the methanol may be oxidised almost quantitatively in this way. (Meharg and Adkins. U.S.Pat.1913404) Again, Taylor (J.Am.C.S.1934.56.1685) suggested that the relative rates of dehydration and dehydrogenation of an alcohol over zinc oxide are determined by the relative rates of desorption of water and hydrogen by the catalyst.

Matsumara and others (Inst.Phys.Chem.Res.Tokyo 1940.37.302) attempted to correlate activated adsorption of reactants on cobalt and iron catalysts with the course of the Fischer-Tropsch synthesis. They came to the conclusion that the manner of desorption of the various chemi-sorbed molecules determined the rate of reaction and the nature of the final products obtained.

In view of the notable effect of poisons on catalytic activity, attempts have been made to measure similar effects on adsorption. Griffin (J.Am.C.S. 1939.270) stated that carbon monoxide in small quantities checked the adsorption of hydrogen on supported nickel catalysts. Carbon monoxide was known to check the rate of hydrogenation of organic substances on these catalysts. Maxted and Evans (J.C.S. 1939.1750) also showed that catalyst poisons slowed down adsorption rates and checked catalytic activity in the same degree. Unfortunately, the adsorptions on which these tests were based were all carried out at low temperatures, much below the temperature of reaction. These adsorptions may have been activated (Leipunskii, J.Phys.Chem.U.S.S.R.1937.9.143 detected activated adsorption at a temperature as low as -145°C.) but were not necessarily concerned in the actual reaction.

It is not improbable that activated adsorption at higher temperatures would have been similarly affected. The findings of Barwell and Taylor (J.Am.C.S. 1936.58.1753) on the checking effect of water on the adsorption of gases on zinc oxide have already been referred to, and supported by the course of the practical work of this thesis. It would be very interesting to know what effect water vapour concentration has upon the rate of formation of methanol in the well known synthesis but no work bearing on this point is known to the author. In opposition to the above conclusions, it should be noted that Pevnyi (Ukraine Khem.Zhur.1937.12.317) claimed that oxygen adsorption on a chromium trioxide surface poisoned with arsenic was greater than on the fresh surface.

The adsorbing surface of the catalyst need not be considered as two-dimensional. There seems to be a considerable weight of evidence accummulating in favour of migration below the single molecular layer postulated by Langmuir. Brunauer and Emmett (J.Am.C.S. 1940.62.1732) suggested that certain adsorbed atoms can migrate below the surface of the catalyst. Kawakita (Rev.Phys.Chem.Japan.1940.14.1) was of the opinion that adsorbed molecules might migrate to centres of varying catalytic activity, and this would clearly be easier if the migration paths were not confined to the surface. This migration would be affected by the size of the individual molecules, and it is of interest to note that Sartori (Gazz.Chim.Ital.1937.67.98) claimed that the rates of adsorption of carbon monoxide and hydrogen on zinc oxide catalysts at 430° were proportional to the square root of the individual molecular weights. He also suggested that carbon dioxide would not diffuse in the catalyst and hence showed no adsorption. This idea of diffusion in the catalyst shows some resemblance to the older "thick layer" theory of adsorption, and could be used for explanation of such data as those of Bodenstein on the oxidation of sulphur dioxide.

Of late the importance of quality of adsorption rather than quantity has been stressed - this is in agreement with the author's five minute adsorption period limitation. Joris and Taylor (J.Chem.Phys. 1939.7.893) working with ammonia synthesis catalysts, suggested that the velocity of activated adsorption was in agreement with the catalytic activity, and this was also the finding of Rusof and Roiter (J.Phys.Chem. U.S.S.R.1938.11.390) although the agreement did not seem very close in this case. These workers were more fortunate than Klar (Z.Elektrochem.1937.43.379), who investigated the hydrogenation of ethylene on supported iron catalysts. His adsorption measurement s were based on quantity, and were at a much lower temperature than that chosen for reaction. Perhaps for these reasons, no connection could be traced between adsorption and activity.

This determination of adsorption at a low temperature has, to the author's mind, detracted from the value of much recent work done in Japan (see, for instance, Iijima-Bull.Inst.Phys.Chem.Res.Tokyo 1938. 17.286) Lewis and Taylor (J.Am.C.S. 1938.60.877) worked at higher temperatures with a mixed catalyst of copper on magnesium oxide. They showed that the total adsorption of hydrogen on the mixed catalyst was greater than on either component in the pure form, and this was related to the effectiveness of the mixture as an hydrogenation catalyst.

In the next section the practical results obtained are discussed in the light of these more recent developments.

Discussion Of Results

The first completed curve for the adsorption of hydrogen on zinc-chromium catalysts is so similar in form to the curve for catalytic activity (Fig.25,p.95) that it was hoped to correlate activity directly with amount of adsorption. The form of the corresponding curve for carbon monoxide (Fig.34, p.107) was not in accordance with this idea, while attempts to relate decomposition with amount of hydrogen adsorbed over a range of temperature, instead of at 360°, were not successful (P. 97). Experiments with the second group of zinc-chromium catalysts definitely indicated that the earlier results were in the nature of a coincidence rather than the illustration of a general rule. Figure 36 shows this very clearly; according to the hydrogen adsorption, activity should increase gradually over the whole range of catalysts tested. Instead, the characterisitc sharp maximum with catalyst compositions of just under 70% of zinc was obtained.

This optimum composition was so clearly established (Figures 10 and 35, p.60+109) that there should be some feature of the adsorption figures corresponding to the maximum activity if adsorption is to be correlated in any way with activity. Examination of the adsorption curves for both series of catalysts (Figures 34 and 36) shows that in both cases the adsorption of carbon monoxide and hydrogen is approximately equal in amount when the catalyst composition is between 60 and 70 % of zinc(atomic) From this it would appear that the peak of catalytic activity and the range of equal adsorptive capacity for the two reactants are within the same section of catalyst composition. This rule holds for catalysts of varying activity.

It would seem that the magnitude of the total adsorption is related to the catalyst activity. Thus a catalyst containing 65% of zinc, from the first series, will adsorb 32 ml. of carbon monoxide and 35. ml. of hydrogen - a total of 67 ml. per 100 gm. of catalyst - and decompose some 48% of methanol under standard conditions. A catalyst of similar composition from the second series will adsorb 105 ml. of hydrogen and 120 ml. of carbon monoxide - a total of 225 ml. per 100 gm. of catalyst. The amount of methanol decomposed was not measured under the same conditions as in the first series, but with a diluting gas present - nitrogen - which could only slow down the rate of reaction. Nevertheless, some 84% of the methanol flowing was decomposed, with approximately similar times of contact and the same reaction temperature as in the tests on the first series.

From this it may be said that the relative activities were roughly in the same proportion as the total volumes of reactants adsorbed.

The adsorption of one reactant only is no guide to the activity of the catalyst. Consider in this connection the case of a catalyst of low zinc content, such as catalyst A of Series 2. The capacity of this sample for carbon monoxide is very large - 320 ml per 100 gm.- but it is comparatively inert, despite an adsorptive capacity of 60 ml per 100 gm. for hydrogen.

The curves obtained by plotting catalytic activity against catalyst composition in the decomposition of methyl alcohol are in close agreement with those relating synthesis of the alcohol at higher pressures to these same compositions (P.46) Such a relation indicates a similar course for the two reactions, and a similar orientation of reactants on the surface of the catalyst. If, in the synthesis reaction, the first step is the formation of formaldehyde from one molecule of hydrogen and one molecule of carbon monoxide, then there should be intimate association of these two molecules on the surface of the catalyst. When the gases are present on the surface in equimolecular amounts, conditions are much more favourable for the occurrence of such associations than when unequal proportions of the gases are present.

To take a numerical example, for catalyst A above, some five molecules of carbon monoxide are present on the surface for each hydrogen molecule. As the proportion of zinc in the catalyst increases, the proportion of hydrogen also increases, until approximately equimolecular proportions are present, and the catalyst exhibits its maximum activity. Beyond the catalyst composition corresponding to about 70% of zinc, the proportion of carbon monoxide diminishes very rapidly, and this change is paralelled by the drop in catalyst activity.

The form of the catalyst surface causing this orientation of reactants has clearly been influenced by the change in density of the solid catalysts. It has been shown that with a composition of between 70 and 80% of zinc (atomic) the mixed catalyst exhibits minimum density (P. 54) This minimum density is not coincident with the point of maximum activity, however, nor does the activity calculated on a volume basis differ very much from that calculated on weight.

The form of the carbon monoxide adsorption curve, very similar for both series of catalysts, seems to determine the point of maximum activity by the very rapid alteration of adsorption with composition. There is , however, an important discrepancy. The adsorptive capacity for carbon monoxide falls to immeasurably small values with catalyst C of the second series - a carefully checked result. Thus a matreial with no adsorptive capacity for one of the reactants has a definite catalytic activity. The synthesis for a catalyst of such a composition would appear to start by a reaction between carbon monoxide in the gaseous phase and hydrogen adsorbed on the surface of the catalyst. Such a reaction has, of course, been noted by other workers (P.30)

There is an alternative hypothesis, which will be referred to later, that the actual adsorptions which are active in reaction occur on only a few of the possible points for adsorption. The total amount adsorbed may reflect the number of active adsorptions, but may vary independently of these, and will in any case be very much greater than the amount actually involved in the chemical change. This would put activated adsorption at reaction temperatures in very much the same relationship to catalytic activity as ordinary adsorption of the "van der Waals" type.

It must not be overlooked that this argument rests upon the assumption that the mechanisms of synthesis and decomposition are identical. In the decomposition reaction

$$CH_3OH \rightarrow CO + 2H_2$$

the first step must be the association of one molecule of alcohol with the catalyst surface. This molecule will assume a state of strain, leading to the fission of the alcohol. This breaking up will probably take one of two forms

(1) The formation of formaldehyde and two atoms of hydrogen, or

(2) The formation of carbon monoxide and four atoms of hydrogen.

From the synthesis standpoint, the former course is clearly the more likely if the mechanism of the two reactions is the same. The latter course pre-supposes a tri-molecular reaction in synthesis, which is unlikely and definitely rules out the explanation given above for the activity of catalysts containing some 65% of zinc.

If this explanation is accepted, with the reservation that it does not seem to account for all catalytic activity, then the most active catalysts for the methanol synthesis or decomposition are those which will give a correct proportion of reactants for the synthesis or decomposition of formaldehyde.

The second step in the synthesis, or the first step in the decomposition, seems relatively unimportant. This is rather surprising in view of the well known instability of formaldehyde. These conclusions are in agreement with the third postulation of Adkins (loc.cit.) and the work which was cited in suppprt of this view.

The weakness of the argument lies in the two facts that some catalytic activity can be detected in surfaces which do not adsorb one reactant at all, and that it has been necessary to base reasoning as to the mechanism of synthesis upon experiments involving only decomposition. This second criticism was met by work upon a second reaction, the formation of methane from carbon dioxide over a supported nickel catalyst.

In this case, as with the methanol catalysts, some connection may be traced between the total amount of reactant adsorbed and the activity (Tables 22+24) The connection is so slight as to suggest as to suggest that the two phenomena - catalytic activity and amount of adsorption - are two subsidiary manifestations of a particular type of surface rather than two intimately connected properties.

With these nickel catalysts, there is the distinct difference from zinc-chromium mixtures that only one reactant (hydrogen) appears to be adsorbed in measurable quantities. If all adsorbed molecules are intimately concerned in the reaction, there can be very little change in the proportion of reactants on the surface, whatever the composition of the gaseous mixture above it. There will always be a very large preponderance of hydrogen. In view of the observations of Craxford and Rideal (P.137) on the effect of a surface saturated with hydrogen, it is not surprising that the main product of reaction over a nickel surface, even when associated with other elements, is the fully reduced methane.

The carbon dioxide may react with the adsorbed hydrogen, while itself remaining in the gaseous form. It appears unlikely that the carbon dioxide would react simultaneously with four adsorbed hydrogen molecules, and this mechanism would almost demand a step reaction. Were this the case, then it would be anticipated that, by such devices as high gas velocities, certain intermediate products would be obtained, such as methyl alcohol. Also, as the hydrogen is strongly adsorbed, and presumably activated, there should be an increase in reaction rate as the percentage of of carbon dioxide in the reaction mixture increases, at any rate up to a fairly high figure.

By such an increase, the number of collisions with a surface which is always saturated with hydrogen will also increase, and thereby the reaction rate should increase also.

This has already been dealt with on page 25. It was shown that the reaction rate in a bimolecular reaction passed through a maximum when

$$P_a' = \frac{1}{b'}$$

where P_a' was the partial pressure of the~~m~~ more strongly adsorbed of the two reactants. In the limiting state where one reactant is strongly adsorbed and the other not at all, the value for b' approaches infinity, and the pressure for the maximum rate of reaction approaches zero in the case of the strongly adsorbed reactant. This would appear from adsorption measurements to be the condition of the system under review, and the rate of reaction should therefore be almost proportional to the concentration of the carbon dioxide, at any rate up to pressures at which the catalyst surface ceases to be saturated with hydrogen.

There remains, however, the second possibility already referred to, that activated adsorption, as measured here, is no guide to the mechanism of reaction at all. In that case activated adsorption will fall into line with adsorption at lower temperatures. It was to gain some insight into these points that the work upon conditions for the methane synthesis was commenced.

In considering the results set out in Figures 43 and 44 it must be remembered that the solid catalyst, during each dynamic test, is covered with a layer of more or less stagnant gas. This gas film consists of hydrogen, carbon dioxide, and the products of reaction; as distinct from the actual adsorbed layer, it is certainly several molecules in thickness. In layers immediately adjacent to the surface, there will be a tendency for the products of reaction to be concentrated. Through this inert film the reacting gases - carbon dioxide and hydrogen - will have to diffuse. If this diffusion is at equal rates, then the two gases will arrive at the surface in the proportions originally present in the reacting system.

It may be presumed that the two gases will be associated in some way on the surface, and the rate of reaction will be proportional in the first place to the joint rate of diffusion, and in the second place to some limiting value, characteristic of the two gases mixed in these proportions. This limiting value of reaction rate would be obtained if the gas film hindering migration to the surface were infinitely thin, this condition being obtained by an infinitely high gas velocity. On the basis of this reasoning, the reaction velocity, with any one mixture of gases, would be proportional to the gas mixture velocity. From the results obtained with mixtures rich in carbon dioxide, this does not appear to be the case.

If the hydrogen diffuses faster than the carbon dioxide, which seems very probable, then the surface will always be partially covered with hydrogen molecules awaiting the arrival of carbon dioxide. As the gas film grows thinner with increase in gas velocity, the rate of diffusion of the carbon dioxide to the surface would again increase, and, as before, reaction would increase with gas velocity.

If it be supposed that hydrogen is adsorbed at the surface, and that this adsorption must precede reaction, while adsorbed carbon dioxide does not react, then the accumulation of carbon dioxide on the surface may check reaction in the same way as the accumulation of the reaction products. Then, as the gas velocity is increased, the improvement in reaction rate due to increased diffusion may be offset if too much carbon dioxide is arriving at the surface. If the proportion of carbon dioxide in the gas mixture is low the carbon dioxide molecules arriving at the surface react immediately, and high gas velocity will make for high veloicty of reaction. As the proportion of oxide in the original gas mixture increases, the inert carbon dioxide adsorbed at the surface will also increase, and these adsorbed molecules, unaffected to any marked degree by gas velocity, will remain as a barrier to reaction. Changes in reaction velocity will then follow the lines actually determined experimentally. Here the reaction velocity was proportional to gas velocity while the carbon dioixde content of the gas mixture was below 10%. It may be argued, therefore, that both carbon dioxide and hydrogen are adsorbed on the catalyst surface.

If it is supposed that carbon dioxide requires to react simultaneously with more than one hydrogen molecule, then the proviso made in the preceding paragraph that adsorbed carbon dioxide does not react will not be necessary, but it is clear from the experimental results that the number of hydrogen molecules will be as high as eight.

The theoretical reasoning pursued on p.25, and already referred to in this discussion, ignores the effect of the thick gas layers formed at relatively high pressures in any dynamic test. Conditions for the highest gas velocities may most fittingly be compared with these theoretical considerations. It will be seen from Figures 43 and 44 that reaction velocity increases up to a maximum at about 10% of carbon dioxide and then falls off. This indicates that the limiting state referred to on page 154 has not been reached, and that both reactants are adsorbed for reaction, as postulated above. It is clear, therefore, that the evidence available for the course of the reaction is in conflict with the measurements of adsorption.

It will be remembered that efforts to trace some definite plan for heats of activation and adsorption have failed, probably because of superimposed adsorptions and the difficulty of measuring changes spread over a few seconds. The initial adsoprtions, of these first few seconds after admitting the gas, have admittedly been masked by subsequent effects. The actual reactions which these catalysts bring about are rapid - the contact time is measured in seconds only - and may be confined to the reactants adsorbed during this critical first few seconds. Measurements of the subsequent bulk adsorptions may be of little value.

Considering the evidence for the course of the reaction on the nickel catalysts, it is of interest to note that no evidence of the formation of intermediate compounds, of the type of carbon monoxide,

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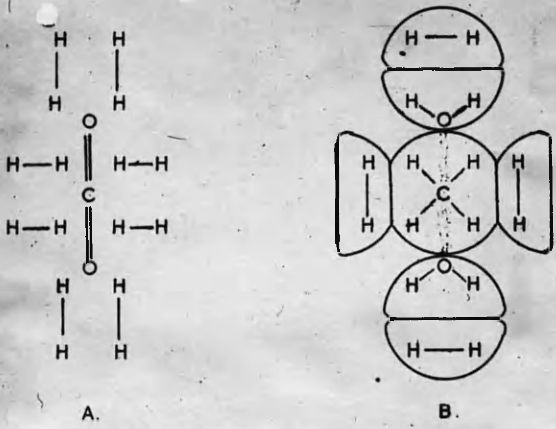
Figure 45.

FIG. 45.



formaldehyde and methyl alcohol was forthcoming in any test. If the reaction had been a stepwise one, as is usually supposed, then with higher gas velocities it would be anticipated that more of these compounds would be detected in the course of the reaction. This is not the case, as a study of Tables 26-29 shows. Formation of carbon monoxide would be shown immediately in the gas analysis (0.1% can be detected) while the other products would be dissolved in the brine solution of the gas holder, and cause a low mass balance.

It might be suggested that the mechanism of reaction is as follows. One molecule of carbon dioxide is adsorbed at the catalyst surface, surrounded by a symmetrical ring of eight hydrogen molecules. These are represented by Pattern A in Figure 45. Interaction then occurs as suggested by the closed rings of Pattern B, leaving in the first stage of the reaction methane, water, and four reformed hydrogen molecules. These reformed molecules could then distil from the surface with too much energy to condense again immediately. In this case a maximum rate might be expected for a gas mixture containing 11.1% of carbon dioxide, which is roughly in agreement with the practical results.

GENERAL CONCLUSIONS

The scope of the work described in the preceding pages has been too narrow for any final conclusions to be drawn. It has been thought desirable, however, to present some tentative findings from which guidance for future work may be sought. These findings are set out below.

(1) The variation in catalytic activity with composition, observed by Frolich and others (loc.cit.) for zinc-chromium catalysts, has been substantiated. It has been demonstrated that the most active catalysts in the decomposition of methanol contain about 70%(atomic) of zinc. This activity is not to any great extent due to the low relative density of catalysts of the above composition.

(2) The phenomenon of activated adsorption has been found to be common to all catalysts tested, and may involve large volumes of reactant relative to the weight of surface-active solid.

(3) Activated adsorption on surfaces can only be measured accurately when the surface is suitably cleaned. This necessitates some type of scouring action as well as thorough evacuation at temperatures higher than the adsorption temperature.

(4) Measurements of adsorption can be carried out conveniently on an apparatus which has been developed in the course of the work. (Figures 29 and 30, p. 99.)

(5) The actual amount of any one reactant adsorbed at reaction temperatures on a catalytic surface is not a measure of catalytic activity.

(6) The relation between the individual volumes of reactants adsorbed appears in some cases to determine catalytic activity. Two series of zinc-chromium catalysts showed a well defined maximum of activity in methanol decomposition with adsorption of equal volumes of carbon monoxide and hydrogen. This maximum occurred at an atomic content of 70% of zinc.

(7) In view of the close parallel between synthesis and decomposition of methanol established by Frolich and others, the adsorption of equal volumes of carbon monoxide and hydrogen by the most active catalysts indicates a stepwise reaction in both cases. In these reactions the first (or alternatively the last) step would be the association of

equal volumes of carbon monoxide and hydrogen.

(8) Heats of adsorption and activation can rarely be measured accurately, owing to the interference caused by several types of adsorption superimposed one upon the other.

(9) Reaction between two different molecules can occur at a surface on which only one of these molecules is adsorbed in measurable quantity. This has been observed with both zinc-chromium and nickel catalysts, and confirms the parallel observations of Griffith (loc.cit.) From this it is suggested that reactions between adsorbed molecules and molecules in the gaseous state are relatively commom phenomena.

(10) Following from (9) above, there is a distinct possibility that both molecules are associated with the surface, but that only one is adsorbed in measurable quantity. It is therefore suggested that only the molecules adsorbed in the first few seconds of any adsorption are active for reaction. Subsequent bulk adsorptions may not necessarily reflect the first critical stages of adsorption. This reasoning is supported by the evidence as to the course of the methane synthesis.

(11) If the suggestion contained in (10) above is correct, then the only section of an adsorption of value as a certain guide to reaction mechanism is the first five seconds or less. This is in accordance with the reaction time required for catalytic reactions.

(12) Some indication has been obtained that a surface reaction may be of a high molecular order, involving several adsorbed molecules. In this connection a mechanism has been suggested for the methane synthesis on nickel catalysts which is supported by the practical resulst.

SUGGESTIONS FOR FUTURE WORK.

The direction which future work on this subject might take is towards a more exact measurement of small adsorptions at very low pressures. This would determine whether some slight adsorption of, for instance, carbon dioxide on a nickel catalyst, does in fact occur. Even when low pressures are used, some means more rapid than the Macleod gauge for tracing the course of adsorption will have to be devised. A gauge of the Pirani type might be suitable.

As volume measurements are seldom so satisfactory as weighing, it might be possible to utilise a weighing method on the lines suggested by McBain (P.R.S.1929. 125A.579) In this connection, an ingenious hydrometer type of instrument devised by Chambers and King (J.C.S. 1939.139) might be effective.

Failing the success of such methods as these, it would be necessary to revert to some alternative process for investigation of reaction. A suggestion has already been made in the Introduction as to the effect of variation in partial pressures of reactants. This method has been applied in the course of the work to the investigation of methane formation, and might be more fully developed. In particular, efforts might be made to apply such variations to a study of the well known synthesis of methanol at high pressures.

APPENDIX.

In the course of the author's industrial work an occasion arose for studying the gasification of carbon under pressures greater than one atmosphere. This important industrial process had already been put on a semi-technical scale in Germany, and since the time that the work described below was carried out several papers have been published on the subject, notably by the Research Committee of the Institution of Gas Engineers. It was this particular piece of work which first turned the author's attention to the whole problem of reaction at surfaces.

The industrial process, in brief, was to gasify coal or coke by measn of a mixture of oxygen and steam, conducting the reaction under a pressure of several hundred pounds per square inch. By this means a gas of high calorific value was obtained directly from the gas producer. Consideration of the primary reactions involved shows that there is a possibility that they may be greatly influenced by variations in pressure. Cobb and his co-workers (Report of the Instit. Gas Engineers. 1927), in the course of investigations upon the reactions of the normal gas producer, had suggested that the reaction between

To Face Page 2 (Appendix)

Figures 1 & 2 (Appendix)

FIG_1 (APPENDIX)

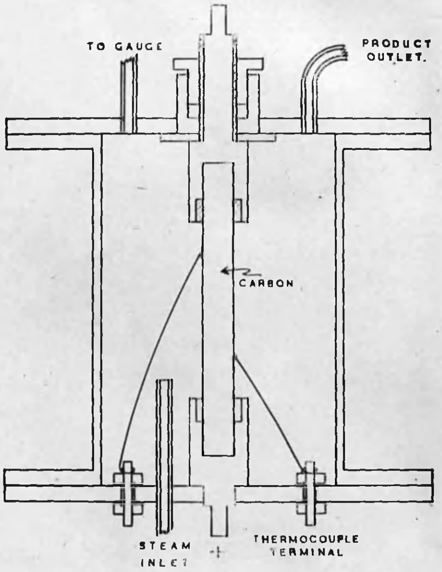
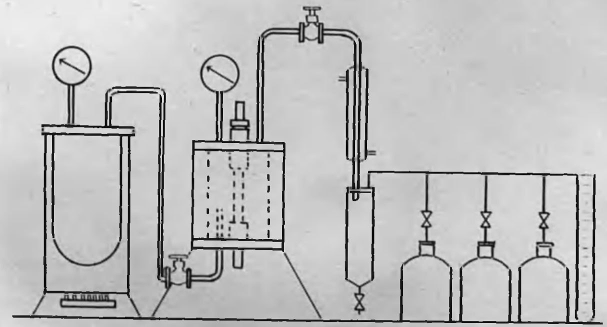


FIG. 2 (APPENDIX)



steam and carbon was of zero order i.e. not affected by pressure. On the other hand, Haslam (J.I.E.C.1923.15.115.) had varied the total pressure of a steam air mixture reacting with carbon at a fixed temperature, and his results indicated that the amount of steam reacting varied with the pressure, or the reaction was of the first order. It was this reaction of steam with carbon that the author investigated.

The reaction

$$C + H_2O \rightarrow CO + H_2$$

goes practically to completion at temperatures from 500° to 1300°C., provided that sufficient time is allowed. The effect of pressure on the equilibrium should be small, whatever its effect on reaction velocity. This possible change in velocity could only be determined experimentally, and, as stated above, results obtained by previous workers were conflicting. For these reasons it was decided to investigate the problem afresh.

The apparatus used for these experiments is shown in Figures 1 and 2 (Appendix) The reaction vessel was a cylindrical container in mild steel, flanged top and bottom, and constructed in 1/8" plate with 1/4" flanges. The diameter of the cylinder was 4", while the flanges were

7" in diameter. The covers, in 1/4" plate, were held in place by 6 bolts of 3/8" diameter, closing on a composition joint. This construction was designed for working pressures up to 100 lbs./sq.in.. Through each cover passed one connection to the 1/2" carbon electrode rod which was used for reaction. This rod, supplied by the G.E.C., was almost ash free. One of the terminals was carefully insulated from the vessel by means of rubber washers and sheathing. It might be added at this point that insulating materials other than rubber broke down rapidly under the operating conditions employed.

The end plate at the base of the unit carried eight small insulated terminals for thermo-couples. The four couples used were of stout chromel-alumel wire, and the tips were bent to lie immediately adjacent to the carbon surface at suitable points along the rod. Steam entered at the base, and the mixture of unchanged steam and reaction products was drawn off through a valve from the top.

In assembling the apparatus, the bottom cover was first fixed in position, and the carbon rod, previously made a tight push fit into the solid brass carriers, was mounted on the lower one. The four thermo-couples were then fixed in position, followed by the top carrier. The top cover was then put into place and screwed down, and finally the stuffing box round the insulated electrode was completed and tightened. The two electrodes were now connected to the terminals of an electrical system capable of giving 200 amps (A.C) at an E.M.F. of 5 volts. This current could be varied at will, and was adjusted to give steady readings to the thermocouples during a test. Actually it was found that very little adjustment was necessary when once conditions had become steady.

The pressure vessel was coupled up to a source of steam, a condenser, and reaction product receivers as shown in Figure 2. After the current chosen had been passing for about 15 minutes, steam was turned on, and the pressure adjusted to the required level, while drawing off the equivalent of 10 ml. of water per minute through the condenser, and discarding the reaction products. This gave a steady flow of steam over the carbon surface, and brought out a steady stream of reaction products, while at the same time a large excess of water vapour over all other components was maintained in the atmosphere surrounding the carbon rod.

After a further fifteen minutes, during which time conditions became steady, samples of reaction product were collected, taking readings of volume against time. As will be seen from the log of a typical experiment given below, the reaction rate seemed to be quite steady, and very consistent results were obtained.

Experiment 4. Temperature 700°C. Press. 1,2 & 3 at.

Time. mins.	Temperature °C. 1	2	3	4	Amps.	Press. lb/IN^2	Gas ml.
0					95		
5	600	650	635	615	95		
10	645	680	655	635	85		
15	675	700	680	635	85	30	
20	680	705	675	670	85	30	
25	685	710	675	675	85	30	
30	680	715	680	681	85	30	
1		710		680	85	30	15.5
2	685		680		85	30	30.0
3		715		685	85	30	45.5
4	690		690		84	30	61.0
5		715		685	84	30	76.0
7	690	710	685	685	84	45	---
9	695	715	690	685	83	45	---
10		715		685	83	45	16.0
11	690		690		83	45	30.5
12		710		680	84	45	44.5
13	690		690		84	45	60.5
14		705		680	84	45	75.5
16	695	695	690	680	84	15	---
18	700	715	695	685	82	15	---
20	700	715	695	690	82	15	---
22	700	710	690	690	82	15	---
23	700		690		82	15	---
24		705		685	83	15	15.5
25	700		685		83	15	31.0
26		705		690	83	15	46.0
27	700		690		83	15	62.0
28		705		695	83	15	77.0

Average rate of gas evolution

At 15 lbs.	30 lbs	45 lbs.
15.4 ml/min	15.2 ml/min	15.1 ml/min

Experiment 4 (cont.)

Gas Composition

Sample	1	2	3
CO_2	32.2%	32.0%	32.0%
CO	0.2%	0.4%	0.4%
H_2	67.0%	67.2%	67.3%
N_2	0.6%	0.4%	0.3%

Carbon reacting (Gm. per minute) × 1000

(1) 2.7 (2) 2.6 (3) 2.6

Equivalent rate in lbs. per sq.ft. per hour × 1000

(1) 11.3 (2) 10.9 (3) 10.9

A series of tests was carried out in which the pressure was varied from 2 lbs. up to 45 lbs. per sq. in. (abs.). The results obtained, set out as pounds of carbon reacting per square foot of surface per hour, are shown in Table 1 (Appendix)

Table 1 (Appendix)

Test	Reaction rate × 1000						Temperature
	at 2	5	10	15	30	45 lbs/in²	in °C.
1				2.3	2.2	2.2	650
2				3.9	3.4	3.5	675
3				16.4	16.1	16.4	750
4				11.3	10.9	10.9	700
5	17.0	16.2		16.9			750
6	15.5	15.1	15.0				750

It was manifest from these results that the reaction between steam and carbon was of an apparent zero order. In no test was there any sign of an increase in rate with increase in steam pressure. As previously stated, the concentration of the steam in the reaction space was very great compared with the concentration of the reaction products. In particular, the partial pressure of the carbon dioxide was roughly constant at about 1 mm Hg.. It may well be that this oxide, or the carbon monoxide which may have formed first at the surface, determined the reaction rate by strong adherence to the carbon surface. However this may be, the reaction provides a clear instance of the lowering of the apparent reaction order from monomolecular to zero, as suggested in the introduction to this thesis (24)