A thesis entitled

THE OXIDATION OF METHANE OVER HETEROGENEOUS CATALYSTS

by

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ABSTRACT.

The purpose of this investigation has been to establish the mechanism of the oxidation of methane over supported palladium catalysts.

The Introduction contains an account of the general features of heterogeneous catalytic reactions, and a survey of the catalytic oxidation of hydrocarbons. The former section discusses chiefly the usefulness and limitations of kinetic measurements in establishing the mechanisms of heterogeneous reactions. In the latter section, the adsorption and catalytic oxidation of some low molecular weight hydrocarbons are described, and previous investigations of the catalytic oxidation of methane are reviewed.

The Experimental Section describes the apparatus and experimental procedures used. Most of the rate determinations were made by a calorimetric method involving measurements of the heat evolved at the surface of a "bead" of the catalyst. In certain systems, these measurements were supplemented by product analysis. The preparation of catalysts, and their investigation by physical methods, are also described.

The principal findings are presented in the Results Section. With 20 atom % palladium / thoria catalysts, the dependence of the reaction rate on the concentrations

of methane, oxygen, carbon dioxide and water vapour have been determined, the concurrent oxidations of methane with methanol, carbon monoxide and formaldehyde have been investigated, and the oxidations of methane and some other hydrocarbons have been compared. Measurements have also been made of the activities of palladium catalysts supported by various materials, and the structures of the catalysts have been investigated by means of X-ray analysis and electron microscopy.

In the Discussion, it is shown that, in the oxidation of methane over palladium catalysts, both the reactants and the products are adsorbed on similar sites. Evidence for this proposition is obtained not only from the results of methane oxidation, but also from measurements involving the concurrent oxidation of methane and its partial oxidation products. Some conclusions are also drawn concerning the nature of the catalyst surface and the mechanism of adsorption of the reactants.

CONTENTS.

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INTRODUCTION.

1. INTRODUCTION.

1.1. The industrial importance of the catalytic oxidation of hydrocarbons.

Large quantities of commercially important materials are made from oxygen-containing organic compounds, and the manufacture of these compounds from hydrocarbons is therefore of considerable interest. Uncatalysed oxidation is not in general suitable for this purpose, mainly because of the high temperatures that have to be employed. As a result of this, the oxidation of a single hydrocarbon in general gives rise to a multiplicity of products, whose separation would be difficult and expensive. Partly because they proceed at lower temperatures, catalytic reactions are generally more specific, and are therefore more suitable for operation on an industrial scale.

With the increasing problems of air pollution, and with the necessity to perfect devices for the estimation of methane in places such as coal mines, attention has also been focussed on the use of catalysts in effecting the complete combustion of hydrocarbons and other fuels. Such complete combustion is favoured by the more active and less selective oxidation catalysts, and some of these have been used as the detecting elements in methanometers [1].

If the course of a reaction is to be controlled scientifically, then its mechanism must first be determined. Even the simplest heterogeneous reaction involves several steps which are not readily studied in isolation. However, much fundamental work has been done on processes such as the adsorption of the reactants, although studies of this kind often have to be carried out under conditions far removed from those used in industrial practice. In addition, a considerable effort has been devoted to the correlation of the activities of catalysts with their physicochemical properties. With regard to the oxidation of hydrocarbons, it will be shown in this review that the mechanism depends both on the properties of the catalyst and on those of the hydrocarbon, and is understood in detail only in a few cases. The oxidation of methane is not one of these, however, and the object of the present work is to remedy this situation.

1.2. Heterogeneous catalytic reactions.

1.2.1. A general description.

Reactions over heterogeneous catalysts involve the interaction of molecules with a surface, the breaking of old bonds and the making of new bonds in the adsorbed species, and finally the return of the resulting products to the gas phase.

Such reactions are generally faster and more specific than the analogous homogeneous processes because each involves the formation of at least one "adsorbed intermediate", and the two separate energy barriers which discourage its formation and further reaction are lower than the single barrier that has to be overcome in the homogeneous process. The adsorbed intermediates may be breakdown products of the reactant molecules, or they may be intermediate products of the reaction which can be desorbed into the gas phase. Since an intermediate product will have less free energy when adsorbed than in the gas phase, it has fewer possible paths for further reaction in the adsorbed state.

Since heterogeneous reactions take place at what may loosely be termed "active sites", reaction rates are proportional to the number of these sites in the system, which in turn is nominally proportional to the area of the catalyst. "Catalytic activity" is therefore most suitably expressed as an overall rate constant per unit area. This procedure permits activities to be compared at a fixed temperature. Alternatively, comparisons may be made of the temperatures required for a fixed area of each catalyst to effect a certain percentage conversion. The usefulness of such measurements is limited because they are too superficial to reveal mechanistic variations. However, for the purpose of assessing the effectiveness of a catalyst in promoting a given reaction, measurements may be made both of its activity and of its selectivity, i.e. the rate of a required reaction compared with the rates of unwanted concurrent and consecutive reactions.

An elementary catalytic reaction must proceed by means of the following sequence of steps:

(a) The diffusion of the reactants from the gas phase to the surface of the catalyst.

(b) The adsorption of the reactants, and their migration to active sites. (The adsorption process may involve dissociation).

(c) The chemical reaction of the adsorbed species to form the adsorbed products.

(d) The desorption of the products from the catalyst surface.

(e) The diffusion of the products back into the gas phase.

With the exception of some adsorption processes, these steps are reversible, and the overall kinetics will depend on the equilibria between the components of the reaction mixture and the surface, as well as on the kinetics of the slowest steps. The surface reaction (c) may involve the formation of reasonably stable intermediates, which may then be partially desorbed into the gas phase.

It will be noted that this formulation, originally due to Sabatier [2], describes the changes taking place in reacting molecules but says little about the mode of action of the catalyst. Two more or less complementary theories place more emphasis on the role of the surface.

The multiplet theory, developed by Balandin [3], is particularly dependent on the geometry of the catalyst. The theory postulates that the dissociation of the molecule AB is achieved by the attachment of groups A and B to different surface atoms, which are separated by a distance greater than that necessary to accommodate the molecule in its normal form. The atoms or groups between which a new bond is to be formed migrate to the same catalyst site, where they react. The course of the reaction is determined principally by the relative spacings of the atoms in the surface and in the reactant molecules.

The electronic theories of catalysis interpret adsorption phenomena in terms of the exchange or sharing of electrons between the adsorbed species and the catalyst surface. Thus the criterion for a substance to be catalytically active is its ability to accept or donate electrons. This is in accord with the high catalytic activity of semiconductors and transition metals and their compounds. These principles have been formulated in terms of valence bond theory and the band theory of solids [5].

The valence bond theory treates a metal as a giant covalent molecule bound by the overlap of filled hybrid orbitals of s, p, and, if available, d electrons. The calculated participation of d electrons in the cohesive binding of the solid is known as the "% d character of the metallic bond", and may be used as an inverse measure of the extent to which the non-bonding d orbitals have been filled. Electron band theory, on the other hand, treats a crystal as an assembly of ions, through which electrons or positive holes move randomly. The electrons in the crystal occupy permitted energy "bands", which replace the energy levels of individual atoms or ions. In transition metals and extrinsic semiconductors the highest energy band is only partially filled, and may therefore be stabilised by either the removal or addition of electrons.

The elucidation of the mechanism of a particular reaction involves an understanding both of the relationship between the overall reaction rate and the rates of the individual steps, and of the dependence of the latter on the physical and physicochemical properties of the catalyst. The present work has concentrated on the determination of the chemical mechanism of the catalytic oxidation of methane by means of kinetic measurements. It is therefore desirable to consider in more detail the thermodynamics and kinetics of adsorption and of surface reactions, as well as to discuss the results of some of the previous studies of the catalytic oxidation of hydrocarbons.

1.2.2. The adsorption of gases on solids.

The primary distinction between various types of adsorption is made by means of the heats of adsorption. Physical adsorption, which is rather similar to condensation, is accompanied by the evolution of less than 5 kcal.mole^{-1}. Chemisorption, on the other hand, involves the formation of chemical bonds between the surface and the adsorbate molecules, so that heats of adsorption usually exceed 10 kcal.mole^{-1}. In the present work, the "relative pressures" of the components of reaction mixtures were much too low for physical adsorption to be of any significance.

Few chemisorption bonds are wholly ionic or covalent, but most may be classified as being either predominantly of the former type, e.g. adsorbed oxygen, or mainly of the latter variety, e.g. carbon monoxide adsorbed on some transition metals. The adsorption of such substances as oxygen and the hydrocarbons may be accompanied by dissociation, and in these cases the geometrical structure of the surface has some influence on the nature and extent of the process. Geometrical factors also influence the adsorption of such gases as carbon monoxide, which may form a terminal bond or a bridging bond with the surface.

Since the geometrical structures of solids are related to their electronic properties, the assignment of catalytic properties to one or the other is not always possible. Nevertheless, many measurements, e.g. of dissociative adsorption on single crystal faces, show clearly the importance of geometric factors, while the measured activation energies of numerous surface activated processes are readily correlated with the electronic properties of the catalysts. Since, as will be shown, the palladium catalysts used in the present work were in the form of small crystallites that were probably randomly oriented, geometric effects will not readily be apparent from the results. It is therefore probably more satisfactory to consider the relationships between heats of chemisorption and surface coverage in terms of electronic theories of adsorption.

The thermodynamics of an adsorption process will depend on the nature of the bond between the adsorbate and the surface. Using the terminology of the band theory of solids [5], the partially filled d band of transition metals may be stabilised either by being emptied by electron transfer from the surface or by being filled up with electrons from the adsorbate. In either case, the adsorptive power of the surface usually decreases as coverage increases, partly because of the accompanying modification of the electrical properties of the surface and partly because of the increasing repulsive interaction between adsorbed particles.

Adsorption on semiconductors follows a similar pattern but a slightly more detailed picture is required of the process on each of three types. "Extrinsic" semiconductors are non-stoichiometric compounds, which therefore contain either an excess of electrons (n-type) or of positive holes (p-type). Adsorption requiring the transfer of electrons from an n-type catalyst soon exhausts the surface supply, so that for further adsorption electrons have to migrate to the surface from within the crystal lattice. This causes potential barriers to be set up, so that the heat of adsorption decreases and the process eventually stops. If, on the other hand, electron transfer to the surface accompanies adsorption on an n-type catalyst, there is plenty of space available in the marginally occupied energy band to accommodate all the electrons acquired in the formation of a monolayer with a very much less marked fall in the heat of adsorption. These two processes are known respectively as depletive and cumulative chemisorption, and the position is reversed for p-type catalysts. "Intrinsic" semiconductors are stoichiometric compounds, some of whose electrons may be thermally excited to a slightly higher band. They will therefore be n-type at low temperatures and p-type at higher temperatures.

With respect to adsorption equilibria, the following points may therefore be noted. Firstly, the electrical properties of the surface of a solid differ from those of the bulk material, so that correlations between bulk properties and catalytic effects are of limited use. (Some calculations of surface properties have been made; e.g. Wolkenstein's calculations on semiconductors [6]). Secondly, heats of adsorption usually vary with coverage. The extent of this variation depends on the nature both of the surface and of the adsorbate. Thirdly, if two gases are adsorbed at the same time on a single surface, and the processes involve electron transfer in opposite directions, then both gases are likely to be adsorbed to a greater extent than they would be on their own. Lastly, not all chemisorption processes are reversible. If, for example, carbon dioxide is adsorbed on to some transition metals such as titanium, molybdenum and tungsten, subsequent desorption yields some carbon monoxide and a surface layer of the metal oxide [7]. Another example is the desorption of water from the surfaces of some metal oxides on to which hydrogen has been adsorbed[8]. In these circumstances, correlations between heats of adsorption and surface coverage cannot be made.

The rates of heterogeneous catalytic reactions may depend on the rates of adsorption or desorption processes, or, if the surface reaction of adsorbed intermediates is rate-determining, on the equilibrium coverages of the surface by the reactants and products. Since the present work is largely concerned with kinetic measurements, the dependence of these on the thermodynamics amd kinetics of the elementary steps will now be considered in the light of the general principles that have been described.

1.2.3. The kinetics of heterogeneous catalytic reactions.

The overall kinetics of a heterogeneous reaction are determined by those of the individual steps. A primary distinction may be made between chemical rates, which increase exponentially with the absolute temperature, and diffusion rates, which are proportional to some power of the absolute temperature between zero and two. As a general rule, therefore, chemical processes control reaction rates at low temperatures, while at high temperatures, diffusion processes are at least of comparable importance. The transition between chemical and diffusion control is marked by a reduction in the overall activation energy as the temperature is increased, so long as the activation energy of the chemical process is not too small.

If the mechanism of a surface reaction is to be investigated, it is preferable that reaction conditions are chosen such that diffusion processes are relatively rapid. This is not always practicable, however, and it is necessary first of all to describe the experimental features by which diffusion control may be recognised, and the effects which diffusion may have on the overall kinetics of surface reaction

1.2.3.1. The effects of diffusion processes[9].

In describing the kinetics of gaseous reactions over porous catalysts, account must be taken of two gaseous diffusion processes: mass transport through the gas phase to the outside surface of the catalyst, and the diffusion of the reactants within the pores of the catalyst.

The rates of bulk diffusion in gas mixtures are proportional to their concentration gradients, and to the absolute temperature to a power between 1.5 and 2; they also depend on the composition of the mixture. Mass transfer in the pores of a catalyst may, if the pores are large, occur by bulk diffusion, or, if the pores are narrower than the mean free path of the molecules, by diffuse reflection of the molecules from the walls of the pores. This latter process is known as "Knudsen diffusion", and the relevant diffusion coefficients are independent of the composition of gas mixtures.

Bulk diffusion is much more rapid than pore diffusion. Thus the Arrhenius plot for a reaction over a porous catalyst usually consists of three sections. At low temperatures, diffusion processes are relatively rapid, and the activation energy E obtained from the slope of the graph is that of the surface reaction. As the temperature is increased, Knudsen diffusion progressively slows down the increase in overall rate, and the apparent activation energy decreases to a limit of E/2. This transition may occur over a temperature range as wide as 200°. Then at still higher temperatures, bulk diffusion becomes the rate controlling process, and the observed activation energy decreases much more rapidly to about 1 kcal.mole^{-1}. In the first region, the observed kinetics are those of the surface reaction, whereas in the second they are modified so that an nth order reaction appears to have an order of $(n+1)/2$, and in the third the apparent order is half the true order. (It should be noted, however, that these results have been deduced for a spherical particle under isothermal conditions. If there is a temperature gradient between the surface of each catalyst pellet and its centre, then these effects may be somewhat blurred.) Coefficients both of bulk diffusion and of pore diffusion are inversely proportional to the square root of molecular weight. Thus the heavier the gas, the lower the temperature range over which diffusion processes become important.

Although not of great importance in the present work, it is of interest to note that the pore structure of a catalyst has considerable influence on its selectivity. The position may be summarised briefly as follows. Firstly, if there is competition for surface sites between different reactions of the same order, then the process in which reactants diffuse most rapidly is favoured by more porous catalysts. Secondly, if a single reactant undergoes two concurrent reactions of the same order, the selectivity of the catalyst is not affected by its pore structure. If, however, the orders differ, then the process with the lower order is favoured by more porous catalysts, since its rate is less affected by the depletion of reactants inside the pores. Thirdly, if the reaction proceeds via an intermediate product, the yield of this product is greater if a non-porous catalyst is employed. This is because intermediate product molecules formed inside the pores stand a high chance of reacting further, by collision with the walls of the pores, before they can escape into the gas phase.

It may be seen from this account that diffusion processes modify but do not override the kinetics of surface reactions. There now follows, therefore, a discussion of the kinetics of the surface processes.

1.2.3.2. The kinetics of the chemical surface processes.

Three distinct chemical processes are involved in an elementary heterogeneous reaction: the adsorption of the reactants, the surface reaction itself, and the desorption of the products. It is necessary to consider the overall kinetics observed when each of these steps is rate determining. They cannot be completely isolated from each other however, because, for example, the rate of adsorption depends on the availability of surface sites, which in turn depends on the equilibrium coverage by the products.

Adsorption and desorption will be considered first. These processes may be represented by the equations:

(a) Dissociative adsorption: $AB + 2^* \rightleftharpoons A^* + B^*$

(b) Non-dissociative adsorption: $AB + n^* \rightleftharpoons AB(n^*)$

where A and B are atoms or groups, * represents an adsorption site and n is any number greater than or equal to one. ("n" only exceeds one if AB is a large molecule which occupies an appreciable surface area). Taking equation (a), the rate of adsorption, r_a, is given by

$$\begin{aligned} r_a &= \sigma \; [**] \; p_{AB} \; (2\pi mkT)^{\frac{1}{2}} \; e^{-E_a/RT} \\ &= k_a \; (1 - \theta)^2 \; e^{-E_a/RT} \qquad (1.1) \end{aligned}$$

where k_a and E_a are respectively the rate constant and activation energy of adsorption, m is the mass of the molecule, θ is the fraction of surface covered, σ is the "sticking probability", more or less analogous to the "steric factor" of collision theory, and other symbols have their usual meanings. The rate of desorption, r_d, is given by

$$r_d = k_d \, \theta^2 \, e^{-E_d/RT} \qquad (1.2)$$

where k_d and E_d are respectively the rate constant and activation energy of desorption.

The further development of these equations depends on the adoption of simplifying assumptions. For example, the Elovich equations [10], which account for the observed rates of chemisorption in a number of systems, have been deduced by assuming firstly that adsorption is mobile, so that σ is approximately equal to one, and secondly that the activation energies vary linearly with coverage, according to the equations

$$E_a = (E_a)_o + \alpha\theta \qquad (1.3)$$

$$E_d = (E_d)_o - \beta\theta \qquad (1.4)$$

where α and β are constants, and the subscript "o" indicates zero coverage. These assumptions lead to the equations:

$$\begin{aligned} r_a &= (1-\theta)^2\, e^{-\alpha\theta/RT} \\ r_d &= \theta^2\, e^{+\beta\theta/RT} \end{aligned} \qquad (1.5)$$

Over intermediate ranges of coverage, changes in θ^2 and $(1-\theta)^2$ are relatively unimportant, so that to a reasonable approximation,

$$\left.\begin{aligned} r_a &= a \exp(-\alpha\theta/RT) \\ r_d &= b \exp(+\alpha\theta/RT) \end{aligned}\right\} \text{Elovich Equations} \qquad (1.6)$$

where a and b are constants.

It is considered probable [10] that chemisorption is localised at lower temperatures, so that the Elovich equations are then less likely to be obeyed. However, the activation energy of surface migration is usually less than that of desorption, so that the mobility of reversibly adsorbed layers does increase as the temperature is increased. With dissociatively adsorbed species, this tendency is less marked because desorption involving association is likely to require a lower activation energy. Mobility is also likely to increase as coverage increases, since the heat of adsorption concurrently decreases.

The overall kinetics of a reaction whose rate is controlled by adsorption may be seen from equation (1.1). The initial rate is proportional to the partial pressure of the reactant, so long as the partial pressures of other gases in the reaction mixtures are kept constant. If the products are slowly desorbed, or their strengths of adsorption are appreciable, then the concentration of unoccupied adsorption sites will decrease as the reaction proceeds, and the apparent order with respect to the reactant will increase.

When product desorption is rate controlling, the overall kinetics depend partly on the strengths of adsorption of the reactants. If the reactants are only weakly adsorbed, then for most of the reaction the surface is almost completely covered by product molecules, so that the order with respect to the reactants is zero.

In considering the kinetics of the surface reaction itself, it is assumed that the gas phase components are all in equilibrium with their respective adsorbed species, so that the coverage of the surface by each component depends on its strength of adsorption, its partial pressure and the coverage by the other components. Three possibilities must be considered:

(i) the reactants may be adsorbed on similar sites,
or (ii) they may be adsorbed on different sites, or
(iii) the reaction may take place between one adsorbed reactant and another in the gas phase.

In all these cases, the reaction products may compete with the reactants for surface sites.

In the first instance, the discussion will be simplified by the assumption that strengths of adsorption do not vary with coverage. The fractional coverage of the surface, θ_x, by a component x, whose partial pressure in the presence of other components i is p_i, is given by:

$$\theta_x = \frac{b_x \ p_x}{1+b_x p_x + \sum b_i p_i} \quad \text{for non-dissociative adsorption} \qquad (1.7)$$

$$\theta_x = \frac{\sqrt{b_x \ p_x}}{1+\sqrt{b_x p_x} + \sum b_i p_i} \quad \text{for dissociative adsorption} \qquad (1.8)$$

where the "b" terms are the equilibrium constants for adsorption. The observed kinetics will then depend on the molecularity of the surface reaction. Two cases will be sufficient to illustrate these principles.

(a) in which the rate determining step is:

$$A_{(g)} + B_{(ads)} \longrightarrow (\text{Intermediate and/or final products})_{(ads)}$$

(Rideal-Eley mechanism[10])

(b) in which the rate determining step is:

$$A_{(ads)} + B_{(ads)} \longrightarrow (\text{Intermediate and/or final products})_{(ads)}$$

(Langmuir-Hinshelwood mechanism[11])

In case (a), the rate is proportional to the frequency with which gas-phase molecules of A collide with adsorbed species of B. Two rate expressions are therefore possible.

(i) for the non-dissociative adsorption of B,

$$\text{rate} = \frac{k_1\ p_A\ p_B}{1 + b_B\ p_B + \sum b_i p_i} \qquad (1.9)$$

(ii) for the dissociative adsorption of B,

$$\text{rate} = \frac{k_2\ p_A \sqrt{p_B}}{1 + \sqrt{b_B\ p_B} + \sum b_i p_i} \qquad (1.10)$$

In both cases, the reaction is first order with respect to A throughout its course. The dependence of rate on the concentration of B depends, however, on the strengths of adsorption of B and the products, If both are equally weakly adsorbed, and the reaction mixture is stoichiometric, then the order with respect to B is initially slightly below 1.0 (case (i)), or slightly below 0.5 (case (ii)), but increases as the reaction proceeds. The kinetics in other circumstances may be deduced by inspection.

In case (b), if it is assumed either that the adsorbed species are randomly distributed over the surface, or that they are mobile, then the reaction rate is proportional to the product of the surface coverages of A and B. Rate equations may therefore be formulated as follows.

(iii) all species adsorbed on similar sites; no dissociation,

$$\text{rate} = \frac{k_3 \; p_A \; p_B}{(1 + b_A p_A + b_B \, p_B + \sum b_i p_i)^2} \qquad (1.11)$$

(iv) all species adsorbed on similar sites; A dissociated, other species not dissociated,

$$\text{rate} = \frac{k_4 \sqrt{p_A} \; p_B}{(1 + \sqrt{b_A p_A} + b_B \, p_B + \sum b_i p_i)^2} \qquad (1.12)$$

(v) all species adsorbed on similar sites; both reactants dissociated,

$$\text{rate} = \frac{k_5 \sqrt{p_A \; p_B}}{(1 + \sqrt{b_A p_A} + \sqrt{b_B \, p_B} + \sum b_i p_i)^2} \qquad (1.13)$$

(vi) reactants adsorbed on different sites; products adsorbed on one type of site; no dissociation,

$$\text{rate} = \frac{k_6 \; p_A \; p_B}{(1 + b_A p_A)\,(1 + b_B p_B + \sum b_i p_i)} \qquad (1.14)$$

(vii) A dissociatively adsorbed on one type of site; B and products non-dissociatively adsorbed on the other,

$$\text{rate} = \frac{k_7 \sqrt{p_A} \quad p_B}{(1 + \sqrt{b_A p_A})\ (1 + b_B p_B + \sum b_i p_i)} \qquad (1.15)$$

(viii) A adsorbed without dissociation; B dissociatively adsorbed on similar sites to those on which the products are adsorbed,

$$\text{rate} = \frac{k_8 \quad p_A \sqrt{p_B}}{(1 + b_A p_A)\ (1 + \sqrt{b_B p_B} + \sum b_i p_i)} \qquad (1.16)$$

The overall reaction kinetics in any given circumstances may again be deduced by inspection. Taking cases (vii) and (viii) as examples, if reactant A is strongly adsorbed and its partial pressure is high, then the rate will depend only upon the strengths of adsorption of B and the products and on whether or not these adsorptions involve dissociation.

Clearly, the number of rate equations required to cover all possible cases of uni-, bi-, and ter-molecular surface reactions is very large. The possibility that some of the products may be dissociatively adsorbed has in any case been ignored. However, it may be noted that each variable factor has an effect on the overall kinetics, and should therefore be detectable from experimental measurements. The amount of mechanistic detail that may be deduced depends chiefly on the accuracy and comprehensiveness of these measurements. For example, initial rate measurements indicate whether or not the reactants are dissociated on adsorption, and also permit their strengths of adsorption to be compared qualitatively. Measurements of rate as a function of time show whether or not the reaction is inhibited by its products, and if this is so, experiments in which the products are previously introduced into the reaction mixtures should indicate whether the inhibition is kinetic or thermodynamic in nature.

There are certain ambiguities in this approach, some of which may be resolved by means of further kinetic measurements under different conditions. If, for instance, the order with respect to the initial concentration of B is between 0.1 and 0.5, it is not clear whether B is dissociatively and moderately strongly adsorbed or whether it is non-dissociatively and weakly adsorbed. This question might be decided by means of experiments in which mixtures containing much lower concentrations of B are allowed to react. A more serious difficulty arises if the kinetics show a first order dependence on the initial concentration of B and an indication of inhibition by the products or the other reactants. It is not then possible to distinguish whether the non-dissociative adsorption of B on sites different from those on which A is adsorbed is the rate-determining process, or if the slow step involves the reaction of adsorbed A with gaseous B.

A further objection to this approach is that it is based on a premise that is usually false, namely, that the heat of adsorption of a component is independent of the coverage of the surface by itself and other components. Some attempt should therefore be made to assess the effect of variations in heats of adsorption. The generalised adsorption isotherm [11] is too complex for this purpose. The Freundlich isotherm [11], which is based on the exponential decrease of the heat of adsorption with coverage, and the Temkin isotherm [11], in which a linear decrease is implicit, may however be used. A large number of chemisorption measurements are found to fit one or the other quite well, particularly at moderate coverages.

The Freundlich isotherm for a single adsorbate is:

$$\theta = (b_o\ p)^{RT/q_m} \quad \text{for non-dissociative adsorption} \qquad (1.17)$$

$$\theta = (b_o\ p)^{RT/2q_m} \quad \text{for dissociative adsorption} \qquad (1.18)$$

where b_o is the initial strength of adsorption and q_m is a constant (units: cal.mole^{-1}).

For intermediate coverages, the Temkin isotherm, which is the same both for dissociative and for non-dissociative adsorption, may be reduced to:

$$\theta = \frac{RT}{q_o \alpha} \ln \left(b_o\ p\ e^{q_o/RT}\right) \qquad (1.19)$$

where q_0 is the initial heat of adsorption and α is the proportionality constant according to which the heat of adsorption decreases with increasing coverage. It may be noted that, if a reactant is adsorbed in this way, then there will be no kinetic distinction between its dissociative and non-dissociative adsorption prior to reaction.

The formulation of rate equations from these isotherms is not useful unless values of q_m etc. are available from chemisorption measurements made under conditions comparable with those used in making rate measurements. Even if these were available, the assessment of the effects of different adsorption processes on each other would be extremely complicated. It may however be said that marked variations of heats of adsorption with coverage are liable to blur the distinctions that may be made between different mechanisms on the basis of the Langmuir - Hinshelwood approach.

1.2.4. Summary.

The essential features of heterogeneous catalytic reactions have now been described, and rather more attention has been paid to the reaction kinetics than to the properties of the catalysts. This is because the relative activities of numerous catalysts for the oxidation of methane have already been determined, and it is now of more interest to focus attention on the mechanism of the reaction. Although some physical measurements, for example of the changes in the magnetic properties and electrical conductivities of catalysts during reaction, might be expected to yield some information regarding the mechanism, it is considered probable that kinetic measurements will in the first instance be most useful in establishing the general outlines. It has been shown that, in ideal circumstances, the mechanism could probably be established from kinetic measurements alone. The difficulties of interpretation that have been mentioned limit only slightly the usefulness of this approach.

The remainder of this introduction will consist of a survey of some previous investigations of the catalytic oxidation of hydrocarbons. A general review of the catalytic oxidation of low molecular weight hydrocarbons will first be given, and then the oxidation of methane will be considered in more detail.

1.3. The catalytic oxidation of hydrocarbons.

1.3.1. A general survey.

Many investigations of these reactions have been concerned with the production of partial oxidation products in useful quantities. Varying degrees of success have been achieved in this respect, as may be seen from the general review by Margolis [12], and a more recent survey of the catalytic oxidation of olefins [13].

The general results show that moderate yields of intermediate products may be obtained by means of the less active and more selective oxidation catalysts such as the oxides of the transition metals of groups VA, VIA, and VIIA. Catalysts of nickel, palladium, platinum and copper tend to be more active, and so to favour complete combustion. Gold is hardly active at all, but silver is of moderate activity, and is by far the most suitable catalyst for the oxidation of ethylene to ethylene oxide.

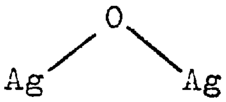
The ease with which intermediate products are formed also depends on the nature of the hydrocarbon. High unsaturated hydrocarbons may be oxidised at lower temperatures than low saturated hydrocarbons, and the yields of intermediates produced from the former are usually much greater. Again, the oxidation of ethylene over silver catalysts is something of an exception to this generalisation.

In discussing the factors that give rise to these effects, it is convenient to describe the chemisorption of the reactants on the catalysts before considering the reaction mechanisms.

1.3.1.1. The adsorption of oxygen on oxidation catalysts.

According to the classification originally due to Trapnell [14], oxygen is readily adsorbed on almost all metals and on many metal oxides. Measurements of the electrical conductivities of some catalysts during their adsorption of oxygen [15], indicate that negative ions are formed on the surface. More detailed information has been obtained from desorption measurements and from studies of the homonuclear oxygen exchange reaction [12,16], which show that, in decreasing order of thermal stability, the species O^{2-}, O^- and O_2^- may all be present on a catalyst surface.

At least in some cases, the chemisorption of oxygen is accompanied by its dissolution into the bulk of the catalyst. For example, when oxygen is adsorbed on silver, several surface layers of silver oxide are formed. The actual nature of the oxygen adsorbed on top of these layers is not known, but the existence of such complexes as



has been suggested by Twigg [17] to explain his observations of the oxidation of ethylene over silver films.

On the other hand, the reverse process is also possible. For example, when oxygen is sorbed on cuprous oxide [18], Cu^+ ions migrate through the crystal lattice to surround the O^{2-} ions on the surface, thus leaving positive holes in the catalyst.

It is clear that oxidation reactions over oxides may involve either adsorbed oxygen or lattice oxygen.

Kinetic measurements do not readily distinguish between these possibilities, but ^{18}O tracer studies have in some cases succeeded in doing so. It has been shown, for example, that the oxidation of carbon monoxide over cupric oxide almost exclusively involves adsorbed oxygen [19]. On the other hand, it is thought likely that many catalytic oxidations over vanadium pentoxide proceed by means of the alternate reduction of the surface by the hydrocarbon and the re-oxidation of the surface by gaseous oxygen [20,12].

The formation of surface oxide layers on silver in the presence of gaseous oxygen has already been mentioned. Similar processes occur on most metals at room temperature [21]. Over rhodium, palladium and platinum, however, only chemisorption is observed at room temperature [21], and bulk oxidation occurs only at temperatures exceeding 200°C [16]. At these higher temperatures, the adsorbed oxygen is in the form of monatomic ions. Whether or not a surface layer of oxide plays an important part in a metal-catalysed oxidation is likely to depend firstly on whether an adequate partial pressure of oxygen is maintained for the formation of the layer, and secondly on the relative rates of bulk oxidation and of hydrocarbon oxidation over the pure metal.

Volumetric and calorimetric measurements show that, over most catalysts, the heat of adsorption of oxygen varies appreciably with coverage. Adsorption measurements on several metal oxides are satisfactorily fitted by the Freundlich isotherm, and in some other cases a better correlation is achieved with the Temkin isotherm [12]. Except when bulk oxidation accompanies adsorption, the surface is usually saturated when the coverage is less than complete. It is reasonable to expect that the oxygen which is least strongly bound to the surface is that which is most likely to take part in a catalytic reaction, and this supposition is frequently borne out by experiment; see, for example, studies of homonuclear oxygen exchange [16].

1.3.1.2. The adsorption of hydrocarbons on oxidation catalysts

Experimental measurements of hydrocarbon adsorption and of concurrent changes in the electrical conductivity of catalysts show that the process may or may not involve dissociation of the adsorbate [12]. Non-dissociative adsorption is found to involve the formation of adsorbed RH^+ ions, whereas the dissociative process leads to the formation of R. and H. groups bound to the surface by largely covalent bonds.

The former process is more usual over metal oxides, and occurs more readily with unsaturated hydrocarbons than with saturated hydrocarbons. For example, Margolis has shown [12] that ethane, ethylene and a number of higher hydrocarbons are adsorbed as RH^+ ions both on n-type catalysts and on p-type catalysts. Hydrocarbon adsorption on all these catalysts is extremely rapid, and it appears that heats of adsorption decrease as coverage increases. At higher temperatures, the adsorbed species undergo pyrolysis and/or oxidation by the surface. Since pyrolysis involves bond fission, it is possible that the adsorption process becomes dissociative at high temperatures.

It is generally accepted that saturated hydrocarbons are dissociatively adsorbed on metals [22]. At lower temperatures, this process is more likely to involve the breaking of C-H bonds than of C-C bonds. Thus, two adsorption mechanisms are possible:

(a) $$RH_{(g)} \quad + \quad 2^* \longrightarrow R^* \quad + \quad H^*$$

(b) $$RH_{(g)} \quad + \quad H^* \longrightarrow R^* \quad + \quad H_{2(g)}$$

At higher temperatures, adsorbed alkyl groups tend to decompose:

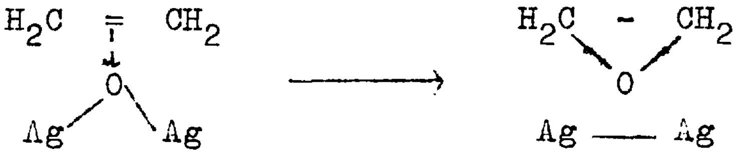
(c) $$\begin{tikzcd} CH_3 \quad + \quad 3^* \arrow[r] & CH_2^{**} \arrow[d] & + \quad H^* \\ {}_{**}\underset{*}{C}{}_{*} & + & CH_{4(g)} \end{tikzcd}$$

Unsaturated hydrocarbons tend to be adsorbed by means of π electron donation on metals as well as on oxides. There are, however, exceptions to this: for example, the adsorptions of ethylene on nickel [23] and on palladium [24] are thought to proceed via the formation of 1.2.diadsorbed ethane.

Some measurements have been made of the adsorption of hydrocarbons on oxide films at metal surfaces. It has, for instance, been shown [20] that whereas ethylene is rapidly and reversibly adsorbed on a pure silver film, the process is much slower and only partially reversible over an oxidised surface. It appears that not many measurements of this type have been made, but it seems reasonable to suppose that, generally speaking, the adsorption of a hydrocarbon on a surface oxide layer resembles the process on the bulk oxide more than the process over the pure metal.

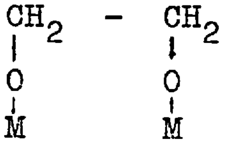
1.3.1.3. <u>The reactions of the adsorbed species</u>.

The ready formation of partially oxidised products from hydrocarbons appears to be associated particularly with the attachment of unsaturated groups to adsorbed oxygen. This is illustrated, for example, by the oxidation of ethylene, which follows different routes over different catalysts. The main products from the reaction over silver are ethylene oxide, acetaldehyde, carbon dioxide and water[17]. It is suggested that ethylene oxide is formed by means of the reaction:



Although the acetaldehyde is probably formed by the rearrangement of some of the ethylene oxide, it has been shown by means of tracer studies [26] that, at least at lower temperatures, most of the carbon dioxide is formed directly from ethylene.

When palladium catalysts are used [24], the major products of the reaction are carbon dioxide and water, and no ethylene oxide is formed. At lower temperatures, however, the catalysts are progressively poisoned by the formation of formic acid, which is thought to be formed from acetaldehyde. It has been suggested that in this case ethylene is initially adsorbed as:



$$\begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ O & & O \\ | & & | \\ M & & M \end{array}$$

It is much more difficult to obtain partially oxidised products from the catalytic oxidation of saturated hydrocarbons, particularly from those of low molecular weight. Low percentage yields may sometimes be obtained by means of high area catalysts of moderate activity, such as the oxides of chromium, molybdenum and vanadium, either supported or in the form of powder. Trace amounts of intermediate products have also been obtained using silver and platinum, but none appear to be formed over palladium catalysts. These results may in part be attributed to the higher temperatures required for the oxidation of saturated hydrocarbons, and in part to the mode of adsorption of these compounds.

The kinetics of the complete oxidation of hydrocarbons are hard to determine, because the reactions are highly exothermic. A number of comparisons of catalytic activities have, however, been made using reaction mixtures with small hydrocarbon concentrations, and those for methane oxidation are referred to below. Margolis and Todes [27] have found that, over copper chromite, magnesium chromite and platinum catalysts, the oxidations of normal and unsaturated hydrocarbons are first order with respect to fuel, while the oxidations of alkyl-substituted paraffins are second order. In contrast, Accomazzo and Nobe [28] have obtained orders of less than one for the oxidation of C_1 to C_3 hydrocarbons over copper oxide supported on alumina. Reaction orders were found to decrease and ease of oxidation to increase with increasing unsaturation of the hydrocarbons. Moro-oka et al.[29] have obtained a wide range of orders, both with respect to fuel and with respect to oxygen, in their investigation of the oxidations of acetylene, ethylene, propylene, propane and i-butane over a series of transition metal oxides. Their results show clear correlations between reaction rates, reaction orders, strengths of adsorption of the hydrocarbons as compared by means of competitive oxidation experiments, and the heats of formation of the metal oxides. There is evidence in this work, in Margolis' work, and in several investigations of the catalytic oxidation of methane, of compensation effects, i.e. the connection of the activation energies, E, and the pre-exponential factors, A, for a reaction over different catalysts by the relationship:

$$\ln . A = E_a + \text{Constant.}$$

To summarise, it appears that the mechanism of the catalytic oxidation of hydrocarbons depends to a considerable extent on the experimental conditions as well as on the properties of the reactants and the catalyst. Although some broad outlines have been drawn in some of the investigations cited, little precise mechanistic information is available.

The catalytic oxidation of methane has been the subject of a number of studies of catalytic activity, and more recently a number of kinetic investigations of the reaction have been carried out. These will be considered in more detail, but first it is of interest to describe the general features of the homogeneous reaction, which may in some circumstances influence the processes occurring on the surface of catalysts.

1.4. The oxidation of methane.

1.4.1. The slow homogeneous oxidation of methane.[30]

1.4.1.1. General characteristics of the reaction.

At sub-atmospheric pressures, the homogeneous oxidation of methane begins to occur at temperatures above about 350°C. It is a chain reaction, characterised [31], in a constant volume system, by an induction period, followed by a pressure rise stage, during which the reaction rate increases to a maximum before decreasing again. The major products of the overall reaction are carbon monoxide, carbon dioxide and water, but small amounts of formaldehyde, hydrogen peroxide, methanol, hydrogen and ethane may also be isolated as intermediates and final products. Formaldehyde is an intermediate under most reaction conditions [32], but its yield as a percentage of the initial methane concentration rarely exceeds 3%. The role of hydrogen peroxide depends much more on the reaction conditions [33]. Thus this compound is decomposed by basic surfaces (e.g. PbO) and at high temperatures. Carbon monoxide may also be regarded as an intermediate, since it is oxidised further to carbon dioxide [34]. This reaction is, however, inhibited both by methane and by formaldehyde.

These variations in the behaviour of intermediates are reflected in the sensitivity of the overall reaction kinetics to experimental conditions. The trends of observed reaction orders and activation energies as temperature is increased are summarised in table 1.1.

Table 1.1.

General kinetic features of the slow homogeneous oxidation of methane.

Temperature range (°C.)	Order in methane	Order in oxygen	Activation energy (kcal.mole^{-1})
380 - 450	2	0.5 - 1.0	90
450 - 550	2 - 1.5	1.0 - 1.6	60
550 - 650	1.5 - 0.0	1.6 - 2.8	40

1.4.1.2. The reaction mechanism.

It has been shown [30] that the slow thermal oxidation of methane proceeds by means of a free radical chain mechanism, which involves the formation of one or more molecular chain-branching intermediates. A comprehensive reaction scheme has been proposed which accommodates most of the observed features of the reaction over a wide range of experimental conditions (see Table 1.2).

Not all the reactions in this scheme are important under a single set of conditions: the following comments refer to reactions at sub - amospheric pressures. Below 500°C., all three major propagation chains may play an important part in the reaction, and heterogeneous termination steps are more important than homogeneous termination processes. Most of the hydrogen atoms formed combine with oxygen molecules according to step 13. As the temperature is increased, the chain branching step 14 overtakes step 13, and there is an increased likelihood of explosion taking over from slow reaction. This possibility increases in a single experiment as the reaction proceeds, and the competition for hydrogen atoms from methane and formaldehyde decreases [34]; this competition will also be increased by the addition of small amounts of carbon monoxide to initial mixtures. At temperatures exceeding 650°C, further variations in the mechanism occur. It has been shown that, even at 950-1000°C, formaldehyde is still the principal chain-branching intermediate [35], but there appears to be no general agreement as yet regarding the details of the mechanism at these high temperatures.

1.4.1.3. The possible effects of homogeneous processes on the heterogeneous catalytic reaction.

It has been stated that stoichiometric mixtures of methane and oxygen react slowly at temperatures below 500°C, but rapidly or even explosively at temperatures exceeding 650°C. Thus a catalyst of relatively low surface area introduced into a stoichiometric mixture at high temperatures will provide only a minor alternative route for the reaction, and may serve as a local heat source by means of which an explosion is initiated. Under less severe conditions, e.g. if the reaction mixture contains only a small proportion of methane and a high area catalyst is used, some initiation and propagation steps may proceed to a certain extent in the gas phase, and produce species which are more readily oxidised at the catalyst surface than is methane itself. Thus the general effect of these gas-phase processes will be to increase the apparent rate of the surface reaction. If the surface reaction itself is under investigation, then the experimental conditions should be chosen so that the importance of homogeneous processes is negligible. In practice, this means that only dilute mixtures of methane in oxygen or air should be used at temperatures below about 650°C.

Table 1.2. Reaction scheme for the homogeneous oxidation of methane[30].

Initiation:

$CH_4 + O_2 \longrightarrow CH_3 + HO_2$ 1

$CH_2O + O_2 \longrightarrow HCO + HO_2$ 2

Propagation:

Methane chain:

$CH_3 + O_2 \longrightarrow CH_2O + OH$ 3

$CH_4 + OH \longrightarrow CH_3 + H_2O$ 4

$CH_4 + HO_2 \longrightarrow CH_3 + H_2O_2$ 5

Formaldehyde chain:

$CH_2O + OH \longrightarrow HCO + H_2O$ 6

$CH_2O + HO_2 \longrightarrow HCO + H_2O_2$ 7

$HCO + O_2 \longrightarrow HO_2 + CO$ 8

Carbon Monoxide chain:

$CO + OH \longrightarrow CO_2 + H$ 9

$CO + HO_2 \longrightarrow CO_2 + OH$ 10

Other propagation steps:

$2HO_2 \xrightarrow{\text{gas phase}} H_2O_2 + O_2$ 11

$H_2O_2 + (M) \longrightarrow 2\,OH + (M)$ 12

Low temperatures:

$H + O_2 + (M) \longrightarrow HO_2 + (M)$ 13

Table 1.2 (continued)

High Temperatures:

$H + O_2 \longrightarrow OH + O$ 14

$O + CH_4 \longrightarrow H_2 + HCO$ 15

Low oxygen concentrations:

$H + CH_4 \longrightarrow H_2 + CH_3$ 20

$H + CH_2O \longrightarrow H_2 + HCO$ 21

<u>Termination</u>:

Low temperatures:

$HO_2 \xrightarrow{\text{surface}} \frac{1}{2} H_2O + \frac{3}{4} O_2$ 16

$H_2O_2 \xrightarrow{\text{surface}} H_2O + \frac{1}{2} O_2$ 17

High temperatures, acid treated vessels:

$H_2O_2 + OH \longrightarrow H_2O + HO_2$ 18

$H_2O_2 + H \longrightarrow OH + H_2O$ 22

$2CH_3 \longrightarrow C_2H_6$ (and other radical combinations) 23

1.4.2. The heterogeneous catalytic oxidation of methane.

1.4.2.1. Catalytic activities, and the formation of intermediate products.

The main products of the heterogeneous catalytic reaction are carbon dioxide and water, although small amounts of intermediate products are formed over some catalysts. The results of some of the earlier investigations are summarised in Table 1.3, and it appears from these that the formation of formic acid is usually associated with platinum catalysts, whereas aldehydes (usually formaldehyde) are more generally formed over copper and nickel catalysts and some metal oxides. Carbon monoxide and hydrogen are usually produced under conditions favouring partial oxidation (e.g. over nickel oxide [36]) but some workers claim to have obtained up to 60% yields of formaldehyde [37,66]. More recently, it has been claimed that quite high yields of formaldehyde may be obtained from reaction mixtures containing traces of nitric oxide which are allowed to react over rather inactive catalysts [38]. In general, however, it appears that conditions favouring the formation of intermediate products from the heterogeneous catalytic oxidation of methane are hard to produce.

Some of the more recent investigations [28, 39-41] have been concerned with comparing the activities of different

Table 1.3. Reaction products obtained from the heterogeneous catalytic oxidation of methane.

(a) Metal catalysts.

Catalyst	Support	Temperature (°C.)	Products MAIN (trace)	Ref.
Platinum	-	800	CARBON DIOXIDE WATER, (formic acid)	50
"	Asbestos	250-600	ditto	51
"	-	800	ditto	52
"	Asbestos	250-500	ditto	53
"	Asbestos	172-700	ditto	54
"	Silica Gel	200-400	ditto	55
"	-	150-350	ditto	56
"	-	200	ditto	57
Palladium	Asbestos	250-600	CARBON DIOXIDE WATER.	51
"	Asbestos	172-700	ditto	54
"	Silica Gel	200-400	ditto	55
"	Asbestos	200	ditto	58
"	Asbestos	450-700	ditto	59
Silver	Silica Gel	200-400	CARBON DIOXIDE WATER (aldehydes)	55
"	-	500	ditto	60
Copper	-	500	CARBON DIOXIDE WATER (formaldehyde)	61
"	Silica Gel	200-400	CARBON DIOXIDE WATER (acetaldehyde)	55

Table 1.3 (continued)

(a) Metal Catalysts.

Catalyst	Support	Temperature (°C)	Products: MAIN (trace)	Ref.
Copper	Pumice	172-700	CARBON DIOXIDE WATER.	54
Gold	-	150-500	CARBON DIOXIDE WATER	51
Nickel	-	150-900	CARBON DIOXIDE WATER FORMALDEHYDE	62

Oxide Catalysts.

Catalyst	Support	Temperature (°C)	Products: MAIN (trace)	Ref.
V_2O_5	Asbestos	172-700	CARBON DIOXIDE WATER	54
V_2O_5	Pumice	500	ditto	
CuO	Asbestos	250-350	ditto	53,54,64
NiO	"	250-500	ditto	53
NiO	"	100-350	CARBON DIOXIDE WATER FORMALDEHYDE	64
PdO	"	350-500	CARBON DIOXIDE WATER	53
CeO_2	"	50-500	ditto	53
ZnO	"	350-1000	CARBON DIOXIDE WATER FORMALDEHYDE	65
PdO	"	350-1000	ditto	65
ZnO	"	350-500	CARBON DIOXIDE WATER	53
U & Be Oxides	-	500-600	FORMALDEHYDE	66

Table 1.3 (continued)

(c) Under Conditions for Low Conversion.

Catalyst	Support	Temperature (^{0}C)	Products MAIN (trace)	Ref.
Pt(wire) (hetero-homogeneous mechanism)	-	750-850	HYDROGEN CARBON MONOXIDE	67
Cu/CuO	-	700	ditto	68
Cu/UO_2	-	700	ditto	68
Cu/MoO_3	-	700	ditto	68
Pt,Pd Ag,Au	-	700	ditto	69
V_2O_5, CeO_2	-		HYDROGEN CARBON MONOXIDE CARBON DIOXIDE	70
Pt, Pd	Silica Gel		CARBON DIOXIDE WATER (formic acid)	71

catalysts for the complete oxidation of methane. For example, Stein et al.[39] have compared the activity of the oxides of some of the first-row transition metals, together with that of palladium, platinum, silver, gold and molybdenum trioxide. Activation energies of between 16 and 31 kcal.mole^{-1} were obtained, and these values did not vary appreciably with the nature of the support. Pre-exponential factors were also measured, but are of less interest because the surface areas of the catalysts were not determined. Comparison of the activities "per gram of active metal" of catalysts supported by one type of alumina gave the following decreasing order:

$$Pt > Pd > Cr > Mn > Cu > Ce > Co > Fe > Ni > Ag$$

1.4.2.2. Previous investigations of the reaction mechanism.

Previous studies of the reaction mechanism have usually involved the use of the more active catalysts such as palladium and platinum, but some workers have instead used less active materials such as silver or copper oxide.

The reaction over platinum was first studied in detail by Davies [42], who measured the heat evolved on the surface of a platinum wire maintained at the appropriate temperature (200-900°C) in dilute reaction mixtures. His results indicated that the process involved the reaction of adsorbed methane with adsorbed oxygen. This was in contrast with the oxidations of hydrogen and carbon monoxide over the same catalyst, which appeared to proceed by means of the collision of gas phase fuel molecules with adsorbed oxygen. In a more recent study, using temperatures between 600 and 1300°C, Lintz et al.[43] have confirmed Davies' conclusions with respect to methane oxidation by showing that the reaction does not proceed unless the temperature is high enough for methane to compete effectively with oxygen for adsorption sites. These workers have also concluded that carbon monoxide, which was formed in increasing quantities as the temperature was raised, is an intermediate product of the reaction over this catalyst. At very high temperatures [44], platinum atoms and surface complexes are vapourised from the catalyst, so that the mechanism is no longer wholly heterogeneous in character.

The reaction over silver films has been studied at 580°C by Enikolopyan and Bel'gorskii [45]. It was found that, although under their experimental conditions the homogeneous reaction was faster than the heterogeneous process, the latter occurred exclusively in the presence of the catalyst. Furthermore, the small yield (ca. 3%) of formaldehyde from the homogeneous reaction was completely eliminated by the catalyst. The same catalyst was, however, much more active in the oxidation of methanol, and high yields of formaldehyde were obtained from these experiments. Thus formaldehyde cannot be formed as a surface intermediate in the oxidation of methane over silver.

The investigation of the reaction over copper oxide by Bransom et al.[46] emphasises the importance of lattice oxygen. In each of their experiments, a regenerated catalyst containing both cuprous and cupric oxide was used for the oxidation of a number of hydrocarbons, including methane, in the absence of gaseous oxygen. Thus most of the cupric oxide was reduced to cuprous oxide during each experiment. The addition of oxygen reduced the reaction rate. These workers have concluded that the reaction starts by means of the process:

$$\text{Hydrocarbon} + CuO \longrightarrow CO_2 + H_2O + Cu_2O$$

Then, when the resulting surface layer of cuprous oxide has built up to an appreciable thickness, the diffusion of O^{2-} ions through this layer to the surface becomes rate-controlling. The adsorption of the hydrocarbons is thought to involve their acceptance of electrons, and their increasing ease of oxidation with increasing molecular weight is attributed to the concurrent increase in electron affinity.

It has been noted that palladium is one of the most active catalysts in the oxidation of methane, and that it is rarely associated with formation of intermediate products. Firth [47] has investigated the importance of the electronic properties of the metal by means of kinetic measurements over a series of palladium/gold alloys. His results indicate that, at temperatures exceeding 400°C, the rate-determining step is the slow reaction of an adsorbed intermediate formed by the reaction of methane from the gas phase with adsorbed oxygen. Palladium-rich alloys appeared to be saturated with adsorbed oxygen, but on gold-rich alloys, i.e. those containing more than 60 atom % gold, the adsorption of oxygen was weaker and decreased in strength with increasing gold concentration. The products did not appear to inhibit the reaction. Over palladium-rich alloys, the activation energy was found to be 11 kcal.mole^{-1}, and over gold-rich alloys it increased in proportion to the gold concentration. A compensation effect was observed over gold-rich catalysts. Mezaki and Watson [48], and Ahuja and Mather [49], have studied the kinetics of methane oxidation over palladium catalysts, in the temperature range 320-380°C. Mezaki and Watson [48] also concluded that the surface reaction involved gaseous methane and adsorbed oxygen. Ahuja and Mather [49] have critised this work, and claim that the surface reaction involves methane and oxygen both adsorbed on similar sites. In contrast to the results of Firth's study these later investigations both indicate that the products inhibit the reaction. These apparent discrepancies may, perhaps, however, be attributed partly to the different experimental conditions.

1.4.2.3. Summary.

It has been shown that, while intermediate products are not formed in large quantities from the heterogeneous oxidation of methane, those that are produced tend to be associated with particular catalysts. It is therefore quite possible that the overall reaction may proceed by a number of alternative routes, one of which involves the direct conversion of methane to carbon dioxide, while others involve the formation of intermediate products which may be either desorbed or oxidised further. Over all the heterogeneous catalysts so far investigated the routes involving the formation of intermediates are comparatively unimportant, and appear to be of least importance over palladium.

Since alternative mechanisms would perhaps involve different forms of adsorbed methane, the observed overall kinetics would be a complex function of the various processes, It seems advisable in the first instance to determine the kinetic features of the main reaction. The present work is therefore concerned with the oxidation of methane over low-area palladium catalysts at relatively high temperatures. As has been shown, the mechanism of the oxidation of methane over palladium catalysts has not been clearly established. It is therefore intended to make further investigations by means of classical kinetic measurements both on the oxidation of methane itself and on the further oxidations of possible reaction intermediates. It is also proposed to study the behaviour of other hydrocarbons under similar experimental conditions.

EXPERIMENTAL.

2. EXPERIMENTAL

2.1. Apparatus.

2.1.1. General description.

The apparatus, illustrated in Fig. 2.1 and Plate 1, was used to measure the heat changes taking place during catalytic reactions. Its essential feature was the calorimeter, or "bead", onto which the catalyst material was deposited. This bead, and an uncoated compensating bead, were mounted in the reaction vessel of a static gas-handling system. The beads were maintained at a pre-set temperature by means of internal electrical heating, and temperature changes taking place at the surface of the catalyst were measured indirectly by comparing the electrical resistances of the beads, using a double Wheatstone's Bridge circuit.

2.1.2. Detailed description.

2.1.2.1. Catalyst and compensator beads.

The design of the catalyst beads, as shown in Fig. 2.2, was based on commercial "methanometer" elements, originally developed at the Safety in Mines Research Establishment, Sheffield[1]. Each consisted of a bead of alumina, in which was embedded an eleven turn, 0.005 in. pitch coil of platinum wire (0.002 in. diameter). The electrical resistance of these coils was between 1.0 and 1.5 ohms at room temperature. Each bead was formed by successively

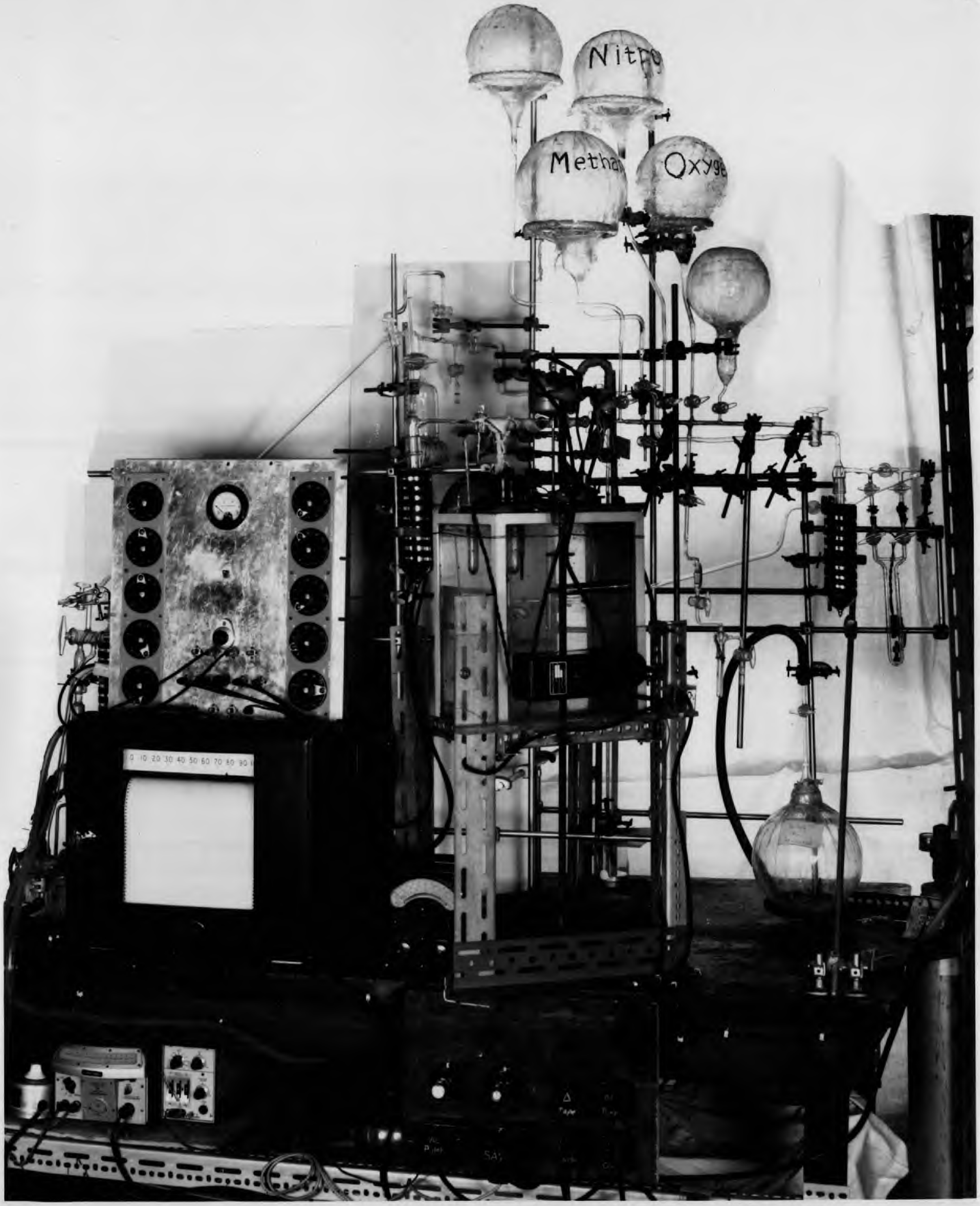


Plate 1 The apparatus

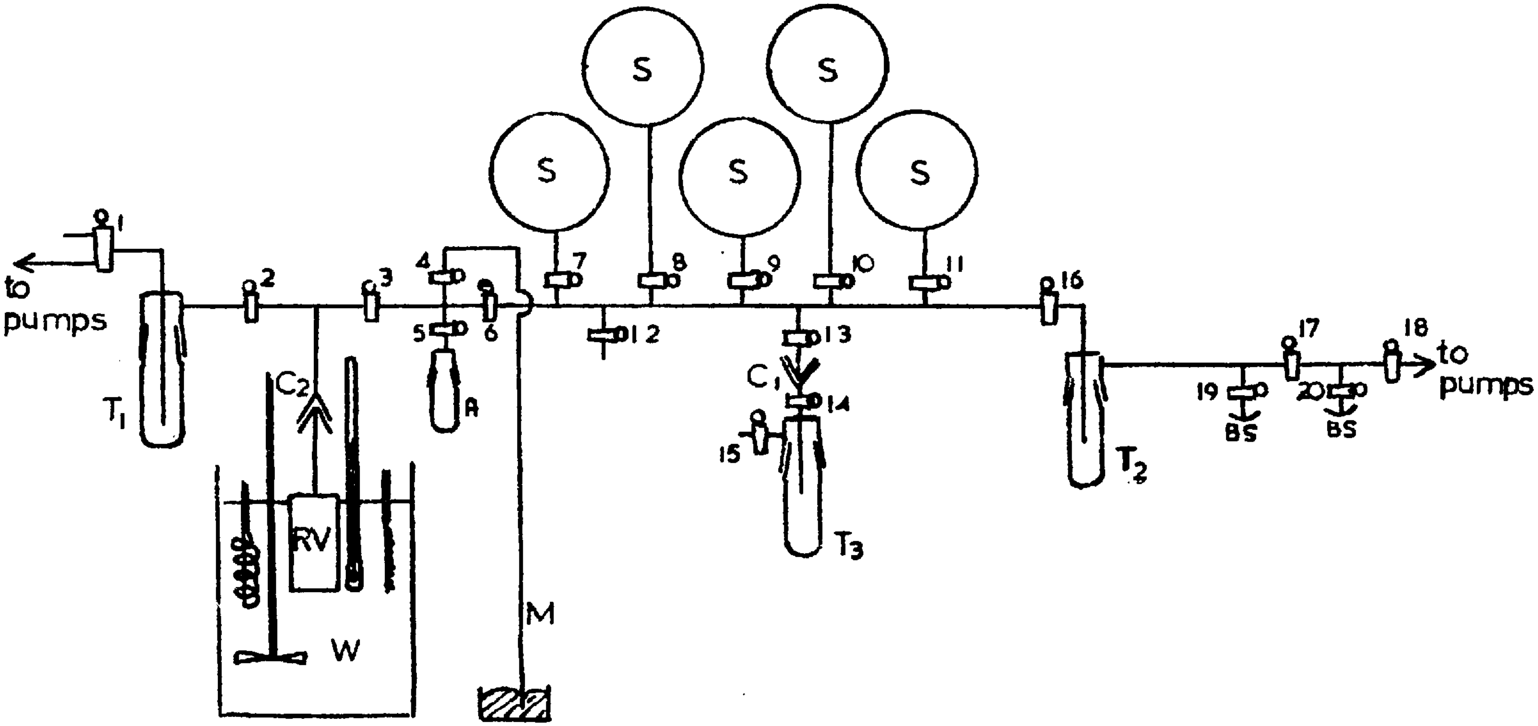


Fig. 2.1. The gas-handling system.

Key to Fig. 2.1.

Component.	Description
1 to 20	High vacuum stopcocks.
S	Gas storage globes.
RV	Reaction vessel.
T_1 to 3	Traps.
C_1	Ground glass joint, B.10.
C_2	Ground glass joint, B.7.
BS	Ball and socket joints.
A	Side arm, capacity 5 ml. approx.
M	Mercury manometer.
W	Water bath, fitted with 0.75Kw. immersion heater, stirrer, "Sunvic" temperature control unit and 0-110°C thermometer.

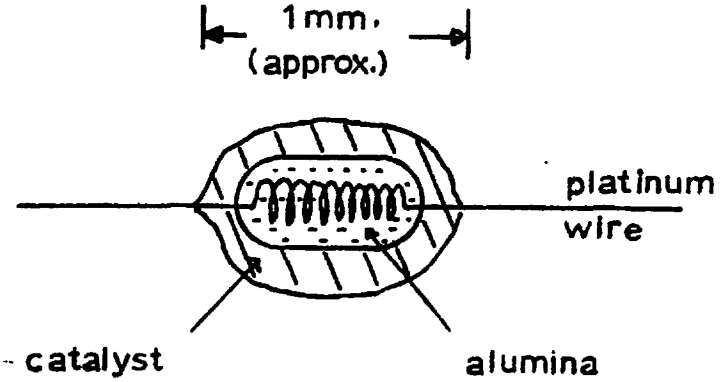


Fig. 2.2. A catalyst "bead".

dipping the coil into a concentrated aqueous solution of aluminium nitrate, and heating it electrically to around 600°C. The process was repeated eleven times to produce a bead of approximately 1 mm. diameter. A catalyst bead was then coated further by a similar process using an aqueous solution of the appropriate metal salts. Further details of the preparation of the various catalysts will be given in section 2.2.

During a reaction, a constant fraction of the heat change taking place at the surface of a catalyst bead was registered as a change in the electrical resistance of the platinum wire. It was necessary, however, to compensate for other changes, due to variations in the thermal conductivity and ambient temperature, by comparing the resistances of catalyst and compensator beads maintained at about the same temperature. The compensator beads were uncoated, but were poisoned to prevent their playing any chemical part in the reaction.

2.1.2.2. <u>Reaction vessels</u>.

The catalyst and compensator beads were mounted in a reaction vessel of volume ca. 80 cm^3 as illustrated in Fig.2.3. Each was constructed from a B.34 pyrex cone and socket, the four support wires and the capillary tube leading to the vacuum line being mounted in the socket, and the cone

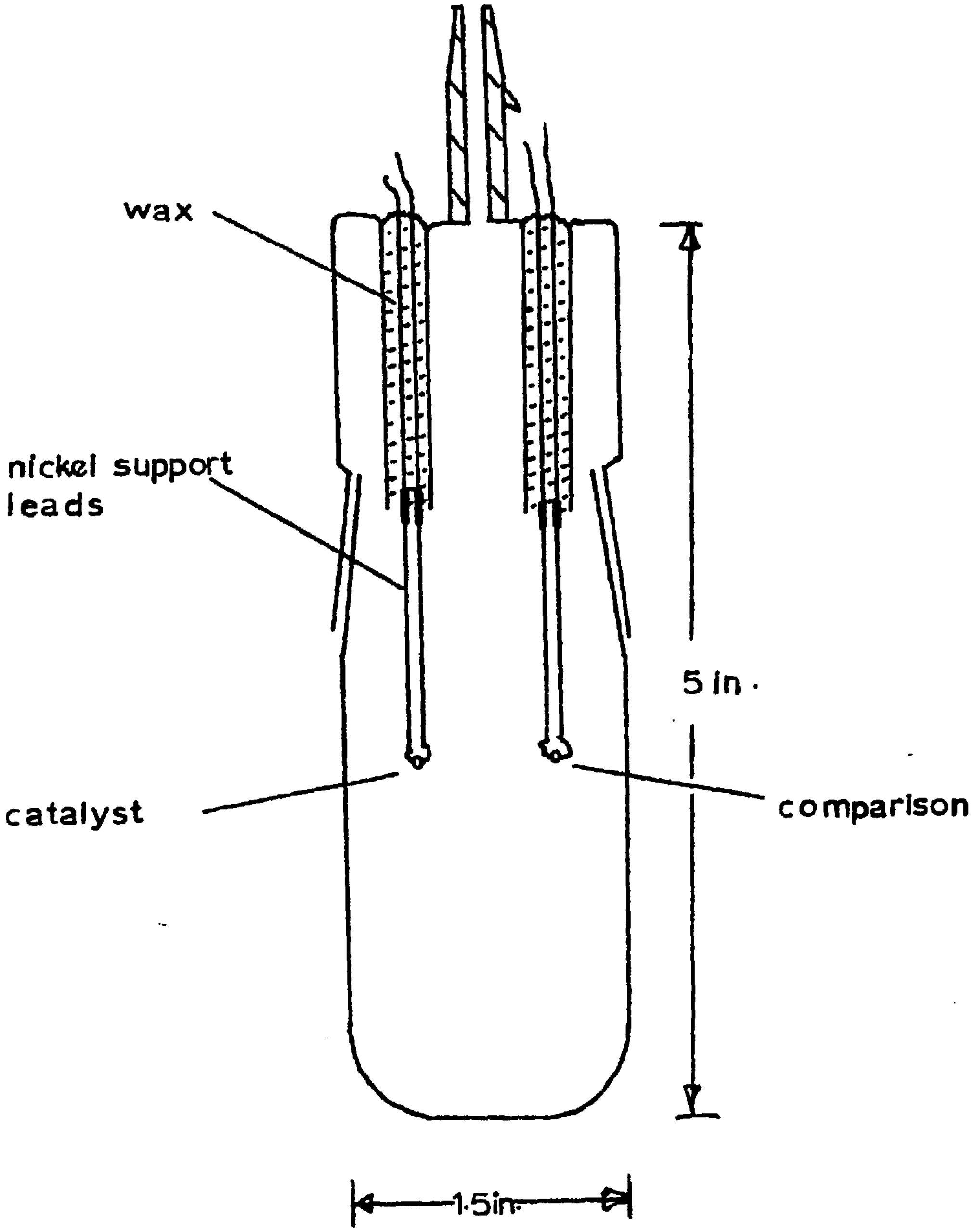


Fig. 2.3. The reaction vessel.

being sealed off to form an envelope. The vessel was attache to the vacuum system by a B.7 capillary cone and socket.

The support wires, obtained from Jencons Ltd. (Scientific Glassware), consisted of nickel/tungsten + glass/ copper-nickel braid "electrodes". The copper-nickel braid wires, which were coated with wax to minimise atmospheric corrosion, were soldered to coaxial cable leads connected to the bridge circuit. The catalyst and compensator beads were mounted by spot-welding their platinum leads to the nickel support wires. Care was taken to keep the platinum leads as short as possible.

2.1.2.3. The static gas-handling system.

The vacuum system, which was constructed of pyrex glass, is shown diagrammatically in Fig.2.1. The "dead space" above the reaction vessel, between stopcocks 2,4,5 and 6, was made as small as possible. Furthermore, this section was lagged with heating tape and maintained at about 70°C during experiments, in order to prevent the condensation of vapours. As shown, the system was connected at various points to a high vacuum line, which was maintained by a two-stage mercury diffusion pump backed by a rotary oil pump.

Joints and stopcocks in the reaction section were lubricated with Apiezon T, a grease which, though hard at room temperature, was found to be both reliable and suitably fluid under operating conditions. All other taps were lubricated with silicone high vacuum grease. Benzene and acetone were used for cleaning purposes: trichloroethylene, a more satisfactory solvent, was avoided because of its drastic inhibiting effects on catalytic oxidation reactions.

Condensable gases entering the system were liquified in trap T_2 at -189°C, and were purified by redistillation, while non-condensable gases were passed through trap T_3, which was also maintained at -189°C. Vapours, such as water and methanol, were admitted to the system from vessels attached to side arm A. Samples of the reaction products for gas chromatographic analysis were collected in tube U, which could be attached either to the vacuum line or to the gas chromatography apparatus by ball-and-socket joints. When necessary, the calibration vessel was attached to the vacuum line by ground glass cone C_1.

The reaction vessel was maintained at a constant temperature ($\pm$ 0.5°C, measured with a mercury-in-glass thermometer) by means of a thermostatically controlled water bath.

2.1.2.4. The bridge circuit.

The electrical network for the measurement and comparison of bead resistances is shown diagrammatically in Fig.2.4., and the specifications of the components are as

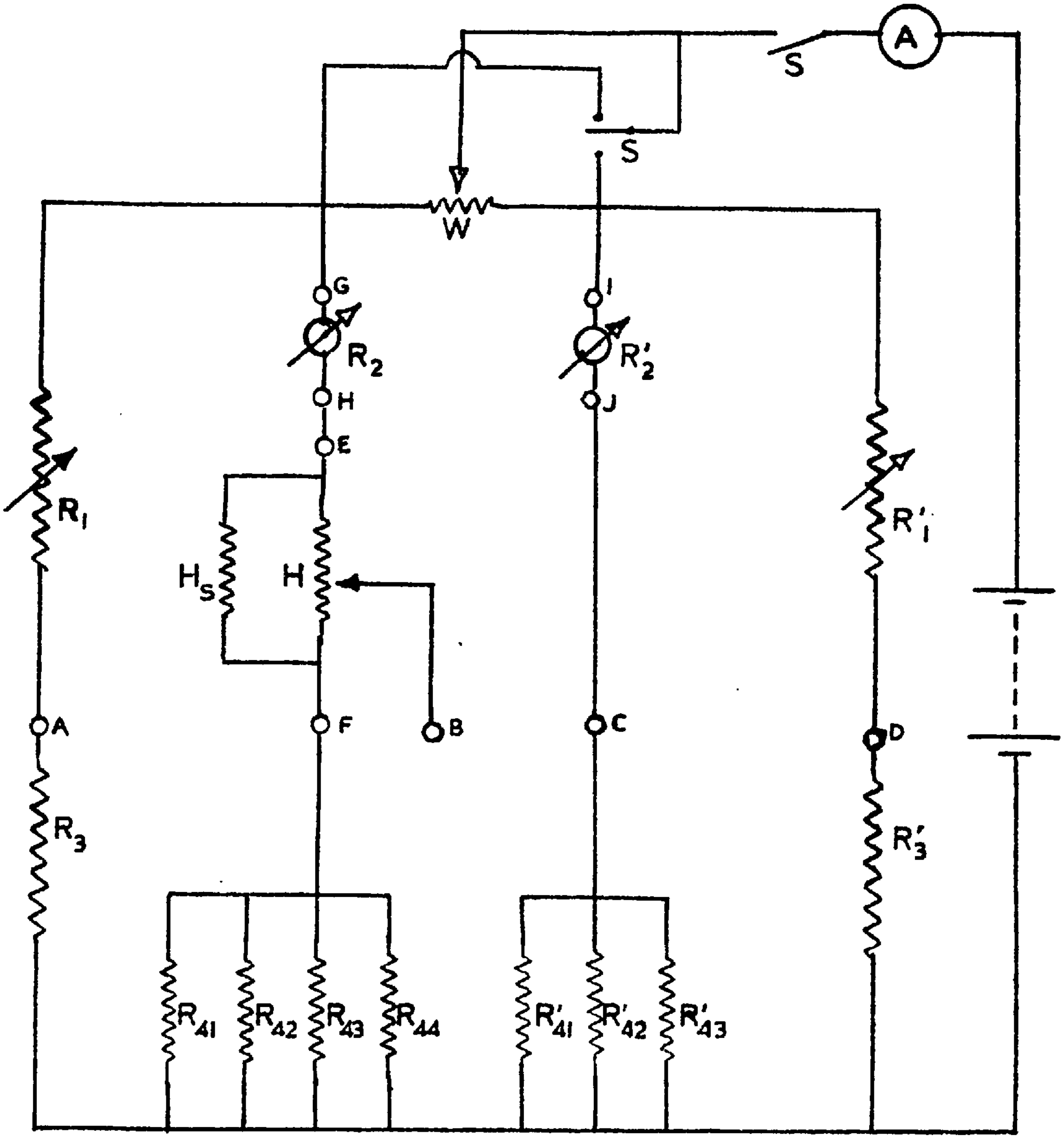


Fig.2.4. The circuit for the measurement of the electrical resistances of the catalyst and comparison beads.

Key to Fig. 2.4.

Component	Description
R_1, R_1'	Decade resistance box, 0.1 to 9999.9 ohm in steps of 0.1 ohm.
R_3, R_3'	Standard resistance, 3000 ohm ± 1%.
R_{4}.1,2 & 3	Standard resistances, 9.00 ohm ± 1%.
R_4'.1,2 & 3	
R_{44}	27 ohm ± 5%.
A to J	Coaxial plugs and sockets, type BNC.
H	10 turn oil filled helical potentiometer, with dial and lock, 1 ohm + 0-20%.
H_s	0.5 ohm ± 5%.
W	1 ohm wire wound helical potentiometer.
A	"Avometer".

Supplementary apparatus:

Pye "Scalamp" galvanometer.

A.E.I. 10 in. potentiometric recorder, model 10 M.

Solartron power unit type AS 1410.

shown in the key. All internal connections were made with thick copper wire and soft solder, and the system was mounted in an aluminium box (see Plate 1). External connections to the galvanometer, recorder and beads, were made with earthed coaxial leads which were connected to the circuit by means of type BNC plugs and sockets, lettered A to J in Fig.2.4.

The circuit was powered by a Solartron type AS 1410 supply unit with the following specifications:

Voltage: 0 - 30 V., variable in steps of 0.1 V.
Current: 0 - 1.1 A., continuously variable.
Temperature coefficient: 0.01% per degree Centigrade.
Long term stability: 0.05% in 1000 hours.

2.1.3. Calibrations.

2.1.3.1. The bridge circuit (see Fig.2.4).

Resistances $R'_{4(1,2 \text{ and } 3)}$, R_3 and R'_3 were measured by means of a post-office box, and were found to be within the makers' specifications, (see key to Fig.2.4). The combined resistance R_4 of the parallel components $R_{4(1 \text{ to } 4)}$, and the combined resistance H' of the helical potentiometer H and its shunt H_s were measured by balancing the bridge formed by short-circuiting W and connecting points C with D, and A with E or F. (It was not necessary to disconnect resistances R_3 and R'_3 on account of their large values). Five separate measurements using decade-box resistances of between 1000 ohms and 9000 ohms gave values of R_4 and H' which were consistent to within 0.05%.

The resistances of the leads from the bridge circuit to the beads were measured by short-circuiting the nickel support wires inside the reaction vessel at the points where the beads would otherwise be connected, and balancing the two bridges R_1, R_2, R_3, R_4, and R_1', R_2', R_3', R_4', (see section 2.3.2). The resistances of the leads to R_2 and R_2' were 0.103 and 0.106 ohms respectively.

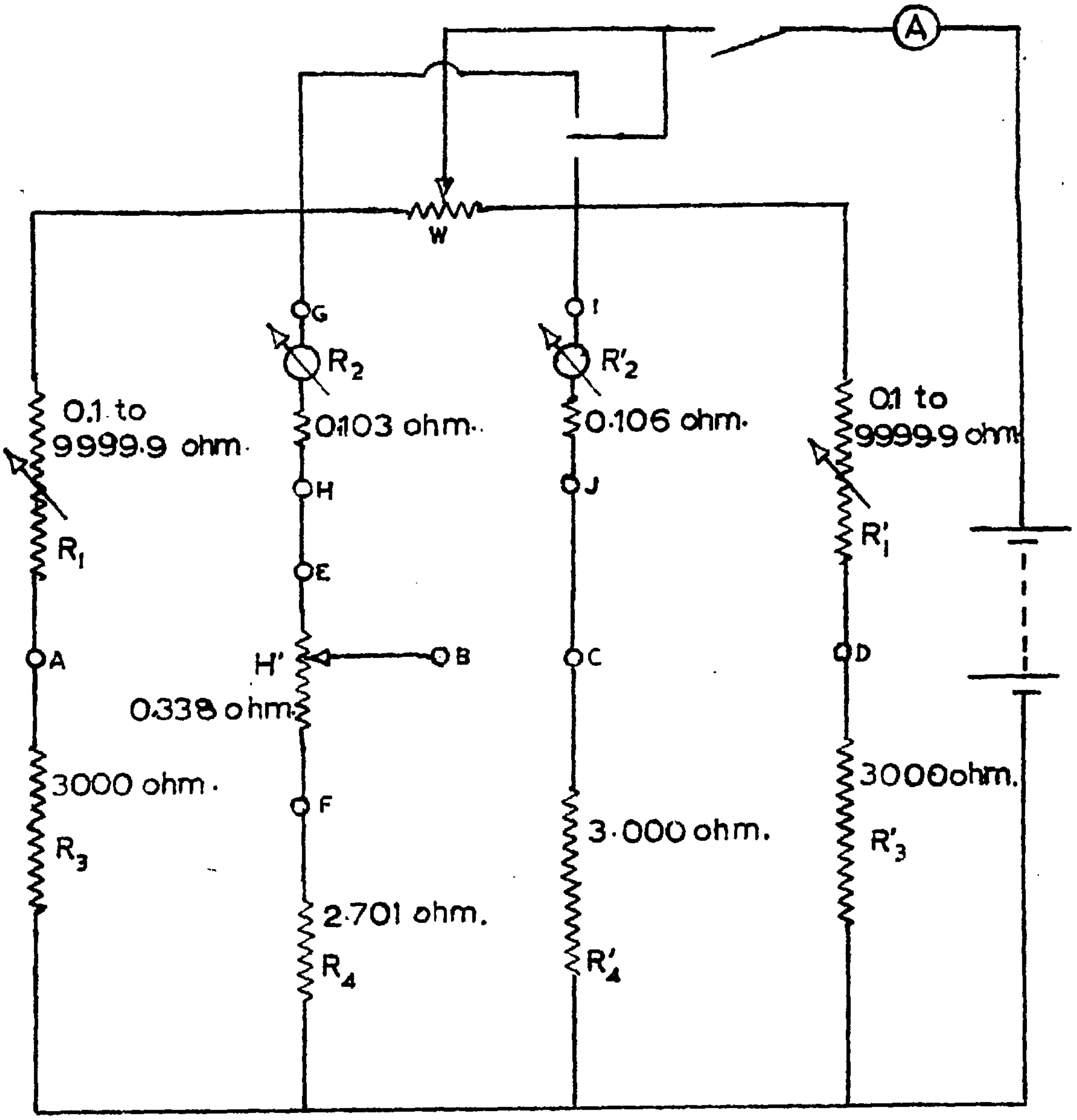
The results of these calibrations, and the combined limitations of the electrical components, are set out on the simplified circuit diagram shown in Fig.2.5.

2.1.3.2. The temperature-resistance characteristics of catalyst beads.

The temperature variation of the resistances of a number of catalyst and comparison beads between 20 and 750°C was determined by maintaining each bead at the required temperature in a furnace and measuring the voltage drop across it on passing a known current of between 10 and 30 mA. Some typical plots of resistance vs. temperature are shown in Fig.2.6; the behaviour both of catalyst beads and of comparison beads conformed to the equation:

$$R_T = R_{20} \left(1 + (0.00325 \pm 0.00006)(T - 20)\right) \quad (2.1)$$

where R_T is the resistance of the bead at T°C, and R_{20} is the resistance of the bead at 20°C.



R_1, R_1'	± 0.1 ohm.
R_2, R_2'	± 0.003 ohm.
R_3, R_3'	± 3 ohm.
R_4 R_4'	± 0.003 ohm.

Fig. 2.5. The simplified circuit diagram.

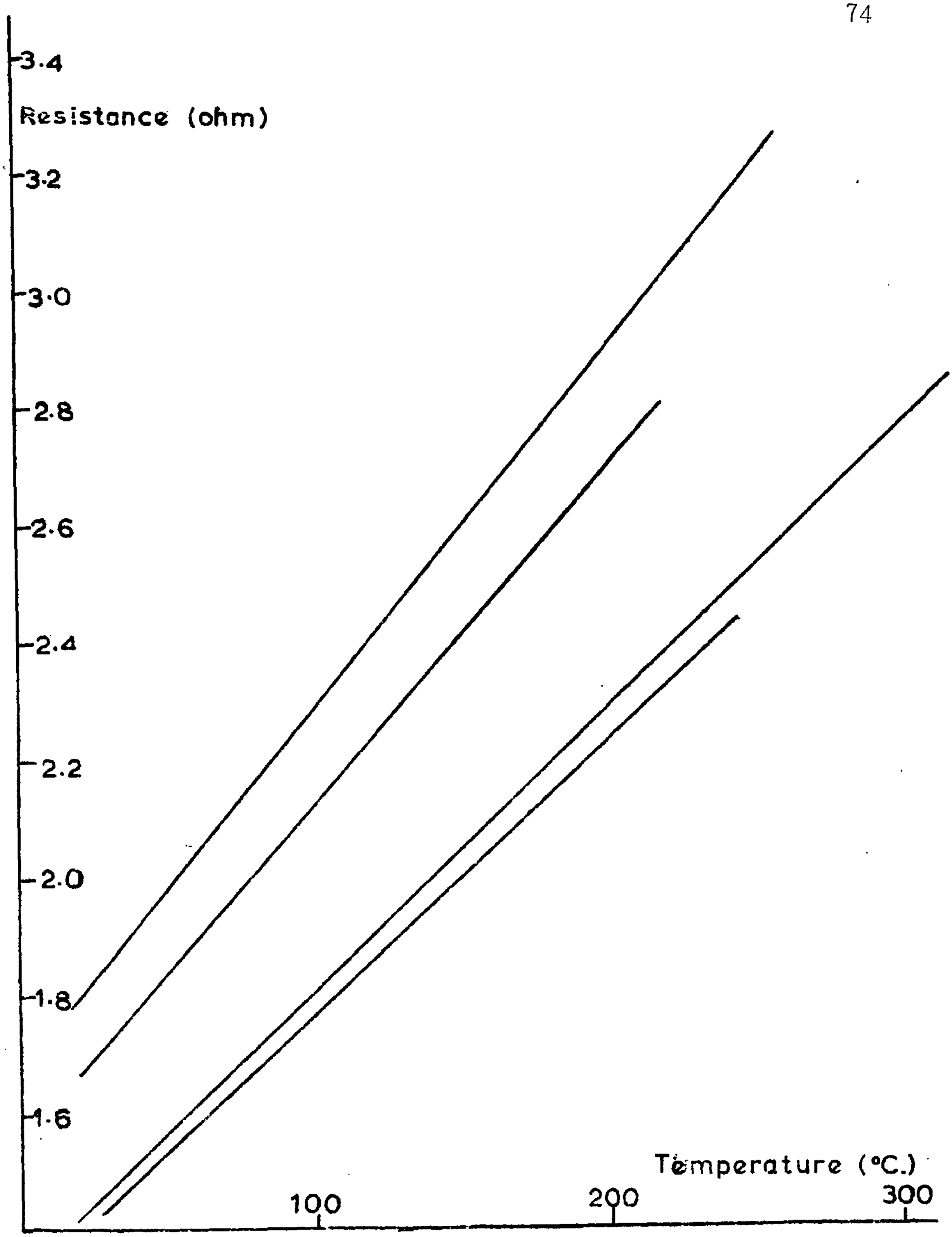


Fig. 2.6. Some plots of electrical resistance against temperature for "catalyst" and "comparison" beads.

It should be noted that an unavoidable uncertainty is introduced into calculations of temperature from resistance measurements by the platinum leads from the nickel support wires to the beads, since there is a temperature gradient across these leads. As previously stated, the leads were made as short as possible, but it was not practicable to standardise their length.

2.1.3.4. Volume calibrations.

The volumes of reaction vessels and of the appropriate sections of the static system were measured by expanding some known amounts of gas from a standard volume attached at cone C_1. Measurements were made with reaction vessel maintained at 21°C, and were found to be consistent to within 0.8%.

2.2. Materials and reagents.

2.2.1. The preparation of catalysts.

Catalyst coatings were deposited on the alumina beads as already described, by dipping in standard solutions of individual metal salts, followed by strong heating of the adhering material.

Where possible, solutions were prepared by dissolving the metal salts in water, but in some cases it was necessary to dissolve the metal oxides in the minimum quantities of A.R. concentrated nitric acid and then to make up the solutions to standard volumes with water. Solutions of each catalyst and support material were prepared separately, and appropriate proportions of both were mixed to form the solutions used for coating the beads. The solutions used in the preparation of various catalysts are summarised in Table 2.1. All the chemicals used were Johnson Matthey "Specpure" reagents, in which the concentrations of single impurities did not exceed 5 p.p.m. Distilled water was purified further by means of a "Deeminac" model 32-6 de-ioniser, and solutions prepared in clean pyrex apparatus were used immediately.

The catalyst coatings were deposited as follows. Each bead was suspended between two stainless steel artery clips, which were connected across a 12 V accumulator via an ammeter, a variable resistance, a switch and a 1-amp fuse. The current passed when the bead was hot (i.e. about eight seconds after the circuit had been switched on) was adjusted to 0.40 A, which corresponded to a temperature of approximately 700°C. With the circuit switched off, a drop of solution was placed on the bead, which was then electrically heated in air for 15 sec. This process was repeated according to the thickness of coating required. With 0.23 M. solutions, the process was repeated six times, and the number of times the process was repeated increased with increasing dilution of the

Table 2.1. <u>Solutions used in the preparation of catalysts</u>.

	Substance dissolved to form				Proportions of solutions used	No.of coats
Catalyst	Palladium	Conc. (M)	Support	Conc. (M)		
Pd/CeO_2	$(NH_4)_2PdCl_4$	0.460	$Ce(NO_3).6H_2O$	1.843	1:1	6
Pd/Sm_2O_3	"	"	Sm_2O_3	0.457	1:2	6
Pd/Pr_6O_{11}	"	"	Pr_6O_{11}	0.152	1:2	6
Pd/UO_2	"	"	$(UO_2)(NO_3)_2$ $.6H_2O$	0.185	1:10	20
Pd/Er_2O_3	"	"	Er_2O_3	0.0922	1:10	20
Pd/Tl_2O_3	Pd *	0.24	$TlNO_3$	0.183	2:5	12
Pd/ThO_2 in various proportions	$(NH_4)_2PdCl_4$	0.255	$Th(NO_3)_2$ xH_2O	0.260	1:9, 2:8, etc.	12

* Used because of the formation of a precipitate by thallous nitrate and ammonium chloropalladite.

solutions. The beads were then mounted in the reaction vessel of the static system.

The usual procedure for activation was as follows. A 12% methane/air mixture was admitted to the reaction vessel at a pressure of about one atmosphere, and the bridge circuit was switched on at a current that would heat the bead to about 450°C in one atmosphere of pure air. The bead temperature on admission of the reducing mixture was increased by the heat of reaction to an initial value of between 750 and 900°C. After one minute, the current was switched off and the reducing mixture was replaced by dry air, in which the bead was maintained at about 600°C for 15 sec. These two processes were repeated four times for 15 sec. each.

Compensator beads were poisoned so that they would play no chemical part in the system over the temperature ranges investigated. This was done by dipping the uncoated bead into a boiling 1% solution of potassium hydroxide and then heating it to 800°C for about 1 min.

2.2.2. Gases and vapours.

Methane, with a specified purity of 99.98%, was obtained from Air Liquide (Division Belge). It was transferred to its storage globe from the cylinder and was used without further purification.

Carbon monoxide and oxygen, supplied by the British

Oxygen Company, were purified by redistillation. Care was taken on each occasion to store only a small middle fraction of the boiling liquid.

Air, "oxygen free" nitrogen, and hydrogen, also supplied by the British Oxygen Company, were further purified by being passed slowly through cold trap T_3, which was surrounded by liquid nitrogen.

Water vapour was evacuated from distilled and deionised water, and methanol vapour was produced from A.R. methyl alcohol supplied by Burroughs Ltd., which was used without further purification.

Formaldehyde vapour was generated by gently warming paraformaldehyde. The powder was previously dried by cautious evacuation (via a U-tube trap separated from the main vacuum system) accompanied by very gentle warming. The dry paraformaldehyde was stored under vacuum. When introducing formaldehyde into the reaction vessel, the heat source was removed from the paraformaldehyde before the vapour was admitted to the apparatus through stopcock 5, so as to minimise the risk of powder being blown into the reaction system.

2.3. Procedure.

2.3.1. Gas handling.

In each experiment, the manometer M, the reaction vessel and the line from the storage globes, were first evacuated to ca. 10^{-4} mm.Hg. Gases and gas mixtures could then be admitted to the reaction section of the apparatus from the storage globes. Reaction mixtures were prepared in the reaction vessel, and their compositions were determined by means of pressure measurements using M. For the more accurate measurement of small partial pressures of methane, a mixture containing about 20% methane in oxygen was prepared previously in one of the storage globes. Vapours of substances normally liquid at room temperature were introduced into the reaction vessel before the gaseous components.

2.3.2. Electrical measurements.

Before each series of kinetic experiments, it was necessary to measure the cold resistance of the catalyst bead, so that the temperature variation of its resistance could be calculated. This was done by passing a small current (ca. 25 mA.) through the circuit and balancing the bridge containing the catalyst bead with the aid of a Pye Spot galvanometer.

In each experiment, the power unit was first set to give the required constant current, and the recorder was connected across terminals B and C so as to measure the "out-of-balance potential" across the bridge network formed by R_2, R_2', R_4 and R_4'. Then, when the gas mixture had been prepared and the reaction section had been closed off, the recorder chart motor and the bridge circuit were switched on simultaneously, and the helical potentiometer H was quickly adjusted so that the balance point was within the scale of the recorder. This state of affairs was maintained by means of further periodic adjustments of the potentiometer. At the end of the reaction, indicated by a constant balance point, the recorder was disconnected, and the resistances ofthe catalyst and compensator beads were measured by balancing bridges R_1, R_2, R_3, R_4 and R_1', R_2', R_3', R_4'. Before each experiment, the catalyst was degassed by heating under vacuum at ca. 800°C. for $1\frac{1}{2}$ to 2 minutes.

2.3.3. Analytical.

2.3.3.1. The analysis of reaction products by gas chromatography.

Reaction mixtures were analysed by means of a Pye Series 104 gas chromatograph, which used a thermal conductivity detector. The instrument was fitted with two 2-metre columns containing silica gel and Linde 5A molecular sieve respectively, so that either could be used for the separation of the components of the sample. In all measurements, the columns and the detector were maintained at 50°C, and the flow rate of the argon carrier gas was controlled at 50 ml. min^{-1} at atmospheric pressure. The retention times and the response of the instrument to various gases is shown in Table 2.1. All peaks were sharp and symmetrical, so that peak heights were proportional to concentrations. It should be noted that the limit of detection of carbon monoxide in the presence of appreciable quantities of oxygen is not as low as would be expected from the sensitivity of the instrument, because the separation of these two components is not quite adequate.

Samples were taken by sharing the contents of the reaction vessel with the larger section of a previously calibrated double "U" tube, shown in Figs. 2.7 and 2.4. Water vapour was removed by means of trap T_2, which was loosely packed with glass wool and cooled by an ice-salt mixture. The pressure of the sample was measured by means of manometer M. The tube was then removed and connected to the carrier gas supply to the chromatograph, as shown in Fig. 2.8. Air from the connecting arms was then swept out by passing carrier gas through the by-pass tube. When this air had passed through the chromatograph, the carrier gas was diverted through the tube containing the sample. All analyses were carried out in duplicate.

Gas mixtures containing methanol or formaldehyde were also analysed on a Perkin Elmer F.11 gas chromatograph with a single flame-ionisation detector, fitted with a

Table 2.2. Gas Chromatograph Calibrations.

(a) Calibrations for the thermal conductivity detector and the silica gel column maintained at 50°C, argon carrier gas flowing at 50 ml. min^{-1} at 1 atmosphere pressure and room temperature. "x" is the amount of gas, in moles, giving a peak 1 cm. high on the chart paper.

Gas	x (moles)	Response time (sec.)
Hydrogen	$5.2 \pm 0.2 \times 10^{-9}$	56
Oxygen	$2.4 \pm 0.1 \times 10^{-8}$	86
Carbon monoxide	$4.0 \pm 0.1 \times 10^{-8}$	102
Methane	$2.0 \pm 0.2 \times 10^{-8}$	138
Carbon dioxide	$5.2 \pm 0.4 \times 10^{-7}$	758

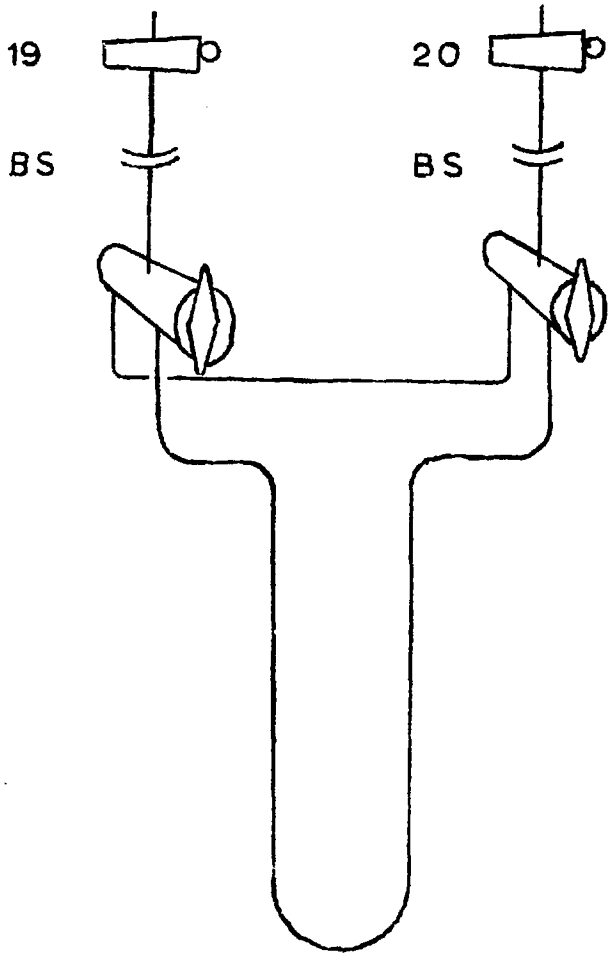
(b) Calibrations for the thermal conductivity detector and the molecular sieve column, with conditions as in (a)

Gas	x (moles)	Response time (sec.)
Hydrogen	$3.3 \pm 0.2 \times 10^{-9}$	96
Oxygen	$5.4 \pm 0.2 \times 10^{-8}$	130
Methane	$6.3 \pm 0.1 \times 10^{-8}$	354
Carbon monoxide	$2.0 \pm 0.1 \times 10^{-7}$	578

N.B. continued

Table 2.2 (continued)...

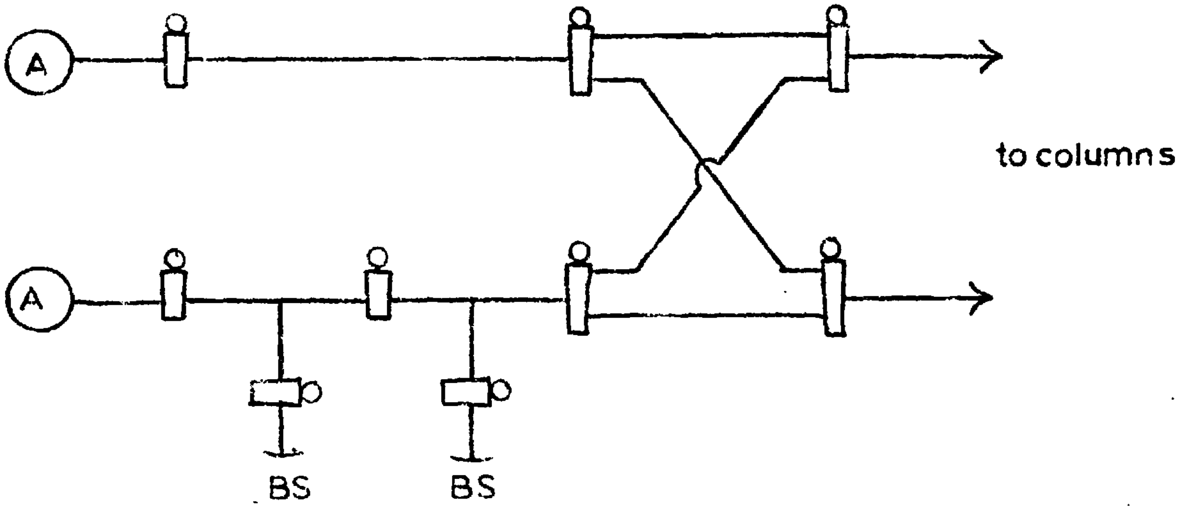
<table>
<tr><td colspan="2">(c) Calibrations for the flame ionization detectors and the squalane column maintained at 30°C, with nitrogen carrier gas flowing under a pressure of 4.5 lb. in.$^{-2}$.</td></tr>
<tr><td>Methane :</td><td>1 cm. peak height is equivalent to 1.72 ± 0.4 x10^{-3} mm.Hg in a sample of 1 ml.. The response time was 42 sec.</td></tr>
<tr><td>Methanol:</td><td>100 cm^2 peak area are equivalent to 2.9 ± 0.02 cm. Hg in a sample of 1 ml.. The response time was 180 sec.</td></tr>
</table>



BS = Ball and socket joint

For the location of stopcocks 19 and 20, see Fig.2.1.

Fig. 2.7. The calibrated double "u" tube for the sampling of reaction products.



A = Argon cylinder (with reducing valve).

BS = Ball-and-socket joint.

Fig. 2.8. The gas supply system for the dual column gas chromatograph.

2-metre column of squalane (15% w/w) coated on "Chromosorb P". The optimum operating conditions were found to be:

Hydrogen pressure:	10 $lb.in^{-2}$	to the flame
Air pressure:	25 $lb.in^{-2}$	
Nitrogen pressure:	4.5 $lb.in^{-2}$	carrier gas
Oven temperature:	30°C.	

Under these conditions, the methane peak was very sharp, so that the peak height was proportional to the concentration of methane. The methanol peak, however, exhibited considerable "tailing", so that peak area measurements were necessary for the estimation of this component. Retention times and sensitivities are shown in Table 2.2.

Samples for this instrument were taken by sharing the contents of the reaction vessel with an evacuated volume, fitted with a stopcock, connected to the main vacuum line at C_1 (see Fig. 2.1). This volume was then transferred to a vacuum line connected to the gas-sampling valve of the chromatograph. This line was fitted with a manometer, so that standard samples of 0.5 ml. at known pressures could be introduced onto the column by means of the gas-sampling valve.

2.3.3.2. Colorimetric Analysis.

Investigations were made of the usefulness of the chromotropic acid test [72] for detecting formaldehyde among the reaction products. This test involves the measurement of the intensity of the purple colour formed by adding a small quantity of chromotropic acid solution, and then a larger amount of concentrated sulphuric acid, to a small sample of an aqueous solution of formaldehyde. The absorption intensity of the solution is normally measured at 570 mμ However, it was confirmed that, as stated in the literature, the smallest quantity of formaldehyde that can be detected by this method is ca. 3×10^{-6} moles. Typical reaction mixtures contained 5×10^{-5} moles methane, so that formaldehyde would only be detected at conversions of more than 6%. No previous investigations of methane oxidation over palladium have reported formaldehyde formation in anything like this quantity, and reaction mixtures were not therefore analysed in this way.

2.3.3.3. X-ray analysis of the catalysts.

The structures of the catalysts used were studied by procedures similar to the "powder diffraction pattern method" of X-ray analysis. Since the quantity of catalyst material in each bead was insufficient for the preparation of a sample in a thin-walled glass capillary tube, two less satisfactory methods of sample preparation were used. The first merely involved suspending the bead in the sample holder of the camera by means of its platinum lead wire. It will be noted that the sample diameter (ca. 1 mm.) was rather larger than is desirable. In the second, a cylindrical sample approximately 0.5 mm x 10 mm was formed by crushing the bead, removing the platinum wire and mixing the powder with gum tragacanth and a trace of water. Samples of palladium and platinum were in wire form, and samples of metal oxides were prepared by sealing some of the powdered form of each oxide in a thin-walled capillary tube (0.25 mm. internal diameter).

Samples were mounted in a circular "rotating sample" camera of diameter 9 cm. and were photographed using nickel screened copper-alpha radiation accelerated across 50 kV, (Wavelength 1.542Å). Exposure times of 0.5 to 3 hr., with a filament current of ca. 15 mA., were used. Microdensitometer traces of some of the films were kindly made by the Safety in Mines Research Establishment, Sheffield.

2.3.3.4. Electron microscopic studies of the catalyst surfaces.

Electron micrographs of the surfaces of catalyst beads were kindly taken by Mr.A.E.B.Presland of the Department of Chemical Engineering and Chemical Technology, Imperial College. It was not possible to photograph the surfaces directly because of their curvature. Instead, a plastic "replica" of each was made by covering the bead with cellulose acetate, and then stripping this material off the surface. The replica was covered with carbon by evaporation, and in some cases also "shadowed" with gold, and it was then photographed under the electron microscope at magnifications of between 8,000 and 40,000.

2.4. The interpretation of experimental rate measurements.

The measurement of reaction rate from the out-of-balance potential from a Wheatstone's Bridge circuit was described in section 2.3.2. In addition to the surface reaction itself, a number of physical factors are involved in producing the observed rate. The effects of these factors must therefore be analysed so that the significance and limitations of the measurements can be assessed.

The catalyst reached the reaction temperature within about ten seconds of the start of each experiment. Thereafter, electrical energy was dissipated from both catalyst and comparison beads by convection, conduction and radiation, while heat was evolved by the reaction at the surface of the catalyst bead. A reaction proceeding at x moles of methane per second evolves heat at the rate of $x.\Delta H.J$ joules sec^{-1}, where ΔH $cal.mole^{-1}$ is the standard heat of reaction under the prevailing conditions, and J is the electrical equivalent of heat. If a fraction, f, of this, transferred through the bead to the central platinum wire, raises the temperature of the wire by ΔT degrees, the resistance of the wire increases by an amount ΔR ohms, given by:

$$\Delta R = \Delta T.\, dR/dT \qquad (2.2)$$

Neglecting the small reduction in the current through the bead, and the consequent small increase of power dissipated by the comparison bead, the out-of-balance potential V mV. is proportional to ΔR, and thus to the rate of reaction. Thus, if power of dh/dt watts is required to maintain the bead at $T^{o}K$, then the increment $\Delta(dh/dt)$ required to increase the bead temperature by ΔT^{o} is given by:

$$\Delta \frac{dh}{dt} = \Delta T.\, \frac{d(dh/dt)}{dT} \qquad (2.3)$$

Since:

$$\Delta \frac{dh}{dt} = x.f.\Delta H.J \qquad (2.4)$$

we have, combining 2.2, 2.3, and 2.4, that:

$$\Delta R = x.f.\Delta H.J.(dR/dT).(d(dh/dt)/dT)^{-1} \qquad (2.5)$$

Now, if the total bridge current is i A., then the current through the catalyst bead i_x is given by:

$$i_x \simeq i.(R_2' + R_4') / (R_2 + R_2' + R_4 + R_4') \qquad (2.6)$$

Therefore:

$$V = \frac{i.10^3.(R_2' + R_4')}{(R_2 + R_2' + R_4 + R_4')} .J.x.f.\Delta H.(dR/dT) .(d(dh/dt)/dT)^{-1} \qquad (2.7)$$

so that:

$$\log x = \log V + \text{constant} \qquad (2.8)$$

Equation (2.8) provides a basis for the calculation of kinetic data. However, certain factors in the constant term may vary during the course of a reaction, and furthermore, the reaction conditions are not strictly isothermal. Thus both the thermal properties of catalyst beads and the effect of temperature variations on reaction rate must be considered in more detail.

2.4.1. The effects on rate measurements of temperature variations during reaction.

In most experiments, the measured initial rates corresponded to surface temperatures which were 7 to 15° higher than the "final" reaction temperature. The effects of these non-isothermal conditions are less marked at higher temperatures, and in reactions with low activation energies. For example, it may readily be shown by means of the Arrhenius equation that the rate constant of a reaction the activation energy of which is 11 kcal.mole^{-1} decreases by approximately 15% as the temperature falls by 13° from 427°C, and by about 9% for the corresponding temperature fall from 627°C. The effects of these variations on kinetic measurements are to increases slightly both the order with respect to concentration and the order with respect to time. It is therefore necessary to correct the experimental results for these effects wherever practicable.

2.4.2. The rate of dissipation of energy of catalyst beads, dh/dt, as a function of temperature.

In a non-reacting system, the electrical power required to maintain a bead at a fixed temperature, $T^{\circ}C$, is readily measured as a function of T and of the atmosphere surrounding the bead. Fig.2.9 illustrates the parabolic form of this function. It appears, (see Tables 2,3 and 2.4) that the power required to maintain a bead at a constant temperature is proportional to the pressure of the gas surrounding the bead, and is also approximately proportional to the thermal conductivity of the gas. With respect to the experimental measurments, it is necessary to assess the variation of dh/dt over small ranges of temperature, and also its variation with small changes in the composition of the surrounding atmosphere. Values of the temperature coefficient $d(dh/dt)/dT$ may be measured as the slopes of curves of the type shown in Fig. 2.9, and the variation of this coefficient as a function of temperature is shown in Fig.2.10. It may be noted that the coefficient increases both with increasing temperature and with increasing thermal conductivity of the gas. Values of the fractional increase, y, in $d(dh/dt)/dT$ over 30° intervals at various temperatures were found to be independent of temperature and pressure, but to be higher in gases with higher thermal conductivities (see Table 2.5). Thus, for a bead cooling in oxygen or carbon dioxide, d(dh/dt)/dT may be expected to decrease by about 7% for each 30° fall in temperature. This variation tends to offset the effect of temperature change during the reaction.

The situation in a mixture in which composition is changing is less easily clarified. It may be seen from Fig. 2.10 (curves 3 to 6) that the variation of d(dh/dt)/dT with composition at constant temperature is appreciable. For example:

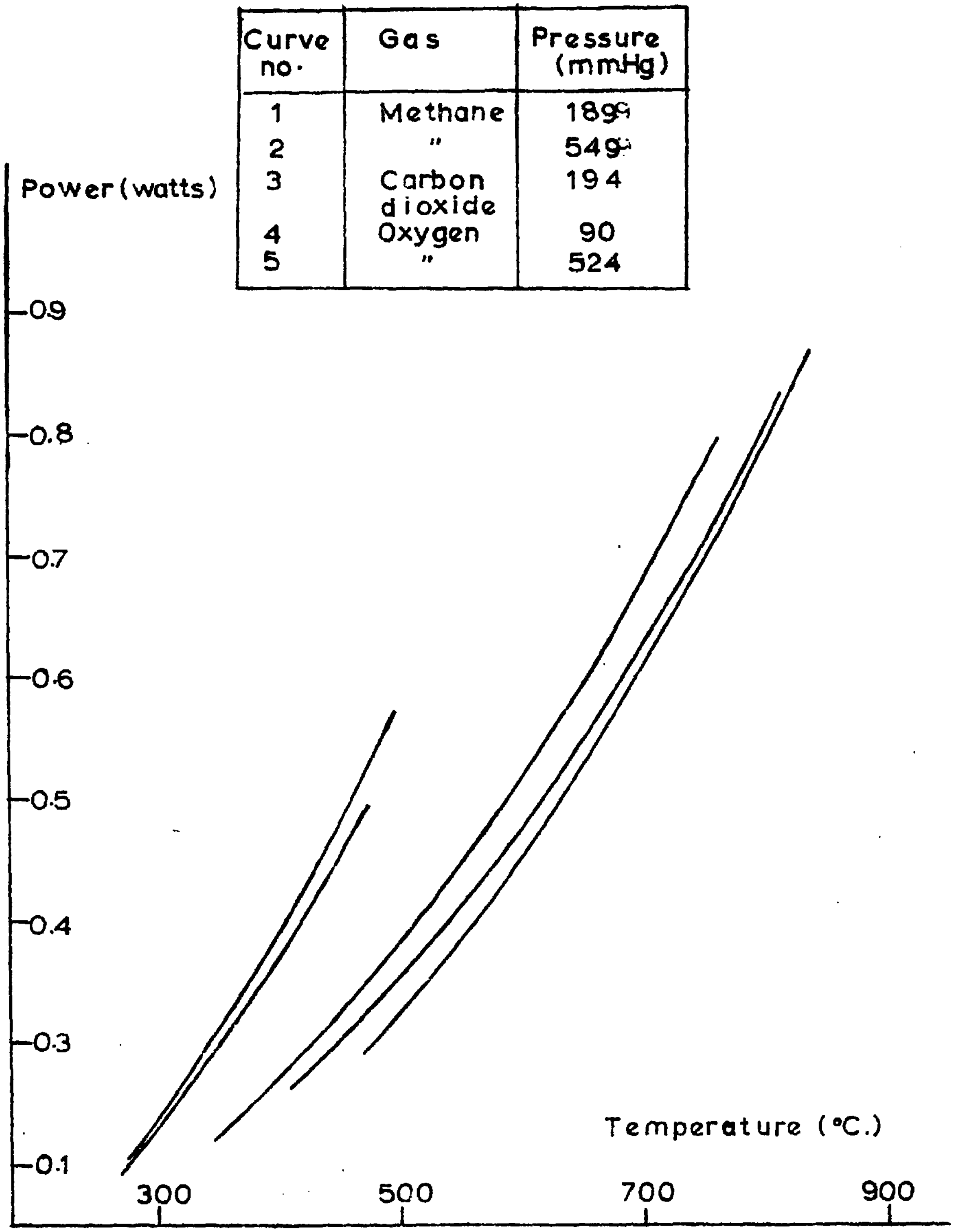
$$\frac{d\,(dh/dt)}{dT}_{4\,,750^{\circ}K} = 0.8\,\frac{d\,(dh/dt)}{dT}_{3\,,750^{\circ}K} \qquad (2.9)$$

$$\frac{d\,(dh/dt)}{dT}_{6\,,750^{\circ}K} = 0.64\,\frac{d\,(dh/dt)}{dT}_{3\,,750^{\circ}K} \qquad (2.10)$$

However, the differences in composition between mixtures C,D etc. are very much greater than the variation in the composition of a typical reaction mixture during an experiment. It seems reasonable therefore to suppose that the variation in the temperature coefficient due to the small composition changes involved in most experiments is negligible.

2.4.3. The variation with temperature of the fraction, f, of the heat of reaction transferred to the centre of the bead.

The heat of reaction liberated at the catalyst surface is dissipated partly by conduction through the bead



Curve no.	Gas	Pressure (mmHg)
1	Methane	189
2	"	549
3	Carbon dioxide	194
4	Oxygen	90
5	"	524

Fig. 2.9. The power required to maintain a catalyst bead at various temperatures in different gases.

Curve no.	Gas mixture composition (mm.Hg)		
	Methane	Carbon dioxide	Oxygen
1	549	—	—
2	139	—	—
3	53	268	—
4	85	105	—
5	50	165	—
6	—	—	342
6	—	281	57
7	—	—	90
8	—	194	—
9	—	120	—

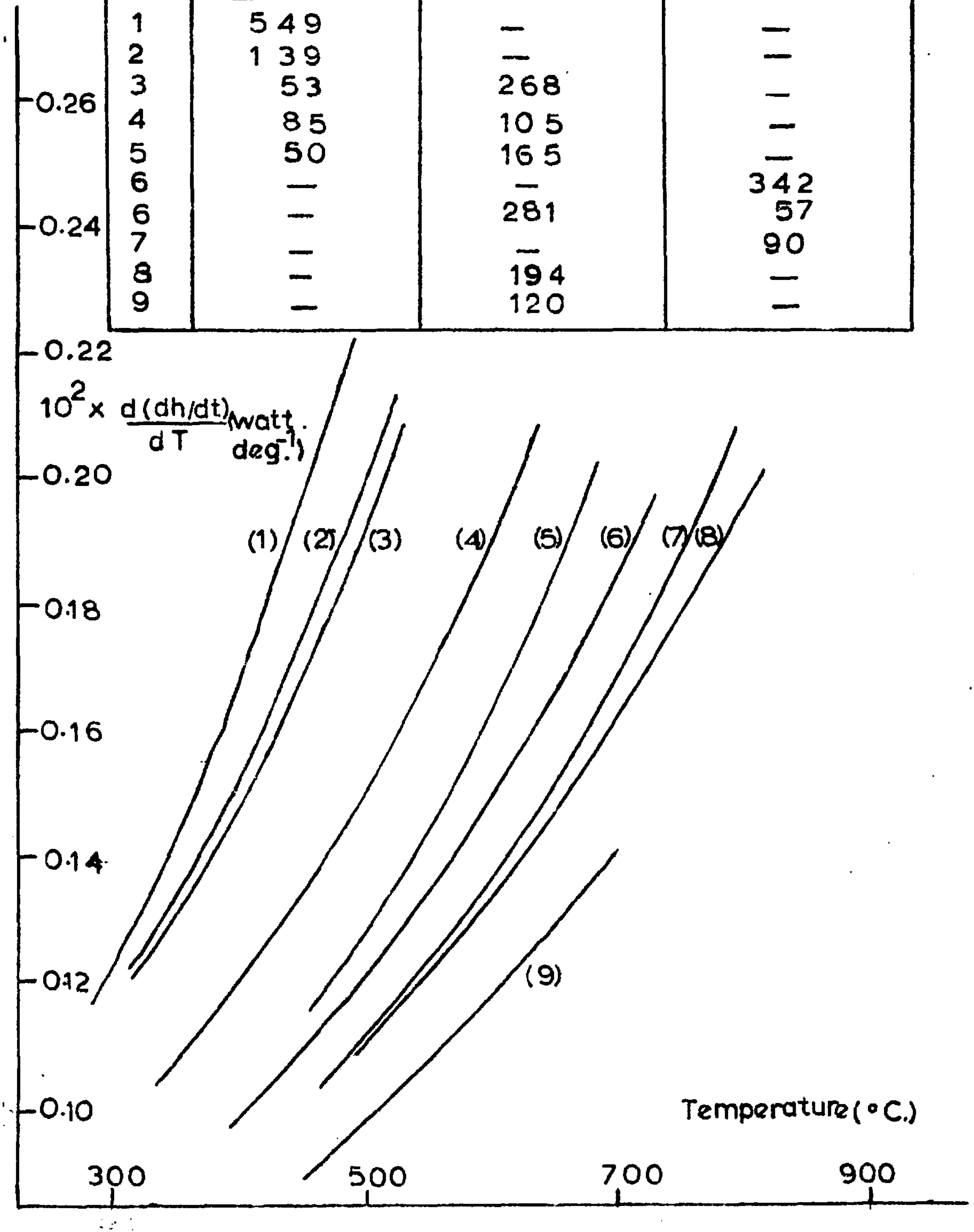


Fig.2.10. Some plots of the temperature coefficient of the power dissipation against temperature in various gases.

Table 2.3. The rate of dissipation of energy by a catalyst bead at various temperatures in a number of gases and gas mixtures.

Composition of gas mixture		Power dissipated (watts) at temperatures:				
Pressure (mm.Hg)	Component(s)	310°C	377°C	534°C	691°C	808°C
90	Oxygen		0.229	0.394	0.612	
181	Oxygen		0.222	0.400	0.629	
402	Oxygen		0.245	0.415	0.642	
524	Oxygen		0.246	0.427	0.664	
139	Methane	0.178	0.327	0.609		
273	Methane	0.182	0.340	0.620		
439	Methane	0.194	0.348	0.639		
549	Methane	0.199	0.354	0.655		
120	Carbon dioxide			0.361	0.557	0.731
194	Carbon dioxide			0.362	0.591	0.801
85	Methane and		0.264	0.478		
105	Carbon dioxide					
50	Methane and		0.234	0.423	0.682	
165	Carbon dioxide					
53	Oxygen and		0.211	0.374	0.540	0.813
155	Carbon dioxide					
57	Carbon dioxide,		0.234	0.403	0.631	
281	Oxygen					

Table 2.4. <u>Comparisons of the power dissipated by a catalyst bead in different gases at constant temperature and pressure</u>.

Gases	Temp. (°C)	Ratio of power dissipated at pressures:				Ratio of Thermal Conductivities *
		20 mm.Hg	30 mm.Hg	40 mm.Hg	50 mm.Hg	
Oxygen : Methane	377	0.695	0.695	0.694	0.693	0.77
Oxygen : Methane	534	0.656	0.654	0.655	0.653	0.77
Carbon dioxide Methane	534	0.592	0.598			0.49
Carbon dioxide Oxygen	534	0.905	0.914			0.63
Carbon dioxide Oxygen	691	0.941	0.898			0.63

* Calculated from values at 25°C given in "Tables of Physical and Chemical Constants" G.W.C.Kaye and T.H.Laby, 13th Ed., Longmans, 1966.

Table 2.5. The fractional increase, y, in d(dh/dt)/dT over 30° temperature intervals.

Gas	Partial pressures (mm.Hg)	Temperature range (°C)	y
Methane	130 - 500	287 - 467	0.079 ± 0.008
Methane + Carbon dioxide	53 + 268	287 - 467	0.080 ± 0.002
Methane + Carbon dioxide	85 + 105	357 - 577	0.081 ± 0.002
Methane + Carbon dioxide	50 + 165	317 - 637	0.076 ± 0.002
Carbon dioxide	120 - 190	477 - 767	0.065 ± 0.005
Oxygen	90 - 530	387 - 707	0.063 ± 0.005

to the central platinum wire, and partly by conduction, convection and radiation through the surrounding atmosphere. Thus, although the direct measurement of f is not possible, the quantity may in principle be calculated for a hollow spherical bead by the application of the simple physical laws of heat transfer. Approximate calculations for a bead of internal radius 0.005 cm and external radius 0.05 cm, shows that, as the temperature is increased from 350 to 650°C, f decreases from 0.57 to 0.43. Thus f might increase by about 2% during the course of a single experiment. It appears that the remaining heat is dissipated mainly by conduction through the surrounding atmosphere and by radiation, and that it is the increasing importance of radiation that leads to the decrease in f as the temperature is increased. The calculations are likely to have underestimated the values of f, since a proportion of the reaction may take place at pore surfaces inside the catalyst bead. Thus the relative importance of radiation losses has probably been overestimated, so that the variation of f during a single experiment is probably negligible. Over wider temperature ranges, however, possible variations in the value of f cannot be ignored.

2.4.4. Summary.

It has been possible to make only a qualitative assessment of the validity of the kinetic results obtained with the present experimental system. However, this assessment does show clearly, firstly that the main source of experimental error will be due to the effect of non-isothermal conditions on the reaction rate, and secondly that the effects of temperature induced rate variations on the measured bridge output are likely to be counteracted by the concurrent variations both in d $(dh/dt)/dT$ and in f. The lack of absolute values of f as a function of temperature make it necessary to use equation (2.8) for the interpretation of experimental data, rather than to substitute equation (2.7) into integrated rate equations.

RESULTS.

3. RESULTS.

3.1. A general survey of the experiments performed.

The oxidation of small amounts of methane by air or oxygen over 20% palladium/80% thoria catalysts has been studied over the temperature range 350 - 650°C. The dependence of the rate of reaction on the concentrations of the reactants and products has been determined by means of thermal measurements made with the catalyst bead system. The effects of possible reaction intermediates have also been investigated in this way. A number of experiments involving product analysis have been carried out, both to correlate composition of the reaction mixture with reaction rate, and to detect any products of incomplete oxidation.

The oxidations of several other low molecular weight hydrocarbons have been carried out over the same type of catalyst, for comparison with the oxidation of methane.

For the purpose of assessing the effect of the catalyst support on the catalytic properties of palladium, the activities of palladium catalysts supported on several different materials have been measured. Furthermore, the activities of catalysts consisting of palladium and thoria in various proportions have been determined. The catalysts used in this work have been analysed by means of X-ray powder diffraction photographs, and the pore structures of their surfaces has been investigated by means of electron microscopy.

3.2. The kinetics of the oxidation of methane over 20% palladium/80% thoria catalysts.

3.2.1. The dependence of the rate of reaction on the concentration of methane.

3.2.1.1. The order with respect to methane.

The order in methane, n_c, has been determined by measuring initial reaction rates as a function of the initial concentration, $[CH_4]_o$, in gas mixtures containing 3-25 mm.Hg methane and 200-600 mm.Hg oxygen. Measurements were made at various temperatures between 380 and 680°C. Initial rates were obtained as voltage output measurements, V_o mV, from the electrical circuit, and values of n_c were obtained from the slopes of plots of $\log_{10} V_o$ against $\log_{10} [CH_4]_o$. Corrections for the small temperature fluctuations between experiments nominally at the same temperature made no significant difference to the results, which are shown in Table 3.1 and in Fig.3.1. It appears that the order with respect to methane is about 0.8 over a wide temperature range.

3.2.1.2. The order with respect to time.

The order with respect to time, n_t, has been assessed from measurements of the quarter-life, $t_{1/4}$, the half-life, $t_{1/2}$, and the three-quarter life, $t_{3/4}$, these values being defined (somewhat unconventionally) as the time taken for the reaction rate to decrease from its initial value by the appropriate factor. Thus, if the rate expression for the reaction is :

$$\text{rate} = k \cdot [CH_4]^n \qquad (3.1)$$

then the methane concentration, $[CH_4]_{1/2}$, corresponding to the half-life is related to the initial methane concentration by the equation:

$$[CH_4]_{1/2} = 2^{-1/n}\,[CH_4]_o \qquad (3.2)$$

where the subscript "t" has for convenience been omitted. Substitution of equation (3.2), and similar expressions for the methane concentrations corresponding to the quarter-life and three-quarter life, into the integrated form of the rate equation (3.1) leads to the following relationships:

$$\frac{2^{(1 - 1/n)} - 1}{(4/3)^{(1 - 1/n)} - 1} = t_{1/2}/t_{1/4} \qquad (3.3)$$

$$\frac{4^{(1 - 1/n)} - 1}{(4/3)^{(1 - 1/n)} - 1} = t_{3/4}/t_{1/4} \qquad (3.4)$$

$$\frac{4^{(1 - 1/n)} - 1}{2^{(1 - 1/n)} - 1} = t_{3/4}/t_{1/2} \qquad (3.5)$$

Equation (3.5) is readily rearranged to give:

$$n_t = (\log 2) / (\log 2 - \log(c-1)) \qquad (3.6)$$

where $c = t_{3/4}/t_{1/2}$, $c \neq 1$, $c \neq 3$.

The roots of equations (3.3) and (3.4) may be computed* by means of an approximation method.

Alternatively, the different reaction "lives" may be compared for the reaction at a given temperature of mixtures containing different amounts of methane. In these cases, the lifetime, t_x, is related to the initial methane concentration by the equation:

$$kt_x = \text{constant} \,.\, ([CH_4]_o)^{1-n} \tag{3.7}$$

Thus the apparent order may be obtained from a plot of $\log_{10} t_x$ against $\log_{10} [CH_4]_o$.

Neither method can be expected to give more than a qualitative outline of the overall reaction kinetics as a function of the extent of reaction, because the rate expression (3.1) cannot be applied to heterogeneous reactions. Indeed, all methods of analysis based on integrated rate equations are liable to give misleading results when applied to complex reactions [73]. It is, however, possible to decide whether or not the products inhibit the reaction by determining whether n_t, as obtained from equations (3.3), (3.4) and (3.5), exceeds or is equal to n_c. Thus in the present case, values of n_t between 1.0 and 2.5 may be taken to indicate moderate inhibition of the reaction by its products. Larger positive values and all negative values of n_t probably indicate much stronger product inhibition.

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* Acknowledgment is due to Mr. P. Sharkey of the Department of Mathematics at Portsmouth College of Technology, for assistance with these calculations.

Table 3.1. Orders with respect to methane at various temperatures.

Temperature ($^\circ$C)	Range of initial methane pressure (mm.Hg)	Oxygen pressure (mm.Hg)	n_c	Mean deviation (%)
403	7 to 10	330 ± 10	0.82	2
451	6 to 10	300 ± 10	0.19*	-
	10 to 16		0.76*	-
497	8 to 15	330 ± 10	0.75	2
554	6 to 15	290 ± 10	0.9	5
587	6 to 15	330 ± 10	0.8	7
600	6 to 16	320 ± 10	0.60	1
658	3 to 14	300 ± 10	0.62	2

* See Fig. 3.1.

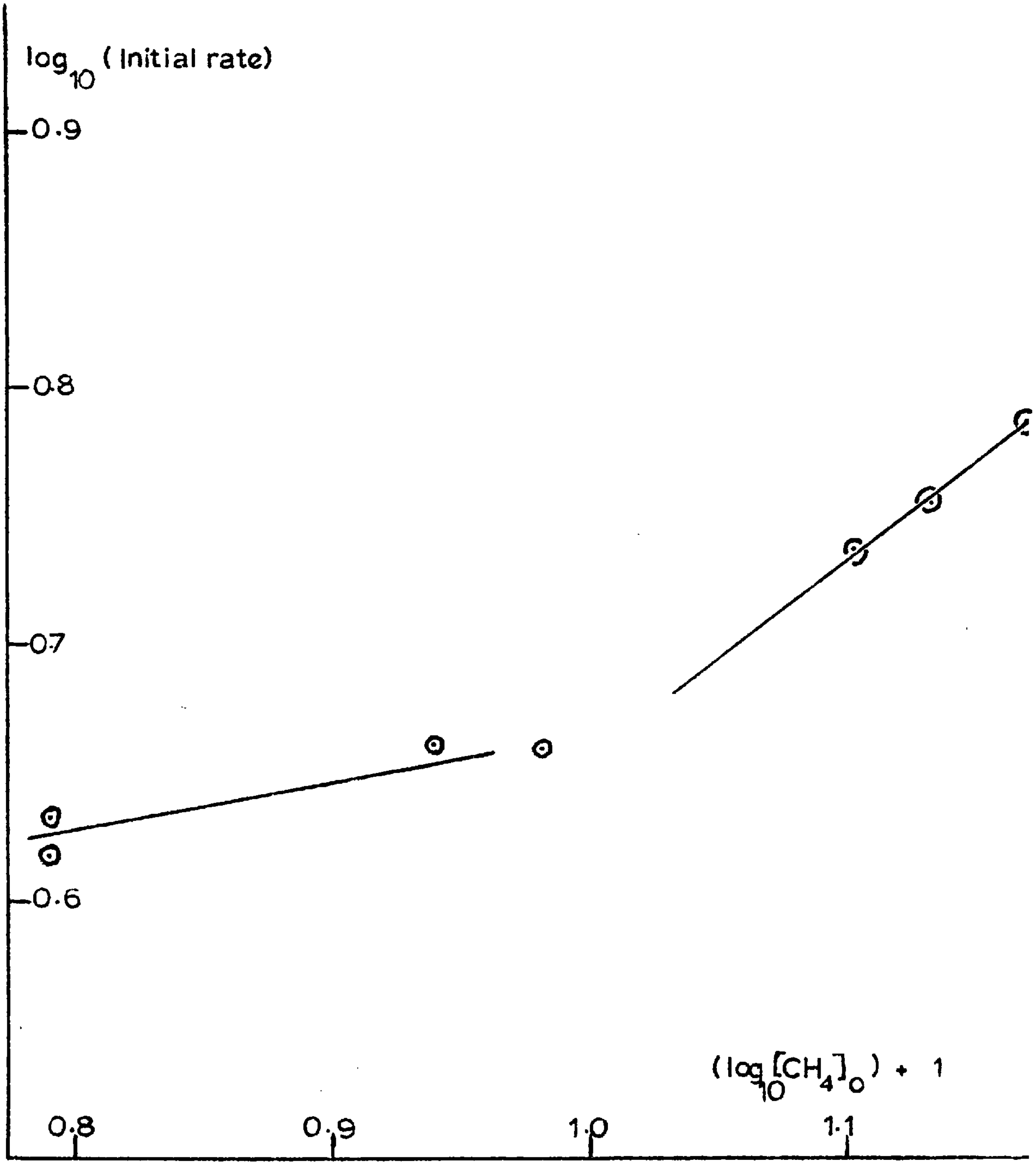

Fig.3.1. A plot of $\log_{10}$ (initial rate) against $\log_{10}$ (initial methane concentration) for the oxidation of methane at 451°C.

Table 3.2. Apparent values of the order with respect to time (n_t) obtained from run-to-run comparisons of quarter-lives and half-lives.

Temperature (^oC)	Values of n_t obtained from:			
	$t_{1/4}$	error %	$t_{1/2}$	error %
451	0.25	1.3	0.35	1.3
600	1.0	3	1.0	10
658	0.45	1.0	0.47	0.9

Table 3.3. Values of the order with respect to time, n_t, for the oxidation of methane, obtained by comparing the half, one-quarter and three-quarter lives of each reaction.

Temperature (°C)	Initial methane pressure (mm.Hg)	Values of n_t obtained from	
		$t_{1/2}/t_{1/4}$	$t_{3/4}/t_{1/2}$
451	6.2	6.9	*
	7.1	2.9	*
	8.7	1.7	*
	9.6	-ve	*
	12.7	-ve	*
	15.5	1.1	*
534	9.1	-ve	1.3
	9.4	1.6	1.4
	9.6	1.3	1.0
	12.6	1.0	1.0
600	5.8	-ve	1.4
	7.7	1.0	1.6
	10.0	1.0	1.0
	12.6	1.1	*
	15.7	1.2	1.3
658	3.3	1.1	1.0
	4.9	1.9	1.3
	5.7	1.7	1.3
	10.6	1.2	1.2
	15.0	1.0	1.5

* unobtainable

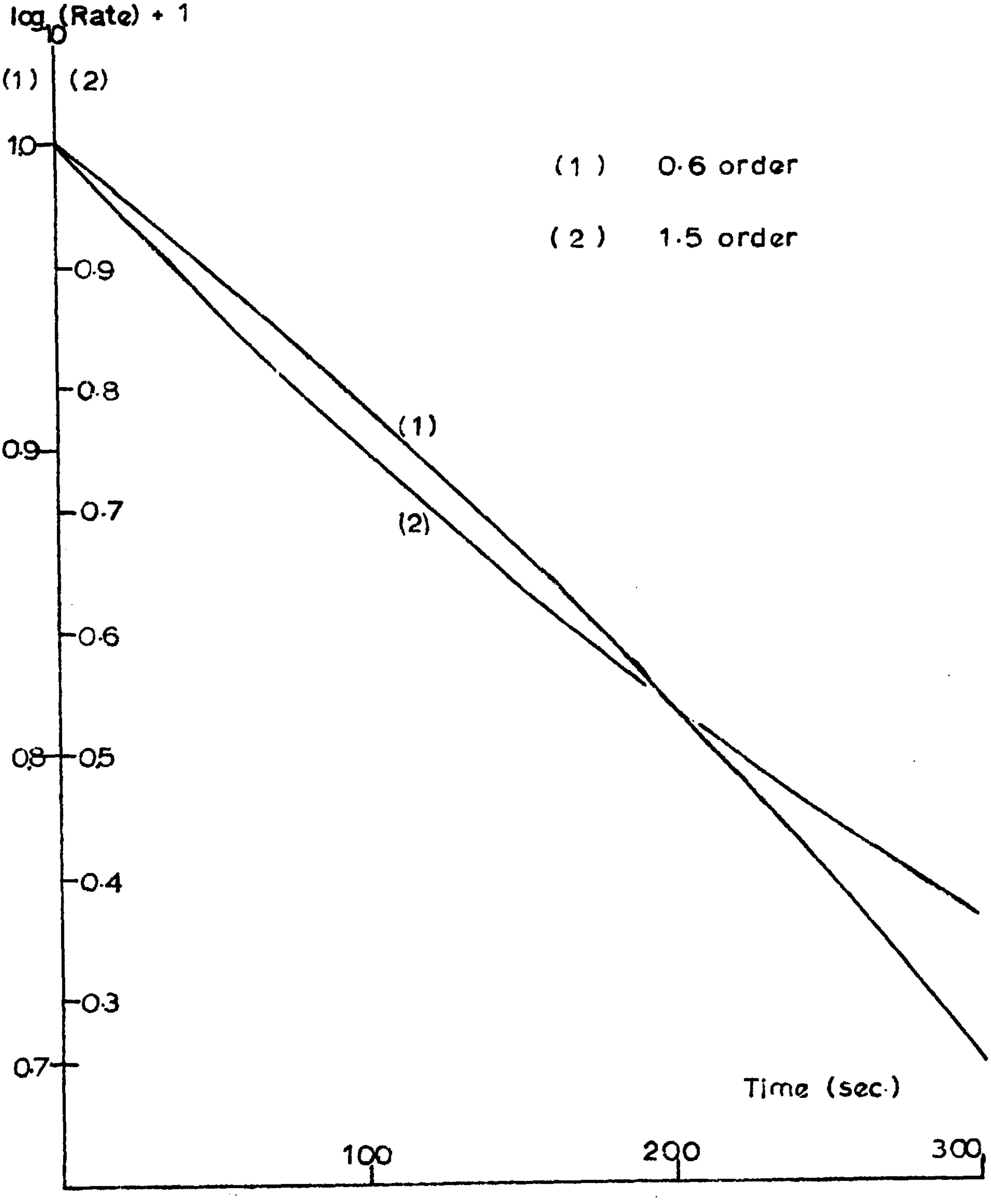

Fig. 3.2. Plots of $\log_{10}$ (rate) against time for 0.6 and 1.5 order reactions with half lives of 200 sec.

Curve no.	Initial mixture composition (mm.Hg)		Temperature (°C.)
	Methane	Oxygen	
1	15·7	320	590
2	10·0	320	590
3	15-5	330	430
4	6·2	330	430

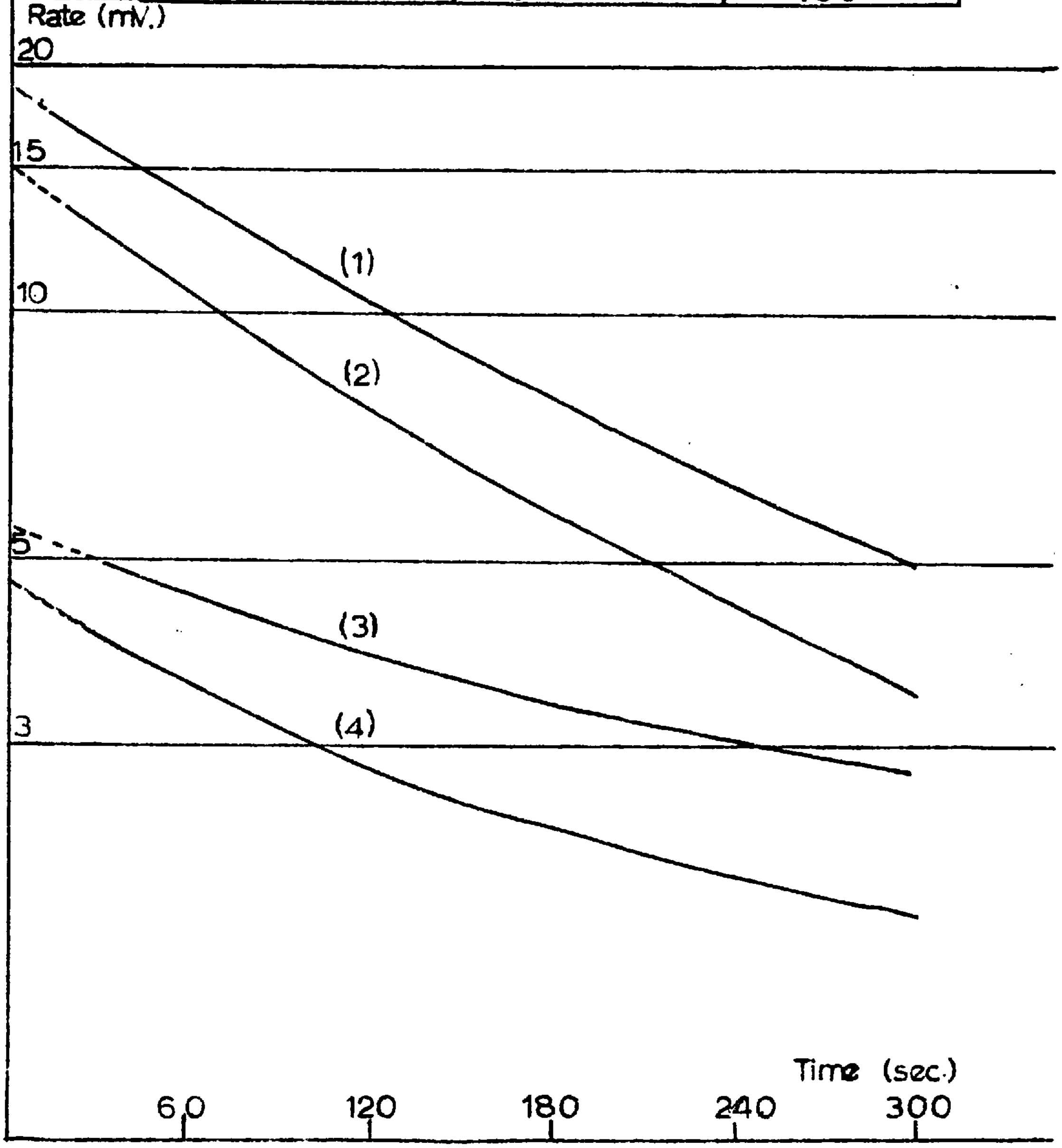

Fig. 3.3. Some typical plots of $\log_{10}$ (rate) against time for the oxidation of methane.

The run to run comparisons give apparent orders with respect to time that are much lower than the order with respect to concentration, particularly at lower temperatures (see Table 3.2). The measurements on individual runs show, however, that, in methane oxidation, the order with respect to time was almost invariably greater than one. This may be seen by comparing the hypothetical curves of "$\log_{10}$ (rate) against time" for reactions with orders of 0.6, 1.0 and 1.5 (Fig.3.2) with some typical plots obtained in methane oxidation experiments, (Fig.3.3). Values of n_t in these experiments have been calculated from equations (3.3), (3.4) and (3.5), and a selection of these is presented in Table 3.3. It may be noted that n_t exceeds n_c over the whole range of temperature, but that n_t decreases as the temperature is raised.

3.2.1.3. Catalyst poisoning.

The necessity to de-gas the catalyst at ca. 800°C under vacuum between experiments in order to obtain consistent results has already been mentioned (see Section 2.3.2). The process was carried out for ca. 90 sec. each time; more vigorous conditions were liable to result in the failure of the resistance wire in the bead. It was usually found, however, that the activity of the catalyst was not completely restored by this process. Most of the catalysts used in this experimental work were deactivated by about 2% per run. There were, however, a number of appreciable variations on either side of this figure, the cause for which was not apparent. The rate at which the catalyst was deactivated was strongly influenced by the contents of reaction mixtures. For example, the presence of small quantities of water vapour considerably increased the rate of deactivation (see below, Section 3.2.6) while the oxidation of methanol together with methane prevented deactivation completely (see below, Section 3.2.7.1). These effects are described in more detail in the appropriate sections.

3.2.2. The dependence of the rate of reaction on the concentration of oxygen and on the total pressure.

Since, in all experiments, the reaction mixtures contained oxygen in considerable excess, the dependence of the rate of reaction on the concentration of oxygen was not directly observable from the kinetic measurements. Thus the experimental rate constant, k, in equation (3.1), is related to the true rate constant, k_{tr}, by the equation:

$$k = k_{tr} \cdot [O_2]^x \cdot P^y \qquad (3.8)$$

where x and y are the experimental reaction orders in oxygen and the total pressure, P. (It should be noted that this formulation is over-simplified for a heterogeneous reaction, and that the orders in methane and in oxygen may not be independent).

Two series of experiments were carried out. One involved reactant mixtures containing a fixed pressure of methane (ca. 10 mm.Hg) and pressures of oxygen varying between 150 and 650 mm.Hg, while the other involved mixtures containing a constant ratio of methane and oxygen, at total pressures of between 100 and 650 mm.Hg. Experiments were carried out at between 517 and 600°C. Values of n_t were calculated for individual experiments (Table 3.4), and values of x or of (x+y) were obtained from plots of $\log_{10}$ k against $\log_{10} [O_2]$, (Table 3.5). Due to the considerable run-to-run variations in the overall order of reaction, an average order of 1.5 was assumed for the calculation of values of k from half-life measurements.

If values of n_t are taken as an indication of the importance of product inhibition, then the results presented in Table 3.4 show firstly that the inhibition is not affected by the concentration of oxygen (see results at 555°C) and secondly, that the inhibition increases as the initial concentration of methane is decreased (see results at 517°C and at 600°C). The values of x and (x+y) in Table 3.5 indicate that the kinetics with respect to oxygen vary little over the range 517-587°C, and that the total pressure, as varied by the addition of an inert gas, has no appreciable effect on the kinetics.

Table 3.4. Orders with respect to time in experiments to determine the reaction kinetics in oxygen and total pressure.

Reaction conditions	Initial pressures (mm.Hg)		Values of n_t from	
	Methane	Oxygen	$t_{\frac{1}{2}}/t_{\frac{1}{4}}$	$t_{\frac{3}{4}}/t_{\frac{1}{2}}$
Variable methane	7.1	401	3.7	2.7
and oxygen; pressure	7.0	223	2.6	1.6
made up to 430±10	7.4	336	1.7	2.1
mm.Hg with nitrogen.	5.8	396	2.3	3.1
Temperature: 600°C	7.7	332	1.0	1.6
	10.0	326	1.0	1.0
	15.7	327	1.1	1.3
Reaction mixtures		191	3.3	1.1
containing 12.6± 5		195	1.6	1.6
mm.Hg methane and		489	1.2	1.8
various amounts of		488	1.0	1.8
oxygen (no nitrogen)		340	1.4	1.6
Temperature: 555°C		590	1.2	1.5

N.B. continued...

Table 3.4 (continued) ....

Reaction conditions	Initial pressures (mm.Hg)		Values of n_t from	
	Methane	Oxygen	$t_{\frac{1}{2}}/t_{\frac{1}{4}}$	$t_{\frac{3}{4}}/t_{\frac{1}{2}}$
Reaction mixtures containing methane and oxygen in the ratio 0.0216$\pm$0.0015 :1, at various total pressures. Temperature: 587°C.	3.9	186	-ve	2.2
	6.1	297	2.6	2.4
	8.4	388	3.5	2.2
	10.6	491	-ve	-
	12.8	591	3.2	2.0
Reaction mixtures containing methane and oxygen in the ratio 0.0214$\pm$0.0005 : 1 at various total pressures. Temperature: 517°C.	2.2	106	-ve	9.6
	2.7	128	-ve	3.3
	4.1	189	-ve	3.1 - 4.1
	4.6	219	-ve	2.7 - 4.4
	5.6	265	-ve	2.6 - 3.0
	6.3	297	1.5-2.7	1.4(0)

Table 3.5 Orders of reaction in oxygen, and in total pressure.

Temperature ($^{\circ}C$)	Conditions	Order in oxygen	Order in oxygen + order in total pressure
600	Constant total pressure (P) and initial pressure of methane.	-0.14±0.09	-
555	Constant initial pressure of methane $P=(p_{CH_4}+p_{O_2})_{initial}$	-	0.14±0.05
587	Constant ratio of initial methane and oxygen pressures	-	0.8±0.2
517	Constant ratio of initial methane and oxygen pressures		0.9±0.2

3.2.3. The dependence of rate on temperature.

The oxidation of 5-15 mm.Hg of methane in mixtures containing 200-400 mm.Hg of oxygen proceeds at a conveniently measurable rate over palladium bead catalysts at temperatures greater than ca. 380°C. Two methods have been used for calculating the overall activation energy, both of which use rate measurements obtained for mixtures of fixed composition. The first involves calculating rate constants from the "average slope" of $\log_{10}$ rate against time plots, assuming first order kinetics. The second involves measuring the half life of the reaction, as defined in 3.2.1.2, at various temperatures. The first method, applied to a large set of results, produced an activation energy of 11 ± 2 kcal.mole^{-1}. The second, applied to several sets of results, produced a wider scatter, with most values in the range 4-10 kcal.mole^{-1}. The greater importance of product inhibition at lower temperatures has the effect of reducing the reaction rate more rapidly in the early stages of the reaction, so that half lives at low temperatures obtained from rate measurements are misleadingly short. Thus the value of 11 kcal,mole^{-1} for the overall activation energy is probably the more reliable.

As the temperature is increased above ca. 650°C the observed reaction rate decreases rapidly, and at ca. 750°C, the surface process apparently becomes endothermic; that is to say, negative rate - time curves are obtained (see Fig. 3.~~12~~13).

3.2.4. The correlation of the experimental rate measurements with the analysis of the reaction products.

These measurements were made in order to check the validity of the overall kinetic results obtained, and to detect possible reaction intermediates. Rather than using a flow system to produce relatively large quantities of products, mixtures from the static system were sampled in order to maintain comparability between the rate measurements and the analytical determinations.

Two series of experiments were carried out with methane-oxygen mixtures using the silica gel column for separation, and a third series was performed using the molecular sieve column for the more clear cut detection of carbon monoxide (see Table 2.2, Section 2.3.3.1). Each series consisted of a number of runs in which gas mixtures of a constant composition were allowed to react at a fixed temperature for various times between 15 sec. and 90 min. At the end of each run, the equilibrium was "frozen" by switching off the bridge current and the products were analysed as previously described. The first and last runs in each series were taken to completion so that composition and rate measurements could be compared and the progressive deactivation of the catalyst could be assessed.

One result common to all series was that about 5% of the initial concentration of methane was left unoxidised the the end of each "complete" reaction, i.e. when the measured reaction rate was zero. This indicated that the bead was temporarily deactivated by the reaction itself, and/or that the methane from the "dead space" was diffusing only very slowly into the reaction vessel. That both effects were probably operating is shown firstly by the necessity to de-gas the catalyst between runs, and secondly by the consistent discrepancy between the duplicate samples taken from each reaction mixture; the first sample was generally slightly richer in methane than the second. Accordingly, average values were taken for the analysis of each run, and corrections were made for the amount of reaction mixture contained in the "dead space".

A second result is that no formation of hydrogen or carbon monoxide was observed. The lower limits of detection (Table 2.1) correspond to about 1.1×10^{-7} moles of hydrogen and 1.1×10^{-6} moles of carbon monoxide in a reaction mixture. Typical reaction mixtures contained 5×10^{-5} moles of methane, so that carbon monoxide cannot exceed 2% and hydrogen cannot exceed 0.4% of the initial quantity of methane.

Measurements of reaction rate have been compared with those of product analysis by plotting on the same axis:

$$\frac{\text{Rate at time } t}{\text{Initial rate}} \quad \text{vs.} \quad t$$

and

$$\frac{\text{Methane concentration at time } t}{\text{Initial methane concentration}} \quad \text{vs.} \quad t.$$

In both cases (see Figs. 3.4 and 3.5) the rate decreased more rapidly than the concentration of methane, thus indicating, in agreement with the rate measurements, that the reaction order with respect to time is greater than one.

3.2.5. The effect of added carbon dioxide on the rate of oxidation of methane.

It has been established that the overall order with respect to time exceeds the order with respect to methane. This indicates that the reaction is being inhibited by at least one of the products, or perhaps by an intermediate whose presence was not detected. Measurements were therefore made of the effects of several additives on reaction rates.

In the experiments involving added carbon dioxide, the dependence of the reaction rate on the amount added was measured for mixtures containing 6-16 mm.Hg of methane, 200-400 mm.Hg of oxygen and 10-350 mm.Hg of carbon dioxide, at temperatures between 450 and 660°C, but mainly at around 590°C. Some product analysis measurements were carried out on the variation of rate with concentration, and in order to detect carbon monoxide and hydrogen. In this latter

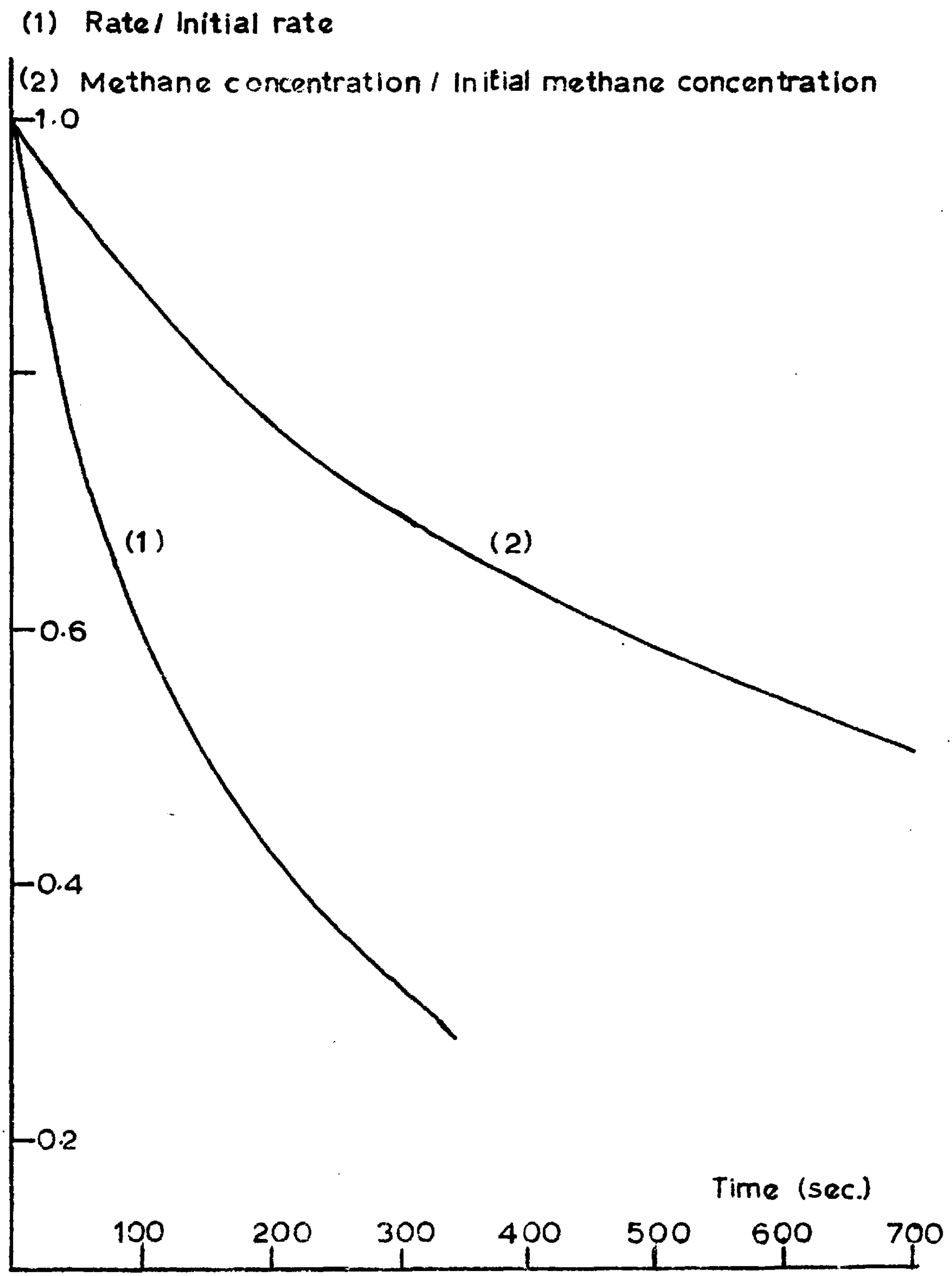

Fig.3.4. A comparison of rate measurements with product analysis for methane oxidation at 590°C.

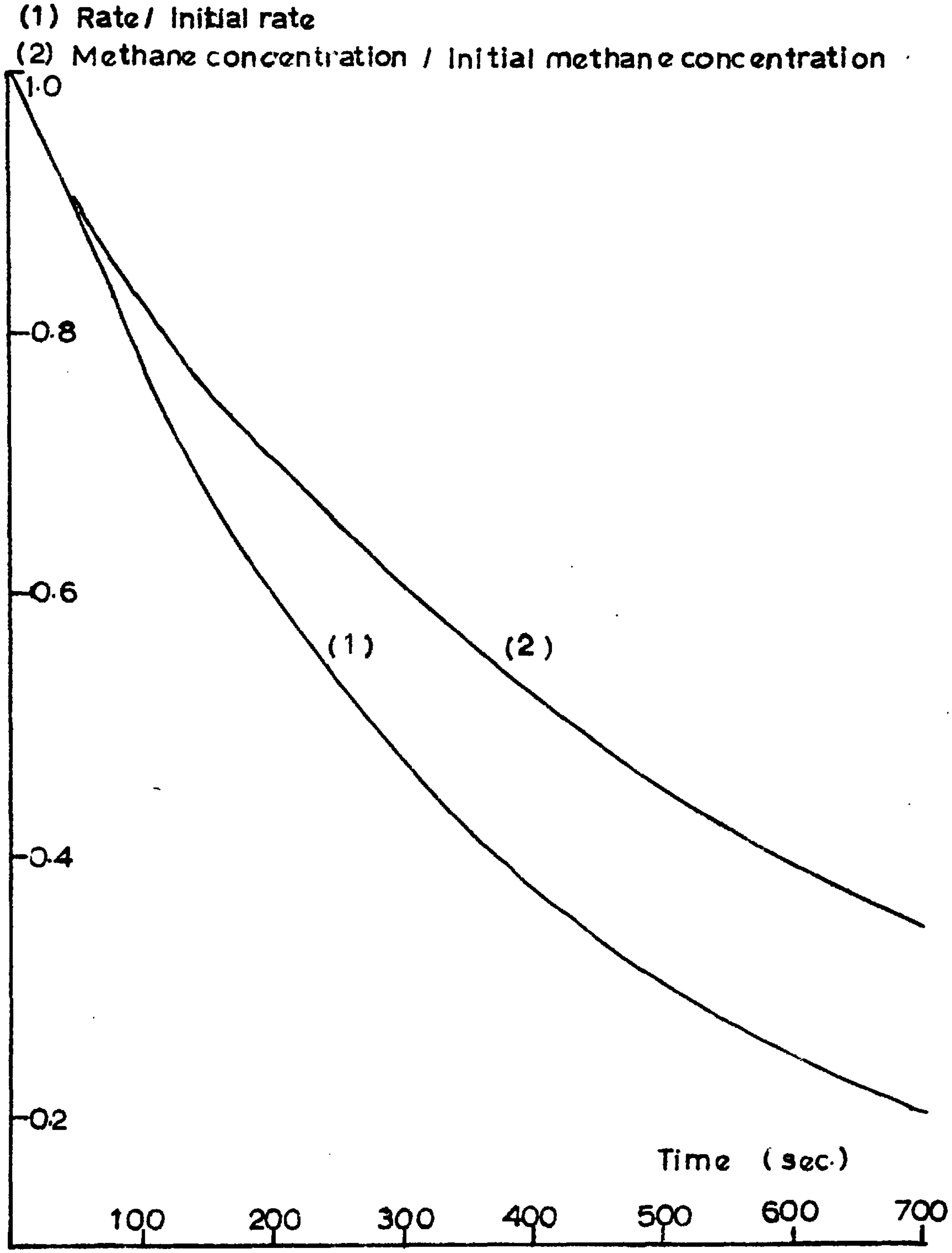

Fig.3.5. A comparison of rate measurements with product analysis for methane oxidation at 554°C.

connection, a few experiments were performed in which methane was allowed to react with carbon dioxide in the absence of oxygen. The results were as follows.

(a) Rate measurements at $587 \pm 6^{\circ}C$. *

It was shown, by carrying out periodic check runs involving the reaction of mixtures of methane and oxygen only, that the presence of large amounts of carbon dioxide does not cause additional poisoning of the catalyst. Furthermore, the addition of up to 100 mm.Hg of carbon dioxide to reaction mixtures had no measurable effect on the reaction kinetics. However, larger pressures (100-200 mm. Hg) reduced the initial rate of reaction and altered its overall kinetics: the overall order with respect to time increased. By plotting:

$$\log_{10} \frac{\text{(Initial rate)}}{([CH_4]_o)^{0.8}} \quad \text{vs.} \quad \log_{10} [CO_2]_o$$

it was found that the apparent order with respect to carbon dioxide at partial pressures of 100-350 mm.Hg was approximately -0.3 (see Fig.3.6). It should be noted that the graph indicates that the influence of carbon dioxide cannot be expressed in terms of any fixed order, and also that the inhibiting effect shown may be exaggerated by the increasing thermal conductivity of the reaction mixture as

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* The uncertainty in the final reaction temperatures is due to the differences between the thermal conductivities of the gas mixtures, which made it difficult to adjust the power supply correctly for each experiment.

the partial pressure of carbon dioxide is increased.

The reaction of some mixtures containing 200-280 mm.Hg of carbon dioxide showed unusual kinetic behaviour. The reaction rate decreased rapidly over the first few minutes, and then suddenly increased quite sharply, subsequently decreasing only very slowly until the reaction was complete (see Fig.3.7). The precise experimental conditions required to produce this unusual behaviour were not obtained. The presence of still larger amounts (300-350 mm. Hg) of carbon dioxide was found to inhibit the reaction considerably, and in these conditions the bridge output became unstable about two minutes after the start of a reaction.

(b) Rate measurements at 654 ± 3°C.

Measurements at this temperature, summarised in Table 3.6, indicate that the presence of excess carbon dioxide causes appreciable poisoning which may be partially reversed by more prolonged de-gassing (compare initial rates and half-lives for experiments 1, 7 and 8).

(c) Rate measurements at 450 ± 3°C.

Additions of up to 200 mm.Hg of carbon dioxide to mixtures containing 6.6 mm.Hg of methane and 320 mm.Hg of oxygen made little difference to the observed initial rates of reaction, but caused the rate to decrease more rapidly as the reaction proceeded. The presence of larger amounts of carbon dioxide caused almost complete inhibition.

(d) Product analysis measurements.

These measurements were made at intermediate temperatures. The products of one series of experiments at 510°C were analysed using the molecular sieve column, and those of another series at 494°C were analysed using a silica gel column. Reaction mixtures contained $4.0 - 5.4 \times 10^{-5}$ moles of methane, $0.6 - 1.3 \times 10^{-3}$ moles of carbon dioxide and $0.8 - 1.4 \times 10^{-3}$ moles of oxygen.

No hydrogen was detected among the reaction products. With the molecular sieve column, however, small carbon monoxide peaks were obtained, indicting the formation of appreciable amounts of this product. Both sets of results (see Tables 3.7 and 3.8) show that the presence of large amounts of carbon dioxide prevents the conversion of methane approaching completion.

The products of the reaction of mixtures of methane and carbon dioxide, in the absence of oxygen, were also analysed, and found to contain quite large amounts of hydrogen, and, in some cases, small quantities of carbon monoxide (see Tables 3.9 and 3.8).

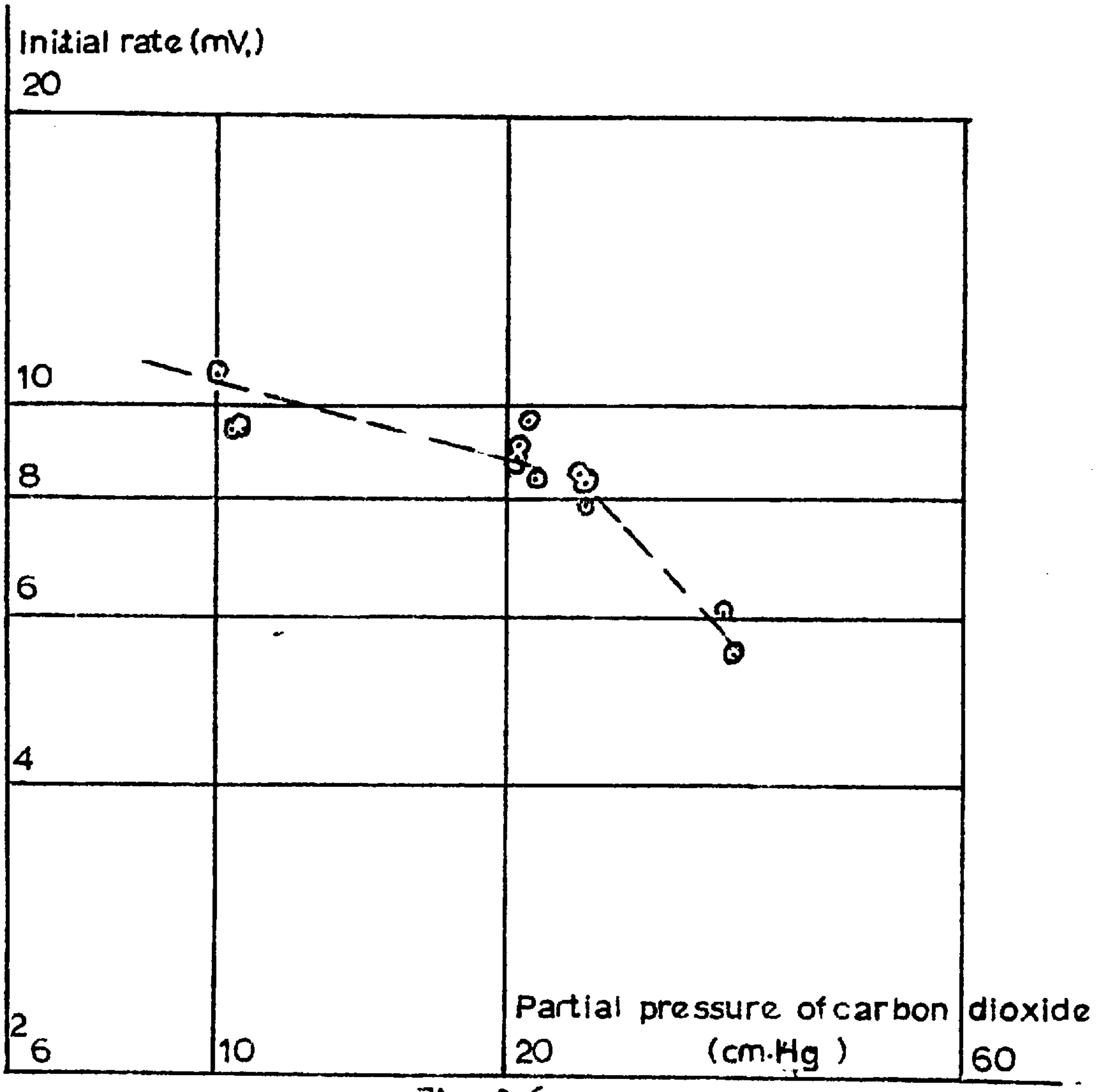


Fig. 3.6.

The dependence of the initial rate of methane oxidation on the initial partial pressure of carbon dioxide at 587°C.

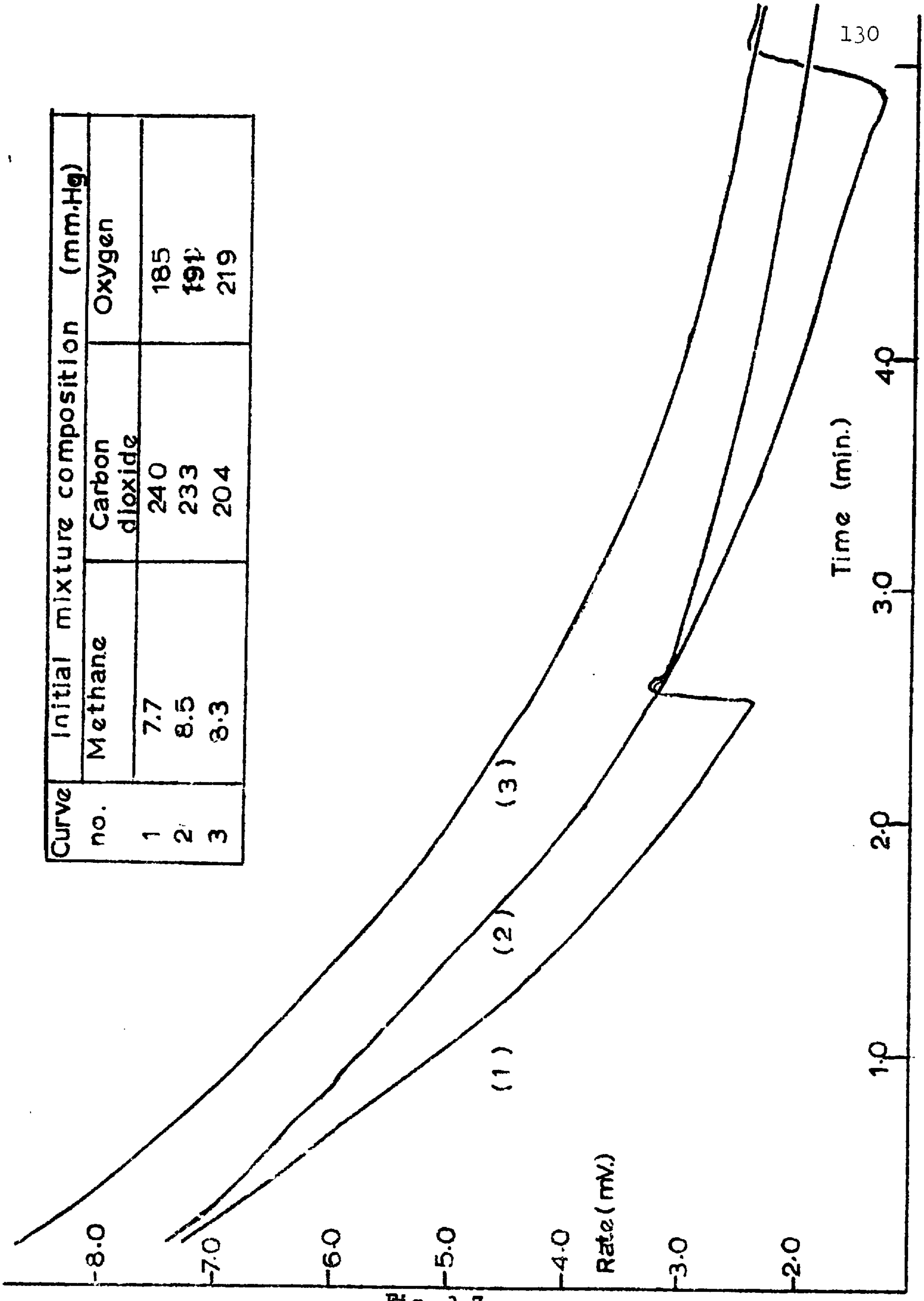


Fig. 3.7.

Some plots of rate against time for the oxidation of methane at 587°C in the presence of relatively high pressures of carbon dioxide.

Table 3.6. The effects of carbon dioxide at 654°C.

Run no.	Partial pressures(mm.Hg) of:			$\frac{\text{(Initial rate)}}{([CH_4]_o)^{0.8}}$	$t_{\frac{1}{2}}$(sec.)
	CH_4	CO_2	O_2		
1	6.2	-	328	13.0	106
2	6.3	151	327	11.6	133
3	6.3	258	322	10.8	104
4	6.3	258	315	11.0	106
5	6.4	211	324	9.4	91
6	6.5	-	322	9.0	128
7	6.5	-	329	9.8	122

Table 3.7. Product analysis measurements on the reaction of methane-oxygen-carbon dioxide mixtures at 510°C.

Run no.	Initial mixture composition (moles)			Analysis (moles)		Length of run	$t_{\frac{1}{2}}$
	$CH_4 x 10^5$	$CO_2 x 10^3$	$O_2 x 10^3$	$CH_4 x 10^5$	$CO\ x 10^5$	(sec.)	(sec.)
1	5.4	1.06	1.40	2.2	14	5400	-
2	5.7	1.04	1.38	0.9	3.6	infinity	360±30
3	4.0	0.87	0.95	1.2	2.3	"	360±30
4	4.0	1.30	0.97	4.0	3.2	360	-
5	4.2	1.24	0.99	3.0	-	720	-
6	4.1	0.64	0.99	0.6	2.7	infinity	400±50
7	4.0	0.71	0.94	0.4	1.4	"	417±5
8	4.2	0.87	0.83	2.0	0.97	180	-
check	4.2	0.98	1.08	4.2	-	0	-

Table 3.8. Product analysis measurements on the reaction of methane - carbon dioxide - oxygen mixtures at 494°C.

Run no.	Initial mixture composition (moles)			Analysis (moles)		Length of run (sec.).
	CH_4x10^5	CO_2x10^3	O_2x10^3	CH_4x10^5	H_2x10^6	
1	5.3	8.5	9.9	3.3	-	"infinity"
2	5.4	8.9	10.1	1.3	0.03*	242
3	5.2	8.8	10.8	3.0	0.02*	600
4	5.4	8.8	10.0	5.0	0.04*	120
5	12.9	10.5	-	12±1	50±10	"infinity"

Carbon monoxide was not detected.

* These quantities are probably due to traces of hydrogen present in some initial gas mixtures.

Table 3.9. Product analysis measurements on the reaction of methane - carbon dioxide mixtures at 597°C.

Run no.	Initial mixture comp. (moles x10^5)			Analysis (moles x10^5)		(moles x10^7)		Length of run (sec.)
	CH_4	CO_2	O_2	CH_4	CO_2	CO	H_2	
1	5.5	-	141	0.45	5.0	-	0.2	infinity
2	18.8	18.6	-	19 ± 1	19 ± 1	1.1	53	600
3	18.4	51.1	-	missed	50 ± 2	1.2	25	600
4	40.3	19.3	-	40 ± 2	missed	-	8	1800

N.B. Reaction mixtures were found to contain up to 5 x10^{-7} moles of hydrogen as impurity.

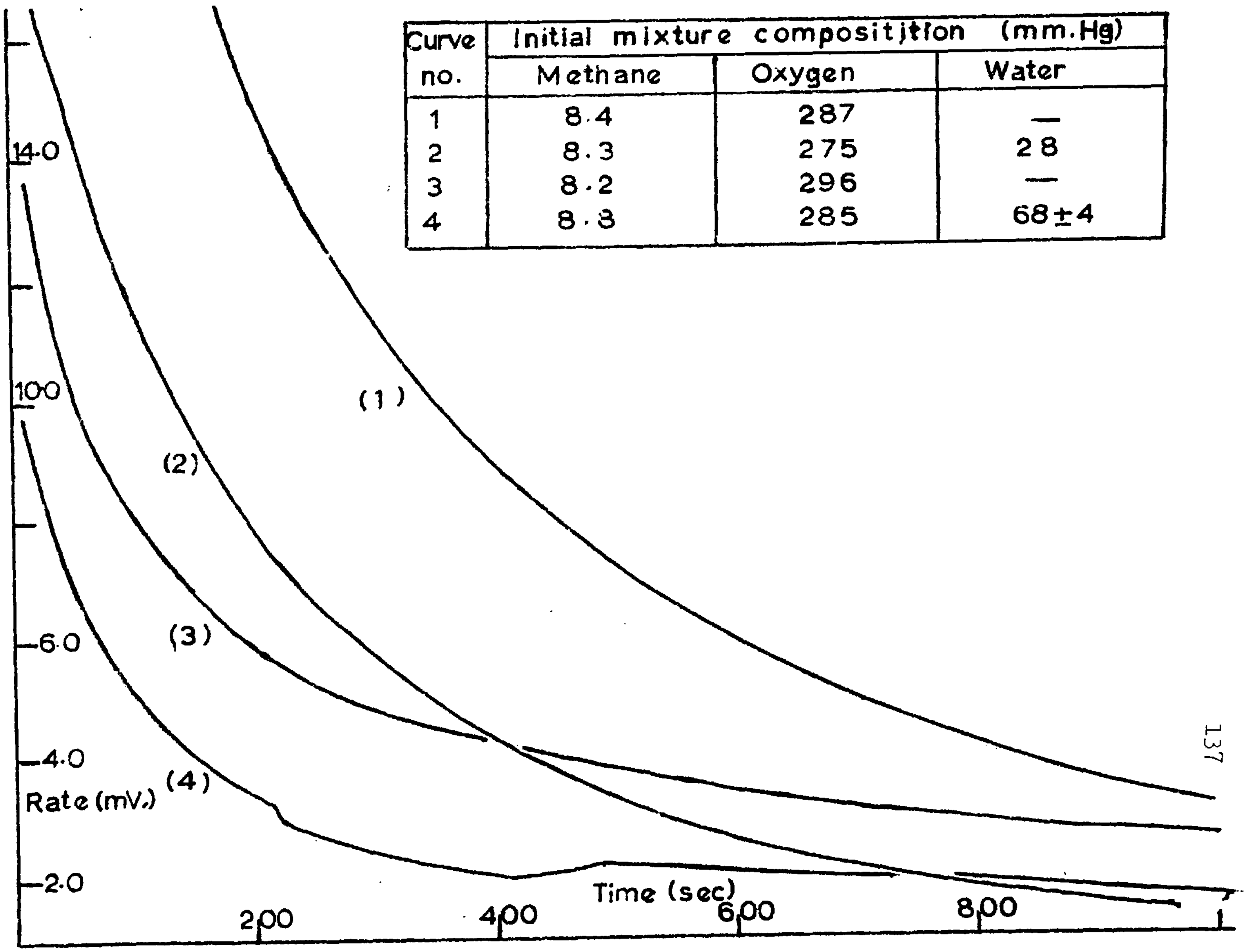
3.2.6. The effect of added water vapour on the rate of oxidation of methane.

Experiments to determine the dependence of reaction rate on the amount of added water vapour were carried out at 480 and 547°C. In addition, one series of product analysis measurements was carried out at ca. 582°C. Reaction mixtures contained 8.2 - 8.8 mm.Hg of methane, 285 ± 11 mm.Hg of oxygen and up to 70 mm.Hg of water vapour.

In contrast to the small inhibiting effect of carbon dioxide, water vapour was found to reduce the rate of methane oxidation considerably. Thus at 480°C, the presence in the initial reaction mixture of 20 mm.Hg of water vapour was almost sufficient to stop the reaction completely, and no quantitative measurements were obtainable at this temperature. Some comparable rate-time curves for the reaction at 547°C both in the presence and absence of added water vapour, are shown in Fig.3.8. Since it is probably impossible to assign a fixed order with respect to water vapour, the magnitude of the inhibiting effect is best expressed as the fractional reduction in initial rate of reaction. Values of this quantity, corresponding to various initial partial pressures of water vapour are presented in Table 3.10.

The poisoning effect of the presence of water vapour may be estimated by comparing the initial rates and overall orders of "check runs", using mixtures not containing water vapour (see Table 3.11). It appears that water vapour greatly increases the rate at which the catalyst becomes deactivated. Furthermore, the overall order of methane oxidation increases as deactivation of the catalyst progresses. There is some indication that more prolonged degassing between experiments restores the activity of the catalyst to a slight extent (compare experiments 5 and 6).

One series of product analysis measurements was carried out at 582°C using a silica gel column. Also, mixtures containing only methane and water vapour were allowed to react completely at 460°C, and the products were analysed in the same way. Neither hydrogen nor carbon monoxide were detected in mixtures containing oxygen, and the rate vs. time curves obtained in these experiments confirmed the inhibiting and poisoning effects of water vapour. However, both carbon monoxide and hydrogen were obtained from the reaction at the lower temperature of mixtures containing no oxygen. For example, a mixture containing 11.1×10^{-5} moles of methane and 11.9×10^{-5} moles of water vapour yielded 1.3×10^{-5} moles of carbon dioxide, 1.8×10^{-5} moles of hydrogen and 8×10^{-7} moles of carbon monoxide. It is clear therefore that water and methane may interact at the surface of palladium catalysts to produce partial



Curve no.	Initial mixture compositjion (mm.Hg)		
	Methane	Oxygen	Water
1	8.4	287	—
2	8.3	275	28
3	8.2	296	—
4	8.8	285	68±4

Fig.3.8. Some plots of rate against time for the oxidation of methane in the presence of added water vapour at 547°C.

Table 3.10. The % reduction in the initial rate caused by the presence of water vapour.

(Reaction mixtures containing 8 mm.Hg of methane and 285 mm.Hg of oxygen).

Pressure of water vapour (mm.Hg)	Reduction in initial rate (%)
28	34
69	42
75	50

Table 3.11. Catalyst poisoning due to the presence of water vapour: half-lives, initial rates and orders with respect to time for check runs.

Run No.	Initial mixture comp. 285±5 mm.Hg Oxygen,&		n_t*	$t_{\frac{1}{2}}$ (sec)	Initial rate,V (mV)**	Poisoning*** per run (%)
	CH_4 (mm.Hg)	H_2O (mm.Hg)				
1	8.5	-	1.0	180	29.5	2.7
2	8.4	-	1.0	176	28.4	
3,4	8.4	28	-			10.0
5	8.5	-	1.0	249	20.2	
6	8.4	-		231	21.7	
7,8	8.5	76	-			7.0
9	8.2	-	1.0	160	16.5	

* Calculated from $t_{1/2}/t_{1/4}$

** Corrected for the effect of temperature on rate

*** Poisoning $= \dfrac{V_{(1)} - V_{(2)}}{V_{(1)}} \times 100$

$$\text{or } \frac{1}{3} \; \frac{V_{(2)} - V_{(5)}}{V_{(2)}} \times 100$$

(corrections made for varying initial partial pressures of methane.)

oxidation products of methane in the absence of oxygen, but that formation of such products is very slow in comparison with their further oxidation.

3.2.7. The effects of added intermediates on the rate of oxidation of methane.

The purpose of these experiments was to see whether the addition of substances which could conceivably be formed as intermediates during the catalytic oxidation of methane have any effect on the rate of reaction. It was anticipated that the two fuels might either be oxidised independently, or that they might compete for the available catalyst surface, or that the presence of appreciable quantities of an intermediate might facilitate the oxidation of methane. Of the various possible C_1 products, methanol, carbon monoxide and formaldehyde were chosen for these experiments.

3.2.7.1. The concurrent oxidations of methane and methanol.

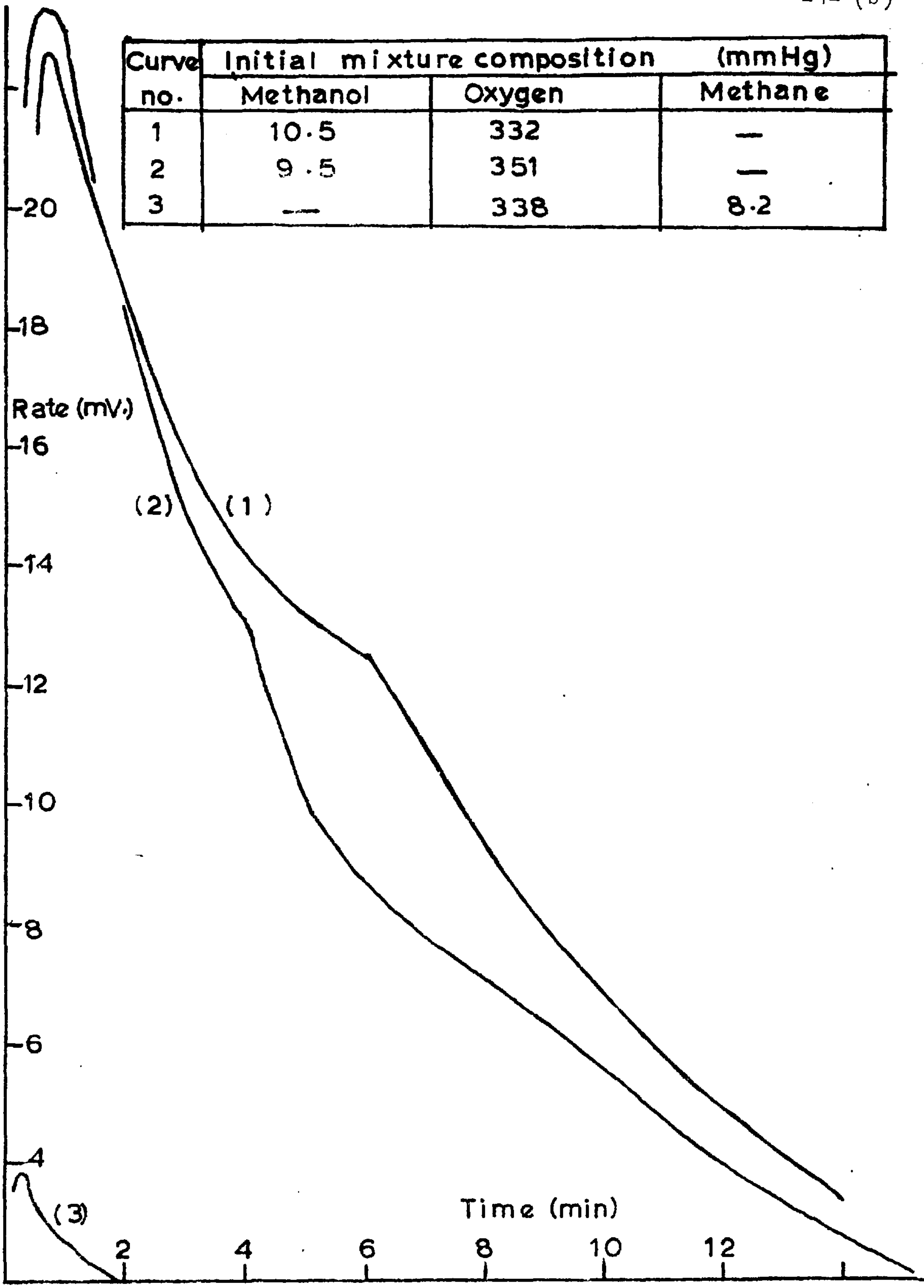
Measurements were made of the rates of oxidation of methane and methanol, both separately and together, at 410, 554 and 722°C. Reaction mixtures contained 5-15 mm.Hg of methane, 4 - 20 mm.Hg of methanol and ca. 300 mm.Hg of oxygen. Product analysis measurements were also carried out at 496°C. using both the silica gel column/katharometer detector system and the squalane column/flame ionisation detector system (Section 2.3.3.1). The results were as follows.

(a) Rate measurements at 410°C.

Methanol was found to be oxidised fairly rapidly at this temperature, while the rate of oxidation of methane was only just measurable over the catalyst used. The rate-time curves for methanol oxidation were rather irregular, Fig.3.9, suggesting that the reaction proceeds via an intermediate formed in appreciable quantities. Examples of the rate-time curves for the concurrent oxidation experiments are shown in Fig.3.10. It appears that the rates of concurrent oxidations are appreciably higher than would be expected from the measured rates of the separate oxidations of methane and methanol. The "kink" in the rate-time curve for methanol oxidation is accentuated by the presence of methane. However, quantitative comparisons are not possible between these two sets of rate-time curves.

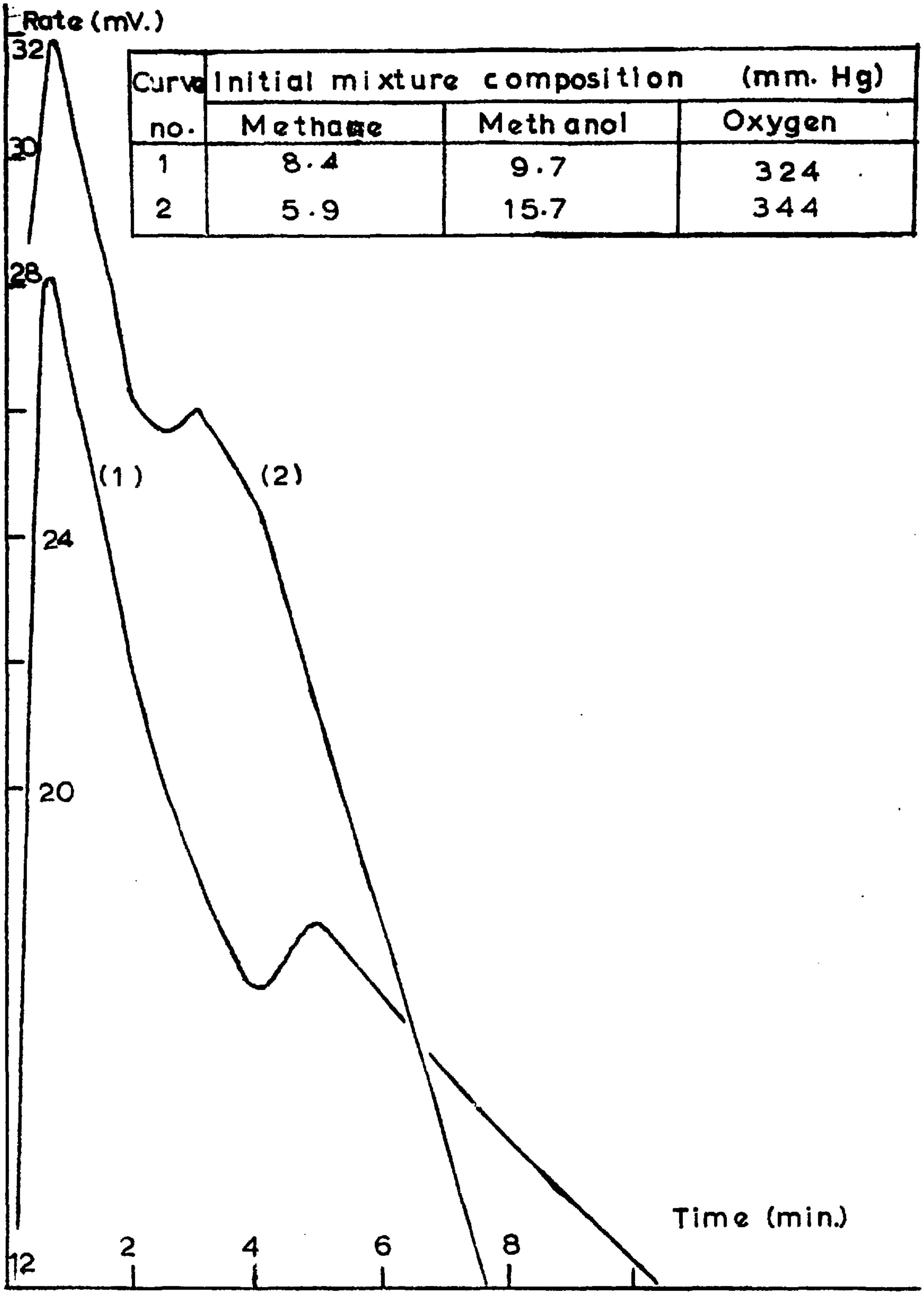
(b) Rate measurements at 554°C.

Both methane and methanol are oxidised rapidly and smoothly at this temperature (see Fig.3.11), but methanol oxidation is by far the faster process. Some kinetic measurements of methanol oxidation were made at 517, 554, and 587°C, and the results are given in Table 3.12 (orders with respect to methanol) and 3.13 (orders with respect to time). It may be noted from these that the kinetics of methanol oxidation are similar to those of methane oxidation, except



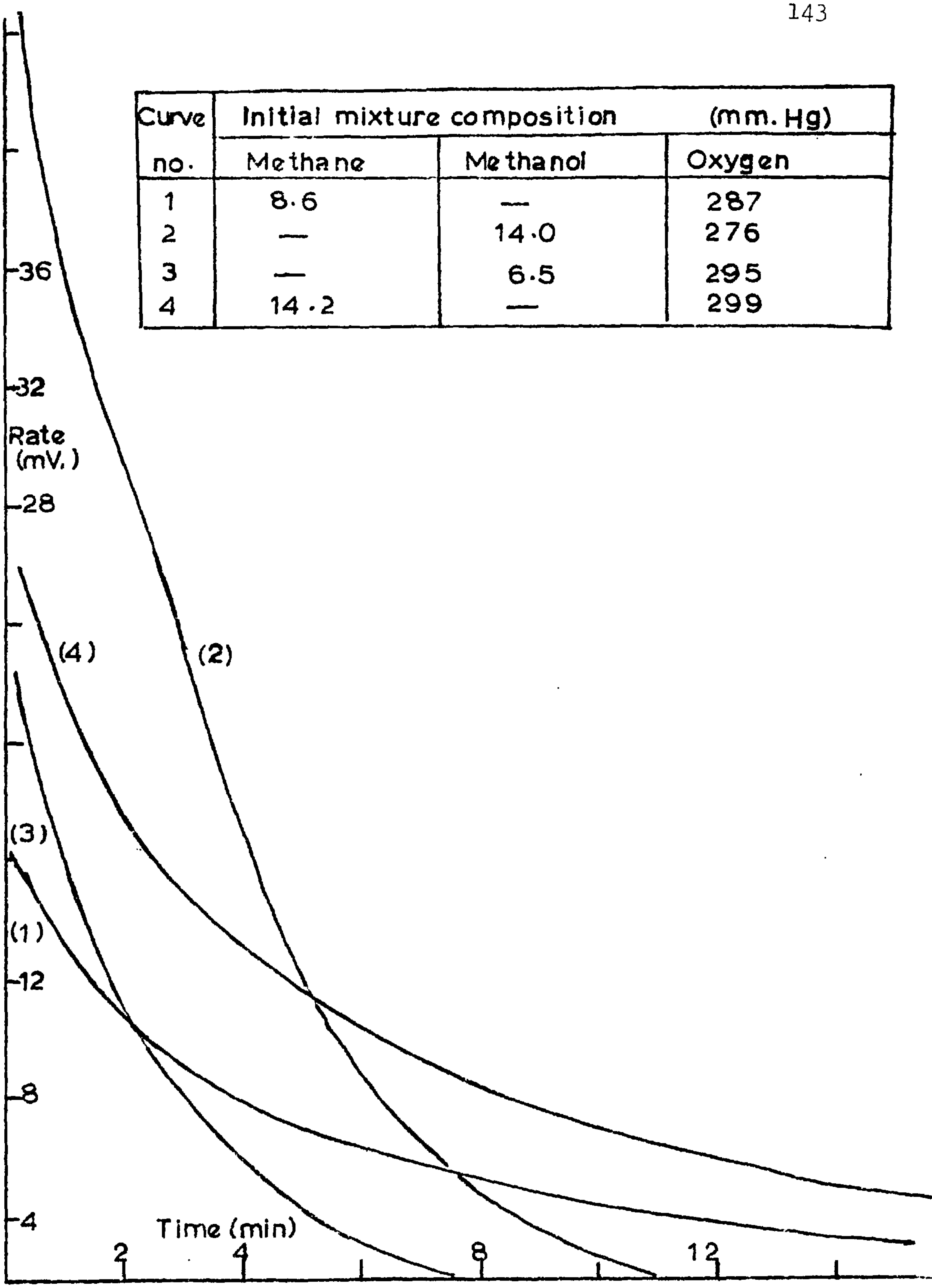
Curve no.	Initial mixture composition (mmHg) Methanol	Oxygen	Methane
1	10·5	332	—
2	9·5	351	—
3	—	338	8·2

Fig. 3·9. Some plots of rate against time for the oxidation of methanol at 410°C.



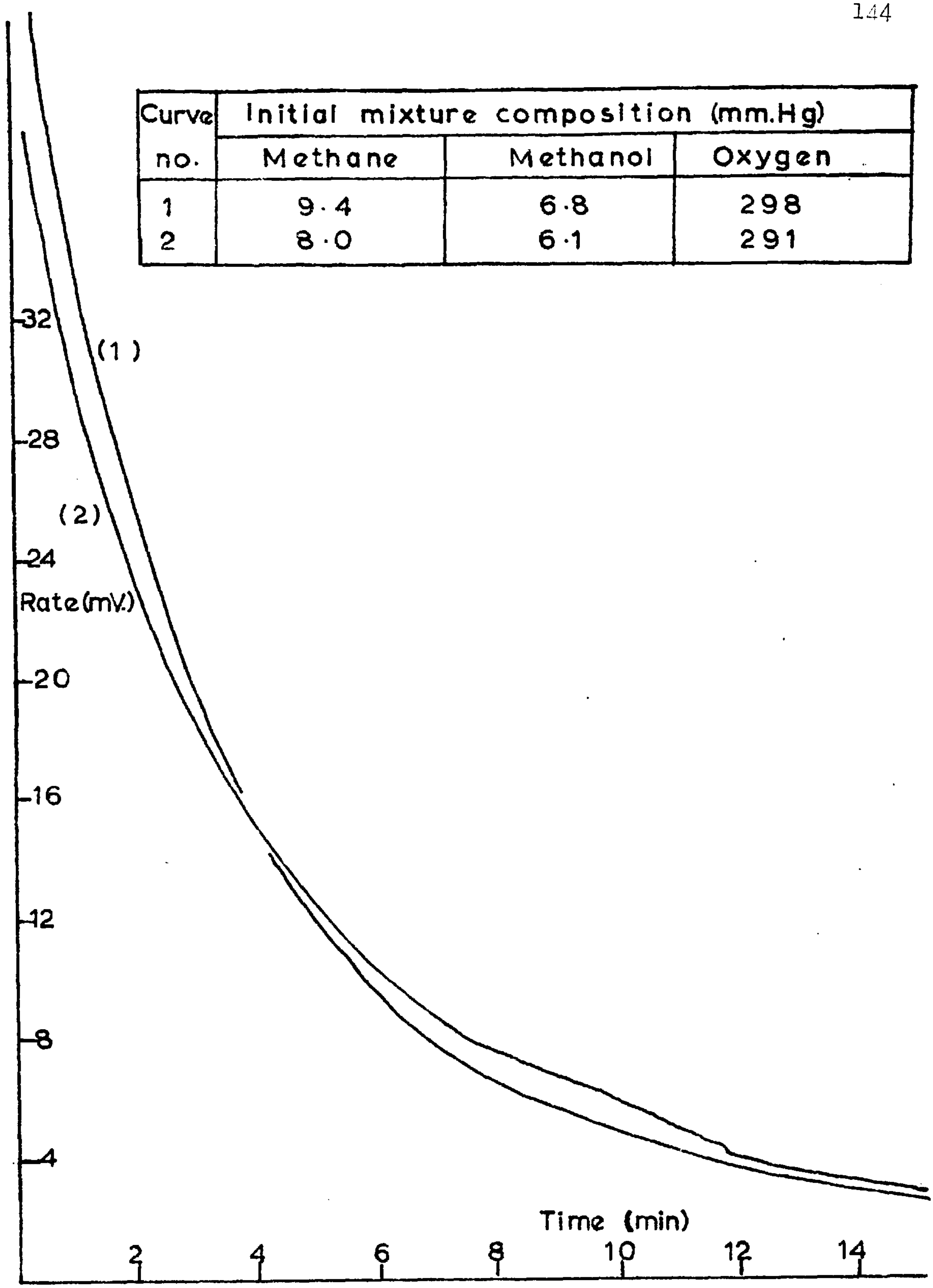
Curve no.	Initial mixture composition (mm. Hg)		
	Methane	Methanol	Oxygen
1	8.4	9.7	324
2	5.9	15.7	344

Fig. 3.10. Some plots of rate against time for the concurrent oxidation of methane and methanol at 410°C.



Curve no.	Initial mixture composition (mm. Hg)		
	Methane	Methanol	Oxygen
1	8·6	—	287
2	—	14·0	276
3	—	6·5	295
4	14·2	—	299

Fig. 3.11. Some plots of rate against time for the separate oxidations of methane and methanol at 554°C.



Curve no.	Initial mixture composition (mm.Hg)		
	Methane	Methanol	Oxygen
1	9·4	6·8	298
2	8·0	6·1	291

Fig. 3.12. Some plots of rate against time for the concurrent oxidation of methane and methanol at 554°C.

Table 3.12. The kinetics of methanol oxidation: orders with respect to methanol.

(Initial mixtures contained ca. 300 mm.Hg oxygen and various amounts of methanol)

Temperature (^{o}C)	Orders with respect to methanol	Range of partial pressures of methanol (mm.Hg)
517	0.73 ± 0.01	4 - 19
554	0.90 ± 0.02	6 - 14
587	0.8 ± 0.1	4 - 19

Table 3.13. The kinetics of methanol oxidation: orders with respect to time.

Temperature (^{o}C)	Partial pressure of methanol (mm.Hg)	$t_{\frac{1}{2}}$ (sec)	Orders with respect to time	
			$t_{1/2}/t_{1/4}$	$t_{3/4}/t_{1/2}$
410	10.5	370	-ve	0.7
517	4.2	62	1.0	2.2
517	7.4	70	3.2	1.4
517	10.2	85	1.2	1.5
517	14.0	87	-ve	1.1
517	19.0	94	1.0	3.0
554	6.5	108	1.8	0.9
554	14.0	172	1.8	1.4
587	4.5	52	-ve	1.8
587	8.1	68	-ve	1.2
587	12.7	85	4.1	1.1
587	18.4	104	1.3	1.1
722	10.1	123	1.4	0.8

that product inhibition is much less marked in the former process. The activation energy for methanol oxidation over the range 517-587°C was 3.7 ± 0.5 kcal.mole^{-1}.

Some of the rate vs. time curves obtained from concurrent oxidation experiments at this temperature are shown in Fig.3.12. These curves were sufficiently smooth for initial rate measurements to be obtained, by the backward extrapolation of plots of $\log_{10}V$ against t, for comparison with the initial rates of "separate" oxidations. Calculations were made on the basis of orders of 0.8 with respect to both methane and methanol, and activation energies of 11 kcal. mole^{-1} and 4 kcal.mole^{-1} for the respective oxidation processes. Each calculation was made as follows.

If x_1 mm.Hg of methane are oxidised at an initial rate corresponding to P_1 (mV) then the expected contribution, P_1', of methane oxidation to the initial rate measurement for a reaction mixture containing y_1 mm.Hg of this fuel is given by:

$$P_1' \quad = \quad P_1\ (y_1/x_1)^{0.8} \qquad (3.9)$$

If the corresponding values for methanol are P_2, P_2', y_2 and x_2, then the total initial rate, R, which would be expected if the two oxidations proceeded independently is given by:

$$\begin{aligned} R \quad &= \quad P_1' \quad + \quad P_2' \\ &= \quad P_1(y_1/x_1)^{0.8} \quad + \quad P_2(y_2/x_2)^{0.8} \qquad (3.10) \end{aligned}$$

R, P_1 and P_2 have to be corrected to the same temperature; in other words, account has to be taken both of the increase in the temperature due to the reaction at the catalyst surface, and of the small differences in the temperatures of the catalyst at the end of different experiments. In each case this is done by substituting into the Arrhenius equation the difference between the temperature at which the initial rate has been measured and the arbitrarily chosen final temperature T. This difference, δT, is given by:

$$\delta T = \frac{d + R_0/10^3 i}{R_0 \alpha} \qquad (3.11)$$

where d is the difference between the final resistance of the bead and the resistance corresponding to a temperature of T, i is the current through the bead, and R_0 and α are the cold resistance and the temperature coefficient of the bead respectively.

The comparisons of the initial rates of "concurrent" and "separate" oxidation experiments are shown in Table 3.14. These show that the oxidations of methane and methanol on the same catalyst do not in any way inhibit each other, and there is a strong indication (e.g. result (2)) that a cooperative effect is involved. This effect is not as large as it appears to be at lower temperatures (see above). In interpreting the effect, the possibility must be borne in mind that the observed behaviour is due to differences between the

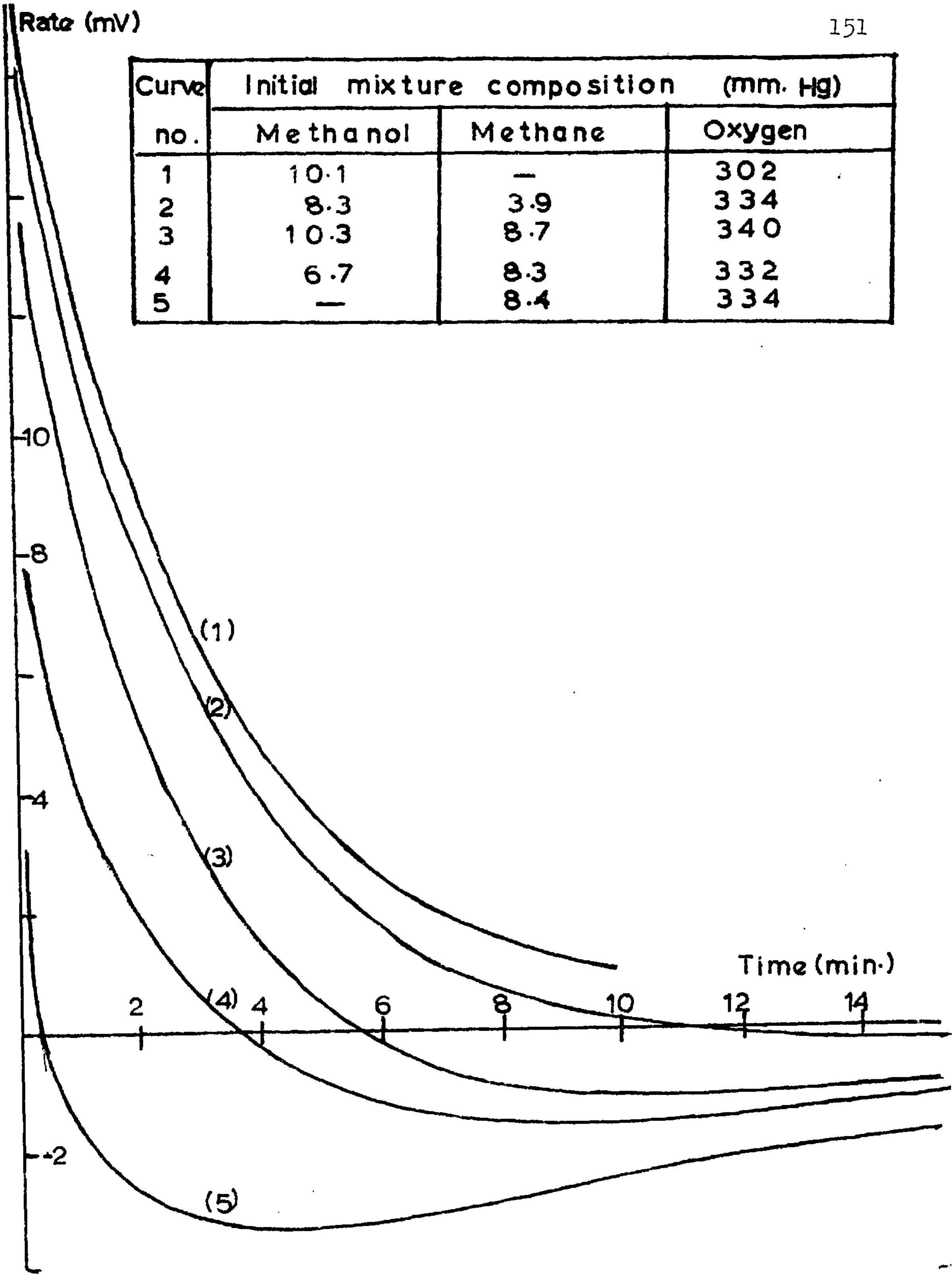
Table 3.14. <u>Comparisons of the calculated and measured values of the initial rates in the concurrent oxidation of methane and methanol at 554°C.</u>

Run no.	Initial mixture composition (mm.Hg)			R(obs.)	R(calc)*
	CH_3OH	CH_4	O_2		
1	6.8	9.4	294±4	53.0±1.0	51.9±4
2	6.1	8.0	294±4	53.0±1.0	46.8±4
3	4.2	14.4	294±4	53.0±1.0	49.7±3

* The uncertainty in calculated values of R includes possible errors both in the gas mixture composition and in the calculations.

Table 3.15. The absence of catalyst poisoning during methanol oxidation experiments: the kinetics of methane oxidation before and after the series of methanol oxidation runs.

Run no.	Initial mixture composition (mm.Hg)		Initial rate (mV)	$t_{\frac{1}{2}}$ (sec.)
	CH_4	O_2		
1	8.7	289	16.6	213
26	8.3	332	16.1	207



Curve no.	Initial mixture composition (mm. Hg)		
	Methanol	Methane	Oxygen
1	10·1	—	302
2	8·3	3·9	334
3	10·3	8·7	340
4	6·7	8·3	332
5	—	8·4	334

Fig. 3. 13. Some plots of rate against time for the oxidation of methane and methanol at 722°C.

thermal conductivities of the gas mixtures.

It will be noted that the progressive poisoning of the catalyst (see above, 3.2.1.3), has not been allowed for in these comparisons. This is because methane oxidation experiments carried out at intervals during the series showed, within the limits of experimental error, that no deactivation occurred. The kinetics of the first and last methane oxidation runs, between which some 24 other runs were carried out, are compared in Table 3.15.

(c) Rate measurements at 722°C.

The oxidation of methanol proceeded very rapidly at this temperature, but, as found previously (3.2.3), the oxidation of methane was accompanied by a relative cooling of the catalyst bead (see Fig. 3.13). No reaction orders were determined at this temperature. The rate-time curves for concurrent oxidation experiments (Fig. 3.1) indicate that the two surface processes take place independently, but quantitative comparisons of the rates of "separate" and "concurrent" reactions are not possible.

(d) Product analysis measurements.

A series of experiments was carried out at 496°C. in which reaction mixtures of approximately constant composition were allowed to react for various lengths of time, and then analysed by gas chromatography (2.3.3.1).

The results are presented in Table 3.16. These show that, while methanol is reacting extremely rapidly until over 95% has been oxidised, the oxidation of methane proceeds much more slowly, and stops with at least 10% of the methane unchanged. No carbon monoxide or hydrogen were detected in the reaction products. In some analyses, two unidentified carbon-containing products, denoted I and II, were detected in small quantities, appearing between methane and methanol in the separation. Neither could have been formaldehyde, since the squalane column used for separation would not allow this compound to pass. Both products are probably intermediates in the catalytic oxidation of methanol, whose formation was suspected in view of the irregular rate-time curves for methanol oxidation obtained at low temperatures. The results indicate that yields of intermediate II, which was formed before intermediate I, were increased by the presence of methane.

3.2.7.2. The concurrent oxidations of methane and carbon monoxide.

A series of rate measurements was carried out at 557°C and some product analysis measurements were made at 521°C.

At 557°C, the order with respect to carbon monoxide was found to be 0.75 ± 0.1. Orders with respect to time,

Table 3.16. Product analysis measurements for the concurrent oxidation of methane and methanol at 496°C.

Run no.	Length of run. (sec.)	Initial mixture comp. (moles)			Analysis (moles)					
		CH_3OH x10^5	CH_4 x10^5	O_2 x10^3	CH_4 x10^5	CO_2 x10^5	O_2 x10^4	CH_3OH x10^5	peak* I	peak* II
1	"infinity"	4.3	6.0	1.06	1.2 ±.1	8.6 ±.6	9.3 ±.2	0.28 ±.01	-	-
2	600	4.2	5.4	1.02	2.84 ±.08	8.3 ±06	9.6 ±.2	0.5 ±.1	-	-
3	360	4.3	5.8	1.01	2.95 ±.07	7.7 ±.4	9.45 ±.05	0.74 ±.02	1.3 ±.5	2.1 ±.3
4	240	5.2	4.7	1.12	3.5 ±.1	6.0 ±.2	10.2 ±.1	1.12 ±.09	3.0 ±.9	7.8 ±.3
5	150	4.2	5.3	0.99	4.10 ±.03	5.4 ±.2	9.5 ±.2	1.16 ±.16	3.0	16 ±.1
6	90	4.4	5.4	1.00	3.8 ±.1	4.7 ±.1	9.7 ±.3	2.06 ±.03	3.5 ±.4	12.8 ±.8
7	60	4.2	5.5	0.98	4.7 ±.3	2.2 ±.2	9.5 ±.3	1.9 ±.4	1.8	4.3 ±.9
8	42	4.5	5.3	0.98	4.9 ±.2	1.5 ±.1	9.6 ±.2	2.7 ±.3	2.6 ±.7	18 ±6
9	20	4.2	6.0	0.99	5.9 ±.4	0.8 ±.2	9.8 ±.1	2.8 ±.6	-	10.8 ±1.0

N.B. continued....

Table 3.16 (continued) ....

Run no.	Length of run (sec)	Initial mixture comp. (moles)			Analysis (moles)					
		CH_3OH $\times 10^5$	CH_4 $\times 10^5$	O_2 $\times 10^3$	CH_4 $\times 10^5$	CO_2 $\times 10^5$	O_2 $\times 10^4$	CH_3OH $\times 10^5$	peak* I	peak* II
10	15	4.5	5.4	1.00				2.9 ±.3	-	27 ±2
11	"infinity"	4.2	-	0.84				0.31 ±.3	-	-
12	15	4.3		0.88				3.2 ±.1	2.2 ±.1	2.8 ±.1
13	30	4.4		0.87				3.8 ±.2	2.7 ±.1	2.4 ±.1

$$* \text{ Value given } = \frac{\text{peak area} \times \text{pressure of reaction mixture}}{\text{pressure of sample}}$$

N.B. Peaks I and II were absent from analyses both of initial mixtures and of much larger samples of the methanol used in these experiments.

shown in Table 3.17, indicate that some product inhibition takes place in the oxidation of carbon monoxide. The catalyst was slowly poisoned during the course of these experiments, but its activity was restored by heating it in about 1 atmosphere of oxygen at ca. 700°C for several minutes.

The initial rates of "separate" and "concurrent" oxidation experiments were compared in the same way as those for the oxidation of methane and methanol. The results were not corrected to take account of the catalyst poisoning, but nevertheless show clearly (Table 3.18) that the two oxidation reactions inhibit each other.

The product analysis measurements showed that, at equilibrium, all the carbon monoxide had been oxidised, while 25-30% of the methane remained unchanged.

3.2.7.3. The concurrent oxidations of methane and formaldehyde.

A series of rate measurements was performed at 558°C. Product analysis was not carried out because the squalane column used with the flame ionisation gas chromatograph would not allow formaldehyde to pass.

The oxidation of formaldehyde proceeded extremely rapidly, but caused a marked loss of catalytic activity, which was only partially restored by prolonged heating in oxygen at ca. 700°C. This rapid loss of activity prevented the full determination of the kinetics of formaldehyde oxidation and the quantitative comparison of the rates of "separate" and "concurrent" oxidations. Some information with regard to the former is however shown in Table 3.19, and some rate-time curves obtained are illustrated in Fig. 3.14.

3.2.8. A comparison of the catalytic oxidation of methane and of other low molecular weight hydrocarbons.

The purpose of these experiments was to compare the kinetics of the oxidation of methane over palladium with that of other hydrocarbons, which are known to be more readily oxidised and which may give appreciable quantities of intermediate products in some circumstances. The hydrocarbons used were ethane, ethylene, acetylene, propane, n-butane and isobutane. The same catalyst bead was used for all experiments, and periodic methane oxidation runs were carried out to check its activity.

In each case, rate measurements for the reaction of low fuel : oxygen mixtures were made over a range of temperatures, and the lowest temperature at which the reaction would proceed was determined. Orders with respect to fuel were measured at one or two temperatures, and orders with respect to time were calculated for each run. Activation energies for each oxidation were obtained from measurements of the half-lives of the reaction of mixtures of constant initial composition at various temperatures.

Table 3.17. <u>The kinetics of the oxidation of carbon monoxide: orders with respect to time at 557°C.</u>

(Reaction mixtures initially contained ca. 230 mm.Hg of oxygen and various amounts of carbon monoxide.)

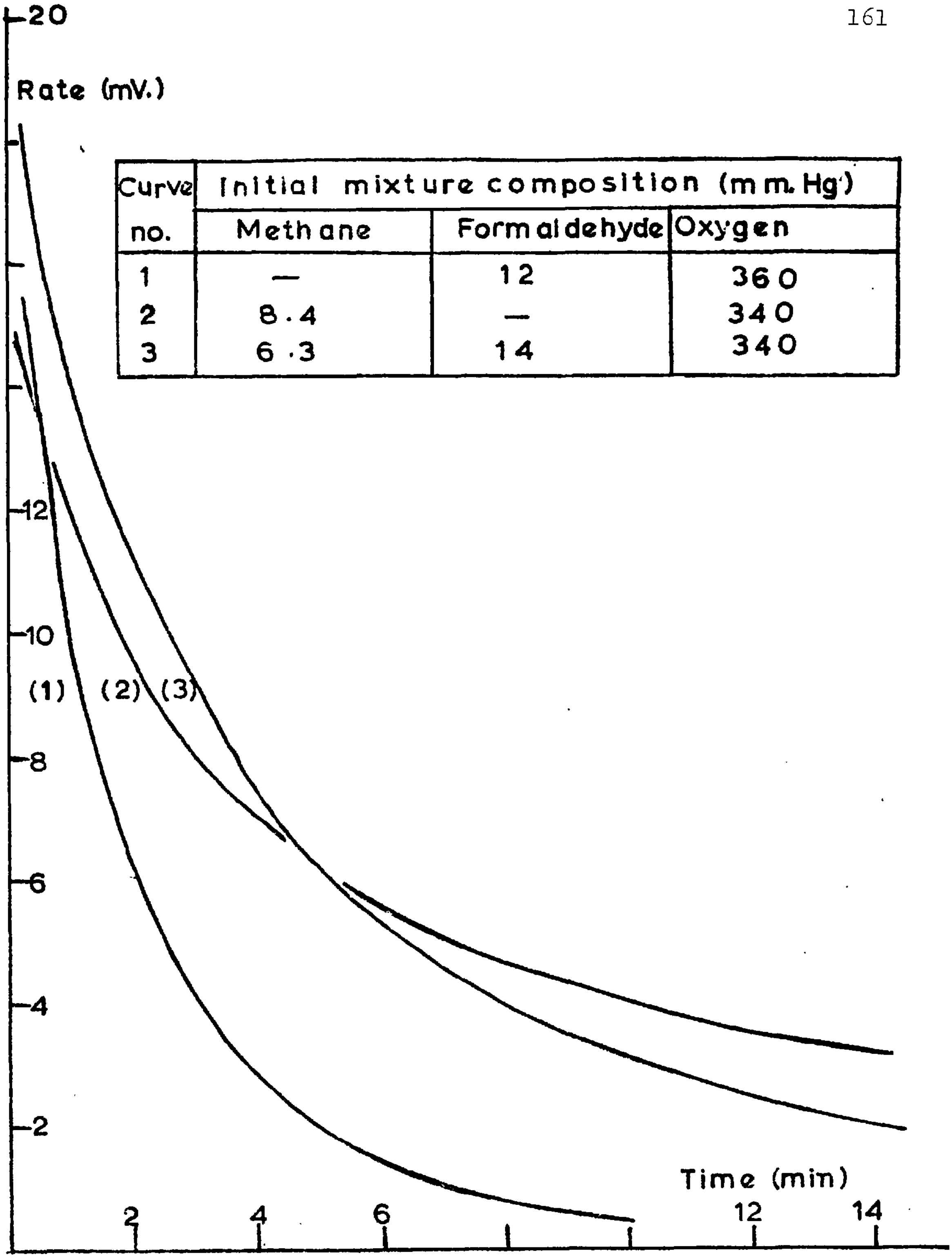
Partial pressure of carbon monoxide (mm.Hg)	$t_{\frac{1}{2}}$ (sec)	Values of n_t calculated from:	
		$t_{1/2}/t_{1/4}$	$t_{3/4}/t_{1/2}$
5.8	73	1.8	2.5
11.0	78	2.0	1.2
18.4	98	1.7	0.9

Table 3.18. Comparisons of the calculated and measured values of the initial rates of the concurrent oxidation of methane and methanol at 557°C.

Run no.	Initial mixture composition (mm.Hg)			Initial rates(mV): Calculated contributions			Observed	Difference (%)
	CH_4	CO	O_2	CH_4	CO	Total		
1	8.6	15.3	305	15.0	23.6	38.6	27.2	30
2	6.2	10.3	312	11.3	17.2	28.5	16.1	44
3	6.2	16.8	308	11.3	25.2	36.5	24.9	32
4	4.4	20.2	310	8.3	29.5	37.8	22.4	41
5	8.2	4.1	308	13.7	8.2	21.9	15.6	29

Table 3.19. Some kinetic measurements of the oxidation of formaldehyde at 558°C.

Run no.	Initial mixture comp. (mm.Hg)			Initial rate (mV)	Values of n_t from		$t_{\frac{1}{2}}$ (sec)
	CH_2O	CH_4	O_2		$t_{\frac{1}{2}}/t_{\frac{1}{4}}$	$t_{\frac{3}{4}}/t_{\frac{1}{2}}$	
2	-	8.4	338	15.5	large +ve	-ve	192
3	4.2	-	363	15.7	1.8	1.9	56
4	4.3	-	332	12.9	large +ve	large +ve	46
5	17.7	-	317	22.1	-ve	0.9	161
6	11.8	-	330	17.7	large +ve	1.3	78
11	-	8.6	334	8.0	-ve	-ve	280



Curve	Initial mixture composition (mm.Hg)		
no.	Methane	Formaldehyde	Oxygen
1	—	12	360
2	8.4	—	340
3	6.3	14	340

Fig. 3.14. Some plots of rate against time for the oxidation of methane and formaldehyde at 558°C.

Table 3.20. Kinetic measurements on "check runs" carried out at 530°C during experiments on the catalytic oxidation of various low molecular weight hydrocarbons.

Run no.	Initial pressure of methane (mm.Hg)	Other fuel	Initial rate (mV)	$t_{1/2}$ (sec)	n_t*
1	9.2	-	-	120	1.2
5-20	-	Acetylene			
21	9.4	-	50.0	113	1.3
23-32	-	n-Butane			
33	9.1	-	47.1	121	2.1
34-44	-	Isobutane			
45	9.5	-	45.7	121	2.3
46-57	-	Ethane			
58	9.2	-	42.5	124	1.0
59-70	-	Ethylene			
71	12.6	-	50.0	135	1.0

* Calculated from $t_{3/4}/t_{1/4}$

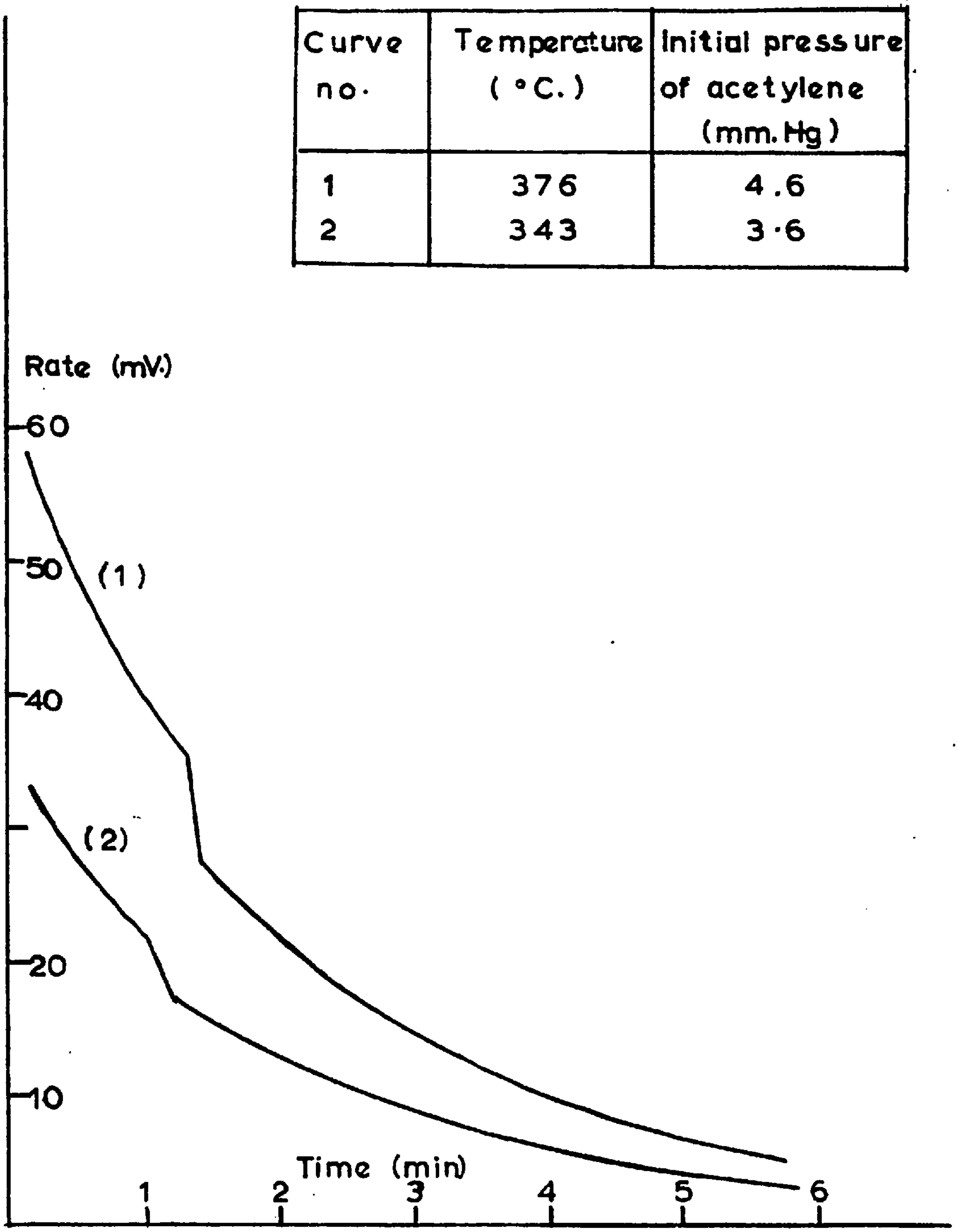
Table 3.21. Kinetic measurements of the catalytic oxidation of some low molecular weight hydrocarbons: orders with respect to time and orders with respect to hydrocarbon.

Fuel	Order w.r.t. hydrocarbon n_c	Temp. (°C)	Order w.r.t. time n_t*	Temp. (°C)	Partial pressure of hydrocarbon (mm.Hg)
Methane	0.83	403	1.0	401	7.6
			1.7	466	9.7
			1.5	530	9.4
Acetylene	1.7	343	1.7	343	4.7
	0.8	417	1.0	378	4.6
			1.8	417	4.6
Ethylene	0.74	534	1.6	373	4.4
			2.1	477	4.5
			1.0	534	4.4
Ethane	0.72	536	1.6	411	4.8
			2.3	477	4.9
			1.5	535	4.8
Propane	0.76	487	1.0	374	4.5
			1.6	476	4.4
			1.0	529	4.4
n-Butane	0.7	492	1.3	346	2.8
			2.4	414	2.7
			2.9	482	2.7
Isobutane	0.6	492	1.0	345	3.3
			3.2	415	3.4
			1.6	482	3.3

* Calculated from $t_{3/4}/t_{1/4}$

Table 3.22. Kinetic measurements of the catalytic oxidation of some low molecular weight hydrocarbons: minimum temperatures at which the reactions proceed, and comparisons of catalytic activity at 372°C.

Fuel	Minimum oxidation temperatures			Catalytic activity at 372°C.
	p_{CH_4} (mm.Hg)	p_{O_2} (mm.Hg)	T_o (°C)	$t_{\frac{1}{2}}$ (sec.) (to the nearest 10 sec.)
Methane	7.8	330	337	160
Acetylene	4.6	338	333	90
Ethylene	4.3	344	279	120
Ethane	3.3	340	327	190
	5.0	338	No reaction at 337	
Propane	4.4	349	305	240
n-Butane	2.8	355	314	230
Isobutane	3.4	331	303	260



Curve no.	Temperature (°C.)	Initial pressure of acetylene (mm.Hg)
1	376	4.6
2	343	3·6

Fig. 3.15. Some plots of rate against time for the oxidation of acetylene.

It was found that the catalyst used for these experiments was, for no obvious reason, rather more active than most of the others used in this work, and that its progressive deactivation was much slower than usual. The kinetic measurements on "check runs", presented in Table 3.20, show that the activity of the catalyst remained constant over about the first 40 runs and only decreased by about 12% over the whole series of experiments. None of the hydrocarbons contributed more than the others to the poisoning of the catalyst.

The orders of reaction, shown in Table 3.21, indicate that all the hydrocarbons except acetylene are oxidised by similar mechanisms at temperatures exceeding ca. $400^{\circ}C$. The orders with respect to hydrocarbon are all around 0.8, and the values of n_t indicate the occurrence of product inhibition, the importance of which increases as the temperature is decreased. The oxidation of acetylene appears, however, to proceed in two stages, separated by a sudden drop in the heat output at the surface of the catalyst (see rate-time curves in Fig.3.15).

The minimum oxidation temperatures (Table 3.22) appear to depend as much on the partial pressures of fuel and oxygen as on the nature of the hydrocarbon. The value for ethylene was however much lower than all the others. The activation energies for the saturated hydrocarbons were between 3 and 5 kcal.mole^{-1}, and those for ethylene and acetylene were 1.3 ± .2 and 9 ± 2 kcal.mole^{-1} respectively. Thus, at temperatures at which the reactions were all well established, the oxidation of acetylene was by far the fastest (Table 3.22).

3.3. The influence of the support on the activities of palladium catalysts.

The purpose of these experiments was to investigate the influence of the support on the mechanism of the surface reaction, on the resistance of the catalyst to progressive deactivation, and on the mechanical stability of the catalyst. An attempt has also been made to discover the precise form of the catalysts, which were prepared by the thermal decomposition of aqueous solutions of salts of palladium and the support (see Section 2.2.1).

Two series of experiments were carried out. The first consisted of measurements of the activities of a series of catalysts containing different proportions of palladium and thoria, and the second involved similar measurements on catalysts of palladium supported by a number of other metal oxides. X-ray "powder" photographs were taken of most of the catalysts used, and electron micrographs were obtained for a few of them.

3.3.1. The activities of catalysts containing various proportions of palladium and thoria.

The activities with respect to methane oxidation of palladium/thoria catalysts containing 100, 90, 60, 40, 20, 10 and 0 atom % palladium were measured at various temperatures. The orders of reaction obtained are shown in Table 3.23, and the reaction half-lives at 575°C are compared in Table 3.24. Activation energies were also calculated.

The reaction orders agreed with those already presented (see Section 3.2.1.) and no significant variations were observed. The activation energies for catalysts containing palladium, calculated from half-life measurements, lay between 3 and 13 kcal.mole^{-1}, and showed no significant dependence on catalyst composition, thus illustrating the large influence of variations in overall order with temperature on the results of these calculations. The half-lives at 575°C, showed no significant dependence on the composition of the catalyst, except that the sample containing 10 atom % of palladium was considerably less active than the others. It was found that the reaction only proceeded over thoria alone at temperatures higher than ca. 750°C. No thermal changes were detected at the surface of this "catalyst" below this temperature.

Most of the catalysts were deactivated at about the usual rate, i.e. ca. 3% per run. The 100% palladium catalyst, however, maintained undiminished activity throughout 42 experiments, and showed no sign of mechanical failure. (It should be noted that no mixture containing more than 15 mm.Hg methane was used in these experiments).

X-ray powder photographs of the catalysts used have been compared with similar photographs of standard materials, and with values of the reflections for palladium, palladium oxide and hydrated palladium oxide given in the A.S.T.M. Index [74]. Some of the diffraction patterns obtained are illustrated in Plates 2 and 3.

The 100% palladium catalyst, in both bead form and powder form, gave a diffraction pattern corresponding to the palladium metal standard, which in turn corresponded with the major peaks shown in the A.S.T.M. Index (see Table 3.25). Furthermore, the pattern from the bead sample showed lines corresponding to the platinum standard and the uncoated bead, while that from the powdered sample, from which the platinum lines were absent, showed, in addition, quite a number of faint lines. The 100% thoria bead pattern contained platinum lines and a distinctive "thoria" pattern, which did not, however, correspond well with the index data for thorium oxide. Patterns from catalysts containing between 40 and 60 atom % of palladium showed the stronger lines of palladium and thoria, while those from catalysts containing more than

80 atom % or less than 20 atom % of palladium gave only faint indications of the minor component. It was notable, however, that no measurable variations (± 1 to 3%) were observed in the positions of the diffraction peaks from catalysts containing both palladium and thoria. All the unused catalysts showed rather broad peaks for both components in comparison with the standard patterns. However, some catalysts which had been used extensively gave much sharper patterns.

It is therefore established that the bulk of the catalyst consisted of palladium metal and thorium oxide. It also seems probable that the aggregation of the components into larger crystallites accompanied the prolonged use of the catalyst at high temperatures.

Electron micrographs were taken of a 20 atom % palladium/80 atom % thoria bead, and also of beads coated with the separate components. Some of the photographs obtained are illustrated in Plates 4 and 5. These show that catalysts containing an appreciable amount of thoria have a fairly extensive pore structure, with many pores which are hundreds of Angstrom units wide and deep. These catalysts also have a very small proportion of relatively smooth surface (see photographs 5 and 7). The 100% palladium catalysts appear to have a predominantly smooth surface, broken up by widely spaced cracks.

Table 3.23. Kinetic measurements of the oxidation of methane over catalysts of palladium supported by various proportions of thoria.

Atom % Palladium	Order w.r.t. to methane n_c	Temp. (°C)	Order w.r.t. time n_t	Temp. (°C)	Partial pressure of methane (mm.Hg)
100	0.83 ± 0.01	630	2.6	347	12.6
	0.7 ± 0.1	527	1.3	431	12.4
	0.8 ± 0.1	377	1.2	527	12.1
			1.2	579	12.6
90			2.3	373	12.6
			2.1	495	12.6
			1.5	559	12.4
80	1.0 ± 0.1		-ve	382	12.4
			1.2	467	12.4
			-ve	575	12.4
60			-ve	348	9.3
			1.0	440	9.4
			1.0	497	12.1
50			-ve	352	12.5
			1.2	453	12.8
			1.1	521	12.4
40			-ve	380	12.3
			2.1	433	12.5
			1.2	554	12.2
20	0.75 ± 0.01	497	1.4	407	9.3
			1.1	466	9.7
			1.0	519	9.2
10			-ve	435	12.5
			+ 5	579	12.6
			2.7	679	12.4
0	NO REACTION.				

Table 3.24. The activities of various palladium - thoria catalysts for the oxidation of methane at $575^{\circ}C$.

Atom % palladium	$t_{1/2}$ (sec.) (all values ± 10 sec.)
100	148
90	143
80	134
60	105
50	105
40	137
20	111
10	171
0	-

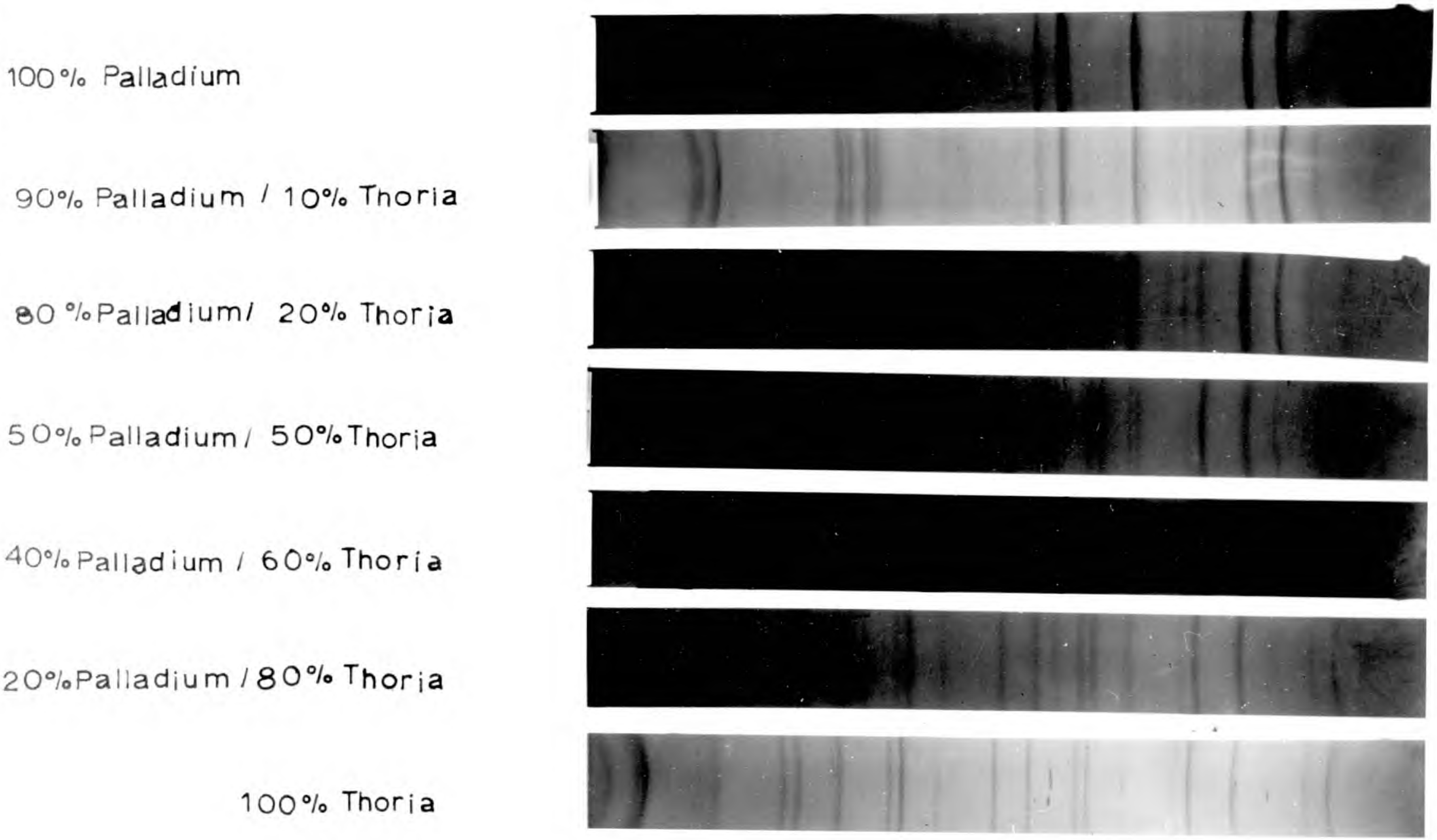


Plate 2 X-ray diffraction photographs of catalysts (1).

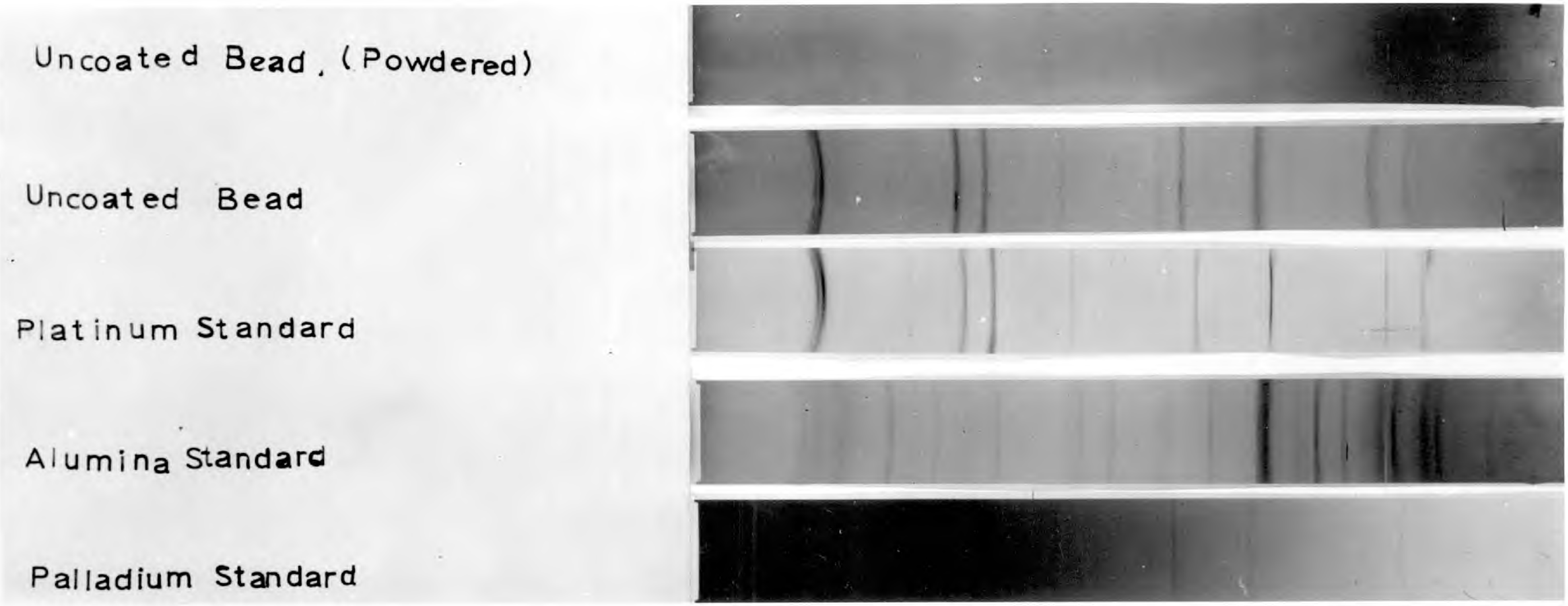
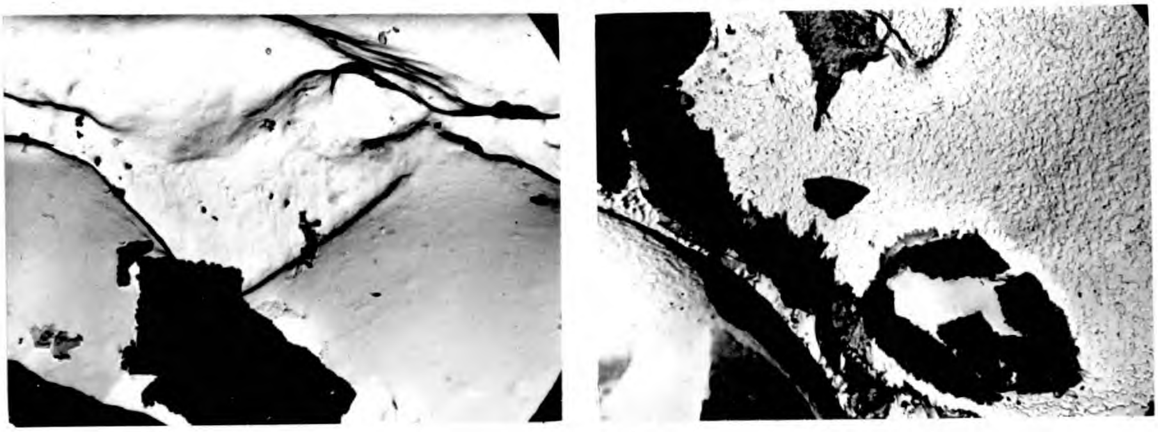


Plate 3 X-ray diffraction photographs of catalysts (2)

100 % PALLADIUM



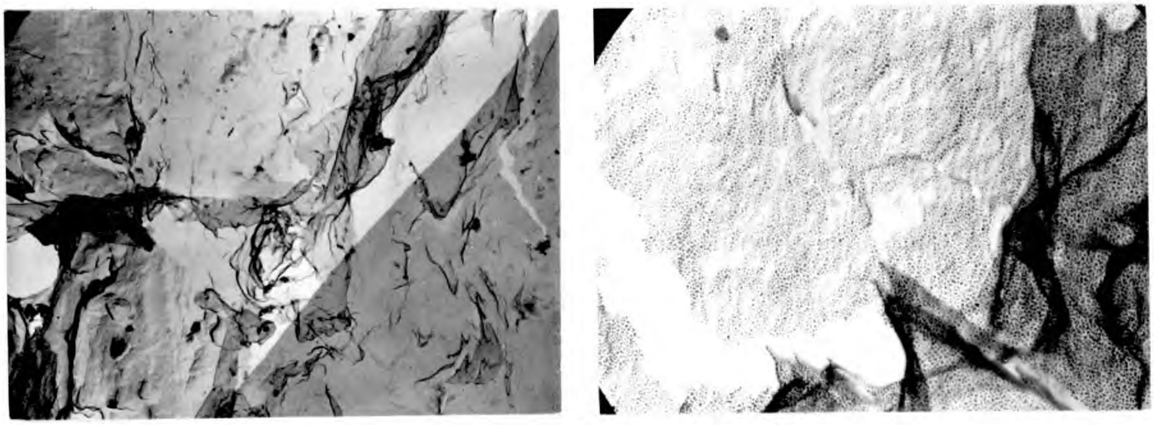
X 8000

1.

X 8000

2.

100 % THORIA



X 8000

3.

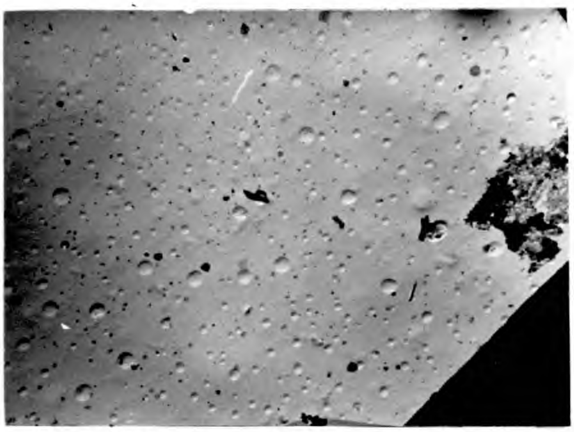
X 40,000

4.

PLATE 4

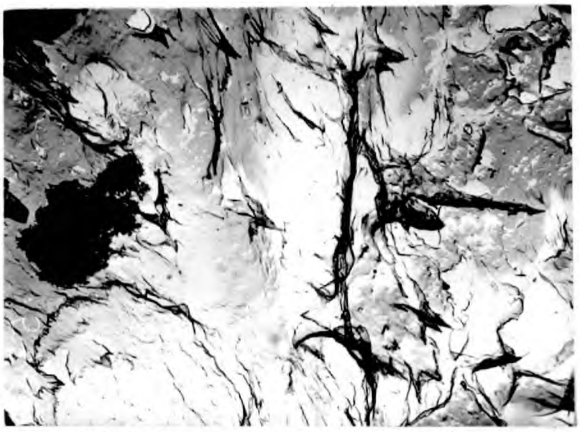
ELECTRON MICROGRAPHS OF THE SURFACES OF CATALYST BEADS - (1)

20 ATOM % PALLADIUM DEACTIVATED CATALYST



X 8000 (very small areas)

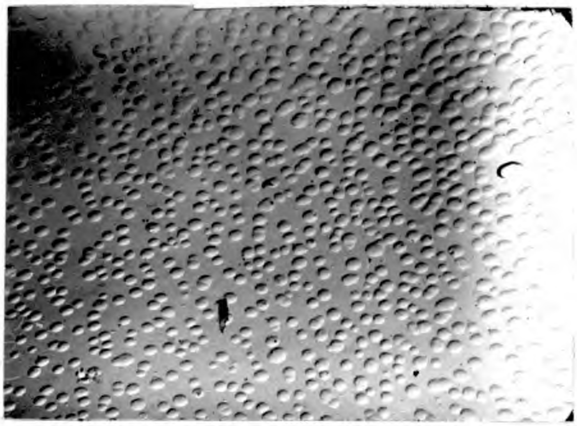
5.



X 8000 (most of the surface)

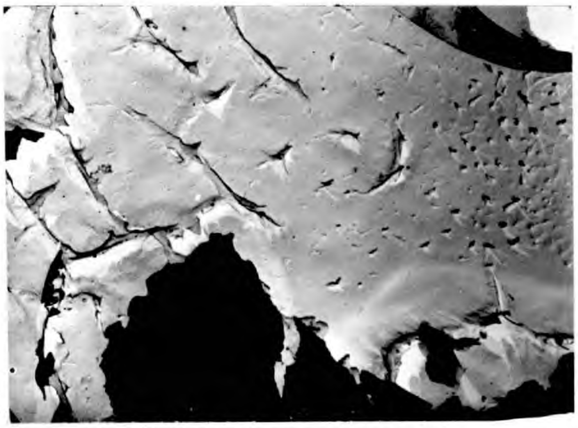
6.

20 ATOM % PALLADIUM - UNUSED CATALYST



X 8000 (very small areas)

7.



X 8000 (most of the surface)

8.

PLATE 5

ELECTRON MICROGRAPHS OF THE SURFACE OF CATALYST BEADS - (2)

Table 3.25. Values of inter-layer spacings obtained from X-ray diffraction photographs of palladium/thoria catalysts, together with reference values taken from the A.S.T.M. index.

From photographs of catalysts and of palladium wire		From the A.S.T.M. index					
		Palladium		Palladium Oxide		Hydrated Palladium Oxide	
Interlayer spacing, d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
				2.667	35	2.704	20
				2.644	100	2.615	100
2.21	100	2.246	100				
				2.153	20	2.120	30
1.96	40±5	1.945	42				
				1.674	30	1.668	60
				1.536	18	1.545	40
						1.499	30
1.37	30±5	1.376	25				
						1.353	20
				1.314	20	1.303	60
1.25	25±5	1.173	24				
						1.142	20
						1.074	30
						1.016	20
						1.004	20
		0.9723	3			0.981	30
						0.945	20
0.91	20±5	0.8924	13			0.892	50
0.87	20±5	0.8697	11			0.872	30 B
						0.840	50 B
						0.829	60 B
						0.882	50 B

N.B. (a) Only relative intensities (I/I_0) exceeding 18% have been quoted from the available data for palladium oxide and hydrated palladium oxide.

(b) "B" = blurred.

3.3.2. The activities of catalysts of palladium supported by various refractory oxides.

The activities of a number of supported palladium catalysts have been measured in order to find out whether the support has any effect on the activity of the palladium. As in the experiment described in Section 3.3.1, kinetic data were measured for each catalyst tested. The supports used were samarium oxide, erbium oxide, cerium oxide, praseodymium oxide, thallium oxide and uranium oxide, and each catalyst contained 20 atom % of palladium. With the exception of palladium supported by uranium oxide, which was almost completely inactive, all the catalysts behaved in a similar manner. The overall kinetics did not differ significantly from those already described for the reaction over palladium/thoria. Each catalyst was active at temperatures exceeding 420 ± 20°C, and at these 'low' temperatures, the reaction had a high order with respect to time, and took a long time (ca. 3 - 4 hr.) to go to completion. As the temperature was increased to about 550°C, the half-life, as determined from rate measurements, decreased from ca. 450 sec. to ca. 125 sec. Above this temperature, the half life did not decrease significantly and the bridge output signal, which is proportional to the reaction rate, decreased up to ca. 900°C, where it became insignificant or negative. Plots of

$\log_{10}$ $(1/t_{\frac{1}{2}})$ against $1/T^{\circ}K$ produced a wide scatter of points in most cases, but an activation energy of 7 ± 1 $kcal.mole^{-1}$ over the range 450 - 550°C was obtained for the palladium/thallium oxide catalyst. X-ray "powder" photographs taken of the catalysts used in these experiments showed only the patterns of the oxide supports.

Although there were few significant differences between the activities of the catalysts, there were some variations in their durability and resistance to poisoning; which were established by the testing of several samples in each case. Apart from uranium oxide, the least satisfactory support was cerium oxide; catalysts containing this material could only be used for about 20 experiments. The other rare-earth oxides were more satisfactory, but the most suitable support material was thallium oxide. The palladium/thallium oxide catalysts were also rather more active than the other specimens.

DISCUSSION.

4. DISCUSSION.

The primary aim of this investigation has been to establish the chemical mechanism of the oxidation of methane over supported palladium catalysts. For this purpose, kinetic measurements have been made of the oxidation of mathane and of the oxidation of some possible intermediate products. While it is not always possible to arrive at an unambiguous and detailed mechanism for a heterogeneous reaction solely from measurements of this type, one can usually obtain a general picture covering several mechanisms, which could perhaps be differentiated by means of more specialised techniques. In this section, the extent to which the results obtained elucidate the mechanism will be considered and possible further lines of investigation will be suggested.

Since mass transfer of the reactants and products to and from the catalyst surface must occur in all heterogeneous reactions, the effects of these processes on the experimental measurements must be considered. It must also be shown that homogeneous processes are not important under conditions where the measurements are carried out. Only then will it be permissible to discuss the observed kinetics as reflecting the true mechanism of the surface reaction, and to formulate the possible paths by which the reaction may occur. It may be possible to eliminate some of these effects, and to obtain a more detailed picture, by consideration of the results of the experiments on the oxidation of intermediate products.

4.1. The oxidation of methane.

4.1.1. Evidence for the heterogeneous nature of the rate-controlling process.

4.1.1.1. Concerning the possible effects of homogeneous oxidation.

The reaction is characterised by a low activation energy. The value obtained from the present measurements is of the order of 10 kcal.mole^{-1}. This compares with 11.0 kcal.mole^{-1} and 21 kcal.mole^{-1} obtained by previous workers using supported palladium catalyst in static and flow systems respectively. These differences are probably due to variations in reaction conditions, and it is clear that the reaction must be a genuine surface process, since the homogeneous oxidation of methane has a much higher activation energy (see Section 1.4.1.1). Moreover, the reaction products did not contain carbon monoxide even at low conversions, and this compound is produced in appreciable quantities during homogeneous oxidation.

The homogeneous reaction becomes very rapid as the temperature is increased above 650°C, and it is possible that this process is occurring to some extent in the envelope of hot gas that surrounds the catalyst bead. Previous workers (see ref. 45 for example) have found that a catalyst introduced into a system quenches any homogeneous reaction by destroying the free radicals by which it is propagated. One might expect however that the free radicals and intermediates would react at the catalyst surface more rapidly than would methane itself, so that the rate of complete conversion would be marginally increased. Rate measurements at these temperatures (see Section 3.2.3) indicate, however, that heterogeneous oxidation does not occur. At the same time, heterogeneous oxidation takes place over the supposedly inert "comparison" bead at temperatures exceeding 700°C. It is likely that these measurements made at higher temperatures reflect the effects of other processes besides the oxidation of methane over palladium, and they will therefore be ignored.

4.1.1.2. <u>Diffusion control</u>.

It has been explained in Section 1.2.3.1 that, as the temperature is increased, control of the overall reaction rate is taken over first by pore diffusion and then by bulk diffusion. However, the observed kinetics still partially reflect the kinetics of the chemical reaction. Thus, a chemical interpretation may be put on any of the results, so long as it is known in which of the three regions -

chemical control, pore diffusion control and bulk diffusion control, - the measurements were made.

The primary characteristic of the three regions is the overall activation energy: in the region of pore diffusion control, the observed value is about half that for the chemical process, and in the bulk diffusion control region it is about [9] 2 kcal.mole^{-1}. In the present case, the observed activation energy is high enought to rule out bulk diffusion control except at temperatures exceeding 600°C, but it is not high enough to exclude the possibility of pore diffusion control. On the contrary, the present value is about half that reported by one group of previous workers (see Section 4.1.1.1).

On the other hand, it has been found that several other fuels are oxidised much more rapidly than methane over the same catalyst. The rates of oxidation of similar concentrations of methane, methanol, carbon monoxide, acetylene and ethylene are compared in Table 4.1. Of these reactions, the oxidation of methane is the slowest at all temperatures. The differences between the reaction rates at a fixed temperature are quite large, so that diffusion processes are probably unimportant in the oxidation of methane (which gas, having the lowest molecular weight, would be expected to diffuse most rapidly).

Table 4.1. The comparative rates of oxidation of methane and other fuels.

* Temp. (°C)	Half-life (sec) for the oxidation of the following fuels					
	Methane	Carbon monoxide	Methanol	Formaldehyde	Ethylene	Acetylene
394	156				113	71
395	318	97		78		
441	138				106	44
496	125				100	
554	210		108			

* Each set of measurements has been made using different catalyst beads, so that only "horizontal" comparisons may be made.

(N.B. no page 186)

The unimportance of pore diffusion control is also supported by the values of the order with respect to methane, n_c, at various temperatures (see Table 3.1). It might be expected that, if n_c is less than 1, its value would increase towards $(n_c + 1)/2$ as the temperature is increased if the importance of pore diffusion increased concurrently. This trend would be augmented by any concurrent weakening in the strength of adsorption of methane on the catalyst. However, the values obtained show little sign of such a tendency, so that there can be no variation in the importance of pore diffusion over the whole range 400-590°C. Diffusion is not likely to be rate-controlling at the lower temperature, at which the reaction is very slow, and it is therefore probable that the process is unimportant over the whole range.

To summarise therefore, most of the evidence points to the conclusion that the overall rate of the reaction is controlled by chemical processes at the surface of the catalyst, but the possibility that pore diffusion may also be important cannot be completely discounted.

4.1.2. The nature of the rate-controlling step.

The mechanism of the surface reaction, which is reflected by the observed kinetics, must involve the chemisorption of the reactants and products as well as the reaction between the adsorbed species. The possible alternative routes may conveniently be shown on a block diagram (see Fig. 4.1). In this section, the extent to which the results distinguish between these alternatives will be discussed.

4.1.2.1. Reaction intermediates.

It is first considered whether or not the reaction involves the formation of discrete intermediates. Since the conversion of each methane molecule involves the rupture of all the bonds in three molecules, there is quite a number of intermediate species which might be present on the surface during the reaction. Any that are moderately stable would be detectable in the gas phase at low conversions. Previous workers (see Section 1.4.2.1) have reported the formation of small amounts of formaldehyde over catalysts of relatively low activity, including platinum, and the reaction of stoichiometric mixtures, diluted with inert gas, over supported nickel catalysts at high temperatures (700-900°C) produces measurable quantities of carbon monoxide and hydrogen [36]. Recent studies of the reaction over palladium catalysts [47,48,49] have not reported the formation of intermediates.

In the present work, the formation of intermediates was not detected. Although the experimental methods used were not very suitable for the detection of traces of formaldehyde, the formation of 2% of carbon monoxide and of

Fig. 4.1. Alternative routes for the heterogeneous catalytic oxidation of methane (after Ref.20).

(1) (a) Oxidation of the catalyst surface; and/or

(b) Adsorption of oxygen, and/or methane.

(2) Diffusion of adsorbed species to active sites.

(3) Electron transfer processes at active sites

(a) $O_2(\text{ads}) + e \longrightarrow O^-(\text{ads}),\ O^{2-}(\text{ads}),\ O_2^-(\text{ads})$

(b) $CH_4(\text{ads}) \longrightarrow CH_4^+(\text{ads}) + e$

or $CH_4(\text{ads}) \longrightarrow CH_3(\text{ads}) + H(\text{ads})$

followed by further dissociation steps.

(4) The surface reaction between gaseous or adsorbed species of methane (X) and gaseous or adsorbed species of oxygen (Y)

$$\begin{tikzcd}
X + Y \arrow[r] \arrow[d] & \left(\begin{array}{c}\text{Activated}\\\text{Complex I}\end{array}\right) \arrow[r] & \text{Products (ads)} \\
\left(\begin{array}{c}\text{Activated}\\\text{Complex II}\end{array}\right) \arrow[r] & \begin{array}{c}\text{Intermediate}\\\text{Products(ads)}\end{array} \arrow[r] & \left(\begin{array}{c}\text{Activated}\\\text{Complex III}\end{array}\right) \arrow[u]
\end{tikzcd}$$

(5) The desorption of products.

0.5% of hydrogen (with respect to the initial concentration of methane) would have been observed. More recent work using a flow system [75] confirms the absence of most possible intermediates down to much lower limits of detection. It should be noted, however, that the present analytical results (see Sections 3.2.5 and 3.2.6) show that palladium does catalyse the reactions between methane and carbon dioxide and methane and water vapour which, in the presence only of traces of oxygen, form carbon monoxide and hydrogen. Both processes, though measurable at temperatures exceeding 450°C, are much slower than methane oxidation. Several reactions may be formulated to account for these results, and some distinction may be made between them on thermodynamic grounds. The standard free energies corresponding to some of them are shown in Table 4.2.

It was also found that the substances which might have been formed as intermediates underwent much more rapid oxidation than methane under the same conditions. It may be concluded therefore that, even if one of them was formed as a surface intermediate, it would be oxidised directly to carbon dioxide and water, before it could be desorbed. The activation energy for methanol oxidation, 4 kcal.mole^{-1} is in accord with this conclusion. It may be emphasised that the relatively high temperatures which have to be employed

Table 4.2. Standard free energies for some possible interaction between methane, carbon monoxide, carbon dioxide, water, hydrogen and oxygen.

Reaction	Standard free energies (cal.mole^{-1}) at the following temperatures (^{o}K)			
	298	600	800	1000
$2CO_2 \rightleftharpoons 2CO+O_2$	+122904	+110172	+101744	+93334
$CH_4+2O_2 \rightleftharpoons CO_2+2H_2O$	-191392	-191266	-191282	-191298
$CH_4+3CO_2 \rightleftharpoons 4CO+2H_2O$	+54416	+ 29078	+ 12206	- 4630
$CH_4+H_2O \rightleftharpoons CO+3H_2$	+33968	+ 17288	+ 5525	- 6514
$CH_4+CO_2 \rightleftharpoons 2CO+2H_2$	+40784	+ 21218	+ 7752	- 5886
$CH_4+2H_2O \rightleftharpoons CO_2+4H_2$	+27152	+ 13358	+ 3298	- 7142
$CO+H_2O \rightleftharpoons CO_2+H_2$	- 6816	- 3930	- 2227	- 628
$C + 2H_2 \rightleftharpoons CH_4$	-12140	- 5491	- 547	+ 4610
$C + \frac{1}{2}O_2 \rightleftharpoons CO$	-32808	- 39359	- 43667	- 47943
$C + O_2 \rightleftharpoons CO_2$	-94260	- 94445	- 94539	- 94610
$H_2+ \frac{1}{2}O_2 \rightleftharpoons H_2O$	-54636	- 51156	- 48645	- 46039

for the catalytic oxidation of methane and of other saturated hydrocarbons of low molecular weight reflect the considerable amounts of energy required to "break into" these stable molecules.

To summarise therefore, it may safely be stated firstly that no stable intermediate can be formed when methane is oxidised by a large excess of oxygen over palladium, and secondly that any proposed mechanism must account for the formation of carbon monoxide and hydrogen when oxygen is scarce.

4.1.2.2. The overall reaction kinetics.

The general results may be summarised as follows. The order with respect to methane, n_c, is about 0.8 and does not vary appreciably with temperature. The order with respect to time, n_t, is approximately 1.0 at high temperatures, exceeds 1.0 at intermediate temperatures, and is a complex function of the extent of reaction at low temperatures. The reaction is slightly inhibited by oxygen. The presence of carbon dioxide, except in very large amounts, does not appreciably reduce the rate of reaction; water vapour has, however, a marked inhibiting effect even when present in a concentration lower than that of methane. Analytical results, in addition to confirming that n_t exceeds n_c, show that up to 5% of the methane remains unchanged when the reaction stops. (This would not be expected on thermodynamic grounds; the equilibrium constants for methane oxidation at 327, 527 and 727°C respectively are 8.6 $x10^6$, $1.6x10^5$ and 1.4 $x10^4$).

From these results taken in conjunction with information available in the literature, conclusions may be drawn with regard to the nature and strength of adsorption of the reactants and products. In particular, it may be shown whether the various species are adsorbed on similar sites, on different sites, or not at all, and whether or not the adsorption processes involve dissociation. With these objects in view, the parts played in the reaction by the products and the reactants will be considered in turn and then possible mechanisms will be considered.

(a) The influence of the reaction products.

It is clear from the fact that n_t exceeds n_c that the reaction is inhibited by its own products. The "added product" experiments showed that this inhibition is due to water and not to carbon dioxide.

It is reported [7] that carbon dioxide is strongly adsorbed on some transition metals at 0 and 100°C up to limited coverages. Palladium is not one of these metals, however, and, except for its inhibiting effect on the oxidation of carbon monoxide, observed in the present studies (see

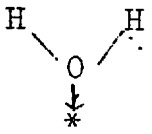
Section 3.2.7.2 and Table 3.16), no other reports of carbon dioxide adsorption on this metal have been found. It has been suggested [7] that, since the observed heats of adsorption of carbon dioxide are high even at saturation point, the absence of further adsorption, and of any adsorption at all on some metals, is due to prohibitively high activation energies. If this were true in the case of palladium, then one would expect carbon dioxide to inhibit the reaction appreciably, since the activation energy for its desorption would be very high indeed. This is consistent with the apparently contradictory experimental observations that added carbon dioxide does not further inhibit the oxidation of methane, while the oxidation of carbon monoxide is subject to mild product inhibition (see below). This "kinetic inhibition" by carbon dioxide cannot be very great in the oxidation of methane, however, since its effect on the much faster oxidation of carbon monoxide is not very large.

No information appears to be available regarding the adsorption of water on palladium, or on palladium-catalysed reactions of water. The deuterium/water exchange reaction has, however, been studied over platinum [76]. It is suggested that water may be adsorbed either as:

(a) $$H_2O \quad + \quad 2* \longrightarrow *OH \quad + \quad *H$$

or as:

(b) $H_2O \quad + \quad * \longrightarrow$

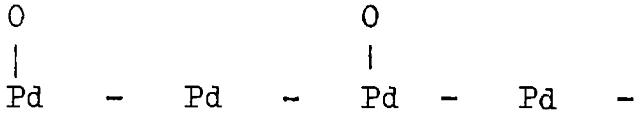


(where * represents an "active site") and that (b) is more likely at high temperatures (250 - 550°C).
Extrapolations from one catalyst to another tend to be misleading, but it may perhaps be suggested that the adsorption of water on palladium is similar in nature. The experimental results certainly suggest that water is strongly adsorbed: it reduces the reaction rate and prevents the complete oxidation of methane. It seems probable that the water produced by the reaction is almost entirely responsible for the product inhibition observed in almost all methane oxidation experiments.

(b) The dependence of rate on oxygen concentration.

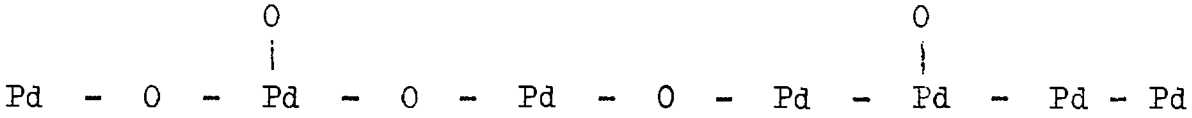
The slightly negative dependence observed indicates that the catalyst is saturated with oxygen under all conditions used in the present work. It also almost certainly shows that methane and oxygen are adsorbed on similar sites and that oxygen is the more strongly adsorbed. It is not clear, however, whether saturation is equivalent to complete coverage.

A considerable amount of work has been dome on the adsorption of oxygen on palladium. The rather wide range of heats of adsorption under different conditions probably reflect a large variation in this quantity with coverage. Brennan, Hayward and Trapnell [21] showed that at 25°C, the surface of a palladium film is saturated at a coverage of 0.6 - 0.7, and found initial and integral heats of adsorption of 67 and 44 kcal.mole^{-1} respectively. Measurements at 227°C by Bortner and Parravano [77] produced a heat of 48 kcal.mole^{-1} at coverages between 1 x10^{-4} and 0.7, and this value is not very different from the heat of formation of palladium oxide, 42 kcal.(mole oxygen)$^{-1}$. In more recent work on the exchange reaction between $^{18}O_2$ and $^{16}O_2$, Boreskov [16] observed that at 200°C, bulk palladium oxide was formed rather slowly (30 monolayers in 20 hr.) and that very little of the oxygen on the surface takes part in the reaction. It seems possible therefore that at low temperatures oxygen is adsorbed to form



$$\overset{\mathrm{O}}{\overset{|}{\mathrm{Pd}}} - \mathrm{Pd} - \overset{\mathrm{O}}{\overset{|}{\mathrm{Pd}}} - \mathrm{Pd} -$$

with the evolution of a high initial heat which falls off very rapidly as the coverage increases. At high temperatures, however, adsorption of this type only occurs up to the point beyond which bulk oxidation is energetically more favourable. Thus the surface would be something like:



$$\mathrm{Pd} - \mathrm{O} - \overset{\mathrm{O}}{\overset{|}{\mathrm{Pd}}} - \mathrm{O} - \mathrm{Pd} - \mathrm{O} - \mathrm{Pd} - \overset{\mathrm{O}}{\overset{|}{\mathrm{Pd}}} - \mathrm{Pd} - \mathrm{Pd}$$

If this is the case, then so long as the prèssure of oxygen is greater than that required to form the first oxide layer, the state of the surface will not depend on the oxygen concentration, and nor will the reaction rate, to any great extent. The oxygen which takes part in the surface reaction is probably that which is least strongly adsorbed on the surface. It is also possible that lattice oxygen is involved, since this is the least strongly held; this has been observed when hydrocarbons are oxidised over copper oxide [46]. The apparent "induction period" observed for the reaction at low temperatures over some catalysts may be due to the time taken for an oxide layer to be formed. In view of the fact that the catalytic activity of palladium appears to decrease at high temperatures, it would be of interest both to calculate the equilibrium constants for bulk oxide formation used in the experimental work and to estimate the extent of surface coverage by adsorbed oxygen over this same temperature range.

Approximate calculations ofthe equilibrium constant for bulk oxide formation have been made using the standard free energy of formation -14.4 kcal.mole^{-1}, and the standard heat of formation, -20.4 kcal.mole^{-1} at 25°C. The equilibrium pressure of oxygen above palladium and palladium oxide is plotted as a function of temperature in Fig.4.2. This shows that the temperature range, 580-700°C, over which

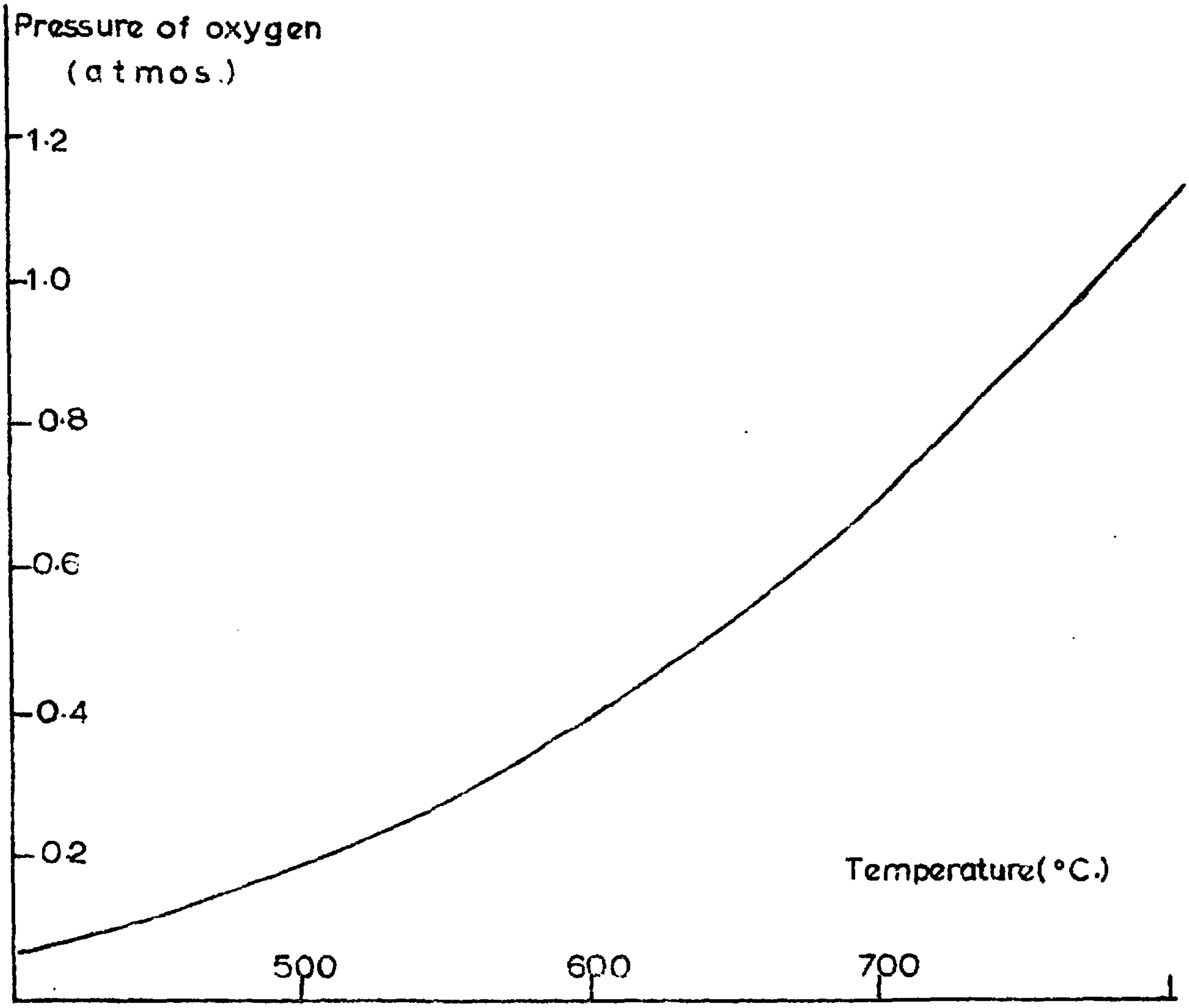


Fig. 4.2. The equilibrium pressure of oxygen above palladium oxide as a function of temperature.

the equilibrium pressures of oxygen over palladium oxide correspond to the oxygen pressures used in the experimental work, is just that over which a decrease in catalytic activity is observed.

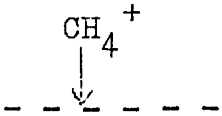
With respect to adsorbed oxygen, it seems unlikely that calculations made for adsorption on palladium metal will be applicable to adsorption on the oxide, whose formation appears to be a pre-requisite for the oxidation of methane. The finding of palladium metal by means of X-ray analysis does not necessarily contradict this, because <u>surface</u> layers of oxide would not be detected. No information has been found regarding the adsorption of oxygen on palladium oxide, and the theoretical prediction of coverages from adsorption isotherms in the absence of such information is impracticable. However, the slight negative dependence of the rate of reaction on oxygen concentration does indicate that it is adsorbed oxygen rather than lattice oxygen which takes part in the reaction.

(c) The dependence of rate on methane concentration.

The factors which might control the dependence of the reaction rate on the concentration of methane are the frequency with which methane molecules collide with the catalyst surface, the rate of chemisorption, and the rate of the surface reaction. The first two are directly proportional to the concentration of methane, and so are probably ruled out by the observed kinetics. The dependence of rate on the initial methane concentration (rate $\propto p_{CH_4}^{0.8}$) indicates fairly low coverage of the surface and it also appears that all the reactants and products occupy similar sites and that all except carbon dioxide have comparable strengths of adsorption.

Little information on the adsorption of methane on palladium is available in the literature. This compound is less strongly adsorbed than oxygen and the process is slow at room temperature[78]. It has also been observed [79] that at higher temperatures (> 400°C) the breakdown of methane to carbon and other hydrocarbons takes place. This is not surprising, since methane is thermodynamically unstable with respect to its elements in their standard states at temperatures exceeding ca. 550°C. As in the case of oxygen, the heat of adsorption falls and the activation energy of adsorption rises as the coverage increases. Thus the coverage of the surface is never complete, and at low temperatures is independent of pressure except when this is very low. In addition to these chemisorption measurements, studies of the exchange reaction between methane and deuterium over palladium [80] are of some interest. Between 200 and 300°C the order in deuterium is 1.0 and in methane 0.5 for stepwise exchange and -0.9 for multiple exchange. These results show that the rate-controlling step is the reaction between adsorbed CH_3 and adsorbed D_2 (or H_2) and that although adsorbed CH_2, CH, and C may be formed on the surface, their concentrations are relatively small.

As it has already been established that the surface of the palladium catalyst used probably consists largely of an oxide film, the results of chemisorption and exchange measurements cannot strictly be compared withthose obtained in the present work. It seems likely that the adsorption of methane on the catalyst used is dissociative, but that the hydrocarbon may alternatively be adsorbed by a process involving electron donation to the catalyst surface to form:



$$\overset{CH_4^+}{\downarrow}$$

Some indication of which process occurs might be expected from the comparative rates of oxidation of saturated hydrocarbons under similar conditions. However, since both the C-H bond strengths and ionisation potentials of these hydrocarbons show similar trends (see Table 4.3), and the differences between their rates of oxidation are not large, no distinction may be made on the basis of the results of the present work.

In either case, it is not unreasonable to suppose that, at temperatures exceeding 400°C, adsorption is not

Table 4.3. The ionisation potentials and C-H bond energies of some low molecular weight hydrocarbons [87].

Hydrocarbon	Ionisation potential (eV.)	C-H bond energy (kcal.mole^{-1})
CH_3 - H	12.99	10.3 ± 2
C_2H_5 - H	11.65	98
n-C_3H_7 - H	11.21	98
i-C_3H_7 - H		94
n-C_4H_9 - H	10.80	101
i-C_4H_9 - H	10.79	93
t-C_4H_9 - H		89
C_2H - H	11.40	115 ± 10
C_2H_4 - H	10.60	104

rate-controlling, but that the degree of coverage is small enough to depend on the partial pressure of methane. It is, however, surprising that there is no marked variation with temperature of the order with respect to methane. One might have expected an increase from some low value at low temperatures to unity at high temperatures, unless the temperature variations of the strengths of adsorption of methane and oxygen are very similar.

4.1.2.3 Possible reaction mechanisms.

It has been established that the catalytic oxidation of methane over palladium involves:

(a) a complete layer of adsorbed oxygen, and/or some oxygen from the lattice of a surface layer of oxide;

(b) Methane chemisorbed either as CH_3* or as $CH_4^+ *$;

(c) Chemisorbed water;

(d) Fairly rapidly desorbed carbon dioxide.

It is possible therefore to set up rate equations to decide whether or not the various adsorptions involve dissociation. As has been pointed out (see Section 1.2.3.2) the applicability of these equations is questionable, since they are based on the Langmuir isotherm. However, functions based on a more realistic model would be too complex for satisfactory interpretation, so that the Langmuir-Hinshelwood approach has to be used in the absence of anything better.

The reaction to be considered is therefore:

$$CH_4(ads) + 2O_2(ads) \longrightarrow CO_2(g) + 2H_2O(ads)$$

Since oxygen coverage is complete and carbon dioxide is at most only weakly adsorbed, only the adsorptions of methane and water need be considered, and there will be no kinetic distinctions between reactions involving the various possible forms of adsorbed oxygen. The kinetics will however vary according to whether methane, water and oxygen are adsorbed on the same or on different sites, so that, assuming all adsorptions are mobile, the alternatives to be considered are:

(1) All sites similar
or
(2) Methane and oxygen adsorbed on different sites;

(a) methane dissociated,
or
(b) methane undissociated;

(i) water dissociated
or
(ii) water undissociated.

Let p_i represent the partial pressure of component i;
" a " " strength of adsorption of methane)
" b " " " " " " oxygen) at a fixed temp.
" c " " " " " " water)
" θ_i " " fractional surface coverage by component i

and let the superscript "o" indicate initial partial pressures.

Case

Case 2.a.i. In this case, the surface coverage by oxygen and hence the reaction rate, would be proportional to some power of the partial pressure of oxygen between 0 and 1.0. Since a slight inhibiting effect by oxygen has been observed, this and all other cases of (2) may be dismissed.

Case 1.a.i. The surface coverages by the reactants are given by:

$$\theta_{CH_4} = (a.p_{CH_4})^{\frac{1}{2}}/(1 + (a.p_{CH_4})^{\frac{1}{2}} + (b.p_{O_2}) + (c.p_{H_2O})^{\frac{1}{2}}) \quad \ldots \quad (4.1)$$

$$\theta_{O_2} = (b.p_{O_2})/(1 + (a.p_{CH_4})^{\frac{1}{2}} + (b.p_{O_2}) + (c.p_{H_2O})^{\frac{1}{2}}) \quad \ldots \quad (4.2)$$

Since:

$$\text{rate} \propto \theta_{CH_4} . \theta_{O_2} \quad \text{or} \quad \theta_{CH_4} . \theta_{O_2}^{2} \quad \ldots \quad (4.3)$$

$$\text{rate} \propto [(a.p_{CH_4})^{\frac{1}{2}}.b.p_{O_2}]/y^2 \, ,$$

or

$$[(a.p_{CH_4})^{\frac{1}{2}} .b^2.p_{O_2}^{\;2}]/y^3 \quad \ldots \quad (4.4)$$

where y is the denominator of equations (4.1) and (4.2). These equations may be ruled out because they would give an order with respect to methane of 0.5. Case 1.a.ii may be discounted for the same reason.

Case 1.b.i. If the following substitution is made for the partial pressure of water:

$$p_{H_2O} = 2(p_{CH_4}^{\;o} - p_{CH_4}) \quad \ldots \quad (4.5)$$

then the possible rate equations become:

$$\text{rate} \propto [(a.p_{CH_4})(b.p_{O_2})]/[1+(a.p_{CH_4})+(b.p_{O_2}) + 2c(p_{CH_4}{}^{o} - p_{CH_4})\ ]^2 \quad \ldots \quad (4.6$$

or:

$$\text{rate} \propto [(a.p_{CH_4})(b.p_{O_2})^2]/[1+(a.p_{CH_4})+(b.p_{O_2}) + 2c(p_{CH_4}{}^{o} - p_{CH_4})\ ]^3 \ldots \quad (4.7$$

Both these expressions are consistent with an order in methane, n_c, of less than unity. They also indicate that the order with respect to time, n_t, would be greater than n_c so long as a and c are of the same order of magnitude. The order with respect to oxygen, according to these equations, could vary between +1 (equation 4.6) or +2 (equation 4.7) for weak adsorption to -1 (both equations) for strong adsorption. The observed values of about -0.1 indicate moderately strong oxygen adsorption.

Case 1.b.ii. This case differs from 1.b.i only in the contribution to the denominator made by the term for the strength of adsorption of water vapour. There is no clear-cut way of distinguishing between these two mechanisms.

To summarise, therefore, the rate-determining step of the reaction probably involves undissociated adsorbed methane reacting with oxygen which is somewhat more strongly adsorbed on similar sites. The reaction is retarded by the product water.

4.1.3. Catalyst poisoning.

It was mentioned in Section 3.2.1.3 that the activity of most of the catalysts gradually decreased with use and also (in Section 3.2.4), that a small amount of methane remained unchanged at the end of each run. It was also necessary to reactivate the catalyst between runs by heating it to ca. 800°C under vacuum for 90 sec. The possible causes of this deactivation are carbon decomposition, sintering and the formation of some compound not decomposed by the activation process.

With regard to carbon deposition, electron probe microanalysis gave some indication of this on catalysts used for the oxidation of intermediates, but not on catalysts used for the oxidation of methane only. Unfortunately, the method is not very sensitive to carbon, and these results must therefore be treated with reserve. They are supported to some extent, however, by the finding that catalysts deactivated by use for the oxidation of formaldehyde and carbon monoxide were more satisfactorily restored by heating in oxygen than by heating under vacuum, which was the best way of reactivating a catalyst used for the oxidation of methane. It appears therefore that if methane is adsorbed dissociatively, this dissociation does not proceed beyond the first stage to any great extent.

It is well established that a catalyst surface is liable to sinter if it is heated to a temperature greater than about half its melting point, and that sintering occurs at lower temperatures in the presence of readily adsorbed gases. Thus, since the melting point of palladium is 1549°C, catalyst sintering would be expected in the present instance. There was a noticeable difference in the sharpness of the peaks of the X-ray diffraction photographs of used and unused catalysts, (see Section 3.3.1). On the other hand, there was no clear distinction between the pore structures of activated and deactivated catalysts, as shown by the electron micrographs (see Plates 4 and 5). It seems likely that sintering is partly responsible for the gradual reduction in activity, although it cannot be responsible for the complete deactivation of the catalyst. It is probable that the differences between the suitability of the different oxides tested as catalyst supports probably reflect their surface area and resistance to sintering.

One further cause of deactivation is indicated, and this is the formation of a surface compound which is not desorbed even under the fairly extreme conditions used. The most likely compound is palladium hydroxide, since water is known to inhibit the reaction. The stability of palladium (II) hydroxide exceeds that of palladium oxide (see Table 4.4), while that of palladium(IV)

Table 4.4. Some thermodynamic properties of palladium compounds [88].

Compound	ΔH^{o}_{298} (kcal.mole^{-1})	ΔG^{o}_{298}(kcal.mole^{-1})
Pd (g)	93	84
PdO (s)	-20.4	-14.4
$PdO_2.xH_2O$	decomposes at	about 200°C
$Pd(OH)_2$	-92.1	-72
$Pd(OH)_4$	-169.4	-126.2 (?)

hydroxide is very much greater. It seems probable that the degassing conditions used between runs were not sufficiently rigorous to decompose the surface hydroxide, which had built up until the whole catalyst surface was covered. There must be an appreciable difference between the strength of adsorption of water and the stability of the crystalline hydroxide, since adsorbed water may be removed by degassing. There is, however, one objection to this hypothesis. Clearly the hydroxide layer should have been present from the beginning, since the catalyst is deposited from aqueous solution. It can only be assumed that the initial activation processes (see Section 2.2.1) destroy the hydroxide.

4.2. The oxidation of intermediates.

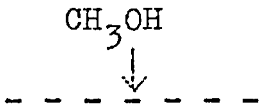
It has already been noted that formaldehyde, methanol and carbon monoxide are all oxidised more rapidly than methane under the experimental conditions used. It is worthwhile at this stage to consider in more detail the oxidations of these compounds, and some of the concurrent oxidation results.

4.2.1. Methanol oxidation.

At fairly low temperatures ($<400^\circ$C) this reaction involves the formation of at least two intermediates other than formaldehyde and formic acid, which could not be detected b the analytical methods used. These substances were not identified, but both must contain carbon, and both were eluted after methane but before methanol on the squalane column. At 500°C, these intermediates are formed only in small quantities, and the overall kinetics are rather similar to those for methane oxidation, except that product inhibition is almost non-existent. The activation energy is even lower than that for methane oxidation, although it is likely that the kinetics of this reaction are influenced by diffusion. The reaction proceeds satisfactorily at temperatures well outside the range in which methane oxidation occurs.

These observations all point to the conclusion that methane and methanol are adsorbed by different mechanisms. Their strengths of adsorption are presumably comparable, since orders with respect to fuel are similar. A greater inhibition of methanol oxidation by water would be expected if this compound were blocking methanol adsorption sites, since this surface reaction is so much faster than the oxidation of methane. This conclusion is confirmed by the concurrent oxidation rate measurements, which show that the initial rate of oxidation of each fuel is not reduced by the presence of the other. On the contrary, it appears that the combined rate of oxidation is greater than would be expected on the basis of "side-by-side" reactions.

Both fuels appear to be adsorbed by non-dissociative mechanisms. Both are adsorbed on different sites, and assist each other's adsorption to a slight extent. It is probable therefore that one is adsorbed by electron donation to the surface, and the other by electron transfer from the surface. This is difficult to justify completely, however, because whichever fuel accepts electrons would be dissociated in the process. Methane is, however, the more likely to be able to be dissociatively adsorbed, which would imply that methanol is probably adsorbed as



$$\begin{array}{c} CH_3OH \\ \downarrow \\ \text{- - - - - - -} \end{array}$$

Few kinetic results on the catalytic oxidation of methanol have been reported. Jiru et al [81] have shown that, over ferric oxide/molybdenum trioxide catalysts, at 270°C, the reaction proceeds by a reduction-oxidation mechanism of the form:

$$CH_3OH\ (g) \ + \ \text{oxidised catalyst} \longrightarrow HCHO\ (g) + H_2O\ (g) \\ + \text{reduced catalyst}$$

$$O_2\ (g) \ + \ \text{reduced catalyst} \longrightarrow \text{oxidised catalyst}$$

Other workers [82] have reported, however, that adsorbed oxygen is involved, so that the mechanism probably varies from one catalyst to another. It would therefore be unwise to attempt to predict the mechanism over palladium catalysts in the absence of detailed experimental measurements. The indications from the present results are that methanol is initially adsorbed by electron donation to the surface, and that the mechanism involves concurrent and/or consecutive reactions, by which intermediates are formed. These intermediates will not, however, affect the initial rates of comsumption of methane and methanol.

4.2.2. Carbon monoxide oxidation.

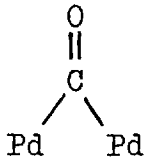
This reaction proceeds at high but measurable rates over a wide temperature range. The kinetic results (order with respect to carbon monoxide 0.9; order with respect to time 1.0) indicate that carbon dioxide and carbon monoxide are both weakly adsorbed on similar sites, and that the adsorption of the latter compound is non-dissociative. The results of experiments in which methane and carbon monoxide were allowed to undergo oxidation side by side show that the two reactions interfere with one another, suggesting that the adsorption of the fuels is competitive. Since the oxidation of methane is not appreciably inhibited by carbon dioxide, it may be concluded either that carbon monoxide is the less strongly adsorbed fuel, and/or that the slow desorption of carbon dioxide has more effect on the faster oxidation of carbon monoxide.

A number of investigations of the oxidation of carbon monoxide over palladium catalysts have been carried out. Schwab and Gossner [83] found that the activation energy for the reaction over the temperature range 250-320°C is 22.2 kcal.mole^{-1}, and suggested on the basis of their kinetic results that the reaction involves strongly adsorbed carbon monoxide and weakly adsorbed oxygen. This work is comparable with that of Daglish and Eley [84], who, using similar experimental conditions, obtained an activation energy of 30 kcal.mole^{-1}, and concluded that the rate-determining step is the adsorption of oxygen onto two neighbouring sites in a nearly saturated layer of carbon monoxide. These results however are not directly comparable with those obtained in the present work, since the concentrations of oxygen used were probably too low for bulk oxidation to occur. A mechanism of the type proposed for the reaction over nickel may well be more appropriate:

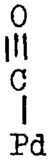
$$\begin{aligned} CO\ (g) &\longrightarrow CO\ (ads.,\ bridge) \\ O_2\ (g) &\longrightarrow 2O\ (ads.) \\ CO\ (ads) + 2O\ (ads) &\longrightarrow CO_3\ (ads.) \\ CO_3\ (ads) + CO\ (g) &\longrightarrow 2CO_2\ (g) \end{aligned}$$

Carbon dioxide has been found to inhibit the reaction over cuprous oxide [19], and ^{18}O tracer studies show that the reaction over this catalyst involves mainly chemisorbed oxygen, rather than lattice oxygen.

Since methane and carbon monoxide are adsorbed competitively, the electron transfer processes accompanying each adsorption are probably similar, so that information on the adsorption of carbon monoxide may have some relevance to the adsorption of methane. Infra-red studies [85] have shown that carbon monoxide is adsorbed on the surface of palladium mainly as:



but also to a small extent as:



Calculations of the % ionic character of surface-carbon bonds indicate that such bonds are largely covalent, so that very little electron transfer is involved in their formation. This is in accord with the theories of metal bonding in carbonyl compounds. In terms of the molecular orbital formulation [86], the M-C bond in terminal carbonyls is formed by σ-donation of two electrons from the carbon atom into empty orbitals of the transition metal, together with π-donation of metal d - electrons into π-antibonding orbitals of the carbon monoxide. These effects are of comparable importance, so that the net electron transfer is approximately zero. In the bridged carbonyls, however, the π-bonding is probably more extensive, so that there would be a small net electron transfer from the metal to carbon. In the case of palladium, carbonyl formation has not been reported. However, carbon-oxygen stretching frequencies obtained from infra-red adsorption studies indicate that the metal-carbon bond is strong, so that the extent of π-electron donation from metal to carbon is considerable. Measurements have not been made using palladium oxide, but it is not unreasonable to suppose that the situation here is similar.

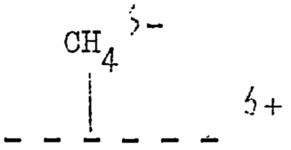
It may therefore be inferred that the adsorption of methane also involves electron transfer from the catalyst. This would fit in with the mutual enhancement of the rates of oxidation of methane and methanol, but is at variance with the observed kinetics of methane oxidation, which do not coincide with those expected on the basis of a dissociative mechanism.

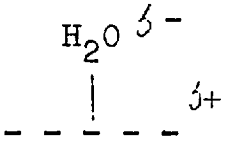
4.3. A general assessment.

The conclusions drawn from the findings of this work may be summarised as follows. The heterogeneous catalytic oxidation of methane over palladium appears to lead, via the reaction of adsorbed methane with adsorbed oxygen and/or lattice oxygen from surface layers of palladium oxide, to the formation of carbon dioxide and water only. The reactants and products are adsorbed on similar sites (or at any rate by similar mechanisms) with strengths of adsorption decreasing in the order:

$$O_2 > CH_4 \simeq H_2O > CO > CO_2$$

The adsorption of these compounds involves electron transfer from the catalyst surface, whereas the adsorption of methanol involves electron donation to the catalyst surface. Since the formation of adsorbed species such as:





is highly unlikely, the adsorption of both these compounds probably involves dissociation. Thus the presence of adsorbed CH_3, H and OH groups on the catalyst surface is quite probable. The existence of more highly unsaturated adsorbed carbon-containing species is also possible but less likely, except when the gas-phase concentration of methane is high. Since the conclusion that methane adsorption involves dissociation is at variance with the interpretation of the kinetic results, this interpretation, which is based on Langmuir-Hinshelwood mechanisms, is considered unsatisfactory.

The existence of surface-carbon bonding could go some way toward explaining the formation of carbon monoxide by the partial oxidation of methane; this would involve reaction between adsorbed methyl or methylene groups and adsorbed oxygen, or hydroxyl groups or carbon dioxide depending on the components of the reaction mixture.

The progressive deactivation of the catalyst is probably mainly attributable to the gradual formation of palladium hydroxide, which is not readily reconverted to palladium.

The results of other investigations using palladium catalysts appear to be in accord with these conclusions. Some recent experiments have involved the use of micro-catalytic flow reactors, through which pulses of reaction mixtures are carried by means of an inert gas. This method incidentally has the advantages firstly that mixtures containing comparable amounts of methane and oxygen are allowed to react, and secondly that catalysts of much higher surface area may be used. It must be realised, however, that the kinetic interpretation of the results is a complex matter. Stein et al[39] detected carbon monoxide among the products of the reaction over palladium, and found an activation energy of 21.8 kcal.mole^{-1} over the temperature range 180-250°C. Oxygen was used as carrier gas in this work, so that it is difficult to decide whether or not the catalyst was covered by a surface layer of oxide. However, in view of Boreskov's finding (see above) that the rate of bulk oxide formation is very slow at 250°C, and since the activation energy is so much higher than that reported in the present work, it seems likely that the reaction involves oxygen adsorbed on palladium metal. Mezaki and Watson [48], and Ahuja and Mathur[49], have studied the reaction at temperatures between 320 and 380°C. Activation energies were not reported but appear to have been fairly low; intermediate products were not detected. The former work involves the use of air as carrier/oxidant, while oxygen was used in the latter investigation. The two studies appear to be otherwise comparable, and both groups of workers used similar methods for analysing their results. However, while Mezaki and Watson considered that the rate-controlling step is the reaction between gaseous methane and oxygen adsorbed on dual sites and that either or both products may inhibit the process by appreciable adsorption, Ahuja and Mathur concluded that all four substances are appreciably adsorbed on similar sites, that the surface reaction is rate-controlling, and that the adsorption of oxygen is non-dissociative. Mezaki and Watson's calculations indicate that carbon dioxide is the more weakly adsorbed product, but that the difference between the two strengths of adsorption is not large, and decreases with increasing temperature.

These findings are to some extent in accord with the results of the present work. It is agreed that the products inhibit the reaction, but it has here been shown that the adsorption of carbon dioxide is negligible at temperatures exceeding 450°C. The finding that methane and oxygen are competitively adsorbed agrees with the conclusions of Ahuja and Mathur; it is interesting that their kinetic results also indicate the non-dissociative adsorption of methane. Thus, either the applicability of Langmuir-Hinshelwood mechanisms to this type of problem is limited, or the current theories of the modes of adsorption of saturated hydrocarbons are inadequate; the former possibility seems more likely.

The principal problem which remains unsolved is the nature of the oxygen species which takes part in the rate-determining step. It is clear that surface palladium oxide is the effective catalyst, since the catalytic oxidation of methane does not proceed under conditions where a layer of oxide is not readily formed. However, whether it is lattice oxygen or adsorbed oxygen that takes part in the reaction cannot be decided from the present results, and neither can the nature of the adsorbed oxygen. (Since the Langmuir-Hinshelwood approach gives a dubious conclusion with respect to methane adsorption, Ahuja and Mathur's conclusion with respect to oxygen adsorption must remain open to question).

^{18}O tracer studies, and adsorption and conductivity measurements, using both palladium metal and palladium oxide, would help to answer these questions. The adsorption of methane under conditions where reaction takes place could not readily be studied in isolation, however, since the pressure of oxygen required to maintain the oxide film would also be adequate to oxidise the adsorbate.

REFERENCES.

1. A.R.Baker, Safety in Mines Research Establishment Research Report No.162, March 1959.

2. P.Sabatier, "La Catalyse en Chemie Organique " (Librairie Polytechnique, Paris), 1912.

3. A.A.Balandin, "Catalysis and Chemical Kinetics" ed. A.A.Balandin, (Academic Press), 1965.

4. G.C.Bond, "Catalysis by Metals" (Academic Press), 1962, p.21.

5(a) W.Hume-Rothery and G.V.Raynor, "The Structure of Metals and Alloys" (Institute of Metals, London) 1954. (For other sources see Reference 4, p.17).

(b) F.F.Vol'kenstien, Adv. Catalysis, 12, 259, (1960).

6(a) F.F.Vol'kenstien: "The Electronic Theory of Catalysis on Semiconductors" translated by N.G.Anderson, ed. E.J.H.Birch (Pergamon), 1963.

(b) F.F.Vol'kenstien and O.Peshev, J.Catalysis, 4, 301, (1965).

7. D.O.Hayward and B.M.W.Trapnell, "Chemisorption", 2nd edition (Butterworths), 1964, pp.244,245.

8. W.E.Garner and F.E.T. Kingman, Trans.Faraday Soc., 27, 322, (1931).

9(a) C.N.Satterfield and T.K.Sherwood: "The Role of Diffusion in Catalysis" (Addison-Wesley),1963.

(b) O.Levenspiel: "Chemical Reaction Engineering" (J.Wiley), 1962, Chapter 14.

10. Reference 7, p.93.

11. Reference 7, pp. 189, 169, 176.

12. L.Ya.Margolis, Adv. Catalysis, 14, 429, (1963).

13. H.H.Voge and C.R.Adams, Adv. Catalysis, 17, 151,(1967).

14. B.M.W.Trapnell, Proc. Roy. Soc., A.218, 566, (1953).

15. Reference 7, pp. 230, 261.

16. G.K.Boreskov, Disc. Faraday Soc., 41, 263, (1966).

17. G.H.Twigg, Proc. Roy. Soc., A.188, 92, (1946).

18. W.E.Garner, T.J.Gray and F.S.Stone, Proc. Roy. Soc., A.211, 472, (1952).

19 (a) E.R.S.Winter, J.Chem.Soc., 2726, (1955).
(b) F.S.Stone, Adv. Catalysis, 13, 1, (1962).

20. C.F.Cullis, Ind. Eng. Chem., 59 (12), 18, (1967).

21. D.Brennan, D.O.Hayward and B.M.W.Trapnell, Proc. Roy. Soc., A.256, 81, (1960).

22. Reference 4, p. 183.

23. G.H.Twigg and E.K.Rideal, Proc. Roy. Soc., A.171, 55, (1939).

24. C.Kemball and W.R.Patterson, Proc. Roy. Soc., A.270, 219, (1962).

25. L. Ya. Margolis and S.Z. Roginski, "Problemy Kinetiki i Katalize" ed. S.Z.Roginski et al., Vol. 9, p.107 (Akad.Nauk S.S.S.R. Moscow) 1957.

26. L. Ya. Margolis, Izvest. Akad. Nauk. S.S.S.R., Otdel Khim. Nauk. No.10, 1175, (1958).

27. L. Ya. Margolis and O.M.Todes, Zhur. Obshchei Khim., 18, 1043, (1948).

28. M.A.Accomazzo and K.Nobe, Ind. Eng. Chem. Proc. Des. and Dev. 4, 425, (1965).

29. Y. Moro-oka, Y.Morikawa and A.Ozaki, J.Catalysis, 7, 23, (1967).

30(a) D.E.Hoare, "Low Temperature Oxidation" ed. W.Jost (Gordon and Breach Science Publishers), 1965, Chapter 6.

(b) Y. Ya. Shtern, "The Gas Phase Oxidation of Hydrocarbons" (Pergamon), Chapter 7, 1964.

31. W.A.Bone and J.B.Gardner, Proc. Roy. Soc., A.154, 329, (1936).

32. N.S.Enikolopyan, L.V.Karmilova and A.B.Nalbandyan, Zhur. Fiz. Khim., 34, 990, (1960).

33(a) Sir A.C.Egerton, G.J.Minkoff and K.C.Salooja, Proc. Roy. Soc., A.235, 158, (1956).

(b) D.E.Hoare and A.D.Walsh, 5th International Symposium on Combustion, 467, (1954).

(c) D.E.Hoare, J.B.Protheroe and A.D.Walsh, Trans. Faraday Soc., 55, 548, (1958).

34(a) D.E.Hoare and A.D.Walsh, Trans. Faraday Soc., 50, 37, (1954).

(b) M.Vanpee and F.Grard, Fuel, 34, 433, (1955).

35(a) J.H.Burgoyne and H.Hirsch, Proc. Roy. Soc., A.227, 73, (1954).

(b) E.M.Magee, J.Amer. Chem. Soc., 81, 278, (1959).

36. M.Prettre, C.Eichner and M.Perrin, Trans.Faraday Soc., 42, 335, (1946).

37(a) J.K.Dixon and J.E.Longfield, "Catalysis" ed. P.H.Emmett (Rheinhold, New York), 7, 183, (1960).

37(b) V.I.Astroshchenko, N.A.Gavrya, Z.M.Shchedrinskayi, Tr. Khar'kovsk, Politekhn. Inst., 39, 11 & 19, (1962).

38(a) German Patent No. 1,181,192, Huettenwerk Oberhausen A.G. (W.B.H. Gertges and O.Heinze) (see also C.A. 62, (6), 6396 c).

(b) E.Otsuka and H.Watanabe, Nenryo Kiokaishi, 43, (442), 118, (1964). (See also Fuel Abstracts Current Titles No.5994, (1964).

39. R.B.Anderson, K.C.Stein, J.J.Feenan and L.J.E.Hofer, Ind. Eng. Che., 53, 809, (1961).

40. H.Schachner, "Cobalt", 9, 12, (1960).

41. E.J.Rosenbaum, R.W.Adams and H.H.King, Anal. Chem., 31, 1006, (1959).

42. W.Davies, Phil. Mag., 21, 513, (1936).

43. H.G.Lintz, A.Pentenero and P.le Goff, J.phys. Chim., 59, 933, (1962).

44. P.Bussiere, P.Devore, B.Domanski and M.Prettre, 2nd International Congress on Catalysis, (Edition Technip, Paris), 2, 2247, (1961).

45. N.S.Enikolopyan and V.Bel'gorskii, Zhur. Fiz. Khim., 34, 1571, (1960).

46. S.Bransom, L.Hanlon and B.Smythe, Trans. Faraday Soc., 52, 672, (1956).

47. J.G.Firth, Trans. Faraday Soc., 62, 2566, (1966).

48. R.Mezaki and C.C.Watson, Ind. Eng. Chem., Proc. Des. and Dev., 5, 63, (1966).

49. O.P.Ahuja and G.P.Mathur, Can. J. Chem. Eng., 45, 367, (1967).

50. H.Davy, Phil. Trans. Roy. Soc., (1817).

51. G.Philips, J. Amer. Chem. Soc., 16, 164 & 255, (1894).

52. S.A.Fokin, Zhur. Russ. Fiz-Khim Obshchestva, 40, 276, (1908).

53. S.S.Medvedev, Trudy Khim. Inst. im Kappova, 3, 54,(1924

54. J.R.Campbell, J.Soc. Chem.Ind., 48, 93T, (1929).

55. L.H.Reyerson and L.E.Swearingen, J.Amer. Chem.Soc., 50, 2872, (1928); J.Phys. Chem., 32, 192, (1928).

56. W.P.Yant and C.O.Hawk, J.Amer. Chem. Soc., 49, 1454, (1927).

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

58. N.Hempel, Ber., 12, 1006, (1879).

59. H.Richard, Z. anorg. Chem., 38, 76, (1904).

60. E.H.Boomer, V.Thomas and C.A.Johnson, Canad. J. Res., B.15, 360, (1937).

61. E.H.Boomer and S.N.Naldrett, Canad. J. Res., B.25, 494, (1947).

62. K.Yoschikawa, Bull. Inst. Phys. Chem. Res., Tokyo, 10, 251, (1931).

63. A.P.Kreshkov, Zhur. Obshchei Khim., 10, 1605, (1940).

64. K.Neumann and H.Wang, Z. angew. Chem., 46, 57, (1933).

65. A. Janes, J.Soc. Chem. Ind., 70, 636A, (1923).

66. J.Matui and B.Jasuda, J.Soc. Chem. Ind. Japan, 43, 117, (1940).

67. M.V.Poljakow and K.K.Gryanenko, Acta Physiochim. URSS., 6, 587 & 755, (1937); Ibid. Zhur.fiz. Khim., 9, 260, (1937).

68. A.Arneil, J. Soc. Chem. Ind., 53, 89, (1934).

69. W.A.Bone and T.Andrew, Proc. Chem. Soc., 22, 78, (1906).

70. W.L.Faith, S.Swann and D.B.Keyes, Ind. Eng. Chem., 25, 224, (1933).

71. A.A.Kobe and E.B.Brookbank, Ind. Eng. Chem., Anal. Ed., 6, 35, (1934).

72. C.E.Bricker and H.R.Johnson, Ind. Eng. Chem., Anal. Ed., 17, 400, (1945).

73. K.J.Laidler, "Chemical Kinetics" 2nd ed. (McGraw-Hill) 1965, Chapter 2.

74. X-Ray Powder Diffraction Data Pile (Publication No. ~~#~~ PDIS-16i, American Society for Testing and Materials), 1966.

75. C.F.Cullis, D.Keene and D.L.Trimm, unpublished work.

76. Reference 4, p. 218.

77. M.H.Bortner and G.Parravano, Adv. Catalysis, 9, 424, (1957).

78. Reference 7, pp. 74, 75.

79. B.M.W.Trapnell, Trans. Faraday Soc., 52, 1618, (1956).

80. Reference 4, p. 192.

81. P.Jiru, B.Wichterlova and J.Tichy, Proc. 3rd International Congress on Catalysis, Amsterdam, 1, 199, (1964, pub. 1965).

82. J.K.Dixon and J.E.Longfield, in "Catalysis" ed. P.H.Emmett (Rheinhold, New York), 7, 183, (1960).

83. G-M. Schwab and Z.Gossner, Z. physik. Chem. neue Folge, 16, 39, (1958).

84. A.G.Daglish and D.D.Eley, Proc. 2nd International Congress on Catalysis (Editions Technip, Paris) 1961.

85. R.P.Eischens, W.A.Pliskin and S.A.Francis, J.Chem.Phys., 22, 1786, (1954); ibid. J.Phys.Chem 60, 194, (1956).

86(a) E.W.Abel, Quart. Rev., 17, 133, (1963).

(b) F.A.Cotton and G.Wilkinson, " Advanced Inorganic Chemistry" 2nd edition (Interscience) 1966, p.720.

87. V.I.Vedeneyev, L.V.Gurvich, V.N.Kondrat'yev, V.A.Medvedev, Ye.L.Frankevich, "Bond Energies and Ionisation Potentials" (Edward Arnold) 1966.

88. W.M.Latimer, "Oxidation Potentials" 2nd edition, (Prentice-Hall) 1952.