EXCHANGE REACTIONS OF HYDROCARBONS WITH DEUTERIUM ON PLATINUM AND NICKEL CATALYSTS

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[redacted]

SUMMARY

The object of this investigation was to study the self poisoning of the exchange reactions of hydrocarbons with deuterium on platinum and nickel catalysts. The exchange of methane, propane, butane, and neopentane has been studied on various platinum catalysts; and the exchange of cyclopentane and cyclohexane has been studied on evaporated nickel films.

The mass spectral data for the hydrocarbons, with the exception of propane, were analysed by statistical methods using a general computer program. In the case of the isotopic propanes, where the variation between the fragmentation patterns of propane and perdeuteropropane made it impossible to correct the mass spectral data accurately by statistical methods, the data were analysed using a computer program which allowed for the variation of the fragmentation patterns of the isotopic molecules with deuterium content.

The surface areas of evaporated platinum films were calculated from krypton adsorption measurements at 77°K by application of the B.E.T. equation and the 'Point B' method; and an excellent correspondence was observed between the areas calculated by the two methods. Presintering a film at 250°C for 1 hr. in vacuo decreased the apparent surface area relative to that of an unsintered film by a factor of 4.6.

On the unsintered platinum films propane, butane, and neopentane exchanged readily at temperatures greater than 30°C. Presintering the films at 250°C for 1 hr. in vacuo, however, necessitated reaction temperatures in excess of 80°C to propagate the exchange of butane and neopentane. Methane, in contrast to the other molecules, was much more difficult to exchange; reaction only occurring at temperatures greater than 180°C on both the unsintered and sintered films. The specific activities of the unsintered

All the molecules studied on the platinum catalysts underwent extensive multiple exchange. The product distributions for the exchange of propane, butane, and methane showed that all the possible isotopic species were produced initially, whereas those for neopentane usually did not contain isotopic species with more than three dueterium atoms. It is suggested that the exchange of propane and butane is propagated by the interconversion between α-, $\alpha\beta$- and π-allylic intermediates, whereas that for methane and neopentane occurs by the interconversion between α- and $\alpha\alpha$-adsorbed intermediates.

The exchange of cyclopentane and cyclohexane on unsintered nickel films occurred readily below 0°C, cyclopentane being the more reactive molecule. Presintering the films at temperatures greater than 270°C, however, required temperatures in excess of 200°C to propagate the exchange of cyclopentane. At temperatures less than room temperature on the unsintered films only half of the hydrogen atoms in cyclopentane and cyclohexane were readily exchangeable initially, and it is suggested that exchange occurs by the interconversion between α- and $\alpha\beta$-adsorbed intermediates. For the exchange of cyclopentane and cyclohexane on the unsintered films at higher temperatures, and for the exchange of cyclopentane on the sintered films all the possible isotopic species were produced initially, indicating that a π-allylic intermediate was participating in the mechanism of exchange. The exchange of both molecules on the nickel films was extensively self poisoned, deviation from the Arrhenius equation occurring with the activation energy tending to negative values; and it is thought that this self poisoning was occurring by the formation of $\alpha\alpha\beta$- and, or $\alpha\alpha\beta\beta$-adsorbed intermediates on the sites catalytically active for the exchange reaction.

films for the exchange of propane, butane, and neopentane were similar, as were the specific activities of the sintered films for the exchange of butane and neopentane. No evidence was obtained to indicate that the primary hydrogen atoms in propane and butane were substantially less reactive than the secondary hydrogen atoms; and the activity of both types of films for the exchange reactions could be correlated with the hydrocarbon primary carbon-hydrogen bond dissociation energies. Presintering the films reduced their activity for the exchange of methane, butane, and neopentane to a greater extent than could be accounted for by the decrease in the apparent surface area, indicating that the proportion of the surface which was catalytically active varied slightly with the hydrocarbon studied. The exchange of neopentane was also studied on platinum γ-alumina and on two samples of a platinum-silica catalyst which had been reduced at different temperatures. The platinum-silica catalysts were less active than the platinum γ-alumina catalyst which had an activity similar to that of a sintered film.

The apparent first order rate plots obtained for the exchange of the hydrocarbons on the unsintered platinum films were slightly retardedly curved. This curvature was ascribed to progressive sintering, and not to self poisoning of the films during the reaction, because the exchange reactions on the sintered films and on the supported catalysts obeyed the kinetic equation, and because the presorption of saturated hydrocarbons at 105°C for 1 hr. on unsintered films produced only a very slight reduction in the activity of the films for the subsequent exchange reaction of neopentane. The presorption of neopentane or a neopentane-deuterium mixture at temperatures greater than 200°C on sintered films substantially reduced the activity of the films for the exchange of neopentane, indicating that irreversibly adsorbed species could be formed at high temperature.

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PART I

INTRODUCTION, EXPERIMENTAL AND ANALYSIS

CHAPTER I

GENERAL INTRODUCTION

1.1. Historical Background

The influence of catalytic agents upon reactions has been known for a very long time, for example, the alchemists in the middle ages produced ether by the action of sulphuric acid on alcohol. There was, however, very little understanding of how, or why, catalysts acted. This understanding of the fundamental nature of a catalyst had to await the development of chemistry as an exact science.

The concept of catalysis was first introduced by Berzelius (1) to group together the results obtained by a number of other workers (2-7). He only considered, however, the amounts of the products produced by the catalyst, and not their rate of formation, leading him to suggest that the catalyst acted by a kind of chemical affinity which produced increased yields of material. It is now known that a catalyst does not increase the yield of a reaction but that it increases the rate of approach to the thermodynamically possible equilibrium position. The reaction rate as a measure of catalytic activity was first introduced by Ostwald (8) who defined a catalyst as "any substance which alters the velocity of a chemical reaction without appearing in the end product of the reaction".

More recently, Hinshelwood (9) has stated that a catalyst offers the possibility of an alternative and more speedy reaction route, and that a catalysed reaction can usually be explained in terms of normal chemical reactions between the catalyst and substrate, to give intermediates, which eventually break down to yield products and regeneration of the catalyst. Thus in order to understand how a catalyst functions, it is necessary to know the nature of the intermediates formed between the catalyst and substrate, the reactions in which they are produced and those they undergo in yielding the products, and also the reasons why the kinetic mechanism introduced by the catalyst gives a faster rate than is possible in its absence. This pattern of formation and reaction of intermediates is common to all catalysed reactions, but there is, however, a great diversity of kinetic mechanisms and rather than try to find one complete explanation of catalytic behaviour, it is easier to consider catalysed reactions in various groups, the mechanisms in one group being alike in kind if not in detail.

Catalysed reactions can be classified broadly into three main groups:

(a) Heterogeneously catalysed reactions.

(b) Homogeneously catalysed reactions.

(c) Catalysed chain reactions.

The work in this thesis ~~being~~ is concerned exclusively with the first of the above classes.

1.2. Heterogeneously Catalysed Reactions

A heterogeneously catalysed reaction is one in which the catalyst and the substrate are in different phases, the most widely applicable case being that between a solid catalyst and a gaseous reactant. For catalysis to take place there must be an interaction of some kind between the catalyst and the substrate. The first hypothesis proposed was that the gas molecules were brought into a chemically active state by mechanical impact with the solid surface. However, the consideration of catalyst specificity, as shown by Sabatier (10), ruled out immediately this simple hypothesis. It was shown by

Langmuir (11-13) that metal surfaces could adsorb gases and it was reasonable to suppose that these adsorbed species could participate in chemical reactions. The simplest supposition to make was that the increased concentration in the adsorbed layer could bring about the increased velocity of reaction by virtue of a purely mass action effect. The clearest proof of the inadequacy of this theory is afforded by the study of those reactions in which the same substance can undergo transformation in alternative ways. Thus alcohol vapour can be decomposed according to the following scheme.

$$\begin{tikzcd}
 & C_2H_4 + H_2O \quad \text{I} \\
C_2H_5OH \arrow[ur] \arrow[dr] & \\
 & CH_3CHO + H_2 \quad \text{II}
\end{tikzcd}$$

Reaction I may be brought about over alumina at 300°C, while copper at the same temperature favours reaction II. Although the mass action theory is inadequate, the concept of adsorption developed by Langmuir, and the equations he derived (14) relating the amount of gas adsorbed to the pressure in the gas phase have proved of great value in the interpretation of the kinetics of many catalytic reactions.

1.3. Adsorption

It is now a well established fact that catalytic reactions involve the adsorption of at least one of the reactants upon the catalyst surface, and experimental studies made of adsorption phenomena have established that there are two main ways by which a molecule can be held on a catalyst surface. These types of adsorption are referred to as physical adsorption and chemisorption.

Physical Adsorption: Here the molecules are held to the surface by Van der Waals forces, comparable to those holding a liquid together.

Since these forces are weak they are probably not very important from a catalytic viewpoint except in very special cases (15).

The heat of physical adsorption is similar in magnitude to the heat of condensation of the gas being adsorbed; and the rates of adsorption and desorption are rapid, provided the surface is accessible, and the processes readily reversible. From this viewpoint, physical adsorption, although not catalytically important, can be very useful for obtaining values for certain surface properties of the catalyst by measuring the amounts of gas adsorbed under certain conditions. The most important of these are the measurement of the surface areas of catalysts by the method of Brunauer, Emmett and Teller (16), and the determination of the pore size distribution of supported or solid catalysts (17-19).

Chemisorption: This type of adsorption consists essentially in the formation of a chemical compound at the surface of the catalyst. The bonds formed between the reactant and the solid surface being similar to those that occur in chemical compounds. Adsorption of the molecule results, therefore, in an exchange or sharing of electrons between the adsorbate and the adsorbent. When the molecule is adsorbed on the surface some degrees of freedom are lost, resulting in a decrease in entropy. Since chemisorption is a spontaneous process the Gibbs free energy must be negative and utilization of the equation

$$\Delta G = \Delta H - T\Delta S$$

shows that the heat of chemisorption must be negative. Chemisorption is therefore an exothermic process with a heat of adsorption usually in the range 80-200 k J mole^{-1}, and chemisorbed species are thought to be a prerequisite of catalytic reactions. The rates of adsorption are very fast with small activation energies, a value of 2.0 k J mole^{-1}

having been reported for the adsorption of nitrogen on tungsten (20). Chemisorption may, however, be an activated process and is known in two distinct types. One is the adsorption of nitrogen on iron catalysts (21,22), where slow adsorption occurring on the bare surface has been ascribed to the difficulty of dissociating the nitrogen-nitrogen bond; and the second refers to the further slow uptake of gas which sometimes follows fast initial chemisorption.

The velocity of slow chemisorptions often obey the Elovich equation (23)

$$\frac{\partial v}{\partial t} = a\,e^{-bv} \qquad 1.1.$$

where v is the volume of gas adsorbed, t is the time, and a and b are constants.

It has been shown that surfaces do show slow adsorption at relatively high coverages. Thus Rideal and Trapnell (24) reported a slow adsorption of oxygen on tungsten after the occurrence of an instantaneous process. The Elovich equation also applies quite well to these slow processes which sometimes follow fast initial chemisorptions, thus on iron and nickel films the kinetics of the uptake of hydrogen and carbon monoxide have been shown to be Elovichian in nature (25-28). Ehrlich (29-32) has shown that the occurrence of weakly chemisorbed surface structures are the precursors of strongly bonded structures on tungsten and Taylor and Thon (33) suggested that if the value of b in equation 1.1 was characteristic of the nature of the sites involved in the adsorption, then the abrupt changes in the slope given by the plot of the integrated Elovich equation for some systems, indicated a changeover from one kind of site to another at a certain stage of the adsorption. Thus, the results of Maxted and Evans (34) for the adsorption of hydrogen on clean platinum, and on platinum poisoned with hydrogen sulphide, which showed breaks in the Elovich plot, could be explained on this basis.

It is, however, possible that more than one surface - adsorbate structure influences the kinetics of adsorption. For example, Eischens et al.(35) reported that studies of the infra red spectra of carbon monoxide chemisorbed on palladium showed evidence for two structures. As the coverage increased the chemisorbed carbon monoxide molecule, which had been bonded to two palladium atoms, changed over into a form in which it was only bonded to one palladium atom. The more important aspects of chemisorption have been discussed in a review by Gundry and Tompkins (36).

The amount of gas adsorbed by solids varies with the pressure of the gas, and the simplified treatment proposed by Langmuir (13) gave the equation

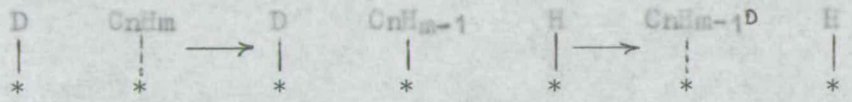
$$\theta = \frac{ap}{1 + ap}$$

where θ is the fraction of the surface covered by adsorbed molecules, p is the gas pressure and a is a constant related to the heat of adsorption.

Langmuir's equation assumed that there were no lateral interactions between the adsorbed molecules, and so does not account for the fact that the heat of adsorption decreases with coverage. Isotherms that have been derived to take account of this phenomenon include those of Brunauer, Emmett and Teller (16), Freundlich (37) and Tempkin (38).

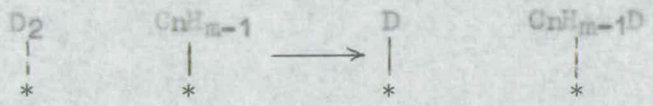
1.4. The Mechanism of Catalytic Reactions

Chemisorption of at least one of the reactant molecules is a prerequisite to any heterogeneous catalytic reaction. Two main mechanisms have been suggested to explain the combination of the reactants at the metal surface. For saturated hydrocarbons, it is generally agreed that adsorption of the hydrocarbon on the surface necessitates the dissociation of at least one of the carbon-hydrogen bonds, whereas unsaturated hydrocarbons may be chemisorbed either dissociatively or associatively. There are, however, two well established mechanisms by which dissociatively chemisorbed species may react. One is the Langmuir-Hinshelwood mechanism, where all the species are chemisorbed[*], i.e.,



$$\begin{array}{ccccccccc} D & C_nH_m & & D & C_nH_{m-1} & H & & C_nH_{m-1}D & H \\ | & \vdots & \longrightarrow & | & | & | & \longrightarrow & \vdots & | \\ * & * & & * & * & * & & * & * \end{array}$$

and the other, is the Eley-Rideal mechanism where one of the reacting species is gaseous or physically adsorbed, i.e.,



$$\begin{array}{ccccc} D_2 & C_nH_{m-1} & & D & C_nH_{m-1}D \\ \vdots & | & \longrightarrow & | & \vdots \\ * & * & & * & * \end{array}$$

Detailed arguments have been put forward in support of each of these mechanisms for the exchange of hydrogen and deuterium, but there is no clear evidence that one of these mechanisms operates to the total exclusion of the other.

It might be assumed that a catalytic reaction occurs over the whole of the available surface. Evidence that this is not true,

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[*] a continuous line denotes a chemisorbed species, and a dotted line a physically adsorbed species.

has been found from a study of the hydrogenation of ethylene on nickel films (39). The proportion of the catalytic surface that is active for catalysis is a function of the catalyst and the reaction that is being catalysed. Evidence for the presence of highly active sites has been presented by Kemball (40) for the exchange of alkyl benzenes with deuterium. Heating a nickel film to 200°C, or presorbing carbon monoxide on it, inhibited the exchange of the ring hydrogens to a much larger extent than the hydrogens in the substituent alkyl groups.

For a catalytic reaction five rate determining steps may be possible:

(1) The diffusion of reactant molecules to the surface.

(2) Chemisorption on the surface.

(3) The surface reaction.

(4) Desorption from the surface.

(5) The diffusion of the products away from the surface.

When studying the kinetics of a catalytic reaction, it is important to know which of the above steps is the one which controls the overall rate of the reaction. For the catalysts studied in this work it was highly improbable that steps (1) and (5) were rate determining. If a reaction is diffusion controlled, the rate of reaction is only very slightly dependent upon the temperature, and as the rates of exchange reported in this work gave good straight Arrhenius plots, it was concluded that diffusion controlled processes were not playing any significant part in the reactions studied. The methods for deciding which of the other steps is rate determining are usually based on other kinetic data. A typical approach is that of Kummer and Emmett (41) who found that the rate of exchange of $^{28}N_2$ with $^{30}N_2$ agreed well with the rate of formation of ammonia from nitrogen and hydrogen, thus concluding that chemisorption of the nitrogen was the rate determining step.

The exact mechanism of the surface reaction is very difficult to determine, since the nature, properties and concentrations of the various chemical species cannot easily be derived from an examination of the kinetics of a catalytic reaction. Only the direct techniques such as E.S.R., I.R., and other types of spectroscopy are capable of giving direct information on the nature of surface species, and even here the results are often difficult to interpret. Much interesting information concerning the bonding of molecules, and of hydrocarbons in particular, may be obtained by the use of 'tracer' elements or deuterium. Thus, Anderson et al. (42) used ^{13}C tracer methods to determine the mechanism of the isomerization of aliphatic hydrocarbons on platinum and palladium films, and Kummer and Emmett (43) used radioactive alcohols to elucidate the mechanism of Fischer-Tropsch syntheses. The major use of a 'tracer' element to elucidate the mechanism of a catalytic reaction has been that of exchanging the hydrogen atoms in hydrocarbons with deuterium, and following the deuterium incorporation by mass spectrometry. These chemical 'reactions' are of a very special type as both reactants and products are the same chemically, only differing in mass. The literature in this field has been excellently summarized in a number of reviews (44-48).

The exchange reactions of hydrocarbons with deuterium can be separated into two main categories, viz, processes which give stepwise replacement of hydrogen by deuterium and those which lead to multiple exchange. Both of these processes can occur together although they will be treated separately.

In a stepwise exchange reaction, only a single hydrogen atom is replaced by a deuterium atom in each molecule which reacts on the catalyst surface. The initial product distribution will only contain the monodeutero species, and species containing more than one deuterium atom can only be formed by successive reactions of the reactant on the catalyst surface. The adsorbed intermediate which is responsible for simple exchange must, therefore, be a comparatively stable entity on the catalyst surface, with a very small probability of undergoing further reaction involving the introduction of a second deuterium atom.

In the multiple exchange reaction, more then one deuterium atom is introduced into the molecule on each interaction with the surface, and the initial product distribution will contain species having more than one deuterium atom.

We may consider as an example the exchange of ethane with deuterium on evaporated metal films. It was found (49) that on films of tungsten and molybdenum ethane tended to exchange only one hydrogen atom per visit to the surface, whereas on palladium and rhodium all six hydrogen atoms were exchanged initially. Two mechanisms were proposed for the reaction; the formation of an adsorbed ethyl radical was postulated on the former two metals, while on the latter the exchange was achieved by the interconversion between an adsorbed ethyl radical and an adsorbed ethylene species. Various other adsorbed intermediates have been postulated to account for the exchange of hydrocarbons. Thus a π bond, similar to that in ferrocene, was proposed (50) to explain the exchange of the hydrogen atoms in polymethylcyclopentanes, and an $\alpha - \gamma$ adsorbed intermediate has been proposed to explain the exchange of neopentane on tungsten and rhodium films (51).

The deuterium exchange technique, does not give an absolute proof of the mechanism of the catalytic reaction, but by assuming that the hydrocarbon may form certain types of adsorbed intermediates, and drawing an analogy with previous results, the catalytic mechanism may be inferred but not rigorously proved.

1.5. Catalysts and Catalytic Activity

The geometrical properties of reactant molecules and the crystal habit of contact catalysts can play a very important role in catalytic reactions. Catalytic activity may be favoured if the reacting species interacts with the surface in such a way that its atoms have a particularly favourable fit relative to the array of the atoms in the solid surface. This approach has been applied essentially to hydrogenation reactions, and the relationship between stereochemical considerations and the mechanism of olefin hydrogenation has been reviewed by Siegel (52) and by Bond and Wells (53).

It was clear, however, that the operation of a geometric effect alone could not explain all the observed phenomena. The development of the more general electronic factor in a precise manner had to await advances in the theory of the solid state. For most reactions, transition metals have a far higher activity than non-transition metals, and this must be associated with the vacant d-orbitals of the former (54). The percentage d-character has been used as a correlation of the heats of adsorption of ethylene and hydrogen on evaporated films by Beeck (55). Alloys offer a very convenient method of continually varying the percentage d-bond character of a catalyst, and results (56,57) obtained using them show a definite correlation between the percentage d-bond character of the catalyst and catalytic activity.

The concept of electronic factors in metal catalysts has, however, recently been criticized (58), and the emphasis placed, instead, upon the relation between the energetics of surface and bulk compounds. It has been found (59) that the activity of metals for the decomposition of formic acid could be related to the heat of formation of the metal formates by a 'volcano-shaped' curve. The interpretation proposed was that, when the heat of formation is low (e.g. gold), the rate is low because of the low concentration of adsorbed species; but when the heat of formation is high (e.g. nickel) the rate is low because the adsorbed species are too strongly held. A maximum rate may, therefore, be expected when the heat of formation is such as just to give a fully covered surface.

It can be seen that both the electronic factor and the chemical factor have their proponents. It would, however, seem likely that no catalytic reaction can be described completely as being due to either one factor or the other, but probably as a combination of both. The factor which is predominant will probably depend upon the system. For a complete description of the catalytic system, one would need to treat the interaction between the chemisorbed species and the surface by a molecular orbital approach.

1.6. The Use of Metals as Catalysts

For a metal to be of use as an effective catalyst, it must present to the gas phase as large a surface area as possible. The metal to be used can be in a number of forms; sponges and skeletal metals, such as Raney nickel, are not, however, used very much because of the difficulty in obtaining a non-contaminated metal surface. A lot of attention has, therefore, been paid to methods of preparing metals in a state of high surface purity. Of these, the one which has the widest industrial application is the metal supported catalyst. Metal supported catalysts are usually prepared by impregnating a support, such as silica, with a solution of the metal salt, drying it, and then reducing the salt to the metal at high temperature. Although exchange reactions have been carried out on metal supported catalysts (60-62), it would be fair to say that they have been mainly used for the study of hydrogenation-dehydrogenation (63-67), hydrogenolysis (68-71), isomerization (72-74), or aromatization (75) reactions. The main difficulty in studying reaction mechanisms on these catalysts has been in deciding which mechanistic steps may be attributed to the metal and which to the support (76).

Metals can be prepared in a state of high surface purity and surface area by evaporating them from a thin wire onto a substrate, by resistance heating. The use of these evaporated metals as catalytic systems dates from the work of Beeck et al. in 1941 (77). The method used is that a thin wire of the metal is sealed into a 'pyrex' glass container, the container being outgassed by external heating while dissolved species are removed from the wire by resistance heating. After attaining a sufficient state of purity, the vessel is brought to some convenient temperature and the current passing through the wire is increased until atoms evaporate from its surface and condense on the walls.

Metal films prepared by this technique are porous in structure as can be seen from the fact that their apparent surface area is several times greater than the geometric area. The films themselves consist of large crystallites, the non-coherence of which is shown, in for example the case of nickel (77), by the fact that the electrical conductivity of the film is much less than that of the bulk metal. Films prepared by deposition in vacuo tend to be unoriented. It was originally claimed, however, that if the evaporation of nickel was carried out in a vessel containing an inert gas at a pressure of about 0.1 kNm^{-2}, the film was preferentially oriented (77). This has since been disproved (78), and it appears that the degree of orientation is not affected by this procedure. Films may however be prepared in an orientated form by deposition upon a suitable substrate and these oriented crystal planes have been shown to have important catalytic properties (42). The metal films used in this work were not deliberately oriented; it was possible, however, that sintering at high temperature, which caused a consequent decrease in surface area, also oriented the films to a small degree.

1.7. Object of the Present Investigation

As has been mentioned previously in this thesis, for a catalyst to be effective, chemisorption of at least one of the reactants upon the catalytic surface is necessary. When a hydrocarbon is adsorbed upon the catalyst surface a number of 'adsorption phases' are possible:

(1) Reversible adsorption of the hydrocarbon by dissociation of the carbon-hydrogen bonds.

(2) Irreversible adsorption of the hydrocarbon by dissociation of the carbon-hydrogen bonds but without dissociation of the carbon-carbon bonds.

(3) Irreversible adsorption of the hydrocarbon with dissociation of the carbon-carbon bonds.

For any catalyst, and dependent upon the temperature, reaction of the hydrocarbon with hydrogen or deuterium may involve either all or some of these 'adsorption phases'. If we consider an idealized case, as the reaction temperature is increased a gradual change in the nature of the adsorbed species occurs, viz, phase 1 progressively going to phase 2 and then to phase 3.

Numerous investigations have been carried out upon the exchange of hydrocarbons with deuterium with adherence to apparent first order kinetics (phase 1) (79,80), and upon the hydrocracking of saturated hydrocarbons (phase 3) (81,82). Very little attention has been focussed, however, upon the intermediate stage (phase 2), where the gradual formation of irreversibly adsorbed species causes breakdown of the apparent first order kinetics. One of the clearest examples of this 'self poisoning' of an exchange reaction is shown by the exchange of n-hexane with deuterium on rhodium films (83), and it has been argued (84) that self poisoning of exchange reactions should occur more widely than has been apparent from the literature.

According to the results obtained with polymethyl cyclopentanes (50), platinum is quite active as a catalyst for forming $\alpha\gamma$-diadsorbed intermediates. Anderson and Avery (42) showed that the hydrocracking of saturated hydrocarbons on platinum films was brought about by the formation of an $\alpha\alpha\gamma$-triadsorbed intermediate. If we consider the exchange of neopentane with deuterium on a platinum film, then for neopentane to exchange all twelve hydrogen atoms by a multiple exchange mechanism it must form an $\alpha\gamma$-diadsorbed intermediate. The question in which we were interested was:- If the neopentane starts to exchange by an $\alpha\gamma$ intermediate, will this be reversibly adsorbed or will it form the $\alpha\alpha\gamma$ intermediate postulated by Anderson and Avery, and hence self poison the reaction? For this reason it was decided to study the exchange reactions of the lower aliphatic hydrocarbons on platinum films, and if they began to self poison, to try and find out some information about the nature of the adsorbed species responsible for self poisoning by presorbing hydrocarbons upon the film, and determining their effect upon the rate of exchange and the product distribution of the subsequent exchange reaction.

Metal films are very active catalysts but do not really bear very much resemblance to the catalysts used industrially. Industrial supported catalysts have been fired at a high temperature and thus the metal crystallites can be regarded as being in a stable configuration. The metal film crystallites, however, are only stable below the temperature at which they were deposited, and hence at temperatures greater than the deposition temperature may be regarded as being in a state of flux. More knowledge was required about the ways in which films differ from supported catalysts. For this reason it was decided to study the exchange of neopentane with deuterium on both platinum films and platinum supported catalysts, to see how they compared with respect to the rates of exchange, and the nature of the exchange reaction taking place.

When the exchange of ethane with deuterium was studied on nickel films (49) some very strange observations were noted. After some initial activity, on increasing the temperature activity ceased, but started again on increasing the temperature. It seemed, therefore, that some type of self poisoning phenomenon was occurring, and it was hoped to study this in the same way that it was to be studied on platinum.

CHAPTER II

APPARATUS AND EXPERIMENTAL TECHNIQUE

2.1. Introduction

The apparatus used in this investigation can be divided essentially into three parts:

(a) A gas handling system which enabled mixtures of pure gases and liquid vapours of definite composition and pressure to be prepared.

(b) A reaction vessel in which clean evaporated metal film catalysts could be prepared. The same reaction vessel system was also used for the reactions on supported catalysts.

(c) An Associated Electrical Industries Ltd. M.S.10 mass spectrometer which was joined to the reaction vessel by a fine capillary leak, enabling continuous analysis of the composition of the gas mixture in the reaction vessel to be made.

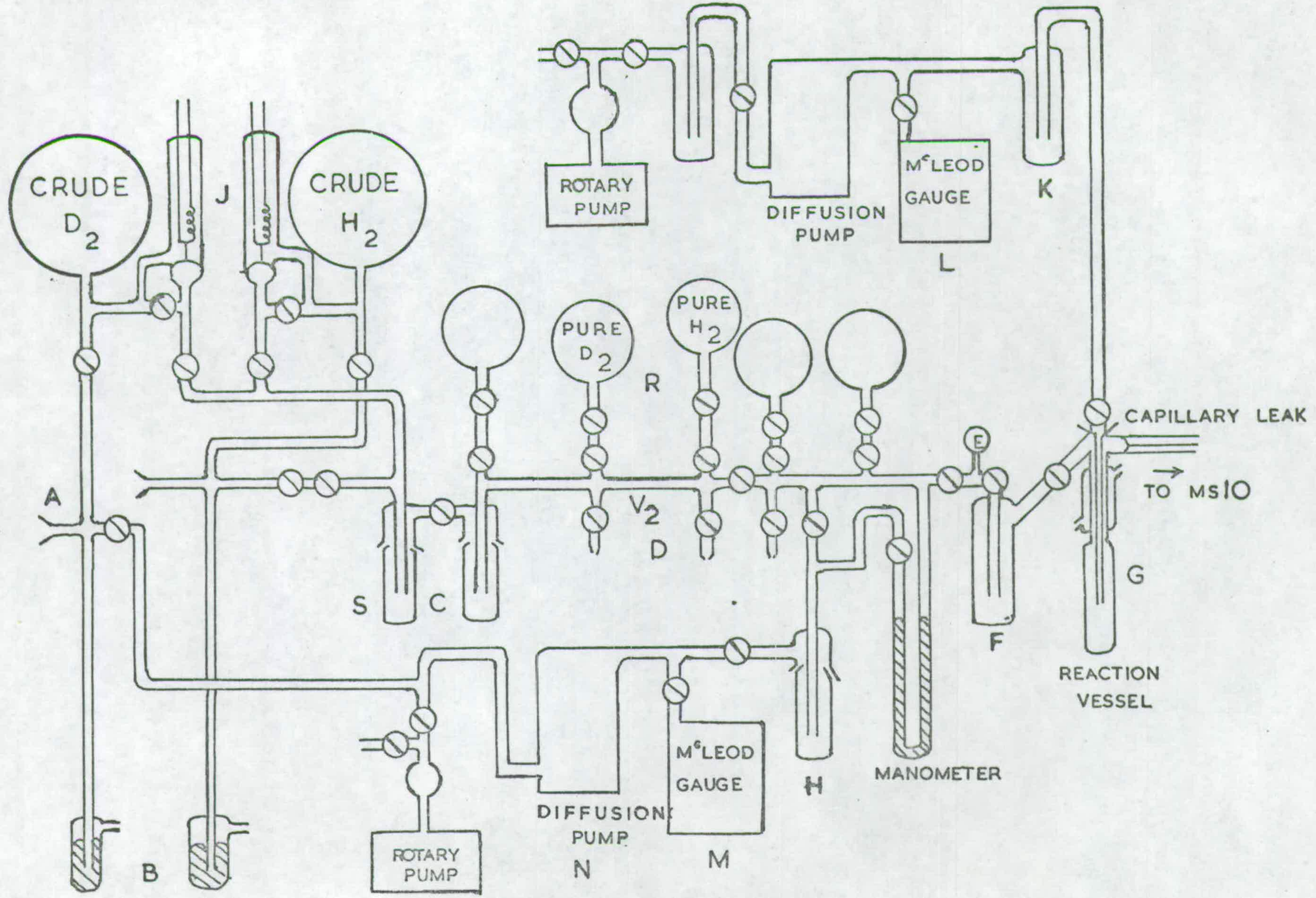
Each of these parts is described in detail later.

Simultaneously with this research the apparatus was used to study the self poisoning of the butane-deuterium exchange reaction on tungsten evaporated films (85), and the exchange and self poisoning of saturated hydrocarbons with deuterium on molybdenum and cobalt evaporated films (86). Using the same gas handling system and mass spectrometer but a different reaction vessel, investigations on the exchange of olefins with deuterium oxide and the hydrogen-deuterium exchange reaction on cation exchanged molecular sieves were carried out (87).

2.2. The Gas Handling System

A diagrammatic representation of the gas handling system is shown in Figure 2.1. It consisted of a general purpose vacuum system

FIG. 2.1 APPARATUS



constructed throughout of 'Pyrex' glass. All the ground glass stopcocks and joints were lubricated with 'Apiezon L' high vacuum grease. It could be evacuated to a pressure of 0.667 $\mathrm{mNm^{-2}}$ using an electrically heated single stage mercury diffusion pump 'N', backed by a two stage 'Speedivac' rotary pump 'P'. Mercury was excluded from the gas line by means of the liquid nitrogen trap 'H', and the pressure measured by the McLeod gauge 'M', volume 56.3 ml.

The gas handling system provided permanent facilities for the purification and storage of hydrogen, deuterium, and the hydrocarbon gases in the bulbs 'R' attached to the apparatus. Bulbs to store other gases could be attached at 'D' by means of ground glass joints. The liquid hydrocarbons used were stored in tubes fitted with stopcocks and were attached to the apparatus at 'D' by means of ground glass joints. The system also provided a means of purifying these compounds by repeated distillation between the traps 'C' and 'S'.

2.3. The Reaction Vessel and Capillary Leak

The reaction vessel was constructed from 'Pyrex' glass and is shown in Figure 2.2. The removable portion consisted of a cylindrical vessel 35 mm. in diameter and 0.13 m. in length, and was joined to the apparatus by means of a B24 ground glass joint which fitted into a water cooled socket, and permitted easy removal between experiments. Two 0.5 mm. diameter tungsten rods encased in glass, were sealed through the top of the joint and carried internal mild steel connectors, to which the wires used in the evaporation of the metal films were attached. Later this reaction vessel system was replaced by one containing 2 mm. diameter tungsten rods and a greaseless water cooled socket. The detachable reaction vessel was cleaned thoroughly with chromic acid, washed well with distilled water, and dried before mounting it on the apparatus.

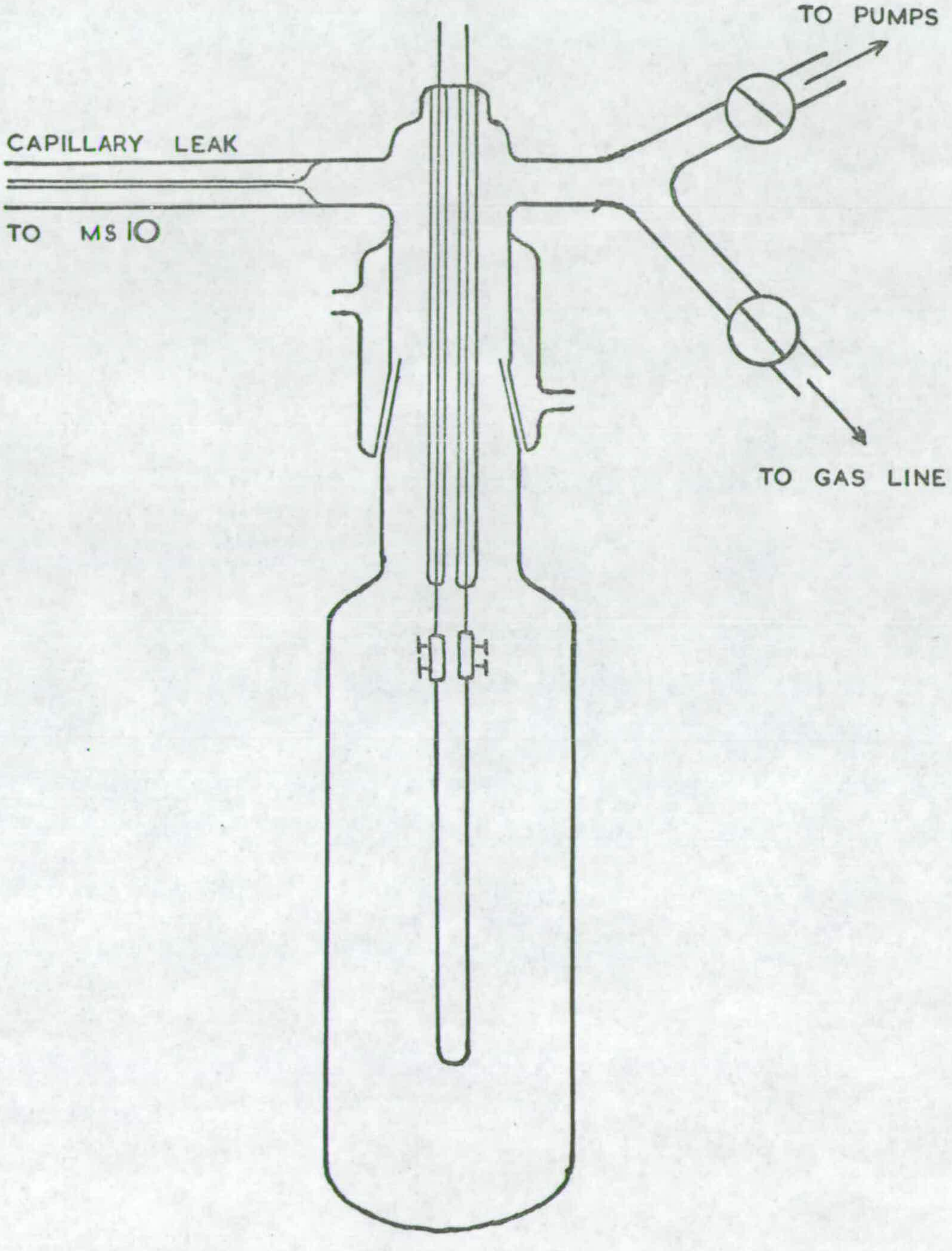


FIG. 2.2 REACTION VESSEL

The reaction vessel system could be evacuated to a pressure of 0.133 mNm^{-2} by use of a mercury diffusion pump, and a rotary pump similar to those used to evacuate the gas handling system. Mercury was excluded from the reaction vessel by the liquid nitrogen trap 'K', and the pressure measured by the McLeod gauge 'L', bulb volume 0.2855 l. Pressures of the order of 0.1 mNm^{-2} were very easily attained.

The reaction vessel was heated by one of two electrical furnaces:

(a) An aluminium block furnace.

(b) A close fitting furnace constructed from an iron tube 55 mm. in diameter, and 0.2 m. in length, wound with resistance wire and overwound at the top and bottom to minimise temperature gradients. This furnace was capable of very rapid heating, and the temperature could be raised 50°C and stabilized within five minutes.
The temperature of the furnace was kept at a constant value using a Fielden Electronics Ltd. 'Bikini' Temperature Controller (Type TcB7) which was accurate to ± 0.5°C. The actual temperature of the reaction vessel was measured by a chromel-alumel (T_1-T_2) thermocouple, the ends of which had been spotwelded in an argon atmosphere. The thermocouple was calibrated against a platinum resistance thermometer (Type 11433 No. CT 729577) using a Smiths Difference Bridge; the potential produced by the thermocouple being measured on a Sangamo Weston millivolt meter (model S82 No. BB17247). The equations used for the calculation of the temperature are shown below, and some of the results obtained are shown in Table 2.1.

The resistance P_T of the platinum resistance thermometer at temperature T°C is given by;

$$P_T = 100 \frac{R_T - R_0}{R_{100} - R_0}$$

where R_0 and R_{100} have the values 23.976 ohms and 33.391 ohms respectively;

the temperature T°C is given by;

$$T = 3398.962 + 33.48962\,(10300.83 - 5.972\,R_T)^{\frac{1}{2}}$$

all the temperatures were measured with the thermocouple cold junction at 0°C.

TABLE 2.1.

THERMOCOUPLE CALIBRATION

T°C	Millivolts
54.79	2.20
99.22	3.89
125.19	4.92
161.01	6.22
215.74	8.22
275.98	10.51
304.23	11.64
344.49	13.15
399.24	15.28
521.60	20.18

Temperatures below 0°C were obtained using slurries of low melting organic compounds. These were prepared by the addition of liquid nitrogen to a suitable organic solvent contained in a dewar flask. By adding the correct amount of liquid nitrogen a slush of constant temperature was obtained. The solvents used and their melting points are given in Table 2.2. The temperature of the slurries was measured using the negative portion of the thermocouple calibration graph, the values for which agreed with those given in the 'Rubber Handbook'.

TABLE 2.2.

CONSTANT TEMPERATURE BATHS

Solvent	T°C
Acetone	-95
Ethyl acetate	-84
Chloroform	-64
Chlorobenzene	-45
Carbon Tetrachloride	-23

A fine capillary leak, similar in design to one used by Nier (88), was attached to the top of the reaction vessel opposite the inlet tube, and led directly into the ionization chamber of the mass spectrometer. The leak itself was about 0.15 m in length and was constructed by collapsing a piece of 'pyrex' tubing into a fine capillary, and then drawing it out. Pieces of this capillary were then broken off until the rate of leakage into a volume of 20 ml. was 2.67 kNm^{-2} in 20 mins, with a pressure difference of 101.325 kNm^{-2} across the capillary. When in use the pressures on either side of the leak were approximately 4.0 kNm^{-2} and 0.27 mNm^{-2} respectively, and under these conditions, the rate of leakage of the reaction mixture into the mass spectrometer was approximately 3% hr^{-1}. As the reactions were not usually followed for more than 3 hrs., the leak enabled analysis of the gas mixture to be made at any time, without appreciable alteration of the pressure in the reaction vessel. Also, by eliminating manipulation difficulties, it enabled reasonably fast reactions to be followed. The leak and the glass tubing connecting it to the mass spectrometer were heated continually, by means of an electrical heating tape to minimize adsorption of the reactants on the walls.

The importance of leak design has been discussed by various authors (89-91). It is impossible, however, to make a leak of the type used, in which viscous flow occurs over its entire length. Since the pressure is low at the ion chamber side of the leak, flow will be molecular in this region, and will be viscous on the reaction vessel side, with an intermediate region over which a change from viscous to molecular flow will occur. There will thus be a tendency for the heavier molecules to concentrate on the high pressure side of the leak and to diffuse back into the reaction vessel. The capillary tube, however, increases the velocity of flow of gas at the entrance to the leak, and effectively prevents back diffusion. This increased mass flow, combined with the similarity of the masses in an isotopically exchanged mixture, means that the gas entering the mass spectrometer will be representative of that in the reaction vessel. When the gas enters the mass spectrometer, however, some fractionation occurs, due to the mass spectrometer pumping system removing the molecular species at a speed inversely proportional to the square root of their mass. As the masses of the molecular species involved in the exchange reactions were similar, it was assumed that effects due to their mass were minimal.

The arrangement used constituted a static reaction system, so that the same bulk of gas was in contact with the catalyst surface throughout the duration of the experiment. Mixing of the gases was caused by convection and diffusion. It is unlikely that diffusion to and from the surface was rate determining, or that any appreciable time lag existed between the molecules leaving the surface, and their appearance in the mass spectrometer. This was shown by the very rapid response of the instrument to reactions occurring on the catalyst.

Also, since the rate of diffusion is proportional to the square root of the absolute temperature, if a process is diffusion controlled this will be shown by the slight temperature dependence of the rate of reaction compared to that for a surface process. It may be concluded, however, that since the rates of reaction obtained in this work obeyed the Arrhenius equation, diffusion to and from the catalyst surface was not important.

2.4. The Mass Spectrometer

The Associated Electrical Industries Ltd. MS10 mass spectrometer used for the analysis of the reaction mixtures was a general purpose 180° sector instrument, suitable for the analysis of gases and volatile liquids. A diagrammatic representation of the instrument is shown in Figure 2.3. The gas was leaked into the ion source 'C', by the capillary leak described above, where it was ionized by electrons produced by the electrically heated rhenium filament 'F'. The ions were then accelerated through the slit 'S_1', into the uniform magnetic field, by a variable accelerating potential. Equation 2.1. shows that with a constant accelerating voltage and a constant magnetic field the ions follow semicircular paths the radii R of which vary with the m/e ratio of the ion.

$$m/_{e} \quad = \quad R^2H^2/2V \qquad\qquad 2.1.$$

where H is the magnetic field strength and V is the accelerating voltage. By variation of either the magnetic field or the accelerating voltage all the ions of one m/e ratio could be focussed through the alpha slit 'S_2' and the collector slit 'S_3' onto the collector plate 'I'.

The ion current was preamplified using an electrometer head type ME1403 with an input resistance of 10^{11} ohms and a time constant of

1 s. The signal was then further amplified by a 'plug in unit' and recorded as a trace on a 'Sunvic' pen recorder. A sensitivity range changing device of 1000 to 1 in seven ranges on the amplifier, allowed each peak to be measured and recorded at its maximum sensitivity.

Initially the instrument was operated using a fixed magnetic field strength of 1830 G. provided by a permanent magnet, the ions being focussed onto the collector by a variable accelerating voltage of 40 to 2000 V d.c. Later the permanent magnet was replaced by an electromagnet of variable field strength 0 to 9 kG. Four fixed accelerating voltages of 2 kV, 1 kV, 500 V, and 250 V allowed four mass ranges to be scanned, the automatic scanning time being variable from 100 to 5000 s. Using the electromagnet modified instrument and smaller slits 'S_1', 'S_2' and 'S_3', the unit mass resolution of the instrument was increased from 80 to 300.

The ion chamber of the mass spectrometer could be evacuated to a pressure of 1.3 μNm^{-2} using a Metrovac 033 water cooled diffusion pump backed by a Metrovac GDR1 rotary pump, an orifice plate situated at 'O' reducing the pumping speed to 1 ls^{-1}. Oil from the diffusion pump was prevented from reaching the ion chamber by a liquid nitrogen trap. The pressure inside the ionization chamber was measured by a Metrovac VC-3A ionization gauge using a gauge head 'A' style No. 298092. The mass spectrometer cold trap required replenishing every twelve hours. If the instrument was to be left unattended for longer than this period, the ion gauge was turned off, the electrometer head and the voltage supplies to the source were disconnected, and the tube heated by the band heaters provided, to prevent diffusion pump oil contaminating the source.

2.5. Volume Calibrations

A bulb of volume 143.31 ml at 23°C, determined by calibration with water, was attached to the gas handling system at 'D', in Figure 2.1., by means of a ground glass joint. The apparatus was then evacuated and the bulb filled with air to a pressure measured on the manometer. The tap to the bulb was closed, the remainder of the apparatus was evacuated and, then, by successive expansions into the various parts of the apparatus, the corresponding volumes were obtained at 23°C and at 0°C. Those necessary for the calculation of partial pressures are given below.

Reaction Vessel 'G'	at 23°C	201.82 ml
Reaction Vessel 'G'	at 0°C	211.33 ml
Ice Trap 'F'	at 0°C	90.17 ml
Mixing Bulb 'E'	at 23°C	578.22 ml
Dosing Volume 'V',	at 23°C	60.68 ml

Knowing the pressures of the reactants in the dosing volume 'V', and the mixing volume 'E', the pressure of the gas, and hence the number of molecules in the reaction vessel could be calculated at any temperature.

2.6. Preparation and Purification of Materials

Before attempting to purify any of the gases used in this work, the apparatus was evacuated until a 'sticking' vacuum was obtained on the McLeod gauge. The storage bulbs were then flamed repeatedly, while under evacuation, to desorb any impurities from the glass walls.

Hydrogen and Deuterium: Hydrogen and deuterium were obtained in lecture bottles from the Matheson Co. (99.98% 'pure') and were admitted to the storage bulbs at 'A' by means of the mercury bubblers 'B' (Figure 2.1.). The "hydrogen"* was then purified by diffusion through the electrically heated palladium thimbles 'J'. Before collection was commenced the apparatus was flushed with "hydrogen" and the flaming of the bulbs repeated. The gas line was then isolated from the pumps, and the

* In this section "hydrogen" is used as the generic term for hydrogen or deuterium.

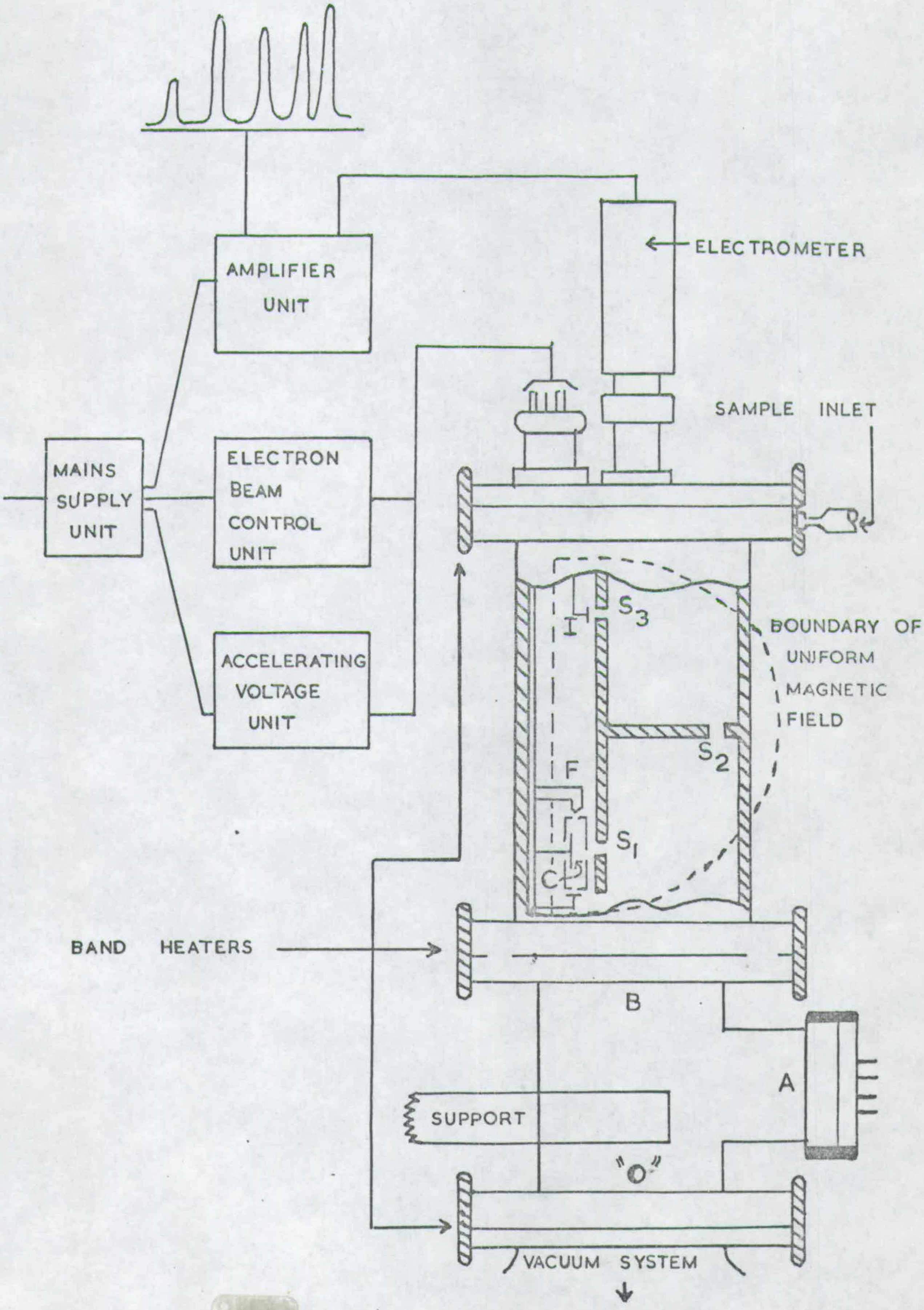


FIG. 2.3 MS 10 MASS SPECTROMETER

traps 'S' and 'C' surrounded by liquid nitrogen; these traps served to prevent mercury vapour reaching the hot palladium thimbles where it caused rapid deterioration and leakage and, secondly, to condense out any remaining impurities in the "hydrogen". The palladium thimble was then heated and the pure "hydrogen" collected in a two litre bulb. Diffusion was generally carried out overnight, the "hydrogen" being generated at approximately 2 kNm^{-2} hr^{-1}. After a suitable quantity of "hydrogen" had been collected the palladium thimble was turned off and the bulb isolated from the rest of the apparatus. The purity of the "hydrogen" was then measured mass spectrometrically, it always being air free and having an atom purity greater than 98%, the impurity, if any, always being the other "hydrogen" isotope.

Deuterium gas was always available in cylinders, but could be generated, if required, by the electrolysis of deuterium oxide, the details for which may be found elsewhere (92).

Liquids and Gases: The gases used were stored in bulbs attached to the apparatus. The liquids were held in tubes attached to the apparatus by cone and socket joints. They were thoroughly degassed by repeating a cycle of freezing, pumping, and thawing the sample several times. The liquids were stored at liquid nitrogen temperature to prevent the liquid vapour dissolving in, and eating away the stopcock grease and hence contaminating the liquid with grease.

The sources and methods of purifying the various gases and liquids used are given in the appropriate sections dealing with their reactions.

2.7. The Preparation of the Metal Catalysts

The platinum-silica and platinum on γ-alumina catalysts are described in Part II section 3.1.

The technique of using evaporated metal films in the study of catalytic reactions is well established (77, 93) and, provided that adequate precautions have been taken, they provide a reproducible, clean metal surface. Full details of their preparation are given in Table 2.3. Nickel was prepared by direct evaporation from a filament of the metal, but because the platinum tended to melt before its vapour pressure was high enough to cause evaporation it was supported on tungsten. Due to the thickness of the tungsten wire, used as a support, and the large temperature difference between their evaporation temperatures, it was extremely unlikely that evaporation of the support occurred simultaneously with the evaporation of the platinum. With both metals, to clean the surface, a light preliminary film was thrown and discarded. If this was not done the first film from these wires was not as active as subsequent ones. Only one film could be thrown from a platinum wire as later ones were very light and irreproducible. With nickel more than one film could be thrown from each wire, though in the case where the exchange reaction was carried out on heavy films the wires were evaporated until they burnt out.

2.8. Experimental Procedure

The gas line was pumped and the reaction vessel baked at 450°C overnight, whilst under continual evacuation by their separate pumping systems. After evacuation 'sticking' vacuums were registered on the respective McLeod gauges. An ice bath was then placed around the trap at 'F' (Figure 2.1.). While the filament was being outgassed with the reaction vessel at 450°C, a reaction mixture was prepared in the mixing bulb 'E' by admitting the hydrocarbon first and pumping the excess away; the deuterium was then admitted by slowly opening the tap to the mixing bulb until the desired pressure was attained, always keeping a pressure head across the tap to prevent any back diffusion of

TABLE 2.3.

THE PREPARATION OF SOME EVAPORATED FILMS

Metal	Source of supply and quality	Method of preparation	Outgassing current (A)	Evaporation current (A)	Time (min.) for 10 mg. film
Platinum	Johnson, Matthey & Co. Ltd. spectroscopically standardised	0.30 m of 0.1 mm dia. Pt wire wound on 0.15 m of 0.3 mm W wire	6.5	7.7	20
Nickel	"	0.15 m of 0.5 mm dia. Ni wire	4.7	6.6	10

the hydrocarbon. The mixtures were always prepared to the nearest 0.1 mm with the aid of a burette reader. After outgassing the wire the furnace was removed and the reaction vessel closed off from the pumps. While the reaction vessel was cooling down, the mass spectrometer filament was turned on and allowed to stabilize. After checking to see that the mass spectrometer was operating satisfactorily the reaction vessel was surrounded by an ice bath and the film prepared. For a normal exchange experiment the reaction mixture was admitted to the film either at 0°C or at temperatures below zero if the reaction occurred at low temperatures. The reaction vessel was then brought rapidly to the desired temperature by means of the low melting slurries, or the close fitting electric furnace. Normally only one reaction was carried out on each film, the film weight being determined by weighing the filament before and after evaporation.

The procedure described above was used when films were used as the catalyst. For the solid catalysts, however, an activation treatment had to be used. This was applied at the stage in the procedure described above, where previously the filament was being outgassed and the film thrown. For the platinum-silica catalysts, after outgassing at 140°C overnight, the catalyst was heated at 80°C for 1 hr. in 10.0 kNm^{-2} of deuterium. The reaction vessel was then pumped for 5 mins. at 80°C, and a further 8.0 kNm^{-2} of deuterium admitted to the reaction vessel at 80°C. After heating at this temperature for 1 hr., the reaction vessel was pumped for 10 mins. and the reaction mixture admitted to the catalyst at reaction temperature. For the platinum supported on γ-alumina catalyst the activation treatment used was that described by Hightower and Kemball (94).

CHAPTER III

EXCHANGE REACTIONS AND ANALYSIS

3.1. Introduction

The satisfactory quantitative analysis of chemical mixtures by mass spectrometry requires certain conditions to be satisfied. These have been described by Beynon (95):

(1) The mass spectrum of any component must be unaffected by the presence of another component.

(2) The mass spectrum of a mixture must be a linear superposition of the spectra of the various components.

(3) The ion beam intensity for any component must be proportional to the partial pressure of that component in the reaction vessel.

(4) The mass spectrum, which is characteristic of any particular molecule, must remain stable over a reasonably long period.

(5) The sensitivity of the mass spectrometer must remain reasonably constant. In this work, changes in absolute sensitivity were not very important as the percentages of isotopic species present were calculated from their sum at a particular time.

(6) For exchange reactions all the above parameters must be independent of the weight of the molecule.

Conditions 1,2,3, and 5 have been shown by other workers to be satisfied. Condition 4 was shown to be satisfied by the reproducibility of the mass spectra from experiment to experiment. Condition 6, however, is not always satisfied and parameters such as the extent of fragmentation can be different for non exchanged and fully exchanged species. This aspect will be dealt with in greater detail later.

3.2. The Mass Spectrometric Analysis of the Reaction Mixture

The experimentally produced mass spectral data could not be used directly to compute the percentages of the isotopic species. It was first necessary to subject the observed mass spectra to a preliminary treatment, and then to apply corrections to account for background in the mass spectrometer, the occurrence of natural isotopes, and fragmentation of the molecules caused by electron impact in the ion source. The treatment of, and corrections to, the data were applied in the following order.

Preliminary Treatment: A typical mass spectrum is shown in Figure 3.1. It can be seen that this consists of a number of peaks of varying intensity, which, provided the ions are all singly charged, are separated by one mass unit. A kinetic run at a fixed temperature consisted of a number of these spectral scans taken at definite time intervals. The preliminary treatment involved measuring the height of each of the peaks, to the nearest millimetre, and converting them to a common sensitivity. The peak height corresponding to each mass was then plotted against the time at which the scan was taken, no allowance being made for the fact that within each scan the peaks were separated by definite time intervals. Smooth curves were then drawn through the points for each mass, to eliminate small variations of the mass spectrometer sensitivity and also any minor fluctuations due to the recorder. To analyse the data kinetically, six to eight times were selected at regular time intervals, and the peak height for each mass corresponding to a particular time read from the graph, the heights at any time being interpolated to allow for the fact that the masses were separated by a finite time interval.

Background: Background was always present in the mass spectrometer and was due to two causes:

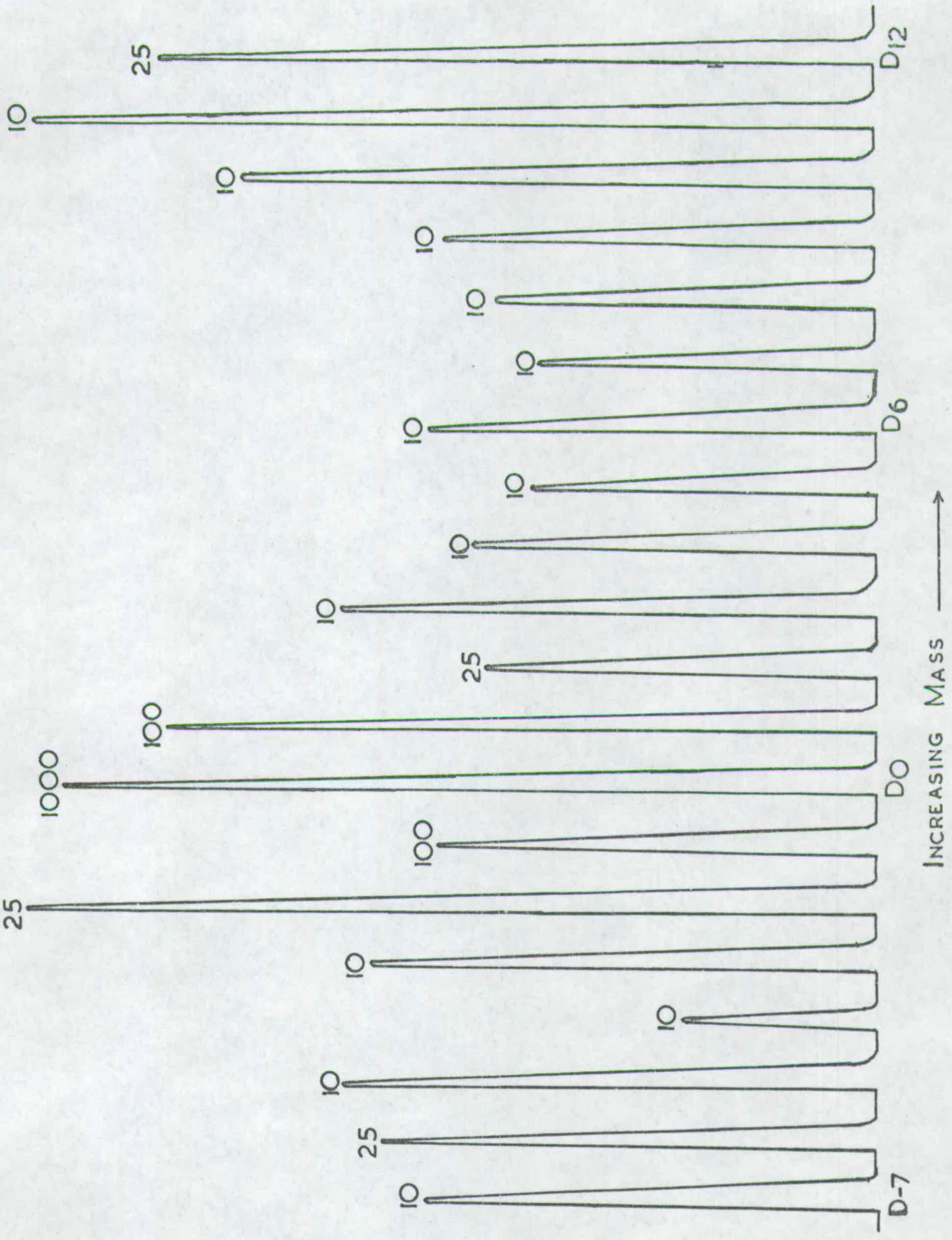


Fig. 3.1 Mass Spectrum of a Mixture of Deuterated Cyclohexanes

The Numbers are the Range Factors by which the Peak Heights are to be Multiplied

(a) Residual gas in the mass spectrometer ion chamber.

(b) Inherent background.

The background spectrum due to the residual gas was produced by ionization of the air molecules and water vapour always present in the ion chamber, and the carbon monoxide given off by the filament. Corrections for this were applied by taking a background scan during the catalyst preparation, and after the reaction mixture had been pumped away upon completion of the reaction. The two background scans were then averaged and subtracted off the peaks to which they contributed in the hydrocarbon mass spectrum.

The inherent background was much more difficult to determine. It was produced by hydrocarbon species from previous experiments which had been adsorbed on the walls of the ion chamber and the glass walls of the inlet tube. Leakage of the reaction products into the mass spectrometer caused desorption of these species, whose mass spectra contributed to the mass spectra of the reaction products. This inherent background could be measured by leakage of the reaction mixture into the mass spectrometer at a temperature at which the hydrocarbon would not react over the catalyst, any peaks present in the mass spectrum corresponding to deuterated molecules would thus be due to this inherent background. After measurement it was allowed for in the normal way.

Natural Isotopes: Many of the elements as they occur in nature contain small amounts of heavy isotopes. Carbon and hydrogen are found in two isotopic forms, ^{12}C and ^{13}C, and ^{1}H and D respectively, thus the mass spectra of hydrocarbons will contain peaks at mass numbers greater than that of the parent molecule due to the presence of these heavier isotopes. Since in exchange reactions the rates are measured by the increase in the peaks at higher masses as the hydrogens in the hydrocarbon are replaced by deuterium, in order to obtain an accurate measure of the amount of exchange it is necessary to take into account the contributions to these peaks from the ^{13}C and D originally present in the hydrocarbon. Since naturally occurring carbon and hydrogen contain 1.081% ^{13}C and 0.016% D respectively, the heights of the peaks at M + 1 and M + 2 for a hydrocarbon of mass M can be calculated relative to the peak height PM at mass M by suitable use of the isotopic abundances given above. For a hydrocarbon C_nH_m

$$100\,\frac{PM+1}{PM} = \left\{ n\left(\frac{1.081}{98.919}\right) + m\left(\frac{0.016}{99.984}\right)\right\}100 \qquad 3.1.$$

and

$$100\,\frac{PM+2}{PM} = \left\{ n\,\frac{(n-1)}{2}\left(\frac{1.081}{98.919}\right)^2 + \frac{m(m-1)}{2}\left(\frac{0.016}{99.984}\right)^2\right\}100. \qquad 3.2.$$

The values of these factors will vary with the isotopic content of the molecules since as the hydrogens are replaced by deuterium the probability of the presence of naturally occurring deuterium decreases. Thus for any isotopic species $C_nH_{m-x}D_x$ the values of the corrections are obtained by substituting m-x for m in the above equations.

Correcting for isotopes thus entailed the subtraction of these isotopic contributions due to peaks at low masses. This was done on a systematic basis starting with the lowest masses and working upwards to the higher masses using the corrected heights at every mass to calculate the contributions to the higher masses.

Fragmentation Corrections: When the hydrocarbon molecules leak into the ion source, they are subjected to impact from the electrons produced by the filament. On colliding with the hydrocarbon molecules, an electron can transfer its energy and cause transitions between the electronic energy levels of the molecule. If the energy of the electron is greater than the ionization potential of the molecule, positive ions may be produced in accordance with the Franck-Condon principle. As the energy of the electron beam is not homogeneous, higher energy electrons may produce further dissociation of the molecule by breakage of the carbon-hydrogen bonds. A typical mass spectrum of a hydrocarbon of mass M will thus show peaks at masses M-1, M-2, M-3 etc. due to this secondary process. In order to determine the isotopic content of the partially exchanged hydrocarbon molecules the contributions of these isotopic fragments to isotopes at lower masses must be taken into account.

To reduce these contributions to as small a value as possible, the mass spectrometer was operated at low electron voltages. However, because the sensitivity decreased with decreasing electron energy, a compromise had to be reached between sensitivity and extent of fragmentation. The values of the electron energy normally used were from 13-25eV depending upon the hydrocarbon.

For the majority of the hydrocarbons used in this work, the cracking or fragmentation pattern of the hydrocarbon was assumed to be independent of either the isotopic substitution or the position of isotopic substitution in the molecule. The fragmentation corrections could then be calculated on a statistical basis. This was normally calculated by computer, the programs being given in a later section; an illustration of how this was done by hand calculation is given below. To calculate the corrections on a statistical basis the fragmentation pattern of the light hydrocarbon was determined before each experiment, this was necessary because the fragmentation pattern varied from day to day.

If the peak heights for the masses at M-1, M-2, etc of a hydrocarbon of mass M, after correction for naturally occurring isotopes, are described by PM-1, PM-2 etc., then the fragmentation factors f_i may be defined by

$$f_i = \frac{PM-i}{PM} \quad . \qquad 3.3.$$

Taking butane as our model, and applying statistical reasoning to the molecule $C_4H_6D_4$, the fragmentation scheme shown in Table 3.1. may be derived .

TABLE 3.1.

CALCULATION OF THE FRAGMENTATION SCHEME FOR $C_4H_6D_4$

Number of Mass Units lost	Method of loss	Probability of loss taking place
1	H	$6/10\ f_1$
2	D	$4/10\ f_1$
	HH	$(6/10\cdot 5/9)\ f_2$
3	HD or DH	$2(6/10\cdot 4/9)\ f_2$
	HHH	$(6/10\cdot 5/9\cdot 4/8)\ f_3$
4	DD	$(4/10\cdot 3/9)\ f_2$
	HHD, HDH, DHH	$3(6/10\cdot 5/9\cdot 4/8)\ f_3$
5	HDD, DDH, DHD	$3(6/10\cdot 4/9\cdot 3/8)\ f_3$
	HHHD, HHDH, HDHH DHHH	$4(6/10\cdot 5/9\cdot 4/8\cdot 4/7)\ f_4$
	HHHHH	$(6/10\cdot 5/9\cdot 4/8\cdot 3/7\cdot 2/6)\ f_5$
6	DDD	$(4/10\cdot 3/9\cdot 2/8)\ f_3$
	HHDD, DDHH, DHDH, HDDH, HDHD, DHHD	$6(5/10\cdot 5/9\cdot 4/8\cdot 3/7)\ f_4$
	HHHHD, combinations	$5(6/10\cdot 5/9\cdot 4/8\cdot 3/7\cdot 4/6)\ f_5$
	HHHHHH	$(6/10\cdot 5/9\cdot 4/8\cdot 3/7\cdot 2/6\cdot 1/5)\ f_6$
etc.		

If this procedure is carried out for each of the deuterated species, the fragmentation scheme given in Table 3.2. may be drawn up. By substitution of the numerical values of f_i into Table 3.2. the actual numerical values for the corrections may be calculated.

The fragmentation corrections were made by a process similar to that used for the isotope corrections but starting instead with the highest mass. The resultant peak heights after correction were then used to calculate the isotopic distributions and phi value of the hydrocarbon entering the mass spectrometer at the time the scan was taken.

The methods used for the mass spectrometric analysis of the isotopic propanes, which due to the large differences between the fragmentation patterns of C_3H_8 and C_3D_8 could not be calculated statistically, will be discussed fully later.

3.3. The Final Equilibrium of an Exchange Reaction

In the exchange reaction between a hydrocarbon C_nH_2m and deuterium, two kinds of equilibria will be established at equilibrium:

(a) An equilibrium distribution between the total amount of deuterium in the gas phase hydrogen and the total amount of deuterium in the hydrocarbon.

(b) An equilibrium between the relative amounts of the different isotopic species of hydrocarbon present.

If the hydrogen and the deuterium have an equal probability of being found in the hydrocarbon, at equilibrium the "hydrogen" will be randomly distributed between the hydrocarbon molecules, and the value of ϕ at equilibrium (where ϕ is the average number of deuterium atoms in 100 molecules of hydrocarbon) can be calculated by purely statistical reasoning. Thus for a hydrocarbon C_nH_m

TABLE 3.2.

FRAGMENTATION FACTORS FOR ISOTOPIC BUTANES

arent lecule	Mass.	Number of mass units lost					
		1	2	3	4	5	6
$_4D_{10}$	68	0	f_1	0	f_2	0	f_3
$_4HD_9$	67	$\frac{1}{10} f_1$	$\frac{9}{10} f_1$	$\frac{1}{5} f_2$	$\frac{4}{5} f_2$	$\frac{3}{10} f_3$	$\frac{7}{10} f_3$
$_4H_2D_8$	66	$\frac{1}{5} f_1$	$\frac{4}{5} f_1 + \frac{1}{45} f_2$	$\frac{16}{45} f_2$	$\frac{28}{45} f_2 + \frac{1}{15} f_3$	$\frac{7}{15} f_3$	$\frac{7}{15} f_3 + \frac{2}{15} f_4$
$_4H_3D_7$	65	$\frac{3}{10} f_1$	$\frac{7}{10} f_1 + \frac{1}{15} f_2$	$\frac{7}{15} f_2 + \frac{1}{120} f_3$	$\frac{7}{15} f_2 + \frac{7}{40} f_3$	$\frac{21}{40} f_3 + \frac{1}{30} f_4$	$\frac{7}{24} f_3 + \frac{3}{10} f_4$
$_4H_4D_6$	64	$\frac{2}{5} f_1$	$\frac{3}{5} f_1 + \frac{2}{15} f_2$	$\frac{24}{45} f_2 + \frac{1}{30} f_3$	$\frac{1}{3} f_2 + \frac{3}{10} f_3 + \frac{1}{210} f_4$	$\frac{1}{2} f_3 + \frac{4}{35} f_4$	$\frac{1}{6} f_3 + \frac{3}{7} f_4 + \frac{1}{42} f_5$
$_4H_5D_5$	63	$\frac{1}{2} f_1$	$\frac{1}{2} f_1 + \frac{2}{9} f_2$	$\frac{5}{9} f_2 + \frac{1}{12} f_3$	$\frac{2}{9} f_2 + \frac{5}{12} f_3 + \frac{1}{42} f_4$	$\frac{5}{12} f_3 + \frac{5}{21} f_4 + \frac{1}{252} f_5$	$\frac{1}{12} f_3 + \frac{25}{252} f_5 + \frac{10}{21} f_4$
$_4H_6D_4$	62	$\frac{3}{5} f_1$	$\frac{2}{5} f_1 + \frac{1}{3} f_2$	$\frac{8}{15} f_1 + \frac{1}{6} f_3$	$\frac{2}{15} f_2 + \frac{1}{2} f_3 + \frac{1}{14} f_4$	$\frac{3}{10} f_3 + \frac{8}{21} f_4 + \frac{1}{42} f_5$	$\frac{1}{30} f_3 + \frac{5}{21} f_5 + \frac{3}{7} f_4 + \frac{1}{210} f_6$
$_4H_7D_3$	61	$\frac{7}{10} f_1$	$\frac{3}{10} f_1 + \frac{7}{15} f_2$	$\frac{7}{15} f_2 + \frac{7}{24} f_3$	$\frac{1}{15} f_2 + \frac{21}{40} f_3 + \frac{1}{6} f_4$	$\frac{7}{40} f_3 + \frac{1}{2} f_4 + \frac{3}{36} f_5$	$\frac{1}{120} f_3 + \frac{5}{12} f_5 + \frac{3}{10} f_4 + \frac{1}{30} f_6$
$_4H_8D_2$	60	$\frac{4}{5} f_1$	$\frac{2}{10} f_1 + \frac{28}{45} f_2$	$\frac{16}{45} f_2 + \frac{7}{15} f_3$	$\frac{1}{45} f_2 + \frac{7}{15} f_3 + \frac{1}{3} f_4$	$\frac{1}{15} f_3 + \frac{8}{15} f_4 + \frac{2}{9} f_5$	$\frac{2}{15} f_4 + \frac{5}{9} f_5 + \frac{2}{15} f_6$
$_4H_9D$	59	$\frac{9}{10} f_1$	$\frac{1}{10} f_1 + \frac{4}{5} f_2$	$\frac{1}{5} f_2 + \frac{7}{10} f_3$	$\frac{3}{10} f_3 + \frac{3}{5} f_4$	$\frac{2}{5} f_4 + \frac{1}{2} f_5$	$\frac{1}{2} f_5 + \frac{2}{5} f_6$
$_4H_{10}$	58	f_1	f_2	f_3	f_4	f_5	f_6

$$\phi_{\infty st} = 100\,m\,\frac{(\text{no. of deuterium atoms})}{(\text{no. of deuterium atoms + no. of hydrogen atoms})} \quad 3.4.$$

Thus if the ratio of deuterium molecules to hydrocarbon molecules initially present in the gas mixture was P:1, then $\phi_{\infty st}$ is given by equation 3.5.

$$\phi_{\infty st} = 100\,m\,\left(\frac{2P}{2p+m}\right) . \quad 3.5.$$

Experimentally it is found that ϕ_{∞} is slightly greater than $\phi_{\infty st}$. This is due to the fact that the carbon-deuterium and the carbon-hydrogen bonds do not have the same bond strengths, the deuterium prefering to be incorporated into the "hydrocarbon" rather than into the gas phase "hydrogen".

Values obtained for the second type of equilibrium are fairly close to those expected for a random distribution of the hydrogen and deuterium atoms among the various isotopic hydrocarbon species. Thus the values of the equilibrium constants for the reactions

$$\begin{aligned} &CnHm + CnH_{m-2}\,D_2 \xrightleftharpoons{K_1} 2CnH_{m-1}D \\ &CnH_{m-1}D + CnH_{m-3}\,D_3 \xrightleftharpoons{K_2} 2CnH_{m-2}\,D_2 \\ &\quad \text{etc.,} \end{aligned} \quad 3.6.$$

can be calculated from a combination of terms in the appropriate binomial expansion and may be expressed in general terms as

$$Ki = \frac{\binom{i}{m}^2}{\binom{i-1}{m}\binom{i+1}{m}} \quad 3.7.$$

where the symbol $\binom{i}{m}$ represents the number of ways of selecting i objects from a group of m identical objects. The interconversion equilibrium constants calculated in this way were in good agreement with those derived experimentally.

3.4. Determination of Rate Constants

The rate of incorporation of deuterium into the hydrocarbon can be determined from the parameter ϕ, defined by equation 3.8.

$$\phi = \sum i \; d_i \qquad 3.8.$$

where d_i is the percentage of the isotopic species containing i deuterium atoms at time t. As has been mentioned in the previous section, the calculated value of $\phi_{\infty\,st}$ is usually less than the experimental value. If we derive a parameter a from equation 3.9.

$$\phi_{\infty\,exp.}/\phi_{\infty\,st} = a \qquad 3.9.$$

then for any experiment using a specific hydrocarbon

$$\phi_{\infty} = a \; \phi_{\infty\,st} . \qquad 3.10.$$

Provided all the hydrogen atoms in the hydrocarbon are equally susceptible to exchange, and isotope effects upon the rate of reaction are ignored, the course of the exchange reaction will be given by the first order equation

$$\frac{\partial \phi}{\partial t} = k_{\phi} \left(1 - \frac{\phi}{\phi_{\infty}}\right) \qquad 3.11.$$

where k_{ϕ} is the rate constant equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time, and ϕ_{∞} is the equilibrium value of ϕ defined by equation 3.10.

Integration of equation 3.11 yields the first order equation

$$- \log \frac{\phi_\infty - \phi}{\phi_\infty} = \frac{k_\phi t}{2.303 \phi_\infty} . \qquad 3.12.$$

Failure to obey this equation may be due to a number of factors which, as they are of fundamental importance to the results in this thesis, will be discussed more fully later. The rate of disappearance of the light hydrocarbon is given by the empirical equation 3.13 analogous to equation 3.12.

$$- \log \frac{(d_0 - d_{0\infty})}{(100 - d_{0\infty})} = k_0\ t/_{2.303}\ (100 - d_{0\infty}) \qquad 3.13.$$

where d_0 is the percentage of the 'light' hydrocarbon at time t and $d_{0\infty}$ and 100 are the equilibrium and initial percentages of this species respectively. If the ratio of deuterium to hydrocarbon used is large, $d_{0\infty}$ will be negligible and equation 3.13. simplies to

$$- \log d_0 = \frac{k_0 t}{230.3} - 2 . \qquad 3.14.$$

Equation 3.14. is the one that has been used exclusively in this work.

The value of the parameter M defined by

$$M = {}^{k_\phi}/_{k_0} \qquad 3.15.$$

is a very important quantity because it represents the mean number of deuterium atoms entering the hydrocarbon molecule in the initial stages of the reaction.

3.5. Kinetics

The rate constants calculated from equations 3.12 and 3.14 are constant only for the course of an exchange reaction with a single mixture of reacting gases. They are pressure dependent and vary as the relative pressures of the gases in the reaction mixture are altered. The true pressure dependencies of the reaction can thus only be determined by carrying out the reaction with a series of different reaction mixtures.

The reason for this apparent first order kinetic behaviour of an exchange reaction can be seen from a consideration of the processes occurring during the reaction. On admission of the reaction mixture to the catalyst, two things happen:

(a) The surface concentrations of the adsorbed species build up to their equilibrium values and remain constant.

(b) The exchange reaction commences and eventually leads to equilibrium between all the species in the system.

Process (a) will be rapid but (b) cannot go to completion until all the gas phase has been adsorbed and desorbed and hence throughout most of the time required for the exchange reaction there will be equilibrium concentrations of the different types of adsorbed species. The only thing which reduces the rate of exchange from its initial value is the approach of the isotopic content of the "hydrogen" and "hydrocarbon" to their equilibrium values and this as can be seen from equation 3.11. leads to apparent first order kinetics.

3.6. Computer Program for the Statistical Analysis of the Results

The mass spectral data for the hydrocarbons (excluding propane) were analysed on a statistical basis, as described in Section 3.2. by means of a computer. The flow chart showing the steps followed by the computer is given in Figure 3.2., and the general program, which was written in Atlas Autocode and run on an English Electric KDF9 computer, is given in Appendix I.

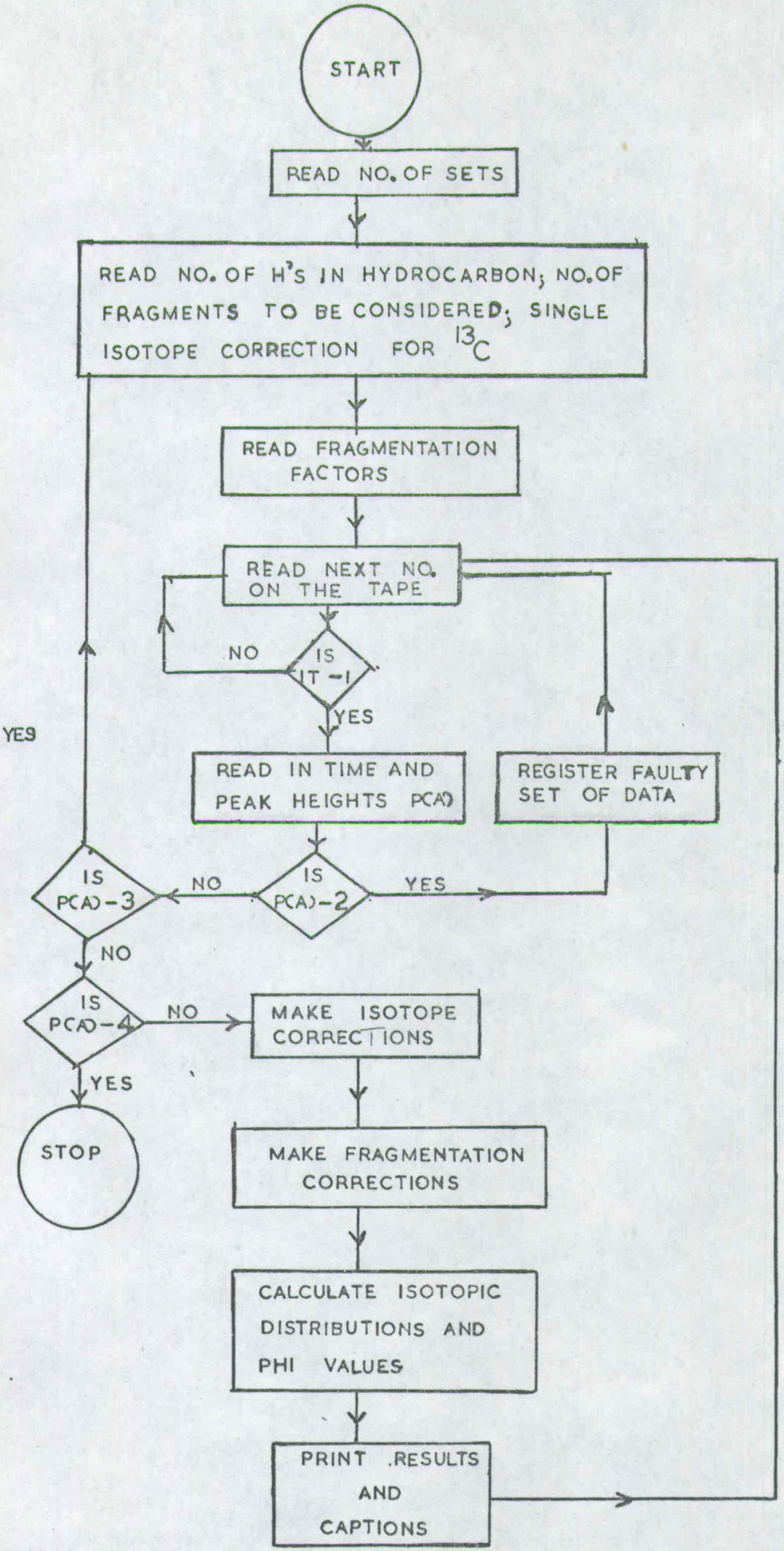


FIG. 3.2 FLOW CHART FOR THE ATLAS AUTOCODE PROGRAM

PART II

THE EXCHANGE OF THE LOWER ALIPHATIC HYDROCARBONS WITH DEUTERIUM ON PLATINUM CATALYSTS

CHAPTER I

INTRODUCTION

The diversity of the reactions which organic molecules undergo in the presence of platinum catalysts have been the subject of many extensive investigations. The published literature reports studies of the catalytic fission of the C-halogen bond (96-98), C-O bond (99) and the C-N bond (100); and of the exchange reactions of amines (101), and diethyl ether (102) with deuterium. The majority of the investigations have, however, been concerned with the exchange reactions of hydrocarbons with deuterium (79, 103, 104) or heavy water (105), hydrogenation-dehydrogenation reactions (71, 106, 107), and hydrocracking and isomerization reactions (108-110).

Although self poisoning has been reported for the exchange of hydrocarbons with deuterium on other metals (83), so far as is known, the literature does not contain any report on the self poisoning of exchange reactions on platinum catalysts. As has been mentioned previously, the classic work by Anderson and Avery (42) showed that the hydrocracking and isomerization of saturated hydrocarbons on platinum films at high temperature, proceeded by the formation of an $\alpha\alpha\gamma$-triadsorbed intermediate. Since platinum is known to be capable of propagating the multiple exchange process past a quaternary carbon atom via an $\alpha\gamma$-diadsorbed intermediate (50), and because the high isomerization activity relative to the hydrocracking activity is due to the ready formation of this $\alpha\alpha\gamma$-triadsorbed intermediate, it was hoped that the self poisoning of the exchange reaction might be exhibited by the use of neopentane, which can only exchange all twelve hydrogen atoms initially by the interconversion between α- and $\alpha\gamma$-adsorbed intermediates. It will be shown that at lowish temperatures (20 to 180°C) no discernible self poisoning of the exchange reaction was observed for the exchange of propane, butane or neopentane with deuterium; but presorbing neopentane or a neopentane-deuterium mixture at high temperature on a presintered film did reduce the activity of the film for the subsequent exchange reaction of neopentane with deuterium.

One of the most surprising features found in this work was the very large reduction in activity that was observed when the exchange of butane and neopentane was carried out on presintered films. This decrease in activity, which was not accompanied by any fundamental change in the reaction mechanism, could not be completely explained by a decrease in the apparent surface area of the film upon sintering.

Although the texture of, and the nature of chemisorbed molecules on, the surface of platinum supported catalysts have been well characterized (111-116), little attempt has been made, however, to correlate the activity of platinum films with that of platinum supported catalysts. The exchange of neopentane with deuterium was, therefore, carried out on some supported catalysts to determine how the activity and mechanistic characteristics of the exchange reaction on these catalysts compared with those on the films.

If one looks at the broad spectrum of reactions, involving hydrocarbons, which can be catalysed by platinum, is each type of reaction a separate entity proceeding through its own specialized intermediates; or are they all related in some manner via an underlying mechanism, the particular facet of which is predominant being determined by the experimental conditions? Why does platinum appear to differ in its catalytic properties from the other metals in Group VIII of the periodic table? It is hoped to answer these questions, as well as explaining why platinum acts in the way it does towards the hydrocarbons studied in this work.

CHAPTER II

EXPERIMENTAL

2.1. Surface Areas

The surface areas of the platinum films were measured by two methods:

(a) Krypton adsorption at -196°C. This method gave the surface area of the platinum which was available for physical adsorption.

(b) Hydrogen-deuterium exchange at 0°C. This method gave the surface area of the platinum which was capable of chemisorbing hydrogen, and thus an indication of the catalytically active area.

Krypton adsorption: The apparatus used to study the adsorption of krypton on the films is shown in Figure 2.1. It consisted of a general purpose gas line and a reaction vessel system identical to that shown in Figure 2.2. (Part 1). The apparatus was built and used by Mr. G.B.B. Scott to study the surface areas of, and the decomposition of alcohols on, titanium films.

The volumes needed for the calculation of the results were measured at 23°C using helium gas and the results extrapolated to zero pressure. The following values were found:

V_R	The volume of the reaction vessel	188.0 ml
V_2	The volume bounded by taps T_1-T_7	36.2 ml
V_3	The volume bounded by the tap T_5 and the McLeod gauge cut off	7.80 ml
V_4	The McLeod gauge bulb volume	68.9 ml
V_x	The total gas volume $(V_2 + V_3 + V_4)$	112.9 ml

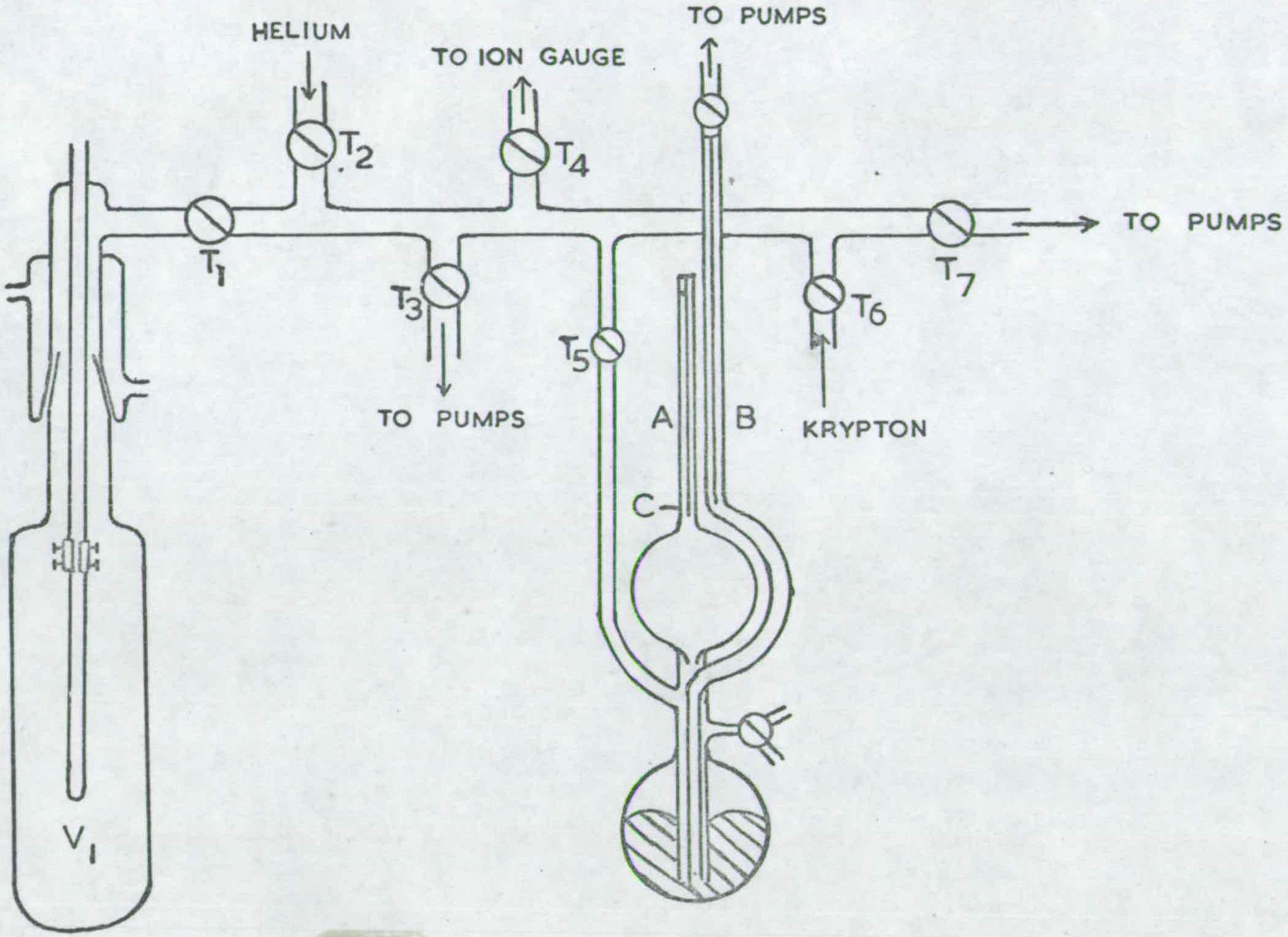


FIG. 2.1 B.E.T. APPARATUS

With taps T_2, T_6 and T_7 closed and taps T_1-T_5 open the gas line and reaction vessel were evacuated, while the reaction vessel was being outgassed. After outgassing the wire, tap T_1 was closed and the film prepared at 0°C; taps T_3 and T_4 were then closed and T_5 left open. The reaction vessel was then surrounded by liquid nitrogen and a dose of krypton admitted to V_x. The krypton pressure was measured by raising the mercury in the McLeod gauge to the standard mark 'C' on the closed capillary limb 'A'. The height of the mercury level in limb 'B' from the standard mark 'C' was then read and the mercury level lowered to just below the McLeod gauge cut-off. T_1 was then opened and the krypton expanded into the reaction vessel where some was adsorbed on the film. After equilibration T_1 was closed and the residual pressure in V_x measured as before. A further dose of krypton was then admitted to V_x, the pressure read, and the gas expanded into V_A by opening T_1. After equilibration T_1 was closed, the pressure read, and the dosing procedure repeated a number of times. After completion of the adsorption isotherm the film was warmed to 0°C, the krypton was pumped off and the adsorption isotherm remeasured.

The surface area of the sintered platinum film was determined by presintering the film at 250°C in vacuo for 1 hr, cooling to -196°C and measuring the adsorption isotherm as previously described.

Due to the large temperature difference between the reaction vessel (-196°C) and the gas line (23°C), when T_1 is opened, the thermal transpiration effect will tend to make the pressure in the reaction vessel less than would be expected on the basis of the gas laws. Since this effect V_R is dependent upon the equilibrium pressure, a factor f allowing for it was determined by using helium which does not adsorb on the glass. Using a blank reaction vessel, the apparatus was evacuated and T_1 closed. The reaction vessel was then surrounded by liquid nitrogen, and some helium admitted to V_x. The pressure was read, T_1 opened, and the equilibrium pressure read.

The equations used for the calculation of the results are given below, all heights being in mm, and pressures in units of Nm^{-2}.

The relation between the height H of the mercury in the capillary 'B' and the Pressure P is given by

$$P = 0.0303997\ H. \qquad 2.1.$$

In general, if P is the gas pressure contained in V_x, then the volume V of gas in V_x is given by

$$V = V_x \cdot \left(\frac{273}{296}\right)\left(\frac{P}{1.01332}\right) \cdot 10^{-2}\ \mu l \text{ at N.T.P.}, \qquad 2.2.$$

letting $V_x\ (273)/(296)(1.01332)\ .10^{-2}$ be denoted by A, then A has the value $1.041\ \mu lm^2N^{-1}$, and hence the volume of gas contained in V_x corresponding to any pressure P is given by

$$Vml\ (\text{N.T.P.}) = 1.041 \cdot 10^{-3}\ P. \qquad 2.3.$$

If P_B is the helium pressure before equilibration and P_C is the helium pressure after equilibration, then the volumes of helium before and after equilibration are given by

$$V_B = 1.041\ P_B \cdot 10^{-3}\ \text{ml (N.T.P.)}$$
$$V_C = 1.041\ P_C \cdot 10^{-3}\ \text{ml (N.T.P.)}$$

and the volume of helium V_G contained in the reaction vessel is given by

$$\begin{aligned} V_G &= V_B - V_C \\ &= 1.041\ (P_B - P_C) \cdot 10^{-3}\ \text{ml (N.T.P.)}. \end{aligned}$$

Defining f as the volume of gas contained in the reaction vessel per unit pressure then

$$f = V_G/P_C \quad \text{ml m}^2\,\text{N}^{-1},$$

and
$$f = 1.041\,(P_B - P_C)/P_C \;.\; 10^{-3} \quad \text{ml m}^2\,\text{N}^{-1}.$$

Hence for any equilibrium pressure P_e the volume of gas V_R contained in the reaction vessel during krypton adsorption is given by

$$V_R = 1.041\,(P_B - P_C)\,P_e/P_C \;.\; 10^{-3} \quad \text{ml (N.T.P.).} \qquad 2.4.$$

The equations used for calculating the volumes of krypton adsorbed on the film are given below.

For the first dose of krypton the volume of gas in V_x is denoted by V_T. For the second and subsequent doses the volume of gas in V_x is denoted by V_x. After expansion into V_A (the reaction vessel) the volume of gas remaining in V_x is denoted by V_L, and finally the volume of krypton adsorbed is denoted by V_a

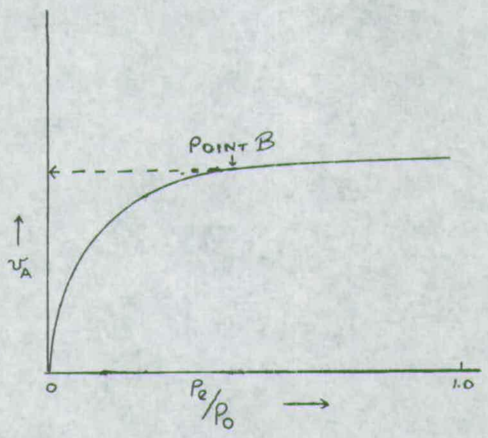
$$Va_1 = V_{T1} - (V_{L1} + V_{R1}) \qquad 2.5.$$
$$V_{a2} = (V_{T1} + V_{x2}) - (V_{L1} + V_{L2} + V_{R2}) \qquad 2.6.$$
$$Va_3 = (V_{T1} + V_{x2} + V_{x3}) - (V_{L1} + V_{L2} + V_{L3} + V_{R3}) \qquad 2.7.$$

etc.

Thus from a knowledge of the initial and equilibrium pressures and using equations 2.1. - 2.7., the volumes of krypton adsorbed on the film for different values of the equilibrium pressure may be calculated.

The surface areas of the films may be calculated from the adsorption data by two methods:

(a) By plotting the adsorption isotherm, and using the "Point B" as a measure of the monolayer volume.



or (b) By utilizing the Brunauer, Emmett and Teller (16) equation

$$P_e/(P_o - P_e)\,v = 1/v_mC + \frac{(C-1)}{v_mC} . \ P_e/P_o \qquad 2.8.$$

where v_m is the monolayer volume of krypton and P_o is the saturation vapour pressure of krypton at -196°C.

Inspection of equation 2.8. shows that a plot of $P_e/(P_o - P_e)v$ against P_e/P_o should be a straight line, the monolayer volume being obtained from a combination of the intercept I and the slope S.

$$v_m \ \text{ml (N.T.P.)} = 1/I + S \qquad 2.9.$$

The surface area A may then be calculated from

$$A = \frac{6.023}{22.414} . \ 19.5\ v_m \ \ m^2. \qquad 2.10.$$

<u>Hydrogen-Deuterium exchange</u>: In the present work an attempt was made to measure the surface area of the platinum films by a variation on the method reported by Hall and Lutimski (117) for supported catalysts.

Basically this method consisted of covering the surface of the metal with chemisorbed deuterium and then exchanging it with hydrogen. The resultant mixture of isotopic hydrogens being analysed mass spectrometrically, using 70 V as the ionising potential.

Before the experiment the mass spectrometer was calibrated for hydrogen and deuterium as the sensitivity fluctuated from day to day. After baking out, the reaction vessel was surrounded by an ice bath and the background mass spectrum measured. A known pressure of hydrogen was then expanded into the reaction vessel, and the peaks at masses 2,3 and 4 scanned manually using the mass spectrometer fitted with the permanent magnet in place of the electromagnet. The gas phase was then pumped off and the background mass spectrum remeasured. Further doses of hydrogen were then expanded into the reaction vessel and the procedure repeated. This calibration was then repeated using deuterium instead of hydrogen.

The reaction vessel was rebaked, and the film prepared at 0°C. Deuterium was then admitted to the film at 0°C, the gas phase pumped off, and the chemisorbed deuterium exchanged with hydrogen at 0°C. The hydrogen deuteride produced being measured mass spectrometrically. The film was then flushed with deuterium to remove all traces of hydrogen and hydrogen deuteride from the system, and the area remeasured. The film was then sintered in vacuo at 250°C for 1 hr. and the area measured as described above.

As a basis for calculating the surface area it was assumed that all the chemisorbed deuterium was produced as hydrogen deuteride after exchange with the hydrogen. From the calibration graph the number of chemisorbed deuterium atoms could be calculated, and by assuming that each deuterium atom occupied an area of 0.08 nm^2 the area of the film could be calculated.

2.2. Mass Spectrometric Analyses

The electron potentials used to ionize the molecules, along with some typical fragmentation patterns are given in Table 2.1. The potentials used provided adequately large peaks and only a moderate amount of fragmentation of the molecules.

TABLE 2.1.

FRAGMENTATION PATTERNS OF THE MOLECULES

Molecule	Ionizing Potential V	f_1*	f_2	f_3	f_4	f_5	f_6
Methane	20	0.546	0.0196	0	0	-	-
Propane	17	1.135	0.1695	0.393	0.0361	0.1665	0.0324
Perdeuteropropane	17	0.781	0.1015	0.2385	0.064	0.127	0.0224
Butane	30	0.198	0.078	0.0782	0.0129	0.0374	0.0044
Neopentane	20	0.041	0.0088	0	0	0	0

* The f factors have been described by equation 3.3., (Part I).

The isotopically substituted methanes, and butanes were determined, assuming statistical loss of hydrogen and deuterium atoms under electron impact, as described in Part I. section 3.2. The isotopic neopentanes could not be analysed in terms of substituted neopentyl molecules because, under electron impact, neopentane quantitatively loses a methyl group even at ionising potentials close to the appearance potential. The isotopically substituted neopentanes were therefore analysed as the tert-butyl ions, though still assuming statistical loss of both hydrogen and deuterium atoms.

With an ethylene-ethane mixture, the ethane fragments contribute to the peaks due to ethylene. Analysis of the gas mixture from the hydrogenation of ethylene on platinum was therefore based on the mass 30 peak for ethane, and the mass 26 peak for ethylene. Thus if the mass spectrum of the ethylene-ethane gas mixture at any time t is described by a_i where a_o corresponds to mass 30 and a_4 to mass 26, and the ethane fragmentation pattern is similarly described by b_i, then after natural isotope corrections have been applied

at time t the amount of ethane present is given by a_o,

and the amount of ethylene present is given by $a_4 - a_o b_4$.

However, since the sensitivity of the mass spectrometer is not the same for both ethylene and ethane, in order to calculate the actual percentage of the ethane and ethylene present, these sensitivity factors must be introduced.

If 133.322 Nm^{-2} of C_2H_6 in the reaction vessel give a peak height at mass 30 of C mm,

and 133.322 Nm^{-2} of C_2H_4 in the reaction vessel give a peak height at mass 26 of D mm,

Then the sensitivity factor G is given by

$$G = C/D$$

$\therefore$ actual C_2H_6 present in the reaction vessel at time t

$$= a_o$$

and the C_2H_4 present $= G\,(a_4 - a_o . b_4)$

$$\text{and } \%\ C_2H_6 = 100\, a_o / \left[a_o + G(a_4 - a_o b_4)\right]$$

$$\%\ C_2H_4 = 100\, G(a_4 - a_o b_4) / \left[a_o + G(a_4 - a_o b_4)\right].$$

The isotopic propanes could not be analysed statistically due to the large differences between the mass spectra of propane and perdeuteropropane. The various schemes devised, and the results obtained, from them are described in section 3.2.

2.3. Chemicals

Hydrogen and Deuterium: The preparation and purification of these gases have already been described in Part I. section 2.6.

Methane, Ethane and Ethylene: These gases were obtained in cylinders from the Matheson Co. Inc., and were "C.P." grade pure. Before use they were frozen in liquid nitrogen and degassed by repeated pumping, thawing, freezing, pumping cycles. They were then fractionated on the apparatus, the middle fractions being stored in bulbs attached to the gas line.

Propane and Butane: Propane and butane were obtained in cylinders from the Phillips Petroleum Co. and were of "research grade" purity. Before use they were frozen in liquid nitrogen and degassed before being stored in bulbs on the gas line.

Neopentane: Neopentane was a standard sample obtained from the Department of Scientific and Industrial Research, Chemical Research Laboratory (99.98% "pure"). Before use it was degassed and stored in a bulb.

2.4. Procedure

The standard reaction mixture consisted of 0.67 kNm^{-2} and 6.7 kNm^{-2} of hydrocarbon and deuterium respectively in the mixing volume which, after expansion, gave pressures of 0.45 and 4.5 kNm^{-2} in the reaction vessel at 0°C. The reaction mixture was normally prepared during the period when the film was being thrown and was allowed to equilibrate for 30 mins to ensure adequate mixing of the gases. The gas mixture was normally admitted to the film at 0°C and the temperature then raised rapidly to that at which the reaction began to occur.

In experiments involving presorption the procedure was to admit the material to be presorbed as described above for a reactant. While it was remaining in contact with the film at the desired temperature the excess was removed from the mixing volume and the subsequent reaction mixture prepared. The removal of the presorbate was achieved by pumping for 10 mins at the presorption temperature. The admission of the reaction mixture was then accomplished in the usual way.

In experiments using the solid catalysts, the gas mixture was prepared while the catalyst was being stabilized at the reaction temperature. After stabilization the gas mixture was admitted at this temperature.

CHAPTER III

RESULTS

3.1. Surface Areas of the Catalysts

The platinum-silica catalysts used were obtained from Dr. R.L. Moss at the Warren Springs Laboratory, Stevenage. Dr. Moss also kindly supplied the catalyst characteristics and these have been summarized in Table 3.1.

TABLE 3.1.

PLATINUM - SILICA CATALYSTS

10.0% Platinum on Davison grade 70 silica. Surface Area 215 m^2g^{-1}

Catalyst	Reduction temperature °C	X-ray size nm (111)(200)(220)	Proportion of platinum > 5.0 nm	Platinum area m^2g^{-1} X-ray	Rate C_2H_4/H_2 at -80°C, mols $s^{-1}m^{-2}$ $.10^{-16}$
S68/AP/140	140	7.0 6.5 7.5	0.77	4.84	14.6
S68/AP/500	500	10.0 9.5 10.0	0.89	3.03	1.6

The platinum on γ-alumina was a sample of a commercial platforming catalyst supplied by Universal Matthey Products Ltd.; the catalyst consisting of 0.375% platinum on γ-alumina with fluorine promoter. The characteristics of this catalyst have been described by Hightower and Kemball (94). They did not, however, give the actual platinum surface area of the catalyst, and so by utilizing their results, an estimate of the available platinum area was made in the following manner.

Catalyst contains 0.375% platinum

$\therefore$ 1 g of catalyst contains $0.375.\ 10^{-2}$ g of platinum

1 g mole of platinum = 195.1 g

$\therefore$ 1 g platinum contains $\frac{6.023}{195.1}.\ 10^{23}$ atoms

$\therefore$ 1 g catalyst contains $\frac{6.023(0.375)}{195.1}.\ 10^{21}$ atoms of platinum

If one assumes that the area of a spherical atom when it is projected onto a plane is the same as that of a square the dimensions of which are given by the diameter of the atom, then since the Pt-Pt bond length is 0.275 nm, the area of one platinum atom is approximately given by $0.275^2.\ 10^{-18}m^2$.

$$\therefore 1 \text{ g catalyst} = \frac{60.23}{1.951}(0.375)(0.275)^2(1.1)m^2 \text{ of platinum}$$

$$= 0.9631 \text{ m}^2 \text{ of platinum,}$$

and this value was used to convert the experimentally determined rates into absolute units.

Krypton Adsorption: The results obtained for the adsorption of krypton on an unsintered platinum film are given in Table 3.2. and the adsorption isotherms and B.E.T. plots are shown in Figures 3.1. and 3.2. respectively. Isotherm II was obtained by evacuating the krypton from the film at 0°C, recooling to -196°C and then measuring the adsorption of krypton upon the film. Figure 3.1. shows that the adsorption of the krypton was not reproducible. The reasons for this will be discussed fully later, but it indicated that the krypton might be diffusing between the platinum crystallites.

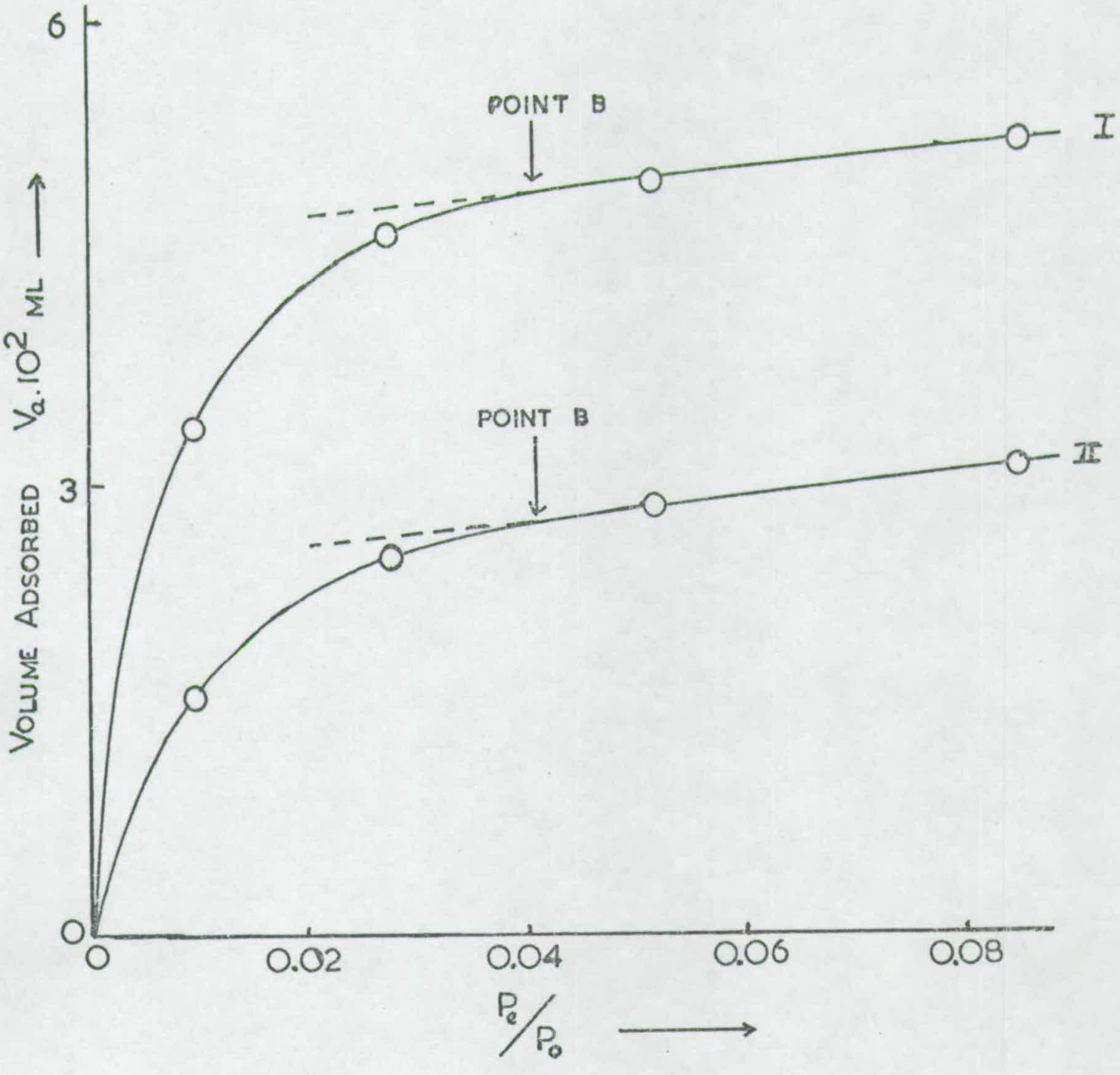


Fig. 3.1 Adsorption Isotherms of Krypton on an Unsintered Platinum Film

I Initial Adsorption Isotherm

II Readsorption after Desorption of Isotherm I

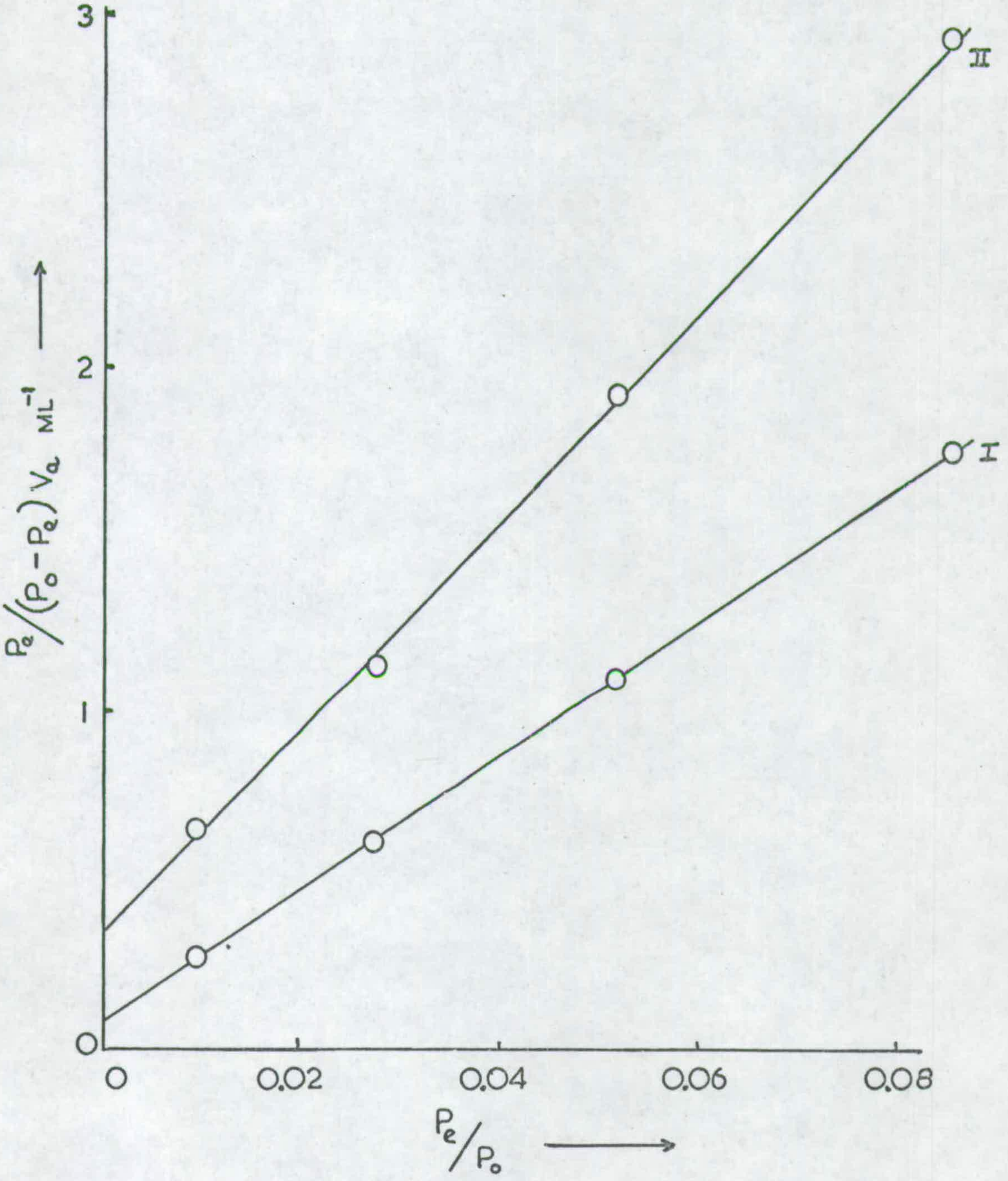


FIG. 3.2 B.E.T. PLOTS FOR THE ADSORPTION OF KRYPTON ON AN UNSINTERED PLATINUM FILM

TABLE 3.2.

ADSORPTION OF KRYPTON ON AN UNSINTERED PLATINUM FILM

$P_o = 0.3906\ kNm^{-2}$

Isotherm	Pressure P Nm^{-2}	Equilibrium pressure P_e Nm^{-2}	Vol. of gas adsorbed $V_A.10^2$ ml	P_o-P_e Nm^{-2}	$^{P_e}/(P_o-P_e)v$ ml^{-1}	$^{Pe}/_{P_o}$
I	51.56	3.678	3.40	386.9	0.2796	0.0094
	78.30	10.70	4.64	379.9	0.609	0.0274
	62.24	20.23	4.93	370.4	1.108	0.0518
	87.84	33.20	5.27	357.5	1.76	0.085
II	51.56	3.68	1.47	386.9	0.655	0.0094
	39.18	4.41	2.54	386.19	1.140	0.0274
	44.99	9.27	2.84	381.33	1.922	0.0518
	55.16	20.13	3.17	370.47	2.933	0.085

For the sintered film, the reaction vessel was warmed to 0°C and the krypton pumped off. The temperature was then raised to 250°C and the film sintered, while under evacuation, at this temperature for 1 hr. The results obtained for the adsorption of krypton are given in Table 3.3., and the isotherm and B.E.T. plots are shown in Figures 3.3. and 3.4. respectively.

The figures show that in the range of relative pressure used, the adsorption of krypton on platinum gave isotherms with a very pronounced plateau. It was thus possible to measure the monolayer volumes accurately from both the B.E.T. plots, and the 'point B' values obtained from the adsorption isotherms. The results obtained are given in Table 3.4, which shows the excellent correspondence between the areas

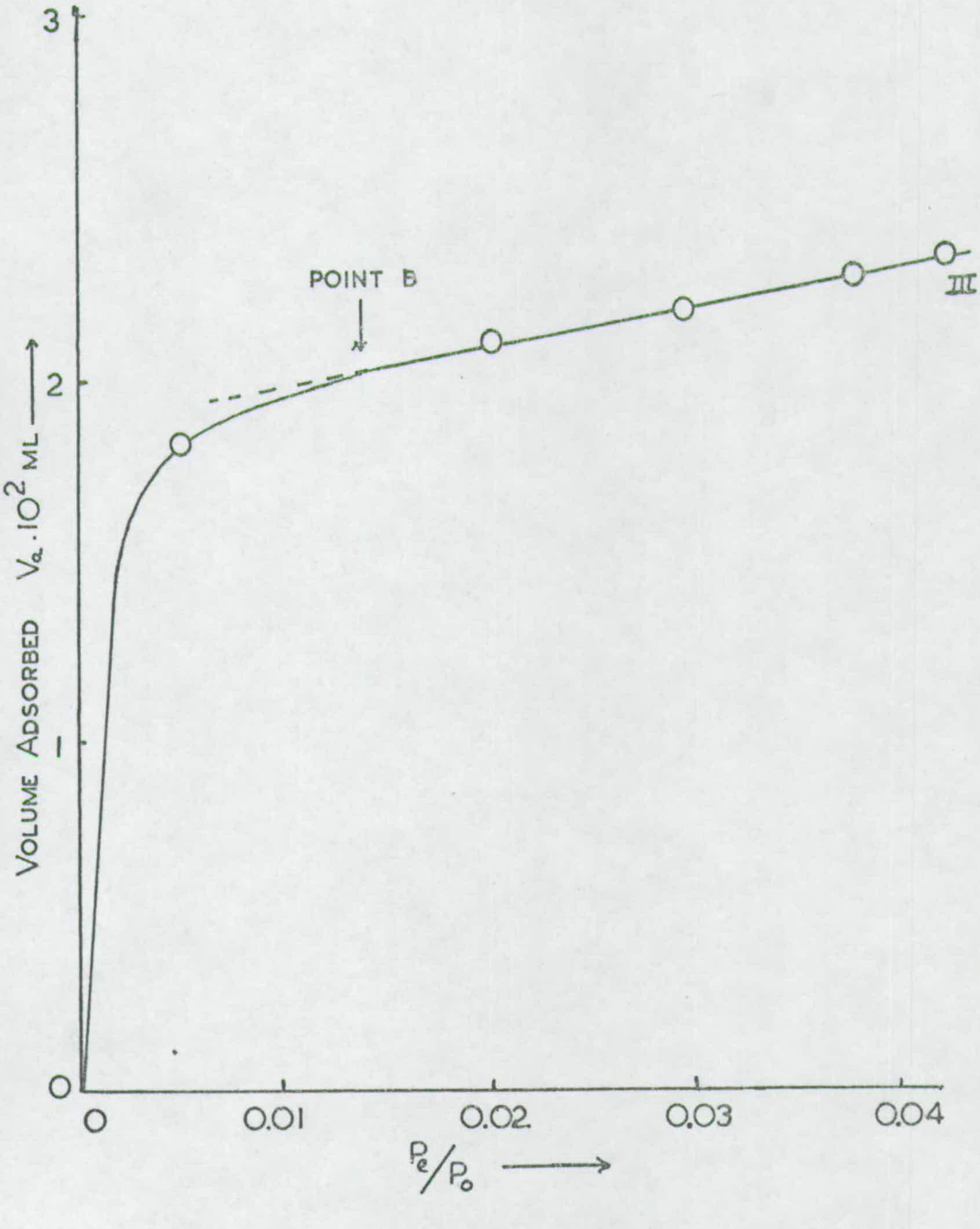


Fig. 3.3 Adsorption Isotherm of Krypton on a Sintered Platinum Film

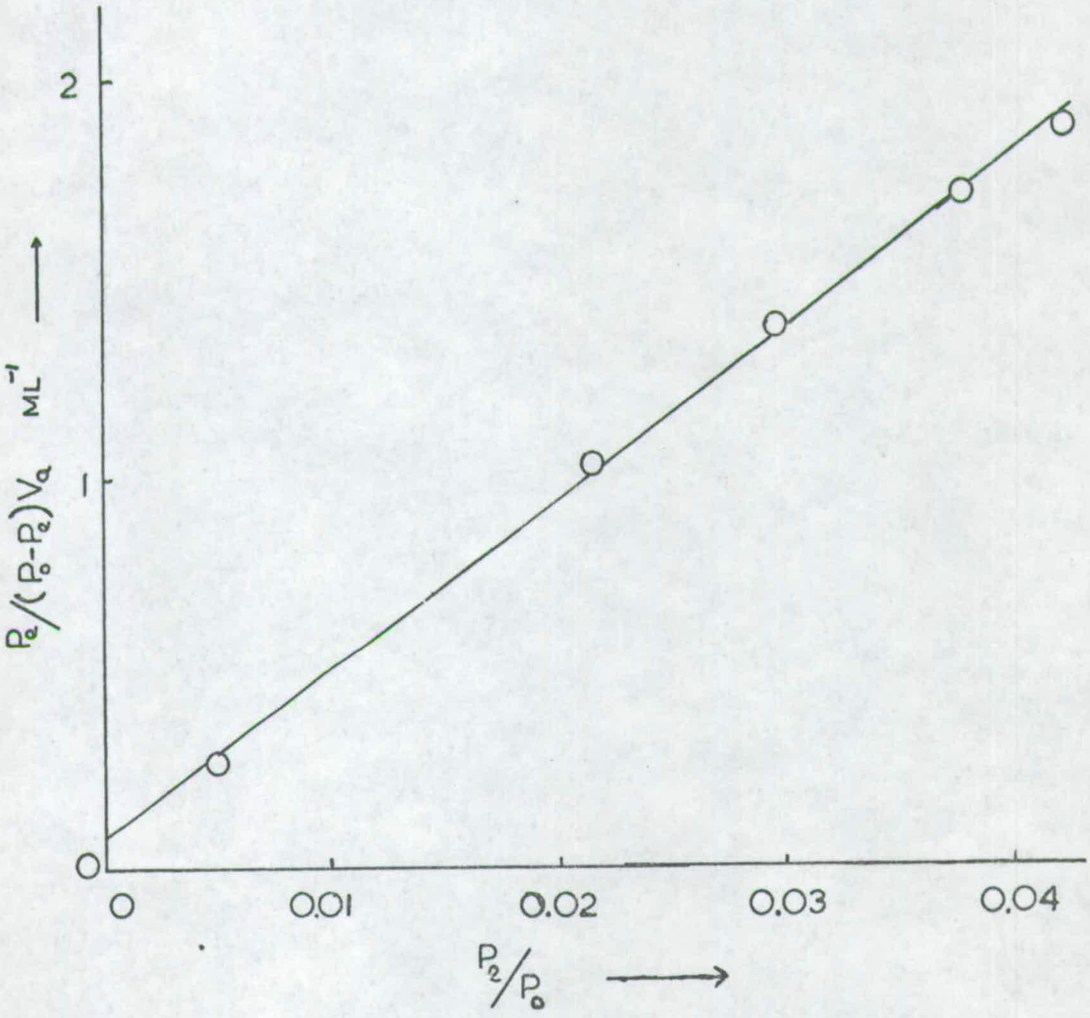


FIG. 3.4 B.E.T. PLOT FOR THE ADSORPTION OF KRYPTON ON A SINTERED PLATINUM FILM

TABLE 3.3.

ADSORPTION OF KRYPTON ON A SINTERED PLATINUM FILM

Isotherm	Pressure P Nm^{-2}	Equilibrium pressure P_e Nm^{-2}	Vol. of gas adsorbed V_A. 10^2 ml	P_o-P_e Nm^{-2}	$P_e/(P_o-P_e)v$ ml^{-1}	P_e/P_o
III	27.50	1.92	1.836	388.68	0.2691	0.0049
	36.87	8.36	2.109	382.24	1.037	0.0214
	24.98	11.49	2.188	379.11	1.385	0.0294
	28.81	14,73	2.283	375.87	1.717	0.0377
	24.32	16.51	2.347	374.09	1.880	0.0423

calculated by the two methods. These areas could not, however, be used directly to convert the experimental rates into absolute units. It was first of all necessary to correct the areas obtained for the adsorption of the krypton upon the glass surfaces of the gas handling system. This blank area was determined by measuring the geometric surface area of the glass and then multiplying it by a 'roughness' factor of 1.7. The blank area of 0.0794 m^2 obtained was then subtracted from the experimental areas to give the film areas shown in Table 3.5., which also includes the results obtained by other workers.

TABLE 3.4.

SURFACE AREAS OF THE FILMS

Isotherm	Type of film used	Point B monolayer vol. V_m. 10^2 ml	B.E.T. monolayer vol. V_m. 10^2 ml	Point B surface area m^2	B.E.T. surface area m^2
I	unsintered	4.85	5.03	0.2541	0.2634
II	unsintered	2.73	3.28	0.1431	0.1721
III	sintered	2.02	2.28	0.1059	0.1194

TABLE 3.5.

CORRECTED SURFACE AREAS OF THE PLATINUM FILMS

Isotherm	Type of film	B.E.T. surface area m^2
I	unsintered	0.1840
II	unsintered	0.0927
III	sintered	0.040
	unsintered	0.1989 (118)
	unsintered	0.1000 (119)
	sintered	0.040 (119)
	unsintered	0.1200 (120)

The surface areas obtained by solution of the B.E.T. equation were considered to be more accurate than those obtained from the 'Point B' values, and so the areas of isotherms I and III contained in Table 3.5. were used to convert the experimental rates into their absolute values.

Hydrogen-deuterium exchange: The results obtained for the calibration of the mass spectrometer for hydrogen and deuterium are given in Table 3.6., and have been plotted in Figure 3.5. No attempt was made to measure the calibration line for hydrogen deuteride.

The results that were obtained for the calibration of the mass spectrometer are subject to an error in the pressure measurements. Due to the construction of the gas line, the calibration doses of hydrogen and deuterium had to be expanded from the dosing volume (60 ml) to a final volume of 880 ml. The pressure of the gas in the dosing volume was read

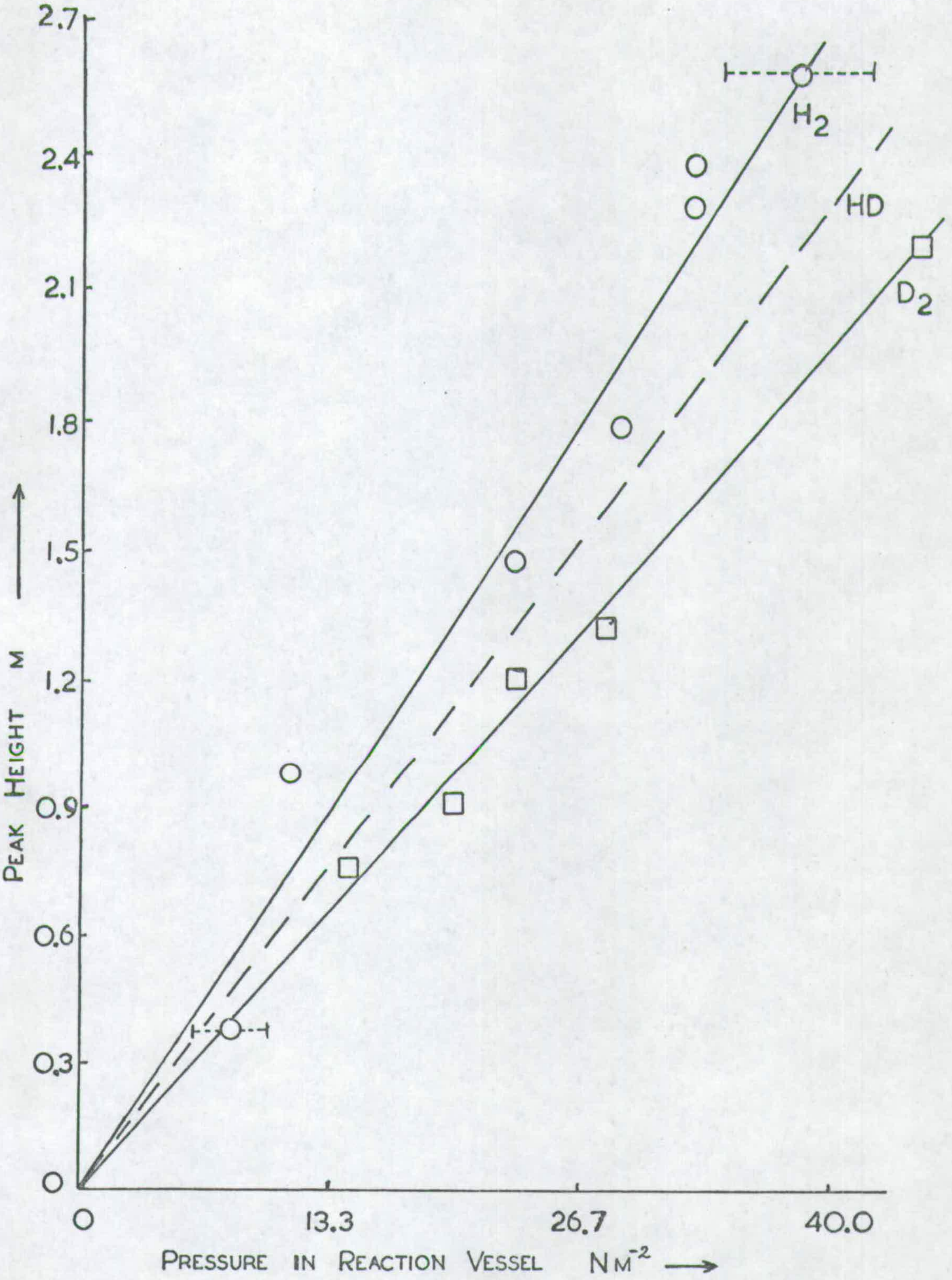


Fig. 3.5 Calibration of the Mass Spectrometer for Hydrogen and Deuterium

TABLE 3.6.

CALIBRATION OF THE MASS SPECTROMETER

Pressure of hydrogen in reaction vessel Nm^{-2}	Hydrogen peak height m	Pressure of deuterium in reaction vessel Nm^{-2}	Deuterium peak height m
38.13	2.575	43.66	2.200
32.58	2.375	28.00	1.420
32.58	2.275	23.20	1.200
28.80	1.775	20.00	0.920
23.20	1.475	14.67	0.750
11.20	0.975		
8.40	0.375		

to an accuracy of ± 13.3 Nm^{-2}, and since the pressure varied from 133 to 540 Nm^{-2} calculation showed that the error in reading the pressure varied from approximately ± 20% to ± 5%respectively. Thus, assuming that the gas expansion from the dosing volume to the reaction vessel can be carried out accurately, the pressure of the gas in the reaction vessel will be subject to an error varying from ± 20% for the lowest pressure used, to ± 5% for the highest pressure. The above argument assumes that there was no error in the volume measurements, or that there was no adsorption of the gas on the glass walls of the gas line during the expansions. This latter assumption is very unlikely and adsorption of the gas would, therefore, reduce the pressure from that calculated. The error in the volume calibrations has been estimated to be ± 5% ; thus the total error in the pressure of the gas in the reaction vessel has been estimated to vary from ± 25% for the lowest pressure used to ± 10% for the highest pressure. These error ranges have been shown on the calibration graph.

The calibration curve for hydrogen deuteride was assumed to lie equidistant between the calibration curves for hydrogen and deuterium. The validity of this assumption can be shown as follows.
If one takes a mixture of hydrogen and deuterium and exchanges it over a catalyst, at equilibrium the interconversion equilibrium equation predicts that

$$2HD \overset{K}{\rightleftharpoons} H_2 + D_2$$

$$\therefore \quad K \quad = \quad \frac{4[HD]^2}{[H_2][D_2]}.$$

Due to the isotope effect, if one uses equimolar quantities of hydrogen and deuterium $K \neq 4$. For the purpose of this argument it is assumed that $K = 3.9$. From Figure 3.5. at a pressure of 26.7 Nm^{-2}

$$[H_2] \; = \; 0.180 \text{ m} \; ; \quad [D_2] \; = \; 0.1305 \text{ m}$$

and substitution of these values gives $[HD] = 0.151$ m, compared with the value obtained from the graph of $[HD] = 0.1525$ m. This supports the assumption that the sensitivity of the mass spectrometer for hydrogen deuteride would lie equidistant between the sensitivities for hydrogen and deuterium.

The surface areas obtained by this method are given in Table 3.7. It is apparent that they are much lower than those obtained by the adsorption of krypton. This is due to the fact that this method gives the area which is available for the chemisorption of deuterium, which may not necessarily be the same as that available for the physical adsorption of krypton.

No attempt was made to estimate the error in the surface areas obtained by this method. It might be thought that one should use these

TABLE 3.7.

SURFACE AREAS OF PLATINUM FILMS

Type of film	Peak height of hydrogen deuteride produced mm	Surface area m^2	Average
unsintered	500	0.0385	
	570	0.0444	0.0428
	620	0.0454	
sintered	430	0.0284	
	370	0.0266	0.0262
	250	0.0237	

surface areas to convert the experimental rates into their absolute values. This was not done for a number of reasons:

(a) The large error inherent in the pressure measurements.

(b) The gases used may not have been 100% atom pure.

(c) The amount of hydrogen deuteride produced was very small, the accuracy of its measurement depending upon how accurately the background hydrogen deuteride could be measured.

3.2. Mass Spectral Analysis of the Isotopic Propanes

As has been mentioned in Part I section 3.3., for the satisfactory analysis of a mixture of isotopic molecules, several criteria must be obeyed:

(a) The product distribution obtained after the correction of an equilibrium mixture should be the same as that calculated from the appropriate binomial expansion.

(b) The interconversion equilibria must be obeyed. In general this is not quite true. However, the correlation between the observed and calculated interconversion equilibrium constants becomes better with increasing size of the paraffinic hydrocarbon. Thus the constants hold for hexane, but not for methane. It was assumed that in the case of propane, the correlation would be exact.

(c) After correction of the mass spectrum for natural isotopes and fragmentation the peaks at masses less than that of the parent molecule should disappear, as they can only arise from contributions due to the fragmentation of the molecules at higher masses.

Table 3.8. shows the effect of correcting the mass spectrum of an equilibrium mixture of isotopic propanes by a statistical treatment. This indicates that the contributions of the peaks at higher masses to those at lower masses, due to fragmentation, have been overestimated; indicating the inaccuracy of using the same set of fragmentation factors for both the carbon-hydrogen and carbon deuterium bond dissociations.

TABLE 3.8.

EQUILIBRIUM DISTRIBUTION OF ISOTOPIC PROPANES UTILIZING A STATISTICAL TREATMENT

Deuterium Content	d_{-2}	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Experimental Peak heights	132	47	135	236	305	274	592	923	984	639	336.0
Peak heights after isotopic and fragmentation corrections	-32.2	-0.7	-3.42	-68.2	-25.1	35.7	0.72	156.1	509.3	606.8	315.5
Percentage of isotopic species			-0.21	-4.2	-1.55	2.2	0.04	9.61	31.36	37.37	19.43
Binomial distribution with Ø = 659.93			0	0	0.05	0.52	3.05	11.48	27.05	36.41	21.44

It is known (121) that the carbon-deuterium bond strength is approximately 10% greater than that of the carbon-hydrogen bond. Thus under electron impact in the mass spectrometer there will be a tendency for the C-H bonds to be dissociated more easily than the C-D bonds. The presence of deuterium atoms in the molecule also has an enhancing effect upon the relative probability of losing hydrogen and deuterium atoms under electron impact. Thus as the number of deuterium atoms in the molecule increases, the easier it becomes to dissociate hydrogen atoms and conversely more difficult to dissociate deuterium atoms. These effects are apparent in the differences between the fragmentation patterns of C_3H_8 and C_3D_8 (83), and because the extent of fragmentation was large even for low electron energies, this variation between the mass spectra of C_3H_8 and C_3D_8 made it impossible to calculate the fragmentation corrections quantitatively by the statistical treatment used for the other hydrocarbons in this work.

To obtain an equivalent set of fragmentation factors describing carbon-deuterium bond dissociations, perdeuteropropane was prepared by repeated exchange of propane with deuterium over a tungsten film at 100°C. Table 3.9. shows the result obtained from this experiment. The perdeuteropropane prepared contained approximately

TABLE 3.9.

MASS SPECTRUM OF PERDEUTEROPROPANE AFTER ISOTOPIC CORRECTION

Deuterium content	d_{-4}	d_{-3}	d_{-2}	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Peak height	9.5	4.2	41.9	2.4	6.2	2.8	17.7	4.4	21.6	1.1	108	2.2	196.9

1% of C_3D_7H. The contributions that this would make to the d_6, d_4, d_2 and d_0 peaks would be negligible and so the fragmentation factors for C_3D_8 were calculated directly from the data in Table 3.9. The fragmentation factors for C_3H_8 and C_3D_8 are shown in Table 3.10. Due to the very large variation between these two sets of factors it was not surprising that overcorrection of the mass spectral data occurred when the results were calculated on a statistical basis. It was therefore necessary to evaluate a correction scheme which took into account the different probabilities of losing hydrogen and deuterium atoms from the deuterated molecules.

TABLE 3.10.

FRAGMENTATION FACTORS FOR C_3H_8 AND C_3D_8

Electron voltage V	Molecule X	f_0 $C_3X_8^+$	f_1 $C_3X_7^+$	f_2 $C_3X_6^+$	f_3 $C_3X_5^+$	f_4 $C_3X_4^+$	f_5 $C_3X_3^+$	f_6 $C_3X_2^+$
17	C_3H_8	1.000	1.1350	0.1695	0.393	0.0361	0.1665	0.0324
17	C_3D_8	1.000	0.781	0.1015	0.2385	0.064	0.127	0.0224

Two methods of measuring absolutely the fragmentation scheme were considered. It would be possible to correct the mass spectrum of an isotopic mixture if the mass spectrum of each of the deuterated species was known. Theoretically, each of the deuterated propanes could be prepared and their mass spectra measured. The difficulty with this is that the mass spectrum not only varies with deuterium content but also with the substitution position of the deuterium atoms in the molecule. Thus the mass spectrum of $CD_3CH_2CH_2D$ would not be expected to be the same as that of $CHD_2CD_2CH_3$. Effects of this nature would make the preparative and analytical problems almost insuperable.

It may be readily shown that if one uses a high resolution mass spectrometer, it would be possible to determine the parent ion content of the isotopic mixture absolutely. If the heights of the parent ions as determined by high resolution mass spectrometry, for example an MS903, are described by a_i for $i = 0$ to 8; and if the mass spectrum obtained from the low resolution MS10 used in this work is similarly described by b_i for $i = 0$ to 8, where i is the deuterium content of the molecule; then after natural isotope correction b_7 and b_8 will be fragment pure. By normalizing the two sets of spectra so that $b_8 = a_8$ the following scheme may be devised.

$$a_8=b_8$$

$$a_7=b_7$$

$$a_6=b_6-a_8f_2^{\,8}-a_7f_1^{\,7}$$

$$a_5=b_5-a_7f_2^{\,7}-a_6f_1^{\,6}$$

$$a_4=b_4-a_8f_4^{\,8}-a_7f_3^{\,7}-a_6f_2^{\,6}-a_5f_1^{\,5}$$

$$a_3=b_3-a_7f_4^{\,7}-a_6f_3^{\,6}-a_5f_2^{\,5}-a_4f_1^{\,4}$$

$$a_2=b_2-a_8f_6^{\,8}-a_7f_5^{\,7}-a_6f_4^{\,6}-a_5f_3^{\,5}-a_4f_2^{\,4}-a_3f_1^{\,3}$$

$$a_1=b_1-a_7f_6^{\,7}-a_6f_5^{\,6}-a_5f_4^{\,5}-a_4f_3^{\,4}-a_3f_2^{\,3}-a_2f_1^{\,2}$$

$$a_0=b_0-a_8f_8^{\,8}-a_6f_6^{\,6}-a_5f_5^{\,5}-a_4f_4^{\,4}-a_3f_3^{\,3}-a_2f_2^{\,2}-a_1f_1^{\,1}$$

etc.,

where $f_A^{\,B}$ refers to the fragmentation factor for the loss of A mass units from a molecule containing B deuterium atoms.

By using five mass spectral scans, for different extents of exchange, the various $f_A^{\,B}$ factors may be calculated. Both of these methods of analysing the data were not considered further due to the very involved nature of the work, and so a method of analysis using a general computer program was looked for.

If f_{1H}, f_{2H} etc. refer to the probability of losing one hydrogen and two hydrogens atoms etc. from the completely protonated species; and f_{1D} and f_{2D} etc. refer to the probability of removing one deuterium atom and two deuterium atoms etc. from the perdeuteropropane, then the first improvement applied to the purely statistical approach was to replace the f_{1H}, f_{2H} etc. terms by f_{1D}, f_{2D} etc. in cases where the particular fragmentation being corrected for involved only carbon-deuterium bond dissociation. For mixed fragmentation, i.e., fragmentation involving the loss of both hydrogen and deuterium atoms, the 'light' hydrocarbon factors were still used. The results of applying this treatment to the experimental data of Table 3.8. are shown in Table 3.11.

TABLE 3.11.

EQUILIBRIUM PRODUCT DISTRIBUTION OBTAINED BY SUBSTITUTION OF 'HEAVY' FACTORS FOR DEUTERIUM LOSS IN THE STATISTICAL METHOD

Deuterium content of molecule	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Peak height after correction	-18.9	-35.6	-63.7	31.1	0.27	24.8	312.3	620.9	606.8	315.5
Percentage of isotopic species		-1.86	-3.33	1.63	0.01	1.30	16.34	32.48	31.74	16.50
Binomial distribution with ϕ=639.27		0.00	0.01	0.12	0.94	4.65	14.80	29.43	33.44	16.63

Assuming that the hydrogen only and deuterium only fragmentations have been adequately corrected for, the persistently low value for d_4 as shown in Table 3.11. suggested that there was an overcorrection for the fragmentation involving the loss of one hydrogen atom and one deuterium atom from C_3D_7H. It would appear from these results that, for systems like propane where considerable fragmentation occurs, the mixed fragmentation corrections are sensitive to the type of fragmentation factors used; so incorporation of the 'heavy' propane factors into the mixed fragmentation correction terms appeared necessary.

Gault and Kemball (83) in their study of the exchange of propane with deuterium on palladium films devised a method of analysing the isotopic mixtures. They assumed:

(a) That the sensitivities of the parent peaks of the nine isomers C_3H_8 to C_3D_8 were equal.

(b) That the chance of fragmentation of each carbon-hydrogen or carbon-deuterium bond was independent of the nature of the other bonds in the molecule.

(c) That the formation of each fragment ion could be described by a successive dissociation of carbon-hydrogen bonds, selected on a statistical basis and multiplied by factors for the chance of each individual dissociation.

Let ${}^{m}_{n}A^{y}_{x}$ be the height of the peak corresponding to the fragment ion $C_3H_{x-n}D^{+}_{y-m}$ relative to the height of the parent ion $C_3H_xD_y{}^{+}$. Let the fragmentation pattern of C_3D_8 be described by

$$\alpha_i = f_i/f_{i-1}$$

where f_i represents the amount of the i th fragment and corresponding factors β_i apply to the fragmentation of C_3H_8. Then the general expression for the relative height of any fragment ion is given by

$${}^{m}_{n}A^{y}_{x} = \frac{x(x-1)--(x-n+1)y(y-1)---(y-m+1)}{(8)(7)\ ---\ (8-n-m+1)} \sum_{i \neq j < m+n+1} \overset{m\ \text{terms}}{\prod} \alpha_{1 \cdot\cdot i} \overset{n\ \text{terms}}{\prod} \beta_j$$

and this expression was used to calculate and hence to eliminate the contributions of fragment ions to the mass spectra of mixtures of isotopic propanes. The effect of this treatment upon an equilibrium mass spectrum is shown in Table 3.12. Comparison of Table 3.12. with Table 3.11. shows that the values of the corrected peak heights for d_5-d_8 are unchanged, because they are not dependent on mixed fragmentation corrections: The d_o to d_4 corrected peak heights are, however, dependent upon these mixed corrections and show increased values over the previous methods used.

TABLE 3.12.

CALCULATION OF THE EQUILIBRIUM PRODUCT DISTRIBUTION BY THE METHOD OF GAULT AND KEMBALL (83)

Deuterium content of the molecule	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Peak heights after correction	-6.73	-38.1	-48.8	58.4	7.0	30.5	313.3	620.9	606.8	315.5
Percentage of isotopic species		-1.95	-2.50	2.99	0.36	1.56	16.01	31.82	31.10	16.17
Binomial distribution with Ø = 631.26		0.0	0.01	0.15	1.15	5.37	16.08	30.07	32.14	15.03

The lack of improvement obtained for the isotopic analysis by using this method was disappointing, but it indicated that there must be an effect involved in the extensive fragmentation of isotopic propanes that had not yet been accounted for in the correction scheme. One of the assumptions made by Gault and Kemball (83) was that the chance of fragmentation of each carbon-hydrogen or carbon-deuterium bond was independent of the nature of the other bonds in the molecule. This assumption is not quite true because as mentioned earlier the carbon-deuterium bond dissociation energy is 10% greater than that of the carbon-hydrogen bond (121). It therefore seemed appropriate to develop a scheme where this effect would be taken into account.

Evans et al. (122) developed a quantitative description of the differing probabilities for the loss of hydrogen or deuterium atoms from a molecule, in terms of the π and Γ factors given below.

$$\pi = \frac{\text{probability of deuterium leaving } CH_3D}{\text{Probability of an individual hydrogen leaving } CH_3D}$$

$$\Gamma = \frac{\text{Probability of individual hydrogen leaving } CH_3D}{\text{Probability of individual hydrogen leaving } CH_4} .$$

These definitions have since been modified so that the π factor is the measure of the probability of removing a deuterium atom from a partially deuterated molecule as compared to the probability of removing a hydrogen atom from the completely protonated isomer.

The π and Γ factors defined above refer to the probability of losing one hydrogen or deuterium atom from the monodeuterated species. Schissler et al. (123), however, painted out that as the number of deuterium atoms in the molecule increased there was a tendency for Γ to increase. It has also been found (124, 125) that the probability of removing a hydrogen atom from the deuteroethylenes relative to the probability in C_2H_4 increased progressively with the number of deuterium atoms in the molecule; similarly the probability of removing a deuterium atom was less than that of removing a hydrogen atom from C_2H_4 and decreased with the number of hydrogen atoms in the molecule. For the ethylenes the probability of removing a deuterium atom is 0.90 in perdeuteroethylene and is very nearly equal to the a priori probability times $(0.90)^2$, $(0.90)^3$ and $(0.90)^4$ in molecules containing 1,2 and 3 hydrogen atoms. The probability of removing one hydrogen atom is equal to the a priori probability times 1.10, $(1.10)^2$ and $(1.10)^3$ for molecules containing 1, 2 and 3 deuterium atoms. Since the factors 1.10 and 0.90 are nearly reciprocal, all the factors could be represented by positive and negative powers of the constant 1.10. The relative probability, $R_{l,m,n}$ of removing l hydrogen atoms and m deuterium atoms from an ethylene molecule $C_2H_{4-n}D_n$ as compared with the probability of removing hydrogen from C_2H_4 is given by

$$R_{l,m,n} = A_{l,m,n} \; K^{[ln+m(n-5)]}$$

where $A_{l,m,n}$ is the *a priori* probability and K = 1.10 for ethylene.

For the propanes it was hoped that an equation of this form could be used for analysing the isotopic mixture. By writing a computer program utilizing

$$R_{l,m,n} = A_{l,m,n} \; K^{[ln+m(n-9)]} \qquad 3.1.$$

Where $R_{l,m,n}$ is the relative probability of removing l hydrogen atoms and m deuterium atoms from a propane molecule $C_3H_{8-n}D_n$ as compared with the probability of removing hydrogen from C_3H_8 and by varying the value of K used to calculate the equilibrium distribution from the data in Table 3.8. it was hoped to find the best value of K which gave an adequate analysis of the experimental data. The results obtained are shown in Table 3.13. Assuming that the terms allowing for loss of hydrogen or deuterium atoms only are correct, the changing values of the peak heights d_0-d_4 with increasing K must be due to inaccuracies in the mixed fragmentation terms.

Amenomiya and Pottie (126), however, showed that for the deuteroethanes, the weighting factors a_n for the loss of hydrogen from a molecule containing n deuterium atoms could be expressed as a power series

$$a_n = 1.095^n$$

TABLE 3.13.

VARIATION OF THE EQUILIBRIUM PRODUCT DISTRIBUTION WITH PARAMETER K

Parameter	Deuterium content of the isotopic molecules												
K	d_{-4}	d_{-3}	d_{-2}	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1.00	14.51	-14.33	-21.92	- 3.24	-10.20	-61.14	-14.76	16.50	-8.93	175.12	521.34	603.03	313.10
1.01	16.00	- 8.51	-19.80	- 1.70	- 4.02	-54.56	-16.66	20.71	-0.02	178.49	518.76	603.03	313.10
1.02	17.13	- 3.74	-17.90	- 1.30	0.68	-47.38	-20.25	20.03	8.44	181.31	515.75	603.03	313.10
1.03	18.00	- 0.77	-16.82	- 4.84	4.95	-40.71	-23.69	19.28	16.47	183.61	512.29	603.03	313.10
1.04	18.80	2.00	-15.82	- 7.92	8.83	-34.51	-27.01	18.44	24.10	185.41	508.36	603.03	313.10
1.05	19.54	4.59	-14.91	-10.58	12.35	-28.74	-30.23	17.47	31.33	186.76	503.94	603.03	313.10
1.06	20.23	7.02	-14.08	-12.86	15.55	-23.35	-33.37	16.35	38.18	187.70	499.02	603.03	313.10
1.07	20.27	9.30	-13.34	-14.80	18.45	-18.33	-36.43	15.06	44.65	188.28	493.57	603.03	313.10
1.08	21.48	11.45	-12.67	-16.43	21.09	-13.64	-39.42	13.57	50.74	188.55	487.58	603.03	313.10
1.09	22.06	13.49	-12.07	-17.80	23.50	- 9.27	-42.36	11.89	56.44	188.57	481.01	603.03	313.10
1.10	22.61	15.42	-11.54	-18.92	25.70	- 5.20	-45.24	10.02	61.73	188.40	473.86	603.03	313.10
1.11	23.14	17.25	-11.08	-19.85	27.73	- 1.43	-48.10	7.97	66.59	188.12	466.09	603.03	313.10
1.12	23.50	19.63	-11.03	-18.63	27.41	2.05	-50.94	5.80	70.98	187.80	457.69	603.03	313.10
1.13	23.75	22.31	-11.27	-16.13	25.69	5.22	-53.82	3.55	74.82	187.53	448.61	603.03	313.10
1.14	23.98	24.84	-11.55	-13.77	24.15	8.09	-56.81	1.30	78.05	187.42	438.85	603.03	313.10
1.15	24.16	27.14	-11.84	-11.79	22.88	10.35	-60.87	-0.83	80.57	187.37	428.37	603.03	313.10
1.16	24.30	29.19	-12.12	-10.27	21.89	11.93	-66.43	-2.69	82.26	188.10	417.14	603.03	313.10
1.17	24.44	31.10	-12.42	- 8.93	21.11	13.28	-72.12	-4.09	82.96	189.15	405.13	603.03	313.10
1.18	24.58	32.88	-12.74	- 7.80	20.51	14.43	-77.91	-4.76	82.47	190.85	392.32	603.03	313.10
1.19	24.73	34.55	-13.09	- 6.90	20.31	15.46	-83.72	-4.40	80.59	193.37	378.66	603.03	313.10
1.20	24.87	36.14	-13.46	- 6.23	20.30	16.47	-89.49	-2.58	77.02	196.89	364.13	603.03	313.10

and, similarly that the weighting factors b_m, for the loss of a deuterium atom from a molecule containing m hydrogen atoms could also be expressed as a power series

$$b_m = 0.910^m.$$

Since the mass spectral analysis of the deuteroethanes can be adequately explained by a geometric power series, it would be interesting to look at equation 3.1. in greater detail to see why it does not explain the mass spectra of the deuteropropanes. For an adequate analysis of the mass spectrum, equation 3.1. must explain:

(a) The fragmentation pattern of C_3H_8.

(b) The fragmentation pattern of C_3D_8.

(c) The increased probability of losing hydrogen atoms and the decreased probability of losing deuterium atoms from a partially deuterated molecule.

If f_{iH} and f_{iD} for i = 1 to 6 are the fragmentation factors of propane and perdeuteropropane respectively, then from equation 3.1. the fragmentation pattern of propane is given by

$$R_{l,m,n} = A_{l,m,n} K^o.$$

Since $R_{l,m,n}$ for l = 1 to 6 and m=n=o equals f_{iH}/f_{yH} for y=i=1 to 6 and $A_{l,m,n}$ equals 1 for l = 1 to 6 and m=n=o, then criterion (a) must hold. For perdeuteropropane equation 3.1. becomes

$$R_{l,m,n} = A_{l,m,n} K^{-m}$$

and since $A_{l,m,n}$ is the a priori probability, that is 1 for i=1 to 6 and m=n=o then $R_{o,1,8}$ only equals K^{-1} for K equal to 1.455. Calculation has shown that

$$R_{1,m,n} \neq A_{1,m,n} (1.455)^{-m} \text{ for } m = 2 \text{ to } 6,$$

therefore criterion (b) does not hold.

It is rather difficult to decide whether criterion (c) is or is not adequately satisfied by equation 3.1. If we take the case of $C_3H_3D_5$, for the loss of one hydrogen atom equation 3.1. gives

$$R_{1,m,n} = 3/8\ K^{5} = f_x/f_{1H} \qquad 3.2.$$

where f_x is the probability of losing one hydrogen atom from $C_3H_3D_5$.

For the loss of one deuterium atom

$$R_{1,m,n} = 5/8\ K^{-4} = f_R/f_{1H} \qquad 3.3.$$

where f_R is the probability of losing one deuterium atom from $C_3H_3D_5$, and for the loss of one hydrogen deuteride molecule

$$R_{1,m,n} = 2.3/8.5/7.\ K^{1} = f_{xR}/f_{2H} \qquad 3.4.$$

where f_{XR} is the probability of losing one HD molecule from $C_3H_3D_5$.

It is likely that equation 3.2. would be obeyed since it has been based upon the fragmentation factor for the loss of a hydrogen atom from the completely protonated isomer. Equations 3.3. and 3.4., however, which involve the loss of deuterium from the molecule are not based upon the fragmentation factors for the loss of deuterium atoms but upon the fragmentation factors for the loss of hydrogen atoms from the completely protonated isomer. It is therefore unlikely that any of the fragmentations involving deuterium atoms have been adequately corrected for.

The scheme that was finally evolved for correction of the mass spectra of the isotopic propanes may be regarded as a combination of the methods of Gault and Kemball (83) and Dibeler et al. (124). In this final form, however, the Dibeler approach has been extended to include the use of deuterium fragmentation factors based upon the mass spectrum of perdeuteropropane *. Table 3.14. column 2 shows the peak heights for the experimental (natural isotope corrected) amounts of the isotopic propanes d_5 to d_8. Using the values of the d_7 and d_8 peaks shown, along with the interconversion equilibrium constants, the peak heights expected for the d_5 to d_8 compounds, after allowance for fragmentation may be calculated. These values are shown in Table 3.14. column 3.

In terms of fragmentation corrections

$$d_{6\text{calc.}} = d_{6\text{expt.}} - d_8.f_{1D}^{d8} - d_7.f_{1H}^{d7}$$

where f_A^B is the fragmentation factor for the loss of A atoms of hydrogen or deuterium from a molecule containing B deuterium or hydrogen atoms.

TABLE 3.14.

Deuterium content	Experimental peak heights	Expected value for corrected peak height
d_8	315.50	315.50
d_7	606.81	606.81
d_6	953.43	510.70
d_5	903.19	245.60

$$\therefore \quad f_{1H}^{d7} = \frac{d6\text{expt.} - d6\text{calc.} - d8\, f_{1D}^{d8}}{d_7},$$

substitution of the relevant values gives

$$f_{1H}^{d7} = 0.3234.$$

---

* Thanks are due to Mr. R.S. Dowie who derived this section of the work.

Previous methods of analysis would have given the result as

$$f^{d7}_{1H} = \frac{1}{8} f^{H8}_{1H} = 0.1419.$$

Thus the presence of the deuterium atoms in C_3D_7H enhances the fragmentation of the hydrogen atom by a factor of 2.279. In keeping with the ideas of Amenomiya and Pottie (126)

$$a_7 = (1.125)^7.$$

Table 3.15. gives the values for the fragmentation factors for the loss of one hydrogen atom from each of the isotopic propanes.

Similarly

$$d_{5calc} = d_{5expt.} - d_7 f^{d7}_{1D} - d_6 f^{d6}_{1H}$$

$$\therefore f^{d7}_{1D} = \frac{d_5 \text{ expt} - d_5 \text{ calc} - d_6 f^{D6}_{1H}}{d_7}.$$

Substitution of the relevant values gives

$$f^{d7}_{1D} = 0.5998.$$

Previous methods would have given the result as

$$f^{d7}_{1D} = \frac{7}{8} f^{d8}_{1D} = 0.6834.$$

So the secondary fragmentation effect has in this case reduced the extent of fragmentation of a deuterium atom from C_3D_7H by a factor of 0.8776.

$$\therefore b_m = (0.8776)^m$$

The corresponding factors for the loss of a deuterium atom from each of the deuterated propanes are shown in Table 3.16.

TABLE 3.15.

FRAGMENTATION FACTORS FOR THE LOSS OF ONE HYDROGEN ATOM FROM THE DEUTERATED MOLECULES

Deuterium number	Fragmentation correction factor	f_A^B
d_8	0	$f_{1H}^{d_8}$
d_7	$1/8 \cdot f_{1H}^{H8} \cdot (1.125)^7$	$f_{1H}^{d_7}$
d_6	$2/8 \cdot f_{1H}^{H8} \cdot (1.125)^6$	$f_{1H}^{d_6}$
d_5	$3/8 \cdot f_{1H}^{H8} \cdot (1.125)^5$	$f_{1H}^{d_5}$
d_4	$1/2 \cdot f_{1H}^{H8} \cdot (1.125)^4$	$f_{1H}^{d_4}$
d_3	$5/8 \cdot f_{1H}^{H8} \cdot (1.125)^3$	$f_{1H}^{d_3}$
d_2	$6/8 \cdot f_{1H}^{H8} \cdot (1.125)^2$	$f_{1H}^{d_2}$
d_1	$7/8 \cdot f_{1H}^{H8} \cdot (1.125)^1$	$f_{1H}^{d_1}$
d_0	$8/8 \cdot f_{1H}^{H8} \cdot (1.125)^0$	$f_{1H}^{d_0}$

TABLE 3.16.

FRAGMENTATION FACTORS FOR THE LOSS OF ONE DEUTERIUM ATOM FROM THE DEUTERATED MOLECULES

Deuterium number	Fragmentation correction factor	f_A^B
d_8	$8/8 \cdot f_{1D}^{d8} \cdot (0.8776)^0$	f_{1D}^{d8}
d_7	$7/8 \cdot f_{1D}^{d8} \cdot (0.8776)^1$	f_{1D}^{d7}
d_6	$6/8 \cdot f_{1D}^{d8} \cdot (0.8776)^2$	f_{1D}^{d6}
d_5	$5/8 \cdot f_{1D}^{d8} \cdot (0.8776)^3$	f_{1D}^{d5}
d_4	$4/8 \cdot f_{1D}^{d8} \cdot (0.8776)^4$	f_{1D}^{d4}
d_3	$3/8 \cdot f_{1D}^{d8} \cdot (0.8776)^5$	f_{1D}^{d3}
d_2	$2/8 \cdot f_{1D}^{d8} \cdot (0.8776)^6$	f_{1D}^{d2}
d_1	$1/8 \cdot f_{1D}^{d8} \cdot (0.8776)^7$	f_{1D}^{d1}
d_o	0	f_{1D}^{do}

If we redefine

$$\pi = \frac{\text{Probability of one deuterium leaving } C_3D_7H}{\text{Statistical probability of one deuterium leaving } C_3HD_7}$$

and

$$\Gamma = \frac{\text{Probability of one hydrogen leaving } C_3H_7D}{\text{Statistical probability of one hydrogen leaving } C_3H_7D}$$

then, $\pi = 0.8776$ and $\Gamma = 1.125$, and $\pi \approx 1/\Gamma$.

Examples of same correction terms are given below

For an isotopic propane containing L deuterium atoms, the correction term for the loss of one hydrogen atom is

$$T = (8-L)/8 \cdot A\ (1) \cdot ZH,$$

where $ZH = \Gamma^{L}$ and A (1) is the appropriate Gault and Kemball expression; similarly for the loss of one deuterium atom

$$T = L/8 \cdot B\ (1) \cdot ZD,$$

where $ZD = (\pi)^{8-L}$ and B (1) is the appropriate Gault and Kemball expression. If A refers to the Gault and Kemball expression for the case under consideration, then for the loss of x hydrogen atoms from a molecule containing L deuterium atoms

$$T = A \cdot (ZH)^{x}, \text{ where } ZH = (\Gamma)^{L},$$

and for the loss of y deuterium atoms

$$T = A\ (ZD)^{y} \text{ where } ZD = (\pi)^{8-L}$$

In the cases where both hydrogen and deuterium atoms are lost from the isotopic molecule this mixed fragmentation term is obtained by regarding the loss of the hydrogens and deuteriums as being two distinct occurrences.

The total probability will then be the product of these separate probabilities. Thus for a molecule containing L deuterium atoms, the correction factor for the loss of x hydrogen atoms and y deuterium atoms is given by

$$T = A\,(ZH)^{x}\,(ZD)^{y}.$$

This correction scheme was applied to the equilibrium isotopic propane data of Table 3.8., with the result shown in Table 3.17.

TABLE 3.17.

EQUILIBRIUM PRODUCT DISTRIBUTION OF ISOTOPIC PROPANES

Deuterium content	d_{-3}	d_{-2}	d_{-1}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Corrected peak heights	40.31	22.45	-12.96	-13.47	-3.45	-40.21	15.40	75.19	243.35	516.7	606.81	315.50
Percentage of isotopic species				-0.76	-0.19	-2.27	0.87	4.24	13.74	29.14	34.22	17.79
Binomial distribution with φ = 64.98				0.00	0.01	0.10	0.80	4.17	13.88	28.87	34.32	17.85

$\pi = 0.8929; \quad \Gamma = 1.1200$

The correlation between the observed and calculated equilibrium distributions is excellent for the isotopic propanes d_3-d_8. Although the d_2 corrected peak is still quite negative, it does not devalue the results greatly, since negative peaks are not included in the calculation of the percentages of the isotopic species. Thus with respect to the latter the d_2 peak is regarded as zero, which is more or less the value given for the d_2 species by the binomial distribution.

The scheme which has been developed for the analysis of the isotopic propanes is a very flexible one. In general, the values of

π and Γ to be used are determined from the experimental equilibrium mass spectrum after isotopic correction. If the 'equilibrium' mass spectrum used to calculate π and Γ is not in fact an equilibrium mixture of isotopic propanes, then little correlation will be found between the experimental distribution of propanes after correction, and that calculated from the binomial expression. It also follows from the correction scheme that π must be $\leqslant 1$ and Γ must be $\geqslant 1$. The values of π and Γ also depend upon the mass spectrometric conditions but should be constant for any series of related propane and perdeuteropropane fragmentation patterns.

Although it has been shown that for adequate analysis of the isotopic propanes the extended Gault and Kemball-Dibeler treatment is necessary, in cases where the extent of fragmentation is low and the differences between the 'light' hydrocarbon and perdeutero hydrocarbon fragmentation patterns are small, the fully extended scheme may not be required. Thus the analysis of a mixture of isotopic isomeric butenes can be adequately analysed by the Gault and Kemball treatment (127).

The computer program used for the analysis of the isotopic propanes is given in Appendix II.

3.3. The Exchange of Propane with Deuterium

At temperatures greater than 40°C the exchange of propane with deuterium on unsintered platinum films proceeded at a readily measurable rate. The rates of exchange k_o and k_ϕ, which were calculated from plots of the apparent first order equations 3.12. and 3.14., were converted into their absolute values by assuming that the surface areas of the films, as measured by krypton adsorption, were independent of their weight. Figure 3.6. shows two typical rate plots obtained for the incorporation of deuterium into the molecule; and

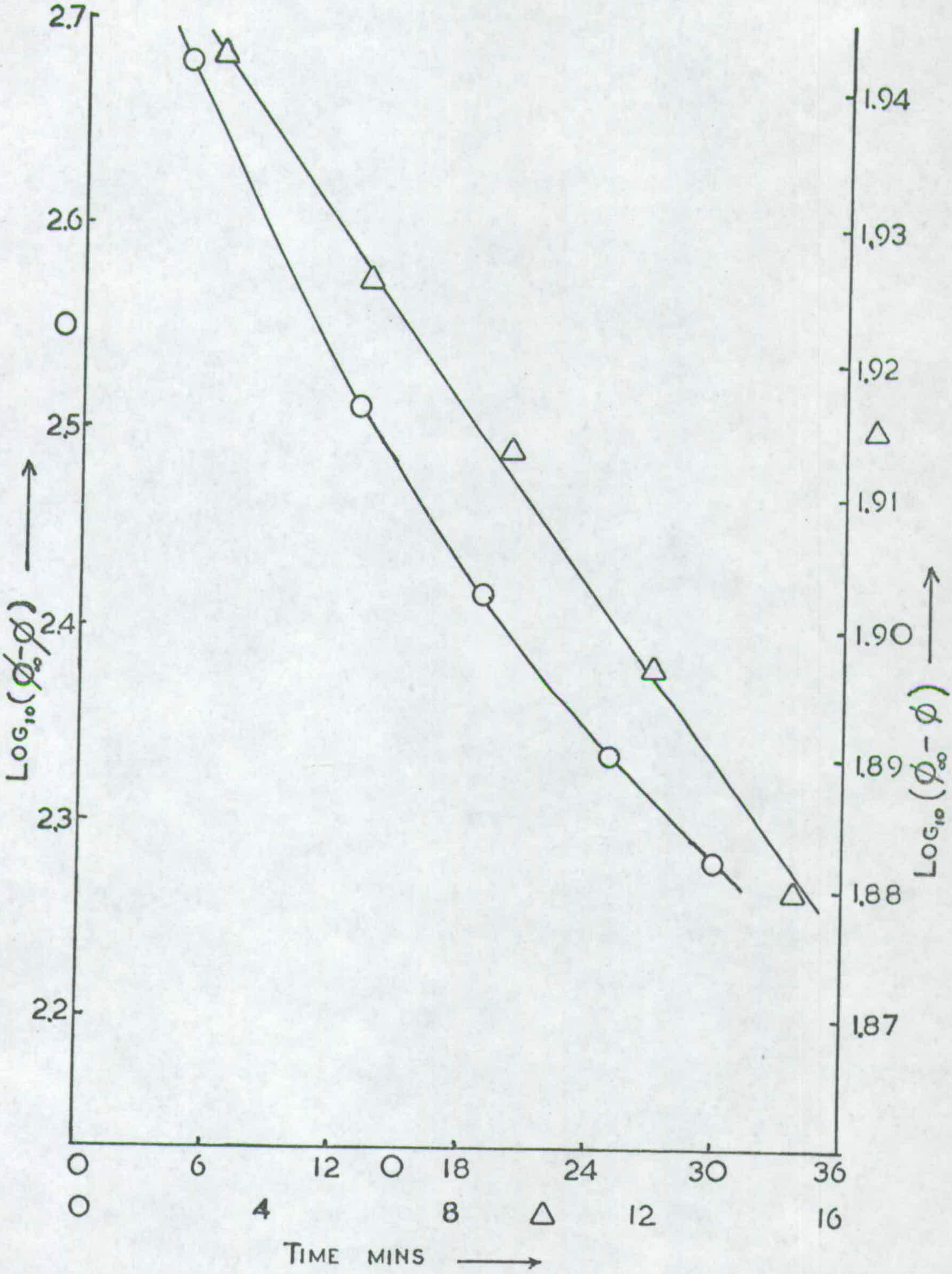


FIG. 3.6 φ Plots for the Exchange of Propane

○ Reaction at 76°C

△ Reaction at 144°C

the rates of exchange and the type of rate plots obtained are summarized in Table 3.18. All the rates quoted, apart from those for the reaction at 76°C, were obtained from a single experiment by admitting the reaction mixture to the film at 0°C and then progressively increasing the reaction temperature. In the case of the reaction at 76°C, the reaction mixture was admitted to the film at 0°C and the temperature then rapidly increased to this temperature.

The shapes of the rate plots could be divided into two groups:

(a) That containing straight line rate plots, i.e., the reaction obeyed apparent first order kinetics.

and (b) That containing curved rate plots, indicating that the reaction was slowing down with time.

This retarded curvature occurred at reaction temperatures of 76°C and 118°C; above and below these temperatures straight line rate plots were obtained. This curvature, which was tentatively ascribed to progressive sintering of the film and not to progressive self poisoning of the surface during the reaction, will be discussed fully later.

TABLE 3.18.

EXCHANGE OF PROPANE WITH DEUTERIUM ON UNSINTERED PLATINUM FILMS

Run No.	Reaction temperature °C	Rate of reaction mols $s^{-1}m^{-2}$. 10^{-16}		M= $\frac{k_\varphi}{k_0}$	Type of rate plot		Carbon count †
		k_φ	k_0		$\log(\varphi_\infty - \varphi)$	$\log \delta_0$ *	
4	39	1.596	0.284	5.61	S	S	C
	118	46.13→16.24	7.43→2.68	6.2→6.05	CR	CR	C
	114	17.59	5.331	3.30	S	S	C
	172	20.87	4.311	4.84	S	S	C
	191	11.71	8.00	1.46	S	S	C
1	76	55.3→26.25	7.84→4.62	7.05→5.68	CR	CR	C

* S:- strgight line apparent first order plot

CR:- curved rate plot; reaction slowing down

† C:- constant carbon balance

The constancy of the carbon balance at any temperature indicated that little progressive loss of 'propane' was occurring either by poisoning or hydrocracking. It may also be shown that, apart from the small quantity which was leaking into the mass spectrometer, no 'propane' was being lost from the system over the duration of the experiment.

For a closed system the pressure of the propane is proportional to the absolute temperature; and the total carbon count determined mass spectrometrically is proportional to the total pressure of the isotopic propanes in the reaction vessel. Therefore, the carbon count will be proportional to the absolute temperature. If the amount of gas adsorbed on the surface at the lowest temperature used in the experiment remains constant as the temperature is increased, then any deviation of the experimental carbon balance from that calculated on the basis of the gas laws, must be due to either desorption of 'propane' from the surface of the film, or further adsorption of 'propane' in some form upon the surface. Figure 3.7., which was obtained by applying the above argument to the data of experiment 4, shows that 'propane' was desorbed from the film surface upon increasing the reaction temperature.

The Arrhenius equation plot for the rate of disappearance of the 'light' propane shown in Figure 3.8., also includes the results that were obtained by Addy and Bond (128) for the exchange of propane with deuterium on a 5% platinum-pumice catalyst. They (128) did not, however, give any indication of the surface area of the platinum on the catalyst; nor did they give any details about the volume of their reaction vessel system. Their experimental rates were, therefore, converted into absolute units by assuming a value of 210 ml for the volume of the reaction vessel system; and using a value of 11.67 m^2g^{-1} for the surface area of the platinum, which was calculated by the same

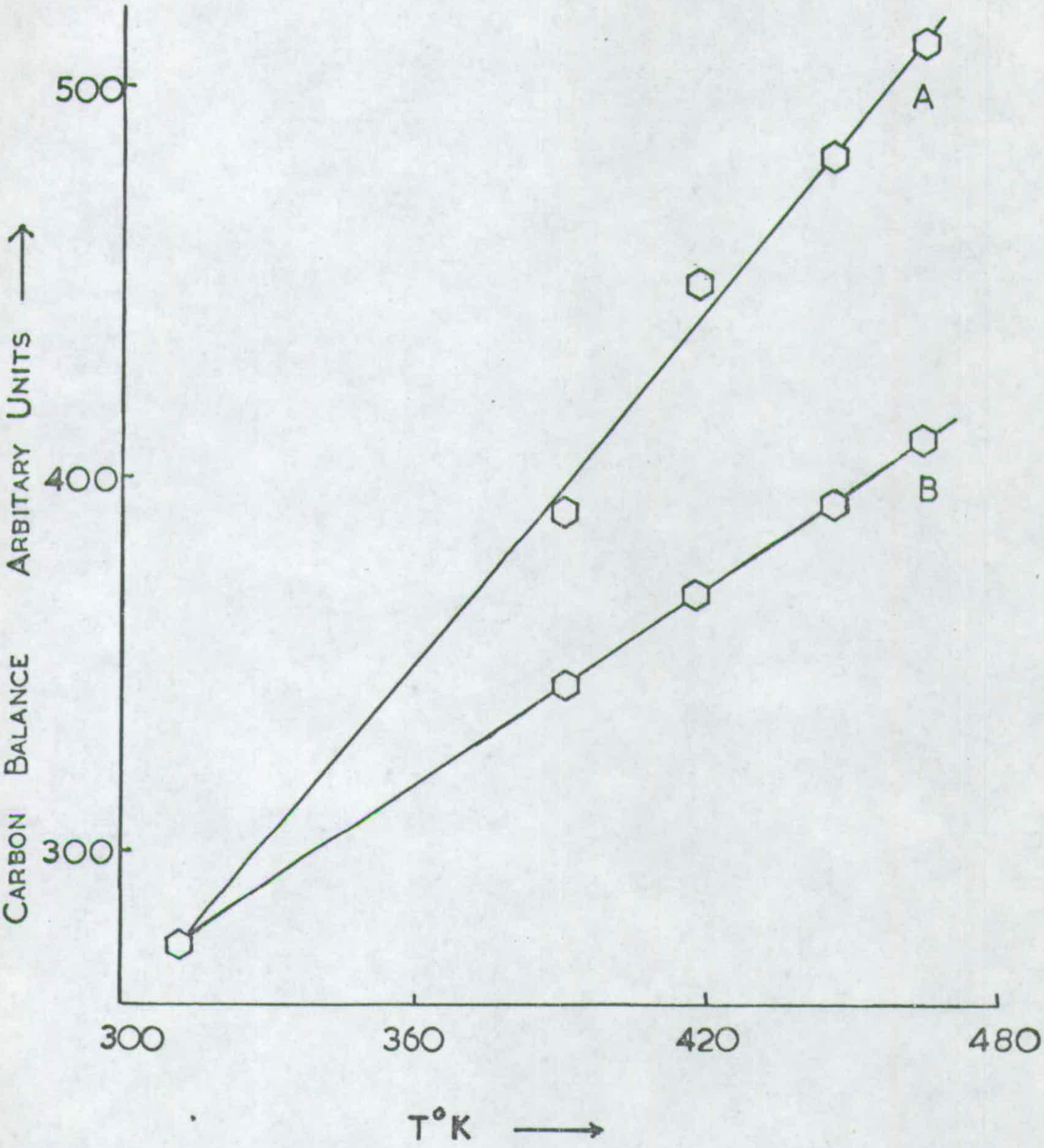


Fig. 3.7 Plot of Carbon Balance against the Absolute Temperature for the Exchange of Propane with Deuterium

A Experimental Results

B Calculated from the Gas Laws

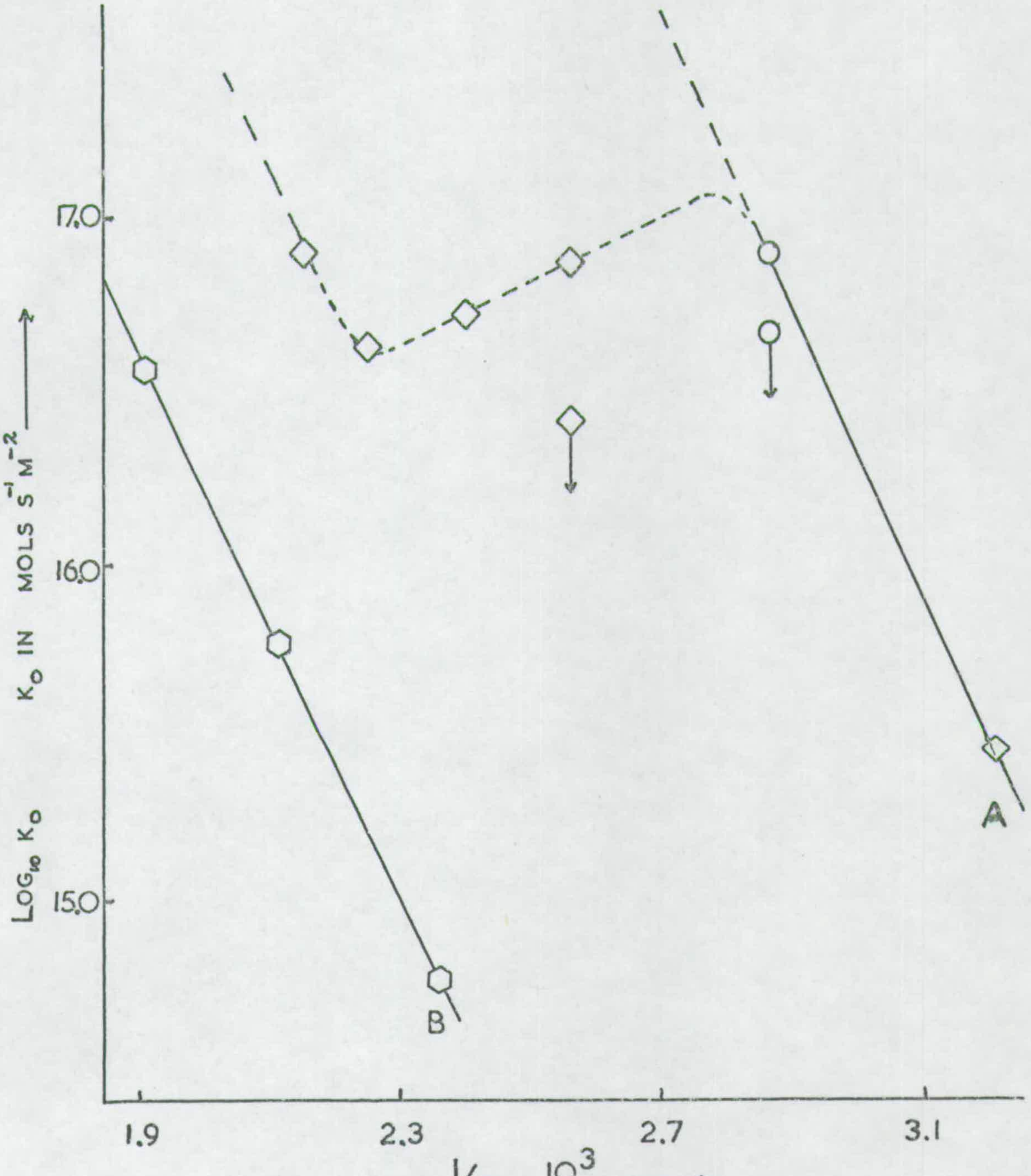


FIG. 3.8 ARRHENIUS PLOTS FOR THE EXCHANGE OF PROPANE WITH DEUTERIUM ON PLATINUM CATALYSTS

A ON UNSINTERED FILMS, symbols refer to different experiments

B ON 5% PLATINUM – PUMICE (128)

method used to estimate the surface area of the platinum on the platinum γ-alumina catalyst. These assumptions will produce a degree of uncertainty in the relative position of the Arrhenius equation plot for their results. It is considered, however, that the rates will not be affected by more than a factor of ± 3.

On the unsintered films the exchange reaction did not obey the Arrhenius equation over the complete range of temperature. The rates of exchange k_o and k_ϕ at 39°C and 76°C were, since these were the initial reaction temperatures used in the experiments, judged to be the ones least liable to have been affected by changes in the nature of the films. The activation energy (E_O = 81.34 k J $mole^{-1}$) and pre-exponential factor ($\log_{10} A = 29.07$; A in mols $s^{-1}m^{-2}$) were, therefore, calculated from the line drawn through these two points. At temperatures greater than 80°C deviation from the Arrhenius equation was observed, the apparent activation energy tending to a negative value. Above this temperature the M values were less than those obtained initially, i.e., the rate of incorporation of deuterium into the 'propane' was being affected to a greater extent than the rate of disappearance of the 'light' propane.

From Figure 3.9. which shows the course of a typical reaction with time, and Table 3.19. which gives the initial product distributions for the exchange reaction, it is apparent that all eight hydrogen atoms were readily exchangeable and that all possible isotopic propanes were produced in substantial amounts initially. This coupled with the fact that the M values were greater than one indicated that the molecule was undergoing extensive multiple exchange. The initial product distributions obtained, which showed maxima in one case at the d_2, d_4 and d_8 deuteropropanes and in the other at the d_3 and d_8 deuteropropanes, did not vary much with temperature, although the M values did increase with

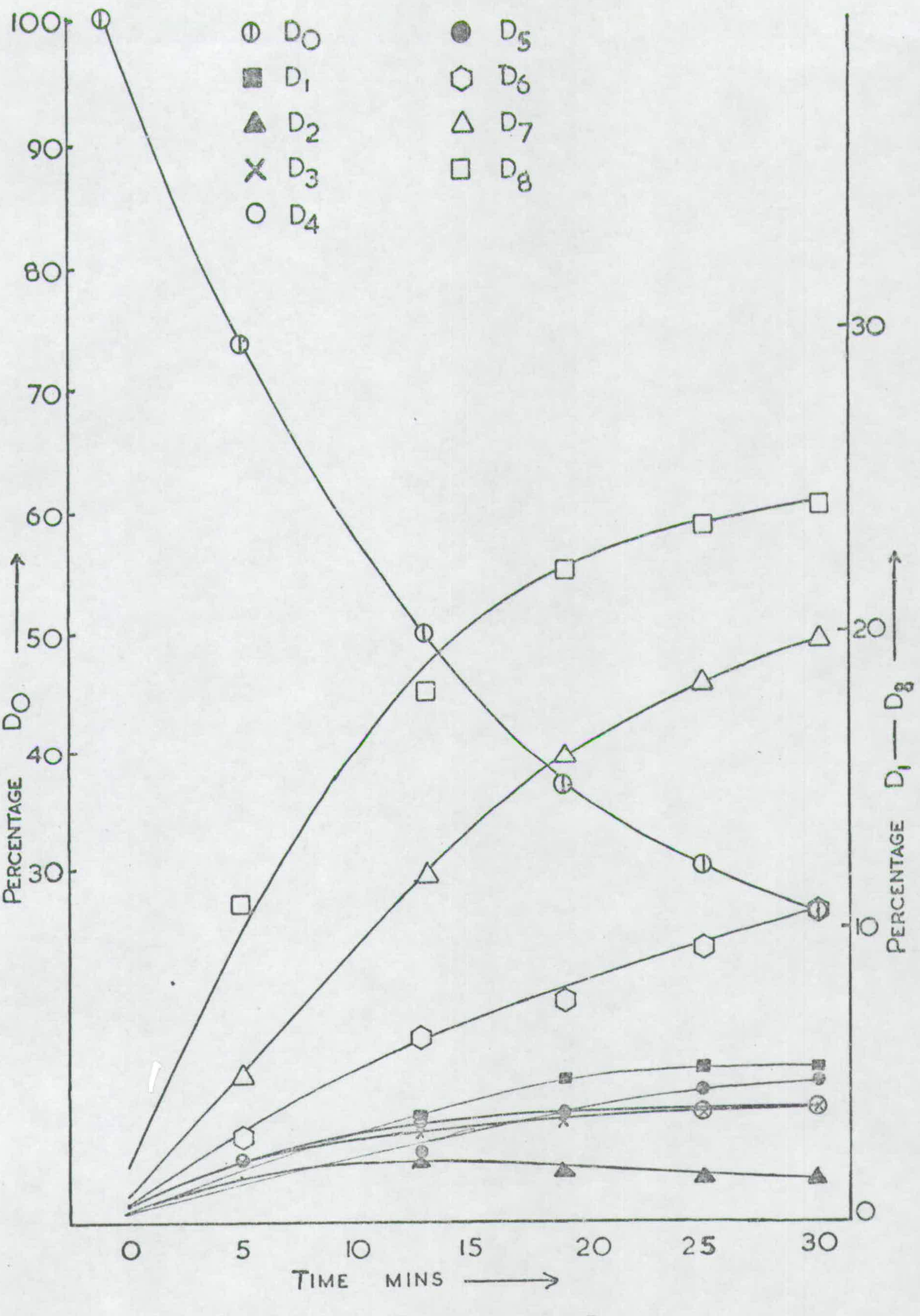


Fig. 3.9 Exchange of Propane with Deuterium at 76°C on an Unsintered Platinum Film

TABLE 3.19.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF PROPANE WITH DEUTERIUM

	Catalyst	T°C	Percentage deuterium content								$M = \frac{k_\phi}{k_0}$	$M = \frac{\sum nd_n}{100}$
			d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
	film	39	5.5	12.8	5.8	14.5	3.8	7.3	17.4	33.0	5.61	5.55
	film	76	6.5	8.5	11.5	8.0	5.5	12.0	17.0	31.0	7.05 -5.68	5.57
(128)	5% Pt-pumice	100	11.8	14.6	14.4	12.7	9.1	8.0	12.8	16.6	-	4.51
	"	150	20.9	12.5	13	8.8	7.4	7.6	11.7	18.1	-	4.29
	"	200	18.0	7.7	7.9	9.1	7.4	6.9	13.8	29.2	-	5.02
	"	250	17.0	5.7	7.2	10.5	8.0	6.3	13.3	32.0	-	5.19
(129)	"	200	17.7	8.4	6.2	6.5	7.8	9.7	13.7	30.0	-	5.12

temperature up to 118°C. Although these isotopic distributions agreed quite well with those obtained by Addy and Bond (128), the large maximum which they found for the monodeuteropropane was not observed for the reaction on the films. However, when the fragmentation corrections were applied to the results by the method of Gault and Kemball (83) the initial product distribution for the exchange reaction at 39°C did show a large maximum at the monodeuteropropane. It is thus possible that the correction scheme used by Addy and Bond (128) did not provide an adequate analysis of the data and so some doubt must be cast upon the accuracy of their initial product distributions.

3.4. The Exchange of Butane with Deuterium

The exchange reaction of butane with deuterium was studied on sintered and unsintered films, the weights of which varied from 7.25 to 11.50 mg. At temperatures greater than 30°C butane exchanged readily on the unsintered films; however, presintering the films at 250°C in vacuo for 1 hr necessitated reaction temperatures greater than 110°C to give readily measurable rates of exchange. The nature of the rate plots and the rates of reaction obtained are summarized in Table 3.20.

TABLE 3.20.

THE EXCHANGE OF BUTANE WITH DEUTERIUM
ON PLATINUM FILMS

Catalyst conditions	Temp. °C	Rates of reaction mols $s^{-1}m^{-2}$. 10^{-16}		Type of rate plot obtained*		$M=\frac{k_\phi}{k_o}$	Carbon† count
		k_ϕ	k_o	$\log_{10}(\phi_\infty-\phi)$	$\log_{10}d_o$		
unsintered	38	5.00	1.03	VSCR	VSCR	4.85	C
"	48	17.15	2.62	VSCR	VSCR	6.55	C
"	61	37.87	5.80	VSCR	VSCR	6.54	C
"	73	103.70	12.14	S	S	8.54	C
sintered at	116	25.74	3.75	S	S	6.9	C
250°C in	120	37.96	6.16	S	S	6.15	C
vacuo for	148	212.60	27.98	S	S	7.67	C
1 hr	162	149.0	19.22	S	S	7.76	C
"	196	355.8	76.38	S	S	4.65	C

* VSCR :- very slightly curved, i.e. a retarded reaction

S :- straight line rate plot, i.e. the reaction obeyed apparent first order kinetics

† C :- Carbon balance constant

The shapes of the rate plots were similar to those that had been obtained for the exchange of propane with deuterium. For the exchange reaction on unsintered films a slight retarded curvature of the plots was generally observed; but when using presintered films this curvature was no longer apparent, the reaction obeying apparent first order kinetics.

In all cases, for the reaction at any temperature, a constant carbon balance was observed. The criterion for this constancy was based upon there being less than a 5% change in the total carbon count for the isotopic butanes during the course of the reaction at any temperature. Within this constancy limit, however, a certain degree of variability was observed. In some cases the carbon count was found to either increase or decrease slightly with time, and in others the behaviour was variable. No overall trend in the behaviour of the carbon count was apparent.

Figure 3.10. which shows the Arrhenius plots for the rate of disappearance of the 'light' butane, also includes the results that were obtained by Anderson and Avery (42) for the hydrocracking and isomerization of butane on sintered platinum films. It is apparent that, even after allowance for the decrease in the apparent surface area of the films upon sintering, there was still a considerable difference in activity for the exchange reaction between the two types of films; and that the activity of the sintered films for the exchange reaction was much greater than that for the hydrocracking reaction. The Arrhenius parameters and activity factors for the exchange reaction are given in Table 3.22.

At all temperatures on both the sintered and unsintered films, all ten hydrogen atoms in the butane molecule were readily exchangeable, each of the deuterated species being produced in

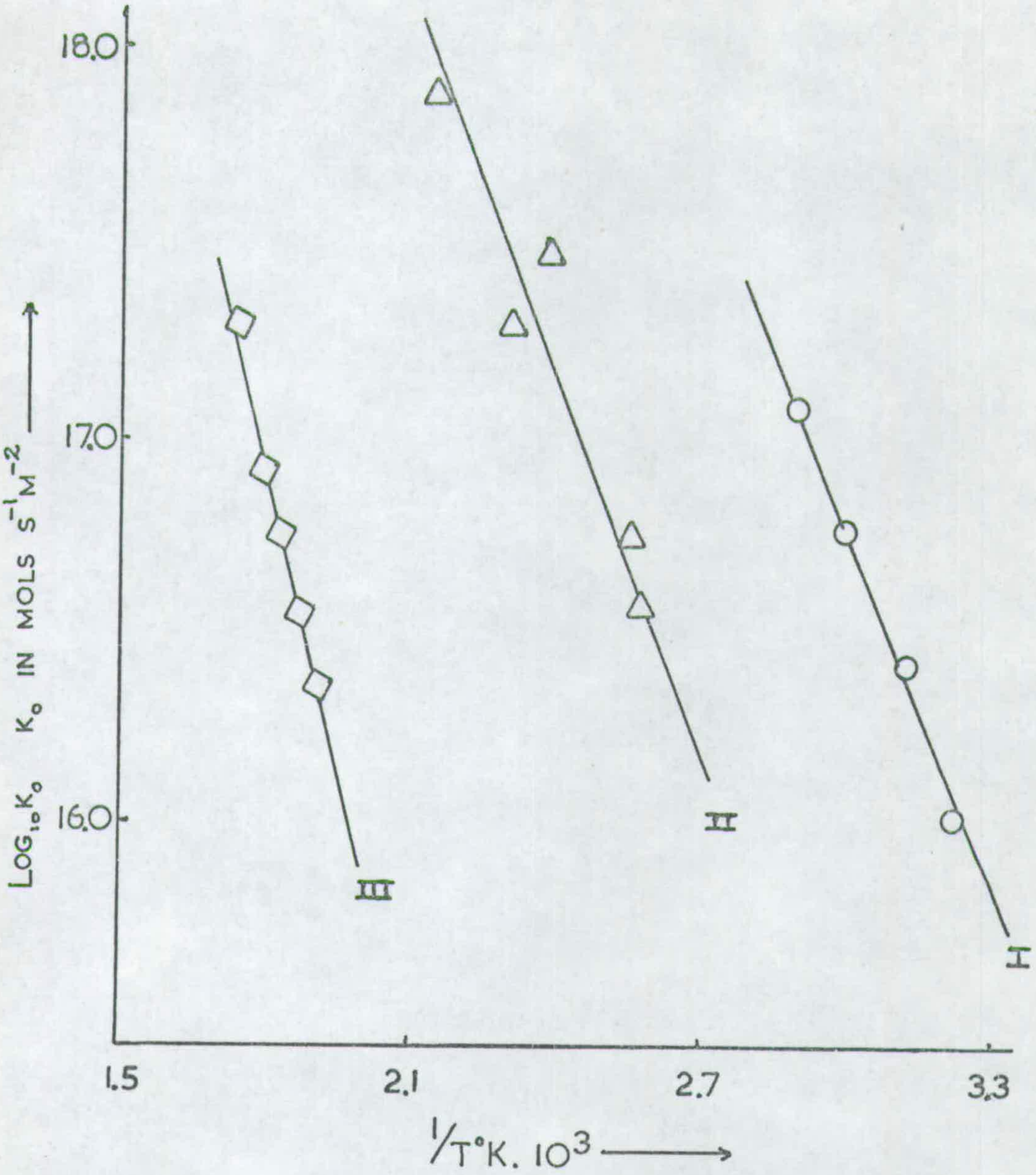


FIG. 3.10 ARRHENIUS PLOTS FOR THE REACTION OF BUTANE ON EVAPORATED PLATINUM FILMS

I EXCHANGE ON UNSINTERED FILMS

II EXCHANGE ON FILMS SINTERED AT 250°C FOR 1 HR

III RESULTS OF ANDERSON AND AVERY (42)

TABLE 3.22.

ARRHENIUS PARAMETERS AND ACTIVITY FACTORS

Catalyst	Apparent activation energy E_0 kJ $mole^{-1}$	Pre-exponential factor $log_{10}A$ A in mols $s^{-1}m^{-2}$	Activity factor at 78°C
I	58.39	25.88	1.00
II	61.80	24.89	0.031

substantial amounts. This behaviour is illustrated by Figure 3.11. which shows the course of a typical reaction with time, and by Table 3.23 which gives the initial product distributions for the exchange reaction at different temperatures.

TABLE 3.23.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXGHANGE OF BUTANE WITH DEUTERIUM ON PLATINUM FILMS

Catalyst and conditions used	Temp. °C	Percentage of isotopic species										$M=\frac{k_0}{k_o}$	$M=\frac{\Sigma nd_n}{100}$
		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}		
unsintered	38	7.45	15.3	8.0	6.2	6.5	5.9	9.0	10.8	14.0	17.0	4.85	5.98
"	48	25.0	6.4	6.3	5.7	6.9	7.0	7.8	8.5	14.0	25.0	6.55	6.52
"	49	18.1	7.7	7.2	5.2	6.2	10.3	8.3	6.7	10.3	20.1	5.8	5.73
"	62	17.0	7.0	4.3	3.5	4.0	6.5	6.0	7.0	12.5	32.2	6.5	6.50
"	69	13.7	6.8	6.8	6.4	7.8	11.2	8.8	10.3	12.7	15.6	5.8	5.93
sintered at 250°C for 1 hr.	116	13.6	4.7	4.5	1.8	2.4	6.8	4.2	1.3	12.0	48.7	6.9	7.3
	120	18.3	9.4	7.6	4.0	4.2	4.7	4.5	6.9	9.9	30.4	6.15	6.05
	148	15.8	5.0	5.0	2.5	2.8	2.9	2.1	11.0	19.9	34.0	7.11	6.95
unsintered	47.5	24.5	26.5	19.5	10.0	7.5	5.0	3.5	2.0	0.5	0	2.74	2.74

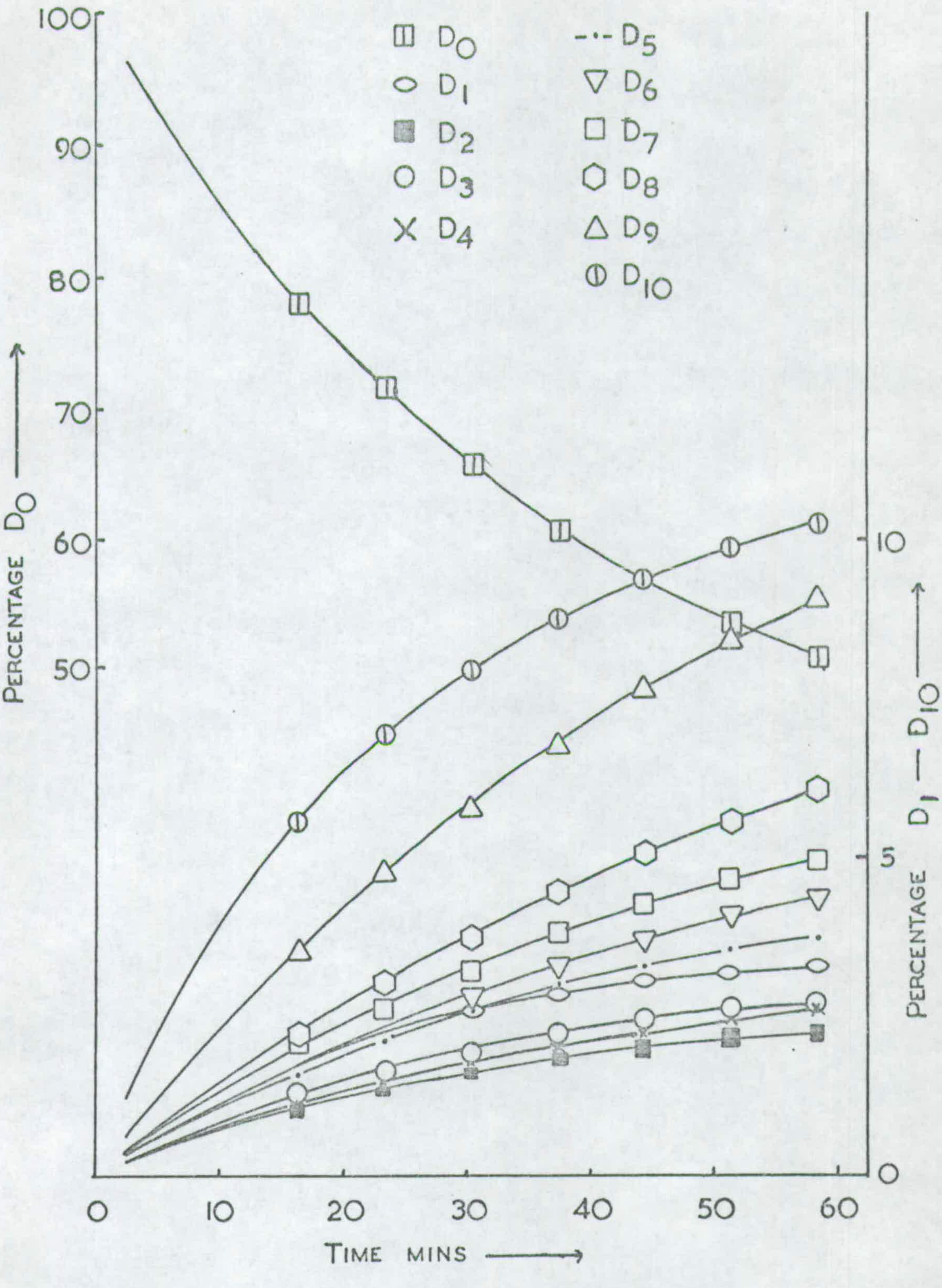


FIG. 3.11 EXCHANGE OF BUTANE WITH DEUTERIUM AT 48°C ON AN UNSINTERED PLATINUM FILM

For both types of film the initial product distributions were similar in shape, and within the limitations of catalyst reproducibility the amounts of the more highly deuterated species and the M values increased with increasing temperature. The initial product distributions generally showed maxima at the d_1, d_6 and d_{10} deuterobutanes. In only two cases was divergence from this pattern observed, the initial product distributions for the reaction at 38°C and 48°C on unsintered films showing maxima in the former case at the d_2, d_5 and d_{10} deuterobutanes, and in the latter case at the d_1 and d_{10} deuterobutanes.

The exchange reaction on the unsintered films showed some degree of irreproducibility with respect to both the initial product distributions and the rates of exchange. In general the rates of exchange in these cases were less than those plotted in Figure 3.10. When butane was presorbed on an unsintered film at 145°C for 45 min. the subsequent exchange reaction showed a small reduction in rate from that of a normal exchange reaction, but the rates obtained were comparable to those for some of the irreproducible 'unpoisoned' reactions. Presorbing oxygen at 145°C for 45 mins. enhanced the rate of the subsequent exchange reaction by a factor of 4.5, though in this case approximately 38% of the 'butane' was lost over the duration of the experiment. The initial product distributions obtained for these irreproducible experiments were similar to those obtained for the reaction on the unsintered films, but differed from them with respect to the amounts of the more highly deuterated species that were produced. The final distribution given in Table 3.23. is an extreme example of this behaviour, where the production of the large amounts of the perdeuterobutane has been suppressed. There appeared to be some degree of correlation between the reduction in activity and the divergence of the initial product distributions from normality. This irreproducibility was also observed, but to not quite the same degree, for the reaction on the sintered films.

Presintering a film at 145°C for 45 mins. in vacuo reduced the activity of the film for the subsequent exchange reaction by a factor of 80, compared with a reduction in activity by a factor of 450 for a film sintered at 250°C. These values were based upon the experimental rates of exchange because the surface area of a film which had been sintered at 145°C was not known. No estimate of the area could be made because, although the number of the thermodynamically controlled defects could be calculated, sintering of the film will be both temperature and time dependent.

3.5. The Exchange of Neopentane with Deuterium

The exchange reaction of neopentane with deuterium was studied on sintered and unsintered evaporated films, and on platinum supported on silica and γ-alumina. The catalysts used are described in Table 3.24.

TABLE 3.24.

CATALYSTS USED

Catalyst symbol	Nature of Catalyst
A	unsintered film
B	Film presintered at 250°C in vacuo
C	Film presintered at 200°C in deuterium
I	0.375% Pt on γ-alumina; fluorine promoted
II	10.0% Pt on silica; reduced at 140°C
III	10.0% Pt on silica; reduced at 500°C
IV	10.0% Pt on silica; reduced at 500°C (reactivated)

The rates of exchange k_0 and k_ϕ were calculated from the plots of the apparent first order equations 3.12. and 3.14. (Part I), and were converted into absolute units by assuming that for the films, whose weights varied from 5.4. to 16.4 mg, the surface areas as measured by krypton adsorption were weight independent; and by using for the supported catalysts the known surface area of platinum which was available for chemisorption. The shapes of the rate plots and the rates of exchange for the reaction on the different catalysts used are summarized in Tables 3.26.-3.28.; while Table 3.25. gives an explanation of the symbols used in these tables.

TABLE 3.25.

SYMBOLS USED

Symbol	Meaning
S	Straight line apparent first order rate plot
VSCR	Slightly curved rate plot; reaction slowing down
CR	curved rate plot; reaction slowing down
CA	curved rate plot; reaction accelerating
C	constant carbon count
↓	carbon count decreasing with time
↑	carbon count increasing with time
V	variable carbon count

The shapes of the rate plots, which were similar to those that had been obtained for the exchange of propane and butane with deuterium, depended upon the catalyst used or its pretreatment. When the exchange reaction was carried out on unsintered films a very slight

TABLE 3.26.

EXCHANGE OF NEOPENTANE WITH DEUTERIUM ON UNSINTERED PLATINUM FILMS

Catalyst	Sorption conditions	Temp. °C	Reaction rate mols $s^{-1}m^{-2}$. 10^{-15}		M $= \frac{k_\phi}{k_0}$	Type of rate plot		Carbon count
			k_0	k_ϕ		$\log(\phi_\infty - \phi)$	$\log \partial_0$	
A	None	20	2.083	2.809	1.35	VSCR	VSCR	C
		41	20.80	26.48	1.43	S	S	C
		48	14.14	19.68	1.40	S	S	C
		50	28.18	45.96	1.63	VSCR	VSCR	C
		65	47.51	70.98	1.49	S	S	C
		68	59.58	99.17	1.67	VSCR	S	C
		80	80.85	119.8	1.48	VSCR	VSCR	C
		90	-	295.4	-	VSCR	-	C
		94	148.1	269.6	2.14	VSCR	S	C
		122	-	655.4	-	VSCR	-	C
A	Methane at 150°C for 1 hr.	59	16.48	23.91	1.45	S	S	C
		60	31.47	45.38	1.44	S	S	C
		68	123.2	214.8	1.74	S	S	C
		80	83.99	149.0	1.77	S	S	C
		88	84.43	125.9	1.49	VSCR	VSCR	C
		103	-	532.8	-	S	S	C
A	Ethane at 105°C for 1 hr.	57.5	15.79	23.45	1.49	S	S	C
		77	62.77	104.6	1.66	VSCR	VSCR	C
		98	-	199.4	-	VSCR	-	C
A	Propane at 105°C for 1 hr.	66	58.25	89.89	1.54	VSCR	VSCR	C
		89	127.5	205.0	1.61	VSCR	VSCR	C
		105	-	298.8	-	S	S	C
A	Neopentane $-D_2$ at 105°C for 1 hr.	81.5	63.05	102.8	1.63	S	S	C
		109	-	403.3	-	VSCR	VSCR	C
A	Ethylene at 105°C for 1 hr.	78	7.213	10.86	1.51	S	S	C
		105	17.35	31.45	1.81	S	S	C
		149	19.16	28.34	1.48	S	S	↓

TABLE 3.27.

EXCHANGE OF NEOPENTANE WITH DEUTERIUM ON SINTERED PLATINUM FILMS

Catalyst	Sorption conditions	Temp. °C	Reaction rates mols $s^{-1}m^{-2}$. 10^{-16}		$M = \frac{k_\phi}{k_0}$	Type of rate plot		Carbon count
			k_0	k_ϕ		$\log(\phi_\infty - \phi)$	$\log \partial_0$	
C	None	87	0.847	1.654	1.95	S	S	C
		122	8.47	19.56	2.31	S	S	C
		170	69.58	195.6	2.81	S	S	C
B	None	101	3.74	5.57	1.49	S	S	C
		106.5	7.49	12.35	1.65	S	S	C
		138.5	35.70	59.88	1.68	S	S	C
		147.5	39.32	75.53	1.92	S	S	C
		178	182.7	481.5	2.64	S	S	C
		178.5	127.5	288.7	2.26	VSCR	S	C
B	Neopentane at 220°C for 1 hr.	155	2.16	3.31	1.53	VSCR	VSCR	C
		189	5.623	9.50	1.69	VSCR	VSCR	C
B	Neopentane -D_2 at 250°C for 1hr.	152	6.67	11.00	1.65	S	S	C
		199	22.59	42.67	1.89	S	S	C

TABLE 3.28.

EXCHANGE OF NEOPENTANE WITH DEUTERIUM ON PLATINUM SUPPORTED CATALYSTS

Catalyst	Catalyst weight mg.	Temp. °C	Reaction rates mols $s^{-1}m^{-2}$. 10^{-15}		H $= \frac{k_\phi}{k_\theta}$	Type of rate plot		Carbon count
			k_θ	k_ϕ		$\log(\phi_\infty - \phi)$	$\log \partial_\theta$	
I	20.9	100	141.3→41.9	280.9→58.64	1.97→ 1.40	CR	CR	C
	19.5	100	168.6	238.3	1.42	S	S	C
	16.5	116	109.6	159.1	1.45	S	S	↓
	6.4	134	237.0	735.7	3.10	S	S	C
	20.9	144	52.38	115.8	2.21	S	S	C
	19.5	149	342.6	637.5	1.86	S	VSCR	↑
	6.4	179	610.5	2694.0	4.42	S	VSCR	↑
II	72.2	54	2.26	2.46	1.09	S	S	C
	72.2	56	4.39	6.58	1.50	S	S	C
	72.2	88	10.88	15.72	1.45	S	S	C
	72.2	90.5	8.92	14.25	1.60	S	S	C
III	114.8	129	1.34	2.70	2.02	S	S	↓
	116.9	137	1.83	3.91	2.14	CA	CA	C
	114.8	176	2.45	3.84	1.57	S	S	↓
	114.8	236	15.15	27.28	1.81	S	S	C
IV	117.1	223	3.11	5.08	1.63	CR	CR	V
	117.1	295	8.87	15.63	1.71	S	S	V

retarded curvature of the rate plots was usually observed; however, on presintering the films at high temperature this retarded curvature was no longer apparent the reaction obeying apparent first order kinetics. In the cases where either methane, ethane, propane, ethylene or a neopentane-deuterium reaction mixture was maintained over unsintered films for 1 hr. at 105°C, the shape of the rate plot obtained for the subsequent exchange reaction depended upon the hydrocarbon presorbed. When methane, ethylene or a neopentane-deuterium reaction mixture was presorbed, straight line rate plots were obtained. However, when ethane or propane was presorbed a slight retarded curvature of the rate plots was obtained. Differences in the rate plots were also observed for the experiments where neopentane, or a neopentane-deuterium mixture was presorbed at high temperature upon a sintered film. When neopentane itself was presorbed at 220°C for 1 hr., the subsequent exchange reaction obeyed apparent first order kinetics. However, when a neopentane-deuterium mixture, (deuterium:neopentane = 10:1), was presorbed at 250°C for 1 hr., the subsequent exchange reaction showed a slight retarded curvature of the rate plots. The exchange reaction on the supported catalysts obeyed apparent first order kinetics. In only one case, that for the reaction on γ-alumina at 100°C was retardation of the exchange reaction observed; and in only one case, that for the reaction on the silica catalyst which had been reduced at 500°C, was an accelerating rate observed.

Tables 3.26.-3.28 also give the carbon counts that were obtained for the exchange reaction. The films gave constant carbon balances at all temperatures. With the supported catalysts, however, the behaviour was variable, though mainly constant. In those cases where carbon was being lost from the system the change was of the order of 15%.

The Arrhenius equation plots for the rate of disappearance of the 'light' neopentane are shown in Figures 3.12. - 3.14. At temperatures greater than 20°C neopentane exchanged readily on the unsintered films. At these low temperatures no evidence was obtained for progressive self poisoning of the exchange reaction. This is illustrated by Figure 3.12. which shows that the presorption of saturated hydrocarbons upon the unsintered films at 105°C for 1 hr., only produced a very small reduction in the activity of the film for the subsequent exchange reaction. The presorption of ethylene at 105°C for 1 hr. upon an unsintered film, however, reduced the activity of the film for the subsequent exchange reaction by a factor of 12; on increasing the temperature above the presorption temperature the exchange reaction continued at a steady rate, the apparent activation energy tending to zero k J mole^{-1}.

In order to study the self poisoning that might occur at high temperatures it was necessary to eliminate any effects due to the film progressively sintering during the reaction. The exchange reaction was, therefore, carried out on presintered films to provide a base to which presorption effects upon the subsequent exchange reaction could be referred. Presintering the films necessitated reaction temperatures greater than 80°C to propagate the exchange process and Figure 3.13. shows that even after allowing for the decrease in apparent surface area of the films upon sintering, there was still a large reduction in activity for the exchange reaction. Some evidence for the formation of irreversible species upon the surface of a platinum film was found when a hydrocarbon was presorbed upon a presintered film. Presorption of neopentane itself at 220°C for 1 hr. produced a large reduction in the activity of the film for the subsequent exchange

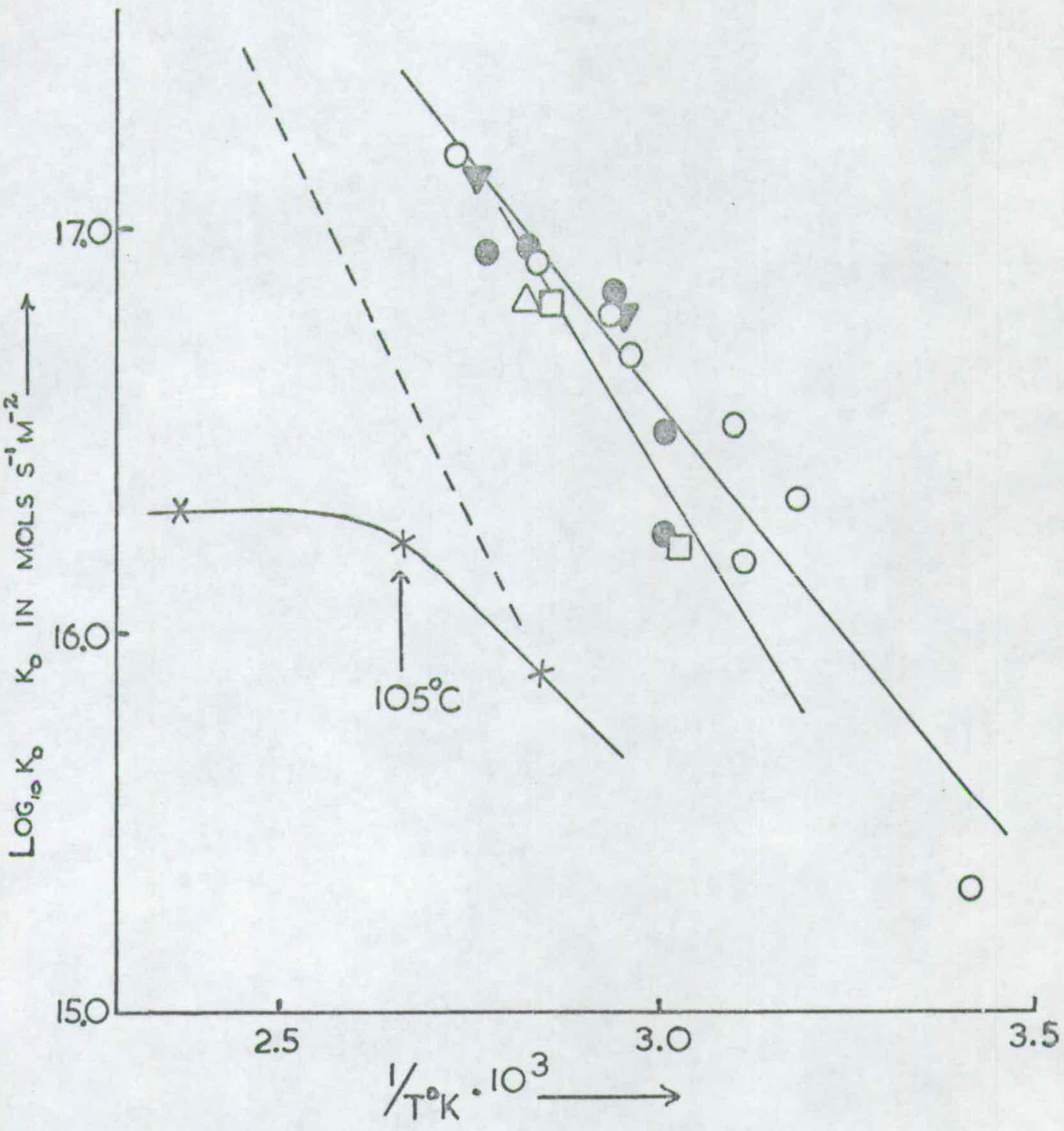


Fig. 3.12 Arrhenius Plots for the Exchange of Neopentane with Deuterium on Unsintered Platinum Films

○ Normal Exchange

● Film Pretreated with Methane at 105°C for 1 hr.

□ " " " Ethane " " " "

▼ " " " Propane " " " "

× " " " Ethylene " " " "

--- Exchange Reaction on Sintered Platinum Films

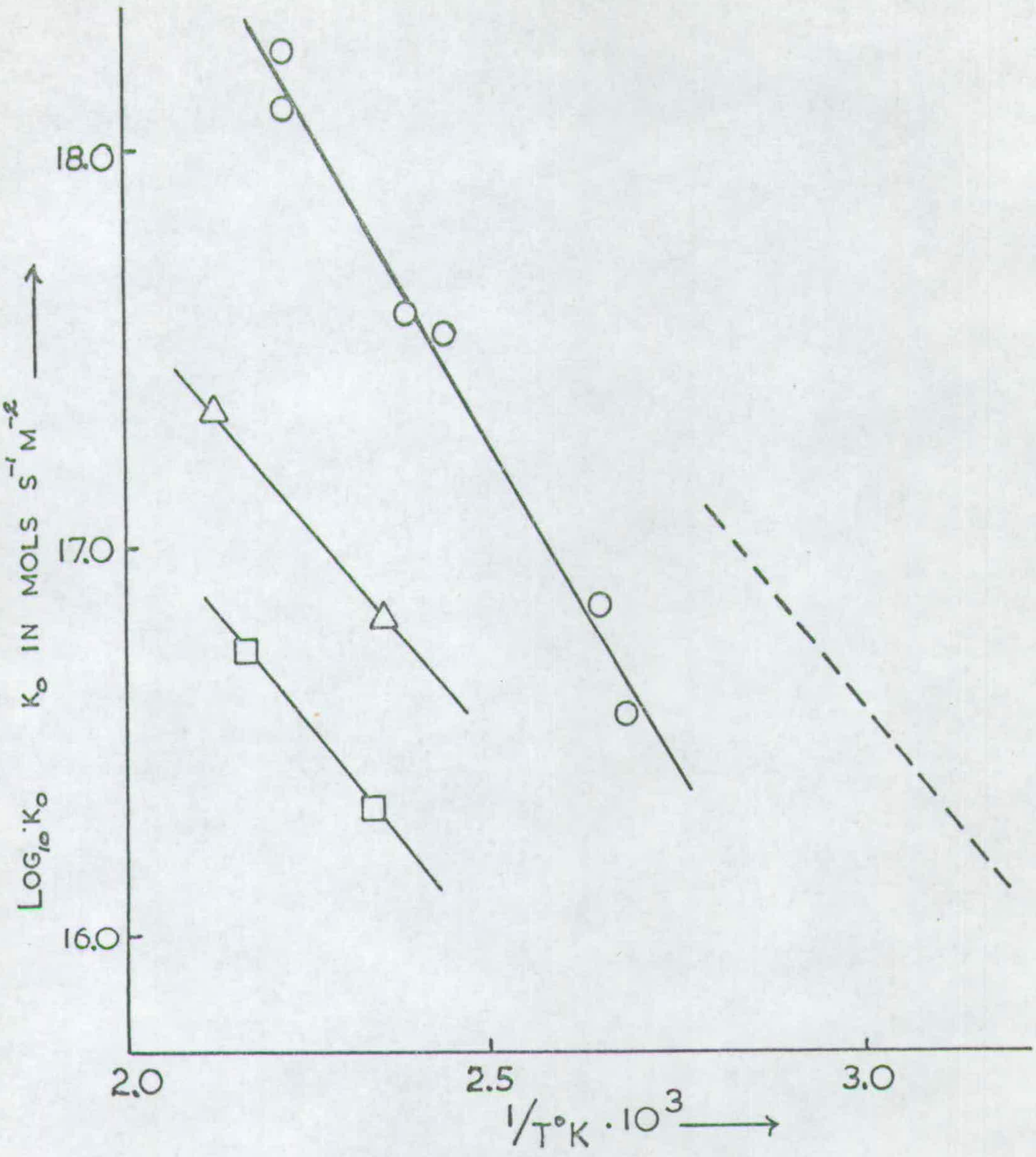


FIG. 3.13 ARRHENIUS PLOTS FOR THE EXCHANGE OF NEOPENTANE WITH DEUTERIUM ON SINTERED PLATINUM FILMS

○ EXCHANGE ON FILMS SINTERED AT 250°C FOR 1 HR, AND AT 250°C FOR 0.5 HR.

△ EXCHANGE ON A FILM PRESINTERED AT 250°C AND PREPOISONED WITH NEOPENTANE – D_2 AT 250°C FOR 1 HR.

□ EXCHANGE ON A FILM PRESINTERED AT 250°C AND PREPOISONED WITH NEOPENTANE AT 220°C FOR 1 HR.

--- EXCHANGE ON UNSINTERED FILMS.

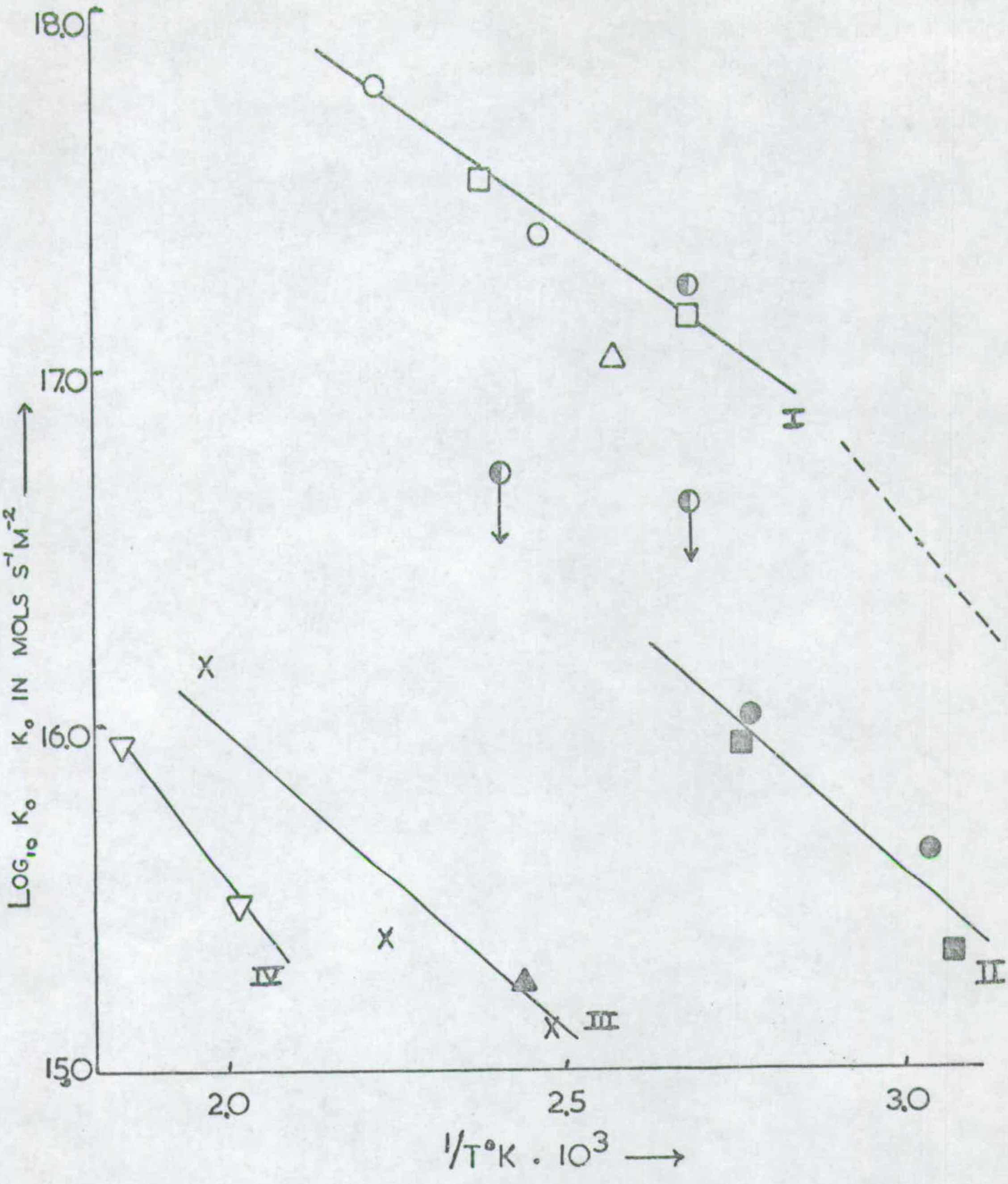


FIG. 3.14 ARRHENIUS PLOTS FOR THE EXCHANGE OF NEOPENTANE WITH DEUTERIUM ON PLATINUM SUPPORTED CATALYSTS

I	0.375 % PLATINUM - γ-ALUMINA	FLUORINE	PROMOTED		
II	10.0 %	PLATINUM - SILICA	REDUCED	AT	140°C
III	"	"	"	"	" 500°C
IV	"	"	"	"	" 500°C

REACTIVATED CATALYST

--- EXCHANGE ON AN UNSINTERED FILM

DIFFERENT SYMBOLS REFER TO DIFFERENT EXPERIMENTS reaction; and this reduction in activity was greater than that observed when a neopentane-deuterium reaction mixture was presorbed at 250°C for 1 hr.

The Arrhenius plots for the reaction on the supported catalysts are shown in Figure 3.14. Although the rates of exchange were reproducible there were considerable differences in activity between the catalysts; the platinum on γ-alumina catalyst being the most active, and the platinum on silica catalyst which had been reduced at 500°C the most inactive. The downward pointing arrows shown for some of the rates of exchange on the platinum on γ-alumina catalyst, refer to the experiment quoted in Table 3.28. where a retarded rate plot was obtained. At the initial temperature used in this experiment the rate of exchange decreased with time giving a final rate which was one third that of the initial rate. On increasing the temperature, the rate of exchange did not increase markedly from the final rate mentioned above, and was still much less than the initial rate.

The Arrhenius equation parameters for the exchange reaction are given in Table 3.29., which also includes the temperature for which the rate of disappearance of the 'light' neopentane $k_o = 3.4.10^{16}$ mols $s^{-1}m^{-2}$. This corresponded, for the reaction on the unsintered films, to an experimental rate of 1 min^{-1}. The table shows that presintering the film, or presorbing saturated hydrocarbons on an unsintered film increased the apparent activation energy of the exchange reaction; whereas presorbing saturated hydrocarbons on a sintered film decreased the apparent activation energy. The temperatures given in column 5 are a little misleading as a measure of catalytic activity. Although the reaction on the films can be correlated by this method, as can the reaction on the supported catalysts, due to the differences in the Arrhenius parameters between the films and the supported catalysts any correlation between the two groups of catalysts by this method would be misleading.

TABLE 3.29.

ARRHENIUS PARAMETERS

Catalyst used	Sorption conditions	Apparent activation energy E_0 k J mole^{-1}	$\log_{10}A$ A in mols s^{-1}m^{-2}	T°C for k_0=3.4.10^{16} mols s^{-1}m^{-2}
A	none	46.43	23.80	60
A	Saturated hydrocarbons at 105°C for 1 hr.	55.14	25.00	67
A	Ethylene at 105°C for 1 hr.	43.27 †	21.28 †	120.5*
B	none	62.80	25.39	97
B	Neopentane at 220°C for 1 hr.	45.31	21.27	171
B	Neopentane-D_2 at 250°C for 1 hr.	40.36	22.40	127
I	none	25.08	20.67	44
II	none	32.17	20.65	135
III	none	32.83	19.42	321

* Extrapolated

† less than 98°C

Activity factors for the catalysts could, however, be calculated by using the rates of exchange at constant temperature. In order to avoid using extrapolated rates, the catalysts were divided into two groups:

(a) The exchange reaction on the unsintered films, and the normal exchange reaction on the sintered films.

and (b) The exchange reaction on the supported catalysts and the sintered films.

For group (a) the temperature chosen was 84°C, and the activity factors were calculated relative to the reaction on the unsintered films. In the case of group (b) the temperature chosen was 152°C, and the activity factors were calculated relative to the reaction on the sintered films. The results obtained are given in Table 3.30, which shows that in terms of the absolute rates of exchange, the activity of the supported catalysts for the exchange reaction was similar to that of a sintered film.

TABLE 3.30.

ACTIVITY FACTORS

Group	Catalyst used	Sorption conditions	Activity factor
A	A	none	1.0
	A	Saturated hydrocarbons at 105°C for 1 hr.	0.841
	A	Ethylene at 105°C for 1 hr.	0.0852
	B	none	0.1580
B	B	none	1.0
	B	Neopentane - D_2 at 250°C for 1 hr.	0.148
	B	Neopentane at 220°C for 1 hr.	0.0412
	I	none	0.813
	II	none	0.106
	III	none	0.0051

The initial product distributions obtained for the exchange of neopentane were different to those observed for the exchange of propane and butane. This is illustrated by Figure 3.15. which shows the course of a typical reaction with time, and by Table 3.31. which gives the initial product distributions for the exchange reaction on the catalysts studied.

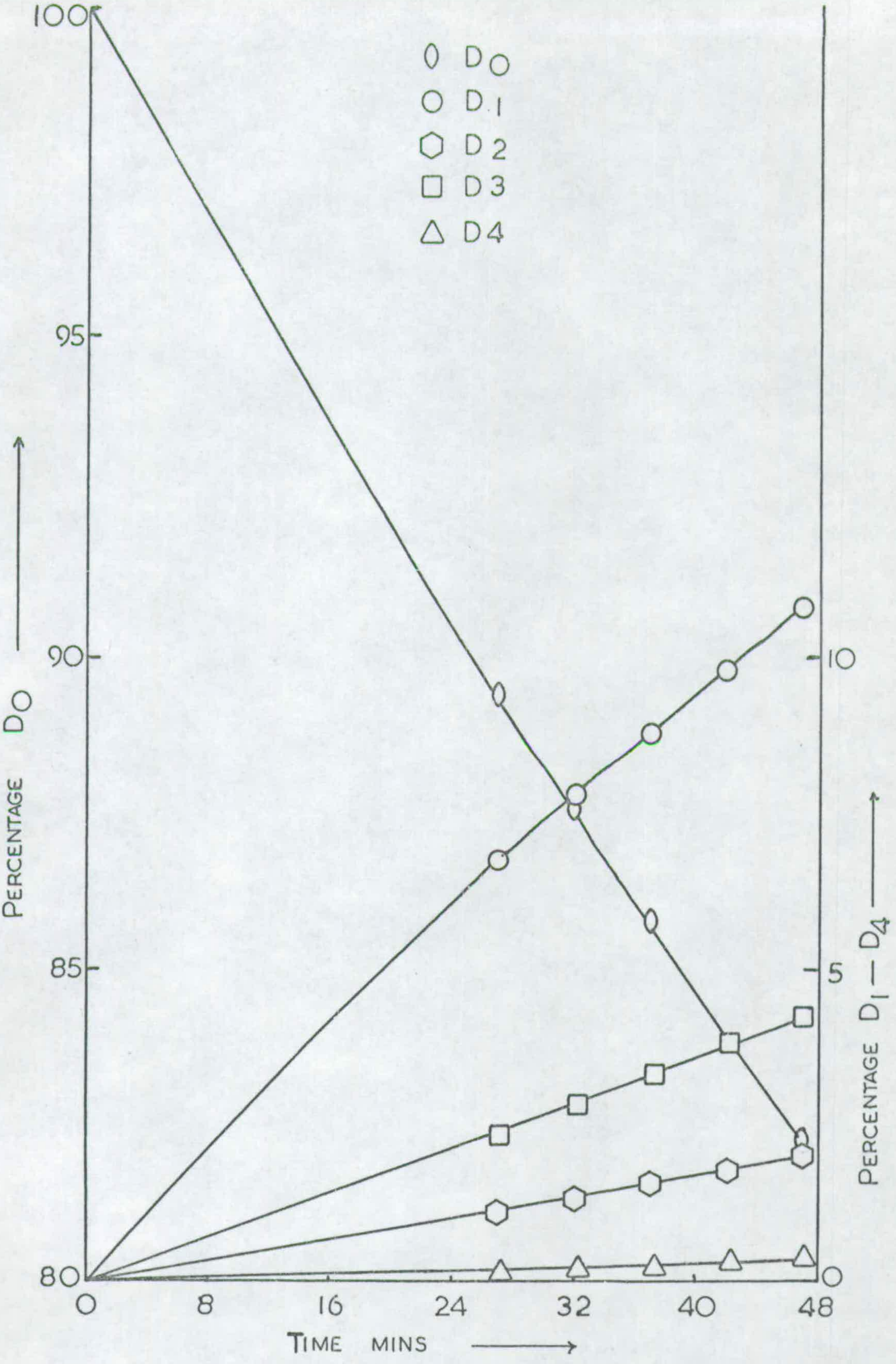


FIG. 3.15 EXCHANGE OF NEOPENTANE WITH DEUTERIUM AT 122°C ON A SINTERED PLATINUM FILM

TABLE 3.31.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF NEOPENTANE WITH DEUTERIUM

Catalyst used	Sorption conditions	Temp. °C	Percentage deuterium content									$M=\frac{1}{2}\frac{k_\phi}{K_o}$	$M=\sum\frac{nd_n}{100}$
			d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9		
A	none	20	95.5	3.0	1.5	-	-	-	-	-	-	1.01	1.05
A	none	65	81.6	15.3	2.6	0.5	-	-	-	-	-	1.12	1.22
B	none	101	90.7	4.6	4.4	0.25	-	-	-	-	-	1.12	1.14
B	none	106.5	89.1	4.1	5.6	0.3	0.15	0.15	0.15	0.15	0.3	1.24	1.22
B	Neopentane at 220°C for 1 hr.	155	88.7	5.01	5.26	0.5	0.5	-	-	-	-	1.15	1.19
B	Neopentane - D_2 at 250°C for 1 hr.	152	94.0	2.5	3.6	0.15	-	-	-	-	-	1.24	1.10
A	CH_4 at 105°C for 1 hr.	59	91.0	4.9	3.9	0.1	-	-	-	-	-	1.09	1.13
A	CH_4 at 105°C for 1 hr.	60	87.3	10.3	2.1	0.4	-	-	-	-	-	1.08	1.16
A	C_2H_6 at 105°C for 1 hr.	57.5	95.2	2.57	2.06	0.4	-	-	-	-	-	1.12	1.08
A	C_3H_8 at 105°C for 1 hr.	66	89.5	7.5	2.5	0.5	-	-	-	-	-	1.15	1.14
A	Neopentane - D_2 at 105°C for 1 hr.	81.5	77.1	15.0	6.0	1.0	0.4	0.25	0.13	0.05	0.05	1.22	1.34
A	C_2H_4 at 105°C for 1 hr.	78	95.0	4.4	0.85	-	-	-	-	-	-	1.06	1.13
A	C_2H_4 at 105°C for 1 hr.	105	89.5	7.0	3.1	0.5	-	-	-	-	-	-	1.13
I	none	116	92.2	6.0	1.8	-	-	-	-	-	-	1.09	1.10
II	none	56	95.3	4.0	0.65	0.1	-	-	-	-	-	1.11	1.06
III	none	129	87.1	8.3	4.6	-	-	-	-	-	-	1.2	1.5

Although neopentane reacted readily on the catalysts, only the d_1, d_2 and d_3 deutero tert-butyl ions were produced in substantial amounts initially, the relative amounts being $d_2 \ll d_1 \gg d_3$. The distributions almost invariably showed the absence of isotopic species containing more than four deuterium atoms; in only two cases was propagation of the exchange process to produce all nine isotopic tert-butyl ions observed. The distributions can be divided into two groups depending upon the relative amounts of the species containing two and three deuterium atoms present:

(a) Those for which $d_2 > d_3$, this group arising from the reaction on the unsintered films and the supported catalysts.

and (b) Those for which $d_2 \approx d_3$, this group arising from the reaction on the sintered films.

The M values although close to were significantly greater than one, and increased with increasing temperature. This effect was also shown by the initial product distributions, the amounts of the isotopic species containing more than one deuterium atom increasing with increasing temperature.

The Arrhenius equation plots for the exchange reaction on the catalysts showed the excellent reproducibility that was obtained. This is also illustrated by Table 3.32. where the results obtained in this work are compared with that briefly reported by Gault et al. (82) in their study of the hydrogenolysis of gem dimethylcyclopropane with deuterium on platinum films.

TABLE 3.32.

EXCHANGE OF NEOPENTANE WITH DEUTERIUM
ON UNSINTERED PLATINUM FILMS

Temp.	Experimental rate k_0 % min^{-1}	Percentage of isotopic species									M	
		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9		
50	0.6	96.21	2.65	1.14	0.1	-	-	-	-	-	1.44	(82)
48	0.77	93.4	5.05	1.5	0.1	-	-	-	-	-	1.44	

In contrast to the straight chain paraffins studied neopentane did not exchange readily to produce isotopic species containing more than four deuterium atoms. Figure 3.16., which compares the Arrhenius plot for the exchange of neopentane with deuterium on sintered films with that obtained by Anderson and Avery (42), shows that the rate of disappearance of the 'light' neopentane k_o at 127°C was faster than the rate of hydrocracking and isomerization by a factor of 4365. An attempt was, therefore, made to rationalize this discrepancy in the following manner. For neopentane to exchange all twelve hydrogen atoms initially it must form an $\alpha\delta$-diadsorbed intermediate. If one looks at the initial product distributions for the exchange reaction on sintered films, then any isotopic species containing more than three deuterium atoms must have been produced by the formation of this intermediate. Therefore, if A denotes the total percentage of the isotopic species d_4-d_9, the rate R of the exchange process producing these species is given by

$$R = A\, k_o/100 \quad ;$$

and similarly the rate S of the exchange process producing the isotopic species d_1-d_3 is given by

$$S = k_o - R.$$

Figure 3.17., which compares the Arrhenius plots for these two rates of exchange on sintered films with that of Anderson and Avery (42), shows that at the temperatures required to propagate the exchange reaction the rate of multiple exchange R is comparable to the rate of hydrocracking and isomerization. Due to the small amounts of the isotopic species containing more than three deuterium atoms that were present in the initial distributions, and the limited temperature range over which the initial distributions could be accurately measured, the rate of multiple

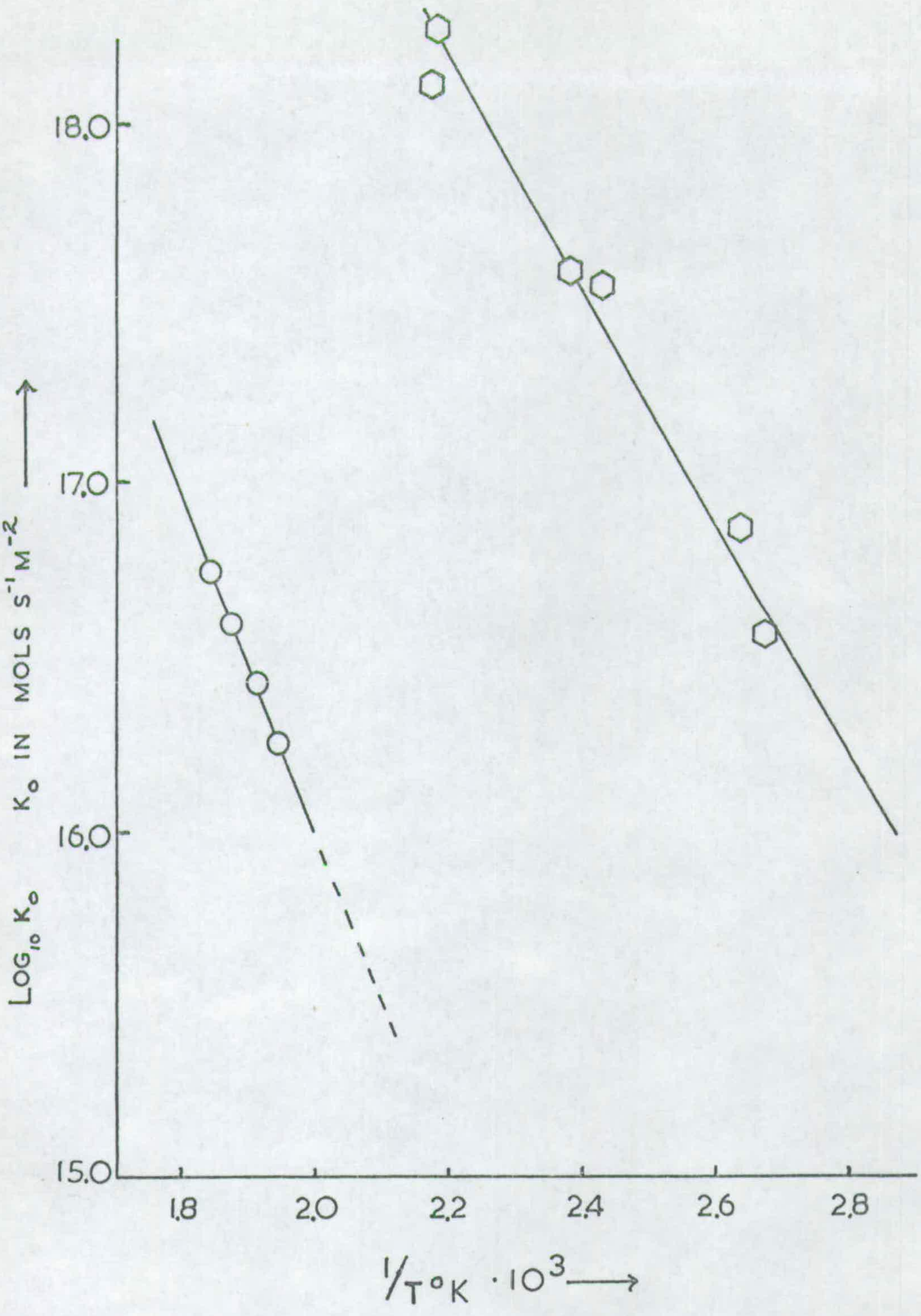


Fig. 3.16 Arrhenius Plots for the Reaction of Neopentane on Sintered Platinum Films

○ Results of Anderson and Avery (42)

⬡ Normal Exchange Reaction

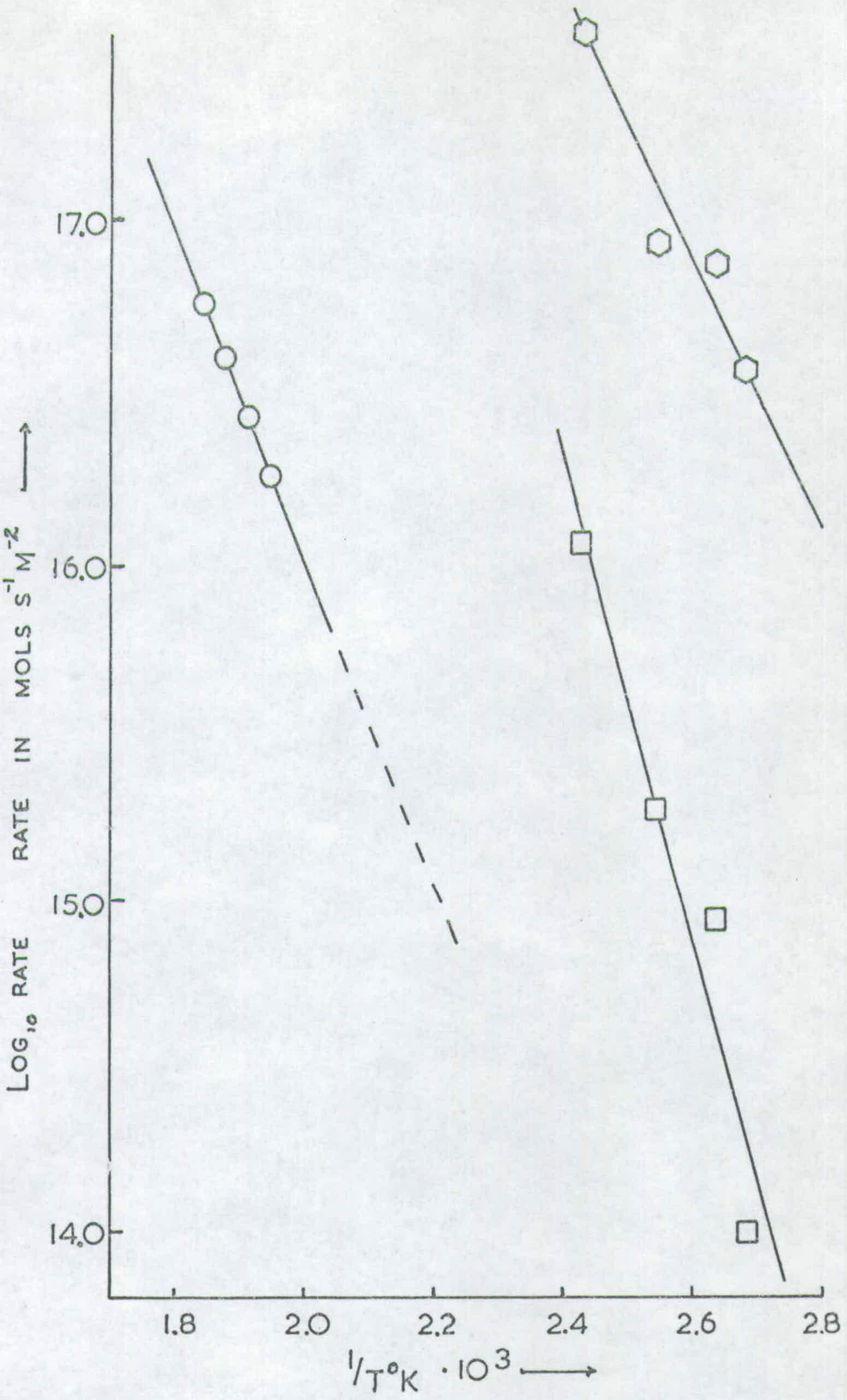


FIG. 3.17 ARRHENIUS PLOTS FOR THE REACTION OF NEOPENTANE ON SINTERED PLATINUM FILMS

○ RESULTS OF ANDERSON AND AVERY (42)

⬡ EXCHANGE PROCESS S

□ EXCHANGE PROCESS R

exchange R will be subject to some error. An attempt was, therefore, made to extend the temperature range and accuracy of measurement by measuring the initial distribution at high temperature. It was proposed to do this by admitting the reaction mixture to the sintered film at the reaction temperature. However, when the reaction mixture was admitted to the film at temperatures ranging from 145°C to 170°C no exchange of the molecule was observed at temperatures less than 250°C.

The Arrhenius equation parameters for the exchange processes R and S given in Table 3.33. will be subject to quite a substantial error, due to the inaccuracy in the measurements described above. Though this error will amount to probably ± 6 k J mole^{-1} in the activation energy, the results will still be qualitatively correct.

TABLE 3.33.

ARRHENIUS PARAMETERS

Process	Activation energy E_o k J mole^{-1}	Pre-exponential factor $\log_{10} A$ A in mols $s^{-1}m^{-2}$	Activity factor at 127°C
Hydrocracking (42)	87.86	25.2	0.0002
R	138.80	33.71	0.021
S	74.29	26.97	1.0000

3.6. The Exchange of Methane with Deuterium

The exchange of methane with deuterium has been studied on unsintered and sintered platinum films, the weights of which varied from 8.1 to 12.7 mg. Methane in contrast to the other hydrocarbons studied was much more difficult to exchange, reaction temperatures greater than 180°C being required to give readily measurable rates. The rates of exchange k_o and k_ϕ are summarized in Table 3.34.

TABLE 3.34.

EXCHANGE OF METHANE WITH DEUTERIUM ON PLATINUM FILMS

Group*	Catalyst used	Temp. °C	Rate of reaction mols $s^{-1}m^{-2}$. 10^{-15}		Type of rate plot obtained‡		$M = \frac{k_\varphi}{k_o}$	Carbon balance†
			k_o	k_φ	$\log(\varphi_\infty - \varphi)$	$\log d_o$		
A	Unsintered	195	$26.89 \rightarrow 7.67$	$44.82 \rightarrow 13.57$	CR	CR	1.66	C
A	Unsintered	242	62.99	99.59	S	S	1.58	C
B	Unsintered	195	$5.86 \rightarrow 1.67$	$9.86 \rightarrow 2.98$	CR	CR	1.66	C
B	Unsintered	242	13.72	21.69	S	S	1.58	C
	Sintered at 250°C for 1 hr.	183.5	5.92	8.14	S	S	1.38	C
		212	17.20	28.62	S	S	1.66	C
		214	27.20	41.84	S	S	1.57	C
		239	50.17	88.37	S	S	1.72	C

* A using a value of 0.04 m^2 for the surface area

B " " " " 0.184 m^2 " " " "

‡ S reaction obeyed apparent first order kinetics

C.R. rate plot curved, i.e., reaction slowing down with time

† C carbon balance constant

Figure 3.18. shows two typical rate plots obtained for the rate of incorporation of deuterium into the molecule. As in the case of the other hydrocarbons studied the type of rate plot obtained depended upon the catalyst pretreatment. When the exchange reaction was studied on sintered films the reaction always obeyed apparent first order kinetics. On the unsintered films two types of rate plot were

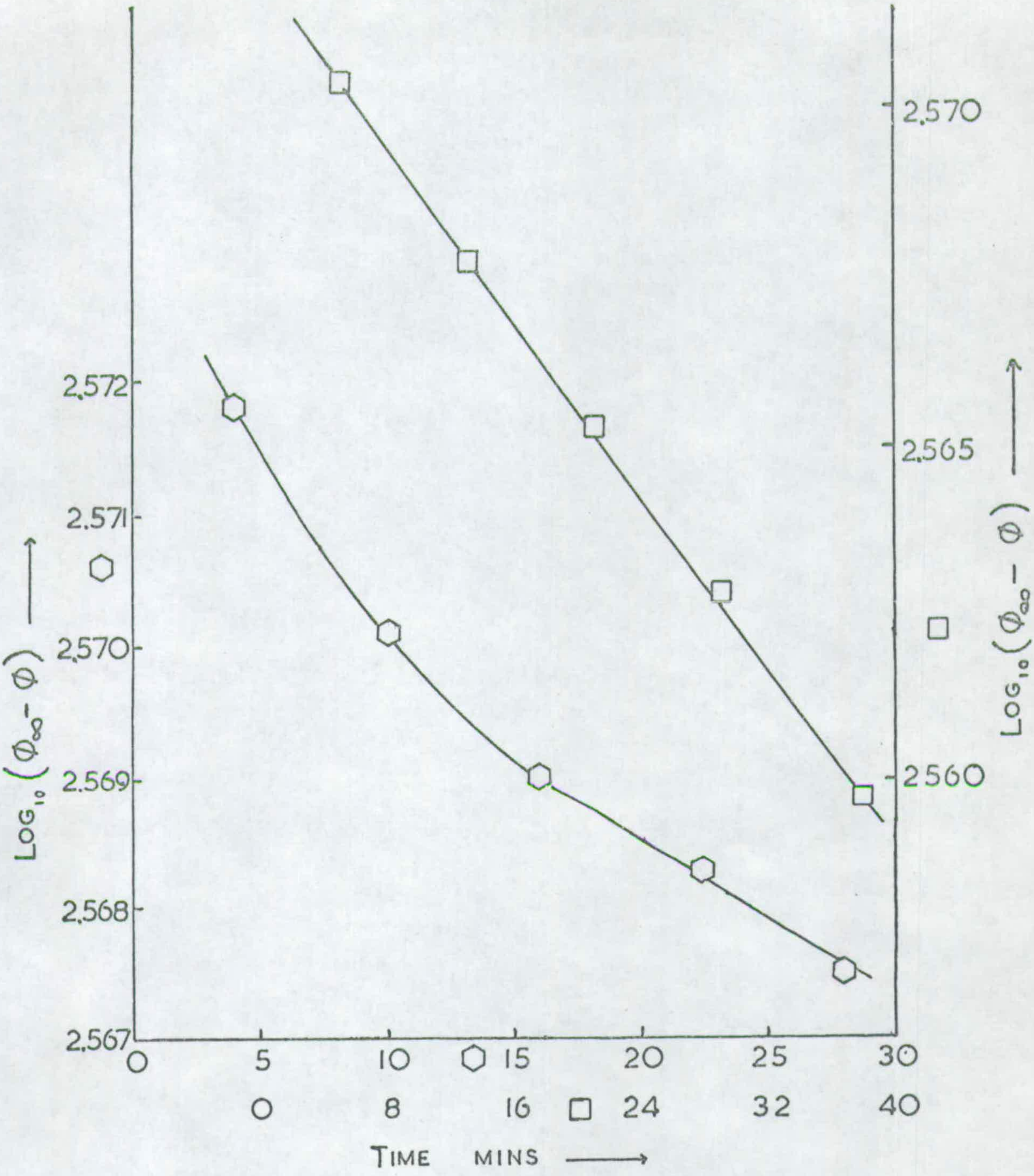


Fig. 3.18 First Order Rate Plots for the Exchange of Methane with Deuterium on Platinum Films

⬡ at 195°C on an Unsintered Film

□ at 212°C on a Sintered Film

obtained. At the initial temperature used a very retarded curvature of the plot was obtained; however, on increasing the reaction temperature, this curvature disappeared and the reaction obeyed apparent first order kinetics.

The Arrhenius equation plot for the rate of disappearance of the 'light' methane k_0 shown in Figure 3.19. also includes the results obtained by Kemball (130) for the exchange of methane on unsintered platinum films. Kemball's results which were obtained using a different gas ratio than that used for the results reported in this thesis, were converted for use in Figure 3.19. by application of the pressure dependency equations which he reported; and by converting the surface area which he had determined by the chemisorption of hydrogen (93) into the equivalent krypton surface area by application of the surface area measurements reported in this thesis. This figure, which shows that the rates of reaction for the exchange on sintered and unsintered films and those reported by Kemball (130) obey the same Arrhenius equation, requires some detailed explanation. The Arrhenius plot was derived by the superposition of the absolute rates of exchange for three groups of catalysts:

(a) The results of Kemball (130) for the exchange reaction on unsintered films.

(b) The results obtained in this work for the exchange reaction on sintered films.

(c) The results obtained in this work for the exchange reaction on unsintered films.

The derivation of groups (a) and (b) has been explained above. In the case of group (c), at the highest temperature used in the experiment the rate of exchange was converted into its absolute value by using the surface area of a sintered film. For the initial reaction temperature

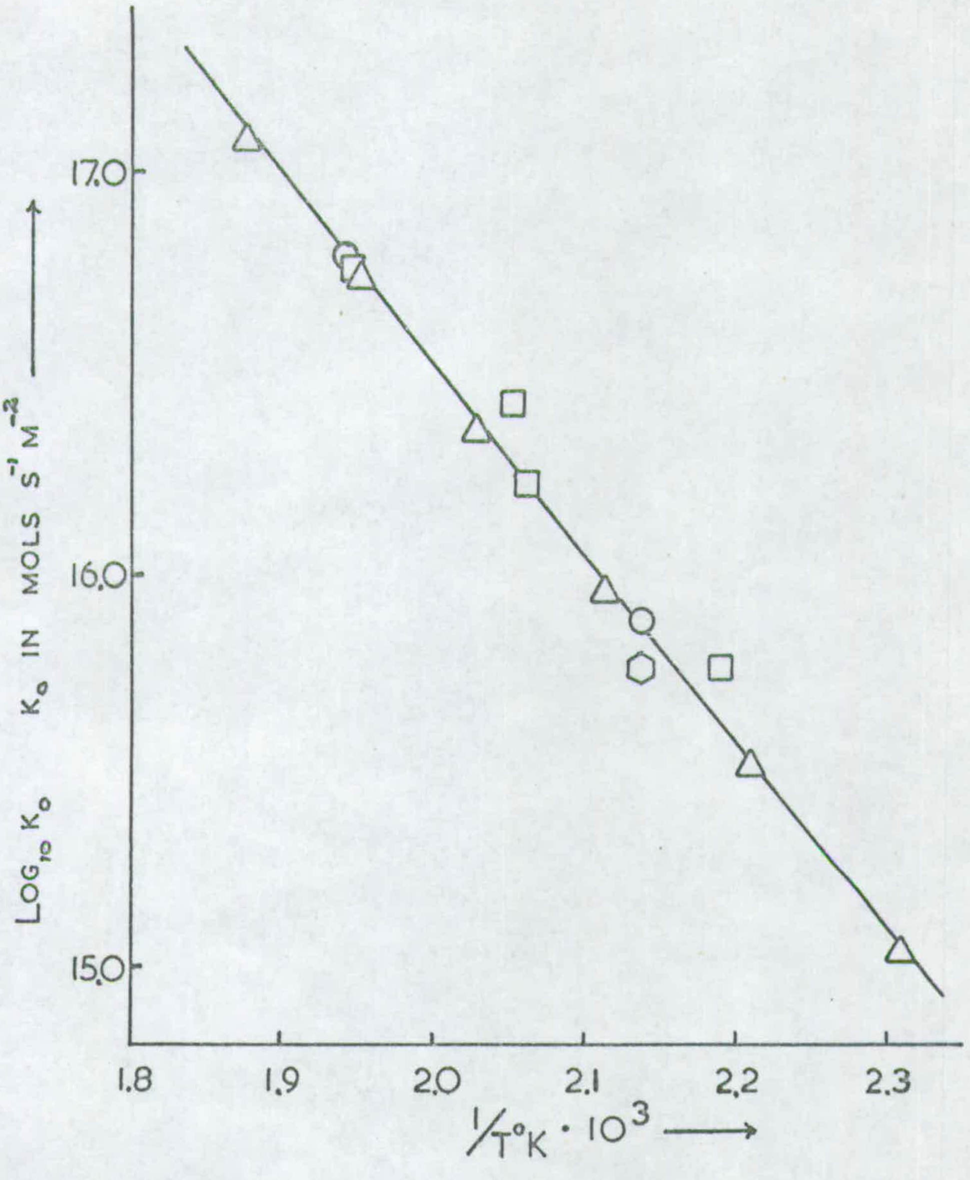


Fig. 3.19 Arrhenius Plot for the Exchange of Methane with Deuterium on Evaporated Platinum Films

□ Using Presintered Films

△ Results of Kemball (130)

○ ⬡ Using Unsintered Films with a Value for the Surface Area of ; ○, 0.04 m^2; ⬡, 0.184 m^2

where a retardedly curved rate plot was obtained, the rates of exchange were converted into their absolute values by using for the initial rate the surface area of an unsintered film, and for the final rate the surface area of a sintered film. It is thus apparent, that in contrast to the other hydrocarbons studied, the exchange reaction of methane does not differentiate between sintered and unsintered films. The Arrhenius parameters for the exchange reaction are given in Table 3.35.

TABLE 3.35.

ARRHENIUS PARAMETERS

Apparent activation energy E_0 k J $mole^{-1}$	Pre-exponential factor $\log_{10}A$ A in mols $s^{-1}m^{-2}$	Temp. °C for $k_o = 3.4. 10^{16}$ mols $s^{-1}m^{-2}$
90.3	25.94	228

On the films all four hydrogen atoms in the molecule were readily exchangeable at all temperatures, each of the deuterated species being produced in substantial amounts. This is illustrated by Figure 3.20. which shows the course of a typical reaction with time, and by Table 3.36. which gives the initial product distributions for the exchange reaction. The distributions always showed maxima at the d_1 and d_4 deuteromethanes, the monodeuteromethane being the predominant isomer. Within each experiment the M values and the percentages of the more highly deuterated species increased with increasing temperature. It was not possible to compare directly these distributions with those of Kemball (130) due to the different gas ratios used. The two sets of results were, however, similar, Kemball observing the production of all four deuteromethanes initially, the species containing one and four deuterium atoms being the predominant isomers.

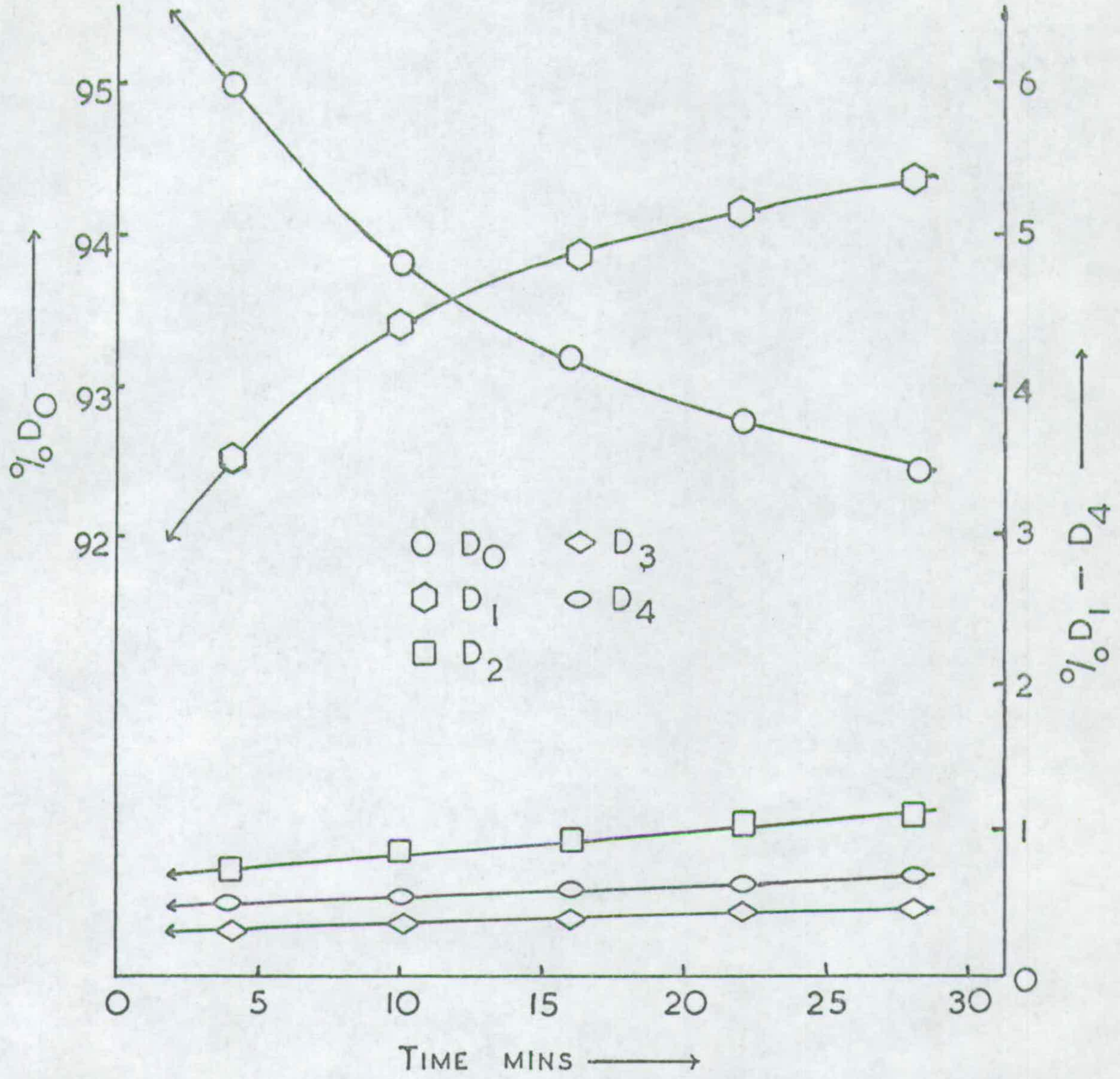


FIG. 3.20 EXCHANGE OF METHANE WITH DEUTERIUM AT 195°C ON AN UNSINTERED PLATINUM FILM

TABLE 3.36.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF METHANE WITH DEUTERIUM

Catalyst	Temp. °C	Percentage of isotopic species				$M=\frac{k_\phi}{k_o}$	$M=\frac{\Sigma ndn}{100}$
		d_1	d_2	d_3	d_4		
Unsintered	195	64.35	16.0	7.25	14.40	1.66	1.83
film	242	62.0	15.0	9.0	14.0	1.58	1.75
"	246	46.75	12.0	14.0	27.25	2.01	2.60
film	183.5	62.2	17.1	8.65	12.0	1.52	1.70
Sintered at	212	65.0	15.25	6.5	13.25	1.66	1.68
250°C	214	64.6	16.15	7.83	11.35	1.57	1.66
for 1 hr.	239	65.0	13.5	7.5	14.0	1.72	1.71

3.7. The Hydrogenation of Ethylene

The hydrogenation of ethylene has been studied on sintered and unsintered films over the temperature range -98°C to -35°C. The mass spectral data were analysed by the method described in Part II section 2.2., and the rates of hydrogenation shown in Table 3.36. were calculated from the zero order plots of percentage ethane against time.
The satisfactory analysis of the mass spectral data that was obtained even at low extents of hydrogenation is shown by the zero order rate plots in Figures 3.21. and 3.22.

One of the surprising features of this work was the non-equivalence of the apparent activation energies for the reaction on the two kinds of films. This is illustrated by the Arrhenius equation plots shown in Figure 3.23., where presintering the film, instead of reducing

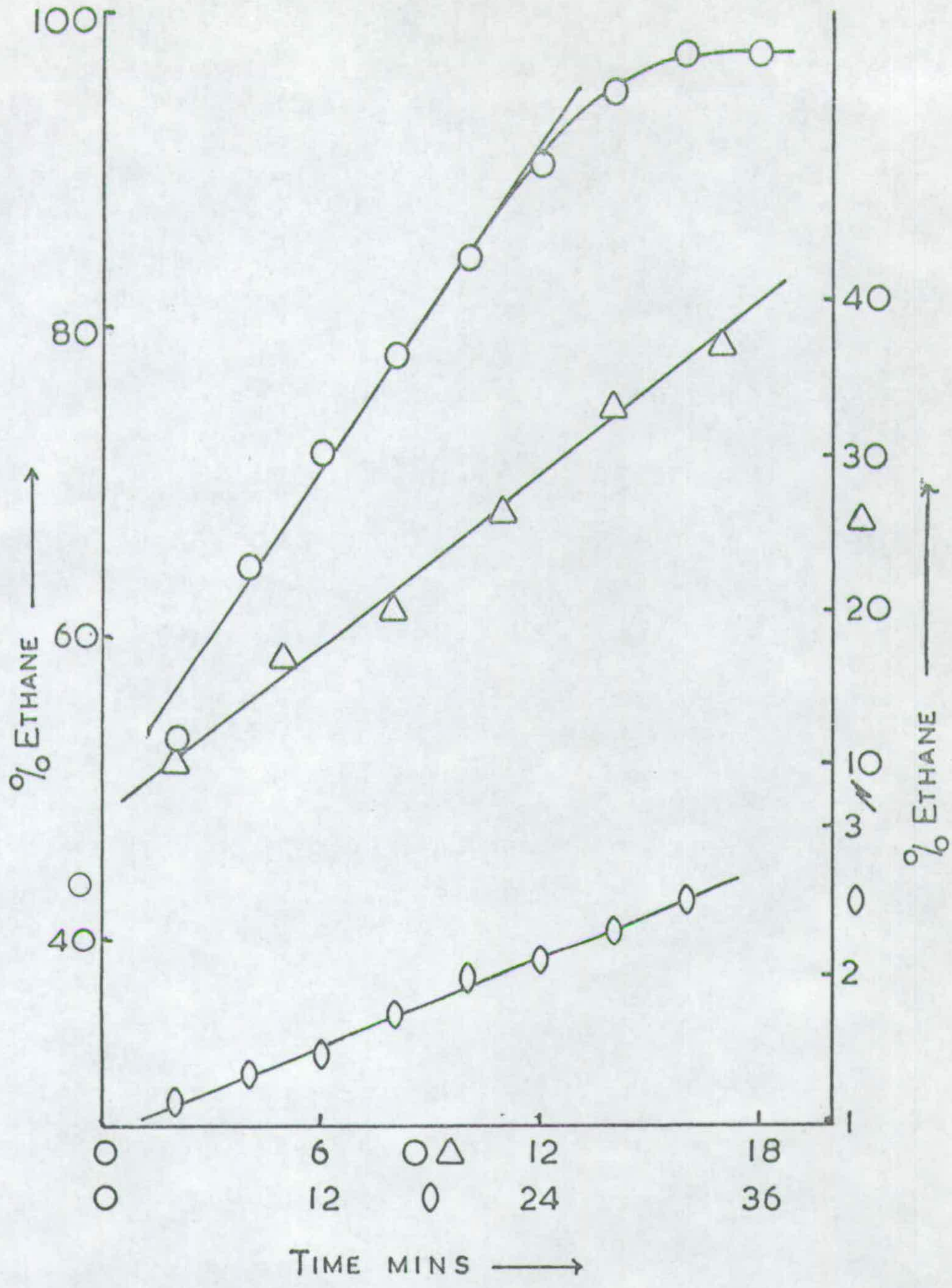


Fig. 3.21 Zero Order Rate Plots for the Hydrogenation of Ethylene on Platinum Films

0 on a Sintered Film at - 74°C

△○ on an Unsintered Film at △, -88°C;

○, at -77°C

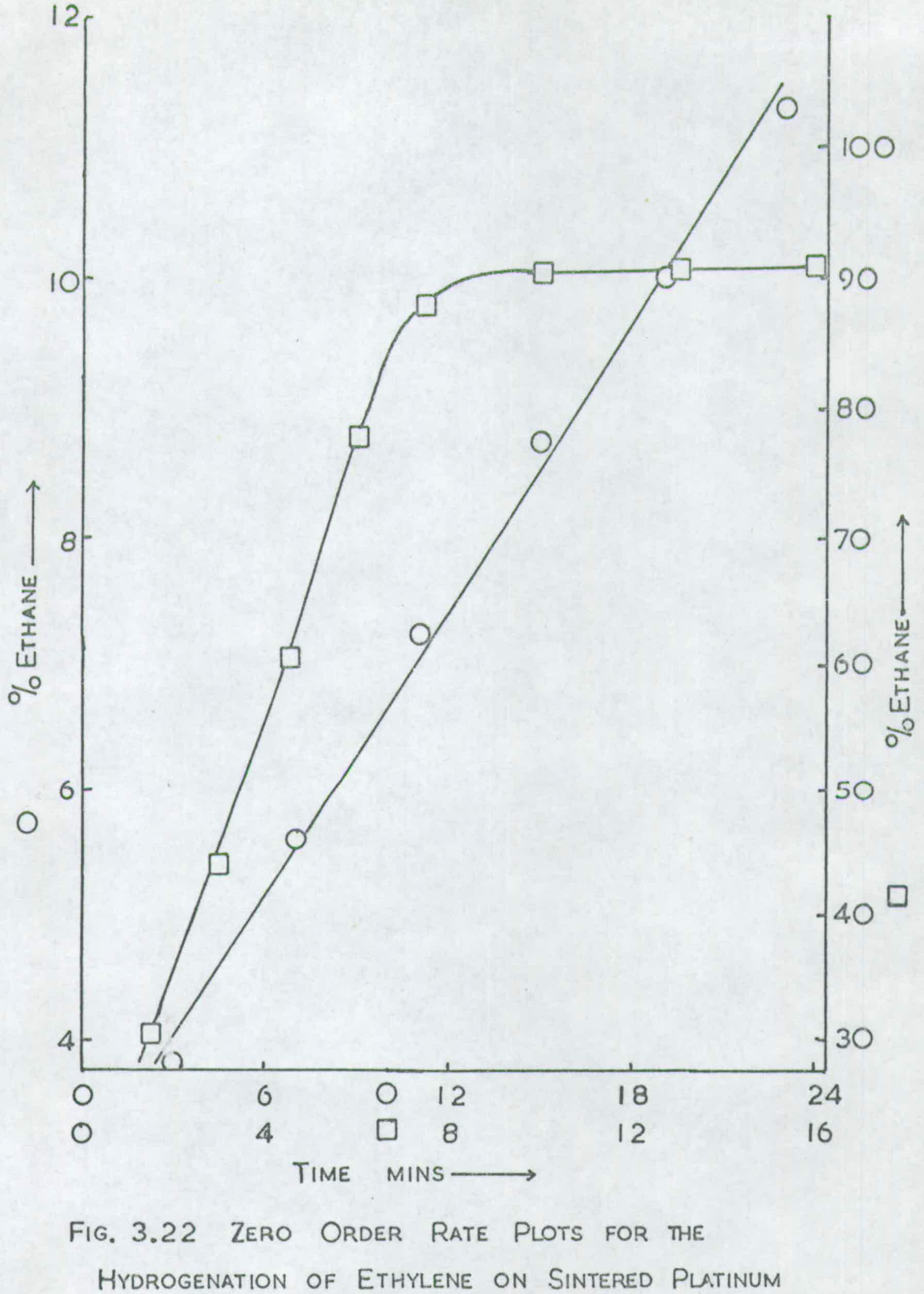


Fig. 3.22 Zero Order Rate Plots for the Hydrogenation of Ethylene on Sintered Platinum Films

○ Reaction at − 59.7°C

□ Reaction at − 35.2°C

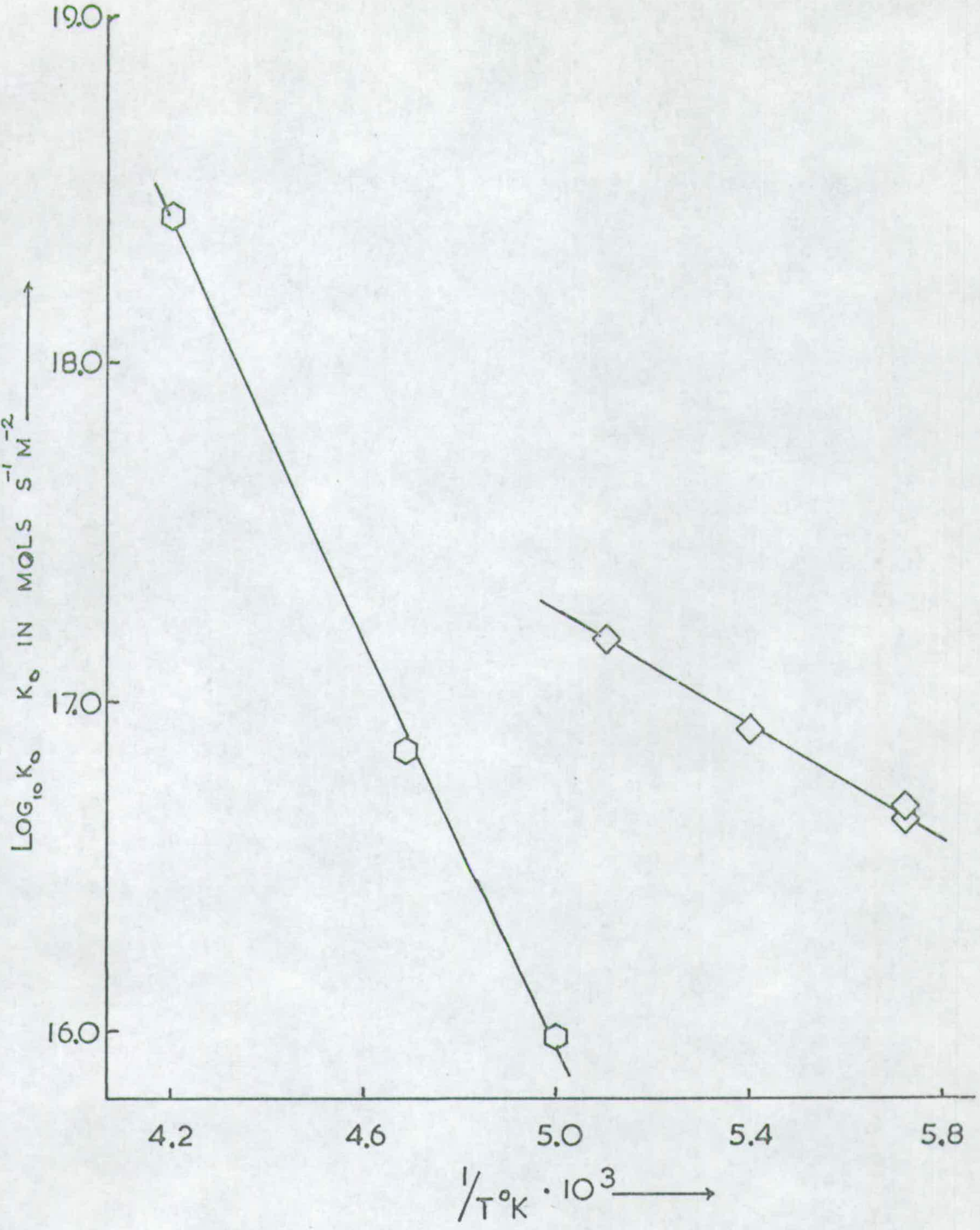


FIG. 3.23 ARRHENIUS PLOTS FOR THE HYDROGENATION OF ETHYLENE ON PLATINUM FILMS

◇ REACTION ON UNSINTERED FILMS

⬡ REACTION ON SINTERED FILMS

TABLE 3.37.

RATES OF HYDROGENATION OF ETHYLENE
ON PLATINUM FILMS

Type of film used	Reaction temperature °C	Rate of hydrogenation mols $s^{-1}m^{-2}$. 10^{-16}
Unsintered	-98.0	4.94
"	-98.0	4.54
"	-88.0	8.30
"	-77.0	15.75
Sintered at	-74.0	0.96
250°C for	-59.5	7.24
1 hr.	-35.0	270.3

the activity of the catalyst by altering the pre-exponential factor as expected, also increased the apparent activation energy for the hydrogenation reaction by a factor of 3.6. This effect could not be attributed to using an ethylene 'poisoned' film because the experiments were carried out on different films; and not by using one film with the reaction cycle, hydrogenation on an unsintered film, sintering at 250°C in vacuo, followed by hydrogenation on a sintered film. The Arrhenius parameters are given in Table 3.38. The low value found for the activation energy on the unsintered films, appears to be a real phenomenon and can not be explained by a diffusion controlled process.

TABLE 3.38.

ARRHENIUS PARAMETERS

Film used	Apparent activation energy E_0 k J $mole^{-1}$	Pre-exponential factor $\log_{10} A$ A in mols $s^{-1}m^{-2}$
Unsintered	16.47	21.56
Sintered	59.01	31.35

3.8. Summary of Results

The exchange reactions of propane, butane, methane, and neopentane with deuterium have been studied on various platinum catalysts. The rate plots that were obtained from the kinetic equations fell into two groups. When the exchange reactions of the hydrocarbons were studied on unsintered films the plots were usually retardedly curved. However, when using presintered films or supported catalysts this curvature was no longer apparent, the reaction obeying apparent first order kinetics. The retarded curvature that was observed was only very slight and was ascribed to sintering of the films during the reaction. In the case of propane and butane no evidence was found to suggest that the secondary hydrogen atoms were exchanging at a significantly fasterrate than the primary hydrogen atoms.

Butane and propane were readily exchangeable on unsintered films at temperatures greater than 35°C, all the isotopic species being produced in substantial amounts initially. The initial product distributions always showed a maximum at the perdeuterocompound, at low temperatures both molecules also showed a maximum at the d_2 deuterocompound; but at higher temperatures this maximum had disappeared and was replaced by one at the monodeuterocompound. Contrary to expectation neopentane exchanged readily on the unsintered films over the same temperature range as propane and butane, but not all the hydrogen atoms were readily exchangeable only species containing up to four deuterium atoms being produced initially. The production of species containing more than one deuterium atom initially indicated that all three hydrocarbons were undergoing a multiple exchange process. That the mechanism for the exchange reaction consisted of a combination of at least two processes with different activation energies was shown by the fact that the M values and amounts of the more highly deuterated species increased with increasing temperature. No evidence was obtained to indicate that the exchange reaction was being progressively self poisoned at the low temperatures required to propagate the exchange process on unsintered films. This is illustrated by the fact that the presorption of saturated hydrocarbons upon an unsintered film at 105°C for 1 hr. only produced a very small reduction in the activity of the film for the subsequent exchange of neopentane.

Presintering a film at 250°C for 1 hr. reduced the activity of the film for the subsequent exchange reaction of neopentane by a factor of 6.3 and of butane by a factor of 32.3. With both molecules reaction temperatures in excess of 80°C were required to propagate the exchange process. Presintering the films did not produce any marked change in the reaction mechanism that was not consistent with the higher reaction temperatures, the initial product distributions being of the same shape as those obtained for the higher reaction temperatures on the unsintered films. No evidence was obtained to indicate that at temperatures less than 180°C the reaction was being progressively self poisoned. Some evidence for the formation of irreversibly adsorbed species was, however, found when the exchange reaction of neopentane was carried out on sintered films which had been prepoisoned with neopentane or a neopentane-deuterium mixture at high temperature. When neopentane itself was presorbed at 220°C for 1 hr. the activity of the film for the subsequent exchange reaction was very much reduced, and this reduction was greater than that observed when a neopentane-deuterium mixture was presorbed at 250°C for 1 hr.

The exchange reaction of neopentane on the platinum supported catalysts was similar to that on the films with respect to the initial product distributions. The Arrhenius parameters were, however, different the apparent activation energies being lower. These catalysts were, however, quite active, the platinum on γ-alumina catalyst having an activity similar to that of a sintered film.

It is often said, especially with reference to organic chemistry, that the first member of a homologous series is anomalous in its reactions. This also appears to be true in the case of exchange reactions. Methane in contrast to the other hydrocarbons studied was very difficult to exchange, reaction temperatures in excess of 180°C being required to propagate the exchange process on both sintered and unsintered films. The Arrhenius plot showed that on both types of film the reaction obeyed the same Arrhenius equation, an exact correlation being found between the results reported in this thesis and those of Kemball (130). Although methane was difficult to exchange all four deuteromethanes were produced initially, maxima being observed at the monodeutero- and perdeuteromethanes. Within each experiment the M values and the percentages of the more highly deuterated species increased with increasing reaction temperature.

The Arrhenius equation parameters for the exchange reactions summarized in Table 3.39. show that sintering the films increased the

TABLE 3.39.

ARRHENIUS PARAMETERS FOR THE EXCHANGE REACTIONS ON PLATINUM CATALYSTS

Catalyst used	Molecule	Apparent activation energy E_0 k J mole^{-1}	Pre-exponential factor $\log_{10} A$ A in mols $s^{-1}m^{-2}$	Temp. in °C for which $k_0 = 3.4.10^{16}$ mols $s^{-1}m^{-2}$
Unsintered	C_3H_8	$81.34 \pm^{x_1}$	$29.07 \pm^{x_2}$	$66 \pm^{x_3}$
films	*n*-C_4H_{10}	$58.39 \pm^{3.84}$	$25.88 \pm^{0.60}$	$53 \pm^{0.2}$
"	*neo*-C_5H_{12}	$46.43 \pm^{4.03}$	$23.80 \pm^{0.60}$	$60.5 \pm^{1.3}$
Sintered	CH_4	$90.24 \pm^{6.70}$	$25.94 \pm^{0.70}$	$180 \pm^{5.5}$
films	*n*-C_4H_{10}	$61.90 \pm^{8.10}$	$24.89 \pm^{1.03}$	$114 \pm^{4.7}$
(250°C for 1 hr.)	*neo*-C_5H_{12}	$62.80 \pm^{4.79}$	$25.39 \pm^{0.62}$	$97 \pm^{2.3}$
Pt-δAl_2O_3	*neo*-C_5H_{12}	$25.08 \pm^{3.11}$	$20.67 \pm^{0.42}$	$44 \pm^{9.3}$
Pt-SiO_2(140°C)	*neo*-C_5H_{12}	$33.17 \pm^{15.50}$	$20.65 \pm^{2.28}$	$135 \pm^{0.8}$
Pt-SiO_2(500°C)	*neo*-C_5H_{12}	$32.83 \pm^{3.45}$	$19.42 \pm^{0.44}$	$321 \pm^{24.7}$

x_1, x_2, x_3 could not be calculated.

apparent activation energy of the reaction; and although the results have not been illustrated by a diagram in this thesis, the exchange reaction of the hydrocarbons on the two types of films showed the compensation effect.

CHAPTER IV

DISCUSSION

4.1. Surface Areas of the Films

Metal films rather than metal supported catalysts have been used for the study of some catalytic reactions, because on the macro scale they can be prepared reproducibly with respect to both activity and mechanistic characteristics; and also because the reactions which compounds undergo on them can be related directly to the nature of the metal and not be influenced by any effects which, for example, the support might introduce. On the atomic scale, however, films of one metal may differ considerably from one another, and if one is attempting to correlate one's own results with those obtained by other workers it is essential to eliminate as many of the catalyst variables as possible. When using metal catalysts the absolute rate of the reaction will usually be proportional to the area of the metal available for reaction, and in the general case the surface area A of, for example, a metal film will be dependent upon the following variables:

(a) The weight of the film.

(b) The geometry of the reaction vessel system.

(c) The preparative conditions.

(d) The temperature of deposition.

That is,

$$A = f(a,b,c,d)$$

and depending upon the metal all or some of these variables will be operative.

Of the variables mentioned above, the geometry of the reaction vessel system was kept constant throughout the duration of this work;

and the position of the filament in the reaction vessel, the outgassing current, the evaporation current, and the deposition time were kept as constant as possible. Even with these precautions, however, the weights of the films still varied slightly, but it is considered that these small variations would not have produced any substantial variation in the surface areas of the films used in this work.

The surface areas and the surface structure of evaporated platinum films have not been extensively studied. In the reports that have appeared in the literature the surface areas of the films were, as in the case of the areas reported in this thesis, usually measured by the physical adsorption of krypton at 77°K. The majority of the reports agree upon the applicability of the B.E.T. equation for measuring the surface area. Thus Trapnell et al. (120) and Brennan et al. (118) agree that for the adsorption of krypton the B.E.T. equation is applicable using relative pressures as low as 0.001, and Anderson and Baker (119) also found that the adsorption of xenon on both sintered and unsintered films obeyed the B.E.T. equation over the range of relative pressure $0.001 < Pe/Po < 0.06$. Frennet et al. (131), however, measured the surface area by both the B.E.T. and Kaganer methods and reported that though the areas as measured by the two methods agreed at high pressures they did not agree at low pressures; while Adamek et al. (132) reported that the adsorption of krypton did not obey the B.E.T. equation but obeyed the Freundlich equation. Although the consensus of opinion supports the applicability of the B.E.T. equation, the values that were obtained for the surface areas varied considerably as shown in Table 4.1. This spread in the results was probably caused by variations in the size of the film crystallites and surface heterogeneity.

TABLE 4.1.

SURFACE AREAS

Gas adsorbed	Sintering temperature °C	Surface area m^2	Reference
krypton	0	0.184	
"	250	0.04	
"	0	0.1989	118
"	0	0.150	131
"	40	0.12	120
xenon	0	0.097	119
"	262	0.04	119

The surface areas of platinum films have also been calculated from "hydrogen" adsorption measurements at 0°C and 13.3 kNm^{-2} pressure (93); and at 0°C using pressures greater than 0.4 kNm^{-2} (119). These conditions were chosen because it is known that at 0°C and at pressures greater than 0.4 kNm^{-2} the hydrogen adsorption isotherm is flat topped (119), and also to ensure that the weakly bonded structures reported for the adsorption of hydrogen at 73°K (133) were no longer present. Using this method Kemball (93) obtained a value of 0.057 m^2, and Anderson and Baker (119) a value of 0.087 m^2 for the surface area of an unsintered film, compared with a value of 0.043 m^2 obtained in this work by the method of Hall and Lutinski (117). The accuracy of the results obtained in this work has been criticized in section 3.1. It is, however, more difficult to explain the variation in the other results quoted. This may be due to slight differences in technique or accuracy of measurement, thus Kemball (93) used deuterium whereas Anderson and

Baker (119) used hydrogen. It is, however, significant that Frennet et al. (131) have reported that the chemisorption of hydrogen was not reliable. Platinum does not form a bulk hydride readily, and at the temperature and pressures used it is unlikely that the variation in the results can be ascribed to hydride formation. The variation may, therefore, be caused by surface heterogeneity.

The results given in section 3.1. (Part II) indicated that the adsorption of krypton on a film which had been deposited at 0°C was not reproducible. After determining the adsorption isotherm at 77°K and pumping off the adsorbed krypton at 273°K, the volumes of krypton adsorbed for the subsequent isotherm at 77°K were less than those obtained initially for the same relative pressures. There are a number of possible explanations for this behaviour:

(a) Sintering of the film by the heat liberated during the adsorption.

(b) Diffusion of the krypton into the bulk metal or between the crystallites.

(c) The presence of high energy sites preventing the desorption of the krypton.

Krypton is physically adsorbed on the surface of the film and hence the heat of adsorption will be similar to the heat of liquefaction of the gas. Trapnell et al. (120) in their study of the chemisorption of oxygen on a platinum film which had been sintered at 40°C obtained a value of 280 $\mathrm{kJmole^{-1}}$ for the heat of chemisorption at a coverage $\theta < 1$. They (120) also found that the ratio of the surface area after the adsorption of oxygen to the surface area before the adsorption of oxygen was equal to 0.97, indicating that the heat liberated during the adsorption had not sintered the film appreciably. It is, therefore, extremely unlikely that the heat of physical adsorption of krypton would cause the film to sinter.

The surfaces of metal films are known to be heterogeneous; for example, the work function has different values on different crystal faces (134), and the variation of the heat of chemisorption with coverage has been ascribed to a variation in the energy of surface sites (135). The basis for using the B.E.T. equation to measure surface areas assumes that the nature of the adsorbent is of secondary importance, the krypton being physically adsorbed on the surface with a structure similar to that found in the liquid. Very little interaction will, therefore, occur between the metal atoms and the physically adsorbed krypton and the presence of high energy surface sites would not be expected to prevent desorption of the krypton upon warming to 0°C.

The variation between the isotherms for the adsorption of krypton may be regarded as a form of hysteresis. It is known (136) that nickel films which have been deposited at 0°C in vacuo are microcrystalline in structure with an average crystallite size of 20-100 nm and intercrystal gaps of approximately 2.0 nm. It is, therefore, reasonable to assume that a platinum film which had been deposited at 0°C in vacuo would have a similar structure. By assuming that an unsintered platinum film consists of cylindrical crystallites 60 nm in diameter and 7 nm in depth separated by intercrystal gaps of 2 nm, it can be shown by an approximate calculation that part of the discrepancy between the results for the unsintered film may be accounted for if the krypton which has been adsorbed between the crystallites is not desorbed on warming the film to 0°C. This calculation assumes that the crystallites have flat tops and are non porous. This is extremely unlikely and the remaining discrepancy may be accounted for if it is assumed that the adsorbed krypton is trapped in pores on the film surface.

Metal films are prepared by evaporating the metal from a filament at high temperature and rapidly quenching it by deposition onto a substrate at a temperature much lower than the evaporation temperature. The structure of the film will thus be characteristic of the difference between the evaporation and deposition temperatures. The film will, therefore, have excess surface energy and will be stable only at temperatures lower than the deposition temperature. On increasing the temperature above the deposition temperature the film will reduce its excess surface energy to that characteristic of the new temperature by crystal growth and the elimination of surface asperities, thereby causing the surface area to decrease. This conclusion is verified by the results reported in this thesis where sintering the film at 250°C for 1 hr. caused the surface area to decrease from 0.184 m^2 to 0.04 m^2, and by the results of Anderson and Baker (119) who found that sintering a platinum film at 262°C decreased the area from 0.0965 m^2 to 0.0386 m^2.

In this work it was assumed that the surface areas of the films were independent of their weight. The experimental rates of exchange were, therefore, converted into absolute units by using a value of 0.184 m^2 for the surface area of an unsintered film, and a value of 0.04 m^2 for the surface area of a film which had been sintered at 250°C for 1 hr. in vacuo. The justification for this assumption is shown by Figure 3.12. for the exchange of neopentane with deuterium on unsintered platinum films whose weights varied from 5.3 to 16.4 mg. It was found that if the rates of exchange were assumed to be proportional to their weight the exchange reaction could not be described by a single solution of the Arrhenius equation. Instead they were separated into two groups which comprised:

(a) The exchange reaction on films weighing 5.3 and 5.8 mg.
and (b) The exchange reaction on films weighing 15.1 and 16.4 mg.

The rates of exchange of saturated hydrocarbons with deuterium on palladium films have also been found to be independent of the weight of the film (83); and this may indicate that even at very low film weights the crystallites of platinum and palladium films are dispersed evenly over the substrate surface. For nickel films the surface area is slightly dependent upon the weight of the film, and it is very unlikely that for platinum films which had been deposited at 0°C the surface area of a film weighing 40 mg would have exactly the same area as a film weighing 5 mg. There will thus be a relationship between the surface area A and the weight of the film W on the form

$$A = B + C\,W,$$

where B and C are constant for a particular deposition temperature. In the case of platinum films $B \gg C$ and the surface area will be virtually weight independent.

4.2. Rate Plots and Poisoning of the Exchange Reaction

It has been mentioned in Part I section 3.4. that for an exchange reaction where the hydrocarbon molecules are reversibly adsorbed on the catalyst surface, the incorporation of deuterium into the molecules follows apparent first order kinetics. Retarded deviation of the reaction from apparent first order kinetics may be due to a number of causes, viz:

(a) Non-equivalent hydrogen atoms in the hydrocarbon molecule.

(b) Progressive self poisoning of the catalytically active sites during the reaction.

(c) Progressive sintering of the catalyst during the reaction.

(d) Inaccurate fragmentation corrections causing inaccuracy in the ϕ values.

(e) Incorrect value of ϕ_∞ used in the kinetic equation.

The results that were obtained for the exchange of the hydrocarbons with deuterium showed that the shapes of the rate plots could be classified into two groups:

(1) Those showing adherence to the apparent first order kinetics.

and (2) Those showing retarded deviation from the kinetics.

It is proposed to discuss individually each of the groups (a) to (e) given above, to determine which is responsible for the effect described in group (2).

The value of ϕ_∞ which is used in the kinetic equation should be determined experimentally. This, however, was usually impractical and the value of ϕ_∞ used was assumed to be $1.14\ \phi_{\infty\ st.}$. If it is assumed that the exchange reactions followed apparent first order kinetics, then if the experimental ϕ values are close to ϕ_∞ adherence to the kinetics will only be observed if $\phi_\infty \approx \phi_{\infty\ exp.}$. If $\phi_\infty \neq \phi_{\infty\ exp.}$ then either retarded or acceleratory deviation from the kinetics will be observed depending upon whether the value of ϕ_∞ used is greater or less than $\phi_{\infty\ exp.}$. As the exchange reactions were not usually studied at ϕ values close to ϕ_∞ it is unlikely that the retarded deviation of the rate plots observed for the reactions on the unsintered films can be explained on the basis of group (e).

The value of ϕ which is used in the kinetic equation is defined for any hydrocarbon C_nH_m by the equation

$$\phi = \sum_{i=1}^{m} i\, d_i$$

This implies that the percentage d_i of each of the deuterated molecules containing i deuterium atoms at time t is accurately known. Since the percentage of each of the deuterated species is calculated from the mass spectral data after applying the fragmentation corrections, the accuracy of the ϕ values will depend upon how accurately the fragmentation corrections can be calculated. Because the fragmentation patterns of the deuterated species vary with deuterium content, the fragmentation corrections when calculated by statistical methods will only be approximately correct for those molecules which fragment to a small extent under electron impact. This argument only applies in those cases where large amounts of the more highly deuterated species are produced. It can be readily shown that for a molecule which reacts slowly by a simple exchange process, the accuracy of the fragmentation corrections does not greatly affect the accuracy of the isotopic distributions. Of the hydrocarbons studied all underwent extensive multiple exchange. In the case of neopentane, since the extent of fragmentation of the tert-butyl ions produced by the quantitative loss of a methyl group from neopentane was very small, it is probable that the deviation from the kinetics shown by the exchange reaction on the unsintered films was not due to any inaccuracy in the statistical calculation of the fragmentation corrections. This conclusion will also apply to the exchange reactions of butane and methane. In these cases, although the extent of fragmentation under electron impact was substantial, the reactions on the sintered films obeyed apparent first order kinetics under the same exchange conditions as those for which the reactions on the unsintered films showed deviation from the kinetics. In the case of the isotopic propanes the mass spectral data were analysed using a computer program which had been derived to take into account the variation of the fragmentation patterns of the deuterated molecules with deuterium content. It can, therefore, be concluded that for the isotopic propanes, although the extent of fragmentation was large, the mass spectral data have been adequately analysed.

From the arguments given above it has been concluded that the retarded deviation shown by some of the rate plots was not caused by inaccurate ϕ values. It cannot, however, be assumed that the converse of this conclusion is correct. Because the ϕ values are accurate, i.e. the plot of $\log_{10}(\phi_\infty - \phi)$ against time is a straight line, does not automatically mean that the product distributions are accurate. It is possible that overcorrection of some of the peaks has been balanced by undercorrection of some of the other peaks, thus leading to 'accurate' ϕ values but inaccurate product distributions.

One of the basic assumptions in the derivation of the kinetic equation is that all the hydrogen atoms in the molecule are equally susceptible to exchange. If the molecule contains groups of hydrogen atoms which are not equally susceptible to exchange they will react at different rates, and the overall rate of reaction will be a composite of the rates of exchange of the different groups of hydrogen atoms. The plot of $\log_{10}(\phi_\infty - \phi)$ against time will, therefore, be non linear; the initial and final regions of which will, if the molecule contains two non-equivalent groups of hydrogen atoms, approximate to straight lines. Initially the rate of reaction will be mainly governed by the rate of exchange k_A of the most easily exchangeable group of hydrogen atoms. After this group has reached equilibrium the rate of reaction will be governed by the rate of exchange k_B of the least easily exchangeable group of hydrogen atoms. The resulting degree of deviation from apparent first order kinetics will, therefore, depend upon the ratio k_A/k_B, and the methods used for separating the overall rate of exchange into its components have been described in the literature (104,137). Of the hydrocarbons studied propane and butane contain both primary and secondary hydrogen atoms, whereas neopentane and methane contain only primary hydrogen atoms. All the hydrocarbons, however, gave a slight retarded deviation of the rate plots for the exchange reaction on unsintered films. This, coupled with the fact that the exchange reactions of methane, butane, and neopentane on sintered films and of neopentane on supported catalysts obeyed the apparent first order kinetic equation, indicates that non-equivalence of the hydrogen atoms in the molecule was not responsible for the retarded deviation of the exchange reaction from the kinetic equation. It follows immediately from this argument that for butane and propane, although the primary carbon-hydrogen bond dissociation energy is approximately 16.5 kJ mole^{-1} greater than the secondary carbon-hydrogen bond dissociation energy, the reactivities of the primary and secondary hydrogen atoms on platinum films are similar.

The exchange reactions of hydrocarbons with deuterium on catalysts being surface phenomena, the activity of the catalyst will depend upon the number of catalytically active sites which will be a function of the surface area and temperature. Progressive self poisoning of the catalytically active sites or progressive sintering of the catalyst during the reaction will reduce the number of active sites available for reaction and hence cause a gradual reduction in catalytic activity with time. Since the retarded deviation of the rate plots shown by the exchange reactions on the unsintered films was only very slight, the reasons for deciding whether progressive sintering or self poisoning was responsible for the effect must be based on small differences in catalytic behaviour.

If it is assumed that the retardation of the rate plots for the exchange reactions on the unsintered films was due to self poisoning, it is necessary to explain why the reactions on the sintered films obeyed the apparent first order kinetic equation. The initial product distributions for the exchange of butane and neopentane on the unsintered films did not differ very much from those on the sintered films. This indicates that presintering the films has not preferentially eliminated some of the exchange sites, and one would, therefore, expect that if the exchange reaction on the unsintered films is being self poisoned it would also show this behaviour on the sintered films. One reason why this is not occurring may be that the irreversibly adsorbed species formed at low temperatures are being reversibly hydrogenated at the higher temperatures required to propagate the exchange process on the sintered films.

There are a number of reasons for rejecting the hypothesis that the retarded curvature of the rate plots was due to self poisoning. Anderson and Avery (42) postulated that an $\alpha\alpha\gamma$-triadsorbed intermediate was the species responsible for the hydrocracking and isomerization of saturated hydrocarbons containing at least three carbon atoms on platinum films. The formation of this species, which it was hoped would be the intermediate responsible for the self poisoning of the exchange reactions of propane, butane and neopentane on platinum films, must occur from the prior formation of either an $\alpha\gamma$- or an $\alpha\alpha$-diadsorbed intermediate. Gault, Rooney and Kemball (50) in their study of the exchange reactions of polymethylcyclopentanes with deuterium on evaporated metal films showed that on unsintered platinum films at 50°C the hydrogen atoms in the gem dimethyl groups were being exchanged by an $\alpha\gamma$-diadsorbed intermediate. They (50) did not, however, obtain any evidence to indicate that the reaction was being self poisoned, nor to indicate that platinum was an active catalyst for the formation of $\alpha\alpha$-diadsorbed intermediates.

If irreversibly adsorbed species are being formed on the surface of unsintered platinum films during the exchange reaction, it would be expected that the adsorption of hydrocarbons in the absence of deuterium would have a greater deactivating effect upon the activity of the films for the subsequent exchange reaction than the adsorption of the hydrocarbons in the presence of deuterium at the same temperature. Also if $\alpha\alpha\gamma$-triadsorbed intermediates are responsible for the self poisoning of exchange reactions on platinum catalysts, the presorption of hydrocarbons which cannot form $\alpha\gamma$-diadsorbed intermediates would not be expected to have the same deactivating effect as the presorption of hydrocarbons which can form $\alpha\gamma$-diadsorbed intermediates. However, when methane, ethane, propane, or a neopentane-deuterium mixture was presorbed at 105°C for 1 hr. on an unsintered film, the activity of the film for the subsequent exchange reaction of neopentane was only very slightly reduced from that observed in the absence of the presorbed hydrocarbons; nor was any evidence obtained to show that the presorption of propane or a neopentane-deuterium mixture produced a greater deactivating effect than the presorption of methane or ethane. Also when butane was presorbed at 145°C for 45 mins on an unsintered film the subsequent exchange reaction of butane proceeded at a rate comparable with those for some of the normal exchange reactions.

The conclusion that may be drawn from this argument is that at the low temperatures required to propagate the exchange reactions on unsintered films the retarded curvature of the rate plots was not due to self poisoning of the exchange reaction. The retarded curvature must, therefore, have been caused by progressive sintering of the film during the reaction. It was mentioned in section 4.1. that at temperatures greater than the deposition temperature platinum films are unstable, and reduce their excess surface energy by crystallite growth and the elimination of surface asperities. At the low temperatures required to propagate the exchange process on the unsintered films the films will slowly sinter, and the resultant decrease in the catalytically active area would be sufficient to explain the slight retarded curvature of the rate plots. The platinum supported catalysts and the sintered films have been thermally treated at high temperature and the metal crystallites may be regarded as being in a stable condition. On both these types of catalyst the exchange reaction of neopentane followed apparent first order kinetics. The most striking evidence for the progressive sintering of the films during the reaction was obtained from the exchange of methane with deuterium on platinum films. On sintered films the exchange reaction always obeyed the apparent first order kinetic equation. On the unsintered films, however, two types of rate plot were obtained. At the initial temperature A the rate plot was curved, and at the final temperature B straight line rate plots were obtained. However, if the initial rate of A was converted into absolute units using a value of 0.184 m^2 for the surface area, and if the final rate of A and the rate of B were converted into absolute units using a value of 0.04 m^2 for the surface area, all the rates of exchange obeyed a single solution of the Arrhenius equation; and this solution was also obeyed by the exchange reaction on the sintered films. This result indicates that the curvature of the rate plot was due to the film sintering during the reaction.

Although no evidence was obtained to indicate that the exchange reactions of the hydrocarbons were being self poisoned at temperatures less than 180°C, evidence was obtained showing that it was possible to form irreversibly adsorbed species at high temperatures on sintered films. The presorption of neopentane at 220°C for 1 hr. on a sintered film reduced the activity of the film for the subsequent exchange reaction of neopentane by a factor of 29.5; and the presorption of a neopentane-deuterium mixture at 250°C for 1 hr on a sintered film reduced the activity of the film for the subsequent exchange reaction of neopentane by a factor of 9.0. These results can only be explained by the formation of irreversibly adsorbed species during the presorption stage, the difference between the effects produced by the two types of presorption indicating that the presence of the deuterium was preventing the extensive formation of irreversibly adsorbed species upon the surface of the film. The carbon balance at any temperature during the exchange reactions was constant, and the rate plots were either very slightly retardedly curved or straight, indicating that the reduction in activity was caused by the presorbed hydrocarbon, and not by the gradual formation of irreversibly adsorbed species during the exchange reaction.

The failure of the exchange reactions of saturated hydrocarbons to self poison of temperatures less than 180°C must be related to the stability of the platinum-hydrocarbon intermediates, because other organic molecules are known to form irreversibly adsorbed species. Thus Kemball and Wolf (101) have shown the exchange reactions of amines, and Kemball and Clarke (102) have shown the exchange reactions of ethers, on unsintered platinum films to be self poisoned by adsorption of the hetero-atom to the surface. Olefins will also poison the surface of platinum films. Thus it has been found (138) that the exchange of propylene with deuterium oxide at low temperatures on unsintered films is self poisoned. This is also illustrated by Figure 3.12. where the presorption of ethylene at 105°C for 1 hr. on an unsintered film caused a large reduction in the activity of the film for the subsequent exchange reaction of neopentane. This deactivation must be due to the extensive formation of irreversibly adsorbed ethylene species upon the surface by the initial adsorption of the ethylene by a

π bond, followed by opening of the double bond coupled with extensive dissociation of the carbon-hydrogen bonds.

4.3. Mechanism of Exchange

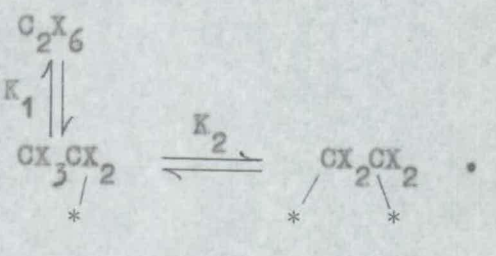
The mechanism for the exchange of saturated hydrocarbons with deuterium on metal catalysts is generally believed to involve dissociative adsorption of the hydrocarbon on the catalyst surface by breakage of at least one of the carbon-hydrogen bonds; and the nature of the adsorbed intermediates responsible for the mechanism can be deduced from the shape of the initial product distributions, their variation with temperature, and the magnitude of the M values and their variation with temperature. In general two main types of mechanism are believed to be responsible for the exchange process on metal catalysts:

(a) A simple exchange mechanism where the hydrocarbon is adsorbed on the catalyst surface by the dissociation of one carbon-hydrogen bond.

and (b) A multiple exchange mechanism which can arise in a number of ways, usually by the interconversion between mono- and multiply-adsorbed species before desorption of the molecule into the gas phase occurs.

Of these mechanistic types either or both may be responsible for exchange depending upon the catalyst used, the hydrocarbon, or the conditions of exchange.

Anderson and Kemball have shown (49) that on metal films the exchange of ethane with deuterium can be represented by the following model



If a parameter P is defined as the ratio K_2/K_1 it is possible by mathematical theory to calculate the expected initial product distribution for certain values of this parameter. Thus it was found that for the exchange of ethane on molybdenum the calculated and observed distributions agreed with a P value of 0.25 (implying mainly a simple exchange process), whereas on palladium a P value of 18 was required to give agreement (implying a multiple exchange process). However, for some metals, notably platinum, where maxima were observed in the initial product distributions at the monodeutero- and perdeutero ethanes, it was not possible to explain the observed distribution by a single value of the parameter P. In the case of platinum agreement between the observed and calculated distributions could only be achieved if it was assumed that 54% of the ethane was reacting with a P value of 2.0, and 46% was reacting with a P value of 20.0. This result must imply that the two processes with high and low values of P are occurring on different parts of the surface, since it is impossible by the mechanistic model shown for the two processes to occur on the same surface site.

As in the case of ethane (49) all the hydrocarbons studied in this work underwent varying degrees of multiple exchange. Although the general shape of the initial product distributions did not vary markedly with temperature, the M values did increase with increasing temperature. This indicates that the mechanism of exchange was a composite of both the simple exchange process A and the multiple exchange process B, the two processes having different activation energies with $E_B > E_A$. The mechanism of exchange for each of the hydrocarbons can, therefore, be represented by a scheme similar to that shown for ethane, but employing different multiply bonded adsorbed intermediates.

The mechanisms of exchange for the hydrocarbons are deduced from the shapes of, and the position of maxima in, the initial product distributions. Therefore, before discussing in detail the mechanism of exchange for each of the hydrocarbons, it is necessary to discuss the accuracy of the distributions. Two criteria will effect the accuracy of the results:

(a) The accuracy with which the fragmentations corrections can be applied to the mass spectral data.

and (b) The accuracy with which the initial product distribution can be calculated from the corrected mass spectral data.

The accuracy of the fragmentation corrections has been discussed in section 4.2. with respect to the calculation of the ϕ values, and it was concluded that although the ϕ values were probably 'accurate' this did not necessarily guarantee that the product distributions were accurate. It can be concluded from the previous discussion that the mass spectral data for propane and neopentane have been adequately corrected. The mass spectral data for butane and methane were, however, corrected for fragmentation by statistical methods. Since the extent of fragmentation of these molecules under electron impact was quite substantial (Table 2.1. p. 50), it is probable that some error has arisen in the application of the fragmentation corrections. Although the general shape of the product distributions will be correct, it is possible that the presence or position of small maxima may be open to question.

The initial product distribution was taken to be the product distribution of the exchange reaction at 2% conversion. With the hydrocarbons used in this work by the time that the reaction temperature had stabilized the conversion of the 'light' hydrocarbon was usually greater than 2%. The calculation of the initial distribution for any hydrocarbon involved plotting the percentage of each of the isotopic species against time and extrapolating the curves to the 'zero time' of the reaction, i.e., the time at which the percentage of the 'light' hydrocarbon was 100. The initial product distribution was then obtained by reading from the graph the percentage of each of the isotopic species at the time for which the percentage of the 'light' hydrocarbon was 98. The accuracy of the initial product distribution depended upon how accurately the extrapolation could be carried out, and this depended upon the initial conversion and the rate of conversion of the hydrocarbon under consideration. The M values calculated from the initial distributions should equal those calculated from the ratio of the rates of exchange and the tables of the initial product distributions given in Chapter III show that an excellent correspondence was usually obtained.

The accuracy of the initial product distributions will, therefore, be mainly determined by the accuracy with which the fragmentation corrections can be applied, and it can be concluded that the initial product distributions for the exchange of methane and butane may be subject to some error.

The exchange of methane with deuterium on platinum catalysts has been studied by a number of workers. McKee and Norton in their study of the reaction on Pt-Ru alloys (139) found that on platinum itself all four deuteromethanes were produced initially in the relative amounts $CH_3D > CH_2D_2 > CHD_3 > CD_4$. The distributions reported in this work and those reported by Kemball (130) showed maxima at the monodeutero- and perdeutero methanes, and it is possible that the distribution obtained by McKee and Norton (139) using a bulk platinum catalyst may be due to a contaminated surface. Kemball (130) has shown that the exchange of methane occurred by a combination of two mechanisms. The monodeuteromethane was produced by a simple exchange mechanism via an α-adsorbed intermediate, and the species containing more than one deuterium atom were produced by the interconversion between α- and

$\alpha\alpha$-adsorbed intermediates. The results obtained in this work can, therefore, be explained by a similar mechanism. The main difficulty is to decide whether this $\alpha\alpha$-diadsorbed intermediate is bonded to one or two platinum atoms. In bulk platinum the nearest neighbour distance is 0.2775 nm, and if it is assumed that the platinum-carbon bond length is the same as that in $[Pt(CH_3)_4]_4$, i.e. 0.225 nm (140), then for the adsorbed methylene radical to be bonded to two platinum atoms without distortion requires a Pt-C-Pt bond angle of 76.2^o, compared with the normal bond angle of 109.5^o found in methane. If however, the adsorbed methylene radical has an sp^2 configuration the carbon atom may bond to a platinum atom by a σ bond utilizing one of the sp^2 hybrid orbitals, the p orbital may then form a π bond with one of the t_{2g} platinum orbitals to give a methylene radical doubly bonded to one platinum atom. This argument can only be qualitative because it makes no allowance for the modification of the platinum orbitals by the neighbouring platinum atoms in the crystal lattice. It is probable, however, that a methylene radical which is bonded to one platinum atom by a carbon-metal σ bond and a p_π-d_π bond will be more stable than a methylene radical which is bonded to two platinum atoms.

The exchange of propane and butane with deuterium on the platinum films gave results similar to those for the exchange of methane and ethane. All possible isotopic molecules were produced in substantial amounts initially, and the percentages of the more highly deuterated species increased slightly with increasing temperature. Since propane and butane contain more than one carbon atom it is possible for the multiply bonded adsorbed species to be bonded to the surface platinum atoms at different carbon atoms, and in keeping with the mechanism proposed for the exchange of ethane (49) it would be possible to exchange all the hydrogen atoms in these molecules by the interconversion between

α- and $\alpha\beta$-adsorbed intermediates.

The exchange of these molecules by the interconversion between α- and $\alpha\alpha$-adsorbed intermediates can be discounted because by such a mechanism it is only possible to exchange a maximum of three hydrogen atoms in each molecule initially. The formation of $\alpha\gamma$-adsorbed intermediates alone can also be discounted as being responsible for the propagation of the multiple exchange process, because by the interconversion between α- and $\alpha\gamma$-adsorbed intermediates it is possible to exchange only five hydrogen atoms in butane and six hydrogen atoms in propane initially. The formation of the large amounts of species containing more than five and six deuterium atoms respectively cannot be explained on the basis of this mechanism alone. It is possible, however, that the formation of $\alpha\alpha$-and $\alpha\gamma$-adsorbed intermediates may be playing a minor part in the exchange mechanism. Thus Gault et al. (50) in their study of the exchange of polymethylcyclopentanes on platinum films found that at 50°C some exchange was occurring in the gem dimethyl groups. They (50) did not, however, obtain any evidence to show that $\alpha\alpha$-adsorbed species were participating in the exchange reaction. It will be shown later that $\alpha\gamma$-adsorbed intermediates are not actively participating in the exchange of neopentane on platinum films, and it is considered extremely unlikely that they are playing any significant role in the exchange reactions of propane and butane. The exchange of propane and butane by a multiple exchange process must, therefore, be propagated by the interconversion between species bonded to the surface at adjacent carbon atoms. A number of intermediates may be formulated, viz., $\alpha\beta$, $\alpha\beta\gamma$, or π allylic; and the initial adsorption of the molecule upon the surface can occur by dissociation of either a primary or a secondary carbon-hydrogen bond.

Kemball and Woodward (129) using an extension of the theory developed for ethane (49) reanalysed the results obtained by Addy and

Bond (128) for the exchange of propane on a platinum-pumice catalyst, and showed that agreement between the observed and calculated distributions for the reaction at 200°C could be obtained if it was assumed that 80% of the propane reacted with a P value of 19.0 and 20% reacted with a P value of 0.30. This dual distribution concept has been criticised by Miyahara (141) who found that a reasonably good correlation could be obtained between the observed and calculated distributions for ethane by applying a steady state treatment to the adsorbed ethane species which were in equilibrium with each other. This is implied by Kemball and Woodward (129) who found that the distributions obtained by Addy and Bond (128) could also be reproduced with a single value of P by introducing the concept of $\alpha\beta\gamma$-triadsorbed intermediates into their theory.

The distributions obtained by Addy and Bond (128), which showed maxima at the monodeutero- and perdeuteropropanes at temperatures greater than 100°C, do not resemble the distributions obtained in this work for the exchange of propane. They do, however, resemble those obtained in this work for the exchange of butane, where pronounced maxima were obtained at the monodeutero- and perdeuterobutanes on both sintered and unsintered films at temperatures greater than 38°C. It is thus likely that at temperatures greater than 38°C the mechanism for the exchange of butane involves the interconversion between α-adsorbed, $\alpha\beta$-diadsorbed, and $\alpha\beta\gamma$-triadsorbed or π allylic intermediates.

Gault et al. (83) have suggested that the presence of a maximum at the d_2-compound in the initial product distributions for the exchange of hexane on rhodium films was due to the direct formation of a diadsorbed intermediate. They concluded, however, that two adjacent secondary carbon atoms was the structural feature necessary for the formation of this intermediate. Although platinum appears to be an active catalyst for dissociating primary carbon-hydrogen bonds the initial product distributions for the exchange of butane do not have a maximum at the d_2-compound, (with the exception of the distribution at 38°C which is considered inaccurate), and it is considered unlikely that the maximum at the d_2-compound in the distribution for the exchange of propane at 39°C is due to the formation of this intermediate.

Kemball and Woodward (129) in their analysis of the results of Addy and Bond (128) developed a theory 'A' which included parameters to allow for differences in the reactivities of primary and secondary carbon-deuterium and carbon-hydrogen bonds. If only the maximum at the perdeuteropropane is considered to be accurate, the distributions obtained in this work resemble some of those calculated by theory 'A'; however, they also resemble that calculated with a P value of 18 by the extension of the theory used for ethane (49). The distributions obtained are summarized in Table 4.2. No evidence was obtained in this work to suggest that the secondary carbon-hydrogen bonds were substantially more reactive than the primary carbon-hydrogen bonds, and the general shape of the distributions obtained in this work may be described on the basis of theory 'B'. Butane and propane are similar in structure,

TABLE 4.2.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF PROPANE

Theory	Percentage of isotopic species								Parameters used*		
	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	S	T	R
This	5.5	12.8	5.8	14.5	3.8	7.3	17.4	33.0	-	-	-
work	6.5	8.5	11.5	8.4	5.5	12.0	17.0	31.0	-	-	-
B	4.4	5.6	6.7	8.1	9.9	12.4	17.2	35.7	-	-	-
A	1.5	2.3	5.7	7.8	9.6	12.1	17.4	43.6	10	40	1.0
A	11.5	2.3	12.4	14.0	13.7	13.4	14.5	28.2	10	40	0.3
A	1.5	2.3	25.1	22.0	16.4	12.2	9.2	11.3	10	40	0.1
A	2.0	2.8	9.5	11.9	12.3	12.1	12.7	36.7	20	20	0.1

* S is the reactivity of a primary carbon-hydrogen bond
T is the reactivity of a secondary carbon-hydrogen bond
R is the reactivity of a carbon-deuterium bond relative to that of a carbon-hydrogen bond.

they both contain primary and secondary hydrogen atoms and a carbon chain of at least three atoms. There is, therefore, no fundamental reason why they should exchange by different mechanisms, and the absence of a maximum at the monodeutero propane may be due to a low probability for forming an $\alpha\beta\gamma$-triadsorbed intermediate, the molecule preferring to exchange mainly by the interconversion between α-adsorbed and $\alpha\beta$-diadsorbed intermediates. Although the mass spectral data for propane were corrected by using the specially derived computer program as described in Part II section 3.2., the presence of the maxima in the initial product distributions at deuterated species containing less than eight deuterium atoms may be open to question. In the case of the first distribution given in Table 4.2. the rate of exchange was slow and hence any errors inherent in the experimental technique, or in the analysis of the results will produce quite a substantial error in the percentages of the deuterated species. In the case of the second distribution given in Table 4.2. the rate of conversion was high and the extrapolation of the experimental product distributions to obtain the initial product distribution will have been subject to a substantial error. Therefore, although the general shape of the initial product distributions will be true as will the absence of a maximum at the monodeuteropropane, the presence and magnitude of the subsidiary maxima are open to doubt. For these reasons no attempt has been made to formulate a mechanism by which they may have been produced, nor to attempt to reproduce the distributions by the insertion of suitable parameters into the theoretical equations of Kemball and Woodward (129).

It is considered that the mechanisms for the exchange of propane and butane are similar, butane exchanging by the interconversion between α-adsorbed, $\alpha\beta$-diadsorbed, and $\alpha\beta\gamma$-triadsorbed or π allylic intermediates; and propane exchanging by the interconversion between

α-adsorbed and $\alpha\beta$-diadsorbed intermediates.

The initial product distributions that were obtained for the exchange of neopentane on the catalysts were different from those obtained for the exchange of the other hydrocarbons. All the hydrogen atoms in the molecule were not equally susceptible to exchange, the initial product distributions showing that only species containing up to three deuterium atoms were produced in substantial amounts, the d_1-species being the predominant isomer. Since neopentane contains only primary carbon-hydrogen bonds and a quaternary carbon atom two schemes can be formulated to explain the multiple exchange process:

(a) The interconversion between α-adsorbed and $\alpha\alpha$-diadsorbed intermediates.

and (b) The interconversion between α-adsorbed and $\alpha\gamma$-diadsorbed intermediates.

The results of Anderson and Avery (42) indicate that at 100°C the rate of hydrocracking and isomerization would be $5.3.10^{12}$ mols $s^{-1}m^{-2}$ compared with the rate of exchange for the species containing four to nine deuterium atoms of $1.9.10^{14}$ mols $s^{-1}m^{-2}$. The difference between the two rates can be explained as follows. In the deuterium exchange experiments the adsorption and desorption of neopentane by an $\alpha\gamma$-adsorbed species without a carbon-carbon bond shift will be characterized by the incorporation of deuterium into the molecule and hence the rate of disappearance of the d_0-neopentane will be large. In the work of Anderson and Avery (42) the reversible adsorption of the neopentane without a carbon-carbon bond shift will have approximately the same rate as in the deuterium exchange experiments; however, because they used hydrogen this reversible rate cannot be measured, and the rate which they obtained will be that arising from the disappearance of the neopentane by a carbon-carbon bond shift. If one uses the rate of hydrocracking and isomerization given above it can be readily shown that if only one hundredth of the surface is catalytically active then the surface of an unsintered film at 100°C would be covered by adsorbed neopentyl radicals in about 2500 s. Taking the extreme case that each neopentane molecule fragments into five adsorbed methyl radicals then the surface would be covered by adsorbed methyl radicals in about 500 s, and if only one hundredth of these species are irreversibly adsorbed then the surface would be covered by irreversibly adsorbed species in about 14 hr. Since the exchange experiments were carried out over a period of about 4 hr., some deactivation of the catalyst with time might be expected. The results reported in this thesis show that at temperatures less than 180°C no self poisoning of the catalyst was observed, and from the rates given above the rate of exchange by an $\alpha\gamma$-diadsorbed intermediate is faster than the rate of hydrocracking and isomerization by a factor of 36. This must indicate that the $\alpha\gamma$-diadsorbed species formed are essentially reversibly adsorbed. This conclusion is also illustrated by the results of Sinfelt et al. (108) who in their study of the hydrogenation of cyclopropane on Pt-SiO_2 found that no hydrogenolysis occurred over the temperature range 79-102°C; and by the results of Anderson and Avery (142) who found that the reaction of cyclopropane and methylcyclopropane with deuterium on platinum films gave only deuterogenation products.

Of the initial product distributions given in Table 3.31. p. 99, only two showed evidence for the extensive formation of species containing up to nine deuterium atoms. Anderson and Avery (42) have shown that $\alpha\gamma$-diadsorbed intermediates can be adsorbed on the surface of an unoriented platinum film with minimum distortion of the molecule. The initial product distributions given in Table 3.31. show that increasing the reaction temperature did not greatly increase the probability of forming $\alpha\gamma$-diadsorbed intermediates from the prior formation of an α-adsorbed intermediate. Gault et al. (50) in their study of the exchange reactions of polymethylcyclopentanes on unsintered platinum films showed that the exchange of the gem dimethyl groups was occurring by the formation of an $\alpha\gamma$-diadsorbed intermediate. The amount of exchange occurring in the gem dimethyl groups was small, and it is possible that the formation of the $\alpha\gamma$-diadsorbed intermediate was being facilitated by the neighbouring π-allylic intermediate, i.e., the intermediate had the form $\pi\gamma$-adsorbed rather than $\alpha\gamma$-adsorbed. Campbell and Kemball (98) have shown that <u>tert</u>-butyl chloride can exchange on platinum films at 0°C without rupture of the carbon-chlorine bond by the interconversion between α-adsorbed and $\alpha\gamma$-diadsorbed intermediates, the chlorine atom being α-bonded to the surface; and they concluded that the adsorption-desorption of the alkyl chloride must be rapid because the initial product distribution showed that the d_1-compound was the predominant isomer. In both these cases the mechanism of exchange may have been influenced by the structure of the molecule. The initial product distributions for the exchange of neopentane on the platinum catalysts showed a pronounced cut-off at the d_3-compound; and it is considered that, although the interconversion between α-adsorbed and $\alpha\gamma$-diadsorbed intermediates may be playing a minor role in the mechanism of exchange, the predominant mode of exchange is the tendency to complete the exchange of the first methyl group to react by the interconversion between α-adsorbed and $\alpha\gamma$-diadsorbed intermediates.

It is possible to formulate two other mechanisms of exchange. Anderson and Avery (42) have shown that for <u>i</u>-butane the isomerization activity relative to the hydrocracking activity was increased by using a [111] oriented platinum film, and this increased activity was explained by assuming that the *i*-butane molecule was adsorbed on the [111] plane by an $\alpha'\alpha''\alpha'''$-triadsorbed intermediate. It would be possible for neopentane to exchange its hydrogen atoms by the formation of this intermediate, giving a maximum at the d_3-compound by the addition of three deuterium atoms. Unoriented platinum films do not have the [111] plane preferentially exposed and this intermediate is not regarded as playing any part in the mechanism for the exchange of neopentane. Another possibility is that some of the neopentane might have isomerized to *i*-pentane which would then have exchanged on the catalysts. Of the catalysts studied the platinum an γ-alumina catalyst had been fired at high temperature, and the formation of the most stable [111] plane would be expected to be most likely on this catalyst. The rate of isomerization of neopentane at 100°C is less than the rate of exchange producing the isotopic *tert*-butyl ions containing one to three deuterium atoms by a factor of 10^4, and the isomerization of neopentane on the [111] planes would not, therefore, introduce any complications into the mechanism of exchange. This is shown by the fact that no isotopic species corresponding to the exchange of *i*-pentane were observed in the initial product distribution for the exchange of neopentane on this catalyst.

4.4. Activities of the Catalysts for the Exchange Reactions

The object of this work was to investigate the self poisoning of the exchange reactions of the lower aliphatic hydrocarbons on platinum catalysts. The results obtained, however, indicated that no discernible self poisoning was observed for the exchange reactions of any of the hydrocarbons on the catalysts studied. It was found that the specific activities of unsintered films for the exchange of propane, butane, and neopentane were similar; but presintering the films at 250°C for 1 hr. caused a large reduction in the activity of the films for the exchange of neopentane and butane. The presorption of saturated hydrocarbons on the surface of unsintered films did not alter the activity of the films for the subsequent exchange reaction of neopentane. However, are these results a feature of platinum as a catalyst or are they caused by using a contaminated surface? In this work the films were evaporated with the reaction vessel closed off from the pumping system. The first few layers of film deposited should, therefore, have removed a large proportion of the residual gas by gettering, and it may be concluded that the films were essentially clean before the admission of the gas mixture. The films may, however, have become contaminated by slight traces of oxygen admitted with the reaction mixture.

There are a number of reasons for concluding that the films used were essentially non-contaminated. Oxygen is known (120) to chemisorb on platinum; the presorption of oxygen on an unsintered film at 145°C for 45 mins. did not, however, reduce the activity of the film for the subsequent exchange reaction of butane but enhanced it slightly. Any oxygen adsorbed on the film would react with the deuterium in the reaction mixture, and it has been shown (138) that the presorption of deuterium oxide at 0°C on platinum films does not affect the activity of the film for the exchange of propylene with deuterium oxide. Platinum films consist of large crystallites and thus have a low platinum dispersion, Boudart et al. (143) have, however, shown that the hydrogenation of cyclopropane at 0°C on low dispersion platinum supported catalysts was not susceptible to oxygen poisoning. The most conclusive evidence for the cleanliness of the surface is given by a comparison of the results obtained in this work with those reported by other workers. The results obtained in this work for the exchange of neopentane on unsintered films agreed with that reported by Gault et al. (82) with respect to both the rate of exchange and the initial product distribution of the deuterated molecules; and an excellent correspondence was observed between the results obtained in this work for the exchange of methane and those reported by Kemball (130). It may, therefore, be concluded that the results reported in this work for the exchange of the hydrocarbons were not obtained by working with a contaminated surface.

Although the initial product distributions for the exchange of neopentane with deuterium show that the mechanism was similar on all the catalysts studied, there was a large variation between the catalysts with respect to both activity and the magnitude of the Arrhenius parameters. The supported catalysts were less active than, and the apparent activation energies and pre-exponential factors were lower than those obtained for the exchange reaction on, the unsintered films.

In section 1.4., p. 8 it was stated that diffusion to and from the catalyst surface was not rate determining for the reactions studied. The lower Arrhenius parameters for the reaction on the supported catalysts cannot be due to this diffusion controlled process because the rates of exchange are not proportional to the square root of the absolute temperature, which is the relation characteristic of a diffusion controlled process. The diffusion of neopentane within the catalyst pores may, however, have important consequences. Kemball (51) has reported that neopentane exchanged on palladium films by a simple exchange process, one deuterium atom being incorporated into the molecule on each interaction with the surface. Dwyer et al. (61) studied the kinetics of the neopentane-deuterium exchange reaction on palladium-silica-alumina and found that the character of the reaction was modified by desorption and diffusion. They (61) observed that more deuterium was being incorporated into the molecule than would have been expected from the results of Kemball (51). However, they found that this discrepancy could be removed by applying corrections to the kinetic data to allow for an enhanced probability of exchange while the molecule was inside the catalyst pores. A comparison of Tables 3.27. and 3.28. shows that at higher reaction temperatures the M values for the exchange reaction on the supported catalysts were significantly greater than those for the reaction on the sintered films, and it is considered that, although this diffusion within the catalyst pores will not have had any significant effect upon the mechanism of exchange, it may be responsible for the lowered Arrhenius parameters for the exchange reaction on the supported catalysts.

The variation in the specific activities of the supported catalysts is more difficult to explain, especially since the specific activities of the unsintered films for the exchange of propane, butane, and neopentane are similar. Boudart et al. (144) have introduced the idea of facile and demanding reactions; a facile reaction being one in which the specific activity of supported catalysts for a reaction is nearly independent of the support or the degree of dispersion of the metal, and a demanding reaction being one in which the specific activity for the reaction is not independent of the support or the degree of dispersion of the metal. Thus the hydrogenation of cyclopropane (143), the dehydrogenation of cyclohexane (145), and the hydrogenation of benzene (146) on various platinum supported catalysts are facile; whereas the hydrogenolysis and isomerization of neopentane on platinum supported catalysts is a demanding reaction (144).

Dorling and Moss (146) have shown that for the hydrogenation of benzene the specific activity of a platinum-silica catalyst which had been fired below 400°C was greater than that for a platinum-silica catalyst which had been fired at 500°C; and Table 3.1., p.54 shows that the platinum-silica catalyst which had been reduced at 140°C was more active for the hydrogenation of ethylene than the platinum-silica catalyst which had been reduced at 500°C by a factor of 9. The results obtained in this work show that the platinum-silica catalyst which had been reduced at 140°C was more active for the exchange of neopentane than the platinum-silica catalyst which had been reduced at 500°C by a factor of 21. This must indicate that the variation in the specific activities of the two platinum-silica catalysts for the exchange of neopentane was due to the demanding nature of the reaction, and the different degrees of dispersion of the platinum on the catalysts coupled with the inaccessibility of some of the platinum crystallites to the neopentane.

The platinum on γ-alumina catalyst used in this work was fluorine promoted, and Myers et al. (147) have shown for the exchange of butane with deuterium that there was an increasing tendency to exchange more hydrogen atoms in the molecule with increasing acidity of the catalyst. This must imply that there is some degree of co-operation between the acid sites on the support and the platinum sites. Table 3.30., p. 98 shows that the platinum on γ-alumina catalyst was more active than the platinum-silica catalyst which had been reduced at 140°C for the exchange of neopentane by a factor of 7.7; and although the degree of dispersion of the platinum on γ-alumina catalyst will be less than that of the platinum-silica catalyst due to the higher reduction temperature, the presence of the fluorine promoter will increase the activity of the platinum on γ-alumina catalyst from that expected on the basis of the degree of dispersion.

The decreased activity of the supported catalysts from that of the unsintered films can thus be explained as being due to the diffusion of the neopentane within the catalyst pores, coupled with the demanding nature of the reaction being influenced by the degree of dispersion of the platinum on, and the nature of, the support.

All the hydrocarbons studied with the exception of propane gave good straight Arrhenius plots for the rates of exchange on the films. In the case of propane the rates of exchange for the reaction on unsintered films deviated from the Arrhenius equation at temperatures greater than 80°C; and the M values at temperatures greater than 118°C were lower than those obtained initially, indicating that the rate of incorporation of deuterium into the "propane" was being affected to a greater extent than the rate of disappearance of the d_o-propane. However, it is believed that this deviation was not due to self poisoning because the apparent first order rate plots were straight, and Figure 3.7. shows that "propane" was desorbed from the surface on increasing the reaction temperature. It is not known whether the exchange reactions of butane and neopentane on unsintered films also exhibited this behaviour, because at temperatures greater than 100°C the ϕ values were close to ϕ_∞. Below 100°C, however, the rates of exchange for propane were comparable to those for butane and neopentane, and the deviation from the Arrhenius equation at temperatures greater than 118°C may be due to sintering of the film. It is not possible, however, to formulate a completely satisfactory explanation for this behaviour.

The activity of the platinum films for the exchange reactions studied varied with the hydrocarbon or the type of film used. The results obtained are summarized in Table 4.3., and the bond strengths of the hydrocarbons are given in Table 4.4.

TABLE 4.3.

ARRHENIUS PARAMETERS

Film used	Molecule	Apparent activation energy E_o kJmole^{-1}	Pre-exponential factor $\log_{10} A$ A in mols $s^{-1}m^{-2}$
Unsintered	C_3H_8	81.34	29.07
"	n-C_4H_{10}	58.39	25.88
"	neo-C_5H_{12}	46.43	23.80
Sintered	CH_4	90.24	25.94
at 250°C	n-C_4H_{10}	61.80	24.89
for 1 hr.	neo-C_5H_{12}	62.80	25.39

TABLE 4.4.

BOND DISSOCIATION ENERGIES (148)

Molecule	Bond dissociation energy kJmole^{-1}	
	primary C-H	secondary C-H
CH_4	436	-
n-C_4H_{10}	420	396
neo-C_5H_{12}	415	-
C_3H_8	410	395

The films have their surfaces exposed to the gas phase and the rate of exchange will not be governed by diffusion within the film structure, nor by diffusion to or from the surface. Deuterium exchanges rapidly with hydrogen on metal films; and the pressure dependency equations for exchange reactions show that the rate is proportional to a negative power of the deuterium pressure, indicating that deuterium is more strongly adsorbed than the saturated hydrocarbon. The specific activity of a metal film for an exchange reaction, as determined by the Arrhenius equation parameters, will thus be dependent upon either adsorption/desorption of the saturated hydrocarbon or the surface reaction. For any exchange reaction the rate of disappearance of the d_0-hydrocarbon will be proportional to the pressure, the number of active sites, and the energetics of the system. At constant temperature and pressure the number of active sites will be constant provided that the exchange reaction is not being self poisoned, and the rate of exchange will depend upon the energetics of the system. For a specific hydrocarbon exchanging on a stable surface the pre-exponential factor in the Arrhenius equation will be approximately constant, and the rate of exchange will be governed by the apparent activation energy, which will be a composite term involving the heats of adsorption and desorption and the activation energy for the multiple exchange process.

The initial product distributions for the exchange reactions give some idea of the processes occurring on the surface of the platinum films. In the case of propane and butane all the deuterated species were produced in substantial amounts initially indicating that the interconversion between mono-adsorbed and multiply-adsorbed species was rapid relative to the rate of desorption. In the case of neopentane isotopic species containing more than one deuterium atom were not produced in substantial amounts initially, indicating that the interconversion between mono-adsorbed and multiply-adsorbed intermediates was slow relative to the rate of desorption. These results indicate that the activation energy for the formation of multiply bonded intermediates is much greater for neopentane than it is for either propane or butane, and that the rate determining step for the disappearance of the d_0-hydrocarbon is mainly governed by the adsorption/desorption of the hydrocarbon.

The comparison between the specific activities of different types of platinum films for the exchange of a particular hydrocarbon, or between the specific activities of a particular platinum film for the exchange of different hydrocarbons is made more difficult because the specific activity may be dependent upon the apparent activation energy, the pre-exponential factor, or a combination of both. Taking the case of butane, Table 4.3. shows that on the sintered and unsintered films the apparent activation energies are similar; the reduction in the specific activity of the film for the exchange reaction on sintering was, therefore, caused by a reduction of the pre-exponential factor, and this must indicate that the catalytically active surface area has been decreased to a greater extent than the apparent surface area.

Although methane reacted by a multiple exchange process the amounts of the species containing more than one deuterium atom were less than those obtained for the exchange of butane, indicating that the activation energy for the formation of an $\alpha\alpha$-diadsorbed intermediate is greater than that for the formation of an $\alpha\beta$-or an $\alpha\beta\delta$-adsorbed intermediate. The coalescence of the Arrhenius equation plots for the exchange reaction on the sintered and unsintered films indicates that the rate of exchange is proportional to the apparent surface area of the film. Therefore, at the much higher temperatures required to dissociate the methane carbon-hydrogen bonds all the available surface area is catalytically active, and the specific activity of the film for the exchange reaction is not sensitive to its structure.

The exchange of neopentane on the unsintered and sintered films is more complex since both the apparent activation energy and the pre-exponential factor increase on sintering; but it is unlikely that the decrease in the apparent surface area of the films on sintering has been accompanied by an increase in the number of the catalytically active sites. The Arrhenius equation can be expressed in a form embodying the entropy of adsorption and the heat of adsorption; and the variation of the Arrhenius parameters with the type of film may be regarded as a form of the compensation effect involving an interplay between the heat of adsorption and the entropy of adsorption. Although it is not possible to give a completely satisfactory explanation for this behaviour, the low value for the pre-exponential factor on the unsintered films despite the favourable activation energy may be due to a low probability of adsorption, i.e., a low sticking coefficient caused by interactions between the adsorbed neopentane molecules.

The exchange of propane, butane and neopentane on the unsintered films occurred over approximately the same range of temperature, as did the exchange of butane and neopentane on the sintered films. A comparison of Table 4.3. with Table 4.4., however, shows that there is no obvious relation between the bond dissociation energies of the molecules and either the apparent activation energies or the pre-exponential factors. The adsorption of the hydrocarbon will necessitate the dissociation of at least one of the carbon-hydrogen bonds, and the specific activity of the films for the exchange of the hydrocarbons must be governed, at least in part, by the strengths of the carbon-hydrogen bonds in the molecules. Since the Arrhenius parameters vary from hydrocarbon to hydrocarbon, the specific activity may be more meaningful if it is based upon the temperature for a constant rate of exchange. Table 3.39., p. 110 shows that the temperatures for which the rate of disappearance of the d_o-hydrocarbon on the unsintered films was equal to $3.4.10^{16}$ mols $s^{-1}m^{-2}$ are similar. Although these temperatures do not fall in the same order as the primary carbon-hydrogen bond dissociation energies, the correlation between them is quite good. Table 3.39., p. 110 also gives the temperatures for which the rate of disappearance of the d_o-hydrocarbon on the sintered films was equal to $3.4.10^{16}$ mols $s^{-1}m^{-2}$; and a comparison of these values with those for the primary carbon-hydrogen bond dissociation energies of neopentane, butane, and methane, shows that an excellent correspondence was obtained. No evidence was observed in this work to indicate that the secondary carbon-hydrogen bonds were substantially more reactive than the primary carbon-hydrogen bonds. This, coupled with the correlations given above, would indicate that even though the mechanisms for the exchange of the hydrocarbons are different the specific activity of the film is governed by the adsorption of the hydrocarbon by dissociation of a primary carbon-hydrogen bond.

4.5. Correlation with Other Results

The specific activity of a metal for a catalytic reaction will depend upon the nature of the metal and the molecule being adsorbed; and for a particular reaction the specific activity may depend upon either the geometric or electronic properties of the metal. One of the more fundamental geometric properties of a metal is its radius, and it might be expected that the hydrogenation of ethylene would only occur on those metals having the correct metal-metal distance to chemisorb ethylene associatively by an $\alpha\beta$-diadsorbed intermediate. Twigg and Rideal (149) have, however, shown that although the ideal metal-metal distance is 0.273 nm the hydrogenation of ethylene is possible on metals having metallic radii between approximately 0.25 and 0.31 nm; and although platinum and palladium have almost identical metallic radii the hydrogenation of ethylene at 0°C on palladium films is faster by a factor of 7 than it is on platinum films (55). The structure of the metal may possibly influence the reaction; thus the results reported in this work show that sintering the films at 250°C decreased the specific activity of the film for the hydrogenation of ethylene and increased both the apparent activation energy and pre-exponential factor. However, this result may not be significant, because it has been shown (150) that sintering a nickel film at 300°C only decreased the specific activity of the film for the hydrogenation of ethylene by a factor of 2.5 without altering the apparent activation energy; and the apparent activation energies for the reaction on platinum, palladium, rhodium, and ruthenium supported on silica are similar (151). It is, therefore, probable that geometric effects play only a very small role in determining the catalytic properties of metal surfaces, and a more likely correlation between platinum as a catalyst and the other Group VIII metals is to be found by considering the electronic properties of the metals.

Although the electron orbitals of an isolated metal atom will be altered when the atom is placed in a crystal lattice, a correlation may be expected between the adsorption properties of a metal surface and the formation of inorganic complexes. Thus the chemisorption of oxygen on platinum, palladium, and rhodium films has been shown (120) to be a true chemisorption, in contrast to the results obtained on iron, cobalt, and nickel films which have been shown to be caused by the formation of an oxide layer. All the Group VIII metals adsorb carbon monoxide; however, platinum and palladium do not form stable inorganic carbonyls, and this may possibly explain why they are not active catalysts for the Fischer-Tropsch synthesis, whereas iron, cobalt, nickel, and ruthenium are. At high coverages the adsorption of carbon monoxide on the metal surface will approximate to one adsorbed molecule per surface metal atom, and the bonding will be similar to that found in the metal carbonyls; i.e., the bond will have two components, a carbon-metal σ bond and a $d_\pi - p_\pi$ bond. Nyholm (152) has concluded that the ease of $d_\pi \rightarrow p_\pi$ bonding is in the order $Ni \gg Pt \gg Pd$, and he has stated that this is the major reason why palladium and platinum do not form stable carbonyls.

For the exchange of methane by a multiple exchange process an $\alpha\alpha$-diadsorbed intermediate is necessary, and the structure of this intermediate may be the same as that of the carbonyls. On the Group VIII metals the order of activity for the simple exchange process is $Rh > Pt \approx Pd > Ni$ and that for the multiple exchange process is $Rh \gg Pt > Ni > Pd$ (90,130). If allowance is made for the fact that hydrocarbons form strongly adsorbed species on nickel surfaces this will explain the low position of nickel in the orders of activity given above; and the order of reactivity for the multiple exchange process will thus probably be $Rh > Ni > Pt > Pd$, which is also the same order as the activities of the catalysts for the hydrocracking of hydrocarbons to methane (153), and the order of $d_\pi \rightarrow p_\pi$ donor bonding given above. Since the multiple exchange of methane can only take place by the interconversion between α-adsorbed and $\alpha\alpha$-diadsorbed intermediates, it would be reasonable to conclude that the formation of $\alpha\alpha$-diadsorbed intermediates is important in the processes leading to the formation of strongly bound hydrocarbon molecules on metal surfaces.

The hydrogenolysis of neopentane and neohexane has been studied on films of nickel, rhodium and platinum (154). On nickel and rhodium films neohexane was more reactive than neopentane, whereas on platinum films the reactivities were similar. However, the tendency for the fission to occur adjacent to the quaternary carbon atom in neohexane to give ethane and i-butane decreased in the order $Pt \gg Ni > Rh$, and the activity sequence for the hydrogenolysis was $Rh > Ni > Pt$. These results support the conclusion of Anderson and Avery (42) that the hydrogenolysis of neopentane on platinum films occurs by the formation of an $\alpha\alpha\gamma$-triadsorbed intermediate. It is not possible, however, to say whether the formation of the $\alpha\alpha\gamma$-triadsorbed intermediate is derived from a precursor $\alpha\alpha$- or $\alpha\gamma$-diadsorbed intermediate. In the case of rhodium and nickel the greater reactivity of neohexane relative to neopentane indicates that on these metals the formation of an $\alpha\alpha\beta$-triadsorbed intermediate is more probable than an $\alpha\alpha\gamma$-triadsorbed intermediate.

The results given above indicate that the ease of $d_\pi \rightarrow p_\pi$ bonding was greatest for nickels and least for palladium. The ease of $d_\pi \leftarrow p_\pi$ donor bonding will be the inverse of the previous order, i.e., the ease of $d_\pi \leftarrow p_\pi$ donor bonding will follow in the order $Pd \gg Pt \gg Ni$. This desire of palladium to increase the electron density in its d_π orbitals is shown by the ready formation of a bulk hydride, and the ready participation of π-allylic intermediates in the exchange reaction of, for example, 1,1,3,3,4-penta methylcyclopentane (50).

The exchange reactions of saturated hydrocarbons on the Group VIII metals can be summarized as follows. For methane on nickel films the perdeuterocompound was the most abundant product initially (90), and this fits in well with the ready formation of a nickel carbide in the Fischer-Tropsch synthesis. Rhodium and platinum are both active for the multiple exchange process, and palladium has a very low activity for the multiple exchange process (130). For ethane and the higher straight chain hydrocarbons all the metals are active for the $\alpha\beta$-mechanism of exchange but some differences exist between them. Thus for ethane the efficiency for the multiple exchange process falls in the order $Rh \approx Pd > Pt > Ni$, but with the higher hydrocarbons where the formation of $\alpha\beta\gamma$- or π-allylic intermediates is possible palladium is by far the most efficient metal for the multiple exchange process. For neopentane a multiple exchange process occurs on rhodium and platinum, whereas only stepwise exchange occurs on palladium and nickel. This result for nickel is a little surprising in view of the results obtained using methane, but it may be due to the reaction self poisoning (51).

There are, however, very wide differences between the metals with respect to the temperatures required to propagate the exchange reactions of the hydrocarbons, and this indicates that the rate determining step may be the adsorption/desorption of the hydrocarbon. Some idea of the relative activities of the metals is given in Table 4.5., which is based upon the temperature for which the rate of disappearance of the d_0-hydrocarbon was $3.4.10^{16}$ mols $s^{-1}m^{-2}$. The values contained in this table for some of the hydrocarbons will be subject to some error, because some of the Arrhenius parameters were based on units other than mols $s^{-1}m^{-2}$ and some assumptions had to be made about the surface areas of the catalysts. However, it does indicate some general trends. Table 4.4. shows that the primary carbon-hydrogen bond dissociation energies of ethane, propane, and neopentane are similar and are approximately 25 kJ $mole^{-1}$ less than the bond dissociation energy of methane; whereas the secondary carbon-hydrogen bond dissociation energy of propane is 16.5 kJ $mole^{-1}$ less than that for the primary carbon-hydrogen bond. The secondary hydrogen atoms IN PROPANE ARE KNOWN TO EXCHANGE

TABLE 4.5.

RELATIVE ACTIVITIES

Metal film	Temperature °C			
	neo-C_5H_{12}	C_3H_8	C_2H_6	CH_4
Pd	132	106	165	203
Pt	97	-	107	180
Ni	-	5	201	290
Rh	17	-40	28	164

this value will be high because ethane is known to exchange on nickel films at low temperatures, but the reaction is self poisoned (49).

approximately ten times faster than the primary hydrogen atoms on nickel films (155), and the greater reactivity of propane on rhodium relative to ethane and neopentane may possibly be due to the adsorption of propane by the dissociation of a secondary carbon-hydrogen bond. The behaviour of palladium is irregular, and the discrepancy between the values for ethane and neopentane makes it difficult to decide whether the greater reactivity of propane is due to the greater reactivity of the secondary hydrogen atoms. The results for platinum have been discussed in section 4.4. where it was concluded that the reactivity of the primary and secondary hydrogen atoms were similar.

In conclusion it may be said that platinum and palladium are relatively inactive for the exchange reactions of saturated hydrocarbons compared to the other metals in Group VIII, and this is probably related to their greater difficulty in dissociating carbon-hydrogen bonds. Some support for this conclusion may be given by the observation that these two metals are very active olefin hydrogenation catalysts, and this may be related to the initial adsorption of the olefin by a π bond. The orders of reactivity given above for the formation of $\alpha\alpha$-diadsorbed and π -allylic intermediates indicates that platinum is a relatively efficient catalyst for both intermediates; the surprising result is that platinum comes before and not after palladium in the order of $d_{\pi} \rightarrow p_{\pi}$ donor bonding, and this is probably linked to the effects of the platinum filled 4 f shell. The adsorbed intermediates on platinum surfaces are relatively stable, as shown by the fact that the exchange reactions do not self poison and by the relative inactivity for hydrogenolysis compared to nickel and rhodium. When hydrogenolysis does occur the major result is the formation of products by the fission of one carbon-carbon bond. The high isomerization activity compared to the other metals must be related to the adsorption of the hydrocarbon by an $\alpha\alpha\gamma$-triadsorbed intermediate with the minimum of strain, the difference between platinum and palladium arising because, although they have almost identical metallic radii, palladium does not readily form an $\alpha\alpha\gamma$-triadsorbed intermediate.

PART III

THE EXCHANGE OF CYCLOPENTANE AND CYCLOHEXANE WITH DEUTERIUM ON EVAPORATED NICKEL FILMS

CHAPTER I

INTRODUCTION

The surface intermediates responsible for the exchange and hydrogenolysis of saturated hydrocarbons on nickel surfaces have been the subject of a large number of investigations (90, 156, 119, 157). The dissociative adsorption of hydrocarbons on nickel surfaces in the absence of "hydrogen" is known to result in extensive dehydrogenation of the molecules. Thus, Wright et al. (158) have shown that ethane adsorbs on a nickel film at 98°C by the dissociation of two carbon-hydrogen bonds; and Galwey and Kemball (159) have shown that the adsorption of cyclohexane on a nickel-silica catalyst at temperatures greater than 50°C, results in the adsorption of the molecule in the boat configuration by the dissociation of four carbon-hydrogen bonds. The presence of deuterium in an exchange reaction presents an added complication, because the formation of irreversibly adsorbed species may not be so probable as it is in the absence of deuterium. However, although it is known that the exchange reactions of ethane (49), propane (155), i-butane (155), and neopentane (51) with deuterium on nickel films are self poisoned, no systematic study of the adsorbed species responsible for this behaviour has been attempted.

The object of this investigation was to study the intermediates responsible for the self poisoning of exchange reactions on nickel films by presorbing hydrocarbons on the film, and observing the effects, if any, that they produced upon the activity of the film for, and the nature of, the subsequent exchange reaction. For this approach to be successful all the criteria outlined in Part II section 4.2. which would introduce ambiguity into the results have to be eliminated. The effects introduced by progressive sintering of the film during the exchange reaction necessitate using a molecule which reacts at temperatures less than the deposition temperature of the film (0°C). The molecule used would also have to have a low extent of fragmentation under electron impact, and not contain groups of non equivalent hydrogen atoms. These conditions immediately eliminated the lower aliphatic hydrocarbons. The use of aromatic compounds was also eliminated because it has been shown (103) that the exchange reaction of benzene on nickel films at - 45°C was too fast for accurate measurement. The molecule chosen for study was cyclopentane, because it is known (159) that cyclopentane adsorbs on nickel-silica at temperatures close to 0°C in the absence of "hydrogen" by extensive dissociation of the carbon-hydrogen bonds.

It will be shown that the exchange reaction of this molecule on both sintered and unsintered films was self poisoned. On the unsintered films reaction occurred at temperatures below 0°C, but presintering the films required reaction temperatures in excess of 200°C to propagate the exchange process. Nickel films are known to be very susceptible to oxygen poisoning (120), and an attempt was made to judge the cleanliness of the system by comparing the results obtained for the exchange of cyclohexane on unsintered films with those obtained by Anderson and Kemball (103). The two sets of results did not compare favourably, however, and the reasons for this will be discussed fully later.

CHAPTER II

EXPERIMENTAL

2.1. Mass Spectrometric Analyses

The isotopically substituted cyclopentanes and cyclohexanes were analysed mass spectrometrically; the fragmentation corrections being applied assuming a statistical loss of hydrogen and deuterium atoms as described in Part I of this thesis. The electron potentials used to produce the positively charged ions, and some typical fragmentation patterns for the molecules are given in Table 2.1. Due to the small extent of fragmentation of the molecules under electron impact an adequate analysis of the mass spectral data was obtained by treating the loss of hydrogen and deuterium atoms by statistical methods.

TABLE 2.1.

FRAGMENTATION PATTERNS OF THE MOLECULES

Molecule	Ionizing potential V	f_1 *	f_2	f_3	f_4	f_5	f_6
Cyclopentane	25	0.0361	0.0199	0.0531	0.0097	0.0084	0
Cyclohexane	25	0.0584	0.0136	0.0082	0.0037	0.009	0.019

* f_i has been described by equation 3.3. (Part I).

2.2. Chemicals

Hydrogen and Deuterium: The preparation and purification of these gases have been described in Part I section 2.6.

Cyclopentane and Cyclohexane: Cyclopentane and cyclohexane were obtained as standard samples from the Department of Scientific and Industrial Research, Chemical Research Laboratory (99.98% pure). Before use the liquids were degassed and stored in sample tubes surrounded by liquid nitrogen.

2.3. Procedure

The standard reaction mixture consisted of 0.67 kNm^{-2} and 6.7 kNm^{-2} of hydrocarbon and deuterium respectively in the mixing volume, the pressures of the gases in the reaction vessel after expansion depending upon the temperature at which the gas mixture was admitted. Due to the ready solution of the hydrocarbons in the tap grease, a small pressure of the hydrocarbon was allowed to dissolve in the tap grease so that on subsequent preparation of the gas mixture the pressure of the hydrocarbon would remain relatively stable while the gas mixture was equilibrating in the mixing bulb. The gas mixture was prepared while the film was being deposited at 0°C or high temperature, and was admitted to the film at low temperature.

Nickel films are very susceptible to oxygen poisoning. To avoid this poisoning by oxygen or other gases liberated from the filament while the film was being deposited the filament was outgassed for 1 hr. instead of the normal 30 mins. In the cases where sintered films were used, in order to reduce the length of time that the film would be out of contact with the gas mixture the films were deposited with the walls of the reaction vessel at the sintering temperature. This method of depositing the films had, however disadvantages, the most serious of which was adequate temperature control of the reaction vessel walls. Since the walls were kept at a constant temperature by external heating, it was possible that the heat given out by the deposition of the film would, if the rate of heat conduction away from the walls was not adequate, cause the film temperature to rise above that of the walls producing film irreproducibility due to the irreproducibility of the sintering conditions. To avoid this, and also to reduce the extent of oxygen poisoning, the film was deposited at 0°C and then sintered at high temperature in a deuterium atmosphere.

The preparation of heavy nickel films was carried out in the normal way, but instead of evaporating the filaments for a constant time they were evaporated until they burnt out.

CHAPTER III

RESULTS

3.1. Surface Areas of the Films

The surface areas of nickel films have been extensively studied by Crawford et al. (150) who found that for a constant sintering temperature the surface area was given by the equation

$$A = B + DW \qquad 3.1.$$

where A is the surface area, B and D are constants, and W is the weight of the film.

They found that increasing the sintering temperature over the range 25-400°C reduced the value of the constant D markedly, but had little influence on the value of the constant B. Since the sintering temperatures used in this work were not the same as those used by Crawford et al. (150) the surface areas of the films were calculated from their data in the following manner. Inspection of the values of D indicated that they decreased exponentially with increasing temperature, and this was confirmed when the plot of $\log_{10} D$ against T°K was found to be a straight line; and the values of B decreased linearly with increasing temperature between 100 and 300°C as shown by a plot of B against T°K. Thus, knowing the temperatures at which the films used in this work had been sintered, the values of B and D were obtained from the graphs, and the surface areas calculated by substitution into equation 3.1.

Some of the films used in this work were sintered at high temperature in deuterium to reduce the probability of oxygen poisoning. No allowance was made for this in the calculation of the surface areas, because it has been shown (103) that although the presence of deuterium decreases the rate of sintering it does not alter the final value of the surface area; and it is considered that after sintering the films at 300°C for 1 hr. the surface area would have attained its limiting value.

3.2. The Exchange of Cyclopentane with Deuterium

The exchange of cyclopentane with deuterium was studied on sintered and unsintered nickel films; and the experimental rates of exchange were converted into absolute units using the known surface areas, which had been calculated by the method described in section 3.1.

On the unsintered films, whose weights varied from 8.3 mg to 13.7 mg, when the gas mixture was admitted to the reaction vessel at temperatures varying from -63°C to -23°C no exchange was observed at temperatures less than 70°C. In all cases the peak heights decreased with time, indicating that the cyclopentane was either being strongly adsorbed on the surface of the film or absorbed in the tap grease of the reaction vessel system. In order to reduce the problems of interpretation caused by the films sintering during the reaction, the reaction temperature was decreased by using heavy nickel films. On these films which weighed from 26-38 mg exchange occurred at temperatures less than 0°C. The rates of exchange and other data are summarized in Table 3.1. and Figure 3.1. shows two of the typical rate plots that were obtained. The carbon count at any temperature did not vary in a systematic manner; and there was no correlation between the shape of the rate plot and the variation of the carbon count.

The curvature of some of the rate plots at temperatures less than 0°C must be due to progressive self poisoning of the reaction, and this is also clearly indicated by the Arrhenius equation plot shown in Figure 3.2. Increasing reaction temperature did not increase the rate of exchange but decreased it, and it is interesting to note

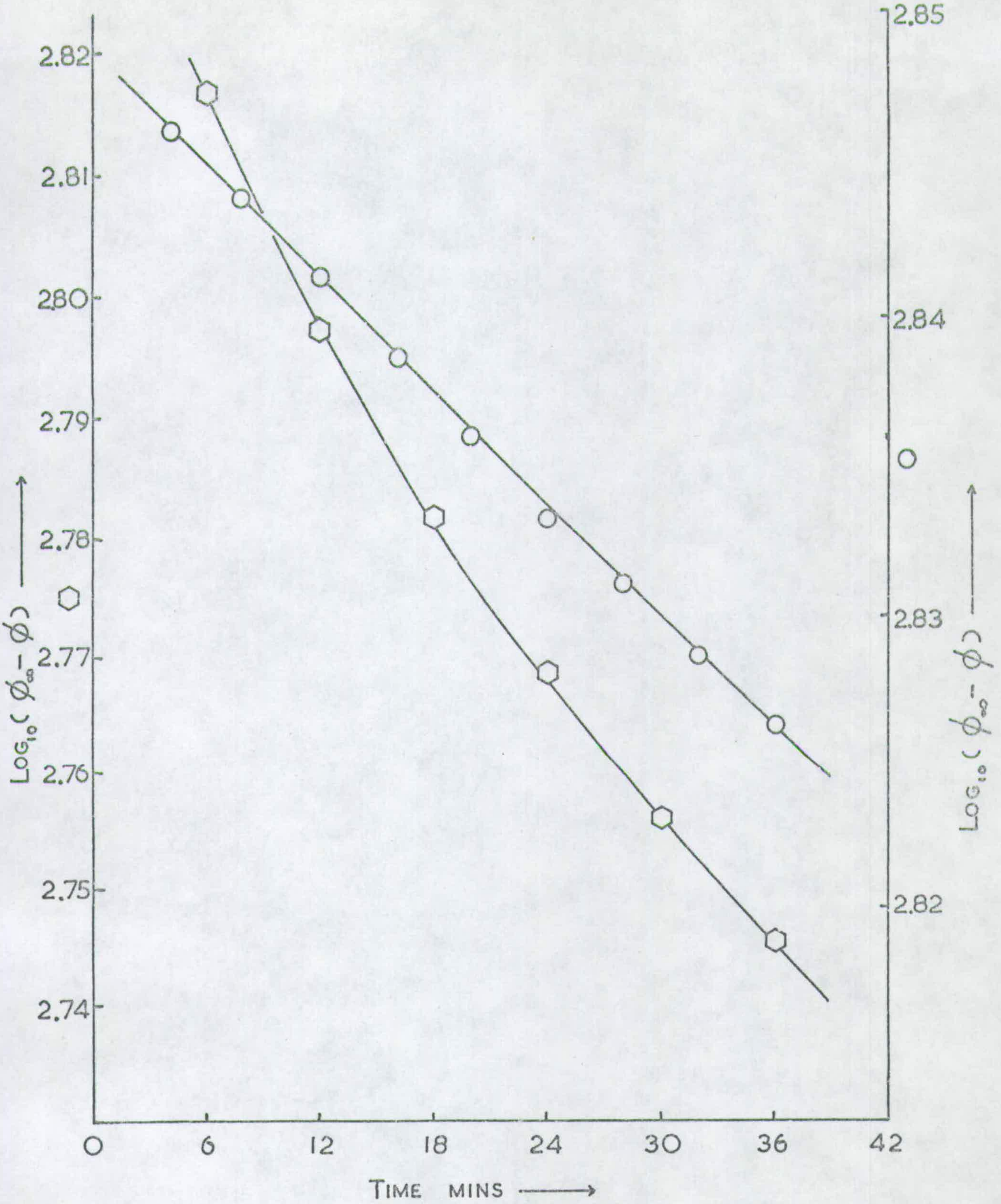


Fig. 3.1 φ Plots for the Exchange of Cyclopentane with Deuterium on Unsintered Nickel Films; ⬡ at −23°C; ○ at 23.5°C

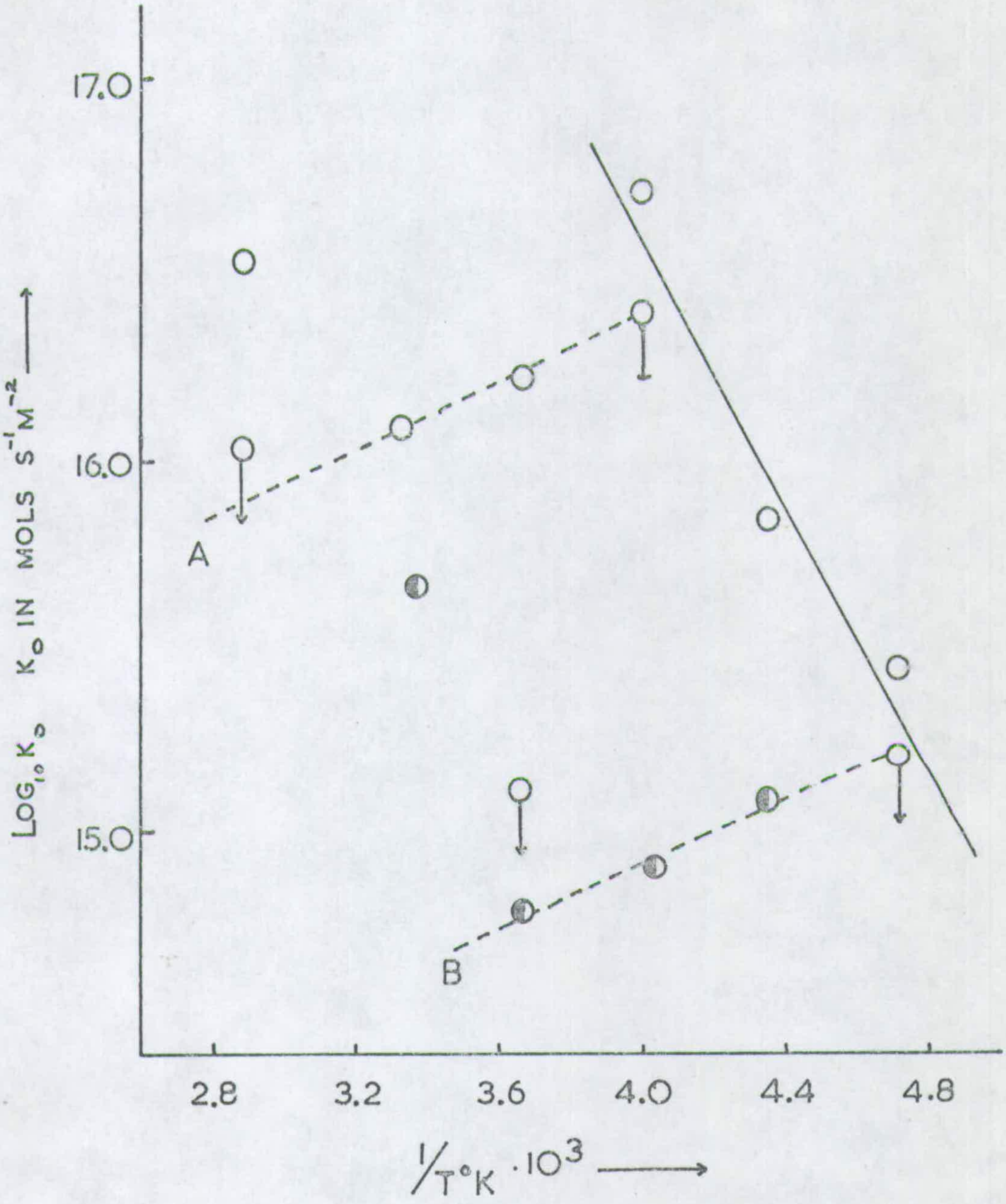


FIG. 3.2 ARRHENIUS PLOT FOR THE EXCHANGE OF CYCLO-PENTANE WITH DEUTERIUM ON UNSINTERED NICKEL FILMS

◐ ONE EXPERIMENT

○ ALL OTHER EXPERIMENTS

TABLE 3.1.

THE EXCHANGE OF CYCLOPENTANE ON UNSINTERED FILMS

Reaction temp. °C	Rate of exchange mols $s^{-1}m^{-2}$. 10^{-15}		$M = \frac{k_\phi}{k_o}$	Type of rate plot obtained *	
	k_ϕ	k_o		$\log_{10}(\phi_\infty - \phi)$	$\log_{10} d_o$
-61	3.37→1.34	2.83→1.61	1	VSCR	VSCR
-43	2.25	1.21	1.86	S	S
-43	7.00	7.03	1.0	S	S
-26	0.90	0.81	1.11	S	S
-23	46.27→25.01	50.2→23.2	1.0	VSCR	VSCR
0	1.52	0.77	1.98	S	S
0	17.13→ 3.5	16.61→1.30	1.03→2.7	CR	CR
23.5	13.02	4.66	2.80	S	S
27.3	41.78	12.55	3.34	S	S
72	157.9→47.1	34.58→10.99	4.55→4.28	CR	CR

* VSCR:- rate plot very slightly curved, reaction slowly down.

S :- straight apparent first order rate plot.

CR :- curved rate plot, reaction slowing down

that the slopes of the lines A and B are identical. The apparent activation energy (E_a = 33.8 kJ $mole^{-1}$) and pre-exponential factor ($\log_{10}$ A = 23.7; A in mols $s^{-1}m^{-2}$) were calculated from the straight line drawn through the initial reaction temperature for each experiment, as these will not have been unduly affected by self poisoning.

The exchange of cyclopentane was studied on two kinds of heavy nickel films:

(a) Those which had been deposited with the reaction vessel walls at the sintering temperature.

and (b) Those which had been sintered at high temperature in deuterium.

In the case of group (a) the reaction vessel walls were kept at a constant temperature within the range 269-276°C while the film was being deposited. After the filament had fused, the film was heated at the deposition temperature for a further period of time such that the total deposition plus sintering time was 1 hr. In the case of group (b) the film was deposited at 0°C in vacuo, and then sintered for 1 hr. within the range 292-298°C under a pressure of approximately 2.5 kNm^{-2} of deuterium. The deuterium was then pumped off at the sintering temperature. Since cyclopentane was known to exchange on unsintered heavy films at temperatures less than 0°C, for the first experiment on the sintered films the gas mixture was admitted to the reaction vessel at -43°C and the temperature then increased gradually; no exchange was observed at temperatures less than 200°C. For the subsequent experiments the gas mixture was admitted at 0°C and the temperature then rapidly increased until exchange was observed at approximately 200°C.

The rates of exchange are summarized in Table 3.2. and have been plotted according to the Arrhenius equation in Figure 3.3. which shows that extensive self poisoning of the exchange reaction was occurring. Increasing reaction temperature did not increase the rate of exchange, but as in the case of the reaction on the unsintered films tended to decrease it. The apparent activation energy (E_o = 75.1 kJ $mole^{-1}$) and pre-exponential factor ($\log_{10} A$ = 24.9; A in mols $s^{-1}m^{-2}$) were calculated from the straight line drawn through the points corresponding to the initial reaction temperature for each experiment. As in the case of the reaction on the unsintered films straight line apparent first order rate plots were usually obtained, and this is illustrated by Figure 3.4. The carbon counts at any temperature were not usually constant, but decreased linearly with time as illustrated by Figure 3.5. In those cases where the carbon count decreased with time, the rate of disappearance of the

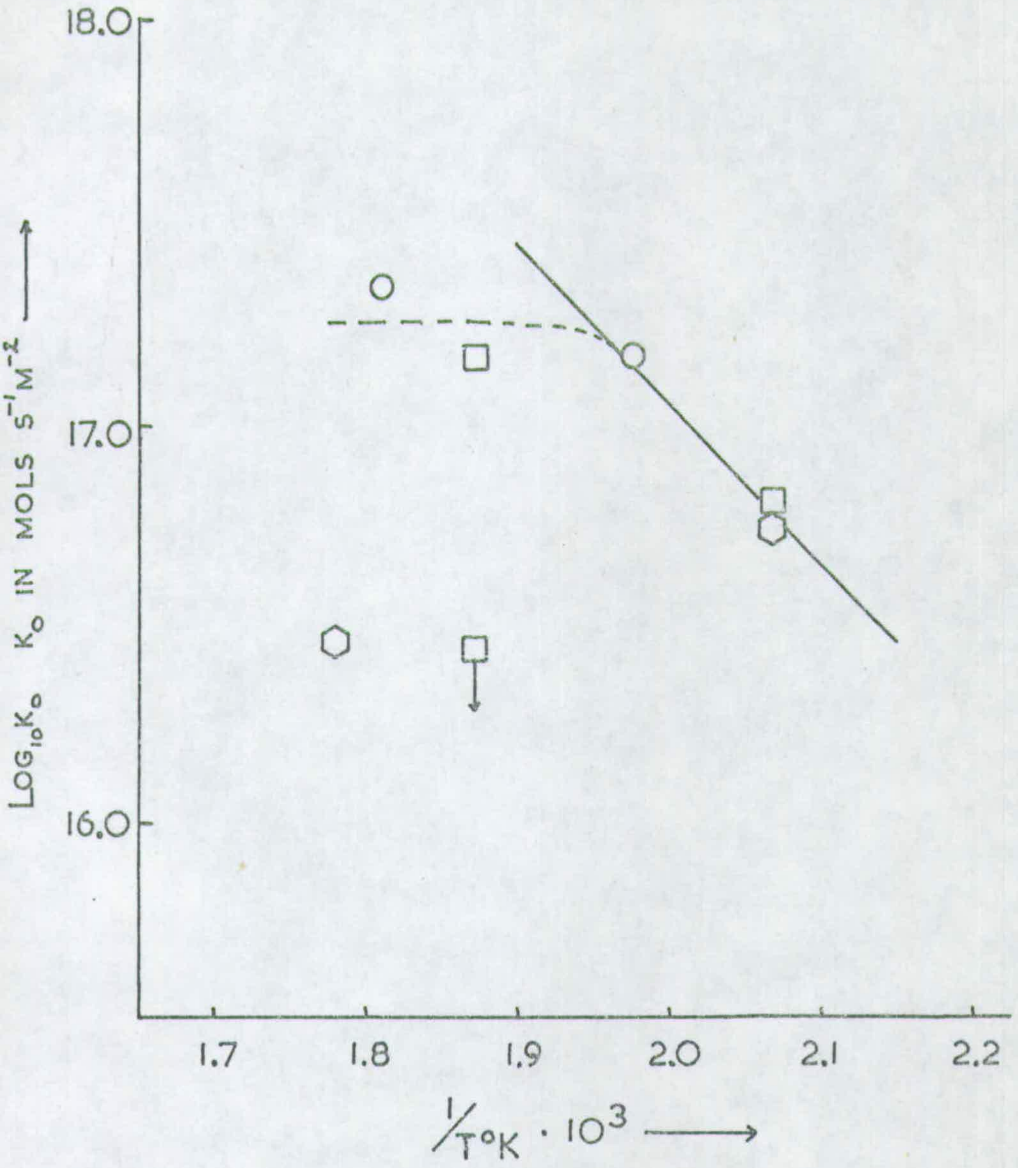


Fig. 3.3 Arrhenius Plot for the Exchange of Cyclo-pentane with Deuterium on Sintered Heavy Nickel Films

different symbols refer to different experiments

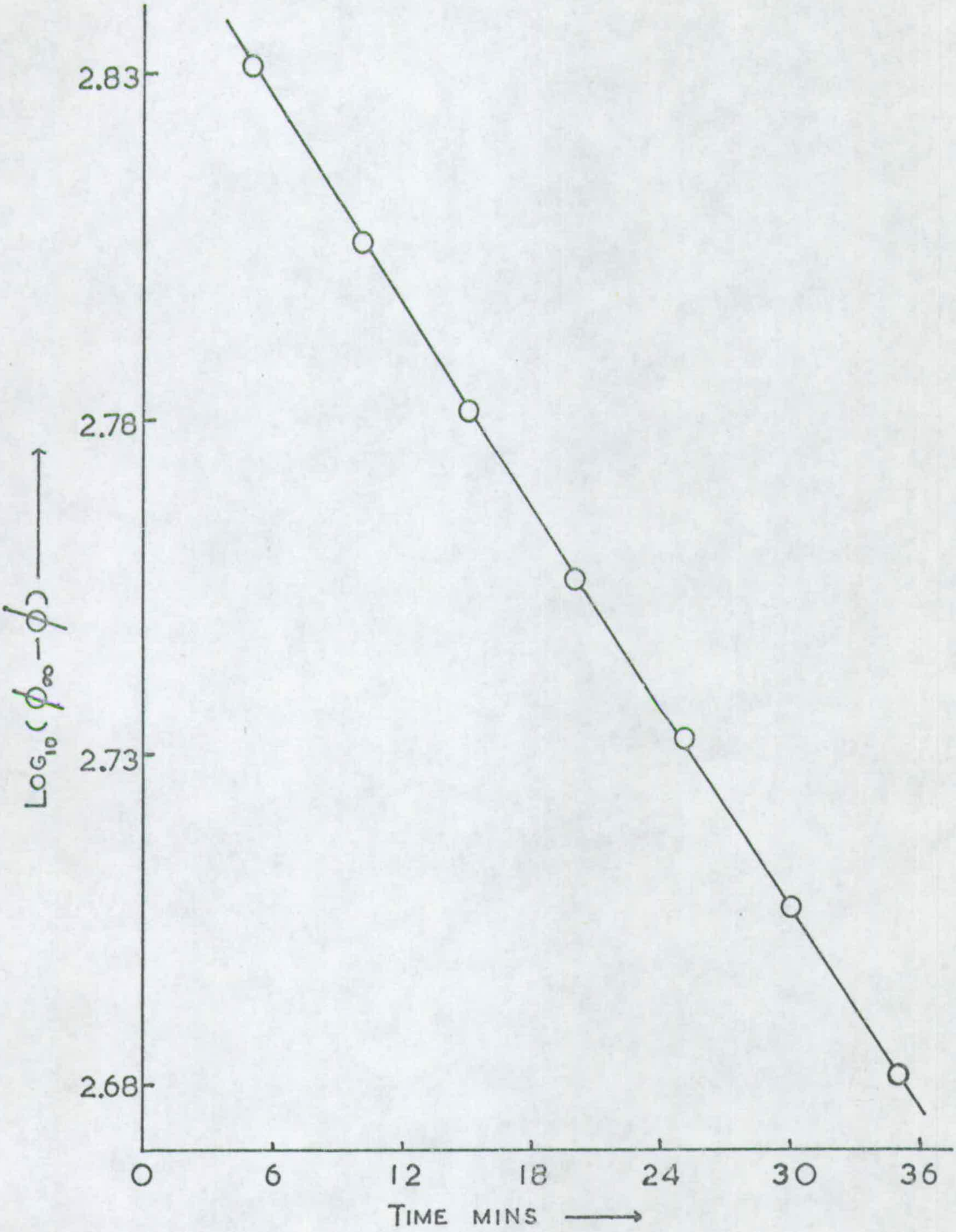


Fig. 3.4 ϕ Plot for the Exchange of Cyclopentane with Deuterium at 210°C on a Sintered Heavy Nickel Film

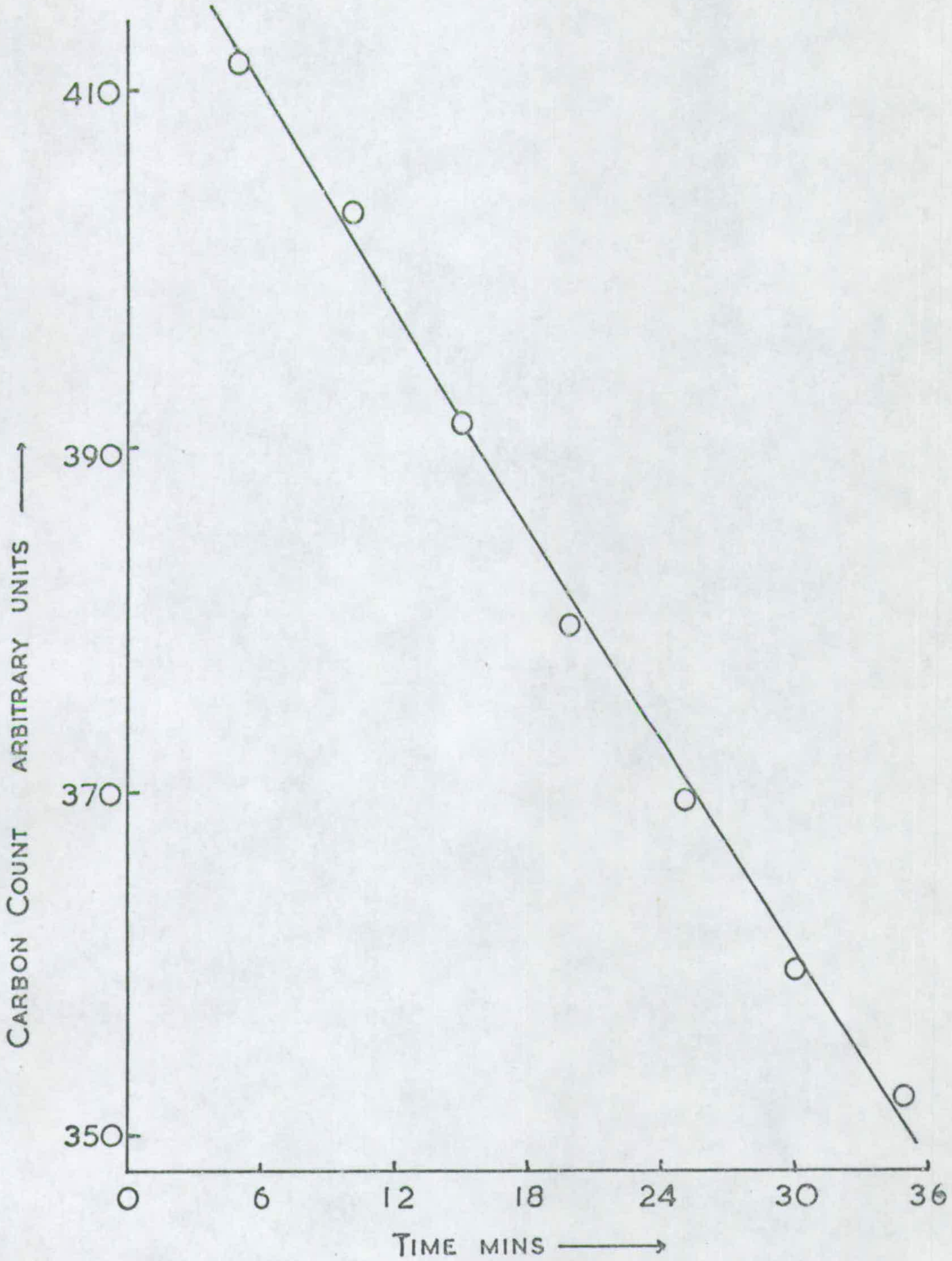


Fig. 3.5 Plot of Carbon Count Against Time for the Exchange of Cyclopentane with Deuterium at 220°C on a Sintered Nickel Film

TABLE 3.2.

EXCHANGE OF CYCLOPENTANE ON HEAVY SINTERED FILMS

Sintering conditions	Reaction temp. °C	Rate of exchange mols $s^{-1}m^{-2}$. 10^{16}		$M = \frac{k_\phi}{k_o}$
		k_ϕ	k_o	
296°C for 1 hr	210	52.78	5.66	9.3
in D_2	221	11.70	1.74	6.75
"	280	19.26	2.20	8.76
"	288	31.12	2.94	-
at 269-	210	44.95	6.65	6.75
276°C in	220	8.85→28.43	1.03→2.80	8.6→ -
vacuo for	232	33.11→54.94	3.72→6.42	8.9→8.56
1 hr	260	154.8→28.83	15.10→2.82	-
"	261	50.29	6.69	7.5
"	"	11.39	1.30	8.75

total "cyclopentanes" was calculated from the zero order plot of the carbon count against time. In order to convert the carbon count into a percentage of the total "cyclopentanes" originally present in the reaction vessel, the "zero time" of the reaction was determined from the plot of $\log_{10} d_o$ against time and the carbon count at this "zero time" determined from the plot of carbon count against time. Table 3.3. which summarizes the data shows that there was no correlation between the shape of the rate plot and the variation of the carbon count with time; and that the rate of disappearance of the total "cyclopentanes" was virtually temperature independent.

The nature of the exchange reaction occurring on the unsintered and sintered films was different; and this is illustrated by Table 3.4. which gives the initial product distributions for the exchange reaction,

TABLE 3.3.

CORRELATION BETWEEN TYPE OF RATE PLOT OBTAINED AND THE CARBON BALANCE

Temp. °C	Type of rate plot obtained *		Carbon † balance with time	Rate of disappearance of the total "cyclopentanes" mols $s^{-1}m^{-2}$. 10^{-16}
	$\log_{10}(\phi_\infty - \phi)$	$\log_{10} d_o$		
210	S	S	C	0
221	S	S	dec	2.56
280	~ S	~ S	dec	5.46
288	~ S	~ S	dec	2.44
210	S	S	dec → inc	-
220	VSCA	VSCA	dec	3.95
232	CA	CA	C	0
260	CR	CR	inc	-
261	S	S	dec	0.65
261	~ S	~ S	dec	2.30

*

S :- straight rate plot

VSCA:- rate plot very slightly curved, reaction accelerating

CR :- curved rate plot, reaction slowing down

CA :- curved rate plot, reaction accelerating

† C :- carbon balance constant

dec:- carbon balance decreased linearly with time

inc:- " " increased " " "

dec → inc:- carbon balance decreases and then increases with time and by Figures 3.6.-3.8. which show the course of some typical reactions with time. The correspondence between the M values calculated from the initial product distributions and from the ratio of the rates of exchange was not very good. Due to the reaction self poisoning it is probable that the rates of exchange will be subject to a substantial error, and the M values calculated from the ratio of the rates of exchange will be less accurate than those calculated from the initial product distributions. It was not possible to measure the initial product distributions for the two results indicated in Table 3.4. due to the large extent of reaction, but they have been included because they give some idea of the processes occurring on the catalyst surface.

On the sintered films all the possible deuterated cyclopentanes were produced in substantial amounts initially. In the case of the distribution at 232°C pronounced maxima were obtained at the monodeutero- and perdeutero-compounds, and the hump in the distribution between the d_5 and the d_6 compounds indicates that there is probably a small maximum at the d_5 isomer. Increasing reaction temperature increased the value of M and caused a shift in the distribution towards the more highly deuterated compounds.

On the unsintered films the M values increased with increasing temperature, and the initial product distributions also varied with temperature. At low temperatures only the d_1 and d_2 cyclopentanes were produced initially, the d_1 isomer being the predominant species. At -43°C and -23°C no species containing more than six deuterium atoms were produced initially. All the isomers containing from one to five deuterium atoms were produced in substantial amounts maxima being observed at the d_1 and d_5 cyclopentanes, and there was a substantial break in the distributions between the d_5 and the d_6 cyclopentanes. At temperatures

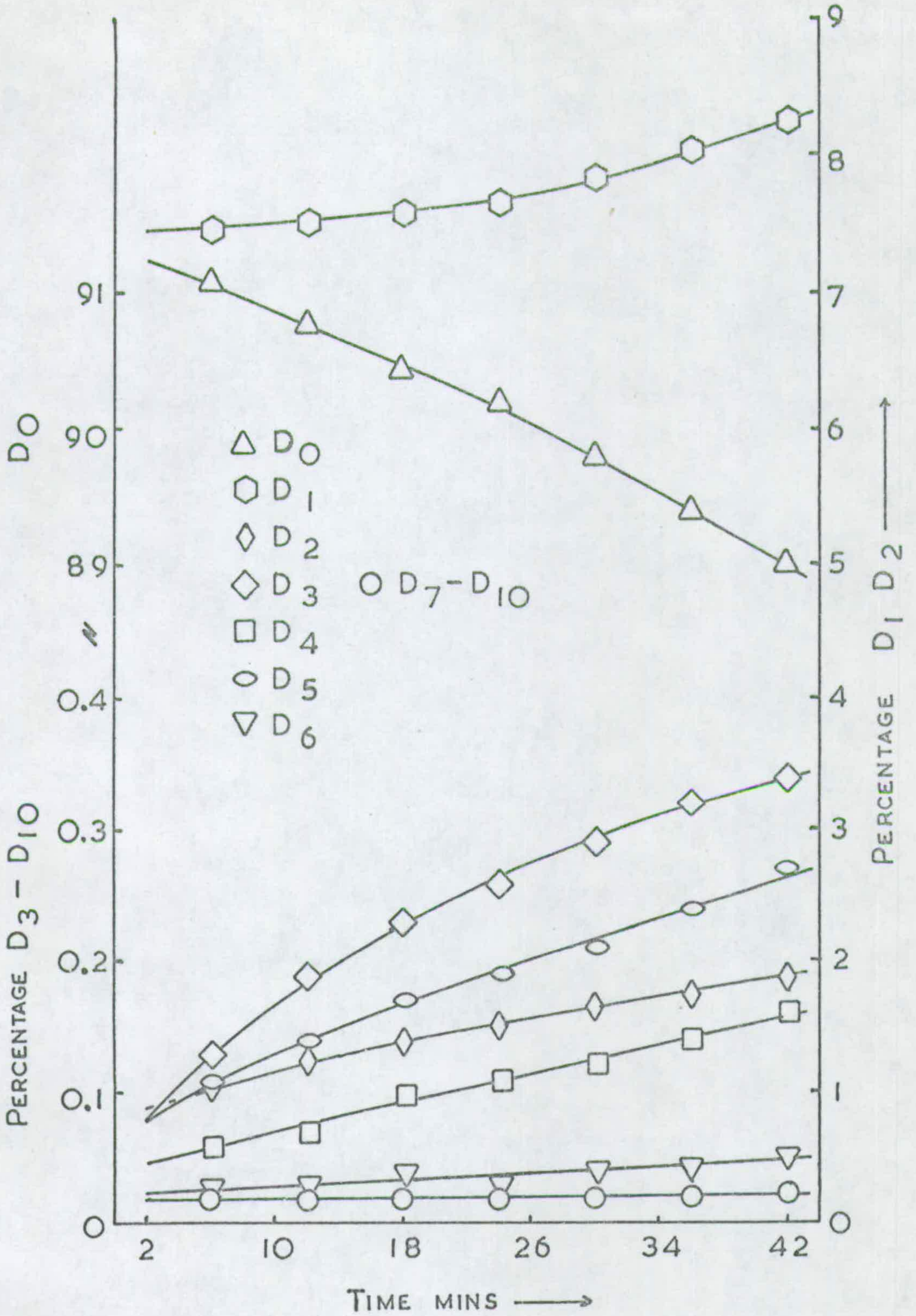


Fig. 3.6 Exchange of Cyclopentane with Deuterium at O°C on an Unsintered Nickel Film

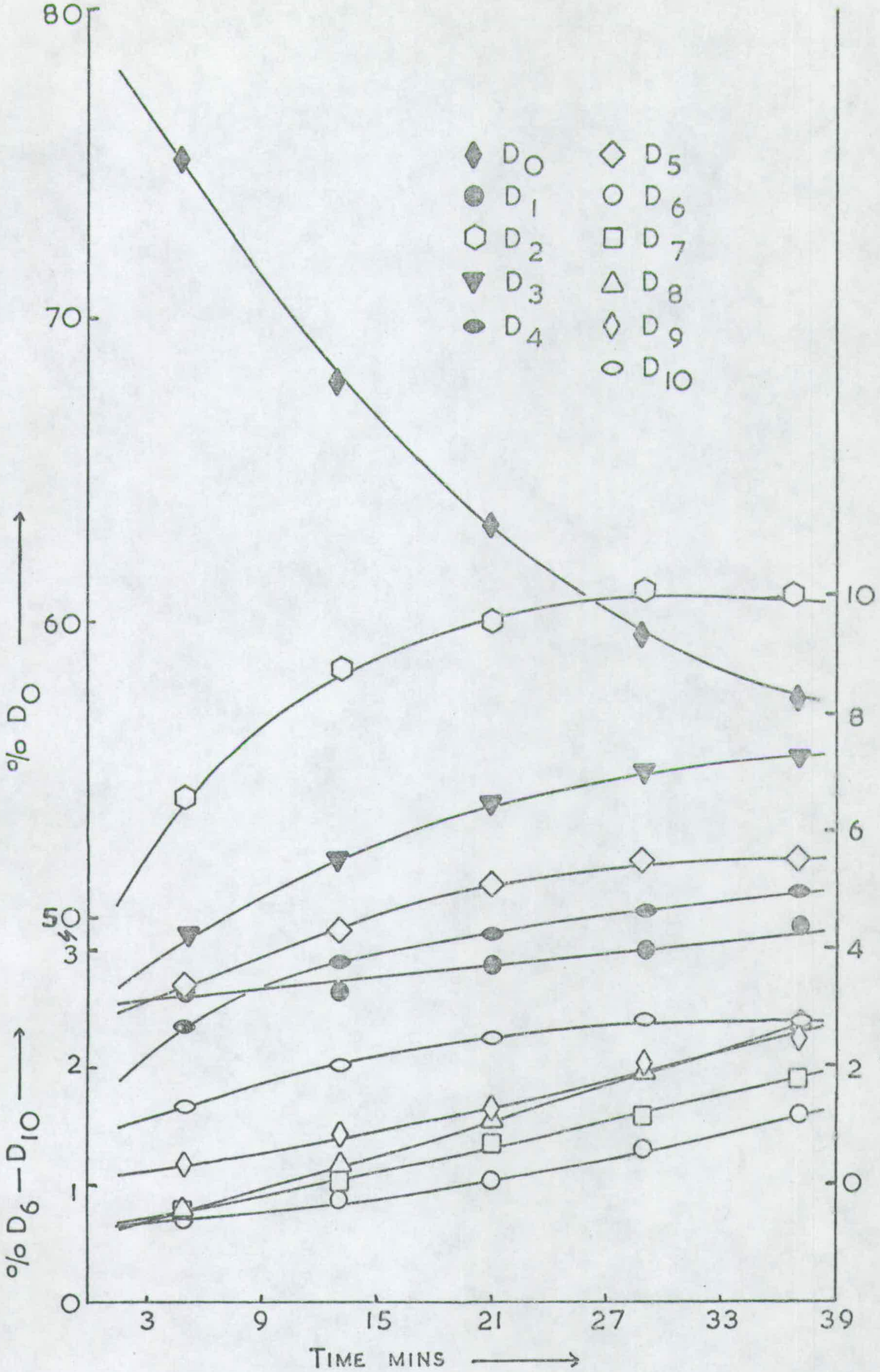


Fig. 3.7 Exchange of Cyclopentane with Deuterium at 72°C on an Unsintered Nickel Film

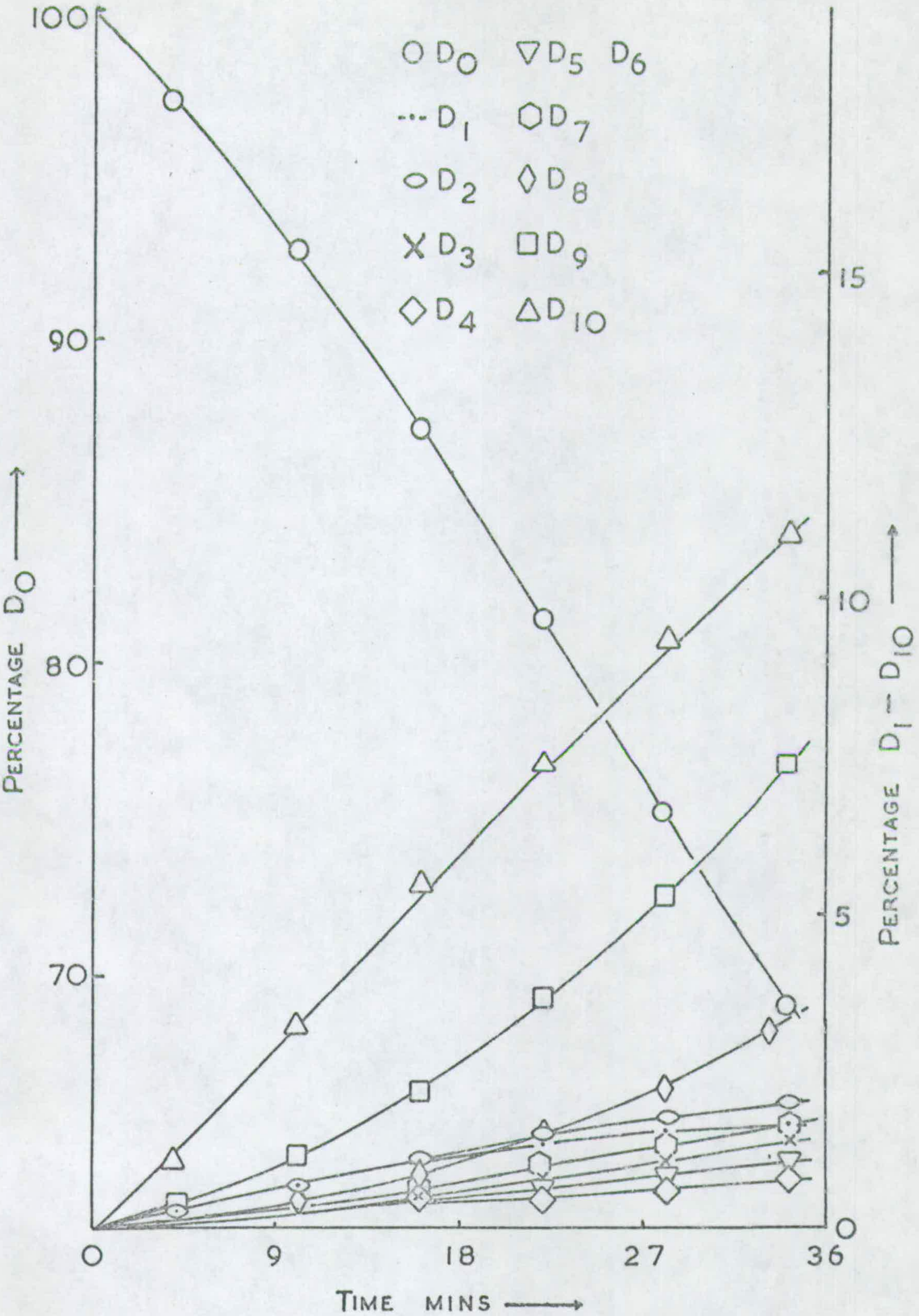


FIG. 3.8 EXCHANGE OF CYCLOPENTANE WITH DEUTERIUM AT 233°C ON A SINTERED NICKEL FILM

TABLE 3.4.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF CYCLOPENTANE

Sintering conditions	Temp. °C	Percentage of deuterated species										$M = \frac{k_\phi}{k_o}$	$M = \sum \frac{nd_n}{100}$
		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}		
none	-61	86.50	13.35	-	-	-	-	-	-	-	-	~ 1	1.13
none	-43	80.25	7.41	2.47	2.47	4.93	1.24	-	-	-	-	1.86	1.44
none	-23	90.61	6.62	0.87	0.52	1.22	0.18	-	-	-	-	1.11	1.16
none †	72	13.30	26.30	17.05	10.80	13.40	2.86	3.18	3.14	4.75	5.15	4.55	3.86
Film deposited at 275°C	232	15.05	7.79	5.11	2.26	3.33	3.33	4.03	5.38	13.42	40.30	8.9	6.88
Film sintered at 298°C*	288	1.84	1.64	0.46	0	1.43	0	5.63	14.15	31.50	43.30	-	8.80

† distribution at ϕ = 95.93; d_o = 75.16

* distribution at ϕ = 407.76; d_o = 53.83

greater than 70°C all the deuterated species were produced in substantial amounts initially. The kinetic data for the exchange reaction at 72°C showed that the isomers containing two and three deuterium atoms were being produced at a faster rate than the monodeuterocyclopentane. It is thus probable that if the initial product distribution could have been measured it would have been similar in shape to that for the exchange reaction on the sintered films; i.e. maxima would have been observed at the d_1, d_5 and d_{10} cyclopentanes, with a distinct break in the distribution at the d_5 cyclopentane.

3.3. The Exchange of Cyclohexane with Deuterium

The exchange of cyclohexane with deuterium has been studied on unsintered heavy nickel films; and the results obtained compared with those reported by Anderson and Kemball (103). On the unsintered films which weighed approximately 30 mg a very slow reaction was initially observed at -30°C; and the reaction was studied at temperatures between -30°C and 93°C. The rates of exchange were converted into absolute units using the known surface areas of the films, which were calculated by the method described in section 3.1., and are summarized in Table 3.5.

TABLE 3.5.

EXCHANGE OF CYCLOHEXANE WITH DEUTERIUM ON UNSINTERED NICKEL FILMS

Reaction temp. °C	Rate of exchange mols $s^{-1}m^{-2}$. 10^{-14}		$M = \frac{k_\phi}{k_o}$
	k_o	k_ϕ	
-30	1.71	2.08	1.22
0	32.66 → 22.69	39.64 → 26.14	1.21 → 1.15
21.3	36.74 → 22.07	48.81 → 35.34	1.33 → 1.60
51	18.52 → 13.78	141.8 → 102.3	7.65 → 7.42
93	65.06 → 12.55	522.5 → 378.4	8.04 → -

The plots of the apparent first order rate equations 3.12. and 3.14. (Part I) were, apart from the reaction at -30°C, very slightly retardedly curved, and this is illustrated by Figure 3.9. The shapes of the rate plots obtained and the variation of the carbon count with time are summarized in Table 3.6., which shows that there was no correlation between the two sets of results. For the reaction at -30°C the carbon count increased at a rate of approximately 0.5% min.$^{-1}$ In the case of the reaction at the other temperatures, increasing the reaction temperature produced an initial increase in the carbon count which then either did not vary with time or decreased at a rate of approximately 0.1% min^{-1}.

Figure 3.10. which shows the Arrhenius equation plot for the rate of disappearance of the d_o cyclohexane also includes the results reported by Anderson and Kemball (103). Their results were converted for use in Figure 3.10. in the following manner. An inspection of the two values which they reported for the pre-exponential factor, indicated that they had assumed that a nickel film which weighed 10 mg would have a surface area of 0.1 m^2. By the method described in section 3.1. an unsintered nickel film which weighed 10 mg would have had a surface area of 0.215 m^2, and this value was used to convert the pre-exponential factor reported by Anderson and Kemball (103) for use in Figure 3.10.

TABLE 3.6.

Reaction temp. °C	Type of rate plot obtained*		Variation of carbon count with time
	$\log_{10}(\phi_\infty - \phi)$	$\log_{10} d_o$	
-30	S	S	increasing
0	VSCR	VSCR	decreasing
21.3	VSCR	VSCR	constant
51	VSCR	VSCR	constant
93	VSCR	CR	constant

* S:-	straight line apparent first order rate plot
VSCR:-	very slightly curved rate plot, reaction slowing down
CR:-	curved rate plot, reaction slowing down

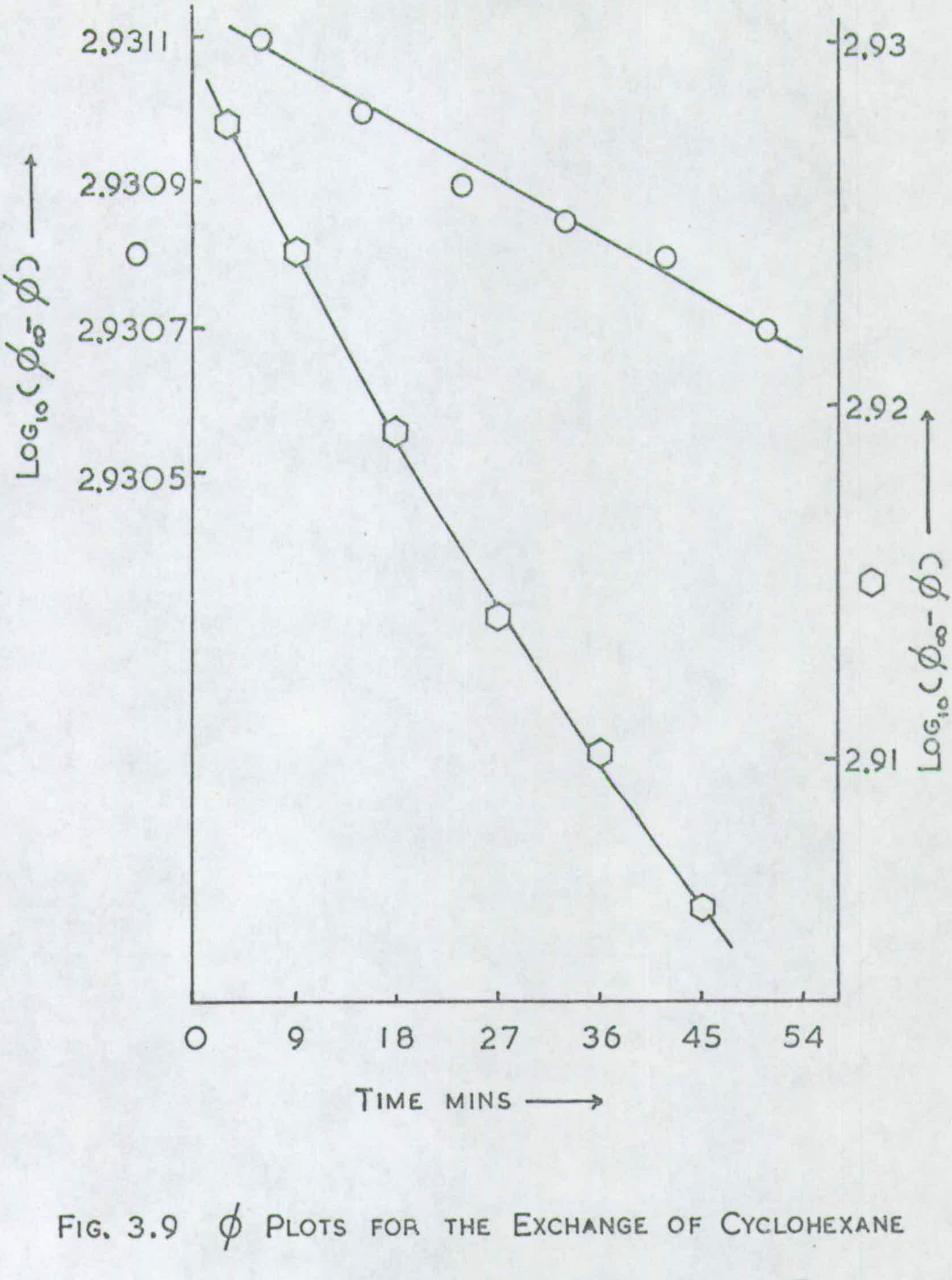


Fig. 3.9 ϕ Plots for the Exchange of Cyclohexane with Deuterium on Unsintered Heavy Nickel Films; ○ at -30°C ; ⬡ at 51°C

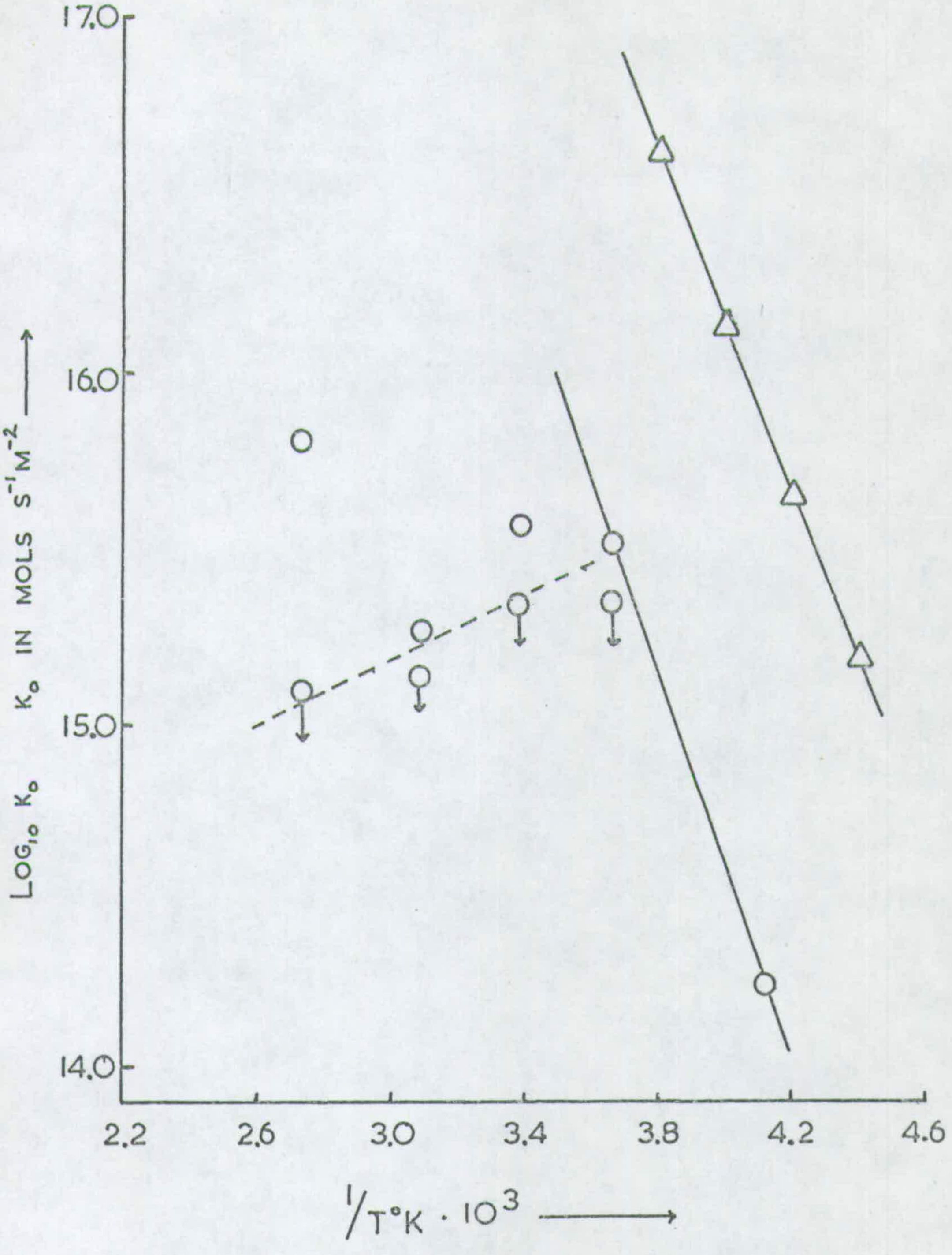


Fig. 3.10 Arrhenius Plot for the Exchange of Cyclohexane with Deuterium on Unsintered Heavy Nickel Films

△ Results of Anderson and Kemball (103)

○ This Work

The results obtained in this work do not compare favourably with those obtained by Anderson and Kemball (103), the films used in this work being less active at -23°C by a factor of 40. The discrepancy may be even larger because the gas ratios used in this work were different from those used in the earlier report. Anderson and Kemball (103) used a gas ratio (deuterium:cyclohexane) of 20:1, whereas the ratio used in this work was 10:1. It was not, however, possible to allow for this difference because they did not give any details relating the rate of exchange to the partial pressure of the deuterium.

The deviation of the rates of exchange k_o from the Arrhenius equation (Figure 3.10) at temperatures greater than 0°C indicates that extensive self poisoning of the exchange reaction was occurring. However, the reaction shows some anomalous features. A comparison of Figure 3.10. with Figure 3.11. which shows the Arrhenius equation plot for the rate of incorporation of deuterium into the cyclohexane, indicates that the rate of disappearance of the d_o hydrocarbon may be being affected to a greater extent than the rate of incorporation of deuterium into the molecule. The Arrhenius parameters for the exchange reaction are summarized in Table 3.7.

TABLE 3.7.

ARRHENIUS PARAMETERS FOR THE EXCHANGE OF CYCLOHEXANE

Based on the rate of exchange	Apparent activation energy E_a kJ mole^{-1}	Pre-exponential factor $\log_{10} A$ A in mols $s^{-1}m^{-2}$	
k_o	45.3	25.6	(103)
k_o	53.5	25.6	
k_ϕ	53.4	25.8	

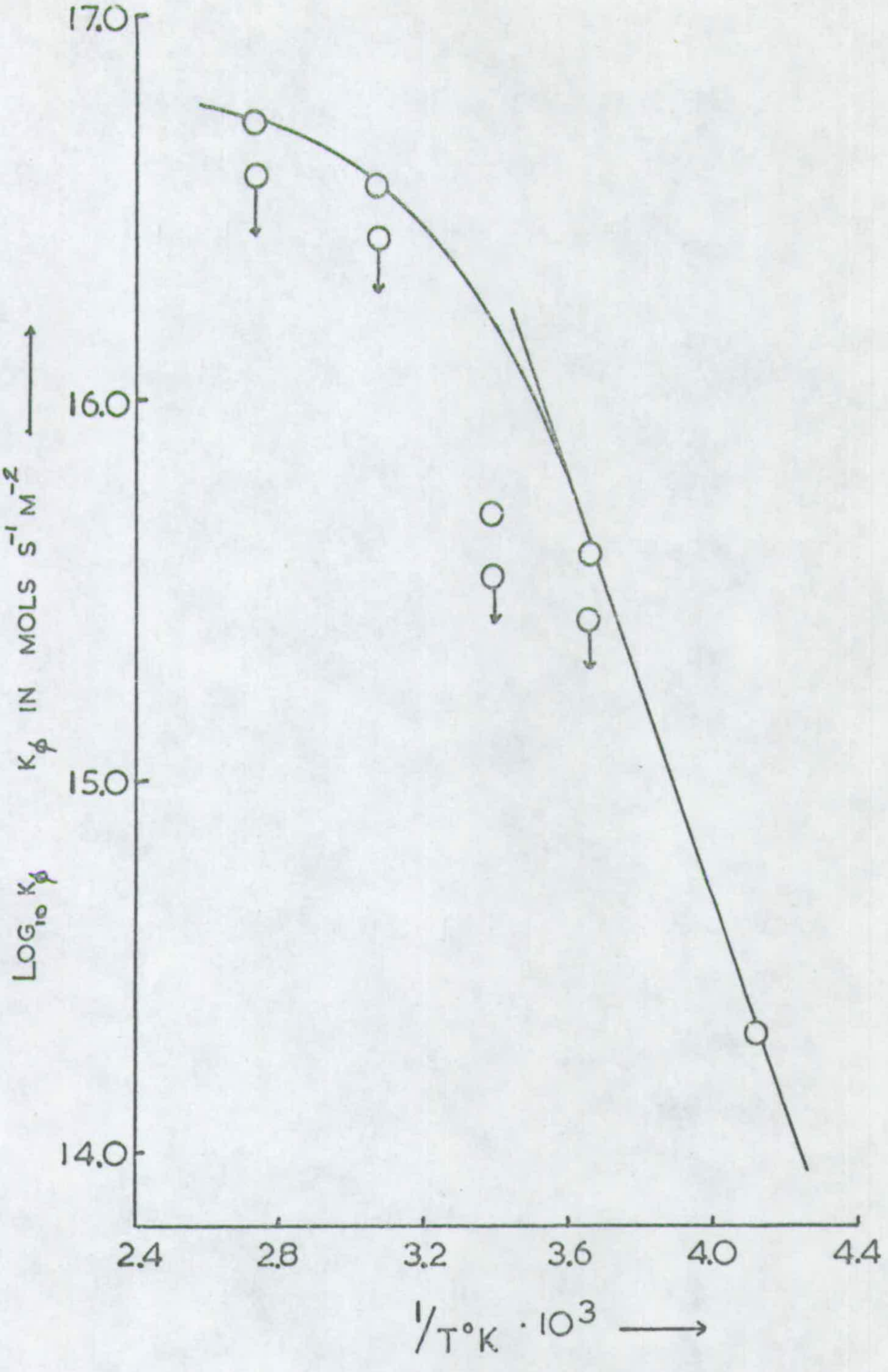


FIG. 3.11 ARRHENIUS PLOT FOR THE EXCHANGE OF CYCLO-HEXANE WITH DEUTERIUM ON UNSINTERED HEAVY NICKEL FILMS

Figures 3.12. and 3.13. show the course of some typical reactions with time, and the initial product distributions for the exchange reaction are given in Table 3.8. The initial distributions obtained were similar in shape to those that had been observed for the exchange of cyclopentane on the unsintered films. At temperatures less than 22°C the only isotopic cyclohexanes produced initially were those containing from one to six deuterium atoms. The d_1 cyclohexane was the predominant isomer and the percentages of the isotopic species decreased in order with increasing deuterium content of the molecule. At temperatures greater than 22°C all the possible deuterated cyclohexanes were produced in substantial amounts initially, maxima being observed at the d_1, d_6, and d_{12} cyclohexanes with a distinct break in the distribution at the d_6 compound. As in the case of the distributions for cyclopentane the correlation between the experimental M values and those calculated from the initial distributions was not very good; and this was probably caused by a substantial error in the M values calculated from the rates of exchange, due to the reaction self poisoning.

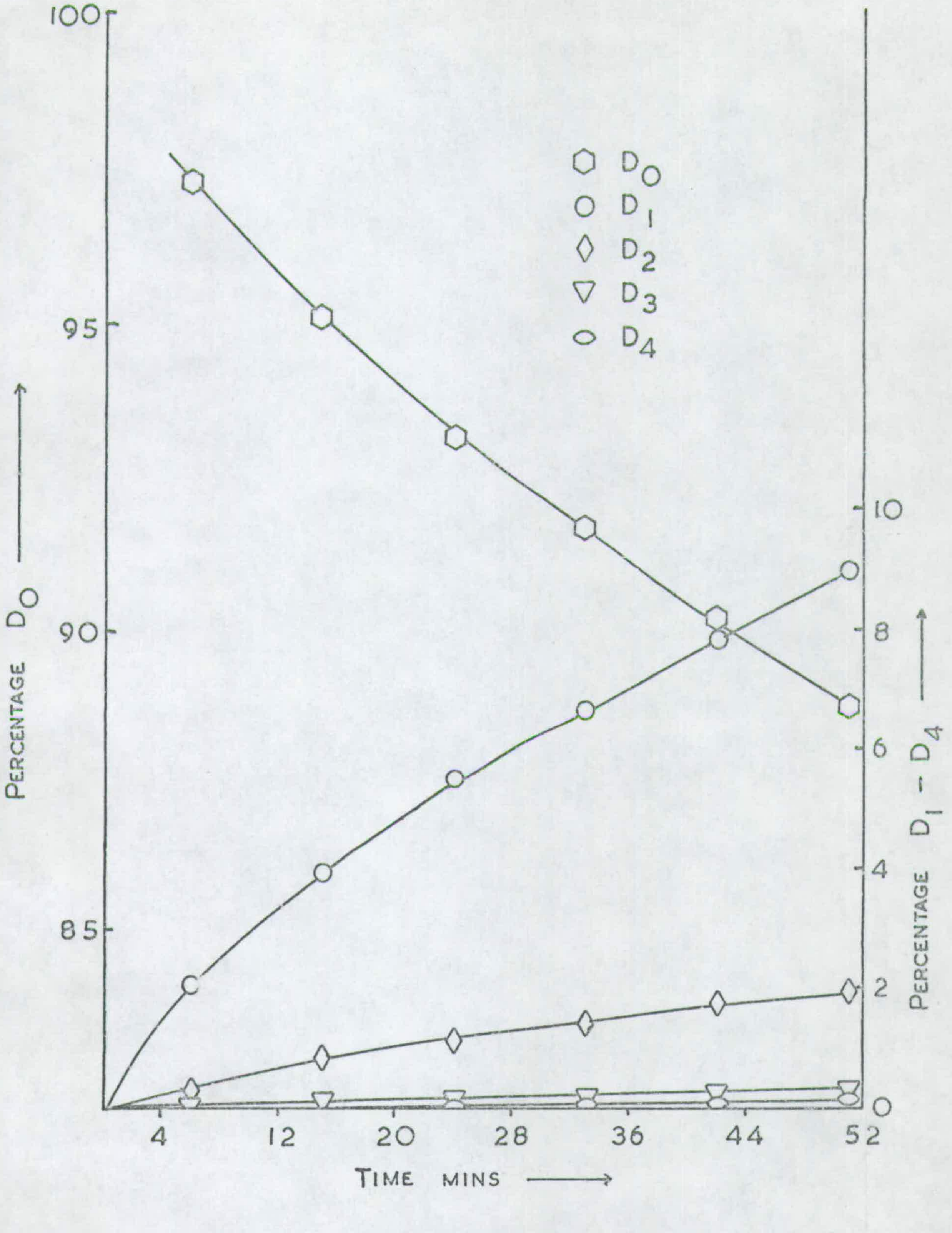


Fig. 3.12 Exchange of Cyclohexane with Deuterium at 0°C on an Unsintered Nickel Film

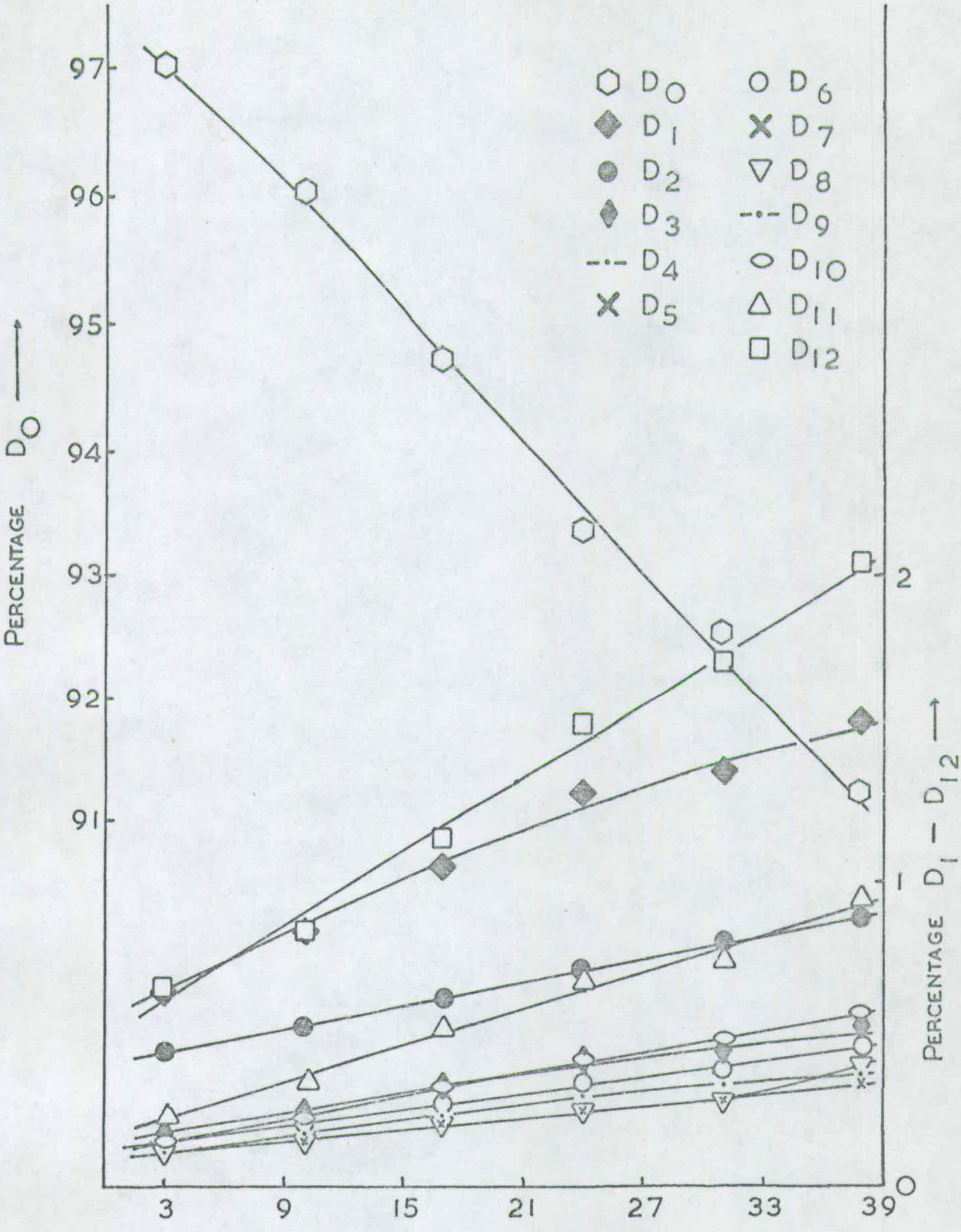


Fig. 3.13 Exchange of Cyclohexane with Deuterium at 51°C on an Unsintered Nickel Film

TABLE 3.8.

INITIAL PRODUCT DISTRIBUTIONS FOR THE EXCHANGE OF CYCLOHEXANE

Temp. °C	Percentage of deuterated species												$M = \frac{k_\phi}{k_o}$	$M = \sum \frac{nd_n}{100}$	
	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}			
-34.5	87.90	6.68	2.59	1.80	0.80	-	-	-	-	-	-	-	-	1.20	(103)
-30	72.75	22.0	2.28	1.52	0.76	0.76	-	-	-	-	-	-	1.22	1.38	
0	73.50	22.85	1.85	1.20	0.44	0.21	-	-	-	-	-	-	1.21	1.33	
51	26.00	16.10	5.78	4.49	2.94	4.73	2.93	2.94	3.78	4.49	5.78	20.35	7.65	5.67	

CHAPTER IV

DISCUSSION

4.1. The Mechanism of Exchange

The initial product distributions for the exchange of cyclohexane and cyclopentane show that the mechanisms of exchange are similar. Both molecules contain only secondary hydrogen atoms and the mechanism of exchange will thus not be influenced by the variation of carbon-hydrogen bond dissociation energies. However, because the molecules are alicyclic the hydrogen atoms can be divided into two groups:

(a) Those above the plane of the ring.

and (b) Those below the plane of the ring.

The presence in the initial product distributions of species containing more than one deuterium atom indicates that a multiple exchange process is operating, and a number of adsorbed intermediates can be formulated to account for this process, viz; $\alpha\alpha$-, $\alpha\beta$- and π-allylic. A consideration of the molecular geometry of the adsorbed species shows that, if the molecules are dissociatively adsorbed with the plane of the ring parallel to the surface, it is only possible to exchange the hydrogen atoms on one side of the ring by the interconversion between α-adsorbed and $\alpha\beta$-diadsorbed intermediates. For the hydrogen atoms which are inaccessible to the surface to be exchanged initially, it is necessary for the adsorbed molecules to undergo a 'turn-over' mechanism. There are two possible ways of achieving this. The α-adsorbed intermediate may form an $\alpha\alpha$-diadsorbed intermediate, thus producing an adsorbed molecule with the plane of the ring perpendicular to the surface. The reversion of this intermediate to an α-adsorbed intermediate will enable the adsorbed molecules to turn over on the surface. However, a change in the hybridization of the carbon electron orbitals from the sp^3 found in an αβ-diadsorbed intermediate to the sp^2 implicit in a π-allylic intermediate will bring the hydrogen atoms bonded to the carbon atoms forming the π-allylic intermediate into the plane of the ring; thus enabling the hydrogen atoms above the plane of the ring to be exchanged by an Eley-Rideal mechanism.

The molecular shapes of cyclohexane and cyclopentane are different; the cyclopentane ring being almost planar, whereas that of cyclohexane is not. The chair conformation of cyclohexane is slightly more stable than the boat form. However, due to the alternation of the axial and equatorial bonds in the chair conformation, the adsorption of cyclohexane by an αβ-diadsorbed intermediate can only occur by distortion of the molecule. It is thus probable that cyclohexane will be adsorbed by an αβ-diadsorbed intermediate in the boat conformation. The formation of a π-allylic intermediate requires that the carbon atoms lie in one plane; and it will be relatively easy to do this from the almost planar cyclopentane. In the case of cyclohexane the formation of a π-allylic intermediate will require distortion of the molecule. It would, therefore, be expected that if π-allylic intermediates are operative in the exchange mechanism, the variation in the ease of their formation from cyclohexane and cyclopentane would have an influence upon the initial product distribution.

On the unsintered films at temperatures less than ambient temperature, the initial product distributions show that for cyclopentane and cyclohexane only half of the hydrogen atoms were readily exchangeable; and this must correspond to the exchange of the hydrogen atoms on one side of the ring. By the interconversion between α-adsorbed and αα-diadsorbed intermediates it is only possible to exchange a maximum of two hydrogen atoms in each molecule initially. The presence of species containing more than two deuterium atoms in the distributions immediately rules out an αα-diadsorbed intermediate as being primarily responsible for the multiple exchange process. The primary mode of exchange must, therefore, be the interconversion between α-adsorbed and either αβ-diadsorbed or π-allylic intermediates. Since the formation of a π-allylic intermediate involves a minimum of three carbon atoms, the desorption of a molecule from the surface after undergoing an α-, αβ- and π-allylic interconversion can only occur by the addition of three deuterium atoms. The initial product distribution for the exchange of cyclopentane at -61°C shows, however, that a maximum of two deuterium atoms were incorporated into the molecule initially, indicating that a π-allylic intermediate was not participating in the exchange mechanism. The evidence cited in section 3.5. (Part II) indicates that nickel has a relatively poor activity for the formation of π-allylic intermediates, and it is considered that this intermediate was not responsible for the exchange of the hydrocarbons at temperatures less than 0°C. The exchange of the hydrogen atoms on one side of the ring must, therefore, be due to the interconversion between α-adsorbed and αβ-diadsorbed intermediates.

On the sintered films all the hydrogen atoms of cyclopentane were readily exchangeable initially; as were the hydrogen atoms of cyclopentane and cyclohexane at temperatures greater than room temperature on the unsintered films. This propagation of the exchange process from one side of the ring to the other can, as mentioned previously, only occur by the formation of either an αα-diadsorbed intermediate or a π-allylic species. It has been shown for the exchange of methane on nickel films that at temperatures greater than 200°C an αα-diadsorbed intermediate is participating in the exchange mechanism (90). Gault et al.(50)

have shown for 1,1,3,3-tetramethylcyclopentane, which cannot form a π-allylic intermediate, that the propagation of the exchange process from one side of the ring to the other by an $\alpha\alpha$-diadsorbed intermediate only became important at temperatures greater than 140°C. It is, therefore, unlikely that $\alpha\alpha$-diadsorbed intermediates are participating in the mechanisms for the exchange of cyclopentane and cyclohexane on the unsintered films at temperatures greater than room temperature.

Gault et al. (50) have shown for the exchange of cis-1,1,3,4-tetramethylcyclopentane on unsintered nickel films, that at 0°C maxima were observed at the d_1, d_4, and d_{12} isomers, indicating that a π-allylic intermediate was being formed on the surface. The amounts of the isotopic species containing from one to four deuterium atoms were greater than those containing from five to twelve deuterium atoms, and corresponded to the exchange of the four hydrogen atoms trans to the cis methyl groups. They also found for the exchange of the same molecule that at 43°C maxima were observed in the initial distributions at the d_1 and d_{12} isomers, and that the percentages of the species containing from one to four deuterium atoms were similar to those containing from five to twelve deuterium atoms. This indicates that the activation energy for the formation of π-allylic species is greater than that for the formation of the σ bonded $\alpha\beta$-diadsorbed intermediate, and that the ratio π/σ increases with increasing temperature. This behaviour of the distributions was also shown by the hydrocarbons studied in this work at temperatures greater than room temperature on the unsintered films; and it is considered that the exchange of cyclopentane and cyclohexane was propagated by the interconversion between α-, $\alpha\beta$-, and π-allylic intermediates, with the formation of π-allylic intermediates becoming increasingly probable with increasing temperature.

At the high temperatures required to propagate the exchange of cyclopentane on the sintered films it is possible for αα-diadsorbed intermediates to participate in the exchange mechanism. However, because π-allylic intermediates are readily formed at lowish temperatures on the unsintered films, it is considered that the interconversion between α-, αβ-, and π-allylic species will be more probable than the intervention of an αα-diadsorbed intermediate into the interconversion between α-adsorbed and αβ-diadsorbed intermediates.

4.2. Activity of the Films for the Exchange Reactions

The absolute rates of exchange were based upon the apparent surface areas of the films, as calculated by the method described in Part III section 3.1. It is well known that the surface areas of nickel films depend upon the sintering temperature (150), and a number of reports have appeared in the literature devoted to their physical structure. Thus Anderson et al. (136) have shown that nickel films deposited at 0°C in vacuo are unoriented, and consist of large crystallites 20-100 nm in diameter with intercrystal gaps of 2 nm. The structure of films deposited at 0°C are extremely porous with a large internal surface, and the surface area is proportional to the thickness of the film; in confirmation of this it has been shown, that the electrical conductivity is about seven times less than for the bulk metal (77), that the surface area is dependent upon the weight (150), and that all the physically adsorbed xenon used to measure the surface area could not be removed by pumping (160). Sintering the films either in vacuo or in hydrogen causes crystallite growth and smoothing of the surface. Thus it has been found that sintering a film at 400°C in vacuo increased the crystallite size to 200-300 nm and eliminated surface asperities (136), and that sintering at 200°C produced a polycrystalline surface with no intercrystal gaps (160); this coherence of the film structure is also shown by the fact that the resistance of a 5 mg film, which had been sintered at 187-257°C, was approximately equal to the resistance of the bulk metal (136).

The specific activity of the films may depend not only upon the surface area, but upon the catalytically active surface area, which will be a function of the hydrocarbon studied. Thus for the hydrogenation of ethylene, the zero order dependence of the rate upon the ethylene pressure (55) indicates that ethylene is much more strongly adsorbed than hydrogen; and it might be expected that almost all of the surface would be catalytically active. It has been shown, however, that all of the surface is not catalytically active (115), and that sintering the films decreases the specific activity for the reaction to a slightly greater extent than the decrease in the apparent surface area (150). For the exchange of alkylbenzenes on nickel films it has been shown that sintering produces a very profound effect upon the character of the reaction (137). It was found for the exchange of cumene, that on unsintered films the m- and p-hydrogen atoms, and the hydrogen atom on the carbon atom α to the ring reacted at approximately the same rate; but on the films sintered at 200°C only the hydrogen atom on the α carbon atom was readily exchangeable. This indicated that sintering or poisoning associated with the sintering process had destroyed the sites responsible for the adsorption of the benzene ring.

The results obtained in this work show that sintering the films decreased their specific activity for the exchange of cyclopentane at -23°C by a factor of 10^7. This value may, however, be misleading because it involved an extreme extrapolation of the resultw for the reaction on the sintered films, and the activation energy may not be temperature invariant. If the specific activities are based on the temperatures required to give a rate of exchange k_o equal to 3.10^{16} mols $s^{-1}m^{-2}$, then for the unsintered and sintered films values of -23°C and 194°C respectively are obtained. The initial product distributions obtained for the reaction on the two kinds of film were similar, indicating that sintering may not have preferentially eliminated certain types of exchange sites.

The decrease in the specific activity may have been caused by using an oxygen contaminated surface; thus the results obtained for the exchange of cyclohexane show that the films used in this work were not as active as those used by Anderson and Kemball (103). Two explanations can be advanced for this behaviour:

(a) The films used in this work were contaminated and those used by Anderson and Kemball (103) were clean.

or (b) Those used in this work were clean and those used by Anderson and Kemball (103) were contaminated.

For the films used in this work the reaction vessel system was outgassed until the pressure was less than 0.3 mNm^{-2}, and the films were deposited with the reaction vessel closed off from the pumping system. The first few layers of film deposited will, therefore, have removed most of the oxygen remaining in the reaction vessel by gettering; and it is considered that the films were essentially clean before the admission of the reaction mixture. If it is assumed that a nickel atom in the surface of the film occupies an area of 0.0625 nm^2, then the surface of an unsintered film will contain approximately 6.10^{18} nickel atoms. For the formation of a monolayer of oxygen atoms on the surface the reaction vessel at 0°C would have had to contain an oxygen pressure of 65 Nm^{-2}, and this would have required the gas mixture to contain approximately 1% oxygen; this is unlikely because the hydrocarbons used were degassed before preparing the reaction mixture. An attempt was made to resolve the problem by contaminating the surface of an unsintered film with oxygen by the thermal decomposition of nitrous oxide (161). After $7.3.10^{18}$ molecules of nitrous oxide had been allowed to remain in contact with the film at 0°C for 30 mins, the excess was removed by pumping at 0°C for 10 mins; however, when the gas mixture was admitted to the film at -40°C no exchange of cyclohexane was observed at temperatures less than room temperature. This result was not entirely unexpected because it is known that hydrogen does not chemisorb on a freshly oxidized nickel surface (162). It can, therefore, be concluded that the disparity between the results was not caused by using nickel oxide instead of nickel.

It is possible, however, that the films may have been contaminated by islands of nickel oxide in a nickel matrix. It has been shown that the adsorption of oxygen on nickel increased with time at -78 and 22°C and was not reversible (163). This indicated that oxygen was being incorporated into the bulk nickel; but it was possible, however, to partially regenerate the surface by heating in vacuo at -78°C. Galvey and Kemball (159) have shown for the adsorption of hydrocarbons on a nickel supported catalyst, that at -35°C little dissociative adsorption of cyclohexane, n-pentane, i-pentane, or 2,2-dimethylbutane was occurring, the adsorption being mainly physical in nature. With cyclopentane, however, extensive dissociation of the carbon-hydrogen bonds was observed at -35°C. It is difficult to correlate these results with those obtained by Anderson and Kemball (103) for the exchange of cyclohexane on unsintered films, because adsorption may occur over the whole surface, whereas only a small proportion of the surface may be active for exchange reactions. The dissociative adsorption of cyclohexane at temperatures greater than -35°C corresponds quite well with the exchange of cyclohexane at temperatures greater than -30°C observed in this work; and it is considered that the films used in this work were essentially non-contaminated. Nickel oxide is a p-type semiconductor, and the chemisorption of hydrogen on its surface will be depletive. If islands of nickel oxide are present in the surface of a nickel film, the nickel metallic orbitals at the nickel oxide - nickel interface will be modified, and the enhanced activity of the films used by Anderson and Kemball (103) may be due to the exchange of cyclohexane taking place readily at this interface.

The results obtained in this work for the exchange of cyclopentane on the sintered films were similar to those reported by Rowlinson et al. (164). A direct comparison between the two sets of results could not be made because they used a different gas ratio from that used in this work; nor did they report the Arrhenius parameters and pressure dependency equations for the reaction. For the results obtained in this work, the rates of exchange on the films sintered in deuterium and on those deposited at the sintering temperature were similar; and it is considered unlikely that this correspondence would have been obtained if the films had been contaminated.

Since no exchange of cyclopentane on the sintered films was observed at temperatures less than 200°C, the large decrease in the specific activity on sintering cannot be due to progressive self poisoning of the reaction, and must have been caused by a change in the nature of the surface. It has been shown for the hydrogenolysis of ethane on a nickel-silica-alumina catalyst, that the specific activity decreased with increasing crystallite size to a greater extent than could be explained by the decrease in the surface area (165). This result shows that for a molecule with a simple molecular structure such as ethane, the reaction is sensitive to the degree of dispersion of the metal. Sintering the films will have increased the mean crystallite size and smoothed their surface; and it is probable that for cyclopentane with its more complex molecular shape, the reaction will be sensitive to the structure of the surface. The large decrease in activity on sintering will thus be due to the lowered degree of dispersion and the elimination of surface defects.

The results obtained for the exchange of cyclohexane and cyclopentane on the unsintered films show that at -23°C cyclopentane was more reactive than cyclohexane by a factor of 100. The results obtained by Galwey and Kemball (159) show that cyclopentane was more readily adsorbed on a nickel catalyst than cyclohexane; and their results correlate quite well with the greater ease of exchange of cyclopentane on the unsintered films. The Arrhenius parameters for the exchange of cyclohexane were greater than those for cyclopentane; and the Arrhenius parameters for the exchange of both molecules showed a normal compensation effect. This indicates that there is an interplay between the heat of adsorption and the entropy of adsorption which is not readily disentangled.

The Arrhenius equation plots for the exchange of cyclohexane and cyclopentane show that both reactions were extensively self poisoned; indicating that on the parts of the surface responsible for exchange there is a competition between the reversible adsorption of the hydrocarbon, and the tendency of nickel to dissociate the adsorbed species further to give strongly bound structures on the surface. A number of reports have appeared in the literature devoted to the adsorption of hydrocarbons on nickel surfaces. Wright et al. (158) have shown that on a nickel film the adsorption of methane was rapid at 140°C and was accompanied by the slow liberation of hydrogen. The breakdown of the adsorbed methane was extensive and increased with increasing temperature. They also found that ethane was adsorbed readily at 0°C and could be displaced from the surface by hydrogen. In the temperature range 60-100°C, however, the adsorption of ethane was accompanied by the liberation of hydrogen from the surface, indicating that the adsorbed ethane species were extensively dehydrogenated. Ethylene can adsorb on a nickel surface either associatively or dissociatively, and Eischens and Pliskin (166) have shown that on a bare nickel surface at 35°C, or on a hydrogen covered nickel surface at 150°C the carbon atoms are mainly saturated. Morrow and Sheppard (167) have shown that for the adsorption of ethylene on a nickel carb-o-sil catalyst, the I.R. spectrum of the adsorbed species varied with the time and temperature of adsorption. At room temperature the spectrum was mainly indicative of n-butyl surface species; and the hydrogenation of the adsorbed species at 20°C resulted mainly in the formation of gaseous or physically adsorbed n-butane. Knor et al. (168) found that on a nickel film at 0°C the adsorption of cyclopropane resulted in the formation of gas phase propane and ethane, indicating that fission of the carbon-carbon bonds was occurring. The hydrogenation of cyclopropane at 0°C was, however, reversible; after pumping off the gas phase, the activity of the film for subsequent hydrogenation reactions was reproducible. The adsorption of cyclohexane has also been studied by Palazov et al. (169), who found that on a nickel silica catalyst at 20°C carbon-hydrogen stretching bands appeared in the I.R. spectrum due to the dissociative adsorption of the cyclohexane; they also found, however, that on a hydrogen covered surface these carbon-hydrogen stretching bands did not appear. These results indicate that nickel is an extremely active metal for dissociating carbon-hydrogen bonds. The strongly held species will thus be probably bound to the surface by an $\alpha\alpha\beta$-type intermediate.

On the unsintered films the exchange reactions of cyclopentane and cyclohexane showed deviation from the Arrhenius equation plot at temperatures of -23°C and 0°C respectively, and the activation energy of -8.63 kJ mole^{-1} obtained for the deviated branch of the plot was identical for both molecules. This self poisoning of the exchange reaction can only occur if the strongly bound species are adsorbed on the same surface sites as those which are responsible for exchange. The formation of strongly adsorbed species on metal surfaces is generally believed to involve the adsorption of the hydrocarbon by intermediates of the type ααβ- ααββ- etc. It was shown in section 4.5. (Part II) that nickel is a relatively good catalyst for the formation of αα-diadsorbed intermediates; and it has been shown that the hydrogenolysis of neohexane on nickel films involved the formation of an ααβ-triadsorbed intermediate (154). The self poisoning of the exchange reactions of cyclopentane and cyclohexane, therefore, probably involves the formation of ααβ-triadsorbed, or ααββ-tetraadsorbed intermediates. For cyclohexane and cyclopentane, if the molecules are strongly adsorbed with the plane of the ring parallel to the surface, the formation of ααβ- etc. intermediates is geometrically impossible. The strongly bound species must, therefore, be adsorbed on the surface with the plane of the ring perpendicular to the surface. It would be possible for the formation of the adsorbed species to occur by hydrogenolysis of the alicyclic ring. It has been shown, however, for the hydrogenolysis of alkylcyclohexanes, that on a nickel-alumina catalyst no cleavage of the cyclohexane ring occurred at 220°C (170); and it is considered improbable that cleavage of the alicyclic ring occurs at low temperatures on the unsintered films. It is believed that the identical activation energy given above for the deviated branch of the Arrhenius plots supports the hypothesis that self poisoning is occurring by the formation of ααβ-type intermediates. The formation of a 1,2,4,5-tetra adsorbed intermediate by the dissociation of the four hydrogen atoms from the boat conformation of cyclohexane, requires four nickel atoms in a square arrangement with a side dimension 0.29 nm. So far as is known a site of this type does not exist on the surface of nickel films. The formation of this intermediate is also possible from cyclopentane but it is not believed to be responsible for the self poisoning of the exchange reactions.

The exchange of cyclopentane on the sintered films was also self poisoned and the carbon count at any temperature usually decreased linearly with time. The kinetics of the exchange reaction and the self poisoning reaction were different; the exchange reaction generally obeyed the apparent first order equation, whereas the decrease in the carbon count obeyed zero order kinetics. Tt is believed that the exchange reaction and the self poisoning reaction were occurring simultaneously on the same surface sites. The activation energy for the self poisoning reaction, i.e., the rate of disappearance of the carbon count, was effectively zero, indicating that the two processes did not have a common intermediate. It is known (50) that on nickel films it is possible for the adsorbed polymethylcyclopentanes to turn over on the surface by the formation of an $\alpha\alpha$-diadsorbed intermediate; and it is believed that this intermediate is the one responsible for self poisoning of the exchange reaction. The exchange and self poisoning reactions may thus be formulated as follows. The initial adsorption of the cyclopentane will occur by the formation of an α-adsorbed intermediate which can then form either an $\alpha\beta$- or an $\alpha\alpha$-diadsorbed intermediate. If the $\alpha\beta$-diadsorbed intermediate is formed the exchange of cyclopentane will be propagated by the interconversion between $\alpha\beta$-diadsorbed and π-allylic intermediates. If, however, the $\alpha\alpha$-diadsorbed intermediate is formed, the plane of the ring will be perpendicular to the surface, and an $\alpha\alpha\beta$-triadsorbed intermediate will be formed in preference to the reversion of the $\alpha\alpha$-species to an α-adsorbed intermediate, hence causing self poisoning of the exchange reaction.

In conclusion it may be said that extensive self poisoning of the exchange reactions of cyclopentane and cyclohexane was observed at low temperatures on the unsintered films. Preadsorption of hydrocarbons on the surface would have increased the reaction temperatures required to propagate the exchange process, and the effects produced by presorption would have been impossible to differentiate from progressive sintering of the films. Presintering the films increased the temperatures required to propagate the exchange process markedly, and the presorption of hydrocarbons on such films would have brought the reaction temperatures necessary to propagate the exchange process into the region of temperature where hydrocracking of the molecules would have occurred. It is, therefore, believed that with the apparatus used it is impossible to study self poisoning of exchange reactions on nickel films by the method proposed.

CONCLUSION, REFERENCES AND APPENDICES

CONCLUSION

The results obtained in this work indicate that platinum and nickel, although they are in the same sub order of Group VIII, are very different in their catalytic properties.

Anderson and Avery (42) postulated that the hydrocracking and isomerization of saturated hydrocarbons containing more than two carbon atoms on platinum films, occurred by the formation of an $\alpha\alpha\gamma$-triadsorbed intermediate. The exchange reactions of the saturated hydrocarbons on the platinum catalysts were not, however, self poisoned at temperatures less than 180°C; and the rates of exchange of neopentane at these temperatures were very much greater than the rate of hydrocracking and isomerization. This indicates that the adsorbed intermediates responsible for the propagation of the exchange process are essentially reversibly adsorbed. The exchange of methane by a multiple exchange process occurred readily at temperatures greater than 180°C; and the results obtained for the exchange of polymethylcyclopentanes on platinum films (50) indicated that an $\alpha\gamma$-diadsorbed intermediate could be formed at low temperatures. These results indicate that if an $\alpha\alpha\gamma$-triadsorbed intermediate is formed during the exchange reactions it is reversibly adsorbed, and hence does not cause self poisoning of the exchange reactions.

Although the mechanisms of exchange were different, the specific activity of the films for the exchange of propane, butane, and neopentane were similar, indicating that the exchange reaction was mainly governed by the ability of platinum to dissociate primary carbon-hydrogen bonds. The main characteristic of the unsintered platinum films was their tendency to sinter slightly during the reaction; and the specific activity of the films was reduced by presintering to a greater extent than the decrease in the apparent surface area. This reduction in activity, which was not accompanied by a change in the mechanism of exchange, depended upon the hydrocarbon studied.

On the nickel films, however, extensive self poisoning of the exchange reactions of cyclopentane and cyclohexane was observed. It is suggested that the exchange and self poisoning occurred by different mechanisms; the exchange being propagated by the interconversion between α-, αβ-, and π-allylic intermediates, whereas the self poisoning was caused by the formation of ααβ- or ααββ- adsorbed intermediates. As in the case of platinum, presintering the films produced a very large decrease in the specific activity of the films for the exchange of cyclopentane; and it is thought that this is due to a pronounced restructuring of the surface on sintering eliminating the catalytically active sites.

It was proposed to study the self poisoning of the exchange reactions of saturated hydrocarbons on platinum and nickel catalysts by presorbing hydrocarbons upon the surface and determining the effects, if any, that they produced upon the characteristics of the exchange reaction. However, is the effect produced by the poison caused by blocking the exchange sites, or by presorption on adjacent sites preventing reaction occurring on the exchange sites? Presorption of saturated hydrocarbons on platinum catalysts at temperatures less than 105°C does not poison the catalyst for the subsequent exchange reaction. However, platinum can be poisoned by molecules which contain lone pairs of electrons, and it would be interesting to see what effects the presorption of such molecules would produce upon the characteristics of an exchange reaction. It would also be interesting to see what effects a series of these compounds would produce, for example, ammonia, methylamine, dimethylamine, and trimethylamine. In the case of nickel the self poisoning of the exchange reactions studied was so extensive that quantitative work upon the effects of presorbing hydrocarbons would have been impossible. It may, however, be possible to deduce the structure of the intermediates responsible for self poisoning by other methods. One way of doing this would be to alter the structure of the molecule being studied. Thus, the exchange reaction of cyclohexane is self poisoned; but is that of norbornane? Although it has been postulated that the exchange of cyclohexane is self poisoned by the formation of an $\alpha\gamma\beta$-triadsorbed intermediate, it would also be possible for the reaction to self poison by the formation of an intermediate resulting from the dissociation of the four carbon-hydrogen bonds when the molecule is adsorbed in the boat conformation. The exchange of cis-hexafluorocyclohexane, which cannot form an $\alpha\gamma\beta$-triadsorbed intermediate, would enable the structure of the intermediate to be resolved; as would the study of the adsorbed intermediates by I.R. or broad line N.M.R. spectroscopy.

One of the interesting facets of this work was the decrease in the specific activity of the films on sintering. This may have been due to the elimination of surface defects or the elimination of crystal faces. Although some work has been published on the exchange of hydrocarbons on epitaxed nickel films (171) it would be interesting to study further the relationship between exchange reactions, self poisoning and the structure of the catalyst surface. This could be done by using epitaxed films, or by inducing surface defects into the catalyst, for example, by etching.

One of the problems encountered in the work with nickel films was related to their cleanliness. So far as is known, no systematic study of the relationship between surface contamination and the characteristics of exchange reactions has been attempted. It has been suggested that the enhanced activity of the nickel films used by Anderson and Kemball (103) for the exchange of cyclohexane relative to those used in this work was due to a contaminated surface. It would be interesting to study this further by exchanging cyclohexane on a series of nickel films, containing increasing quantities of nickel oxide. This study would be difficult experimentally requiring U.H.V. techniques and rigorous deoxygenation of the gases used. The catalysts would also have to be prepared prior to each experiment to prevent oxygen incorporation into the lattice and the chemisorption of "hydrogen" which is known to occur on aged nickel oxide catalysts (162).

If one studies the Group VIII metals, iron, cobalt, nickel and ruthenium are the only elements which are active in the Fischer-Tropsch synthesis. The triad of the metals in the first transition series readily form carbides in the Fischer-Tropsch synthesis, and also tend to self poison during exchange reactions. Iron is the most extensively self poisoned of the three metals, and although cobalt has not yet been fully studied in this respect it might be expected to show effects intermediate between those of iron and nickel. The iron sub order also differ from the other metals in that their crystal structures are different, and it would be interesting to see whether this has an influence upon the characteristics of catalytic reactions. Of the metals in Group VIII it is considered that the exchange reactions of hydrocarbons on iron, cobalt, and nickel films will be self poisoned to such an extent, that the quantitative study of the intermediates responsible would be impossible. This problem would not arise with the metals in the second and third transition series. Of these metals rhodium is known to self poison (83). It is also similar to platinum in that it readily forms $\alpha\alpha$-diadsorbed intermediates. It might, therefore, be expected that those metals on which methane readily exchanges by the formation of an $\alpha\alpha$-diadsorbed intermediate, would also exhibit self poisoning of the exchange reactions of the higher paraffins; and in this context an extensive study of the exchange reactions of saturated hydrocarbons on rhodium, iridium, ruthenium and osmium evaporated films would be worthwhile.

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APPENDIX I

The program given below is written in Atlas Autocode and was used for the statistical analysis of the mass spectral data.

```
  % BEGIN

  % INTEGER I,J,K,L,R,S,Q,A,N,B,M
  % ARRAY   P(-20:20)
  % ARRAY   F(1:6)
  % REAL    Z,T,H,C,D,E,G,TOTAL,PHE,X

  READ (I)
  % COMMENT I SETS OF DATA
7:READ (N)
  % COMMENT NO. OF HYDROGENS TO BE CONSIDERED
  READ (M)
  % COMMENT NO. OF FRAGMENTS TO BE CONSIDERED
  READ (X)
  % COMMENT SINGLE ISOTOPE CORRECTION

  % CYCLE B=1,1,6
  READ (F(B))
  % REPEAT

  % CYCLE J=1,1,I
1:READ (Z)
  →1 % UNLESS Z =-1
  READ T;  % COMMENT T IS TIME

  % CYCLE A=-M,1,N
  READ (P(A))
  % IF P(A)=-2 % THEN ⟶6
  % IF P(A)=-3 % THEN ⟶7
  % STOP % IF P(A)=-4
  % REPEAT

  READ (Z)
  →2 % IF Z=-2
6:% CAPTION~FAULTY␣SET␣OF␣DATA
  PRINT (J,3,0)
  →1

  % COMMENT CORRECTIONS FOR S.I.C., D.I.C., AND NAT. D. FOLLOW

2:% CYCLE K=-M,1,N-1
  H=X+(N-!K!)*0.0002
  P(K+1)=P(K+1)-H*P(K)
  % IF K>(N-2) % THEN ⟶3
  P(K+2)=P(K+2)-H*((H-0.011)/2)*P(K)
3:REPEAT
```

```
  % COMMENT CORR. FOR FRAG. CONS. LOSS OF UP TO 6 MASS UNITS

  % CYCLE L=N,-1,0
  % IF P(L)<0 % THEN → 10

  % COMMENT -1
  P(L-1)=P(L-1)- F(1)*(N-L)/N*P(L)

  % COMMENT -2
  P(L-2)=P(L-2)-((F(1)*L/N)+                                  %C
       (F(2)*((N-1)-L)/(N-1)*(N-L)/N))*P(L)

  % COMMENT -3
   C=P(L)*F(2)*2*L/N*(N-L)/(N-1)
   D=P(L)*(N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2)
   P(L-3)=P(L-3)-(C+D)

  % COMMENT -4
   C=P(L)*F(2)*L/N*(L-1)/(N-1)
   D=P(L)*F(3)*3*L/N*((N-1)-L)/(N-1)*(N-L)/(N-2)
   E=P(L)*F(4)*(N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2) %C
       *((N-3)-L)/(N-3)
   P(L-4)=P(L-4)-(C+D+E)

  % COMMENT -5
   C=P(L)*F(3)*3*L/N*(L-1)/(N-1)*(N-L)/(N-2)
   D=P(L)*F(4)*4*L/N*(N-L)/(N-1)*((N-1)-L)/(N-2)          %C
       *((N-2)-L)/(N-3)
   E=P(L)*F(5)*(N-L)/N*((N-1)-L)/(N-1)*((N-2)-I)/(N-2) %C
     *((N-3)-L)/(N-3)*((N-4)-L)/(N-4)
   P(L-5)=P(L-5)-(C+D+E)

  % COMMENT -6
   C=P(L)*F(3)*L/N*(L-1)/(N-1)*(L-2)/(N-2)
   D=P(L)*F(4)*6*L/N*(L-1)/(N-1)*                          %C
     ((N-1)-L)/(N-2)*((N-2)-L)/(N-3)
   E=P(L)*F(5)*5*L/N*(N-L)/(N-1)*((N-L)-1)/(N-2)          %C
      *((N-L)-2)/(N-3)*((N-L)-3)/(N-4)
   G=P(L)*F(6)*(N-L)/N*((N-L)-1)/(N-1)*((N-L)-2)/(N-2)      %C
      *((N-L)-3)/(N-3)*((N-L)-4)/(N-4)*((N-L)-5)/(N-5)
   P(L-6)=P(L-6)-(C+D+E+G)
10:%REPEAT

  % COMMENT CALCULATION OF PERCENT, PH1 AND PRINT INSTRUCTIONS

  NEWLINES (2)
  TOTAL=0

  %CYCLE S=0,1,N
  % IF P(S)<0 % THEN → 5
  TOTAL=TOTAL+P(S)
 5:%REPEAT

  % CAPTION CORRECTED␣PEAK␣HEIGHTS
```

```
   NEWLINES (1)

   % CYCLE R=-M,1,N
     % CAPTION ␣D;  PRINT (R,1,0)
     % CAPTION ␣=;  PRINT (P(R),1,2)
   % REPEAT

   % CAPTION~TOTAL␣PEAK␣HEIGHT␣NEGLECTING␣D-1␣TO␣
             D-M␣=␣
   PRINT(TOTAL,1,2)
   % CAPTION~PERCENTAGE␣OF␣ISOTOPIC␣SPECIES
   NEWLINES (1)

   % CYCLE R=0,1,N
   % CAPTION ␣D;  PRINT (R,1,0)
   % CAPTION ␣= ;  PRINT (P(R)*100/TOTAL,1,2)
   % REPEAT

   PHI=0

   % CYCLE Q=1,1,N
   % IF P(Q)<0 % THEN→44
   PHI=PHI+Q*P(Q)*100/TOTAL
44:% REPEAT

   % CAPTION~PHI␣=␣;  PRINT (PHI,1,2)
   % CAPTION~TIME␣␣=␣␣;  PRINT (T,1,2)
99:% REPEAT
   % END % OF % PROGRAM
```

The data is fed into the computer in the following form

```
I
N   M   X
F1 F2 F3 F4 F5 F6

-1T P-M   P-M+1   . . .  P0  . . . . .  PN    -2
etc.
-1     0     - 3    )
 N     M       X    }                          A
 F1 F2 F3 F4 F5 F6  )

-1 T P-M  P-M+1   . . .  P0  . . . . .  PN    -2
etc.

-1     0     - 4
```

Section A is only inserted if one is changing any of the hydrocarbon parameters.

APPENDIX II

Fortran IV computer program for the extended Gault-Kemball-Dibeler correction scheme used to analyse the mass spectra of the isotopic propanes.

```
      INTEGER S
      DIMENSION P(21),FH(7),FD(7),A(6),B(6),PER(21),CORP(21)
      READ (5,100) JSETS
      DO 57 JNOS=1,JSETS
      READ (5,100) ISETS
100   FORMAT (I6)
      READ (5,101) N,M,SIC
101   FORMAT (I6,I6,F6.4)
      READ (5,102) (FH(IFRAG),IFRAG=1,7)
102   FORMAT (7F6.4)
      READ (5,102) (FD(IFRAG),IFRAG=1,7)
      DO 1 I=1,6
       IF (FH(I).EQ.0.0000) GO TO 2
      A(I)=FH(I+1)/FH(I)
      B(I)=FD(I+1)/FD(I)
      GO TO 1
2     A(I)=0.0000
      B(I)=0.0000
1     CONTINUE
      S=M+1
      K=N+S
      I=N+M
      IPEAK=I+2
      NA=N*(N-1)
      NB=NA*(N-2)
      NC=NB*(N-3)
      ND=NC*(N-4)
      NE=ND*(N-5)
      DO 56 INOS=1, ISETS
      READ (5,103) TIME
103   FORMAT (F5.1)
      READ (5,104) (P(J),J=1,M)
104   FORMAT (12F6.2)
      READ (5,105) (P(J),J=S,K)
105   FORMAT (9F6.2)
      WRITE (6,33)
 33   FORMAT (10X,25HEXPERIMENTAL␣PEAK␣HEIGHTS//)
      WRITE (6,1002)
1002  FORMAT (3X,3HD-7,5X,3HD-6,5X,3HD-5,5X,3HD-4,5X,
     W3HD-3,5X,3HD-2,5X,3HD-1,4X//)
      WRITE (6,301) (P(J),J=1,M)
 301  FORMAT (7F8.2//)
      WRITE (6,1001)
```

```
1001 FORMAT (4X,2HD0,6X,2HD1,6X,2HD2,6X2HD3,6X,2HD4,6X,
   W 2HD5,6X,2HD6,6X,2HD7,6X,2HD8,21X//)
     WRITE (6,25) (P(J),J=S,K)
  25 FORMAT (9F8.2//)
     I=N+M
     DO 3 J=6,I
     L=J-S
     IF (L.LT.0) GO TO 21
     GO TO 22
  21 L=-L
  22 COR=SIC+(N-L)*0.0002
     P(J+1)=P(J+1)-COR*P(J)
     IF (L.GT.N-2) GO TO 3
     P(J+2)=P(J+2)-COR*((COR-0.011)/2)*P(J)
   3 CONTINUE
     WRITE (6,35)
  35 FORMAT (10x,34HPEAK␣HEIGHTS␣CORRECTED␣FOR␣
    W ISOTOPE,2X//)
     WRITE (6,1002)
     WRITE (6,301) (P(J),J=1,M)
     WRITE (6,1001)
     WRITE (6,25) (P(J),J=S,K)
     D6=7*P(20)**2/(16*P(21))
     D5=7*P(20)**3/(64*P(21)**2)
     FHD7=(P(19)-D6-FD(2)*P(21))/P(20)
     GAMMA=(FHD7/(A(1)/N))**(1,0/7.0)
     FHD6=2*A(1)/N*GAMMA**6
     FDD7=(P(18)-D5-FHD6*D6)/P(20)
     PI=FDD7/(FD(2)*(N-1)/N)
     WRITE (6,2121) GAMMA,PI
2121 FORMAT (6X,6HGAMMA=,F7.4,8X,3HPI=,F7.4,2X//)
     DO71 J=1,21
  71 CORP(J) =P(J)
     DO 72 J=1,21
  72 P(J)=CORP(J)
     DO 4 I=1,IPEAK
     J=IPEAK-I
     IF(J.EQ.M) GO TO 45
     L=J-S
     IF (P(J).LT.0.0) GO TO 4
     NHA=(N-L)*(N-L-1)
     NHB=NHA*(N-L-2)
     NHC=NHB*(N-L-3)
     NHD=NHC*(N-L-4)
     NHE=NHD*(N-L-5)
     NDA=L*(L-1)
     NDB=NDA*(L-2)
     NDC=NDB*(L-3)
     NDD=NDC*(L-4)
     NDE=NDD*(L-5)
     ZH=GAMMA**L
     ZD=PI**(N-L)
     T=(A(1)*(N-L)/N)
   W *ZH
     P(J-1)=P(J-1)-(T*P(J))
     T=B(1)*L/N
   W *ZD
```

```
      U=A(1)*A(2)*NHA/NA
     W *ZH**2
      P(J-2)=P(J-2)-(T+U)*P(J)
      T=(B(1)*A(2)+A(1)*B(2))*L*(N-L)/NA
     W *ZH*ZD
      U=A(1)*A(2)*A(3)*NHB/NB
     W *ZH**3
      P(J-3)=P(J-3)-(T+U)*P(J)
      T=B(1)*B(2)*NDA/NA
     W *ZD**2.00
      U=(B(1)*A(2)*A(3)+A(1)*B(2)*A(3)+A(1)*A(2)*B(3))
     W *L*NHA/NB
     W *ZD*ZH**2
      V=A(1)*A(2)*A(3)*A(4)*NHC/NC
     W *ZH**4
      P(J-4)=P(J-4)-(T+U+V)*P(J)
      T=(B(1)*B(2)*A(3)+B(1)*A(2)*B(3)+A(1)*B(2)*B(3))*NDA*
     W (N-L)/NB
     W *ZH*ZD**2.00
      U=(B(1)*A(2)*A(3)*A(4)+A(1)*B(2)*A(3)*A(4)+A(1)*A(2)
     W *B(3)*A(4)+A(1)*A(2)*A(3)*B(4))*L*NHB/NC
     W *ZD*ZH**3
      V=A(1)*A(2)*A(3)*A(4)*A(5)*NHD/ND
     W *ZH**5
      P(J-5)=P(J-5)-(T+U+V)*P(J)
      T=B(1)*B(2)*B(3)*NDB/NB
     W *ZD*3.00
      U=(B(1)*B(2)*A(3)*A(4)+B(1)*A(2)*B(3)*A(4)+B(1)*A(2)
     W *A(3)*B(4)+A(1)*B(2)*B(3)*A(4)+A(1)*B(2)*A(3)*B(4)
     W +A(1)*A(2)*B(3)*B(4))*NDA*NHA/NC
     W *ZD**2*ZH**2
      V=(B(1)*A(2)*A(3)*A(4)*A(5)+A(1)*B(2)*A(3)*A(4)*A(5)
     W +A(1)*A(2)*B(3)*A(4)*A(5)+A(1)*A(2)*A(3)*B(4)*A(5)
     W +A(1)*A(2)*A(3)*A(4)*B(5))
     W *L*NHC/ND
     W *ZD*ZH**4
      W=A(1)*A(2)*A(3)*A(4)*A(5)*A(6)*NHE/NE
     W *ZH**6
      P(J-6)=P(J-6)-(T+U+V+W)*P(J)
      T=(B(1)*B(2)*B(3)*A(4)+B(1)*B(2)*A(3)*B(4)+B(1)*A(2)*
     W B(3)*B(4)+A(1)*B(2)*B(3)*B(4))*NDB*(N-L)/NC
     W *ZH*ZD**3.00
      U=(B(1)*B(2)*A(3)*A(4)*A(5)+B(1)*A(2)*B(3)*A(4)*A(5)
     W +B(1)*A(2)*A(3)*B(4)*A(5)+B(1)*A(2)*A(3)*A(4)*B(5)+
     W A(1)*B(2)*B(3)*A(4)*A(5)+A(1)*B(2)*A(3)*B(4)*A(5)+
     W A(1)*B(2)*A(3)*A(4)*B(5)+A(1)*A(2)*B(3)*B(4)*A(5)+
     W A(1)*A(2)*B(3)*A(4)*B(5)+A(1)*A(2)*A(3)*B(4)*B(5))*
     W NDA*NHB/ND
     W *ZD**2*ZH**3
      V=(B(1)*A(2)*A(3)*A(4)*A(5)*A(6)+A(1)*B(2)*A(3)*A(4)*A(5)*A(6)
     W +A(1)*A(2)*B(3)*A(4)*A(5)*A(6)+A(1)*A(2)*A(3)*B(4)*A(5)*A(6)
     W +A(1)*A(2)*A(3)*A(4)*B(5)*A(6)+A(1)*A(2)*A(3)*A(4)*A(5)*B(6))
     W *L*NHD/NE
     W *ZD*ZH**5
      P(J-7)=P(J-7)-(T+U+V)*P(J)
      T=B(1)*B(2)*B(3)*B(4)*NDC/NC
     W *ZD**4.00
```

```
      U=(A(1)*A(2)*B(3)*B(4)*B(5)+A(1)*B(2)*A(3)*B(4)*B(5)+
     WA(1)*B(2)*B(3)*A(4)*B(5)+A(1)*B(2)*B(3)*B(4)*A(5)+
     WB(1)*A(2)*A(3)*B(4)*B(5)+B(1)*A(2)*B(3)*A(4)*B(5)+
     WB(1)*A(2)*B(3)*B(4)*A(5)+B(1)*B(2)*A(3)*A(4)*B(5)+
     WB(1)*B(2)*A(3)*B(4)*A(5)+B(1)*B(2) *B(3)*A(4)*A(5))
     W *NDB*NHA/ND
     W *ZD**3*ZH**2
      V=(B(1)*B(2)*A(3)*A(4)*A(5)*A(6)+B(1)*A(2)*B(3)*A(4)*A(5)*A(6)
     W +B(1)*A(2)*A(3)*B(4)*A(5)*A(6)+B(1)*A(2)*A(3)*A(4)*B(5)*A(6)
     W +B(1)*A(2)*A(3)*A(4)*A(5)*B(6)+A(1)*B(2)*B(3)*A(4)*A(5)*A(6)
     W +A(1)*B(2)*A(3)*B(4)*A(5)*A(6)+A(1)*B(2)*A(3)*A(4)*B(5)*A(6)
     W +A(1)*B(2)*A(3)*A(4)*A(5)*B(6)+A(1)*A(2)*B(3)*B(4)*A(5)*A(6)
     W +A(1)*A(2)*B(3)*A(4)*B(5)*A(6)+A(1)*A(2)*B(3)*A(4)*A(5)*B(6)
     W +A(1)*A(2)*A(3)*B(4)*B(5)*A(6)+A(1)*A(2)*A(3)*B(4)*A(5)*B(6)
     W +A(1)*A(2)*A(3)*A(4)*B(5)*B(6))
     W *NDA*NHC/NE
     W *ZD**2*ZH**4
      P(J-8)=P(J-8)-(T+U+V)*P(J)
    4 CONTINUE
   45 WRITE (6,300)
  300 FORMAT (10X,22HCORRECTED␣PEAK␣HEIGHTS//)
      WRITE (6,1002)
      WRITE (6,301) (P(J),J=1,M)
      WRITE (6,1001)
      WRITE (6,25) (P(J),J=S,K)
      TOTAL=0.0
      DO 60 J=S,K
      IF (P(J).LT.0.0) GO TO 60
      TOTAL=TOTAL+P(J)
   60 CONTINUE
      WRITE (6,400)
  400 FORMAT (10X,30HPERCENTAGE␣OF␣ISOTOPIC␣SPECIES//)
      WRITE (6,1001)
      DO 810 J=S,K
  810 PER(J) = P(J)*100/TOTAL
      WRITE (6,500) (PER(J), J=S,K)
  500 FORMAT (9F8.2//)
      PHI = 0.0
      DO 80 J=S,K
      L+J-S
      IF (PER(J).LT.0.0) GO TO 80
      PHI=PHI+L*PER(J)
   80 CONTINUE
      WRITE (6,410) TIME, TOTAL, PHI
      FORMAT (10X,4HTIME,10X,5HTOTAL,10X,3HPHI/F14.1,F15.2,F13.2//)
      YY=PHI/800
      XX=1.0-PHI/800
      D8=100*YY**8
      D7=800*YY**7*XX
      D6=2800*YY**6*XX**2
      D5=5600*YY**5*XX**3
      D4=7000*YY**4*XX**4
      D3=5600*YY**3*XX**5
      D2=2800*YY**2*XX**6
      D1=800 *YY**1*XX**7
      D0=100 *XX**8
      WRITE (6,34) PHI
   34 FORMAT (10X,31HBINOMIAL␣DISTRIBUTION␣WITH␣PHI=,F9.2,2X//)
```

hydrocarbon studied. The exchange of neopentane was also studied on platinum γ-alumina and on two samples of a platinum-silica catalyst which had been reduced at different temperatures. The platinum-silica catalysts were less active than the platinum γ-alumina catalyst which had an activity similar to that of a sintered film.

The apparent first order rate plots obtained for the exchange of the hydrocarbons on the unsintered platinum films were slightly retardedly curved. This curvature was ascribed to progressive sintering, and not to self poisoning of the films during the reaction, because the exchange reactions on the sintered films and on the supported catalysts obeyed the kinetic equation, and because the presorption of saturated hydrocarbons at 105°C for 1 hr. on unsintered films produced only a very slight reduction in the activity of the films for the subsequent exchange reaction of neopentane. The presorption of neopentane or a neopentane-deuterium mixture at temperatures greater than 200°C on sintered films substantially reduced the activity of the films for the exchange of neopentane, indicating that irreversibly adsorbed species could be formed at high temperature.

All the molecules studied on the platinum catalysts underwent extensive multiple exchange. The product distributions for the exchange of propane, butane, and methane showed that all the possible isotopic species were produced initially, whereas those for neopentane usually did not contain isotopic species with more than three deuterium atoms. It is suggested that the exchange of propane and butane is propagated by the interconversion between α-, αβ-and π-allylic intermediates, whereas that for methane and neopentane occurs by the interconversion between α- and αα-adsorbed intermediates.

The exchange of cyclopentane and cyclohexane on unsintered nickel films occurred readily below 0°C, cyclopentane being the more reactive molecule. Presintering the films at temperatures greater than 270°C, however, required temperatures in excess of 200°C to propagate the exchange of cyclopentane. At temperatures less than room temperature on the unsintered films only half of the hydrogen atoms in cyclopentane and cyclohexane were readily exchangeable initially, and it is suggested that exchange occurs by the interconversion between α- and αβ-adsorbed intermediates. For the exchange of cyclopentane and cyclohexane on the unsintered films at higher temperatures, and for the exchange of cyclopentane on the sintered films all the possible isotopic species were produced initially, indicating that a π-allylic intermediate was participating in the mechanism of exchange. The exchange of both molecules on the nickel films was extensively self poisoned, deviation from the Arrhenius equation occurring with the activation energy tending to negative values; and it is thought that this self poisoning was occurring by the formation of ααβ- and, or ααββ-adsorbed intermediates on the sites catalytically active for the exchange reaction.