TRACER STUDIES OF CATALYSED CHEMICAL REACTIONS

THESIS

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SUMMARY

The reaction of cyclopropane with hydrogen has been studied over evaporated and pumice-supported nickel catalysts. It has been found that reproducibility of reaction behaviour on a particular catalyst is controlled by a number of factors. In cases where reproducibility has been obtained poisoning of the hydrogenation reaction by mercury has been studied using a radiotracer technique. The results of this study indicate that, when allowance has been made for differences in film weight, a particular amount of mercury does not produce a comparable effect on different films, although, when only relative effects are considered, reproducibility between films is obtained. A comparison of the poisoning curve so derived with those in the literature confirms that on evaporated nickel films the mechanism of the poisoning process is the prevention by mercury of hydrogen adsorption; a process necessary for hydrogenation of cyclopropane.

The poisoning effect of mercury for cyclopropane hydrogenation has also been studied on pumice supported palladium catalysts which showed reproducible behaviour. It was found possible to reactivate these catalysts to a certain degree subsequent to mercury poisoning. This process has been correlated with the observed migration of mercury through the catalyst bed.

The adsorption of radioactive mercury on evaporated and supported nickel catalysts has been followed and the extent of the adsorption has been found to be critically dependent on the relative temperatures of the mercury source and of the catalyst, under conditions where distillation from the mercury source cannot occur. The results obtained for simultaneous hydrogen desorption and mercury adsorption behaviour have been attributed to the presence of two modes of adsorption, chemisorption and physical adsorption. Difficulty has been found in distinguishing between these under certain conditions.

To study the factors controlling the adsorption of mercury on nickel catalysts, a technique has been developed to determine the mercury vapour pressure above a mercury-poisoned catalyst. It has been shown that this technique, using the absorption of mercury resonance radiation in conjunction with a radiotracer technique, is extremely sensitive for the study of this type of system.

INTRODUCTION

Heterogeneous catalysis - the occurrence of a reaction between chemical species at a much accelerated rate in the presence of certain types of solid surface - has been known for well over a century. Thus, for example, an extensive study of the action of a platinum surface, in promoting the reaction of oxygen with carbon monoxide and with hydrogen, was made by Faraday. It was not until the 20th century, however, that any real attempt was made to develop the basis of an explanation for this remarkable behaviour: indeed it was not until 1916 that the necessary scientific background for this was made available.

In 1913, Sabatier (1) attempted to rationalise catalytic processes in terms of compound formation between the reactants and the catalyst. Recently (2) this same concept has been used to explain the pattern of behaviour of formic acid decomposition on various metals. It was found that the catalytic activity of the metal could be correlated with the thermal stability of its formate. After the discovery of the phenomenon of adsorption by Langmuir in 1916 (3) and particularly of chemisorption, where the mode of attachment to the surface was by a bond which was chemical in nature, it came to be realised that "surface compounds" of this type were responsible for the catalytic action. It was, therefore, no longer necessary to restrict the ability to explain catalysis to those cases where a known compound of the conventional sort existed.

Until this time, therefore, catalysis had been regarded as an interesting phenomenon, which could be utilised to accomplish chemical reactions and its employment was in the nature of an art. In many of its industrial applications the subject has continued to advance along these lines, so that a great deal of useful empirical knowledge has been acquired. On the other hand, the development of the concept of chemisorption opened up the possibility of the study of catalysis on a rigid scientific basis.

It is now generally accepted that the chemisorption of reactants plays an important part in heterogeneous catalysis, and this has led to detailed studies of the interaction between reactants and surfaces. These studies have employed an exceedingly diverse range of techniques, but have developed along two main inter-related lines.

Firstly, it appeared that the arrangement of the atoms on the surface of the catalyst had some bearing on its activity. Striking qualitative evidence for this was found by Balandin (4) from studies of the reactions on metal surfaces of molecules having six membered rings, in particular the hydrogenation of benzene and the converse reaction, the dehydrogenation of cyclohexane. He claimed that catalytic activity for these reactions was only shown by those metals which formed crystals with face-centred cubic or hexagonal close packed structures. Only these metals were capable of presenting crystal faces at the surface which possessed hexagonal symmetry and accordingly it was postulated that in order to undergo reaction, the molecule became attached to the surface by six metal to carbon bonds. Considerations of this kind, which have come to be known as the geometric factor in catalysis, manifest themselves also in catalytic specificity. It has frequently been found that different catalysts produce different products in the same reaction. Thus in the decomposition of ethyl acetate on oxide catalysts a variety of products resulted, but the relative yields of each of these products varied greatly with different oxides (5).

More quantitative information on the effect of spacing of the atoms on the adsorbate surface came from a consideration of ethylene hydrogenation on metals. Twigg and Rideal (6) calculated to what extent the valence angles would require to be distorted in order for ethylene to be chemisorbed by attachment to two adjacent metal atoms on the surface. For this calculation they used values for the various bond lengths which had been established from known compounds. They showed that on the 2.47 A^o spacing of nickel, ethylene would be expected to be chemisorbed with very little distortion of the tetrahedral angles of the carbon atoms. It was left to Beek (7) to provide the experimental observations complementary to this theoretical idea. The specific activities of films of various metals for ethylene hydrogenation were compared. It was found that a relationship appeared to exist between the lattice spacing and the activity (expressed as the logarithm of the rate constant) and that this relationship exhibited a maximum. This maximum activity was shown by rhodium with a lattice spacing of 3.75 A^{o}: a value very much greater than that necessary to achieve an adsorbed species with the least strained structure. From this it appeared, therefore, that conditions which were likely to result in the strongest bonding to the surface were not those which gave the highest catalytic activity. This conclusion will be referred to again later.

It was soon evident that, while the geometry of the surface could explain some of the observations on catalytic behaviour, it was necessary also to take into account the chemical aspect of the process. Consequently, the second main line of investigation studied the bonding of species to the surface, that is, the electronic factor in catalysis. From the mass of empirical observations which had been accumulated it was apparent that, as far as metals were concerned, the most outstanding catalytic activity was exhibited by the transition metals. It was logical, therefore, to examine the possibility of a relationship between their own peculiar characteristic, viz. the possession of an incompletely filled d-band and the catalytic activity. Evidence for chemical bonding involving the electrons of the d-band has been derived from two main types of investigation.

Firstly, it was shown by Dilke, Eley and Maxted in 1948 (8) that the paramagnetic susceptibility of palladium - a property dependent upon the amount of d-band vacancy - was reduced when methyl sulphide was allowed to adsorb on the metal surface. This behaviour was attributed to chemisorption bonds in which the lone pair of electrons on each sulphur atom were donated to the d-band of the palladium. The other evidence came from work on the catalytic activity of binary alloys. In particular, Couper and Eley (9) studied parahydrogen conversion on palladium-gold alloy filaments, and Dowden and Reynolds (10) investigated copper-nickel alloys as catalysts for ethylene hydrogenation and for the decomposition of methanol and formic acid. In both cases the alloy system used was chosen because the two metals had almost identical lattice spacings, so that the alloy composition could be varied widely without having a superimposed geometric effect. It was observed that on varying the alloy composition there was a marked increase in the activation energy for the reaction under study. This increase occurred suddenly when the composition was reached where it would be expected that there was just sufficient gold or copper present for its s electrons to fill the vacancies in the d-band of the palladium or nickel.

Binary alloys such as those mentioned above afforded an elegant way to study the electronic factor in the absence of a variable geometric factor. Unfortunately, it was not possible to study the geometric factor in isolation, so that it is not clear to what extent the conclusions drawn could also be attributed to the electronic factor. As mentioned previously, however, it seemed that the type of chemisorption bond which achieved a chemically active surface species was considerably weaker than that resulting from a strain free structure. Accordingly, it was postulated that the type of adsorption important in catalysis - chemisorption which was rapid yet weak - could be provided by bonding with the d-band of the metal.

The importance of weak bonding can be seen qualitatively in various reactions. Platinum and silver are the only metals which show appreciable catalytic activity for oxidation reactions and the unusually low heat of oxygen chemisorption on these metals appears to be responsible for this. The heats of chemisorption of oxygen on most other metals exceeds 100 K cal/mole. In contrast, many oxides are capable of chemisorbing oxygen with a low heat of adsorption and these comprise the selection of the most active oxidation catalysts. The situation for hydrogenation reactions is very different. Here the catalytic activity is exhibited in some degree by all the group 8 elements and this is paralleled by the fact that in general the heat of desorption of hydrogen is much lower than that of oxygen. Again, to find metals which have sufficiently low heats of chemisorption for nitrogen is the difficulty which severely limits the choice of catalyst for ammonia synthesis. On iron, the heat of nitrogen chemisorption in the high coverage region is only 16 K cal/mole, which is consistent with its establishment as the catalyst for the Haber process.

In view of the requirement that for high activity chemisorption of reactants should be fairly weak, it is not surprising that there exist chemical species which are capable of acting as catalyst poisons. These materials, by being more strongly adsorbed by the surface than are the reactants, can reduce, often drastically, the activity of the catalyst. In certain systems this poisoning effect can be brought about by traces of impurities in the reactants, so that in practice the effect constitutes a serious disadvantage. On the other hand, it is occasionally found that the poison is capable of acting selectively. Thus, a nickel on kieselguhr catalyst, which was active for the hydrogenation of both cyclopropane and propylene, could have its activity for cyclopropane hydrogenation destroyed by mercury. The activity for propylene hydrogenation was virtually unimpaired and this behaviour has been applied by Corner and Pease (11) as the basis of a method for the analysis of mixtures of cyclopropane and propylene. The mechanism of this selective poisoning action has been studied by Campbell and Thomson using a radiochemical tracer technique. It was found that the effect of the mercury was to prevent hydrogen chemisorption, a state of affairs necessary for the cyclopropane hydrogenation (12). In contrast, the reaction of propylene is known to involve this hydrocarbon in the chemisorbed state and its adsorption was unaffected by mercury.

There is evidence that the geometric factor is also important in the manner in which poison molecules interact with the surface and also that steric hindrance can play a part in the poisoning action. Maxted (13) has demonstrated this to be true in a rather novel manner, by studying the relative effects of sulphides and disulphides as poisons. It was found that aliphatic sulphides of the type R-S were much more effective poisons than disulphides, of the type S-R-S, possessing the same chain length. This was presumably because molecules of the latter type were anchored more rigidly to the surface since the sulphur atoms through which bonding occurred were at the extremities of the carbon chain, while the former had a free chain end capable of a rotational motion which could sweep the surface. Herington and Rideal (14) have also considered the effects of poisons on sites for catalysis in terms of the number of sites occupied by each poison molecule and the number required for each reaction event.

All of the foregoing ideas based on surface geometry have implied the simple picture of the surface as being an array of uniformly active sites, which can be progressively eliminated by being blocked by the poison molecule. It has often been noted, however, that very large poisoning effects result from small amounts of poison and from this developed the "active spot" theory of catalysis. This theory suggested that the active sites were concentrated on relatively small areas of the catalyst surface. This may be exemplified by the work of Pease and Stewart (15) in which carbon monoxide, when admitted to a reduced copper catalyst, affected its activity for acetylene hydrogenation to a much greater extent than it affected the adsorption of the reactants. Similarly, using a tracer technique, it was shown (16) that the poisoning of a silica-alumina catalyst for the cracking of isobutane by minute amounts of quinoline was by the adsorption of this on the few active sites on the catalyst.

The object of the work described in this thesis was to study in more detail the poisoning action of mercury in cyclopropane hydrogenation. Beek (17) has reported that a correlation exists between the catalytic activity and adsorptive capacity of metal films and their weight. Consequently, it was hoped, by using such films in conjunction with a tracer technique for mercury, that the poisoning mechanism could be put on a more qualitative basis, in particular that, having regard to the actual fraction of surface covered by poison under any given conditions, some indication would be obtained of the extent and nature of the catalyst surface taking part in the reaction.

CHAPTER 1

THE STUDY OF CYCLOPROPANE HYDROGENATION ON EVAPORATED NICKEL FILMS

The apparatus used by Campbell and Thomson (12) for their study of the mercury poisoning of cyclopropane hydrogenation on evaporated nickel films possessed a number of unsatisfactory features which did not permit a rigorous study of this reaction. The initial object of this work, therefore, was to repeat this study using a system more suitable for following the hydrogenation reactions.

In this chapter only brief details of the experimental procedure and the apparatus used are given. Full details are given in Chapter 9.

(1.1.) Pressure Measuring and Gas Circulating Devices Used in Initial Experiments

In the initial stages of this work hydrogenation reactions were followed using all glass Bourdon "spoon" gauges. These gauges, when used in conjunction with a conventional optical lever, had sensitivities typically about 4 mm per torr of pressure differential.

To maintain a flow of reactants over the catalyst a magnetically operated piston cycling pump was used.

(1.2.) Preparation of Evaporated Nickel Films

The evaporated nickel films were prepared in essentially the

SCHEMATIC DIAGRAM OF
HYDROGENATION APPARATUS

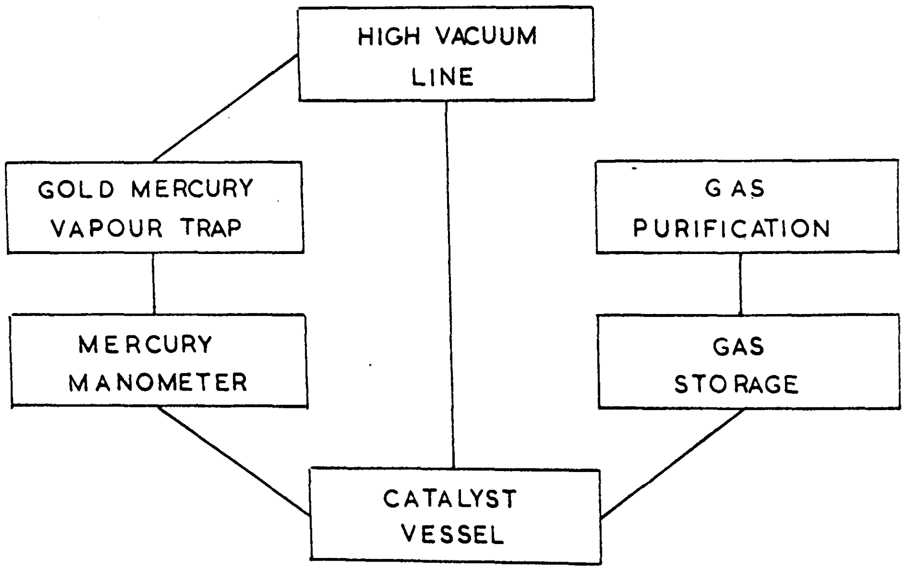


Fig. 1. 1.

same manner as those of Beek et al. (17). The high vacuum required for their preparation was achieved using a mercury free high vacuum system. The ultimate vacuum obtained from this system, measured on a Penning gauge, was 1×10^{-5} torr.

It was not possible to isolate the catalyst vessel from the cycling pump during the evaporation of the film since this would have required the use of break seals which would have greatly reduced the efficiency of the cycling pump. Prior to film evaporation the walls of the Pyrex catalyst vessel were degassed under vacuum at 450 - 500°C for at least 12 hr. During the last few hours of this procedure the hairpin filament of pure nickel wire was heated electrically to just below its evaporation temperature, to remove the copious quantities of gaseous impurities it contained. During the evaporation of the film the walls of the catalyst vessel were cooled by immersion in running water to minimise sintering of the film.

(1.3.) Cyclopropane Hydrogenation

A schematic diagram of the apparatus used is shown in Fig. 1.1. and a detailed diagram is given in Chapter 9.

The carefully purified reactant gases cyclopropane and hydrogen were stored as a 1:1 mixture in a reservoir sealed with a greased tap. This mixture was prepared by admitting cyclopropane to a known pressure into the reservoir and freezing it into a side arm. Hydrogen was then admitted to the same pressure and the cyclopropane allowed to evaporate. Diffusion of the two gases was allowed to proceed for at least an hour and normally much longer before use.

All absolute pressure measurements were obtained using a U-tube mercury manometer. This manometer was isolated from the otherwise mercury-free vacuum system using a greased tap and two gold leaf traps.

(1.4.) Experimental Procedure for Studying Hydrogenation

As soon as possible after the termination of film evaporation the reaction mixture was admitted to the catalyst vessel. The initial gas pressure was noted on the mercury manometer which was then immediately isolated. The reaction being followed, viz.

1 mole hydrogen + 1 mole cyclopropane → 1 mole propane

resulted in an overall pressure drop.

This reduction in pressure was read using the Bourdon gauge at various time intervals until the reaction had proceeded to the desired extent. The contents of the catalyst vessel were then pumped off, a second charge of reactants admitted and the reaction followed as before.

Since the composition of the reactant gas mixture was known it was possible to express the pressure reading at any time in terms of the cyclopropane partial pressure, using the following expression which is derived in section 9.27.

Partial pressure of cyclopropane at any time t

$$= P_t - a = P_o - PD - a$$

where P_t = total pressure at time t

P_o = initial total pressure

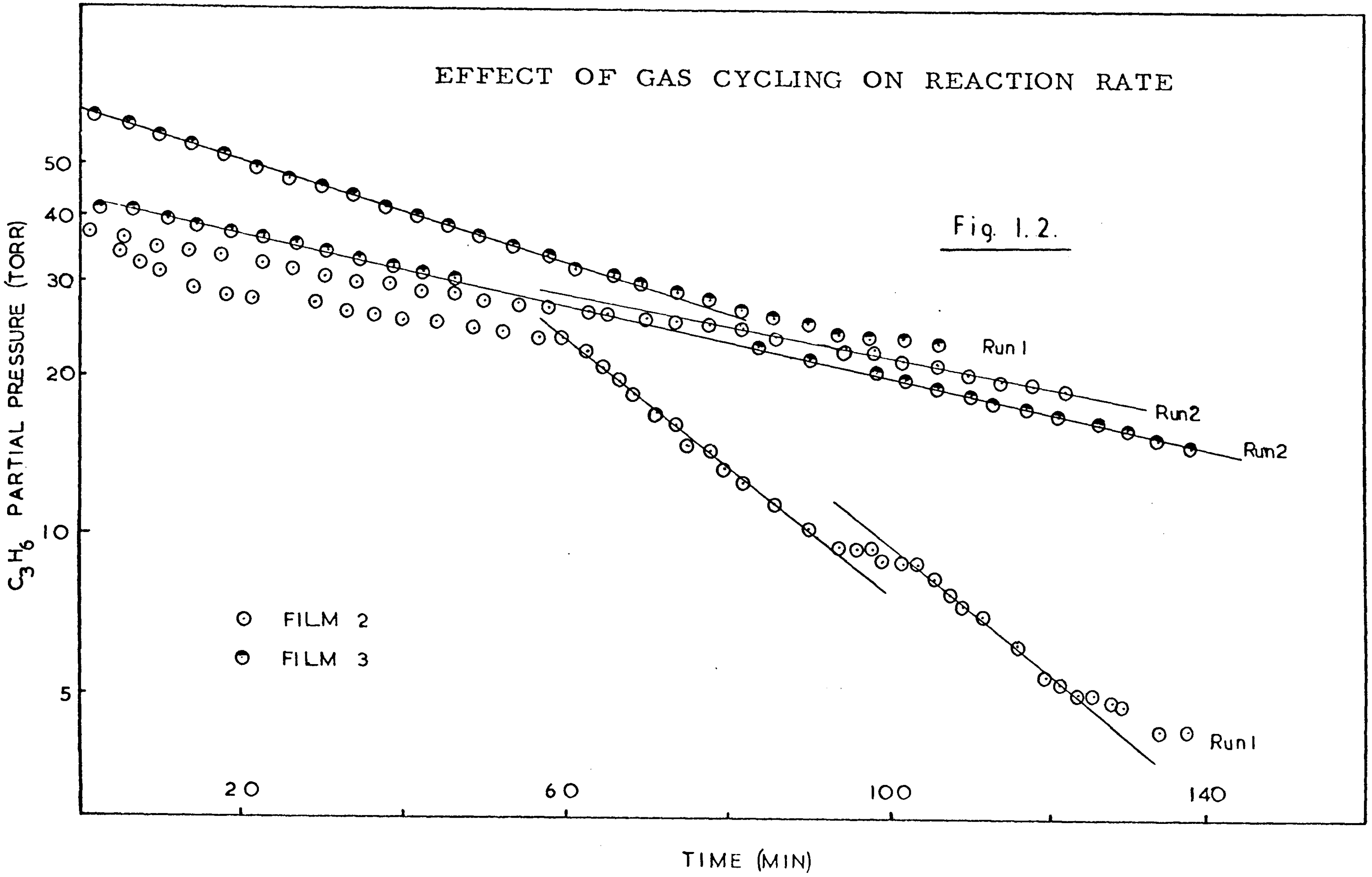
a = fraction of reactant mixture which is hydrogen

PD = observed pressure difference obtained from the pressure gauge.

Since it was intended to study the poisoning effect of mercury on the hydrogenation reaction it was necessary to be able to predict how the reaction would proceed in the absence of mercury. Any change from that expected which occurred after the admission of mercury would then be attributable to the action of the mercury. The characteristics of the reaction in the absence of mercury were determined by studying the effects of certain variables on the reaction such as effect of gas circulation speed, initial gas pressure and ageing effects of the film.

(1.5.) Results Obtained Using Spoon Gauge/Cycling Pump System

The logarithm of the cyclopropane partial pressure (P_c) was plotted against time (t) for each hydrogenation. On Film 1, circulation



EFFECT OF GAS CYCLING ON REACTION RATE

Fig. 1.2.

of the reactants was carried out throughout the duration of the two separate hydrogenation runs and a linear relationship was found between log P_c and t. This would appear to indicate that the reaction being followed was first order.

In Film 2, circulation was not commenced until after 1 hr and was continued for 32 min after which time it was stopped for 6 min and then restarted. The relationship between log P_c and t is given in Fig. 1.2. It can be seen that when no circulation was being carried out this relationship was not linear, the rate was fast initially and then slowed down. When, however, circulation was commenced the rate increased and the relationship became strictly linear. When the circulation was stopped for the 6 min period the linearity was lost but was regained on restarting the circulation.

In Film 3 the results of which are also shown in Fig. 1.2. the circulation was carried out throughout the hydrogenation but the rate of the circulation was varied. This had little effect on the linearity of the relationship.

After the first hydrogenation on each film had been carried out to the desired extent, the catalyst vessel was evacuated using the rotary and the diffusion pumps, for 1 hr in the case of Films 2, 3 and 2.5 hr in the case of Film 1. A fresh charge of reactants was admitted in each case. It was found that the rate of hydrogenation in the second run, under the same conditions of circulation, was slower than that in the first in each case.

The above results enabled a number of conclusions to be made regarding the cyclopropane hydrogenation in this system.

(1) Without circulation occurring the reaction was diffusion controlled.

(2) When circulation occurred the reaction was apparently first order.

(3) The slowest circulating speed used was sufficient to overcome diffusion dependence.

(4) A second hydrogenation on a film did not have the same rate as the first.

(1.6.) Improvements to the Hydrogenation System

It was found that spoon gauges were particularly susceptible to breakage and they were therefore replaced by spiral Bourdon gauges. These gauges were much more robust and proved to be almost twice as sensitive to pressure change as the spoon gauges. In addition, however, these gauges were extremely sensitive to vibration and were unable to be used in conjunction with the gas cycling pump employed previously. Since the spiral gauges possessed so many favourable properties a vibrationless gas circulating system was designed.

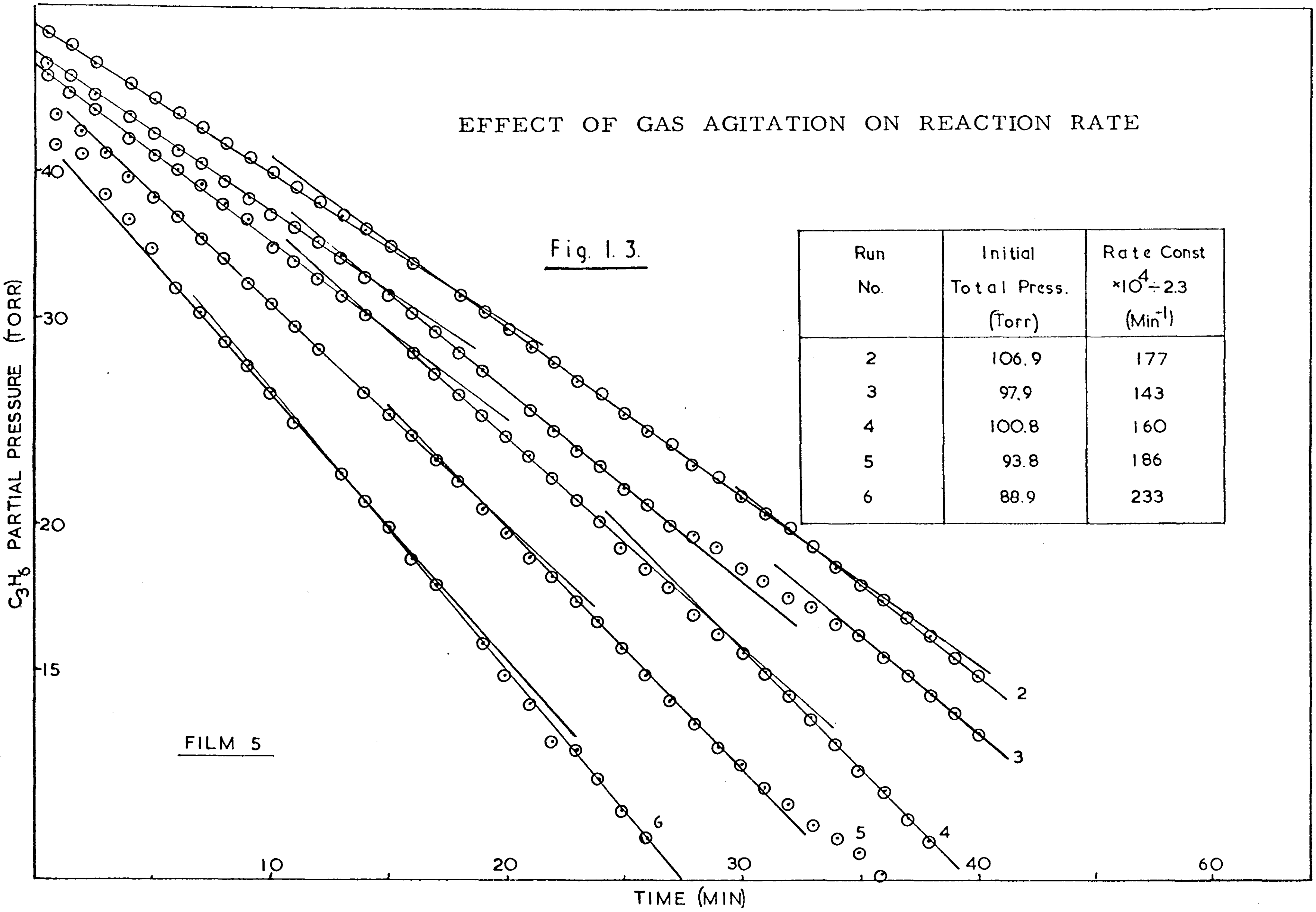
This consisted of a hollow glass piston which was oscillated vertically within the catalyst vessel by means of an electromagnet. This system also enabled the nickel filament to be more efficiently degassed than previously by heating it to its evaporation temperature, the light film thus formed being deposited on the inside of the piston. This design of the hydrogenation system enabled the catalyst vessel to be degassed in a portion of the high vacuum apparatus remote from the pressure measuring system. It was then sealed off at a previously degassed constriction and transferred to the pressure measuring system where the film was evaporated. As soon as possible after the preparation of the film the reactant mixture was admitted by breaking a break seal. The reaction was followed with the catalyst vessel immersed in a water thermostat at 23°C and the gas storage and pressure measuring systems enclosed in an air thermostat at the same temperature.

(1.7.) Preliminary Experiments Using the Improved System

The results of the hydrogenations carried out in the spoon gauge/cycling pump system had indicated that circulation of the reactant gases had an effect on the reaction and that it was not possible

EFFECT OF GAS AGITATION ON REACTION RATE

Fig. 1.3.



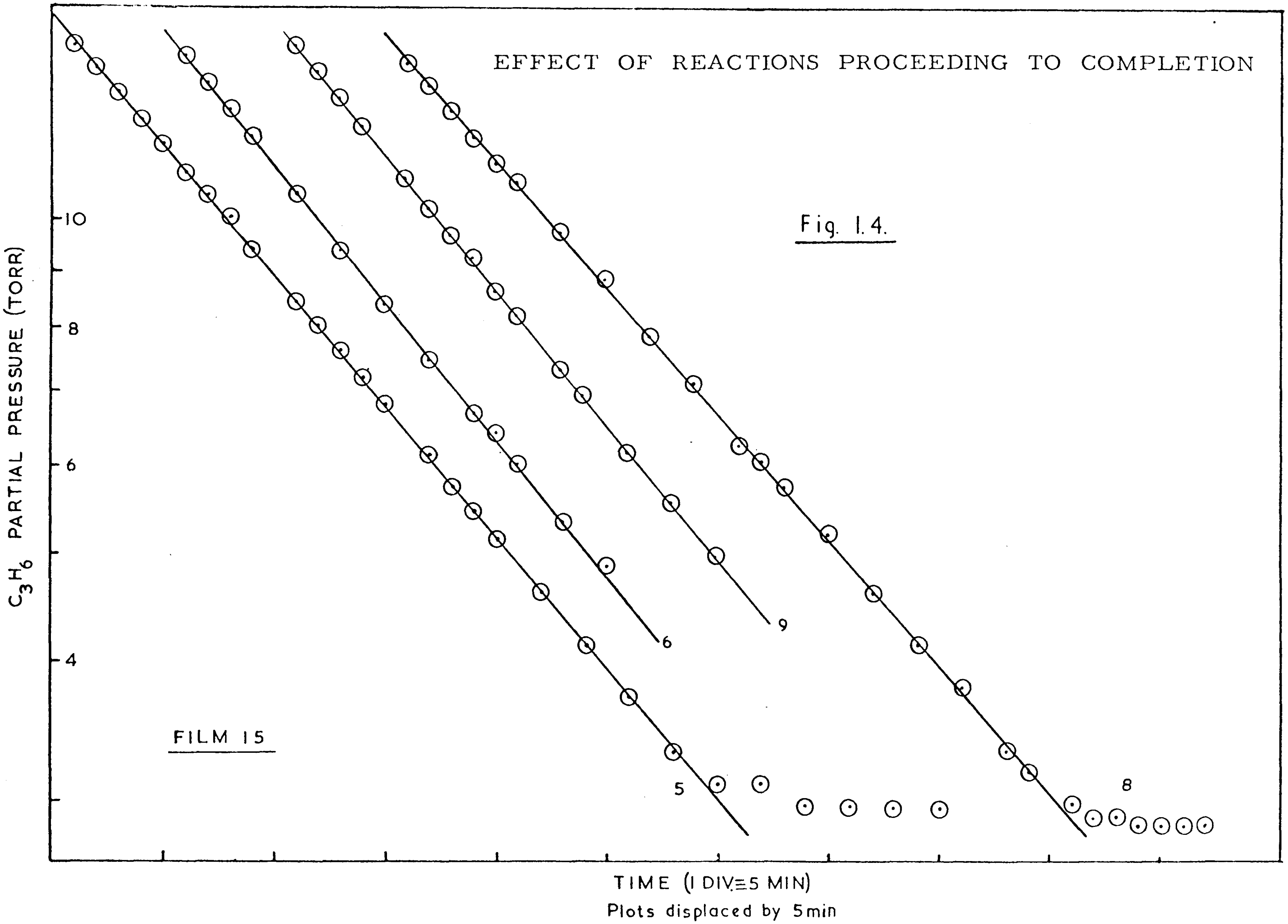
Run No.	Initial Total Press. (Torr)	Rate Const $\times 10^4 \div 2.3$ (Min^{-1})
2	106.9	177
3	97.9	143
4	100.8	160
5	93.8	186
6	88.9	233

to reproduce this rate on the same film. This study was, therefore, repeated to determine the effect of the hollow piston-type gas agitator and spiral gauge system. In this case, however, after each reaction had proceeded to the desired extent the catalyst vessel was evacuated for 3 min only, a further 1 min elapsed before a fresh charge was readmitted. The logarithm of the cyclopropane partial pressure was plotted against time as before. The results are shown for Film 5 in Fig. 1.3.

In runs 2, 3 and 4 the agitator was set in motion after 13 min and stopped after 25 min. In each case the relationship between log P_c and t was linear with or without agitation but the rate of the reaction was increased when the agitator was in operation. In runs 5 and 6 the agitator was switched on at the beginning of the reaction but the rate of agitation was increased to its maximum possible value after 21 min and a slight alteration in the linear relationship was observed. The slope of the log P_c versus t relationship was obtained from the plots for those portions of the reaction in which the same rate of agitation was carried out. These are also indicated in Fig. 1.3.

It was concluded from these results that :

(a) the gas agitation affected the rate of reaction in the improved system also and that a linear relationship between log P_c versus time existed.



EFFECT OF REACTIONS PROCEEDING TO COMPLETION

Fig. 1.4.

(b) the rate of reaction was still not reproducible on the same film although the length of time the film was connected to the vacuum pumps, i.e. potential sources of contamination, was much shorter than before.

(c) the total initial pressure of the reactants might have had some effect on the reaction rate.

On studying hydrogenations using this system on Film 10 it was found that a non linear relationship between log P_c versus time existed when the agitator was not in use but that it became linear when the agitator was switched on. Also, the rate of reaction did not alter if the rate of agitation was raised above a certain value. All hydrogenations in future experiments were, therefore, carried out with the rate of stirring above this value.

Further evidence that the operation of the agitator removed dependence of the rate of reaction on diffusion was shown in a number of hydrogenations on Film 15 which were allowed to proceed to apparent completion. In these cases the linearity of the log P_c versus t relationship was maintained until a sudden break in the linearity took place indicating 80% conversion and no further reaction occurred. This is shown in Fig. 1.4. along with the relationship for the two reactions which immediately followed each of the reactions allowed to proceed to completion. The 80% conversion which was observed when the reaction was followed until no further pressure fall occurred is consistent with the fact that the volume of the catalyst vessel was approximately 150 cc whereas that of the connecting tubing to the gauge was approximately 25 cc. Examples of the experimental data from which the plots shown in Fig. 1.4. were derived are given in Appendix 1.

(1.8.) The Effect on the Hydrogenation Rate of Total Initial Pressure of Reactants

The results of the preliminary experiments suggested that the failure to obtain reproducible rates of hydrogenation as measured by the slope of the linear relationship between log P_c against t on any one film might be due to differences in total initial pressure of reactants. Consequently, a series of hydrogenations were carried out on the one film in which the initial total pressure was different for each run and a constant rate of gas agitation was employed. Each hydrogenation was allowed to proceed for about 20 min after which time the reaction vessel was evacuated for 3 min, before admission of a fresh charge of gas. The gradient of the linear relationship between cyclopropane partial pressure and time was calculated for each hydrogenation as before.

It was found that there was considerable dependence of the

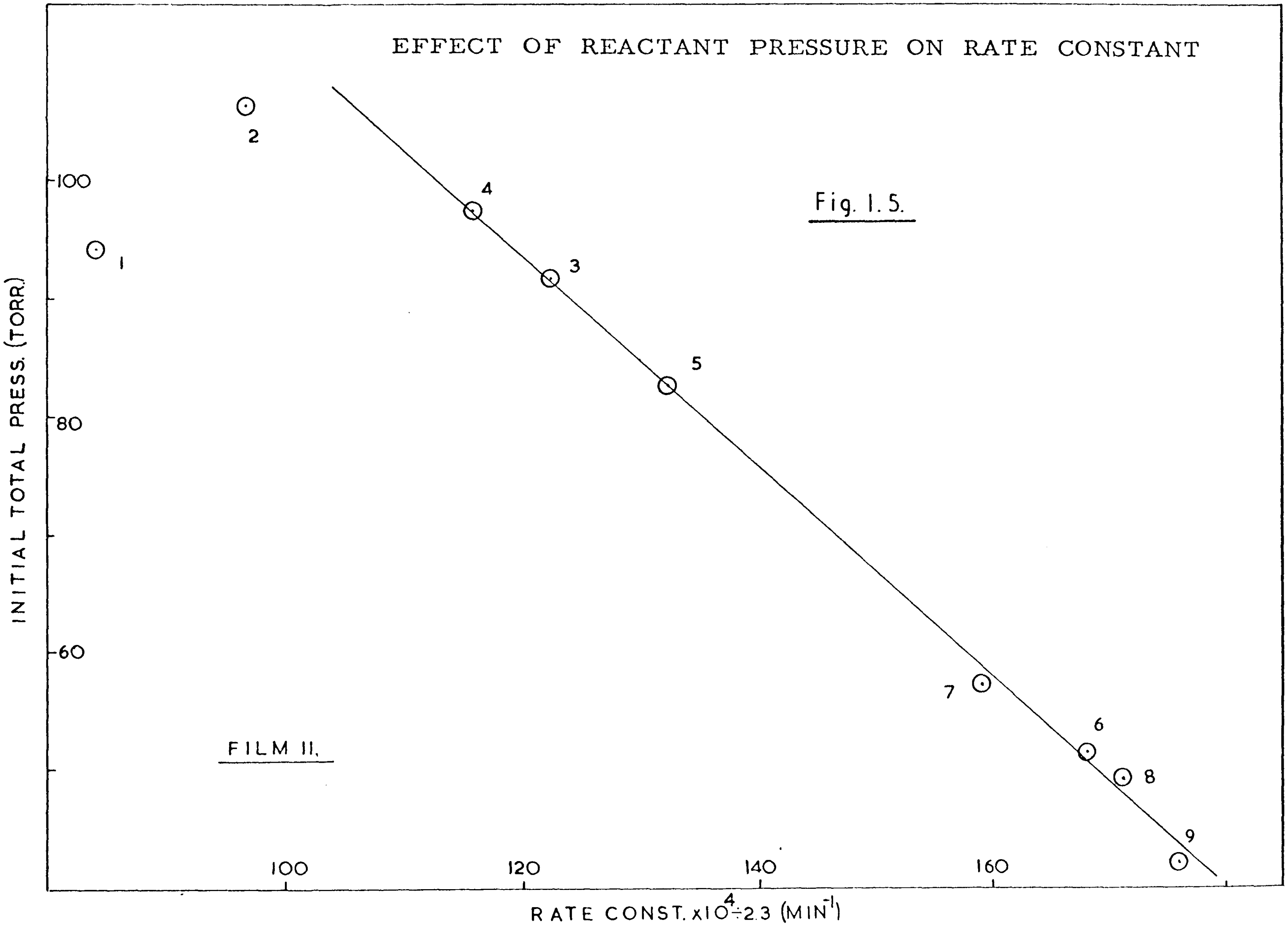
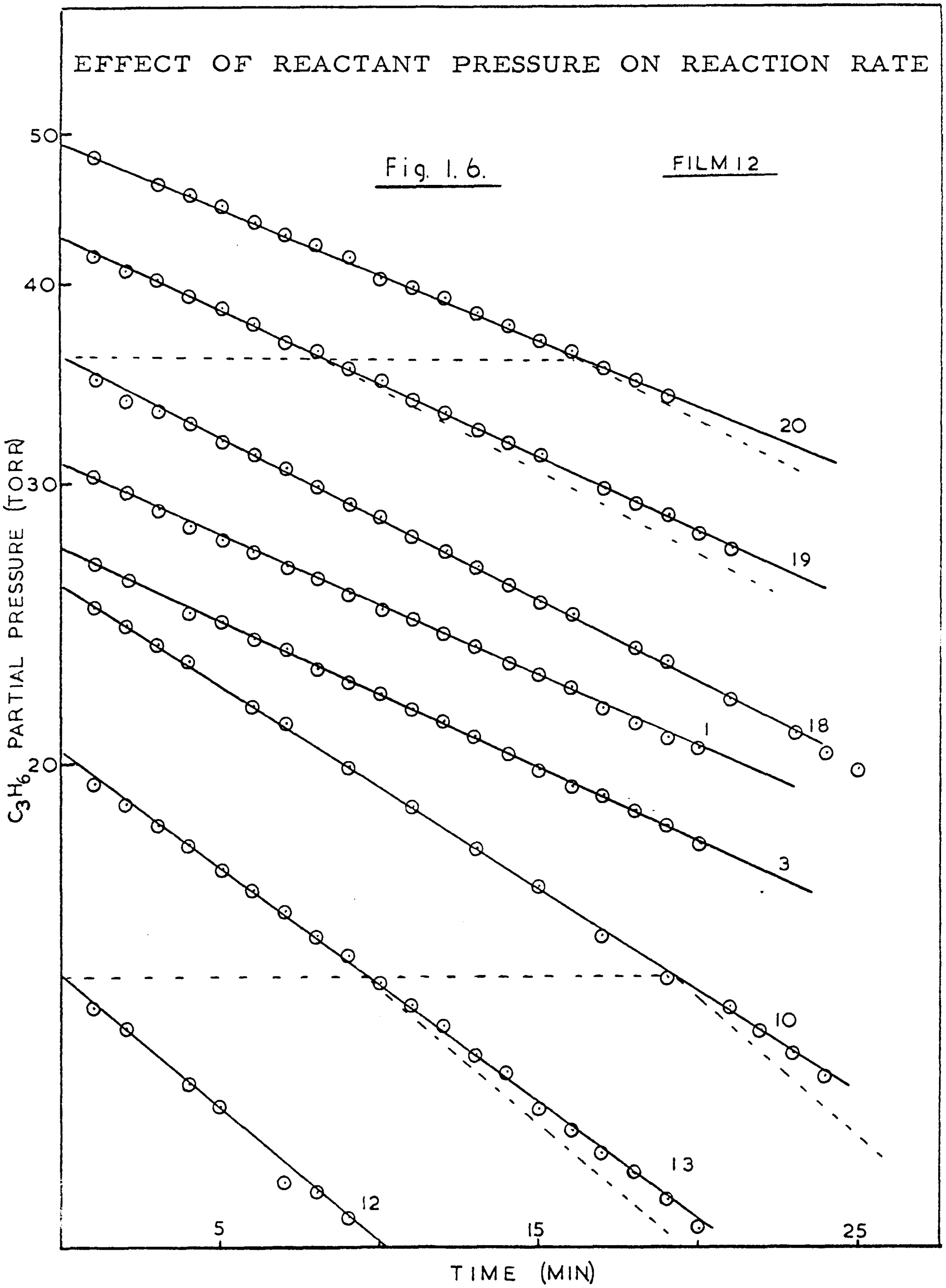

EFFECT OF REACTANT PRESSURE ON RATE CONSTANT

Fig. 1.5.



EFFECT OF REACTANT PRESSURE ON REACTION RATE

Fig. 1.6.

gradient, which will be termed the rate constant, on the initial pressure and this relationship is indicated in Fig. 1.5. Within any particular hydrogenation, however, the relationship between the logarithm of the cyclopropane partial pressure and time was strictly linear. Examples of these relationships are shown in Fig. 1.6. for Film 12.

(1.9.) Additional Factors Affecting Rate of Cyclopropane Hydrogenation

Having determined that the rate of hydrogenation was dependent on the initial total pressure of reactants, further experiments were carried out to determine whether hydrogenation rates were reproducible if this initial pressure was kept constant. Since it was intended to study the effects of various quantities of mercury on the reaction rate and this mercury was to be admitted while the reaction vessel was evacuated between hydrogenations, it was decided to study the effect of leaving the catalyst for varying lengths of time under vacuum between hydrogenations in the absence of mercury.

(a) Time of exposure of catalyst to vacuum between runs

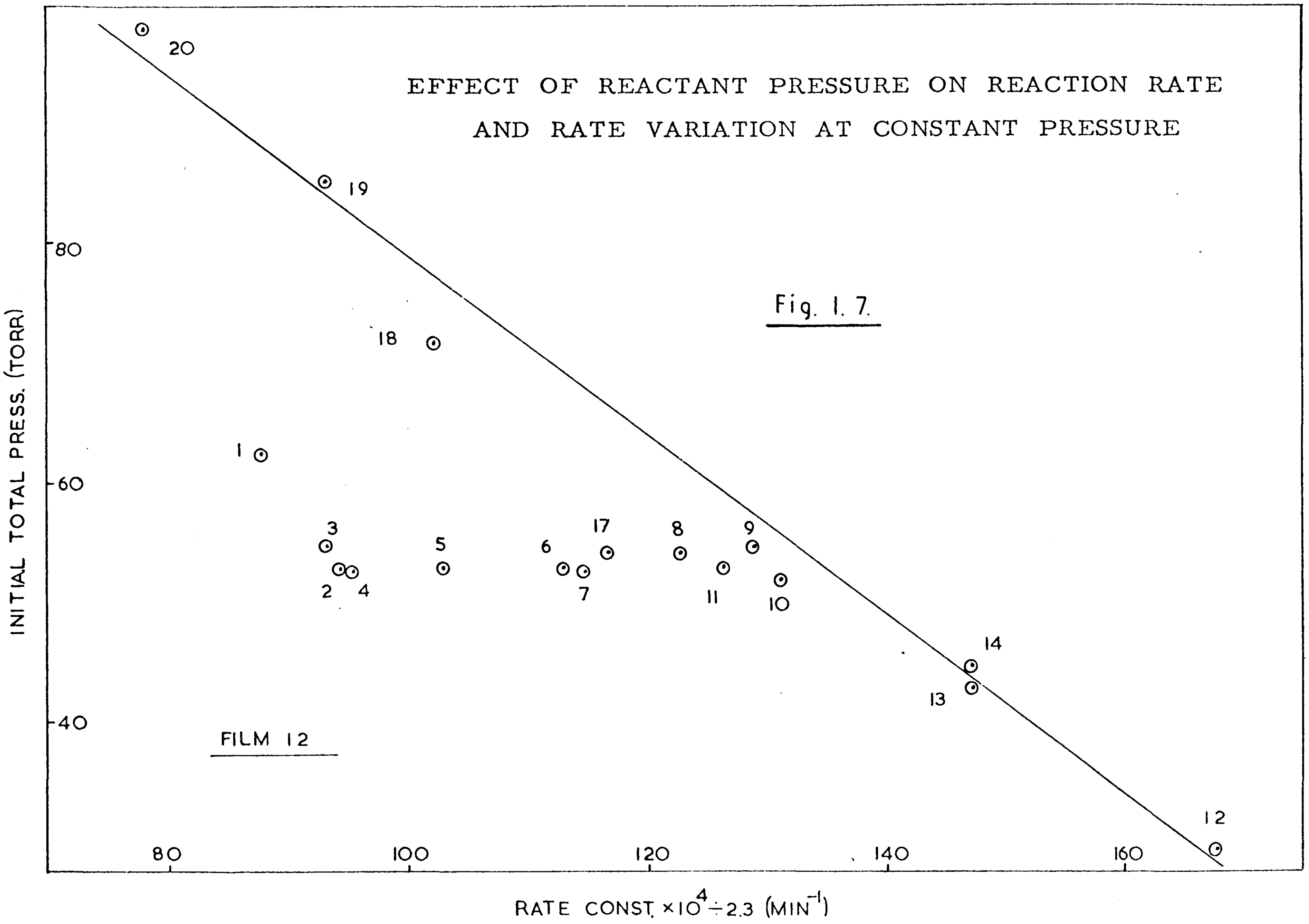
The results obtained are summarised in Table 1.1. Between each hydrogenation the reaction vessel was evacuated for 2 min on the rotary pump. After studying the effect of the time for which the catalyst was left under vacuum the effect of change in total initial

TABLE 1.1.

Effect of Initial Pressure on Reaction Rate

Film 12

Initial Rate (torr min^{-1})	Run No.	Initial Total Pressure (torr)	Length of Run (min)	Exposure to Vacuum (min)	Rate Constant (min^{-1}) x 10^4 ÷ 2.303
0.56	1	62.22	20		88
0.44	2	52.87	20	3.5	94
0.43	3	54.32	20	3	93
0.41	4	52.27	20	3	96
0.45	5	52.82	20	1	103
0.46	6	52.80	20	1	113
0.49	7	52.25	29	3	115
0.54	8	54.06	30	1	123
0.58	9	54.54	20	21	129
0.54	10	51.69	26	33	131
0.54	11	52.78	20	60	126
0.38	12	29.18	20	13	168
0.46	13	40.29	20	3	147
0.47	14	40.48	20	5	147
-	15	80.84	29	3	-
0.24	16	13.42	20	3	236
0.50	17	54.07	20	3	117
0.60	18	71.66	20	2	102
0.64	19	85.18	20	3	93
0.65	20	98.07	20	3	78



EFFECT OF REACTANT PRESSURE ON REACTION RATE AND RATE VARIATION AT CONSTANT PRESSURE

Fig. 1. 7.

pressure was also studied on this film and this is shown in Fig. 1.7.

The results indicate that increasing the length of time for which the film was left under vacuum between runs had little effect on the reaction rate which appeared to increase with the increasing number of hydrogenations carried out on the film. The effect of varying the total initial pressure is the same as that observed previously, an increase in this pressure causing a reduction in the reaction rate, the relationship between rate constant and initial pressure being virtually linear.

(b) Relationship between rate constant and initial rate

To determine whether there was justification for assuming that the value of the rate constant as calculated was a true measure of the rate of reaction the value of the initial rate for each reaction on Film 12 was calculated. This was carried out by plotting the change in gauge readings (which is proportional to the pressure change) against time. Smooth curves were obtained and the gradient of the slope at zero time was taken as the value of the initial rate. The values obtained are also given in Table 1.1. When these values were plotted against the corresponding values of the rate constant a linear relationship was obtained (see Fig. 1.8.) provided reactions with comparable initial total pressures were considered. This indicated that under these conditions the rate constant was proportional to the

RELATIONSHIP BETWEEN INITIAL RATE AND RATE CONSTANT

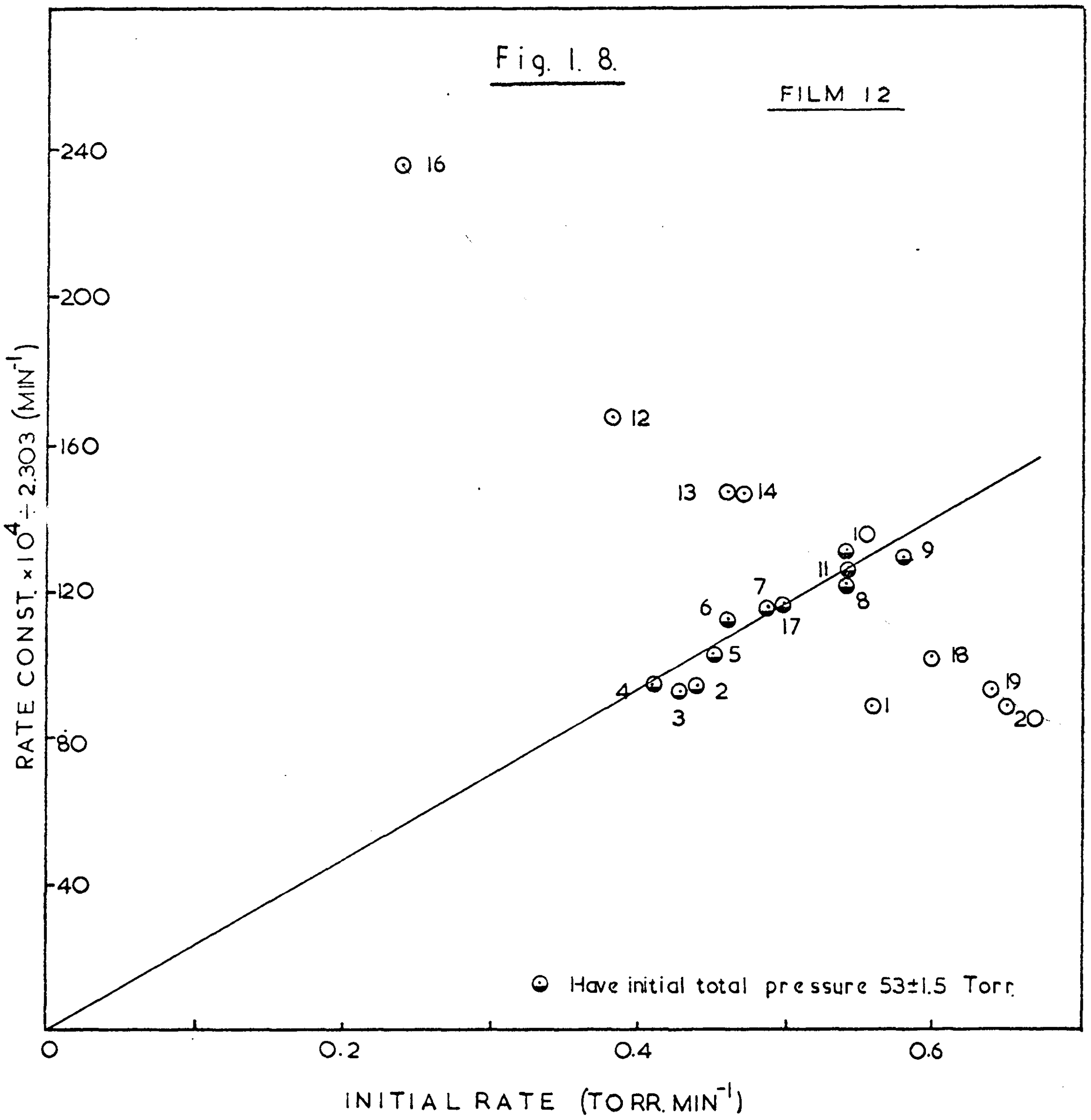


Fig. 1.8.

initial rate and it was, therefore, valid to consider the value of the rate constant as a measure of the hydrogenation rate.

(c) Extent to which previous reaction proceeded

To determine what other factors affected the reaction rate a series of experiments were carried out to determine whether the extent to which a reaction was allowed to proceed had any effect on the rate of a subsequent reaction. There was some evidence from the previous work that this might be the case. Consequently, on Film 14 a standard procedure was adopted. The initial pressures were kept as near to a constant value as possible, the length of time for which the reaction vessel was evacuated was the same in each case, viz. 1 min, and the film was left under vacuum for 4 min between each hydrogenation. A series of hydrogenations were carried out under these conditions, in which the reaction was allowed to proceed for 21 min, to obtain the rate under standard conditions. Several hydrogenations were then allowed to proceed to virtual completion. The results obtained are given in Table 1.2. These results indicate that if a reaction was permitted to continue until it reached completion then the subsequent reaction had an enhanced rate.

To determine whether this effect was due to the presence of adsorbed reactants on the catalyst surface a series of hydrogenations were carried out on Film 15 under standard conditions and values of

TABLE 1.2.

Effect on Reaction Rate if Previous Reaction Proceeds to Completion

Film 14

Run No.	Initial Total Pressure (torr)	Length of Run (min)	Rate Constant (min^{-1}) x 10^4 ÷ 2.303
1	53.90	21	101
2	49.43	20	103
3	50.78	21	102
4	50.51	23	106
5 *	49.79	75	108
6	49.47	21	138
7	50.32	21	123
8 *	49.35	62	121
9 *	49.37	73	138
10	49.31	21	138
11	41.66	21	137
12	49.68	21	119
13 *	3.49	16	360
14 *	6.76	36	145
15	50.24	21	118

Runs marked thus * allowed to go to completion

TABLE 1.3.

Effect of Admission of Single Reactant

Film 15

Run No.	Initial Total Pressure (torr)	Length of Run (min)	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$
1	32.7	24	202
2	30.63	26	197
3	30.10	26	218
4	30.14	26	223
5 *	29.85	62	237
6	29.70	26	233
7	29.26	26	242
8 *	28.92	43	229
9	30.21	26	242
10	31.44	32	223
11	13.42(C_3H_6)	26	-
12	30.60	27	212
13 *	29.84	84	182
14	31.29	26	178
15	30.90	26	136
16	31.07	26	110
17	21.15(H_2)	20	-
18	32.13	26	82
19	30.43	20	67
20	31.06	27	97
21	31.15	45	72

Runs marked thus * allowed to go to completion the rate obtained as before. Cyclopropane was then admitted to the catalyst vessel to a pressure of 13 torr instead of the reactant mixture and was left for the same length of time as a normal hydrogenation mixture. The series of normal hydrogenations were then continued. The process was later repeated using 20 torr of hydrogen. The results obtained are given in Table 1.3.

The admission of cyclopropane had little observable effect on the immediately subsequent hydrogenation but the rate of later hydrogenations became reduced.

The only observable effect of the admission of hydrogen was to reduce this apparent poisoning effect with repeated reaction.

(d) G.L.C. analysis of reactants

In an attempt to determine the factors leading to the lack of reproducible hydrogenation rates (a criterion required before mercury could be admitted) the cyclopropane which had been used as a reactant was investigated for impurities using G.L.C. (see Appendix 2). It was found that this gas contained considerable amounts of propylene and propane as impurities. Cyclopropane from a different source was obtained and this was shown to contain relatively negligible amounts of these gases. This purer cyclopropane was, therefore, used for all subsequent reactions.

A number of experiments were carried out to determine whether

TABLE 1.4.

Run No.	Initial Total Pressure (torr)	Length of Run (min)	Rate Constant (min^{-1}) $\times 10^4$ $\div 2.303$
Run 17			
1	29.09	20	169
2	25.10	21	170
3	25.20	21	166
4	24.54	21	181
5	24.73	21	188
6 *	25.47	46	200
7	26.34	26	228
8	25.58	38	217
Run 18			
1	85.16	30	27
2	21.6	24	54
3	22.09	20	52
4	21.13	21	56
5	21.96	21	55
6	22.14	20	57
7	21.74	21	58
8	33.52	21	45
9	33.72	20	40
10	34.04	20	24

* Run permitted to proceed to completion

TABLE 1.5.

Film 19

Run No.	Initial Total Pressure (torr)	Length of Run (min)	Rate Constant (min^{-1}) $\times 10^4$ $\div 2.303$
1	30.90	40	124
2	32.14	20	108
3	46.59	20	71
4 *	32.52	53	113
5	33.01	19	131
6	31.87	20	139

* Run permitted to proceed to completion

the use of this purer cyclopropane made any difference to the properties of the system already observed. The results of these experiments are given in Tables 1.4. and 1.5. These results did not differ significantly from those using the 'impure' cyclopropane. The reaction rate was still affected by the total initial pressure of the reactants and by the extent to which a previous hydrogenation had been allowed to proceed. There was still a tendency for the reaction rate to increase with the increasing number of reactions carried out; a variation of 10 - 15% in this rate occurred over a series of 5 hydrogenations carried out under the same conditions.

(1.10.) Conclusions from Studies of Cyclopropane Hydrogenation on Evaporated Nickel Films

As a result of the foregoing studies the following conclusions were obtained concerning cyclopropane hydrogenation on evaporated nickel films.

1. The rate of cyclopropane hydrogenation using a 1:1 cyclopropane: hydrogen mixture was controlled by the diffusion of reactants to the catalyst surface when no artificial agitation of the gas was carried out. When circulation or agitation of the gases was employed the rate of hydrogenation increased with the rate of agitation until a limiting value of rate was attained.

2. When agitation of the reactants was carried out the reaction

proceeded with apparently first order kinetics.

3. When a number of hydrogenations were carried out successively on the same film the rate of each reaction, although reproducible within itself, was dependent on a number of factors,

    (a) the total initial pressure of the reactant gases.

    (b) the extent to which the previous hydrogenation had been allowed to proceed.

4. If a series of five or six hydrogenations were carried out under identical experimental conditions a variation of 10 - 15% was observed in the hydrogenation rates.

CHAPTER 2

POISONING BY MERCURY OF CYCLOPROPANE HYDROGENATION ON NICKEL FILMS

The work described in Chapter 1 established that the rate of cyclopropane hydrogenation was affected by a number of factors. Some of these were known, such as total initial pressure of reactants and the past history of the film, but variations in the rate occurred which could not be explained at this stage. It has been reported by other workers (18) that difficulties have been encountered in the reproduction of hydrogenation rates on nickel films for reasons which have not been fully understood. Consequently, although it was desirable to be able to predict the behaviour of the reaction in the absence of mercury with an accuracy better than that obtained, viz. 10 - 15%, it was considered advantageous to study the relative effect of admitting mercury vapour to the system.

(2.1.) The Poisoning Procedure

In order to determine how much mercury was present on the catalyst at any particular time radioactive mercury ^{203}Hg was used to poison the catalyst. This isotope emits gamma radiation of energy sufficient for its absorption in several millimetres of glass to be insignificant. An experimental procedure for the determination of this mercury on the catalyst had been developed by Campbell and Thomson (19) using a halogen quenched counter which was placed parallel to and in contact with the reaction vessel. Owing to counting geometry considerations it was only possible to determine relative amounts of mercury using this method. The absolute weight of mercury present at the end of the experiment was determined by dissolving the film in 10 N nitric acid and comparing the count rate obtained from 10 ml of this in a liquid counter, with that obtained from 10 ml of a solution containing a known weight of mercury of the same specific activity.

Radioactive mercury of a suitable specific activity was distilled into a breakseal tube which was then attached to the catalyst vessel. When it was desired to admit mercury to the film the breakseal was broken and mercury allowed to diffuse to the film while the reaction vessel was evacuated between hydrogenations. It was found that mercury vapour did not diffuse at any appreciable rate when the reactant gases were present in the reaction vessel. During the poisoning experiments an attempt was made to carry out the same experimental procedure for hydrogenations in the presence of mercury as for those in the absence of mercury, in order that any effects observed might only be ascribed to the action of mercury.

When required, the weights of the nickel films were obtained by determining the concentration of nickel in the nitric acid solution, containing the dissolved film, by spectrophotometry using the red, water soluble, nickel III dimethylglyoxime complex (20).

(2.2.) Results of Mercury Poisoning

The results for a series of poisoned and unpoisoned hydrogenations on Film 22 are shown in Table 2.1. The values of the rate constants were obtained from the gradient of the linear graph of the logarithm of the cyclopropane partial pressure versus time. It was found that variations of 2 - 3% were obtained when these values were calculated a number of times from the same experimental points. A variation of the same magnitude was found between the values obtained graphically and those obtained using the method of least squares. This latter technique made use of the KDF 9 computer. Variation of the time for which the film was left under vacuum conditions in the absence of mercury was seen to have a negligible effect on the rate: the overall variation in rate in the seven unpoisoned hydrogenations on this film was 12%.

Mercury was seen to have a definite poisoning effect on the hydrogenation and it was found possible to poison the reaction to such an extent that little activity remained. The effect of the diffusion of mercury vapour through the reactant gases during a hydrogenation was studied in run 13 where the reaction was allowed to proceed

TABLE 2.1.

Film 22 (Wt. = 30.3 mg)

Run No.	Initial Total Pressure (torr)	Time (min) of Exposure	Wt. of Hg Present (mg)	Length of Run (min)	Rate Constant (min^{-1}) $\times 10^4$ $\div 2.303$
1	23.07			35	162
2	18.40	5 +		20	162
3	19.77	5 +		20	163
4	20.61	5 +		20	163
5	19.19	17 +		20	179
6	18.85	27 +		20	171
7	20.86	61 +		90	183
8	19.69	5		20	176
9	18.43	5		20	166
10	18.47	12	0.03	20	156
11	18.29	29	0.15	21	138
12	19.14	20	0.21	21	126
13	20.17	45	0.41	680	106
14	19.94	5	0.44	37	90
15	19.66	61	0.56	83	58
16	19.38	5	0.58	20	55
17	19.99	45	0.70	20	48

For calculation of Hg weights see Appendix 1.b.

\+ indicates film left under vacuum between hydrogenations in absence of Hg

TABLE 2.2.

Film 21 (Wt. = 28.8 mg)

Run No.	Initial Total Pressure (torr)	Time (min) of Exposure	Wt. of Hg Present (mg)	Length of Run (min)	Rate Constant (min^{-1}) $\times 10^4$ $\div 2.303$
1	19.78			35	186
2	20.78	5 +		20	142
3	20.70	5 +		20	138
4	20.47	5 +		20	132
5	20.27	5 +		19	127
6	20.02	5		20	121
7	20.16	11	0.06	20	118
8	19.88	20	0.13	20	109
9	19.49	31	0.29	20	96
10	18.62	76	0.54	20	81
11	20.56	77	0.82	20	67
12	19.67	5	0.87	20	63
13	42.05	3	0.90	20	34
14	19.57	3	0.90	20	69
15	20.18	55	1.09	778	28
16	21.42	3	1.10	20	27
17	21.08	20	1.15	40	8
18	-	30	1.23	24	0

\+ indicates film left under vacuum between hydrogenations in absence of Hg

TABLE 2.3.

Film 20 (Wt. = 36.4 mg)

Run No.	Initial Total Pressure (torr)	Time (min) of Exposure	Wt. of Hg Present (mg)	Length of Run (min)	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$
1	20.72		-	26	296
2	25.14	4.5 +	-	20	228
3	24.64	4.5 +	-	21	214
4	24.28	4.5 +	-	21	225
5	25.08	4.5 +	-	21	229
6	21.75	4.5	0.05	21	237
7	23.93	6.5	0.09	21	219
8	21.02	24	0.15	21	186
9	25.22	28	0.37	21	159
10	21.07	120	0.84	21	122
11	20.97	4.5	0.87	21	115
12	21.22	60	1.15	21	91
13	25.29	60	1.38	708	52
14	25.76	3.5	1.37	22	46
15	24.79	150	1.74	22	13
16	-	30	1.85	22	0

+ indicates film left under vacuum between hydrogenations in absence of Hg

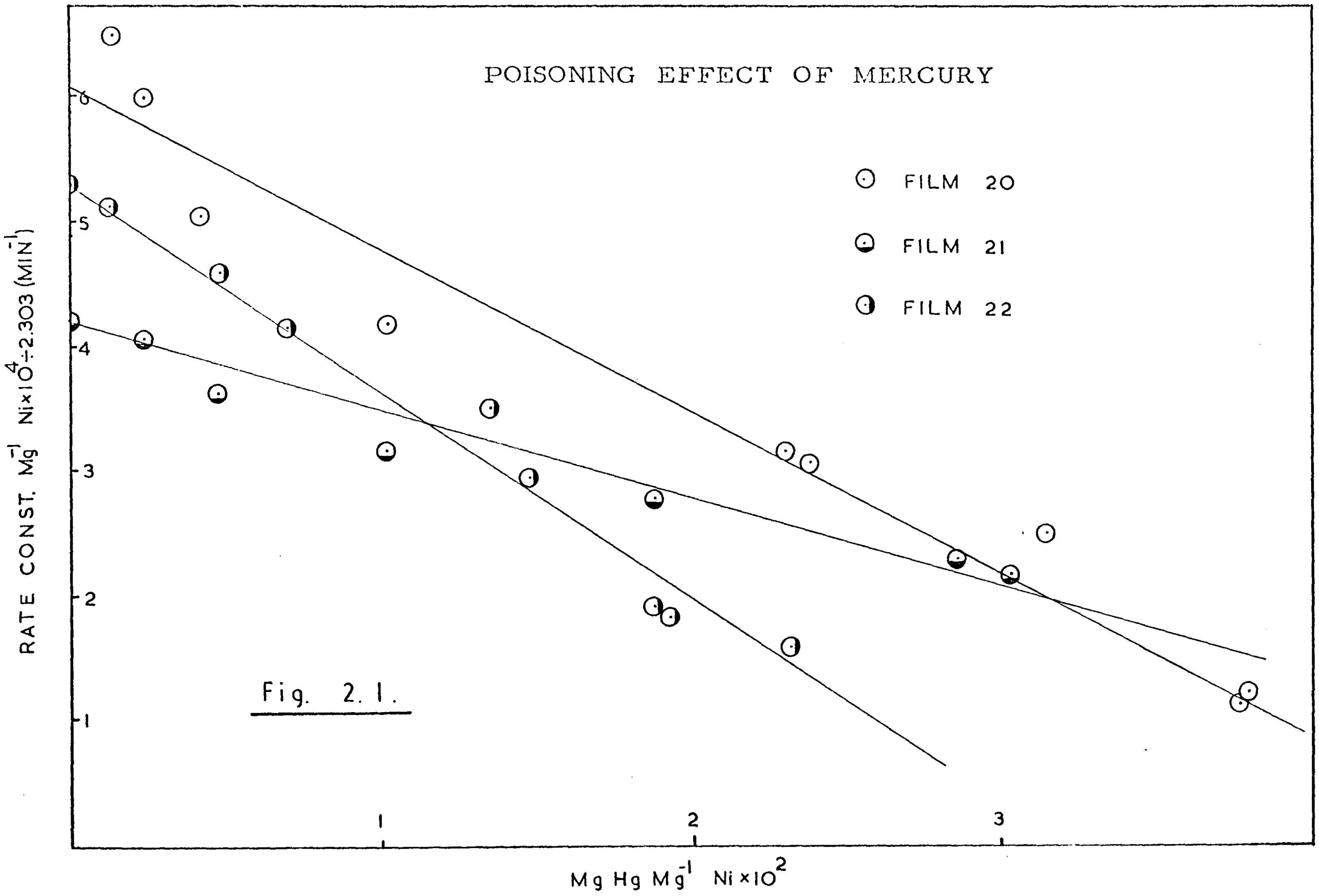

POISONING EFFECT OF MERCURY

Fig. 2.1.

for 12 hr. It was found that the amount of mercury which diffused to the film in this time was negligible. The rate of hydrogenation in run 14 which was carried out after run 13 had been allowed to proceed to completion was not greater as might have been expected. The effect of the small amount of mercury adsorbed between the runs may have reduced the increase normally obtained in these conditions.

Results obtained under similar conditions on Film 21 are given in Table 2.2. A variation in rate of 15% was obtained in the five hydrogenations on the unpoisoned film excluding the initial reaction which was anomalous. The inadvertent use of a higher initial reactant gas pressure in run 13 caused an unexpectedly low rate in run 14.

The variation of rate in the five unpoisoned hydrogenations on Film 20, the results of which are given in Table 2.3., was 6.5%. On this film also the rate of the first hydrogenation was anomalous. A number of the runs on this film were carried out with lower initial reactant pressures but the effect of this was not obvious owing to the relatively greater effect of the mercury.

In order to correlate the results obtained on each film the rate constant per mg nickel was plotted against the weight of mercury present per mg nickel for each run. This is shown in Fig. 2.1. For each film a virtually linear relationship between these functions was obtained but there appeared to be no reproducibility between the films.

NORMALISED POISONING EFFECT OF MERCURY

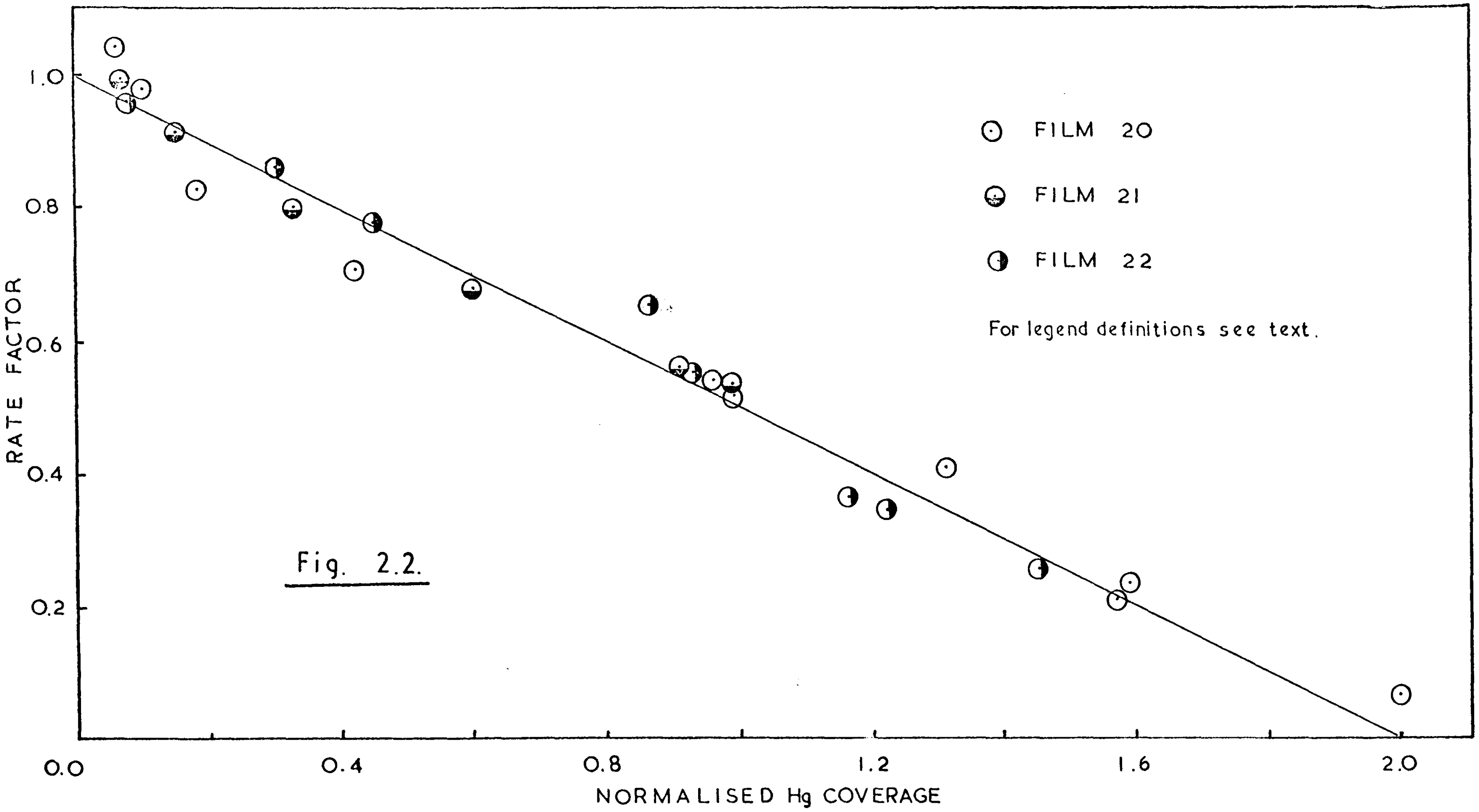


Fig. 2.2.

In an attempt to normalise these results what will be termed the 'rate factor' was plotted against the 'normalised mercury coverage' for each film. These functions were defined as follows :

$$\text{rate factor} = \frac{\text{Rate of hydrogenation at a particular Hg coverage}}{\text{Rate when no Hg present}}$$

$$\text{normalised Hg coverage} = \frac{\text{Wt. of Hg present on film at a particular time}}{\text{Wt. of Hg to make rate factor equal to 0.5}}$$

The result is shown in Fig. 2.2.

(2.3.) Additional Hydrogenation Experiments on Nickel Films

In an attempt to obtain further information concerning the effect of mercury on cyclopropane hydrogenation a series of experiments were carried out using films 23, 24 and 25. It was found on those films that in the absence of mercury the rate of reaction fell considerably with successive hydrogenations although conditions of initial reactant pressure, the time for which the film was left under vacuum between hydrogenations, etc. were kept constant in each case. The results obtained are given in Tables 2.4. and 2.5. On each of these films, allowing hydrogenations to proceed to completion had no observable effect on the rate of the subsequent reaction. In the case of Film 25, Table 2.4., admission of hydrogen in place of the reaction mixture was studied. It was found that this checked the reduction in rate but did not prevent it.

TABLE 2.4.

Films 24 and 25

Run No.	Initial Total Pressure (torr)	Length of Run (min)	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$
Film 24			
1	18.26	28	287
2	17.17	18	219
3	18.61	20	195
4 *	18.81	63	157
5	19.82	20	115
6	18.67	23	87
7	41.03	21	42
8	19.77	26	47
Film 25			
1	28.92	19	602
2	19.62	24	621
3	20.07	20	473
4	20.19	63	357
5	20 H_2 only	23	-
6	19.80	46	333
7	19.18	38	276
8	88.50H_2 only	40	-
9	18.94	29	333
10	18.83	24	95

* Indicates hydrogenation allowed to proceed to completion

TABLE 2.5.

Film 23 (Wt. = 20.2 mg)

Run No.	Initial Total Pressure (torr)	Wt. of Hg Present (mg)	Length of Run (min)	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$
1	18.82		20	403
2	19.69		21	370
3	19.47		21	308
4	18.6		40	218
5	20.27		24	179
6	19.23		21	145
7 *	19.63	0.02	20	94
8 *	19.92	0.06	21	66
9 *	19.13	0.07	20	46
10 *	19.85	0.10	90	30
11 *	21.61	0.13	25	15
12 *	19.50	0.16	20	-
13 *	-	0.26	-	-

Film left for 5 min between each evacuation and admission of fresh charge

* Hg admitted before each reaction after run 6

To determine the relative effect of mercury compared to this unknown ageing influence, i.e. the reduction in rate with successive reactions in Film 23, Table 2.5., mercury was admitted to the catalyst after a series of hydrogenations had been carried out in the absence of mercury. It was found that the weight of mercury required to reduce the hydrogenation rate to a particular extent was very much less in this case than for Films 20, 21, 22.

Films 23, 24 and 25 were prepared from a sample of nickel wire which was not identical with that used for the preparation of all previous films. This may have been the cause of the reduction in hydrogenation activity observed with successive hydrogenations. This wire was stated to be spectroscopically pure, as was that used previously. The observed behaviour could also have been explained if a contaminant had been present in the reactant gas mixture. The possibility of this is remote since the reaction mixture used for Film 23 was freshly prepared and was different from that used for Films 24 and 25.

(2.4.) Conclusions

It may be concluded from the work carried out on the poisoning of cyclopropane hydrogenation on evaporated nickel films that :

(1) Mercury poisons the hydrogenation in such a manner that the

weight of mercury required to reduce the activity of the film to half of its unpoisoned value is half the amount required to remove the activity completely.

(2) The absolute weight of mercury required to produce a particular poisoning effect is not the same for a number of films.

(3) There is evidence to suggest that the behaviour of a film is dependent on small variations in the nature of the wire used for its preparation.

CHAPTER 3

THE STUDY OF CYCLOPROPANE HYDROGENATION ON PUMICE SUPPORTED NICKEL CATALYSTS

The study of cyclopropane hydrogenation on evaporated nickel films and the effect of mercury on this system has been described in Chapters 1 and 2. It was decided to repeat and extend this work using supported nickel catalysts. The reasons for the change to a supported catalyst system were four fold.

(1) A considerable amount of information is available from the work of Bond et al. (see ref. 21) on cyclopropane hydrogenation on a variety of supported metal catalysts in the absence of poisons.

(2) Little information is available concerning the interaction of mercury with supported catalysts.

(3) Supported catalysts are much less time consuming in their preparation and do not require such stringent vacuum conditions in their use as do evaporated films.

(4) Supported catalysts represent more realistic practical catalysts.

Pumice was chosen as the supporting material since :

(a) Pumice has already been used in the majority of the work carried out on the hydrogenation of cyclopropane in the absence of mercury as a poison (21, 32).

(b) It is chemically inert, only slightly porous and of low surface area.

(c) A supply of a suitable mesh size was readily available.

(3.1.) Apparatus

The catalyst vessel had a volume of about 50 cc and was connected to a conventional vacuum apparatus. Pressures, in the region of 10^{-4} torr, measured on a commercially available Pirani gauge, were obtained using a rotary pump and an oil diffusion pump. Pressure changes in the catalyst vessel were measured directly on a thin wall capillary, mercury manometer. This manometer could be isolated from the catalyst when required. Provision was made for protecting the apparatus, otherwise mercury free, from mercury vapour by placing a gold leaf trap between the manometer and the rotary pump. Full details are given in Chapter 9.

(3.2.) Reactants and Catalyst

Anaesthetic grade cyclopropane and cylinder hydrogen were purified as described in section 9.12. and were stored in 2 l storage flasks fitted with greased taps. Equimolar mixtures of these gases were also prepared as before.

5% nickel on pumice catalyst was prepared by evaporating a suitable solution of nickel nitrate hexahydrate onto purified 120 mesh pumice powder. The dry catalyst was ignited to NiO in an open dish at 350°C for 15 hr and reduced in 5 g batches at 480°C in a stream of hydrogen for 10 hr. Before use 0.5 g of the reduced catalyst was activated in the catalyst vessel at 250°C for 1 hr under purified hydrogen at a pressure of 200 torr.

(3.3.) Experimental Procedure

The activated catalyst was found to be inactive at room temperature and hydrogenations were carried out at 78°C. The temperature of the catalyst was kept constant by placing the reaction vessel in a vapour bath containing ethyl alcohol. After removal of the hydrogen used for activation, a charge of the reactant mixture at a pressure in the range 50 - 100 torr was admitted and the pressure fall followed on the manometer. After the reaction had been allowed to proceed for the desired time the catalyst vessel was evacuated and left to stand under vacuum for a fixed time before admission of a fresh charge. Care was taken to evacuate the manometer separately from the catalyst vessel and to avoid connecting them when no gas was present.

(3.4.) Results of Cyclopropane Hydrogenations on Nickel/Pumice

The pressure readings obtained at particular times after the start of a hydrogenation were converted to partial pressures of cyclopropane following a technique similar to that indicated in section 9.27. for nickel films. This was, however, much simplified since the gas mixtures used in this work were prepared such that the fraction of the gas which was hydrogen was 0.5. Moreover, the pressure readings obtained were absolute pressure measurements and no conversion factor was required.

When the logarithm of the cyclopropane partial pressure was plotted against time, a linear relationship was normally obtained. On some occasions, however, this linearity did not include the initial partial pressure and less frequently that after the first minute.

This was presumably due to the lower accuracy with which it was possible to obtain the initial pressure reading after admitting the gas to the reaction vessel since the manometer level was normally oscillating at this stage.

In those hydrogenations which were able to proceed to completion in the standard time allotted for reaction it was consistently found in a series of experiments that from initial partial pressures of 26.5 torr reaction ceased at 5 torr indicating 82% conversion.

Examples of this are shown in Fig. 3.1. This was also found to be the case in a hydrogenation in which the reactants were left over the catalyst for a considerable period. This would appear to indicate, since a 1:1 mixture was used, that all the reactants are unable to reach the catalyst. This might be expected since diffusion of reactants in certain portions of the tubing connecting the reaction vessel to the manometer would be slowed considerably by the presence of the reaction products in the reaction vessel, i.e. the only function of part of the reactant mixture was to communicate the pressure in the reaction vessel to the manometer.

(3.5.) Factors Affecting Rate of Cyclopropane Hydrogenation

At an early stage in the study of cyclopropane hydrogenation on pumice supported nickel it was found that it was not possible to obtain reproducible values of the rate constant. Table 3.1. shows the results obtained from Experiment 3. In this experiment approximately the same initial total reactant gas pressure was used for each hydrogenation. The duration of each hydrogenation was either 11 or 15 min, as indicated, and for a particular length of hydrogenation the time for which the catalyst was under vacuum was varied. The value of the rate constant fell with each successive hydrogenation. There appeared to be little dependence either on the

TABLE 3.1.

Irreproducibility of Reaction Rates

Ni/Pumice Experiment 3

Run No.	Initial Total Pressure (torr)	Rate Constant (min^{-1}) x $10^4 \div 2.303$	Initial Rate (torr min^{-1})	Time (min) of Catalyst Exposure +	Length of Hydrogenation (min)
1	73.0	1380	14.2		11
2	76.0	1015	9.4	6	11
3	77.5	709	5.96	6	11
4	75.8	604	3.6	14	15
5	75.0	463	2.76	8	15
6	76.5	413	2.5	6	15
7	77.2	277	1.81	18	15
8	75.8	212	1.2	24	15
9	76.0	161	1.04	18	15
10	76.0	118	0.78	24	16
11	74.5	63	0.48	36	99
12	76.0	23	0.18	6	55
13	-	19	0.12	5	

+ i.e. to vacuum between pump off and admission of fresh charge

TABLE 3.2.

Ni/Pumice Experiment 6

Run No.	Rate Constant (min^{-1}) x $10^4 \div 2.303$	Initial Total Pressure (torr)	Comments
1	34	50.8	At room temperature
2	663	53.0	At 78°C
3	862	53.0	"
4	657	53.0	"
5	528	53.3	"
6	503	53.0	"
7	426	53.0	"
8	357	53.0	"
9	330	53.3	"
10	279	52.8	"
11	237	52.5	"
12	214	52.2	"
13	189	53.0	"
14	168	53.0	Reaction time 61 min
15	38	52.0	Reaction time 41 min
16	109	53.0	At 100°C
17	69	53.8	"
18	60	54.0	"
19	45	54.0	"
20	40	53.8	"

All reactions followed for 12 min except runs 14, 15
Between reactions, rotary pump evacuation 50 sec,
then 5 min under vac. before admit fresh charge

length of the hydrogenation or on the time for which the catalyst was left under vacuum.

Similar behaviour was obtained in Experiment 2. In this case each hydrogenation reaction was allowed to proceed for 12 minutes, the time for which the catalyst was left under vacuum between reactions was 5 minutes and in all cases except one the initial total pressure of reactants was 82 - 83 torr. In Experiment 2 the only factor which appeared to arrest the steady fall in the value of rate constant with run number was a change in the initial pressure of reactants. As was found with nickel films a decrease of the initial pressure produced an increase in the rate constant.

In Experiment 6 (Table 3.2.) the first hydrogenation was carried out at room temperature and between runs 1 and 2 the temperature of the bath was raised to 78°C. As would be expected this resulted in a considerable increase in rate but after an unexpected high value for run 3 this fell off with subsequent hydrogenations as before. It should be noted that the catalyst had attained the higher temperature before run 2 commenced since linearity of the log P_c versus t relationship was preserved throughout this reaction. The initial pressure, the length of time for which the reactants were in contact with the catalyst and the time of exposure to vacuum were kept constant. Increase in the length of run 14 to 61 min did, however, produce a greater reduction in rate constant for run 15 than was expected. Increase of the bath temperature to 100°C produced an increase in value of the rate constant but this still continued to fall after subsequent hydrogenations to a value indicating negligible activity.

(3.5.) The Effect of Efficient Removal of Reactants and Products

To determine whether the species left on the catalyst were responsible for the reduction in rate with repeated hydrogenations, an attempt was made to remove these more efficiently after reaction by pumping out the catalyst vessel using the diffusion pump. In previous experiments the reactants had been removed by pumping on the reaction vessel between hydrogenations for about 50 sec using the rotary pump. In Experiment 7, therefore, the diffusion pump was also used for 4 min. The results are indicated in Table 3.3.

A spurious result was obtained in run 4 which may have been caused by poisoning with air (see later) and the values obtained for runs 5, 6 may be anomalous. It can be seen, however, that the more efficient pumping did little if anything to improve the deactivation effect.

In Experiment 8 (Table 3.4.) after pumping out the reactants with the rotary pump for 50 sec the next charge of reactant gas was

TABLE 3.3.

Effect of Efficient Catalyst Vessel Evacuation

Ni/Pumice Experiment 7

Run No.	Initial Total Pressure (torr)	Rate Constant (min^{-1}) $\times 10^4 \div 2.303$
1	53.0	1342
2	52.5	809
3	54.0	539
4	53.3	-
5	52.0	199
6	53.8	167
7	53.0	190
8	53.5	142
9	52.3	119
10	51.5	90
11	53.2	62
12	54.2	80
13	54.5	74

All reactions followed for 12 min at 78°C except 12 and 13 at 100°C
Between reactions, rotary pump evacuation for 50 sec,
diffusion pump for 4 min then 5 min under vacuum
before admit fresh charge

TABLE 3.4.

Effect of Reducing Time Catalyst Left Under Vacuum Between Reactions

Ni/Pumice Experiment 8

Run No.	Initial Total Pressure (torr)	Rate Constant (min^{-1}) $\times 10^4 \div 2.303$	Comments
1	64.0	1507	
2	53.0	740	
3	53.5	391	
4	53.5	233	
5	53.8	224	Run followed for 64 min
6	54.0	49	
7	54.0	56	2 min vac.
8	52.8	51	1 min vac.
9	54.8	28	Run followed for 102 min, 2 min to vac.
10	51.8	50	Run followed for 12 min, 1 min to vac.
11	56.8	37	Allow to stand under H_2 10 min
12	56.0	28	Allow to stand under H_2 10 min

Runs 1 - 7 evacuated on rotary pump for 50 sec
and fresh charge admitted immediately
Runs 7 - 12 also used diffusion pump for 5 min
and left under vacuum for time stated
Runs 1 - 9 at 78°C, runs 10 - 12 at 100°C

admitted immediately. This it was hoped would indicate whether the deactivation process occurred during the period in which the catalyst was normally under vacuum and, therefore, more susceptible to poisons. Again it was found that deactivation occurred to an extent comparable to that found before. Changeover to the use of the diffusion pump after run 7 did little to reduce the deactivation. Allowing the catalyst to stand under hydrogen at a pressure of 90 torr for 10 min between runs 11 and 12 also produced no alteration in behaviour.

(3.6.) The Effect of Using a Fresh Reactant Mixture

All of the hydrogenations carried out using the nickel-on-pumice catalyst had employed the same batch of reactant gas mixture. Consequently any impurity which may have been present in this would have resulted in the observed deactivation with successive hydrogenations. For Experiment 9, therefore, a fresh mixture of cyclopropane and hydrogen was prepared. The total reactant pressure was approximately the same for each hydrogenation except for run 6. The reactants and products were pumped off for 50 sec between hydrogenations and a fresh charge admitted immediately without allowing the catalyst to stand under vacuum. The results are shown in Table 3.5.

TABLE 3.5.

Irreproducible Reaction Rates Using Freshly Prepared Reactant Mixture

Ni/Pumice Experiment 9

Run No.	Initial Total Pressure (torr)	Rate Constant (min^{-1}) $\times 10^4 \div 2.303$
1	48.0	
2	53.8	434
3	53.8	441
4	52.9	396
5	54.5	394
6	14.6	189
7	53.2	318
8	50.9	269
9	50.8	238
10	50.8	195
11	50.8	181
12	51.0	164
13	51.0	152
14	50.8	107
15	50.8	96
16	48.0	86
17	50.3	73
18	49.8	59

All reactions followed for 19 min at 78°C except run 1 at room temp.
Between reactions, rotary pump evacuation 50 sec
and fresh charge admitted immediately,
except before 14 when also left under vacuum for 5 min

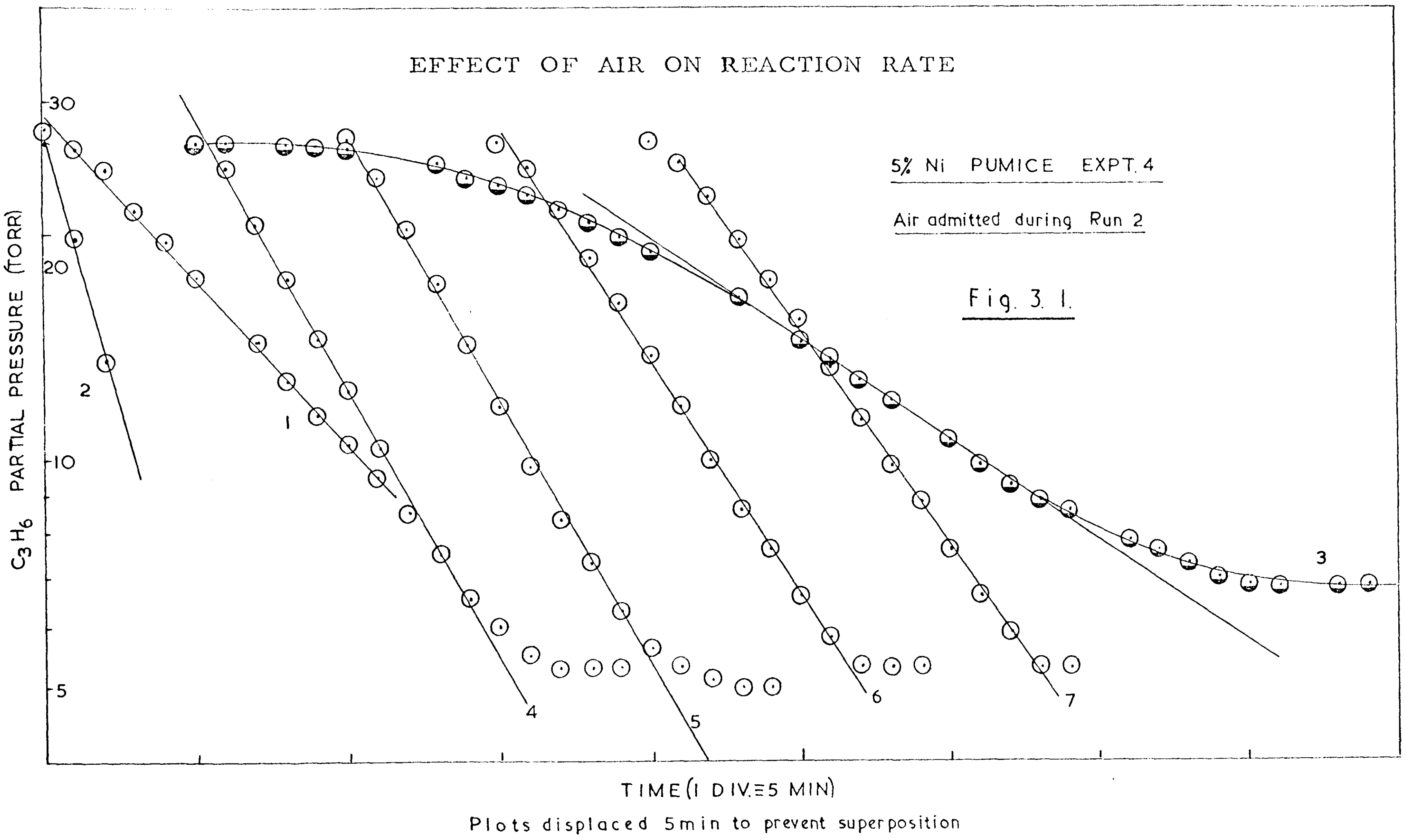
TABLE 3.6.

Effect of Admission of Air

Ni/Pumice Experiment 4

Run No.	Initial Total Pressure (torr)	Rate Constant (min^{-1}) x 10^4 ÷ 2.303	Length of Reaction (min)	Comments
1	55.0	4373	12	
2	52.5	1632	2	Air admitted to gas mixture
3	52.5	max. 264	39	
4	53.0	713	14	
5	52.5	722	14	
6	52.5	635	14	
7	52.5	655	14	Air admitted while under vac.
8	52.5	max. 40	40	
9	52.0	123	14	
10	52.5	-	74	
11	52.0	110	14	
12	52.5	128	14	
13	50.0	118	14	
14	55.0	123	14	
15	54.0	116	14	
16	54.0	111	14	

All reactions followed 14 min at 78°C
Between reactions, rotary pump evacuation for 50 sec
then 5 min under vacuum before admit fresh charge



EFFECT OF AIR ON REACTION RATE

5% Ni PUMICE EXPT. 4

Air admitted during Run 2

Fig. 3. 1.

Plots displaced 5 min to prevent superposition

As was found previously, after the initial hydrogenation had been carried out at room temperature, subsequent runs at 78°C were stabilised, but deactivation soon commenced and after eighteen successive hydrogenations the activity was negligible. The effect of using the diffusion pump between runs 13 and 14 was to increase this deactivation.

(3.7.) The Effect of Admitting Air to the Hydrogenation System

During the second hydrogenation carried out in Experiment 4 air at atmospheric pressure was inadvertently admitted to the catalyst vessel. This was removed after having been present for about one minute and a fresh charge of reactant gas admitted in the normal manner. The subsequent hydrogenation run 3 proceeded at a very much reduced rate but increased to a maximum value before terminating at a percentage conversion less than that obtained by subsequent hydrogenations (see Fig. 3.1. and Table 3.6.). These hydrogenations were carried out in the normal manner and it was found that although the values of the rate constants obtained were less than that before the admission of air, they were much more reproducible. The four immediately succeeding hydrogenations varied by only 12%.

While the reaction vessel was evacuated between runs 7 and 8 air was again admitted at atmospheric pressure for approximately one minute and was then pumped off. The next hydrogenation proceeded extremely slowly but after a considerable induction period attained a maximum value of rate. The percentage conversion attained in the same time interval as run 3 was, however, 45.5% compared with 75% in run 3. Once again the subsequent hydrogenations proceeded with values of rate constant less than those before admission of air and were more reproducible. The subsequent eight hydrogenations varied in their value of rate constant by 18%.

To determine if the phenomena observed in Experiment 4 were general for nickel-on-pumice catalysts the procedure was repeated in Experiment 5. The results are indicated in Table 3.7. A number of hydrogenations were carried out under standard conditions and, as on previous occasions, deactivation of the catalyst was found to have occurred. Between runs 7 and 8 air was admitted to the catalyst at atmospheric pressure and was left in contact for less than one minute before being pumped off. It was not possible to determine accurately the rate constants for the subsequent four hydrogenations owing to a gas lock in the manometer. The next three hydrogenations possessed rate constants differing by 16% and were comparable with those obtained before air had been admitted.

The reproducibility in rate constant was lost, however, when

TABLE 3.7.

Effect of Admission of Air

Ni/Pumice Experiment 5

Run No.	Initial Total Pressure (torr)	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$	Length of Reaction (min)	Comments
1	53.5	1295	12	All hydrogenations at 78°C
2	53.5	621	12	
3	53.5	576	12	
4	55.0	479	12	
5	53.5	397	12	
6	53.5	330	12	
7	53.5	305	12	Air admitted while under vac.
8	53.3	-	40	
9	53.8	-	12	
10	53.3	-	12	
11	53.5	-	11	
12	54.0	309	12	
13	54.0	301	12	
14	53.3	263	40	
15	53.0	135	12	
16	53.0	123	12	
17	53.0	116	12	

Between reactions catalyst vessel evacuated
as for Experiment 4

one of the hydrogenations was allowed to proceed for 41 min instead of 12. Return to the standard time interval for hydrogenations restored reproducibility.

(3.8.) The Effect of Mercury on Cyclopropane Hydrogenation on Nickel/Pumice

To determine the absolute effect produced by mercury on cyclopropane hydrogenation it was necessary to be able to predict the behaviour of the catalyst in the absence of mercury. Since in the majority of the hydrogenations carried out a considerable deactivation occurred in the absence of mercury, no attempt was made to study in any detail the effect of mercury. In those experiments, however, in which air had been admitted to the catalyst, as was stated earlier, much better reproducibility in the value of the rate constant was obtained. Consequently, in Experiments 4 and 5 mercury was admitted to the catalyst when reproducible rates had been attained.

The mercury was situated in a shielded evacuated side arm separated from the catalyst vessel by a tap. When it was required to introduce mercury onto the catalyst this tap was opened during the five minute period after evacuating the vessel and before admission of a fresh charge of reactants. This did not alter the sequence of manipulations under which reproducible rates had been maintained and any observed differences in rate were attributed to the mercury.

The mercury which arrived on the catalyst was detected by a Geiger Muller tube placed under the vapour bath. It was necessary to cool this counter and to maintain it in a rigid position to achieve stable behaviour and constant counting geometry.

(3.9.) Results of Mercury Poisoning

The results obtained for Experiment 4 are given in Table 3.8. It can be seen that admission of mercury produced a considerable poisoning effect as measured by the reduction in value of the rate constant. Owing to the low counting efficiency of the counter and insufficient specific activity of the radioactive mercury accurate values for the weight of mercury at each stage were not obtainable. The total amount of mercury adsorbed was measured by dissolving the catalyst in 10 N nitric acid after the experiment and comparing the count obtained in a liquid counter with that from a standard mercury solution.

In Experiment 5 admission of mercury was again found to have a considerable effect on the rate constant and after five 5 min exposures activity at 78°C was reduced to a negligible value. On leaving the catalyst overnight in presence of the reactants at room temperature, raising the catalyst temperature to 78°C and carrying out a further hydrogenation it was found that some activity appeared

TABLE 3.8.

Effect of Mercury During Experiment 4

Run No.	Initial Total Pressure (torr)	Time of Exposure (min)	Count on G.M. Tube per min	Rate Constant (min^{-1}) x 10^4 ÷ 2.303
14	55.0			118
		5 to vac.		
15	54.0		32 ± 1	111
		5 to vac.		
16	54.0		= Backgd.	111
		4.5 to Hg		
17	54.0		34 ± 2	62
		5 to Hg		
18	54.3		40 ± 2	44
		5 to Hg		
19	53.8		37 ± 2	26
		5 to Hg		
20	53.5		40 ± 2	12
		5 to Hg		
21	54.0		40 ± 2	6

All reactions followed 14 min at 78°C

Total wt. of mercury present after run 21 = 0.066 mg

TABLE 3.9.

Effect of Mercury During Experiment 5

Run No.	Initial Total Pressure (torr)	Time of Exposure (min)	Count on G.M. Tube per min	Rate Constant $(\text{min}^{-1}) \times 10^4 \div 2.303$	Comments
15	53.0		-	135	All at 78°C
16	53.0	5 to vac.	27 ± 1	123	
17	53.0	5 to vac.	= Backgd.	116	
18	51.8	5 to Hg	30 ± 1	99	
19	52.0	5 to vac.	"	93	
20	54.5	5 to Hg	38 ± 2	37	
21	54.0	5 to Hg	39 ± 2	30	
22	54.0	5 to Hg	45 ± 2	14	
23	53.8	5 to Hg	51 ± 0	8	Left for 14 hr
24	53.3	5 to vac.	52 ± 1	10	+ Raised to 100°C
25	55.0	5 to vac.	"	26	"
26	54.8	5 to Hg	54 ± 2	12	"
27	54.0	5 to Hg	61 ± 2	5	"
28	54.0	5 to Hg	67 ± 1		"

+ i.e. after previous reaction carried out at 78°C All reactions followed for 12 min

Total wt. of mercury present after run 28 = 0.105 mg to have been regained. Increase of the catalyst temperature to 100°C produced further activity which was reduced to a negligible value by three further 5 min exposures to mercury. (see Table 3.9.)

The amount of mercury adsorbed on the catalyst in Experiment 5, viz. 0.105 mg, during eight 5 min exposures was less than twice that obtained in Experiment 4 during four 5 min exposures, viz. 0.066 mg. In the former case, however, three of the exposures had been carried out while the catalyst was at 100°C. This adsorption rate is comparable with that found during hydrogenations on evaporated films in Chapter 2.

(3.10.) Conclusions

From the work carried out on cyclopropane hydrogenation in the supported nickel system the following conclusions were reached

(1) The hydrogenation rate is reduced with each successive reaction and this is not attributable to one particular reaction mixture nor to the efficiency of removal of the reaction products.

(2) The reaction proceeds with what appears to be first order kinetics.

(3) The nickel on pumice catalyst becomes poisoned for hydrogenation by the admission of air but is capable of reactivation. In certain

circumstances this reactivation can produce activity comparable to that obtained before the admission of air. After such reactivation the hydrogenation rate is much more consistent than before.

(4) Mercury also poisons the catalyst for hydrogenation and the poisoning is to a certain extent reversible.

The work carried out on supported nickel catalysts has shown that the rate of hydrogenation of cyclopropane was not reproducible by repeating the reaction under standard experimental conditions. In order to determine whether such reproducibility was in fact possible and was not governed by some species produced in the reaction or present in extremely small quantities in the purified reactants it was decided to study the hydrogenation using the same reaction mixture but an entirely different catalyst system. This work is described in Chapter 4.

CHAPTER 4

THE STUDY OF CYCLOPROPANE HYDROGENATION ON SUPPORTED PALLADIUM CATALYSTS

1. 1% Palladium on Carbon

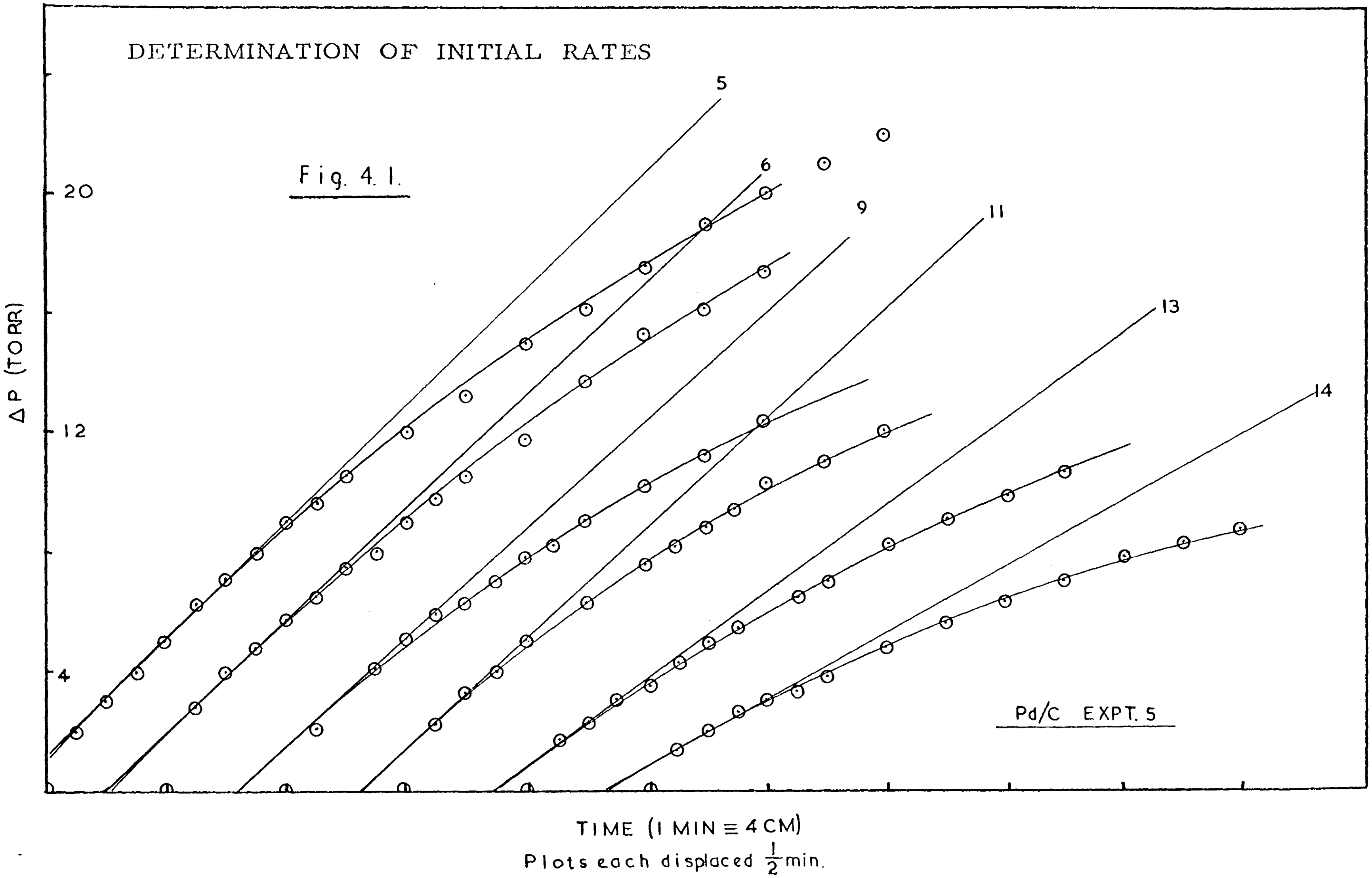
During the study of cyclopropane hydrogenation on pumice supported nickel catalysts and to a certain extent on evaporated nickel it was found that there was a tendency for reaction rate to decrease with successive reactions. In an attempt to determine whether this was due to an inherent property of the nickel system or to the presence of some undetected contamination in the reaction mixture it was decided to study the reaction using a completely different catalyst system but with the same reactant gas mixture. The catalyst chosen was palladium on carbon.

(4.1.) Apparatus and Procedure

The apparatus, purified reactants and experimental procedure were the same as those described previously for the study using pumice supported nickel. The catalyst consisted of 1% palladium on carbon and was obtained commercially. No information was available concerning the origin or the nature of the support or the method of preparation of the catalyst. The palladium was assumed to be present on the catalyst as palladium metal, and no reduction procedure was carried out. A 0.15 g sample of the catalyst was activated in situ at a temperature of 100°C, under hydrogen at a pressure of approximately 200 torr. The hydrogen used for activation was pumped out for 10 min before carrying out the reaction at 100°C.

(4.2.) Results Using 1% Palladium on Carbon Catalyst

It was found that the catalyst was extremely active at 100°C and reaction was virtually complete within the five minute period allowed for reaction. Reduction of the catalyst temperature reduced the activity, but it remained appreciably higher than that obtained with the nickel on pumice catalyst. The pressure fall (Δ P) against time relationship was found to be almost linear, and in the majority of cases did not pass through the origin. This deviation indicated that an anomalous pressure drop occurred within the first quarter minute after admitting the reactant mixture. In many cases, owing to the rapid pressure drop observed, it was difficult to determine with accuracy the value of the initial pressure. The experimental procedure, however, was such that the reactant gas mixture was adjusted to a standard pressure before expansion into the catalyst vessel and by this means the initial pressure was kept constant



DETERMINATION OF INITIAL RATES

Fig. 4.1.

throughout a series of hydrogenations. By carrying out a series of expansions into the catalyst vessel in the absence of the catalyst it was possible to determine an expansion factor. This enabled the initial pressure to be calculated from the pre-expansion pressure. It was found that the difference in the calculated and observed value of the initial pressure was never greater than 1 torr.

An indication of the activity of the catalyst under any particular conditions was obtained by measuring the initial rate. This was carried out by drawing a smooth curve through the pressure fall against time relationship and drawing the tangent to this at zero time. Examples of these taken from Experiment 5 are shown in Fig. 4.1.

(4.3.) Anomalous Behaviour

During the reactions using the palladium on carbon catalyst it was found that the pressure fall proceeded to an extent which was greater than the partial pressure of either of the reactants. In reactions carried out at 100°C using an initial reactant pressure of about 44 torr, reaction ceased within the 5 min interval allotted. The overall pressure drop obtained was in the region of 30 torr. For reactions at 78°C, using comparable initial pressures, reaction was not complete within a 5 min period but the pressure drop observed was greater than half the initial total pressure. When reaction at this temperature was allowed to proceed to completion an overall drop of about 33 torr was obtained.

It is difficult to find a simple explanation for this unexpected behaviour. In terms of chemical effects, it is necessary to firstly postulate that a gross error was present in the preparation of the reaction mixture such that cyclopropane was in excess. Secondly, it must be assumed that considerable quantities of hydrogen remained chemisorbed by the catalyst during the reduction procedure. This was rejected as the basis of an explanation for the following reasons,

(a) the anomalously large pressure drop could be observed in all reactions on the catalyst, not only during the first, as would be expected if hydrogen contained in the catalyst were responsible.

(b) removal of the cyclopropane from the mixture by cooling a portion of the reactant gas reservoir in liquid nitrogen, while not completely quantitative nevertheless gave a pressure fall consistent with a 1:1 mixture.

(c) another carefully prepared 1:1 mixture gave an identical G.L.C. analysis, and

(d) this new mixture also showed anomalously large pressure reductions when hydrogenated on the catalyst.

It was, therefore, concluded that the phenomenon was not a function of the gas mixture. This was confirmed using a 2:1 hydrogen:cyclopropane mixture, which gave a pressure fall greater than the expected $^1/3$, as shown by the results in Table 4.1.

(4.4.) Effect of Temperature

The same catalyst as had been used for the experiments already described was reactivated by heating it at 78°C for 4½ hr under hydrogen at a pressure of 200 torr. It was found that the activity at 78°C was comparable with that obtained at 100°C during an earlier series of hydrogenations on the same catalyst using the same pressure of reactants as an equimolar mixture. This indicated that the effects of a considerable number of hydrogenations carried out on this catalyst and also of several intentional exposures to mercury had been completely removed.

Three reactions were then carried out at 62°C and the results are given in Table 4.2. The first of these was rejected for technical reasons but the other two, although they had not attained completion in the interval allowed, produced a pressure drop which represented 160% of the initial cyclopropane partial pressure. Reduction of the catalyst temperature to 32°C produced reactions with a much reduced rate which were complete within 18 min and resulted in a pressure

TABLE 4.1.

2:1 H_2:C_3H_6 at 78°C on Pd/C

Run No.	Total Initial Pressure (torr)	Time to Constant Pressure (min)	Pressure Fall ΔP (torr)	Initial Rate (torr min^{-1})	ΔP as % of C_3H_6 Partial Pressure
1	142.0	40	50.7	4.8	108
2	82.8	21	29.8	3.6	108
3	64.5	15*	24.8	4.3	115
4	63.8	15	25.8	5.0	121
5	64.0	13	27.8	5.0	132

* This run did not reach a constant value of pressure

The values in above table should be compared with 150% conversion at 78°C obtained in 67 min at an initial rate of 6.1 torr min^{-1} when using a 1:1 mixture.

TABLE 4.2.

Effect of Temperature on Rate Using Pd/C

Run No.	Temp. °C	Total Initial Pressure (torr)	Time of Run (min) *	Pressure Fall ΔP (torr)	Initial Rate (torr min^{-1})	ΔP as % of C_3H_6 Partial Pressure
1	78	43	4	28	33	130
2	62	44	-	-	-	-
3	62	43	(5)	34	27	160
4	62	42	(4)	33.5	23.5	160
5	32	42	20(18)	35.5	3.35	169
6	32	42	40(16)	39.5	3.75	188
7	26	42	78(35)	37.5	1.45	178
8	22	41	93(10)	36.5	1.3	180

* The pressure fall had not ceased at the times given in brackets

drop corresponding to 180% of the cyclopropane partial pressure. Similar behaviour was found at 22°C and 26°C after longer time intervals. It appeared, therefore, that decrease in the temperature of the catalyst increased the overall pressure drop expressed as a percentage of the initial cyclopropane partial pressure.

(4.5.) Study of Reaction Products

It has been shown that the phenomena observed were not a function of the reactant gas mixture used and must consequently have been a property of the system. In order to obtain a reduction in pressure greater than the partial pressure of the reactant present to the smaller extent it is necessary to postulate that molecules of reactants or products were being removed from the vapour phase by one of the following mechanisms.

(1) Physical adsorption onto the carbon.
(2) Chemisorption onto the palladium or carbon.
(3) Polymerisation of reactants or products or both.

These will be considered more fully in the discussion given in Chapter 5. Although it was not possible to explain the magnitude of the observed pressure drop in terms of polymerisation alone, it might be expected that any polymerisation which occurred would produce species which could be observed in the vapour phase.

In order to determine if these species existed, a 1:1 hydrogen: cyclopropane reaction mixture was admitted to the reaction vessel to a pressure of about 50 torr at 78°C. The reaction was then allowed to proceed for 45 min during which time reaction should have reached completion. A sample of the gas mixture above the catalyst was then removed and analysed using G.L.C. Only two resolvable peaks were found and by comparison with retention times for known samples these were attributed to air and propane. No traces of any compounds having a retention time greater than that of propane were obtained. Compounds such as ethylene, methane and ethane having shorter retention times than propane would not have been observed but these would not have been able to produce the observed effect in any case.

(4.6.) Effect of Mercury

In Experiment 5 a series of reactions were carried out at 100°C in the absence of mercury and under standard conditions. It was found that a variation of less than 10% was obtained in the values of the initial rates. This included reactions carried out after the catalyst had been allowed to stand for 10 and 20 min intervals under vacuum. Exposure of the catalyst to mercury for 10 min produced a considerable reduction in rate. Reactions carried out in the

TABLE 4.3.

Mercury Poisoning of Pd/C Catalyst

Run No.	Exposure Time of Catalyst (min)	Initial Rate (torr min^{-1})	Run No.	Exposure Time of Catalyst (min)	Initial Rate (torr min^{-1})
1		3.74	12		1.13
	5 to vac.			10 to vac.	
2		3.50	13		1.11
	5 " "			6 " "	
3		3.75	14		1.28
	5 " "			10 " "	
4		3.70	15		1.28
	5 " "			20 to Hg	
5		3.61	16		0.58
	10 " "			20 to vac.	
6		3.43	17		0.52
	20 " "			20 " "	
7		3.50	18		0.56
	5 " "			10 to Hg	
8		3.46	19		0.18
	5 to Hg			10 to vac.	
9		2.89	20		0.18
	10 " "			10 to Hg	
10		2.20	21		0.10
	10 " "				
11		2.23			
	10 " "				

All runs lasted 5 min except 1 - 4, viz. 10 min

In all runs initial total pressure = 50 ± 0.03 torr absence of mercury on a poisoned catalyst indicated little reactivation. The catalyst was poisoned to an extent which indicated negligible activity. In this case also little reactivation occurred after leaving the poisoned catalyst overnight at room temperature and at $100^{\circ}C$ for 45 min. It was found that the amount of mercury required to poison the catalyst was small, viz. 4.4×10^{-2} mg mg^{-1} Pd. Owing to this small quantity of mercury present finally it was not possible to determine the amounts present at intermediate stages.

(4.7.) Conclusions

It was concluded from the work carried out with 1% palladium on carbon catalysts that

(1) The catalyst was extremely active for the reaction of cyclopropane with hydrogen and under standard conditions the reaction rate was reproducible without a decrease in rate with successive reactions as was found with nickel on pumice.

(2) The catalyst system exhibited anomalous behaviour which resulted in pressure falls which were greater than the partial pressure of the reactant present to the smaller extent.

(3) Mercury poisoned the catalyst for reaction and the poisoning appeared to be irreversible.

2. Palladium on Pumice

The work carried out on the palladium on carbon catalyst indicated that reproducibility of reaction rate of cyclopropane with hydrogen was attainable on a supported catalyst, and that the reaction could be poisoned by mercury. It was, therefore, decided to determine in more detail the poisoning effect of mercury on a palladium catalyst, and to compare this with the results obtained from nickel films. The palladium on carbon catalyst was considered unsuitable for this study for two reasons. (a) the finely divided nature of the catalyst required that considerable precautions be taken to prevent the distribution of catalyst throughout the vacuum system whenever the reaction vessel was being evacuated. (b) the anomalous pressure drop introduced an unknown variable into the system. Consequently further investigation was carried out using palladium on pumice catalysts.

(4.8.) Apparatus and Procedure

The apparatus and purified gaseous reactants were the same as those used for the previous studies using supported catalysts, and are described in detail in Chapter 10. A modified catalyst vessel was employed which although of comparable volume to that previously described, possessed a greater percentage of its volume within the thermostatted region of the vapour bath.

Two batches of palladium on pumice catalyst were used. Both were prepared by the dissolution of the appropriate weight of palladium chloride in dilute hydrochloric acid, and the evaporation of this solution onto a slurry of purified 120 mesh pumice. One of these catalysts contained 1% palladium metal and only a small quantity was available, the other contained 5% metal. The hydrogenation procedure was similar to that used previously, except for the modifications in reduction and activation which will be mentioned later.

(4.9.) Results Using 1% Palladium on Pumice Catalyst

Preliminary experiments indicated that the 1% catalyst was inactive for cyclopropane hydrogenation when reduced and activated under similar conditions to those used for the 5% nickel on pumice catalyst, viz. reduction at 480°C for 11 hr and activation at 250°C for 1.5 hr. It was found that the 1% palladium catalyst could be made active if milder conditions were employed for activation and reduction. The activities of catalysts prepared under various experimental conditions were compared by taking the initial rate of reaction under standard conditions as a measure of the activity. The results are given in Table 4.4. It can be seen that for reduction of the catalyst at 250°C or 480°C, the lower the temperature of activation, the

TABLE 4.4.

Relative Activities of Palladium Catalysts Resulting from Various Reduction and Activation Procedures

Activity at 100°C (torr min^{-1})	Time and Temp. of Reduction	Time and Temp. of Activation	Catalyst Composition and Weight	Reactant Gas Pressure (torr)
-	11 hr at 480°C	1.5 hr at 250°C	1%, 0.5 g	53.8 *
0.12	11 hr at 250°C	0.75 hr at 250°C	1%, 0.5 g	87.5
0.80	11 hr at 250°C	1.5 hr at 100°C	1%, 0.5 g	86.0
1.23	3-4 hr at 100°C	as reduction	1%, 0.25 g	53.5
21.40	3 hr at 100°C	as reduction	5%, 0.25 g	51.5

* Except for this sample, which used a 1:1, a 2:1 hydrogen: cyclopropane reactant gas mixture was used for all reactions

TABLE 4.5.

Cyclopropane Hydrogenation on 1% Pd/Pumice

Run No.	Initial C_3H_6 Pressure (torr)	Reactant Composition $H_2:C_3H_6$	Initial Rate (torr min^{-1})	Comments
1	17.8	2:1	1.25	Reaction not completed in 56 min after 85% conversion
2	25.7	1:1	0.50	All runs lasted 20 min
3	26.0	1:1	0.44	
4	25.8	1:1	0.44	
5	25.8	1:1	0.46	
6	17.7	2:1	0.36	* Run lasted 10 min
7	17.7	2:1	0.39	
8	17.8	2:1	0.37	
9	10.7	2:1	0.18	Reaction completed in 150 min after 77% conversion

* After run 6 the catalyst was left for 11 hr at 22°C under hydrogen at 200 torr, then reactivated at 100°C for 2.5 hr

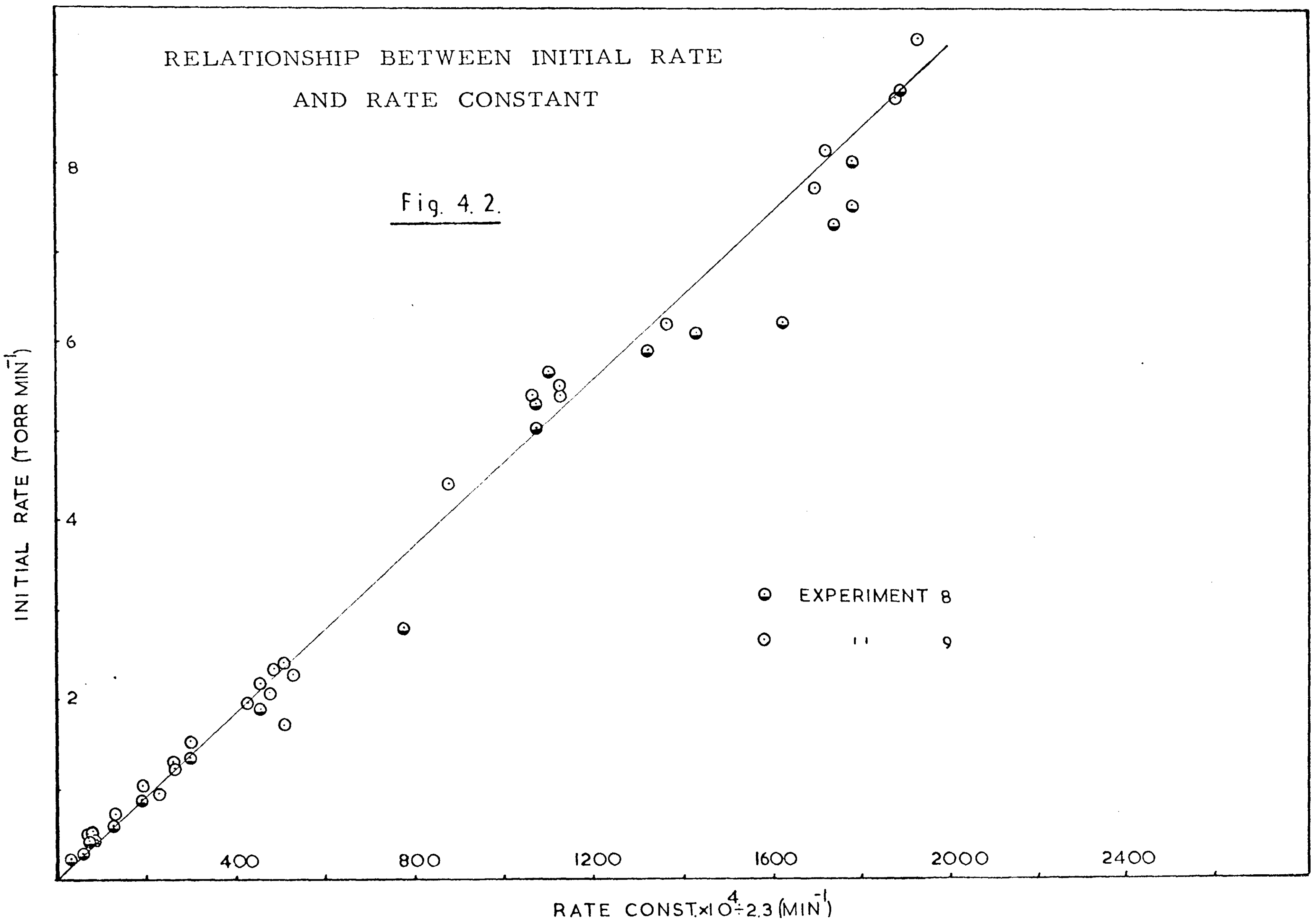
greater was the activity. The greatest activity observed was obtained from a catalyst reduced and activated in one process at 100°C. It was found that the activity of the 5% catalyst prepared under these latter conditions was very much greater than that of the corresponding 1% catalyst.

Using 0.5 g of the 1% catalyst, reduced and activated in one procedure at 100°C a series of hydrogenations were carried out at 100°C to determine whether this system gave reproducible hydrogenation rates. The information obtained is given in Table 4.5.

It can be seen that for runs 3, 4 and 5 carried out under standard conditions of reactant composition and pressure a variation of less than 5% was observed in the initial rates. Run 2, also carried out under similar conditions, had a rate outwith this variation but it was the first hydrogenation carried out under these conditions and followed a hydrogenation allowed to proceed to virtual completion. It might, therefore, be expected to differ. Although reproducibility was maintained with the 1:1 mixture return to the use of the 2:1 mixture in run 6 under conditions similar to those in run 1 indicated that a marked reduction in activity had occurred. This may again have been due to the fact that the properties of a catalyst during the first hydrogenation under a given set of conditions are often found to be anomalous.

RELATIONSHIP BETWEEN INITIAL RATE AND RATE CONSTANT

Fig. 4.2.

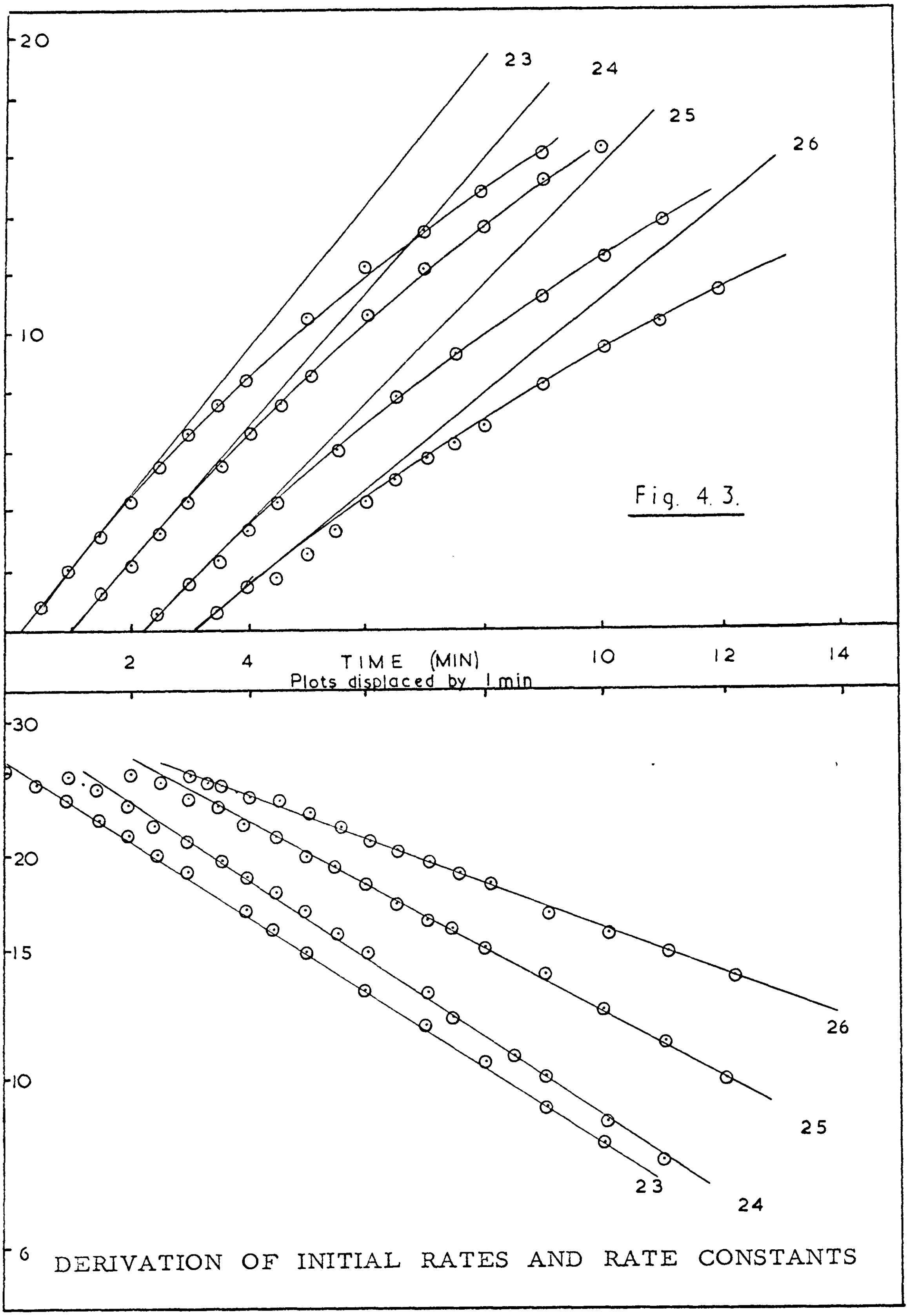


On leaving the catalyst under hydrogen at room temperature for 11 hr and then reactivating it at 100°C for 2.5 hr it was found that a slight increase in activity occurred. Subsequent reactions again showed good reproducibility of rate, providing the standard conditions were used.

(4.10.) Results Using 5% Palladium on Pumice Catalysts

A 0.25 g sample of the catalyst was reduced and activated in one procedure at 100°C. In Experiment 8 a series of hydrogenations were carried out under standard conditions and it was found that a considerable activity was present. This activity was measured by the method of initial rates from the relationship between pressure fall and time. In addition, for the experiments carried out with the 5% catalyst the logarithm of the cyclopropane partial pressure was plotted against time. A linear relationship existed in all cases up to cyclopropane conversions of approximately 85%. The gradient of this line is termed the rate constant as was the practice when using nickel films. Faster reaction rates tended to terminate the linear relationship at lower conversions.

The assessment of the rates by the two different methods was found to be consistent because a linear relationship existed between them. This is shown in Fig. 4.2. This was also the case with



DERIVATION OF INITIAL RATES AND RATE CONSTANTS nickel films. An indication of the experimental points from which the values of the initial rate was derived along with the corresponding derivation of the values of the rate constant are shown in Fig. 4.3.

The results of Experiment 8 are summarised in Table 4.6. The activity for hydrogenation measured both by the initial rate and the value of the rate constant was found to fall initially with each successive reaction at 78°C but between runs 11 - 14 inclusive, a variation of only 10% was observed. This included a hydrogenation carried out after the catalyst had been allowed to stand under vacuum for 10 min before admission of a fresh charge of reactants, instead of the normal 5 min period.

When mercury was admitted to the catalyst during this 5 min period it was found that considerable deactivation occurred. The amount of mercury adsorbed on the catalyst within this period was too small for it to be detected within the counting statistics and consequently approximately 10 min exposure periods were employed. Exposures of the catalyst to mercury were continued until the catalyst showed negligible activity, whereupon the study was terminated. The decrease of activity measured by the value of the rate constant with increasing amounts of mercury on the catalyst is given in Fig. 4.4.

It was found that apart from the effect of small amounts of mercury at the initial stages and the small effect of large amounts

TABLE 4.6.

Mercury Poisoning of Cyclopropane Hydrogenation on 5% Pd on Pumice

Experiment 8 Wt. of Palladium present = 12 mg

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd $\times 10^2$	Initial Rate (torr min^{-1})	Rate Constant $\times 10^4 \div 2.303$
+1*		-	-	21.4	3891
	5 to vac.				
2*		-	-	27.0	-
	" "				
3*		-	-	30.7	-
	" "				
4*		-	-	28.8	4604
	" "				
5		-	-	25.0	-
	" "				
6		-	-	17.2	-
	" "				
7		-	-	15.8	-
	" "				
8		-	-	15.0	3010
	" "				
9		-	-	14.6	-

TABLE 4.6.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^2	Initial Rate (torr min^{-1})	Rate Constant x 10^4 ÷ 2.303
10	5 to vac.	-	-	15.3	-
11	" "	-	-	13.2	2766
12	" "	-	-	13.0	2664
13	" "	-	-	12.1	2548
14	9 to vac.	0	-	12.0	2500
15	$4\frac{1}{4}$ to Hg	-1.3	-	9.9	1979
16	$4\frac{3}{4}$ " "	0.8	0.01	9.7	1911
17	$4\frac{3}{4}$ " "	1.2	0.02	8.8	1905
18	$9\frac{3}{4}$ " "	6.2	0.11	7.9	1790
19	" "	22.1	0.38	7.5	1790

TABLE 4.6.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^{2}	Initial Rate (torr min^{-1})	Rate Constant x 10^{4} ÷ 2.303
20	$9\frac{3}{4}$ to Hg	19.6	0.34	7.3	1749
21	" "	25.1	0.44	6.2	1632
22	" "	40.2	0.70	6.1	1440
23	" "	48.0	0.83	5.9	1327
24	" "	72.8	1.26	5.7	1106
25	" "	85.0	1.47	5.5	1079
26	" "	91.3	1.58	5.1	1000
27	$19\frac{3}{4}$ to Hg	117.1	2.02	2.8	781
28	" "	142.5	2.46	2.0	468
29	" "	174.3	3.02	1.4	301

TABLE 4.6.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^{2}	Initial Rate (torr min^{-1})	Rate Constant x 10^{4} ÷ 2.303
30	$19\frac{3}{4}$ to Hg	184.2	3.19	0.9	198
31	" "	207.8	3.60	0.6	125
32	" "	224.7	3.90	0.5	97
33	" "	255.4	4.40	0.3	58
34	" "	269.2	4.66	0.3	50

All hydrogenations carried out with initial reactant pressure 50 ± 1 torr

Background = 2410 80 = 30.1 c.p.m. All counts taken over 10 min

* Runs 1 - 4 carried out at 100°C, remainder at 78°C

+ Run 1 used 2:1 hydrogen:C_3H_6 mixture, rest 1:1

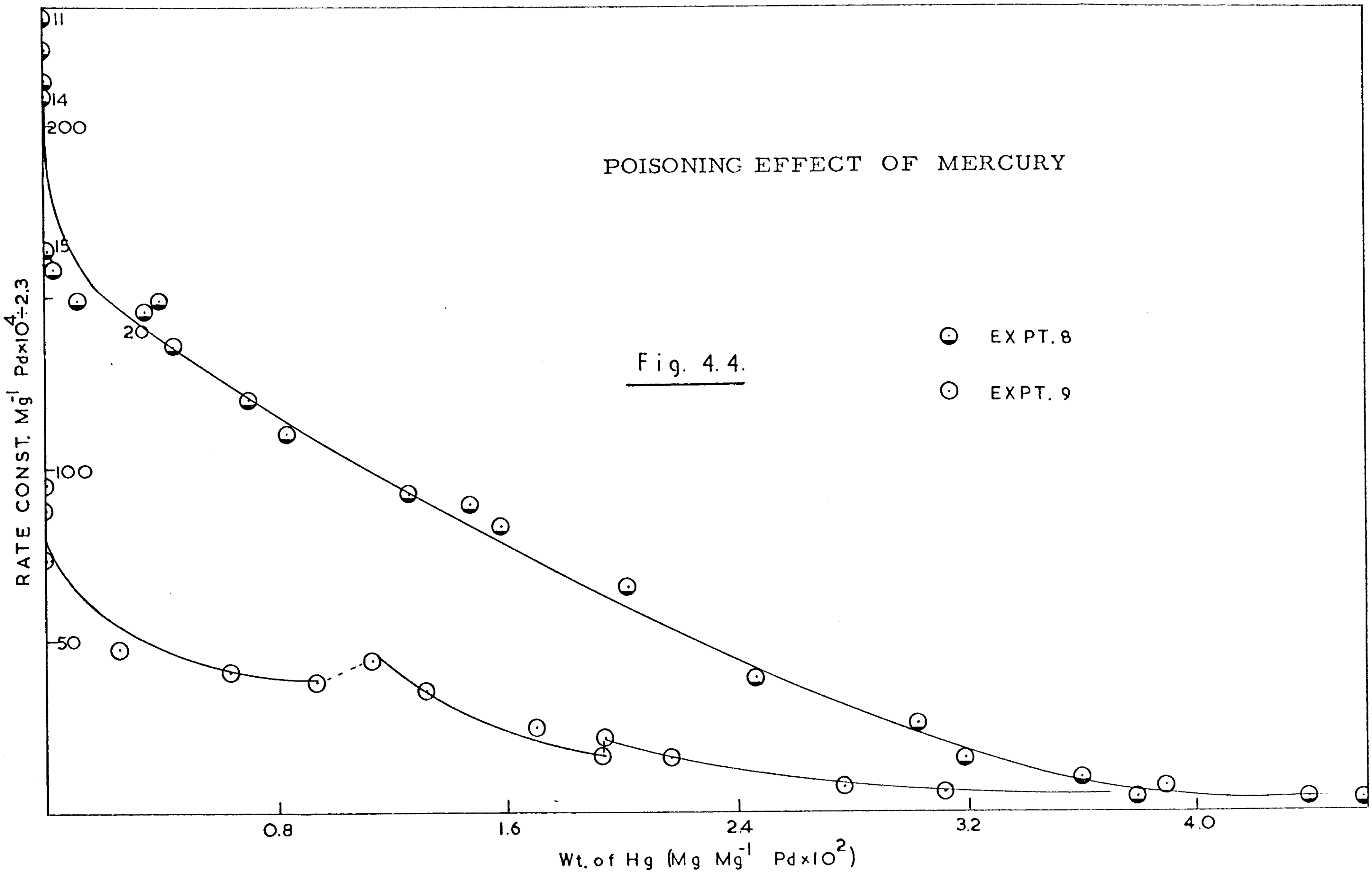


Fig. 4.4.

POISONING EFFECT OF MERCURY

of mercury at the final stage, a virtually linear relationship was obtained between reaction rate and weight of mercury on the catalyst.

Evidence for reactivation after poisoning by mercury had been obtained in the work carried out with pumice supported nickel catalysts. This was further studied in Experiment 9 using a 5% palladium on pumice catalyst prepared in a manner similar to that used for Experiment 8. The activity of the catalyst was again obtained from values of the initial rate and the rate constant. These values are also plotted in Fig. 4.2. A summary of the results of Experiment 9 is given in Table 4.7.

When the catalyst was first exposed to mercury between runs 6 and 7 it was found that a considerable poisoning effect occurred. The amount of mercury which was adsorbed on the catalyst, however, was negligibly small and further attempts to adsorb larger quantities by increasing the time of exposure failed to increase the amount of mercury already present. This was indicated by the virtually constant values both of the surface count and of the activity. After run 14 the mercury source was gently heated, with the connecting tap to the reaction vessel closed, until droplets of mercury were seen to condense in the tube containing the source. Exposure of the source to the catalyst now resulted in adsorption of mercury onto the catalyst and the activity fell. This appeared to indicate that

TABLE 4.7.

Mercury Poisoning of Cyclopropane Hydrogenation on 5% Pd on Pumice

Experiment 9 Wt. of Palladium present = 12 mg

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^2	Initial Rate (torr min^{-1})	Rate Constant x $10^4 \div 2.303$
*1		-	-	25.4	-
	5 to vac.				
2		-	-	20.4	-
	5 " "				
3		-	-	20.0	-
	10 " "				
4		-	-	17.5	-
	20 " "				
5		-	-	15.3	-
	5 " "				
6		1.3	-	15.0	2915
	$4\frac{3}{4}$ to Hg				
7		0.6	-	9.3	1944
	$4\frac{3}{4}$ " "				
8		-0.9	-	8.7	1886
	5 to vac.				
9		2.0	-	8.1	1731

TABLE 4.7.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^2	Initial Rate (torr min^{-1})	Rate Constant x 10^4 ÷ 2.303
10	5 to vac.	3.9	-	7.7	1701
11	5 " "	0.9	-	6.2	1365
12	$9\frac{3}{4}$ to Hg	1.6	-	5.5	1129
13	$9\frac{3}{4}$ " "	-0.8	-	5.4	1138
14	$19\frac{3}{4}$ " "	5.9	-	5.4	1069
15	$19\frac{3}{4}$ " "	0.3	-	4.4	875
16	$9\frac{3}{4}$ " "	13.3	0.25	2.8	573
17	$19\frac{3}{4}$ " "	39.6	0.74	2.4	499
18	$19\frac{3}{4}$ " "	50.0	0.94	1.6	455
19	20 to vac.	53.2	-	1.7	456

TABLE 4.7.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^2	Initial Rate (torr min^{-1})	Rate Constant x 10^4 ÷ 2.303
20	20 to vac.	55.7	-	1.9	431
21	" "	58.2	-	2.2	459
22	" "	58.5	-	2.1	479
23	" "	58.7	-	2.4	513
24	" "	59.8	1.14	2.3	531
25	$19\frac{3}{4}$ to Hg	70.3	1.32	2.0	427
26	" "	90.8	1.70	1.6	300
27	" "	108.1	2.02	0.9	194
28	20 to vac.	106.1	-	1.0	225
29	" "	108.5	-	1.3	258

TABLE 4.7.
(continued)

Run No.	Exposure Conditions (min)	Counts per min Above Background	Wt. of Hg Present mg mg^{-1} Pd x 10^2	Initial Rate (torr min^{-1})	Rate Constant x 10^4 ÷ 2.303
	19¾ to Hg				
30		116.0	2.17	1.1	198
	29¾ " "				
31		148.3	2.77	0.5	88
	19¾ " "				
32		167.2	3.12	0.5	70
	29¾ " "				
33		203.6	3.81	-	41
	20 to vac.				
34		205.5	-	-	51
	8 hr to vac.				
+35		-	-	-	41
36		-	-	-	127

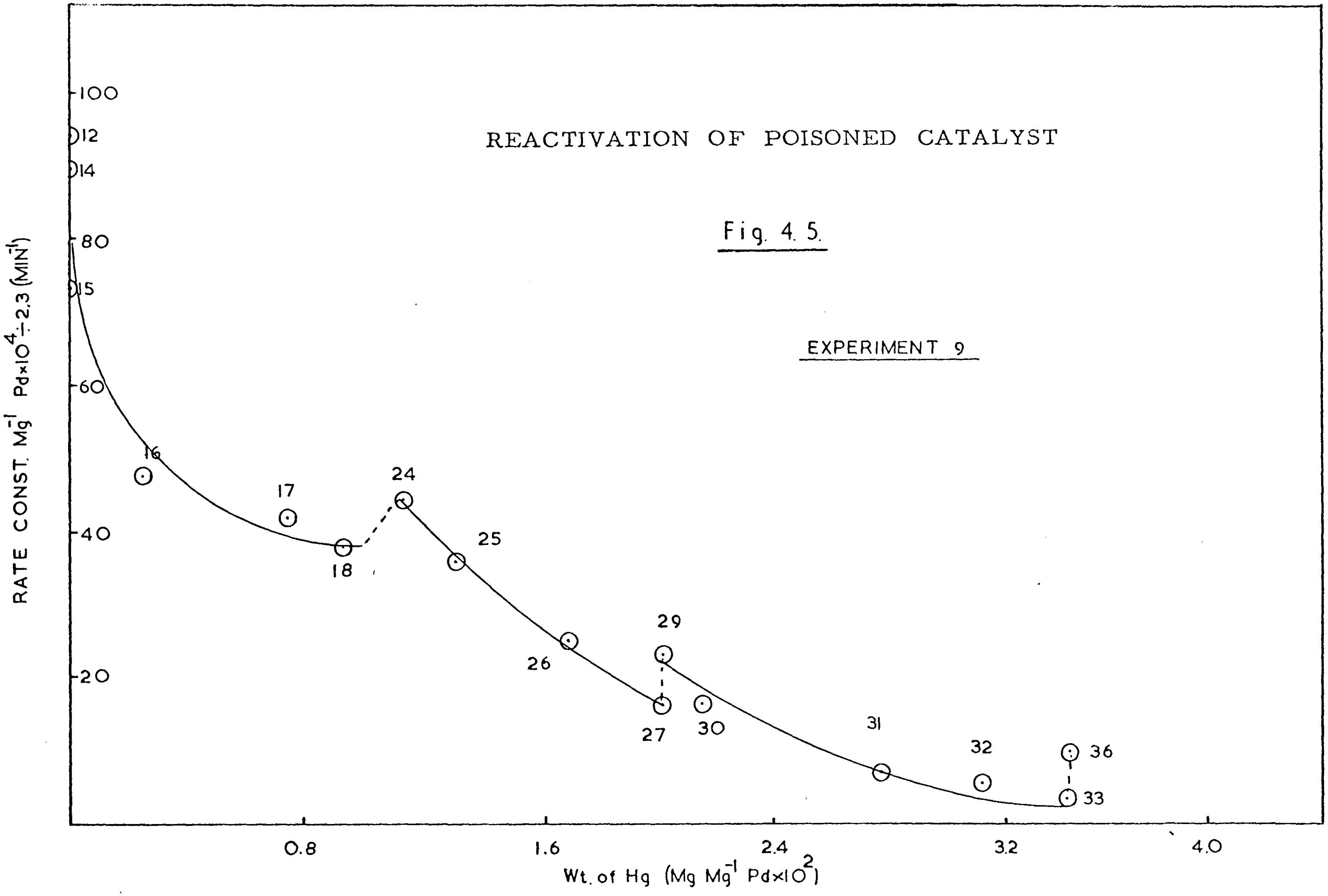
All hydrogenations carried out with initial reactant pressure 50 ± 1 torr

Background = 633   25 = 25.3 c.p.m. All counts taken over 10 min

* Run 1 carried out at 100°C, remainder at 78°C

Run 1 used 2:1 hydrogen:C_3H_6 mixture, rest 1:1

\+ Run 35 was allowed to continue for 11 hr



REACTIVATION OF POISONED CATALYST

Fig. 4.5.

for some reason, before heating, the mercury source was only able to supply a limited quantity of mercury vapour.

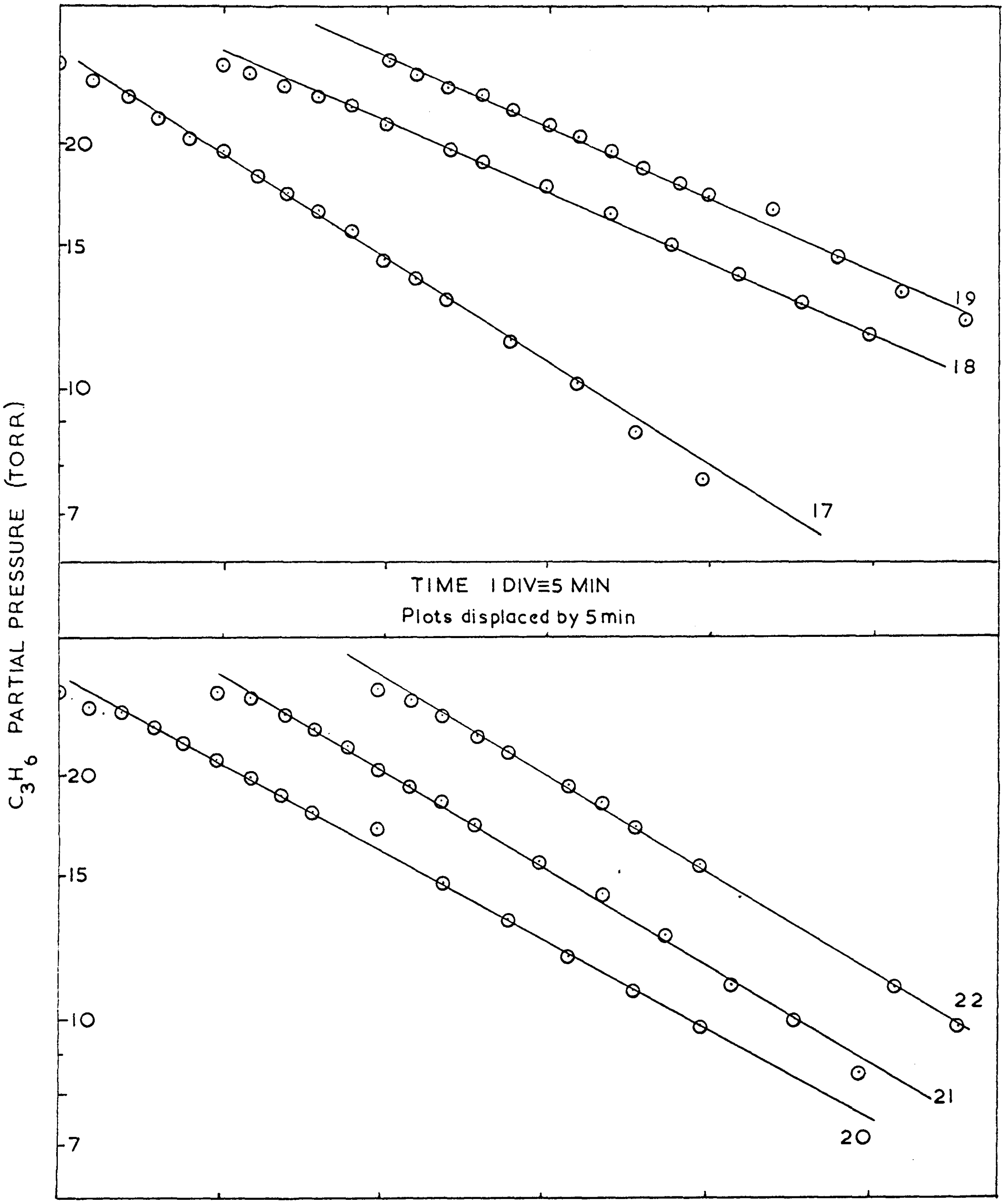
It should be noted that throughout Experiment 9 the mercury source was maintained at a temperature of 20°C and was separated from the catalyst by a 6 mm bore tap. This was to ensure that a constant concentration of mercury vapour was always available to the catalyst. In Experiment 8 the possibility arose that on some occasions the availability of mercury vapour was not constant owing to changes in room temperature or because the grease in the 3 mm bore tap acted as a physical barrier to mercury vapour diffusion.

When a number of runs, 18 - 23, were carried out without additional admission of mercury in Experiment 9 it was found as is indicated in Fig. 4.4. and in more detail in Fig. 4.5. that reactivation of the catalyst did occur. The extent of this reactivation was greater than the deactivation produced by the 20 min exposure to mercury between runs 17 and 18. The plots of the logarithm of cyclopropane partial pressure for runs 17 - 22 are shown in Fig. 4.6. These indicate that no increase in rate occurred during these reactions. It may be concluded, therefore, that any reactivation which occurred during reaction was slow compared with the rate of reaction.

During the period when these hydrogenations were being

REACTIONS ON A POISONED CATALYST

Fig. 4.6.



carried out no mercury was admitted to the catalyst yet an increase in count from the catalyst was observed which was outwith the statistical deviation. This phenomenon is similar to that obtained in the work on the simultaneous determination of mercury in the vapour phase on a supported nickel catalyst which will be described in Chapter 8.

After continued adsorption of mercury, reactivation of the catalyst occurred on two further occasions. These reactivations were not followed to such an extent as previously, and it was not possible to determine whether an increase in count occurred or not. When the activity of the catalyst had been reduced to a negligible value, the catalyst was left under vacuum at room temperature for 8 hr. A further hydrogenation indicated that reactivation during this period was negligible. This latter hydrogenation was continued for 11 hr and it was found on evacuating the reaction vessel after this time and admitting a fresh charge of reactants that a considerable reactivation had now occurred.

The weight of mercury present on the catalyst was calculated by the method already described in Chapter 2.

(4.11.) Conclusions

From the work carried out on cyclopropane hydrogenation on pumice supported palladium catalysts it was concluded that :

(1) The activity of a palladium on pumice catalyst is greatly influenced by the conditions of reduction and activation.

(2) Reproducibility of hydrogenation rate is possible with both 1% and 5% palladium on pumice catalysts, although the first reaction under a given set of experimental conditions is usually anomalous.

(3) The presence of mercury reduces the activity of the catalyst for cyclopropane hydrogenation, but this deactivation is to a certain extent reversible.

(4) During the reactivation process, an increase in the count from the radioactive mercury on the catalyst is observed, although no mercury is admitted.

(5) Initially, small amounts of mercury have a large effect on the rate of reaction, and when poisoning is nearly complete large amounts have little effect.

CHAPTER 5

DISCUSSION OF CYCLOPROPANE HYDROGENATION RESULTS

As stated in the introduction, it was hoped that the use of evaporated metal films would result in the production of reproducible catalysts, the activity of which could be related to the film weight. It was found in practice, however, that under the conditions used, reproducibility of behaviour between films was not obtained and only under certain conditions was reproducibility obtained with repeated reactions using one particular film. Some of the factors affecting reproducibility will now be considered.

(5.1.) Reproducibility of Reaction Rate on Evaporated Nickel Films

Much of the emphasis which has been given to the benefits of the use of evaporated films in catalysis has been based on the reproducibility of behaviour obtained by workers in different laboratories. In many cases, however, this has been achieved only with freshly prepared films and repetition of procedure on the same film has not given reproducibility (22, 23, 24).

The majority of the instances quoted in the literature concerned with lack of reproducibility on repeated reaction on a single film involve reduction in rate with each reaction carried out. This has been particularly so in the study of ethylene hydrogenation on nickel. Foss and Eyring (22) found reduction of activity for this reaction of up to 50% after each hydrogenation, but on reducing the pressure of reactants this deactivation was much reduced. This deactivation was shown to be due to traces of oxygen in the reaction mixture and when these were removed reproducibility of reaction rate was much improved. Oxygen has also been suggested as the cause of the deactivation observed by Jenkins and Rideal (24). In their study of cyclopropane hydrogenation on evaporated nickel films, using small total reactant pressures and purified reactants, Knorr and Ponec (18) observed a steady deactivation of the catalyst. This was shown to be caused by backstreaming of vapour from the oil diffusion pumps during removal of the reactants and products after reaction. When precautions were taken to avoid this, reproducibility of reaction rate within 10% was obtained, provided a standard hydrogenation procedure was carried out. In the present work also, it was found that reproducibility of cyclopropane hydrogenation was possible in the system used for Films 9 - 22 provided a standard technique was employed. There was in fact found to be a tendency for the reaction rate to increase with the number of reactions carried out, and for a definite increase to occur after a hydrogenation had been allowed to proceed to completion.

A change in the type of pure nickel wire used for the film evaporation, however, produced a catalyst which was rapidly deactivated with successive reactions. This was shown not to be due to a contaminant in the reaction mixture, since it occurred with a number of freshly prepared mixtures. It appeared that the properties of the film produced from the two batches of wire were different. Some of the factors which may have produced this difference in behaviour will now be considered.

(5.2.) Possible Factors Affecting Reproducibility

Each of the samples of wire was degassed using the same procedure, viz. heating the wire repeatedly to its evaporation temperature until no further evolution of gas was observed. Differences in physical properties of the wires, however, may have resulted in varying efficiency of gas removal using this technique.

Anderson et al. (25) have shown that nickel films evaporated at a pressure of 2×10^{-7} torr, after degassing of the wire above its evaporation temperature, are deposited on a layer of nickel oxide, which must have been derived from oxygen originating from the degassed walls of the reaction vessel or from the nickel wire itself during its evaporation. Similar effects found with a range of metallic films have been reviewed by Allen (26). If the degassing treatment in the present work had not resulted in comparable removal of oxygen from the two different types of wire, owing to differences in their physical properties, then different amounts of oxide would have been present in the two types of film produced.

The importance of this is indicated by the work of Hall, Cheselke and Lutinske (27), who have correlated the amount of oxygen present in a nickel copper alloy catalyst with the amount of hydrogen which can be accommodated within the catalyst bulk. Moreover, Hall and Emmett (28) have shown that the amount of hydrogen present in a nickel catalyst can affect the activity of the catalyst for ethylene hydrogenation. Later work by Hall and Hassell (29) has shown that the catalytic activity for ethylene hydrogenation is affected by the existence of several types of hydrogen adsorption and possibly dissolved hydrogen, but that contrary to their previous reasoning, this may not be directly related to the amount of oxygen in the catalyst.

The alloy system studied (27) was found to behave quite differently from pure nickel with regard to the enhanced hydrogen uptake, so that it may not be permissible to extrapolate the observations on the alloys to the case of the pure nickel. This effect of dissolved hydrogen has been reviewed by Eischens (30) with reference to the I.R. studies of adsorbed species. It would appear, therefore, that the amount of oxygen present in a nickel catalyst may well affect the activity of the catalyst for reaction.

This effect of occluded gases on the activity of nickel films has also been put forward by a series of Russian work (31). This has shown that nickel evaporated under high vacuum was relatively inactive for ethylene hydrogenation. When, however, it was evaporated under conditions in which one oxygen atom was present per thousand atoms of nickel, the resulting film showed its maximum activity. Similar effects were observed with concentrations of occluded hydrogen ten times greater than this value. In both cases the gas occluded in the evaporation altered the work function in a systematic way.

It has also been shown (28) that the presence of copper can affect the amount of hydrogen which can be occluded within the bulk of a nickel catalyst. It is not seriously suggested that the marked differences in behaviour observed with films from the two batches of wire were due to the presence of copper. If, however, any metallic impurity was present in one of the batches of wire it is likely to have been copper, and this may have contributed to some extent to the overall effect.

(5.3.) Effect of Permitting Reactions to Proceed to Completion

It was also observed using evaporated nickel films that if a reaction was permitted to proceed to completion the rates of the subsequent reactions were increased. This phenomenon, however, did not exist to any great extent when mercury was present on the catalyst, nor on those films in which a steady deactivation occurred with repeated reaction.

It was originally considered that this effect was produced by the presence on the catalyst of species resulting from the reaction itself, which were able to increase the rate of the subsequent reaction. This explanation was, however, rejected since such species would have resulted in an initial increase in rate, which would have fallen as the species themselves took part in the reaction. This was not observed. In addition if such species were formed during reaction, the relationship observed between the logarithm of the cyclopropane partial pressure and time would not have been linear.

It appears, therefore, that the effect produced by permitting a reaction to proceed to completion was the result of some process which occurred between reactions rather than during reaction. In the absence of further evidence it appears most likely that a change in the catalyst itself had occurred.

(5.4.) Effect of Oxygen on Pumice Supported Nickel Catalysts

In the cyclopropane hydrogenations carried out using a pumice supported 5% nickel catalyst it was found, as with Films 23 - 26, that removal of the reactants and products and the admission of a fresh charge produced a considerable reduction in rate. If sufficient hydrogenations were carried out, the activity of the catalyst was reduced to a virtually negligible value. In the light of what has been discussed in section 5.1., this phenomenon can be explained by the presence of some contaminant, such as oxygen, in the reaction mixture. On two occasions, however, oxygen was admitted intentionally to the system and as was to be expected, a reduction in rate of the immediately subsequent reaction occurred. This poisoning effect, however, was short lived and after an induction period the rate of this hydrogenation increased (see Fig. 3.1.). The rate of the subsequent reaction was found in one case to be comparable with that before admission of air and in the second case about one third of this initial value. In both cases, the rate of hydrogenation was much more reproducible and little deactivation with subsequent reactions was observed.

The presence of the induction period after the poisoning of the catalyst with air was comparable with that observed by Foss and Eyring (22) and Jenkins and Rideal (24) during ethylene hydrogenation.

In the former case this induction period was only observed after the catalyst had been considerably poisoned with oxygen derived from traces present in the reaction mixture. The reductions in rate observed with successive reactions before this point was reached were interpreted as the blocking by oxygen of sites having sufficiently high heats of adsorption to prevent the hydrogenation of oxygen at the temperature of reaction. When all of these sites were blocked, adsorption of oxygen commenced on sites with low heats of adsorption, and the adsorbed oxygen was then able to compete with the ethylene for hydrogen. The fact that, in the present work, reproducibility of reaction rate was obtained after the admission and subsequent removal of oxygen, indicates that the reduction in rate observed initially was not due to oxygen. In addition, the relative ease with which it was removed after the poisoning, indicates that if the deactivation observed before the admission of oxygen was due to the blocking of sites by some other adsorbed species, this species must have been situated on sites of higher energy than those occupied by the oxygen or was not capable of reaction with hydrogen.

(5.5.) Conclusions Regarding Reproducibility

The differences in behaviour of the nickel films, produced from similar but not identical nickel wires, and those observed with supported nickel catalysts before and after treatment with oxygen, appeared to indicate that the reaction of cyclopropane with hydrogen was particularly sensitive to small differences in the properties of the catalyst. This behaviour has been noted previously and is not confined to the present work. Thus Bond and Newham (32) have reported that reproducibility of reaction orders with respect to cyclopropane and hydrogen was only obtained when a standard procedure for catalyst reduction was carried out. Similarly, Yates, Sinfelt and Taylor (33) have shown that reproducibility of reaction rate could be achieved in the interaction of hydrogen and cyclopropane when the catalyst was cooled in hydrogen after reduction. Cooling of the catalyst in helium, however, caused the reaction rate to fall with repeated reactions, as was found in the present work with supported nickel catalysts.

Lack of reproducibility in the rate of reaction between cyclopropane and hydrogen has also been reported by Benson and Kwan (34) and this effect has been observed to a lesser extent by Bond and Sheridan (35) over pumice supported nickel.

As far as the study of poisoning by mercury is concerned, it is necessary to be able to predict what the rate of reaction would have been in the absence of mercury, so that the effect of the mercury alone can be determined. Under certain conditions in the present work reproducibility of reaction rate was attained, and only in these cases was mercury allowed to interact with the catalyst. The nature of this interaction and the effects produced will now be considered.

(5.6.) The Poisoning Effect of Mercury

In order to determine the poisoning mechanism of mercury for cyclopropane hydrogenation it is necessary to consider the possible modes of interaction of mercury with the catalyst. These will be considered under the headings (a) alloy formation, and (b) interaction with surface sites.

(a) Alloy Formation

It is well known that mercury alloys with certain metals to form amalgams. Thus formation of gold amalgam is widely used as a method of removal of mercury vapour from vacuum systems (28)(36). Similarly, silver and copper are known to form amalgams (37). The effect which mercury might have on a metal catalyst if an alloy were formed is two-fold, (1) it could alter the d band character of the metal and hence affect the electronic properties of the catalyst, or (2) it could alter the physical characteristics of the metal and introduce a geometric factor. It would appear that small amounts of mercury produced too large a poisoning effect for the first to be operating in the present study (9), although the geometric properties of the metal, particularly on the surface, might well be affected by such small quantities.

If alloy formation occurred, it could result in one of three types of alloy, interstitial, solid solution or intermetallic compound. The type which occurred would depend on the relative atomic radii and properties of the elements concerned, but each might be expected to result in some distortion of the lattice. For the metals under consideration the atomic radii are Hg 1.55 A^o, Ni 1.25 A^o and Pd 1.37 A^o. It is normally accepted that the formation of solid solutions does not occur if the radii of the solute metal is greater by about 15% than that of the solvent (38). For this reason Campbell and Thomson (12) considered the formation of a nickel mercury alloy was an unlikely explanation of the poisoning effect of mercury. It would appear, however, that alloy formation cannot be rejected on this basis alone, as is indicated by the fact that copper has an atomic radius comparable to nickel (viz. 1.28 A^o) yet forms an alloy with mercury. It has in fact been suggested (39), that alloy formation is responsible for particular effects observed using infra-red spectroscopy in the study of carbon monoxide adsorbed on mercury poisoned nickel catalysts. These effects, however, would also appear to be capable of explanation without resort to alloy formation and there appears to be no evidence for the existence of nickel amalgam (40). This is also borne out by the fact that in the present work, under certain conditions, mercury was capable of being removed from the catalyst at room temperature, whereas work on gold amalgam has shown that removal of mercury is only achieved at high temperatures.

In the case of palladium, however, alloy formation may well occur considering the relative sizes of the palladium and mercury atoms. Further evidence may be obtained from the fact that palladium, and particularly palladium hydride Pd $H_{0.6}$ (41), is wetted by mercury, if wetting of a metal by mercury is indicative of a tendency for alloy formation, as might be inferred from the avidity of wetting of silver and gold.

In the absence of evidence for amalgam formation, it is assumed that on nickel the poisoning effect of mercury is due to its interaction with adsorption sites on the catalyst. Confirmatory evidence for this is the approximately atom for atom displacement of adsorbed hydrogen by mercury, as was determined by Campbell and Thomson (19).

(b) Interaction with Surface Sites

It is generally accepted that the mechanism of a catalysed chemical reaction proceeds via the adsorption of one or more of the reactants on the catalyst surface. Furthermore, the rate of the reaction will be governed by the number of active species adsorbed and hence on the number of sites capable of adsorption. As has been indicated in the introduction, Maxted has shown that sites capable of reaction may be eliminated if they become occupied by some strongly adsorbed species. Mercury would appear to be very capable of this strong adsorption on nickel or palladium catalysts, since it possesses a filled d shell which is capable of donating electrons to the transition metal catalyst. The effect which a particular amount of mercury will have on the reaction rate will depend on two factors, (1) the distribution of reaction sites on the catalyst surface and (2) the mechanism of the reaction itself. The first will now be considered in greater detail and a discussion of the second given later.

(5.7.) Properties and Distribution of Reaction Sites in Nickel Catalysts

Evaporated nickel films will be considered initially since they have been studied in greatest detail. From the earliest work, it has been shown that evaporated films possessed a considerable internal structure as indicated by

(a) the difference between the surface area obtained by physical adsorption measurements 10,000 cm^2 and the apparent surface area 30 cm^2 (17),

(b) the dependence of surface area on film weight,

(c) the fact that their electrical resistance is much greater than the bulk metal.

It was originally postulated by Beek that this internal structure was due to the presence of pores within the bulk metal. If this is the case it is possible to postulate that mercury could be adsorbed at the mouth of the pores and hence prevent reaction on the nickel sites within the pore. Recently work has been carried out by Anderson, Baker and Sanders (25) on the structure of nickel films using transmission electron microscopy. They have shown that a nickel film was made up of crystallites, the size of which varied with the conditions of evaporation. For a film evaporated under vacuum at $0^{o}C$, these crystals varied in breadth from 250 - 1,000 A^{o}, were up to 1,000 A^{o} thick and were separated by gaps up to 20 A^{o} wide. Similar observations were made by Sachtler et al. (42) who showed that the growth and orientation of the crystallites was affected by the geometric limitations imposed by neighbouring crystallites. Both sets of workers showed sintering to be the growth of the crystallites and Anderson et al. also observed a simultaneous closing of the intercrystalline gaps and fissures. Assuming this structure for the evaporated films in the present work, it would not be expected that single mercury atoms would be capable of preventing adsorption on a large number of catalyst sites and a situation comparable to a two dimensional surface would be present.

The situation on pumice supported nickel catalyst is less obvious, since direct studies of the system have not been made. It is highly likely, however, that the metal is distributed over the support in a finely divided crystalline form and that the surface area of the metal will be controlled by the area and structure of the support. It is known that pumice, the support used in the present work, is a low area substrate which possesses a course pore system, which makes even the internal area of large pieces accessible (43). Taken along with the fact that the supported nickel catalysts used were reduced at 450°C, and were thus probably highly sintered, this indicates that the supported catalysts too would not be poisoned by a pore blocking mechanism.

Further evidence is given by Wheeler (44) who has indicated the relationships to be expected between the fraction of the surface poisoned to the ratio of activity of a catalyst before and after poisoning, for adsorption of poison at the mouths of pores of different sizes. Only for a system in which poison is adsorbed on a flat surface or at the mouth of large pores is a linear relationship obtained. This is the relationship obtained by the poisoning of cyclopropane hydrogenation on evaporated films as shown in Fig. 2.1.

It may, therefore, be concluded that the mechanism of the mercury poisoning by interaction with the surface does not involve, to any great extent, the adsorption of mercury at the mouths of pores. Owing to the lack of reproducibility obtained with supported nickel catalysts extensive poisoning data was not obtained for these catalysts. With supported palladium, additional phenomena were observed which complicated the poisoning mechanism and these will be discussed in a later section.

The Poisoning Mechanism

(5.8.) Theoretical Considerations

Having concluded that the poisoning of the catalytic activity is caused by the strong adsorption of mercury onto the metal and that pore effects do not operate to any great extent, it is necessary to determine how this adsorption interferes with the mechanism of the hydrogenation process.

Assuming random adsorption on a model catalyst surface, which was considered to be homogeneous, Herington and Rideal (14) have obtained theoretical poisoning curves, i.e. the relationship between catalyst activity and the amount of poison present, for a series of poisons and a series of adsorbed species. They have shown that, if the reaction rate is dependent on the number of adsorbed reactant species, different shapes of poisoning curves will be obtained depending on the number of surface sites occupied by each molecule of the adsorbed species and of the poison. From these results it can be shown that the linear type of poisoning curve obtained from the mercury poisoning of cyclopropane hydrogenation in the present work can result, if reaction is dependent on the concentration of a reactant occupying one site, and if the poison is also adsorbed on one site. In the theoretical treatment, the result of increasing the number of sites occupied either by the reactant or by the poisoning species, was to produce a greater poisoning effect for any particular amount of poison, especially at low poison concentrations. The overall result was non linear poisoning curves which tended to approach the poison concentration axis to a greater extent the more sites required for poison or reactant adsorption.

It is now necessary to determine whether this process is compatible with the available information concerning the mechanism of the reaction of cyclopropane with hydrogen.

(5.9.) Kinetics of Cyclopropane Hydrogenation on Nickel

The reaction of cyclopropane with hydrogen on a metal catalyst to form propane has been known for many years (45). Considerable interest, however, was stimulated in this reaction after the kinetics were studied over pumice supported Ni, Pd and Pt by Bond and Sheridan (35). These workers showed that, unlike the kinetics normally found in the hydrogenation of hydrocarbons, the kinetic orders were first with respect to the hydrocarbon and zero with respect to hydrogen, over wide pressure ranges. As a result of these kinetics it was concluded that the catalyst surface was covered with chemisorbed hydrogen and that the rate determining step involved physically adsorbed or gaseous cyclopropane.

Three alternative modes of interaction of cyclopropane with hydrogen appeared possible, (a) addition of two hydrogen atoms in one step, (b) successive additions of two hydrogen atoms singly and (c) isomerization of cyclopropane to propylene (rate determining) followed by rapid hydrogenation. Mechanisms (a) and (c) were eliminated after further study of the interaction of cyclopropane and propylene with deuterium, in which it was found that propanes having more than 2D atoms were present and also that the distribution of deuterated products from cyclopropane and propylene was entirely different.

Consequently, the above evidence suggested that cyclopropane hydrogenation occurred by the interaction of chemisorbed hydrogen with gaseous or physically adsorbed cyclopropane to form an adsorbed n-propyl radical. If this is the case, as suggested by Campbell and Thomson (12) the poisoning effect of mercury for cyclopropane hydrogenation may be due to the fact that mercury is able to displace hydrogen (19) from the surface and thus prevent the hydrogenation. The results of the mercury poisoning studies in the present work have indicated that the rate of reaction is controlled by the concentration of a species which appears to occupy a single surface site. This is in agreement with the above mechanism, if it is assumed that this species is adsorbed hydrogen. In the light of this information the above mechanism for the reaction of cyclopropane with hydrogen and the effect of mercury is satisfactory. More recent work, however, has shown that it is necessary to consider the mechanism of poisoning further.

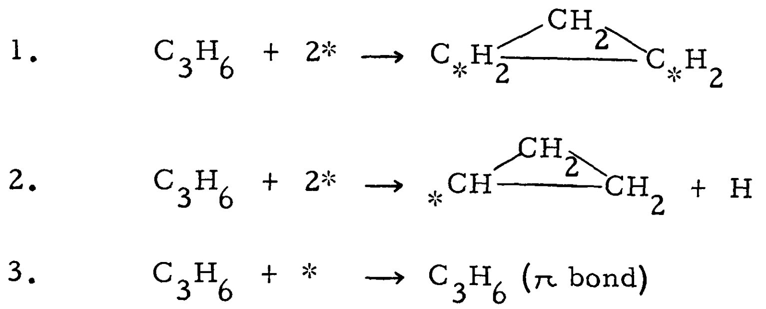
Bond and his co-workers have carried out a detailed study of the kinetics of cyclopropane hydrogenation on a variety of pumice supported metals - Rh, Pd, Pt and Ir - at temperatures ranging from 0 - 200°C, with reactant pressures in the range 10 - 500 torr (21). It has been shown that the orders of reaction for cyclopropane varied between 0.2 and 1.0. For any particular catalyst, the order in cyclopropane tended to rise with temperature and with fixed hydrogen pressure to a limiting value of unity. With fixed cyclopropane pressure, increasing hydrogen pressure produced an increase in rate to a maximum value. Further pressure increase either produced a decrease in rate (i.e. negative order), or the rate remained constant (i.e. zero order). The orders obtained after the maximum had been attained varied from - 0.8 at 0°C to a limiting value of zero with increasing temperature over all catalysts.

No comprehensive study of the variation in reaction order has been carried out using a nickel catalyst other than that by Bond and

Sheridan (35), in which reactions on nickel were not studied at temperatures below 129°C. It does not, therefore, appear possible to state definitely, in the light of the evidence from other metals, that because the orders with respect to cyclopropane and hydrogen at higher temperatures on supported nickel are one and zero respectively, that these orders occur at the temperatures at which the present work was carried out. This is especially valid since the present work was carried out on evaporated nickel films whereas that of Bond and Sheridan was on supported catalysts and it has been shown that the orders obtained can depend on the method of catalyst preparation (32).

To explain the observed fractional positive orders in cyclopropane which have been observed on the metals, it was necessary to postulate that some chemisorption of this reactant occurs. It has been shown that the overall rate of cyclopropane hydrogenation on evaporated films at 23°C in the present work was first order, or approximately first order, but no detailed study of the orders with respect to each reactant has been made. If under the conditions used in the present work the rate was dependent on a positive fractional order in cyclopropane and hence on the existence of chemisorbed cyclopropane, the effect of mercury on this adsorbed species must be considered.

Three possible mechanisms for cyclopropane chemisorption have been suggested (21, 46).



1. $C_3H_6 + 2* \longrightarrow C_*H_2\overset{CH_2}{\text{———}}C_*H_2$

2. $C_3H_6 + 2* \longrightarrow {}_*CH\overset{CH_2}{\text{———}}CH_2 + H$

3. $C_3H_6 + * \longrightarrow C_3H_6$ (π bond)

1

Of these 1. has been considered the least likely, although it is interesting to note that evidence from the I.R. study of cyclopropane on nickel-silica catalysts favours this mode of adsorption (47). There is considerable evidence for the existence of both 2. and 3. and further study seems necessary to determine which represents the true mechanism.

The adsorbed species which result from these different modes of adsorption vary in the number of surface sites which they occupy. Obviously 1. occupies at least two sites, but the situation for 2. and 3. is not obvious. In order to obtain maximum overlap of the orbitals constituting the π-bond in 3. the plane of the cyclopropane ring must lie parallel and as close to the catalyst surface as possible. Consequently it might be expected that the presence of other strongly adsorbed species, such as mercury or carbonaceous residues, on neighbouring nickel sites would prevent strong adsorption of this species. It is possible, however, that adsorption on single sites situated on elevated regions of the surface, or edges of crystals, might occur where interaction with neighbouring sites is much less. Although the geometric structure of the adsorbed species produced in 2. is not known, it appear the most likely to be capable of being adsorbed on a single site. The steric effect of the CH_2 groups, however, might be expected to interfere with species on neighbouring sites.

From the above discussion it may be concluded that even if adsorption of cyclopropane does occur and this influences the rate of the reaction, it cannot do so to any great extent since the possible modes of adsorption of cyclopropane indicated above would all result in poisoning curves which were different from the one obtained in actual practice.

In all the previous studies of the reaction of cyclopropane with hydrogen which have been discussed, it has always been found, or assumed, that propane is the only reaction product. Recent results obtained by a number of workers, however, have shown that under certain conditions this is not the case. It is now necessary to consider how this new evidence is likely to affect the proposed poisoning mechanism.

(5.10.) Reaction of Cyclopropane with Hydrogen to Produce Products Other Than Propane

McKee (48) has shown that, using a platinum black catalyst, reaction of cyclopropane with hydrogen results in demethanation, i.e. cracking, as well as hydrogenation, as indicated by the presence of ethane and methane in addition to propane in the reaction products. In addition, a surface residue of average composition $CH_{1.1}$ was found. Demethanation and hydrogenation have also been obtained by Sinfelt, Yates and Taylor (49) over a range of temperatures on 10% silica-supported nickel and cobalt, although no signs of demethanation were present under similar conditions on platinum and copper.

A further study of these reactions was made by the same workers (33) to determine the factors which controlled the specificity of reaction. This indicated that in addition to the effect of different metals, variation in prereaction treatment of the catalyst and the nature of the catalyst support influenced the nature of the products obtained. Thus specific activity at $42^{o}C$ for hydrogenation on a nickel on silica catalyst was 16 fold greater than on a nickel on silica-alumina catalyst, whereas the specific activity for demethanation was about 44 fold greater. When the catalyst was cooled in helium after reduction it was found that the production of methane and ethane was much lower than when the catalyst was cooled under hydrogen, prior to carrying out the reaction. Sinfelt et al. attributed the non-observance of demethanation in previous work to the fact that this had been carried out on catalysts which had been evacuated after reduction. They considered that, under these conditions, hydrogen would not have been present and catalyst conditions comparable to those used by them after cooling in helium would have existed. That this is not a valid assumption is indicated by the results of the present work, which has shown that even after evacuation hydrogen is present on reduced supported nickel catalysts, as indicated by its displacement with mercury. Nonetheless, it appears that the nature of the catalyst support and the pre-reaction treatment affect the distribution of products. Since standard treatment and preparation procedures were not employed in the different laboratories it is not surprising that differing results were obtained.

In addition to the work carried out on supported catalysts it has also been shown by Knorr and Ponec (18) that hydrogenation of cyclopropane, using low reactant gas pressures, on evaporated nickel films involves the formation of ethane and methane. They have also shown that ethane is obtained along with propane when cyclopropane is adsorbed on nickel films in the absence of hydrogen and there is evidence that methane is also present. This latter product may account for part of the non-condensible residue obtained by Campbell and Thomson (12) after displacement of cyclopropane by mercury from evaporated nickel films.

It may be concluded, from the above discussion of the evidence, that for a particular catalyst under a given set of experimental conditions the reaction of cyclopropane with hydrogen is much more complex than the original work suggested. Knorr and Ponec (18) have shown that when cyclopropane was chemisorbed on evaporated nickel films in the absence of hydrogen the extent of the adsorption at 200°K corresponded to an area of approximately four times that of a nickel site. Owing to the fragmentation which must occur during chemisorption to account for the observed products, it is not possible to determine from this result the mode of adsorption of the cyclopropane. What is possible, however, is to state that even if cyclopropane adsorption occurred in the present work, under hydrogenation conditions, it could not have played a large part in controlling the kinetics, since the poisoning curve obtained does not satisfy the large number of sites required for its adsorption.

In conclusion, even considering the formation of products other than cyclopropane, it would appear that the poisoning effect of mercury on the reaction of cyclopropane with hydrogen is to prevent the adsorption of hydrogen, the presence of which controls the rate of reaction.

(5.11.) Surface Heterogeneity

This conclusion is based on the theoretical findings of Herington and Rideal (14) and it must be borne in mind that these were based on the assumption that a homogeneous surface was present. Recent work by Wishlade and Thomson (50) has shown that there is evidence that the surface of evaporated nickel films is heterogeneous towards ethylene hydrogenation.

A mixture of ethylene and hydrogen was admitted to a nickel catalyst on which was pre-adsorbed ethylene C-14. The hydrogenation and subsequent removal to the gas phase of the radioactive ethylene was followed using a G.M. tube. The reduction in count from the surface after reaction indicated that 40% of the sites were catalytically active in the hydrogenation. Owing to certain limitations in this technique it was not possible to determine the nature of the species which were adsorbed on the apparently inactive sites. Neither was it possible to decide how the active sites were situated relative to those on which the residues were adsorbed.

There is evidence from the work of McKee (48) to suggest that carbonaceous residues are formed during cyclopropane hydrogenation, using a platinum catalyst. This might also be the case on various other metals, including nickel, considering the demethanation reactions which have been found to operate. If this does occur, resulting in a heterogeneous catalyst surface, the fact that linear poisoning curves were still obtained was additional evidence that a one site poisoning process was occurring. Alternatively, the heterogeneity results from the residues being concentrated in large patches which enabled the active surface to be considered as homogeneous although the overall surface would be heterogeneous.

(5.12.) The Effect of the Initial Reactant Pressure on the Rate of Cyclopropane Hydrogenation

Although apparently not connected directly with the foregoing discussion, a phenomenon was observed during the study of the cyclopropane hydrogenation experiments which is considered worthy of further mention at this stage.

Thus it has been shown in Chapter 1 in the work on nickel films and to a certain extent on 1% palladium on pumice that a strictly linear relationship existed between the logarithm of the cyclopropane partial pressure and time. Since this linearity was maintained until all of the available reactants had reacted, it appeared that the reaction being followed was first order or very nearly first order.

In contrast to this, however, the value of the rate constant obtained from the gradient of the apparently first order plot was found to vary considerably with the initial pressure of the reactants. The higher the initial pressure the lower was the value of the rate constant obtained. In this hydrogenation reaction a 1:1 reactant mixture was used. At any time during the reaction, equal pressures of each reactant would have been present, since the reaction proceeded by interaction of 1 mole of cyclopropane with 1 mole of hydrogen to form 1 mole of propane. Thus the pressure of each reactant at the beginning of a reaction, using a particular initial total pressure, would for example have been the same as that present when a reaction using an initial pressure of twice this amount had been permitted to proceed until half of the reactants had reacted. It would, therefore, have been expected that the rates of these reactions would have been comparable when comparable pressures of reactants were present. That this was not in fact the case is indicated in Fig. 1.6. in which it can be seen that the plots are strictly linear and do not accelerate as the reaction proceeds. Consequently it appears that the presence of propane somehow affects the rate of reaction. It is difficult to determine a mechanism for this, however, since any poisoning or promoting effect of the propane would have resulted in a decrease or an increase in the rate during the reaction, neither of which were observed.

In order to investigate this phenomenon further it is proposed to study the rates of a series of reactions in which a constant initial pressure of a 1:1 mixture is used. Mixtures using the same partial pressures of the reactants as before but with added amounts of propane will then be studied to determine whether any alteration in rate occurs. In addition, the investigation will be repeated using additions of an inert gas such as argon, to determine if the propane merely acts as an inert diluent.

The Reaction of Cyclopropane with Hydrogen over Supported Palladium Catalysts

(5.13.) Introduction

The reaction of cyclopropane with hydrogen has been studied over palladium supported on pumice and on carbon. The results of the studies using the pumice supported palladium catalysts can be summarised as follows :

1. The activity of the catalyst was dependent to a large extent on the pre-reaction treatment.
2. Reproducible rates of reaction were obtainable.
3. The activity of a 5% palladium on pumice catalyst was apparently much greater than that of a 5% nickel on pumice catalyst.
4. Mercury reduced the rate of reaction, but in a manner different from that found with evaporated nickel films, and the poisoning action was to a certain extent reversible under reaction conditions.

5. There was an apparent increase in count from mercury on the catalyst during a period when no further mercury was being adsorbed.

(5.14.) Factors Governing the Activity of the Catalyst

The dependence of the activity of the palladium catalyst on the pre-reaction treatment, and its apparent higher activity compared with a similar nickel catalyst, may be considered as effects of
(a) sintering (b) absorption of hydrogen.

Sintering is the process whereby an inherently metastable material reverts to the corresponding stable condition. The higher level of energy which the material possesses is a result of various properties such as high surface area and the number of defects present. These factors depend critically on the method of preparation and the treatment of the catalyst.

For metals, this sintering process is normally made manifest by reduction in surface area. As has already been described (25), sintering of evaporated metal films has been shown to result in crystal growth and in removal of surface asperities, with consequent reduction in surface area. Some indication of the magnitude of this sintering effect with increasing temperature for nickel films is given by Gundry and Tompkins (51).

On supported palladium and nickel catalysts, as used in the present work, it might be expected that sintering would occur by a comparable mechanism to that on films, and that the temperature to which the catalyst is raised, and the time for which it is maintained at that temperature, will affect the extent of sintering. This would explain the differences in activity observed with palladium after various treatments. It might also be expected that for two metals raised to comparable temperatures the extent of sintering would depend on the relative melting points of the metals. On this basis, the low activity of palladium catalysts observed compared with that of nickel after comparable high temperature treatments cannot be ascribed to sintering, since these metals possess comparable melting points of 1554°C and 1455°C respectively. Various other factors contribute to the sintering process, however, as indicated by the acceleration of crystal growth of palladium in the presence of oxygen (52).

In addition to any sintering effect which may be operating, palladium is capable of absorbing large quantities of hydrogen. The amount of hydrogen absorbed rises considerably with temperature as has been found by a number of workers studying the phenomenon as a method of hydrogen purification (53). It has already been stressed in section 5.2. that hydrogen present within the metal lattice can exert a considerable effect on the catalytic properties of the metal. The reasons for this are still the subject of controversy but such factors may well control the differences in activity observed between nickel and palladium and between the various palladium catalysts used in the present work.

In conclusion, it appears to be extremely difficult to assess the relative activities of a series of metals for a particular reaction. Attempts have been made to accomplish this by comparing specific activities derived using some normalising factor such as surface area measurements for chemisorption (33). Such normalisation is incomplete since it is also necessary to include simultaneous comparison of such factors as defect concentrations, and relative amounts of occluded gases, to mention only two of the factors known to influence the activity for a particular reaction.

(5.15.) Poisoning of Palladium on Pumice Catalysts

In the absence of mercury it was found, using the 5% palladium on pumice catalyst, that reproducibility of rate was obtained. In contrast to the behaviour found using the 5% nickel on pumice catalyst, this indicated that the catalyst surface was stable after repeated reactions and that no contaminant was present in the reaction mixture used.

When the catalyst was exposed to mercury vapour between hydrogenations a reduction in the activity of subsequent reactions was observed, indicating that the mercury exerted a poisoning effect on the reaction. When the tap to the mercury source was opened initially in each of the experiments, however, a poisoning effect was produced which was out of proportion to the effects resulting from even longer exposures at later stages. This effect was not observed with nickel films and will now be considered further.

A possible cause of this effect is the presence, in that portion of the apparatus containing the mercury source, of a limited amount of poison which is more efficient in deactivating the catalyst than mercury. Such a poison could not be oxygen since the only possible source of this is that desorbed from the walls of the mercury source tubing. This amount would be insignificant compared with the amount likely to have been desorbed from other regions of the catalyst vessel which had little effect, as indicated by the reproducible reaction rates obtained.

If mercury was in fact responsible for this initial effect, presumably one of the poisoning mechanisms discussed in section 5.8. must have been in operation. The poisoning curves derived from pore-blocking mechanisms suggest that the initial reduction was due to preferential adsorption of mercury at the mouths of pores containing a large internal surface area but a small pore mouth. This is incompatible with the expected structure of the catalyst (43) and also does not explain why subsequent short or long exposures to mercury did not reduce the activity to zero.

The anomalous poisoning effect produced when mercury was first admitted to a palladium catalyst is comparable with that observed by Bond and Wells (54) in the mercury poisoning of palladium catalysts for the hydrogenation of acetylene. In their work this large reduction in rate, termed "type B" poisoning, occurred only with reactions carried out at temperatures of 85°C and higher. This was attributed to the poisoning of the catalyst by mercury from the manometer while the reaction was being followed. This explanation appears unlikely. Considering the long periods of exposure to mercury vapour necessary under vacuum conditions to produce relatively small poisoning effects at lower temperatures, the amount of mercury diffusing through the reactant gas mixture at the higher temperature, in the short time necessary to follow the reaction, must have been extremely small. Any influence of mercury from the manometer in the present work may be eliminated since reproducible unpoisoned rates were obtained before mercury was intentionally admitted.

(5.16.) Reactivation of Poisoned Palladium Catalysts

It was found that mercury was capable of poisoning the pumice supported palladium for cyclopropane hydrogenation. It was further found that if a series of standard hydrogenations were carried out on this poisoned catalyst, without any further admission of mercury, a reactivation of the catalyst occurred. This reactivation was indicated by an increase with successive reactions of both the rate constant and the initial rate. The reactivation was found to operate at both coverages studied. In neither case was reactivation followed until it achieved a constant value and thus it was not possible to determine the full extent of the process. The reduction in activity produced by exposure of the catalyst to mercury for 20 min was shown to be 33%. The original activity could, however, be restored by carrying out six standard 10 min hydrogenations.

This reactivation process was not observed on poisoned nickel films. The experimental procedure, however, was such that with films, evacuation of the catalyst vessel could not be carried out without the possibility of introducing a further quantity of mercury. Consequently any reactivation which may have occurred would not have been observed.

Reactivation of a mercury poisoned pumice supported palladium catalyst was observed by Bond and Wells during their study of the hydrogenation of acetylene and ethylene (54). These workers postulated that adsorbed mercury was capable of migration and coagulation. Thus sites originally poisoned by the presence of mercury became reactivated as the mercury migrated across the catalyst to form areas of high mercury concentration. They found evidence to suggest that the reactivation process occurred as a result of the hydrogenation reaction. Thus reactivation was possible several days after the catalyst was first poisoned, and reactivation did not occur by treating the catalyst with either reactant separately.

Similar behaviour was found in the present work where an almost completely poisoned catalyst regained little activity after being allowed to stand for eight hours under vacuum at room temperature. On allowing a hydrogenation to proceed for 11 hr at 78°C, a considerable reactivation took place. In the present work this reactivation may have been caused by the higher temperature involved during the reaction, particularly if the migration was an activated process. This migration process will now be considered in more detail.

(5.17.) Migration of Mercury over the Catalyst Surface

The idea of mobility of species physically adsorbed on a catalyst surface is readily acceptable since the bonds between the adsorbate and the adsorbent are relatively weak and non-localised, and the activation energy for migration will be low. In the case of chemisorption the bond energies are much greater, and thus surface migration should require a much greater activation energy. It is necessary, however, to postulate that chemisorbed species are mobile, and are able to undergo surface collisions as is required for the Langmuir Hinshelwood theory of bimolecular surface reactions. In apparent contrast to this, chemisorption isotherms are based on localised adsorption which perhaps implies that the adsorbed molecules are immobile.

This "immobility", however, requires only that the surface mobility is small compared to the rate of adsorption and desorption, so that the species being adsorbed or desorbed experience a relatively unchanged surface environment.

It is thus generally accepted that if the activation energy for migration from one site to another is appreciable, but definitely less than that for desorption, adsorption is still localised but the layer is mobile.

In the case of mercury adsorbed on palladium it would be expected that chemisorption would occur owing to the nature of the filled d shell of mercury. Thus an immobile layer is formed which influences reaction to an extent depending on the number of sites required for adsorption of the reactant, as postulated by Herington and Rideal. This layer is still mobile and thus capable of reactivating the surface as indicated by Bond and Wells. However, the time scale required will be long compared with the time necessary for reaction.

In acetylene hydrogenation this reactivation, based on mobility of the mercury to form areas of high mercury concentration, is plausible since an isolated mercury atom can prevent adsorption of acetylene on a number of surface sites, owing to the fact that acetylene requires two sites for adsorption and only certain pairs of sites are suitable. Thus crowding of the mercury releases sites for adsorption, since mercury atoms on a group of neighbouring sites permit more acetylene adsorption than mercury on isolated sites. This crowding effect also explains why complete regeneration is not possible, since the absolute acetylene coverage is less on a poisoned than on an unpoisoned surface.

In the case of cyclopropane hydrogenation, the influence of mercury atoms would not be very different when they were present on isolated sites or when crowded together, since it is assumed that mercury only influences one surface site for hydrogen adsorption. The validity of this assumption is shown by the fact that when mercury was adsorbed on a nickel surface saturated with hydrogen an approximately atom for atom displacement was obtained (19). It would thus appear that a crowding mechanism does not explain the reactivation which was observed during the hydrogenation of cyclopropane, and an alternative mechanism is required. It is suggested that this mechanism is related to the observed increase in count which was obtained during the reactivation process from the Geiger Muller tube, situated below the catalyst bed.

(5.18.) Migration of Mercury Through the Catalyst Bed

The alteration in count obtained from the radioactive mercury adsorbed on the catalyst surface during an interval when no mercury was admitted to the catalyst, was also found during a series of experiments which are described in Chapter 8. On this occasion a reduction in count was observed when the counter was placed above the catalyst. In both cases the change observed can be attributed to migration of mercury down through the catalyst bed. The magnitude of the increase in count to be expected as a result of migration during the hydrogenation reactions may be derived by considering the geometric arrangement of the counter and the catalyst as is indicated in detail in Fig. 10.3. From this it can be seen that the catalyst bed is of the order of 1 mm thick and the top of the bed is approximately 1 cm from the counter window. Assuming that the count seen by the counter varies as the inverse square of the distance from the source, a migration from the top of the bed to the bottom would result in an increase in count by a factor of $(11)^2 \div (10)^2$. The increase in count observed, 50 to 60 c.p.m., was comparable with this. The validity of this mechanism is shown by its use as a standard method of determining diffusion of radioactive material in ionic solids (55).

As indicated previously in this discussion, the migration of chemisorbed mercury might be expected to be an activated process. In the acetylene hydrogenation work there was evidence to suggest that reactivation occurred only when a reaction was being carried out: there was no evidence for reactivation when the poisoned catalyst was left in contact with either one of the reactants. It may be postulated, therefore, that the energy required for migration was derived from that produced in the exothermic reaction.

In the present work it was not possible to determine whether or not migration through the catalyst bed occurred during the hydrogenation reaction. As indicated in Chapter 8, migration was, however, definitely found to take place in the absence of any reaction when the adsorption of mercury was being studied on a nickel catalyst. It must be concluded, therefore, that reaction is not necessary for this migration through the bed to occur and the mechanism of this migration will now be considered in more detail.

In both the experiments carried out in which this migration was observed, the catalyst was placed on the bottom of the reaction vessel and mercury vapour was present above the catalyst. Mercury would, therefore, be chemisorbed on the top of the catalyst bed, and owing to the very fine nature of the catalyst support, very little would be able to penetrate into the bulk of the catalyst bed without becoming adsorbed. Adsorption would occur initially on those sites near the top of the catalyst bed which had the highest energy, and migration from these sites would be unlikely if migration is an activated process. As adsorption continued, however, mercury would be adsorbed on sites near the top surface of the bed which had lower energy. It would then be energetically favourable for this mercury to migrate to higher energy sites within the catalyst bed which were still unoccupied. This process would continue, to produce an overall migration of mercury from the top of the bed to the bottom. The rate of migration would depend on the range of site energies and would be expected to be reduced as the higher energy sites became occupied.

Assuming this process occurs, reactivation of the poisoned catalyst may be explained by considering that hydrogenation occurs more readily near the top of the catalyst bed. Thus successive exposures to mercury poison the hydrogenation, but when a number of hydrogenations are carried out without further exposure to mercury, reactivation occurs as migration into the catalyst bed leaves sites, originally poisoned, free for reaction.

It may be postulated that this process was also operative in the poisoning of acetylene hydrogenation (54). In this case, however, a large size of support was used (viz. 8 - 16 mesh alumina) and it would be expected that the majority of the available metal was capable of taking part in reaction. This would be particularly so if the method of preparation of the catalyst involved pre-soaking of the support before adsorption of the metal salt solution. This has been shown to produce a very fine layer of metal on the surface of the support with little migration into the bulk (56).

If the above poisoning mechanism is correct, it indicates that with catalysts supported on very fine mesh supports reaction may only occur on the topmost portion of the catalyst bed. This could be verified if a system was used in which aliquots of a particular catalyst were removed from the reaction vessel without changing the experimental conditions. With a very finely divided support this could be accomplished by blowing a fraction of the catalyst out of the reaction vessel at various stages, using a stream of hydrogen.

(5.19.) Discussion of the Anomalous Behaviour of Palladium on Carbon Catalysts

If a mixture of cyclopropane and hydrogen were allowed to react to completion, the pressure fall observed would be equal to the initial partial pressure of the reactant which was present to the smaller extent. Using palladium on carbon catalysts, it was found that pressure changes considerably greater than this were observed. This effect was attributed to one or more of the following processes occurring with the products or reactants

1. Polymerisation,
2. Chemisorption on the palladium or carbon,
3. Physical adsorption on the carbon.

These will now be considered in more detail.

At first sight it might be supposed that the formation of fairly long chain polymers would account for anomalously large pressure falls during reaction. Thus several cyclopropane molecules would be required to produce one polymer molecule and the overall pressure drop would be dependent on the number of cyclopropane molecules taking part and on the volatility of the product. Since long chain polymers are the least volatile their formation might be expected to result in the largest pressure fall. In addition to this, however, an opposing factor must be considered. In the formation of long chain polymers the unsaturation resulting from the breakage of the cyclopropane ring is largely satisfied by carbon bond formation. Only the terminal unsaturation of the chain is satisfied by hydrogen addition. The larger the polymer molecules envisaged, the more hydrogen is left which is incapable of reacting, owing to lack of potentially unsaturated reactants. In practice, therefore, polymer formation is likely to result in pressure falls only slightly greater than those in hydrogenations, so that the observations cannot be explained on this basis.

Likewise, chemisorption effects are unlikely to be the cause for the following reasons

1. Chemisorption would not be readily reversible so removal during the short non-rigorous evacuation would be negligible. Thus saturation would soon be reached and chemisorption would not be consistently observed in several reactions carried out consecutively.
2. The amount of metal present is very limited.
3. Chemisorption on the carbon is unlikely to occur at the temperature used.

It would appear that the most feasible explanation of the observed anomalous pressure fall is physical adsorption onto the carbon support. The support used, due to its very fine particle size, to say nothing of its pore structure, details of which are unknown, would possess a very large surface area and hence a large adsorption capacity. In addition physically adsorbed species would be expected to be relatively easily removed under non-rigorous vacuum conditions.

In order to explain the magnitude of the pressure fall observed, it is necessary to postulate either that both reactants are physically adsorbed or else that the products of reaction are physically adsorbed. The fact that hydrogen is not physically adsorbed on carbon to any great extent above - 78°C (57) appears to rule out the first of these. The second postulate requires the physical adsorption of the product of reaction of cyclopropane and hydrogen. This product would appear most likely to be propane, although polymerisation may not be excluded. Data is not available for the physical adsorption of propane on charcoal although this is available for the adsorption of ethylene at 30°C (58). Comparison of the boiling points of these two substances (- 42.17°C and - 103.9°C respectively) would suggest that at any particular temperature more propane would be adsorbed than ethylene. It has been calculated that the amount of charcoal used was sufficient to adsorb ethylene in amounts comparable to the volume of propane formed during reaction. It would appear feasible, therefore, to explain the large pressure falls observed as being due to physical adsorption of propane. This is supported by the fact that greater pressure falls were observed when the catalyst was at lower temperatures, as would be expected if physical adsorption was operating.

The study of this system was not continued further since the observed phenomena simply complicated the poisoning study which was the main project in the present work.

CHAPTER 6

ADSORPTION OF MERCURY ON NICKEL CATALYSTS

Adsorption of Mercury on Clean Nickel Films

(6.1.) Introduction

In the experiments described in Chapter 2 mercury was allowed to adsorb onto nickel films in the time interval between successive hydrogenations, and the weight of mercury present on the film at any time was determined using the gamma counter. From the point of view of studying the poisoning effect of this mercury it was relatively unimportant to know at what rate the mercury was adsorbed, provided that a true adsorption did occur and transfer of mercury from the source to the film did not take place by distillation and condensation. For this reason an attempt was made to maintain the temperature of the mercury source at a value at least 1 C^{o} less than that of the film.

On consideration of the weights of mercury adsorbed in known periods of time, however, it was found that equal weights of mercury were not adsorbed in equal times of exposure of the film (see Table 6.1.). This was in apparent contrast to what was found by other workers (19, 59) in this laboratory during the study of the desorption of tritiated hydrogen by mercury, in which the mercury was adsorbed in a linear fashion with respect to time.

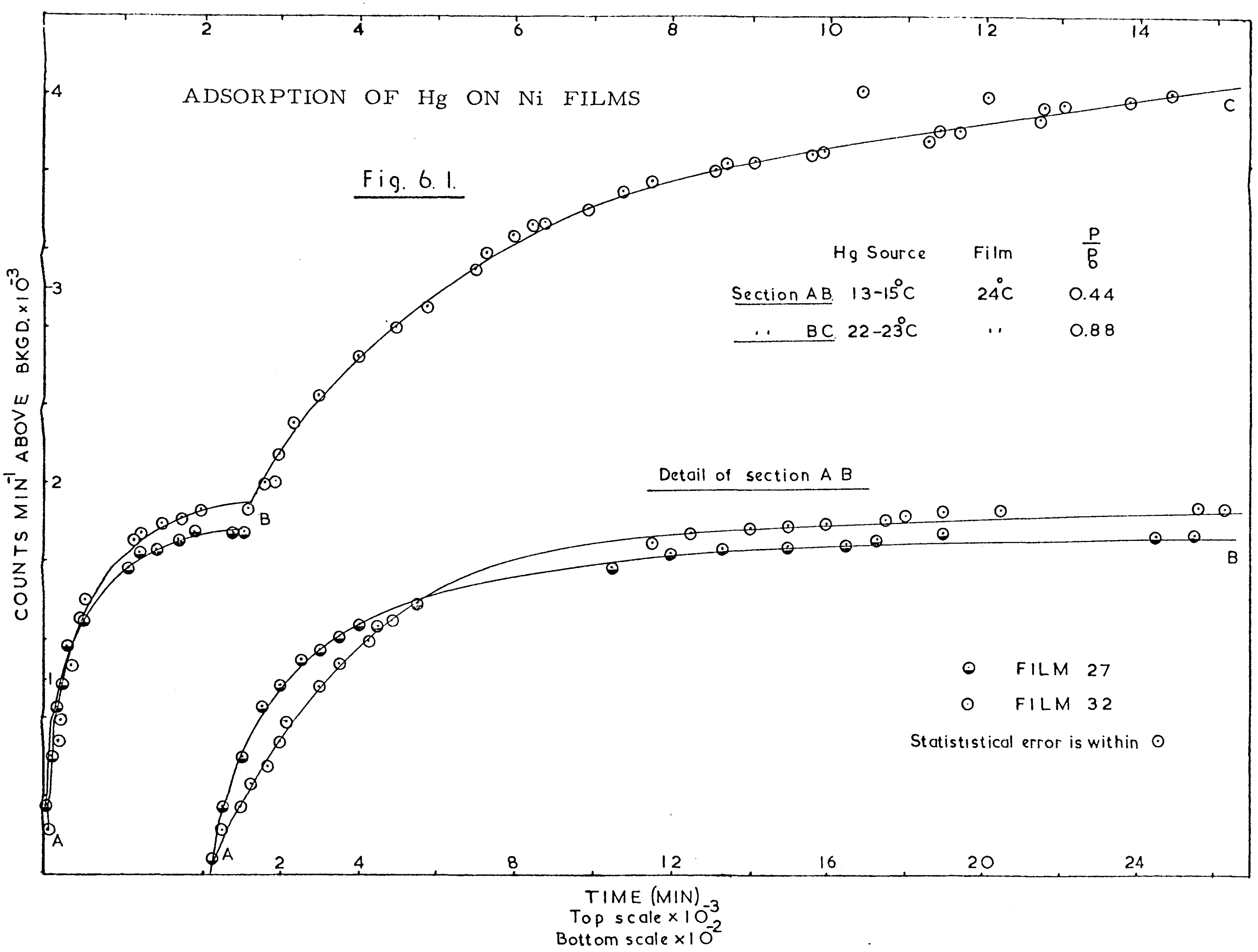
TABLE 6.1.

Summary of Rates of Hg Adsorption on Films

Film 20		Film 21		Film 22	
Time of Exposure (min)	Wt. of Hg Adsorbed (mg)	Time of Exposure (min)	Wt. of Hg Adsorbed (mg)	Time of Exposure (min)	Wt. of Hg Adsorbed (mg)
30	0.11	30	0.08	45	0.11
150	0.37	20	0.05	5	0.02
3.5	0	3	0.01	61	0.11
60	0.23	55	0.19	5	0.03
60	0.28	3	0	45	0.20
4.5	0.03	3	0.02	20	0.07
120	0.47	5	0.05	29	0.11
28	0.22	77	0.28	12	0.04
24	0.07	76	0.24	-	-
6.5	0.03	31	0.16	-	-
4.5	0.05	20	0.07	-	-
-	-	11	0.06	-	-

ADSORPTION OF Hg ON Ni FILMS

Fig. 6.1.



It was decided, therefore, to study in more detail the adsorption of mercury on evaporated nickel films in the present system.

(6.2.) Experimental Procedure

The films were prepared in exactly the same manner as those used for the hydrogenation experiments. In this case, however, after evaporation of the film, mercury vapour was admitted immediately, without carrying out any hydrogenations. The catalyst vessel was maintained at 24°C in the thermostat tank and the mercury source was surrounded by a spiral of lead piping through which water at a temperature of 13 - 15°C was passed. The arrival of mercury on the surface was followed using the cylindrical gamma counter. Details of the procedure are given in section 9.29.

(6.3.) Results

The results obtained for Films 27, 32 are shown in Fig. 6.1. in which the counts per minute from the catalyst are plotted against total time of exposure.

In the case of Film 27 adsorption was carried out with the film in the presence of a greased tap, i.e. tap T8, Fig. 9.6. It was found that adsorption proceeded initially at a fast rate which gradually decreased until after approximately 1900 min, no further adsorption took place during 600 min. The adsorption experiment was then terminated.

Two reasons why the adsorption had ceased suggested themselves

(a) the nickel surface had become saturated with mercury,

(b) some poison had competed with the mercury for the available nickel sites.

Considering the linear relationship of mercury adsorption with time found after total hydrogen displacement by Campbell and Thomson (19) and considered by these workers to be due to the presence of physical adsorption, it appeared that (b) was the most likely explanation. Two sources of contamination which could have produced this effect were 1. hydrocarbon vapours originating from the tap grease, 2. gases which were desorbed under vacuum conditions from that portion of the glass tubing which had not been as thoroughly degassed as the catalyst vessel.

In Film 32 the connecting tubing was thoroughly degassed under vacuum by heating it with a soft gas flame. Before breaking the breakseal of the mercury source, the catalyst vessel was isolated from the greased tap by sealing off the connecting tubing at a previously degassed constriction. Under these conditions similar results were obtained as with Film 27, i.e. a steep initial rise in adsorption which gradually decreased to a constant value (see Fig. 6.1.). In this case, however, instead of terminating the experiment when the adsorption had ceased, the temperature of the source was raised to a value of 21 - 23°C with the film still maintained at a temperature of 24°C. It was found that further adsorption now took place and continued for a considerable time (12000 min) without reaching a saturation value. The rate of adsorption did, however, decrease with time.

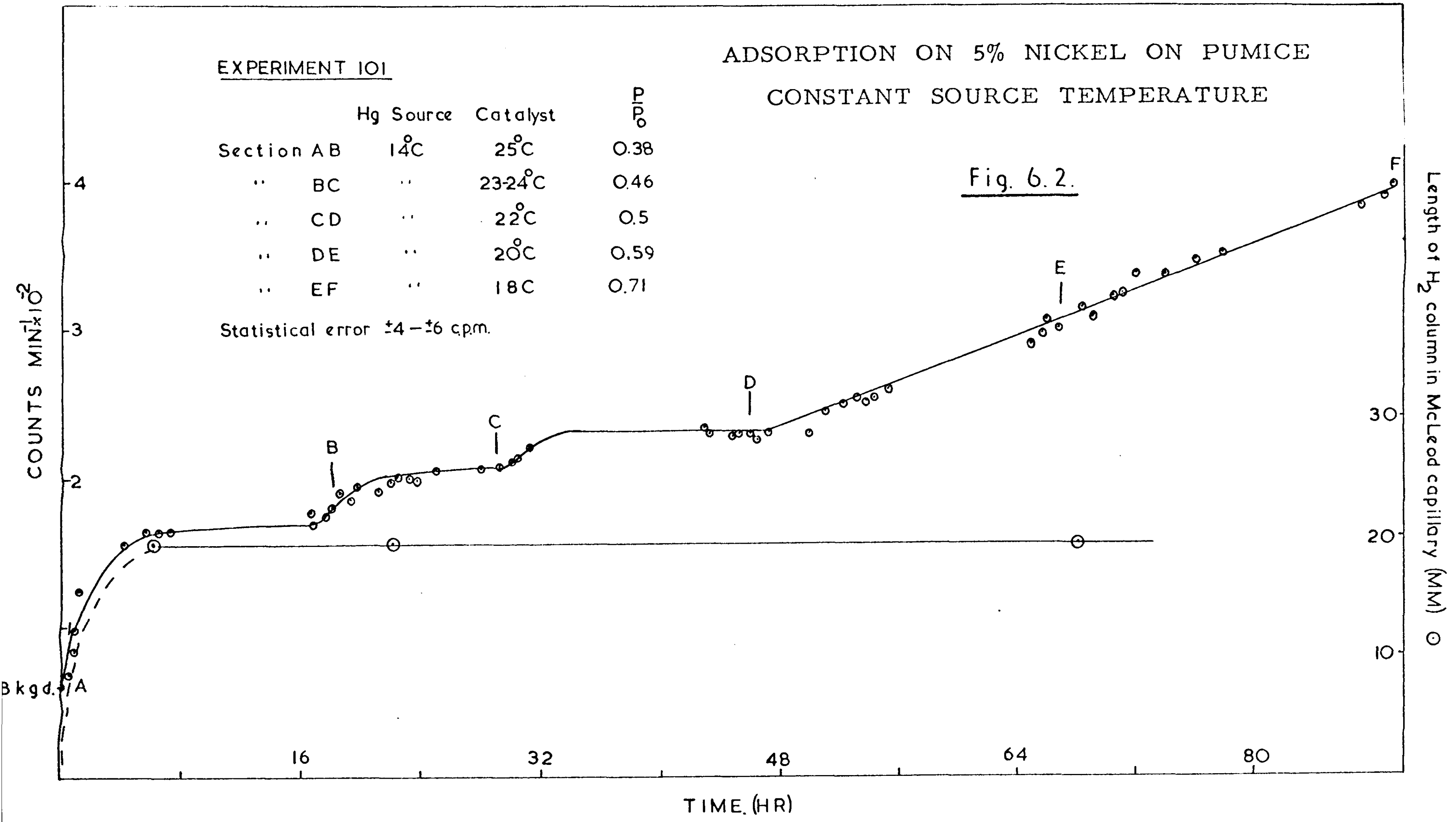
Adsorption of Mercury on Reduced Supported Nickel Catalysts

(6.4.) Experimental Procedure

As will be described in section 7.5. it was found necessary to determine to what extent hydrogen present on a reduced supported nickel catalyst was displaced by mercury. Radioactive mercury was used for this study and the arrival of the mercury on the catalyst was followed using a suitably modified G.M. tube. This study, consequently, also enabled information to be obtained concerning the adsorption of mercury on supported nickel catalysts. A diagram of the apparatus is shown in Fig. 11.5. and a detail of the counter assembly given in Fig. 11.6. Details of the catalyst preparation and experimental procedure are given in section 11.10.

(6.5.) Results Using Constant Mercury Source Temperature

In Experiment 101, the mercury source was surrounded by a cooling coil through which cold water was passed. The temperature



ADSORPTION ON 5% NICKEL ON PUMICE
CONSTANT SOURCE TEMPERATURE

Fig. 6.2.

of this water was maintained in the range 13 - 15°C. Initially the catalyst was thermostatted at 25°C in a water bath and, as was found in the case of the evaporated films, the amount of mercury adsorbed on the catalyst reached a constant value. The results obtained are shown in Fig. 6.2.

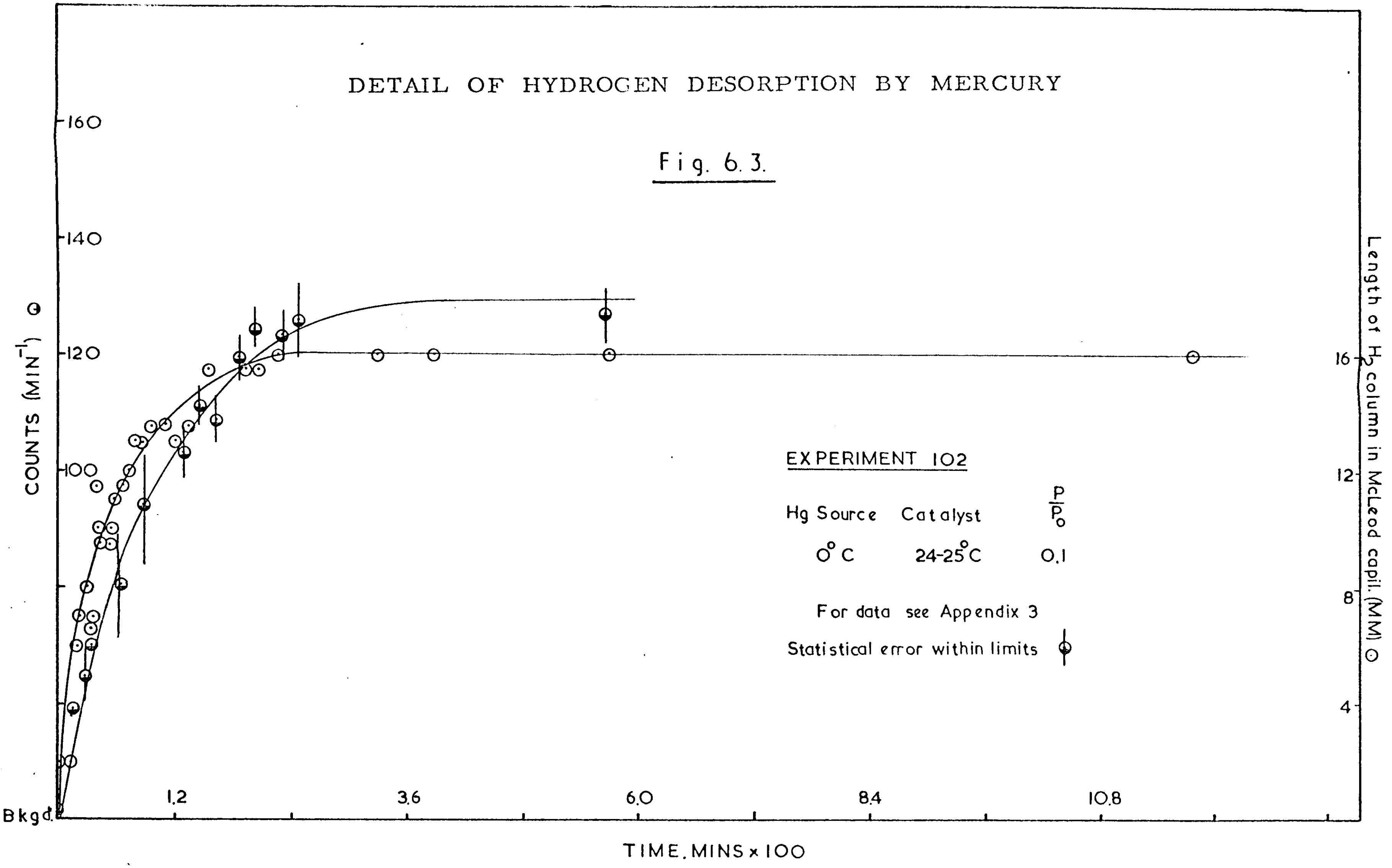
During the adsorption of the mercury the pressure of the desorbed hydrogen was measured using a McLeod gauge. The McLeod gauge capillary readings are also indicated in Fig. 6.2. It was not possible during this experiment to obtain values of the hydrogen pressure during the initial stages of mercury adsorption owing to practical difficulties. It was found, however, that the hydrogen pressure attained within the first five hours did not vary for the remainder of the experiment, indicating that the hydrogen desorption was completed within the five hour period.

Since it was not convenient to increase the temperature of the source in order to determine whether any further mercury could be adsorbed on the catalyst,the temperature of the water bath was reduced to 23°C by the use of a cooling coil. It was found that an increase in adsorption above the original constant value immediately occurred and a new constant value for the amount of mercury adsorbed was attained. Reduction of the bath temperature to 22°C produced a further adsorption which again attained a constant value. When the bath temperature was reduced to 20°C an increase in adsorption again occurred but in this case it did not become constant and continued to increase linearly with time. No reduction in this adsorption rate was indicated after leaving the catalyst in contact with the source for periods of time comparable with those in which the adsorption had ceased on previous occasions. Further reduction of the catalyst temperature had no effect on this linear adsorption.

Although the source of radioactive mercury was kept at a constant temperature of about 13 - 15°C throughout the experiment the variation in the room temperature was considerable. If a secondary source of mercury had been present, the temperature which was controlled by the room temperature, variations of the type observed in the amount of mercury adsorbed on the catalyst might have been obtained by distillation. That this did not occur was shown by the fact that throughout the major part of the experiment the room temperature did not rise to a value greater than 4 C° below that of the catalyst. During the latter half of the period at which the catalyst was at 20°C and also during part of the time when the catalyst was at 18°C, the temperature of the air was, however, comparable with that of the catalyst. During the remainder of the time when the catalyst was at these temperatures the air temperature was lower than that of the catalyst. If distillation was responsible for the linear adsorption

DETAIL OF HYDROGEN DESORPTION BY MERCURY

Fig. 6.3.



rate obtained when the catalyst was at 20°C and 18°C, then a break in the linearity would be expected when the air temperature was below this. This was not observed, nor was there any indication of a mercury source other than that maintained at 13 - 15°C.

The adsorption was repeated in Experiment 102. In this case the mercury source was surrounded by a Dewar flask containing ice and was, therefore, maintained at 0°C throughout the experiment. With the catalyst thermostatted at 25°C the adsorption again tended to attain a constant value. Owing to a fault which developed in the counter it was not possible to study the adsorption at other catalyst temperatures. During this experiment the pressure of the desorbed hydrogen was followed closely from the commencement of mercury adsorption. The results are given in Fig. 6.3. along with the counts obtained from the mercury on the surface. As in the case of Experiment 101, desorption of hydrogen was rapid and was complete in about three hours. No further hydrogen adsorption was observed although mercury continued to be adsorbed.

(6.6.) Results Using Constant Catalyst Temperature

In order to determine whether the amount of mercury adsorbed on a supported nickel catalyst was dependent on the temperature of catalyst or on some other factor, a further study was carried out

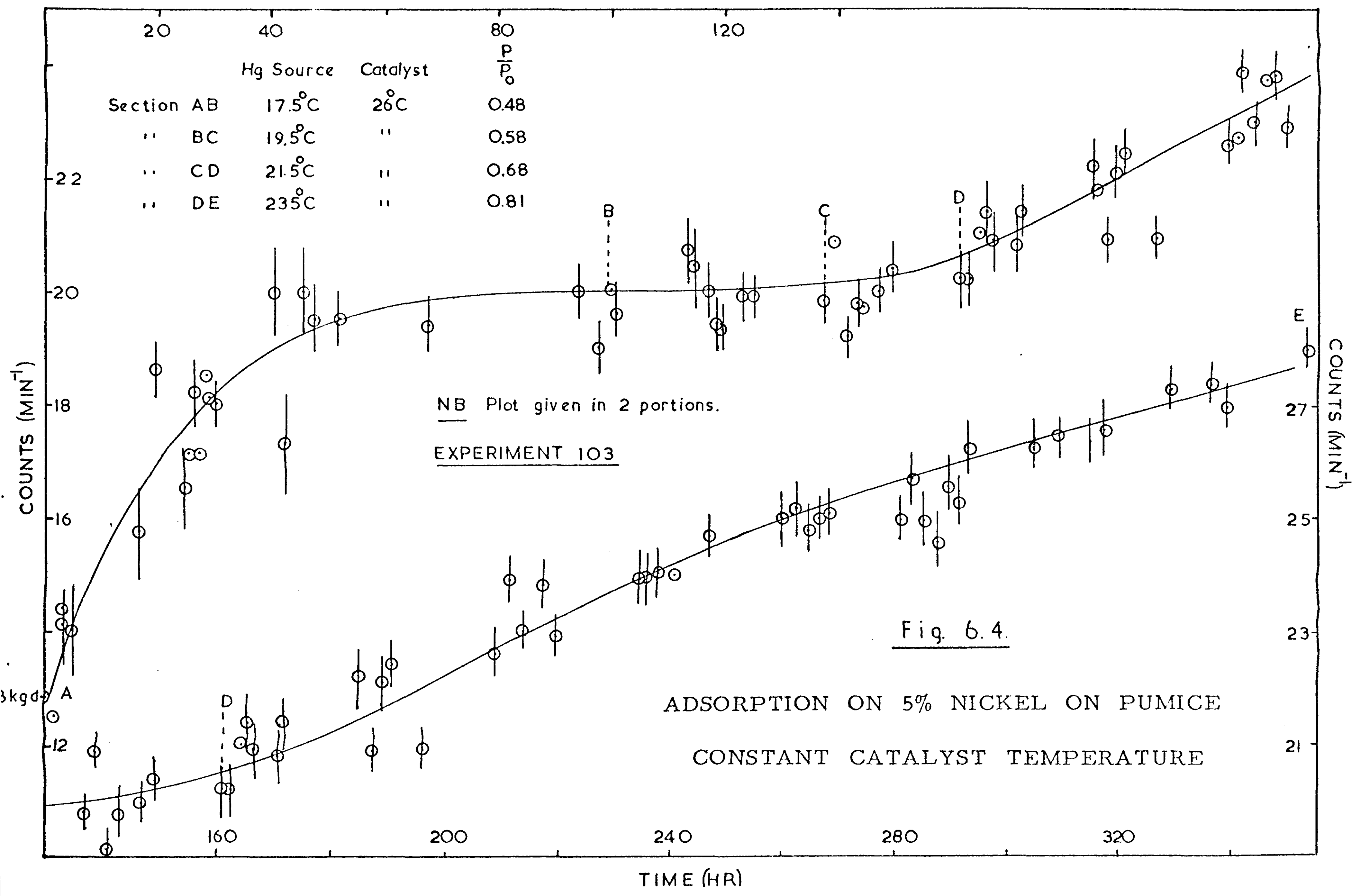


Fig. 6.4.

ADSORPTION ON 5% NICKEL ON PUMICE

CONSTANT CATALYST TEMPERATURE

in Experiment 103.

In this case the mercury source was placed in a copper calorimeter, which was enclosed in a tightly wound coil of copper tubing. The temperature of the mercury was controlled by pumping water through the coil from a thermostat tank. The calorimeter was filled with fine mesh copper powder to act as a heat transfer medium. The catalyst vessel was placed in a second thermostat tank, which was maintained at 26°C throughout the experiment. Water from this tank was pumped over the tubing connecting the mercury source to the catalyst vessel to reduce any effects due to changes in room temperature. No McLeod gauge was fitted to this apparatus and the displacement of hydrogen was not followed.

With the mercury source at 17.5°C it was found, as is shown in Fig. 6.4., that mercury was adsorbed on the catalyst extremely slowly. After about 50 hr the amount of mercury adsorbed had reached a constant value, which did not alter for the remaining 50 hr that the source was maintained at this temperature. Increase of the source temperature to 19.5°C for 40 hr had no apparent effect on the amount adsorbed, nor did 20 hr at 21.5°C. This was in contrast to what was found in Experiment 101. When the temperature of the source was raised to 23.5°C, however, with the catalyst still at 26°C, an increase in count was observed which continued in a virtually linear fashion for 180 hr without attaining a constant value. This latter behaviour was comparable to that found in Experiment 101. Owing to the counting statistics it cannot be stated definitely that this linear adsorption process did not commence when the source temperature was at 21.5°C. The overall amount of mercury adsorbed on the catalyst was extremely small, viz. 0.11 mg.

At the end of the experiment a secondary source of mercury was found to have developed in a portion of the apparatus which had been at room temperature. This could only have been formed by distillation when the source was at 23.5°C, since this was the only temperature attained which was greater than room temperature. The fact that this source was produced simultaneously with adsorption of mercury onto the catalyst, indicated that the slow adsorption of mercury on the catalyst was not due to a limited supply of mercury vapour from the source.

(6.7.) Summary of Results of Adsorption Experiments

A summary of the results obtained from the mercury adsorption experiments is given in Table 6.2. The experimental values and calculations for those experiments involving hydrogen displacement are given in Appendix 3.

TABLE 6.2.

Summary of Mercury Adsorption Experiments

	$^{P}/P_o$	Wt. of Hg Present (mg)	No. of Hg atoms x 10^{18}	No. of Hg atoms mg^{-1} Ni x 10^{17}	No. of Ni per Hg
Experiment 101,					
1st Plateau	0.38	1.02	3.02	1.28	80.7
2nd Plateau	0.46	1.36	4.08	1.73	59.4
3rd Plateau	0.50	1.61	4.84	2.05	50
Final value	0.59-0.71	3.39	10.10	4.27	24
Experiment 102,					
1st Plateau	0.1	0.78	2.34	0.98	104.2
Hg to displace all H_2	-	0.70	2.10	0.88	117
Experiment 103,					
1st Plateau	0.48-0.58	0.05	0.14	0.069	1500
Final value	-	0.11	0.33	0.17	612
Film 27,					
Final value	0.44	2.38	7.1	4.43	23
Film 32,					
1st Plateau	0.44	4.08	12.2	4.52	23
Final value	0.88	9.76	28.5	10.6	9.8

Discussion of the Results Obtained from the Adsorption of Mercury on Nickel Catalysts

The results obtained from the study of the adsorption of radioactive mercury on evaporated and supported nickel catalysts may be summarised as follows

(1) The adsorption of mercury from a cooled source onto supported and evaporated nickel increases with time, until a point is reached where it attains a constant value.

(2) This constant value is dependent on the temperatures of the mercury source and of the metal surface.

(3) If the temperature differential between the source and the catalyst is smaller than a certain value, then a constant amount of adsorbed mercury is not attained.

(4) Hydrogen is completely desorbed from a reduced supported catalyst by an amount of mercury which is less than that present when mercury adsorption first ceases.

(6.8.) Comparison with Previous Work

Mercury is a well known catalyst poison and a number of reactions have been studied to determine the modus operandi of this poisoning effect (12, 54). The results of these studies indicate that the mercury is adsorbed on the catalyst surface. In addition, it has been shown (51, 60) that mercury can displace adsorbed hydrogen from evaporated metal films. Thomson and his co-workers (19, 59) have studied this displacement in detail using a radiotracer technique and have shown that the mercury is adsorbed on the catalyst linearly with respect to time. Moreover they found that the mercury adsorption brought about an atom for atom displacement of the hydrogen and that the adsorption continued linearly with time, even after all of the hydrogen had been displaced.

In contrast to this the present work has shown that adsorption of mercury on clean nickel films is not linear with respect to time and reaches a constant value. The amount of mercury which had been adsorbed when this constant value was attained was virtually the same in the two experiments carried out, viz. 4.43 and 4.52×10^{17} atoms of mercury per mg of nickel. Calculation showed that the amount of mercury present on the evaporated films used by Campbell and Thomson, after all of the hydrogen had been displaced, was about 2.9×10^{17} atoms of mercury per mg nickel. Allowing for the fact that in the original work the films had been evaporated in argon and would, therefore, be expected to have a larger surface area, it appears that in this earlier study adsorption had not been followed to such an extent as in the present work. This was confirmed on closer examination of the experimental results obtained by Campbell (20). This showed that at later stages, after hydrogen displacement was complete, the rate of mercury adsorption was not linear, and the amount adsorbed tended to a constant value, which was comparable with that observed in the present work. Accurate assessment of the amount of mercury present at this stage was not possible owing to insufficient information being available.

It is concluded in the light of this evidence that the attainment of a constant amount of adsorbed mercury on nickel catalysts is a general feature of this system and possible mechanisms will now be considered.

(6.9.) Factors Producing Constant Amounts of Adsorbed Mercury

If a source of liquid mercury is placed in the apparatus containing the catalyst, the apparatus will be filled with mercury vapour to a pressure equal to that of the vapour pressure of mercury at the temperature of the source. Transport of bulk mercury from the source to the catalyst can only occur if one of two processes is operating, (a) condensation (b) adsorption of the mercury vapour onto the catalyst. If the temperature of the source is always lower than that of the catalyst condensation will not occur and process (b) only will operate. In the present work and also in that of Campbell, care was taken to prevent distillation. If the catalyst is able to adsorb mercury vapour the concentration of the vapour will be reduced above the catalyst and more mercury at the source will evaporate to restore equilibrium. Once adsorption has commenced, termination of adsorption can only occur if one of the following conditions occurs :

(a) the source is unable to produce vapour, either because all the mercury has been transferred to the catalyst, or else the surface of the source has become contaminated,

(b) the surface is unable to adsorb any more mercury because (1) a monolayer has been formed, (2) it has become covered by some other adsorbent,

(c) the adsorption of the mercury is reversible and the rate of desorption of mercury from the surface becomes equal to the rate of adsorption, i.e. adsorption equilibrium is established.

If, as in the present work, on evaporated films, adsorption ceases but recommences after the temperature of the source is raised by only a small amount, conditions (a), (b) cannot be responsible for the cessation of adsorption and it must be due to condition (c). In this case increase of the source temperature, which is still below that of the catalyst, produces an increase in mercury vapour pressure and the equilibrium above the catalyst is upset. The possible processes which govern this equilibrium will now be discussed.

(6.10.) Processes Governing Adsorption Equilibrium

(a) Predominance of physical adsorption

Both in the present work and in that of Campbell and Thomson, mercury was found to be capable of displacing hydrogen from a nickel catalyst. In the previous work using films the amount of hydrogen displaced was measured accurately using a radiotracer technique and an atom for atom displacement was obtained. In the present work, using a less rigorous technique on supported catalysts, approximately 2 mercury atoms were found to displace 1 hydrogen. These results indicate that the mercury occupies sites originally occupied by hydrogen. If this is the case, as postulated by Campbell and Thomson, chemisorption of mercury can be envisaged up to a stage where all the hydrogen has been displaced. Any further mercury which is adsorbed will then be present in physically adsorbed layers, i.e. assuming the monolayer for mercury adsorption to be comparable with that for hydrogen.

On this basis the constant values attained after prolonged exposure to mercury vapour under standard temperature conditions were due to equilibrium set up between vapour phase mercury and physically adsorbed mercury, since the constant values occurred after all of the hydrogen had been displaced. The extent to which physical adsorption of a particular species occurs on a substrate depends on the value of the ratio $^P/P_o$, where P is the equilibrium pressure of the species above the substrate at a particular temperature, and P_o is the saturated vapour pressure of the species at the same temperature.

It is generally accepted that significant physical adsorption can occur when the value of $^P/P_o$ is greater than 0.01 (61). As indicated in Table 6.2. the values attained during the present work were very much higher than this, viz. 0.1 - 0.9, and thus physical adsorption would be expected to operate. Changes in temperature of the source or the catalyst alter the value of $^P/P_o$ and thus reduction of the catalyst temperature, or increase in the source temperature, would be expected to increase the amount of mercury on the catalyst. This was in fact observed. On Film 32, after equilibrium had been attained at a $^P/P_o$ value of 0.44, considerably more mercury was adsorbed when this value was increased to 0.88. Similarly with Experiment 101 in which changes in $^P/P_o$ were produced by lowering the temperature of the catalysts, and equilibrium was attained after each change. In Experiment 103 the $^P/P_o$ value was varied by increasing the temperature of the source. In this case, no additional adsorption was observed initially, although this may have been hidden by the counting statistics.

In both of the experiments (101, 103) in which mercury was adsorbed on supported catalysts, increase in $^P/P_o$ above a particular value, in the region of 0.6, resulted in adsorption of mercury which did not attain a constant value, although the time for which the adsorption was followed was much greater than that in which adsorption had ceased on previous occasions. On the basis that previous increments of adsorption had occurred as a result of increase in the value of $^P/P_o$, it may be postulated that this enhanced adsorption also was due to the increase in value of $^P/P_o$. This may have been the case if it is considered that $^P/P_o$ had reached a value which permitted condensation into pores. Such a process would be expected to result in an enhanced adsorption, if a negative surface tension effect was operating. A calculation has shown that under the conditions used, condensation would only occur in pores of diameter 40 A^o or less.

(b) Predominance of chemisorption

The above mechanism satisfactorily explained the observed adsorption phenomena on the assumption that only the values of $^P/P_o$ controlled the amount of adsorption, and not the actual values of P and P_o. Thus it was postulated that there was no difference between the effect of raising the temperature of the source or lowering the temperature of the catalyst, and the absence of adsorption increments in the former case was due to counting statistics.

It is possible, however, that the absence of adsorption increments in this case was a true effect, and if this was so, a second mechanism may be postulated.

Because of the systematic displacement of hydrogen by mercury, it must be considered that mercury interacted rapidly with sites originally occupied by hydrogen and became chemisorbed. In the former mechanism this replacement was considered to continue until all the hydrogen had been displaced, whereupon physical adsorption occurred, the assumption being made that mercury could only be chemisorbed on sites capable of hydrogen adsorption. If, however, there were sites available for reversible mercury chemisorption on which hydrogen was not adsorbed, it may be postulated that the first equilibrium conditions obtained in all cases occurred when mercury was still being chemisorbed on the catalyst, and the mercury monolayer had not yet been reached. Under these conditions the rate of chemisorption would equal the rate of desorption. Decrease in temperature of the catalyst would favour adsorption, but equilibrium would again be reached at some higher coverage. Thus adsorption increments would be observed with successive temperature reductions until a stage was reached at which all the sites capable of chemisorbing mercury were occupied; thereafter physical adsorption would occur. This physical adsorption, it is postulated, is the cause of the steady increase in adsorption observed after the temperature of the catalyst had been reduced below 22°C in Experiment 101.

In Experiment 103, once the first equilibrium had been reached the temperature of the catalyst was kept constant and only the temperature of the source varied. This would have resulted in a smaller increase in the amount of mercury adsorbed, because the change in the vapour pressure was now the only factor which could affect the adsorption equilibrium. This factor would also have been operating in Experiment 101 but would have been masked by the increased adsorption due to reduction in the catalyst temperature. The steady increase in adsorption also observed at a later stage in Experiment 103, would again have been due to physical adsorption occurring on top of the chemisorbed mercury.

Thus the two mechanisms proposed both account for the initial adsorption as being due to chemisorption, and the final adsorption as due to physical adsorption or condensation into pores. What is not evident is the stage at which chemisorption ceases and physical adsorption commences. To determine this it is necessary to consider the relative sizes of the mercury and the hydrogen monolayers.

(6.11.) Factors Affecting Sizes of Mercury and Hydrogen Monolayers

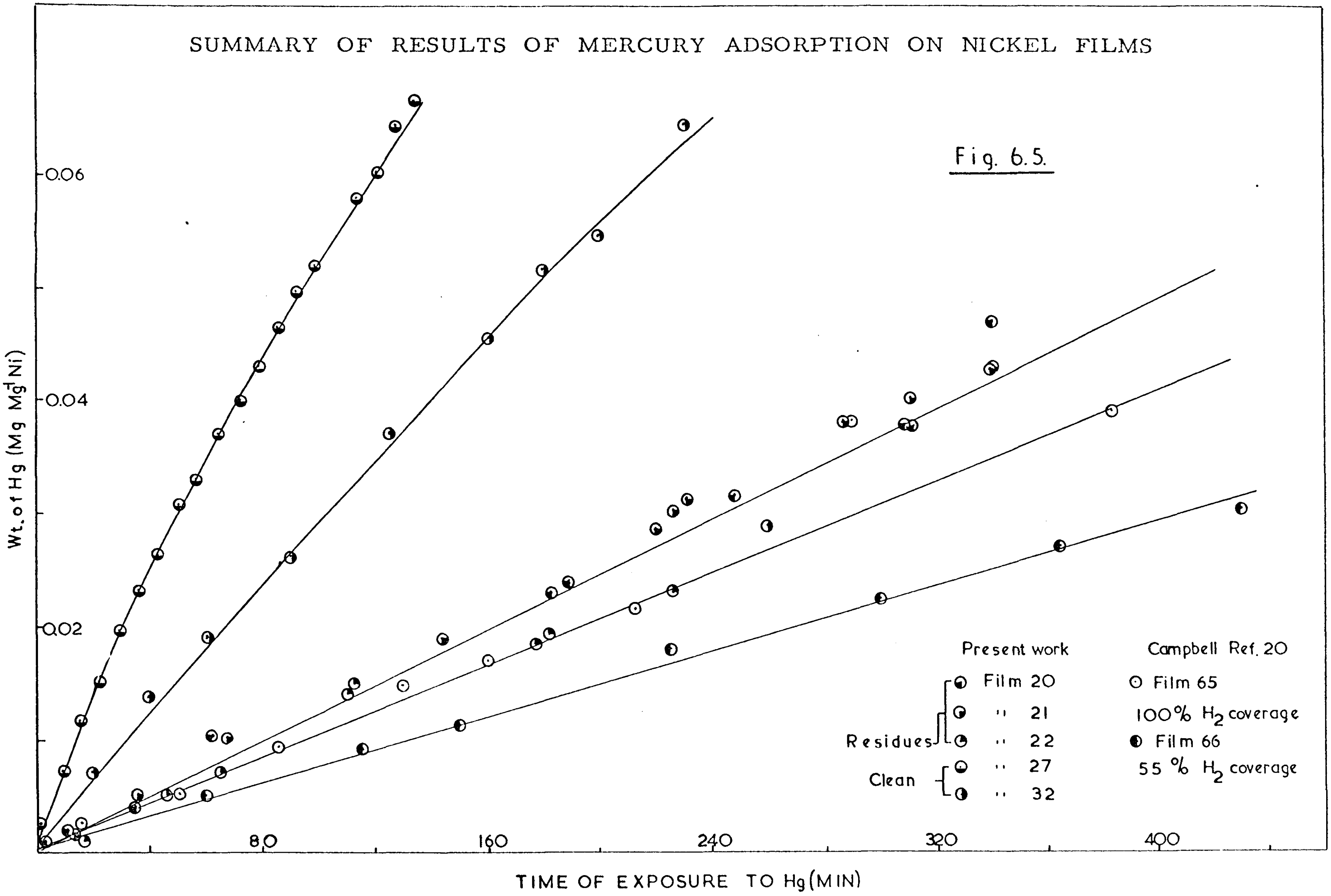
If the monolayer for mercury adsorption is greater than that for hydrogen, mercury must be capable of adsorption on sites incapable of hydrogen adsorption and this implies that hydrogen is not adsorbed on all the available nickel sites. This phenomenon has been reported previously by Klemperer and Stone (62), who found that hydrogen was only adsorbed on 40% of the available nickel surface, as measured by physical adsorption of krypton. This figure may well be inaccurate since it has recently been shown (63) that the surface area occupied by the inert gas atoms used for physical adsorption can vary considerably with the type of substrate used.

On the other hand there is evidence that, on platinum at least, hydrogen chemisorption is only limited by the availability of metal atoms exposed on the surface. On a supported catalyst in which the platinum was sufficiently dispersed, it was shown that hydrogen could be adsorbed such that the number of atoms was comparable with the number of metal atoms (64).

Unfortunately, no data is available on the heat of adsorption of mercury on nickel or how this varies with coverage. It is known, however, that the heat of adsorption of hydrogen and oxygen on nickel are 30 and 107 Kcal mole^{-1} (65) respectively and since mercury is able to displace hydrogen but not oxygen from nickel, the value of the heat of adsorption of mercury must be somewhere intermediate. If mercury is adsorbed on sites which are not occupied by hydrogen, it is difficult to explain why hydrogen is displaced immediately mercury is admitted to the surface. For this to occur it must be energetically more favourable for mercury to displace the hydrogen than to adsorb on the sites unoccupied by hydrogen. Until information is available on how the heat of adsorption of mercury varies relative to that of hydrogen, with increasing coverage, this mechanism must remain speculative.

An attempt was made during the present work to determine whether the first adsorption equilibrium reached was due to mercury adsorbed physically or chemically on the catalyst. It was felt that an indication of the type of adsorption present would be obtained by studying the vapour pressure of mercury above the catalyst with increasing coverage. Since chemisorption requires strong attachment to the surface, it would be expected that the vapour pressure above mercury chemisorbed on the catalyst would be less than that above physically adsorbed mercury. It was also hoped using this technique to determine how the heat of adsorption of mercury varied with coverage. The technique employed for this study entailed the use of U.V. spectrophotometry and is described in Chapters 7 and 8. Unfortunately, the results obtained, owing to practical difficulties, were unable to supply the required information. The technique employed, however, was shown to be a powerful tool for the study of this system.

No matter what mechanism is considered, the increased adsorption obtained in the later stages of a particular experiment is attributed to some form of physical adsorption. If this is the case, it might be expected that under comparable conditions two samples from the same batch of catalyst would adsorb mercury at a comparable rate since, unlike chemisorption, physical adsorption is not dependent on the activity of the metal surface. In actual fact the rates of adsorption obtained (derived from Table 6.2.) were 2.3×10^{-4} mg hr^{-1} for Experiment 103 and 4.5×10^{-2} mg hr^{-1} for Experiment 101. That the reduced rate in Experiment 103 was not due to unavailability of mercury from the source is indicated by the presence of the secondary mercury source which formed simultaneously with this type of adsorption in this experiment. Even during the early stages of adsorption, which are attributed to chemisorption, the rate of adsorption was very much less for Experiment 103 than for 101. It must be concluded, therefore, that two samples of supported nickel catalyst from the same batch, reduced and activated under comparable conditions, possess very different powers of adsorption for mercury. In contrast to this, however, the rate of adsorption of mercury on



SUMMARY OF RESULTS OF MERCURY ADSORPTION ON NICKEL FILMS

Fig. 6.5.

evaporated nickel films appeared to indicate reproducibility of adsorption rates and this will now be considered in more detail.

(6.12.) Effect of Adsorbed Species on the Adsorption of Mercury on Nickel Films

The general pattern of adsorption behaviour observed on nickel films has been given in Fig. 6.1. In order to compare the absolute rate of mercury adsorption both between these films and those carried out by Campbell and Thomson (19) the weight of mercury per milligram of nickel has been plotted against time in Fig. 6.5. Also in this figure have been plotted the total amounts of mercury present after total exposure times of the catalyst to mercury vapour during the poisoned hydrogenations on nickel films described in Chapter 2. It can be seen that in all cases, except Film 27, a virtually linear relationship exists between the amount adsorbed and time. The values obtained from the films on which hydrogenations have been carried out show an unexpectedly reproducible linearity, considering the disagreement between the differential amounts of mercury adsorbed in equal time intervals as mentioned in section 6.1.

From consideration of the rates of adsorption obtained between films prepared under identical conditions, i.e. those prepared under vacuum at room temperature in the present work, it appears that the presence of adsorbed residues on the surface of the catalyst reduced the rate of mercury adsorption. Since the results derived from the previous work were obtained from films evaporated under argon it is doubtful whether they can be compared directly with the present work. It has been stated (17) that such argon deposited films possess a different activity from vacuum deposited films. If it is valid for such films to be considered, it appears that the rate of adsorption on hydrogen covered films is comparable with that on films covered with the species resulting from cyclopropane hydrogenation.

It is not obvious why the adsorption on Films 27, 32 varied both in rate and in its relation with respect to time,since in both cases mercury was adsorbed on clean films from sources at comparable temperatures. It might have been expected that adsorption on Film 27 would have been slower since it was carried out in the presence of a greased tap which was a possible source of contamination, whereas this was not present in Film 32. That the overall adsorption properties of the films were comparable is shown by the fact that the amount of mercury adsorbed, per milligram of nickel, when adsorption ceased at its first constant value was similar in both cases. It is suggested, in the absence of further evidence, that Film 27, by means of some factor in its preparation, contained a proportion of sites with relatively high energy. Adsorption on these sites would have been rapid and once they were removed the rate of adsorption would have fallen.

If it is a true effect that the rate of adsorption of mercury on a nickel catalyst is dependent on the species which are already adsorbed on the surface, this presents an elegant method of determining the extent to which particular species are present. In addition, it indicates that it is not always a valid assumption, if a catalyst is exposed to mercury for various time intervals between reactions, that proportional amounts of adsorbed mercury are obtained. The amount of mercury adsorbed in a particular time interval will depend on the nature and the extent of the species adsorbed. This in turn will depend on the extent to which the previous reaction has been allowed to proceed and on the efficiency of the removal of the reactants and products.

CHAPTER 7

DEVELOPMENT OF TECHNIQUE FOR MEASURING MERCURY VAPOUR PRESSURE

(7.1.) Introduction

After consideration of the phenomena observed in Chapter 6 when mercury was allowed to adsorb onto clean nickel films, it was decided to pursue this study in greater detail. In particular it was considered of value to study how the vapour pressure of the mercury above the nickel surface varied with increasing adsorption of mercury on the surface.

It was decided to carry out this study using supported nickel catalysts since these were much more convenient to prepare than evaporated nickel films and the vacuum conditions required for their use were much less stringent. This latter consideration was important in those experiments which were to proceed for long periods of time.

(7.2.) Detection of the Mercury Vapour

The vapour pressure of the mercury at any time was determined by measuring the absorbance of 2537 A^{o} radiation by the mercury vapour. Radiation of this wavelength is strongly absorbed by mercury, since it provides the resonance energy for an electronic transition within the mercury atom. Its use for determining concentrations of mercury has been widely reported (66).

The apparatus used for the present study consisted of three basic sections, a source of mercury vapour, a quartz cell in which the mercury vapour pressure could be measured and, between these, a section containing the nickel catalyst. Diagrams and full details are given in Chapter 11. The apparatus was designed such that the absorption cell fitted into the cell compartment of a Hilger Uvispek spectrophotometer. The apparatus was thermostatted so that the absorption cell and a reference cell, along with the catalyst containing section, were kept at 24°C. The mercury source was kept at a lower temperature, normally 20°C or 22°C.

Initial experiments indicated that the "white" radiation produced by a deuterium lamp already present in the spectrophotometer was unsuitable for this study and a source of monochromatic 2537 A° radiation was provided from an external mercury lamp.

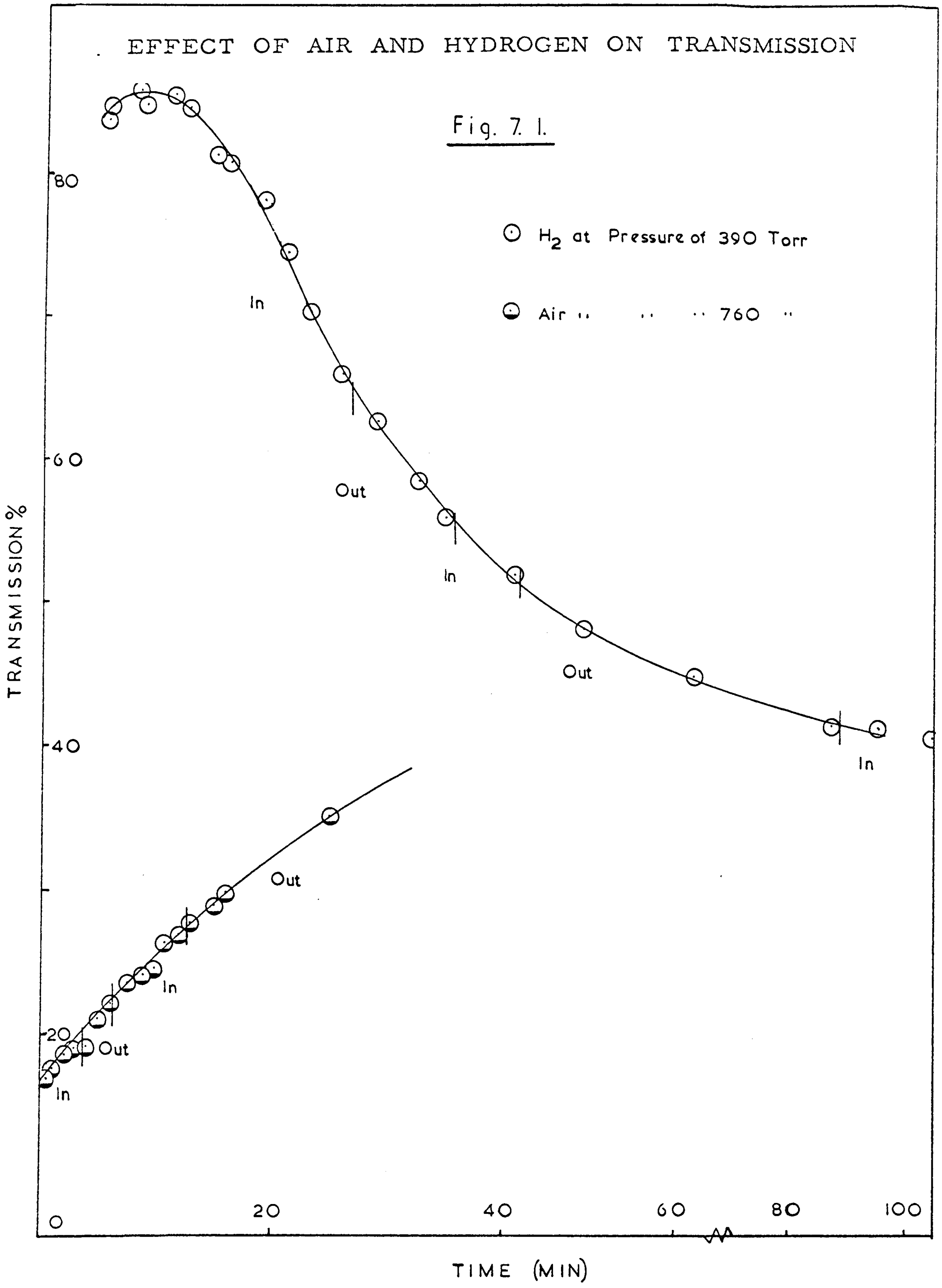
(7.3.) Preliminary Experiments

Before attempting to calibrate the apparatus it was necessary to carry out a number of preliminary experiments. During these experiments no catalyst was present in the apparatus. The difference in absorbing power of the absorption cell attached to the apparatus and that of an identical reference cell was determined with each cell containing air. The reference cell was then evacuated, sealed off and the difference again noted. The process was repeated, comparing the absorbing power of the evacuated reference cell with the other cell under various conditions. The results obtained from these are given in Table 7.1.

TABLE 7.1.

	Transmission % i.e. T%
With both cells containing air	101
With reference cell evacuated and the other cell containing	
(a) air	101
(b) vacuum	103
(c) H_2 at pressure of 100 torr	103
(d) H_2 at pressure of 400 torr	101
(e) Hg under vacuum at 21°C	88
(f) Hg under vacuum at - 196°C	102
(g) Hg at 21°C and air at 760 torr	24 - 40
(h) Hg at 19°C and H_2 at 56 torr	46
(i) Hg at 19°C and H_2 at 390 torr	84 - 41

It can be seen that the presence of mercury, at room temperature, in the cell increased the absorption (i.e. decreased the transmission). If, however, the mercury source was surrounded by liquid nitrogen,



EFFECT OF AIR AND HYDROGEN ON TRANSMISSION

Fig. 7.1.

then in the space of 6 min all of the mercury was removed from the cell. This removal was not at a constant rate, the greater proportion was removed within the first minute, as indicated by a change in transmission from 85% to 98%. The remaining 5 minutes were required to remove the small residual portion.

After the mercury had been allowed to warm up to room temperature to give its original transmission reading, air was admitted to the apparatus at atmospheric pressure. An immediate decrease in transmission occurred to a value of 17 T% (where T% = % transmission) but this did not remain constant and rose to a value of 40 T% in about half an hour. This variation is shown in Fig. 7.1. Comparable effects were also found to occur on numerous later occasions.

In order to determine whether this effect was brought about by some chemical action of the U.V. radiation, the absorption cell was left in the beam between readings on some occasions and removed on others. These are also indicated in the figure. It was found, however, that this had little effect on the decrease of the absorption. Reducing the temperature of the mercury source from 19°C to 0.2°C after 4 min also had no effect, as can be seen from Fig. 7.1.

The effect of refilling the apparatus with mercury vapour and hydrogen to a pressure of 56 torr was to increase greatly the absorbing power of the mercury vapour. In order to determine the effect of larger pressures of hydrogen the apparatus was filled with hydrogen to a pressure of 390 torr. It took approximately 5 min after sealing the apparatus to replace it in the spectrophotometer and to determine the absorption. It was found that a very much reduced value was obtained but that this increased with time to give a constant value of 41 T%. This value remained constant on leaving the apparatus for a week. The variation of transmission with time is also indicated in Fig. 7.1. In this case also, any effect of leaving the cell in the beam compared with leaving it out appeared insignificant.

(7.4.) Conclusions from Preliminary Experiments

From the results of the preliminary experiments a number of conclusions may be drawn.

(1) Mercury vapour alone at room temperature absorbs 2537 A^{o} radiation to a greater extent than hydrogen at pressures up to 400 torr or air at atmospheric pressure.

(2) Both hydrogen and air when mixed with the mercury vapour ultimately increase the absorbing power of the mercury considerably.

(3) The absorbing power of mercury vapour for 2537 A^{o} radiation increases with increasing hydrogen pressure.

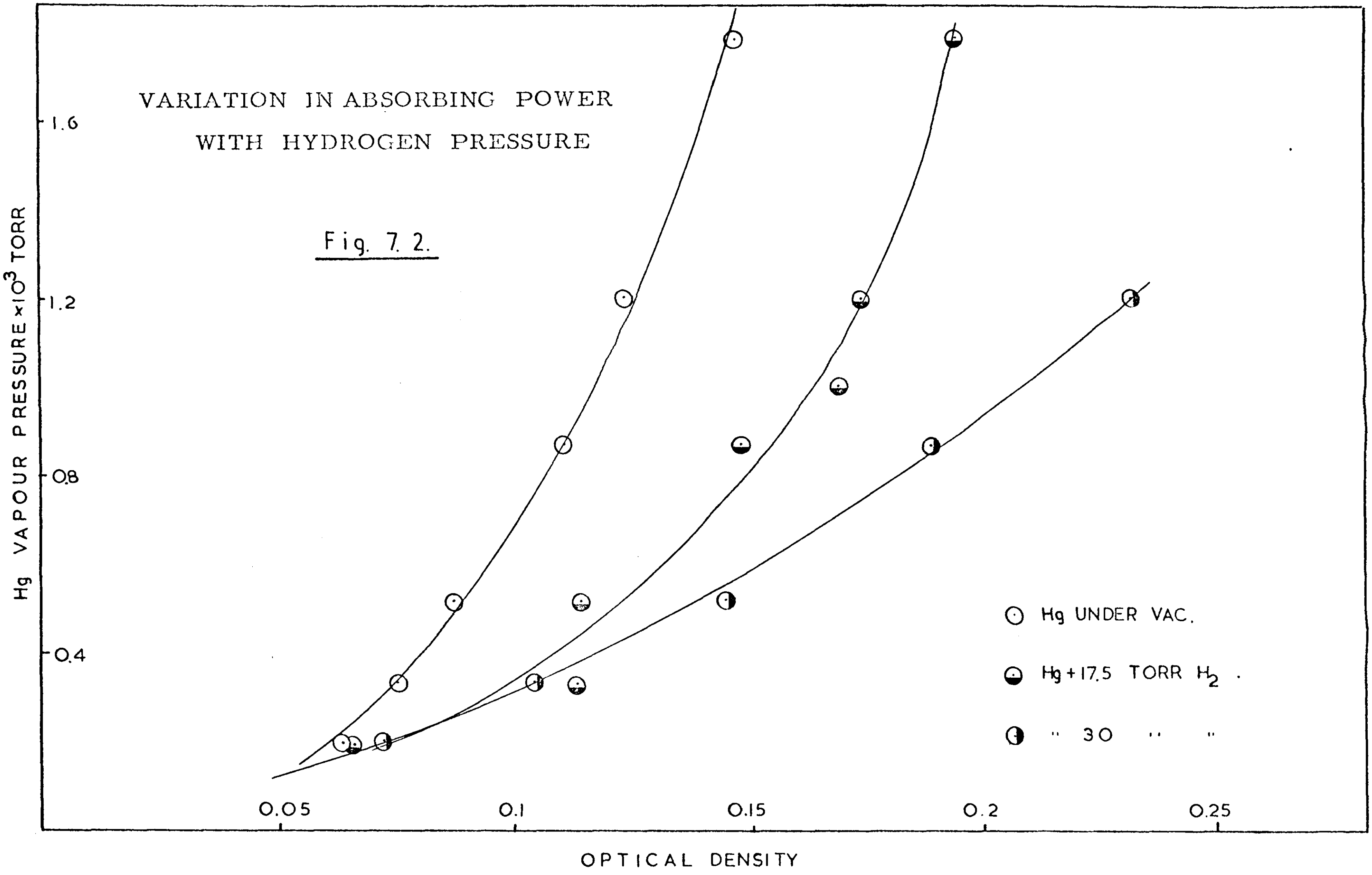
(4) When large pressures of air or hydrogen are admitted to

mercury vapour they produce effects which vary with time. Absorption in the presence of hydrogen increases with time, whereas a decrease is observed with air present.

(7.5.) Determination of the Effect of Various Hydrogen Pressures on the Absorbing Power of Mercury

It was proposed to study the absorption of mercury vapour above a supported nickel catalyst using the U.V. absorption technique outlined. Such nickel catalysts are produced by reduction of nickel oxide in a stream of hydrogen and would be expected, therefore, to contain a considerable amount of adsorbed hydrogen. It has been shown by various workers (19, 59) that mercury vapour is able to displace hydrogen from hydrogen-covered nickel films, and it appeared likely that similar behaviour would be obtained on supported nickel catalysts. If this is the case this hydrogen would affect the absorbing power of the mercury as was indicated in the previous section. Since the amount of hydrogen present in the gas phase would vary with the amount of mercury adsorbed, it was necessary to study in greater detail to what extent hydrogen affected mercury absorption for 2537 A^{o} radiation, especially at low pressures of hydrogen.

The apparatus was the same as that used for the preliminary experiments, except that in this case the absorption cells were thermostatted at 24°C. The apparatus was filled with hydrogen to



VARIATION IN ABSORBING POWER WITH HYDROGEN PRESSURE

Fig. 7.2.

a pressure of 17.5 torr and sealed off. The constant values of the optical density obtained by placing a Dewar flask containing water successively at temperatures of 0, 10.6, 16.2 and 20°C were noted. The procedure was then repeated with the apparatus filled with hydrogen to a pressure of 30 torr and again with the apparatus under vacuum. The results are given in Table 7.2. together with the vapour pressure of mercury at the appropriate temperatures (67). The variation in absorbing power with increasing hydrogen pressure is plotted in Fig. 7.2.

It can be seen that even at low pressures of admixed hydrogen the absorbing power of mercury is enhanced and the effect of the hydrogen is greatest at high vapour pressures of mercury and relatively high hydrogen pressures.

(7.6.) Effects Observed Immediately After Switching On the Mercury Lamp

It was observed on a number of occasions that the absorption readings obtained for a particular amount of mercury in the absorption cell varied with time immediately after switching on the mercury lamp. An apparent high absorption occurred immediately after switching on the lamp but this gradually decreased to a constant value. It is known that the intensity of radiation produced by such lamps varies with arc voltage, which in turn is temperature dependent, and that this would

TABLE 7.2.

Variation in Optical Density of Hg with Increasing Hydrogen Pressure

Temp. of Hg Source °C	Vapour Pressure of Hg torr x 10^3	Optical Density (T%) with Hg under vacuum	Optical Density (T%) Hg under 17.5 torr of H_2 (19°C)	Optical Density (T%) Hg under 30 torr of H_2 (16°C)
0.2	0.19	0.063(86.5)	0.067(85.8)	0.072(84.6)
5.6	0.32	0.076(84)	0.114(77)	0.109(77.9)
10.6	0.51	0.082(82.5)	0.115(76.8)	0.143(73)
16.2	0.86	0.11 (79)	0.149(71)	0.188(64.7)
18.0	1.01	-	0.17 (67.5)	-
20	1.2	0.123(75.5)	0.174(67)	0.231(58.8)
24.6	1.79	0.145(71.5)	0.192(64.2)	-

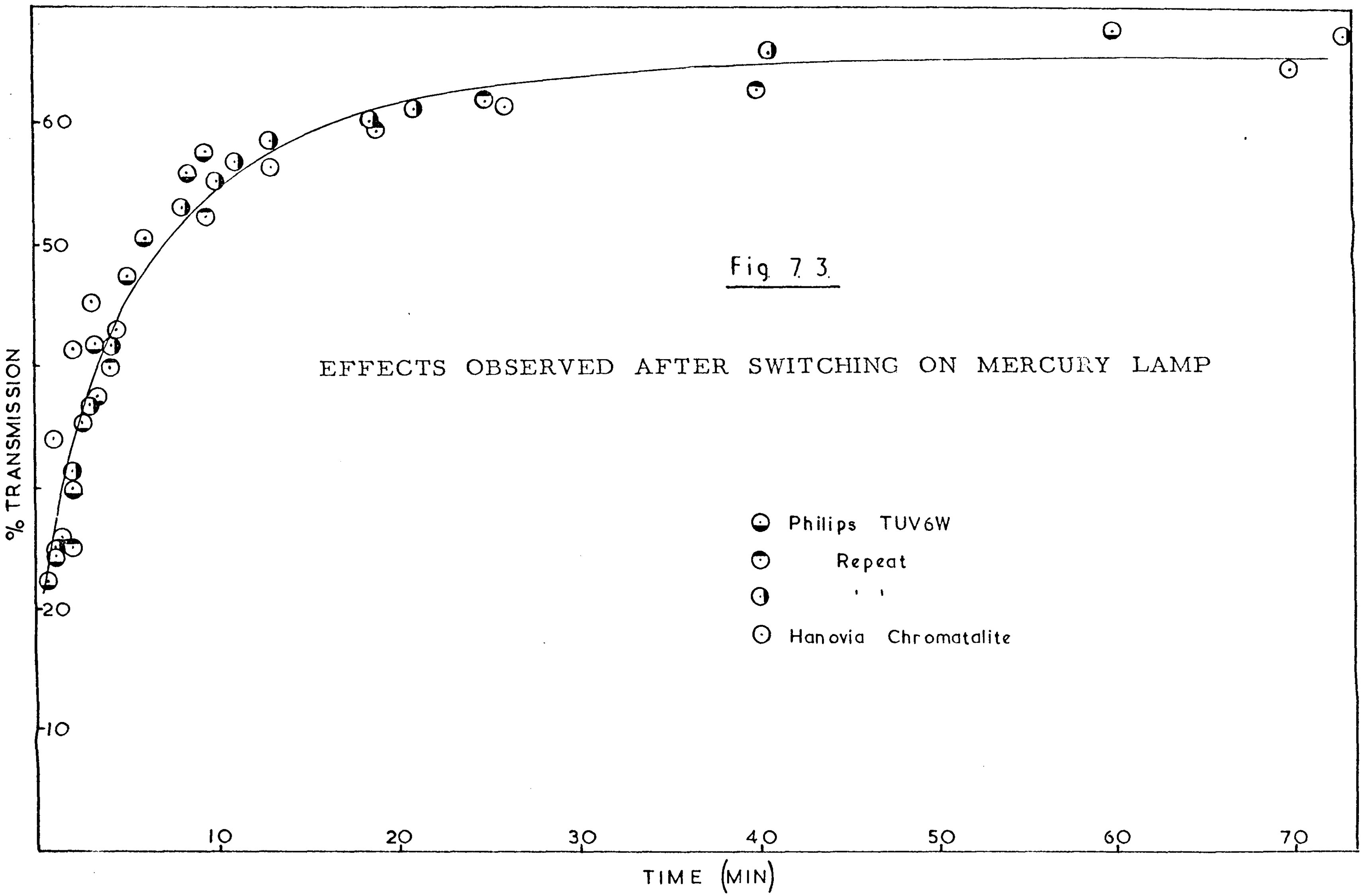


Fig 7.3.

EFFECTS OBSERVED AFTER SWITCHING ON MERCURY LAMP be expected to vary with time (68). It was shown, however, that this phenomenon was not due to intensity changes since the method of obtaining the absorption readings compensated for this.

It appeared that the phenomenon, as well as being dependent on changes in the lamp, also depended on the contents of the absorption cell. It was not observed when the absorption cell did not contain mercury. The magnitude of the effect is shown in Fig. 7.3. for the apparatus containing mercury vapour at 20°C and hydrogen at a pressure of 17.5 torr. It was also shown to be present when using a Hanovia Chromatalite portable U.V. lamp. All the measurements which are given in previous sections were taken after the lamp had been allowed to warm up for a period of at least three-quarters of an hour.

(7.7.) Displacement of Hydrogen from a Reduced Supported Nickel Catalyst by Mercury

In the previous section it has been shown that small quantities of hydrogen are capable of altering the absorbing power of a particular concentration of mercury. It is now necessary to determine how much hydrogen is able to be desorbed from a supported nickel catalyst when mercury is adsorbed.

Beek et al. (17) have given information regarding the volume of hydrogen adsorbed on evaporated nickel films but similar information is not available for supported nickel catalysts. If it is assumed that the amount of hydrogen adsorbed per milligram of nickel is comparable in each case, then it is possible to calculate the order of magnitude of the total volume of hydrogen expected to be desorbed, if a reduced supported catalyst is completely poisoned by mercury. From this value can consequently be calculated the ultimate pressure of hydrogen to be expected in the absorption apparatus and hence an apparatus can be designed to measure this.

Calculation of hydrogen pressure to be expected after mercury adsorption

Wt. of 5% Nickel on Pumice catalyst used = 0.2 g

Assume 1 mg of Nickel adsorbs 1×10^{17} atoms of hydrogen (17)

Volume of the absorption apparatus = 35 cc

$\therefore$ If all hydrogen displaced, will get

$$= \frac{5 \times 0.2 \times 10^{17} \times 1}{105 \times 10^{-3} \times 2} \text{ mol}$$

$\therefore$ Volume of gas to be expected at N.T.P.

$$= \frac{5 \times 0.2 \times 10^{20} \times 22.4 \times 10^{3}}{105 \times 2 \times 6.023 \times 10^{23}} \text{ cc}$$

$$= 1.86 \times 10^{-2} \text{ cc}$$

Converting this to a pressure of gas in a volume of 35 cc at 20°C using the Gas Equation

$$= \frac{760 \times 1.86 \times 10^{-2} \times 293}{35 \times 273} \text{ torr}$$

$$= 0.43 \text{ torr}$$

i.e. pressure of hydrogen expected if all is desorbed = 0.43 torr.

In order to determine the actual pressure of hydrogen displaced from a known weight of reduced metal catalyst this desorption was carried out under approximate experimental conditions. The apparatus used was not the same as that used for the absorption experiments, but consisted of a cylindrical reaction vessel with a volume of approximately 25 cc. On the bottom of this vessel was placed a thin layer of catalyst of known weight. The apparatus had facilities for attaching it to the high vacuum system and for sealing it off once evacuated. Full details are given in section 11.10.

Radioactive mercury was used for the displacement and was placed in a suitably cooled side arm. This permitted the arrival of the mercury on the catalyst to be followed using a G.M. counter. Since the reaction vessel was maintained at a constant temperature in a water thermostat this counter was suitably adapted for use under water (see section 11.11.).

The pressure of the displaced hydrogen was measured using a McLeod gauge. This was isolated from the catalyst system using two ground glass/steel ball valves and a cold trap surrounded by liquid air. While attached to the vacuum apparatus the catalyst was activated under conditions comparable to those used in section 3.2. It was then evacuated, sealed off and counts of mercury and pressure of displaced hydrogen taken with respect to time.

(7.8.) Results of Hydrogen Displacement from Supported Nickel Catalysts

This experiment was carried out on two occasions using two apparatuses of different volumes. The results obtained are indicated below. The calibration of the McLeod gauge is given in Appendix 4.

	Expt. 101	Expt. 102
Length of gas column in capillary before desorption	0.3 cm	0 cm
Length of H_2 column in capillary after desorption	1.9 cm	1.6 cm
Wt. of 5% Ni/Pumice catalyst used	0.4969 g	0.4978 g
Average temperature of apparatus	$20^\circ C$	$15^\circ C$
Volume of apparatus including McLeod gauge	66.5 cc	76.3 cc

Experiment 101

Pressure of gas before desorption (see Appendix 4)

$$= (0.3 + 4.7) \times 2.43 \times 10^{-2} \times 0.3 \text{ torr}$$

$$= 3.6 \times 10^{-2} \text{ torr}$$

Pressure of gas + H_2 after desorption

$$= (1.9 + 4.7) \times 2.43 \times 10^{-2} \times 1.9 \text{ torr}$$

$$= 3.06 \times 10^{-1} \text{ torr}$$

$\therefore$ Pressure of H_2 displaced = 0.27 torr

Converting this to a volume at N.T.P.

$$= \frac{273 \times 0.27 \times 66.5}{293 \times 760} \text{ cc}$$

$$= 0.0227 \text{ cc}$$

Experiment 102

Pressure of H_2 after desorption

$$= (1.6 + 4.7) \times 2.43 \times 10^{-2} \times 1.6 \text{ torr}$$

$$= 0.246 \text{ torr}$$

Converting this to a volume at N.T.P.

$$= \frac{273 \times 0.246 \times 76.3}{288 \times 760} \text{ cc}$$

$$= 0.0234 \text{ cc}$$

$\therefore$ the average volume of H_2 at N.T.P. displaced from 0.5 g catalyst

$$= 0.0227 \text{ cc}$$

Consequently using 0.2 g of catalyst in an apparatus of volume 35 cc would expect H_2 to be displaced to a maximum pressure of

$$\frac{760 \times 2.27 \times 10^{-2} \times 293 \times 2}{273 \times 35 \times 5} \text{ torr}$$

$$= 0.22 \text{ torr}$$

This indicates that there is less hydrogen capable of being desorbed on a reduced supported nickel catalyst than on an evaporated nickel film of comparable nickel weight.

Details of the mercury adsorption on the supported catalyst with respect to time and temperature of the catalyst have already been given in Chapter 6. It was found that the hydrogen was desorbed from the catalyst completely within 3 hr although adsorption of mercury continued for a much longer period.

Having determined that hydrogen was displaced from a reduced catalyst, and also to what extent, it was now possible to study the vapour pressure of mercury above a mercury poisoned catalyst in the presence of hydrogen. This will be described in the next chapter where experiments are carried out under a pressure of hydrogen greater than that desorbed from the catalyst.

Discussion of Effects Observed During Development of Technique

(7.9.) Introduction

Before considering the results obtained using the U.V. absorption technique, some of the work which has previously been carried out using mercury resonance radiation will be considered. This will enable a better understanding of the phenomena observed during the present study, and allow an assessment of the value of the results in the light of previous work.

One of the first studies of the absorption of 2537 A^{o} radiation by mercury vapour was made in 1912 by Wood (69). He showed that mercury vapour at room temperature emitted resonance radiation when stimulated by monochromatic light of wavelength 2537 A^o, and that air admixed with the vapour had the effect of quenching this resonance radiation. The source of 2537 A^o radiation used was a hot running mercury arc. To prevent the radiation produced in the arc from being absorbed by the cooler mercury vapour near the lamp walls, thus causing self inversion, measurements were made in the first few seconds after switching on the lamp. The true absorption of the radiation by the vapour in a quartz cell was measured, and was found to have an extremely high absorption coefficient for the 2537 A^o radiation.

A further study of the absorption properties of the vapour was carried out by Hughes and Thomas (70) using as a source of 2537 A^o radiation the resonance radiation produced in mercury, contained in a quartz bulb under vacuum, when excited by an external U.V. source. This study showed that the absorption of the radiation in the vapour did not obey Beer's Law. It was concluded that the resonance radiation was inhomogeneous and contained a component which was able to penetrate considerable distances in the vapour.

Owing to the toxicity of mercury vapour, a number of apparatuses have been developed (71, 72) to measure the concentrations of mercury vapour in air using the absorption phenomenon. The absorption of the vapour of 2537 A^{o} radiation at any time was compared with that from a known concentration of mercury.

The most advanced practical application of mercury absorption of its resonance radiation has been developed by Gunning et al. This work has employed the phenomenon to provide an efficient method of separating the isotopes of mercury in naturally occurring mercury. It has been shown (73), as would be expected from theory, that the 2537 A^{o} absorption and emission lines from natural mercury are made up of a hyperfine structure of 10 components. Each isotopic component of the natural mercury produces one or more hyperfine lines depending on its nuclear spin. Gunning has shown (74) that if resonance radiation from a monoisotopic source is directed into an absorption cell containing vapour derived from natural mercury, the radiation is only absorbed by the same isotope as that used to produce the resonance radiation. Admission of some species which will react with the excited mercury atoms produces an isotopically specific method of separation. In order to make this technique operate satisfactorily Gunning has greatly increased the knowledge of the factors affecting the absorption.

The small separation (ca. 0.01 A^{o}) in the five resolvable hyperfine components of the 2537 A^{o} line requires that, to excite a single isotope in natural mercury vapour, the corresponding emission hyperfine line from the monoisotopic exciting source must be extremely narrow. If this were not the case its frequency distribution would extend into the range of absorption of other mercury isotopes and consequently these would become excited. Moreover, the broadening of the absorption frequencies of adjacent mercury isotopes must be minimised for the same reason. To achieve such conditions, all factors affecting the broadening of both the emission and the absorption lines (75) must be eliminated, or reduced as much as possible. Consequently, a well cooled, low pressure, electrodeless discharge lamp is used which is operated at the minimum power level consistent with steady radiation output. This reduces the effects of self inversion and Stark broadening. In addition, the pressure in the absorption cell of the mercury vapour and any foreign gases must be kept low, to minimise pressure broadening effects.

From this work it can be concluded that in order to obtain efficient absorption of radiation by a particular species, the match between the absorption properties of the absorber and the emission properties of the source must be virtually perfect. Slight differences can produce a considerable effect.

Some of the phenomena observed in the present work will now be considered in the light of this information.

(7.10.) Effect of Hydrogen

It has long been known that the intensity of emitted resonance radiation from mercury vapour is reduced as the pressure of an admixed gas is increased (69). The resonance radiation is produced by the excitation of mercury in the ground state to a higher level

$$\mathrm{Hg}\ ({}^1S_o) \xrightarrow{hv} \mathrm{Hg}^*\ ({}^3P_1)$$

which can return to its original level with the emission of the characteristic radiation.

In the case of mercury under vacuum the majority of the excited atoms return to their original state by this mechanism and consequently a larger proportion of the incident energy is re-emitted as secondary radiation, as reported by Wood (69). When an admixed gas is present, however, atoms of this may collide with the excited atoms, and the excitation energy is normally dissipated by some other process which may include the emission of radiation of a slightly different wavelength. The greater the pressure of admixed gas, the greater the number of collisions and the smaller the number of excited mercury atoms able to emit radiation at the resonance wavelength. Hydrogen is particularly efficient in this quenching procedure since the energy transfer causes the molecule to dissociate.

In the present work, when the absorption cell contained mercury vapour under vacuum, the percentage of the radiation received by the photo cell which was derived from resonance radiation produced in the absorption cell would have been small. Even if a high percentage of the radiation incident on the cell was converted to resonance radiation this would be spread over a solid angle of 4π and only a small portion of this would fall on the photocell. Consequently, in contrast to the radiation produced from the lamp source, a beam of which is directed onto the photo cell, the contribution of this secondary radiation is small and changes in its intensity due to pressure of hydrogen would be relatively undetectable. The observation that the absorbing power of the mercury <u>increased</u> with increase in hydrogen pressure also indicates that this process is not being observed to any great extent.

If, on the other hand, the effect of the admixed hydrogen in the absorption cell is to broaden the absorption band of the mercury by collision, the broader the band the greater the amount of the incident radiation which would be absorbed. Consequently, an increase in hydrogen pressure would produce an increase in absorption.

For this phenomenon to occur, however, it is necessary for the source to emit radiation in a band of wavelength as broad, or broader, than that attained by the absorbing atoms by collision. If the emitted band is smaller than the absorbed band then a point is reached when a further increase in hydrogen pressure has no effect on the absorption because radiation of the correct energy is not being emitted from the source. That this did not occur in the present work indicates that the emission line is relatively broader than the absorption line at its maximum breadth.

Consideration of the source indicates that such a state of affairs could well exist. The type of lamp used was chosen because it was known to possess little self inversion (76) and produced a high intensity of 2537 A^o radiation (as indicated by the maker's specifications). Little was known about the breadth of this line. Since, however, the lamp contained neon as a carrier gas at a pressure of 3 - 5 torr, it would be expected to be appreciably broadened. The effect of the arc field and the running temperature (60^oC) would also be to produce broadening. It has recently been reported by Yang (77) that this broadening phenomenon is a point which has been overlooked by many workers using 2537 A^o for photochemical investigations. He states that the low pressure mercury lamp commonly employed in such work emits 2537 A^o resonance radiation with a Doppler half breadth 4.5 times that of the absorption line. This mismatch in the two line breadths drastically reduces the light absorption in spite of the high absorption coefficient. The addition of foreign gases sharply increases the light absorption because the absorption line becomes collision broadened. Further evidence supporting the theory that the emission source used in the present work possesses a broad line will now be given.

(7.11.) Effects Observed Immediately After Switching On Mercury Lamp

The absorbing power of a particular concentration of mercury gradually decreased with time after switching on the lamp source. This phenomenon was not due to changes in overall lamp intensity. When first switched on, it would be expected that the lamp would emit a relatively narrow line and that this would, therefore, be efficiently absorbed by the mercury in the absorption cell, resulting in a high absorption reading. As the lamp is allowed to warm up, increased broadening of the line will occur so that a larger percentage of the radiation will possess energies in the wings of the frequency contour. Consequently, less of the radiation at any particular intensity is able to be absorbed and a decreased absorption reading is observed. When the lamp comes to equilibrium the radiation produced has a constant line breadth and the absorbing power of the mercury for this will be constant, as is observed.

The effects of broadening which have been discussed in this and the previous section although large when compared with theoretical 'fine lines' are still relatively small compared with the resolution of the monochromator system of the spectrophotometer. It is essential, however, that the centre of the emission line is always in the middle of the spectrophotometer slits and the procedure described in section 11.3. accomplishes this efficiently.

(7.12.) Changes of Absorption with Time, After Admission of Air or Hydrogen

The effects which have already been discussed have arisen from the spectroscopic properties of the source or of the absorber. Consequently, except insofar as they were dependent upon some external factor, such as the warming up of the light source, they did not vary with time. On the other hand, in the experiments where air was admitted at atmospheric pressure, or hydrogen at 390 torr, the absorption observed varied over periods of time of up to half an hour. While this phenomenon did not interfere with the use of the U.V. absorption technique for mercury vapour pressure measurement, it was felt that these effects were sufficiently interesting to justify some comment.

The effect of the hydrogen initially was to produce a system with a fairly low absorption which gradually increased. A purely physical explanation for this was considered. It was possible that the admission of hydrogen to the apparatus displaced the mercury vapour to parts of the system which were not within the light beam, and that the increase in absorption was a measure of its slow return by diffusion. This was rejected as the basis of an explanation because this same effect was not observed with air. The change in this latter case was from a low to a high value, but it is interesting to note that the ultimate value achieved was (perhaps fortuitously) almost the same with air as with hydrogen.

Chemical interactions of some kind, therefore, appeared to be operating. A decrease in absorption to a greater extent than was found in the present work has been reported by Ballard and Thornton (72) in their study of mercury vapour in the presence of nitrogen. This they attributed to adsorption of ionised mercury atoms, produced by the action of the U.V., onto the walls of the absorption cell. In the present work, after admission of air or of hydrogen it was found that whether the cell was left in or out of the U.V. light beam had little, if any, effect on the change in absorption. It is not, however, possible to eliminate chemical effects produced by this radiation, especially during the periods in which readings were being taken. This is particularly so in the case of air, which contains oxygen capable of being converted to ozone, which reacts with mercury to produce the well-known "tailing" effect.

Before coming to any definite conclusions concerning these effects, it is felt that further information concerning the chemical action of the radiation must be available. In particular whether, if the appropriate gas was admitted to the apparatus and allowed to stand for half an hour in the absence of U.V. radiation, this would result, immediately measurements were made, in the same absorption value as that ultimately achieved in the present work.

CHAPTER 8

SIMULTANEOUS DETERMINATION OF MERCURY ADSORBED ON A SUPPORTED CATALYST AND THAT IN THE VAPOUR PHASE

(8.1.) Introduction

The development work carried out in the previous chapter had enabled a number of conclusions to be made regarding the factors involved in studying the absorption of mercury vapour for 2537 A^{o} radiation in this system.

(1) The absorbing power of mercury vapour was influenced by the pressure of hydrogen admixed with it. The greater the pressure of hydrogen the greater was the absorption for a given number of mercury atoms present.

(2) Hydrogen was present on reduced nickel catalysts and was able to be desorbed by mercury.

With these factors in mind it was decided to carry out the adsorption of mercury in the presence of a known pressure of hydrogen. The pressure of hydrogen used was considerably greater than the pressure which would be produced as a result of desorption, and consequently the effect of this latter on the absorbing power of mercury was made relatively negligible. Although it was preferable to use a large pressure of hydrogen in order to obtain as large an absorption as possible from any particular number of mercury atoms, the greater the hydrogen pressure the slower was the diffusion of mercury from the source to the catalyst. A compromise was chosen between these two effects by following the mercury adsorption in the presence of hydrogen at a pressure of 17.5 torr. A relationship between the absorbing power of mercury and the mercury vapour pressure had already been obtained under these conditions.

(8.2.) Preparation of the Catalyst

The catalyst used was 5% nickel on pumice, prepared as described in section 10.6. A sample of 0.2 g was placed in an ignition boat between the mercury source and the absorption cell. For practical reasons it was necessary to activate the catalyst in situ by heating it at approximately 200°C for 2 hr under hydrogen at a pressure of 200 torr. To prevent uncontrolled contamination of the catalyst with radioactive mercury a tap was fitted between the mercury source and the catalyst. Care was taken to use a tap lubricant which was unlikely to produce vapours absorbing 2537 A° radiation.

(8.3.) Pre-absorption Procedure

After activation of the catalyst the apparatus was evacuated, hydrogen to a pressure of approximately 17.5 torr was admitted and the apparatus sealed off. It was then placed in the spectrophotometer. The thermostats round the absorption cells and the mercury source were allowed to come to equilibrium at the required temperatures.

During early experiments it was discovered that great care was necessary to prevent the temperature of the mercury source rising above that of any other portion of the apparatus. If this occurred distillation took place and secondary sources of mercury vapour were produced. It was found necessary, therefore, to thermostat the room containing the spectrophotometer at a temperature higher than that of the mercury source.

On opening the tap isolating the radioactive mercury source, mercury was able to diffuse toward the catalyst and the rate of adsorption was measured using a gamma radiation counter. This counter was of the cylindrical type previously used for studying the adsorption of radioactive mercury on nickel films (section 9.23). It was placed directly above and parallel to the catalyst-containing section of the apparatus with the ignition boat containing the catalyst in the centre of the working region of the counter. The background with this counter and the mercury source suitably shielded was obtained before adsorption of mercury on the catalyst was commenced.

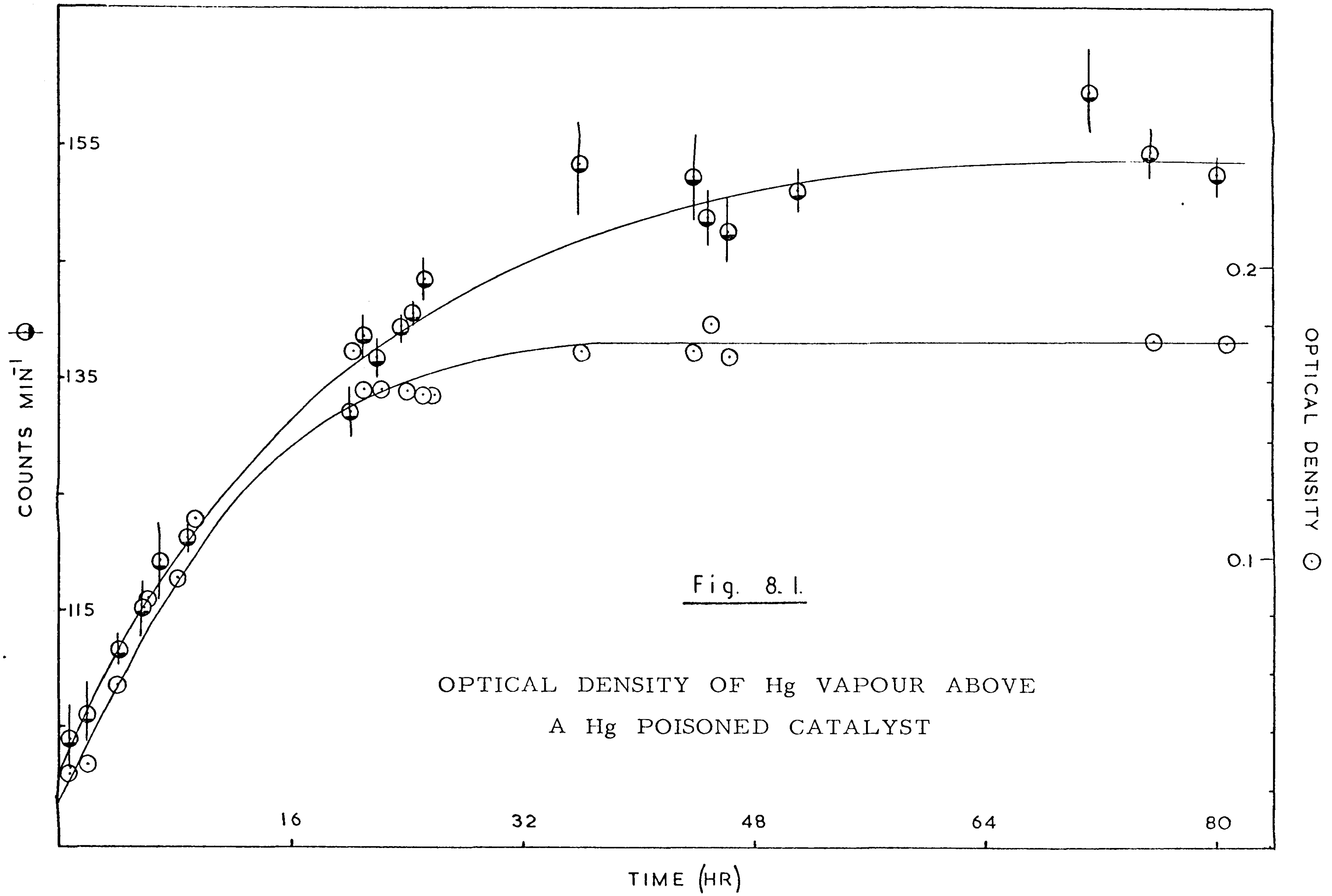


Fig. 8.1.

OPTICAL DENSITY OF Hg VAPOUR ABOVE
A Hg POISONED CATALYST

(8.4.) Results

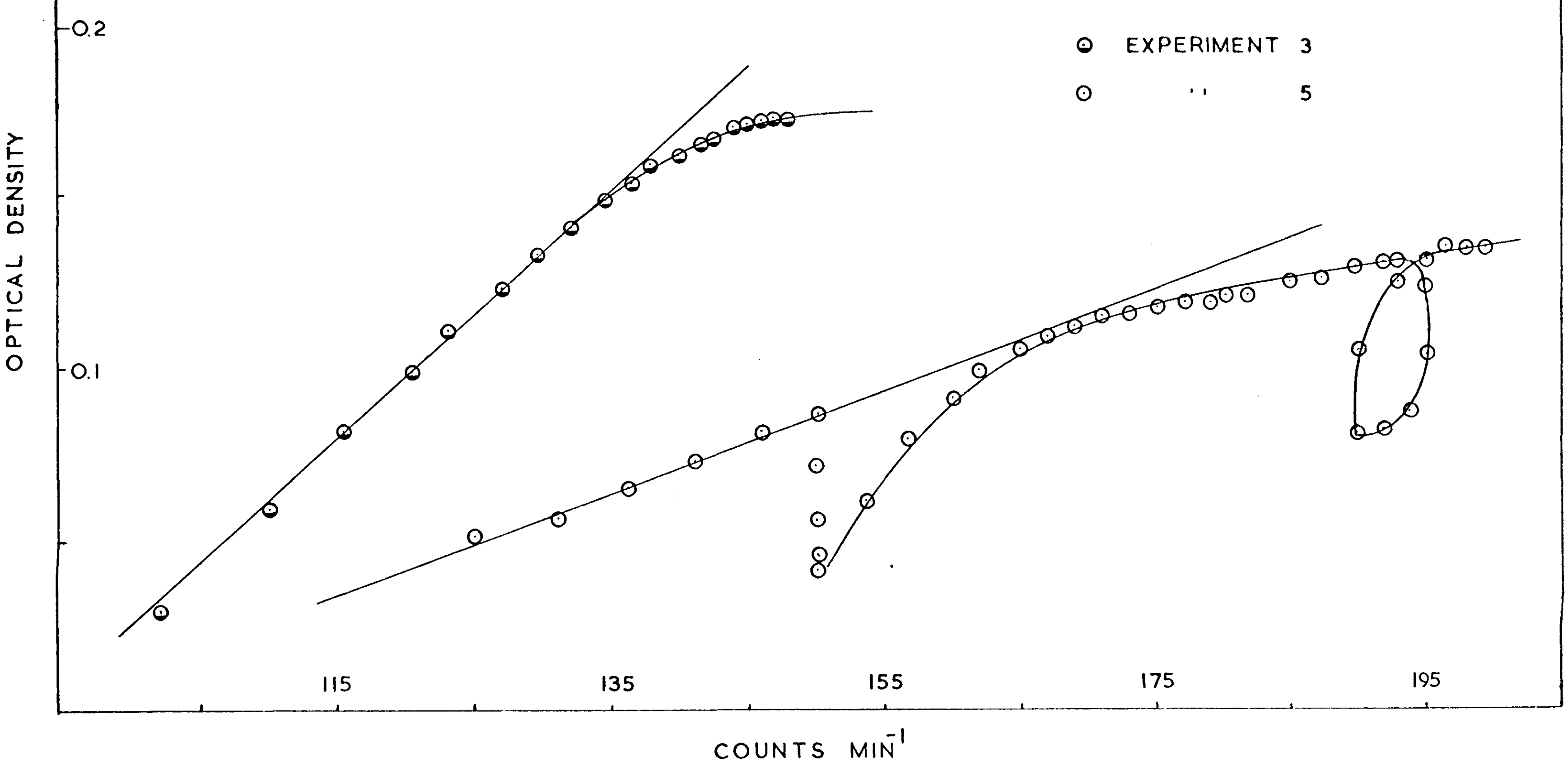
On opening the tap isolating the mercury source it was found that no sudden change in absorption took place. This was in direct contrast to the effect observed when the tap was opened in the absence of the catalyst and of hydrogen. In this case an increase in absorption was observed. Provided a second source of mercury vapour was not present the absorption readings at the beginning of the experiment indicated an absorption only slightly greater than that obtained with the cell under vacuum. It was found that adsorption of the mercury on the catalyst was extremely slow. Counts were taken for long enough time intervals to give a statistical accuracy of about 2 per cent although at low coverages the error was slightly greater.

Readings of the absorption of the 2537 A^o radiation in the absorption cell compared to that in the evacuated reference cell were taken with respect to time. Fig. 8.1. shows the counts and the absorption readings plotted against time, for Absorption Experiment 3. In this case the catalyst and the cells were maintained at 24°C and the mercury source was at 20°C.

It can be seen that the amount of mercury adsorbed on the catalyst increased with time, as did the concentration of mercury vapour in the absorption cell. After approximately 28 hr the value of the absorption became constant and remained at this value for the next 60 hr.

VARIATION OF OPTICAL DENSITY WITH COUNT FROM ADSORBED Hg

Fig. 8.2.



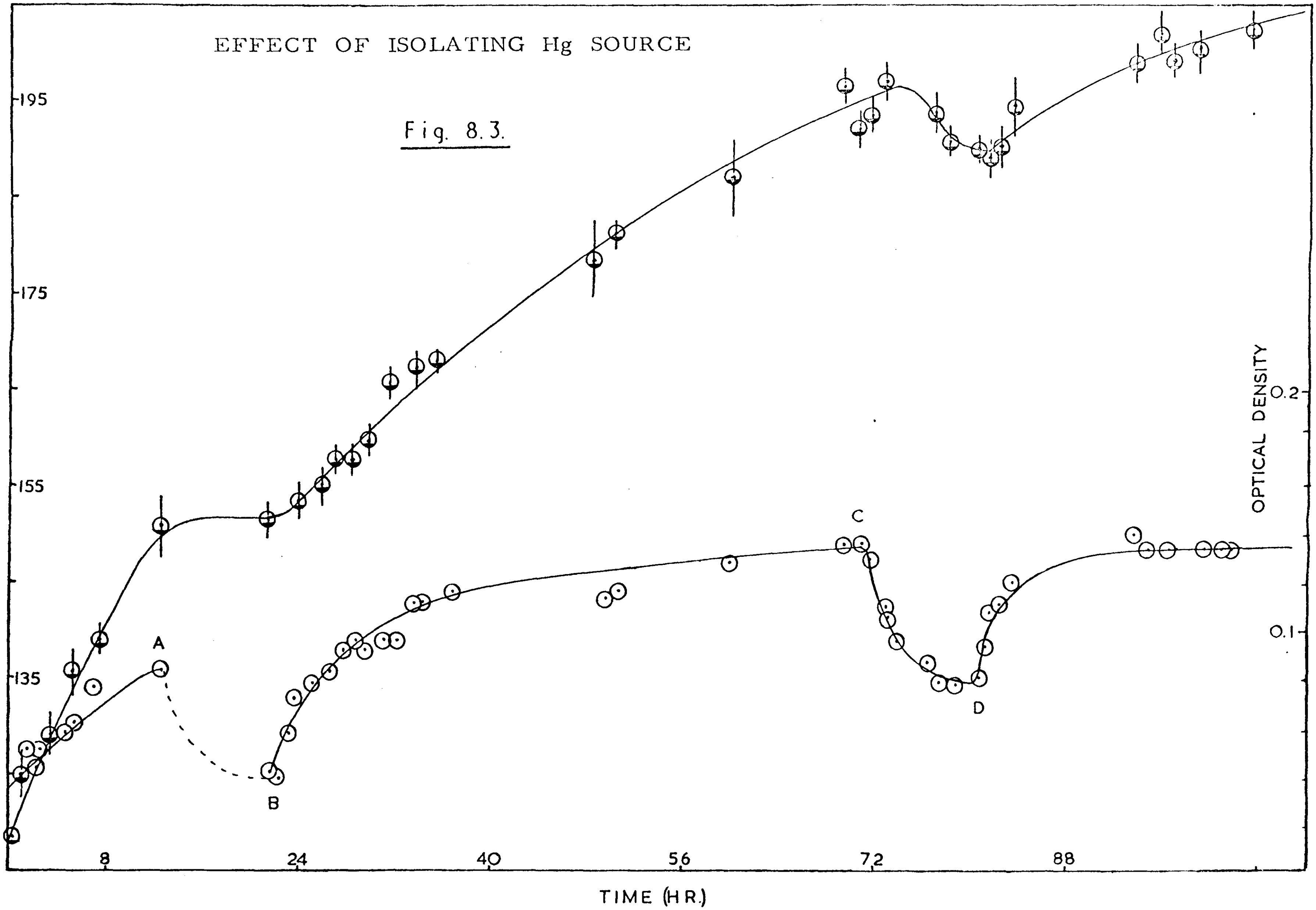
The vapour pressure of mercury which this absorption represented under the experimental conditions was just less than the saturated vapour pressure at the temperature of the mercury source.

The adsorption of mercury onto the catalyst continued at a fairly constant rate for approximately 48 hr and then tended to fall to a lower rate, but, in the time in which the adsorption was followed, it did not reach a constant value.

In order to determine how the values of optical density and the counts obtained from the catalyst varied relative to each other these were plotted for Experiment 3 in Fig. 8.2. It can be seen that the amount of mercury vapour in the absorption cell increased in a linear manner during the earlier stages of the adsorption process.

From the results obtained from Absorption Experiment 3 it was not possible to determine whether the amount of mercury above the catalyst at any particular time was the equilibrium concentration obtained as a result of adsorption/desorption processes over the whole of the nickel surface of the catalyst, or whether it resulted only from these processes occurring on nickel surfaces at the top of the catalyst bed.

This was investigated in Absorption Experiment 5. This study was carried out with the apparatus at a temperature of 26°C and containing hydrogen initially at a pressure of 18.5 torr. The temperature



EFFECT OF ISOLATING Hg SOURCE

Fig. 8.3.

of the mercury source was kept constant at 22°C. On opening the tap isolating the mercury source again no immediate change in absorption occurred. In this case, however, on leaving the source connected to the catalyst no increase in surface count was observed outwith the statistical deviation, even after eight hours. Similarly the value of optical density did not vary from its original value. This appeared to indicate that no mercury vapour was present. Consequently the mercury source was heated gently until beads of mercury were seen forming on the glass. During this procedure the tap was kept shut and the glass between the mercury source and the tap surrounded by cotton wool soaked in liquid nitrogen. The tap was then opened but no increase in absorption was observed. On leaving the system overnight and opening the tap again the counts were seen to increase with time, as did the readings of optical density, indicating that mercury vapour was, in fact, present. The values obtained are indicated in Fig. 8.3.

After 12 hr, indicated by the point A, the tap to the source was closed and was reopened 9 hr later, i.e. at point B. During the period in which the tap was closed, the optical density fell from the value of 0.083 which it had attained to 0.043, i.e. virtually the same value which it had possessed before adsorption occurred. No observable change in the surface count occurred during the period when the source was isolated. On reopening the tap both the surface count and the optical density increased, the latter initially at a faster rate and the former at a slower rate than previously. After a further exposure of 48 hours the tap was again closed at point C and in this case optical density readings were taken for the twelve hours until it was reopened at point D. In this time the optical density again fell and reached a constant value which it maintained for two hours. This value of the optical density indicated that at this stage mercury was still present above the catalyst at a vapour pressure of 0.2×10^{-3} torr. The counts obtained from the catalyst surface also fell on this occasion while the source was isolated. On opening the tap the optical density readings increased to their original value in a relatively short time and the surface counts also increased. With prolonged further exposure the optical density measurements appeared to reach a constant value and in the time for which measurements were taken this did not attain a value corresponding to the mercury vapour pressure at the temperature of the source or the catalyst.

(8.5.) Determination of the Weight of Mercury Present During Adsorption

The absolute weight of mercury present at the end of the reaction was determined by dissolving the catalyst in nitric acid and comparing the count in a liquid counter obtained from this with that obtained from a standard solution. Since the final count obtained on the external

TABLE 8.1.

Weights of Mercury Present During Absorption Experiment 5

Liquid counter background = 1953 ÷ 115 = 17 c.p.m.

10 cc of soln. containing catalyst = 8101 ÷ 65 - 17 = 108 c.p.m.
(dissolve catalyst in 12 ml)

10 cc of standard soln. = 25134 ÷ 45 - 17 + 2 = 544 c.p.m.
(5.4 mg in 100 ml)

$$\therefore \text{ Total wt. of Hg present } = \frac{0.54 \times 108 \times 1.2}{544} \text{ mg}$$

$$= 0.13 \text{ mg}$$

Wt. of catalyst = 0.2 g = 9.54 mg of nickel

$$\therefore \text{ Ratio of Ni/Hg at end } = \frac{6.023 \times 10^{23} \times 9.54 \times 10^{-3} \times 200.6}{58.7 \times 6.023 \times 10^{23} \times 0.13 \times 10^{-3}}$$

$$= 250$$

Source	Time After Start (hr)	Count per min	Wt. of Hg (mg)	Ratio Ni/Hg atoms
Background	-	4978 ÷ 42 = 118	-	-
Total wt. of Hg	128	6232 ÷ 30 - 118 = 90	0.13	250
" " "	16	219 - 118 = 101	"	"
" " "	82	212 - 118 = 94	"	"
Wt. of Hg at pt A (Fig. 6.3.)	16	151 - 118 = 33	0.04	810
Wt. of Hg at pt C	82	195 - 118 = 77	0.11	294

gamma counter was derived from this calculated weight of mercury, the weights of mercury producing the observed counts at other stages of the reaction could be calculated. Necessary corrections for the radioactive decay of the mercury over the period of the adsorption were made. The results obtained are given in Table 8.1. with details of the method of calculation.

(8.6.) Discussion of Simultaneous Study of Mercury Adsorbed on a Supported Catalyst and That in the Vapour Phase

The striking feature of the mercury adsorption results was the steady rise in mercury vapour pressure which occurred as adsorption proceeded. Even in the very early stages of the process, an increase in the optical density of the vapour was observed. In order to explain the observed phenomena, it is postulated that this adsorption occurred by two processes, chemisorption and physical adsorption. The first of these resulted in strongly adsorbed mercury, but the second permitted reversibility of adsorption such that the adsorbed mercury was in equilibrium with a measurable vapour pressure.

In the initial stages, chemisorption occurred and it is envisaged that, owing to the finely divided nature of the catalyst, this occurred preferentially on top of the catalyst bed, as has been discussed in Chapter 5. Since the number of sites for chemisorption on the top of the bed was limited, the mercury was soon being supplied at a greater rate than it could be chemisorbed. The continued adsorption, as indicated by the increase in count, occurred mainly by physical adsorption. Thus an increase in the amount of mercury in the vapour phase was observed. The long time intervals involved in this work, compared with the time required for mercury to reach the cell in the absence of the catalyst, suggested that the vapour pressure measured in the absorption cell was that in equilibrium with the catalyst on top of the catalyst bed.

When the mercury source was shut off, however, as in Experiment 5, a fall in the vapour pressure was observed to a value which indicated that negligible amounts of mercury vapour were present. This may be explained if mercury originally physically adsorbed on the surface was capable of migration into the catalyst bed, to become chemisorbed on sites previously unoccupied. This migration thus vacated space on the surface for physical adsorption and the equilibrium with the vapour was upset, resulting in removal of mercury from the vapour phase. On the first occasion when the source was isolated, little mercury had been adsorbed and consequently only a short migration was necessary before the physically adsorbed mercury became chemisorbed. On the second occasion, however, much more mercury was present, as indicated by the higher values of the vapour pressure and the count rate, and consequently more extensive migration of the mercury was necessary. The decrease in count rate indicated that this diffusion of mercury into the bed, and consequently away from the counter, was taking place.

The extensive migration also accounted for the slower rate of removal of mercury from the vapour phase on the second occasion that the source was isolated. Because of the reversible nature of the physical adsorption, relatively large quantities of mercury would require to diffuse to reduce the vapour pressure appreciably. That this did in fact happen was confirmed by the time taken for the vapour pressure to recover its original value after the access of mercury was temporarily interrupted. This was very much greater than would have been required to provide only that amount of mercury which disappeared from the vapour phase. The fact that the vapour pressure fell to a constant, but still appreciable, value on the second occasion indicated that not all of the physically adsorbed mercury on the top of the bed had been able to migrate.

In addition, the idea of the migration process was capable of explaining why the rate of increase of vapour pressure after opening the tap on the second occasion was greater than that on the first occasion, which in turn was greater than at the beginning of the experiment. The rate of appearance of mercury vapour at the beginning of the experiment would be expected to be slowest since at this stage there were more sites available for chemisorption. As the adsorption proceeded, the sites for chemisorption would become progressively less accessible. The rate of chemisorption would, therefore, decrease so that competition with the physical adsorption process for the available mercury would continuously diminish. After a period of migration when the upper region of the bed was well covered by physically adsorbed mercury, therefore, the vapour pressure would be able to rise to its original value in a shorter time, as was observed experimentally. Similarly in Experiment 3, in which the source was never isolated from the catalyst throughout the experiment, the vapour pressure above the catalyst surface built up rapidly to the saturated vapour pressure, since the rate of supply of mercury at the surface of the bed was greater than the rate of diffusion of physically adsorbed mercury into the catalyst bed. It should be realised, however, that this migration process would still occur and that the observed rate of increase of the count would be controlled by both the rate of arrival of mercury and its rate of diffusion into the catalyst bed.

It was not practical to study the desorption of hydrogen during these absorption experiments, and thus it was not known at what stage all of the hydrogen had been displaced. Assuming that the hydrogen monolayer was comparable with that for mercury, however, it was necessary to postulate that hydrogen was being desorbed at least up until point D, Fig. 8.3., since the presence of sites capable of mercury chemisorption is a prerequisite of the migration process envisaged. It is interesting to note that this adsorption process, which permits physical adsorption before all the sites capable of chemisorption have been occupied, explains why about two mercury atoms were adsorbed for each hydrogen atom displaced from the supported nickel catalysts, whereas an atom for atom displacement was found on nickel films (19).

Although the picture presented above was a suitable model for explaining the phenomena observed in these experiments it is not entirely complete. In order to explain the reactivation of mercury-poisoned palladium catalysts for cyclopropane hydrogenation, it was necessary to postulate that mercury was able to migrate from poisoned sites on top of the catalyst bed onto other chemisorption sites further down the catalyst bed. This process, therefore, resulted in regeneration of chemisorption sites on the most easily accessible part of the catalyst which were capable of continuing reaction, but it also required that the sites capable of chemisorption varied in energy. It would appear, therefore, that it must be postulated that chemisorption and physical adsorption occur during the absorption experiments, but that the chemisorption sites vary in their strengths of adsorption. It is in fact possible to explain all of the observed phenomena on the basis of this heterogeneous chemisorption alone, if the less firmly bound species are capable of producing a measurable vapour pressure. Unfortunately no information is available on how the heat of chemisorption of mercury varies with coverage although it would be expected that this variation would occur, considering the effects which are observed with other chemisorbed species such as hydrogen (78). In the case of mercury the heat of physical adsorption might be expected to be comparable with the heat of vapourisation of 15 Kcal mole^{-1}, which is much higher than is normally found for physical adsorption. Thus the distinction between mercury chemisorbed at high coverages, and mercury physically adsorbed might well be ill defined.

It is difficult to explain why the vapour pressure in Absorption Experiment 3 rose to the saturated vapour pressure of the source although this did not occur in Experiment 5. This may be explained if the rate of adsorption in the second case was much slower and the adsorption not studied to the same coverage as in Experiment 3. On the other hand, difficulty was encountered at the beginning of Experiment 5 with contamination of the mercury source and it may be that this reduced the availability of the mercury vapour. The presence of this contamination, which would appear to have been derived from the silicone greased tap, might also explain why the initial rate of adsorption in Experiment 5 was so low (3.5×10^{-4} mg Hg mg^{-1} Ni hr^{-1}). This rate of adsorption on a nickel catalyst was not, however, the lowest obtained. In Experiment 103 in Chapter 6 the rate was 8.4×10^{-5} (units as before) compared with 8.6×10^{-3} in Experiment 101, 6.5×10^{-3} in Experiment 102 and 3.2×10^{-2} on Film 27. These differences in rate of adsorption cannot be attributed entirely to differences in availability of mercury from the source since the slower rates were attained with some of the higher source temperatures. It would appear, considering the high rates of adsorption obtained with films, that the activity of the catalyst and the surface area exposed to the vapour control the rate of adsorption.

(8.7.) Conclusions and Suggested Further Studies

A number of comments may be made concerning the technique for the study of the vapour pressure of mercury above a poisoned catalyst using mercury resonance radiation.

(1) The mercury resonance radiation source used in the present work, although satisfactory, did not possess the best properties for the optimum application of the spectrophotometric technique under the given conditions.

(2) The rate of mercury adsorption on the catalysts used was extremely slow and long periods of time were necessary before

sufficient amounts of mercury were adsorbed on the catalyst to produce a significant count.

(3) The detection of mercury adsorbed on the catalyst was complicated by the migration of mercury through the catalyst bed.

In addition to these, difficulty was encountered in interpreting the observed results on the basis of physical or chemisorption of mercury on the catalyst. Difficulties of the same nature have been discussed in Chapter 6 with regard to the adsorption of mercury on nickel catalysts and in the simultaneous displacement of hydrogen. In particular, it was not possible to distinguish clearly which type of adsorption was prevalent at certain stages. It is felt, however, that valuable information could be obtained which might cast some light on this problem, if the techniques described in Chapters 6 and 8 were combined.

Thus it is envisaged that radioactive mercury should be adsorbed on evaporated metal films which contain adsorbed hydrogen and the volumes of hydrogen displaced, along with the values of the vapour pressure, determined. In this way it should be possible to determine whether any significant increase in vapour pressure occurs at the stage when all the hydrogen has been desorbed and to thus determine the relative sizes of the hydrogen and mercury monolayers.

Evaporated films would be most suitable for this study since, although they provide practical difficulties in their preparation, they combine considerable activity with large surface area, resulting in fast adsorption rates. Moreover they would not give rise to bulk migration problems. In addition a fine line mercury source, such as that described by Gunning (73), should be used which would result in strong absorption by the mercury vapour even in the presence of varying pressures of hydrogen.

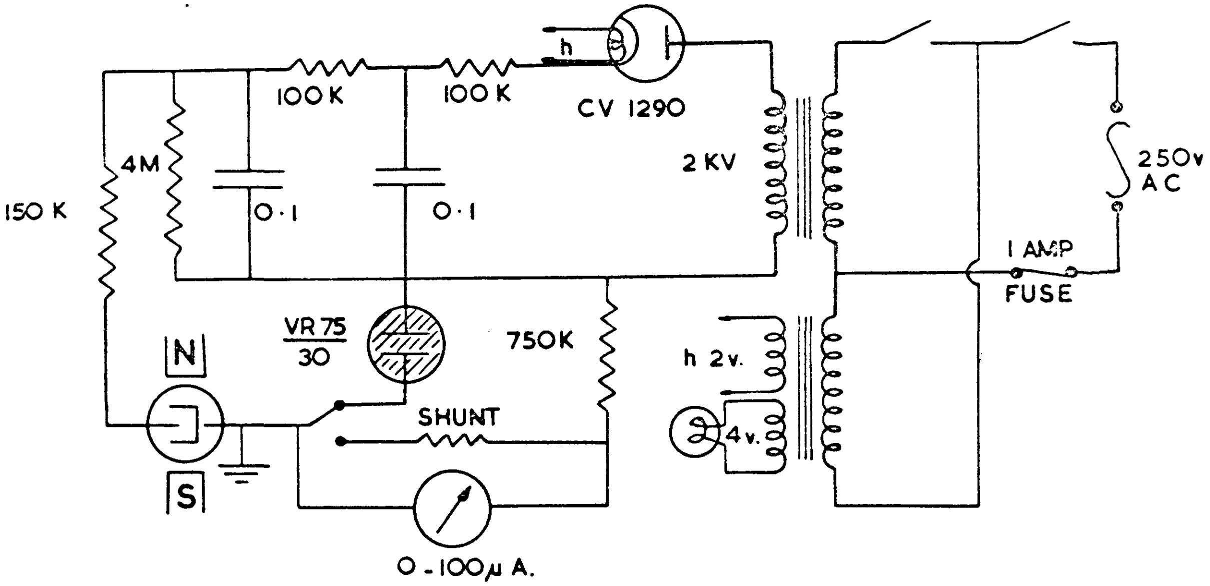
CHAPTER 9

THE STUDY OF CYCLOPROPANE HYDROGENATION ON EVAPORATED NICKEL FILMS: EXPERIMENTAL

The purpose of the experimental study was to examine the effect of poisons, deliberately added to the system, on the rate of hydrogenation of cyclopropane. It was therefore necessary to construct a high vacuum apparatus so that uncontrollable sources of contamination could be avoided. Furthermore, the undesirability of having mercury in the system imposed restrictions on the use of many of the techniques employed in conventional high-vacuum systems.

(9.1.) The High Vacuum System

The apparatus was constructed throughout from Pyrex glass and the stop cocks greased with Apiezon N grease. The high vacuum was achieved using an Edwards Speedivac rotary oil-pump to back a "Metrovac" oil diffusion pump charged with Edwards 704 silicone oil. Traps cooled with liquid nitrogen were situated between the pumps and the high vacuum line. It was found that filling these traps with copper strips did little to affect the ultimate vacuum as indicated by Alpert (79) although the



PENNING GAUGE

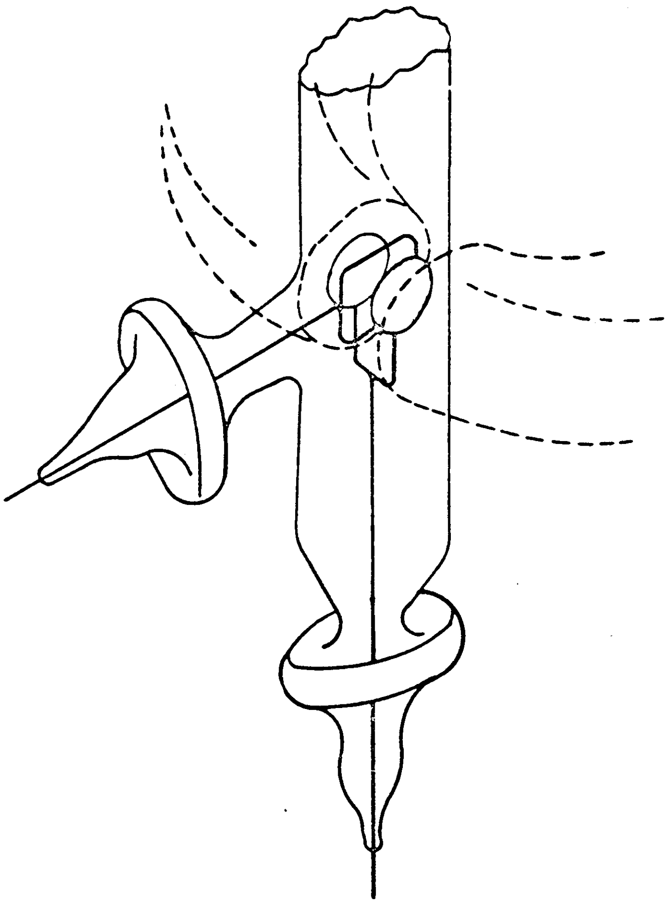


Fig. 9. 1.

copper did increase the efficiency of the traps when the liquid nitrogen reservoirs were low. The apparatus was designed so that it was possible to by-pass the high vacuum line and diffusion pump when large pressures of gases were to be pumped away. Pressures as low as 1×10^{-5} torr measured on a Penning ionisation gauge could be obtained.

(9.2.) The Penning Gauge

The Penning Gauge (80) consisted of a discharge tube attached to the end of the high vacuum line, the principle of its operation being that the current carried by the discharge was a function of the gas pressure.

The construction of this gauge and the accompanying electrical circuit are indicated in Fig. 9.1. The calibration of the current produced at various pressures was obtained from the literature (80).

(9.3.) Pressure Measuring Devices for Studying Hydrogenation

For the study of cyclopropane hydrogenation it was intended to work with gas pressures in the region 10 - 200 torr and it was found (81, 82) that a number of gauges were capable of use in this range. These may be conveniently classified, depending on their mode of action, into fluid manometers and mechanical manometers.

The majority of the fluid variety were unsuitable since they contained mercury, consequently McLeod gauges and various types of accurate mercury manometers (83, 84) were not considered. Oil manometers (85) were suitable in that they did not present contamination problems but the solution of gas and its subsequent spontaneous evolution when under vacuum were sources of error and inconvenience.

A compromise between these two types of fluid manometer was provided by use of a layer of high vacuum oil to suppress mercury vapour in mercury manometers (86). This, however, still showed tendencies to degas but to a lesser extent.

Very few of the mechanical manometers were considered to contain sources of contamination. Many, however, such as metal bellows gauges (87) and diaphragm gauges (88) were constructed using a high proportion of metal. Since the catalytic behaviour of this under experimental conditions and also whether it would amalgamate with the radioactive mercury to be used as a catalyst poison was unknown, these gauges were not considered suitable.

A type of mechanical manometer which contained no source of contamination and which was constructed completely from glass was the Bourdon gauge. Two basic designs of this gauge have been described, the spoon gauge (89) and the spiral gauge (90). Of these the spiral gauge was much more satisfactory since it could be made very sensitive in the appropriate pressure range yet could withstand a large pressure difference, as might be applied inadvertently. An attempt was made to construct these gauges using an apparatus which was available in the laboratory. This, however, was abandoned since gauges of sufficient sensitivity were not produced. Consequently, in the initial experiments of the hydrogenation study the course of the reactions was followed using a Bourdon spoon gauge the construction of which is indicated in section 9.4.

(9.4.) Construction of Bourdon Spoon Gauge

This gauge consisted of a very thin walled glass bulb, shaped in such a manner that a distortion was produced in the bulb when the pressure inside was different from the external pressure. This movement was magnified by a pointer attached to the bulb and an optical lever system.

The gauge was constructed by drawing out 8 mm, external diameter, thin walled tubing into a capillary about 15 - 20 cm in

CYCLING PUMP, SPOON GAUGE SYSTEM

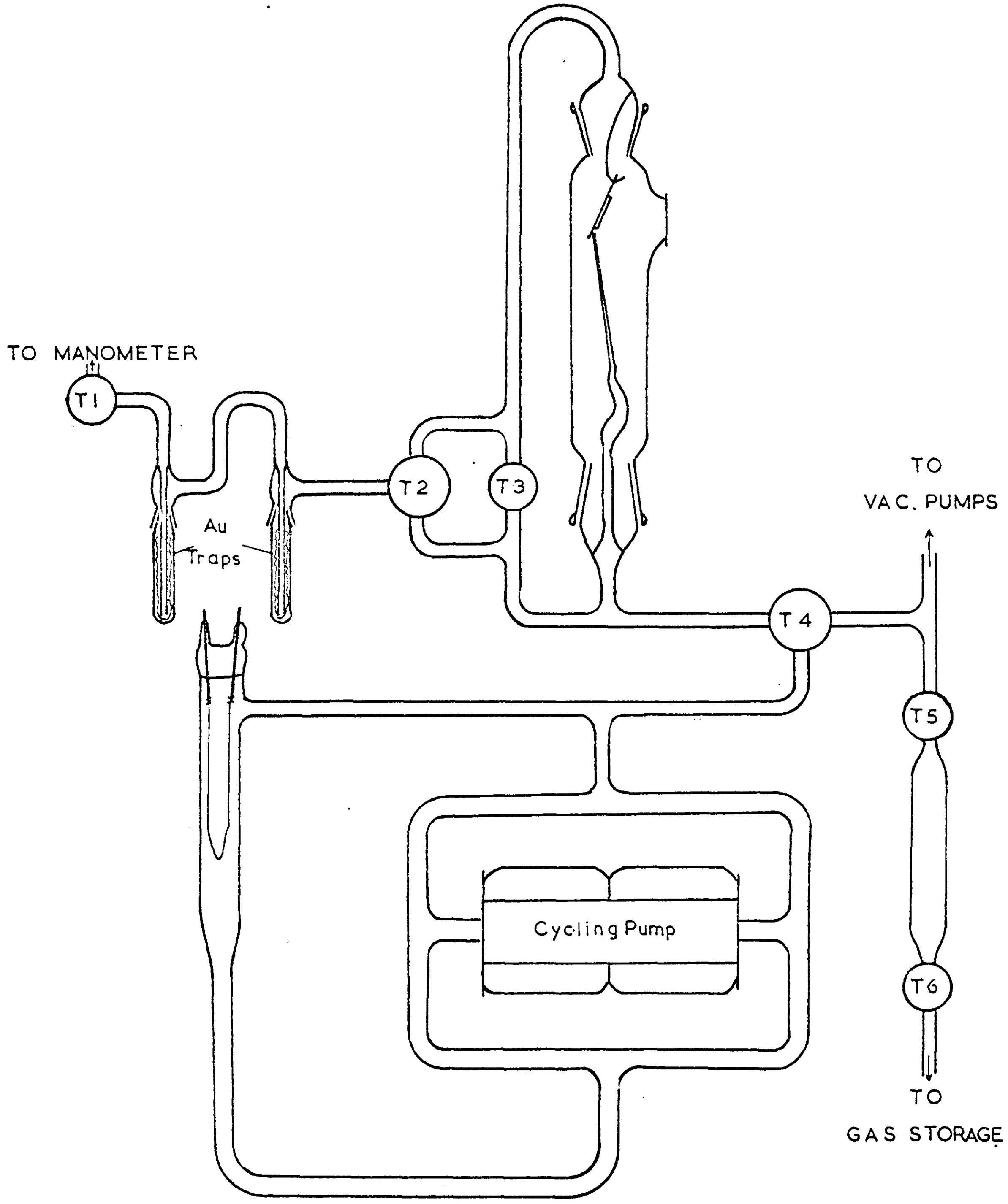


Fig. 9.2.

length and 1 mm in diameter. The end of the capillary was sealed in a flame and a thin walled, oval shaped bulb approximately 3 cm wide was blown in the tubing in the region where it tapered into the capillary.

The bulb was then partially rotated in a soft gas flame causing it to collapse inwards around the circumference, except for a region about 1 cm wide. A rough estimation of the relative sensitivity of the gauges was obtained by sucking the tube gently with the mouth and observing the movement of the capillary pointer. Gauges which did not produce a movement of at least 2 - 3 cm under these conditions were rejected.

(9.5.) Mounting of Spoon Gauge and Optical Lever System

The gauge was enclosed in an outer glass envelope as indicated in Fig. 9.2. This envelope was designed using B 34 joints so that it could easily be removed in the event of breakage of the gauge. A B 14 cone was fitted to the gauge, the corresponding socket being attached by means of a ring seal to the lower end of the B 34 cone onto which was fitted the glass envelope.

A light weight, plane mirror was fitted using Apiezon W wax. A stainless steel knife edge was also attached to the top of the framework and this was suspended from two V shaped supports of 3 mm glass rod attached to the B 34 cone which fitted into the top of the outer glass envelope. This assembly was used as an optical lever, by allowing the lower edge of the glass frame to rest against the capillary pointer of the gauge. When the pressures inside and outside the gauge were equal, the mirror suspended from the knife edge was tilted about 10 degrees from the vertical. Any change in pressure across the gauge caused this angle to alter.

A side arm, 2 cm long and 3 cm in diameter was fitted to the outer envelope at a height corresponding to the position of the mirror and to the end of this was fixed a plane glass disc using Apiezon W wax. This enabled the image of extremely fine metal cross wires to be projected onto the mirror and reflected out again without aberration. This image was then reflected from two plane mirrors, placed at opposite sides of the apparatus, onto a vertical, translucent graduated glass scale. This system required a considerable amount of adjustment before the image could be successfully produced on the scale. Once so adjusted any slight movement of the gauge pointer produced a much magnified movement of the image of the cross wires on the scale.

(9.6.) Calibration of Spoon Gauge using a Mercury Manometer

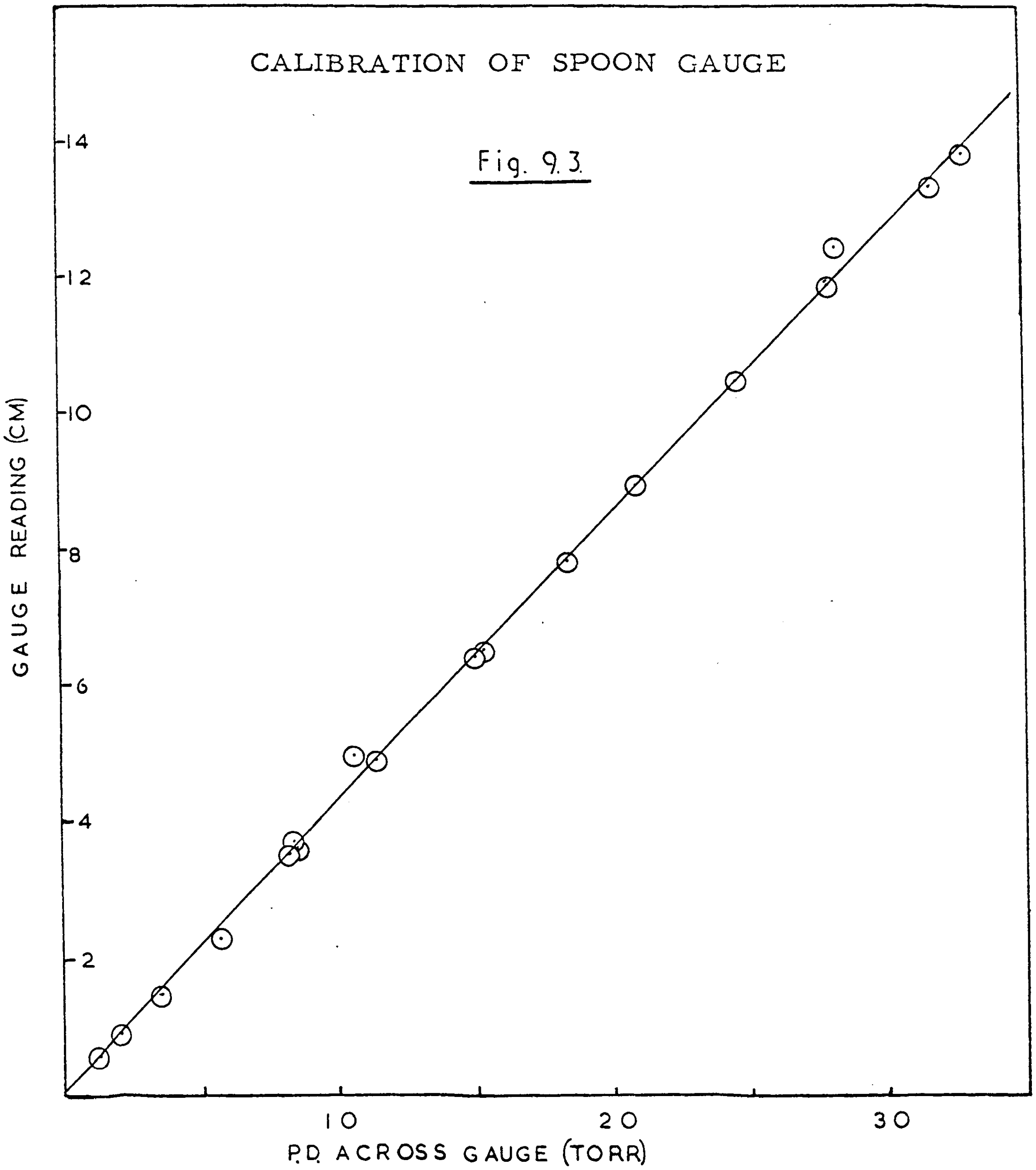
In order to convert the readings obtained on the scale to absolute pressure differences between the inside and the outside of the gauge it was necessary to calibrate the gauge against a mercury manometer.

Several errors inherent in mercury manometers have been reported (91, 92) and an attempt was made to reduce as many of these as possible.

The manometer was of the U-tube type constructed from Pyrex tubing 14.5 mm (outside diameter) and wall thickness 1.2 mm. The limbs were each 80 cm long and were made as parallel as possible. The manometer was thoroughly cleaned with hot chromic acid which was allowed to remain in the limbs overnight. It was then rinsed with distilled water and dried under vacuum. The manometer was filled under vacuum with trebly distilled mercury after the limbs had been thoroughly flamed out. The level of the mercury meniscus in each limb was read using a cathetometer mounted on a vertical graduated scale. The standard deviation on a reading of the mercury meniscus was 0.008 cm. This was improved at a later stage (see section 9.17.) by illuminating the meniscus with diffuse light.

One limb of the manometer was connected to an external vacuum source and could be pumped out to a vacuum better than 10^{-2} torr. This limb was kept under this vacuum throughout any series of experiments. The other limb of the manometer was connected to the otherwise mercury free apparatus by means of two gold traps containing several sheets of gold leaf. This trapping material was activated for mercury adsorption by intentionally amalgamating a small portion of its surface before placing it in the traps. To prevent continuous adsorption of mercury a tap was placed between the manometer and the traps and this was only opened when it was required to take a pressure measurement.

In order to calibrate the spoon gauge a particular pressure of dry air was admitted to both sides of the gauge, i.e. with the tap T3 (Fig. 9.2.) connecting the inside and the outside of the gauge open. The absolute pressure of this air was measured on the manometer by opening the three-way tap T2 and the manometer tap T1. The connecting tap T3 was then closed and the pressure of the gas inside the gauge was reduced by expanding it into another portion of the apparatus. This reduced pressure was measured on the manometer via tap T2 as was the change in reading on the gauge scale. Since the movement of the gauge causes no change in the volume of the gas in the outer envelope and any changes in temperature during the short time required for calibration would



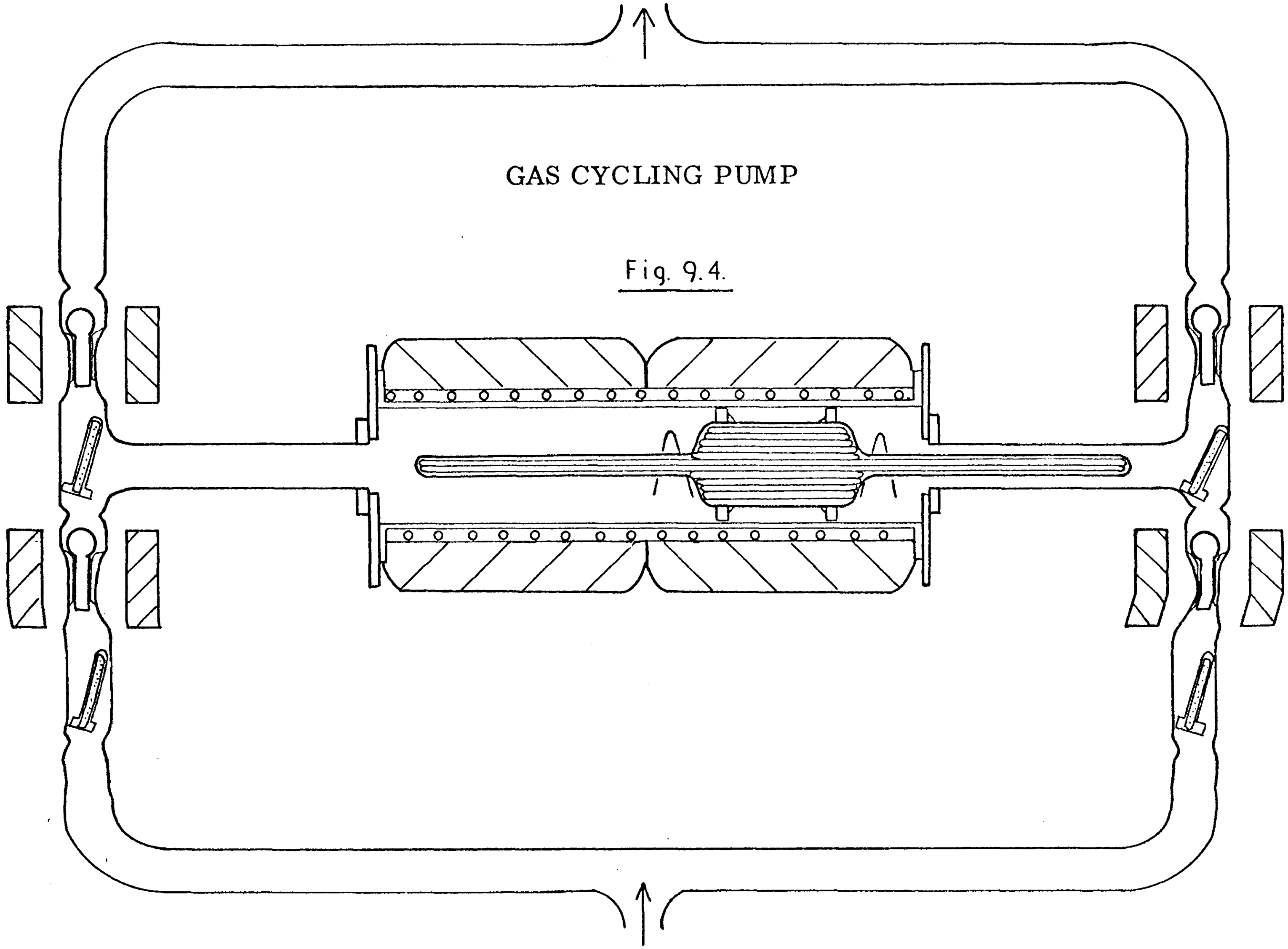
CALIBRATION OF SPOON GAUGE

Fig. 9.3.

be small, the difference between the pressure of the gas in the inside of the gauge and that originally present represents the pressure difference operating across the gauge. By removing aliquots of gas from the inside of the gauge, keeping the pressure of the gas in the outer envelope at its original constant value, a series of gauge readings at various pressure differences was obtained. The relationship between gauge reading and pressure difference is shown in Fig. 9.3. It can be seen that a good linear response was obtained over a range of 35 torr. Pressure differences greater than this were not attempted for fear of breaking the gauge.

(9.7.) Gas Circulating Systems

As in the case of pressure measuring devices for use in the study of cyclopropane hydrogenation the choice of gas cycling systems necessary to circulate the reactant gases over the film was also limited, since those types containing mercury (93) were unsuitable. In addition designs which did not operate at constant volume (94) or those which, although suitable, involved difficulties in construction, e.g. an efficient rotor type (95), were also not considered. The design of the pump constructed was based on that of Brunfield and Holm (96).



GAS CYCLING PUMP

Fig. 9.4.

It is described in section 9.8.

(9.8.) Gas Cycling Pump

The pump consisted of a Pyrex glass cylinder 16 cm long and 3.75 cm in diameter with ground flanges at the ends. These flanges enabled a vacuum tight joint to be made, using Apiezon W wax, to flat ground glass plates covering the ends of the cylinder. These plates, which had a 1.25 cm hole in the centre, were in turn sealed to two 3 cm diameter flanges with Apiezon W wax (Fig. 9.4.). A glass piston, on to which were fixed two Teflon collars 4 cm apart, was inserted in the cylinder. These collars were of size such that the piston fitted into the cylinder to achieve a compromise giving freedom of movement yet with negligible displacement of gas past the collars. This piston was packed with lengths of soft iron wire held in place with paraffin wax. The space inside the piston assembly was evacuated and sealed off.

The piston was made to oscillate horizontally in the cylinder by activating alternately the two electromagnets wound round the outside of the cylinder. These electromagnet coils were wound on top of a coil of 0.3 cm O.D. copper piping through which water was passed to remove the heat generated by the induction within the electromagnets. The coils were each wound with 1500 turns of 23 S.W.G. lacquered copper wire.

The current for the coils was supplied from a Variac variable transformer. An applied voltage of 100 - 120 volts was sufficient to move the piston through the cylinder. Under these conditions the current taken by a coil varied between 1 A and $1\frac{1}{2}$ A, depending on the position of the piston.

The current was switched to each coil by means of a relay activated by current pulses from a micro switch. This relay was necessary since the current to energise the coils was too great to be switched through the micro switch directly. For this reason, switching devices consisting of a mercury rocker switch and probes dipping in and out of two pools of mercury were also shown to be unsuitable.

The movement of the piston into either of the coils was not, as originally intended, stopped by the energising of the other coil. It was, therefore, necessary to fit buffers to each end of the piston to prevent it from striking the glass end plates.

Latterly a small hairpin of phosphor bronze strip was used for this purpose, polythene having been found to be unsatisfactory owing to degassing of the plasticiser.

A system of four light ground glass valves was included in the pumping system to operate as the valves of a double-acting piston pump. It was found that at gas pressures greater than 60 torr the gas displaced from the cylinder was sufficient to open the valves, but at lower pressures this was not so. Consequently it was subsequently found necessary to fit short lengths of soft iron, enclosed in glass, under each valve and to activate these in pairs with electromagnets fitted round the valve seatings. These electromagnets were fitted in series with the main coils and, therefore, operated simultaneously with the piston movement.

Under experimental conditions this pumping system was found to operate satisfactorily, the main disadvantages being the large amount of dead-space it possessed and the vibration which it produced in the apparatus. Under normal working conditions the piston made about 30 oscillations per minute, producing a theoretical displacement of $2\frac{1}{2}$ litres/min^{-1}.

(9.9.) Preparation of Catalyst Vessels

The design of the catalyst vessels varied with the type of gas agitating device which was used but the basic features remained the same. Details of the differences in design will be given under the appropriate sections and the common features of construction given here. The vessel consisted of a 2.3 - 2.5 cm diameter

Pyrex glass tube through one end of which passed two tungsten leads connected with a hairpin shaped filament of nickel wire. Two types of nickel wire were used, both having diameter 0.02 inches, the first for Films 1 to 22 and the second for Films 23 to 32. The first wire was that used in all previous work on nickel films carried out in this laboratory (97, 59). This was pure grade nickel wire obtained from Johnson Matthey. The second wire was also obtained from Johnson Matthey and was spectroscopically pure.

The tungsten to glass seals were prepared by cutting 1 mm annealed tungsten wire into 9 cm lengths taking care to prevent splitting the laminae of the wire. The wire was cleaned by heating it to red heat and then rubbing it with a stick of solid sodium nitrite. The resulting violently exothermic reaction left the wire, when cooled and washed with water, with a bright, silvery appearance. The wire was then passed slowly through a soft gas flame whereupon it was reoxidised to give a green or purple interference film. Pyrex glass tubing 2 mm bore and 7 cm long, previously washed with nitric acid and distilled water, was then slipped over the tungsten wire. The wire and tubing were heated gently, to remove any traces of moisture, and then more fiercely in an oxygen flame. This caused the glass to melt onto the metal, care being taken to exclude air bubbles. If the preparation of the seals had been correct they possessed a characteristic bronze colour throughout their length. Any which did not possess this were rejected. While the tungsten was still hot a piece of 18 gauge copper wire was attached to one end. The silver solder used for this was brought as close to the glass sleeving as possible. This prevented any leakage of gas along the laminae of the tungsten and the copper wire provided a flexible lead for the connection of electrical contacts. A suitable length of nickel wire, normally 16 cm, was connected between the free ends of two of these tungsten leads and spot welded in position. This ensured an adequate electrical contact. In some cases the nickel wire was held in place on the tungsten using stainless steel connectors. The 23 - 25 mm Pyrex glass tubing used for the preparation of the catalyst vessels was cleaned out with concentrated nitric acid and distilled water before use. Difficulty was encountered while sealing the tungsten leads into the catalyst vessel using a pinch seal, owing to the distortion this process produced in the hairpin filament. This was overcome by clamping the two tungsten seals, with the filament in the correct position, using a screw clamp across the copper extension leads. Both seals were retained in this position while the pinch seal was made and the screw clip removed when the glass had cooled.

(9.10.) Pre-evaporation Treatment of Catalyst Vessels in the Cycling Pump/Spoon Gauge System

The normal procedure for the preparation of evaporated nickel films used in this laboratory was to degas the catalyst vessel and evaporate the film in a portion of the apparatus remote from that used for studying reaction. This procedure entailed the use of a breakseal which was broken when the catalyst vessel containing the film was in position in the reaction system. In the present system the efficient operation of the cycling pump depended on an unrestricted flow of gas through the catalyst vessel and any breakseal present in this system would have greatly reduced this efficiency. It was necessary, therefore, to degas the catalyst vessel and evaporate the film in that portion of the apparatus where the reaction was to be followed.

The design of the catalyst vessel and its position relative to the cycling pump are indicated in Fig. 9.2. The catalyst vessel and pump were connected to the spoon gauge, to the vacuum pumps and gas storage system by means of the three-way tap T4.

In order to degas the catalyst vessel prior to the evaporation it was necessary to heat it at 500°C under vacuum. This was accomplished using an electrically wound cylindrical furnace. Experience had indicated that 250 watts had to be supplied to maintain a temperature of 500°C in such a furnace. Consequently it was constructed by wrapping 6.5 yds of 34.55 ohm/yd nichrome wire round an asbestos insulated, 7 inch length of iron tube of diameter 1 inch. When operated on the 240 v mains supply this furnace was capable of reaching temperatures in excess of 500°C and was normally operated using a Variac transformer. The temperature was recorded on an iron-constantan thermocouple in series with a 2.5 mA meter. The meter deflections were calibrated against a 500°C mercury thermometer. It was necessary to fit the furnace in position round the catalyst vessel before attaching the latter to the cycling pump.

The catalyst vessel was pumped out at room temperature for several hours and when the furnace was switched on a considerable increase in pressure was observed on the Penning gauge.
The catalyst vessel was maintained under vacuum at 450 - 500°C for at least 12 hours. During the final three or four hours of this baking out process a current of 4 A was passed through the nickel filament. This current was sufficient to raise the temperature of the nickel wire to just below its melting point as was indicated by the light metallic film obtained on the walls of the catalyst vessel when the current was raised slightly above this value. In previous

work (97, 59) it had been assumed that this treatment was sufficient to remove any gases adsorbed on the surface of the wire and to free any gases occluded within the metal.

In initial experiments this procedure was adopted for degassing the wire but in later experiments it was modified to give a more rigorous purification,as is described in section 9.25.

The ultimate pressure obtained in the catalyst vessel after the degassing of the walls and the filament was in the region of 4×10^{-5} torr.

(9.11.) Evaporation of Nickel Films in the Cycling Pump/Spoon Gauge System

Since considerable heat has to be dissipated during the evaporation process and since it was necessary to avoid undue sintering of the film, the evaporation was carried out with the walls of the catalyst vessel surrounded in a cold water bath.

Owing to the necessity of evaporating the film in situ it was not possible to immerse the catalyst vessel in a conventional water bath and it was necessary to construct a demountable cooling system which could be fitted round the catalyst vessel after the degassing was complete. This consisted of a sheet of 1 mm thick brass, 18 cm by 30 cm,which was wrapped round two 7 cm diameter rubber bungs attached to the top and bottom of the catalyst vessel. Holes had been bored in the centre of these bungs and they had been split along a radius to enable them to be fitted round the tubing of the catalyst vessel. The brass sheet was held in place round the bungs using 7 cm diameter Jubilee hose clips. Water was circulated round the catalyst vessel within this cylinder, passing through glass tubes fitted into holes in the bungs. Leaks in the system were sealed using 5 cm wide plastic masking tape. Before fitting the water bath it was necessary to lower the furnace, originally round the catalyst vessel, but this could not be removed completely owing to the enclosed nature of the system.

The current necessary for the evaporation of the film as well as for the degassing of the wire was obtained from a 70 A,12 v mains transformer, fed by a Variac transformer. The current passing through the wire was measured on an ac ammeter which had a full scale deflection of 10 A. The wire was evaporated by the passage of a current of 6.2 - 6.4 A, the rate of evaporation being between 30 and 40 mg per hour. Evaporation was continued until the wire became so thin that the current passing through it caused it to break. This normally occurred after evaporation had proceeded for at least half an hour. Film weights varying from 15 to 30 mg were obtained.

APPARATUS FOR H_2 PURIFICATION

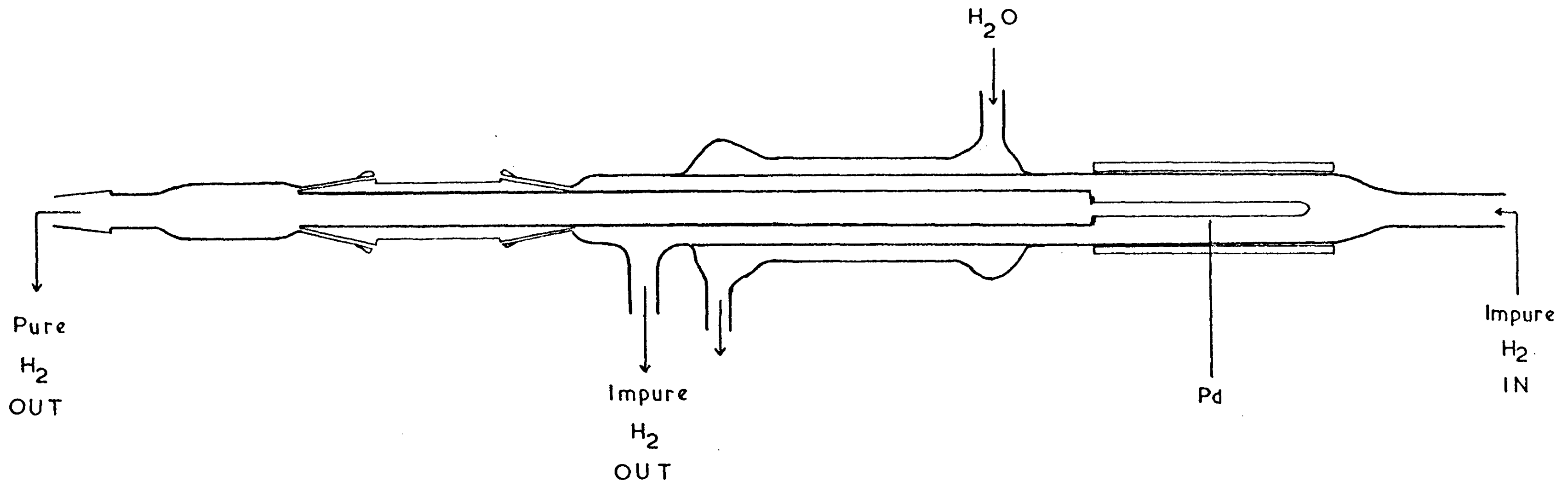


Fig. 9.5.

(9.12.) Purification of Reactants

(a) Hydrogen

Cylinder hydrogen obtained from the British Oxygen Co. was purified by passing it through a palladium thimble obtained from Johnson Matthey. This thimble was brazed onto the end of an open brass tube the other end of which was machined to fit into a B19 socket which was attached to the high vacuum apparatus.

Since the rate of diffusion through palladium is greatly increased by an increase in temperature (98) the thimble was surrounded by a cylindrical furnace wound from nichrome wire. The resistance of this furnace was 40 ohms and the nichrome wire was maintained just at red heat by the application of 50 v supplied from a Variac transformer. In order to prevent heat from this furnace from travelling along the brass and melting the Apiezon W wax used to seal it into the B19 socket it was necessary to surround the brass with a water cooled condenser type system as is shown in Fig. 9.5. According to Young (53) the hydrogen purified by passage through palladium has an impurity content as low as a few parts in 10^{10}.

(b) Cyclopropane

The cyclopropane used for this study was obtained from two sources. That used for Films 1 - 15 was from the same cylinder as used by Campbell (12, 20), supplied by Light & Co. A G.L.C. analysis of this gas indicated that it contained an impurity which was shown to be propylene (see Appendix 2). This was, therefore, rejected in favour of anaesthetic grade cyclopropane supplied by the B.O.C. and conforming to British Pharmacopoeia. This was shown to have traces of propylene less than 0.05% and was used for all other work involving cyclopropane.

Before use the cyclopropane was further purified by carrying out the following procedure. The cylinder was attached to the apparatus by means of a brass B 14 cone held in position by Apiezon W wax. The apparatus, including two 2 l storage flasks with cold fingers attached, was pumped to a vacuum of 4 x 10^{-5} torr and the gas storage portion of the apparatus isolated from the vacuum pumps. Cyclopropane was admitted to one of the storage bulbs to a pressure of approximately 700 torr, this pressure was read on the mercury manometer described in section 9.6. Care was taken to open the tap to the manometer only long enough for the pressure reading to be taken. The storage flask was then isolated from the rest of the system and the cyclopropane it contained was solidified to a fibrous white solid by cooling the finger using liquid nitrogen. This solid was then pumped to a pressure of 8 x 10^{-5} torr, whereupon the storage flask was again isolated and the cyclopropane allowed to warm up until it had all evaporated. This solidification process and subsequent evacuation of the storage vessel to remove traces of non-condensible contaminants was repeated once more. On this occasion the storage vessel was kept in contact with the rotary pumps while the solid was liquefying and until approximately one third of the liquid had been distilled off,thus removing any relatively lower boiling components. The system was then isolated from the pumps and the middle fraction of the cyclopropane distilled into the second storage flask by placing liquid nitrogen round the appropriate cold finger. When only approximately one third of the original volume of liquid was left in the first storage flask the second flask was isolated and the cyclopropane which it contained allowed to return to room temperature, which was noted.

The cyclopropane pressure in the system between the manometer and the storage flask was reduced and then the storage flask opened to the manometer and the pressure of the gas noted. The storage flask was isolated once more and contained pure cyclopropane at the pressure observed on the manometer, normally 250 - 300 torr at 22°C.

(9.13.) Preparation of 1:1 Cyclopropane:Hydrogen Mixture

All reactions, unless otherwise stated, involving the hydrogenation of cyclopropane used a premixed gas mixture containing cyclopropane and hydrogen at the same partial pressure. This mixture was prepared by solidifying the pure cyclopropane already at a known pressure into the cold finger of the flask and maintaining it in this condition using a Dewar flask filled with liquid nitrogen. Hydrogen was then admitted to the storage vessel by passage through the palladium thimble. The rate of hydrogen diffusion into this system was slow, a pressure increase of 80 torr per hour when the system was under vacuum, and decreased as the hydrogen pressure in the system increased to 20 - 30 torr per hour when the system was at 300 torr. The pressure of the hydrogen at any stage was read on the manometer. Care was taken to open the tap for the minimum time and always to have a higher pressure in the system relative to the manometer so that there would be little transfer of mercury vapour into the system. The diffusion of hydrogen was continued until the pressure in the storage vessel above the solidified cyclopropane was the same as that originally attained by the cyclopropane when gaseous, allowing for any changes in room temperature. The storage flask was then isolated, the liquid nitrogen removed and the gases allowed to diffuse through each other for at least one hour and normally several days, before use.

(9.14.) Experimental Procedure for Studying Hydrogenation using the Cycling Pump/Spoon Gauge System

As soon as possible, normally within two or three minutes, after the breaking of the nickel filament terminating the evaporation of the film, a sample of the reactant mixture was admitted to the catalyst vessel. This was accomplished by turning tap T4 (Fig. 9.2.) so as to expand the gases already at a prenoted pressure in the gas pipette and connecting tubing into the catalyst vessel/cycling pump system. The time of admission was noted on a stop watch. As soon as the level of the manometer had become steady, indicating the pressure of the gas in the catalyst vessel and both inside and outside the spoon gauge, the taps T1, T2 were closed and tap T4 was turned clockwise through 90°. This isolated the catalyst vessel from the gas burette system but left it connected to the gauge. One minute after the admission of the reactant gases the tap connecting the inside and the outside of the gauge T3 was closed. Any changes in pressure of the gas in the catalyst vessel, which was connected to the inside of the gauge, which now occurred caused a movement of the gauge pointer and a change in reading on the scale. The value of the initial gas pressure registered on the manometer was read at some stage during the reaction. The cycling pump was set in operation as soon after the admission of the gas as was desired. Readings of the scale with respect to time, normally at one minute intervals, were taken. When the pump was in operation it was found that the vibration it produced made it impossible to read the scale accurately. It was necessary, therefore, about 5 sec before taking a reading to switch off the pump and restart it again about 5 sec after. It was found that the mirror resting against the gauge pointer had a definite damping effect and the pointer came to rest very soon after the pump was switched off.

After the reaction had proceeded for the desired time the tap T4 was turned anti-clockwise through 180° and the gases in the catalyst vessel and cycling pump pumped off via the rotary pump for some particular time interval, normally one minute. The gauge tap T3 was then opened to equalise the pressure inside and outside the gauge and this portion of the system was also pumped out by turning tap T4 anti-clockwise through 90°, simultaneously isolating the catalyst vessel. The manometer was also evacuated with this portion of the system although for only approximately 15 sec. The tap T1 was then closed isolating the manometer.

After pumping out the gauge system, the vacuum pumps were isolated and the gas pressure in the gas burette, i.e. the region between taps T5 and T6, adjusted prior to readmission of reactants into the catalyst vessel after the desired time interval.

(9.15.) Spiral Bourdon Gauges

Bourdon spoon gauges, particularly those of high sensitivity, were found to break readily under sudden shock or on the application of too great a pressure difference. Since a considerable amount of work was necessary to install and calibrate replacements for these gauges it was decided to abandon their use in favour of spiral Bourdon gauges. An attempt had been made to prepare these in the laboratory. This proved unsuccessful and the gauges used were obtained commercially from Springhams.

These spiral Bourdon gauges consisted essentially of a very thin walled glass spiral, mounted vertically. To the top end of the spiral a vertical pointer was attached, bearing a light weight mirror. A pressure difference between the inside and outside of this spiral produced a torque in the pointer which in turn moved the mirror through an angle proportional to the pressure difference.

(9.16.) Installation and Optical Lever System for Spiral Bourdon Gauges

The installation of the spiral Bourdon gauge was very similar

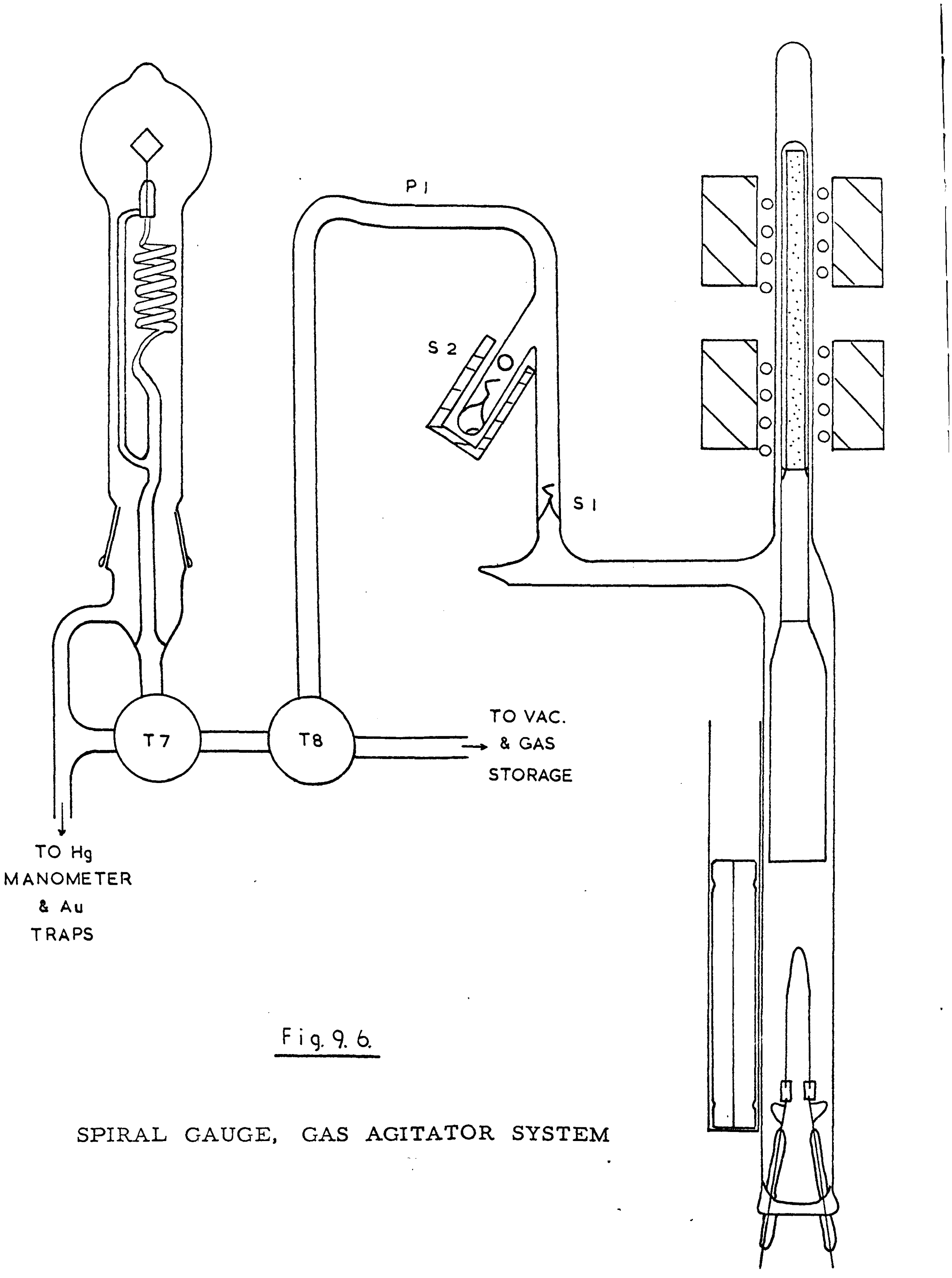


Fig. 9. 6.

SPIRAL GAUGE, GAS AGITATOR SYSTEM

to that of the spoon gauge it replaced and is described in section 9.4. The gauge was supplied in an outer glass envelope which was fitted with a plane window at the height of the gauge mirror. The connections to the interior and exterior of the gauge were situated below the B 24 cone of this outer envelope and this greatly simplified installation. The dead space involved, particularly in the outer glass envelope was also very much reduced by the use of this gauge. A diagram of the gauge and manometer assembly is shown in Fig. 9.6.

Owing to the very small mirror (5 mm x 5 mm) fitted to the spiral gauge and the small amount of light it reflected it was not possible to use the same optical system as that used for the spoon gauges unless the work was to be carried out in darkness. As this was impractical,an alternative system was devised. This was basically the system normally used with a spot galvanometer. The image of the bulb filament was focused on the mirror from a distance of 1 m. After reflection, the image of the cross wire attached to the collimator lens was produced on a translucent screen at a distance of 1.2 m by passage through a condenser lens placed 3 cm from the plane glass window.

(9.17.) Calibration of Spiral Bourdon Gauge

This was similar to, but not identical to, the method used for the calibration of the spoon gauges described in section 9.6. A sample of gas was admitted to both the interior and exterior of the gauge and its pressure noted on the mercury manometer. The interior was isolated from the exterior and the gas pumped from the interior on the vacuum pump to a pressure of at least 10^{-2} torr. The gauge reading so produced was due to the observed pressure reading on the manometer. The process was repeated by isolating the pumps and equalising the gas pressure on both sides of the gauge after each evacuation of the interior. A fresh sample of gas was not admitted until the pressure difference was too low for expansion to produce any appreciable change in the gauge reading. When the gauge readings were plotted against the corresponding pressure differences across the gauge a linear relationship was found to exist. The gradient of this line was calculated by the method of least squares using the computer programme described in Appendix 5 . From this it was found that the pressure difference (torr) = (gauge reading x 0.134 - 0.015) ÷ 10.

It was found during the calibration of the spiral gauge that the accuracy with which the level of the mercury meniscus in the manometer could be determined was improved by illuminating it with diffuse light and viewing it against a contrasting background. These refinements were carried out by drawing a series of lines, 2 mm apart at 45 degrees, in Indian ink on a sheet of translucent tracing linen, 4 cm by 3 cm. This was mounted between two sheets of Perspex, behind which was placed a 24 w bulb. This assembly was attached by means of a Terry spring clip to one limb of the manometer and could be adjusted to take up a position behind the meniscus in either of the limbs. This device, as well as increasing the accuracy of the readings, greatly reduced the eye strain involved in determining the mercury level.

It was also found, before carrying out this calibration, that with both limbs of the manometer at pressures less than 10^{-3} torr the levels in the two limbs were not equal, the so called reference side, attached to an independent vacuum system, showing a positive pressure of 3 torr. On dismantling the manometer it was found that when atmospheric pressure was present in both limbs this effect was not present, the levels in both limbs being equal. This would appear to indicate that the cause is not irregularities in the bore of the manometer tubing. On recleaning the tube with hot chromic acid, redistilling the mercury and thoroughly flaming out the limbs under vacuum before reassembling the manometer it was found that the discrepancy was greatly reduced, a positive pressure of about 0.4 torr in the reference tube being obtained. This discrepancy could not be explained in terms of capillary depression due to the observed differences in meniscus height (92) since the observed maximum difference in meniscus height, viz. 0.18 mm, would only have produced a capillary depression of less than 0.035 torr. In the calibration of the spiral gauge and in all subsequent absolute pressure measurements a correction has been made to the observed pressure readings to allow for this non-zeroing of the manometer.

(9.18.) The Electromagnetic, Hollow Piston Type, Gas Agitators

It was found that owing to the extreme sensitivity of the spiral Bourdon gauge to vibration, it was not possible to use it in conjunction with the gas cycling pump described in section 9.8. It was necessary, therefore, to construct some device which would effectively agitate the gases in the catalyst vessel without producing any vibration in the system attached to the gauge. In addition, the volume of the system in which the film had to be evaporated was required to be as small as possible. Further, any device had to be made from completely inert materials to avoid contamination of the film. These requirements were satisfied by use of a hollow cylindrical glass piston which fitted loosely into the catalyst vessel itself as indicated in Fig. 9.6. This was constructed from 18 mm O.D. Pyrex tubing, 9 cm in length. This length was sufficient to prevent the piston coming in contact with the hairpin filament of nickel wire. To the closed end of the piston was attached a 20 cm length of 10 mm O.D. tubing into which was fitted a 12 cm length of soft iron, 6 mm in diameter. The iron was held in position at the top of the tube by a constriction. The iron-containing section of the piston was evacuated and sealed off.

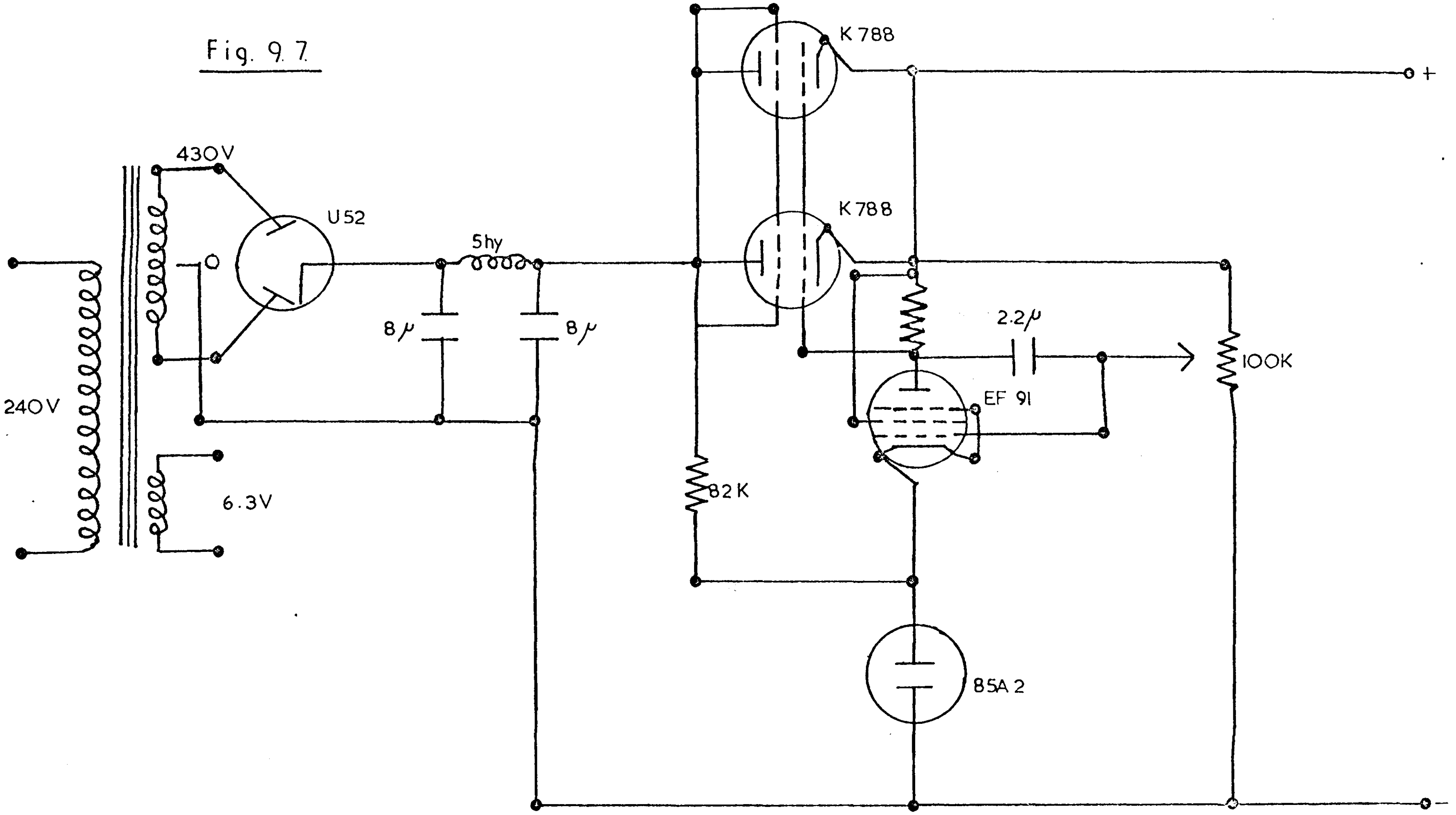
It was necessary to increase the volume of the catalyst vessel from that used previously to enable the piston to be kept clear of the nickel filament during the evaporation of the film. This is the position of the piston indicated in Fig. 9.6. It was also necessary to attach to the opposite end of the catalyst vessel from the tungsten seals a connecting tube whose bore was sufficiently large to admit entry of the iron-containing portion of the piston.

The position of the piston within the catalyst vessel was controlled by placing the coil of an electromagnet round that portion of the piston containing the iron. The coil was energised using a 240 dc supply and drew a current of 0.02 A. The heat produced by this current was quite considerable and the inside of the coil which surrounded the catalyst vessel was cooled by passing water through a spiral of 3 mm diameter copper tubing wound inside the coil.

In the initial experiments using this system the catalyst vessel was mounted vertically and the electromagnet coil placed round the connecting tube. On energising the coil the piston was suspended in the catalyst vessel and by oscillating the coil vertically the piston could be made to oscillate within the catalyst vessel. The coil was attached to a metal framework which slid vertically on two parallel rods. The movement of the coil vertically on these rods was controlled by connecting the framework to a cam, operated by a Citenco motor. In order to produce a smooth movement, especially when the coil was moving downwards, a counter-weight was fitted, connected to the coil over a smooth pulley. The movement of the piston within the catalyst vessel caused an agitation of the gases across the surface of the film. The vibration caused by the movement of the piston itself was small. It was found, however, under experimental conditions that the movement of the counter-weight became irregular, particularly at high pumping speeds, and this caused a significant vibration in the apparatus which was transmitted to the spiral gauge. It also tended to cause the piston to fall out of the influence of the electromagnet and break on the bottom of the catalyst vessel.

STABILISED dc POWER SUPPLY

Fig. 9.7.



As a result of this a number of modifications were introduced in later experiments. The piston was suspended in the same electromagnetic coil as used previously, but this coil was now kept stationary, and a second coil similar to the first was fitted directly above it. This second coil was energised at intervals by passing the energising dc current through a suitable switching device which is described in section 9.19. This caused the piston to rise and fall while still suspended under the influence of the lower coil. This system produced virtually no vibration and it was found unnecessary to switch it off while taking a gauge reading. In order to prevent the piston from fracturing itself on the catalyst vessel if it fell out of the influence of the lower coil, buffers were fitted to the ends of the tungsten leads. These consisted of lengths of nickel wire similar to that used for film evaporation, attached to the tungsten leads so that they protruded at right angles to the leads and cushioned the fall of the piston.

(9.19.) The dc Power Supply and Electronic Switching Device

A dc power supply was used to energise the coils of the gas agitator, as it was found that this produced less heat in the coils due to self induction than did the corresponding ac supply. This supply was capable of producing a stabilised dc voltage of 200 - 240 v

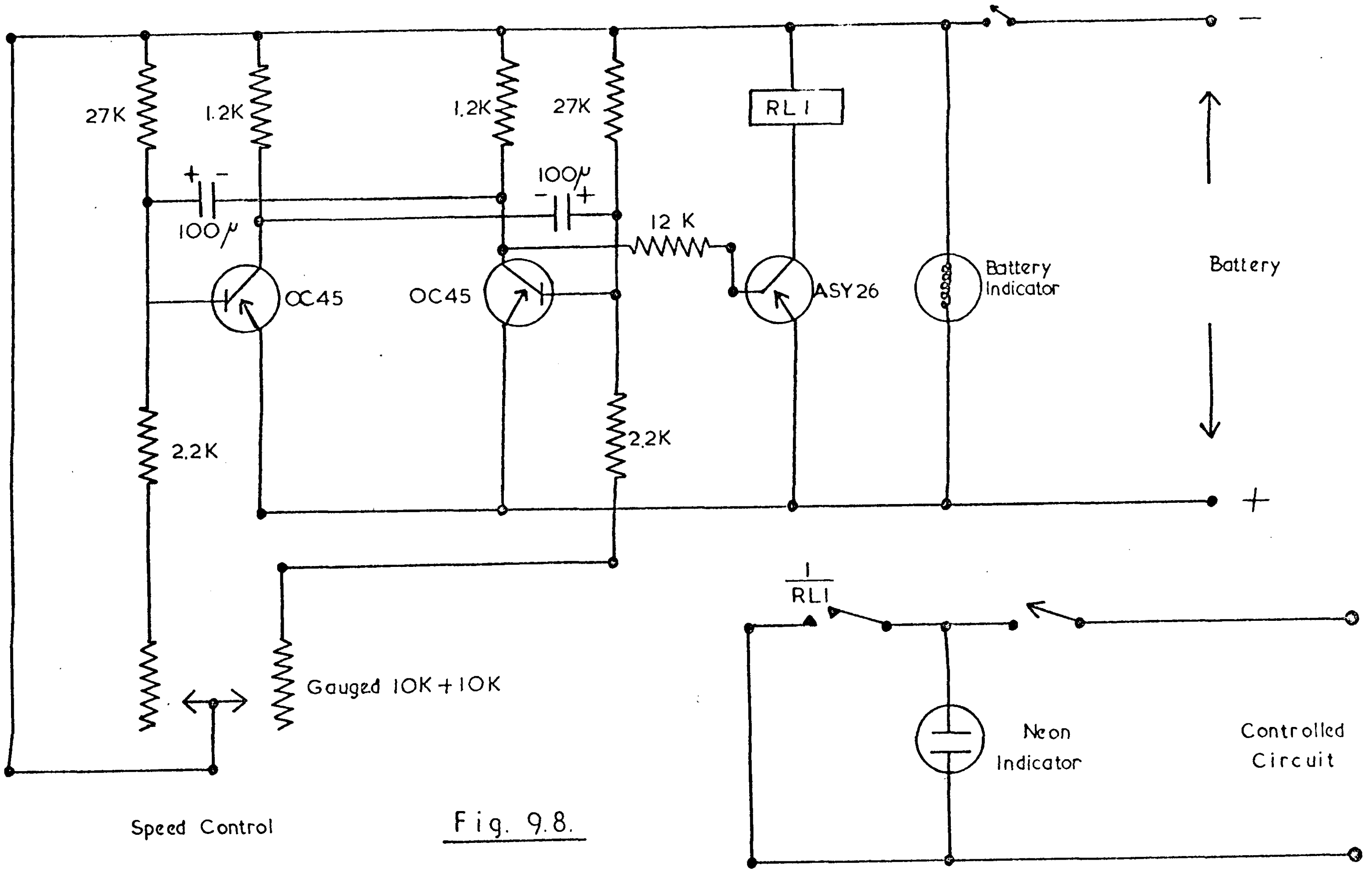


Fig. 9.8.

ELECTRONIC SWITCHING DEVICE

at a current of up to 200 mA. The circuit diagram is given in Fig. 9.7.

Experience of various types of switching devices had indicated that those operated mechanically, particularly those entailing the use of a belt or chain drive, were unreliable. Consequently a robust, reliable, electronic device was produced. This consisted essentially of a 12 v powered circuit, employing two transistors in oscillation, which activated a relay through which the dc current was controlled. The circuit diagram is given in Fig. 9.8.

(9.20.) The Air Thermostat

It was discovered that the air temperature of the laboratory in which the hydrogenation apparatus was constructed could vary considerably in the time necessary to carry out a series of experiments. Since it was found that this temperature could not be controlled efficiently without the production of variable temperature gradients across the apparatus, it was considered advisable to thermostat that portion of the apparatus containing the gas storage and pressure measuring systems. This was achieved by enclosing the appropriate portion of the system with a cardboard framework. The front of this framework was covered with a large polythene sheet which permitted access to the interior of the thermostatted region without greatly altering the internal air temperature. The temperature of the air in the thermostat, which had a volume of 600 l, was maintained at a constant value using a 150 w electric light bulb and a temperature controller. This controller consisted of a 500 cc gas thermometer fitted with electrical contacts of platinum and filled with dry air to a pressure of 100 torr. The controlling device was used in conjunction with a Sunvic type F 102-3 hot wire vacuum switch. The air in the thermostat was circulated using a fan attached to a 12 v electric motor positioned such that it increased the circulation due to convection caused by the electric light bulb. It was found that the temperature throughout the thermostat could be controlled within half a centigrade degree of the desired temperature provided that the room temperature did not rise appreciably above this. Usually the thermostat was maintained at 23°C as a suitable compromise between temperatures above which the normal room temperature might occasionally rise and temperatures which would lead to excessive softening of the tap grease.

(9.21.) The Water Thermostat

The design of the catalyst vessel used with the hollow piston gas agitator permitted use of a conventional water thermostat bath both for controlling the temperature during film evaporation and during hydrogenation. This tank was normally maintained at $24 \pm 0.2^\circ C$ using a 60 w electric light bulb and a Sunvic type TS3NC temperature controller. The tank itself which had a capacity of 30 l was fitted with a heat exchanger through which cooling water could be passed. The water was circulated in the tank using a Stewart and Turner, type 10R8806, mains operated, water pump which had a pumping speed of 5400 l per hour.

(9.22.) Preparation of Radioactive Mercury

Radioactive mercury was obtained from the Atomic Energy Research Establishment, Harwell, and it contained the active mercury isotopes ^{203}Hg and ^{197}Hg. The initial activities were 30 mC ^{203}Hg and 750 mC ^{197}Hg obtained by irradiation of 2 g mercury for 2 weeks in a flux of 10^{12} neutrons/cm^2/sec.

These isotopes had half-lives of 47 d and 65 hr respectively. After removal from the reactor the mercury was allowed to decay for at least a fortnight to reduce the activity of the shorterlived isotope to a relatively negligible value. A sample of this mercury was diluted with inactive mercury if necessary to give a count of about 3000 counts min^{-1} when 10 mg were counted on a nickel tray

PURIFICATION OF RADIOACTIVE Hg

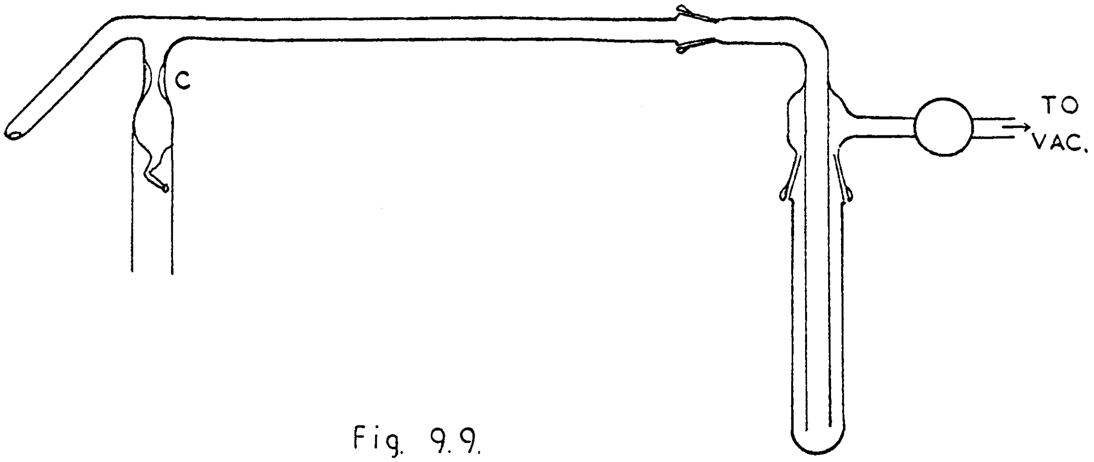


Fig. 9.9.

PLATEAU OF GAMMA COUNTER MX120

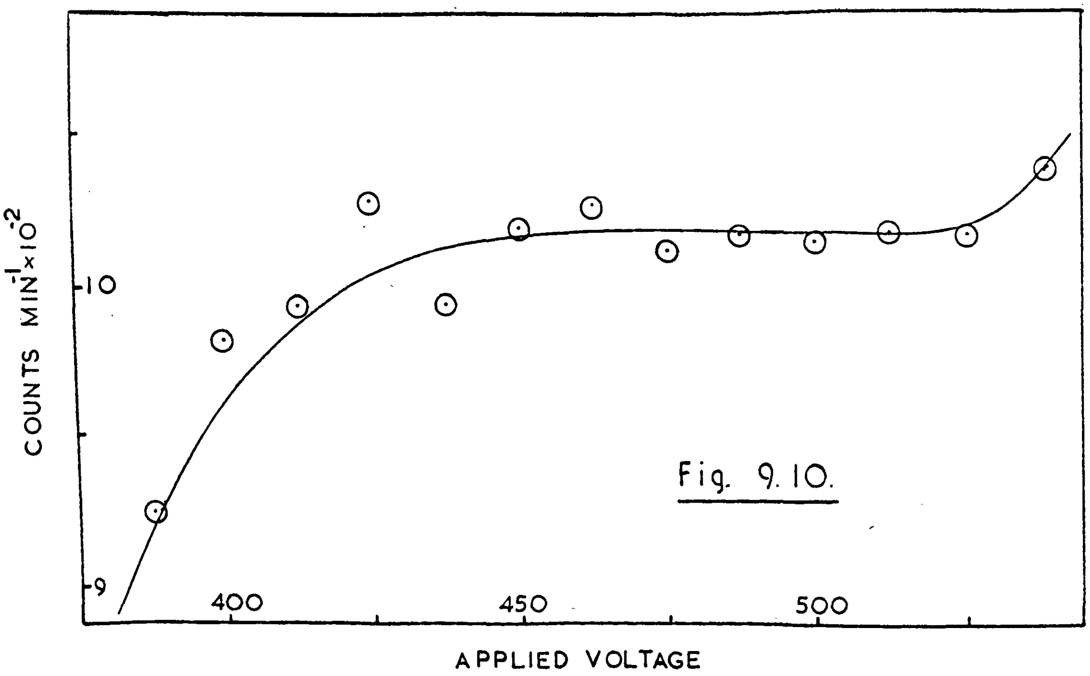


Fig. 9.10.

4 cm from the window of an end-window counter. The mercury was distilled into break-seal tubes using the apparatus shown in Fig. 9.9. This was attached to the mercury free vacuum system by means of a large liquid nitrogen trap and a tap which prevented contamination of the apparatus. The tap was opened only when a high vacuum (10^{-5} torr) was required in the system, before distillation and again prior to sealing off the break-seal at the previously degassed constriction, C. The break-seal tube containing the purified radioactive mercury was attached to the hydrogenation system as indicated in Fig. 9.6.

(9.23.) Continuous Estimation of Mercury Adsorbed on Nickel Films

It was necessary to determine how much mercury was present on the nickel film at any particular time and this was obtained by counting the radiation produced by the ^{203}Hg. The energy of the gamma radiation resulting from the decay of this isotope (0.29 meV) was sufficiently high for it to pass through several millimetres of glass without significant absorption. The counter used was a Mullard MX 120. This had a cathode consisting of a stainless steel cylinder 17.5 mm long and 2.2 cm in diameter and was filled with a neon argon mixture with bromine as quenching agent. This counter operated at a voltage of 475 v and had a plateau of length about 100 v, as shown in Fig. 9.10.

The counter was fitted inside a 24 mm diameter Pyrex tube which was placed parallel to and in contact with the catalyst vessel in the thermostat tank so that the complete length of the film was accommodated in the working sector of the counter. Rigid geometry was obtained by positioning the counter tightly inside its outer tube and attaching this to the catalyst vessel with plastic adhesive tape. Campbell and Thomson (20) have studied the effect of radial distribution of mercury on such a counting system. They have shown that, provided the filament was not locally close to the vessel walls during evaporation, thus causing an uneven distribution of metal and hence of mercury, this technique for the determination of mercury was satisfactory. Care was, therefore, taken to position the filament in the centre of the catalyst vessel during its construction.

The ancillary counting equipment used in conjunction with this counter consisted of an Ericsson Telephones Ltd. type 110A probe unit with a 500 micro second paralysis time, and an Ekco Electronics type N529B scaling unit. The counter was shielded from the mercury source by surrounding the latter with 1 cm thick lead and in order to further reduce the background the catalyst vessel and counter in the thermostat were surrounded by a cylinder of 3 mm lead sheet having a diameter of 15 cm. This cylinder was so designed that it did not impede efficient circulation of water round the catalyst vessel.

When the specific activity of the mercury obtained on this counter had been determined a calculation showed that the amount of mercury present in the vapour phase in the volume of the catalyst vessel seen by the counter was insufficient to be detected on the counter.

(9.24.) Determination of Absolute Weight of Mercury Present on Nickel Films

Owing to geometrical considerations, it was not possible to determine the absolute weight of mercury present on the film using the counting system described in section 9.23. Consequently when a film had been completely poisoned, it was dissolved in 25 cc of 10N nitric acid and 10 cc of this solution counted in a 20th Century Electronics liquid counter type M 64, using the same ancillary equipment as described in section 9.23. The count rate obtained from this solution was compared with the count rate obtained, under exactly the same conditions, from 10 cc of a standard solution. This standard was prepared by dissolving an accurately known weight of mercury, derived from the same mercury source as that used to poison the film, in a known volume of 10N nitric acid. By proportion the weight of mercury finally present on the film could then be obtained. Since the count produced by this weight of mercury on the halogen quenched counter was also known, it was possible to calculate the weights of mercury present on the film at various intermediate stages, knowing the counts these produced on the halogen quenched counter.

In order to determine whether there was a self-absorption effect of the nickel ions in solution, nickel nitrate was added to the standard solution to give a nickel ion concentration similar to that of the solution containing the film. This produced no difference in count rate indicating that self-absorption effects were negligible.

(9.25.) Pre-evaporation Treatment of Catalyst Vessels in the Hollow Piston Containing System

The design of the catalyst vessel used with this system is indicated in Fig. 9.6. A side arm containing a break-seal S1 and a constriction C1 was attached to the catalyst vessel. This enabled the vessel to be thoroughly degassed in a part of the system which did not contain greased taps and which was remote from the pressure measuring device. It was found possible to use one catalyst vessel for the production of a number of films, thus eliminating the need to construct a new vessel for each film. The used catalyst vessel was split open at a level just below where the nickel wire was connected to the tungsten leads and the film removed with 10N nitric acid, as indicated in section 9.24. The nickel wire was removed and replaced with an unused length. The vessel was then reconstructed by holding the two portions tightly against each other, making sure that they were in exactly the same relative positions as before, and rotating them in an increasingly hotter gas/oxygen flame until a vacuum tight seal was produced.

The procedure for degassing the glass of the catalyst vessel was similar to that described in section 9.10., the main portion of the catalyst vessel being enclosed in a cylindrical, electrically wound furnace capable of reaching 500°C. In addition those parts of the vessel which could not be included in the furnace were covered with several layers of insulated heating tape, operated by means of a Variac variable transformer. This was capable of maintaining a temperature of about 450°C. Care was taken to degas the constriction C1 completely, using a soft gas flame. This was carried out by heating the constriction until the glass was seen to soften slightly and cause a yellow colouration in the flame.

During the evaporation of films in the cycling pump system it was observed that an appreciable increase in pressure occurred in the catalyst vessel when the current passing through the filament was increased to a value above 4 A, the current at which the wire had supposedly been completely degassed. Using the piston containing system this phenomenon was investigated further. With the furnace and heating tape at 450 - 500°C the catalyst vessel was pumped to a pressure of 5×10^{-5} torr.

The tap connecting the catalyst vessel to the vacuum pumps was then closed for 20 sec, although the catalyst vessel was still connected to the Penning Gauge, and in this time the pressure measured on the gauge was seen to rise to 1.1×10^{-4} torr. The catalyst vessel was then pumped to its original pressure and the procedure repeated, this time with a current of 4 amps flowing through the filament. It was now found that the pressure of the system rose to 1.3×10^{-4} torr in 20 sec indicating that gas was being given off from the wire. The catalyst vessel was, therefore, pumped for at least 6 hours with a current of 4 A passing through the filament, after which time on shutting off the pumps the pressure read from the gauge increased to 3×10^{-5} torr in 20 sec. The current passing through the filament was then increased to 6 A and on closing off the pumps the pressure in the catalyst vessel rose to 1.5×10^{-4} torr indicating that gas was now being given off from the wire which had been unable to escape during the six hours that the current had been at 4 A. Consequently the current was repeatedly raised to 6 amps for short intervals of time until an increase of pressure was not observed in the catalyst vessel when this current had been flowing for half a minute. It was found the total time required at 6 amps to attain this condition was about 5 - 6 minutes. During this time an appreciable film had been deposited from the wire. It was arranged, therefore, during this degassing process that the piston was covering the filament and the film was deposited on its internal walls. The film so produced was found to be inactive for hydrogenation as would be expected, since it was evaporated at a high temperature and would be considerably sintered. This film was kept separate from the main film and was assayed independently; it was found to have weights varying between 3 and 8 mg.

(9.26.) Experimental Procedure for Poisoning Cyclopropane Hydrogenation with Mercury

After the catalyst vessel and filament had been thoroughly degassed as described in the previous section and the ultimate pressure obtained was in the region of 2×10^{-5} torr, the catalyst vessel was sealed off at the constriction Cl. It was then transferred to the thermostat tank, the leads for the evaporation current connected and the gamma counter fitted. After adjusting the position of the vessel and of the electromagnetic coils to ensure that the piston would operate vertically, the catalyst vessel was glass-blown onto the pressure measuring portion of the apparatus. By energising the topmost coil, the piston was lifted clear of the nickel filament and was maintained in this position while the film was evaporated onto the walls of the vessel by the passage of 6.4 A. During this process the connecting tubing P1 was evacuated and flamed with a soft gas flame to obtain an ultimate pressure of about 1×10^{-4} torr.

As soon as possible after the breaking of the filament, normally within one or two minutes, the reactant mixture, already at a predetermined pressure, was admitted to the catalyst vessel by fracturing the break-seal S1 with a steel ball. It was necessary to adjust the pressure of the gas to a predetermined value before expansion into the catalyst vessel in order to reproduce the initial gas pressure in the catalyst vessel from run to run. The initial pressure of the gas in the catalyst vessel and on both sides of the gauge was measured on the manometer as indicated in section 9.14. One minute after admission of the gas the tap T8 was turned to isolate the catalyst vessel from the gas storage system and the tap T7 turned to connect the catalyst vessel to the inside of the pressure gauge. As before any change in pressure which now occurred in the catalyst vessel produced a reading on the gauge. The piston was then set in motion and it was not necessary to stop it in order to take a gauge reading,as little vibration was produced if the catalyst vessel had been properly aligned. Pressure readings were usually taken at one minute intervals until the reaction had proceeded to the desired extent. The gas in the catalyst vessel was then pumped out via tap T8,using the rotary pump for 30 sec. The catalyst vessel was isolated by turning tap T8, the pressure inside and outside the gauge was equalised and this along with the manometer was pumped out, also on the rotary pump, taking the precautions indicated in section 9.14. When it was decided to admit mercury to the film the break-seal S2 was fractured, using the same steel ball as was used for S1, while the catalyst vessel was isolated after it had been pumped out. After the appropriate length of time a fresh charge of gas was admitted to the catalyst vessel as before and the procedure described above repeated. Before admitting mercury to the film a background count on the counter had been taken. During the hydrogenation immediately following an admission of mercury a further count was taken, normally for 20 min, indicating the relative amount of mercury present on the film during the hydrogenation. It was assumed that while gas was present in the catalyst vessel mercury was unable to diffuse onto the film. This was verified by leaving a film in contact with the mercury, under the experimental pressure of gas, for a number of hours. No mercury was found to arrive at the surface during this time.

(9.27.) Treatment of Results

It was necessary to convert the gauge readings obtained to absolute pressure differences. This was carried out either by direct conversion, using the calibration graph, as in the case of Films 1 and 2 or more normally by multiplying the gauge reading by a suitable conversion factor obtained from the gradient of the calibration graph. In the case of the first spiral Bourdon gauge, as used for Films 13 to 24, an additional intercept term, derived from the calibration graph, was also considered. As was stated in section 9.6. owing to the fact that the manometer did not zero satisfactorily, a non-zeroing correction, normally 0.039 torr, was added to pressure readings measured directly from the manometer.

It was found that a linear relationship existed between the $\log_{10}$ of the cyclopropane partial pressure and time indicating that apparently first order kinetics were operating. The gradient of this linear relationship was taken as a measure of the reaction rate. The cyclopropane partial pressure (P_c) was calculated as follows:

Let initial partial pressures of hydrogen and cyclopropane be a, b respectively

therefore, the total initial pressure $P_o = a + b$

Let hydrogen react until a fraction x is left

Partial pressure of hydrogen at that stage $= ax$

Partial pressure of cyclopropane $= b - a(1 - x)$

Partial pressure of propane $= a(1 - x)$

$\therefore$ total pressure (P_t) $= b + ax$

Partial pressure of cyclopropane at any time $= b - a + ax$

$= P_t - a$

where $a = P_o$ x the fraction of the gas which is hydrogen

i.e. $P_c = P_t - a$

but the pressure difference (PD) measured on the gauge

at any time $= P_o - P_t$

$\therefore P_t - a = (P_o - a) - PD = P_c$

$(P_o - a)$ being a constant for each hydrogenation reaction

The values of P_c with respect to time were plotted on semi-logarithmic paper and the gradients calculated to the base 10. Since as many as thirty hydrogenations were carried out on one film, each hydrogenation containing twenty results, the calculation of the rate constants proved to be a tedious process. Consequently two simple computer programmes for the English Electric KDF 9 computer were prepared. The first of these converted the gauge readings into pressure differences and expressed these in terms of cyclopropane partial pressures. The solution material was designed such that it could be fed directly into the computer as data for a second programme which calculated the rate constant for each hydrogenation using the method of least squares. Further details of the programmes and their use are given in Appendix 5.

(9.28.) Determination of Weights of Nickel Films

The weights of the nickel films were obtained using a procedure well tried in this laboratory involving the colorimetric analysis of the nickel III dimethylglyoxime complex. The film to be analysed was dissolved in 25 cc of warm 10N nitric acid. If the film had contained mercury 10 cc of this solution had already been counted in a liquid counter as was described in section 9.24. The 25 cc of solution containing the film were diluted to 1 litre with distilled water. 10 ml of this solution were measured out with a pipette and transferred to a 50 ml standard flask. 10 ml potassium bromate-bromide solution (3 g $KBrO_3$ and 12 g KBr per litre, giving 0.1N bromine on acidification) were added to oxidise the nickel to the trivalent state. The solution became yellow because of liberation of excess bromine. 1 ml dimethylglyoxime (1% in ethanol) was added followed by 10 ml ammonia solution (0.88 ammonia diluted 1:10). The resulting red solution was diluted to 50 ml with distilled water.

It had previously been shown (20) that the optimum conditions for carrying out a colorimetric analysis of this solution were to allow the colour to develop for at least 30 min and to use light of a wavelength 465 μ. The optical density of the unknown solution at this wavelength was determined in duplicate and was compared with that from a series of accurately prepared standards.

In order to obtain reproducible results it was found that considerable care was required in the preparation of the nickel complex solutions and in determining that the absorption cells were perfectly clean and free of bubbles. When such precautions were taken the results were found to be reproducible within 1 - 1.5%.

(9.29.) Study of Mercury Adsorption on Clean Nickel Films

The design of the catalyst vessel and its treatment before and during evaporation of the film were identical with that described in section 9.25.

As soon after the breaking of the filament as possible the break seal S1 (Fig. 9.6.) was broken and the catalyst vessel section isolated at the tap T8. The mercury was admitted to the film by breaking the seal S2 as before. In later experiments in this study a constriction was constructed in the tubing between tap T8 and the mercury source. This was sealed off after the connecting tubing had been pumped to a high vacuum and prior to breaking the seal S1. This enabled adsorption of mercury to occur in the absence of the greased tap T8.

Since it was desired to follow the uninterrupted arrival of mercury onto the film with time it was not possible to take counts over such long periods of time as in the poisoning experiments. Consequently, in order to maintain the same counting efficiency, viz. about 2%, it was necessary to increase the specific activity of the mercury by a factor of four or five. As the amount of mercury arriving on the catalyst increased, the statistical error on the count decreased since the length of time for which the count was taken was kept the same. In practice the error varied from 5% in the initial stages to less than 1% at high coverages. Owing to the increased specific activity increasing the background count, and in an attempt to control the mercury source at a lower temperature than the film, to avoid distillation from the source, the original shielding round the source was replaced by a cylinder of 3 mm thick lead sheeting enclosed in 6 cm diameter, closely wound spiral of lead piping, of 1 cm bore, through which cooling water was passed.

CHAPTER 10

THE STUDY OF CYCLOPROPANE HYDROGENATION ON SUPPORTED METAL CATALYSTS: EXPERIMENTAL

(10.1.) The High Vacuum System

The apparatus was a conventional vacuum system constructed from Pyrex glass and having stopcocks greased with Apiezon N grease. An Edwards Speedivac rotary pump and an Edwards ES 35 air cooled, single stage, oil diffusion pump were used to produce the vacuum which was measured by means of an Edwards type GSB-2 Pirani gauge. A two vacuum line system was used to enable large pressures of gas to be removed using the rotary pump, without affecting the high vacuum maintained by the diffusion pump. The use of oil pumps and the electronic pressure measuring device resulted in a mercury free system.

(10.2.) Gas Storage and Purification

The reactants were purified in the manner described in section 9.12. and the method of preparation of the equimolar reaction mixture of cyclopropane and hydrogen was also similar to that already described. In addition a 2 l bulb was filled with purified hydrogen for use in the activation of the catalysts.

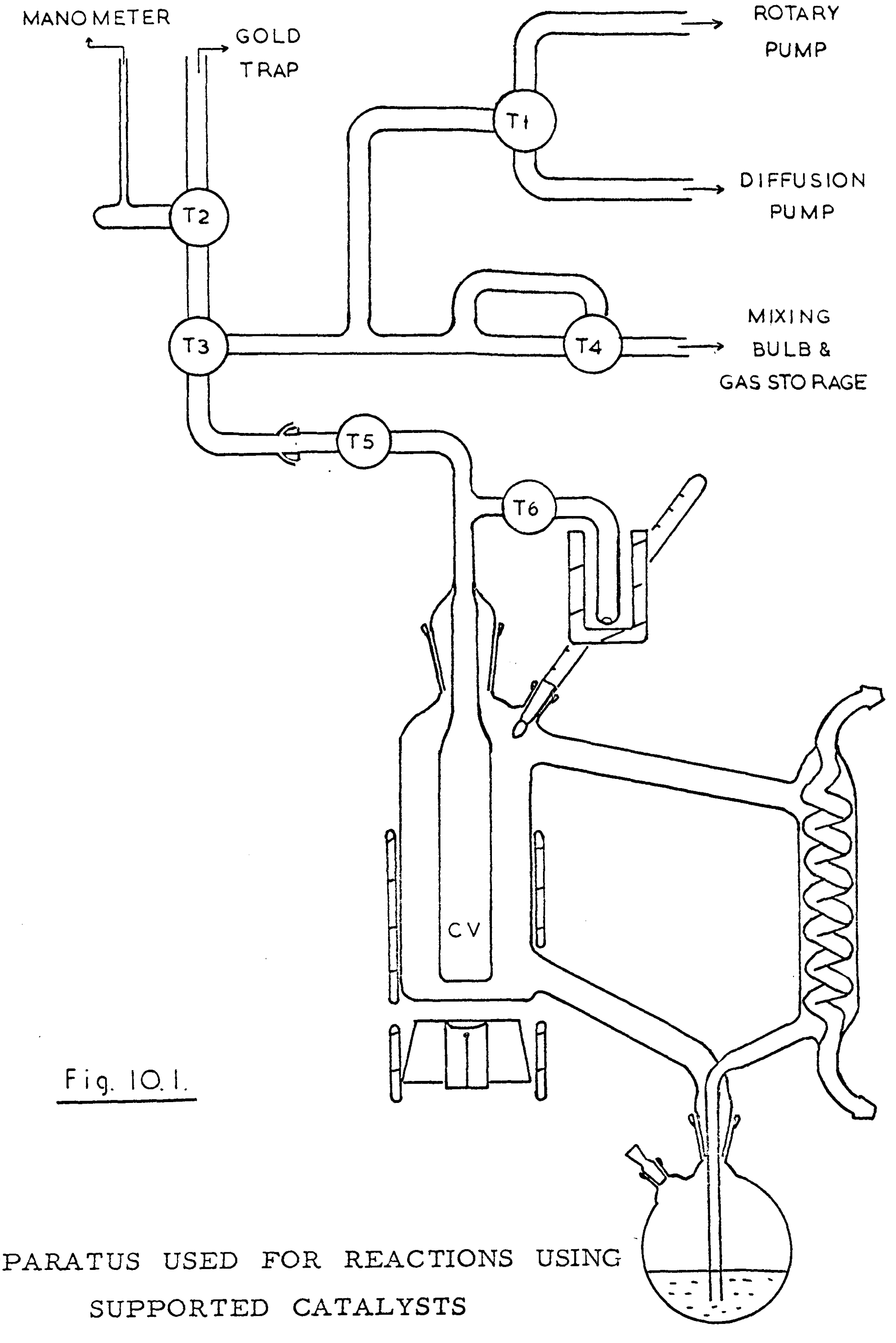


Fig. 10.1.

APPARATUS USED FOR REACTIONS USING SUPPORTED CATALYSTS

The storage bulbs were attached to a common manifold to which was also attached a 500 cc mixing bulb which enabled mixtures other than 1:1 hydrogen:cyclopropane to be prepared. This manifold was connected to the reaction vessel and the pressure measuring system by means of a three-way tap T4 as is indicated in Fig. 10.1. This enabled the reactant gases to be admitted to the reaction vessel directly or by means of a capillary leak.

(10.3.) The Mercury Manometer

It was decided to use a mercury manometer to follow the course of the hydrogenation reactions since experience had indicated that mercury vapour cannot diffuse through the reactant gases under experimental conditions at any appreciable rate. In addition such manometers have commonly been used by other workers in the field of hydrogenation kinetics without any adverse reports of poisoning effects. It was considered that, provided adequate precautions were taken to protect the catalyst from mercury vapour, particularly when the catalyst was under vacuum, a mercury manometer was much more satisfactory than indirect pressure measuring devices.

The manometer was of the single limb type and was constructed from an 85 cm length of 2 mm bore, thin walled, Veridia glass tubing.

One end of the limb was immersed in a reservoir of mercury and the other was connected to the rotary pump vacuum line by means of a three-way tap T2, Fig. 10.1. This tap also enabled the manometer to be connected to the catalyst vessel. The pumping system was protected from mercury vapour by a gold trap. This trap was prepared by soaking glass wool, which had previously been cleaned in boiling aqua regia, in a concentrated aqueous solution of gold chloride. Most of the water was removed by evacuating the tube, and the chloride was reduced to metallic gold by heating it in a furnace at 200°C for 25 hours in a stream of hydrogen. Care was taken to isolate the gold trap from the manometer when not in use to prevent distillation of the mercury into it.

The manometer tube was mounted vertically on a meter rule. A second meter rule was placed on top of the first and was clamped in position before each hydrogenation such that the mercury level in the manometer was at 60 cm on this scale when the manometer was under vacuum. On the few occasions that changes in atmospheric pressure occurred during hydrogenations suitable pressure corrections were made. It was found that a considerable surface tension effect was present in the manometer which was most obvious when the pressure in the manometer was changing. This effect was removed by tapping the manometer vigorously before taking a pressure reading.

(10.4.) The Catalyst Vessel and Constant Temperature Vapour Bath

Two catalyst vessels were used during the course of the hydrogenation studies each having a volume of about 50 cc. The vessel (CV) was constructed with a flat base,as is indicated in Fig. 10.1., so that the catalyst could be distributed evenly across it in an attempt to idealise the counting geometry of the system when the adsorbed mercury was estimated. The catalyst vessel was fitted with a side arm which contained a small bore greased tap T5 and a 12/5BS ground glass socket. This enabled the catalyst vessel to be sealed, removed from the vacuum apparatus and transferred to a furnace for activation of the catalyst.

Preliminary experiments indicated that unlike nickel films, 0.5 g of 5% nickel on pumice catalyst was inactive for the hydrogenation of cyclopropane at room temperature. Owing to considerations of counting efficiency it was not feasible to increase the weight of catalyst used. Thus to obtain a measurable rate it was necessary to carry out the reaction at a higher temperature. Experience had shown that use of a nichrome wire wound furnace was not advisable where accurate temperature control was required, because of temperature gradients within the furnace and variations in temperature caused by fluctuations of the mains voltage. Consequently a constant temperature vapour bath was designed and is also shown in Fig. 10.1.

A liquid boiling at a suitable temperature was heated in the round bottom flask and the vapour produced was directed into the main vessel into which was fitted the catalyst vessel. Vapour which did not condense in the main vessel was led into a water cooled spiral condenser and the liquid formed returned to the flask. A thermometer inserted between the main vessel and the condenser indicated the vapour temperature. The catalyst vessel was positioned such that liquid drained from the bottom of it completely and did not form a continuum with the liquid lying at the foot of the vapour bath. The level of the liquid at the foot of the main vapour bath vessel was kept constant by allowing it to overflow into the heating flask. These precautions ensured that the quantity and hence the absorbing power of liquid through which the radiation from the mercury had to pass was always constant. Normally the temperature of the bath was maintained at 78°C using ethanol, but water, methanol or ether have been used.

The first catalyst vessel was used for the majority of the supported catalyst work and the second for the later work on pumice supported palladium. Each vessel possessed a different proportion of its volume within the vapour bath.

	Vol. at bath temp.	Vol. at intermediate temp.	Vol. at ambient temp.
Vessel 1	41 ml	3 ml	8 ml
Vessel 2	50 ml	3 ml	6 ml

(10.5.) Purification of Pumice

150 g of British Drug Houses powdered pumice (less than 120 mesh) was purified by boiling with 300 cc concentrated hydrochloric acid for half an hour. A brisk effervescence occurred and after allowing the pumice to settle the supernatant liquid was found to be yellow in colour. This supernatant liquid was decanted and the residue boiled with a further 200 cc of acid for half an hour. This procedure was repeated and after decanting the acid, 200 cc of distilled water were added and the solution again boiled for half an hour. After decanting, a further 200 cc of acid were added. This procedure was repeated until the supernatant liquid after boiling was a faint yellow colour. The pumice was freed from acid by repeated washing with distilled water. The residue was allowed to settle for about 2 min before decanting but after this time not all the pumice had settled out. Particles in suspension after this time were discarded with the washings. When free of acid the pumice was dried in an oven at 130°C for 10 hours. The approximate weight of

the pumice after purification was 80 g.

(10.6.) Preparation of 5% Nickel on Pumice Catalyst

Preliminary experiments indicated that the following was the most successful method of preparing a homogeneous catalyst. A smooth slurry was prepared by adding 60 cc of distilled water to 25 g of purified pumice in an evaporating basin. A solution containing 18.574 g of Analar nickel nitrate hexahydrate in 25 cc of distilled water was then added to the slurry, which was stirred vigorously. The basin was transferred to a sand bath maintained at a temperature of about 150°C and the water evaporated off with continual stirring, leaving the green nickel nitrate deposited on the pumice. Care was taken to mix the catalyst thoroughly, particularly when little water was left. Evaporation was continued until the catalyst became almost dry, when it was placed overnight in an evacuated vacuum desiccator.

The pumice-supported nickel nitrate was decomposed to nickel oxide by ignition in a muffle furnace at 350°C for 15 hours.

Batches of this oxide catalyst, 5 g in weight, were reduced to metallic nickel as required by heating them in a furnace at 480 ± 20°C in a stream of hydrogen for 10 hours and were allowed to cool in hydrogen. The reduced catalyst was stored in a stoppered bottle in air. Before use it was activated by heating it in the catalyst vessel under hydrogen at a pressure of 200 torr for 2 hr at a temperature of 250 ± 20°C.

(10.7.) Preliminary Experiments Using 5% Nickel on Pumice

Initial experiments were carried out using 1.0 g of 5% nickel on pumice catalyst, prepared as described in section 10.6., and a 1:1 hydrogen:cyclopropane mixture with initial pressures varying from 200 - 100 torr. These showed that at room temperature hydrogenation occurred at an inconveniently slow rate, less than 0.2 torr per minute. Consequently it was necessary to increase the temperature at which the reaction was carried out. Because of this, it was necessary to investigate whether measurement of the true rate of the reaction would be obscured by the change in pressure caused by the increase in temperature of the reactants.

The catalyst vessel was placed in a nichrome wire wound furnace which was allowed to reach equilibrium at 80°C. Hydrogen was admitted to the apparatus, except for the catalyst vessel, to a pressure of about 200 torr. This gas was then expanded into the catalyst vessel and readings of pressure taken at one minute intervals. It was found that the pressure attained after one minute did not alter over the next 5 min. This expansion was repeated on a number of occasions with the same result, indicating that the expansion which took place occurred extremely rapidly and was not observable beyond one minute after the gases had been admitted.

(10.8.) Experimental Procedure for Studying Hydrogenation on Supported Catalysts

A weighed amount of catalyst was placed in the catalyst vessel after breaking the side arm between the vessel and the tap T5 (Fig. 10.1.). The catalyst vessel was placed in position in the vapour bath and the side arm reconnected.

The catalyst vessel was then evacuated using the diffusion pump for about 10 min. Within this time the pressure in the vessel became insufficient to produce a Tesla coil discharge. The vessel was flushed out with purified hydrogen at a pressure of a few torr and evacuated once more. Hydrogen to a pressure of 200 torr was then admitted and the vessel isolated by closing the tap T5. The ball and socket joint was disconnected and the catalyst vessel removed from the vapour bath and placed in a tubular furnace which had reached equilibrium at a temperature of $250 \pm 10^{\circ}C$. After a period of one hour the catalyst vessel was removed from the furnace and allowed to cool before being returned to the vapour bath and reconnected to the apparatus by means of the ball and socket joint. The hydrogen used for activation was removed using the diffusion pump for a period of 10 min, the ultimate pressure obtained being about 1 x 10^{-3} torr. During this time the vapour bath had been switched on and had reached its equilibrium temperature.

The catalyst vessel was isolated by closing the tap T5 (Fig. 10.1.) and the cyclopropane/hydrogen mixture admitted to the connecting tubes between the gas storage system and the manometer. Unless otherwise stated, a previously prepared 1:1 hydrogen:cyclopropane mixture was used. The pressure of this mixture was adjusted to a predetermined value using the capillary leak. Before any pressure measurements were taken the manometer was evacuated using the rotary pump which was protected from mercury vapour by the gold trap. The tap T5 was opened and the three-way tap T3 turned clockwise through 90°, thus expanding the gas in the system up to the tap T4 into the catalyst vessel. The time of admission was noted and immediately the tap was turned clockwise through a further 180°, thus connecting the catalyst vessel to the manometer. As soon as the level of the mercury stopped oscillating, the pressure of the gas was measured (normally within 10 sec of admitting the gas mixture to the catalyst vessel). Further pressure readings were then taken (usually at 1 min intervals), care being taken to tap the manometer vigorously, to reduce surface tension effects, before each reading. The manometer normally remained connected to the catalyst vessel during the course of the reaction.

After the reaction had proceeded for the desired time, (usually 12 - 15 min) the three-way tap T2 was turned anticlockwise by 90^{o}, thus isolating the manometer. The catalyst vessel was then evacuated for about 50 sec using the rotary pump. During this time the pump had regained its original "hard" note. The catalyst vessel was not evacuated using the diffusion pump on this occasion since it was feared that in cases when the catalyst had been poisoned intentionally with radioactive mercury such an evacuation would contaminate the high vacuum system with mercury vapour. In any case the object in evacuating the catalyst vessel was merely to remove reactants and products to such an extent that those remaining in the vessel had a pressure which did not register on the manometer. The catalyst vessel was then isolated by closing the tap T5 and the gas mixture readmitted to the tubing between the capillary leak and the manometer, after turning tap T3 clockwise through 180^{o}. After a suitable time interval (usually 5 min) this mixture was expanded into the catalyst vessel as before.

(10.9.) Preparation of 5% Palladium on Pumice Catalyst

A 5% palladium on pumice catalyst was prepared using a similar technique to that described in section 10.6. 2.016 g palladium chloride ex Baker and Co., stated to be 60% palladium, was placed in a 50 cc round bottom flask along with 2 cc of concentrated hydrochloric acid and 13 cc of distilled water. This was then heated under a reflux condenser until all of the palladium chloride had dissolved. This solution was then added to a slurry containing 25 g of purified pumice, prepared as described in section 10.5., with 20 cc of distilled water and evaporated to dryness with constant stirring as before.

(10.10.) Reduction and Activation of Palladium Catalysts

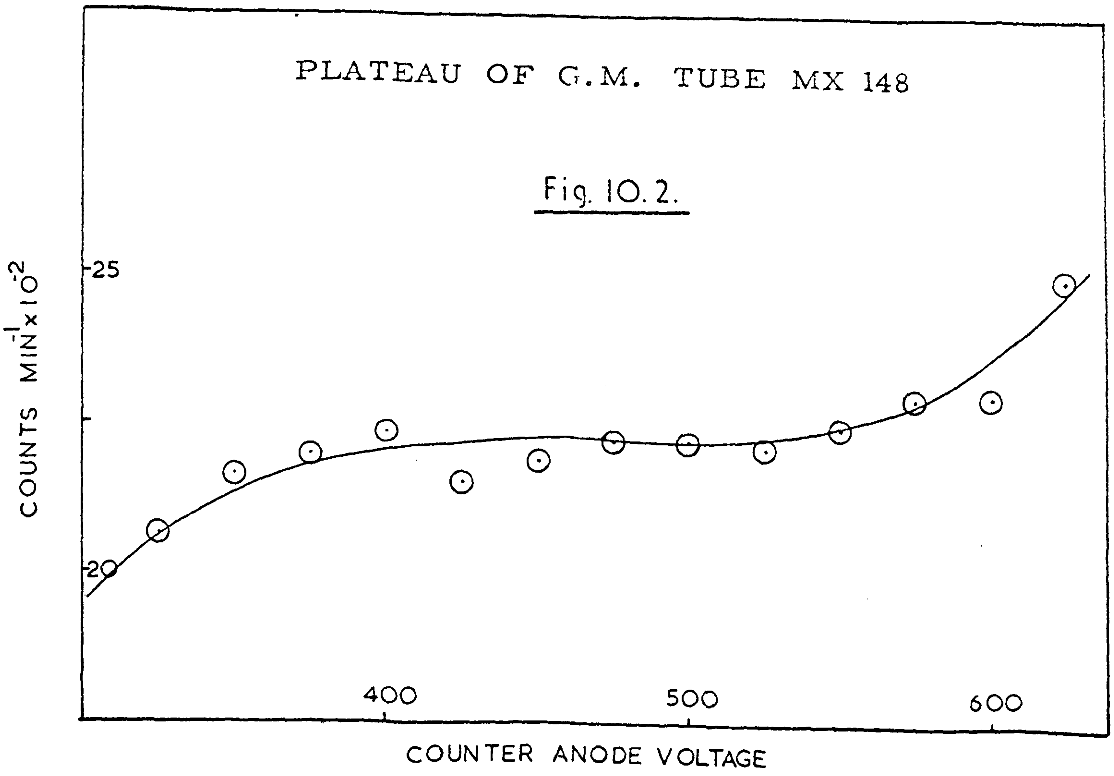
1. Palladium on Pumice

Initial experiments indicated that a 5% palladium on pumice catalyst reduced and activated in a similar manner to the nickel catalysts (see section 10.6.) and was inactive at 70°C and 100°C for cyclopropane hydrogenation. Since palladium salts are reduced much more readily than nickel, it was decided to reduce and activate these catalysts in situ in one process at 100°C.

The catalyst, 0.2 g, was placed in the catalyst vessel which was fitted onto the apparatus and evacuated as before. During the evacuation the vapour bath was kept at 100°C using water as the boiling liquid. Hydrogen was then admitted to the catalyst vessel and its pressure noted. It was found that the catalyst immediately turned from its original pink colour to black and there was an increase in gas pressure corresponding to the formation of hydrogen chloride. This increase was extremely rapid within the first minute after admission of hydrogen and became constant after a further three or four minutes. The total pressure increase for an initial hydrogen pressure of 120 torr was 20 torr. After 10 min the catalyst vessel was evacuated for 10 min using the diffusion pump and a further sample of hydrogen admitted. On this occasion also, a pressure increase was observed during the first minute after admission but was not nearly so great as previously observed, being in the region of 2.5 torr. During the next hour a negligible increase in pressure was observed. The catalyst vessel was evacuated once again and a further pressure of hydrogen admitted. On this occasion a negligible increase in pressure was observed within two hours. After evacuation using the diffusion pump for 10 min a pressure of about 1×10^{-3} torr was obtained. The catalyst vessel was then isolated, prior to admission of the gas mixture as before.

2. Palladium on Carbon

The 1% palladium on carbon catalyst used was obtained from Baker and Co., batch P10152. Owing to the very fine nature of the catalyst it was found necessary to fit a plug of clean glass wool in



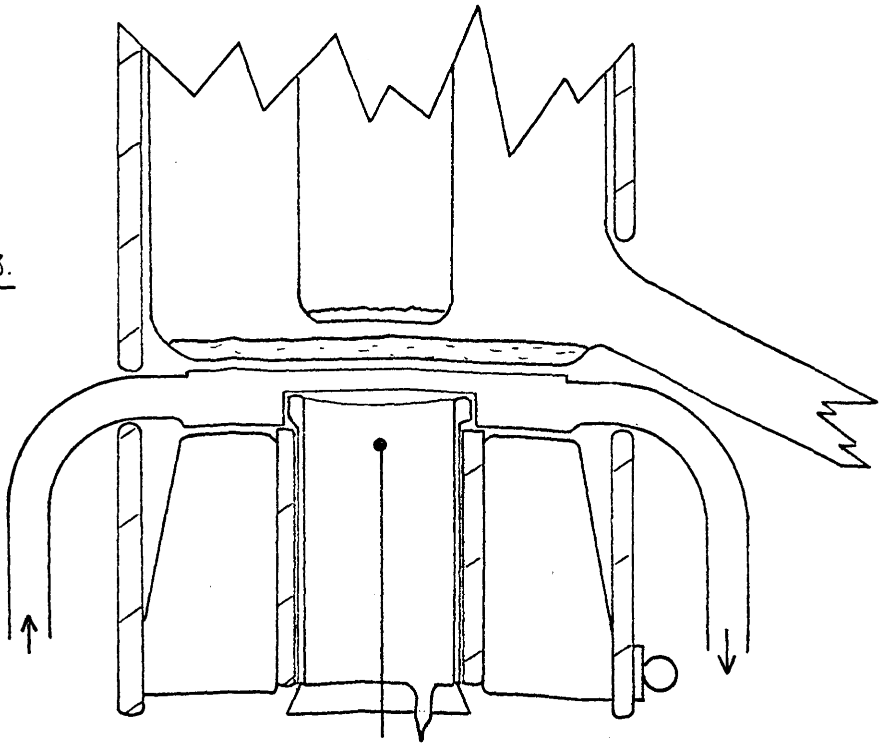
PLATEAU OF G.M. TUBE MX 148

Fig. 10.2.

DETAIL OF COUNTER COOLING SYSTEM

(Actual Size)

Fig. 10.3.



the neck of the catalyst vessel to prevent the catalyst being dispersed throughout the apparatus when evacuating the catalyst vessel. The catalyst was activated in situ in a similar manner to the palladium on pumice catalyst using only one charge of hydrogen. Further details are given in the results section.

(10.11.) The Detection of Radioactive Mercury on Supported Catalysts

The counter used for the detection of mercury adsorbed on the supported catalysts was a Mullard MX 148 end window, Geiger Muller tube. This counter was used in conjunction with the same ancillary equipment as described in section 9.23. It possessed a window area of 300 mm^2 and a window thickness of 1.5 - 2 mg per cm^2. The plateau obtained with this counter is shown in Fig. 10.2. In order to obtain the maximum possible count from the mercury present it was necessary to place the counter as near to the catalyst vessel as possible. Since the characteristics of G.M. tubes vary considerably with changes in temperature and during measurements the catalyst vessel was maintained at temperatures up to 100°C it was necessary to fit a cooling device, particularly round the window of the counter.

The device used is shown in detail in Fig. 10.3. It consisted of two concentric copper collars soldered to a copper disc having a circular hole in the centre, of diameter equal to that of the smaller collar. To the top edges of these collars, the smaller of which was 2 mm shallower than the larger, were soldered discs of 0.002 inch copper foil. Lengths of 8 mm diameter copper tubing were soldered into holes cut at opposite sides of the larger collar, enabling cold water to be circulated between the two copper foil discs. The internal diameter of the smaller collar was such that the window end of the counter fitted tightly into it. This enabled the metal casing of the counter to be in contact with the cooled copper. Copper foil was used in the construction of this cooling device for two reasons. Firstly, the foil was strong yet was of a thickness which did not absorb to any great extent the gamma radiation produced by the radioactive mercury to be counted. The β radiation also emitted by the mercury was of insufficient energy to penetrate the glass of the catalyst vessel. Secondly, the excellent thermal conductivity of the copper ensured that efficient cooling of the counter window was accomplished. The counter itself was enclosed in a cylinder of 3 mm lead sheet and inserted in a suitably drilled rubber bung, as is indicated in Fig. 10.3. An additional cylinder of lead sheet was fitted round the vapour bath and was held in position around the rubber bung using a Jubilee hose clip.

At a later stage in the work using this counter an attempt was made to increase the efficiency of the counter for the detection of gamma radiation. This was carried out by placing very thin sheets of lead between the gamma source and the counter window. It was found that lead foil of thickness 87 mg per cm^2 so placed produced a significant increase in the recorded count. This effect occurred by the interaction of the gamma radiation with the lead to produce electrons by the photoelectric effect,which were much more efficiently counted. When a disc of this lead foil was placed between the counter window and the cooled copper foil, the count obtained from a mercury source increased by a factor of four. The effect of the lead on the background seen by the counter was insignificant. Details of this effect are given in Appendix 6.

(10.12.) The Poisoning of Cyclopropane Hydrogenation on Supported Catalysts Using Radioactive Mercury

When a series of reproducible hydrogenation rates under standard experimental conditions had been obtained, the effect of introducing mercury to the system, without affecting these conditions, was studied.

The mercury vapour was admitted to the catalyst after the gas mixture used for the previous hydrogenation had been pumped away. The side arm containing the mercury had been evacuated previously using the rotary pump and had been left under vacuum. During the admission of the mercury vapour the catalyst vessel tap T5 (Fig. 10.1.) was kept closed. Before admitting mercury vapour to the catalyst vessel the background on the counter was taken. This was found to be in the region of 20 - 30 counts per minute. The relative amount of mercury present during each hydrogenation was obtained by taking a count for approximately 10 min during the course of the hydrogenation. The absolute amount of mercury present was calculated once the weight of mercury present at the end of the series of hydrogenations was determined as indicated in section 10.13.

(10.13.) The Determination of the Absolute Weight of Radioactive Mercury Present on Supported Catalysts

The weight of mercury adsorbed on supported nickel catalysts had already been determined using a technique similar to that used with evaporated films (see section 9.24.). In this technique the count from the dissolved catalyst was compared with that from a standard solution using a liquid counter. Further consideration of this technique, as applied to supported catalysts, introduced the possibility that the undissolved catalyst support might show a preferential adsorption for mercury and the resulting supernatant solution would show an activity lower than the correct value.

In order to determine whether this effect occurred, and if so to what extent, a different method for radioactive mercury assay was attempted.

The most direct method of determining how much radioactive mercury was present on the catalyst was to count the solid catalyst using a standard end window counter. The main disadvantage of this, however, was the difficulty of reproducing the counting geometry conditions when counting the standard mercury source, assuming that a satisfactory standard could be prepared. This difficulty was overcome by using a well-crystal scintillation counter which was much less susceptible to geometric counting losses, since the source was placed inside the well of the crystal and counts were taken over a large solid angle.

The crystal used was thallium-activated sodium iodide. The counting equipment used was a Panax type 100C scaler in conjunction with an automatic timer type T 300. The photomultiplier operated on a voltage of 1000 v and the signal obtained was amplified before being received by the counter. The counter was adjusted to a discriminator voltage of 5 v which resulted in electronic noise being eliminated. The paralysis time was 10 micro seconds and the background measured was in the region of 10 counts per second.

Accurately weighed samples of the catalyst ranging from

20 - 40 mg were placed in 4,1cm diameter glass test tubes. Care was taken to ensure that all of the catalyst was at the bottom of the tube and that none adhered to the walls. To accomplish this the catalyst was introduced through a glass tube which could be inserted almost to the bottom of the tube. A standard solution was prepared by dissolving 12.8 mg of radioactive mercury in 500 ml of 10N nitric acid. Aliquots of 1 ml of this standard were transferred to four test tubes two of which contained 20 mg samples of inactive catalyst. The counts obtained from the unknown samples and the standards are given in Appendix 7; these were taken to at least 10,000 counts to produce a statistical error of ± 1%. Since the energy of the beta radiation produced by ^{203}Hg is only 0.21 meV, this would be unable to penetrate the glass of the test tube so that the count produced was due to the effect of the gamma radiation alone. It was found that the difference in count rate from the four standards was within the statistical error of the count.

To one of the unknown samples was added 1 ml of 10N nitric acid, to determine the effect of dispersing the activity through a larger volume than that occupied originally by the solid catalyst. This was found to have no effect on the count rate, showing that the counting geometry obtained by using a well-crystal made possible the comparison of a liquid standard with the solid unknown. The effect on the count rate of raising the test tube within the well of the crystal was also studied.

The samples of catalyst used for this study were then dissolved in 10N nitric acid and the count from the solution obtained using a liquid counter as before. The results of the two techniques were then compared.

CHAPTER 11

THE STUDY OF THE VAPOUR PRESSURE OF MERCURY OVER A MERCURY POISONED CATALYST: EXPERIMENTAL

Because it constitutes a health hazard (99) a number of workers (66) have studied how the concentration of mercury may be measured accurately in the vapour phase. The most common procedure utilises the fact that mercury vapour absorbs very strongly light of wavelength 2537 A^o, this wavelength corresponding to the resonance energy necessary to bring about an electronic transition in the mercury atom converting it from the $6\,^1S_o$ state to the $6\,^3P_1$ state. This strong adsorption may be shown visually as indicated by Leighton and Leighton (100). They showed that if a source of mercury vapour was placed between an ultraviolet lamp whose main component was the 2537 A^o line and a screen which fluoresced visibly when excited by light of this wavelength a dark shadow was produced on the screen owing to the absorption of the radiation by the mercury vapour.

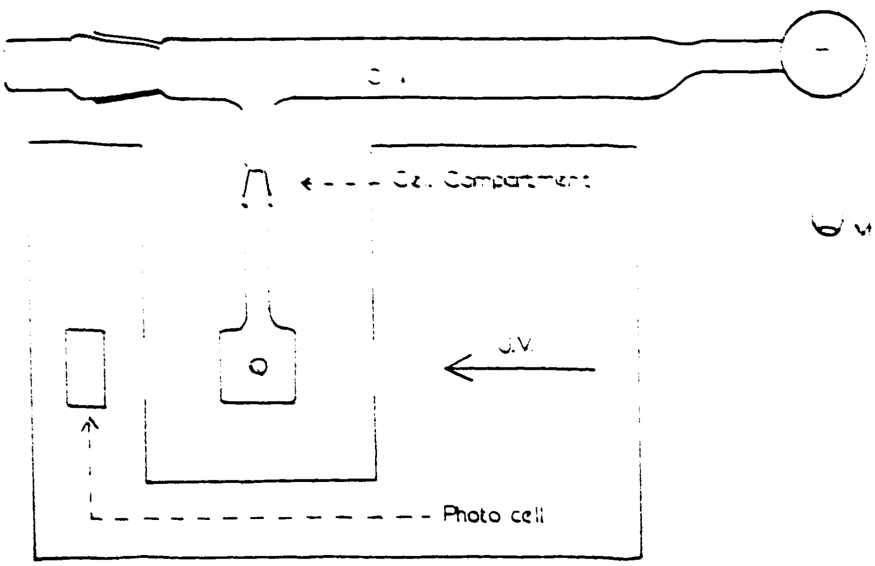
It was decided, therefore, to study the vapour pressure of mercury using this absorption technique.

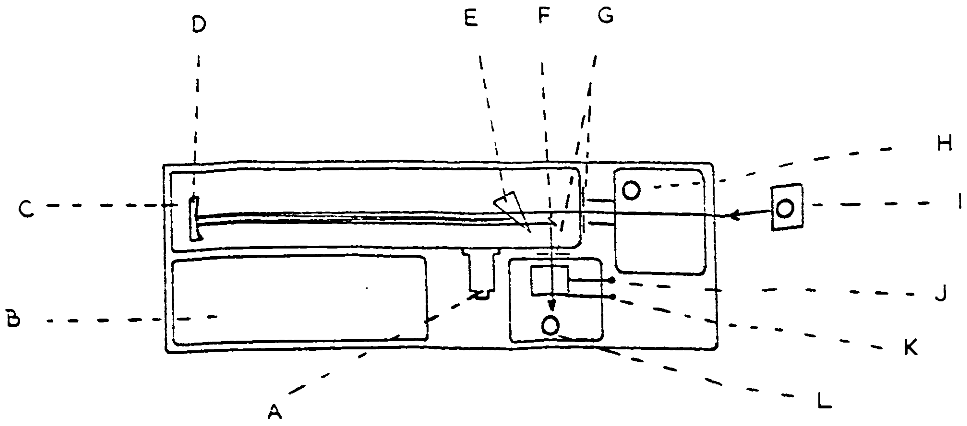
(11.1.) The Spectrophotometer

Preliminary experiments, using a source of mercury in a 1 cm

THE ABSORPTION APPARATUS

Fig. II.2





THE SPECTROPHOTOMETER

Fig. II.1.

quartz cell, in a Unicam SP 800 automatic spectrophotometer showed no detectable absorption in the region of 2537 A^{o}. A similar result was obtained using a Hilger Uvispek spectrophotometer. This could be explained by the fact that both of these machines used a deuterium lamp as the source of U.V. radiation and this produced a "white" spectrum of radiation. Consequently although the 2537 A^{o} line was being absorbed by the mercury the other wavelengths, on either side of this line, were unaffected and the relative decrease of intensity due to removal of this line could not be detected by the photocells of the spectrophotometer, even with the narrowest waveband attainable by the instrument. It was possible to overcome this difficulty by using a monochromatic source of 2537 A^{o} radiation. The source used is described in section 11.2.

A Hilger Uvispek spectrophotometer was used for all the absorption studies since its flame photometry facilities enabled an external light source to be used. A diagram of the spectrophotometer assembly is given in Fig. 11.1. The key to the letters used is as follows:

A	λ Control
B	Measuring Unit
C	Monochromator
D	Concave Mirror
E	Dispersing Prism
F	Plane Mirror
G	Slits
H	D_2 Lamp
I	Hg Lamp
J	Carriage Control
K	Shutter
L	Photocell

After passing into the monochromator system of the spectrophotometer via an entrance slit, the light from the 2537 A^{o} source entered the cell compartment through the exit slit and was detected by the photocell. The sizes of the entry and exit slits were controlled simultaneously, each being the same at any time. The resolution of the machine was such that at 2537 A^{o}, using a slit width of 0.48 mm the band width of the radiation incident on the photocell was 10 A^{o}. During the procedure for adjusting the wavelength described in section 11.3. the slit width was 0.01 mm, and during the majority of the absorption experiments it was 0.1 mm producing band widths of about 0.2 A^{o} and 2 A^{o} respectively.

(11.2.) The U.V. Light Source

The source of 2537 A^{o} radiation used was a Philips Electrical Ltd. T.U.V. 6w germicidal tube. This lamp, which was operated on 240 v ac, was 15 cm long and 2.6 cm in diameter. It was mounted vertically in a 10 cm diameter cardboard container and placed at the "flame source" aperture of the spectrophotometer. The lamp operated at low temperature, maximum wall temperature approximately 60^{o}C, and consisted of an inert gas-filled low pressure mercury arc.

According to the manufacturers' specifications the energy output at 2537 A^{o} was 85 mW and this was the only energy emitted in the region of 2400 - 3000 A^o. The output of this lamp was stated to be temperature dependent, the arc voltage changing by 1% per degree centigrade. Consequently it was switched on and allowed to come to equilibrium for at least three quarters of an hour before use.

(11.3.) Procedure for Obtaining the Correct Wavelength

Although it was known that in the region of the spectrum under consideration the U.V. lamp only emitted 2537 A^o radiation, it was found by varying the wavelength control of the spectrophotometer that light apparently covering a range of wavelengths as read on the control was being received by the photocell. It was further found that the narrower the slit width the smaller the range of wavelengths over which the radiation could be detected. Since the 2537 A^o emission line is a resonance line it was assumed that it would be reasonably sharp but it was not known whether broadening effects would occur in the lamp and if so to what extent the line could become broadened. Because of this uncertainty and also because the wavelength control showed the radiation being emitted from the lamp had a wavelength greater than 2537 A^o it was decided to standardise the procedure for determining the wavelength to be used for absorption studies. This was carried out as follows:

A piece of filter paper soaked in Eosin indicator was placed in the light beam in the cell compartment. Reducing the external lighting to as low a level as possible and moving the wavelength control slowly in one direction in the region of 2540 A^{o} it was possible to observe a yellow fluorescence where the beam passed through the paper; further movement caused this to disappear. Reducing the slit width reduced the range of wavelengths on the control at which fluorescence was seen. For a slit width of 2 mm a fluorescence was observed while the wavelength control indicated a change in wavelength of 70 A^{o}. When the slit width was reduced to 0.25 mm the fluorescence was only present for a change in wavelength of 1 A^{o}.

This technique was made much more dependable by using the photocell of the spectrophotometer which was much more sensitive to light detection than the eye. The method employed was to balance the instrument using as small a slit width as possible in a portion of the spectrum in which no radiation was being produced. Moving the wavelength control extremely slowly it was possible to determine when light was falling on the photocell by the sudden increase in current obtained on the spectrophotometer meter. At low slit widths the position of the line could be determined extremely accurately.

It was found that the line occurred at an apparent wavelength of 2542 A^{o}. Using the same technique with the same light source on a different Hilger Uvispek it was found that the position of the line was at 2537 A^{o} indicating that the wavelength calibration on the original machine was faulty. Since the procedure using the photocell, as described above, was carried out before each absorption experiment this error was unimportant. After the wavelength had been determined at a narrow slit width (0.01 mm), the slit width was increased to a wider value for the absorption experiments (0.1 mm). Since both edges of each slit were moved when the slit width was increased this procedure did not alter the wavelength of the radiation seen by the photocell, only its intensity.

(11.4.) The Absorption Apparatus

The absorption apparatus contained three main components, as shown in Fig. 11.2. A source of mercury (M) which could be isolated when desired using the tap (T), a region in which the vapour pressure of the mercury was studied (Q) and, between these, a region in which the catalyst was placed (CV). It was decided to use supported catalysts rather than evaporated films in this study since these were much easier to prepare and did not require such stringent vacuum conditions for their preparation. The limiting factor in the design of this apparatus was that the region of the apparatus in which the mercury vapour was to be determined had to fit into the cell compartment of the Hilger spectrophotometer.

Since Pyrex glass does not transmit light with wavelength less than 3600 A^{o} (101) it was necessary to construct the absorption cells from quartz. Two cells were required one being used as a reference cell. These cells consisted of quartz cylinders, 2 cm in diameter, to the ends of which were fused optically pure quartz plates giving a path length of 2 cm. A quartz side arm containing a B 7 cone was attached to each cell. This enabled the cells to be attached by means of a B 7 socket to the main portion of the apparatus which was constructed from Pyrex glass. This portion of the apparatus containing the catalyst was constructed from a 13 cm length of 16 mm O.D. Pyrex tubing to one end of which was attached a B 14 socket and to the other a 6 mm three-way tap. The lower side arm of the tap contained the mercury source and the upper side arm was connected to a vacuum system and sealed off at the constriction (C) when the necessary vacuum had been attained.

In order to determine whether their vapours absorbed to any great extent in the 2537 A^{o} region, the absorption spectra of Apiezon W wax, Apiezon N grease and Dow Corning silicone grease were obtained using a Unicam SP 800 spectrophotometer. It was assumed that the absorption spectra of the solid phases would not vary considerably from those of the vapours which were derived from them. Specimens were prepared by smearing the greases in

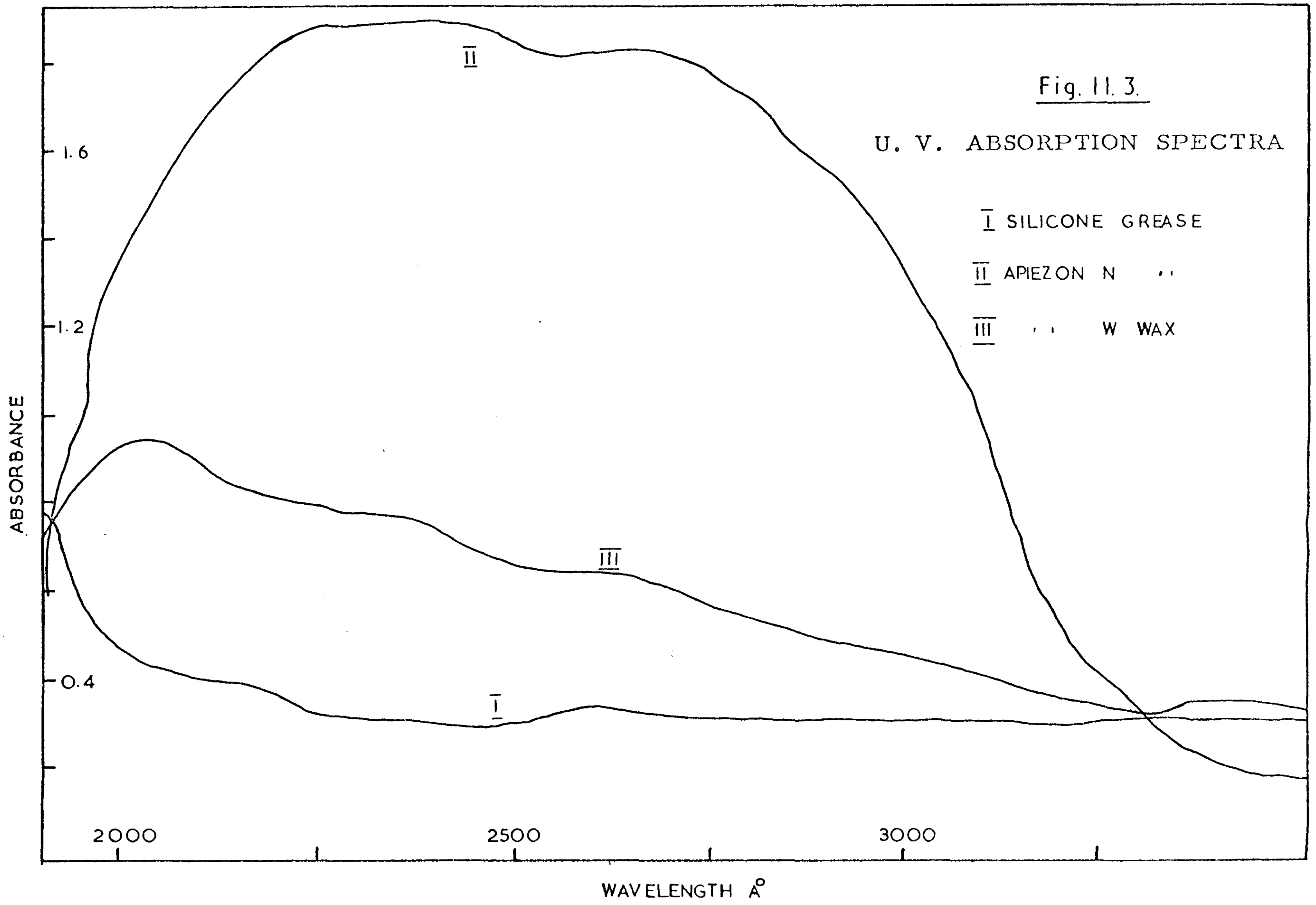


Fig. 11.3.

U. V. ABSORPTION SPECTRA

turn on one face of a quartz 1 cm cell. In the case of the Apiezon W wax a dilute solution in carbon tetrachloride was evaporated onto the cell face. The spectra obtained are shown in Fig. 11.3. Although the relative concentrations of the samples were not known it would appear unsatisfactory to use Apiezon N grease in the system due to its high absorption in the 2537 A° region. Consequently the cone and socket joints were sealed using the minimum amount of Apiezon W wax. Since this wax was used both in the apparatus containing the mercury vapour and in the evacuated reference cell any absorption it may have produced would be the same in each case. The three-way tap was greased with the Dow Corning silicone grease.

(11.5.) The Thermostat System

As a result of the study of the adsorption of mercury on evaporated nickel films it was known that rigid temperature control of both the mercury source and the catalyst would be required in this system. Consequently a box was constructed from 2 mm thick perspex sheet which contained both the mercury absorption apparatus and the reference quartz cell. The quartz cells were so positioned that when the box was placed on the cell carriage of the spectrophotometer movement of this carriage enabled each cell in turn to be brought into the light beam. A wooden ledge was fitted round the thermostat box so that when the box was in position no stray light could enter the cell compartment.

The box contained two spirals made from 3 mm diameter copper tubing through which water could be pumped from a thermostat tank. The spirals were positioned such that temperature gradients within the box were kept to a minimum. After the spirals and the cells had been fitted, the box was filled with 60 - 80 mesh copper powder which acted as an efficient heat-transfer medium. The thermostat tank used, a Calora Ultra thermostat type NB 30527, contained a built-in pumping and stirring unit and could be maintained within 0.1°C of the desired temperature, normally 25°C. It was found that owing to the narrow bore of the copper tubing and the distance from the tank the temperature of the spirals did not reach that of the tank but remained at equilibrium at some value lower by about 1 C°.

The mercury source was maintained at a constant temperature by enclosing the side arm in a copper calorimeter 3 cm in diameter. This calorimeter was fitted tightly inside a closely wound spiral of 8 mm diameter copper tubing through which was pumped water from a second thermostat tank. Like the thermostat box described above the calorimeter was filled with 60 - 80 mesh copper powder. The outside of the spiral was surrounded with a shielding of 3 mm thick lead sheet. The thermostat tank used in this case was the same as that described in section 9.21. A by-pass was fitted into the pumped circulating system which enabled water to be circulated through the copper coil round the mercury source. Since it was desired to maintain the mercury at a temperature lower than room temperature it was always necessary to have water flowing through the heat exchanger built into this tank. The temperature of the water in the tank was controlled to within 0.1°C using a Jackson Thermoregular type TM-700 temperature controller in conjunction with a hot wire vacuum switch. Heat was supplied from a 150 w electric light bulb.

In the later experiments using this apparatus it was found necessary to thermostat the room containing the spectrophotometer at a temperature of 23°C. This was accomplished using a Jumo Shandon 6-64 mercury thermometer type temperature controller in conjunction with a Jumo type GKT IS-O switching unit. The heat was supplied using a 2 kw electric convector heater. This system was found to operate satisfactorily provided draughts were excluded. It was found that control within ± 0.5°C was obtained.

(11.6.) Experimental Procedure for Determination of U.V. Absorption

The spectrophotometer and the mercury lamp were switched on and allowed to warm up for approximately three quarters of an hour before use. The correct wavelength was selected using the procedure described in section 11.3. The absorption apparatus was then fitted into the spectrophotometer, thermostat connections made and the shutter opened when the required temperatures had been attained. With the reference cell in the beam the current derived from the photocell was balanced using the 'check' control. The absorption cell was then slid into position and the photocell current rebalanced using the 'measure' control, the reading obtained being noted. The reference cell was then replaced in the beam to confirm that no drift had occurred on the check control. This procedure automatically eliminated changes in intensity produced by the lamp source, provided that no drift had occurred. If this was present the absorption reading was retaken. To prevent fatigue of the photocell the shutter was normally closed after use unless some sudden effect was being observed.

(11.7.) The Effect of Pressure of Admixed Hydrogen on the Absorbing Power of Mercury Vapour for Resonance Radiation: Experimental

The apparatus used was similar to that shown in Fig. 11.2. except that the greased tap was not present, the relative positions of the mercury source and the side arm used for evacuation were, however, identical. No catalyst was present during this study and inactive mercury was used.

The apparatus was attached to the high vacuum apparatus and evacuated using the rotary pump only. Prolonged pumping was not employed for fear of contaminating the vacuum apparatus with mercury. Hydrogen was then admitted to a pressure of 17.5 torr and the apparatus sealed off. The apparatus was placed in the spectrophotometer and the leads from the thermostat box connected to the thermostat tank which had previously reached equilibrium at 25°C. Both the spectrophotometer and the U.V. light source had been switched on previously and had been allowed to come to equilibrium. After verifying that the absorption reading obtained with the mercury source at room temperature was comparable with that found before, the side arm containing the mercury source was surrounded by a Dewar flask containing a water/ice mixture. An immediate reduction in absorbance occurred and came to a value after 3 min which remained constant for 20 min. On removal of the ice bath the absorbance again increased reaching its original value after 25 min. The Dewar flask was then replaced round the mercury source, on this occasion containing water at a temperature of 10.6°C. The value of absorbance which had remained constant for 20 min was again read. It was found that the water in the Dewar flask retained its temperature without variation throughout this period.

The procedure was repeated surrounding the mercury source with water at temperatures of 16.2°C, 20°C and 24.6°C and noting the absorbance, when it became constant, in each case. Following the same procedure the value of absorbance at each of the above temperatures was determined a second time. The apparatus was then evacuated as before, hydrogen at a pressure of 30 torr admitted and the apparatus sealed off. The values of absorbance at the same temperatures as used when 17.5 torr hydrogen was present were then obtained in duplicate using the same procedure as before. A similar series of results were obtained with the apparatus under vacuum.

(11.8.) Activation of the Catalyst

It was found necessary to fix the quartz cells into the thermostat box permanently in order to obtain reproducible readings, consequently it was necessary to carry out the activation of the catalyst in situ. The catalyst used was 5% nickel on pumice from the same batch as that described in section 10.6. After reduction in a stream of hydrogen at 450°C 0.2 g was weighed into a 4 cm long ignition boat and placed in the apparatus through the B 14 socket.

To activate this catalyst before use it was necessary to heat it in an atmosphere of hydrogen at approximately 200°C. The furnace necessary to produce this temperature had to fit round the appropriate section of the apparatus and was unable to be removed once in position. In addition it required to be as thin as possible since in order to determine the activity of the mercury later to be adsorbed on the catalyst a counter similar to that used in the film work (section 9.23.) had to be placed as close to the catalyst as possible. With these restrictions in mind the furnace was prepared by winding 2 yd of 32 ohm/yd nichrome wire on a 7 cm length of 1.8 cm bore glass tubing. The wire was then enclosed in a thin layer of Cataloy fibre glass paste which hardened to produce a robust heat resisting covering. A temperature of 260°C was obtained with this furnace using an applied voltage of 56 v dc obtained from a series of heavy duty lead accumulators. It was considered that the temperature obtained using this source would be more reproducible and stable than that produced by the mains, owing to observed fluctuations in mains voltage.

The temperature produced in the tube containing the catalyst was measured on a Quickfit 360°C thermometer the B 14 cone of which fitted into the B 14 socket on the absorption apparatus. It was found that a temperature gradient of 40°C was present inside

DETAIL OF ABSORPTION APPARATUS

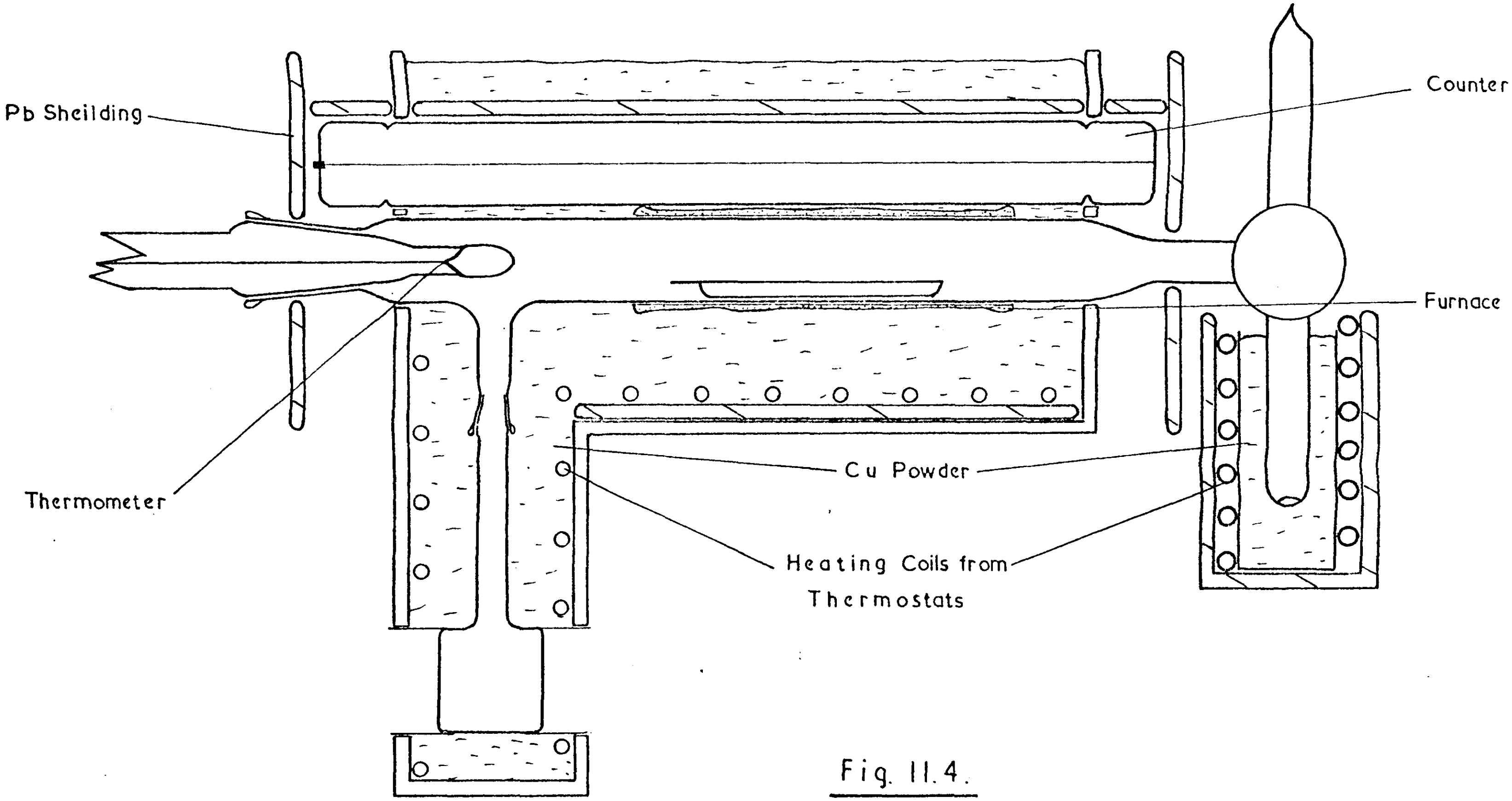


Fig. II.4.

the activating furnace and consequently the boat containing the catalyst was always placed in the centre of the furnace.

The catalyst was activated by attaching the absorption apparatus to the high vacuum apparatus described in section 10.1. and with the furnace heated, pumped to a vacuum of 1×10^{-3} torr. Purified hydrogen was then admitted to the apparatus to a pressure of about 200 torr and left at 220 - 240°C for about one hour. During the time that the furnace was switched on cold water was passed through the copper spirals in the thermostat box, to prevent overheating of the perspex. After activation the catalyst was pumped to a pressure of 1×10^{-3} torr.

(11.9.) The Detection of Mercury Adsorbed on the Catalyst

The mercury adsorbed on the supported catalyst was detected in a similar manner to that adsorbed on the evaporated nickel films (section 9.23.). A similar tubular halogen quenched counter (Mullard type 120X) was fitted into recesses in the perspex thermostat box so that it was positioned parallel to and directly above the tube containing the catalyst (see Fig. 11.4.). The recesses were moulded into the shape of the counter, using fibre glass paste, so that the counter fitted tightly and retained a constant counting geometry. When in position the counter was as close to the tube containing the

APPARATUS FOR SIMULTANEOUS Hg ADSORPTION AND H_2 DESORPTION

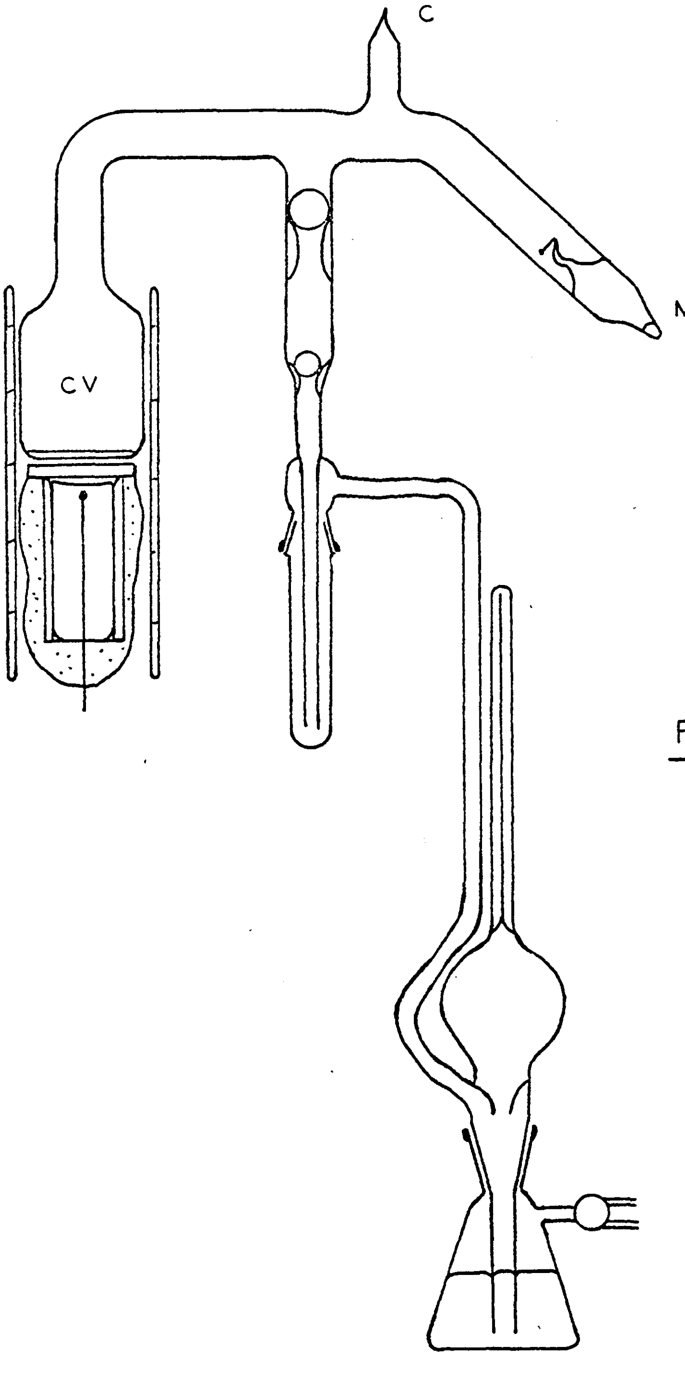


Fig. II. 5.

catalyst as the presence of the small activating furnace would permit and the catalyst was in the centre of the "working region" of the counter.

The counter was shielded from background radiation by enclosing the top and sides with an inverted U-shaped sheet of 4 mm thick lead. Suitably shaped pieces of lead sheet shielded the ends of the counter.

Determination of the Volume of Hydrogen Displaced by Mercury from a Reduced Supported Metal Catalyst: Experimental

(11.10.) The Apparatus

The apparatus is shown in Fig. 11.5. The catalyst was placed at the bottom of the catalyst vessel (CV) which had a volume of about 25 cc and to which was attached a side arm containing a source of radioactive mercury (M). A McLeod gauge with a low volume bulb was used to measure the hydrogen pressure and was separated from the catalyst vessel by means of two steel ball/ground glass valves. In Experiment 101 a side arm, surrounded with liquid nitrogen, was fitted between the McLeod gauge and the ball valves to prevent poisoning of the film by inactive mercury. In Experiment 102 this was replaced by a low volume cold trap as indicated in Fig. 11.5. A connecting tube fitted with a constriction (C) enabled the whole apparatus to be attached to a vacuum system and evacuated. In

Experiment 101 the source of radioactive mercury was surrounded by a shield of 4 mm lead sheet which was cooled by surrounding it with a 3 cm diameter spiral of thin walled rubber tubing, through which cold water was passed. In Experiment 102 a Dewar flask filled with ice was used. The catalyst vessel was placed in a 10 l capacity thermostat tank which was stirred mechanically. Temperature control was maintained within $0.2^{o}C$ of the desired temperature using a Sunvic type TS3 controller in conjunction with a hot wire vacuum switch.

(11.11.) The Counter

Since the catalyst vessel had to be maintained in the thermostat tank the end window counter which was used to detect the mercury present on the catalyst had to be modified to enable it to operate under water. It had also been intended to use this counter to detect radioactive mercury in a catalyst vessel which was to be maintained at a temperature of at least $100^{o}C$ in an electrically wound furnace. This was later rejected in favour of the vapour bath counting system described in section 10.4. With these considerations in mind, the following system was developed.

The counter, a Mullard M x 147 β, γ end window counter, having a window area of 63.5 mm^2 was fitted tightly into a closely wound

G.M. TUBE ADAPTED FOR USE UNDER WATER
OR AT HIGH TEMPERATURES
(actual size)

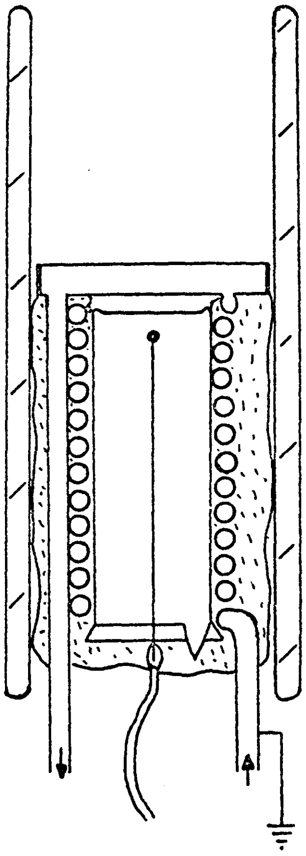


Fig. 11. 6.

spiral of 3 mm diameter copper tubing. A diagram of this system is shown in Fig. 11.6. The end of the spiral nearest the window was levelled using Cataloy fibre-glass paste and covered with a disc of 0.002 inch copper foil, held in position with Araldite. A second disc of copper separated by a 3 mm deep 2.5 cm diameter ring of copper was sealed in position above the first. A connection was made from the main spiral of tubing into this compartment and an outlet was also fitted, so that water could be circulated round the counter and across the counter window. The outside of the spiral was covered with fibre-glass paste, as was the bottom of the counter, after insulated leads had been attached to the anode and cathode. A length of 3 cm diameter lead piping was found to fit tightly round the counter and provided adequate shielding. The catalyst vessel fitted into an extension of this piping and rested on the copper above the counter window. This ensured constant counting geometry. This counter was found to operate satisfactorily under water. Care was taken to connect the cathode to earth. It was found that the absorption of the gamma radiation by the copper foil and the water was small.

(11.12.) The Experimental Procedure

A weighed amount of catalyst from the same sample, the preparation of which is described in section 10.6., was placed in the catalyst vessel which was glass blown onto the apparatus. The apparatus was then evacuated using the rotary pump of the vacuum equipment described in section 10.1. Hydrogen was admitted to the apparatus to a pressure of 200 torr and a nichrome wire-wound furnace at a temperature of 220°C placed round the catalyst vessel. After activating the catalyst at this temperature for an hour, the furnace was switched off and the catalyst allowed to cool. The hydrogen was then pumped out using the rotary pump and the apparatus sealed off at the constriction, the ultimate pressure read on the McLeod gauge being 3.6×10^{-2} torr in Experiment 101 and 1×10^{-4} torr in Experiment 102. The catalyst vessel was placed in position in the lead shielding in the thermostat tank which was at a temperature of 25°C. The catalyst was distributed as evenly as possible on the bottom of the catalyst vessel. The lead shielding and appropriate cooling system were placed round the mercury source and the cold trap surrounded by liquid nitrogen. Lead shielding was also placed between the counter and the liquid nitrogen trap to prevent a contribution to the measured count from radioactive mercury which might have diffused to the trap through the ball valves.

Counts were then taken for 10 min periods along with readings of the McLeod gauge. Care was taken to raise the ball valves before making a pressure measurement since they were found capable of maintaining a pressure difference across them. Experiment 101 was carried out during a period when the room temperature was particularly low and the temperature of the mercury source did not rise above 15°C.

The volumes of the apparatuses were determined by filling them with water after the experiment and the McLeod gauge was calibrated as indicated in Appendix 4.

APPENDIX 1

(a) Determination of Value of Rate Constant from Experimental Data

The data given were obtained from runs 5 and 8 on Film 15.

From the expressions derived in sections 9.17. and 9.27.

$P_c = (P_o - a) - PD$ and $PD\,(\text{torr}) = \text{Gauge Reading} \times 1.34 - 0.15$

$\therefore\; P_c\,(\text{torr}) = (P_o - a + 0.15) - \text{Gauge Reading} \times 1.34$

In both runs the same gas mixture was used in which the fraction of hydrogen was 0.5, therefore $a = 0.5\,P_o$.

The values of the logarithm of P_c were plotted against time. Semilogarithmic paper was used to facilitate this and the best straight line drawn through the points as shown in Fig. 1.4. The gradient of this line, giving the value of the rate constant, was calculated as follows :

$$\text{Gradient (run 5)} = \frac{\log 13.74 - \log 3.72}{2 - 26} = \frac{-0.5675}{24} = -0.0237$$

$$\text{Gradient (run 8)} = \frac{\log 13.28 - \log 3.19}{2 - 29} = \frac{-0.6194}{27} = -0.0229$$

Experimental Data for run 5 Film 15

Level of Hg meniscus in evacuated limb of manometer = 49.604 cm

" " " " " other " " " = 46.658 cm

2.985 cm

Non zeroing factor (see section 9.17.) = .039 cm

$\therefore$ Initial Total Pressure (P_o) = 29.85 torr

Continued over ...

Time (min)	Gauge Reading (GR)	GR x 1.34	P_c torr
1	0.50	0.67	14.41
2	1.00	1.34	13.74
3	1.50	2.02	13.06
4	2.00	2.69	12.39
5	2.50	3.36	11.72
6	3.00	4.03	11.05
7	3.40	4.57	10.51
8	3.80	5.11	9.97
9	4.20	5.65	9.43
11	4.95	6.65	8.43
12	5.25	7.06	8.02
13	5.55	7.46	7.62
14	5.85	7.86	7.22
15	6.15	8.27	6.81
17	6.65	8.94	6.14
18	6.95	9.34	5.74
19	7.15	9.61	5.47
20	7.40	9.95	5.13
22	7.80	10.48	4.60
24	8.15	10.95	4.13
26	8.45	11.36	3.72
28	8.75	11.76	3.32
30	8.90	11.96	3.12
32	8.90	11.96	3.12
34	9.00	12.1	2.98
52	9.00	12.1	2.98

(b) Specimen Calculation of Weight of Mercury Present on Film During Reaction

Film 22, Summary of Counts

	Count	- Background + Paralysis Time
Background of liquid counter	2466 ÷ 122	20 = Bkgd
Count from 10 cc of soln. containing film (Film dissolved in 25 cc)	5619 ÷ 40	119
Count from 10 cc of standard (34.6 mg Hg in 100 cc)	11849 ÷ 8	1479
Background on cylindrical counter	34725 ÷ 191	181 = Bkgd
Count during run 9	3391 ÷ 19	0
" " " 10	3966 ÷ 21	8
" " " 11	4502 ÷ 21	33
" " " 12	5266 ÷ 23	48
" " " 13	9610 ÷ 35	94
" " " 14	8474 ÷ 30	101
" " " 15	7387 ÷ 24	127
" " " 16	3751 ÷ 12	132
" " " 17	10503 ÷ 31	158

$$\text{Total wt. of Hg on film} = \frac{3.46 \times 119}{0.4 \times 1479}\ \text{mg}$$

$$= 0.70\ \text{mg}$$

Since count on cylindrical counter from this weight of Hg was 158 c.p.m. To convert counts on cylindrical counter to corresponding weights of Hg multiply counts by factor 0.7 ÷ 158.

Determination of Weight of Film 22 (see section 9.28.)

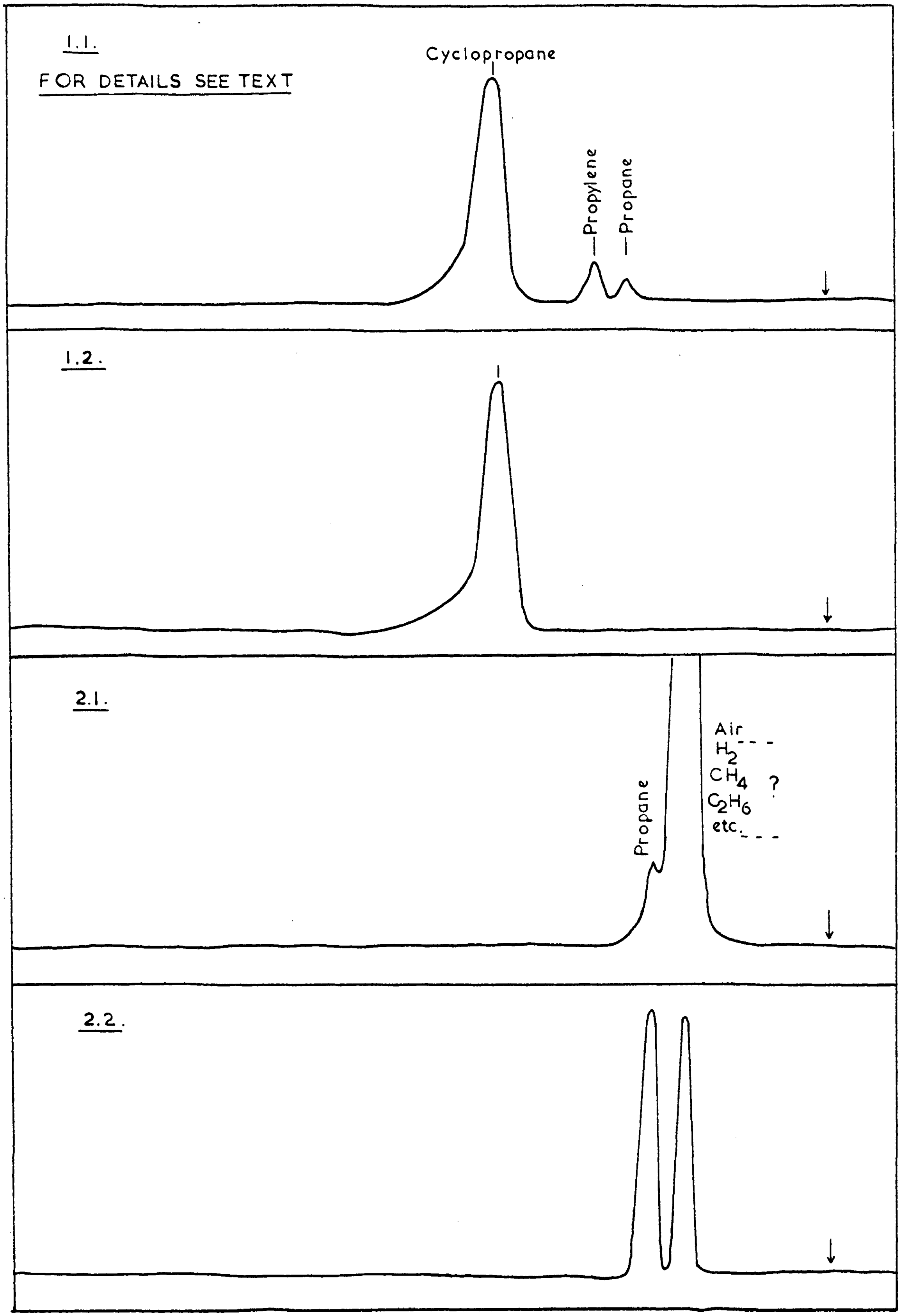
	Standard solutions		Film solutions	
	27.3 mg/l	32.5 mg/l	A	B
Optical Density	0.000	0.176	0.111	0.092
	0.000	0.175	0.111	0.093

Optical density of 0.176 from 5.2 mg

$\therefore$ " " " 0.101 " $\frac{5.2 \times 0.101}{0.176}$ mg = 3 mg

i.e. Film soln. contains 3 mg Ni/l more than 27.3 standard

$\therefore$ Wt. of film = 30.3 mg


1.1.
FOR DETAILS SEE TEXT
Cyclopropane
Propylene
Propane
1.2.
2.1.
Propane
Air
H_2
CH_4
C_2H_6
etc.
?
2.2.

APPENDIX 2

Gas-Liquid Chromatographic Analyses

The G.L.C. analyses were carried out using a Beckman GC2A Gas Chromatograph and a 12 ft column of dimethylsulpholane, 30% on C22 Firebrick 42 - 60 mesh. Samples for analysis were transferred using a Hamilton gas syringe.

Analysis 1.1. Unpurified cyclopropane, ex Light and Co.
Sample: 0.4 ml at 760 torr. Attenuation: 10.
Carrier gas: N_2 at 30 ml min^{-1}.
Retention times (obtained from standards under comparable conditions).
Cyclopropane 5.1 min, Propylene 3.7 min, Propane 3.1 min.
Relative peak areas 48 : 2.7 : 1.2.

Analysis 1.2. Unpurified cyclopropane ex British Oxygen Co.
Conditions as for analysis 1.1.
No detectable peaks other than that for cyclopropane were observed.

Analysis 2:1. Analysis of products of reaction of cyclopropane and hydrogen over 1% Pd on carbon.
Carrier gas: He at 36 ml min^{-1}.
Sample: 1 ml at 30 torr + air to atmospheric pressure.
Attenuation: 1.
Retention times: Propane 2.6 min, Air, etc. 2.0 min.

Analysis 2:2. As for 2:1 but attenuation 100 for first peak.

APPENDIX 3

Data for Simultaneous Mercury Adsorption/Hydrogen Desorption from Supported Nickel Catalysts

Experiment 101

Wt. of 5% Ni on Pumice used = 0.4969 g
(100 g pumice contained 5 g Ni)

$\therefore$ Wt. of Ni present = 23.6 mg

No. of Ni atoms present $= 6.023 \times 10^{23} \times 0.0236 - 58.7$

$= 2.42 \times 10^{20}$

No. of H atoms displaced
(vol. calc. in section 7.8.)

$$= \frac{6.023 \times 10^{23} \times 2.27 \times 10^{-2} \times 2}{22.4 \times 10^{3}}$$

$= 1.18 \times 10^{18}$

Estimation of Radioactive Mercury

Wt. of catalyst after Expt. 101 = 0.5054 g

Wt. used for analysis = 0.4990 g

Background on liquid counter = 788 ÷ 45 = 17 c.p.m.

Count from 10 ml standard soln. $= \frac{38264}{45} = 850$ c.p.m.
(11.5 mg Hg in 100 ml acid)

Corrected for paralysis time and background = 839 c.p.m.

Count from 10 ml soln. containing catalyst $= \frac{19472}{46}$
(0.5 g dissolved in 12 ml acid)

(10 ml made up to 50 ml) = 423 c.p.m.

Corrected = 407 c.p.m.

$$\therefore \text{ Total wt. of Hg on catalyst } = \frac{1.15 \times 407 \times 5 \times 1.2 \times 0.505}{839 \times 0.499} \text{ mg}$$

$= 3.39$ mg

Calculation of Wt. of Mercury Present on Plateaux in Fig. 6.2.

Background on G.M. tube $= 595 \div 10 = 59.5$ c.p.m.

Count from 3.39 mg Hg (91 hr after start of Expt.) $= \frac{4483}{11} - 59.5$

$= 347$ c.p.m.

Calculated count rates from above after various times, t :

(hours)	12	27	40	91
Count rate (c.p.m.)	360	358	356	347
Count from Hg present corrected for background	108	145	170	347

$\therefore$ Wt. of Hg present on plateaux $= \frac{3.39 \text{ x count on plateau}}{\text{corrected count from } 3.39 \text{ mg}}$

No. of Hg atoms present $= \frac{6.023 \times 10^{23} \text{ x wt. of Hg}}{200.6}$

Summary of results is given in Table 6.2.

Experiment 102

Wt. of 5% Nickel on Pumice catalyst used = 0.4978 g

No. of H atoms displaced (vol. calc. in section 7.8.) $= \frac{6.023 \times 10^{23} \times 2.34 \times 10^{-2} \times 2}{22.4 \times 10^{3}}$

$= 1.26 \times 10^{18}$

Estimation of Radioactive Mercury

Total wt. of Hg present on catalyst (calculated as for Expt. 101) $= \frac{1.65 \times 102 \times 5 \times 1.2 \times 0.500}{1094 \times 0.498}$ mg

$= 0.93$ mg

Calculation of Wt. of Hg to Displace all Hydrogen in Expt. 102

Background on G.M. tube $= \frac{493}{12} = 41$ c.p.m.

Count from 0.93 mg Hg $= 150 - 41 = 109$ c.p.m.

Count when on plateau $= 135 - 41 = 94$ c.p.m.

$\therefore$ Wt. of Hg on plateau $= \frac{0.93 \times 94}{109} = 0.78$ mg

$= 2.34 \times 10^{18}$ atoms

Count when all H_2 displaced $= 123 - 41 = 82$ c.p.m.

$\therefore$ Wt. of Hg to displace H_2 $= \frac{0.93 \times 82}{109}$ mg $= 0.7$ mg

$= 2.1 \times 10^{18}$ atoms

Summary of Results of H_2 Displacement

	Expt. 101	Expt. 102	Expt. 103
No. of Ni atoms	2.42×10^{20}	2.44×10^{20}	2.02×10^{20}
No. of H atoms displaced	1.18×10^{18}	1.26×10^{18}	-
Ratio of Ni to H atoms	205	194	-
No. of Hg atoms to desorb 1 H atom	2.5	1.85	-

Run 101

McLeod gauge reading = 19.5 mm after 5 hr
and constant throughout

Time of Count (hr)	Length of Count (min)	Counts per min	Time of Count (hr)	Length of Count (min)	Counts per min
0	10	59.5	47-16	18	232.1
0-6	10	66	47-45	10	227.8
0-17	10	69.6	49-47	10	230.5
0-28	10	74.5	50-56	28	245.5
0-40	11	82.7	51-25	18	246.5
0-57	10	98.2	52-15	12	250.9
1-11	10	125	53-17	10	254.9
4-3	10	156	53-37	10	258.1
5-26	10	165.4	53-52	22	253.5
6-33	10	164.6	54-24	20	254.2
7-1	10	165.0	55-22	30	260.9
16-40	10	177.8	65-7	10	290.6
16-51	11	170.1	65-22	16	296
17-39	12	174	65-38	14	303.1
18-6	12	182	65-54	18	305.5
18-31	24	192.8	66-11	12	308.4
19-12	10	186.9	66-24	12	307
19-36	10	196.2	66-46	28	304.8
21-10	14	192.5	67-10	20	301.4
21-54	10	199.2	68-27	10	316.2
22-28	10	201.8	68-39	14	308.2
23-3	10	200.7	69-15	36	312.3
23-22	10	199.8	70-32	20	324.6
25-7	10	205.2	70-47	10	328.7
28-9	26	206.2	70-59	10	326.4
29-29	10	209.6	71-15	20	332.3
29-53	10	211.5	71-42	32	332.2
30-34	10	215.5	72-6	11	338.1
31-15	10	222.7	72-45	10	336.5
43-21	10	235.6	74-9	42	337.6
44-42	12	229	76-15	12	347.4
45-41	18	235	78-22	6	353.5
45-55	10	230.2	87-41	10	384.2
46-12	10	223.8	88-45	16	389.5
46-28	10	228.5	89-15	26	399
46-40	10	226.4	89-22	14	393.5

Run 102

Time of * Count (min)	Length of Count (min)	Counts per min	McLeod Gauge Reading (mm)	Time of * Reading Gauge (min)
0	12	41	2	2
7	12	59.5	2	10
16	10	63.6	6	19
27	10	70.3	7	23
65	1	80	8	26
82	10	94	7	34
			11.5	37
111	1	92	10	39
130	7	103	9.5	41
145	10	111	10	49
158	10	107.8	11	55
188	10	120	11.5	62
202	12	124.9	12	67
225	9	124.4	13	78
242	2	126	13.5	91
565	4	126	13.5	106
-	-	-	13	120
-	-	-	13.5	131
-	-	-	15.5	152
-	-	-	15.5	190
-	-	-	15.5	203
-	-	-	16	227
-	-	-	16	327
-	-	-	16	383
-	-	-	16	569
-	-	-	16	1170

* Time after admission of mercury vapour

APPENDIX 4

Calibration of McLeod Gauge

Under the constant temperature conditions used $P_1V_1 = P_2V_2$, where P_1 torr was the unknown pressure in the bulb of volume V_1 cc, V_2 cc was the volume of the compressed gas in the capillary $= \pi \times r^2 \times h$cc where r was the radius of the capillary and h was the length of the gas column. The pressure of the compressed gas was equal to the vertical distance from the bottom of the gas column to point to which the mercury reference column was raised.

Wt. of mercury to fill bulb at 18°C	=	272.02 g
Vol. of 1 g Hg at 18°C	=	0.0738 cc
$\therefore$ Vol. of bulb (V_1)	=	20.13 cc
Radius of capillary tubing (Veridia)	=	0.125 cm
The vertical distance from the sealed end of the capillary to the ref. mark	=	4.70 cm

If h = length of compressed gas column

$$(h + 4.7) \times (\pi \times r^2 \times h) = P_1 \times V_1$$

$$\therefore P_1 = (h + 4.70) \times 2.43 \times 10^{-2} \text{ torr}$$

PROGRAMME 2.

Includes solution of equation:

$$m = \frac{n \times sxy - sx \times sy}{n \times sx^2 - (sx)^2}$$

Where $s \equiv \sum$, x = time (t), $y = \ln P_c$

```
DA030017LSJH  L.S.PROGRAM.→

begin  integer  n, i, p;
real  sx, sy, sxy, sx2, m,c, d;
open(20);  open(10);
start:  n:= read(20);
begin  array  x,y [ 1:n];
sx:=sy:=sxy:=sx2:=0.0;
for i:=1 step 1 until n do
begin  x[i]:= read(20);
y[i]:= read(20);
y[i] := ln(y[i])
end;
for i:=1 step 1 until n do
begin sx:= sx + x[i];
sy:= sy + y[i];
sxy:=sxy + x[i]×y[i];
sx2:=sx2 + x[i]↑2end;
d:= n×sx2 -sx↑2;m:= (n × sxy -sx × sy)/d;
c:= (sx2 × sy - sx × sxy)/d;
sx:=0.0;
for i:= 1 step 1 until n do
begin  x[i] := (y[i] - c)/m - x[i];
sx := sx + x[i]↑2  end;
 d := sqrt (sx/n);


write text (10, [[4c] m*=*]);
write (10, format ([-d.ddddd₁₀-nd]), m);
write text (10, [[3s] c*=*]);
write (10, format([-d.ddddd₁₀-nd]), exp(c));
write text (10, [[3s] rms*=*]);
write (10, format ([-d.ddddd₁₀-nd]), d);
write text (10, [[2c] Deviations [c]]);
for i := 1 step 1 until n do
write (10, format ([ 12s -d.ddddd₁₀-ndc]), x[i]);

p := read (20);
if p = 1 then goto start;
close (10);
close (20)
end  end  →
```

APPENDIX 5

The Computer Programmes

Two computer programmes were prepared using KDF 9 Algol. The first solved the expressions derived in sections 9.17. and 9.27., viz.

$$P_c = P - G \times 0.1344$$

where $P = (P_o - a + 0.015)$ and G = gauge reading with P_o and a in units of torr x 10. The solution material from this programme was arranged such that it could be fed directly as data for the second programme. This programme determined the best straight line through the values of $\ln P_c$ against time by the method of least squares. In practice, however, it was found advisable to plot the values obtained from the first programme to verify the linearity of the relationship, before using the second programme. Thus any points at the beginning or end of the reaction which did not conform to the linearity, as a result of an induction period or termination of the reaction, were omitted.

Programme 2 is indicated opposite. The data for this was prepared in the following manner. The values of P_c and t were given for each run, preceded by the number of points in each run. In the case of the first run the total number of runs was also given. At the end of the data for each run an indication was given that more data was to follow using the symbol (1;) except in the case of the last run in which (0;) was used. This programme, as well as giving the gradient of the relationship between $\ln y$ and t, also gave the values of the intercept , the root mean square error and the deviation of each point.

APPENDIX 6

Study of the Gamma ray Photoelectric Effect in Lead

In an attempt to improve the counting efficiency of the G.M. tube for γ radiation produced from the radioactive mercury adsorbed on supported catalysts the following study was carried out. The counter was fitted at the top of a lead castle which contained a number of shelves numbered as below :

Counter
—— Shelf 1
—— Shelf 2
—— Shelf 3
—— Shelf 4

A source of radioactive mercury ^{203}Hg was placed on shelf 4 and a sheet of 69 mg cm^{-2} aluminium was placed on shelf 3. This amount of aluminium was sufficient to absorb the β radiation produced by the source without affecting the amount of γ radiation. Sheets of various metals were placed on shelf 2 and the counts obtained from the counter are listed in the table overleaf.

It was found that the presence of aluminium or copper had little effect on the count observed but a sheet of lead of thickness comparable to that of these metals produced a considerable increase. Increase of the thickness of lead to twice the original value did little to affect the count but increase to three times produced a reduction which was still substantially higher than that obtained with the other two metals or with no metal present at all. This indicated that lead in the range of thicknesses used was able to increase the efficiency of the counter. This was brought about by the interaction of the gamma radiation with

Metal on Shelf 2	Thickness mg cm^{-2}	Counts per min
None	-	4,636
Aluminium	79.3	4,518
Copper	84.7	5,062
Lead	87	10,150
Lead	153	10,053
Lead	240	9,259

the high atomic number metal to produce electrons which were more efficiently counted by the counter. That the absorption occurred by this process was verified by placing the 79.3 mg cm^{-2} sheet of aluminium on shelf 1 when the 153 mg cm^{-2} lead was present on shelf 2. Although this thickness of aluminium had little effect on the count when no lead was present a reduction to 3895 c.p.m. was observed in this case owing to the more efficient absorption by the aluminium of electrons compared with γ radiation.

The efficiency of the counter used in the supported catalyst work was, therefore, increased by placing a sheet of 87 mg cm^{-2} lead as close to the counter window as possible.

APPENDIX 7

Use of a Well-Crystal Scintillation Counter to Determine the Weight of Radioactive Mercury Present on a Supported Catalyst

Pd Experiment 8

Summary of Counts (all counts taken over 10 sec, Background 1023 ÷ 100)

Source	Counts sec^{-1}	+ Paralysis Time - Background	Counts sec^{-1} mg^{-1}
20.6 mg unknown cat.	1115.2	1117.6	54.25
23.7 mg unknown cat.	1245.7	1251.2	52.79
28.8 mg unknown cat.	1544.2	1558.1	54.10
43.5 mg unknown cat.	2249.4	2291	52.67
20.6 mg + 1 ml HNO_3	1125.6	-	-
1 ml standard soln. (+ 24.9 mg inactive cat.)	562.6	-	-
1 ml standard soln. (+ 20.3 mg inactive cat.)	556.4	550.7 av.	-
1 ml standard soln.	553.8	-	-
1 ml standard soln.	558.6	-	-

Standard soln. contained 12.8 mg ^{203}Hg in 500 ml HNO_3

Total wt. of catalyst = 225.6 mg

$$\therefore \text{ Total wt. of mercury } = \frac{12.8 \times 53.45 \times 225.6}{500 \times 550.7} \text{ mg}$$

$$= 0.56 \text{ mg}$$

Comparison with Liquid Counting Technique

0.1725 g of catalyst containing mercury dissolved in 12 cc HNO_3. Standard soln. contained 12.8 mg ^{203}Hg in 500 cc HNO_3.

Summary of Counts

Source	Counts min^{-1}	+ Paralysis Time - Background
Background	18.5	18.5
10 cc unknown	445	427
10 cc standard	328	310

Total wt. of catalyst = 225.6 mg

$$\therefore \text{ Total wt. of } {}^{203}\text{Hg} = \frac{12.8 \times 427 \times 12 \times 0.226}{0.173} \text{ mg}$$

$$= 0.55 \text{ mg}$$

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