INVESTIGATION OF SURFACE PHENOMENA

BY

RADIOACTIVE TRACERS

THESIS

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by

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CONTENTS

ABSTRACT

This thesis describes investigations of a catalyst system which have been made by means of a new radioactive-tracer technique whereby ethylene-C14 was observed directly on the surface of a nickel film during hydrogenation.

A thin-wall G.-M. counter of special design, capable of detecting the radiation from carbon-14, was mounted within a catalyst vessel in such a way that the surface of an evaporated nickel film could be monitored directly. In this way the adsorption and desorption of carbon-14 labelled ethylene at the surface could be followed continuously.

Hydrogen and non-labelled ethylene were admitted to the catalyst on which ethylene-C14 had been adsorbed, and the change in the count rate due to the adsorbed ethylene-C14 was followed continuously as hydrogenation proceeded. It was found that only a fraction of the preadsorbed ethylene was removed from the catalyst surface during hydrogenation; the remainder was firmly held during prolonged hydrogenation of the non-labelled ethylene.

Experiment also showed that there was negligible exchange between adsorbed and gas-phase ethylene.

A number of films were prepared by evaporation in an inert atmosphere; the results of experiments on these films have provided new information on the role of film orientation and the effect of particular crystal planes on catalysis.

A series of experiments was carried out which involved the adsorption on the nickel film of both labelled and non-labelled ethylene. By investigating the effect of different admission sequences on the fraction of the adsorbed ethylene-C^{14} removed during hydrogenation it has proved possible to arrive at conclusions as to the factors which influence the magnitude of the active ethylene fraction.

The results of this research have implications for the correlation between chemisorption and catalysis.

INTRODUCTION

Heterogeneous catalysis involves the reaction of one or more chemical species in a given phase through the intermediacy of a second phase - the catalyst - which has the effect of accelerating the rate at which the reaction system attains equilibrium. It is most common for the reactants to be either in the liquid or gaseous phase while the catalyst is in the solid phase, although exceptions to this rule are known.

Catalysis has been studied with the reactants in either the liquid or the gaseous phase, but more fundamental and significant information can be obtained in gaseous systems with a solid catalyst. In this way the number of variables, such as the solvent and its effects on the system, can be eliminated. Investigations of heterogeneous catalysis can be divided broadly into two classes: those in which the reaction system is studied in its own right, and those in which the reaction system, simple or complex, is used to investigate the properties of the catalyst surface itself. In studies of the reaction system what is sought is information regarding the actual mechanism of the reaction, although the properties of the catalyst and their influence on the reaction system can never be completely divorced from the mechanistic studies. In the alternative procedure the simplest reactions, often nothing more than adsorption and desorption, are employed in an attempt to elucidate some of the many subtlties of the solid state which can influence the catalytic behaviour of the given solid.

In this research we have endeavoured to combine these two approaches into a unified study. Attempts have been made to relate the results of adsorption research to studies of catalysed reactions. Of these attempts mention may be made of the deduction of kinetic laws on the basis of the theories of adsorption of Langmuir (1). Other workers have approached this problem by way of magnetic and other method, but none of the theories which have been developed can be said to be completely successful.

Among the many aspects of adsorption the study of heats of adsorption has been of major prominence. One outcome of these investigations has been the concept of heterogeneity of an adsorbent surface and this concept has been studied in this research - whether a surface has uniform adsorptive and reactive properties, or whether its properties are different on different parts of the surface.

That the heat of adsorption of a gas on an adsorbent decreases with increasing coverage of the adsorbent surface has long been known and this evidence, along with that of workers such as Pease (2), led Taylor and Constable to their theory of "active centres" in catalysis (3) and, more generally, to the concept of a heterogeneous catalyst surface.

This effect of degree of coverage on the heat of adsorption has been extensively reviewed in the literature (see for example, refs. 4,5,6,7). Recently a large volume of work has been carried out on this subject (8), the initial impetus stemming from the development of the use of evaporated metal films in catalysis by Beeck (9).

Three main reasons for this fall in heat of adsorption can be put forward. The first is the inherent heterogeneity of the surface, the second interactions between the adsorbed species, and the third induced heterogeneity, brought about by modification of the properties of the metal surface by the adsorbed species.

The inherent heterogeneity of the surface has two main causes - crystal effects, and the defect structure of the solid state. That different crystal faces have different activity has been shown by Gwathmey and his co-workers (10,11) and also by Müller and others using the elegant technique of the field-emission microscope (12). Defect structure includes lattice vacancies and interstitial atoms, dislocations, grain boundaries, etc., and these irregularities in the metal have been postulated as the basic cause of the fall in the heat of adsorption (13).

Interaction between adsorbed molecules is postulated as taking the form of dipole-dipole interactions and the overlap of electron shells but calculation of the extent of these effects (14) shows that the reduction in the heat of adsorption, brought about by an increase in the surface energy of the adsorbed layer, is not sufficient to account for the large heat falls found for most metals.

Heterogeneity can be induced in the surface by the adsorbed molecules as they increase the work-function of the metal and thereby decrease the heat of adsorption of subsequent molecules (4). This type of heterogeneity plays some part in the overall behaviour of the surface, but its precise contribution has not yet been elucidated. Thus the heterogeneity of a metal surface lies chiefly in the mechanical nature of the surface; in geometric effects and defect structure.

Several workers have attempted to investigate this heterogeneity, using either a "differential" or a "kinetic" isotope technique.

The "differential" technique was that employed by Roginskii and Keier (15) utilising hydrogen and deuterium. The surface under study was partially covered with the heavy isotope of hydrogen, followed by saturation of the remaining surface with the normal isotope. The composition of the gas obtained on desorption was investigated and from these results it was concluded that the surface of a reduced nickel catalyst was heterogeneous.

Eley has employed the "kinetic" method in the study of tungsten and other metals (16). He compared the observed and the calculated values for the rate of *para*-hydrogen conversion on these surfaces and came to the conclusion that the surface of tungsten was also heterogeneous. Eischens (17) has also employed the kinetic method by studying the exchange between two labelled forms of carbon monoxide over a reduced iron catalyst, again with the result that the surface was largely heterogeneous.

All these investigations, however, have been concerned with the total catalyst surface and have employed reactions such as exchange and straightforward adsorption-desorption methods. It has been the purpose of the work described in this thesis to investigate the extent and influence of heterogeneity of a surface during an actual chemical reaction catalysed by the surface.

If one accepts the reasoning that a catalyst has a range or spectrum of energies over its surface, then although this surface is capable of adsorbing molecules to a certain degree it does not follow that all these molecules will be capable of taking part in a subsequent catalytic reaction. An instance of this (18) is the poisoning of a catalyst surface by foreign molecules which is believed to occur by the formation of strong adsorptive bonds. (For example, the initial heat of adsorption of oxygen on evaporated nickel films ranges from 100 to 150 Kcal./mole while the initial heat of adsorption of ethylene on a similar surface is only 58 Kcal./mole and therefore oxygen acts as a poison in ethylene hydrogenation). It is quite possible that the initially adsorbed molecules on the surface, adsorbed with a higher heat of adsorption, will be characterised by strong chemisorptive bonds and will take no part in the subsequent reaction with a second species. This effect can also be seen in the poisoning of a catalyst by the reaction products, when adsorbed product molecules compete to a greater or lesser extent with reactant molecules for catalyst sites and thereby inhibit the reaction.

If, on the other hand, the heat of adsorption of a particular molecule is very low, then the bonds formed will be weak. If we accept the premise that the effect of a catalyst is to induce a molecule to take up a configuration close to that of the transition state (8), then the extent of interaction between adsorbate and adsorbent will influence this configuration. Thus it can be seen that a weak chemisorption bond could result in the adsorbed molecule being unreactive since the lowering of the activation energy would be insufficient to enhance the reactivity of the species in question.

The problem under investigation, then, was to study the fraction of the molecules adsorbed on a catalyst surface which was capable of participation in a catalysed reaction and hence, by inference, the fraction of the surface which was capable of exerting the necessary activating influence on the reactants. Arising out of this question was also the problem of whether this fraction consisted of those molecules adsorbed first on the catalyst surface, or those molecules adsorbed last; or whether it was the adsorbate at some intermediate coverage which participated in reaction.

Of the many methods available for the study of solid surfaces the majority may be classed as "indirect" methods where the experimental conclusions must be inferred from indirect evidence. Among such methods are those of adsorption isotherms and isobars, heats of adsorption, magnetic methods and studies of work function and the existence of dipoles. The direct methods, on the other hand, enable the phenomena occurring on the catalyst surface to be deduced without the necessity for such inference. Perhaps the most spectacular experimental technique of this type is that of the field-emission microscope, By this method the actual crystal faces and, more recently, the atoms of a metal have been observed by virtue of their electron emission in high potential fields. The method has been restricted so far to observation of the adsorption and migration of simple species such as oxygen and hydrogen molecules and atoms of the alkali metals. This technique is severely limited, also, by the extremely small area of metal observed, which precludes thesimultaneous study of a catalysed reaction.

A second method, which can also be a "direct" one, involves the use of radio-active isotopes. The method is extremely sensitive and amounts of, say, carbon-14 of the order of 10^{-10} moles can be detected readily. In view of the sensitivity of the radio-tracer method, and also its flexibility, it was decided to employ this technique in the research described in this thesis.

The experimental approach which was devised was to adsorb on the catalyst surface a given species of molecule, labelled with a radio-active tracer. The arrival of these molecules, and their subsequent behaviour, would then be followed by means of a detector which monitored the catalyst surface directly. In this way it was hoped to observe the fate of chemisorbed molecules under various conditions.

The reaction system chosen had to be such that the reaction rates were of a sufficient order of magnitude to permit their ready determination. The products of the reaction had to be relatively simple and incapable of poisoning the catalyst surface.

Hydrogenation reactions are among the easiest to study on evaporated metal films, and the hydrogenation of ethylene fulfilled all the requirements outlined. The reaction has been extensively studied and is well documented (19). It was hoped, also, to elucidate some of the details of the mechanism of ethylene hydrogenation on metal films.

Ethylene can be obtained labelled with carbon-14 from the Radiochemical Centre, Amersham. The low energy of carbon-14 β particles makes the counting of the labelled species very difficult and precludes the use of a G.-M. counter external to the reaction vessel. A G.-M. tube of the required geometry and adequate efficiency which could be fitted inside a catalyst reaction vessel had to be designed and constructed. The satisfactory outcome of the development of this G.-M. tube has resulted in this research being possible.

CHAPTER 1

EXPERIMENTAL PROCEDURE AND RESULTS

1.1. Introduction

The object of this research has been to ascertain the fraction of a catalyst surface which is active during actual catalysis. The experimental method adopted was as follows.

One of the reactants in the catalytic process, labelled with a radio-active isotope, was allowed to saturate the surface. The radio-activity adsorbed on the catalyst could be monitored continuously by means of a special G.-M. tube. The second reactant, or a reaction mixture containing both reactants, neither of which was isotopically labelled, was then admitted into contact with the catalyst. As the reaction proceeded the labelled molecules adsorbed in an active form took part in the reaction and were thereby removed into the gas phase and the reaction presumably proceeded on the vacant sites made available by this desorption. The molecules incapable of reaction by virtue of their particular location on the surface remained adsorbed and their contribution to the radio-activity of the surface was ascertained by the counting technique. By proper design of the catalyst vessel the labelled molecules removed to the gas phase were sufficiently diluted so as to make little or no contribution to the observed radio-activity.

1.2. Choice of Reaction System

The reaction which was chosen to be employed was the hydrogenation of ethylene. This reaction is, at first sight, the simplest of the olefin hydrogenations - a class of reactions of paramount importance in catalysis by metals, especially those metals of the Transition series. The reaction has many advantages for the study of olefin hydrogenation. Both the reactants are in the gaseous phase at room temperature, and so a large range of pressures can be investigated without increasing the experimental complications.

In addition the reaction system is not complicated by the adsorption of product molecules, and the rates of hydrogenation are readily determinable at room temperature.

A complicating factor in the study of ethylene is the so-called "surface complexes". It has been claimed by Beeck (20) and other workers that 80% of the surface of a nickel film is poisoned by the formation of complexes of dissociatively adsorbed ethylene. This research has assisted in giving information regarding the reactivity of these complexes.

1.3. Choice of Catalyst System

The metal employed in catalytic studies can take many different forms (8). Metal in the form of tapes and wires has been employed, but the very low surface areas of these forms means that the absence of contamination of the metal cannot be ensured unless modern ultra-high-vacuum techniques are employed. The same objection applies to the study of individual faces of massive single crystals of the metal. Ultra-high-vacuum has now reached a point where it can be readily utilised, but only for simple reaction systems. In experiments involving large-scale reactions and the complex reaction vessels required for this work ultra-high-vacuum techniques were impracticable.

Supported metal catalysts have been very widely employed in research on surface chemistry, principally because of the absence of stringent vacuum requirements, and the similarity between the supported catalysts and those catalysts employed in industrial processes. These arguments also apply to metal powders. Since these catalysts are prepared by the reduction in hydrogen of some compound of the metal it is very difficult to ensure that the surface is prepared completely free from adsorbed impurities. The nature of the support material can also influence markedly the behaviour of the metal being studied (see, for example, ref. 21). An additional complication was introduced by the nature of this research. It was planned to adsorb on the catalyst surface ethylene molecules labelled with carbon-14. The β particles from carbon-14 have a maximum energy, E_{max}, of 0·155 MeV which means that absorption of the activity in the source is of significance. Supported catalysts have a greater thickness, for a given area and weight of metal, than an evaporated film, and it was felt that the self-absorption of the radiation in the bulk of the catalysts would be significantly high.

Bearing in mind all these factors it was concluded that the most satisfactory catalyst for study would be a metal in the form of an evaporated film. Evaporated metal films were first developed for use as catalysts by Beeck et al. (9) and since then they have found increasing use in fundamental studies of catalysis owing to their reproducibility and freedom from contamination. Many workers have employed films in their research and there is a large body of literature devoted to the structure, properties, and nature of the films themselves.

Hydrogenation reactions are efficiently catalysed by most of the Transition metals and of these those most extensively studied are iron, nickel, palladium, rhodium, tungsten, and platinum. Of these the most widely studied has been nickel and because of the large amount of knowledge concerning this metal, and also because of the fact that that its use was well established in this laboratory, nickel was chosen as the catalyst in this work.

1.4. Apparatus and Catalyst Preparation

The general layout of the apparatus is shown in fig. 1. It was a conventional high-vacuum apparatus with pumping by diffusion pumps. Gas handling was achieved with orthodox high-vacuum stopcocks lubricated with high-vacuum grease.

The apparatus consisted essentially of the catalyst vessel and its associated apparatus. The remainder of the apparatus comprised gas purification and storage sections and a gas handling and pipetting system. Facilities were also provided for the measurement of gas pressures and the vacuum, and a section was also included for the filling of the G.-M. tube.

The catalyst vessel was designed so that catalyst preparation and the monitoring of radioactivity adsorbed on the catalyst surface could be

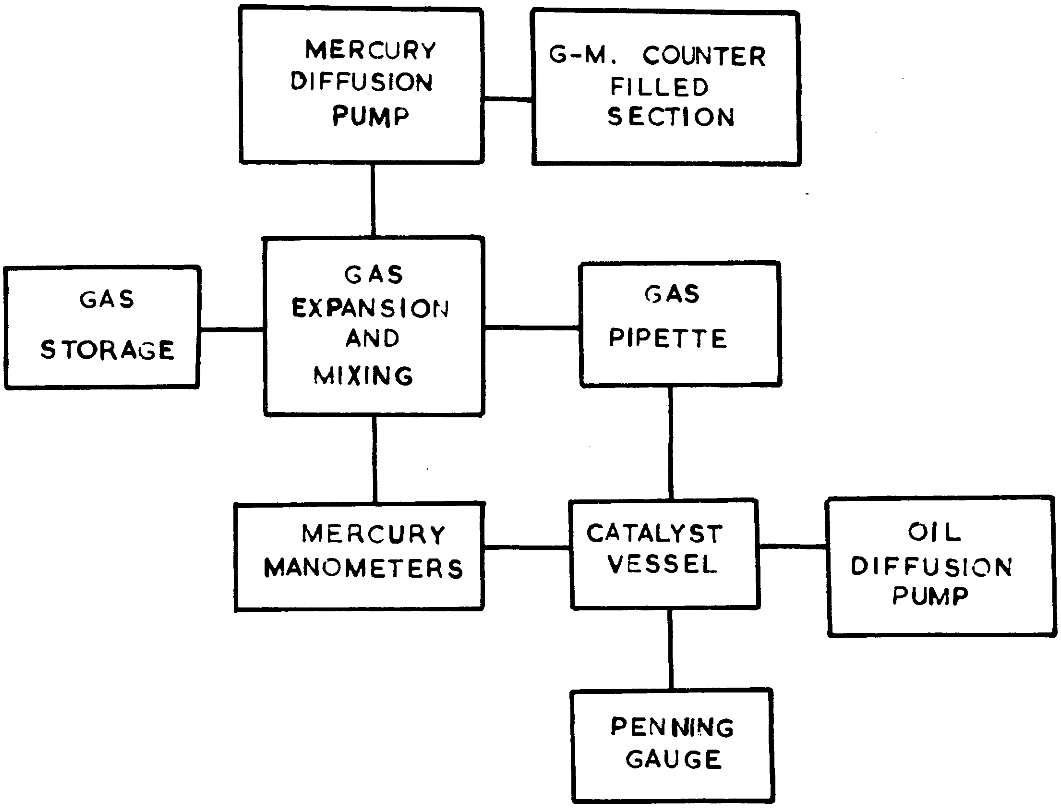

MERCURY DIFFUSION PUMP
G-M. COUNTER FILLED SECTION
GAS STORAGE
GAS EXPANSION AND MIXING
GAS PIPETTE
MERCURY MANOMETERS
CATALYST VESSEL
OIL DIFFUSION PUMP
PENNING GAUGE

FIG. 1

carried out in the same apparatus. The vessel consisted of a tube into the end of which was sealed a hairpin-shaped nickel filament from which the nickel could be evaporated onto the inner surface of a second tube within the outer tube. This second tube could then be moved to the other end of the catalyst vessel when it completely surrounded the specially designed G.-M. counter. The catalyst vessel also had facilities for circulating the reactant gases over the surface of the catalyst. Full details of the catalyst vessel are given in Chapter 5.

The nickel films were prepared by electrically heating the nickel wire filament to bring about evaporation of the nickel atoms onto the inner glass tube. To minimise sintering of the film during evaporation the outer walls of the catalyst vessel were cooled to -78°C. with solid carbon dioxide.

To obtain films free from contamination (9) it was necessary to thoroughly outgas the catalyst vessel by heating it at 500°C. under high vacuum for several hours. The nickel filaments themselves were outgassed by being heated electrically to just below their evaporation temperature during the last stages of the outgassing treatment. Once outgassing was complete, and all occluded gases had been evolved, the pressure within the catalyst vessel fell to less than 1×10^{-5} torr as measured on a Penning ionisation gauge (22). Evaporation of the filament was carried out at this pressure. Full experimental details are given in Chapter 5.

1.5. Measurement of Radio-Activity

The activity of the molecules adsorbed on the nickel film was measured by means of a specially-designed G.-M. tube. The tube was of cylindrical form so that it could be surrounded by the nickel film and thereby monitor virtually the whole area of the film. Being of cylindrical form, the β radiation was monitored through the walls of the counter and a thin-wall construction was therefore required. The counter as finally evolved consisted of a copper tube cathode in which were drilled a large number of holes. The tube was covered with thin "Melinex" film which allowed penetration by a certain fraction of the β particles. The overall efficiency of the counter was determined by experiment and found to be 0.6%. Full details of the counter and its characteristics will be found in Chapter 6.

1.6. Reactants

All reactants were carefully purified before use, either by chemical processes or by a physical technique. Full details of the purification of each reactant will be found in Chapter 7.

1.7. Experimental Procedure

After the preparation of the nickel film (Section 5.4.) and the filling of the G.-M. tube with the necessary gases the background count rate was determined.

Ethylene-1,2-C14 was expanded from its storage bulb into the section of the apparatus of known volume where its pressure was determined. This amount of ethylene was then expanded again, this time into an evacuated bulb of accurately known volume. By a simple calculation it was thus possible to calculate the pressure of gas within this bulb and hence the quantity of ethylene admitted to the nickel film through a calibrated gas pipette. This pipette was in direct connection with the calibrated bulb previously mentioned and the product of the gas pressure and the pipette was a measure of the number of molecules admitted to the catalyst. Gas quantities were measured in cm^3.mm., 1 cm^3.mm. containing 3.29×10^{16} molecules at 20°C. The gas was admitted in small increments and the count rate due to this gas was determined each time. All count rates were corrected for the background count rate and the dead time of the counting circuit which was preset at 500 microseconds.

Admission of ethylene-1,2-C14 was made through a trap cooled in an acetone/solid carbon dioxide mixture to prevent contamination of the catalyst surface by mercury or tap grease vapours.

Ethylene admission was continued until an excess pressure had built up. The first and second increments of ethylene were adsorbed with a residual pressure of less than 2×10^{-3}torr which was the maximum pressure that the vacuum gauge was capable of measuring. Thereafter the excess pressure was in excess of 2×10^{-3}torr and so it could only be estimated. From the quantity of gas admitted, usually about 100 to 150 cm^3.mm., and the volume of the catalyst vessel, about 900 cm^3., the excess pressure was commonly of the order of 0.05 to 0.1 mm. of mercury. At this stage count rates of the order of 4000 to 5000 c.p.m. were obtained. The excess gas was then pumped off until the pressure fell to a value of approximately 1×10^{-4} torr, the count rate falling similarly to a value of 1500 to 2500 c.p.m. although the actual count rate depended also on the specific activity of the ethylene and the weight of the nickel film. Pumping was continued for one half to one hour, but no further decrease in count rate was observed.

The two reactants were mixed as follows. Inactive ethylene was expanded from the storage bulb into a calibrated mixing system to a known pressure. It was then condensed in a cold finger until the gas-phase pressure was negligible. Hydrogen was similarly expanded into the same section to a determined pressure, after which the ethylene was allowed to evaporate. The composition of the reaction mixture was therefore known. Mixing of the two gases was achieved by means of a small glass fan fitted with a soft iron rotor which was driven by an external rotating magnet.

Following on the adsorption procedure pumping on the catalyst vessel was stopped and an accurate value for the count rate due to the adsorbed ethylinic species was determined. The reaction mixture was then admitted and a stop-clock was started. The initial pressure was measured and the pressure was subsequently measured at regular time intervals, usually every three minutes. The count rate was also determined throughout the hydrogenation reaction by a series of two-minute counts, the average count rate for each two-minute count being taken to be the count rate at the particular instant one minute after the commencement of the count.

Readings of pressure and count rate were taken at regular intervals until the reaction had virtually ceased. The gas-phase component was then pumped off in order to determine the contribution to the total count rate made by the ethylene-C14 remaining adsorbed on the catalyst surface. The labelled ethylene removed to the gas phase as ethane made a small contribution to the total count rate, the precise value of this contribution being determined by the total ethylene removed from the surface as ethane, and the initial count rate of the surface gas.

The fall in the number of radio-active molecules was then numerically equal, as a percentage, to the fall in the count rate, taking into account the contribution from gas-phase activity. For example, a final count rate of 2048 c.p.m. fell to 1779 c.p.m. when the gas-phase component was pumped off. In the results which follow the graphs show only the total activity at any particular time, but the percentage falls in radio-activity given in the tables are corrected to give the fall in adsorbed activity alone.

This procedure was followed in every experiment, but minor alterations to the method were necessitated by experiments carried out with slight modifications. For instance, when ethylene or hydrogen alone was admitted to the pre-adsorbed ethylene pressure measurements during the reaction were not required.

1.8. Accuracy

All pressure measurements were made on mercury manometers which were read through a 100 cm. cathetometer mounted on a solid table. Pressures so determined could be measured with ease to 0.05 cm. which in a total pressure of 10 cm. is equivalent to an accuracy of 0.5%.

The initial and final count rates and the background count rate were determined to within at least ±1%. To achieve this at least 10,000 counts were registered. The standard deviation was then equal to 100, i.e. ±1% of the total count rate. The count rates during a run could not be ascertained to this accuracy as only two-minute counts were feasible. With a count rate of say 1000 c.p.m. over a period of two minutes the accuracy was then ±2.3%. The graphical results of the experiments on film 13 are given, in figs. 8, 9, and 10, with the range of the standard deviation shown diagramatically. Film weights could be determined colorimetrically to within 1% (see Section 5.5.).

Surface coverage of the catalyst with

ethylene was rather more difficult to determine accurately. Although the pressure and volume of the gas admitted to the catalyst via the gas pipette was known to within at least 0.5%, the amount of gas adsorbed was difficult to determine owing to the phenomena of self-hydrogenation. The overall efficiency of the G.-M. counter was determined experimentally as described in Chapter 6 and, together with the value for the specific activity of the ethylene-C14, it has been possible to arrive at a value for the number of molecules adsorbed from the observed count rate. The percentage coverages given in the tables have been calculated on the basis of there being 1.99×10^{17} sites available per milligram of catalyst (23).

1.9. Presentation of Results

In the graph associated with each experiment (figs. 2 to 15) is plotted the partial pressure of the particular reactant not in excess against time. The partial pressures have been corrected for the dead-space of the catalyst vessel as is described in Chapter 5. In those experiments where the partial pressures of the two reactants were the same the hydrogen pressure has been plotted. The variation of the count-rate with time has also been plotted on the same graphs where applicable.

1.10. Results

In the following pages the results of experiments on each film or group of films are given in the following sequence:

(a). Brief statement of the object behind each experiment.

(b). Relevant data from each experiment presented in tabular form and as graphs.

(c). Short summary of the major conclusions derived from each experiment.

Films 4 and 5

The experiments on these two films were carried out with the object of establishing, and confirming where possible, the basic phenomena of ethylene hydrogenation. The experiments were all carried out at 20°C. (as were all subsequent experiments) with simultaneous admission of the two reactants to the clean film. After the first run on film 5 the film was found to be inactive - presumably through poisoning - but the activity of the catalyst was restored by exposure of the film to 21.5 cm. of hydrogen for a period of 16 hours.

Table 1

Film 4			Fig. 2
Film Weight (mg.)			46.0
Deposition Temperature (°C)			-78
First Run - Graph I.			
	Reactants (mm) :	Ethylene	154.0
		Hydrogen	141.0
	Initial Rate :	mm/min	10.5
		mm/min/30mg Ni	6.85
	Rate at 15 min :	mm/min	1.75
		mm/min/30mg Ni	1.14
Second Run - Graph II.			
	Reactants (mm) :	Ethylene	92.5
		Hydrogen	89.5
	Initial Rate :	mm/min	0.70
		mm/min/30mg Ni	0.456
	Rate at 15 min :	mm/min	1.58
		mm/min/30mg Ni	1.03
Third Run - Graph III			
	Reactants (mm) :	Ethylene	40.4
		Hydrogen	118.0
	Initial Rate :	mm/min	4.11
		mm/min/30mg Ni	2.68

Table 1 (cont.)

Fourth Run - Graph IV.

Reactants (mm) :	Ethylene	135.0
	Hydrogen	118.7
Initial Rate :	mm/min	0;5
	mm/min/30mg Ni	0.33

after an induction period of 30 minutes.

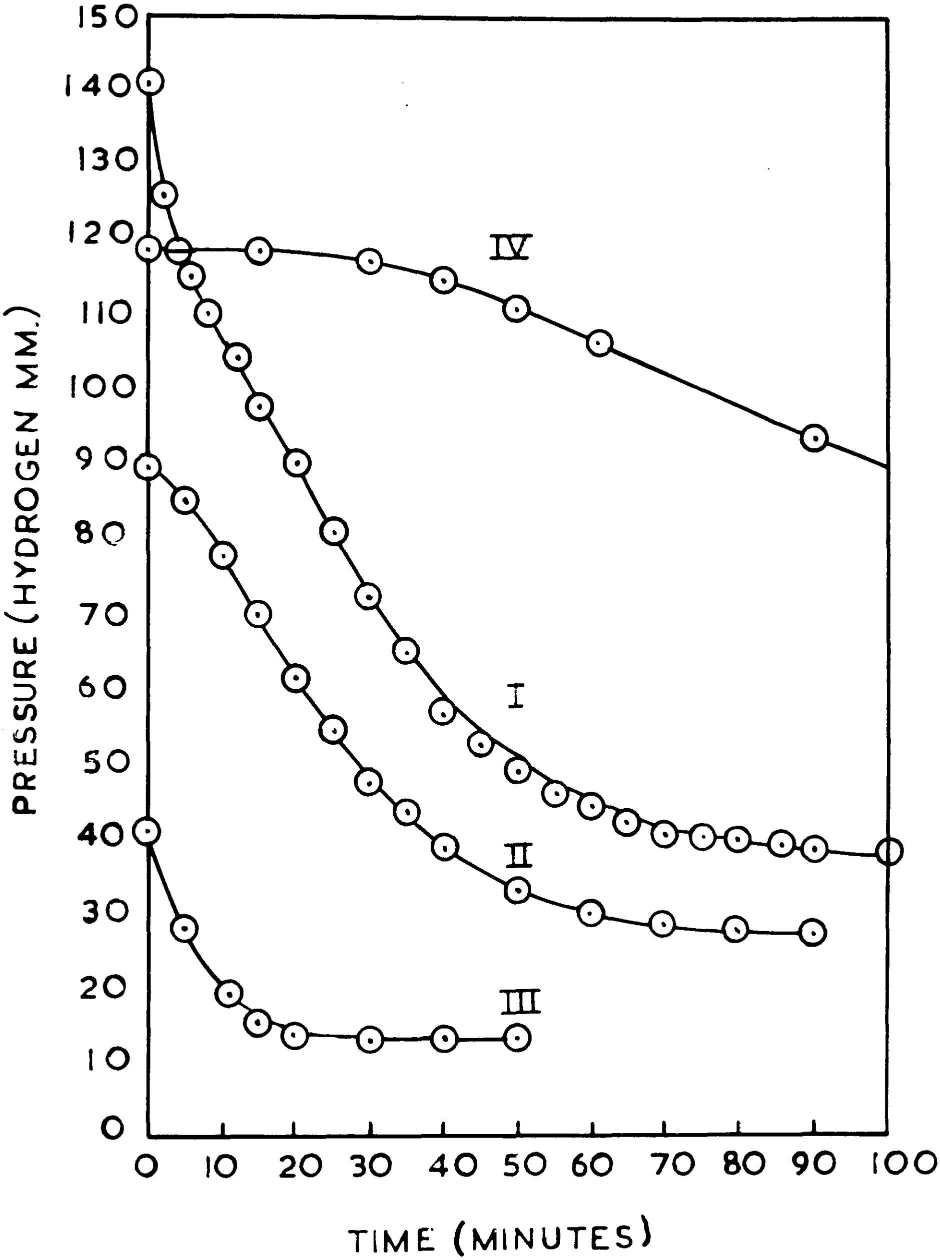

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PRESSURE (HYDROGEN MM.)
0
10
20
30
40
50
60
70
80
90
100
TIME (MINUTES)
IV
I
II
III

FIG. 2

Table 2

Film 5		Fig. 3
Film Weight (mg)		38.1
Deposition Temperature (°C)		-78
First Run - Graph I.		
Reactants (mm) :	Ethylene	123.0
	Hydrogen	125.0
Initial Rate :	mm/min	10.0
	mm/min/30mg Ni	7.88

Thereafter, film inactive. Admit 21.5 cm. hydrogen for 16 hours. Pump off.

Second Run - Graph II.		
Reactants (mm) :	Ethylene	61.0
	Hydrogen	61.0
Initial Rate :	mm/min	3.0
	mm/min/30mg Ni	2.6

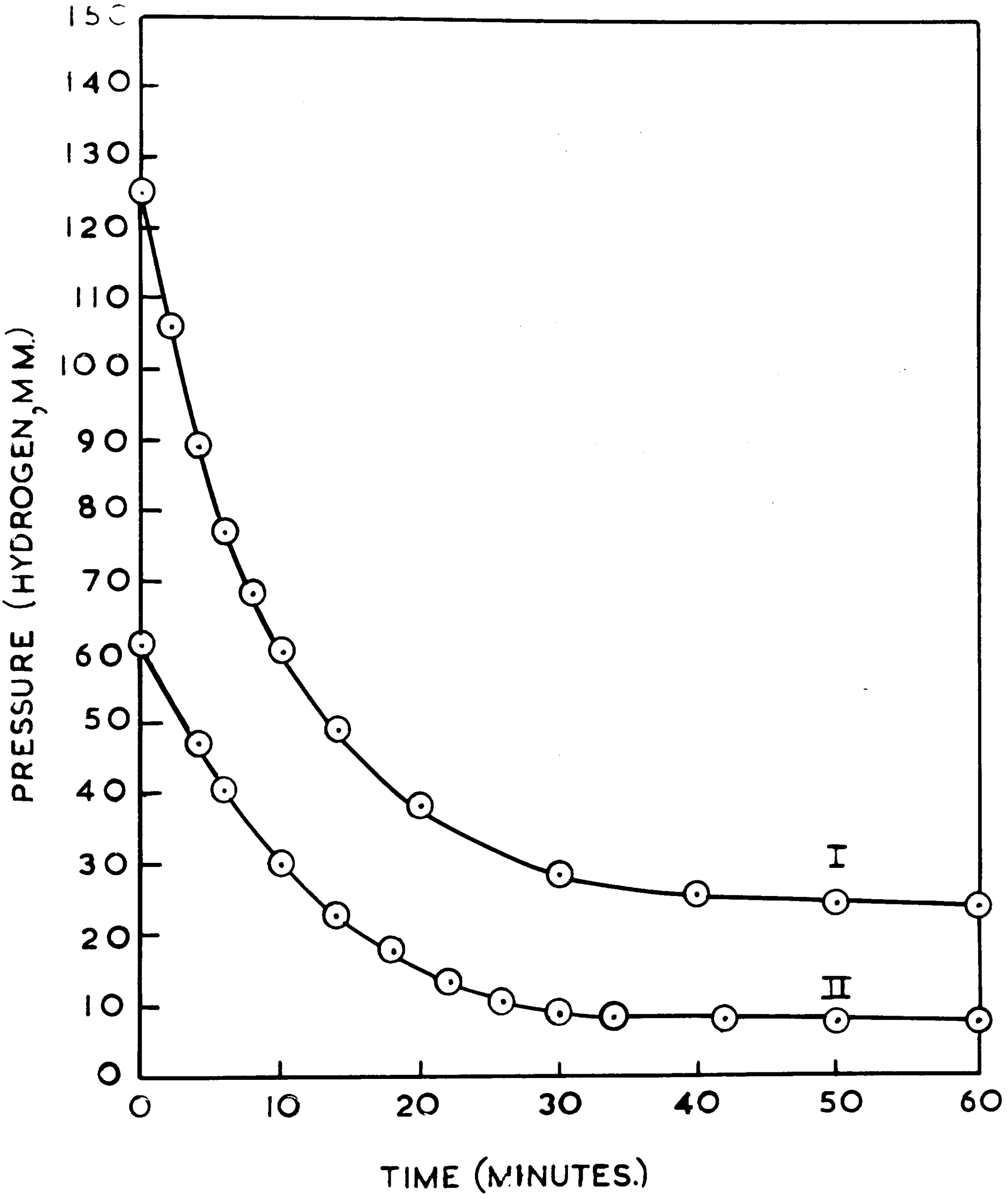

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PRESSURE (HYDROGEN, M.M.)
0
10
20
30
40
50
60
TIME (MINUTES.)
I
II

FIG. 3

The results of the experiments on these two films show the effect of progressive poisoning of the film. In fig. 2 it can be seen that there was a short induction period in the case of run II. This was most probably brought about by poisoning of the film by oxygen which is selectively hydrogenated before the ethylene hydrogenation commences. Run III does not show this behaviour, but a prolonged induction period was observed in the case of the fourth run (graph IV).

The two experiments on film 5 (fig. 3) show similar behaviour, the rate of the second hydrogenation being lower than the rate of the first.

Films 8 and 9

These experiments were carried out in a manner similar to that of films 4 and 5. The major point of difference was that a layer of ethylene was allowed to chemisorb on the film before the reaction mixture was admitted. These experiments were necessary as this was to be the technique employed in the experiments with ethylene-C14.

Table 3

Film 8		Fig. 4
Deposition Temperature (°C)		-78
Film Weight (mg)		47.3
Film with a preadsorbed monolayer of ethylene		
Reactants (mm) :	Ethylene	72.0
	Hydrogen	72.8
Initial Rate :	mm/min	4.5
	mm/min/30mg Ni	2.85

Table 4

Film 9		Fig. 5
Deposition Temperature (°C)		-78
Film Weight (mg)		43.7
Film with a preadsorbed monolayer of ethylene		
Reactants (mm) :	Ethylene	43.0
	Hydrogen	43.7
Initial Rate :	mm/min	1.06
	mm/min/30mg Ni	0.73

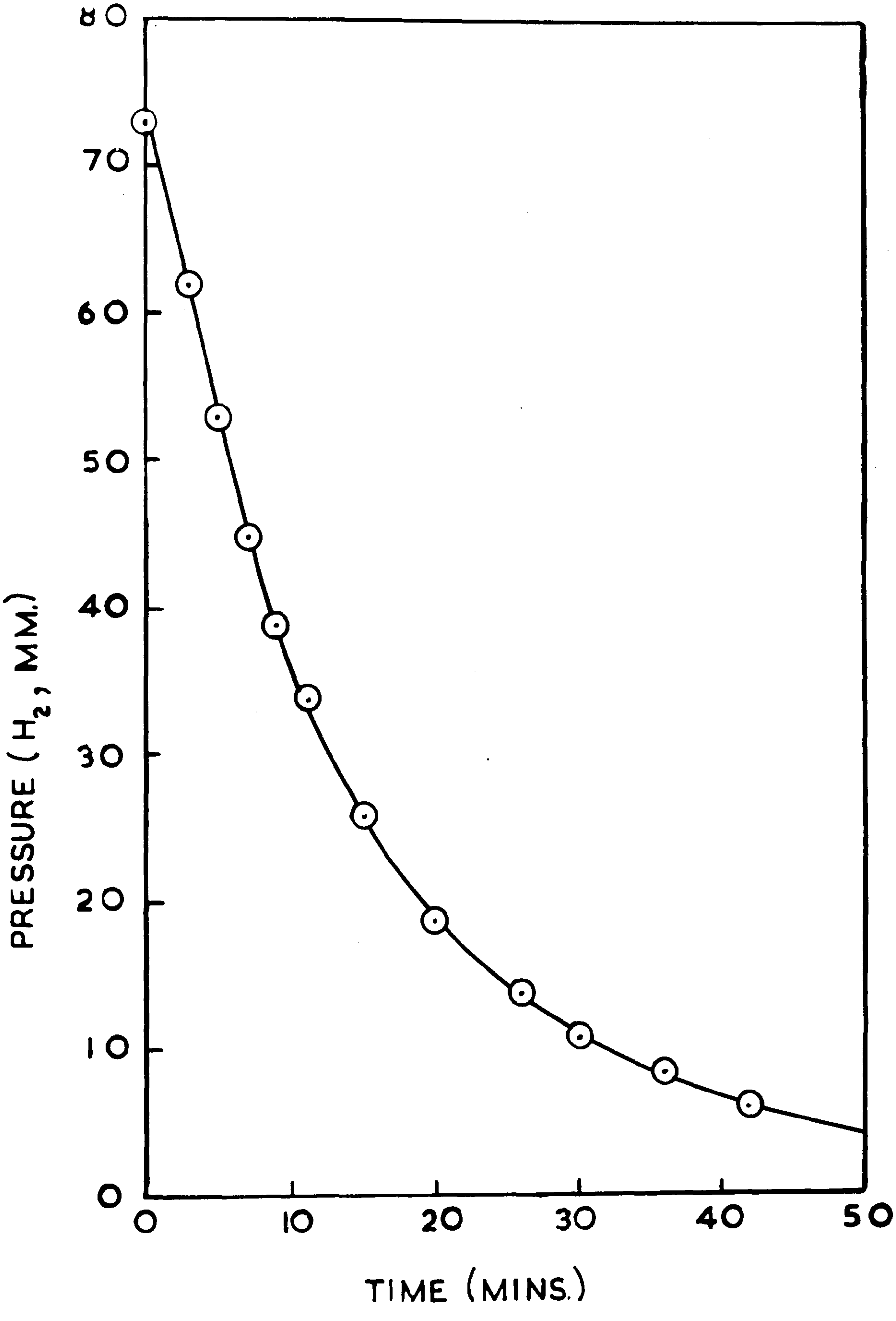


FIG. 4

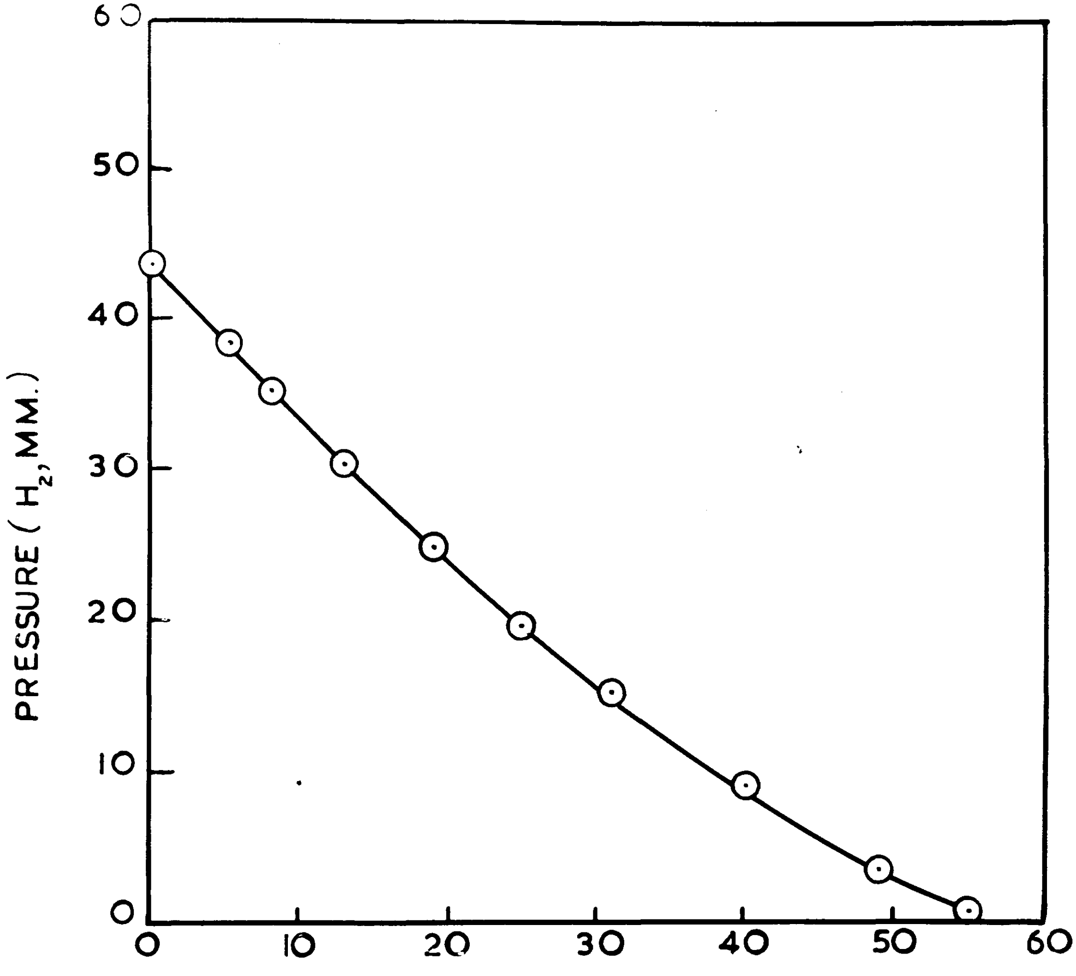


FIG. 5

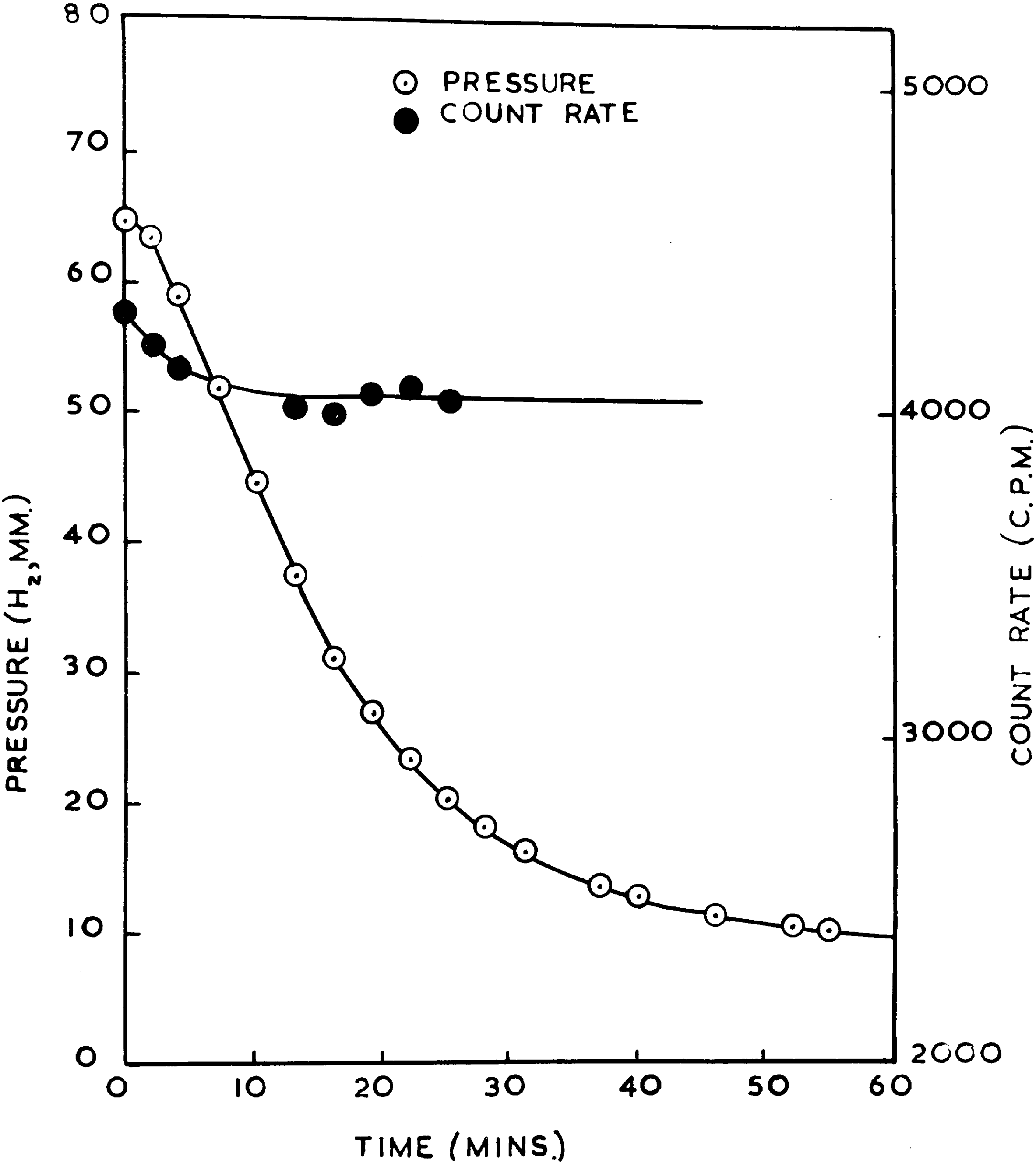
The main point of difference between the results obtained on these two films and the results of films 4 and 5 lies in the initial rate of the hydrogenation. It can be seen from figs. 4 and 5 that the rate of the reaction is constant over an appreciable period, indicating a zero-order mechanism.

Films 10 and 11

The experiments carried out on these two films were the first to give results with ethylene-C14. Ethylene-C14 was preadsorbed on each film and the count rate from the adsorbed species was monitored continuously during the subsequent reaction.

Table 5

Film 10		Fig. 6
Deposition Temperature (^{o}C)		-78
Film Weight (mg)		34.4
Number of sites		6.85×10^{18}
Sp. activity of ethylene-C14 (mc/mM)		0.1113
Background count rate (c.p.m.)		128
Initial count rate (c.p.m.)		4,300
Volume ethylene-C14 admitted (cm^3mm)		204
Volume adsorbed (from count rate) (cm^3mm)		109.3
No. C_2H_4 molecules adsorbed		3.6×10^{18}
Percentage coverage of film by C_2H_4-C14		105%
Fall in count rate		12%
Reactants (mm) :	Ethylene	65.2
	Hydrogen	64.9
Initial Rate :	mm/min	1.0
	mm/min/30mg Ni	0.87
Rate at 5-10 min:	mm/min	2.38
	mm/min/30mg Ni	2.08



○ PRESSURE
● COUNT RATE
PRESSURE (H₂, MM.)
COUNT RATE (C.P.M.)
TIME (MINS.)
80
70
60
50
40
30
20
10
0
5000
4000
3000
2000
0
10
20
30
40
50
60

FIG. 6

Table 6

Film 11		Fig. 7
Deposition Temperature (^oC)		-78
Film Weight (mg)		41.6
Number of sites		8.29×10^{18}
Sp. activity of C_2H_4-$C14$ (mc/mM)		0.1113
Background count rate (c.p.m.)		170
Initial count rate (c.p.m.)		3,270
Vol. C_2H_4-$C14$ admitted (cm^3mm)		91.3
Vol. C_2H_4-$C14$ adsorbed (cm^3mm)		83.3
No. of molecules adsorbed		2.74×10^{18}
% coverage of film		66.1
Fall in count rate		47%
Reactants (mm) :	Ethylene	60.5
	Hydrogen	60.5
Initial rate :	mm/min	1.0
	mm/min/30mg Ni	0.721
Rate at 5-15 min:	mm/min	2.23
	mm/min/30mg Ni	1.61

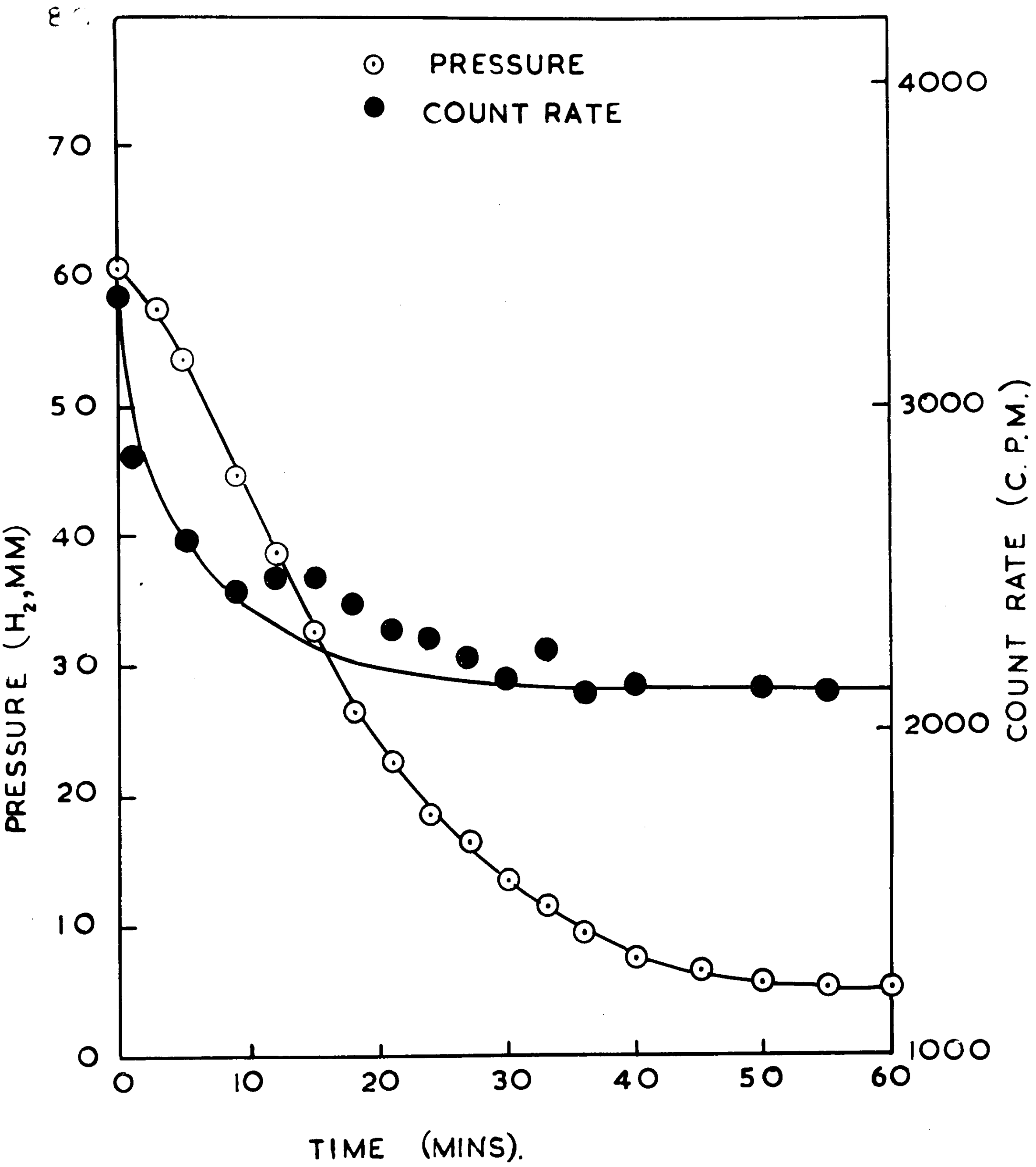

PRESSURE
COUNT RATE
PRESSURE (H₂,MM)
80
70
60
50
40
30
20
10
0
COUNT RATE (C.P.M.)
4000
3000
2000
1000
0
10
20
30
40
50
60
TIME (MINS).

FIG. 7

These results show the characteristic fall in count rate which amounted in one case to 12% of the total ethylene adsorbed, and in the other to 47%. It will be seen from the graphs also that the fall in surface count rate takes place rapidly in comparison with the rate of the overall reaction as measured by the change in pressure.

Film 13

The experiments on film 13 were designed to show the extent of the exchange, if any, between adsorbed ethylene-C14 and gas-phase ethylene in the absence of hydrogen as it was felt that at least part of the observed fall in count rate during hydrogenation could be caused by surface exchange in addition to hydrogenation. The method was to preadsorb, as before, ethylene-C14 on the surface and then to monitor the surface count rate when the surface was allowed into contact with an excess pressure of gas-phase non-labelled ethylene. Further runs with hydrogen alone, and with ethylene-hydrogen, were carried out to verify the activity of the film to catalysis.

Table 7

Film 13	Figs. 8, 9, 10
Deposition temperature (°C)	-78
Film weight (mg)	44.7
Number of sites	8.9×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)	0.184
Background count rate (c.p.m.)	114
Initial count rate (c.p.m.)	2,500
Vol. C_2H_4-C14 admitted (cm^3mm)	100
Vol. C_2H_4-C14 adsorbed (cm^3mm)	38.6
No. of molecules adsorbed	1.27×10^{18}
% coverage of film	28.6
A. Exchange Experiment	Fig. 8
Initial count rate (c.p.m.)	2,500
Ethylene pressure: (mm)	25.0
Fall in count rate	approx. 1%
B. Hydrogenation	Fig. 9
Initial count rate (c.p.m.)	2,400
Fall in count rate	32%
Reactants (mm) : Ethylene	zero
Hydrogen	26.0

Table 7 (cont.)

C. Second Hydrogenation		Fig. 10
Initial count rate (c.p.m.)		1,790*
Fall in count rate		zero
Reactants (mm) :	Ethylene	53.6
	Hydrogen	53.5
Initial rate:	mm/min	1.10
	mm/min/30mg Ni	0.74
Rate at 5 min:	mm/min	1.8
	mm/min/30mg Ni	1.21

(*This value for the count rate differs from that at the end of experiment B owing to a malfunction of the counter, rectification of which increased the apparent count rate.)

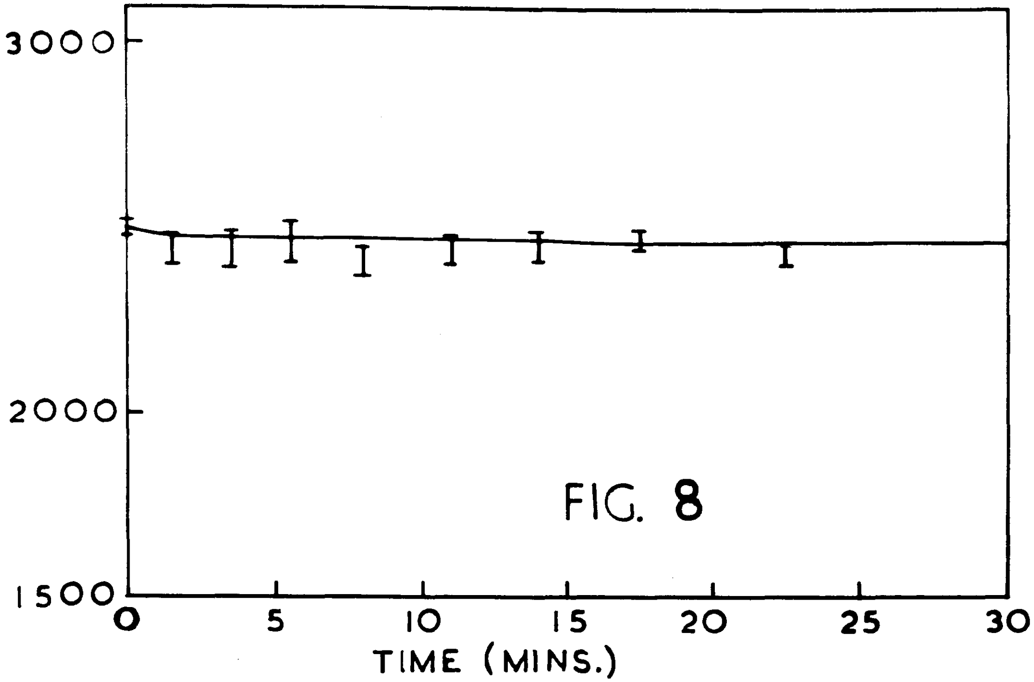

3000
2000
1500
0
5
10
15
20
25
30
TIME (MINS.)

FIG. 8

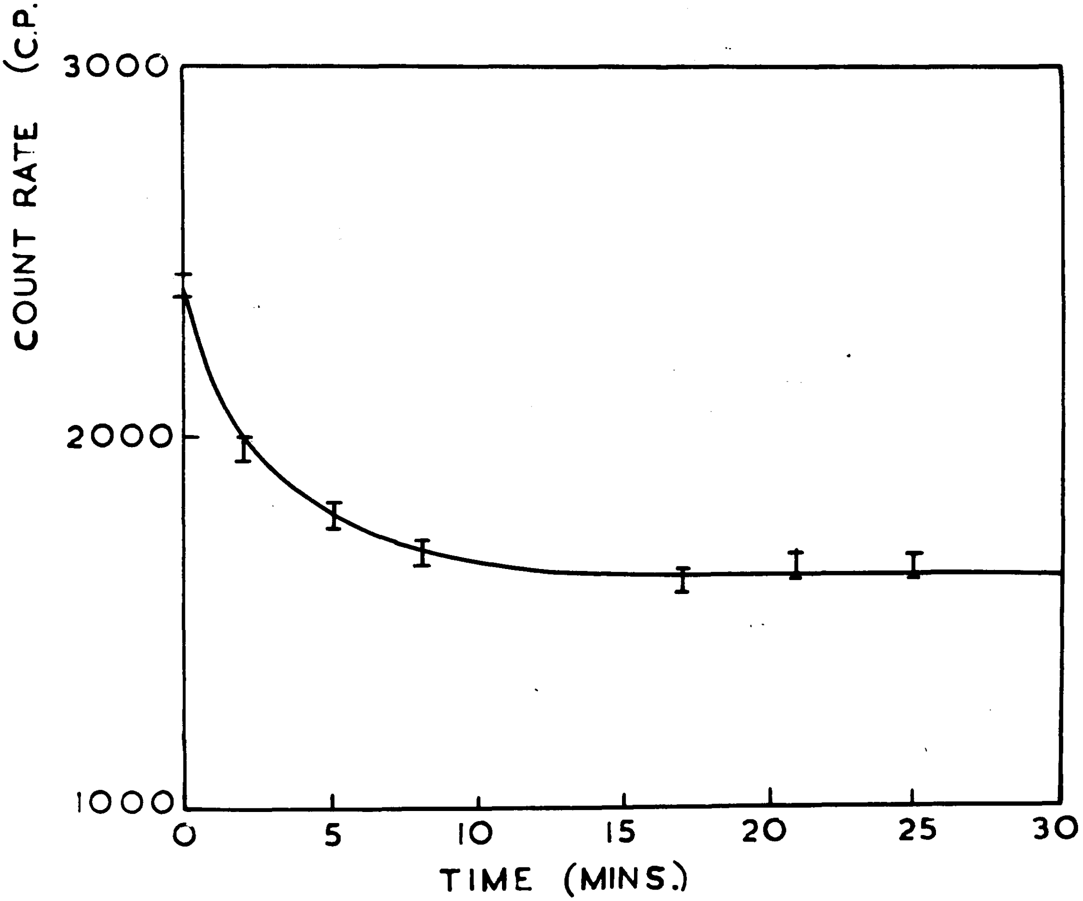

COUNT RATE (C.P.M.)
3000
2000
1000
0
5
10
15
20
25
30
TIME (MINS.)

FIG. 9

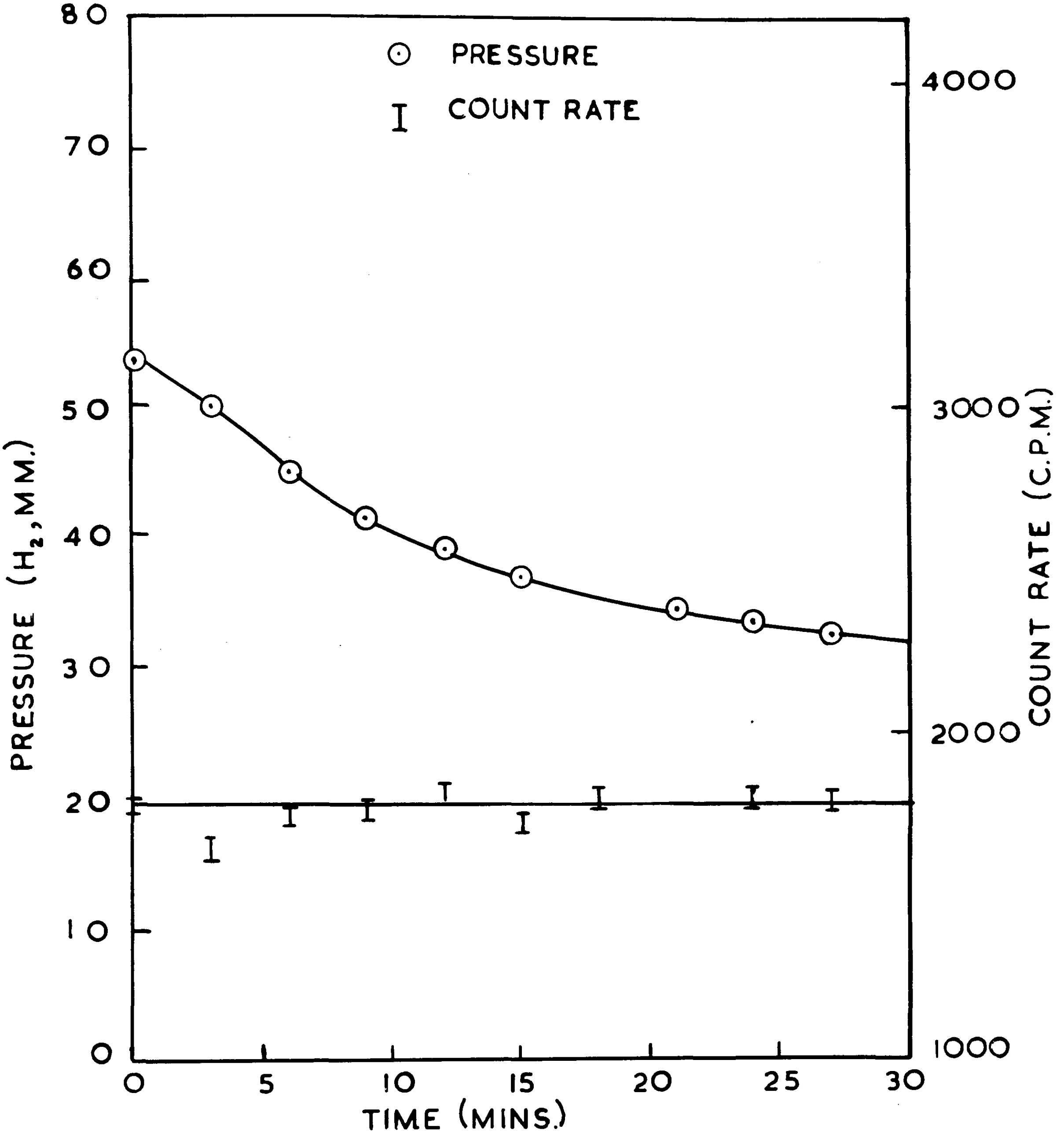

PRESSURE
COUNT RATE
PRESSURE (H_2, MM.)
COUNT RATE (C.P.M.)
TIME (MINS.)
0
10
20
30
40
50
60
70
80
1000
2000
3000
4000
0
5
10
15
20
25
30

FIG. 10

It can be seen from fig. 8 that exchange was negligible, amounting to approximately 1% of the total number of adsorbed ethylene-C14 molecules, whereas after pumping off the gas-phase ethylene hydrogen alone (fig. 9) produced a fall of 32%, in accordance with previous results and substantiated by further work. Removal of gas-phase products and replacement of these by an ethylene-hydrogen mixture produced the normal reaction pattern (fig. 10), but this time with no further fall in the count rate, indicating that all the reactive ethylene had been removed from the surface by the previous treatment with hydrogen alone. It should also be noted that after the rapid initial fall in the count rate there was no further decrease with prolonged exposure of the surface to hydrogen.

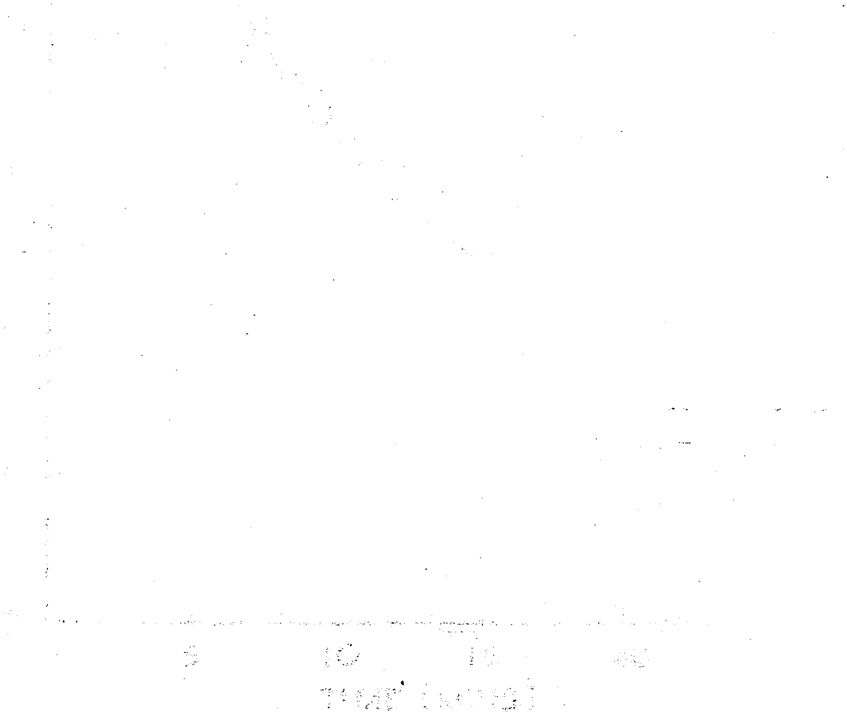
Films 15, 16, 18

Films 15, 16, and 18 were all evaporated in an atmosphere of argon to investigate the effects of orientation of the film on its behaviour.

Film 14, an experiment carried out on a vacuum-evaporated film, has been included as another example of the kinetic behaviour of the reaction system.

Table 8

Film 14		Fig. 11
Deposition temperature (°C)		-78
Film weight (mg)		47.5
Reactants (mm):	Ethylene	125.2
	Hydrogen	33.8
Initial rate:	mm/min	3.2
	mm/min/30mg Ni	2.02



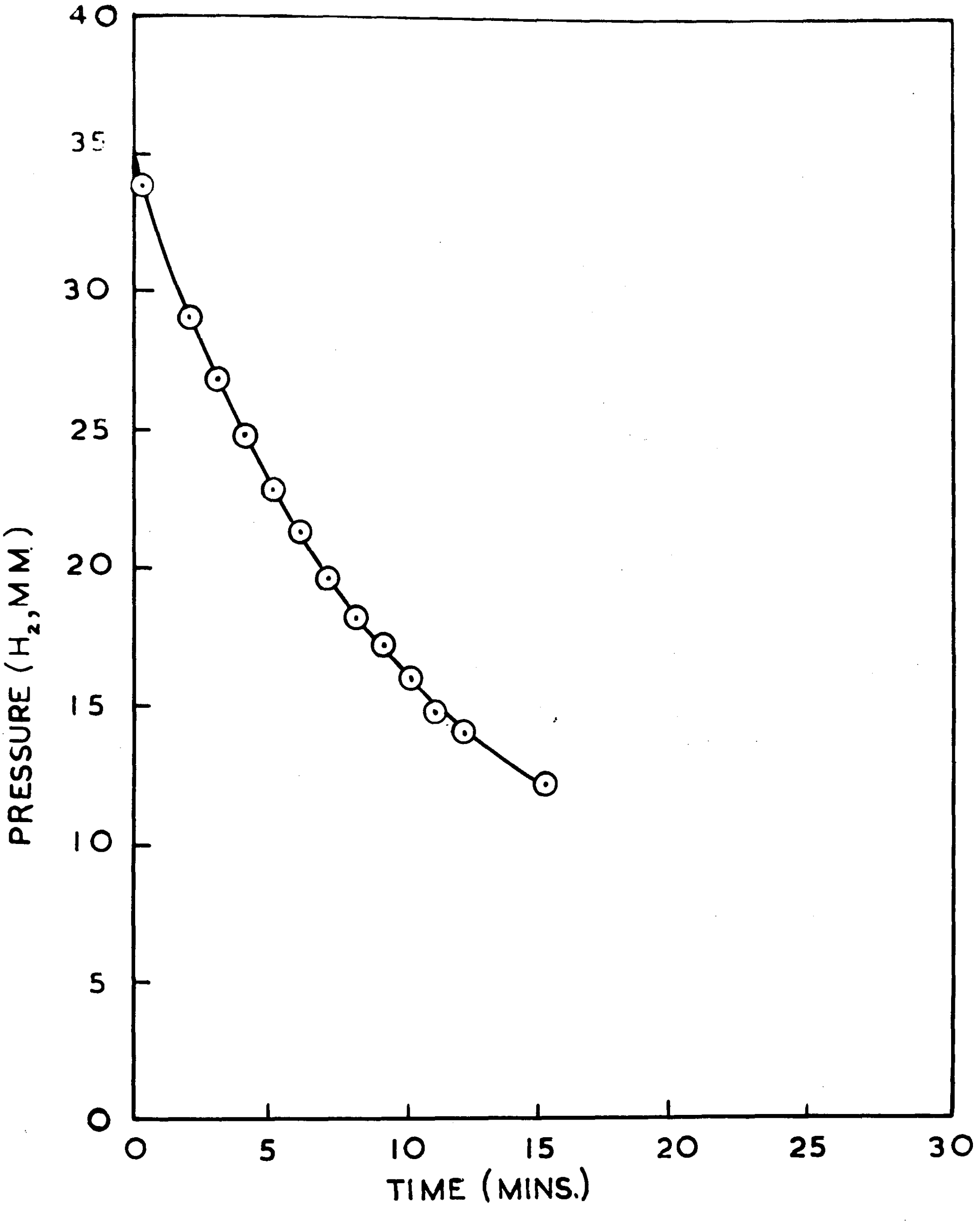


FIG. 11

Table 9

Film 15 Fig. 12

Evaporated under a pressure of 1mm of argon

Deposition temperature (°C)	-78
Film weight (mg)	9.8
Number of sites*	3.9×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)	0.148
Background count rate (c.p.m.)	123
Initial count rate (c.p.m.)	1,170
Vol. C_2H_4-C14 admitted (cm^3mm)	48.9
Volume C_2H_4-C14 adsorbed (cm^3mm)	22.5
No. of molecules adsorbed	0.74×10^{18}
% coverage of film*	38
Fall in count rate	33%

(N.B. This fall is only approximate as the count rate continued to fall with the pressure (see fig. 12).)

Reactants (mm):	Ethylene	32.5
	Hydrogen	132.0
Initial rate:	mm/min	0.3
	mm/min/30mg Ni	0.93

(*Assuming that evaporation in argon gives double the surface area per milligram of vacuum-evaporated films).

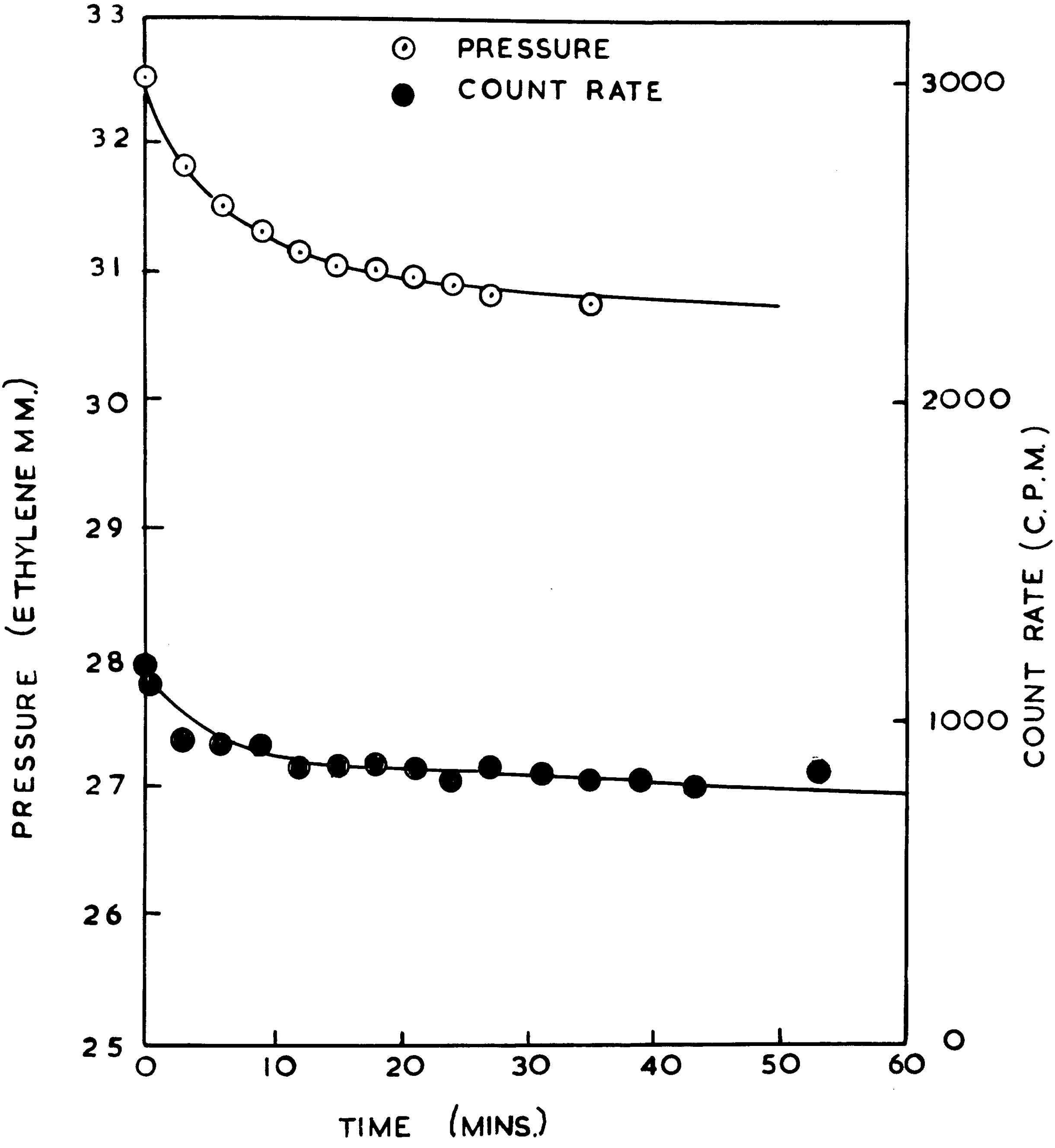

⊙ PRESSURE
● COUNT RATE
PRESSURE (ETHYLENE MM.)
COUNT RATE (C.P.M.)
TIME (MINS.)
33
32
31
30
29
28
27
26
25
3000
2000
1000
0
0
10
20
30
40
50
60

FIG. 12

Table 10

Film 16 — Fig. 13

Evaporated under a pressure of 1mm of argon

Deposition temperature (^{o}C)		-78
Film weight (mg)		11.4
Reactants (mm):	Ethylene	75.0
	Hydrogen	82.0
Initial rate:	mm/min	2.0
	mm/min/30mg Ni	5.26

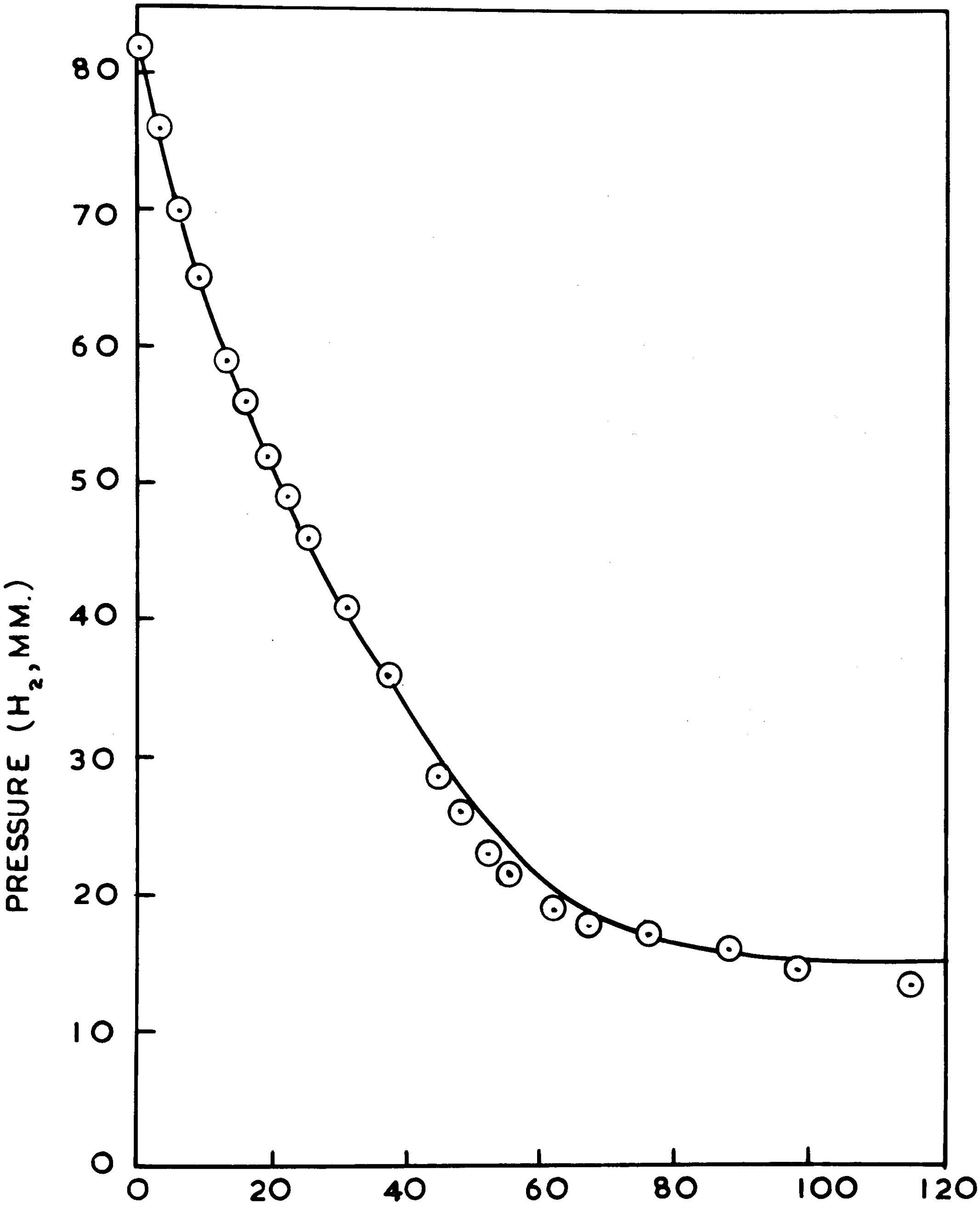

PRESSURE (H_2, MM.)
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
TIME (MINS.)

FIG. 13

Table 11

Film 18 Figs. 14 and 15

Evaporated under a pressure of 1mm of argon

Deposition temperature (^{o}C)	-78
Film weight (mg)	12.4
Number of sites	4.94×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)	0.118
Background count rate (c.p.m.)	180
Initial count rate (c.p.m.)	2,276
Vol. C_2H_4-C14 admitted	unknown
Vol. C_2H_4-C14 adsorbed (cm^{3}mm)	54.6
No. of molecules adsorbed	1.8×10^{18}
% coverage of film	73

A. First Hydrogenation Fig 14

Initial count rate (c.p.m.)		2,276
Fall in count rate		33%
Reactants (mm):	Ethylene	zero
	Hydrogen	62.0

B. Second Hydrogenation Fig. 15

Reactants (mm):	Ethylene	25.2
	Hydrogen	75.6
Initial rate	mm/min	2.4
	mm/min/30mg Ni	5.8

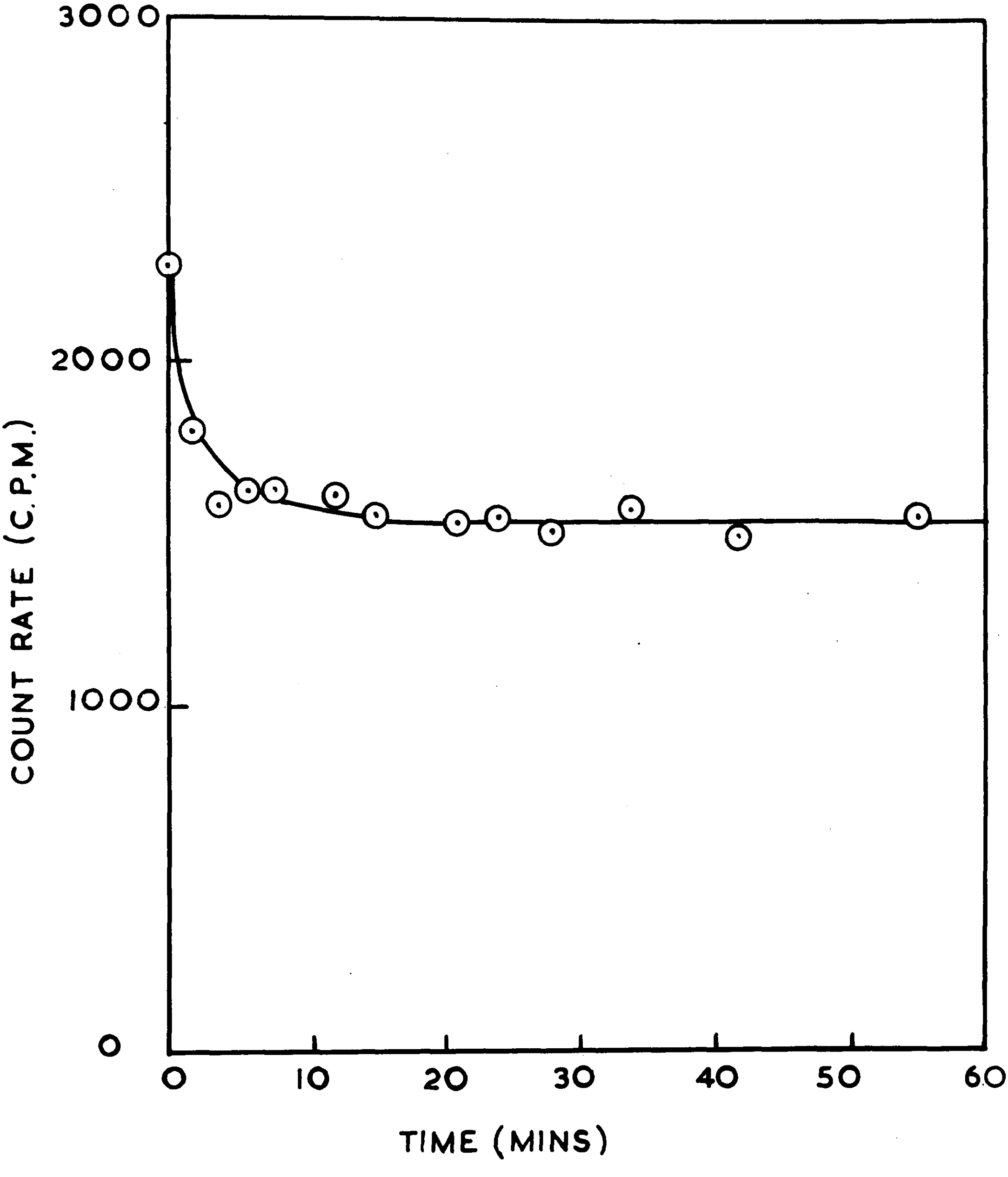


FIG. 14

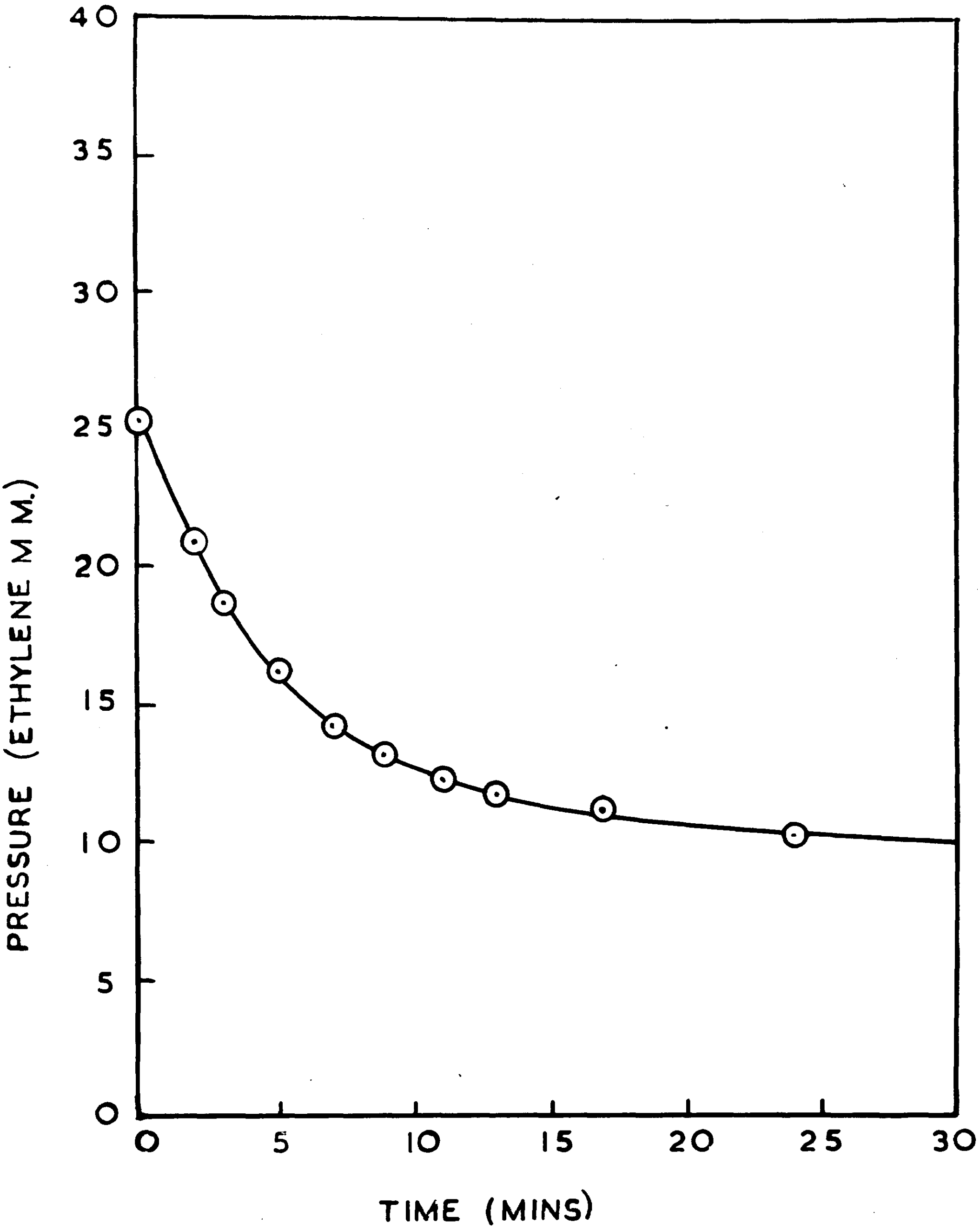

40
35
30
25
20
15
10
5
0
PRESSURE (ETHYLENE M M.)
0
5
10
15
20
25
30
TIME (MINS)

FIG. 15

All the films were characterised by low weight and it is possible therefore that they were poisoned to a larger degree than the vacuum-evaporated films. The film, as it is deposited, exerts a gettering action on any remaining residual gas and it can be concluded from this that the first few milligrams deposited will be poisoned.

The behaviour of the films, both as regards the active fraction of the adsorbate, and as regards the general kinetics, appears to be very much in line with that of the vacuum-evaporated films.

Composite Table

Table 12 on the following page summarises the more important results from each of the experiments. It should be noted that the number of sites on the argon-evaporated films has been calculated on the basis of there being double the number of sites compared with the vacuum-evaporated films.

Table 12

Film Number	10	11	13	15	18
Argon or vacuum evacuated	V	V	V	A	A
No. of sites ($\times 10^{-18}$)	6.85	8.29	8.90	3.90	4.94
Mols. ads. ($\times 10^{-18}$)	3.60	2.74	1.27	0.74	1.80
% coverage	105	66.1	28.6	38	73
% coverage active in hydrogenation	12	47	32	33	33

Surface Coverage

As has already been mentioned in Section 1.8, it proved very difficult to determine the number of ethylene-C^{14} molecules adsorbed on the metal films. The method adopted involved calculation of the number of molecules from the observed count rate and the experimentally determined efficiency of the G.-M. tube.

The efficiency of the G.-M. counter was determined by counting the radiation from a very thin film of "perspex" plastic with a known specific activity. The results of these experiments showed the efficiency to be 0.29% and this value has been used in all the calculations of surface coverage. Full details of the efficiency determination are to be found in Section 6.5.

If N is the observed count rate in counts per minute, and E is the overall counting efficiency, then the true disintegration rate is given by $\frac{N.100}{E}$

Now if the specific activity of the adsorbed species is S millicuries per millimole, then one millimole will give rise to $S \times 3.7 \times 10^7 \times 60$ disintegrations per minute. The number of millimoles is then given by:

$$\frac{N \times 100}{E \times S \times 10^7 \times 60 \times 3{\cdot}7}.$$

The number of molecules present is therefore given by:

$$\frac{N \times 6.023 \times 10^{20} \times 10^{2}}{E.S. \times 3.7 \times 10^{7} \times 60}$$

When E = 0.29% this expression simplifies to:

$$\frac{N}{S} \times 9.35 \times 10^{13}$$

This term can be converted to cm^3mm by dividing by 3.29×10^{16}, the number of molecules in $1cm^3mm$ at 20°C.

The coverage of the surface, expressed as a percentage of the total number of sites available has been calculated on the basis of there being, for a nickel film, 1.99×10^{17} sites available for adsorption per milligram of metal (23), and each adsorbed ethylene molecule has been assumed to occupy two surface sites.

CHAPTER 2

DISCUSSION

It will be seen from the foregoing results that the following conclusions may be drawn:

a). The behaviour of the adsorbed molecules can be observed directly, without the necessity for inferring this behaviour from externally recorded observations.

b). Not all the adsorbed species are active in hydrogenation, i.e., the ethylene-nickel surface system is heterogeneous.

c). This retention of ethylene on the film is in general agreement with the results of Beeck (20) and of Rideal (37).

d). Chemisorbed ethylene does not exchange with gas-phase ethylene at 20°C, although a substantial proportion of the adsorbed species can be hydrogenated readily.

These differences in the reactivity of the adsorbed species can probably be correlated with the structure and topography of the metal film, and with the results of infra-red studies of adsorbed ethylene.

2.1. The Structure of Evaporated Metal Films

The structure of evaporated metal films, and the bearing of the structure on the reactivity has been extensively studied.

The three factors which influence the properties of a catalytic metal, not necessarily in the form of a film, are:

the geometric structure,

the nature and extent of the surface imperfections and,

the electronic nature of the metal.

In his early papers on evaporated nickel films Beeck (9) showed that if the film was evaporated in a low pressure of an inert gas the film was preferentially oriented with the (110) plane parallel to the film support. He found that these films had, on a weight-for-weight basis, twice the surface area of unoriented vacuum-evaporated films and that these oriented films, for an equivalent surface area, posessed five times the activity towards ethylene hydrogenation of the unoriented metal. This contention has been challenged (6) and it appears that the increased surface area is brought about by better transfer of the heat of condensation of the film through the inert gas present during film evaporation. This improved transfer results in a lowering of the temperature of the film and thereby reduces the degree of sintering (13). Studies of ethylene on particular faces of single crystals have shown that a face with a specific atomic spacing can be more active that other crystal planes (11). This work is open to criticism, however, since it is very unlikely that the crystal faces were completely free from contamination. Trapnell has also shown (24) how the interatomic distances in a metal surface can affect the reactivity of an adsorbed molecule such as ethylene.

It is difficult to assess the part played by surface disorders in catalytic reactivity. Such disorders can take the form of lattice vacancies and interstitial sites, dislocations, grain boundaries, and stacking faults. Tompkins (25) has judged these defects to play an important part in catalysis. It has been shown experimentally (26,27,28) that the introduction of a large number of dislocations into a catalyst surface increases catalytic activity. Evaporated films are produced by the rapid condensation on a cold surface of metal atoms driven off a wire at high temperature. Under these conditions the resulting film is expected to possess a high degree of bond unsaturation, and therefore a highly defect structure, which causes the film to sinter readily. Klemperer and Stone have shown (13) that the high energy of these surfaces is manifested by the high heat of adsorption of hydrogen and other gases, as compared with adsorption on reduced metals.

The electronic factor in adsorption and catalysis was first suggested by Dowden (29) when he proposed, to account for the high catalytic efficiency of the Transition metals, that chemisorption occurred by the donation of an electron from the adsorbate into the unfilled d band of the metal. Work on metal alloys of varying composition (30,31) has tended to support this view. It has been shown that as the unfilled d band of the Transition metal is progressively filled by electron donation from the second metal of the alloy there appears a sudden change in the chemisorptive properties of the alloy, and this change occurs at the alloy composition at which the Transition metal d band has been completely filled. It has been pointed out, however, by Trapnell (24) that it is difficult to isolate the two factors of crystal structure and percentage d character, since d character is calculated from the binding energy of the metal atoms, the same factor also affecting the crystalline structure of the metal.

Bearing in mind these considerations, and the arguments discussed in the Introduction, it appears then that a catalyst surface is heterogeneous owing to its physical and chemical nature. On this basis a distribution of surface energies has been calculated (32) which gives a good fit with the Freundlich and the Temkin adsorption isotherms. On the other hand, several workers have postulated that in catalysis, as opposed to adsorption, the nature and extent of the active surface is determined not by the surface itself, but by the nature of the complexes adsorbed on it. (33). Thon and Taylor (34) have also suggested that the rate of a catalytic reaction is determined by the density of the active centres on the catalyst surface, these active centres being formed from dissociatively adsorbed species from one of the reactants. They have stated that reaction rates decrease during reaction owing to the consumption of these active centres. In this case the kinetics as determined from the initial rate will differ from the kinetics studied from the point of view of the rate course of any one particular reaction.

Laidler (1) has criticised this theory and pointed out that it is just as feasible to explain this discrepancy in terms of a heterogeneous surface with a distribution of site energies. (35).

When one comes to consider the hydrogenation of ethylene on nickel two factors are of importance. One of these is the kinetics of the hydrogenation reaction and, associated with it, the kinetics and mechanism of the exchange reaction between ethylene and deuterium. The second factor is the behaviour of ethylene when it is adsorbed on nickel at room temperature in the absence of hydrogen.

The rate of the hydrogenation reaction is dependent on the order of admission of the two reactants. If ethylene is admitted to the catalyst first the subsequent rate of hydrogenation is lower than it would be had the two reactants been admitted together. This was interpreted by Beeck (20) as being caused by poisoning of the surface by adsorbed complexes. As it appears that the formation and reactivity of these complexes will determine the apparent heterogeneity of the surface to ethylene hydrogenation the major work of this research has been directed towards the study of this phenomenon.

A study of the results of this work reveals a simple division of the data into that concerning "static" ethylene and that concerning "active" ethylene. The active fraction is that ethylene whose behaviour can be studied by the kinetics of the reaction system, while the static ethylene is best studied from the point of view of Beeck's "surface complexes". As the static ethylene forms one of the major interests in this research it will be discussed first, although this separation of the two parts of the system is somewhat arbitrary and a certain amount of overlap between the two topics is bound to occur.

The adsorption of ethylene on metals has been studied basically by four methods. These are: chemical methods, magnetic and conductimetric methods, and, more recently, infra-red methods. The findings from each method of study, and the bearing on them of the results of this research, will be discussed in that order.

2.2. Chemical Methods for the Study of Ethylene Adsorption

Beeck's early study of ethylene on evaporated nickel films (20) showed that at 23°C, 5 x 10^{16} molecules of ethylene were adsorbed rapidly on each milligram of nickel. Further addition of ethylene produced gas-phase ethane, and when 12.5 x 10^{16} molecules/mg were adsorbed there was an equal number of ethane molecules in the gas phase. Complete saturation of the surface with ethylene produced a surface complex with an average composition of $C_nH_{0.4n}$. Taking into account the formation of polymers, it appears from this that the surface was largely covered with C_2H_2 species which Beeck designated "acetylinic complexes". He claimed that these species behaved differently from adsorbed acetylene and, furthermore, that 20% of the adsorbed species were removed from the surface by reaction with hydrogen over a period of one hour, although he did not state the rate of removal.

In 1952 Trapnell (36) studied the adsorption of ethylene on tungsten films at 0°C. He adsorbed ethylene until there was a small equilibrium pressure, when he found that each ethylene molecule occupied four sites and 18% of the surface was free to adsorb hydrogen. When he carried the adsorption to completion he arrived at an average composition of 0.55 molecules for each surface site and the surface was then incapable of adsorbing hydrogen, as evidenced by the poisoning of the surface towards the <u>para</u>-hydrogen conversion. He claimed that the stoichiometry of the adsorption process was

$$2W + 2C_2H_4(g) \longrightarrow W_2C_2H_2(a) + C_2H_6(g)$$

and thus half of the molecules admitted were adsorbed.

An extensive investigation of the adsorption of ethylene on nickel films was carried out in 1955 by Jenkins and Rideal (37). At 20°C they found that at saturation the surface was 80% covered with acetylinic complexes on dual sites, and 10% of the surface consisted of dual sites on which hydrogen could be adsorbed. The remaining 10% consisted of isolated single sites. They found no evidence for the adsorption of undissociated, or "associatively adsorbed" ethylene.

Statistical calculations were carried out in which an idealised "surface" of 100 sites was randomly covered with ethylene on double sites, with the two hydrogen atoms from the dissociation of the ethylene on two adjacent sites. This hydrogen was removed (supposedly by reaction with gas-phase ethylene) and the adsorption process carried on until no more groups of four sites remained. At this stage 78% of the surface was covered with ethylene and 13% of the surface remained free, as double sites, with 9% of the surface consisting of single sites. This result was in good agreement with experiment.

On admission of hydrogen they observed a rapid pressure fall, followed by a slow fall. The rapid fall was attributed to hydrogen chemisorption on the free surface, while the slow pressure fall was believed to have been brought about by reaction of some of the adsorbed complexes with hydrogen. This reaction was claimed to be the same as that observed by Beeck when 20% of the adsorbed complexes were removed in one hour.

Stephens (38) has carried out similar experiments on palladium films. He found that adsorption of ethylene took place on 70% of the surface, assuming four-site adsorption. Beyond this stage self-hydrogenation set in and gas-phase ethylene removed the hydrogen atoms resulting from the dissociative adsorption of the ethylene. The surface ultimately became almost completely covered with acetylinic residues.

He found, however, that reaction with hydrogen removed 80% of the adsorbed complexes, compared with 20% as claimed by Beeck for nickel. Stephens also formulated the adsorption process as being

$$2C_2H_4(g) \longrightarrow C_2H_2(a) + C_2H_6(g),$$

in which case the film should adsorb 50% of the ethylene admitted to it.

The same adsorption process on nickel has also been studied recently by McKee (39) over a wide range of temperatures. The experiments were carried out on a reduced nickel carbonyl catalyst and so the results are open to some objection on the grounds that the experiments were carried out on an impure surface.

The results appear, however, to substantiate those of previous workers. At 20°C it was found that the average composition of the adsorbed species was $C_nH_{1.1n}$, thus indicating that the adsorption process at this temperature is also

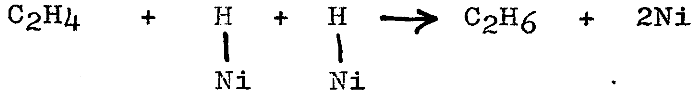
$$2C_2H_4(g) \longrightarrow C_2H_2(a) \quad + \quad C_2H_6(g)$$

At lower temperatures the degree of dissociation of the ethylene is smaller and there appears to be a large proportion (depending upon the precise temperature) of associatively adsorbed ethylene: $\underset{|}{CH_2}-\underset{|}{CH_2}$. At higher temperatures the dissociatively adsorbed ethylene, $\underset{\backslash}{CH}=\underset{|}{CH}$ appears to undergo further dissociation and carbonisation of the surface occurs.

The results of these workers can therefore be summarised as follows. The initial adsorption of ethylene appears to occur by a dissociative mechanism which forms an acetylinic complex plus two adsorbed hydrogen atoms:

$$C_2H_4 + 4Ni \longrightarrow \underset{Ni}{\underset{|}{CH}}{=}\underset{Ni}{\underset{|}{CH}} + \underset{Ni}{\underset{|}{H}} + \underset{Ni}{\underset{|}{H}}$$

This process continues until the surface no longer has groups of four sites left, so that at this point each ethylene molecule is adsorbed on four sites. Further addition of ethylene gives rise to gas-phase ethane as the ethylene reacts with the adsorbed hydrogen atoms:



$$C_2H_4 + \underset{Ni}{\underset{|}{H}} + \underset{Ni}{\underset{|}{H}} \longrightarrow C_2H_6 + 2Ni$$

As this process continues groups of four sites will once more become available and dissociative adsorption of ethylene will again occur. This process continues until no more groups of four sites remain, when the surface is saturated with acetylinic complexes.

In this research the experiments on films 10, 11, and 13 were all carried out with the films covered solely with ethylene-C^{14}, the films having been evaporated under vacuum.

The coverage of the film has been difficult to assess, especially in view of the self-hydrogenation reaction which has been shown to occur as the surface is progressively covered with ethylene. The method adopted has been to rely on the observed count rate and to calculate the number of molecules on the surface by the procedure described at the end of Section 1.10. The number of sites available for adsorption has been taken from the results of Brennan, Hayward, and Trapnell (23). These workers studied the chemisorption of hydrogen and oxygen on nickel films evaporated at 20°C. On the assumption that each hydrogen atom occupied one site they calculated the number of surface sites to be 1.99×10^{17} per milligram, these amounting to 2.0% of the total number of nickel atoms in one milligram of the film.

Our films were evaporated at -78°C, but the transfer of heat from the condensing film to the cooling agent was restricted by the necessity for the double tube construction. (See details of the catalyst vessel in Chapter 5). In view of this we have taken the area of our films to be comparable with those of Brennan, Hayward, and Trapnell which were evaporated at 20°C. Calculations of the degree of surface coverage have therefore been made on the basis of 1.99×10^{17} sites/mg, with each ethylene molecule being adsorbed on two sites.

The relevant data for films 10, 11, and 13 are shown in Table 13.

Table 13

Film Number:	10	11	13
Volume C_2H_4-C14 admitted (cm^3mm)	204	91.3	100
Volume C_2H_4-C14 adsorbed (cm^3mm)	109.3	83.3	38.6
Degree of coverage (%)	105.0	66.1	28.6
Fraction C_2H_4-C14 removed by hydrogenation (%)	12	47	32

It can be seen that this method of calculating the coverage of the film is reasonably accurate. On the basis of the mechanism of adsorption being

$$2C_2H_4(g) \longrightarrow C_2H_2(a) + C_2H_6(g)$$

it appears that 50% of the ethylene admitted should be adsorbed.

In the case of film 10 the volume of ethylene adsorbed amounts to 53.6% of that admitted, so it can be assumed that the surface was saturated with ethylene molecules each adsorbed on two sites. The results of film 11 show that 91.1% of the ethylene-C14 admitted was adsorbed so it can be taken that film coverage took place this time with a large degree of four-site adsorption, as evidenced also by the value of 66.1% for the surface coverage assuming double site adsorption. It is assumed therefore that the majority of the ethylene was in the dissociated form, but that many of the hydrogen atoms had not been removed by reaction with gas-phase ethylene. Thus the two values of 105% and 66.1% for the film coverage can be taken as being accurate, bearing in mind the uncertainties of the calculation, such as the actual film area.

In the case of film 13 38.6% of the admitted ethylene was adsorbed, showing that the film should have been saturated, and yet the percentage film coverage is calculated to be only 28.6%. It seems likely therefore that a certain degree of poisining occurred during the preparation of this film.

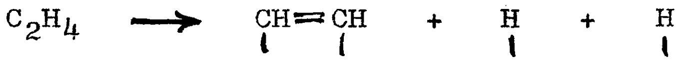
It can be seen from Table 13, and from the relevant graphs (figs. 6, 7, and 9), that an appreciable fraction of the adsorbed ethylene was removed by reaction with an equimolar ethylene-hydrogen mixture (films 10 and 11) or with hydrogen alone (film 13). These falls in the number of adsorbed ethylene molecules are of the same order as those observed by Beeck (20) but it should be noted that the fall in activity occurred very rapidly - the majority of the reactive ethylene had been desorbed within 5 or 10 minutes and thereafter the number of adsorbed ethylene-C14 molecules remained constant.

It will be seen from later results that the number of reactive ethylene molecules on film 10, 12% of the total, is lower than the average number for several experiments. Why this should be is not clear, but this anomalous result does not alter the main findings of the research at this stage.

2.3. Magnetic and Conductimetric Methods

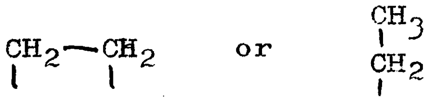
Magnetic studies have chiefly been made on supported nickel catalysts. Selwood has investigated the magnetic properties of a nickel on silica catalyst during ethylene adsorption (40). The investigation was carried out over a range of temperatures, with results similar to those reported by other workers. At 0°C all the adsorption took the associative form, but as the temperature was raised the proportion of dissociatively adsorbed ethylene increased. At 28°C the number of bonds per molecule of ethylene adsorbed was approximately three and at the same temperature 54% of the adsorbate was removable by hydrogen. The value of three for the number of bonds per molecule was explained by postulating a certain amount of polymerisation and C-C bond rupture. Selwood was, however, of the opinion that at this temperature the degree of dissociation of the ethylene was small.

Measurements of the conductivity of metal films have been made by Zweitering, Koks, and Van Heerden (41). They adsorbed ethylene on evaporated titanium films and found a linear fall in conductivity with the amount of ethylene adsorbed. The conductivity fall indicated that each molecule of ethylene formed four bonds with the surface, again indicating the reaction



$$C_2H_4 \longrightarrow \underset{|}{CH}{=}\underset{|}{CH} + \underset{|}{H} + \underset{|}{H}$$

The full coverage of ethylene amounted to 0.85 x 10^{15} molecules/cm^2, but at a coverage of roughly 0.48 x 10^{15} molecules/cm^2 the linear conductivity - coverage graph began to decrease in slope. This decrease in the rate of fall of conductivity indicated that fewer bonds were being formed per molecule of ethylene adsorbed, indicating possible adsorbed species such as



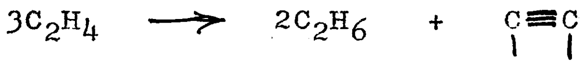
$$\underset{|}{CH_2}-\underset{|}{CH_2} \quad \text{or} \quad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \end{array}$$

These results appear to indicate a further stage in the adsorption process. Afterrdissociative adsorption has occurred it is possible that ethylene adsorbs in the associative form on the remaining pairs of sites. This postulate is substantiated by the results of infra-red studies of adsorbed species.

2.4. Infra-Red Methods

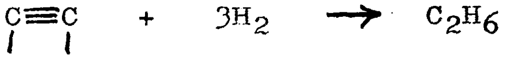
The majority of these studies have been carried out on supported catalysts. Although it is known that adsorption on an evaporated film can differ from adsorption on a supported catalyst, it is still possible to draw some general conclusions from the infra-red studies which can be related to the previous work on evaporated films.

Pickering and Eckstrom (42) have studied the adsorption of ethylene on rhodium and they propose the mechanism for the adsorption of ethylene to be



$$3C_2H_4 \longrightarrow 2C_2H_6 + \underset{|}{C}\equiv\underset{|}{C}$$

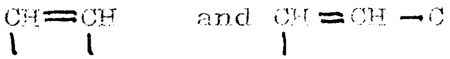
but they find the adsorbed species react readily with hydrogen



$$\underset{|}{C}\equiv\underset{|}{C} + 3H_2 \longrightarrow C_2H_6$$

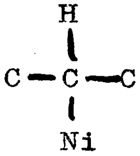
They were unable, however, to identify the adsorbed species present.

Little, Sheppard, and Yates (43) have studied ethylene adsorption on palladium and nickel supported on porous silica glass. On palladium they found evidence for C-H stretching frequencies of both olefinic and paraffinic C-H bonds. They therefore postulated the existence of both saturated species and species such as

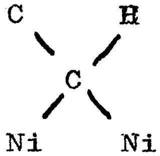


$$\underset{|}{CH}=\underset{|}{CH} \quad \text{and} \quad \underset{|}{CH}=CH-C$$

On nickel a similar situation was evident, with predominantly saturated species. Since the carbon to hydrogen ratio was found to be about 1:1 they suggested that bridged and other complex species are present, such as



and



Extensive studies of adsorption using infra-red spectroscopy have been carried out by Eischens and his associates (44). Their results are roughly in accordance with those of Jenkins and Rideal and other workers. Olefinic C-H frequencies are detectable, but the intensity of the paraffinic C-H frequencies indicated that the adsorbed species are not wholly olefinic, although the C/H ratio is again fairly close to unity.

The main point of disagreement with previous work lies in the effect of hydrogen. At 35°C gas-phase hydrogen rapidly removed olefinic C-H frequencies, indicating that ready hydrogenation of any acetylinic complexes was occurring, although it was not clear whether the species were removed from the surface to the gas phase. This is in agreement with the results of experiments on films 10, 11, and 13 as shown in figs. 6, 7, and 9. Admission of hydrogen, either alone or with ethylene gives rise to rapid removal of chemisorbed ethylene from the surface.

The situation may be summed up therefore as follows. When ethylene is admitted to a metal such as nickel, palladium, or rhodium, the molecules dissociate to give an adsorbed species C_2H_2 plus two adsorbed hydrogen atoms. These atoms may be removed by reaction with gas-phase ethylene. This adsorption process requires groups of four sites; when these groups become no longer available adsorption of ethylene probably occurs on double sites without dissociation.

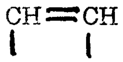
Admission of hydrogen to the catalyst can convert dissociatively adsorbed species into the associative form:

$$C_2H_2(a) \quad + \quad H_2(g) \rightarrow C_2H_4(a)$$

This process can probably go a further stage and give rise to gas-phase ethane:

$$C_2H_4(a) \quad + \quad H_2(g) \rightarrow C_2H_6(g)$$

The precise nature of the dissociatively adsorbed ethylene is not clear. Although termed "acetylinic" complexes by Beeck it seems doubtful whether they do have the structure of associatively adsorbed acetylene, viz:



$$\underset{|}{CH}=\underset{|}{CH}$$

Calculations of the initial heat of adsorption of ethylene assuming the complex to be in the form above have been unsuccessful (45) and it appears from this that the complexes have the form  $HC-CH$ or similar structures. This conclusion is also supported by the results of the infra-red work.

When one considers the results of this research in conjunction with the magnetic, conductimetric, and infra-red ivestigations the following possibilities emerge.

1). The ethylene which can be removed from the surface by hydrogen may be situated on a particular crystal face which, by virtue of its individual atomic spacing, adsorbs ethylene in a reactive form. As stated earlier (page 46), Beeck found that argon-evaporated films had enhanced activity towards ethylene hydrogenation compared with films evaporated under vacuum. If the supposedly active plane is preferentially exposed (the (110) plane in Beeck's research) this could account for the enhanced activity.

2). Chemisorption of ethylene occurs on groups of four sites by a dissociative mechanism until no further groups of four sites remain, when the adsorption occurs by an associative mechanism on dual sites. It is this associatively adsorbed ethylene which is reactive with hydrogen.

3). The surface sites exhibit a large range of energies and the precise configuration of the adsorbed species is determined solely by the energy of the sites on which the ethylene is adsorbed. The argument then follows that only ethylenic species adsorbed with a certain configuration are subsequently reactive with hydrogen.

Each of these theories has been examined in turn, but a fourth possibility required to be examined before further work could be carried out. This was the possibility that the adsorbed ethylene was removed from the surface by molecular exchange rather than by hydrogenation.

2.5. Exchange

It could be possible for the adsorbed ethylene to exchange with gas-phase ethylene and for a reduction on the number of ethylene-C14 molecules on the film surface to occur by this mechanism. The first experiment on film 13 was carried out to test this hypothesis. The film was covered with ethylene-C14 as has been discussed and then the catalyst vessel was evacuated.

No fall in count rate was observed on pumping for about 30 minutes, indicating that the ethylene was irreversibly chemisorbed. Inactive ethylene was then admitted to the catalyst vessel to a pressure of 25.0mm. The change in count rate with time is shown in fig. 8. It can be seen that there was negligible exchange. If exchange took place it only amounted to 1% of the adsorbed ethylene, and in view of the errors in the counting technique (about 1%) it is doubtful whether this small fall can be considered to be significant.

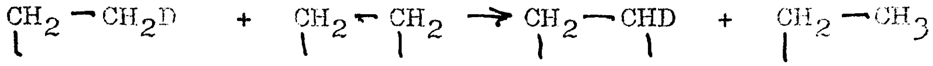
Isotopic exchange between C_2H_4 and C_2D_4 has been studied by a few workers (46,47). Their experiments were concerned with C_2H_4-C_2D_4 exchange over a nickel catalyst with both reactants initially in the gas phase. They found a certain degree of exchange yielding mixed deutero-ethylene products. The mechanism as postulated is initiated by the dissociative adsorption of one of the species:

$$C_2D_4(g) \rightarrow D\underset{|}{C}{=}\underset{|}{C}D + \underset{|}{D} + \underset{|}{D}$$

Associatively adsorbed ethylene can then react with the deuterium atoms to form the "half-hydrogenated state" (48):

$$\underset{|}{C}H_2{-}\underset{|}{C}H_2 + \underset{|}{D} \rightarrow \underset{|}{C}H_2{-}CH_2D$$

A simple interchange between adjacently adsorbed species can then occur:



$$CH_2-CH_2D + CH_2-CH_2 \rightarrow CH_2-CHD + CH_2-CH_3$$

etc. Subsequent desorption of the olefinic species can give rise to partially deuterated olefins in the gas phase. Although this mechanism is feasible, it requires the adsorption of both species on the surface. If, however, one of the labelled species (whether labelled with deuterium or carbon-14) occupies the whole surface then the exchange process cannot occur. This we believe to be the reason for the absence of exchange as the experiment on film 13 showed. It should be noted that the mechanism outlined above is for isotopic exchange, whereas the mechanism of interest in this work is molecular exchange. However it would seem that both forms of exchange can occur by the same mechanism.

The fact that hydrogenation of some of the adsorbed species will still occur (see fig. 9) can be explained on the basis of there being a number of vacant sites which are capable of adsorbing hydrogen but which are not available to ethylene for steric reasons. Reaction will then occur between adsorbed ethylene and adsorbed hydrogen.

2.6. Argon-Evaporated Films

As has been described at the beginning of this Chapter, it has been shown (9) that on an area-for-area basis films evaporated in an atmosphere of an inert gas possessed five times the activity towards ethylene hydrogenation of films evaporated under vacuum. Beeck claimed that this enhanced activity was due to preferential exposure of the (110) nickel plane.

To examine this theory a series of experiments was carried out on nickel films evaporated in an atmosphere of argon at 1mm pressure. The evaporation was carried out with the catalyst vessel and substrate at a temperature of -78°C. Following on evaporation, the films were exposed to ethylene-C14 in a manner identical with that employed for films 10, 11, and 13. The results of the experiments carried out on these films, 15 and 18, are shown in Tables 9 and 11. The results are summarised below in Table 14.

Table 14

Film Number	Admitted Volume (cm^3mm)	Adsorbed Volume (cm^3mm)	Coverage (1) (%)	Coverage (2) (%)	Fall in Count Rate (%)
15	48.9	22.5	76	38	33
18	?	54.6	146	73	33

Coverage (1): Based on there being 1.99×10^{17} sites/mg.

Coverage (2): Based on there being $2 \times 1,99 \times 10^{17}$ sites per milligram.

It appears from these results therefore that argon-evaporated films do have roughly double the area of the films prepared under vacuum. 46% of the ethylene-C14 admitted to film 15 was adsorbed, indicating full coverage, but the low value for the coverage, 38%, can be explained by assuming poisoning of the film owing to its very low weight (9.8mg). It is known that during film evaporation the initial metal deposited exerts a gettering action within the catalyst vessel and adsorbs any residual contaminant gases present. On this basis the low coverage is quite feasible.

The relevant feature of the results of experiments on these films, however, lies in the fall in the number of adsorbed ethylene-C14 molecules. In both cases with both ethylene-hydrogen (film 15) and hydrogen alone (film 18) the observed fall in adsorbed radioactivity amounted to 33%, this result being in good agreement with those obtained with vacuum-evaporated films (Table 13).

The results of these two experiments indicate therefore that argon-evaporated films have a greater surface area per milligram than vacuum-evaporated films, but there is no difference in their activity from the point of view of the fraction of the film surface active in catalysis. Of films 10, 11, and 13 the active fraction had an average value of 30%, while the active fraction of films 15 and 18 was 33%. These results show therefore that particular crystal face and preferential orientation of the film crystallites has no effect on the fraction of the film surface on which ethylene will react with hydrogen. The conclusion follows therefore that the factor which influences the active fraction of the film is the structure and configuration of the adsorbed ethylinic species. As stated earlier, this can arise from two sources - the mechanism of the stepwise adsorption process, and the intrinsic nature of the surface. To examine the first of these a number of statistical experiments were carried out.

2.7. Statistical Models for Adsorption

The experimental method was based on the random filling of an idealised surface consisting of 100 sites. The "surface" was in the form of a square, subdivided into 100 squares, each side of the large square having ten coordinates from 0 to 9. 100 numbers, from 00 to 99, were marked on 100 table-tennis balls and one of these at a time was selected randomly. This number gave the coordinate of the site upon which a molecule, or part of a molecule, could be "adsorbed". For double-site adsorption the other coordinate adjacent to this first coordinate was selected by a similar procedure involving the numbers from 0 to 7 as shown:

6	7	0
5		1
4	3	2

End effects were eliminated by considering the surface to be in the form of a torus, so that the top edge was "adjacent" to the bottom edge, and the two sides were similarly contiguous. On this basis then, the four corner sites were nearest neighbours as shown:

99	09
90	00

where 00 marked the position of the bottom left-hand site.

The results obtained with this type of calculation depend on the model chosen for the adsorption process. The first model chosen was for adsorption of ethylene molecules on four sites, this simulating the dissociative adsorption process:

$$C_2H_4 \quad + \quad 4Ni \quad \longrightarrow \quad Ni_2C_2H_2 \quad + \quad 2NiH$$

Adsorption was allowed to take place only on pairs of "horizontal" or "vertical" sites, with no diagonal adsorption. The two hydrogen atoms were adsorbed on sites adjacent to the sites carrying the two carbon atoms so that the adsorbed entity took the form of a square. On this basis the results given in Table 15 were obtained.

Table 15

		Coverage
C_2H_4 molecules adsorbed	20	80%
Vacant pairs of sites	9	18%
Vacant single sites	2	2%

If we assume that associative adsorption of ethylene can occur on the vacant pairs of sites, and that it is this ethylene which is reactive with hydrogen, then the fraction of the adsorbed molecules which is removable by hydrogen is 9/29 = 31%.

The second model employed allowed for the process of self-hydrogenation. After saturation of the surface with ethylene adsorbed on four sites as described for the first model the hydrogen atoms were removed in pairs by a random process. Further four-site adsorption was carried out, together with removal of pairs of hydrogen atoms, until only pairs of sites and single sites remained. Ethylene was then allowed to adsorb on pairs of sites by a random process until the surface was completely saturated. The results for this model are given below in Table 16.

Table 16

		Coverage
Dissociatively adsorbed C_2H_4 mols.	25	50%
Associatively adsorbed C_2H_4 mols.	17	34%
Number of isolated H atoms	6	6%
Number of vacant single sites	10	10%

On this basis the coverage of the surface by ethylene is 84%. If it is again assumed that only the associatively adsorbed ethylene is reactive with hydrogen, the fraction of the adsorbed gas which is removable is 40.5%.

The third model adopted was very similar to the second, but adsorption of ethylene was allowed to take place in any configuration, including linear arrangement of the C_2H_2 residue and the two hydrogen atoms. On this basis the figures shown in Table 17 were obtained.

Table 17

		Coverage
Dissociatively adsorbed C_2H_4 mols.	22	44%
Associatively adsorbed C_2H_4 mols.	16	32%
Isolated H atoms	10	10%
Vacant single sites	14	14%

The surface coverage is therefore 76% and 42% of the adsorbed ethylene is removable.

From consideration of these figures it is very difficult to decide unequivocally between the three postulated mechanisms. The results obtained should be compared with those obtained in 1955 by Jenkins and Rideal (37). On the evidence of volumetric measurements they concluded that 83.4% of the surface adsorbed ethylene, while 8.3% of the surface consisted of paired sites which were capable of adsorbing hydrogen, but not ethylene. The remaining 8.3% of the surface was in the form of single sites incapable of adsorption. They also carried out stochastic calculations similar to those described above. The results obtained by Jenkins and Rideal were:

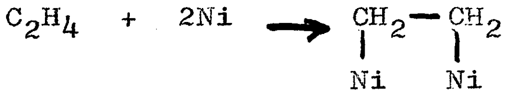
Dissociatively adsorbed C_2H_4	78%
Vacant paired sites	13%
Vacant single sites	9%

thus giving good agreement with experiment.

It will be seen therefore that none of these theories gives good agreement with our experimental results. The value for the active ethylene fraction obtained with our first model (31%) is perhaps the best value, but that particular model ignores the phenomenon of self-hydrogenation. Taking this factor into consideration both models two and three, and Rideal's results, do not give the correct value Assuming that ethylene could be adsorbed on the vacant paired sites in Rideal's model the removal of this ethylene will only amount to 14% of the total adsorption.

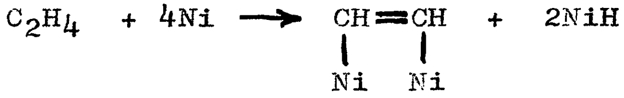
The site arrangement employed by us is an array of squares and therefore corresponds to the (100) nickel plane. In a randomly oriented nickel film it is to be expected that other planes such as the (110) and the (111) will be exposed to the gas phase. Different packing arrangements are therefore possible on the other crystal planes and this itself is bound to lead to different values for the degree of coverage and the active proportion of the adsorbed species. The results of Zweitering (41) do indicate however that a different mode of adsorption sets in as the degree of ethylene coverage increases. In connection with this theory it is of interest to consider the heats of adsorption of different postulated models for ethylene adsorption. The heat of adsorption of ethylene on nickel at 23°C is 58 Kcal/mole at zero coverage and falls rapidly to a value of about 15 Kcal/mole for a fully covered surface. On the basis of these figures it is to be expected that species with a high initial heat of adsorption will tend to be formed preferentially on a clean surface, while as the degree of coverage increases those species with a low heat of adsorption will tend to be favoured.

The heats of adsorption of the different models, calculated for zero coverage (19) are given below.

I. 
$C_2H_4 + 2Ni \rightarrow \underset{\underset{Ni}{|}}{CH_2}-\underset{\underset{Ni}{|}}{CH_2}$ Q = 34 Kcal/Mole

II. $C_2H_4 + Ni \rightarrow Ni-CH=CH_2 + \frac{1}{2}H_2$ Q = 3

III. $C_2H_4 + Ni \rightarrow Ni=CH-CH_3$ Q = 26

IV. 
$C_2H_4 + 4Ni \rightarrow \underset{\underset{Ni}{|}}{CH}=\underset{\underset{Ni}{|}}{CH} + 2NiH$ Q = 23

V. 
$2C_2H_4 + 2Ni \rightarrow \underset{\underset{Ni}{|}}{CH}=\underset{\underset{Ni}{|}}{CH} + C_2H_6$ Q = 17

It will be seen then that the associative mechanism (I) and the dissociative mechanism(IV) of

Beeck will be favoured, with their high heats, at low initial coverages. The onset of self-hydrogenation (V) would be expected to occur at intermediate filling of the catalyst surface, as has been observed. The single site mechanisms (II and III) would be expected to increase in importance as the surface becomes saturated and the number of paired sites becomes less. This will be seen to be in accordance with the findings of infra-red studies and the conductimetric measurements.

In order to examine this theory more closely a series of experiments was devised which relied on adsorption on the metal film of both ethylene-C14 and non-labelled ethylene. These experiments are dealt with in Chapter 3.

CHAPTER 3

SURFACE LOCATION OF THE ACTIVE ETHYLENE
and
KINETICS OF HYDROGENATION

3.1. Surface Location of the Active Ethylene

If the ethylene adsorbed last on the surface, and amounting to 30% of the total adsorbed, is indeed the active part of the adsorbate, then it should be possible to detect this by adsorbing both ethylene-C14 and non-radioactive ethylene. If the surface is first partially covered with ethylene-C14 and then the remainder of the surface is covered with non-labelled ethylene, reaction of the adsorbed ethylene with hydrogen should produce no decrease in the observed count rate, providing that the ethylene adsorbed last covers more than 30% of the surface. Conversely, if the ethylene-C14 is adsorbed last onto the surface the fall in count rate should correspond to the fractional coverage of the nickel by the labelled form.

Results

In the results given on the following pages in Tables 18, 20, and 21, and summarised later in Table 22, the coverage of the film by ethylene has again been calculated on the basis of 1.99 x 10^{17} sites per milligram. The total coverage of the surface has been assumed to be 80% of the available sites and the coverage of the film by the non-labelled ethylene has been derived by difference.

It was very important to establish in these experiments that adsorption of both forms of ethylene took place. In the case of the experiments on films 21 and 22 it can be seen readily from the observed count rate that adsorption of ethylene-C14 ocurred after adsorption of the non-labelled ethylene, even though 59.7% (by difference) of the surface was originally covered with the non-labelled form. By a converse reasoning process it is possible to deduce that adsorption of non-labelled ethylene occurred on film 19 after adsorption of ethylene-C14.

Additional confirmation of this came from observation of the gas pressure during adsorption. After admission of the first form of ethylene the gas phase was pumped away to a residual pressure of 5 x 10^{-5}torr. Admission of the first increment of the second form of ethylene produced an initial rise in pressure which then fell to 1×10^{-3} torr, indicating that adsorption was occurring.

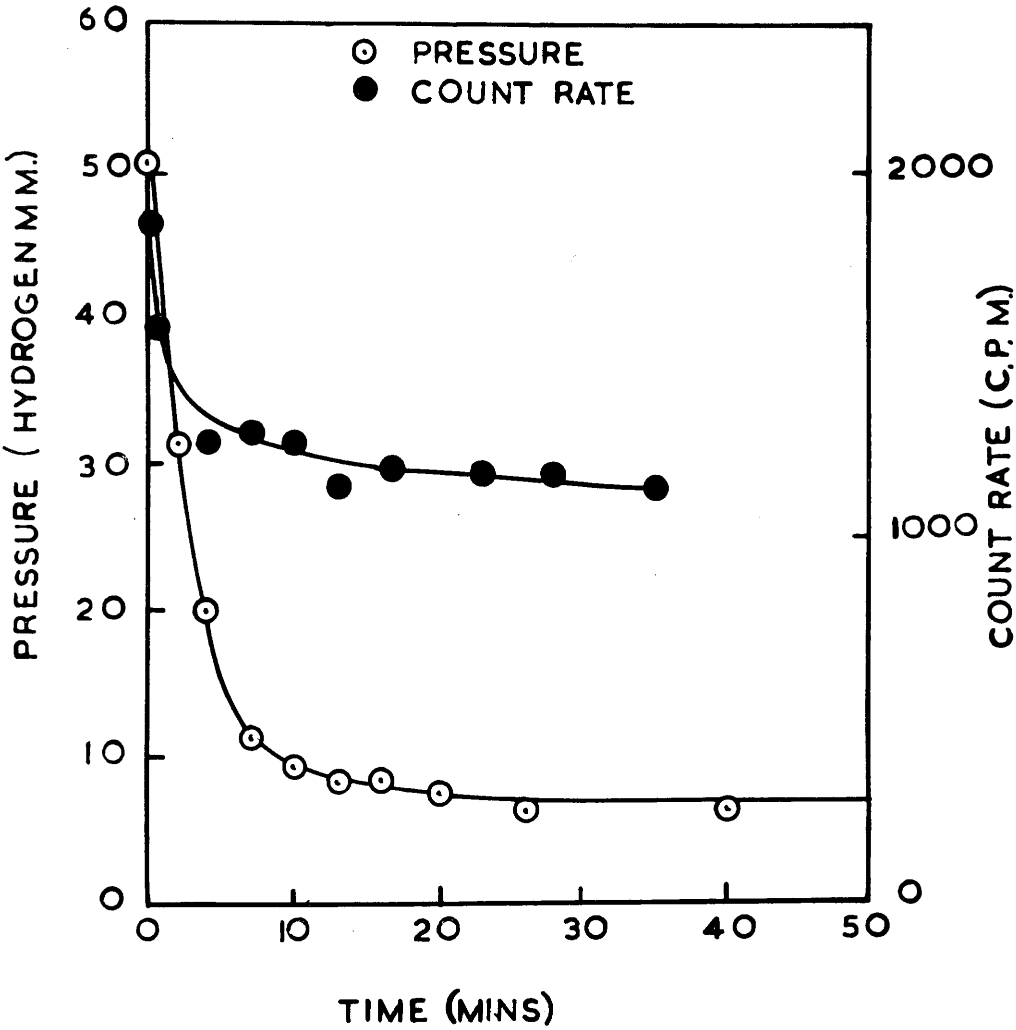
Table 18

Film 19		Figs. 16 and 17
Deposition temperature (°C)		-78
Film weight (mg)		38.8
Number of sites		7.73×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)		0.118
Background count rate (c.p.m.)		261
Vol. C_2H_4-C14 admitted (cm^3mm)		60.5
Initial count rate (c.p.m.)		1,840
Vol. C_2H_4-C14 adsorbed (cm^3mm)		44.4
No. of molecules adsorbed		1.46×10^{18}
% coverage of film by C_2H_4-C14		37.8
Vol. C_2H_4-C12 admitted		-
Vol. C_2H_4-C12 adsorbed		-
% coverage of film by C_2H_4-C12		45.2*
A. First Hydrogenation		Fig. 16
Initial count rate (c.p.m.)		1,840
Fall in count rate		45%
Reactants (mm):	Ethylene	51.3
	Hydrogen	50.3
Initial rate:	mm/min	9.25
	mm/min/30mg Ni	7.15

Table 18 (cont.)

B. Second Hydrogenation		Fig.17
Initial count rate (c.p.m.)		800
Fall in count rate		zero
Reactants (mm):	Ethylene	50.0
	Hydrogen	50.0
Initial rate:	mm/min	6.0
	mm/min/30mg Ni	4.65

(*By difference, from 80%)



⊙ PRESSURE
● COUNT RATE
PRESSURE (HYDROGEN M M.)
COUNT RATE (C.P. M.)
TIME (MINS)
60
50
40
30
20
10
0
2000
1000
0
0
10
20
30
40
50

FIG. 16

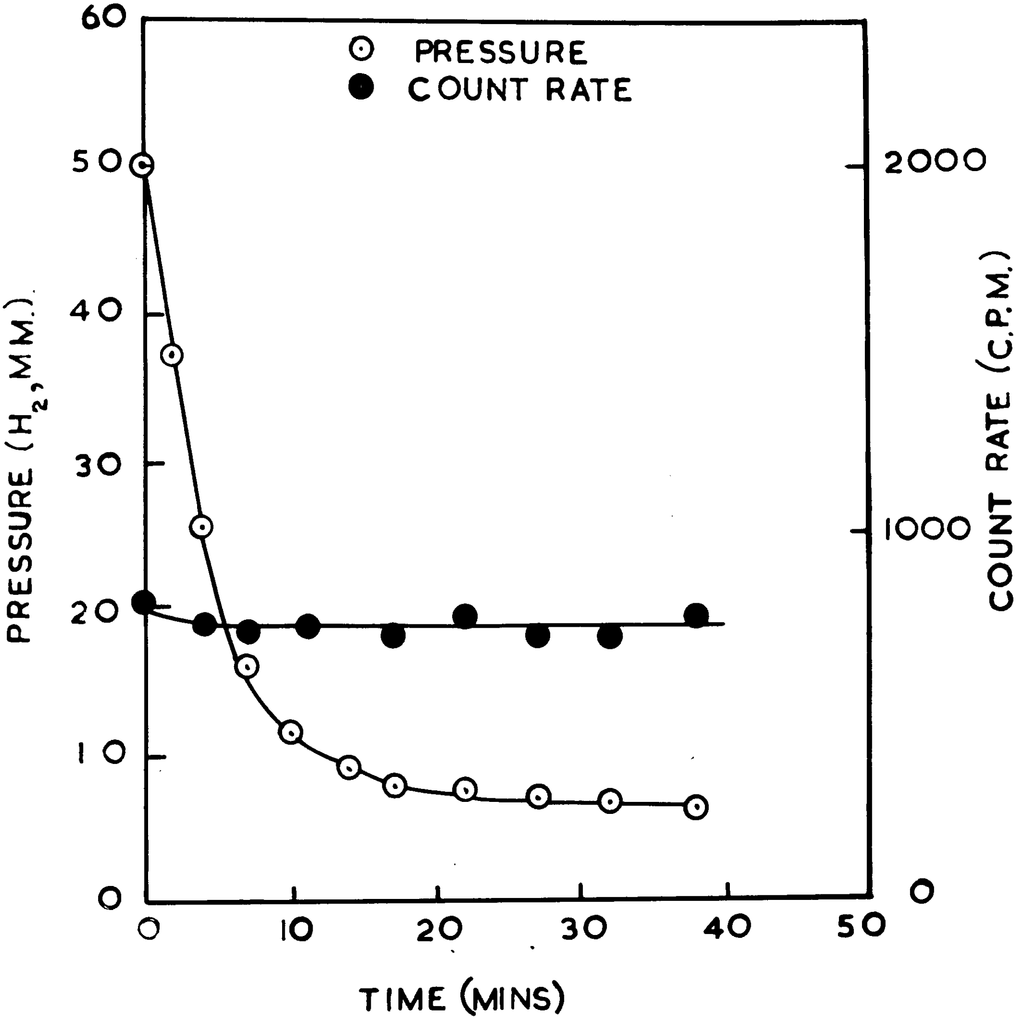

PRESSURE
COUNT RATE
PRESSURE (H_2, MM.)
COUNT RATE (C.P.M.)
TIME (MINS)
60
50
40
30
20
10
0
2000
1000
0
0
10
20
30
40
50

FIG. 17

Table 19

Film 20		Fig. 18
Deposition temperature (°C)		-78
Film weight (mg)		34.2
Reactants (mm):	Ethylene	25.0
	Hydrogen	122.0
Initial rate:	mm/min	2.75
	mm/min/30mg Ni	2.42

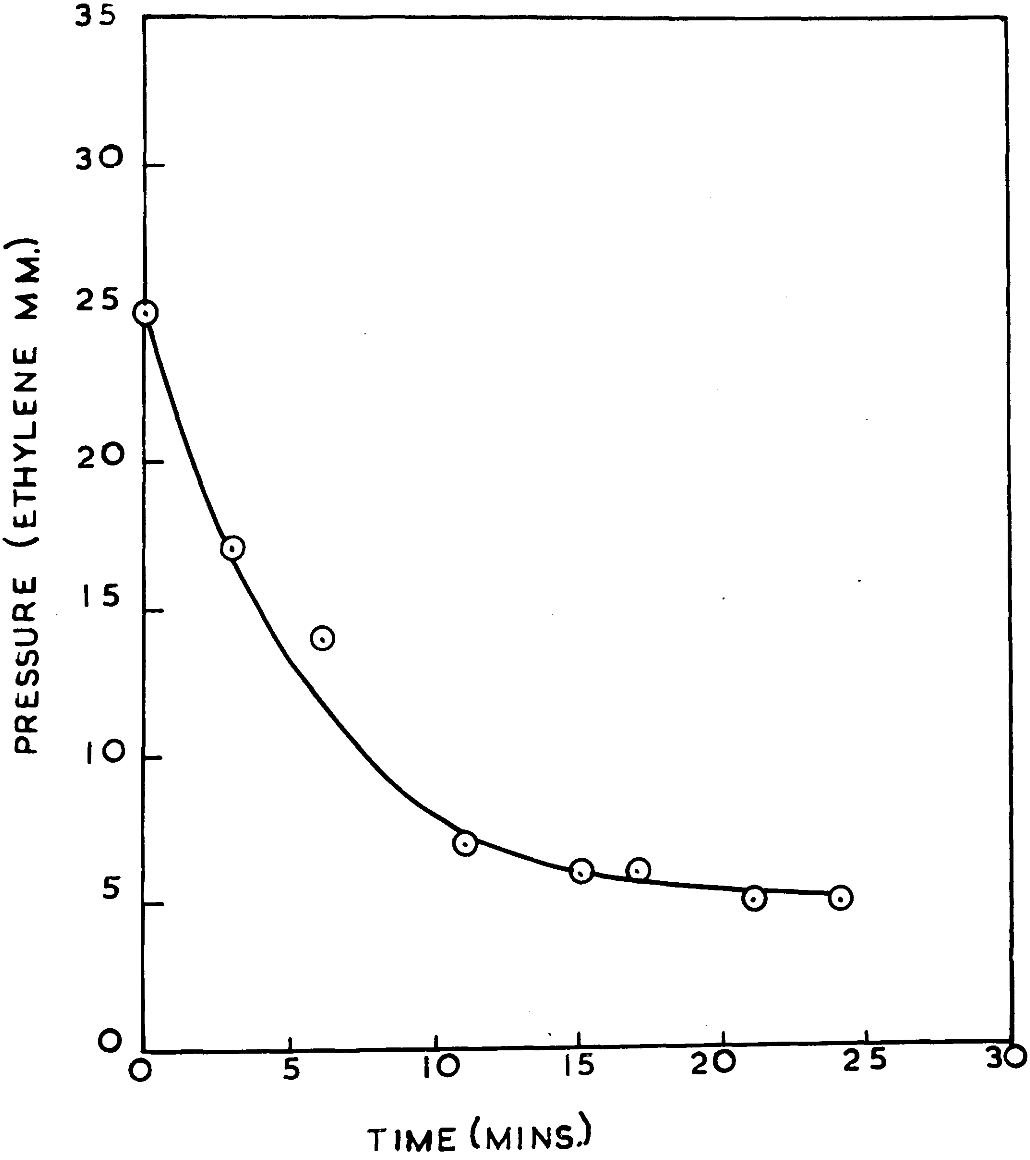

PRESSURE (ETHYLENE MM.)
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
TIME (MINS.)

FIG. 18

Table 20

Film 21		Fig. 19
Deposition temperature (^{o}C)		-78
Film weight (mg)		29.0
Number of sites		5.78×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)		0.0905
Background count rate (c.p.m.)		281
Vol. C_2H_4-C12 admitted (cm^3mm)		42
Vol. C_2H_4-C12 adsorbed (		-
% coverage of film by C_2H_4-C12		19.5*
Vol. C_2H_4-C14 admitted (cm^3mm)		100
Vol. C_2H_4-C14 adsorbed (cm^3mm)		53.1
No. of molecules adsorbed		1.75×10^{18}
% coverage of film by C_2H_4-C14		60.5
Initial count rate (c.p.m.)		1,690
Fall in count rate		34%
Reactants (mm):	Ethylene	47.6
	Hydrogen	52.1
Initial rate:	mm/min	9.5
	mm/min/30mg Ni	9.84

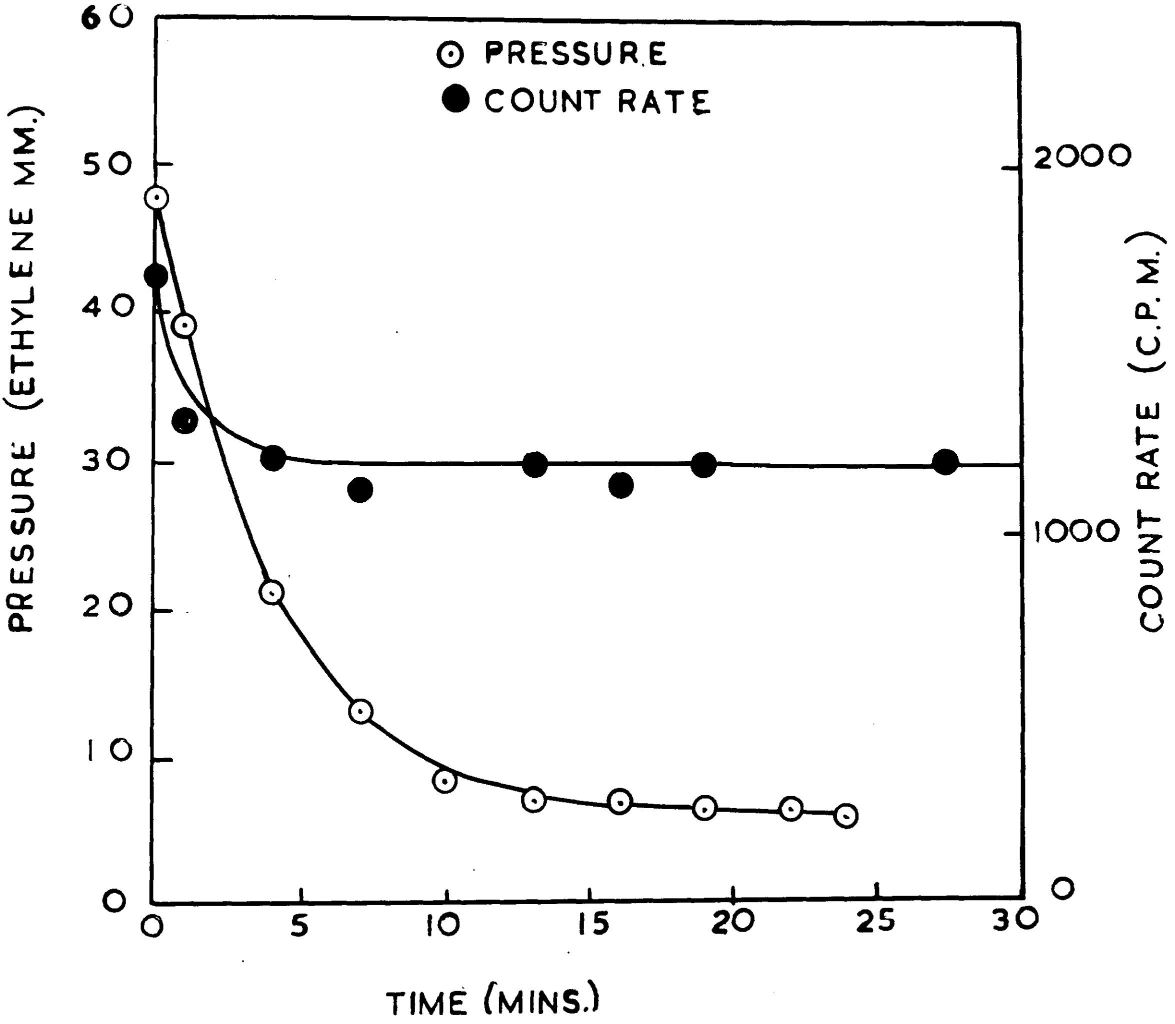

⊙ PRESSURE
● COUNT RATE
PRESSURE (ETHYLENE MM.)
COUNT RATE (C.P.M.)
TIME (MINS.)
60
50
40
30
20
10
0
2000
1000
0
0
5
10
15
20
25
30

FIG. 19

Table 21

Film 22		Fig. 20
Deposition temperature (°C)		-78
Film weight (mg)		38.3
Number of sites		7.62×10^{18}
Sp. activity of C_2H_4-C14 (mc/mM)		0.0905
Background count rate (c.p.m.)		221
Vol. C_2H_4-C12 admitted (cm^3mm)		83.0
Vol. C_2H_4-C12 adsorbed (cm^3mm)		-
% coverage of film by C_2H_4-C12		59.7*
Vol C_2H_4-C14 admitted (cm^3mm)		31.0
Vol. C_2H_4-C14 adsorbed (cm^3mm)		23.6
No. of molecules adsorbed		0.775×10^{18}
% coverage of film by C_2H_4-C14		20.3
Initial count rate (c.p.m.)		750
Fall in count rate		35%
Reactants (mm):	Ethylene	50.0
	Hydrogen	132.0
Initial rate:	mm/min	4.5
	mm/min/30mg Ni	3.52

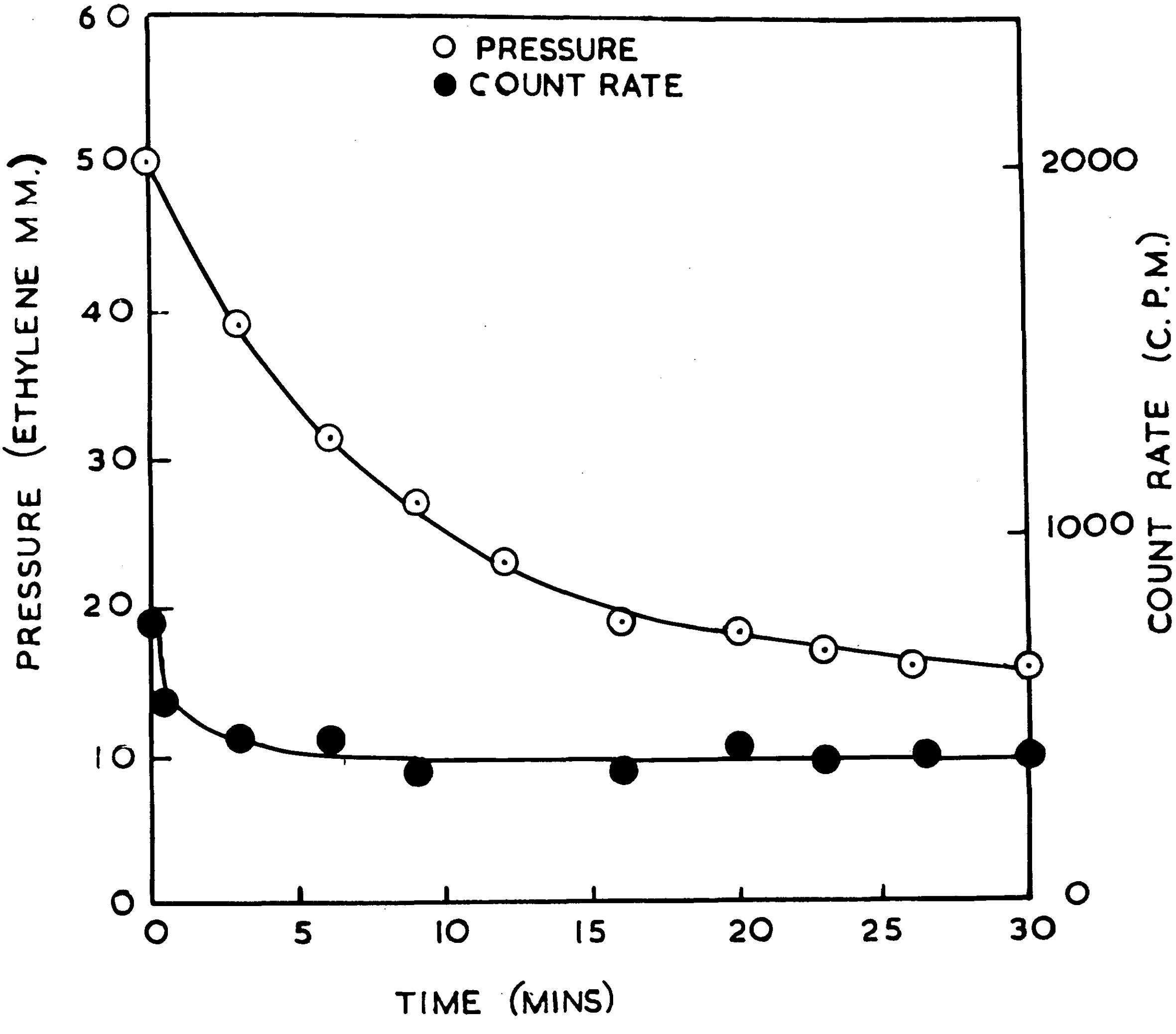

○ PRESSURE
● COUNT RATE
PRESSURE (ETHYLENE M.M.)
60
50
40
30
20
10
0
COUNT RATE (C.P.M.)
2000
1000
0
0
5
10
15
20
25
30
TIME (MINS)

FIG. 20

Discussion

The results of these three experiments are summarised in Table 22.

Table 22

Film	19	21	22
First admission	C_2H_4-C14	C_2H_4-C12	C_2H_4-C12
Vol. admitted (cm^3mm)	60.5	42.0	83.0
Vol. adsorbed (cm^3mm)	44.4	-	-
% coverage	37.8	19.5*	59.7*
Second admission	C_2H_4-C12	C_2H_4-C14	C_2H_4-C14
Vol admitted (cm^3mm)	-	100	31
Vol. adsorbed (cm^3mm)	-	53.1	23.6
% coverage	42.2*	60.5	20.3
% fall in count rate	45	34	35

*By difference, from 80%

It can be seen from these results that irrespective of the number of ethylene-C14 molecules adsorbed, or the sequence of admission of the labelled and non-labelled species, the fraction removed during hydrogenation remains constant, and is of the same order of magnitude as those fractions removed in previous experiments. The implications of this observation are of importance in our understanding of the nature of the adsorbed species and the nature of the adsorption process.

We are now in a position to review all the experimental findings and to correlate them with the results of other workers. The first point to be established, and which arises out of the results of the experiments on films 19, 21, and 22, is that ethylene adsorbed on a nickel film at room temperature is immobile. By postulating immobility an explanation of the results obtained on films 19, 21, and 22 is possible.

If one assumes that the activation energy for ethylene adsorption is zero, and that evaporated nickel films possess a porous structure, both of these assumptions being valid, then the following picture of ethylene adsorption emerges.

The initial increment of ethylene will be adsorbed on the first sites with which it comes into contact. These will not necessarily be be the sites of highest energy since the non-activated adsorption will occur instantaneously before an appreciable degree of diffusion of the gas through the film can occur. The adsorbed molecules will therefore cover a small fraction of the surface sites, but they will cover these sites randomly, molecules being adsorbed on sites of all energies. A similar process can be expected to occur with each successive increment, except that the molecules will have to diffuse within the pores of the metal until they encounter further vacant sites. If, then, ethylene-C14 is adsorbed first, these molecules will cover part of the available surface, but they will be adsorbed on sites of varying energy. The second form of ethylene will then be adsorbed by a similar process and thus both the labelled and the non-labelled forms will occupy sites with the same spectrum of energies. Thus it can be seen that on subsequent hydrogenation those molecules adsorbed on sites of the requisite energy will be removed from the the surface, irrespective of at which stage in the adsorption process they reached the surface. The only possible difference between the two forms of ethylene on this basis is that the ethylene adsorbed last, being adsorbed further within the film, could be less reactive owing to its tending to become trapped within the metal. That this is not so can be seen from the results in Table 22 where the fall in the number of adsorbed ethylene-C14 molecules is roughly the same in all three experiments.

An alternative explanation, namely that desorption and subsequent readsorption of the ethylene molecules occurs, thus leading to a net redistribution process, is unfeasible. The heat of adsorption of ethylene on a clean nickel film is 58Kcal/mole, falling to 15 Kcal/mole for a fully covered surface (49) and therefore the activation energy for desorption during the initial stages of film coverage lies somewhere between 45 and 60 Kcal/mole. This value is too large to allow of any rapid desorption process. In fact our results have shown that prolonged pumping on a nickel film covered with ethylene does not result in any ethylene desorption.

A third explanation is that ethylene is mobile on nickel. This mobility would result in rapid interchange of the different adsorbed species over the surface and therefore a net averaging process would occur, giving rise to a constant value for the fraction of ethylene-C14 molecules removed. Mobility, however, would produce an adsorbed layer which was wholly active in hydrogenation as those species adsorbed on unfavourable sites migrated onto more favourable sites left vacant by desorbing molecules.

It will be seen now that the theory suggested earlier (Chapter 2), namely that the active fraction comprises that ethylene adsorbed on isolated dual sites on an essentially homogeneous surface, cannot be supported since those molecules adsorbed on the remaining dual sites in an immobile layer, if reactive, would not give a constant removable fraction of ethylene-C14 irrespective of the admission sequence.

In addition, when one takes into account the results of the infra-red studies of chemisorbed species, there appears to be no one unique species present on the surface. Rather there is a multitude of different species present any one of which, or a combination of them, could constitute the fraction reactive with hydrogen. It is also rather arbitrary to differentiate between surface energy effects and adsorbed complexes *per se*. It can therefore be seen that the structure and distribution of the adsorbed complexes is related intimately to the energy distribution of the surface.

In connection with these conclusions it is of interest to compare the results on nickel with those of similar studies, although not using a radio-tracer technique, on other metals (20,38). For ethylene adsorbed on different metals different values have been obtained for the fraction of the adsorbed ethylene removable by hydrogen.

Stephens (38) claimed 80% removal on palladium and Beeck (20) has quoted figures for rhodium of 60% after 1 minute and 100% with prolonged reaction. In view of these figures it appears that the metal itself plays an important part in determining the heterogeneity of the surface towards ethylene hydrogenation. In addition to the structural nature of the metal surface it is evident that the other factors of electronic structure and crystal faces must play some part. Which of these three factors predominates is very difficult to assess, but in view of the findings discussed in Section 2.6 it appears that crystal face considerations can only be of secondary importance.

The order of reactivity, as determined by the fraction of adsorbed ethylene removable by hydrogen, of the three metals studied is in the order

Rh(20) > Pd(38) > Ni(20, this research).

It is tempting to correlate this with the percentage d character of the three metals:

Rh, 50%; Pd, 46%; Ni, 40% (8),

but at the present state of our knowledge it is not possible to say more than that the activity of a surface towards hydrogenation is determined by some combination of the several factors involved.

It should also be pointed out that our results are at variance with those of Beeck and therefore further work will be required before a definite decision can be made as to the role of the various factors.

To sum up, we believe that the heterogeneity of evaporated metal films towards ethylene hydrogenation is governed largely by the energy distributionsof the film surface, this distribution being influenced by the surface disorders and imperfections introduced during the process of film preparation. Of the ethylene adsorbed in the absence of hydrogen on the surface of an evaporated nickel film at 20°C, 30 to 40% is removable by reaction with hydrogen.. We have found no evidence, as manifested by the differences between vacuum- and argon-evaporated films, for any specific influence of crystal face on the reactive ethylene fraction.

3.2. Kinetics of Hydrogenation

It remains now to discuss the mechanism whereby the ethylene is removed from the catalyst surface by reaction with hydrogen. In effect there are two processes occurring at the film surface; reaction of the preadsorbed ethylene-C14, and reaction of the bulk gas-phase ethylene with hydrogen. The main topic of interest is whether there are two mechanisms operating - one for the preadsorbed ethylene and one for gas-phase ethylene - or whether the same mechanism occurs for both, with fresh ethylene taking the place of the ethylene-C14 as the latter is removed by hydrogenation.

The Mechanism of Ethylene Hydrogenation

There are two basic mechanisms for ethylene hydrogenation. The first is that proposed by Langmuir and developed by Hinshelwood (51), and referred to as the Langmuir-Hinshelwood mechanism, by which reaction occurs between chemisorbed ethylene and chemisorbed hydrogen. Reaction can occur between the two species which compete for the available surface sites, or it is possible that the reaction takes place between the two species adsorbed on two distinct types of site (50). The precise nature of the process is still the subject of controversy and, in addition to the hydrogenation itself, the para-hydrogen conversion and ethylene-deuterium exchange have been employed in attempts to elucidate the finer points of the mechanism.

The second possible mechanism involves reaction between one species in the chemisorbed state and the other species either in the gas phase or in a Van der Waals adsorbed layer. This mechanism was first proposed by Rideal (52) and will be referred to as the Rideal mechanism. There are two possible modifications of this mechanism. Either chemisorbed ethylene reacts with gas-phase or Van der Waals adsorbed hydrogen in a secondary layer, or chemisorbed hydrogen reacts with ethylene in the secondary layer.

Of the three possible mechanisms the Rideal-I mechanism (adsorbed hydrogen reacting with physically adsorbed ethylene) cannot explain the removal of adsorbed ethylene from the surface as observed in this research. The Rideal-II mechanism (adsorbed ethylene reacting with physically adsorbed hydrogen) will explain the observed fall in the number of adsorbed ethylene molecules. However, on the basis of the calculated retention times for physically adsorbed hydrogen at 0°C (53) it appears that this mechanism is statistically unfavourable at temperatures above

0°C. Other information has been put forward to show that this mechanism does not play a large part in ethylene hydrogenation (20,37).

The remaining possible mechanism is that of Langmuir and Hinshelwood. Beeck has criticised this mechanism on the grounds that the heats of adsorption of ethylene and hydrogen, 58 Kcal/mole and 31 Kcal/mole respectively, will not give the required heat of hydrogenation of ethylene which is 32.5 Kcal/mole (49). In the experiments discussed in this thesis however, the fractional coverage of the nickel surface is approaching closely to unity. At these coverages the heats of adsorption of the two reactants are both 15 Kcal/mole. On this basis then, assuming that the heat of adsorption of the product, ethane, is zero, a satisfactory heat of reaction is obtained.

Although the Rideal-I mechanism cannot explain the removal, as observed in this research, of adsorbed ethylene, Rideal claims the mechanism to be the operative one in ethylene hydrogenation on a surface with a preadsorbed ethylene layer (37). He postulates that hydrogen is adsorbed on vacant sites which are unavailable to ethylene and that reaction occurs between this adsorbed hydrogen and gas-phase ethylene.

Analysis of Experimental Results

There are two methods for analysing the kinetics of a heterogeneous reaction. The first is to study the variation of the initial reaction rate with the pressure of either reactant over a series of reactions. The second involves the investigation of the rate course of any one given reaction run.

The first method requires that the catalyst activity be constant from one run to the next. We have found, however, large variations in catalytic activity between each individual film and so it has not been feasible to study the reaction kinetics by reference to a series of experiments on different films. Examples of the observed behaviour are given in Table 23.

Table 23

Film No.	Fig. No.	Reactant Pressure *(mm)	Initial Rate (mm/min/30mg)	Notes
13	10	53.5	1.2	Third run, E = H Rate after induction period
19	16	50.0	7.15	First run, E = H
21	19	47.6	9.84	E = H
22	20	50.0	3.52	E < H

(*The pressure given is the partial pressure of the reactant present in lower concentration)

In view of the observed variation between different films it has been necessary to have recourse to the second method of analysis.

In general, for a bimolecular reaction

$$v = k.P_A^a.P_B^b.$$

If the two reactants are present at equal partial pressures then

$$v = k'.P_A^{a+b},$$

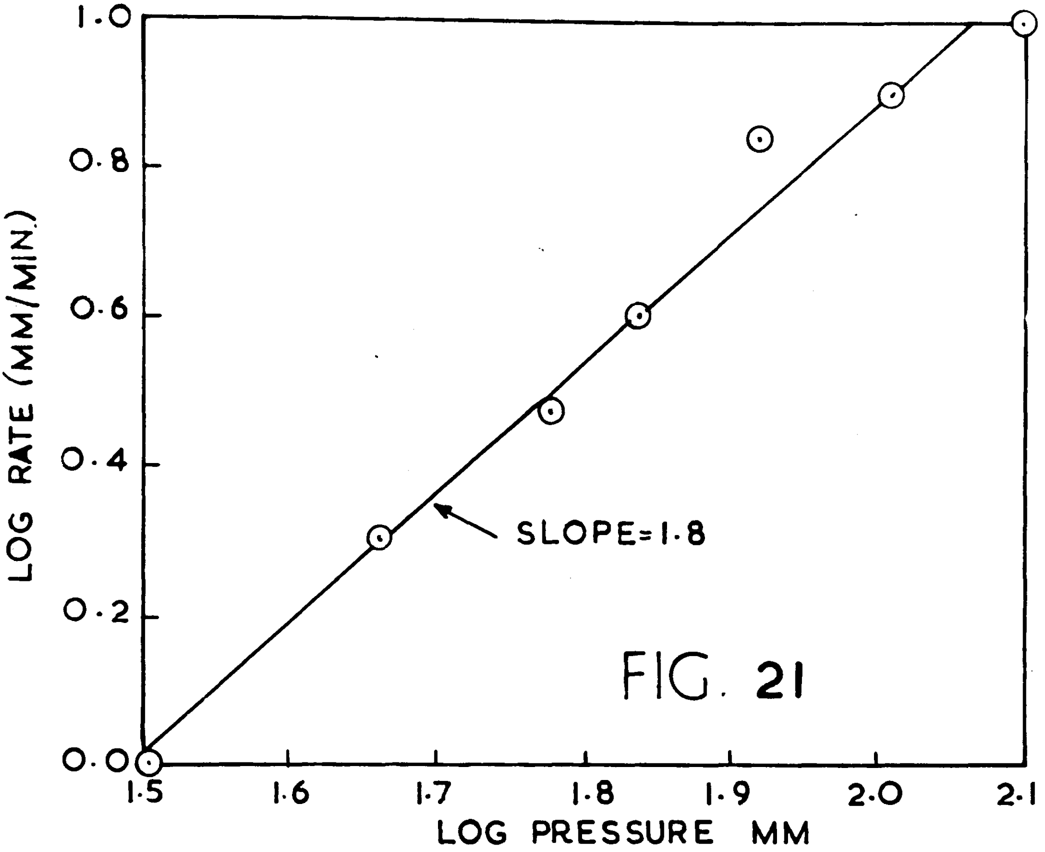
and therefore

$$\log v = \log k' + (a+b)\log P_A.$$

Therefore by plotting the logarithm of the rate at any time t against the logarithm of the partial pressure of one of the reactants at the same time t, a graph is obtained with slope equal to the overall order of reaction. This has been done for the following films (figures in parentheses indicate the graph from which the pressures and rates were obtained): 5(first run)(3), 10(6), 11(7), 19(first run)(16), 20(18), 21(19), and 22(20).

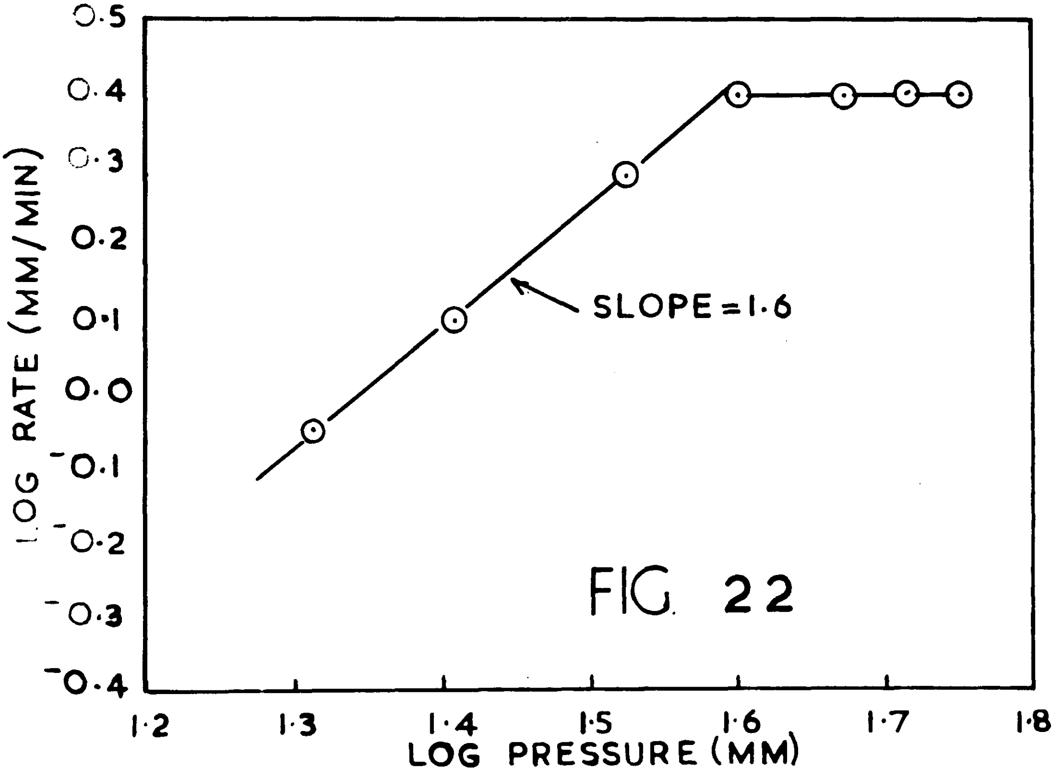
The graphs showing the plots of log.rate against log.pressure are as follows: film5 - fig. 21, film 10 - fig. 22, 11 - 23, 19 - 24, 20 - 25, 21 - 26, film 22 - fig. 27.

Although similar graphs have not been plotted



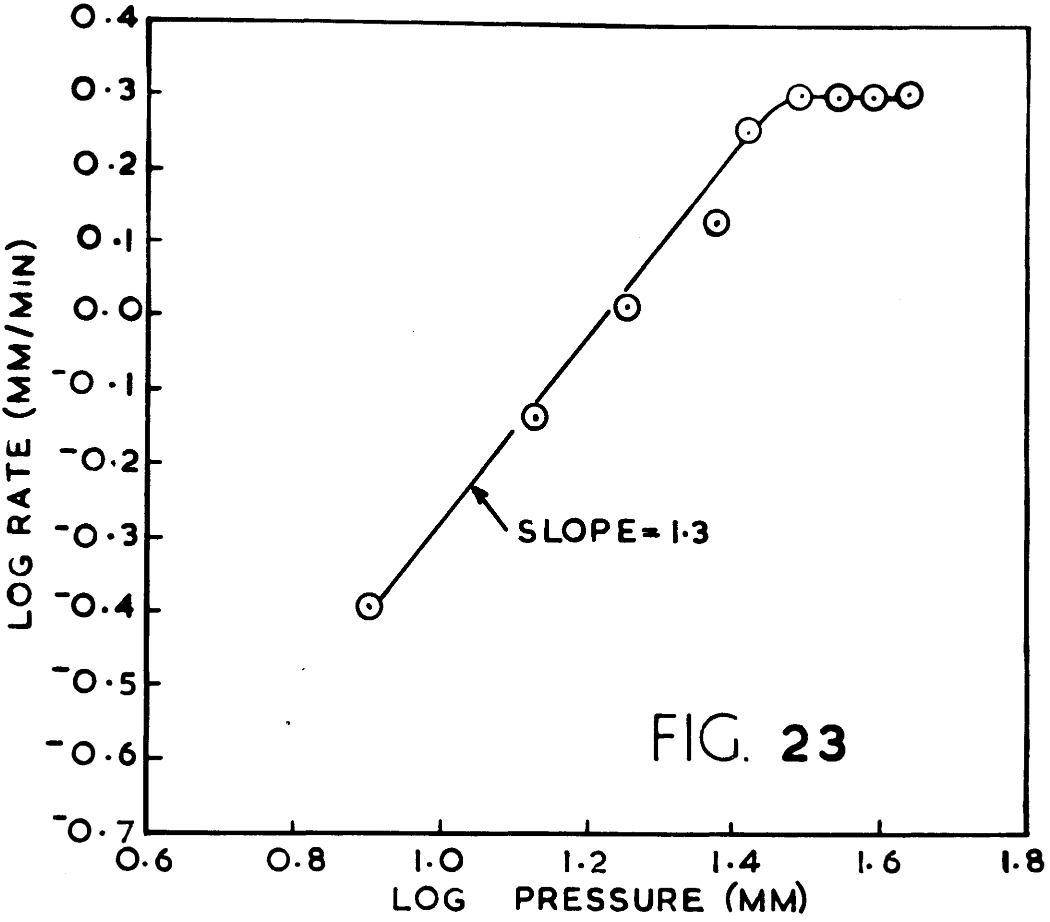
LOG RATE (MM/MIN)
1.0
0.8
0.6
0.4
0.2
0.0
SLOPE=1.8
1.5
1.6
1.7
1.8
1.9
2.0
2.1
LOG PRESSURE MM

FIG. 21



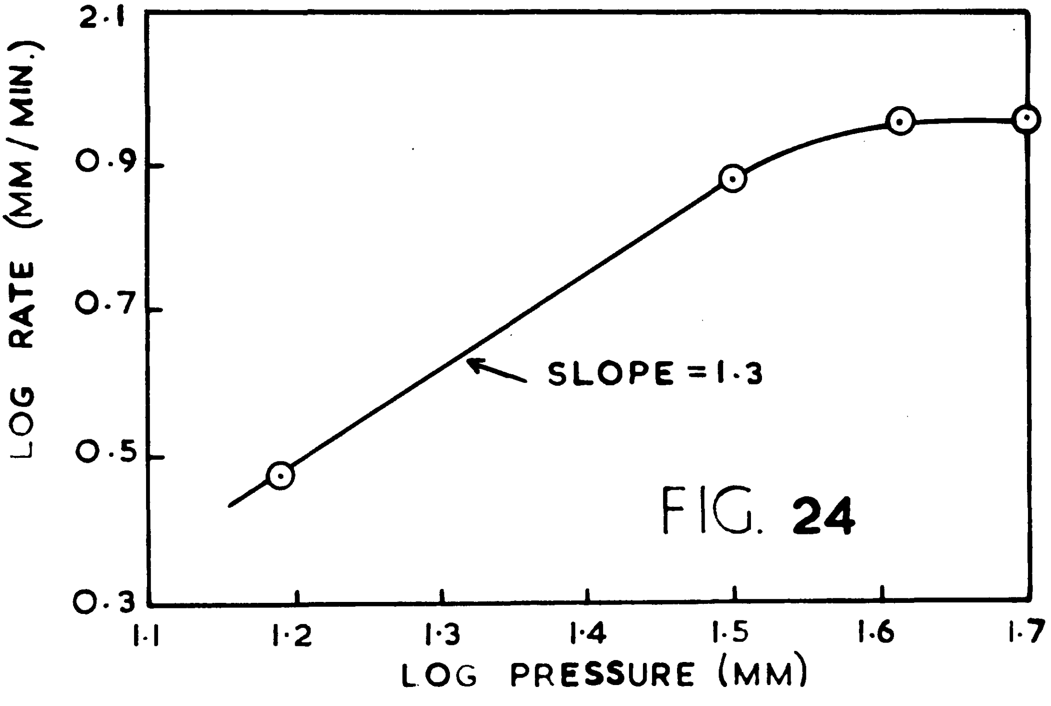
LOG RATE (MM/MIN)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
SLOPE=1.6
1.2
1.3
1.4
1.5
1.6
1.7
1.8
LOG PRESSURE (MM)

FIG. 22



LOG RATE (MM/MIN)
0·4
0·3
0·2
0·1
0·0
-0·1
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
0·6
0·8
1·0
1·2
1·4
1·6
1·8
LOG PRESSURE (MM)
SLOPE = 1·3

FIG. 23



LOG RATE (MM/MIN.)
2·1
0·9
0·7
0·5
0·3
1·1
1·2
1·3
1·4
1·5
1·6
1·7
LOG PRESSURE (MM)
SLOPE = 1·3

FIG. 24

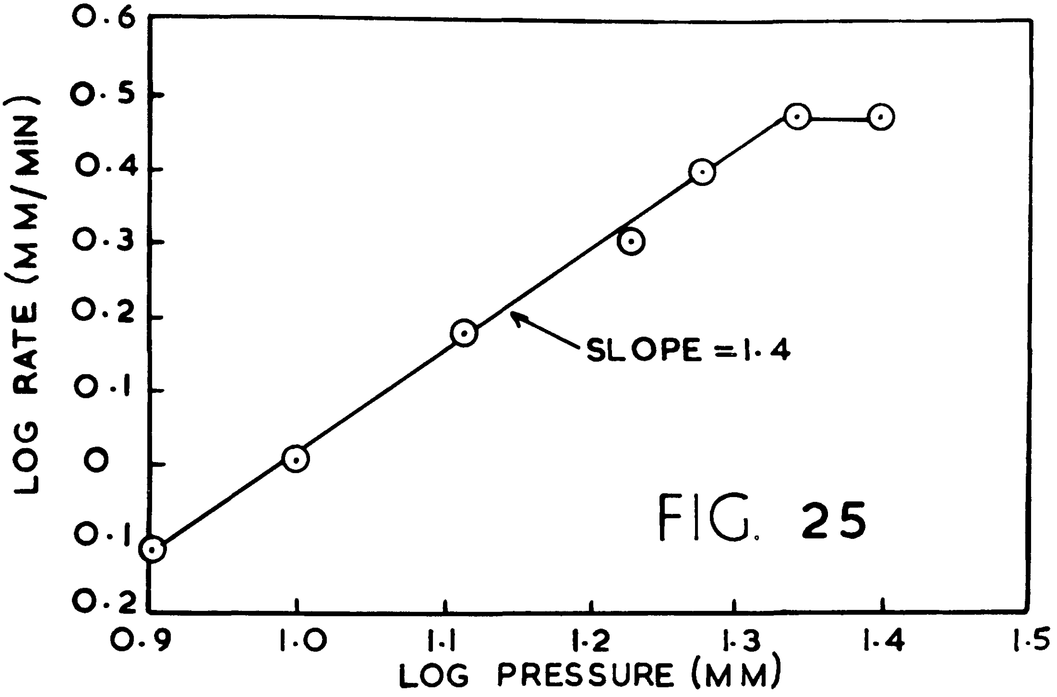

O·6
O·5
O·4
O·3
O·2
O·1
O
O·1
O·2
LOG RATE (MM/MIN)
0·9
1·0
1·1
1·2
1·3
1·4
1·5
LOG PRESSURE (MM)
SLOPE = 1·4

FIG. 25

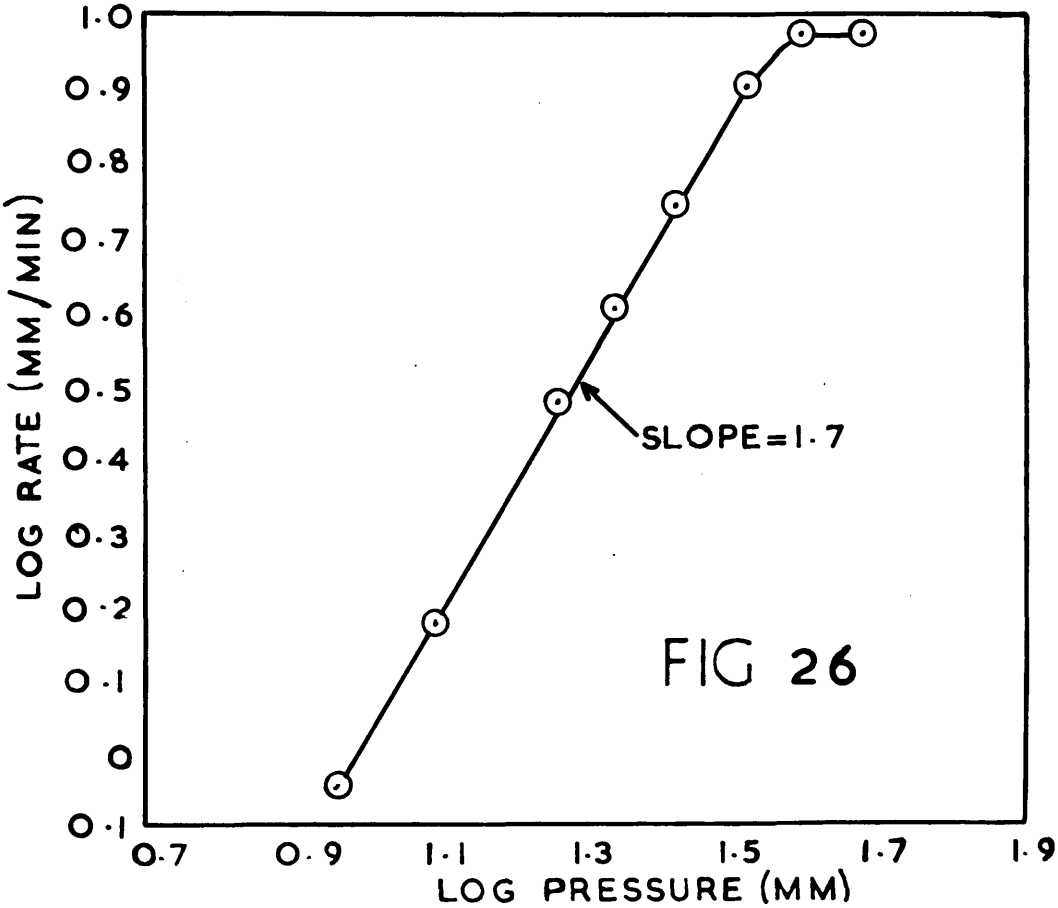

1·0
O·9
O·8
O·7
O·6
O·5
O·4
O·3
O·2
O·1
O
O·1
LOG RATE (MM/MIN)
0·7
0·9
1·1
1·3
1·5
1·7
1·9
LOG PRESSURE (MM)
SLOPE = 1·7

FIG 26

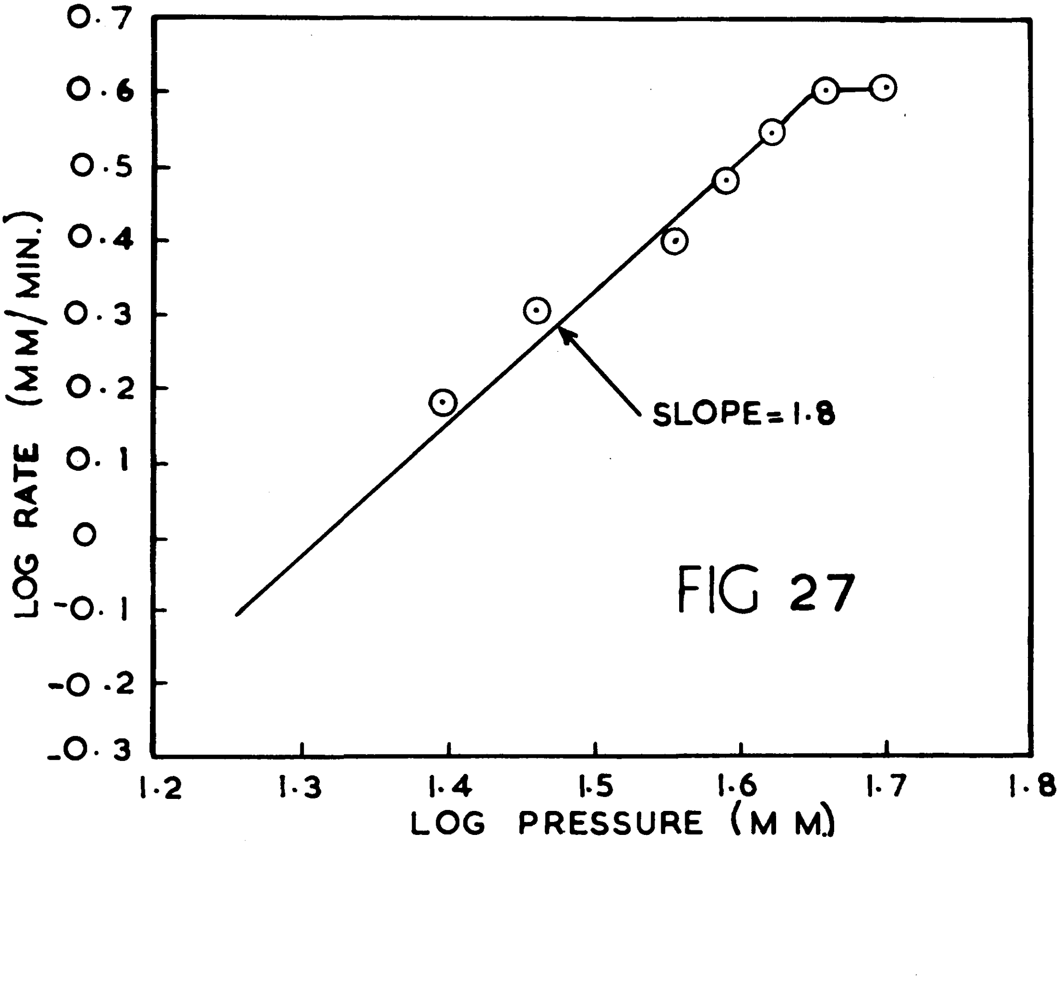

0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
-0·1
-0·2
-0·3
LOG RATE (MM/MIN.)
SLOPE = 1·8
1·2
1·3
1·4
1·5
1·6
1·7
1·8
LOG PRESSURE (M M.)

FIG 27

for all the experiments carried out, inspection shows very similar behaviour in every case. The exceptions which may be noted are: film 13, where poisoning played some part in the pressure variation with time since the run shown in fig. 10 was the third carried out on that particular film; and film 15 which was the first film to be prepared by evaporation in argon. As has been pointed out earlier, this film was poisoned to a certain degree.

The salient feature of interest in each graph is the rapid change in the overall order from zero to an order of between 1.3 and 1.8. An exception to this behaviour is film 5 (fig. 21) where the zero order part of the reaction course is not observed. The point of interest in this zero order behaviour is to study the relationship between it and the fall in count rate observed. In Table 24 is shown the times in minutes at which the zero order reaction course ceased, and the time at which a definite fraction (60%) of the reactive ethylene-C14 was removed during reaction

Table 24

Film Number	10	11	19	21	22
Time of zero order duration (minutes)	12.6	16	1	1	1.25
Obtained from fig. No.	22	23	24	26	27
Time for removal of 60% C_2H_4-C14 (mins)	4	5	1.5	1	0.75
Obtained from fig. No.	6	7	16	19	20

There is good correlation between the two factors for films 19, 21, and 22, but poor correlation for films 10 and 11. In the case of films 10 and 11 it can be seen from figs. 6 and 7 that the removal of ethylene-C14 took place during the short induction period which was observed.

This correlation between the duration of the zero order reaction and the time during which the removal of adsorbed ethylene-C14 molecules occurred can be explained by the equation developed from absolute reaction rate theory (54):

$$v = s^2 LAB^2 c_{g'} \frac{kT}{h} \cdot \frac{1}{F_{g'}} \cdot \exp\left(-\left(\frac{e_0 - e'' - 2e}{kT}\right)\right)$$

for reaction between an adsorbed ethyl radical and an adsorbed hydrogen atom.

The factor of interest in this equation is the term $LAB^2c_{g'}$, where L is the number of sites per cm^2, and A and B are defined by the concentration of adsorbed ethylene molecules and vacant sites resectively, and by a term x which is a function of the adsorption isotherm for ethylene.

The possibility then occurs that as the ethylene-C14 is removed from the surface by reaction the concentration of free sites c_s will increase and will therefore bring about a change in B. Laidler (54) gives graphs which show a marked change of the function AB^2 with x and, if this change is compensated by a change in the opposite sense in $c_{g'}$, a reaction of apparently zero order will occur. Once this variation in AB^2 has ceased, the active ethylene-C14 having been removed, the reaction will revert to an orthodox variation of rate with reactant pressure.

This theory is nullified however by the results shown in fig. 17. This is the result of a second experiment on film 19, the details of which are given in Table 18. It is evident from these results that the reaction follows an identical reaction course of zero order, followed by an overall order of about 1.5, although there is no change in the concentration of the adsorbed ethylene-C14 and therefore the concentration of sites is constant.

The Langmuir-Hinshelwood mechanism gives (1) the rate of ethylene hydrogenation as being:

$$v = \frac{k_2 K_H K_E P_H P_E}{(1 + K_H P_H + K_E P_E)^2}$$

If the hydrogen is weakly adsorbed and ethylene strongly adsorbed the expression simplifies to:

$$v = \frac{k P_H P_E}{(1 + K P_E)^2}$$

It is believed (55) that the data for ethylene hydrogenation obey this equation, although the kinetics of this reaction are still the subject of controversy.

Examination of the equation shows that it will explain the observed reaction pattern found in this research since, if KP_E is large compared with unity, the reaction becomes of overall zero order. As the ethylene pressure falls, however, KP_E will approach more closely to unity and the reaction will tend to a complex order.

By the Rideal mechanism in which adsorbed hydrogen reacts with gas-phase ethylene the rate is given by:

$$v = \frac{k . P_H P_E}{1 + K P_H}$$

This equation will not simplify to give an expression for a zero order reaction course, but it can explain the higher order found at later times during the reaction.

A factor which tends to support the Rideal mechanism as being the operative mode of reaction is the absence of any connection between the observed rate of reaction and the fraction of preadsorbed ethylene which is removed by hydrogen. For instance, the relevant figures for films 10 and 11 are:

Film 10 - fraction removed, 12%; rate at 10 minutes, 2.08 mm/min/30mg Ni.

Film 11 - fraction removed, 47%; rate at 10 minutes, 1.61 mm/min/30mg Ni.

If the Langmuir-Hinshel wood mechanism was operative, then some connection between the two factors would be expected since the active fraction would control the concentration of adsorbed ethylene and hydrogen.

The Rideal mechanism, on the other hand, involving reaction between adsorbed hydrogen and gas-phase ethylene, does not require any such connection.

It appears then that the preadsorbed ethylene is removed by a Langmuir-Hinshelwood mechanism, the mechanism later changing to the Rideal type.

3.3. Conclusions

This research has shown that the technique of observing radioactive molecules on a catalyst surface, and thereby following their behaviour during a reaction, is perfectly feasible and can give useful results. The experiments carried out in this research can be divided into four groups:

1. Straightforward observation of the active fraction of the surface.
2. Exchange between adsorbed and gas-phase ethylene.
3. The behaviour of argon-evaporated films.
4.. Study of the role of different areas of the catalyst surface.

In the case of the ethylene-nickel system 30 to 40% of the ethylene adsorbed on a clean nickel film at 20°C is capable of reacting rapidly with hydrogen, but the remaining ethylene is firmly bonded to the surface and is not removed at a measurable rate over a period of up to one hour.

Chemisorbed ethylene is incapable of molecular exchange with gas-phase ethylene.

The fraction of the ethylene capable of reaction with hydrogen is not affected by the orientation of the film. There is no difference in the fraction of ethylene active in hydrogenation between films evaporated under vacuum and those films evaporated at a pressure of 1mm of argon, although the argon-evaporated films possess approximately double the surface area of the non-oriented films.

Ethylene adsorbed on nickel at room temperature is immobile and is instantaneously and irreversibly adsorbed. The location of the reactive ethylene lies in the precise structure of the surface; it is not determined by the degree of coverage of the film at any particular instant. It is inferred from this that the properties of any adsorbed ethylinic species are determined by the degree of bond unsaturation of the metal, this being closely associated with the degree of sintering of the film and its atomic and micro-crystalline structure. It appears also that the electronic structure of the metal exerts an influence, this also pointing to the conclusion that it is the extent of the adsorbate-adsorbent interaction which determines the reactivity of the adsorbed species. The degree of interaction between an adsorbed species and the metal varies over the whole surface, and it is only those adsorbed species which are activated to the necessary degree by the surface which are capable of reaction.

It ean be postulated from this that the reactivity is determined by some factor such as the electron density in the C-C bond of, say, ethylene, this in turn being affected by the relative strengths of the carbon to metal bonds.

The results of this research also lead to the conclusion that attempts to relate adsorption isotherms, absolute reaction rates, magnetic measurements, heats of adsorption, etc., to the process of catalysis can only be valid if they take into account the fact that only a fraction of the adsorbed species is active in a catalytic reaction.

3.4. Future Work

The technique described in this thesis is a new one, and the work discussed is only the first series of experiments to be carried out using this method. There are many catalytic systems to which it could be applied.

In the ethylene-nickel system alone a large amount of research remains to be done. The two major factors which could be investigated are the effect of temperature and the effect of film structure.

It has been shown (39) that the composition of adsorbed ethylene varies with temperature; it is possible to extend these investigations using this radiochemical technique to other temperatures, and valuable results could be obtained.

The effects of catalyst structure could be investigated in very many different ways - for instance, by different degrees of sintering and annealing of the catalyst, and by techniques such as ion bombardment. The study of the same processes on epitaxially-grown crystals would also give results of interest on the subject of the influence of crystal face on catalysis.

By investigation of ethylene-C14 on different metals it would be possible to ascertain more precisely the effect of the electronic nature of the metal of the reactivity of the adsorbed species.

With systems other than ethylene on nickel many important investigations remain to be carried out. Olefins other than ethylene have only been studied by a few workers; it would be of interest to enquire into the effects of such factors as increasing methyl substitution and cyclisation on the reactivity of the adsorbed molecules.

This radioactive tracer technique therefore provides yet another tool for the investigation of heterogeneous catalysis; one which can help to advance our understanding of the many complications of this difficult subject.

CHAPTER 4

APPARATUS

4.1. General

The block schematic diagram of the apparatus is shown in fig. 1. The basic requirements of the apparatus have been described in Section 1.4. and the actual details of the construction will be discussed in this Chapter.

The apparatus was constructed throughout of thick-walled pyrex glass which was washed with detergent and rinsed with distilled water before incorporation into the vacuum system. Gas control throughout was by means of standard high-vacuum stopcocks manufactured by Messrs. Springham Ltd. When the apparatus was first built the taps were all lubricated with Apiezon 'N' grease, but this was changed at a later date for silicone high-vacuum grease. This change was felt necessary as the viscosity of silicone grease changes far less with temperature than does Apiezon 'N'. This was found to be an advantage since large temperature fluctuations in the laboratory caused Apiezon 'N' grease to "streak" when experiments were carried out with the laboratory heating turned off in the evenings.

The actual apparatus layout is shown in fig. 28. Each section of the apparatus was connected to a common manifold which was pumped by a Messrs. Edwards mercury diffusion pump, type 1M2. The catalyst vessel, which is described in detail in Chapter 5, was evacuated by a separate Edwards silicone oil diffusion pump, type 102, charged with Dow Corning 704 silicone fluid. Both diffusion pumps were connected by a common line to a two-stage rotary pump, Messrs. Edwards type 2S20B.

The vacuum in the apparatus was measured by two independent methods. An Edwards 'Vacustat' miniature McLeod gauge was fitted by a B.14 cone and socket to the end of the main vacuum manifold. This gauge served to measure the vacuum in the whole apparatus apart from the catalyst vessel. The vacuum in the catalyst vessel was measured by means of a Philips PW 7901/00 Penning (22) ionisation gauge.

This gauge had a range of 2 x 10^{-3}torr to 1 x 10^{-5}torr. The instrument was calibrated for dry air by the manufacturer and a calibration chart was supplied. This was used without modification. At 1 x 10^{-5}torr the meter reading was 10 A and, accordingly, the catalyst vessel was always outgassed until the residual pressure gave a meter reading of less than

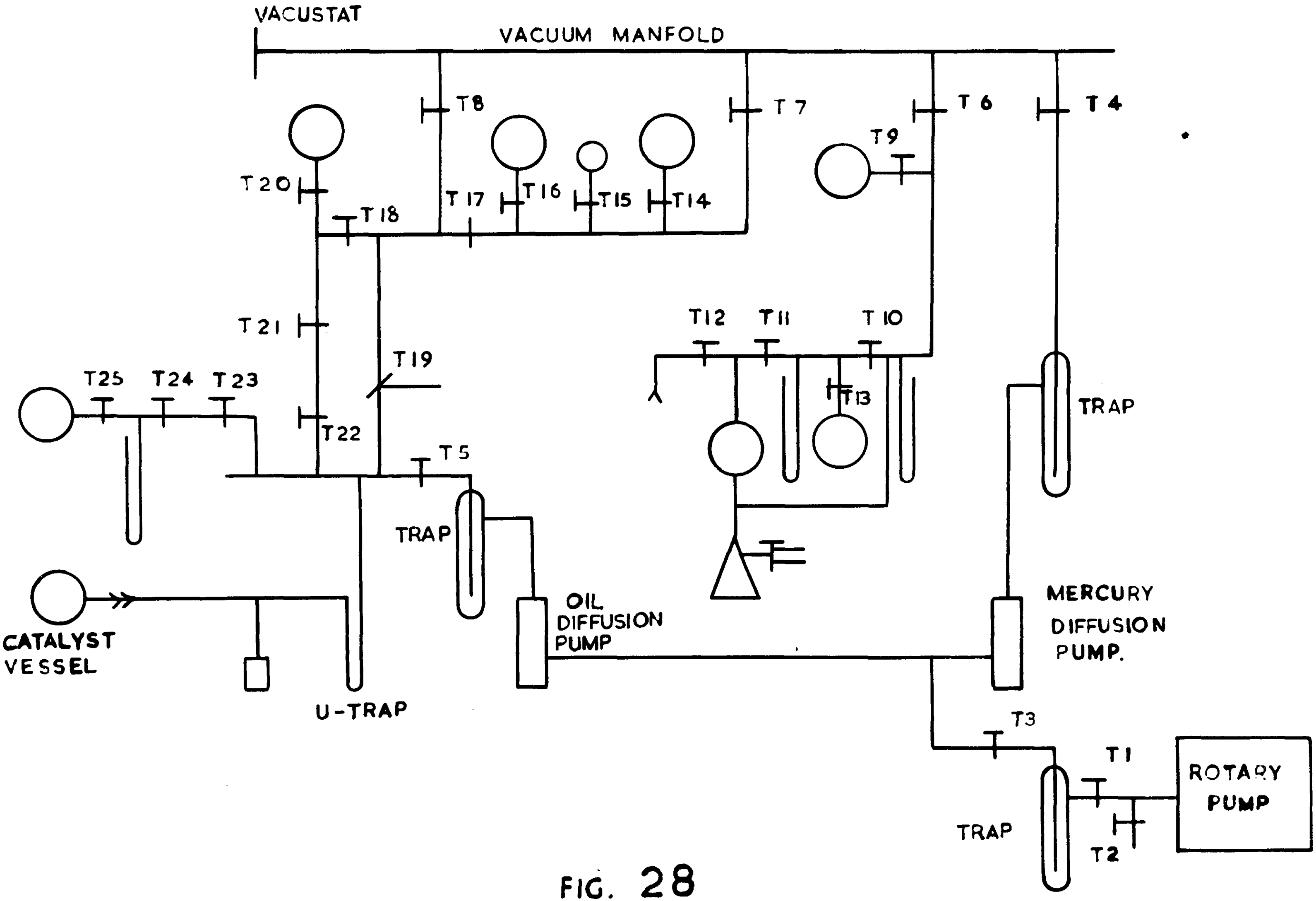

VACUSTAT
VACUUM MANFOLD
T8
T7
T6
T4
T9
T20
T17
T16
T15
T14
T18
T21
T12
T11
T10
T19
T25
T24
T23
T13
T22
T5
TRAP
TRAP
OIL DIFFUSION PUMP
MERCURY DIFFUSION PUMP.
CATALYST VESSEL
U-TRAP
T3
T1
ROTARY PUMP
TRAP
T2

FIG. 28

$10\mu A$, thereby ensuring that the residual pressure was less than 1×10^{-5} torr.

The gauge head was made from "soda" glass and could not be directly attached to the vacuum apparatus. Instead, a B.14 "soda" glass cone was attached to the gauge head and this was then joined to a pyrex B.14 socket in the vacuum line by means of Apiezon 'W' wax, as shown in fig. 34.

Each section of the apparatus will now be discussed in detail.

4.2. Gas Storage

All the reagent gases were stored in the section illustrated in fig. 29. The line G was connected to the vacuum manifold via T7 and to the gas handling section via T17. Hydrogen was stored in a bulb, C, of two litres capacity. Inactive ethylene was stored in bulb F, again of two litres capacity, but fitted with a cold finger E to facilitate purification and handling of the gas. Hydrogen and inactive ethylene were both introduced into the apparatus by way of a No. 4 sintered glass disc, S, over mercury.

Ethylene - C14 was obtained from the Radiochemical Centre, Amersham, in a break-seal tube, A,

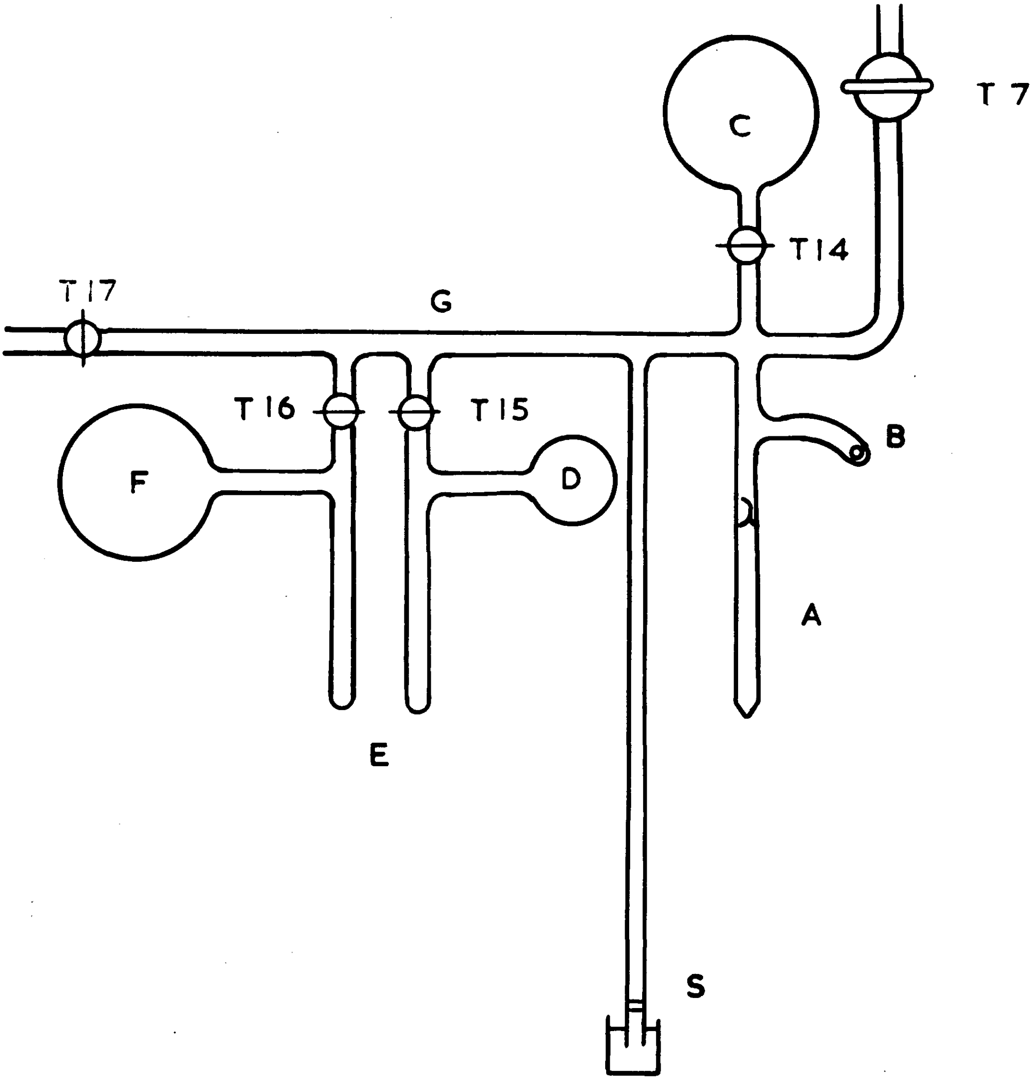


FIG. 29

which was attached to the line G below a side arm, B, holding a stainless steel ball.

The ethylene-C14 was diluted and stored in bulb D, the volume of which was obtained by accurate calibration. The question of calibration is discussed in Section 4.6. The ethylene-C14 was diluted as follows.

After evacuation of volumes D and G to 1 x 10^{-5} torr T7 was closed and inactive ethylene admitted to G and D via T16. The pressure was determined on the main manometers (fig. 33). T15 was then closed and the excess ethylene pumped away until a vacuum of 1 x 10^{-5} torr was again achieved. T7 was closed and the contents of tube A were frozen in liquid nitrogen. The break seal of A was then broken and T15 opened, when the ethylene of bulb D condensed into A. The Dewar flask of liquid nitrogen was then removed from A and placed around the cold finger of D whereupon the inactive ethylene and ethylene-C14 distilled over into D. This cycle was repeated two or three times to ensure that all the ethylene-C14 was transferred to the storage bulb. T15 was then closed.

4.3. Gas Handling

The gas handling section is shown in fig. 30. It consisted of two parts: a mixing section, A, and

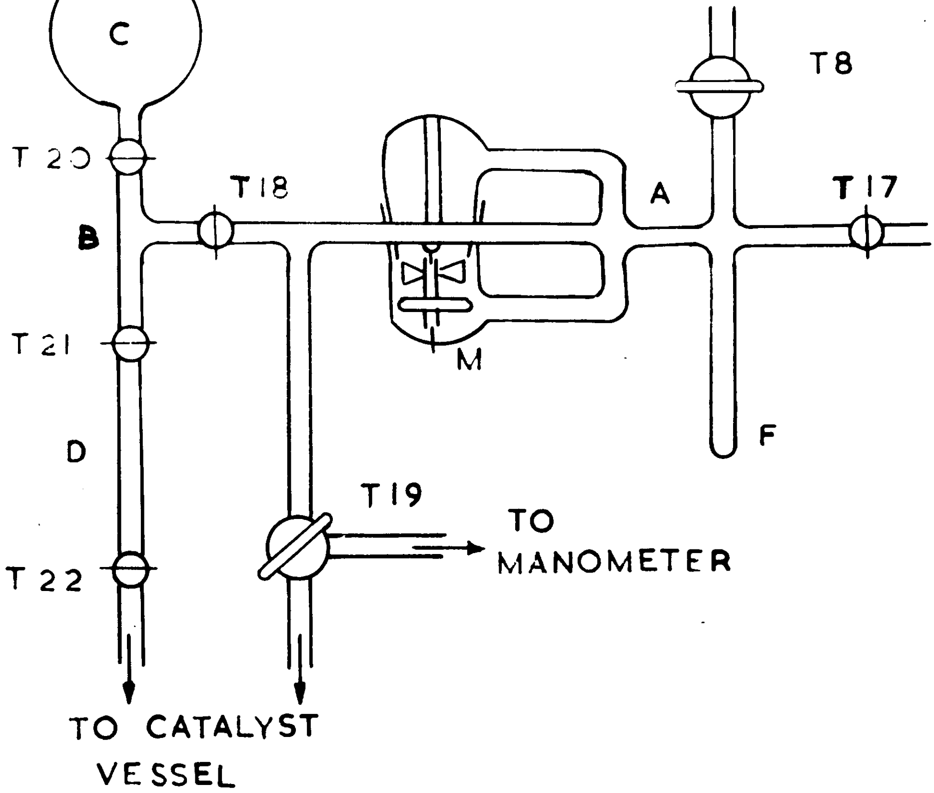

C
T8
T 20
T18
A
T 17
B
T 21
M
D
F
T 19
TO MANOMETER
T 22
TO CATALYST VESSEL

FIG. 30

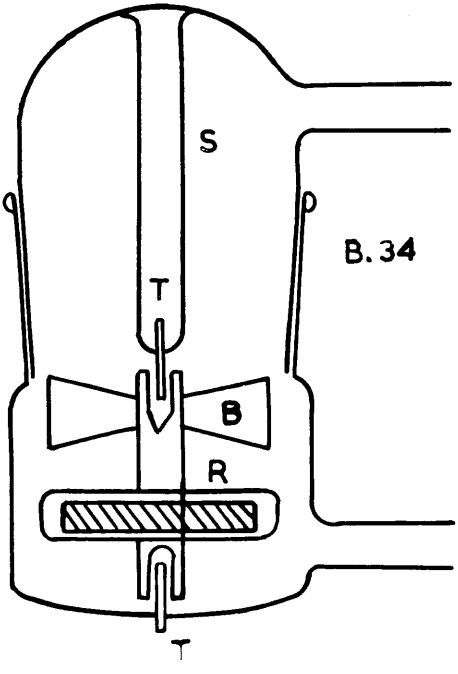

S
B. 34
T
B
R
T

FIG. 31

an expansion and pipetting section, B,C,D.

Reactants were mixed in section A prior to admission to the catalyst vessel. With T19 open to the manometer ethylene was admitted at the required pressure by opening T17. The gas was then frozen into cold finger F with liquid nitrogen and hydrogen admitted, again through T17. The hydrogen pressure was measured on the manometer and the ethylene was then allowed to evaporate.

Mixing of the two gases was achieved by means of the stirrer M which is shown in detail in fig. 31. It was constructed from the two halves of a B.34 joint as shown. A supporting tube, S, was sealed to the upper joint as shown and two 1mm diameter tungsten wires, T, were sealed into the glass to act as bearings for the rotor, R.

The rotor was based on 2mm bore capillary tubing which was sealed onto either side of a transverse tube containing a 3cm length of soft iron rod 1/8in in diameter. The ends of the rotor were cut to the required length on a high-speed carborundum wheel. Four glass blades, B, were affixed to the upper end of the rotor as shown. Each blade was heated at its junction with the rotor and twisted to a pitch of 40-45° to form an impeller. The two halves of the body were joined by means of Apiezon 'W' wax and connection with the vacuum line was made with two side arms of 1.5cm tubing. An 'Eclipse' U-magnet was fitted with a brass pulley and mounted in bearings below the stirrer so that it could be driven by a 'Citenco' variable speed electric motor, hence driving the glass rotor at speeds varying from 250 to 1000 r.p.m.

Gases in section A could be expanded into volumes B and C by opening T18. If little or no expansion was required then T20 was kept closed. The gas or mixture of gases was then pipetted into the catalyst vessel from the gas pipette, D, by opening and closing T21, followed by opening T22.

The pressure in volumes B and C after expansion could be calculated from the known volumes of the apparatus, but as successive increments of gas were pipetted into the catalyst vessel the total pressure in B and C fell. Consequently, two successive volumes of gas from the pipette did not contain the same number of molecules. To overcome this difficulty a mathematical correction procedure was evolved whereby this fall in pressure could be taken into account. This process could be looked upon as a progressive decrease in the volume of the pipette if the pressure in B and C remained constant. The details of this correction, and a table of values of the volume reduction, are given in Appendix I.

4.4. G.-M. Tube Filling

The section shown in fig. 32 was that used to fill the G.-M. tube with the necessary filling gas and quenching agent to the required pressures.

The section was attached to the main vacuum manifold, and evacuated, at T6. The filling gas, argon, was admitted after purification to bulb A through the No. 4 glass sinter S. The quantity of argon present in the bulb could be determined by means of manometer M1. The quenching agent, either ethyl alcohol or ethylene, was stored in bulb C which was attached after filling to the section D by the B.10 joint J1. The G.-M. tube itself was attached by the B.10 joint J2.

With T9 and T13 closed the section and the G.-M. tube were evacuated through T6. T6 and T10 were then closed. Quenching agent at the required pressure was admitted by opening T13. The pressure was measured on the U-tube manometer M3.

The necessary quantity of argon was then admitted to section B to the pressure indicated on M2. This gas was then transferred to the G.-M. tube and sections D and E through the Toepler pump Tp. By

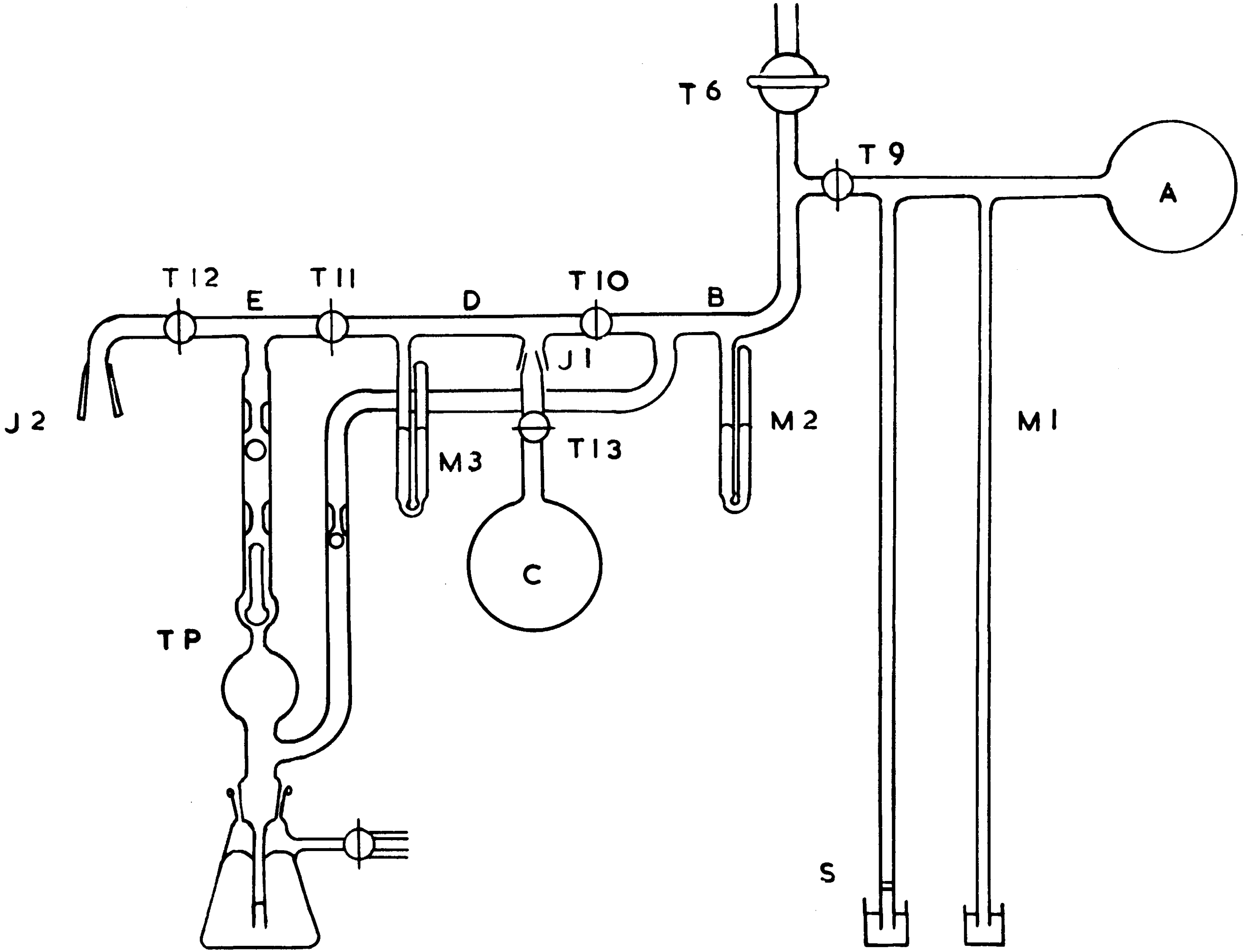


FIG. 32

this procedure contamination of one gas in its storage bulb by the other gas was avoided. The final total pressure of gas in the G.-M. tube could then be read on manometer M3.

4.5. Pressure Measurement

The gas pressures in the various sections were measured on the manometers shown in fig. 33.

The manometers consisted of two 85cm lengths of 2cm diameter tubing,M. These were carefully selected for straightness and evenness of bore. They were carefully cleaned by filling them with approximately 25M sodium hydroxide solution for several hours to remove all grease. They were then washed thoroughly with distilled water and dried with a stream of warm air.

The two tubes were mounted in a 150ml crystallising dish, C, which contained the necessary volume of trebly distilled mercury. Molten paraffin wax was poured onto the surface of the mercury and allowed to set. This cover, W, prevented contamination of the surface of the mercury. Air was allowed into contact with the mercury in the reservoir <u>via</u> the tube, A, which was shaped as shown to prevent dust from entering the air space.

Both manometer tubes were evacuated through

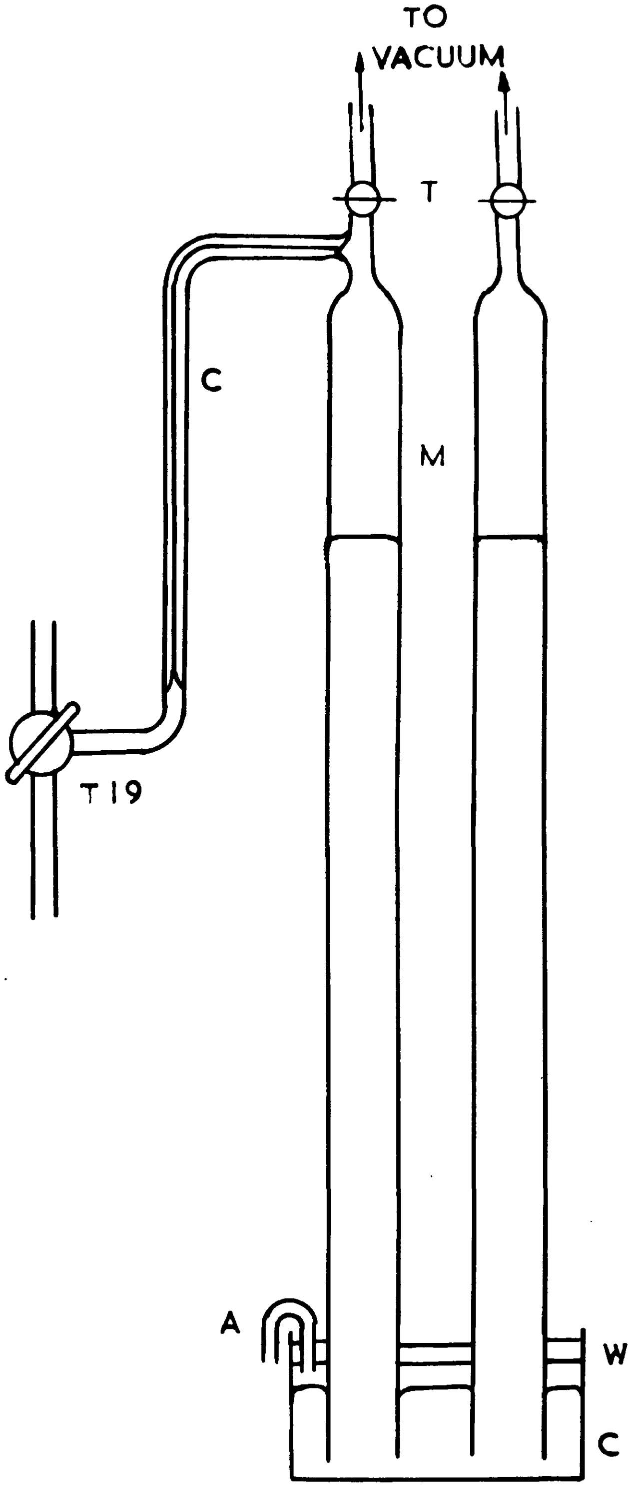


FIG. 33

the two taps T.

The three-way tap T19 was connected to the left-hand manometer by capillary tubing, C, which reduced mercury diffusion into the catalyst vessel to a minimum.

4.6. Calibration

In any vacuum apparatus such as that used in this research it is essential to know accurately the relevant volumes used in handling and storing the various gases. In particular, in this apparatus ethylene-C^{14} had to be accurately diluted to a known specific activity and then expanded to a known pressure and pipetted out, at this pressure, very accurately.

Two basic methods were used in calibration. For those volumes which had to be known very accurately weighing the section when empty and when filled with water was employed. For the other volumes gas expansion was used and the unknown volumes calculated by Boyles Law.

The ethylene-C^{14} bulb (D in fig. 29) was calibrated by weighing with water, as were volumes B and C (fig. 30) and the gas pipette (D in fig. 30).

After each volume had been made, but before it was blown onto the main apparatus, the taps were lightly greased with Apiezon 'N' grease and the section weighed on a sensitive balance capable of weighing up to 2000g. The apparatus was then carefully filled with distilled water so that any air bubbles were eliminated. The apparatus was then weighed again. The volume of water was calculated from its weight, making correction for ambient temperature from the water density tables provided in the "Handbook of Chemistry and Physics" (56). Calibration could be achieved to an accuracy of 0.1% by this method. These calibrated volumes were then employed in the calibration of the remaining sections of the apparatus.

This was achieved by filling the known volume with air to a pressure measured on the manometer at T19. The volume was then isolated and the remainder of the system evacuated. The volume containing the air was then opened to the section whose volume was to be determined and to the manometer. The volume of the unknown section was then calculated by Boyles Law. Since the manometer had to be always accessible to the unknown volume, volume A (fig. 30) was calibrated first, from air expanded from volumes B and C (fig. 30).

A difficulty in this method of calibration was encountered with this apparatus. This was that the total volume of any given section varied as the mercury level in the manometer varied with pressure. The problem was overcome by devising a graphical method for the evaluation of the constants of the system. Having found these constants, then any unknown volume could be determined. The full treatment of this graphical method is given in Appendix II, together with practical details of the determination of the constants.

Table 25 on the following page gives the calibrated volumes of each section of the apparatus.

Table 25

Figure No.	Section	Volume (ml)
Calibrated by weight of water:		
29 D	Ethylene storage bulb	159.6
30 B	Tubing	8.06
30 C	Expansion bulb	1089.0
30 D	Gas pipette	4.365
Calibrated by gas expansion:		
29 G	Vacuum line + open ethylene-C14 tube (A)	103.7
30 A	Tubing and mixing fan	216.0
33 C	Tap T19 to mercury surface at 76.0cm atmos. pressure	40.7
28 & 34	Catalyst vessel and associated tubing	944
35 & 36	Catalyst vessel proper	713
Not calibrated:		
29 C	Hydrogen storage bulb	2000
29 F	Ethylene storage bulb	2000

CHAPTER 5

THE CATALYST VESSEL

5.1. General

The design of the section incorporating the catalyst vessel is shown in fig. 34.

In addition to providing the pumping facilities for the catalyst vessel, the section had connections to the manometers and the gas pipette through T19 and T22 respectively. These taps connected with the sections described in Sections 4.3 and 4.5. In order to provide a high rate of pumping the main tubing connecting the catalyst vessel to the oil diffusion pump was of 15mm diameter and control was achieved by means of a 10mm bore tap T5. The catalyst vessel was protected from stop-cock grease vapour and mercury vapour by a cold trap U which was of U-shape to prevent loss of pumping speed.

The head of the Penning ionisation gauge, I, was attached to the main line, as described in Section 4.1, through a ground glass joint fixed with Apiezon 'W' wax. The catalyst vessel itself was attached to the main line at the B.14 socket shown.

Argon Evaporation

As has already been described, a number of

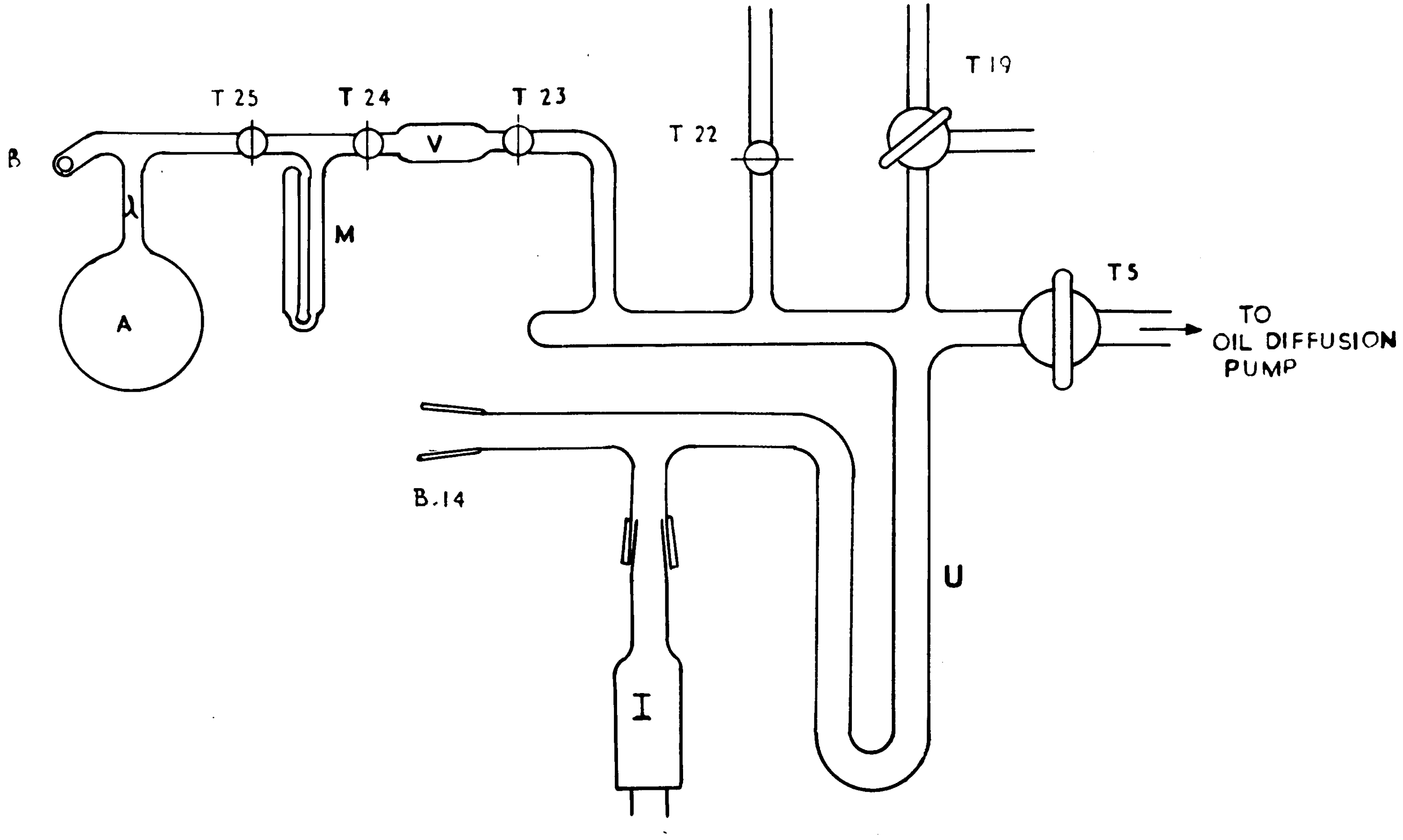


FIG. 34

films were evaporated in an atmosphere of argon. The method of preparation is described in Section 5.4. The apparatus for the introduction of argon to a definite pressure is also shown in fig. 34. Argon, specroscopically pure, was obtained from Messrs. British Oxygen Gases, Ltd. in 1 litre bulbs fitted with break-seals. The bulb, A, was attached to the apparatus below a side arm, B, holding a stainless steel ball for breaking the glass seal. The volume, V, betweem T24 and T23 was constructed, and calibrated with water, to a volume of 10.0ml. With T24 open and T23 closed argon to any required pressure as measured on the manometer, M, could be admitted to volume V by opening and closing T25. T24 was then closed and T23 opened, when argon expanded into the catalyst vessel to a predetermined pressure.

Dead Space

In the graphs of pressure against time given in Chapter 1 the pressures have been corrected for the dead space of the catalyst vessel. Although the volume of the catalyst vessel section as given in Table 25 was 944ml the catalyst vessel itself had a volume of only 713 ml. Ethylene and hydrogen in the dead space of 231ml did therefore not react over the catalyst and consequently the observed pressure change was not the true change due to the reaction. The pressure readings have therefore been corrected for this dead space by the factor of $\frac{713}{944}$.

5.2. The Catalyst Vessel

As was stated earlier, in Chapter 1, the catalyst vessel was designed so as to allow the monitoring, by a G.-M. tube, of the surface of an evaporated nickel film. It was felt desirable to have a catalyst vessel in which the film could be prepared and then used for the experiments. In view of these requirements the catalyst vessel was built as shown in fig. 35. This diagram is not to scale. The vessel consisted basically of a length of pyrex tubing, 45mm diameter and 40cm long. The tube was fitted at one end with a B.40 socket and the G.-M. tube, G, was mounted on a B.40 cone which could be fixed in the socket with Apiezon 'W' wax. The other end of the main tube was fitted with the nickel filament from which the evaporated film was prepared. A pyrex tube, S, was a loose fit inside the main tube of the catalyst vessel. The nickel film was evaporated onto the inner surface of this tube S and the tube could then be moved to the other end of the catalyst vessel where it surrounded the G.-M. tube. The

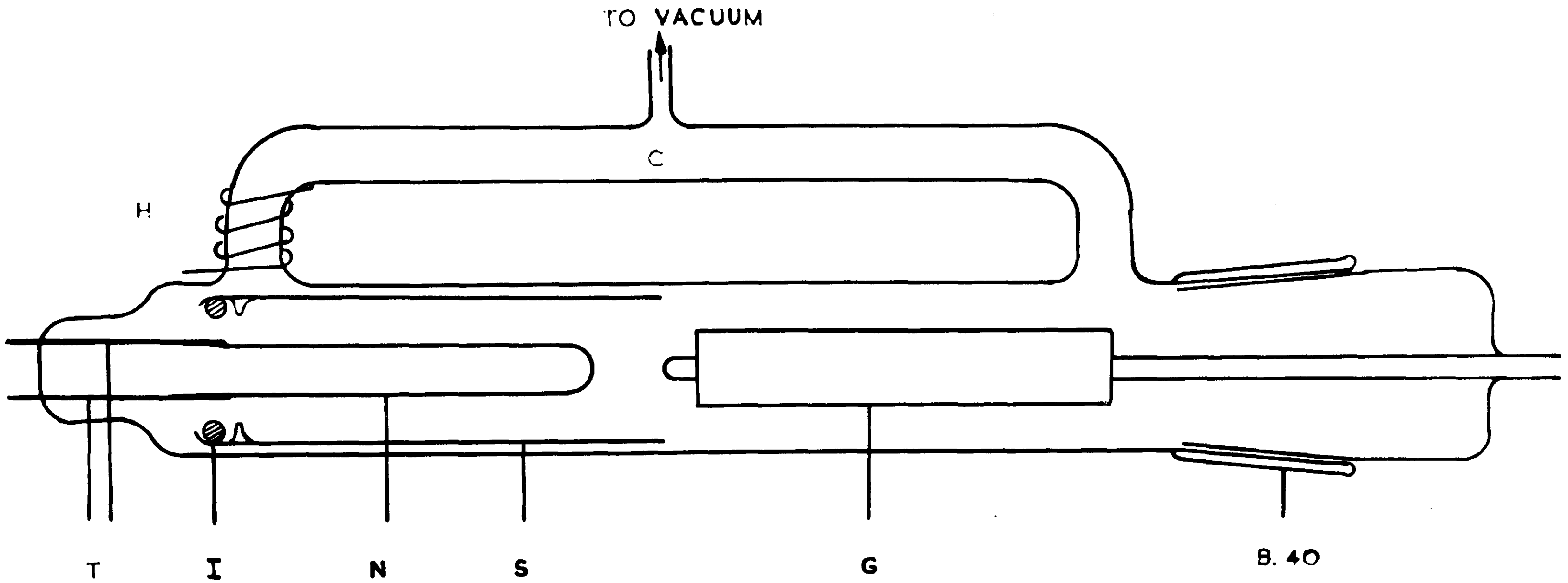


FIG. 35

surface of the nickel film could thus be monitored and the activity of the adsorbed labelled molecules determined.

Two different designs of catalyst vessel were used, and these are shown in figs. 35 and 36. In experiments involving the reaction of two gases over a catalyst diffusion can exert a major influence on the reaction pattern. It was therefore felt to be necessary to have some means of circulating the reactant gases over the catalyst. In the first instance thermal convection was employed. The catalyst vessel was fitted with a side loop, C (fig. 35), of 15mm diameter tubing and a small heating coil, H, was wrapped around one arm of the loop. This heater was made of Nichrome resistance tape and had a resistance of 60 ohms. It was run from a "Variac" variable transformer and thereby achieved a temerature of about 100°C. This temperature is sufficient to maintain an adequate circulation velocity of the gases contained in the catalyst vessel (57).

The catalyst vessel was clamped in a horizontal position, and this raised the problem of moving the tubing carrying the evaporated nickel film. This problem was simply resolved, as follows. One end of the tube S was flanged inwards on a glass-working lathe so as to support a ring of 1/8in diameter soft iron wire, I, which just fitted inside the tube. The iron wire was held in position against the flange by three "dimples" which were formed by softening the glass with an oxy-gas flame and then pushing in the softened area with a pointed carbon rod. The tube could then be moved within the catalyst vessel by means of an external magnet.

Two disadvantages of this design revealed themselves during use. One was that the adequate cooling of the film during evaporation was difficult. As explained in the next Section, the catalyst vessel was cooled by being surrounded with powdered solid carbon dioxide. During evaporation, however, the heat from the condensing film caused evaporation of the solid carbon dioxide. This loss at the top surface of the catalyst vessel was replenished by fresh "Dricold" falling into place. At the bottom of the vessel, however, a large air space formed and cooling in this area therefore became somewhat inefficient.

The second disadvantage concerned the movement of the tube bearing the nickel film. Friction of the glass against the catalyst vessel made it difficult at times to move the tube from one end of the catalyst vessel to the other. Also, the external magnet affected the nickel film itself and sometimes caused the film to flake away from the glass substrate.

Because of these drawbacks a second catalyst vessel was designed as shown in fig. 36. The soft iron ring was dispensed with and the catalyst vessel instead could be rotated in a vertical plane on a B.14 cone shown at B in fig. 36. The position of this cone is illustrated in fig. 36A (viewed from B in fig. 36). The tube could then be moved by gravity, and the catalyst vessel could be cooled during film evaporation by immersion in liquid nitrogen or an acetone/solid carbon dioxide mixture. Gas circulation facilities were also provided, this time by means of a magnetically-driven glass fan, C. This fan was identical with that described in Section 4.3 and shown in fig. 31.

In this type of catalyst vessel, operating in a vertical position, the tube S was inclined to cut off one of the side arms through which the gases circulated. To keep a free passage for the gases two supporting legs, L, were fitted to the sliding tube. These were 2cm lengths of 3mm pyrex rod which were fused diametrically opposite one another onto the end of the sliding tube. The joins were squeezed with glassblowing tweezers before annealing to remove

FIG. 36A

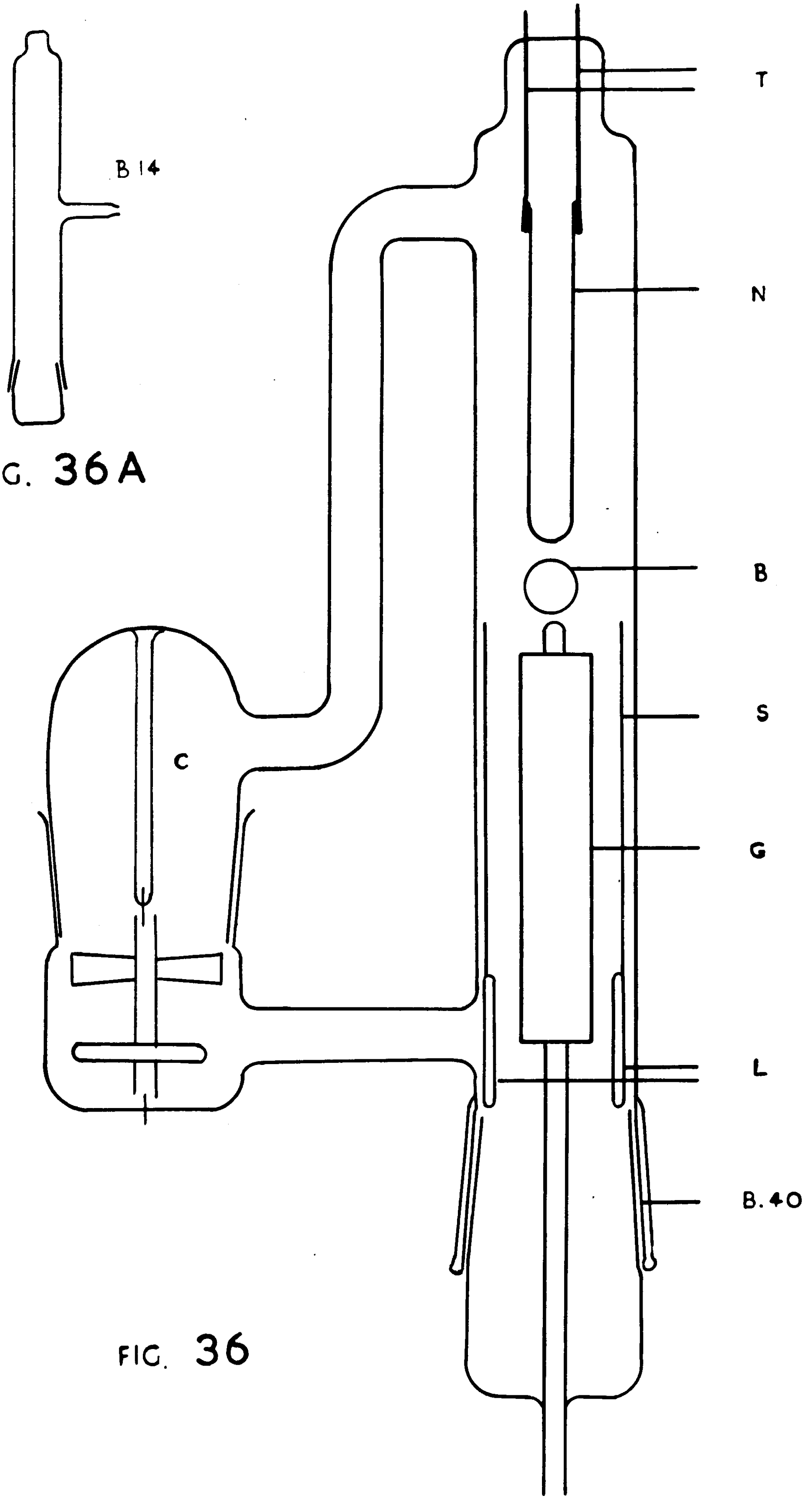


FIG. 36

any thickening of the glass which could restrict the movement of the tube within the catalyst vessel.

The B.14 joint on which the catalyst vessel was rotated was lubricated with silicone high-vacuum grease. It was felt that the risk of contamination of the film by vapour from the grease was more than offset by the better film preparation conditions and therefore the guarantee of more reproducible films.

Following on the publication of their classic paper by Beeck, Smith, and Wheeler (9) the preparation of evaporated metal films for catalysis has become a standard technique and is very well documented. The method of film preparation used in this research is that employed in the work of Campbell and Thomson (58).

The nickel filament, N, was mounted on two tungsten leads, T, (figs. 35 and 36) which were Messrs. Johnson Mathey's 1mm diameter annealed tungsten wire. In cutting this type of wire care is needed to prevent splitting of the tungsten laminae - a possible source of subsequent leakage. It was found that wire cutters having a "shearing" action caused far less splitting of the laminae than did cutters with a "pinching" action.

After having been cut to length and straightened, the wires were carefully cleaned. The wire was heated to red heat in a coal-gas/oxygen flame and then rubbed with a solid sodium nitrite stick. An exothermic reaction ocurred and the wire, after being cooled and washed, had an overall lustrous grey appearance. The wire was then lightly oxidised by passing it rapidly through an oxidising flame until the wire had an irridescent blue appearance. 2mm internal diameter pyrex tubing of the necessary length was positioned on the wire and fused into position. With careful preparation of the wire the glass-to-metal seal had a bronze lustre, denoting a good vacuum-tight seal.

The nickel wire was Messrs. Johnson Mathey's "pure" grade with a purity of 99.9% and a diameter of 0.02in. A 12in length of this wire was cut and each end of the wire carefully wrapped around the end of one of the tungsten seals. The nickel wire was attached firmly to the tungsten by electric spot-welding, thereby ensuring good electrical contact. The filament was bent into a hairpin shape and sealed by a pinch-seal into the end of a length of 20mm pyrex tubing. This tubing, with the filament, was then cut to the required length and blown onto the end of the catalyst vessel as shown in figs. 35 and 36. The filament was aligned centrally within the catalyst vessel and two lengths of 28 S.W.G. copper wire were silver soldered to the outer ends of the two tungsten leads. Silver solder was employed so as to ensure that the tungsten laminae were sealed against leakage into the vacuum system.

5.3. Treatment of the Catalyst Vessel Prior to Film Evaporation

In order to prepare a pure nickel film, free from surface contamination, the apparatus for film evaporation must be thoroughly outgassed by heating under high vacuum. The heating was accomplished in one of two ways, depending on the design of the catalyst vessel. In the case of the vessel shown in fig. 35, heating was achieved by means of a specially-made furnace which was placed around the main catalyst vessel tube before the side arm C was attached.

The furnace was constructed on a former of copper tubing, 16cm long and 5.5cm in diameter. A length of Nichrome resistance tape was wrapped around this cylider, over an insulating layer of asbestos paper. The wire was then insulated with asbestos paper and asbestos string. The furnace had a resistance of 120 ohms and was run from a "Variac" variable transformer. With an applied voltage of 220 to 240 volts the furnace heated the catalyst vessel to a temperature of 450 to 500°C. The temperature was measured by means of a 0-500°C. mercury-in-glass thermometer.

It will be seen from fig. 35 that the furnace could be moved from one end of the catalyst vessel to the other before film evaporation was carried out. This could not be achieved with the catalyst vessel shown in fig. 36 owing to the problem of the side-arm B carrying the B.14 cone. With this catalyst vessel a different form of heating had to be employed, and the method finally decided upon was to use "Electrothermal" heating tape. This tape, manufactured by Messrs. Electrothermal Engineering Ltd., consisted of a fine woven network of resistance wires, knitted within a sleeve of glass-fibre thread. This tape could be wrapped around the catalyst vessel for outgassing, and then removed prior to evaporation of the film. A twelve-foot length of tape was employed and with an applied voltage of 120 volts, supplied from a "Variac", a catalyst vessel temperature of 250°C. was obtained, this being the maximum temperature obtainable with this form of heating.

The G.-M. tube, G, as is discussed in Chapter 6, was covered with a thin sheet of "Melinex" film which has a melting point of about 150°C. The result of this was that the part of the catalyst vessel surrounding the G.-M. tube could not be outgassed by heating and consequently the rate of outgassing was much lower than it would have been had strong heating been possible. In practice complete outgassing of the vessel required a period of some seven to eight days continuous pumping after which the residual pressure was less than 1 x 10^{-5}torr, as indicated on the Penning gauge.

During the last eight hours of this treatment the nickel filament was outgassed by raising the filament temperature to just below the nickel evaporation temperature. This was achieved by passing a current of 4.0 amps through the filament. The current was obtained from a heavy duty 50 volt mains transformer, control being effected by means of a "Variac" connected to the primary of the transformer. The current was measured with a moving iron ammeter in series with the filament. On first raising the filament temperature rapid gas evolution took place and the pressure rode to 1 x 10^{-3}torr. After prolonged heating the pressure fell to less than 1 x 10^{-5} torr and no further pressure rise was observed when the current was increased to 6.0 amps, thus indicating that filament outgassing was complete.

5.4. Film Preparation

In order to prevent sintering of the film it was necessary to cool the catalyst vessel to remove the heat generated during the evaporation process. Cooling was achieved with solid carbon dioxide, either alone or in acetone. The first catalyst vessel employed, that shown in fig. 35, was mounted horizontally and the solid carbon dioxide was packed, as a powder, around the catalyst vessel. The catalyst vessel shown in fig. 36, on the other hand, could be rotated in a vertical plane and evaporation was carried out with the catalyst vessel vertical. The nickel filament was then at the bottom of the vessel and the vessel was immersed, as far as the top of the sliding tube S, in an acetone/solid carbon dioxide mixture contained in a 5 litre Dewar vessel. The catalyst vessel was protected from mercury vapour during film evaporation by cooling the trap U (fig. 34) in liquid nitrogen.

When an argon-evaporated film was to be prepared the argon was admitted via T23 (fig. 34) at this stage.

The nickel was evaporated from the filament by electric heating, employing the same circuit as was used in outgassing of the filament. The evaporation rate was found to be very sensitive to the current passing through the filament. With too high a current overheating and consequent fusion of the nickel wire ocurred, resulting in breakage of the filament. Low currents, on the other hand, gave inordinately long evaporation times. It was found that 5.9 to 6.0 amps gave a satisfactory rate of evaporation in vacuum, while under a pressure of 1mm of argom a current of 7.0 to 7.2 amps was employed.

The rate of evaporation under these conditions was 15 to 20 mg nickel per hour, and films ranging in weight from 20 to 40 mg were normally obtained.

5.5. Estimation of Nickel

The films produced in this work commonly weighed from 20 to 40 mg and therefore gravimetric methods for the determination of the nickel were considered to be impractical. In general, for analysis of samples of this magnitude, colorimetric analysis affords an accurate and relatively straightforward method of determination. There are several methods available (59, 60) which utilise the water solubility of the Nickel IV dimethylglyoxime complex.

The following solutions were prepared:

Nitric acid, approximately 10N.

Potassium bromate-potassium bromide mixture

(3g $KBrO_3$ and 12g KBr per litre, giving

0.1N bromine on acidification).

Dimethylglyoxime solution

(1% in ethyl alcohol).

Ammonia solution

(0.88 ammonia diluted 1:10).

The nickel film to be estimated was dissolved in 25ml of warm 10N nitric acid and the solution diluted to 1 litre with distilled water in a standard flask. 10ml of this solution was pipetted into a 50ml standard flask. 10ml of the bromate-bromide solution was added to the flask to oxidise the nickel II to the quadrivalent state, when the solution became yellow due to the presence of excess bromine, liberated by the acid solution.

1ml of dimethylglyoxime solution was added, followed by sufficient ammonia solution, usually 10ml, to render the solution alkaline, whereupon the red colour of the complex developed. The solution was then made up to 50ml with distilled water.

Previous tests had been carried out to determine the absorption spectrum and the effect of time on the colour intensity of the complex. As shown in fig. 37, the spectrum had an absorption peak at 465Mμ, as measured on a Unicam SP500 UV spectrophotometer. Fig. 38 shows that colour development was complete after 25 minutes, and readings were therefore taken after 30 minutes development. Measurements of the optical density of the solutions were made with the solution in a 1.0cm glass absorption cell at a wavelength of 465Mμ.

Weighed lengths of the same pure nickel wire used for the filaments were dissolved in nitric acid in the same manner as the nickel films and a series of standard nickel solutions thereby obtained. From these standards a calibration curve, shown in fig. 39, was constructed but to ensure complete reproducibility of the method it was found more satisfactory to carry out the same complex formation procedure on 10ml samples of these standard solutions and to measure their optical density simultaneously with the unknown solution. The practice was to employ two standard nickel solutions, and to determine the weight of the unknown film by interpolation. For this purpose solutions containing about 10, 20, 30, and 40mg of nickel per litre were prepared.

Using this procedure results in the range

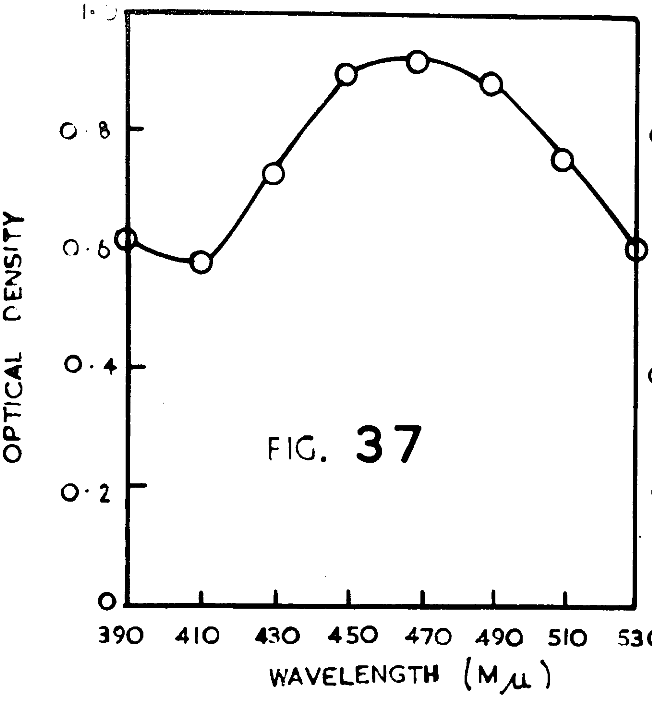


FIG. 37

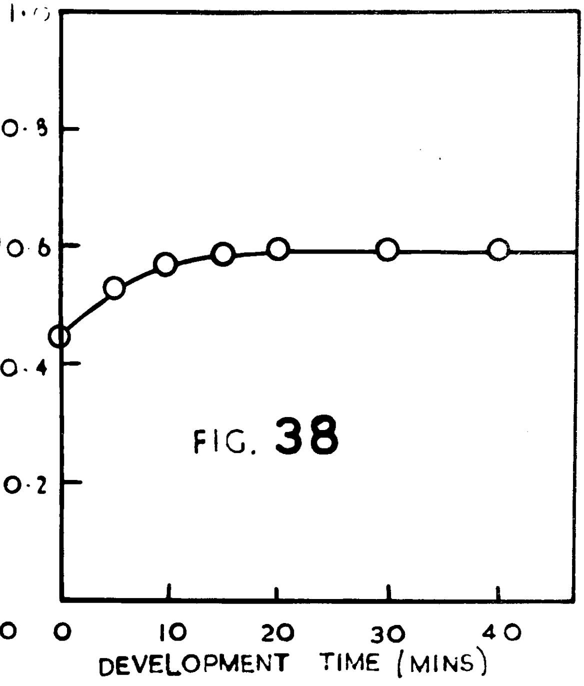


FIG. 38

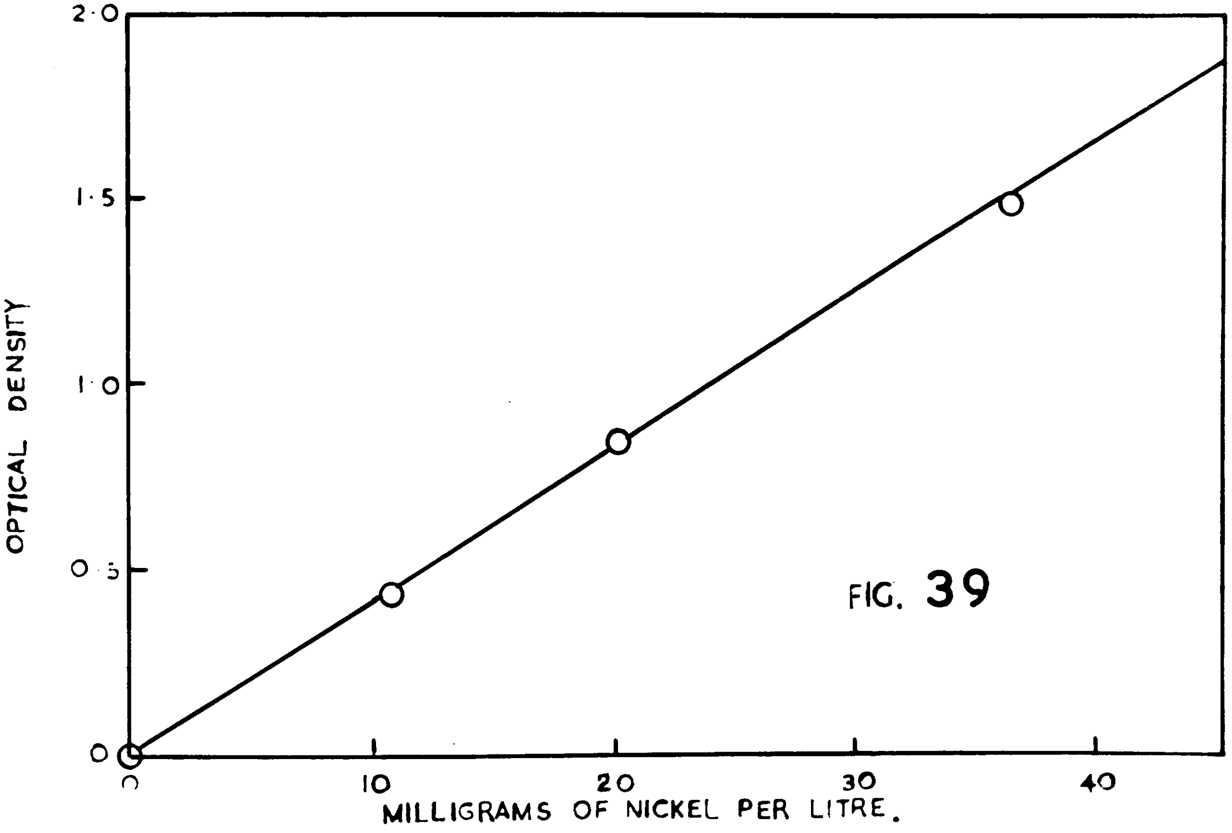


FIG. 39

5 to 45mg nickel per litre were found to be reproducible to within less than 1%.

CHAPTER 6

THE G.-M. TUBE

6.1. Introduction

The design of a G.-M. tube for this research presented special problems which were only overcome after a large amount of development work had been carried out on various designs of tube.

In the research described in this thesis it was necessary to monitor the activity of labelled molecules which were adsorbed on the surface of an evaporated nickel film. Evaporated films are most readily prepared by evaporation onto the inner surface of a glass cylinder, as is described in Chapter 5. In order to monitor the largest possible area of the surface it was necessary to use a cylindrical G.-M. counter which could be placed within the cylinder on which the evaporated film was supported and with which the β particles could be detected through the walls of the G.-M. tube. The principal design difficulty was caused by the nature of the radiation which it was required to detect. Ethylene had been chosen as the reactant to be studied, and ethylene is available from the Radiochemical Centre, Amersham, labelled with the carbon-14 isotope. The β particles from the disintegration of carbon-14 have an E_{max} of 0.155 MeV which is too low for counting with the standard thin-window G.-M. counters. Carbon-14 can be detected with special end-window Geiger counters, but it is more usual to count carbon-14 by other techniques such as scintillation counting or internal gas counting where the carbon-14 is incorporated into a gas, commonly carbon dioxide, which is included as one of the constituents of the counter filling gas.

These techniques were inapplicable to this research, and therefore the thin-wall counter was left as the best possible method for monitoring the carbon-14 labelled ethylene. As has been mentioned, E_{max} for carbon-14 is 0.155 MeV, which means that 95% of the β particles are absorbed by a window thickness of 11mg/cm^2. This is very thin, and glass of a comparable thickness was considered to be too thin for normal laboratory apparatus. Thus it can be seen that a special G.-M. tube had to be designed having walls sufficiently thin to allow penetration by a large proportion of the carbon-14 β particles, and at the same time possessing sufficient mechanical strength to allow the G.-M. tube to be evacuated to enable it to be filled with the necessary gases.

G.-M. counter windows are commonly made from mica or aluminium, but the area of window required for this counter ruled out the possibility of using these two materials. The window was required to be formed from a sheet of about 15cm long and 8cm wide and mica sheets of this area are very difficult to cleave to a sufficient degree of thinness. Thin aluminium sheet can be obtained, but in areas of the order required the prevention of pinholes becomes a considerable difficulty. A third possibility which offered itself was "Melinex" film. "Melinex" is a poly (ethylene terephthalate) plastic which is produced in this country by Messrs. I.C.I. Ltd. and which finds extensive use in physics in the preparation of targets for nuclear machines. The film is extremely tough and can be obtained in various thicknesses. Samples of "Melinex" film were very kindly supplied to us by Mr. J. Lloyd of the Department of Natural Philosophy of this University and three different thicknesses were obtained. These were; 2.0mg/cm^2, 4.54mg/cm^2, and 18.6mg/cm^2. The second of these sizes was selected as having the necessary compromise between mechanical strength and transparency to carbon-14 β particles.

The "Melinex" film was to be bonded to metal during the fabrication of the G.-M. tube and it was necessary to produce a good vacuum-tight joint. A survey of the trade literature showed that several companies, including I.C.I., the Minnesota Mining and Manufacturing Company, and Durham Raw Materials Ltd., produced adhesives suitable for bonding "Melinex" to itself, to glass, and to various metals. However, the majority of these adhesives were solvent adhesives, and the evolution of solvent vapour from the adhesive, even after it had set, could prevent good vacuum conditions being obtained. The epoxy-resin type of adhesive, on the other hand, depends for its action on chemical reaction between two constituents which are mixed before the application of the adhesive. These adhesives contain no solvent, and therefore do not affect a vacuum into which they may be put.

"Araldite", an epoxy-resin adhesive manufactured by Messrs. CIBA (A.R.L.) Ltd., is widely available in this country, and this was the adhesive chosen for the construction of the G.-M. tube. Several different types of "Araldite" adhesive are available, and that chosen was the "Twin-Pack" type which was found to possess the best viscosity properties for this work.

When the two constituents are mixed at room temperature the resulting adhesive is very viscous and its application can be controlled quite accurately. When the adhesive is heated under an infra-red lamp the mixture becomes less viscous and air bubbles and small irregularities are more easily eliminated. At room temperature the setting time is about 12 hours, but with the adhesive heated under the infra-red lamp the setting time is reduced to about one hour.

The mechanical strength of the "Melinex" film was tested as follows. A piece of copper sheet was drilled with a 1/2in diameter hole and a square of 4.54mg/cm^2 "Melinex" film was affixed over the hole with "Araldite" adhesive. A 25mm "Quickfit" flange was then fixed over the film and the hole with "Apiezon" 'W' wax and the interior of the flange was evacuated to 10^{-1}torr for 3 hours. Atmospheric pressure was therefore acting on one side of the "Melinex" film with a net force of 3 pounds. The force was removed by allowing the evacuated section of the apparatus down to atmosphere; pumping was then resumed and vacuum maintained for five minutes. This cycle was repeated ten times, after which no weakening of the film could be detected.

6.2. Design of the G.-M. Tube

As was described earlier, this G.-M. tube was of cylindrical form. The cathode was made from a copper cylinder, 3/4in internal diameter and 5in long. The cathode was drilled with a regular pattern of holes to allow the entry of β particles and the inside of the tube was carefully polished to remove any rough points and edges which could cause sparking and spurious counts. The anode was a fine tungsten wire, 0.1mm diameter, silver soldered to copper wires which were mounted in the end plugs in the copper cylinder. In order to provide insulation of the anode from the cathode polystyrene plugs were used, but difficulties in machining enforced a change-over to poly(tetrafluoroethylene). However, it was found that P.T.F.E. was not wetted by "Araldite" and this was the origin of the difficulties in making the counter vacuum-tight. To remove the necessity for plastics plugs the design shown in fig. 40 was evolved.

The cathode, C, was fitted with two plugs, P, machined from solid brass and affixed in place with soft solder. A 5/16in hole was drilled centrally through each plug, and the outer end of each hole was countersunk. Thick-walled pyrex tubing, selected to be a close fit in each hole, was firmly fixed with

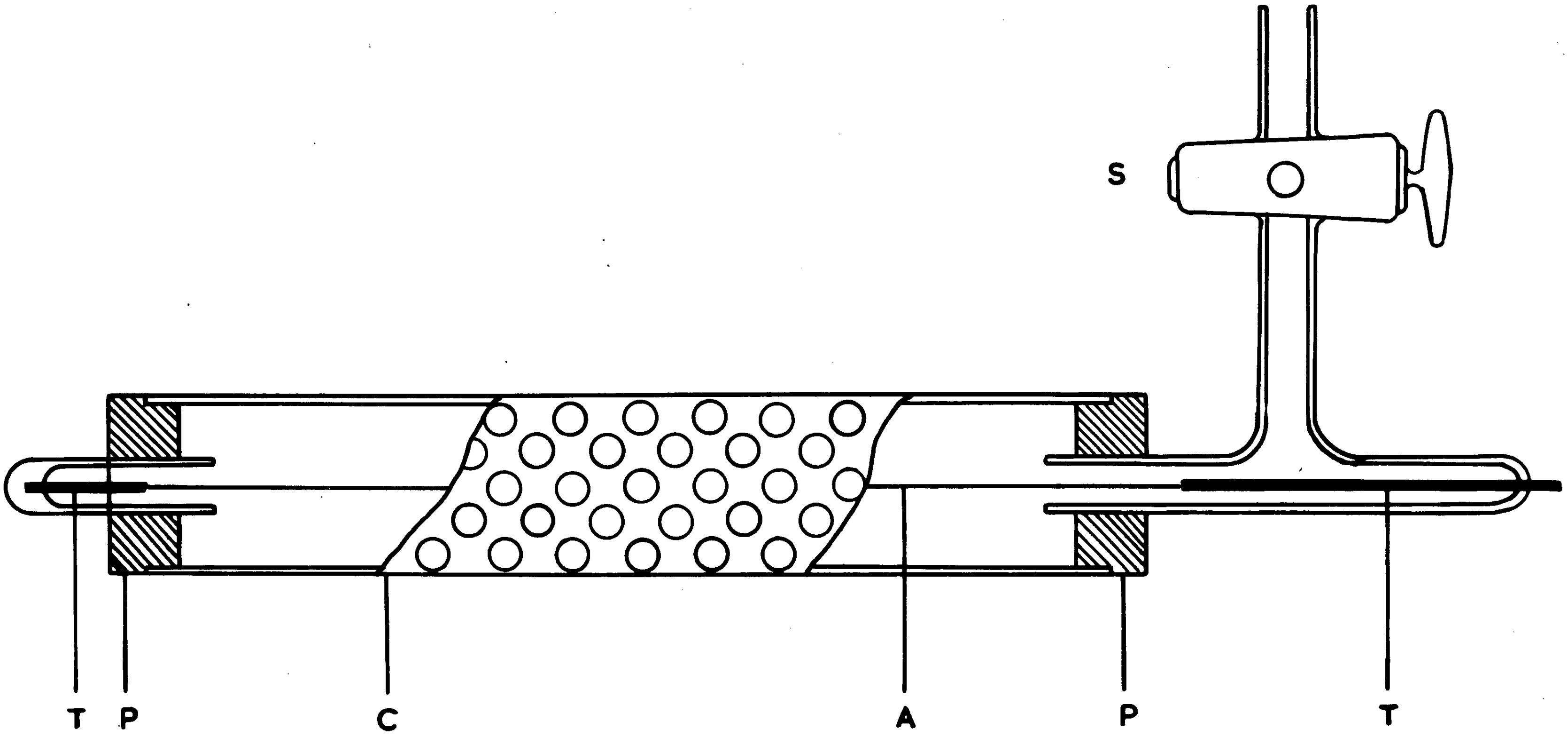


FIG. 40

"Araldite" which was allowed to fill the countersinking to provide a strong joint. The anode wire, A, was silver soldered to two lengths of 1.0mm tungsten wire, T, which were sealed into the ends of the glass tubing as shown. Evacuation and filling of the counter was via the side arm fitted with a high-vacuum stopcock, S. The surface of the cylinder was finally covered with "Melinex" sheet, "Araldite" being confined to each end of the film and to the longitudinal seam. In this way obstruction of the "Melinex" "windows" by the "Araldite" was kept to a minimum.

The inner surface of the "Melinex" covering was made conducting in order to dissipate any electrostatic charges which might have built up during the operation of the counter. The conducting surface was formed by applying a suspension of "Aquadag" colloidal graphite in ethanol to the clean surface of the film. On drying the graphite was found to be bonded firmly to the film. When the counter was evacuated and then filled, however, the flexing of the "Melinex" film caused the graphite coating to flake off in small pieces, and these small flakes gave rise to spurious discharges within the counter. In subsequent counters therefore, only clean "Melinex" film was employed and information was received (61) that any electrostatic charges which built up on the film were dissipated to the cathode very rapidly even when the covering film was not rendered conducting.

Spurious counts still persisted on occasion, and the cause was found to be the central tungsten anode. The tungsten wire had been carefully rubbed down before use to ensure that all rough points had been removed from its surface, but this was not apparently sufficient. The tungsten was therefore replaced with a fine stainless steel wire, 0.02mm diameter, which had a much smoother surface.

Sharp points and rough edges on the inner surface of the copper cathode were difficult to eliminate, chiefly because the holes in the cylinder were drilled from the outside and the consequent "rag" on the inside edges of the holes could not be removed by simple polishing. The most satisfactory method of removing these rough edges was found to be to cut the cylinder longitudinally, open it out flat, and then to slightly countersink each hole from the inside. The final polishing could also be carried out more efficiently when the cylinder was opened out flat. The cylinder was then remade, soldered along the seam and given a final polish.

The holes with which the counter tube was drilled were originally 1/4in diameter, and there were 6 rows of 9 holes each. In later versions these holes were replaced by 1/8in diameter holes, in 4 rows of 16 and 4 rows of 17 holes each. This larger number of smaller holes was found to provide better support for the "Melinex" film when the counter was evacuated.

An alternative method of fabricating the cathode was to use perforated copper sheet. This sheet, obtained from Messrs. Ash and Lacey Ltd., Birmingham, was 22 S.W.G. in thickness and was punched with a hexagonal close-packed array of 1/8in diameter holes. Because the holes were formed by punching, the edges of the holes where the punch had penetrated were rounded and only polishing was required before making the sheet up into a cylinder.

The filling gas used in the counter was argon, obtained in a cylinder from Messrs. British Oxygen Gases Ltd. The gas was dried before use. It was stored in the section of the apparatus described in Section 4.4. The quenching agent employed initially was dry ethyl alcohol. The counter was operated from an Ekco type N529B scaler in conjunction with an Erricson's Telephones probe unit 110A with a dead time of 500μ secs and a quenching pulse of 240 volts.

The counter was tested by connecting the input of a cathode-ray oscilloscope to the input circuit of the scaler. The input pulses from the G.-M. tube, after amplification by the probe unit, could then be observed on the screen of the oscilloscope. Examination of the oscilloscope traces showed that multiple pulses, caused by sparking within the G.-M. tube, had been eliminated by the improvements to the design described earlier in this Chapter. Another characteristic, however, was the occurrence of double pulses and this was put down to the inefficient action of the quenching agent in the G.-M. tube. It was felt, therefore, that although ethyl alcohol is widely used as a quenching agent, its use in this counter might not be completely efficient. Tykva (62) has described the use of ethylene as a quenching agent in G.-M. tubes and this gas was therefore used in place of ethyl alcohol, with satisfactory results. The double pulses no longer appeared when ethylene was used, and a longer plateau with a better slope was obtained.

6.3. Testing of the G.-M. Tube

The final design of the G.-M. tube was tested to determine the best possible filling composition which was known to be about 2cm pressure of ethylene and 8cm pressure of argon. An additional problem was that of overall pressure changes within the counter. The "Melinex" film covering the counter was flexible, and it was thought that a change in the pressure of the gas surrounding the counter might alter the internal counter pressure and hence affect the counter characteristics.

In order to test this the counter was filled with a constant composition of 8.4cm argon plus 2.0cm ethylene and the plateau determined. The total pressure in the counter was then reduced and the plateau redetermined. This procedure was repeated. The three graphs are shown in fig. 41, and it can be seen that the total pressure makes negligible difference to the counter characteristics. The total pressures were as follows: Graph I - 104mm, Graph II - 90mm, Graph III - 77mm. Therefore any changes in the counter pressure transmitted via the flexible "Melinex" film do not affect the counter characteristics sufficiently to cause a change in the observed count rate from this source.

Varying pressures of argon and ethylene were also investigated. The counter was filled with 2.0cm

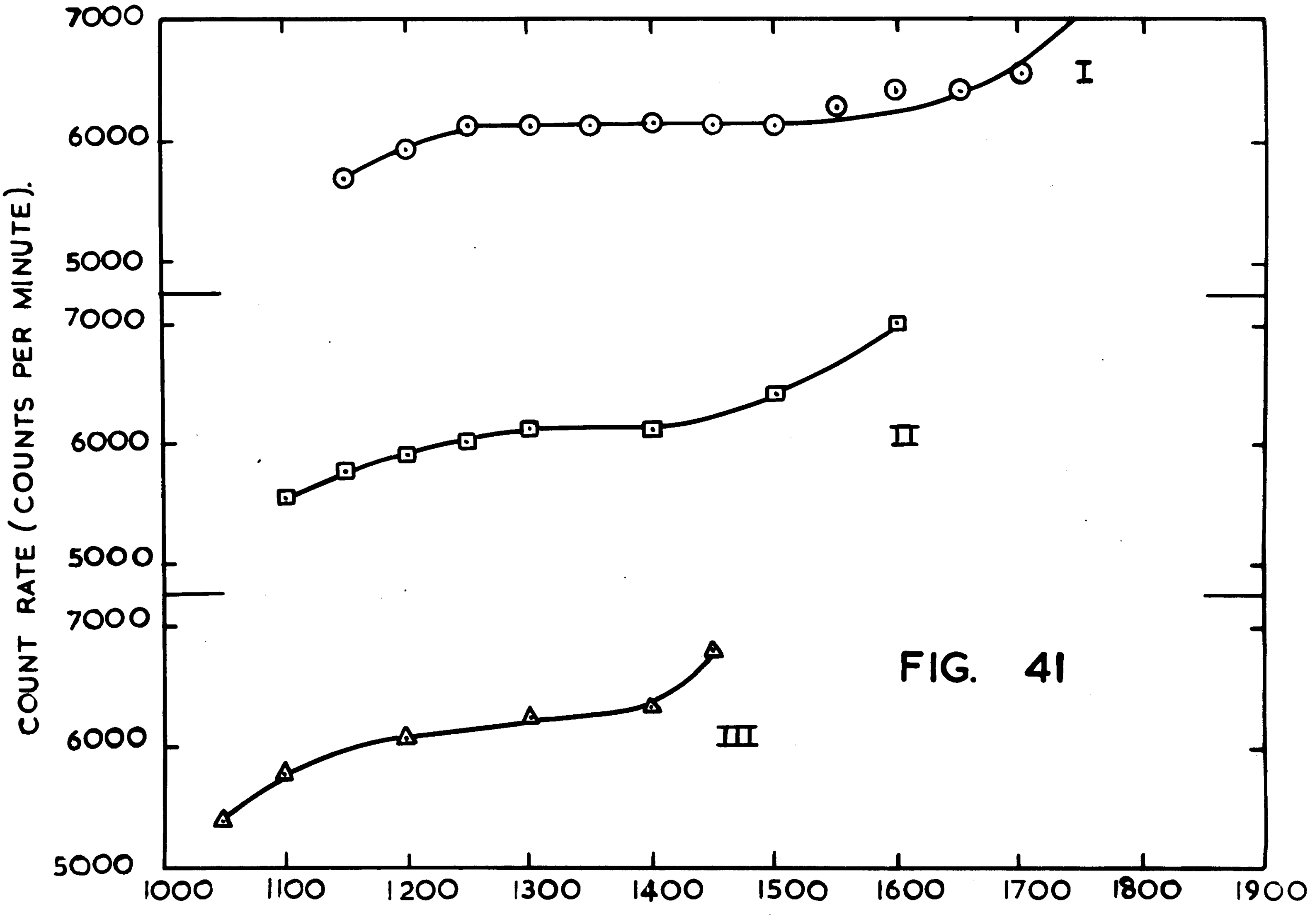

7000
6000
5000
7000
6000
5000
7000
6000
5000
COUNT RATE (COUNTS PER MINUTE).
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
HIGH TENSION (VOLTS)
I
II
III

FIG. 41

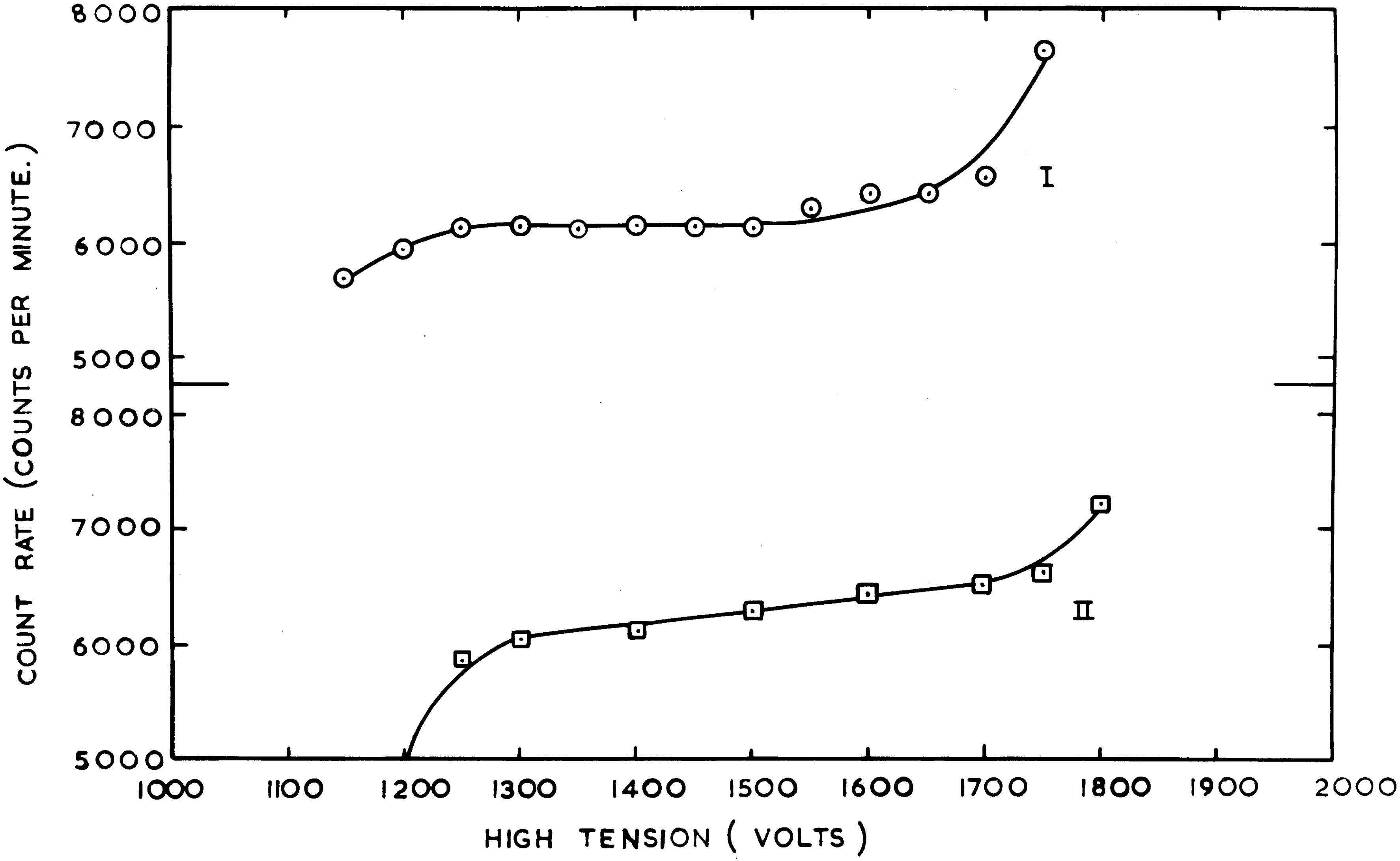

COUNT RATE (COUNTS PER MINUTE.)
8000
7000
6000
5000
8000
7000
6000
5000
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
HIGH TENSION (VOLTS)
I
II

FIG. 42

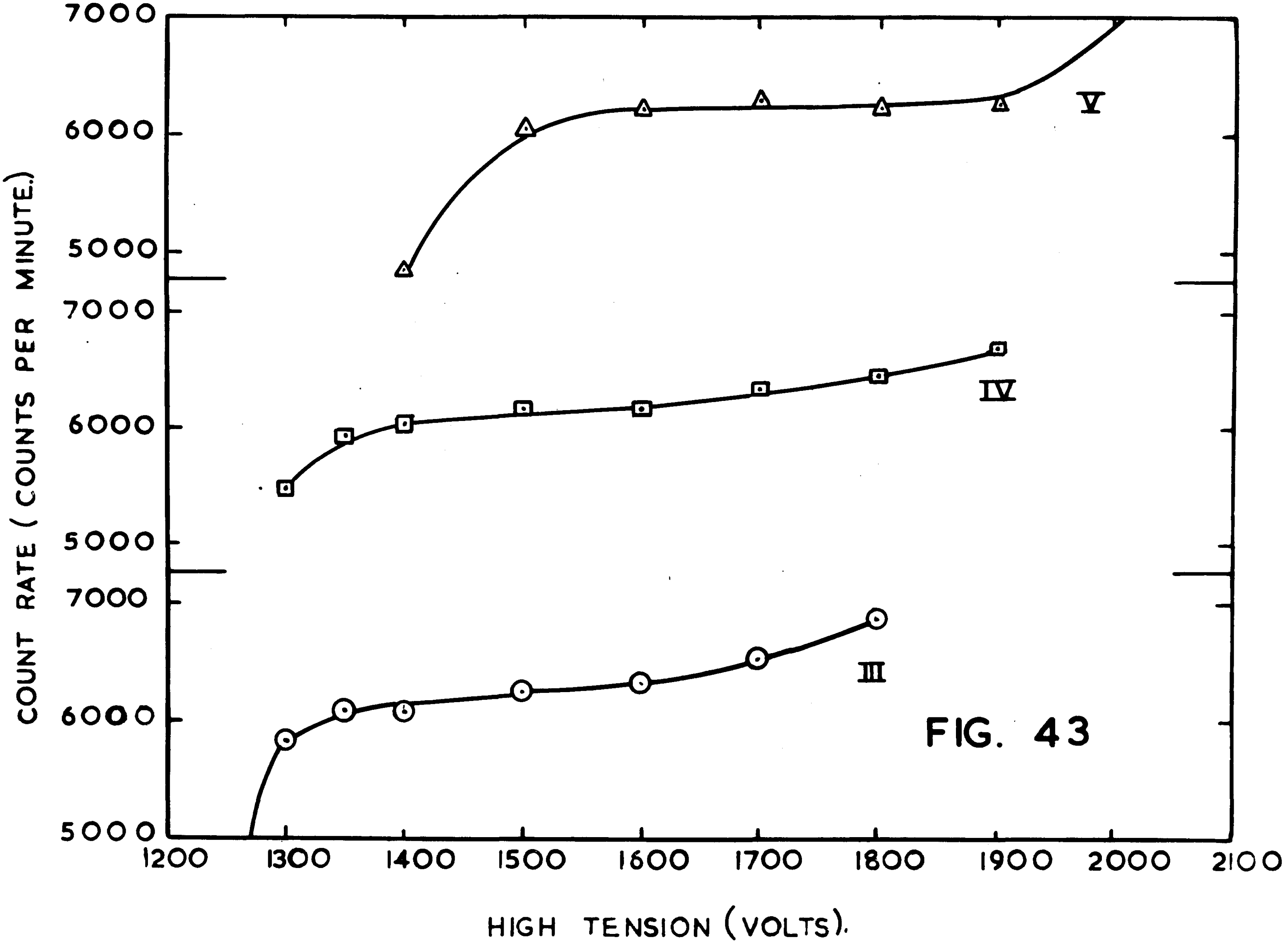

7000
6000
5000
7000
6000
5000
7000
6000
5000
COUNT RATE (COUNTS PER MINUTE.)
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
HIGH TENSION (VOLTS).
V
IV
III

FIG. 43

ethylene plus 8.4cm and 9.6cm argon (fig. 42, Graphs I and II respectively) and with 3.0cm ethylene plus 4.2, 5.4, and 7.5cms argon (fig. 43, Graphs III, IV, and V respectively). From the graphs and the abstract of results given in Table 26 it can be seen that the counter with a filling of 2.0cm ethylene plus 8.4cm argon had the most suitable characteristics.

Table 26

Figure NO.	Pressure (cm)			Plateau Starts (Volts)	Plateau Length (Volts)	Plateau Slope (%/100v)
	Argon	Ethylene	Total			
41 I	8.4	2.0	10.4	1250	300	0.4
41 II	7.3	1.7	9.0	1250	150	0.4
41 III	6.2	1.5	7.7	1200	200	2.05
42 I	8.4	2.0	10.4	1250	300	0.4
42 II	9.6	2.0	11.6	1300	400	1.64
43 III	4.2	3.0	7.2	1350	250	1.55
43 IV	5.4	3.0	8.4	1400	300	1.6
43 V	7.5	3.0	10.5	1600	250	0.4

A second method of investigating the behaviour of a G.-M. counter is by means of the statistical distribution of the observed counts. The observed count rate from an assembly of disintegrating atomic nuclei obeys a Gaussian distribution, but if there should be a malfunction of the counter which is detecting this then the observed counting statistics will not obey the true Gaussian distribution. A statistical study of the counting of the G.-M. tube was therefore carried out.

If a series of N counts is taken on a standard source, counted under standard conditions, then the average count, $\bar{x}$, is given by:

$$\bar{x} = \frac{\sum_i x_i}{N}$$ where x_i is any one count rate expressed in counts per minute.

The "variance" is then given by:

$$\frac{\sum_i (r_i^2)}{N-1}$$

where $r_i = \bar{x} - x_i$, i.e., the difference between any observed result and the average result.

The statistical deviation, σ , is then given by:

$$\sqrt{\frac{\sum_i (r_i^2)}{N-1}}$$

For a Gaussian distribution the number of results lying between $\pm\sigma$ = 68%; between $\pm 2\sigma$ = 95%;

and between $\pm 3\sigma = 100\%$.

The results of the statistical analysis of the results from the G.-M. tube are given in Table 27, and it can be seen that the results obey a Gaussian distribution, indicating no malfunctioning on the part of the G.-M. tube or its associated equipment.

Table 27

Number of 1 minute counts		100
Average count, $\overline{x}$,		10263 cpm
Variance = $\sum r^2/N-1$		15041
Standard deviation = $\sqrt{\text{Variance}}$ =		122
Number of results between:	$\pm\sigma$	67%
	$\pm 2\sigma$	94%
	$\pm 3\sigma$	100%

The frequency distribution of the results is shown in the histogram in fig. 44.

6.4. Factors Affecting the Observed Count Rate

There are four factors affecting the value of the observed count rate in relation to the true disintegration rate of the molecules adsorbed on the nickel film. These are: backscatter of the radiation from the source - the nickel film - and the support - the glass tube; absorption of the

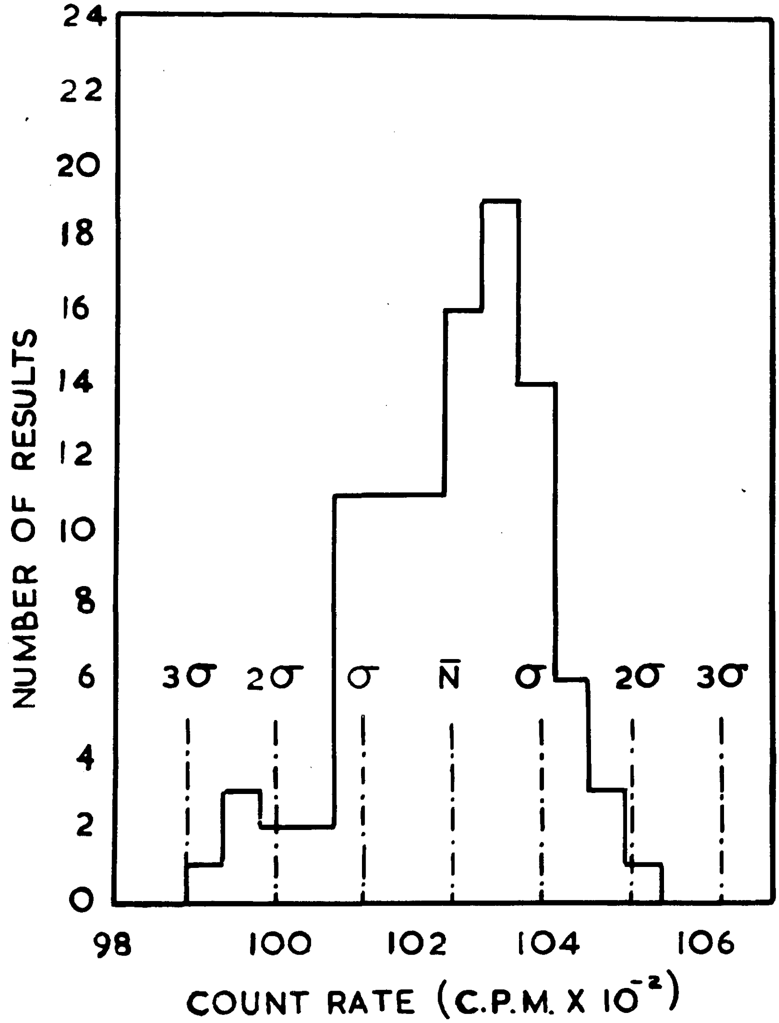

NUMBER OF RESULTS
0
2
4
6
8
10
12
14
16
18
20
22
24
3σ
2σ
σ
N̄
σ
2σ
3σ
98
100
102
104
106
COUNT RATE (C.P.M. X 10⁻²)

FIG. 44

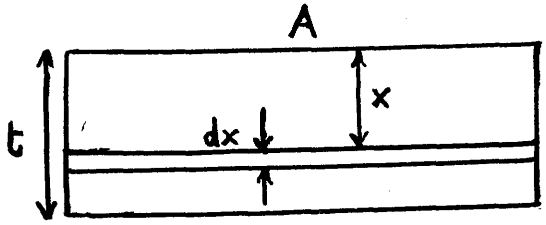
radiation in the source; absorption of the radiation in the gases between the source and the counter; and the net efficiency of the counter, which includes ionisation efficiency, geometric efficiency, and absorption of the radiation in the counter window. The first three factors will be discussed in this Section; while the efficiency of the counter will be dealt with in the following section.

1. Backscatter

The backscattering factor for carbon-14 particles from glass is given in the literature (63) as 1.17 and is approximately the same for nickel.

2. Self-Absorption in the Source

If the ethylene-C14 is evenly distributed throughout the film, allowance must be made for the absorption of the radiation in the film.



If σ = specific activity,

ρ = density of the source,

A = area of surface, and

μ = the linear absorption coefficient, then the surface activity due to an element dx

$$= \frac{1}{2} A \cdot \sigma \rho \, dx . e^{-\mu x}$$

Integrate, $I = \frac{1}{2}.A.\sigma.\rho.\int_0^t e^{-\mu x}.dx$

therefore $I = \frac{A.\sigma.\rho.}{2\mu}\left[1 - e^{-\mu t}\right]$

therefore $I = I_\infty\left[1 - e^{-\mu t}\right]$ where $I_\infty = \frac{A.\sigma.\rho.}{2\mu}$

equals surface activity as $t \rightarrow \infty$

Differentiate:

$$\frac{dI}{dt} = \mu I_\infty . e^{-\mu t}$$

If $t = 0$ $\frac{dI}{dt} = \mu I_\infty$

therefore, corrected activity $I_{corr} = \mu I_\infty t.$

$\therefore$ correction factor $= \frac{I_\infty\left[1 - e^{-\mu t}\right]}{\mu . I_\infty . t}$

$\therefore k = \frac{1 - e^{-\mu t}}{\mu t} = \frac{I}{I_{corr}}$

$\therefore$ True activity without self absorption

$$= \frac{\text{observed surface activity}}{k}$$

Now for carbon-14 $\mu = 0.248$

For a 40mg film evenly distributed over an area of 115cm^2

$t = 0.35\text{mg/cm}^2$

$\therefore \mu t = 0.087$

$\therefore$ $\underline{k = 0.956}$

3. Absorption in the Reactant Gases

Density of ethylene = 1.260g/1 at S.T.P.

Density of hydrogen = 0.090g/1 at S.T.P.

$\therefore$ Wt. of ethylene at 10cm press. = 0.1660mg/cm^3

Wt. of hydrogen at 10cm press. = 0.0118mg/cm^3

$\therefore$ Total wt. at 20cm press. = 0.1778mg/cm^3

If distance between counter and source (film) = 1.0cm

Thickness of gas layer = 0.1778mg/cm^2

$$\text{Now} \quad I/I_0 = 2^{-t/d_{\frac{1}{2}}}$$

$$= 2^{-\frac{0.1778}{2.6}}$$

$$= \underline{0.965}$$

This factor is negligible in comparison with the other corrections which will be made and therefore can be ignored. The backscattering factor and the self-absorption factor are both very small, and will also tend to cancel one another and therefore may also be disregarded.

6.5. Counting Efficiency

There are four factors which influence the counting efficiency of the G.-M. tube.

The first is the ionisation efficiency of the counter filling gas. This can safely be assumed to be 100%.

The second is the absorption of β particles in the copper cathode of the counter. Since the copper was of 'infinite thickness' the efficiency is determined by the fraction of the counter area which is "open" by way of the holes drilled in the cathode. The cathode was drilled with 132 holes, each 1/8in diameter, and hence the area "open" to the β particles was $10.5cm^2$. The total area enclosing the active volume of the counter, as defined by the glass support tubes, was $70.5cm^2$ and therefore 14.9% of the counter was "open" to the β particles.

The third factor influencing the efficiency is the absorption of the β particles in the "Melinex" film.

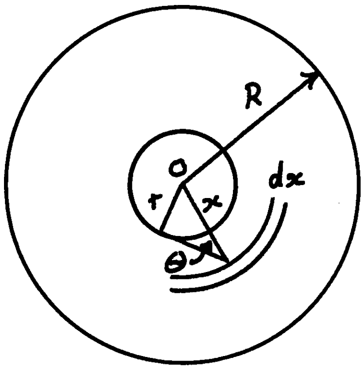
Now, for absorption of β particles in an external absorber

$I = I_o . 2^{-t/d_{\frac{1}{2}}}$ where I is the resultant count rate, t is the thickness of the absorber, and $d_{\frac{1}{2}}$ is the half-thickness for the absorption of the β particles in question. For carbon-14 β particles $d_{\frac{1}{2}} = 2.6mg/cm^2$ (63) and t for the "Melinex" film employed was $4.54mg/cm^2$. Consequently, $I/I_o = 0.3$, or 30% of the incident β particles penetrate the "Melinex" film and are counted. The resultant efficiency of the G.-M. tube is therefore

14.9% of 30% = 4.5%.

A fourth factor, however, is the geometric efficiency of the counting arrangement.

The diagram shows the G.-M. tube concentric with an outer jacket, contained within which is a gas the molecules of which are labelled with radio-tracers.



Consider unit length of this cylinder, and let the count rate = C counts per minute per unit volume.

Then for an element dx at distance x from O the total 2π count rate is given by:

$$C.2\pi x.dx$$

If we then include the efficiency of counting this element at a distance x;

$$\text{Count rate} = C.2\pi x.dx.\frac{2\theta}{2\pi}$$

Now $\theta = \sin^{-1}\frac{r}{x}$

$\therefore$ count rate

$$= C.2x.dx.\sin^{-1}\frac{r}{x}$$

$\therefore$ The total count rate is given by:

$$\int_r^R C.2x.\sin^{-1}\frac{r}{x}.dx.$$

and the overall efficiency is given by:

$$\frac{C\int_{r}^{R} 2x.\sin^{-1}\frac{r}{x}.dx}{C.\pi(R^2 - r^2)}$$

Consider the integral alone;

$$f(r) = \int_{r}^{R} 2x.\sin^{-1}\frac{r}{x}.dx$$

Where $0 \leqslant \sin^{-1}\frac{r}{x} \leqslant \frac{\pi}{2}$

and $0 \leqslant r \leqslant R$

Let $u = \frac{r}{x}$, then $du = -\frac{r}{x^2}.dx$

$$\therefore f(r) = 2r^2 \int_{\frac{r}{R}}^{1} \frac{\sin^{-1} u.du}{u^3}$$

Integrating by parts;

$$f(r) = \left[-r^2.\frac{\sin^{-1} u}{u^2}\right]_{\frac{r}{R}}^{1} + r^2\int_{\frac{r}{R}}^{1} \frac{du}{u^2\sqrt{1-u^2}}$$

Substitute $u = \sin.y$;

$$f(r) = R^2.\sin^{-1}\frac{r}{R} - r^2\frac{\pi}{2} + r^2\int_{\sin^{-1}\frac{r}{R}}^{\pi/2} \frac{dy}{\sin^{-2} y}$$

$$= \left[R^2.\sin^{-1}\frac{r}{R} - \frac{\pi r^2}{2} - r^2.\cot y \right]_{\sin^{-1}\frac{r}{R}}^{\pi/2}$$

$$= R^2.\sin^{-1}\frac{r}{R} - \frac{\pi r^2}{2} + r\sqrt{R^2 - r^2}.$$

$$\therefore \quad f(r) = \int_r^R 2x.\sin^{-1}\frac{r}{x}.dx$$

$$= R^2.\sin^{-1}\frac{r}{R} - r\left(\frac{\pi r}{2} - \sqrt{R^2 - r^2}\right)$$

$\therefore$ the overall efficiency is given by:

$$\frac{f(r)}{\pi(R^2 - r^2)}$$

$$\therefore \quad E = \frac{R^2.\sin^{-1}\frac{r}{R} - r\left(\frac{\pi r}{2} - \sqrt{R^2 - r^2}\right)}{\pi(R^2 - r^2)}$$

For the system in question;

$r = 1.07\text{cm}$ and $R = 1.64\text{cm}$

$$\therefore \quad E = \frac{1.447}{\pi.1.55}$$

$$= \underline{0.297} = \underline{29.7\%}$$

In the specialised case where all the labelled molecules are adsorbed on the nickel film at a distance

R from the centre, the efficiency simplifies to become:

$$E = \frac{2\theta\,(x=R)}{2\pi}$$

When $x = R \quad \theta = \sin^{-1}\frac{r}{R}$

$$\therefore \quad E = \frac{\sin^{-1} r/R}{\pi}$$

$$= \underline{0.226} \quad = \quad \underline{22.6\%}$$

Total efficiency

For gas-phase activity the total efficiency will be 4.5% of 29.7% = <u>1.34%</u>

For activity totally adsorbed on the nickel film the total efficiency will be 4.5% of 22.6%

= <u>1.02%</u>

Experimental Determination of Efficiency

This was determined as follows. Ethylene-C-14 with a specific activity of 0.0905mc/mM was expanded into the catalyst vessel and successive count rates for successive increments determined. Since the catalyst vessel did not contain a nickel film all the activity was in the gas phase. The count rate, corrected for dead-time and background, was plotted against the quantity of gas present. The graph is shown in fig. 45.

The slope of the graph gave the observed count rate per cm^3mm of gas admitted, which was 4.32 $c.p.m./cm^3mm$.

The volume of the catalyst vessel was 944 cm^3 and the volume of gas actually observed by the counter was equal to

$$12.\pi(R^2 - r^2)$$

$$= 58.5cm^3.$$

The factor of 12 above is the length of the section monitored by the counter. It has been determined from the active length of the counter, 10.5cm, plus the contribution from activity beyond the ends of the G.-M. tube. This contribution can only be estimated roughly, but it is approximately 1.5cm in total.

Therefore the percentage volume of the whole which was monitored was 6.2%.

Now 1 cm^3mm at 20°C contains

$$3.29 \times 10^{16} \text{ molecules.}$$

$\therefore$ 6.2% of the total contains

$$2.04 \times 10^{15} \text{ molecules.}$$

$$= \frac{2.04 \times 10^{15} \times 10^3 \times 0.0905}{6.024 \times 10^{23}} \text{ millicuries}$$

By definition 1 millicurie gives rise to 3.7×10^7 disintegrations per second.

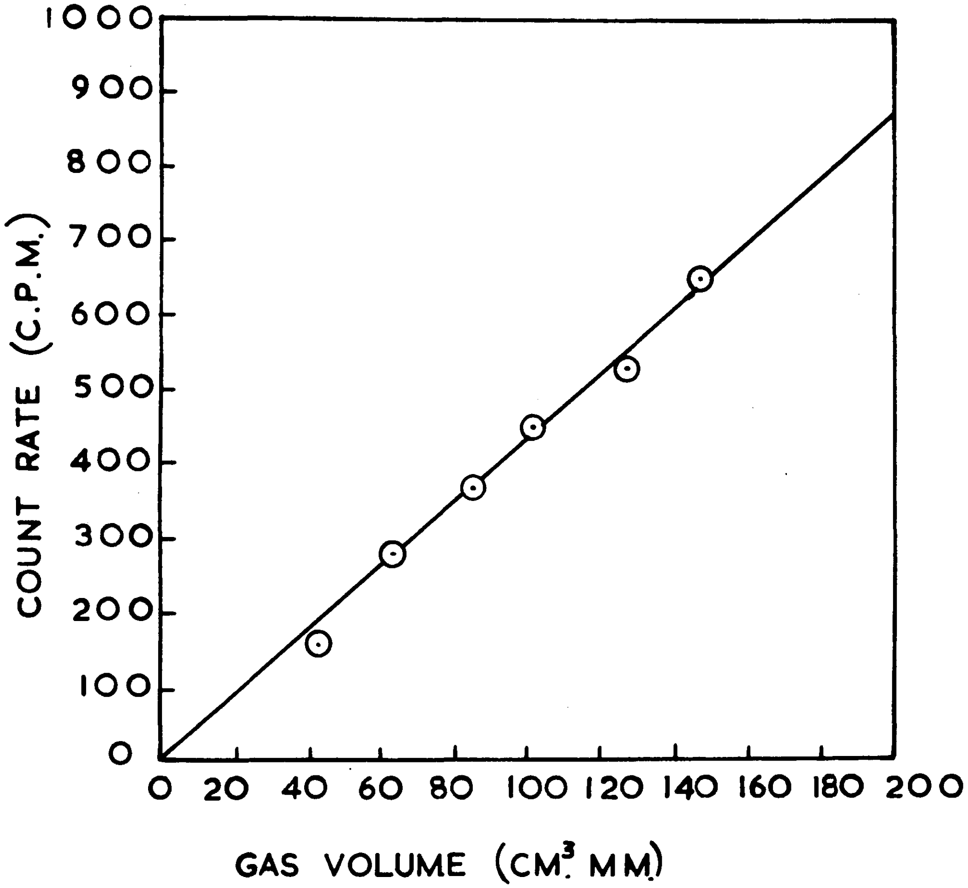

1000
900
800
700
600
500
400
300
200
100
0
COUNT RATE (C.P.M.)
0
20
40
60
80
100
120
140
160
180
200
GAS VOLUME (CM³ MM)

FIG. **45**

Therefore the theoretical count rate per minute

$$= \frac{2.04 \times 10^{15} \times 10^{3} \times 0.0905 \times 3.7 \times 10^{7} \times 60}{6.024 \times 10^{23}} \text{ d.p.m.}$$

= 680 disintegrations per minute.

The actual observed count rate was 4.32 c.p.m.

$$\therefore \text{ Efficiency} = \frac{4.32}{680} \times 100$$

$$= \underline{0.635\%}$$

This is within a factor of 2 of that calculated on theoretical grounds (1.34%) and in view of the unknown factors involved in the calculation this result may be considered to be in quite good agreement.

The disadvantage of this determination is that there are several unknown factors which can influence the observed efficiency. Two of these are the length of the section of gas which is counted, and the effect of oblique entry of the β particles. In order to determine the efficiency by a method more akin to the counting arrangement employed in monitoring the nickel films a technique was used involving the use of a very thin film of "perspex" labelled with carbon-14.

"Perspex" sheet labelled with carbon-14 was obtained from the Radiochemical Centre, Amersham, with a specific activity of 0.1 microcuries per gram. 380mg of this sheet were dissolved in 50ml of chloroform and the solution was poured onto the surface of a layer of mercury which filled a metal tray with the dimensions of 20cm x 15cm. The solvent was allowed to evaporate and the resulting thin film of "perspex" was lifted off by means of a wire loop. A piece of this film measuring 15cm by 10cm was cut and mounted within a glass tube of the same dimensions as those used as catalyst support tubes in the catalyst vessel. The plastic film therefore closely resembled the nickel films with regard to counting geometry and film thickness. The film had an area of 150cm^2 and weighed 233.0mg.

The G.-M. counter was filled as described earlier in this Chapter and operated at 1400 volts. Three series of determinations were carried out with the "perspex" cylinder in place. The background count rate was determined each time with the G.-M. tube surrounded with an identical glass tube to simulate the effect of a catalyst tube without the "perspex" sheet.

The results obtained are as follows:

1.	Background count rate	123±11 c.p.m.
	Count rate + "perspex"	277±4 cpm
	Count rate - "perspex" alone	154±12
2.	Background	179±6
	Count rate + "perspex"	324±9
	"Perspex" alone	145±11
3.	Background	159±6
	Count rate + "perspex"	214±8
	"Perspex" alone	155±10

Average value for "perspex" count rate:

<u>151 c.p.m.</u>

Specific activity of "perspex" = $0.1\mu c/g$.

$\therefore$ 1g gives rise to $0.1 \times 3.7 \times 10^4 \times 60$ c.p.m.

$\therefore$ 233mg give rise to $0.1 \times 3.7 \times 10 \times 60 \times 233$ c.p.m.

$$\therefore \text{Efficiency} = \frac{151 \times 100}{3.7 \times 60 \times 233} \%$$

$$= \underline{0.29\%}$$

This result is much more satisfactory than the previous value for the counting efficiency owing to the more precisely defined geometry, and the better similarity between this counting arrangement and the nickel films. Accordingly, this value of 0.29% has been used in all the calculations of adsorption and film coverage discussed in Chapters 1 and 2.

CHAPTER 7

PURIFICATION OF REAGENTS

7.1. Ethylene

The ethylene used in these experiments was that supplied in cylinders by Messrs. British Oxygen Gases Ltd. The analysis of the ethylene, as given by the suppliers, was as follows:

Ethylene	98.2%
Carbon dioxide	0.3%
Carbon monoxide	0.07%
Hydrogen	0.1%
Methane	0.03%
Oxygen	0.2%
Nitrogen	1.1%

Of the foreign gases, oxygen and carbon monoxide are the most potent catalyst poisons and the purification procedure was directed to their removal, especially oxygen, in addition to the removal of the other contaminants.

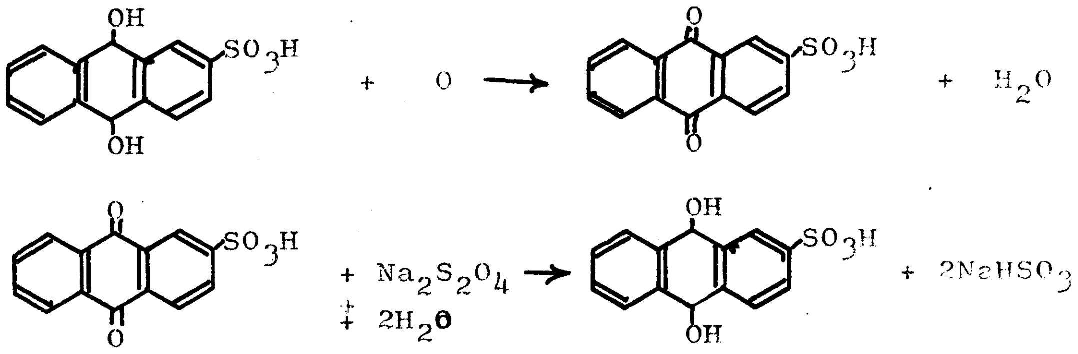
Oxygen in particular was removed by means of Fieser's solution. This solution, investigated by Fieser in 1924 (64), contained anthraquinone-β-sulphonic acid, sodium hydrosulphite, and sodium hydroxide.

The solution was made up as follows:

Anthraquinone-β-sulphonic acid	8g
Sodium hydrosulphite	64g
Sodium hydroxide	53g

dissolved in 400ml of distilled and de-oxygenated water. The solution was first made up with the sodium hydroxide and the sodium hydrosulphite and stored in two Dreschel bottles in the gas purification train which was then flushed with oxygen-free nitrogen. The anthraquinone-β-sulphonic acid, which acted as a catalyst, was added last to the solution under nitrogen when the characteristic deep red colour of the solution developed.

The action of the solution, as described by Fieser, is as follows:



Thus it aan be seen that the anthraquinone-β-sulphonic acid acts as a catalyst and the overall reaction is

$$Na_2S_2O_4 + H_2O + O \longrightarrow 2NaHSO_3$$

Calculation shows that, on the basis of ethylene containing 0.2% oxygen, this solution will purify 2060 litres of ethylene, which is a volume in large excess of that actually required to be purified during the course of this research.

In the gas purification train the two Dreschel bottles containing Fieser's solution were followed by a bottle containing a saturated solution of lead acetate to remove any hydrogen sulphide gas which may have been liberated by the preceding solution.

The gas stream was dried by being passed through a column of Linde molecular seive No. 4A, supplied by Messrs. Union Carbide. The gas was finally passed through a trap cooled at -78°C in an acetone/solid carbon dioxide mixture.

To remove the non-condensable gases remaining; hydrogen, carbon monoxide, and nitrogen, the ethylene was solidified in a cold finger cooled in liquid nitrogen and the free gases pumped off The ethylene was allowed to evaporate and the process was repeated. In this way gases occluded in the solid ethylene were largely eliminated. The ethylene was then distilled into the storage bulb, the upper and lower thirds of the distillate being discarded.

7.2. Hydrogen

Ideally, hydrogen should be purified by diffusion through a palladium leak. In practice, however, it was found that the rate of diffusion was too slow and insufficient hydrogen could be purified in the time available.

As an alternative, the hydrogen was purified by being passed over activated charcoal at -196°C. At this temperature the impurities become physically adsorbed and the main contaminant, oxygen, could be removed readily.

7.3. Argon

The argon used in the G.-M. tube was purified as follows. The gas was passed first through an alkaline solution of pyrogallol to remove oxygen, and then through concentrated sulphuric acid to dry the gas.

Specroscopically pure argon was obtained in 1 litre break-seal flasks from Messrs. British Oxygen Gases Ltd. and was used in the preparation of oriented films, as described in Section 5.4, without further purification.

7.4. Ethyl Alcohol

Ethyl alcohol was used as a quenching agent in the early work on the G.-M. tube. "Absolute" alcohol was used, and it was dried with anhydrous magnesium sulphate before use.

7.5. Ethylene-1,2-C14

This was obtained from the Radiochemical Centre, Amersham, in break-seal ampoules. It had a specific activity of 1.25mc/mM and a radiochemical purity of 102%. The ethylene was used without further purification. The procedure for dilution of the ethylene to the required specific activity is described in Section 4.2 and in Appendix III.

There are several routes available for the preparation of carbon-14-labelled ethylene (65).

Ethylene-1-C14 can be prepared by the dehydration over alumina of ethanol-1-C14 which in turn can be prepared from methyl iodide and labelled potassium cyanide *via* acetic acid.

Ethylene-1,2-C14 can be prepared by several methods, but the most straightforward is the synthesis starting from barium carbonate-C14 (66). Barium carbonate-C14 is reduced with barium metal to barium carbide-C14 which, on treatment with water, yields acetylene-1,2-C^{14}. The acetylene-1,2-C^{14} is then reduced to ethylene-1,2-C^{14} with a solution of chromous chloride according to the method of Arrol and Glascock (67).

APPENDIX I

Gas Quantities from the Gas Pipette

The gas pipette was supplied from a bulb containing the gas in question at a pressure of 2 5mm. As successive volumes were removed from the pipette the pressure in the bulb fell and consequently each succeeding volume contained less gas in terms of actual numbers of molecules.

The gas quantities were expressed in terms of p.v as cm^3mm, where 1 cm^3mm contained 3.29×10^{16} molecules at 20°C.

The volume of the pipette was assumed to decrease as successive increments of gas were removed and the following calculation was used to derive the volume term, at constant pressure, for each increment.

Let the volume of the pipette = a cm^3.

Let the volume of the gas reservoir = b cm^3.

Let the initial pressure = p mm.

Quantity of gas, Q, in the nth sample

$$Q_n = a.p\left(\frac{b}{a + b}\right)^n cm^3mm.$$

$\therefore$ Total quantity in the first n samples

$$Q = a.p(c + c^2 + c^3 + \ldots\ldots + c^n),$$

where $c = \frac{b}{a + b}$.

$$\therefore \quad Q = a.p.c\left(\frac{1 - c^n}{1 - c}\right) \quad \text{if } c \approx 1$$

Let $c = 1 - x$ where x is small

$$\therefore \quad c^n = (1 - x)^n = 1 - nx + \frac{n(n - 1)x^2}{2}$$ ignoring further terms in x.

$$\therefore \quad Q = \frac{a.p.c.\left(1 - 1 + nx - \frac{n(n - 1)x^2}{2}\right)}{1 - (1 - x)}$$

$$= a.p.c\left(n - \frac{n(n - 1)x}{2}\right) \text{ cm}^3\text{mm.}$$

Let $a.c\left(n - \frac{n(n - 1)x}{2}\right) = f(n)$.

Then $Q = p.f(n)$ and therefore Q can be tabulated for different values of n, thus:

n	1	2	3	4
f(n)	$a.c$	$a.c(2 - x)$	$a.c(3 - 3x)$	$a.c(5 - 10x)$

where $x = 1 - c = \frac{a}{a + b}$

The values of f(n) for the apparatus used in this research are given in Table 28.

Table 28

Pipette volume, a $4.365\ \mathrm{cm}^3$

Gas reservoir, b $1097\ \mathrm{cm}^3$

$\therefore$ $x = 0.0040$ and $c = 0.9963$

n	f(n)
1	4.349
2	8.682
3	12.99
4	17.30
5	21.57
6	25.83
7	30.08
8	34.30
9	38.51
10	42.71

APPENDIX II

Method of Calibration by Gas Expansion

As outlined in Section 4.6 the volume of any section was influenced by the pressure of gas within the system as this depressed the level of the mercury in the manometer and thus increased the volume. The prodedure given below was designed to overcome this difficulty.

Let: V_1 = Any known volume
V_2 = Any unknown volume
V_m = Volume of manometer section, from T19 (fig. 33) to the mercury surface.
P_1 and P_2 = initial and final pressures respectively.

Now, if A = cross-section area of manometer, then at any pressure P

$V_m = V_c + P.A$ where V_c is the volume of the manometer above the level of mercury at 76.0 cm atmospheric pressure, with manometer evacuated.

Then $$P_1V_1 = P_2(V_1 + V_2 + V_c \quad P_2A)$$

$$\therefore \quad \frac{P_1}{P_2}.V_1 = V_1 + V_2 + V_c + P_2A$$

$\therefore$ graph of P_1/P_2 against P_2 has a slope of A/V_1 and an intercept of $\dfrac{V_1 + V_2 + V_c}{V_1}$

By this procedure therefore A can be determined and also $V_2' + V_c$.

V_c alone was dtermined by the following procedure. A known volume was filled with carbon dioxide to a pressure P_1. This carbon dioxide was then distilled into the manometer section by cooling the tubing near C (fig. 33) in liquid nitrogen. With condensation complete, T19 was closed and the carbon dioxide allowed to expand to a new pressure P_2. By this means the unknown volume V_2 was eliminated and V_c alone determined.

V_c was found to be 40.7 cm^3.

The plot of P_1/P_2 against P_2 is shown in fig. 46. The slope of the graph is equal to:

$$A/V_1 = 0.001341 \text{ cm}^{-1}.$$

and since $V_1 = 1097 \text{ cm}^3$

$$A = \underline{1.471 \text{ cm}^2}.$$

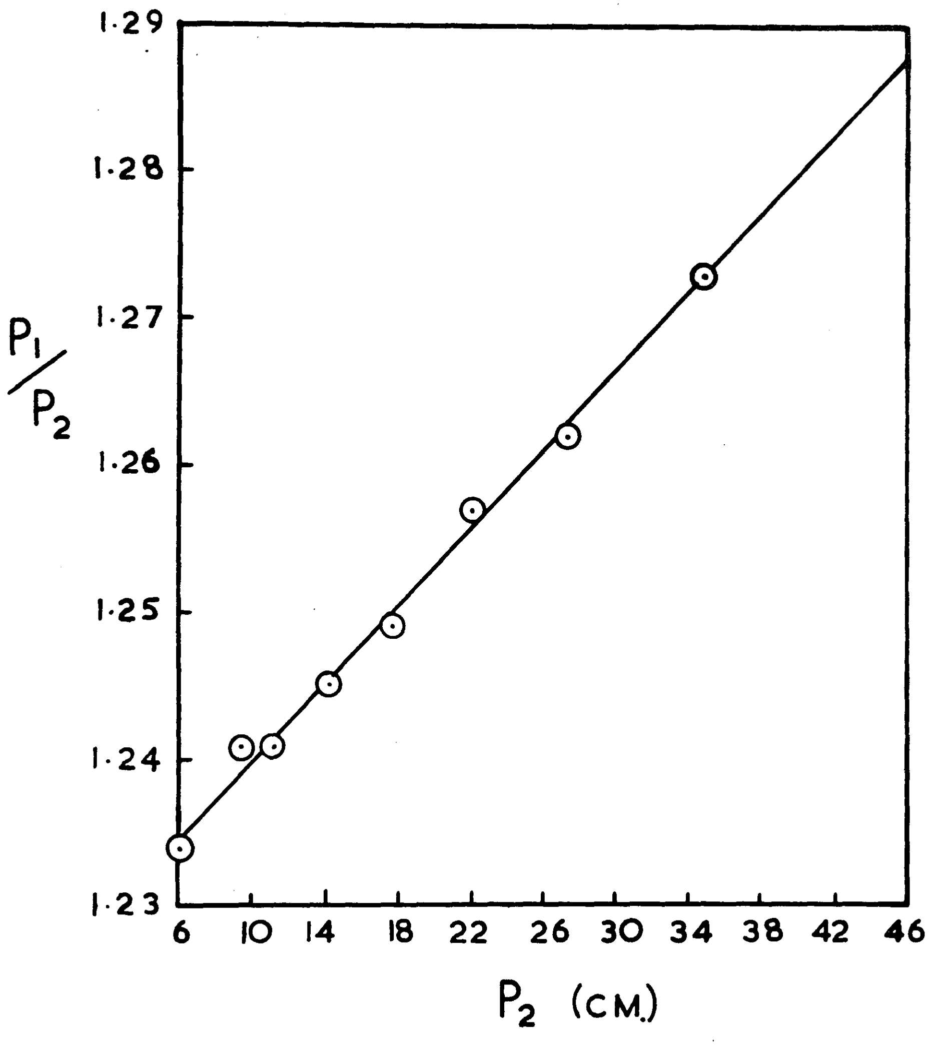

1·29
1·28
1·27
1·26
1·25
1·24
1·23
P_1/P_2
6
10
14
18
22
26
30
34
38
42
46
P_2 (CM.)

FIG. **46**

APPENDIX III

Dilution and Specific Activity of Ethylene-1,2-C14

Ethylene-1,2-C14 was supplied by the Radiochemical Centre, Amersham, with a specific activity of 1.25 mc/mM and a radiochemical purity of 102%, each batch containing 0.1 mc.

It was required to dilute each sample with inactive ethylene to a specific activity of 0.1 mc/mM and therefore the labelled ethylene had to be diluted to a total volume containing 1 mMole of ethylene.

Now $n = PV/RT$ where $R = 82.054$ $cm^3.at.deg^{-1}.mol^{-1}$.

$$n = \frac{1000.P.V}{82.054 \times 293} \quad \text{mMoles at } 20^\circ C.$$

Volume of storage bulb B = 159.6 cm^3 (see Table 25)

$$\therefore \quad n = 1 = \frac{1000.P \times 159.6}{82.054 \times 293}$$

$$\therefore \quad P = \underline{11.48 cm}$$

Of this pressure, a certain fraction will be from the ethylene-C14 already present.

Original specific activity = 1.25 mc/mM

Quantity = 0.1mc

∴ Number of mMoles = 0.1/1.25

= 0.08 mM

By a similar calculation 0.08 mM in a volume of 159.6 cm^3 at 20°C exert a pressure P of

P = 0.915 cm.

This pressure was taken into account when the specific activity of the diluted ethylene-C14 was calculated.

By a converse reasoning process it is quite easy to convert from a known pressure of inactive ethylene to the final specific activity. If the pressure of inactive ethylene is P, then the specific activity (for 0.1mc) is given by:

$$0.1 \times \frac{RT}{PV}.1000$$

APPENDIX IV

Experimental Results for a Typical Experiment

Film 15

Evaporate in argon - pressure: 1.0mm

Evaporation current: 7.0amps.

Time of evaporation: 30 minutes.

Sp. act. C_2H_4-C14 - pressure C_2H_4-C12: 61.95mm

Sp. act: 0.148 mc/mM

Pressure C_2H_4-C14 in bulb C (fig. 30): 3.76mm.

Background count rate: 8601/70 = 123 c.p.m.

Admission of C_2H_4-C14 to catalyst -

Vol. 1 Q = 16.3 cm3mm

Pressure rises to 2×10^{-3} and then falls to 6×10^{-4} torr

Count rate = 4905/3 = 1534 ± 23 c.p.m.

(corrected for background and dead time (500μsecs))

Vol 2 Q = 32.6 cm^3mm

Pressure 2×10^{-3} torr.

Count rate = 6632/5 = 1326 ± 16

Vol. 3 Q = 48.9 cm3mm

Pressure $>2 \times 10^{-3}$ torr

Count rate = 14408/10 = 1336 ± 12 c.p.m.

Pump off gas phase. Pressure = 5×10^{-4} torr.

Count rate = 12902/10 = 1181 ± 11 c.p.m.

Hydrogenation

Reactants: Ethylene 49.9mm

Hydrogen 210.1mm

(N.B. Ethylene pressures in this table have been corrected for dead space as discussed in Section 5.1.)

Time (min)	Ethylene Pressure (mm)	Count Rate (c.p.m.)	Error ±
0	32.5	1170	34
3	31.8	936	23
6	31.5	928	23
9	31.3	920	23
12	31.15	858	22
15	31.05	853	22
18	31.00	866	22
21	30.95	853	22
24	30.90	804	21
27	30.80	852	22
35	30.75	817	21

Initial velocity: 0.3mm/min, 0.93mm/min/30mg Ni

Pump off reactants: count rate = 12444/15

= 712 ± 7 c.p.m.

Analysis of Nickel film.

Wt. of nickel	Optical Density
10.6mg	0.44
20.2mg	0.85
unknown	0.41

Weight of nickel film = 9.8 mg.

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