Tracer investigations of catalysed chemical reactions

Campbell, Kenneth C.

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TRACER INVESTIGATIONS OF CATALYSED CHEMICAL REACTIONS.

THESIS
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Kenneth C. Campbell, B.Sc., A.R.I.C..

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Finally, I wish to acknowledge a grant from the Ministry of Education received during the course of this work.

Kenneth C. Campbell.

CONTENTS

ABSTRACT

The catalytic hydrogenations of propylene and cyclopropane have been studied using evaporated nickel films as the catalysts at 25°C. The effect of the presence of mercury in these two reactions has also been investigated and it was found that the catalyst was poisoned by mercury for the cyclopropane hydrogenation but not for that of propylene. As it was considered that chemisorption differences would explain this selective poisoning of the catalyst, adsorption studies have been made for cyclopropane, propylene, and hydrogen on nickel films and the effect of mercury on the chemisorption investigated. The adsorption of mercury on nickel films has been measured using a radiochemical technique.

Mercury was found to prevent hydrogen chemisorption and the inhibition of the cyclopropane hydrogenation in the presence of mercury has been interpreted in terms of this. Theoretical considerations of the problem of propylene hydrogenation have been made, and these have thrown some light on phenomena observed in the catalytic hydrogenation of ethylene.

A detailed study of the displacement of hydrogen adsorbed on nickel by mercury has been made, and it was

found that the displacement was not complete. The amount of hydrogen retained after the action of mercury on films has been measured at different degrees of coverage by a radiochemical method and has been found to be a function of the adsorptive capacity of the surface rather than of the amount of hydrogen adsorbed. This has been interpreted in terms of the isolation of individual hydrogen atoms on the surface, and the adsorption of hydrogen in pores which are subsequently blocked by mercury.

INTRODUCTION

It has been realised for many years now that the course of a chemical reaction involving heterogeneous catalysis is profoundly influenced by the choice of catalyst to be used, both with regard to the velocity of reaction and the nature of the products obtained.

As early as 1922, Adkins (1) found that the mode of catalytic decomposition of ethyl acetate depended on the catalyst used. The principal products could be either ethylene, or acetone and carbon dioxide, and an explanation was attempted, based on the porous structure of the catalyst. Later in 1922 however Langmuir introduced the concept of surface interactions (2) and the phenomenon of catalyst specificity was attributed to the spacing of the atoms on the catalyst surface used. This was suggested since it was observed that the formation of acetone as the principal product required a larger atomic spacing than the formation of the olefine. The differences undoubtedly occurred because of the different possible modes of attachment of the molecule of ethyl acatate to the surface.

It also came to be realised that another factor besides the "geometric factor" influenced catalytic activity - the "electronic factor" (3). This is concerned with the availability of orbitals in the catalyst by means of which adsorption by surface bonding, or "chemisorption" can take place.

The importance of the transition elements in catalysis lies in their possession of nearly filled atomic d orbitals. The operation of this factor is clearly seen in the results of the experiments on catalysis by alloys of these transition metals with group 1b metals, notably alloys of copper and nickel, and palladium and gold. In these alloys the change of lattice spacing with composition is very small, so that any observed differences in activity could be assumed to be quite independent of the geometric factor.

Couper and Eley investigated the catalytic activity of palladium-gold alloys for the parahydrogen conversion (4), and found that a progressive increase in the proportion of gold resulted in high catalytic activity being maintained until the gold content was 60 atomic % of that of the palladium, at which point the activity dropped sharply to a much lower value.

This can be correlated with the fact that the pure transition metal contains vacancies in the d band amounting to 0.6 vacancies per metal atom. Experiments were also carried out in which the activity for the parahydrogen conversion of an outgassed palladium filament was compared with that of a filament charged with dissolved hydrogen, and again a marked reduction in activity was observed. Similar results were obtained by Dowden and Reynolds for the hydrogenation of ethylene, and in the decomposition of formic acid and methanol on copper-nickel alloys (5, 6). In each case the drastic reduction in activity occurred when an alloy composition had been reached such that the vacant d orbitals of the transition metal were filled by the s electrons of the group lb metal, thus rendering the chemisorption much more difficult.

These developments in the subject of catalysis contributed to the realisation that a detailed understanding of the processes of chemisorption was of fundamental importance in the interpretation of catalysis.

Chemisorption studies have always been difficult because of the need to ensure freedom from initial contamination of the surfaces used. A significant advance was made in 1935 when work was begun on the investigation of the structure and properties of metal films, produced by metal evaporation under high-vacuum conditions (7).

In 1940, Beeck, Smith and Wheeler (8) employed evaporated films of nickel and iron as catalysts in the hydrogenation of ethylene. This investigation met with a great deal of success, as it was found that results were reproducible from one film to another and that the catalytic activity of nickel was proportional to the film weight. Measurements of the chemisorption of ethylene, hydrogen, carbon monoxide, nitrogen, and oxygen were also made, and here again amounts adsorbed were proportional to film weights. This indicated that a "porous" structure was presented to the adsorbing gas.

Investigation, by electron diffraction, of similar films produced by evaporation in argon or nitrogen at about 1 mm mercury pressure revealed that the crystallites of metal were orientated with respect to the substrate. In the case of nickel and iron the orientation was with the (110) and (111) planes respectively parallel to the substrate. Orientated nickel films were found to possess twice the surface per unit weight for adsorption, and ten times the activity for ethylene hydrogenation, when compared with unorientated films.

The use of evaporated films as surfaces for the quantitative study of adsorption and catalysis has since been realised to be of the utmost value, and their use has made possible a great advance in our knowledge of the mechanisms of heterogeneous catalysis.

The investigation to be described in this thesis is concerned with the mechanism of a selective catalyst poisoning process on evaporated metal films. This problem was suggested by an observation by Corner and Pease (9) that it was possible to prepare a nickel-on-kieselguhr catalyst which would selectively hydrogenate propylene in admixture with cyclopropane and hydrogen. This method enabled the analysis of mixtures of propylene with cyclopropane to be effected by successive hydrogenation of the two constituents on poisoned and unpoisoned catalysts.

A nickel catalyst was used which had been prepared by the deposition of nickel carbonate on kieselguhr. The nickel carbonate was decomposed and reduced to nickel by a stream of hydrogen, at a temperature which was gradually raised to 400°C. This catalyst was maintained at a temperature of 150°C and poisoned for cyclopropane hydrogenation by the introduction of a few drops of mercury to the vessel containing the catalyst. In this condition it was found that efficient hydrogenation of propylene in a propylene-cyclopropane mixture could be effected at 150°C by the catalyst, while hydrogenation of the cyclopropane did not occur. Subsequent use of an unpoisoned catalyst prepared in a similar manner enabled the hydrogenation of cyclopropane to be accomplished as a seperate stage. Raising of the catalyst temperature to 300°C resulted in mercury being driven from the poisoned catalyst, thereby restoring its activity for the hydrogenation of cyclopropane.

This phenomenon is of considerable interest because the poisoning action is selective, and because the electronic configuration of mercury is markedly different from that of other known catalyst poisons (10), e.g. compounds of sulphur, nitrogen, phosphorus, arsenic etc. in their lower valency states.

It was therefore decided to find out if this poisoning occurred on nickel films, and if it did then it seemed likely that the mechanism of the selective poisoning might be elucidated by a study of chemisorption.

Bond and Turkevich have shown that in the reactions of deuterium with propylene (11) and cyclopropane (12) over platinum catalysts, the distribution of deuterium in the products was substantially different in the two cases. It seemed unlikely therefore that the isomerisation of cyclopropane to propylene occurred as a first stage in its hydrogenation. Rather it seemed likely that differences in behaviour between cyclopropane and propylene towards hydrogenation on a platinum catalyst lay in the manner in which the reacting species were adsorbed on the surface

In the case of hydrogenation on nickel in the presence and in the absence of mercury it seemed likely that these differences in adsorption would be important and accordingly it was decided to attempt to solve the problem by measuring the adsorption of the species involved upon nickel films, and to investigate the effect of mercury upon this adsorption.

CHAPTER 1

HYDROGENATION OF CYCLOPROPANE AND PROPYLENE, OVER NICKEL IN THE PRESENCE AND ABSENCE OF MERCURY.

Corner and Pease (9) found that mercury acted as a selective catalyst poison for the hydrogenation of cyclopropane over nickel. The mechanism of the poisoning process was unknown, and the main part of this thesis deals with its elucidation.

The catalyst chosen for the investigation was not that used by Corner and Pease - nickel on kieselguhr- for it was decided that the catalyst used must be reproducible from one experiment to the next. For this reason the catalyst chosen was evaporated nickel supported on glass.

The purpose of the first set of measurements on cyclopropane and propylene hydrogenation rates was to find out whether or not mercury would selectively poison nickel in the form of a film as well as nickel on kieselguhr. In this chapter these hydrogenation measurements are described, together with the results which were obtained.

1.1 Preparation of the catalyst.

The nickel films which were used as catalysts were deposited upon the walls of a Pyrex catalyst vessel, by evaporation of nickel from an electrically-heated hair-pin shaped filament. The design of this type of catalyst vessel is described in detail in chapter 7.

To obtain films of good reproducibility (8) it was essential to ensure extreme cleanliness of the catalyst vessels, and to degas these by heating under high-vacuum at 500°C for several hours. The filaments from which the evaporation was to be made were heated electrically to a temperature just below the evaporation temperature during the last hour of this degassing treatment. This freed the filaments from occluded gases. To ensure that the film when prepared was completely mercury free, this proceedure was carried out with the vessel attached to a mercury-free vacuum system. Pressures in this system as low as 10^{-5} mm, measured by a Penning ionisation gauge, were commonly obtained (13).

The catalyst vessels were equipped with break-seals so that they could be transferred from the mercury-free apparatus to another in which the hydrogenation rate measurements were made. When the degassing proceedure had been completed the vessels were sealed-off at their break-seals and removed from the rest of the apparatus. The nickel film was deposited by heating the filament

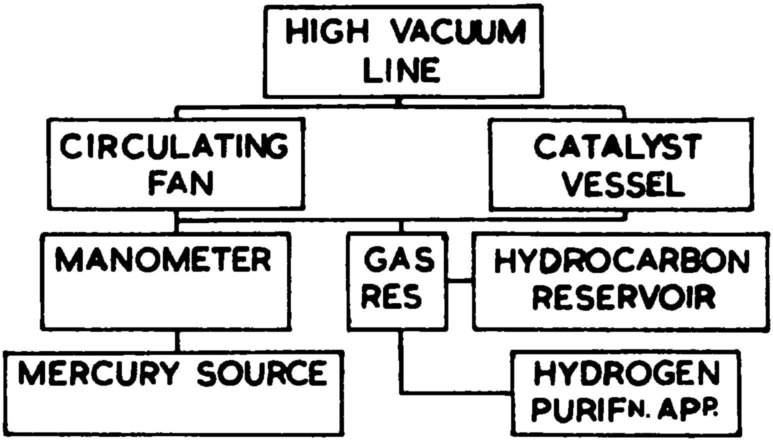

HIGH VACUUM LINE
CIRCULATING FAN
CATALYST VESSEL
MANOMETER
GAS RES
HYDROCARBON RESERVOIR
MERCURY SOURCE
HYDROGEN PURIFN. APP.

FIG. 1

electrically and the walls of the tube were cooled by immersion in running water to minimise sintering of the film during the evaporation. The nickel was deposited at the rate of 0.2 to 0.4 mg per min. Full experimental details will be found in chapter 7.

1.2. The Apparatus for Hydrogenation Measurements.

The apparatus with which hydrogenation measurements were made was part of a conventional mercury-containing vacuum system. This apparatus consisted essentially of the catalyst vessel and its circulating system; this was made as a unit before the preparation of the nickel film and was joined to the rest of the apparatus by means of a break-seal. The remainder of the apparatus comprised gas purification apparatus and reservoirs, a mercury manometer and source of radioactive mercury for use as a tracer in the poisoning experiments. A schematic diagram of the apparatus is shown in fig. 1 and a detailed diagram in chapter 8.

The circulating system was used during the hydrogenation rate measurements to maintain a flow of reactants over the catalyst to ensure that it was accessible to fresh reactants at all times. This circulation was achieved by the use of a glass fan fitted to a glass-enclosed mild steel rotor which was driven by a rotated magnet external to the system.

The hydrogenation rate was observed by following the change of pressure which accompanied reaction; a mercury manometer was used for this purpose. This manometer was constructed from 2 mm bore thick-walled capillary tubing and was filled with ^{203}Hg-labelled mercury, to enable it to be used as a source of mercury vapour for the poisoning experiments.

The reactant gases - cyclopropane or propylene, and hydrogen - were stored in reservoirs attached to the apparatus. An additional reservoir fitted with a side arm was provided in which the reactants could be mixed as follows. A sample of the hydrocarbon was first admitted to the empty reservoir and condensed by cooling the side arm of the reservoir in liquid nitrogen. Hydrogen was then admitted and the hydrocarbon allowed to evaporate. Diffusion of the two gases was allowed to proceed for at least 30 min before the first hydrogenation reaction was carried out. All the materials used in these hydrogenation reactions were very carefully purified before use. Details of the purification proceedures are given in section 8.1.

1.3. The Method of Rate Measurement.

Immediately the break-seal on the catalyst vessel and circulating system was broken, the circulator was set in motion and a sample of the gas mixture admitted at about half the reservoir pressure. Manometer readings were taken at various time intervals until the reaction was almost completed. The gas was then rapidly pumped away, and a further measurement immediately carried out using a gas sample at the full reservoir pressure. This proceedure yielded results for the hydrogenation rates at two different initial pressures and in the absence of mercury, since diffusion of mercury from the manometer was inhibited by the presence of the gas mixture. These two measurements any effect of the variation of initial pressure on the reaction rate to be seen. The results could then be used to compute a correction for the differences in initial pressure arising from the progressive drop in reservoir pressure caused by the removal of samples for the poisoning experiments.

After this second experiment the gases were pumped away. The apparatus was left under vacuum to allow mercury vapour to diffuse from the manometer on to the film. This diffusion of mercury vapour was allowed to proceed for a measured time, and a further hydrogenation measurement was then carried out. Further periods of exposure to mercury vapour were given and these were followed by hydrogenation measurements until any effect of mercury vapour upon the rate could be seen.

The trace amounts of radioactive mercury which had arrived on the film were measured by a radiochemical technique as follows. The catalyst vessel was removed from the apparatus and the nickel film dissolved in 25 ml. 10N nitric acid. Aliquots of 10 ml. of this solution were counted in a liquid counter and the activities compared with that of a 10 ml. sample of a standard solution. This standard solution was prepared from a weighed quantity of mercury of the same specific activity as that used in the manometer. This comparison enabled the weight of mercury on the film to be calculated. The weight of nickel in the film was found by colorimetric analysis; details of the method used are given in section 7.7.

1.4. Results of the Hydrogenation Experiments.

(a) Experiment 1, Cyclopropane Hydrogenation

In this experiment cyclopropane at 6 cm pressure was mixed with hydrogen at 5 cm pressure, and the mixture stored in a reservoir. The circulating fan was set in motion and a sample of this mixture admitted. Pressure readings were taken with respect to time and these readings are shown in table 1. The results are shown graphically in fig. 2 in which $\log_{10} P_0/P$ was plotted against t, where P_0 was the initial pressure and P the pressure t min after the sample was admitted to the reaction system, since previous work had revealed that the reaction was first order (14). The linearity of this graph confirmed this, but deviations occurred towards the end of the reaction. This was possibly because the circulation was not rapid enough to nullify the effect of dilution of the reactants by the propane formed. The catalytic activity of the nickel film was seen to be decreased by exposure to mercury vapour.

(b) Experiment 2, Cyclopropane Hydrogenation.

This was a preliminary experiment in which a different technique was used from that described in section 1.3. Samples of cyclopropane at a constant pressure of about 50 mm were taken in the catalyst vessel and circulating system for each hydrogenation measurement. This constant pressure was obtained by using the cyclopropane from a reservoir fitted with a side arm cooled in acetone-solid carbon dioxide mixture, and was the saturated vapour pressure of cyclopropane at this temperature. The circulating fan was set in motion and a sample of hydrogen admitted. Readings of the pressure indicated by the manometer were taken with respect to

CYCLOPROPANE HYDROGENATION

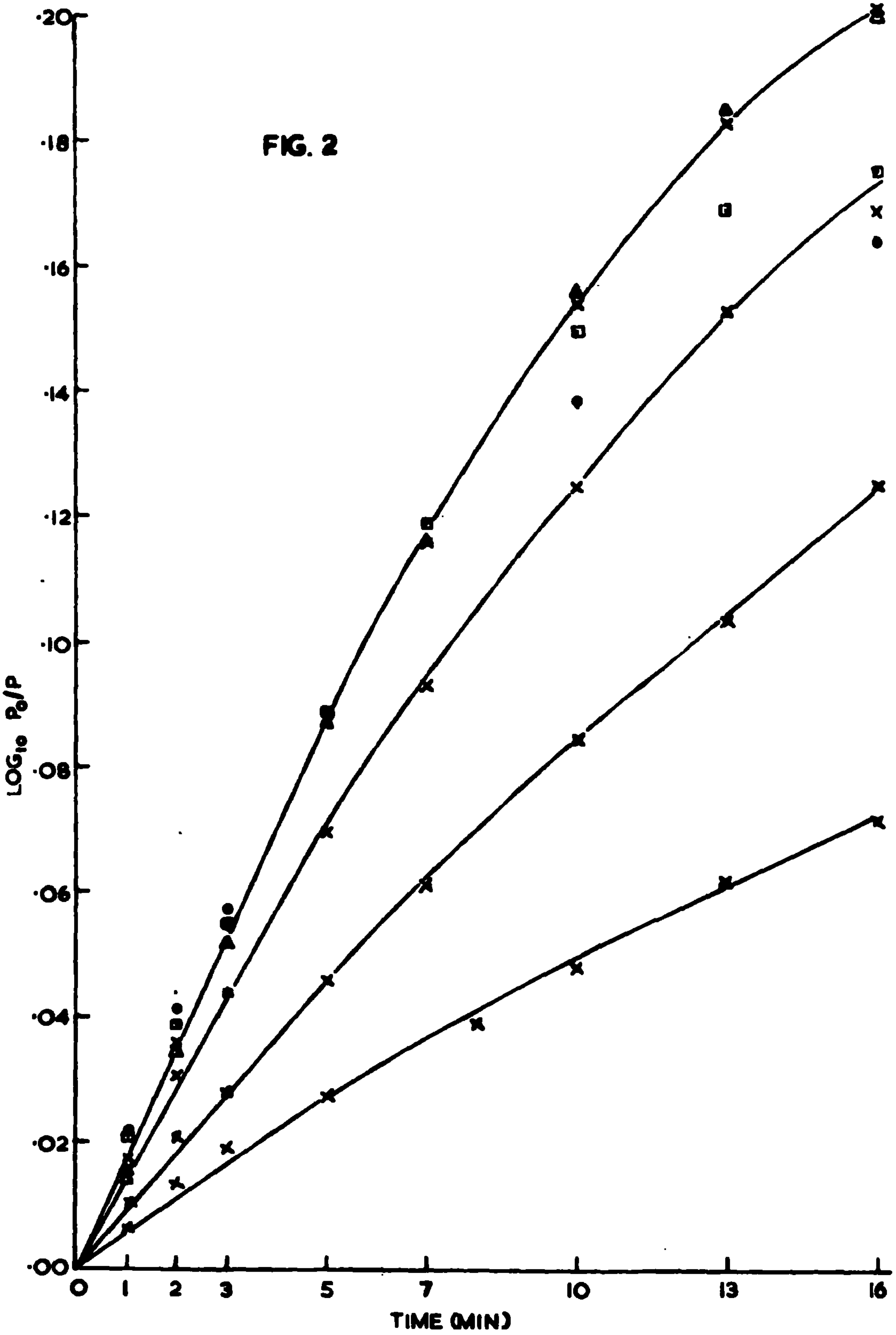


FIG. 2

TABLE 1.

CYCLOPROPANE HYDROGENATION.

Time (min)	Pressure (mm) (1)	(2)	(3)	(4)	(5)	(6)	(7)
0	2.42	8.84	9.80	8.10	7.68	7.56	6.48
1	2.30	8.42	9.48	7.78	7.40	7.18	6.38
2	2.20	8.08	9.06	7.46	7.16	7.00	6.28
3	2.12	7.80	8.70	7.14	6.94	6.90	6.20
5		7.20	8.02	6.60	6.54	6.62	6.08
7		6.72	7.50	6.20	6.20	6.40	5.92
10	1.76	6.26	6.84	5.68	5.76	6.06	5.80
13		5.98	6.40	5.32	5.40	5.80	5.62
16	1.64	5.90	6.18	5.10	5.20	5.52	5.50

Sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)	
Time of exp. to Hg	0	0	0	0	15	55	115	min
Rate constant	.0176	.0176	.0176	.0176	.0142	.0092	.0054	

Mercury Estimation.

Liquid counter background = 18.5 counts/min

Count on 10 ml. film solution = 152.5 counts/min

Count on 10 ml. standard soln. (12.32 mg mercury per 250 ml.) = 309.0 counts/min

∴ Weight of mercury on film = 0.568 mg

Nickel Estimation - see page 18a.

CYCLOPROPANE HYDROGENATION

FIG. 3

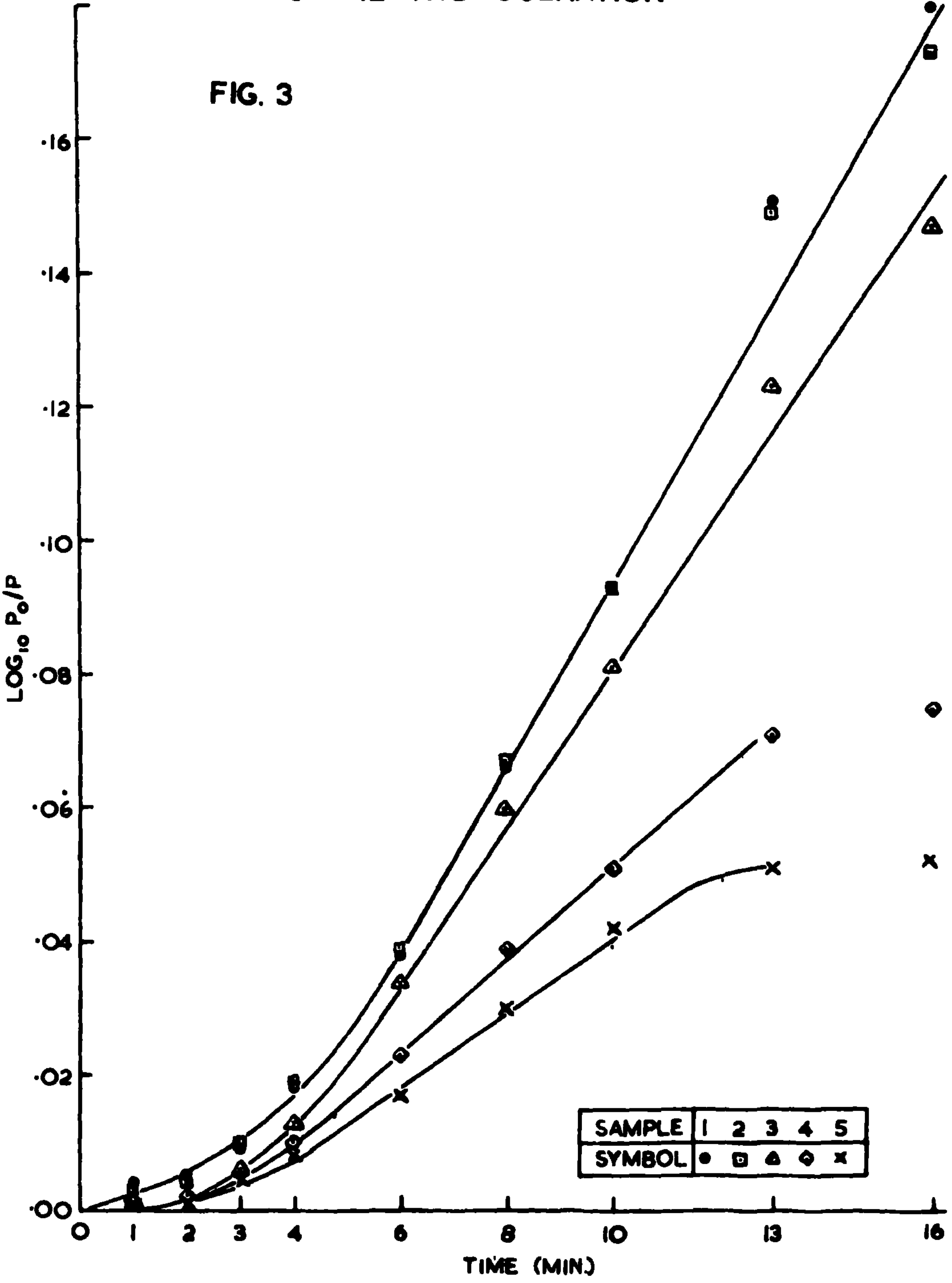


TABLE 2.

CYCLOPROPANE HYDROGENATION.

Time (min)	Pressure (mm) (1)	(2)	(3)	(4)	(5)
0	4.96	9.00	7.44	7.02	6.36
1	4.92	8.94	7.42	7.00	6.36
2	4.90	8.92	7.38	6.98	6.34
3	4.86	8.80	7.34	6.94	6.30
4	4.76	8.62	7.22	6.86	6.24
6	4.54	8.22	6.88	6.66	6.12
8	4.26	7.72	6.48	6.42	5.94
10	4.00	7.26	6.18	6.24	5.78
13	3.50	6.58	5.60	5.96	5.66
16	3.28	6.04	5.30	5.90	5.64

Sample	(1)	(2)	(3)	(4)	(5)
Time of exp. to mercury	0	0	10	50	100
Rate constant	.0139	.0139	.0118	.0070	.0055

__Mercury Estimation.__

Liquid counter background = 15.1 counts/min

Count on 10 ml. film solution = 171.4 counts/min

Count on 10 ml. standard soln. (12.32 mg mercury per 250 ml.) = 315.1 counts/min

∴ Weight of mercury on film = 0.642 mg

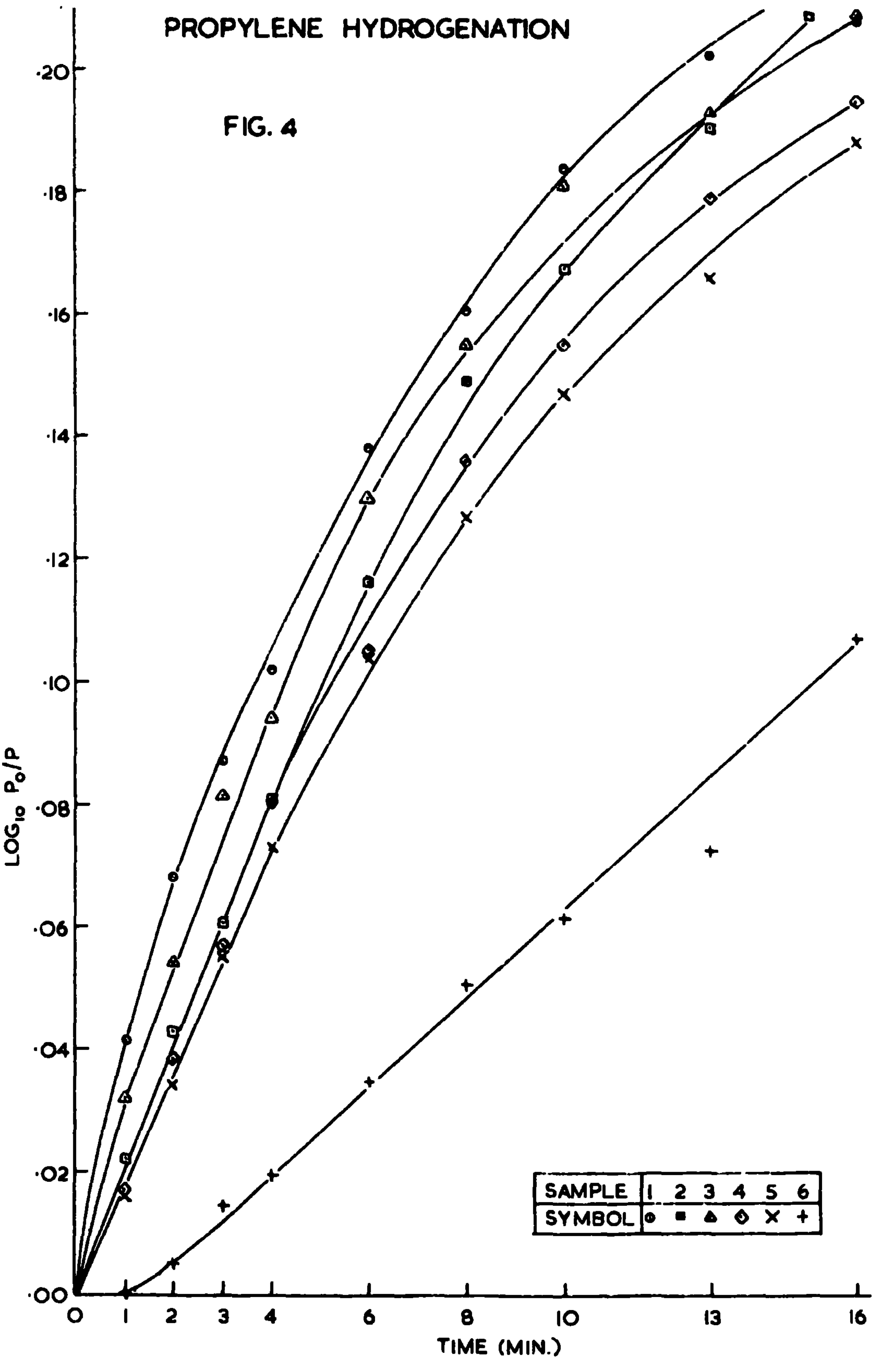
__Nickel Estimation.__ - see page 18a.

time, and these readings are shown in table 2. These pressure readings showed that the reaction was initially slow and increased for several minutes after the hydrogen was admitted. It was concluded therefore that the rate of mixing of the reactants was obscuring the true reaction rate, and the technique described for mixing the reactants before hydrogenation was introduced to obviate this. Fig. 3 shows the graphs obtained when $\log_{10} P_0/P$ was plotted against t. The results were similar to those from experiment 1, apart from the time of mixing effect.

(c) Experiment 3, Propylene Hydrogenation.

Propylene at 2 cm pressure was mixed with hydrogen at 2.5 cm pressure, and this mixture was used for all the hydrogenation measurements. The proceedure for rate measurement used in the previous two experiments was again adopted, and the results are shown in table 3 and fig. 4.

The final sample was hydrogenated after the film had been exposed to air at about 2 mm pressure as a result of the fracture of the rotor of the circulating fan. The results showed clearly that the hydrogenation rate was unaffected by the exposure of the film to mercury vapour.



PROPYLENE HYDROGENATION

FIG. 4

TABLE 3.

PROPYLENE HYDROGENATION.

Time (min)	Pressure (mm) (1)	(2)	(3)	(4)	(5)	(6)
0	2.20	4.00	3.40	2.60	2.20	1.82
1	2.00	3.80	3.16	2.50	2.12	1.82
2	1.88	3.62	3.00	2.38	2.04	1.80
3	1.80	3.48	2.82	2.28	1.94	1.76
4	1.74	3.32	2.74	2.16	1.86	1.74
6	1.60	3.06	2.52	2.04	1.74	1.68
8	1.52	2.84	2.38	1.90	1.64	1.62
10	1.44	2.72	2.24	1.82	1.56	1.58
13	1.38	2.58	2.18	1.72	1.50	1.54
16	1.36	2.46	2.10	1.66	1.44	1.42

Sample	(1)	(2)	(3)	(4)	(5)	(6)
Time of exp. to Hg	0	0	15	45	105	900*
Rate constant			.0180			-

* Film was exposed to air at about 2 mm pressure.

Mercury Estimation.

Liquid counter background = 16.0 counts/min

Count on 10 ml. film solution = 32.6 counts/min

Count on 10 ml. standard soln. (12.32 mg mercury per 250 ml.) = 223.9 counts/min

∴ Weight of mercury on film = 0.098 mg

Nickel Estimation - see page 18a

Nickel Estimations.

First cyclopropane hydrogenation - see page 15.

	Standard solutions		Nickel film solutions	
	38.41mg	58.47mg	A	B
Optical density	0.000	0.710	0.867	0.888
	0.000	0.713	0.880	0.892
Average	0.000	0.711	0.873	0.892

Weight of nickel in film = 63.2 mg

Second cyclopropane hydrogenation - see page 16.

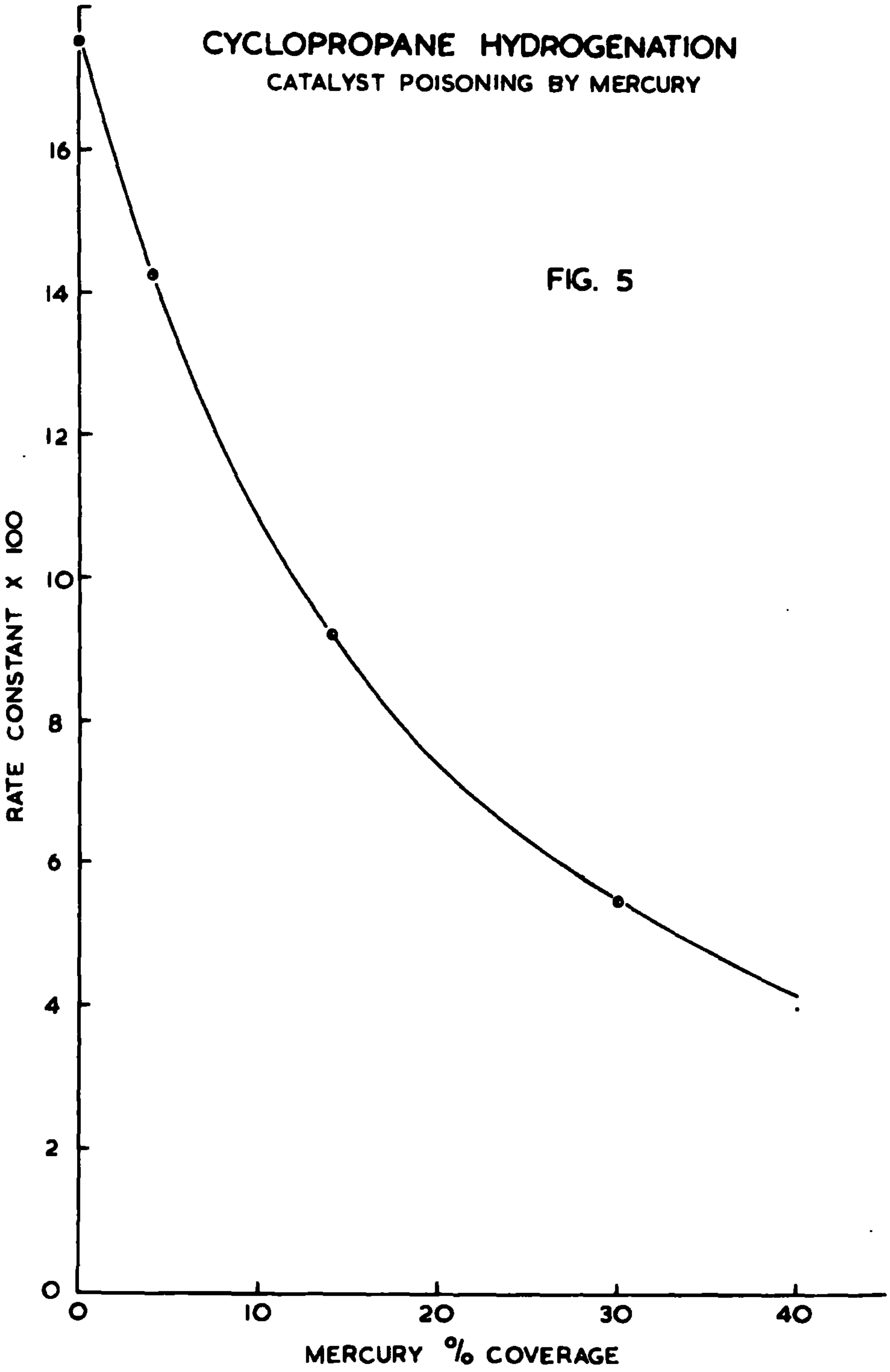
	Standard solutions		Nickel film solutions	
	38.41mg	58.47mg	A	B
Optical density	0.000	0.690	0.730	0.735
	0.000	0.688	0.731	0.733
Average	0.000	0.689	0.730	0.734

Weight of nickel in film = 59.7 mg

Propylene hydrogenation - see page 18.

	Standard solutions		Nickel film solutions	
	30.08mg	38.41mg	A	B
Optical density	0.000	0.517	0.955	0.950
	0.000	0.512	0.950	0.945
Average	0.000	0.512	0.952	0.945

Weight of nickel in film = 45.2 mg



CYCLOPROPANE HYDROGENATION
CATALYST POISONING BY MERCURY

FIG. 5

The results of each of these experiments showed that the rate, expressed as $\frac{d \log P_0/P}{dt}$ was independent of the initial pressure of the reactants, and hence the rate values could be compared directly to show the effect of mercury. Fig. 5 shows this effect on the cyclopropane hydrogenation in which the rate constant is plotted against the fraction of the surface covered by mercury. This fraction of surface covered was calculated for the last hydrogenation on each film from the mercury and nickel estimations, and from the estimated number of surface sites per unit film weight (8). The amount of mercury present at any intermediate time was assumed to be proportional to the time of exposure to mercury vapour, and this assumption was shown to be justified by later results (chapter 5).

Conclusions.

From the results of the experiments described it may be seen that:

1. The rate of hydrogenation of cyclopropane on a nickel film was progressively reduced by the introduction of mercury vapour.
2. The activity was not proportional to the surface free from mercury.

3. The activity of the catalyst in the hydrogenation of propylene was unimpaired when mercury was admitted to the catalyst vessel.

4. The quantity of mercury adsorbed on the catalyst in the presence of propylene was much less than in the case of cyclopropane.

CHAPTER 2.

STUDY OF THE ADSORPTION OF CYCLOPROPANE AND PROPYLENE.

Chapter 1 dealt with the selective poisoning of nickel films by mercury for the hydrogenation of cyclopropane. This phenomenon was investigated in detail by making a study of the adsorption on nickel of the species involved. This chapter is concerned with these measurements for cyclopropane and propylene, and the effect of the presence of mercury upon the adsorption.

2.1. Preparation of the Nickel Surfaces for Adsorption Studies.

Evaporated films of nickel were again used for these adsorption measurements. These films were prepared in a similar manner to those used for the hydrogenation rate measurements, except that they were deposited under 1 mm pressure of pure argon instead of under high-vacuum conditions. When thus deposited, the (110) crystal planes in the film were orientated parallel to the glass support and the film had twice the surface area per unit weight (8).

The design of the catalyst vessel used for these measurements was simpler than that used for the hydrogenation experiments, since it was unnecessary to incorporate a gas circulating system; the practice of using break-seals was however retained. A diagram of the catalyst vessel is shown in section 7.4.

The method of preparation of the catalyst vessels and the deposition of the films was as described for those used for hydrogenation measurements, except that spectrally pure argon was admitted to the catalyst vessel to a pressure of 1 mm before it was sealed off. Full details of the design and construction of the catalyst vessels and of the film preparation are given in chapter 7.

2.2. Apparatus for the Measurement of Adsorption.

The design of the apparatus for the adsorption studies was unconventional because of the difficulties imposed by the necessity to avoid the presence of mercury. To overcome these difficulties mercury-free pressure measuring devices and a technique for gas handling by expansion between sections of apparatus of known volume were used.

The apparatus was built as part of the mercury free vacuum system which was referred to previously in connection with film preparation (1.1.). It consisted essentially of an all-glass Bourdon gauge, an expansion bulb of about 2 litre capacity and a gas pipette into

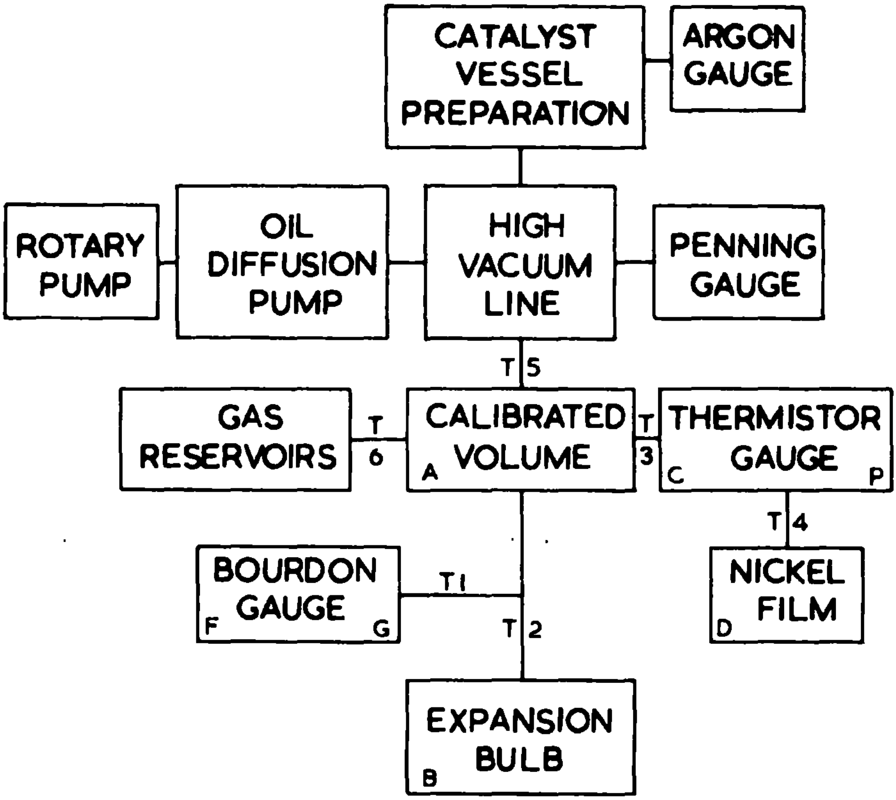

CATALYST VESSEL PREPARATION
ARGON GAUGE
ROTARY PUMP
OIL DIFFUSION PUMP
HIGH VACUUM LINE
PENNING GAUGE
T5
GAS RESERVOIRS
T6
CALIBRATED VOLUME
A
T3
THERMISTOR GAUGE
C
P
T4
BOURDON GAUGE
F
G
T1
T2
NICKEL FILM
D
EXPANSION BULB
B

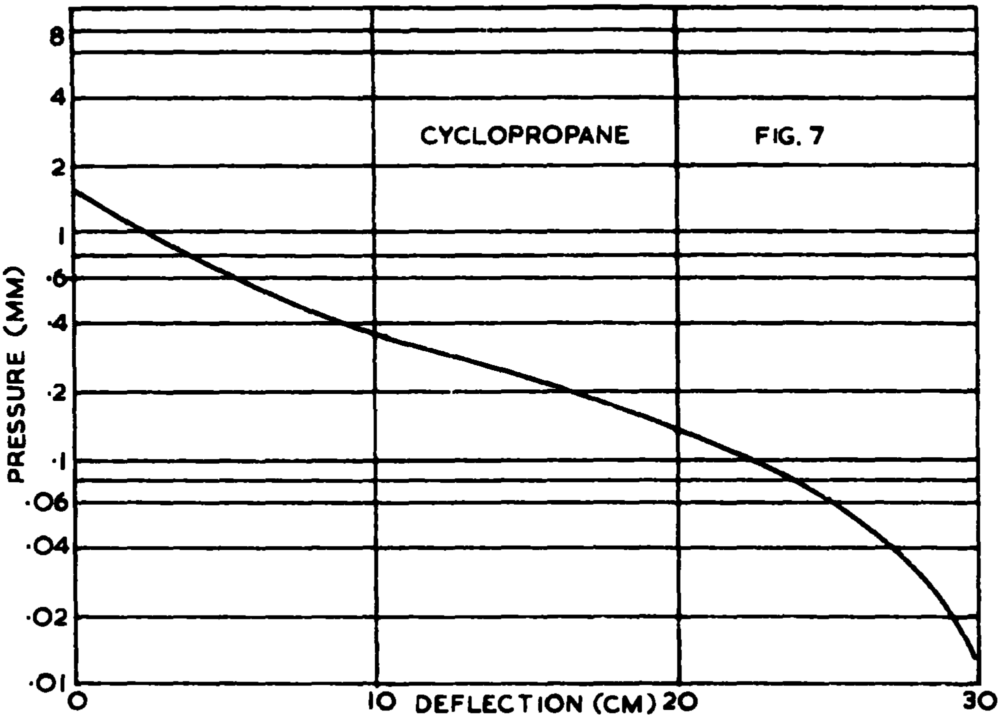
FIG. 6

which was built a thermal conductivity gauge. Each of these components was connected through high-vacuum taps to a calibrated section of about 60 cm^3 capacity, from which connections to high-vacuum and to the gas reservoirs were also taken. The catalyst vessel was connected to this common section through the gas pipette. Fig. 6 shows a block schematic diagram of this arrangement, and a detailed diagram appears in section 8.3 (c).

The construction of the Bourdon gauge is described in section 8.3 (a), and it is sufficient to state here that this device was used as a null instrument in conjunction with an external mercury manometer. Changes of pressure of 0.05 mm mercury from the null position could be detected with this gauge. It was used over the range 10 mm to 60 mm.

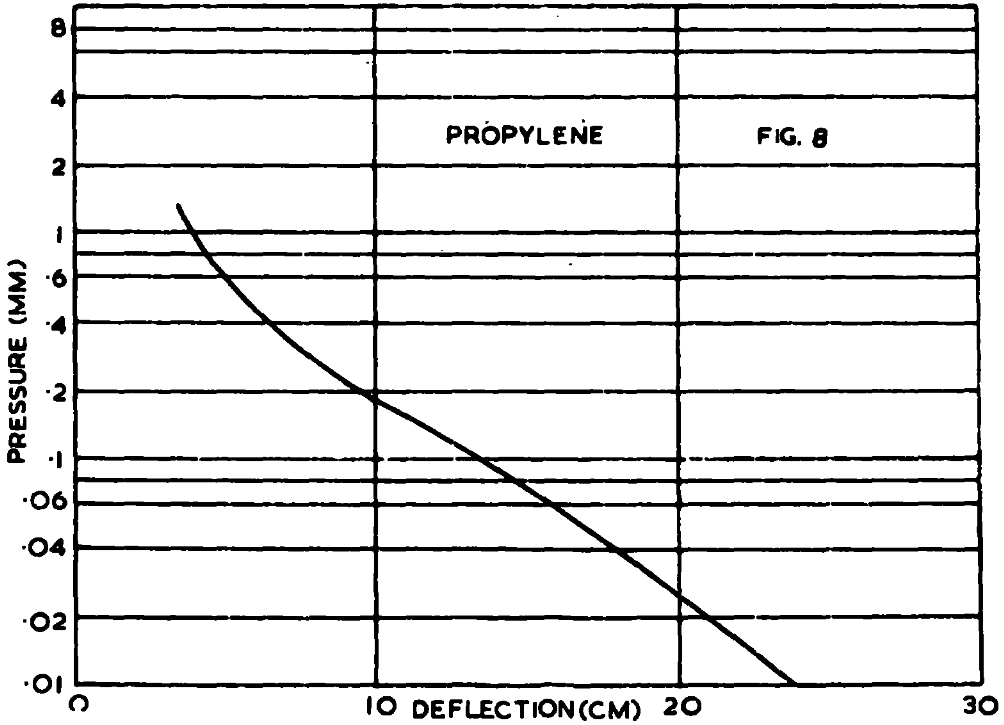
The thermal conductivity gauge was designed to operate in the range 10^{-2} mm to 10 mm, with a wall temperature of 25°C. Thermistors were used as the heat emitters because of their large temperature coefficient of resistance, in order to obtain adequate range and sensitivity under these pressure conditions. The circuit used was essentially a Wheatstone bridge. The thermistor gauge was mounted inside the gas pipette through which samples of gas were admitted to the catalyst vessel, and the gauge, its temperature compensating thermistor,

THERMISTOR GAUGE CALIBRATION



CYCLOPROPANE

FIG. 7



PROPYLENE

FIG. 8

and the catalyst vessel were all immersed in a thermostated water tank at 25°C. The volume of each section of the apparatus, except the Bourdon gauge, was determined during its construction, and that of the catalyst vessel after each adsorption measurement; the vessel was weighed first empty and then full of water, and the volume of water calculated. The volume of each section of the apparatus is given in chapter 8. The thermistor gauge was calibrated for each gas used by noting its galvanometer off-balance deflection under various gas pressures. Typical calibration curves for cyclopropane and propylene are shown in fig. 7 and fig. 8 respectively. A range of pressures was obtained by admitting gas samples in the same manner as during the actual adsorption measurements, to be described in the next section, except that an empty tube was used in place of the catalyst vessel. The reproducibility of calibration results showed that solution of the gases in the Apiezon N tap grease used was either negligible or easily reversible. Experience showed however that long-term galvanometer drifting occurred which displaced all points on the calibration curve by a constant increment. In all except the early experiments therefore a technique was used whereby a calibration appropriate to each experiment could be made, and this is described in section 2.4.

2.3. Materials for Adsorption.

Preliminary adsorption measurements were carried out using propylene supplied by Imperial Chemical Industries Ltd., but this was found to give inconsistent results. Subsequent measurements were carried out using propylene prepared in the laboratory by the debromination of 1.2 dibromopropane with magnesium metal. Cyclopropane was supplied by Messrs. Light & Co.. Both materials were carefully purified by distillation, and full details are given in section 8.1.

2.4. The Measurement of Adsorption.

Adsorption measurements on nickel films were made by the following method. In outline, a sample of gas at about 5 cm pressure was to be measured out and expanded into the expansion bulb B. Aliquots of about 10 cm^3mm were to be allowed to come into contact with the nickel film, in the absence of mercury.

A prepared catalyst vessel was joined to the apparatus at the joint J (fig.6). The apparatus was pumped to a high-vacuum (10^{-5} mm),; the break-seal on the catalyst vessel was broken and the argon pumped away. A sample of the gas to be studied was taken from the reservoirs through the pipette E into section A and the Bourdon gauge F (fig.6) at a pressure of 20 - 50 mm, and this pressure was measured by means of the Bourdon gauge. Tap T1 was closed and T2 opened to allow the sample to expand into B. The pressure was thus reduced to 0.5 to 2.0 mm. Tap T2 was allowed to remain open and a sample of the gas admitted to C by opening T3. The quantity of gas in this sample was of the order of 10 cm^3mm. The deflection produced on the thermistor gauge galvanometer was noted, tap T3 was closed and T4 opened to admit the sample to the catalyst vessel; the fall in pressure due to adsorption and expansion was observed using the thermistor gauge. Further samples were adsorbed if necessary by the same method, until a residual pressure was obtained.

The thermistor gauge was then calibrated as follows. Tap T4 was kept closed throughout the calibration and a further sample of gas from A and B admitted to C and the galvanometer deflection noted. Taps T2 and T3 were then closed and section A pumped to high vacuum; T5 was closed and T3 opened to allow the gas in C to expand into A. The galvanometer deflection was again noted, and the proceedure repeated until the range of the gauge had been covered. The pressure of the gas at any stage could be calculated from the known internal volumes and the initial pressure.

2.5. The Effect of Mercury.

The effect of mercury on the adsorption was studied by admitting mercury vapour to the catalyst vessel after propylene or cyclopropane adsorption. The mercury for this purpose was distilled into a thin-walled capillary tube which was then sealed, and this capillary was mounted in section D in such a way that it could be broken at the appropriate stage in the experiment at will. A diagram of the apparatus used for this is shown in section 8.3; the capillary was broken by turning the B14 cone. Exposure of the film plus hydrocarbon to mercury vapour was generally allowed to continue for a period of one day or more, and any displaced gas detected by means of the thermistor gauge. When the measurements were completed a further sample of gas was taken from the reservoir into the thermistor gauge, and the galvanometer deflection noted and compared with that indicated by the calibration carried out after the adsorption measurements. Any correction necessary for galvanometer zero drift could then be made.

A side arm, which could be cooled in liquid nitrogen, was attached to section D in many of the displacement experiments. If any of the adsorbed hydrocarbon was displaced by mercury it could be quantitatively condensed into this; any hydrogen or lower hydrocarbons produced by hydrocarbon degradation on the catalyst could thus easily be detected by the thermistor gauge.

2.6. Results.

Cyclopropane.

The results obtained from these experiments showed that nickel films adsorbed cyclopropane more rapidly than could be detected by the pressure measuring device (adsorption within 15 - 20 sec). It was found that when cyclopropane samples were admitted to give low surface-coverages no residual pressure was observed. In all cases adsorption was continued until there was a residual pressure, and a study of the amount of gas adsorbed with respect to the residual pressure was made. (In the case of film 26, the amount adsorbed at 1.5×10^{-5} mm was determined by connecting the catalyst vessel to high-vacuum for half an hour after adsorption. Readsorption was then carried out, to find the amount which had been pumped off).

The quantity of cyclopropane adsorbed was low relative to the amount of hydrogen or carbon monoxide adsorbed by similar films, as shown by experiments to be described in the next chapter and by the work of Beeck et al. (8). The amount adsorbed at saturation

ADSORPTION ISOTHERMS AT 25°C

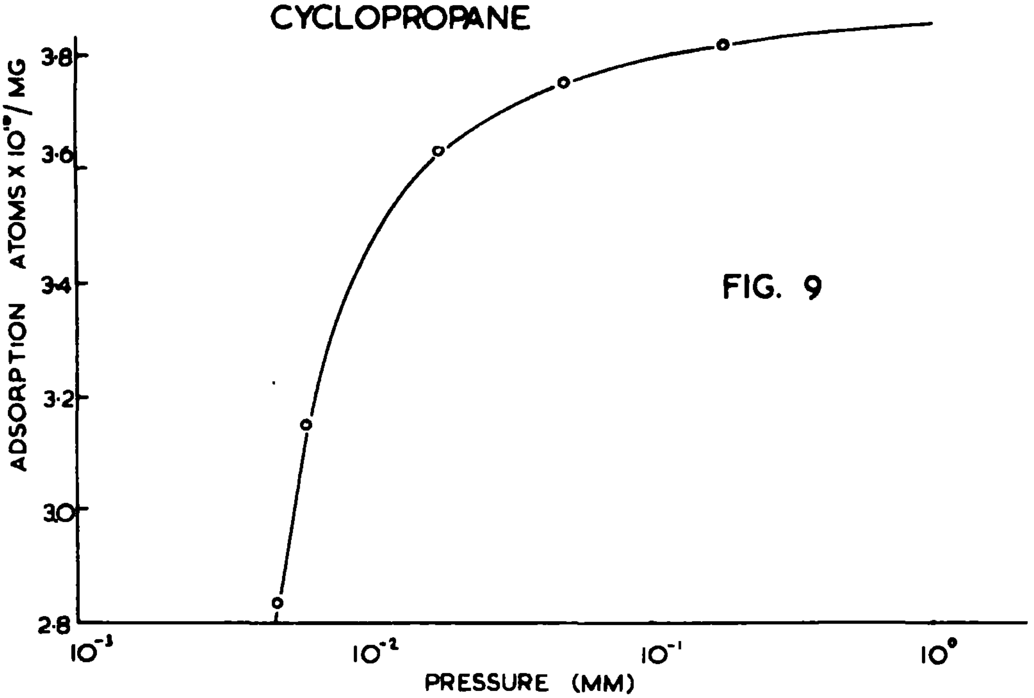

CYCLOPROPANE

FIG. 9

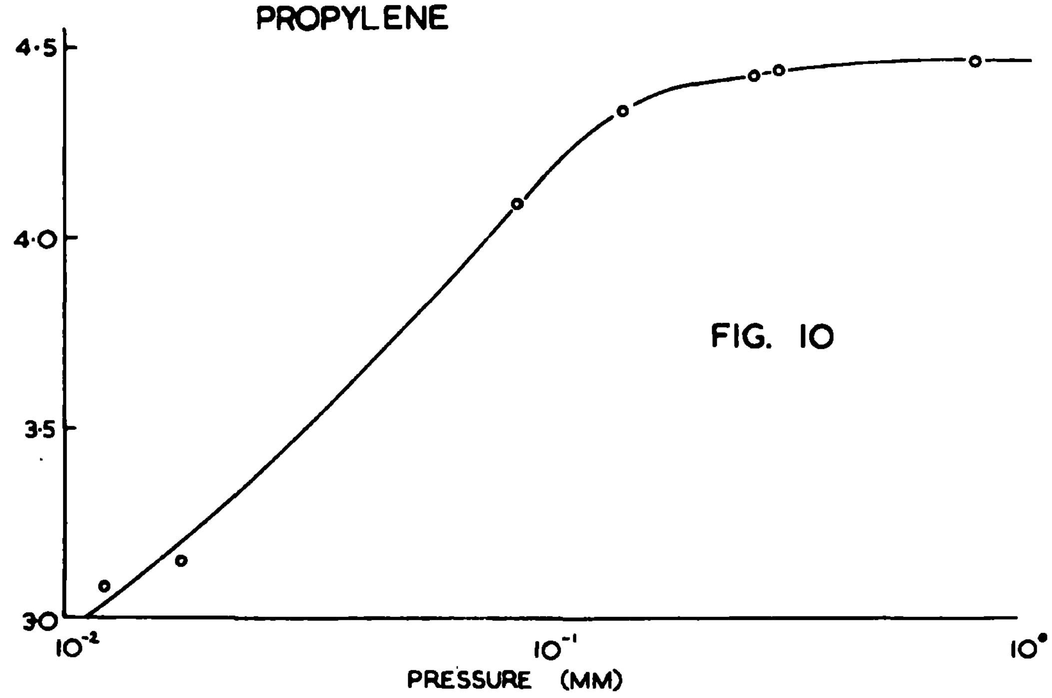

PROPYLENE

FIG. 10

was rather less than 4×10^{16} molecules per mg nickel, compared with the value for hydrogen of 2.5×10^{17} atoms per mg nickel.

Several cyclopropane adsorption experiments were carried out; consistent results were obtained in five experiments and these results are shown in table 4; the effect of equilibrium pressure is shown in fig.9.

Nickel films exposed to mercury vapour were subsequently found to adsorb no cyclopropane. When a sample of cyclopropane was admitted to a vessel containing such a film the equilibrium pressure obtained was that predicted by Boyle's Law. On the other hand, when films were exposed to mercury vapour after cyclopropane adsorption some gas desorption occurred over a period of about 12 hours, as evidenced by the change of thermistor gauge deflection. This gas however could not be completely condensed at liquid nitrogen temperatures; this can be seen from the results obtained with films 30, 32 and 33.

Propylene.

The results obtained from the experiments on propylene adsorption were in many respects similar to those obtained with cyclopropane. Thus the adsorption was more rapid than could be detected by the thermistor

TABLE 4.

CYCLOPROPANE ADSORPTION.

Film no. and weight	Quantity adsorbed ($cm^3 mm$)	Equilibrium pressure mm	Molecules per mg nickel
26*	7.9	1.5×10^{-5}	1.59×10^{16}
(16.26 mg)	8.9	7.5×10^{-3}	1.79×10^{16}
	10.3	1.0×10^{-1}	2.07×10^{16}
30	24.7	7.7×10^{-2}	3.89×10^{16}
(20.73)			
32	16.8	5.5×10^{-2}	3.54×10^{16}
(15.5 mg)			
33	20.5	9.6×10^{-2}	3.62×10^{16}
(18.5 mg)			
90	22.6	5.0×10^{-3}	2.83×10^{16}
(26.1 mg)	30.0	5.0×10^{-2}	3.75×10^{16}
	30.6	1.8×10^{-1}	3.82×10^{16}

* Vacuum deposited film.

gauge, and no residual pressure was obtained at low coverage. The dependance of the amount adsorbed upon residual pressure was again observed, as shown in fig. 10.

The quantity of propylene adsorbed at saturation was greater than in the case of cyclopropane - 4.4×10^{16} molecules per mg nickel. This value was obtained from a set of five consistent results, which were only obtained after very careful purification of the propylene. These results are shown in table 5.

Films which had been exposed to mercury vapour were found to adsorb no propylene. When nickel films were exposed to mercury vapour after propylene adsorption, no change in thermistor gauge deflection was noted, over a period of two days, from that produced by the residual propylene. When the side arm on the catalyst vessel was cooled in liquid nitrogen, this residual propylene condensed and the deflection obtained was the same as under high-vacuum conditions. The adsorption of propylene upon films 69 and 70 was investigated in this manner.

The experimental observations upon which these results were based are reproduced in appendix A.

Conclusions.

Cyclopropane.

1. Cyclopropane adsorbed on nickel films in quantities

TABLE 5.

PROPYLENE ADSORPTION.

Film no. and weight	Quantity adsorbed (cm^3mm)	Equilibrium pressure mm	Molecules per mg nickel
61	10.1	2.4×10^{-2}	3.27×10^{16}
(10.3 mg)	12.8	1.5×10^{-1}	4.05×10^{16}
	13.4	2.8×10^{-1}	4.24×10^{16}
67	11.7	1.7×10^{-2}	3.15×10^{16}
(12.1 mg)	16.1	1.5×10^{-1}	4.33×10^{16}
	16.5	3.1×10^{-1}	4.43×10^{16}
70	23.3	1.8×10^{-2}	3.58×10^{16}
(21.3 mg)	26.8	1.2×10^{-1}	4.11×10^{16}
	29.6	2.1×10^{-1}	4.54×10^{16}
69	27.5	1.2×10^{-2}	3.08×10^{16}
(29.1 mg)	36.5	9.3×10^{-2}	4.09×10^{16}
	39.6	2.9×10^{-1}	4.44×10^{16}
68*	11.3	8.2×10^{-3}	1.20×10^{16}
(30.7 mg)	16.4	1.1×10^{-1}	1.74×10^{16}
	18.9	2.3×10^{-1}	2.01×10^{16}

* Vacuum deposited film.

which were pressure dependent below 10^{-1}mm.

2. The amount adsorbed at saturation was rather less than 4 × 10^{16} molecules per mg nickel for orientated films.

3. The adsorption was prevented by mercury.

4. Mercury vapour displaced gas from the film which was not entirely cyclopropane

Propylene.

1. The amount of propylene which adsorbed on nickel films was dependent upon the equilibrium pressure below about 0.5 mm mercury.

2. The amount adsorbed at saturation was about 4.4 × 10^{16} molecules per mg nickel for orientated films.

3. The adsorption was prevented by mercury.

4. Mercury vapour displaced no gas from the film.

CHAPTER 3.

THE ADSORPTION OF HYDROGEN, AND OF MERCURY UPON NICKEL.

This chapter is concerned with the methods used and the results obtained in an investigation of the adsorption of hydrogen and mercury on nickel.

Measurements of the adsorption of hydrogen were made on evaporated nickel films, and these measurements are described in the first part of the chapter. These measurements were followed by an investigation of the effect of mercury on hydrogen adsorption; two independent methods were used. Finally, the adsorption of mercury upon nickel was investigated.

3.1. The Adsorption of Hydrogen on Nickel.

The adsorption of hydrogen on evaporated nickel films deposited in argon was measured using the same technique as that described in chapter 2 for cyclopropane and propylene adsorption measurements. The thermistor gauge was calibrated for hydrogen pressure measurements, and a typical calibration curve is shown in fig. 11. Samples of the order of 10 cm^3mm were admitted to the catalyst vessel and a total of 50 - 100 cm^3 mm was commonly adsorbed.

Hydrogen for the adsorption measurements was purified

THERMISTOR GAUGE CALIBRATION FOR HYDROGEN

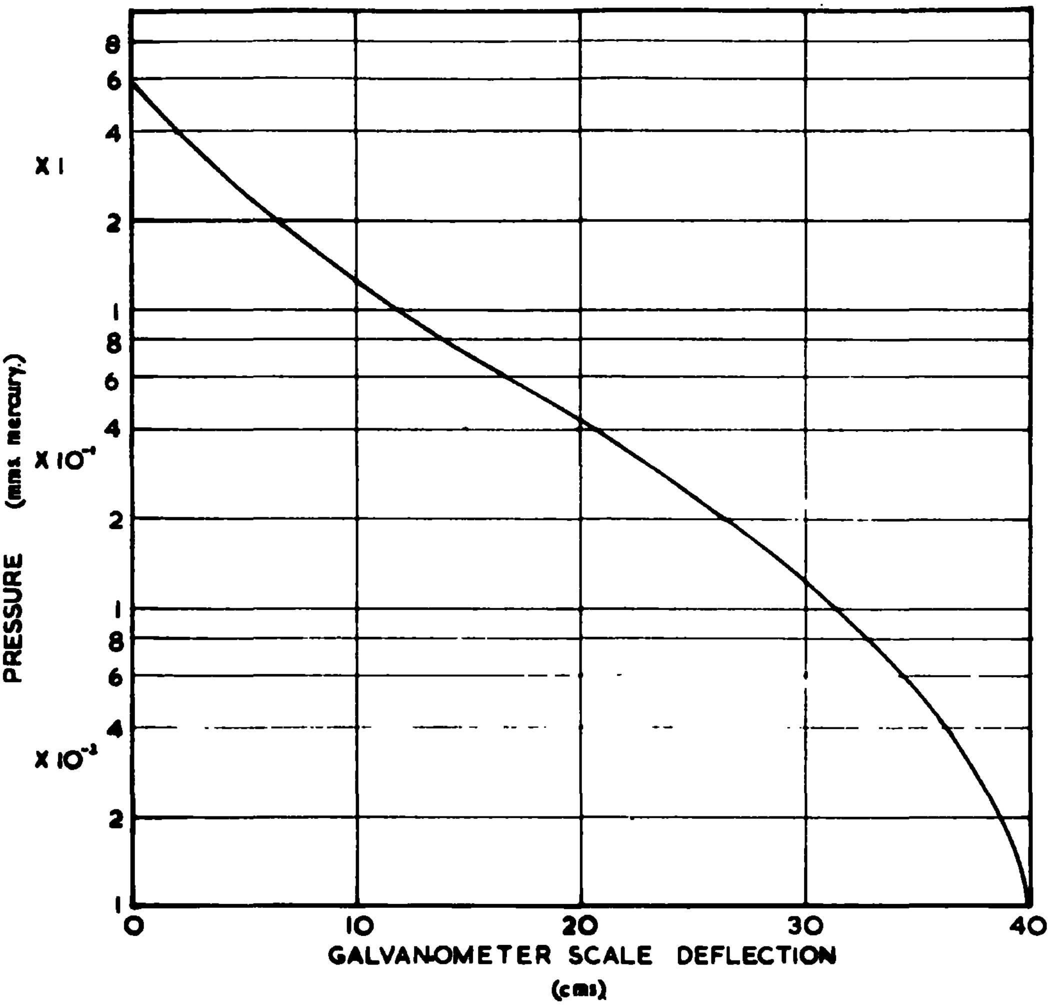


FIG. 11

by diffusion through a heated palladium tube. The experimental details of this method are given in section 8.1.

3.2. Hydrogen Adsorption Results.

Hydrogen adsorption on nickel films was found to take place rapidly - at a rate which could not be measured with the thermistor gauge. Until the surface was saturated the residual pressure was less than 10^{-4}mm. The results of these hydrogen adsorption measurements are shown in table 6.

These results show that the amount of hydrogen adsorbed was proportional to the film weight, and that the average amount was 2.54×10^{17} atoms per mg nickel. This value is in good agreement with the value obtained by Beeck for orientated films (2.50×10^{17} atoms/mg) (8).

An attempt was made to study the slow reversible adsorption process which has been reported to occur after the fast chemisorption (15). This was done during the adsorption measurements with film 7, by observation of the change of thermistor gauge deflection with respect to time. The results obtained are shown in table 7a from which it may be seen that the response of the gauge was not rapid enough to give a reliable measurement. This reversibly adsorbed hydrogen was however from the

TABLE 6

HYDROGEN ADSORPTION ON ORIENTATED NICKEL FILMS AT 25°C.

Film no.	Film weight mg	cm mm hydrogen adsorbed at 25°C	Atoms hydrogen per mg nickel
7	34.3	139.4	2.63×10^{17}
8	26.9	101.8	2.45×10^{17}
12	19.6	77.6	2.57×10^{17}
13	20.4	80.7	2.57×10^{17}
14	19.85	75.5	2.48×10^{17}
15	33.6	129.2	2.51×10^{17}
65	20.2	77.3	2.49×10^{17}
105	30.9	118.4	2.50×10^{17}

TABLE 7a **SLOW HYDROGEN SORPTION.** **Film no.7.**

Time (sec)	Thermistor gauge deflection cm	Hydrogen pressure mm mercury
0	11.8	1.8
10	23.0	3.7×10^{-1}
20	27.9	2.1×10^{-1}
40	31.6	1.4×10^{-1}
60	33.5	1.2×10^{-1}
80	34.6	1.0×10^{-1}
100	35.4	9.8×10^{-2}
120	35.8	9.3×10^{-2}
180	36.8	8.2×10^{-2}
390	37.9	7.0×10^{-2}
800	38.5	6.4×10^{-2}
1500	39.2	5.7×10^{-2}

TABLE 7b **REVERSIBLE SORPTION.**

Film no. and weight	cm^3mm adsorbed	% readsorbed
7 (34.34)	139.4 initially 17.8 after pumping	12.8%
13 (20.40)	80.7 initially 9.4 after pumping	11.6%

film by pumping the catalyst vessel to a high vacuum (10^{-8}mm). Readsorption of the reversible portion was then carried out, and its magnitude measured. The results of these measurements are given in table 7b.

The effect of mercury vapour on nickel films on which hydrogen had previously been adsorbed was investigated by the method described in chapter 2. Hydrogen was adsorbed until a residual pressure (about 0.1 mm) was obtained. The mercury capillary was broken and the thermistor gauge deflection observed over a period of several hours. The pressure was seen to increase, and to attain a steady value after 12 hours exposure of the film to mercury vapour. These results showed that mercury displaced a large proportion of the hydrogen adsorbed on nickel films. The displacement was not quantitative however. The results are shown in table 8.

3.3. Tracer studies of Hydrogen Displacement by Mercury.

From the results of the experiments just described it was seen that hydrogen adsorbed on a nickel film could be displaced by exposure of the film to mercury vapour. The amount of hydrogen displaced was measured by observing the thermistor gauge deflection. This deflection gradually increased as the mercury vapour slowly diffused into the catalyst vessel, and equilibrium was not attained until about one day had elapsed. For

TABLE 8 THE EFFECT OF MERCURY ON HYDROGEN ADSORPTION.

Film no. and weight	cm^3mm hydrogen adsorbed	cm^3mm hydrogen returned to gas phase	% hydrogen remaining on film
14 (19.85mg)	75.5	62.4	17.4%
16 (38.2mg)	39.6 *	30.9	-
	145.6 (calc.)		6.0% *

* Film was not saturated with hydrogen. Amount remaining on film was expressed as %age of adsorptive capacity calculated from the film weight.

TABLE 9 DISPLACEMENT OF TRITIUM BY MERCURY.

Film no. and weight	Calc. ads. capacity cm^3mm	Activity recovered cpm	Specific activity cpm/cm^3mm at 20°C	cm^3mm recovered at 25°C	% retained :ads.cap.
46 (26.9mg)	103.1	761	9.04	85.6	16.9%
43 (28.1mg)	107.6	918	10.87	88.6	17.7%
49	89.3	648	9.04	72.9	18.3%

this reason the method was open to objection because of the galvanometer drift which might have ocurred over such long periods. It was therefore thought desirable to compare the results obtained with those from an independant and more sensitive method of measurement.

The primary feature of this method was the use of ^{3}H-labelled hydrogen (tritium) for the adsorption, so that the hydrogen when displaced by mercury could be detected by gas counting techniques. The tritium-hydrogen was prepared by the reduction of tritiated water with magnesium at 500°C, and purified by allowing it to pass through a glass spiral cooled in liquid nitrogen. This preparation is fully described in section 9.1.

The tritium was estimated by counting in a Geiger-Muller counter. This was filled with hydrogen, containing the tritium sample, to a pressure of 8 cm. Ethyl alcohol was used as the quenching agent, at a pressure of 2 cm. The apparatus was of the standard design used for gas counting and was similar to that described and illustrated in chapter 9.

The method of investigating the tritium displacement by mercury was as follows. A catalyst vessel was prepared in the usual manner on the mercury-free vacuum system, then transferred to the gas counting apparatus. The catalyst vessel could be cut off from the rest of the system by a tap, and was protected from mercury vapour by a U-tube cooled in liquid nitrogen. A small globule of mercury was introduced into this U-tube and the apparatus pumped to a high-vacuum. The break-seal on the catalyst vessel was broken, the argon pumped away, and a sample of tritium-hydrogen admitted to the catalyst vessel to a pressure of about 5 mm in excess of the amount which represented saturation of the film. This excess, after it had remained in the catalyst vessel for 5 min, was rapidly pumped away and the catalyst vessel cut off from the rest of the system. The liquid nitrogen was removed from around the U-tube to allow the mercury to melt. The apparatus was left at this stage for two days, during which time mercury vapour diffused into the catalyst vessel. At the end of this period it was established that mercury vapour in excess of that which had interacted with the film had diffused into the catalyst vessel. This was done by cooling the lower end of the catalyst vessel in liquid nitrogen, when a blue-grey ring of condensed mercury could be observed.

The tritium-hydrogen which had been displaced by mercury was then transferred to the counter by means of the Topler pump and its activity determined. The specific activity of the tritium-hydrogen which had been used for adsorption was determined by counting an aliquot from a calibrated gas pipette. This calibration enabled the quantity of hydrogen which had been desorbed from films by mercury to be calculated from the measured activity. The quantity of hydrogen adsorbed by the film was calculated in each case from the film weight, using the adsorption value quoted in section 3.2. of 2.54 × 10^{17} atoms hydrogen adsorbed per mg nickel.

3.4. Hydrogen Displacement Results.

The results obtained using the tracer method are shown in table 9. These again showed that hydrogen displacement by mercury occurred but was not quantitative; 19 - 20% of the amount necessary to saturate the film was retained in each case. This method was not altogether satisfactory because it was necessary to calculate the amount of hydrogen initially adsorbed from the film weight, and therefore to assume that the film was initially free from contamination. It will be seen that this phenomenon of hydrogen retention on the nickel film will be investigated in detail in chapter 5.

In spite of the disadvantages of the method the results were consistent and in good agreement with that obtained with film 14 by the previous method in which the displaced hydrogen was detected with the thermistor gauge. The apparent anomaly of the result obtained for film 16, in which a smaller amount of hydrogen was retained, will be discussed in chapter 6 in connection with further work on hydrogen displacement to be described in chapter 5.

3.5. Mercury Adsorption.

Following the observation of the marked effect which mercury had on adsorbed layers of hydrogen on nickel films it was decided to measure the adsorption of mercury itself.

Since the magnitude of the amount of mercury which would be adsorbed was unknown, a radioactive tracer technique was used because of its potential sensitivity for the measurement of small quantities of mercury. Mercury labelled with the isotopes ^{197}Hg and ^{203}Hg, which had been prepared by slow neutron irradiation of mercury, was obtained from the Atomic Energy Research Establishment. Samples of this radioactive mercury were distilled into small break-seal tubes and sealed. One of these tubes was connected to a prepared catalyst vessel for each measurement, in such a way that the seals could be broken to admit mercury vapour to the film. This exposure to mercury vapour was maintained for periods ranging from 5 to 50 days, under conditions such that condensation of mercury vapour to free liquid mercury in the catalyst vessel was prevented.

After this period of time had elapsed, the catalyst vessels were dismantled and the nickel film dissolved in 25 ml. 10N nitric acid. 10 ml. of this solution were counted in a liquid counter. 10 ml. of a standard solution, prepared from a weighed amount of mercury of the same specific activity as that used in the adsorption, were counted immediately after the film solution. These determined count rates were corrected for background activity, and were taken to a statistical accuracy of ±1%. The nickel in the film solution was then estimated by the usual method (section 7.7.).

In addition to the mercury adsorption experiments on clean nickel films, an experiment was carried out in the presence of air with a catalyst vessel which was accidentally cracked, and another experiment in which a film saturated with propylene was used. Experimental details of this mercury adsorption method are given in chapter 8.

3.6. Mercury Adsorption Results.

Several mercury adsorption measurements were made

TABLE 10.

ADSORPTION OF MERCURY ON NICKEL AT 25°C.

Film no. and weight	Time of exposure to Hg (d)	Weight of mercury adsorbed (mg)	Atoms mercury per mg nickel
54 (34.6)	5	19.15	16.5×10^{17}
55 (29.1)	7	10.40	10.9×10^{17}
56 (23.0)	5	5.54	7.3×10^{17}
57· (28.2)	30	32.08	34.5×10^{17}
59 (28.3)	30	25.71	27.6×10^{17}
62 (10.1)	50	9.06	27.3×10^{17}
52 * (19.7)	30	0.00	-
79 **	30	0.84	1.2×10^{17}

* Film was exposed to air before the mercury adsorption was commenced.

** Film was exposed to propylene before the mercury adsorption was commenced.

using argon deposited nickel films and the results are shown in table 10. These results show that the adsorption of mercury on nickel was not complete after 7 days. Even after exposure of the film to mercury vapour for 30 days the results were inconsistent. It was clearly seen however that the adsorption was much greater than in the case of hydrogen adsorption by a factor of 10 or more, and was of the order of 3×10^{18} atoms mercury per mg. Mercury adsorption did not occur on a film which had been exposed to air, and only to a limited extent on one upon which propylene had been adsorbed.

3.7. Conclusions.

1. Hydrogen was found to adsorb on argon deposited nickel films to the extent of 2.54×10^{17} atoms per mg nickel.

2. Mercury displaced hydrogen adsorbed on nickel films, but this displacement was not quantitative.

3. Nickel films adsorbed mercury in quantities 10 or more times equivalent to the hydrogen adsorption.

4. The adsorption of mercury was greatly reduced in the presence of adsorbed propylene.

The experimental data from which the results recorded in this chapter were derived are shown in appendix B.

CHAPTER 4.

DISCUSSION OF RESULTS OF HYDROGENATION AND ADSORPTION EXPERIMENTS.

The results of the hydrogenation rate and adsorption measurements have been described in the preceding chapters. The conclusions derived from these results, which any theory about the selective poisoning of the nickel catalyst must explain, may be briefly summarised as follows.

1. Mercury was found to act as a catalyst poison for the hydrogenation of cyclopropane over nickel; the rate of hydrogen did not fall in a linear manner with the amount of poison added.
2. Hydrogen was found to adsorb rapidly on nickel films to an extent in good agreement with the results of Beeck et al. (8).
3. Adsorptions of propylene and cyclopropane were also rapid and in each case it occurred to about one-third of the extent of that of hydrogen, though the adsorption of propylene was rather higher than that of cyclopropane.
4. In no case could gas adsorption be detected on films which had previously been exposed to mercury vapour.
5. Mercury vapour, when admitted to a film upon which

hydrogen had previously been adsorbed, was found to displace hydrogen from the film. The displacement was reproducible but not quantitative.

6. Similar experiments with cyclopropane showed some displacement of gas by mercury but this gas was not entirely cyclopropane, since it could not be completely condensed at liquid nitrogen temperature.

7. Propylene covered films were unaffected by mercury vapour; moreover adsorption of mercury on nickel films was greatly reduced in the presence of propylene.

8. Adsorption of mercury on nickel films was much higher than for the other species studied on corresponding films.

4.1. Discussion of results.

In order to interpret the results and to explain the selective catalyst poisoning phenomenon, it is convenient first of all to consider the nature of the interaction of mercury with nickel. This will be discussed under two headings, viz. the possibility of alloy formation and the possibility of surface interactions only.

The high results which have been observed for mercury adsorption on nickel might be explained in terms of the formation of an alloy. Modification of the properties of the catalyst by alloy formation through its effect on electronic and geometric factors might therefore be expected. The possibility of this being the key to the problem of the selective catalyst poisoning has however been rejected on the following grounds. Firstly, the formation of an alloy between nickel and mercury is unlikely in view of the dissimilarities in their atomic sizes. The formation of solid solutions of the two metals is precluded by these differences in their atomic diameters, 1.25 A^o for nickel and 1.55 A^o for mercury. (16). These values may be contrasted with those for the metals of the alloys used by Couper and Eley, and Dowden and Reynolds (4,5,6,). In the former case the metals, palladium and gold, have atomic radii of 1.37 A^o and 1.44 A^o respectively and in the latter case - nickel 1.25^{o}A and copper 1.28 A^o. In each of these cases the atomic radii of the constituent metals differ by considerably less than 15%, which is considered to be the limit for solid-solution alloys (17).

If a nickel-mercury alloy was formed and a change in lattice spacing in the nickel occurred it might be possible to arrive at a spacing which would be less favourable for the hydrogenation of cyclopropane, but in this case the chemisorption of cyclopropane upon the film would have to be postulated. Measurement of the hydrogenation kinetics led to the view that cyclopropane was not chemisorbed during the hydrogenation, as will be discussed later. Also, the operation of a geometric effect in this way would be accompanied by an electronic effect which would reduce the activity of the catalyst for propylene hydrogenation by a progressive filling of the d levels in nickel with mercury s electrons. Such an effect was not observed, as the results of the propylene hydrogenation showed little or no loss in activity in the presence of mercury.

An alternative explanation of the high results for mercury adsorption therefore seems to be necessary and the possibility of physical adsorption of mercury cannot be neglected. As the same type of forces are concerned in physical adsorption as in liquefaction, the two processes are related. If adsorption is studied at a pressure p and temperature such that the saturated vapour pressure of the adsorbing species is p_0, appreciable fractions of a second monolayer are not usually formed unless p/p_0 exceeds the value 10^{-2} (18). Under the conditions used for the study of mercury adsorption, where the catalyst vessel was at 25°C. and the mercury source at room temperature (15 - 20°C) the value of p/p_0 is only slightly less than unity;

thus some physical adsorption is likely, but it is doubtful whether this would take place to an extent sufficient to explain the observed amounts of mercury - equivalent to ten monolayers. From the results of the hydrogen displacement experiments to be described in the next chapter, it appears that the first layer of mercury atoms is chemisorbed. It is thought that the formation of multilayers upon this first layer effectively blocks the catalyst for chemisorption, and hence no adsorption of any of the species under investigation was observed when the film had been exposed to mercury vapour before the adsorption measurements were made. At temperatures such as that used by Corner and Pease (9) - 150° - it might be expected that this multilayer formation would be greatly reduced and that propylene adsorption would be possible if it could displace the mercury. The state of affairs in their adsorption on mercury treated films would then correspond to that which has been observed in the experiments where adsorbed-gas covered films were subsequently exposed to mercury vapour. If mercury wets nickel there is also the possibility of condensation of mercury into large pores on the nickel surface as a result of surface tension effects because the vapour pressure of the mercury in the pores would be reduced by the concave surface.

Evidence in favour of the poisoning action of mercury being a surface effect was provided by the results to be described in the next chapter. These showed that, apart from certain complicating features, chemisorbed hydrogen was displaced atom-for-atom by mercury. Qualitative evidence for a surface poisoning is also provided by the form of the activity versus amount of poison curve found in the hydrogenation of cyclopropane (fig. 5). Maxted observed a similar form of poisoning curve in an investigation of the poisoning of a platinum catalyst by sulphur compounds in the hydrogenation of crotonic acid (19). The similarity lay not only in the form of the curve but in the amount of poison necessary to produce a comparable effect on the reaction rate in the two cases. In the case of the poisoning of the catalyst by mercury for the cyclopropane hydrogenation the amount of poison was a great many times less than would be necessary to fill the vacant d levels in nickel with s electrons of mercury. Herington and Rideal (20-) have shown theoretically that the form of poisoning curve obtained is to be expected in cases where the adsorbed reactant requires more than one site for adsorption, or where two reactant molecules must be adsorbed on adjacent sites.

Beyond the fact that multipoint adsorption of cyclopropane or hydrogen must occur in cyclopropane hydrogenation, no quantitative conclusions can be drawn from the poisoning data. Herington and Rideal's theory does predict however that the catalytic activity could be reduced to zero by prolonged exposure of the catalyst to mercury vapour, since the vapour is monatomic and therefore capable of covering the surface without leaving gaps. This prediction is in accordance with the observations made by Corner and Pease (9).

It is concluded from this discussion that the sorption of mercury is a surface process.

In order to elucidate the mechanism of the selective poisoning process for cyclopropane it will be profitable to discuss the mechanism of cyclopropane hydrogenation at this stage. Bond and Sheridan (14,21) have studied the kinetics of the hydrogenation of cyclopropane over nickel, palladium, and platinum. Their work showed that the rate of reaction was proportional to the hydrocarbon pressure and independent of the hydrogen pressure; the kinetics were thus anomalous with those found in olefine hydrogenation reactions in which the opposite was true. Two mechanisms were advanced which were in agreement with this observation - the adsorption of hydrogen on the catalyst, with cyclopropane reacting from the gas phase or from a physically adsorbed state; or the isomerisation of cyclopropane to propylene (rate determining) followed by hydrogenation of the propylene. This latter mechanism was rejected in view of the observations by Bond and Turkevich (11,12). They studied the hydrogenation and exchange reactions on platinum between propylene and deuterium,and cyclopropane and deuterium. It was found that the deuterium distribution in the products was quite different in the two cases and it was concluded that the isomerisation of cyclopropane was not one of the steps in its hydrogenation. This conclusion, when based upon this evidence alone, does not appear to be sound because a catalytic isomerisation mechanism would require the chemisorption of cyclopropane and an opening of the ring at some stage. This might be expected to lead to the production of different adsorbed radicles from the case of propylene adsorption, and hence to a difference in deuterium distribution in the products. Mechanisms of cyclopropane hydrogenation involving isomerisation can still be rejected however because there is further evidence, which will now be discussed, in favour of the first mechanism.

Bond and Sheridan also found that cyclopropane acted merely as a diluent when added to the gas mixture in the hydrogenation of propylene. Similar behaviour was found with cyclopropane in the hydrogenation of allene (22) and of methylacetylene (23). Preferential hydrogenation of these latter two compounds was also observed in the presence of propylene (24), so that it appears that the scale of preferential adsorption - methylacetylene, allene, propylene, cyclopropane - exists. From these observations it may be concluded that the chemisorption of cyclopropane is prevented in the presence of hydrogen, olefinic or acetylinic compounds, and that hydrogenation of cyclopropane requires the chemisorption of hydrogen upon the catalyst.

It must be concluded from this argument that the preferential chemisorption of mercury on the surface of nickel films prevents the chemisorption of hydrogen and this in turn inhibits the cyclopropane hydrogenation. This appears to be the key to the mechanism of the selective poisoning phenomenon.

It remains to be explained why the hydrogenation of propylene was uninhibited by mercury in view of the fact that adsorption of mercury, though slight, did occur during the hydrogenation and in view of the fact that hydrogen chemisorption might also be inhibited by mercury.

This problem of why propylene can be hydrogenated in the presence of mercury will now be considered. The presence of hydrogen on the catalyst is thought to be necessary for this process and it seems strange that hydrogenation can occur when the present work has shown that mercury displaces hydrogen.

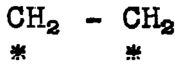
It seems profitable at this stage to examine a theoretical geometrical model for the surface and chemisorbed species and to attempt to draw conclusions from this as to which species can be accommodated together on the nickel surface.

The adsorption of propylene will therefore be considered in relation to the problem of olefine hydrogenation. The extent of propylene adsorption, when adsorbed alone, was found to be such that one molecule was adsorbed to every six sites on the surface (i.e. expressed in terms of sites available for hydrogen adsorption), and it is worth comparing this with ethylene adsorption.

Adsorption measurements with ethylene on nickel films, by Beeck et al. (8), showed that one ethylene molecule was adsorbed for every four sites on the catalyst. If ethylene adsorbed by a dissociative mechanism:

$$\underset{*}{CH} = \underset{*}{CH} \quad + \quad 2\underset{*}{H}$$

(where * denotes a bond to the catalyst), four sites would be covered by one molecule. On the other hand, associative sorption, which the weight of experimental evidence tends to favour (26,27,28), involving an opening of the double bond:



$$\underset{*}{CH_2} - \underset{*}{CH_2}$$

requires only two sites per molecule, and hence considerations of packing must be invoked for an explanation of the figure observed by Beeck.

Such an explanation has been attempted by Twigg and Rideal who have made calculations on the fitting of ethylene and methylethylenes to a nickel surface (29). They predicted that vacant sites would be left in the process in the case of methylethylenes because of the large methyl groups. Evidence in favour of this prediction was provided by the observation that some mercury adsorption on propylene covered films did occur, although the extent of adsorption was small in comparison with the adsorption on a clean nickel film. Further evidence for the existance of these sites available for hydrogen chemisorption comes from the observation that the ortho-para-hydrogen conversion, although inhibited by ethylene on a nickel surface, was not entirely prevented (41). If the dissociative mechanism for olefine adsorption is to be rejected it is necessary to postulate hydrogen adsorption to account for this observation. It seems possible therefore that a considerable surface would be available for hydrogen adsorption on propylene covered films because of the existance of these vacant sites, and that this effect would be more pronounced than in the case of ethylene because of the additional steric effect of the methyl group.

The mechanism proposed by Bond and Turkevich for the hydrogenation of propylene over platinum requires chemisorption of hydrogen:

$$\underset{*}{H} + CH_3 - \underset{*}{CH} - \underset{*}{CH_2} \rightleftharpoons CH_3 - \underset{*}{CH} - CH_3$$

$$\underset{*}{H} + CH_3 - \underset{*}{CH} - CH_3 \rightleftharpoons CH_3 - CH_2 - CH_3$$

This mechanism explains the results obtained with deuterium (11).

The scheme proposed by Twigg for the hydrogenation of ethylene (27) postulates reaction between chemisorbed ethylene and a physically (Van der Waal's) adsorbed hydrogen molecule, but the formation of chemisorbed hydrogen as an intermediate entity is again suggested.

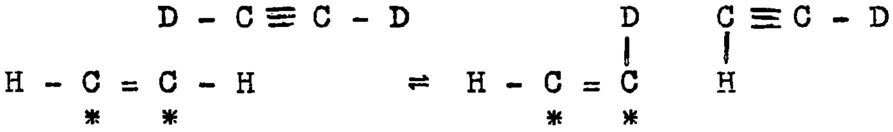
$$\underset{*}{CH_2} - \underset{*}{CH_2} + \underset{:}{H_2} \rightleftharpoons \underset{*}{CH_2} - CH_3 + \underset{*}{H}$$

$$\underset{*}{CH_2} - \underset{*}{CH_2} + \underset{*}{H} \rightleftharpoons \underset{*}{CH_2} - CH_3 \qquad \text{(fast)}$$

In order to explain the observation that mercury has little or no effect on the propylene hydrogenation rate it is necessary either to postulate that hydrogen chemisorption does not occur, and therefore that the reaction does not take place between propylene and hydrogen in chemisorbed states,; or that reaction takes place with hydrogen adsorbed on sites inaccessible to mercury.

The plausibility of a mechanism of the first type, not involving hydrogen chemisorption, will first be considered.

Bond, Sheridan, and Whiffen (30) have postulated the following mechanism for the observed exchange between acetylene and dideuteroacetylene.



$$\begin{array}{ccc} D - C \equiv C - D & & D \quad C \equiv C - D \\ & & | \qquad | \qquad\quad \\ H - \underset{*}{C} = \underset{*}{C} - H & \rightleftharpoons & H - \underset{*}{C} = \underset{*}{C} \quad H \qquad\quad \end{array}$$

If this mechanism of exchange could be postulated for ethylene and propylene, it might be possible to explain the mechanism of the hydrogenayion in terms of simultaneous addition of two hydrogen atoms from a hydrogen molecule. This mechanism must be rejected however on the grounds of the following two observations. Firstly, no exchange between ethylene (C_2H_4) and C_2D_4 has been observed (31). Secondly, by this mechanism the formation of C_3H_7D, and $C_3H_2D_6$ and C_3HD_7 in the reaction of deuterium with propylene would be impossible. The mechanism was thought to be possible in the case of acetylene because of the existance of a dipole,: $\overset{+}{H} - C \equiv C - \overset{+}{H}$

PROPYLENE ADSORPTION

ON (110) FACE OF NICKEL

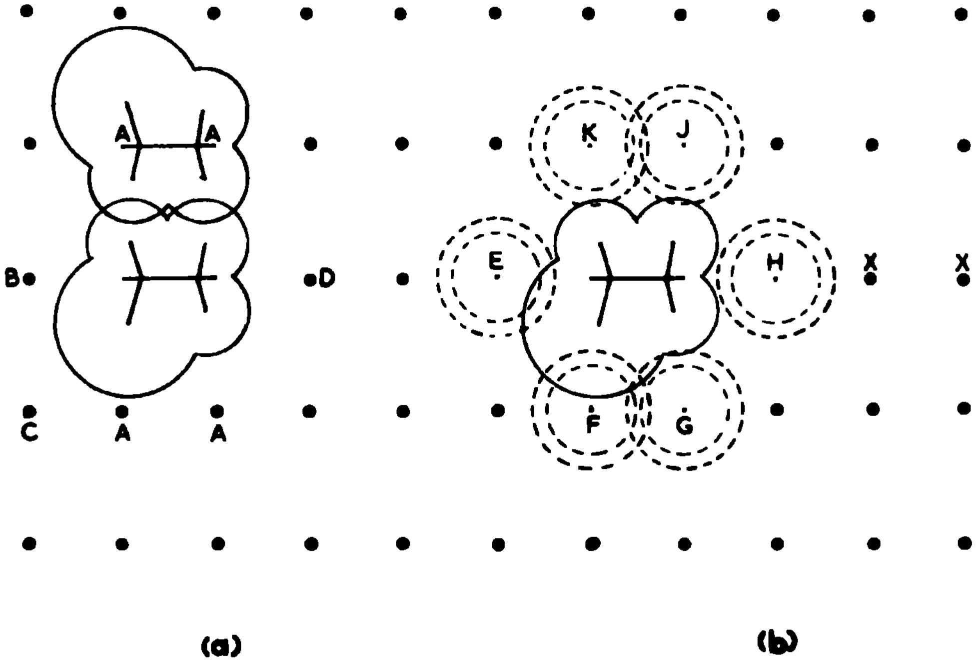


FIG. 12

It seems therefore that a mechanism involving hydrogen chemisorption must be accepted, in spite of the reduced surface available for this to take place. If it is necessary for two adjacent sites to be available before a hydrogen molecule can dissociate to chemisorb as atoms, the extent of hydrogen chemisorption will be still further reduced if the gaps in the propylene film are randomly distributed.

Considerations of the surface packing of propylene molecules, in conjunction with the sizes of mercury and hydrogen atoms, shows that vacancies on the nickel film ought to exist which are accessible to hydrogen but not to mercury. Fig. 12 represents the state of affairs on the (110) plane of nickel. Adsorption is considered to take place by associative chemisorption to sites of 2.47 A° seperation.

In these theoretical considerations the Van der Waal's radii have been used in conjunction with the values used by Twigg and Rideal for the bond lengths, namely:

C-C 1.52 A°, being the carbon-carbon single bond distance, (32),
C-Ni 1.82 A°, as in nickel carbonyl (33),
Ni-Ni 2.47 A° and 3.50 A° (34),
C - H 1.09 A° (35),

H- radius	1.2 A^o	(Van der Waal's) (36),
CH_3 radius	2.0 A^o	(Van der Waal's) (37),
Hg- radius	1.55 A^o	(12-coordination)(38).

The internuclear distance used for Ni-Hg was the sum of the radii for 12-coordination for the two metals, viz. 2.78 A^o. Difficulty was experienced in deciding upon a value for the Ni-H distance in the adsorbed state. The value 1.39 A^o, representing the covalent bond length, was adopted since this gave uniformity with the Ni-C value, which has been obtained from a covalent compound. This value was calculated from: (Ni-C)-(C-C)+(C-H), i.e. the difference between the C-C and C-H bond lengths has been assumed to be the same as the difference in Ni-C and Ni-H lengths.

It may be seen from fig. 12a that any adsorption of a second propylene molecule involving sites A and B adjacent to the first molecule will be impossible, and also in the case of sites C if the methyl group of the second molecule is orientated towards that of the first molecule. As a result of this, adsorption of propylene may take place either after suitable re-orientation of the methyl group or in a manner such that a vacant site is left between the two molecules when adsorbed. Fig.12b shows the availability of sites adjacent to an adsorbed propylene molecule for hydrogen or mercury chemisorption. This represents the projection of the molecules or atoms on to the nickel surface, but since the atoms lie in different planes parallel to the nickel surface the interaction may be less than is apparent from a study of fig.12b. Thus it may be calculated that the centre of the methyl group and the plane of centres of the adsorbed radicle's hydrogen atoms are respectively 3.00 A^{o} and 2.65 A^{o} above the nickel surface plane. From the data available the interactions shown in table 11 may be calculated. These are expressed in A^{o} 'overlap' distances.

TABLE 11 "Overlapping" of adjacently adsorbed atoms.

Site	Mercury adsorbed	Hydrogen adsorbed
E	0.60 A^{o}	NONE
F	1.17 A^{o}	0.30 A^{o}
G	0.25 A^{o}	NONE
H	NONE	NONE
J	0.15 A^{o}	NONE
K	0.15 A^{o}	NONE

The tabulated values show that there are many more sites available for hydrogen adsorption than for mercury adsorption. Site H only is available for mercury adsorption without steric interaction, but in the case of sites J and K this interaction may not be great enough to prevent mercury adsorption. It must be stressed however that the foregoing considerations apply only to an adsorbed, isolated propylene molecule and its six near-neighbouring sites on the catalyst surface. Since these neighbouring sites may be neighbours of other propylene molecules also, further restrictions upon adsorption of hydrogen and, more particularly, mercury will apply. Thus, for example, adsorption of another propylene molecule upon sites X would prevent mercury but not hydrogen adsorption on site H. In these calculations the (110) plane nickel spacings have been used, but as this is the least dense of the planes in nickel the conclusions reached apply also to the (111) and (100) planes for qualitative considerations.

The state of affairs which exists when a high surface concentration of propylene is present is too complex for quantitative explanation, but the important fact emerges that there are many more sites available for hydrogen than for mercury adsorption. It is notable that these occur on adjacent sites on the axis of the adsorbed propylene molecule from which position interaction between chemisorbed hydrogen and a chemisorbed propylene molecule is most likely to occur. If the Van der Waal's adsorbed hydrogen mechanism is accepted the possibility of chemisorption of the dissociated hydrogen atom upon the site left vacant by the formation of the propyl (iso- or n-) radicle is high, and the spacing is then favourable for the rapid addition of this to the adsorbed radicle. Hydrogen adsorbed in such a position is likely to be inaccessible to mercury, but in any case reaction of this chemisorbed hydrogen would be very rapid compared with displacement by mercury. Again, displacement of chemisorbed hydrogen by mercury may only be possible if a hydrogen atom is adsorbed on an adjacent site, so that a molecule can be formed. Any mercury adsorption, by hydrogen displacement from an occupied site, which does occur however would not be cumulative but would attain an equilibrium steady-state because of the postulated displacement of mercury by propylene at the reaction temperature.

This postulated mechanism, which requires the existance of sites accessible to hydrogen but not to mercury, could be investigated by means of the following experiment. Two catalyst vessels containing nickel films could be taken, and propylene adsorbed on the films to saturation. Mercury vapour could then be admitted to one of the catalyst vessels to allow mercury adsorption to take place upon all sites available to mercury. Hydrogen chemisorption could then be studied using the mercury-treated and the untreated film, at a temperature low enough to prevent hydrogenation, and the effect of mercury on the fraction of surface available for hydrogen chemisorption in the presence of propylene found.

4.2. The Hydrogenation of Ethylene.

It appears to the present author that Twigg and Rideal made a fundamental error in the dimensions used in their calculations of the packing of ethylene and methylethylenes on a nickel surface. Although the values for the bond lengths used were justifiable, the use of covalent radii in the determination of the size of the molecules was not. Since no bonding occurred between adjacent molecules when packed together on the surface the appropriate radius to consider was the Van der Waal's radius, as has been done in the considerations of packing of propylene molecules in the previous section.

It is of interest to note that in the case of ethylene adsorption, when the Van der Waal's radius is used for hydrogen, steric interference occurs between adjacent adsorbed ethylene molecules even on the (110) plane - the least dense of the planes. This leads to the conclusion that one ethylene molecule will require four sites on the surface, since it will be associatively chemisorbed to two sites, and will sterically block two others. This is in accordance with the experimental observations of Beeck et al. (8).

It also appears likely that hydrogen chemisorption upon the sites not covered by ethylene would be difficult except on the 110 plane. This may explain the 5-fold activity of (110) orientated films in ethylene hydrogenation relayive to the activity of unorientated films (8), as it is thought that in these orientated metal films the plane parallel to the substrate is the plane predominating on the surface.(39).

4.3. Summary of Conclusions.

1. Adsorption of the reactants under study, by nickel in the following order of preference has been observed or inferred from indirect measurements.: propylene, mercury, hydrogen, cyclopropane.
2. The high observed mercury adsorption values have been concluded to represent chemisorption followed by some other process such as physical adsorption or distillation of mercury into pores on the nickel surface, because of vapour pressure considerations.
3. The inhibition of the catalytic hydrogenation of cyclopropane over nickel in the presence of mercury has been accounted for by the prevention of hydrogen chemisorption.

4. The hydrogenation of propylene over nickel was able to take place in the presence of mercury since the chemisorption of propylene was not prevented by mercury, but it is necessary to postulate some hydrogen adsorption, either chemisorption or Van der Waal's adsorption, in this case. It is suggested that this adsorption occurs on gaps in the propylene film which are inaccessible to mercury. Steric considerations show the feasibility of existance of such vacancies.

CHAPTER 5.

THE DISPLACEMENT OF ADSORBED HYDROGEN BY MERCURY.

In chapter 4 the results obtained from the experimental work described in the first three chapters of this thesis, were considered in relation to the published work on propylene and cyclopropane hydrogenation and exchange. These clearly showed that the selective poisoning of nickel films by mercury for cyclopropane hydrogenation could be explained in terms of the prevention of hydrogen adsorption by mercury. It was of interest however to gain further information about the most interesting features of the displacement, namely the apparent non-quantitative displacement of hydrogen by mercury and the fact that the mercury was adsorbed to a much greater extent than the hydrogen.

5.1. The Experimental Method.

The investigation was carried out by a radiochemical method in which radioactively-labelled mercury and hydrogen labelled with tritium were used.

For the purposes of these measurements a special design of catalyst vessel was used and this is illustrated in fig. 45. Tritium-labelled hydrogen was used for adsorption on to the nickel film and this was prepared

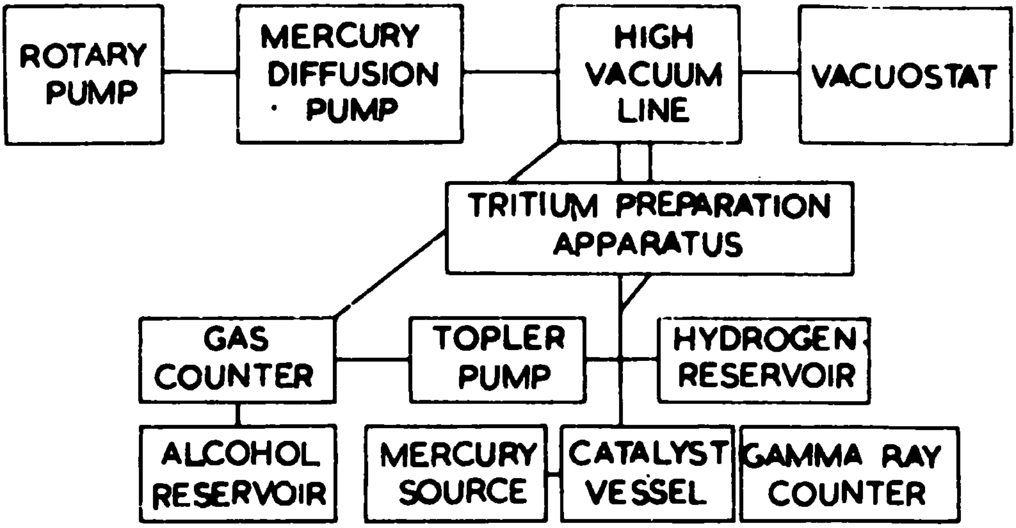

ROTARY PUMP
MERCURY DIFFUSION PUMP
HIGH VACUUM LINE
VACUOSTAT
TRITIUM PREPARATION APPARATUS
GAS COUNTER
TOPLER PUMP
HYDROGEN RESERVOIR
ALCOHOL RESERVOIR
MERCURY SOURCE
CATALYST VESSEL
GAMMA RAY COUNTER

FIG. 14

by reduction of tritiated water with magnesium at 500°C. as described in section 9.1. The adsorption was measured using the thermistor gauge technique described in chapter 2. The catalyst vessel was then sealed off from the adsorption apparatus at the constriction C (fig.45), and transferred to another apparatus to which it was connected by the break-seal D. A schematic diagram of the apparatus is shown in fig. 14. The principle of the désorption study was that two counters could be used, one to respond to the tritium β activity as tritium hydrogen was desorbed from the film and the other to the mercury γ activity as it arrived on the film.

5.2. Tritium Activity Measurement.

The tritium-hydrogen displaced from the film by mercury was estimated by a gas counting technique. A gas counter filled to a pressure of 8cm mercury with hydrogen and a partial pressure of 2 cm ethanol vapour was used, and the tritium-hydrogen transferred into this counter from the catalyst vessel using a Topler pump. This was done in the first instance to estimate the residual gas-phase tritium in the catalyst vessel after the initial sorption and at various time intervals during the exposure of the film to mercury vapour. The gas counter was refilled whenever the accumulated activity exceeded 1000 counts/min. These measurements enabled the amount of tritium-hydrogen displaced from the film, and hence the amount remaining, to be calculated for any time by interpolation. Details of the development of this counting method will be found in chapter 9, together with a detailed diagram of the apparatus (fig.40).

5.3. Mercury Activity Measurement.

In order to be able to measure the activity of the mercury actually present on the film, a long, tubular Geiger-Muller counter was used. This was arranged parallel to and in contact with the catalyst vessel and was shielded from the mercury source by lead bricks which fitted around it and the catalyst vessel. The tritium present on the film did not interfere with the mercury counting because its low energy β emission was too weak to penetrate the glass walls of the catalyst vessel and enter the γ counter. Tests were carried out to estimate the effect on the counter of mercury adsorbed on various parts of the film. These tests are described in chapter 9 and they showed that the technique was valid as a method giving the relative activity of mercury on the film with respect to time. A background activity determination was made with this counter before any mercury was admitted to the catalyst vessel. The break-seal on the mercury tube was then broken and further counts made with respect to time to alternate with the tritium counts.

For the purposes of the study however it was necessary to know the absolute amount of mercury on the film at any time. This was found by the following method. At the end of the experiment, the nickel film was dissolved in 25 ml. 10N nitric acid and 10 ml. of this solution were counted in a liquid counter. The measured counting rate was compared with that given by a standard solution of the same active mercury, as described in chapter 3. From this comparison, the amount of mercury present on the film could be calculated. The counting rate produced by this amount of mercury had been measured with the external counter at the close of the experiment; hence the absolute amount present at any time previous to this could be calculated from the relative values.

5.4. Statistical Errors in the Counting Methods.

Because atomic disintegration is a random process, the radioactive tracer measurements made were subject to statistical errors. In counting rate determinations, whenever possible an error of less than 1% was ensured by prolonging the count until more than 10,000 counts had been recorded. The standard deviation obtained was thus $\sqrt{10,000}$ counts per 10,000 counts, or 1%.

During the actual displacement measurements however it was necessary to tolerate larger errors because of the need to make several counts during the course of the displacement. In spite of this limitation of time, the resultant inaccuracies were not serious. Tritium counts recorded were accurate to at least ±2%, improving to ±½% or better at higher activities. Mercury counts were each taken over a period of 10 minutes, consequently accuracies of ±3% improving to less than 1% at higher activities were obtained.

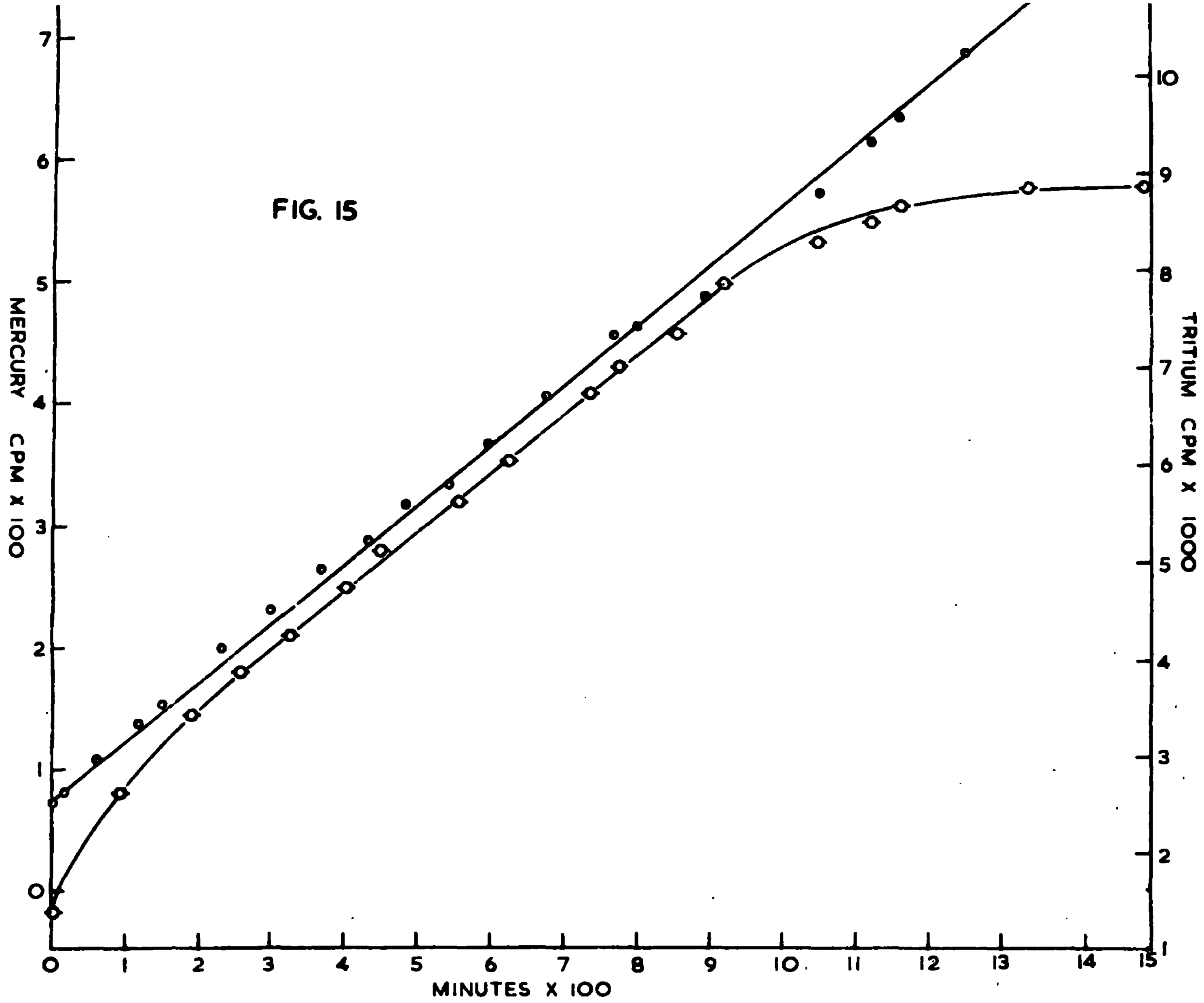
The measured count rates were recorded with respect to time during the displacement measurements. In the case of tritium-hydrogen the appropriate time was that at which the sample was extraced from the catalyst vessel with the Topler pump. For the case of mercury, since mercury adsorption was proceeding during the course of the count rate determination, the average time was taken, that is, five minutes after the beginning of the ten minute count.

5.5. The Isotope Effect.

Tests were carried out to investigate the effect of various factors which might have affected the reliability of the method used for studying the hydrogen displacement by mercury; these are described in chapter 9. Among these factors was the 'isotope effect' which might be expected to occur in the adsorption of tritium-hydrogen on nickel .

Measurements of this isotope effect were made after admitting a sample of tritium-hydrogen to a catalyst vessel containing a nickel film. The amount of tritium-hydrogen was such that about a one-fold excess over that adsorbed remained in the gas phase. A sample of the residual tritium hydrogen was taken in a section of the apparatus containing a Mc.Leod gauge. The pressure was measured with the Mc.Leod gauge, an aliquot of gas transferred to the gas counter and the pressure of the remainder measured. The activity of the sample was determined. Further aliquots from the Mc.Leod gauge section were transferred to the counter and the pressure of the remainder measured in each case. This procedure was repeated with further samples from the catalyst vessel and with a sample of the original tritium-hydrogen, and graphs of Mc.Leod reading against count rate plotted for each sample. The specific activity in each case was obtained from the slope of these plots. This method

FIG. 15


MERCURY CPM X 100
7
6
5
4
3
2
1
0
TRITIUM CPM X 1000
10
9
8
7
6
5
4
3
2
1
MINUTES X 100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

was used to avoid inaccuracies due to non-quantitative transfer of small gas samples, and full details of the method will be found in section 9.7.

5.6. Hydrogen Displacement by Mercury - Results.

The results of two experiments on the hydrogen displacement by mercury are shown in tables 11 and12.

The first of these experiments was carried out with a nickel film completely covered with tritium-hydrogen. Fig.15 shows graphs of the mercury activity and the recovered tritium-hydrogen activity with respect to time, and fig.16 the mercury and tritium hydrogen activities with respect to each other at constant time. From these graphs it may be seen that during the greater part of the displacement, the rate of tritium-hydrogen desorption from the film was proportional to the rate of mercury adsorption. In the early stages of the desorption however the amount of tritium released was much greater relative to the amount of mercury adsorbed, but the opposite was true towards completion of the desorption. When the desorption of hydrogen had ceased, the adsorption of mercury was seen to continue to increase. This increase continued over a period of several days to a mercury adsorption value consistent with those obtained in the study of mercury adsorption described in chapter 3.

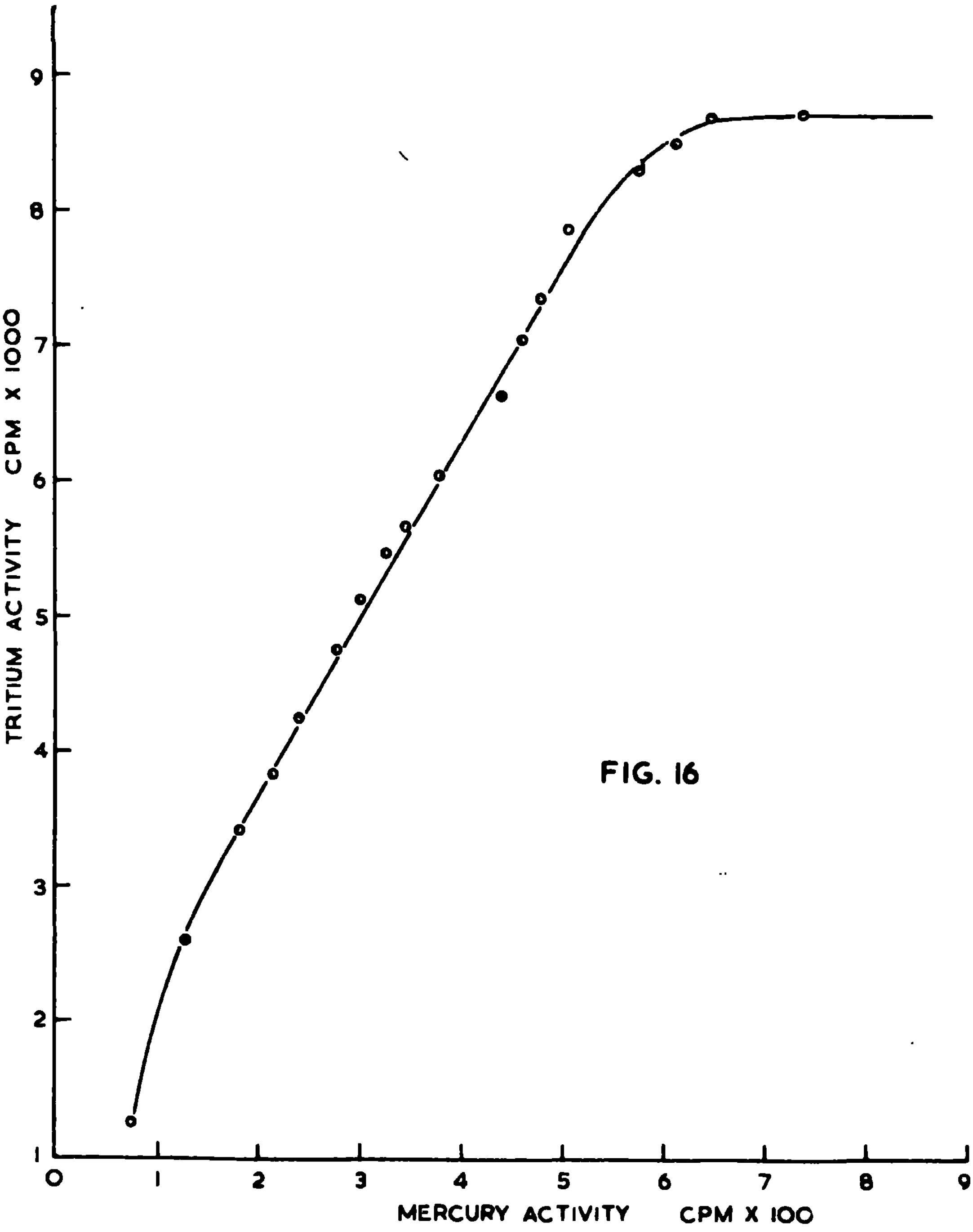

TRITIUM ACTIVITY CPM X 1000
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
MERCURY ACTIVITY CPM X 100

FIG. 16

TABLE 11.

FILM 65 DISPLACEMENT OF HYDROGEN BY MERCURY.

Time (min)	Mercury count	Tritium count - background	Tritium total count
-	-	1267	1267
-	73.5	-	
15	81.0	-	
60	109	-	
90	(125)	1350	2617
115	138	-	
150	152	-	
190	(178)	806	3423
225	200	-	
256	(213)	412	3835
300	231	-	
325	(244)	834*	4257
365	264	-	
400	(277)	490	4747
430	288	-	
450	(299)	863*	5120
485	319	-	
510	(326)	351	5471
540	335	-	
555	(344)	543*	5663

TABLE 11 (cont.)

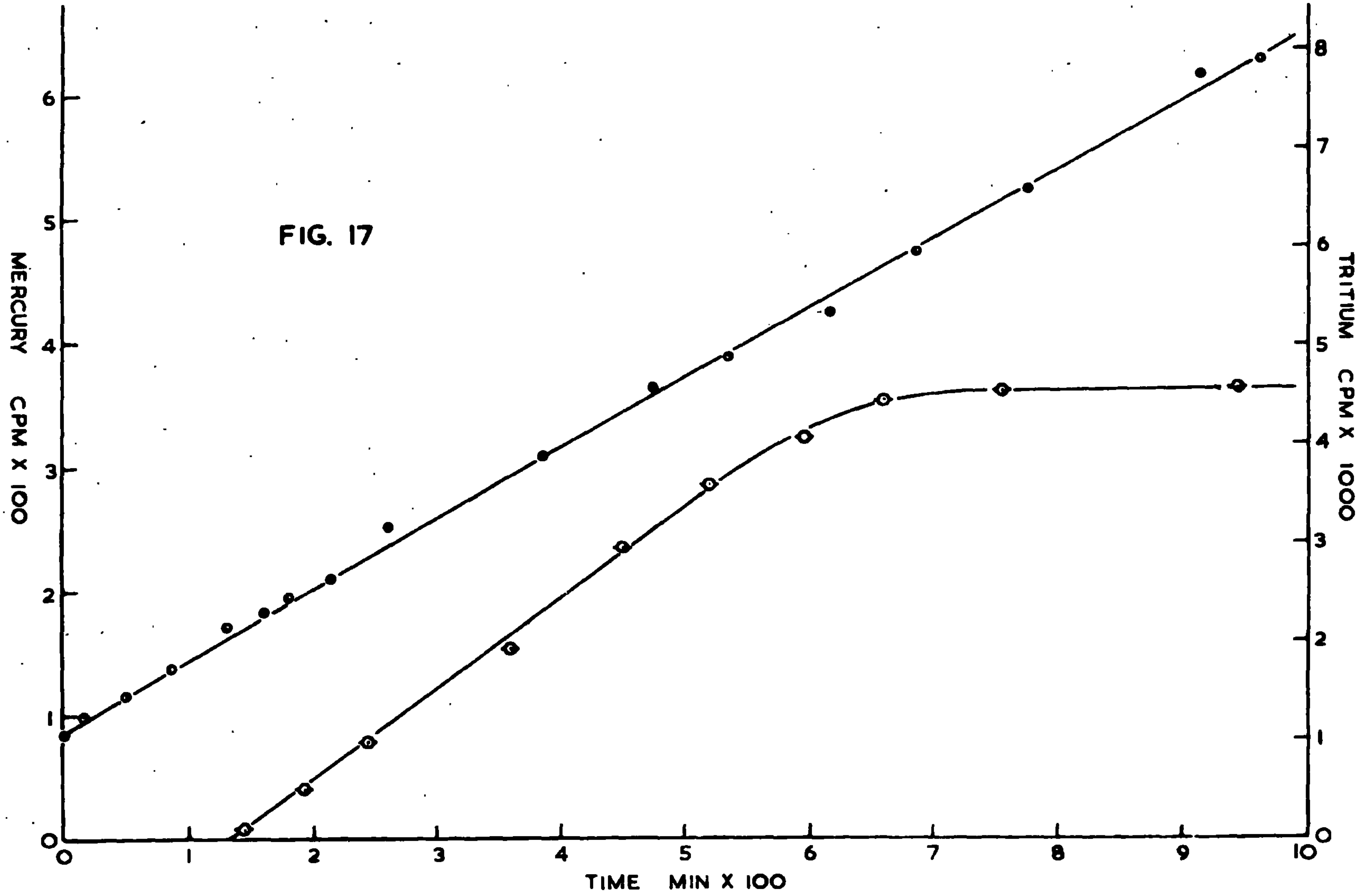
Time (min)	Mercury count	Tritium count - background	Tritium total count
595	368	-	
620	(380)	374	6037
675	407	-	
730	(437)	591	6628
765	457	-	
775	(459)	999*	7036
800	465	-	
855	(480)	1308*	7345
890	490	-	
915	(504)	530	7875
1050	(576)	965*	8310
1120	(614)	180	8490
1160	636	-	
1185	(651)	206	8696
1250	691	-	
1315	740	-	
1330	(741)	21	8716
3760	923	-	
3900		136	8853
Final	1136		

NOTE - Mercury count values in brackets were interpolated. * indicates sample added to previous filling.

The adsorption data are recorded on the following pages and calculations which were made on the amount of tritium-hydrogen retained by the film. Calculation of the amount of tritium-hydrogen present in the catalyst vessel in the gas phase after adsorption showed this to be in reasonable agreement with that calculated from the activity recovered from the gas phase before the desorption was commenced. This indicated that any isotope effect which occurred in the adsorption was unlikely to have interfered with the conclusions to be drawn from the results.

Calculations were also made of the relative rates of mercury adsorption and hydrogen desorption in the region of proportionality. These showed that in this region mercury adsorption was atom-for-atom about 20% greater than the corresponding hydrogen desorption. An attempt was made to calculate the amount of mercury present on the film when hydrogen ceased to be desorbed, but difficulty was experienced in deciding which point represented this condition on the hydrogen desorbed versus time graph. Calculation showed however that an amount of mercury atom-for-atom equivalent to the hydrogen adsorbtive capacity of the film was present on the film at the time the hydrogen desorption curve became horizontal.

FIG. 17


MERCURY CPM X 100
0
1
2
3
4
5
6
TRITIUM CPM X 1000
0
1
2
3
4
5
6
7
8
TIME MIN X 100
0
1
2
3
4
5
6
7
8
9
10

The second experiment, the counting data of which are shown in table 12, was carried out in such a way that no interference from the isotope effect in tritium-hydrogen adsorption was possible. This was done by using for the displacement measurements a film which was not completely covered with hydrogen, so that no residual pressure was obtained after the adsorption. Similar calculations were carried out with the results to those from the previous experiment. It was again found that hydrogen was retained by the film on treatment with mercury. The amount retained, when expressed as a fraction of the amount adsorbed, was in reasonable agreement with the corresponding result for film 65 at complete coverage, obtained from table 11. Later work showed however that this agreement was fortuitous.

Fig.17 shows a graph of the tritium and mercury activities with respect to time. The rate of mercury adsorption was proportional to the rate of hydrogen desorption during the greater part of the displacement, and the relative rates were in good agreement with those found in the previous experiment. It will be recalled that 'end effects' were observed in the displacement in the experiment with film 65. In this experiment a similar effect was noted at the end of displacement but not at the beginning. Mercury adsorption was found

TABLE 12.

FILM 66 DISPLACEMENT OF HYDROGEN BY MERCURY.

Time (min)	Mercury count	Tritium count - background	Tritium total count
0	85	-	
15	100.5		
25		-	
50	115.8		
60		-	
85	137.8		
100		11	11
130	170.1		
145	(176.4)	94.3*	94.3
160	182.8		
180	193.7		
195	(200.0)	478.0*	478
215	208.6		
245	(238.0)	504.8	983
260	252.7		
360	(298.7)	969.8	1953
385	310.0		
450	(349.3)	969.3	2922
475	365.4		
520	(384.4)	977.8	3600

TABLE 12 (cont.)

Time (min)	Mercury count	Tritium count - background	Tritium total activity
535	390.7		
595	(416.9)	444.2	4044
615	425.6		
660	(457.1)	385.9	4430
685	474.3		
755	(514.3)	103.1	4533
775	526.0		
915	617.5		
945		43.8	4577
965	628.8		
1075	670.0		
1820	935.0		
1930		47.0	4624
2005	950.3		
6685	1536		

Final mercury count = 1577 with decay and background corrections.

NOTES. - Mercury count values in brackets were interpolated. * indicates that sample was added to previous filling.

to proceed for some time before any hydrogen was desorbed, but the amount of mercury which adsorbed during this time was not sufficient to cover the surface left bare after hydrogen adsorption. The observed mercury count at the time at which the hydrogen desorption graph became horizontal showed that the amount of mercury adsorbed was equivalent to that required to cover the film on the basis of one mercury atom to one site available for hydrogen adsorption plus that amount of mercury which adsorbed before hydrogen displacement commenced.

Calculations.

Film 65. Adsorption to complete coverage.

1. Tritium Hydrogen Adsorption.

Tritium-hydrogen sample pressure = 37.1 mm

Thermistor gauge deflections:

Sample no.	1	2	3	4	5	6	7	8
Initial defl. (cm)	-3.0	-3.1	-3.0	-3.1	-3.6	-3.6	-3.6	-3.6
Final defl. (cm)	31.0	32.3	31.0	31.1	30.5	31.6	21.7	10.4

2. Thermistor gauge calibration.

Pressure	1.11 mm	0.196 mm	0.035 mm	0.0061 mm
Deflection	-3.1 cm	13.6 cm	26.8 cm	30.5 cm

3. Volume of catalyst vessel = 51.15 cm^3

Volume of catalyst vessel after sealing = 43.20 cm^3

4. Nickel Analysis.

	Standard solns.		Film solns.	
	2o.86mg	28.90mg	A	B
Optical density	0.022	0.324	0.000	0.000
	0.024	0.325	0.000	0.001

Calculated film weight = 20.23 mg

∴Calculated adsorbtive capacity = 77.54 cm^3mm

5. Specific activity of Tritium-hydrogen.

(a) 43.1 mm pressure taken in 4.916 cm^3 gas pipette

Observed count = 20,750 counts/min
= 24,900 counts/min with dead-time correction.

∴Activity per cm^3mm $= \frac{24,900}{43.1} \times \frac{1}{4.916}$ counts/min

= 117.6 counts/min/cm^3mm

(b) 43.2 mm pressure taken in 4.916 cm^3 gas pipette

Observed count = 20,731 counts/min
= 24,877 counts/min with dead-time correction.

∴Specific activity = 117.9 counts/min/cm^3mm

<u>Calculations</u>.

1. Adsorption Calculation.

Six samples were completely adsorbed:

Quantity of tritium-hydrogen adsorbed

$$= 12.83 \times 37.1 \times \frac{60.55}{2370} \times (1 + a + a^2 \ldots\ldots a^5)$$

where $a = \frac{2356}{2369}$

$$= 12.83 \times 37.1 \times \frac{60.55}{2370} \times \frac{(1 - a^6)}{(1 - a)}$$

$$= 72.14 \text{ cm}^3\text{mm}$$

Seventh sample:

Expected final pressure if no adsorption occurred

$$= 37.1 \times \frac{60.55}{2370} \times a^6 \times \frac{12.83}{64.17}$$

$$= 0.184 \text{ mm}$$

Observed final pressure = 0.11 mm

∴ Amount adsorbed = 0.074 × 64.17 cm^3mm
= 4.75 cm^3mm

Total adsorbed tritium-hydrogen
= 77.26 cm^3mm

Total gas phase tritium-hydrogen
= 5.72 cm^3mm from 7th sample
+11.29 cm^3mm from 8th sample
= 17.01 cm^3mm

A fraction $\frac{43.2}{77.2}$ of this remained in the catalyst vessel after sealing = 9.52 cm^3mm

Total tritium-hydrogen in catalyst vessel
= 86.78 cm^3mm

2. Calculation of Recovered Tritium-hydrogen.

Total recovered activity = 8,853 counts/min

Specific activity = 117.6 counts/min/cm^3mm

Quantity of tritium-hydrogen recovered
= 75.37 cm^3mm

Hence, quantity retained by film
= 11.41 cm^3mm

$\therefore$ % retained:adsorbtive capacity $= \frac{11.41}{77.26} \times 100\%$

$= \underline{14.77\%}$

3. Calculation of ratio mercury adsorbed:hydrogen displaced

(a) Specific activity of mercury

Final count on mercury on film = 1136 - background + dead-time

= 1100 counts/min

Film dissolved in 25 ml. nitric acid

Count on 10 ml. film soln. = 745 counts/min

Count on 10ml. standard (25.72 mg per 250 ml.) = 607 counts/min

$\therefore$ Weight of mercury adsorbed $= \frac{745}{607} \times 2.572$ mg

= 3.157 mg

$\therefore$ An external count of 1100 counts/min was produced by 3.16 mg mercury.

(b) Specific activity of tritium-hydrogen

=

= 117.6 counts/min /cm^3 mm

From the graph, fig.15:

$$\frac{\underline{\text{Rate of mercury adsorption}}}{\text{Rate of hydrogen desorption}} = \frac{464b}{6000a} = R$$

where a and b are the specific activities of tritium and hydrogen respectively.

$$\therefore R = \frac{464 \times 3.16 \times 760 \times 117.6 \times 298 \times 11200}{1100 \times 2.006 \times 10^5 \times 6000 \times 273}$$

= 1.210 mercury atoms per displaced tritium-hydrogen.

or 0.826 hydrogen atoms per mercury atom.

This may be compared with the value 82.73% for the amount displaced.

4. Calculation of the amount of mercury required to fill all the sites if one atom occupies one site.

Weight of nickel film = 20.23 mg

Calculated no. of sites for hydrogen adsorption

$$= 20.23 \times 2.54 \times 10^{17} \text{ sites}$$

$$= 5.14 \times 10^{18} \text{ sites.}$$

Weight of mercury required to cover these sites

$$= \frac{5.14 \times 10^{18}}{6.023 \times 10^{23}} \times 2.006 \times 10^{5} \text{ mg}$$

$$= 1.712 \text{ mg}$$

Count rate which would be produced by this amount

of mercury on film $= \left(\frac{1.712 \times 1100}{3.157}\right) + 74$

$$= 674 \text{ counts/min}$$

This count rate corresponds to the amount of mercury which was on the film at the time tritium ceased to be desorbed.

__Film 66__ __Adsorption to incomplete coverage__.

__Experimental Data__.

1. Tritium-hydrogen adsorption.

Tritium-hydrogen sample pressure = 46.1 mm

Thermistor gauge deflections.:

Sample no.	1	2	3
Initial deflection	-4.0 cm	-4.0 cm	-4.0 cm
Final deflection	3o.7 cm	31.4 cm	30.9 cm

2. Thermistor gauge calibration.

Deflection under high-vacuum conditions = 31.0 cm.

3. Volume of catalyst vessel.

This value was not required in the calculation because there was no residual pressure, and was therefore not determined.

4. Nickel analysis.

	Standard solutions		Film solutions	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.385	0.036	0.035
	0.000	0.383	0.037	0.036

Calculated film weight = 21.61 mg

5. Specific activity of tritium-hydrogen

= 117.6 counts/min, as for film 65.

<u>Calculations</u>.

1. Adsorption of tritium-hydrogen.

Three samples were completely adsorbed

Quantity of tritium-hydrogen $= 3 \times 12.83 \times 46.1 \times \frac{6055}{2372}$

$= 45.30 \text{ cm}^3\text{mm}$

2. Recovery of tritium-hydrogen by displacement.

Total recovered activity = 4,624 counts/min

Specific activity = 117.6 counts/min/cm^3mm

∴ Recovered hydrogen = 39.31 cm^3mm

∴ Amount retained = 5.99 cm^3mm

3. Absorbtive capacity.

Film weight = 21.61 mg

∴Absorptive capacity
= 82.83 cm^3mm

% surface covered
= 54.7 %

4.% hydrogen retained on film

(a) As % of adsorbtive capacity $= \frac{5.99}{82.83} \times 100\ \%$

$= \underline{7.23}\ \%$

(b) As % of hydrogen adsorbed $= \frac{5.99}{45.30} \times 100\ \%$

$= \underline{13.22}\ \%.$

5. Calculation of ratio mercury adsorbed:hydrogen displ.

(a) Specific activity of mercury

Final mercury count on film = 1577 counts/min

Film dissolved in 25 ml. nitric acid:

Count on 10 ml. film soln. = 1040.4 counts/min

Count on 10 ml. standard soln. B
(25.72 mg per 25 ml.) = 474.0 counts/min

Count on 10 ml. standard soln. C
(22.60 mg per 25 ml.) = 406.7 counts/min

Background count = 20.5 counts/min

Weight of mercury on film:

From soln. B results $= 2.572 \times \frac{1019.9}{453.5}$ mg

$= 5.784$ mg

From soln. C result $= 2.260 \times \frac{1019.9}{386.2}$ mg

$= 5.969$ mg

Average weight $= 5.88$ mg

Specific activity of mercury

$= \frac{2.006}{5.88} \times 10^5 \times 1577$ counts/min/cm^{3}mm

(b) Specific activity of tritium-hydrogen.

As for film 65.

(c) Calculation of displacement ratio.

$R = 0.0593 \times \frac{a}{b}$ from graph, fig.17.

where a and b are the specific activities of mercury and tritium-hydrogen respectively.

$$\therefore R = \frac{0.0593 \times 117.6 \times 11200 \times 760 \times 298 \times 5.88}{200.6 \times 10^5 \times 1577 \times 273}$$

$= 1.204$ atoms mercury adsorbed per atom hydrogen displaced.

or 0.831 atoms hydrogen per atom mercury.

4. Calculation of amount of mercury required to cover the surface, if 1 mercury atom occupies each site.

Weight of nickel film $= 21.61$ mg

$\therefore$ Weight of mercury $= \frac{21.61 \times 2.54 \times 200.6 \times 10^{22}}{6.023 \times 10^{23}}$ mg

Count rate which would be produced by this amount of mercury on film

$$= \frac{21.61 \times 2.54 \times 200.6}{60.23} + 85 \text{ counts/min}$$

$$= 567 \text{ counts/min}$$

Activity representing mercury which adsorbed during the actual hydrogen desorption

$$= 567 - (140 - 85) \text{ counts/min}$$

$$= 512 \text{ counts/min}$$

This value corresponds to the observed activity at the time mercury-desorption of hydrogen ceased.

5.7. Tritium-hydrogen retention by Nickel Films after treatment with Mercury.

Several further experiments were carried out to measure the amount of hydrogen retained by films after desorption by mercury. The purpose of these measurements was to carry out displacements with mercury on films at different hydrogen coverages and to attempt to correlate the amount of hydrogen retained with either the amount adsorbed or the adsorptive capacity.

The results of these experiments are recorded on the following pages, and the experimental data in appendix C. Table 13 shows the collected results, from which it may be seen that the quantity of hydrogen retained was proportional to the adsorptive capacity, and was 7 - 8 % of this for a partially covered film. Completely covered films however appeared to be exceptional, and in the case of these about 15 % was retained. This was in good agreement with the results obtained using the method described in chapter 3. It was thought that this may have been an effect of the 'slow uptake' which has been observed to follow fast hydrogen chemisorption on nickel. Beeck (40) has stated that the magnitude of the slow uptake was independant of whether the nickel film was orientated or unorientated. An experiment was therefore carried out using an unorientated (vacuum

TABLE 13.

Film no.	% surface covered	% Tritium retained :amt. adsorbed	:ads. capacity
65	100 %	14.77 %	14.77 %
66	54.7 %	13.22 %	7.23 %
83	18.7 %	38.69 %	7.24 %
85	8.6 %	86.40 %	7.43 %
107	20.5 %	34.71 %	7.10 %
105	100 %	16.92 %	16.92 %
108	100 %	14.56 %	14.56 %
113*	100 %	28.92 %	28.92 %

* Vacuum deposited.

deposited) film (film 113) at complete coverage. In this case the amount of hydrogen retained was 28.9 % of the adsorbtive capacity.

Results and Calculations.

Film 83. Argon-deposited, hydrogen adsorbed to incomplete coverage.

Quantity of tritium-hydrogen adsorbed = 13.31 $cm^3 mm$ at 25°C

Film weight = 18.55 mg

Calculated adsorptive capacity = 71.1 $cm^3 mm$

Tritium Recovery

Time of exp. to mercury	Activity	Backgrd.	Activity recovered
11½ hr	796.9	39.8	757.1 counts/min
2 days	60.0	40.1	19.9 counts/min
4 days	41.4	39.1	2.3 counts/min

Total activity = 779.3 counts/min

Tritium specific activity = 95.8 counts/min $cm^3 mm$

Total tritium recovered $= \frac{779.3}{95.8}$ $cm^3 mm$

$= 8.16$ $cm^3 mm$

∴ Quantity retained $= 5.15$ $cm^3 mm$

% retained:adsorptive capacity
= 7.24 %.

% retained:amount adsorbed
= 38.7 %.

% coverage = 18.7 %

Film 85.

This film was argon deposited. Hydrogen was adsorbed to partially cover the film.

Quantity of tritium-hydrogen adsorbed = 10.83 $cm^3 mm$

Film weight = 32.90 mg

Calculated adsorptive capacity = 126.0 $cm^3 mm$

Tritium recovery

Time of exp. to mercury	Activity	Backgrd.	Activity recovered
12 hr	132.8	35.1	97.7
1 day	78.2	36.0	42.2
2 days	36.9	36.1	0.8

Total activity = 140.7 counts/min

Tritium specific activity = 95.8 counts/min $cm^3 mm$

Total tritium recovered = $\frac{140.7}{95.8}$ $cm^3 mm$

= 1.47 $cm^3 mm$

∴ Quantity retained by film = 9.36 $cm^3 mm$

% retained:adsorptive capacity = 7.43 %

% retained:amount adsorbed = 86.4 %

% coverage = 8.59 %

Film 107

This film was argon deposited. Hydrogen was adsorbed to partially cover the film.

Quantity of tritium-hydrogen adsorbed = 22.21 $cm^3 mm$

Film weight = 28.33 mg

Calculated adsorptive capacity = 108.6 cm^3mm

Tritium recovery

Time of exp. to mercury	Activity measured	Background	Activity recovered
5 hr	1379	41.0	1338 counts/min
6 hr	302	35.0	267 counts/min
18 hr	52.4	52.5	0

Total recovered activity = 1605 counts/min

Tritium specific activity = 110.7 counts/min cm^3mm

Total tritium recovered $= \frac{1605}{110.7}$ cm^3mm

= 14.50 cm^3mm

∴ Quantity retained = 7.71 cm^3mm

% retained:adsorptive capacity = 7.10 %

% retained:amount adsorbed = 34.71 %

% coverage = 20.45 %

Film 105

This film was argon deposited. Hydrogen was adsorbed on the film to saturation.

Quantity of tritium-hydrogen present in the catalyst vessel = 124.3 cm^3mm

Film weight = 30.93 mg

Calculated adsorptive capacity = 118.5 cm^3mm

Tritium recovery

Tritium recovery

Time of exp. to mercury	Activity measured	Backgrd.	Activity recovered
30 min	824	61	763
4 hr	8062	51	8011
5.5 h	2683	47	2636
7 h	280	50	230
11 h	239	55	184
1 day	98	54	44

Total recovered activity = 11,868 counts/min

Tritium specific activity = 110.9 counts/min cm^3mm

Total tritium recovered $= \frac{11,868}{110.9}$ cm^3mm

$= 107.0$ cm^3mm

∴ Quantity retained = 17.3 cm^3mm

% retained:adsorptive capacity = 14.56 %

<u>Film 108</u>

This film was argon deposited, and hydrogen was adsorbed upon it to saturation.

Quantity of tritium-hydrogen present in the catalyst vessel = 56.13 cm^3mm

Film weight = 14.19 mg

Calculated adsorptive capacity = 54.38 cm^3mm

Tritium recovery

Time of exp. to mercury	Activity measured	Backgrd.	Activity recovered
0	101	41	60
2 h	2074	40	2034
3 h	804	45	759
4 h	770	41	729
5 h	200	45	155
7 h	90	40	50
1 day	47	40	7

Total recovered activity = 3,794 counts/min

Tritium specific activity= 114.8 counts/min cm^3mm

Total tritium recovered= $= \frac{3794}{114.8}$ cm^3mm

$= 33.06$ cm^3mm

$\therefore$ Quantity retained = 13.28 cm^3mm

% retained:adsorptive capacity = 28.92 %

5.8. Diffusion of Mercury in Nickel.

The results obtained from the experiments described in the earlier sections of this chapter indicated that mercury adsorption on hydrogen covered nickel films caused displacement of the hydrogen, and after hydrogen displacement had ceased the ädsorption of mercury continued. The amount of mercury which adsorbed during the hydrogen displacement was greater than an amount equivalent to the hydrogen displaced. It was

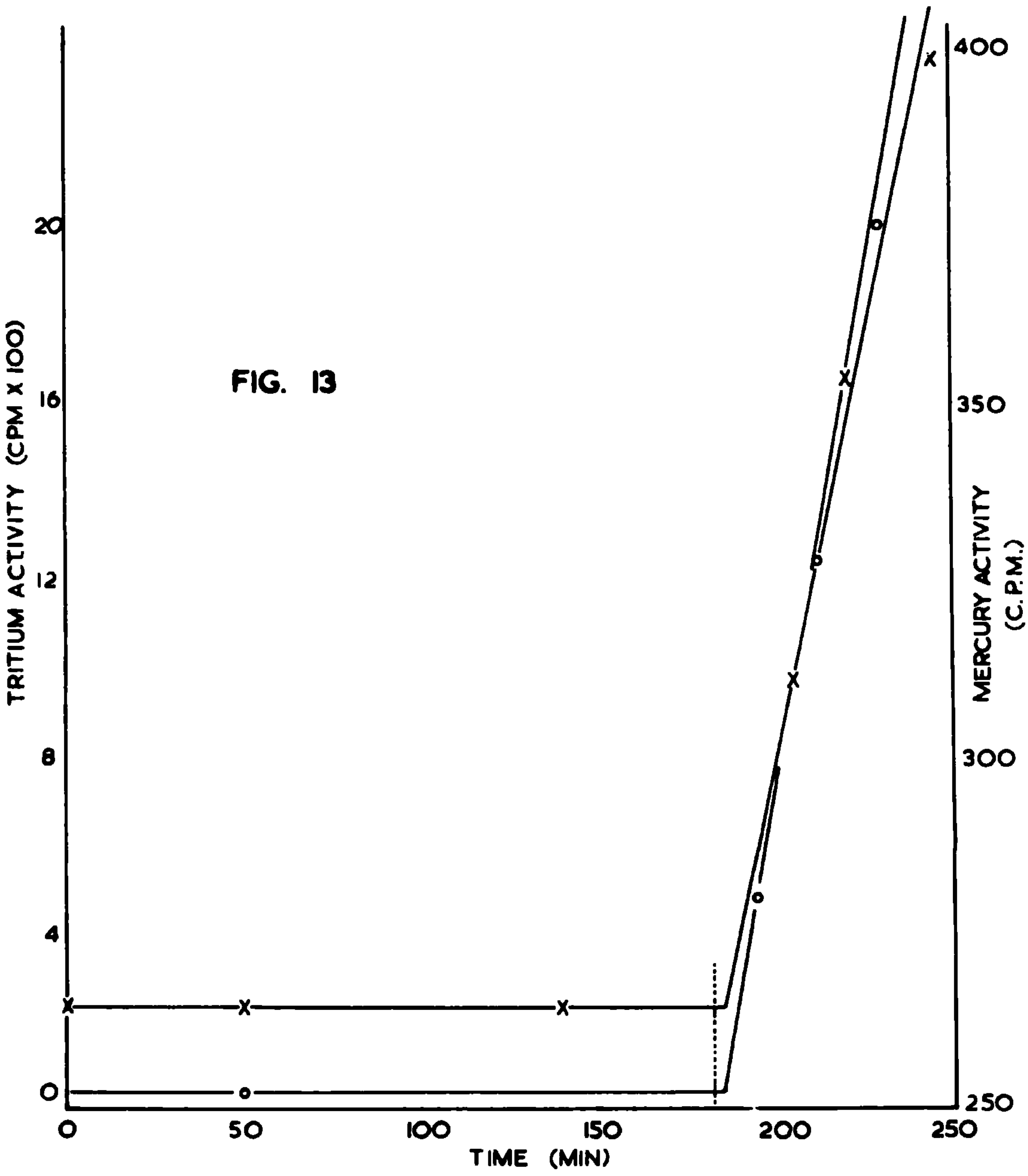

TRITIUM ACTIVITY (CPM X 100)
20
16
12
8
4
0
MERCURY ACTIVITY (C.P.M.)
400
350
300
250
0
50
100
150
200
250
TIME (MIN)

FIG. 13

therefore thought possible that diffusion of mercury into the bulk of the nickel had occurred during the displacement, and a simple experiment which will now be described was designed to investigate this.

An evaporated nickel film was partially covered with tritium-hydrogen, and radioactive mercury vapour admitted by the usual technique. Adsorption of mercury was allowed to proceed until tritium displacement occurred. The mercury source was then cooled in liquid nitrogen to prevent further evaporation, and was maintained at this temperature for three hours, during which time mercury diffusion into the film could occur. At the end of this time the mercury source was rapidly heated to room temperature by surrounding it with a beaker containing cold water. Determinations of mercury and tritium-hydrogen activities were made with respect to time. The results are shown in table 14 and graphically in fig.13, and it may be seen that no time lag occurred between the rise of mercury and tritium activities when exposure to mercury was resumed. It was therefore concluded that either no diffusion of mercury from the surface into the bulk occurred, or that such diffusion only took place when the surface sites were filled.

TABLE 14.

Time (min)	Tritium count + dead-time	Mercury count
0		264 counts/min
50	36 (backgr.)	264 counts/min
140		264 counts/min
182	Mercury heated to 20°C	
194	486	
204		311 counts/min
212	1232	
221		353 counts/min
232	2000	
245		398 counts/min

5.9. Results of Isotope Effect Measurements.

The McLeod gauge readings and counting rates measured during an isotope effect experiment are shown in table 15 and the graphs constructed from the data in fig.18. This experiment was the last of three experiments. The previous two were carried out at a time when acute counter troubles were experienced, and the technique described in section 5.5. and used for this third experiment was introduced as a means for checking the behaviour of the counter as well as to ensure quantitative transfer of measured samples. The graphs show

ISOTOPE EFFECT

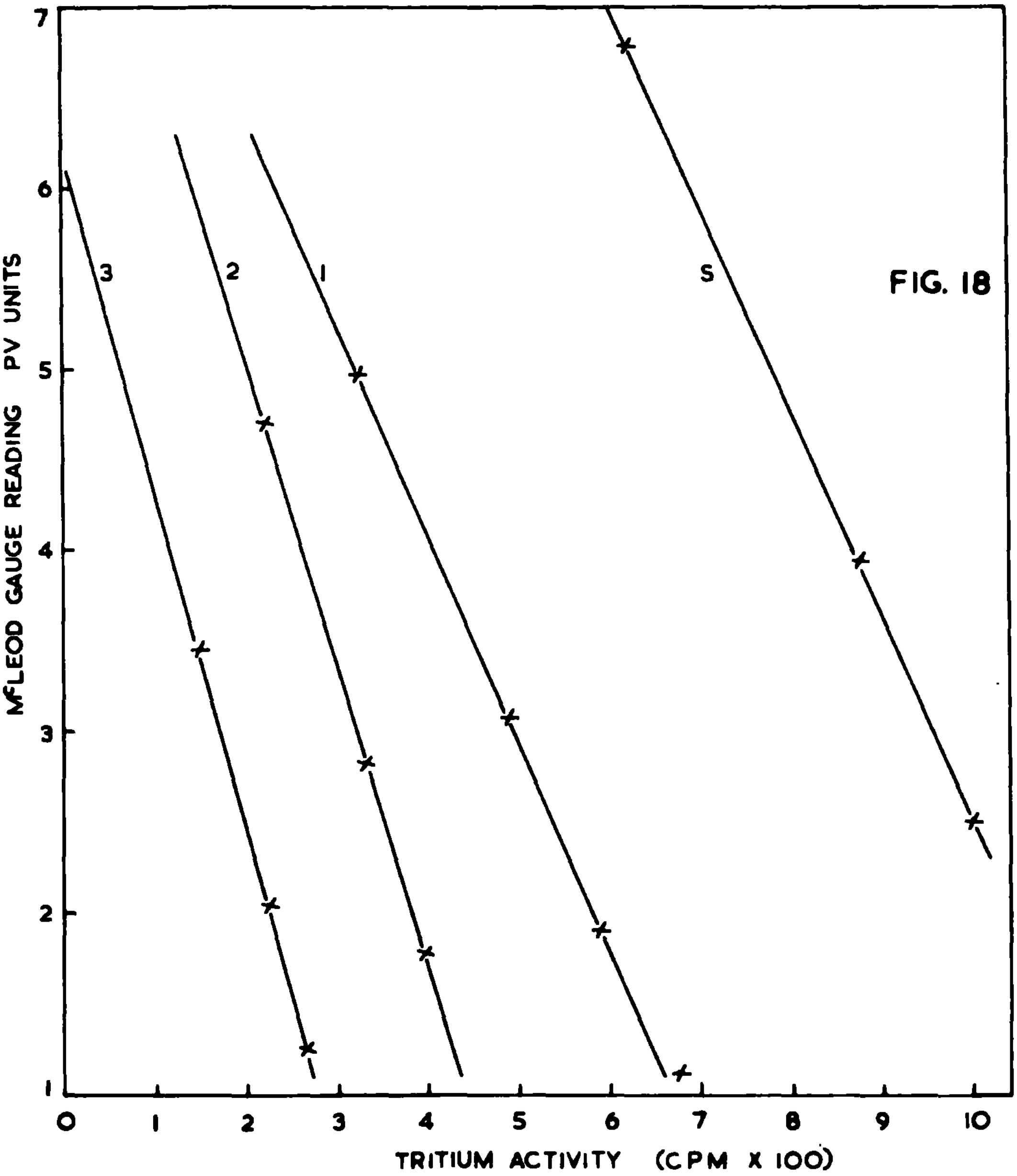


FIG. 18

TABLE 15.

Film 82 ISOTOPE EFFECT.

Pressure (mm)	Volume *(A cm^3)	Gas count Counts/min	PV
Sample 1.			
2.245	2.215	322	4.974
1.730	1.780	488	3.080
1.360	1.400	590	1.904
1.040	1.080	674	1.123
Sample 2.			
2.170	2.170	220	4.710
1.565	1.800	332	2.819
1.315	1.360	398	1.788
Sample 3.			
1.830	1.885	149	3.449
1.395	1.470	222	2.050
1.100	1.145	263	1.260
Sample 4, Calibration Sample.			
3.260	3.325	667	10.91
2.590	2.635	1021	6.825
2.000	1.975	1274	3.950
1.585	1.585	1403	2.513

* A = cross-sectional area of McLeod gauge capillary, in square cm.

by their linearity that the measured counts were proportional to the activity present in the counter, and therefore that spurious counts arising from defective counting equipment were not occurring.

The measured slopes of the graphs however gave rather unexpected results for the specific activities. The first sample extraced from the catalyst vessel had, within the 1 % statistical error, the same specific activity as the sample of hydrogen initially adsorbed. The two subsequent samples had specific activities less than this value, as shown in table 16.

TABLE 16.

Sample	Specific activity (counts/min per unit)
Adsorbed material	88.64
First sample	87.35
Second sample	60.95
Third sample	51.12

CHAPTER 6.

DISCUSSION OF THE EXPERIMENTS ON THE DISPLACEMENT OF HYDROGEN ON NICKEL FILMS BY MERCURY.

The results obtained from the experiments on the desorption of hydrogen from nickel films by the action of mercury may be summarised as follows.

1. Hydrogen desorption proceeded during the course of mercury adsorption in a manner which indicated proportional displacement over a large range of the desorption. The initial rate of hydrogen desorption with respect to mercury adsorption was about twice the rate in the proportional region, and towards the end of the desorption the rate decreased gradually to zero.
2. The adsorption of mercury continued after the hydrogen ceased to be desorbed.
3. The hydrogen displacement was not complete, and the amount retained by the film at the completion of desorption was 7 - 8 % of the adsorptive capacity of the surface, at coverages below about 50 %.
4. At complete coverages the amount of hydrogen retained was 14 - 16 % of the adsorptive capacity for orientated films and 28 % for an unorientated film.
5. The amount of mercury on one of the completely

covered films when hydrogen desorption ceased was equivalent to one mercury atom on every site on which hydrogen could have been adsorbed.

6. The rate of hydrogen desorption was about 85 % of the rate of mercury adsorption in the region of proportionality.

7. Measurement of the isotope effect in tritium-hydrogen adsorption showed that the gas phase residue after adsorption had the same specific activity as the sample adsorbed. Progressive removal of further gas phase samples appeared to result in a decrease in this specific activity.

6.1. Previous Measurements on Hydrogen Adsorption.

In order to attempt to interpret the experimental observations it is desirable to review briefly the subject of hydrogen adsorption on nickel, since it has been observed in the present work that the hydrogen sorbed on nickel can be considered to be in "two states". Particular attention will be given to the two modes of hydrogen sorption, fast and slow, and to the two modes of hydrogen sorption which produce either negative or positive layers of hydrogen on nickel surfaces.

Hydrogen has been found to chemisorb rapidly upon clean nickel surfaces (8) and this observation was confirmed by the experiments described in chapter 3 of this thesis. Several complicating features have been noted in this adsorption, which show that the adsorption process which occurs is far from being simple. Firstly, it was observed by Beeck (42) that the heat of adsorption of hydrogen on nickel decreased with increase of surface coverage. This suggested that the surface was heterogeneous, and that adsorption was taking place in such a manner as to fill the sites of lowest free energy first. Measurements of heat of adsorption on orientated and unorientated films gave the same result, so the heterogeneity is unlikely to be caused by adsorption upon different crystal planes. If however it is concluded from these observations that the surface was heterogeneous it is also necessary to postulate the possibility of surface diffusion, so that diffusion of adsorbed hydrogen atoms to sites of lowest free-energy would be possible.

It was also observed that slow sorbtion of hydrogen occurred on nickel films following the fast, almost instantaneous initial uptake, which suggested that more than one different sorption mechanism might have operated. It was found that hydrogen adsorbed by this slow uptake process could be pumped off and the adsorption repeated. Beeck observed that the amount of hydrogen sorbed on a nickel film during this slow uptake was independant of the sintering temperature of the film. Thus the amount of hydrogen sorbed per unit film weight during this process was constant over a wide range of sintering temperatures. This range of sintering temperatures, 23°C to 400°C was sufficiently wide to cause a 175-fold variation in the surface available for the fast chemisorption. Beeck concluded from these observations (40,43) that the slow uptake was caused by penetration of hydrogen into the bulk of the metal, leading to lattice solution. This sorption was concluded to be partly adsorption and partly absorption, the latter process occurring on positions inaccessible to carbon monoxide and ethylene molecules.

In contrast to these observations by Beeck, Gundry and Tompkins found that the ratio of the amount of hydrogen taken up by the fast process to that by the slow process was substantially constant on nickel and iron films.(44,45). They found that a 15-fold decrease in surface/bulk ratio caused a decrease in fast/slow adsorption ratio of only 47 %. On the basis of their observations the slow uptake was explained in terms of a change in the adsorbed state. This postulated that adsorption took place to an 'initial state' and the change to the 'final state' of lower free-energy required an activation energy. This activation energy was assumed to increase with increase of surface coverage, as the heat of adsorption decreased. The mechanism will however be discussed in more detail later.

In any attempt to explain the variation in heat of adsorption and the mechanism of the slow uptake, it is relevant to consider whether surface diffusion of adatoms is possible and whether the nickel surfaces are homogeneous or heterogeneous (46) for the adsorption of hydrogen. Measurements of certain physical properties of nickel films and supported nickel catalysts have been made from which deductions can be made on these topics. These measurements include studies of contact potentials, electrical conductivity and magnetic properties. These will now be discussed briefly.

Measurements on the electrical conductivities of thin films of nickel have been made by Suhrmann (47), and changes of this conductivity have been observed when hydrogen was adsorbed on the film. Thus, when hydrogen was admitted to the film at room temperature a sudden decrease in film resistance was observed, followed by a more gradual decrease.

This decrease was interpreted as representing electron transfer in the direction nickel to hydrogen, on unsintered nickel films. Using sintered nickel films, work function measurements indicated the opposite effect, that is, the hydrogen appeared to be positive with respect to nickel. An attempt was made to correlate these observations with different modes of adsorption on particles of different size (48), in comparison with the results from the magnetic measurements made by Selwood (49) described in the next paragraph.

Suhrmann has also reported that if the films with sorbed hydrogen were pumped to a high-vacuum, the resistance increased again to a value corresponding to that obtained after the initial sudden change of resistance.

At 90°K, the resistance of the film decreased at equilibrium pressures less than 10^{-6}mm. A sudden decrease in resistance occurred at 10^{-6}mm pressure and continued to decrease at a progressively diminishing rate until above 10^{-3}mm no further change occurred with change in pressure. No change was observed on pumping at 90°K, in contrast to the state of affairs at room temperature. These observations suggest that the sites upon which reversible adsorption occurs are inaccessible to hydrogen at 90°K.

The magnetic measurements carried out by Selwood (49) may also be relevant to the problem of the slow uptake of hydrogen on nickel, since they seemed to suggest that two types of adsorption occurred. These measurements amount of hydrogen adsorbed it was thought likely that hydrogen was adsorbed preferentially on the smaller catalyst particles, and that the slow uptake of hydrogen was the consequence of slow diffusion of hydrogen on to the surface of the less accessible of such particles. As in the case of conductivity measurements, reversibility of the slow sorbed hydrogen accompanied by an increase in magnetisation was observed.

In connection with the use of silica supported nickel catalysts attention should be drawn to the work, which will be discussed later, of Schuit and de Boer (54) who showed the importance of trace oxygen contamination in interpreting the sorption properties of these films.

Measurements of surface potential, by Mignolet (50), and photoelectric work function, by Rideal et al. (51), have been made on evaporated nickel films. The contact potential has also been measured on tungsten and chromium films (52,53). In all cases these surface potentials became more negative when hydrogen was admitted to the film, that is, the work function was increased. This observation indicated that hydrogen adsorption produced a dipole such that the hydrogen was negative with respect to the nickel. At high coverages however the contact potential became slightly less negative, as though nickel-hydrogen dipoles of the opposite sign were being produced. Mignolet (55) has attempted to explain the changes in surface potential at high coverages by postulating that hydrogen molecules may be adsorbed in competition with hydrogen atoms. This he visualises as an activated process. Such a state of affairs would also explain the rapid fall in heat of adsorption which has been observed towards complete coverage.

Although the investigations of surface dipoles recorded above are in agreement with each other, a discrepancy exists between these observations and those of v.Duhn (56), who found that the change in surface potential was positive when hydrogen was admitted. Mignolet points out that this discrepancy could not arise from a systematic error in sign since agreement between the values obtained by Mignolet and v. Duhn for oxygen adsorption on tungsten - in each case an oxygen-negative dipole was obtained. Further discrepancies became apparent when the results for the contact potential, film conductivity and magnetic measurements are compared. The magnetic measurements made by Selwood stand in contradiction to the surface potential work of Mignolet etc.. The surface potential measurements by Suhrmann on unsintered films were in agreement with those of Mignolet, showing a negative-hydrogen dipole, but on sintered films the dipole was found to be positive.

Suhrmann attempted to correlate these observations (48) with those of Selwood in terms of the formation of larger particles during the sintering process.

Any attempt to secure accordance between these results by explaining the anomalies would, in the present state of knowledge of the subject, involve unjustifiable assumptions. It may be mentioned however that de Boer (57, see also 58) has pointed out that the change of sign of the hydrogen - metal dipole could be explained by the presence of impurities on the surface. He states that atoms producing dipoles on adsorption which are of different polarity will aid each other's chemisorption both with regard to rate and strength of adsorption. This implies that the presence of chemisorped oxygen on the surface, with its negative dipole, would favour the adsorption of hydrogen to produce a positive dipole. At the same time the heat of adsorption of hydrogen to form a negative dipole could be decreased to such a value as to make its adsorption impossible.

If the silica supported nickel catalyst used by Selwood was contaminated in this way, it may be possible to explain the anomaly. Selwood (59) states that the catalyst used was contaminated with water vapour which might in turn lead to the presence of oxygen on the film (54). With regard to the measurements by Suhrmann

- no particular mention was made of the precautions taken to free the walls of the conductivity vessel from contaminants; if these precautions were inadequate, contamination of the film may have occurred during the sintering process.

It must be emphasised however that the present state of the subject is too little advanced to draw any definite conclusions from such conflicting observations. It appears however that there is some evidence for the existance of two modes of hydrogen sorption (60).

The question of the homogeneity or heterogeneity of catalyst surfaces has been investigated in its physico-chemical aspects by studies on the adsorption of different isotopic species, but here again anomalies exist between the results of different workers. Thus Keier and Roginskii (61,62) have investigated heterogeneity on supported nickel and on zinc oxide catalysts. The method used was to carry out adsorption in two stages, using hydrogen for one stage and 99 % deuterium for the other. When desorption was carried out by heating the catalyst at progressively higher temperatures the gas desorbed first had the same isotopic composition as that adsorbed last. Continued desorption yielded gas with a higher proportion of the isotope adsorbed in the first stage, and when desorption was almost

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the types of catalyst used by the Russian workers were likely to be impure (64).

It may be mentioned that these observations do not prove the existance of a homogeneous surface, because surface diffusion involving an activation energy may occur between sites of different adsorption energy, but Schuit concludes that this is unlikely in view of the results of Kummer and Emmett (65). These authors have investigated the adsorption of carbon monoxide on an iron catalyst using a similar technique to Schuit's. Two samples of carbon monoxide were admitted to the catalyst, one sample of which was ^{14}C-labelled. They report a tendency of the sample adsorbed last to appear first on desorption, but observed that 50% exchange of the two species occurred even at a temperature of $-196^{\circ}C$. Kwan (64) has concluded from a theoretical treatment of heats of adsorption that the adsorption of hydrogen on nickel is homogeneous.

From the foregoing review of relevant work it may be seen that evidence for or against heterogeneity of catalyst surfaces makes it impossible to draw any firm conclusions in the present state of the work. It is therefore difficult to attempt to explain the slow sorption phenomenon observed with hydrogen on nickel in terms of any concept of the catalyst which involves homo- or heterogeneity. It is appropriate at this point however to consider the observations of Kwan (66), and of Schuit and de Boer (67,54) with regard to the slow sorption process. Using a catalyst prepared by subjecting nickel oxide to a rigorous reduction procedure Kwan was able to show that no slow sorption of hydrogen occurred. A similar catalyst prepared by a less stringent procedure was found to exhibit the slow uptake phenomenon. Kwan also reports that contamination of the surface by minute amounts of vapour from stopcock grease or mercury vapour can appreciably affect the chemisorption rate. Shuit and de Boer found a similar effect with a silica supported nickel catalyst, (67,54), prepared by the reduction of nickel oxide. The fast and the slow types of adsorption were again observed, and it was found that a more thorough reduction procedure gave a catalyst with which the fast type of adsorption was increased at the expense of the slow type. Conversely, the admission of oxygen to a thoroughly reduced surface diminished the amount of fast sorption and increased the slow sorption when hydrogen was subsequently adsorbed on the surface. Furthermore the observed increase of slow sorption was linearly related to the amount of oxygen previously admitted. It was assumed that the slow hydrogen sorption occurred on top of oxygen atoms or molecules already adsorbed on the nickel. The linear relationship already mentioned indicated that the oxygen was adsorbed as molecules at low temperatures and as atoms at higher temperatures. It was further suggested that during adsorption studies on a reduced nickel surface of this type at higher temperatures surface oxidation by reaction of water from the silica support might occur - giving nickel oxide and hydrogen.

From these observations it must be concluded that the presence of oxygen on nickel surfaces causes them to exhibit these slow uptake effects, but it is difficult to decide whether this is the cause of the slow uptake observed with other systems, in particular evaporated films.

Since the surface area of evaporated films is small relative to that of supported catalysts it is difficult to explain the reproducibility of the slow sorption on the basis of spurious contamination. If this was caused by high temperature diffusion of contaminants from the bulk metal of the filament from which the evaporation was made, or by dissociation of the nickel oxide in or on this filament, it might be expected that the resultant amount of contamination would be profoundly changed by changes in the evaporation temperature of the filament. It is difficult to see how this temperature could be sufficiently reproducible from one film preparation to the next to secure the observed reproducibility of the slow uptake.

In spite of the difficulties arising from the conflicting observations in experiments on the nature of catalyst surfaces, attempts to explain the slow sorption of hydrogen have been made by Rideal (51) and by Porter and Tompkins (45,44). These will now be described.

The explanation advocated by Rideal and co-workers requires the assumption of heterogeneity insofar as the existance of sites for adsorption in pores as distinct from sites on the surface are postulated. They found that at 20°C the slow uptake did not occur until there was a measureable pressure of hydrogen in the gas phase, that is, the uptake occurred after but not during the initial fast sorption. This region of the adsorption where a measurable gas phase pressure is observed corresponded to the conditions under which a change in sign of the Ni - H dipole, as shown by the authors' photoelectric work function measurements. From this it was suggested that the sites for the slow uptake may occur in defects or gaps between nickel crystals below the surface of the film, so that the nickel-hydrogen dipole appeared to act in the opposite sense.

It was observed that the rate of the slow sorption was very slow at $-183^{\circ}C$, but proceeded faster as the temperature was increased, as shown by measurements at $-78^{\circ}C$ and $20^{\circ}C$. It appeared therefore that the process involved an energy of activation, and Rideal suggested that the process was one of diffusion of hydrogen from the sites upon which fast chemisorption had occurred to sites in defects or pores in the surface. It was further postulated that these sites upon which slow sorption occurred were sites of lower heat of adsorption than those upon which the fast process occurred; consequently an energy of activation was involved in the diffusion from sites for fast adsorption to sites in pores. Rideal considered it likely that adsorption of hydrogen on to sites below the surface would occur by diffusion from the surface, rather than directly from the gas phase. Consequently, a distribution of hydrogen between the two types of site was visualised which could be represented by the equation

$$N_S = N \exp\left(-\frac{\Delta E_1}{kT}\right)$$

where N is the number of hydrogen atoms adsorbed on sites for slow uptake,

N is the number of hydrogen atoms adsorbed on sites for fast adsorption

and ΔE_1 is the energy difference between the two types of sites.

The experimental results were explained in terms of this model. Thus, the energy difference between the two types of sites decreases as the surface is progressively covered with hydrogen because the heat of adsorption decreases . Consequently, in the region where the heat of adsorption is low and falling rapidly, adsorption on to sites for slow adsorption can occur readily. As it was reasonable to assume immobility of hydrogen at -183°C, these sites for slow adsorption would remain empty when adsorption was carried out at this temperature. This was in accordance with the experimental observations, since it was observed that after carrying out hydrogen adsorption at -183°C, allowing the film to warm up to 20°C and cooling again to -183°C further sorption could be observed. This sorption was considered to be caused by the resorption of hydrogen on sites for fast sorption to replace hydrogen which had diffused into pores. Sorption studies made after prolonged pumping indicated that the slow sorption portion could be removed by this treatment.

This explanation of the slow sorption process may be compared with that of Gundry and Tompkins who, like Rideal, considered the slow uptake to be further chemisorption (44). They considered the adsorption to take place to a 'final' chemisorbed state via an intermediate state. Hence heterogeneity in the method of adsorption rather than in the surface properties was assumed. This 'final' chemisorbed state had a higher adsorption energy than the 'initial' state which in turn had a higher adsorption energy than the Van der Waal's adsorbed state. Energy relationships were postulated such that on admission of hydrogen to a clean nickel surface the hydrogen could enter all the states - particularly the 'final' state since this had the lowest adsorption energy. As the heat of adsorption decreased with increase of coverage the intersection of the potential energy curves representing the two states became such that an activation energy was required for a transition to occur from the 'initial' to the 'final' state. When this point was reached the slow process was observed. This slow process was therefore one of adsorption of hydrogen into the 'initial' state at a rate controlled by the rate of formation of vacancies in this state caused by activated transfer of hydrogen to the final state. When the film was evacuated therefore the hydrogen desorbed was from the 'initial' or the Van der Waal's adsorbed state.

The theory is adequate in explaining the results obtained with the thermal cycling procedure. In this procedure the adsorption is studied at a low temperature, after which the temperature is raised for a length of time then lowered and further adsorption studied. Thus on carrying out thermal cycling without evacuation further rapid sorption was noted followed by slow sorption. This slow sorption took place at a slower rate than in the initial adsorption at the low temperature (78°K). On the other hand, when evacuation was carried out during the thermal cycling procedure the rate of the subsequently observed slow uptake was identical with that at the point where the slow uptake was interrupted after the initial sorption. These observations were explained in terms of the theory by postulating transfer of hydrogen from the 'initial' to the 'final' state during thermal cycling, since the elevated temperature enabled the necessary activation energy to be obtained. On cooling to 78°K and admitting more hydrogen, fast sorption was observed, corresponding to the filling of vacancies in the 'initial' state left after the transfer of hydrogen to the 'final' state at the elevated temperature. The slow sorption observed to follow this fast sorption was slower than that observed in the first adsorption because the number of hydrogen atoms in the 'final' adsorbed state had increased. The effect of this was to increase the activation energy for transfer from the 'initial' to 'final' states and hence to decrease its rate.

It is now worth considering whether there is any explanation of the two states of sorption in terms of a concept of the bonds between hydrogen and nickel.

Dowden has considered the bonding between metals and adsorbed atoms (68) and has suggested that the initial and final states may involve bonding with d-orbitals and with stronger dsp-type hybridised bonds respectively. He has pointed out that as the surface coverage tends to unity the bonding will be predominantly to d-orbitals, and that this may explain the rapid decrease in heat of adsorption in this region. Further, it may be seen from the postulated potential energy diagrams representing the two states (44) that the final adsorption state requires a smaller internuclear distance between the adsorbed hydrogen atom and the nickel surface atom. Dowden has pointed out that on the basis of this the adsorbed hydrogen when in the final adsorbed state might be expected to produce a small negative surface potential, because it would probably be below the electron cloud at the nickel surface. On the other hand, in the 'initial' adsorbed state a positive surface potential would be expected because of the much larger equilibrium distance. He therefore suggests that the observation by Mignolet (50) that the surface potential becomes less negative at high coverages may be consistent with the filling of this 'initial' state in the final stages of adsorption.

From this brief review it may be seen that there are many points of similarity between the theories of Rideal and co-workers, and Porter and Tompkins. The model used in the two theories is quite different however and as a result of this an important difference emerges. In the case of Rideal's theory, the adsorbed hydrogen which has been involved in the slow uptake process is on the sites of lowest adsorption energy and hence is presumably that which is removed on evacuation. On the other hand, Gundry and Tompkin's mechanism involves transfer to a state of high adsorption energy and the filling from the gas phase or Van der Waal's layers of vacancies in the 'initial' state caused by this process. The hydrogen which has taken part in the slow uptake cannot therefore be identified with that which is removed by pumping. The two mechanisms should therefore be distinguishable by experiment.

Having dealt briefly with some aspects of the subject of hydrogen adsorption, the results obtained in chapter 5 will be discussed.

6.2. Discussion of Results.

From the foregoing review of work on the different aspects of hydrogen sorption on nickel there appears to be extensive evidence for the existance of two modes or states of adsorption.

Thus, the dipole moment measurements made by Mignolet and by Rideal show that there appears to be two types of hydrogen adsorption producing dipoles with opposite polarities. A similar state of affairs was indicated by the conductivity measurements on nickel films by Suhrmann and by the magnetic measurements by Selwood using silica-nickel catalysts. In all cases the second type of adsorption appeared at high coverage. It is difficult however to attempt to correlate the slow sorption of hydrogen and the retention of some of the hydrogen after mercury displacement with the observed phenomena in the magnetic, electrical conductivity, and surface potential measurements at the present state of knowledge of the subject, in view of the anomalies which exist. The evidence from the physical measurements is conflicting, when the direction of the electron transfer on adsorption is considered, e.g.,

1. Magnetic measurements indicate electron transfer from hydrogen to nickel.

2. Surface potential measurements indicated that the electron transfer was from nickel to hydrogen.
3. Conductivity measurements showed both effects, depending on the sintering conditions.

In each case the type of adsorption observed at incomplete coverage is considered.

It may be mentioned however that Selwood (59) has suggested that the slow uptake process may take place on the smallest of the catalyst particles. These particles would be those least accessible to hydrogen, and it is possible that sites on these particles would be completely inaccessible for mercury adsorption.

However the results of the present work might be interpreted in terms of a new approach which does not depend on the nature of the Ni - H bond. This is outlined as follows.

It is possible to account for retention of hydrogen on nickel films when mercury displaces hydrogen by considering an idealised homogeneous film and by placing certain reasonable restrictions on the processes of hydrogen adsorption and desorption by mercury. Thus the hydrogen adsorption has been assumed to be dissociative chemisorption to produse an immobile layer. The following additional assumptions have been made.

(a) The nickel lattice was rectangular.

(b) The position taken up on the lattice by one of the hydrogen atoms of any molecule was purely random.

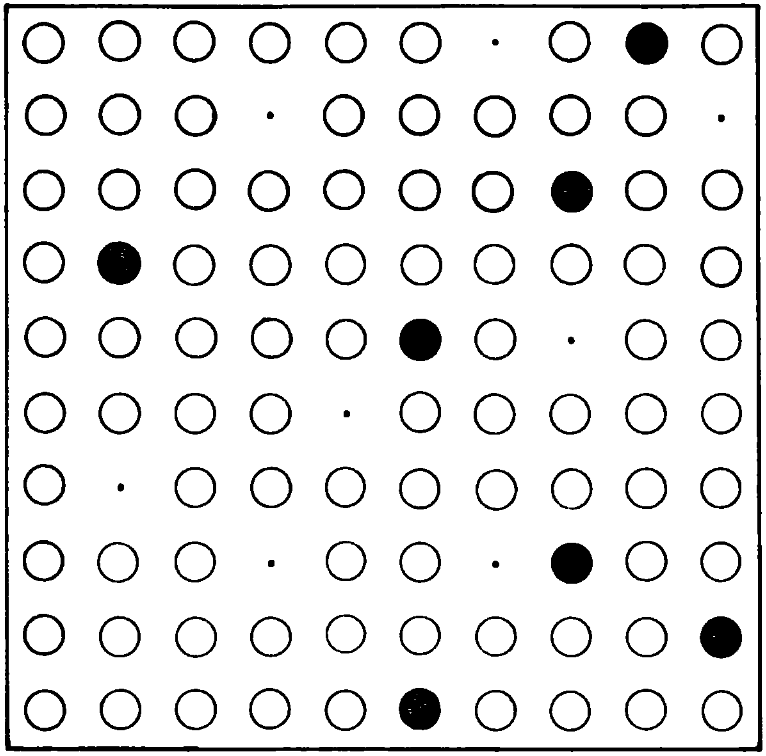
(c) The position of adsorption of the other hydrogen atom of the molecule was restricted to one of the eight adjacent near-neighbouring sites to that occupied by the first atom, but the choice among these eight sites was also random.

(d) Mercury was able to adsorb on any bare site and did so in a random fashion.

(e) Mercury could also adsorb on a site occupied by hydrogen by displacement of this hydrogen, provided the hydrogen had a near-neighbouring hydrogen atom with which it could form a molecule.

(f) In this latter event, the second of the two atoms which formed the molecule of hydrogen left a bare site on the surface.

The problem has been treated theoretically in the following manner. A diagram of a rectangular lattice of 100 sites was constructed, as in fig.19. This took the form of a square 10 units × 10 units, but was considered as a torus. Each of the units was given a coordinate in order from 0 to 9. Random numbers from 00 to 99 were selected (69). The first digit was assigned to the y axis and the second digit to the x axis.



AFTER HYDROGEN ADSORPTION:	AFTER MERCURY DISPLACEMENT:
○ Sites occupied by hydrogen	○ Sites occupied by mercury
● Sites occupied by hydrogen	● Sites occupied by hydrogen
• Vacant Sites	• Sites occupied by mercury

FIG. 19

The site corresponding to these coordinates was then considered to be occupied by hydrogen. The eight sites surrounding this occupied site were each assigned a number from 0 to 7 by an arbitrary rule and the table of random numbers used to select a single digit between 0 and 7. The selected site was then considered to be occupied by the hydrogen atom with which the atom first adsorbed had formed a molecule.

This random selection of sites was continued until no further possible adsorption sites were left, and it was found from the results of many such selections that an average of 7 - 8 % isolated vacancies was obtained on which further atomic hydrogen sorption was impossible.

A similar procedure was carried out with the diagrams of hydrogen filled lattices to represent a random adsorption of mercury. Adsorption of mercury was considered to cause a displacement of hydrogen and a random number selection was made to determine which of its existing neighbours a displaced hydrogen atom would unite with to form a molecule for desorption. This procedure was followed until all the vacant sites had been covered by mercury and all the hydrogen atoms, except those which had become isolated and hence unable to form a molecule, had been displaced. These results indicated the figure 7 to 8 % for the amount of hydrogen retained by isolation. A typical lattice diagram obtained by this theoretical treatment is shown in fig.19.

In attempting to apply these theoretical deductions to the experimental observations it must be remembered that immobility of hydrogen on the surface has been assumed. If this is not the case, the fraction of the adsorbed hydrogen isolated on the surface would be expected to have a lower value dependant upon the possibility of surface diffusion of hydrogen when the remainder of the surface is totally or partially covered with mercury.

The theoretically deduced value for the amount of hydrogen isolated agrees well with that observed experimentally for the retention of hydrogen at incomplete coverage; thus experiments carried out at coverages between 8% and 50% all showed that the amount of hydrogen retained when mercury-displacement was carried out was between 7% and 8% of the adsorptive capacity of the film. It is difficult to explain in terms of the statistical picture why this amount retained should not decrease with decreasing surface coverage. Similar theoretical considerations to those described above show that at 50% coverage about 6% retention might be expected, while at 20% coverage the figure would be about 4%. It is interesting to note that this theoretical treatment predicts that when desorption ceases the amount of mercury present on the film would be equivalent atom-for-atom to the hydrogen originally present, since although 7-8% sites remain occupied by hydrogen there are also 7-8% vacancies available in the complete hydrogen film upon which mercury adsorption can occur. It may also be mentioned that on the basis of this model each mercury atom displaces two hydrogen atoms, leaving one site vacant and available for mercury adsorption. In the early stages of the desorption it may be expected that these bare sites would increase in number since the mercury adsorption is a random process and would cause further displacement rather than adsorption on bare sites (because the number of sites occupied by hydrogen is much greater than the number bare). This might account for the increased rate of hydrogen desorption with respect to mercury adsorption observed in the early stages of the adsorption-desorption process when compared with the steady ratio. This steady ratio would be obtained when a steady-state concentration of vacant sites had been arrived at.

In order to explain the higher amount of hydrogen retained after mercury displacement of hydrogen from films at complete coverage it is suggested that the hydrogen taken up by the slow process is retained in addition to the 7-8% which should be retained on the statistical interpretation. The extra amount of hydrogen retained, 8-9%, is consistent with the expected value for the slow uptake. Thus, although Baker, Jenkins and Rideal (51) found that the amount of hydrogen taken up in the slow process was about 20% of the total amount adsorbed, Beeck has stated that this amount was proportional to the film weight and independant of whether the film was orientated or unorientated (40). Since the films used by Rideal and co-workers were vacuum deposited, the amount of hydrogen taken up on orientated films would be expected to be 10% of the total sorbed. (A distinction may exist between differences in surface area of nickel films caused by orientation from differences caused by sintering, so that in Beeck's statement disagreement with the views of Gundry and Tompkins is not necessarily implied).

The relationship of this extra amount retained to the slow uptake was confirmed by the higher value obtained (28%) in the present work with a vacuum deposited film.

This view that the extra retention of hydrogen is related to the slow uptake is in good accord with Rideal's theory for the slow uptake (51). If the slow uptake process takes place as a result of diffusion of hydrogen into pores it is reasonable to assume that this slow-uptake hydrogen would be in sites inaccessible to mercury. Furthermore, when all the hydrogen available has been desorbed, the hydrogen in pores will presumably be trapped by pore blocking if the subsequent uptake of mercury which has been observed is physical adsorption on the surface.

Gundry and Tompkins (44) report that over 90% of the total sorbed hydrogen could be displaced by mercury vapour at 78°K. This is in accordance with the results which were obtained in the displacement measurements described in chapter 5, since the slow uptake sorption will not have occurred at this low temperature, even though the surface is completely covered. They also report that mercury vapour had little effect if the surface was partially poisoned with oxygen. This implies that the relationship between the slow uptake and oxygen contamination found with supported catalysts may also apply to the slow uptake on nickel films, since it has been observed that mercury appears not to displace hydrogen sorbed by the slow uptake.

It must be mentioned at this point that the hydrogen retention by nickel films after mercury desorption cannot be explained purely by a pore blocking mechanism if the pores were available for sorption to the same extent as the surface, because with this state of affairs the amount of hydrogen retained would be proportional to the amount adsorbed, and not to the adsorptive capacity of the surface as has been observed.

Again, it seems unlikely that the hydrogen molecules which Mignolet thinks might be on saturated nickel films could be that hydrogen retained on displacement with mercury. Since these molecules are in competition with hydrogen atoms for sites at high coverage only their heats of adsorption must be small.

It may also be mentioned that this increased retension phenomenon appears only at complete coverage, and not in a gradual manner as the degree of coverage is increased. This implies that, if this retention is related to the slow uptake, the slow uptake must proceed via the "fast sorbed" state in agreement with the views of Rideal and co-workers.

The above considerations of the problem all assume homogeneity of the surface. If however the surface is heterogeneous for adsorption, and if surface diffusion is possible so that hydrogen fills the sites of highest adsorption energy first, it is possible that there would exist a definite fraction of the surface for which the heat of hydrogen adsorption would be so high that the mercury displacement would be energetically impossible. Such a mechanism would lead to hydrogen retention in proportion to the adsorptive capacity of the surface, and thus could account for the observed retention at incomplete coverage.

The previous interpretation has been concerned with surface processes. The possibility of a bulk process being involved has not been overlooked and it is convenient to reconsider the possibility of alloy formation in the interaction of mercury with nickel.

Alloys of palladium, mercury and hydrogen have been observed by Ubbelohde (70,71) and it would be interesting to consider if the formation of a similar alloy of nickel-mercury-hydrogen could explain the observed hydrogen retention by nickel films when mercury displacement is carried out. It has also been shown by Selwood and Morris (72) that mercury can penetrate into crystallites rich (60-90%) in nickel in copper-nickel catalysts at 175°C. The formation of an alloy under the experimental conditions which have been used is considered to be unlikely for two reasons. Firstly, the temperature at which the displacement measurements were made (25°C) was such that mercury diffusion into the bulk of the film was less likely. Secondly, it was observed that the tritium-hydrogen desorption began immediately the mercury vapour was admitted to the catalyst vessel, and this would be unlikely if the displacement mechanism was one of alloy formation. Couper and Eley (4) have shown that the filling of the d band vacancies must be almost complete before a palladium catalyst is deactivated and so it would be expected that hydrogen would remain chemisorbed on the nickel-mercury alloy surface until the d band vacancies were filled. This would not happen until 30 atomic % mercury was present since each nickel atom has 0.6 d band vacancy and each mercury atom could donate 2 electrons. Recent work by Eley (73) on palladium-gold alloys has shown that an increase in activation energy occurs for the formic acid decomposition at alloy compositions well below that at which the d band of the palladium becomes filled. This has however been explained in terms of the requirement of two point chemisorption and so does not appear to affect the present argument.

It is therefore concluded that the retention of hydrogen following mercury displacement is a surface process, although the 'surface' in this context may be considered to include surfaces inside pores.

It must be stressed once again that the present state of advancement of the subject of hydrogen adsorption is such that no definite interpretation can be placed on the observations recorded.

The foregoing discussion has dealt with possible alternative explanations, and it is hoped that when more is known about the homogeneity or heterogeneity of catalyst surfaces, and about the slow sorption process it may be possible to distinguish between these alternatives.

The conclusions may be summarised as follows.

1. Part of the observed retention at high coverages appears to be accountable for in terms of the slow hydrogen uptake, This is concluded to take place either on sites inaccessible to mercury or by a mechanism which precludes displacement by mercury, such as by adsorption on impurities on the surface.
2. The remainder of this hydrogen, and all the hydrogen observed to be retained at low coverage, is considered to be lost by isolation on the surface or by the operation of adsorption energy effects. Although the observed relative rates of hydrogen desorption and mercury adsorption are as predicted by the theoretical model for random displacement, the constancy of the value for the amount retained when the initial coverage is changed is not in keeping with the model.

As a result of this present work therefore, several possible future lines of investigation present themselves, and these will now be mentioned.

6.3. Future Experimental Work.

From the foregoing discussion it may be seen that it appears to be necessary to postulate more than one mechanism for the retention of hydrogen by nickel films when mercury-displacement of hydrogen is carried out. One of these mechanisms appears to operate at all degrees of coverage and the other is an additional mechanism which occurs only at or near complete coverage.

First of all it would be of interest to know at what coverage this latter mechanism commenced to operate. Apart from the experiments which were carried out at complete coverage, all the experiments on the hydrogen displacement by mercury have been carried out at coverages of less than 60%. This happened quite by chance, since no control could be exercised over the coverages used, because the adsorptive capacity could only be calculated from the determined film weight at the end of the experiment. It is hoped that it will be possible to develop a technique whereby experiments at selected coverages in the range 50-100% can be made, by evaporating the films under very carefully controlled conditions of time and filament temperature. If this fails, it may be possible to observe the course of film coverage by hydrogen by means of electrical conductivity measurements on the film.

With regard to the first mechanism which operates at all coverages it would be interesting to know if this was an effect produced by heterogeneity of the surface. It should be possible to test this hypothesis by means of a technique similar to that used by Roginskii and Keier, and Shuit. Thus a small sample of tritium-hydrogen could be admitted to the surface, followed by inactive hydrogen to saturation. If the hydrogen is then displaced by mercury and examined for its radioactivity it should be easily seen if the activity which has been unrecovered represents the full amount of hydrogen which is retained by the film.

Another interesting topic for investigation would be to measure the slow uptake of hydrogen on nickel films to which traces of oxygen had previously been admitted, and to see if a linear relationship existed between the amount of oxygen present and the amount of hydrogen sorbed by the slow process, as has been observed with supported catalysts (67,54). This investigation could then be extended to a measurement of the displacement of hydrogen by mercury from films to which traces of oxygen had been admitted. The second part of such an investigation might throw some light on the relationship between the slow uptake and the retention of hydrogen in the mercury displacement experiments.

Finally, it is suggested that the anomalous results obtained in the isotope effect measurements justify further investigation. The first specific activity measurement made on the residual gas phase tritium hydrogen after adsorption appeared to indicate that no obvious isotope effect had occurred. (This was supported by the linear relationship which was observed during the displacement of tritium-hydrogen by mercury.) Samples which were removed for further activity measurements however appeared to have a smaller specific activity. As the method used was designed to overcome all the obvious experimental difficulties it is considered that the method was sound. It seems desirable therefore to carry out further experiments on the isotope effect.

It may be stated then, in conclusion, that the scope for future work on this topic of hydrogen sorption on nickel is extensive, and it is hoped that when more is known about the subject the present work will have proved to have been of some contribution.

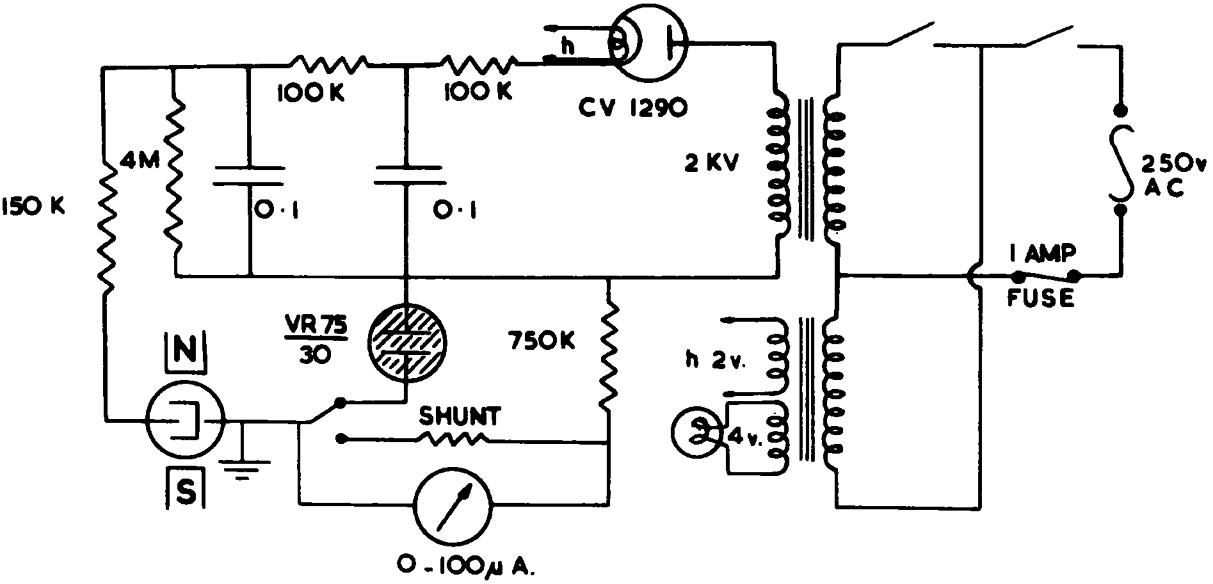
CHAPTER 7.

THE PREPARATION OF NICKEL SURFACES FOR ADSORPTION AND CATALYSIS.

Since it was proposed to study the interaction of adsorbed species on evaporated nickel films in the absence of mercury, or under conditions in which the presence of mercury could be carefully controlled, it was necessary to design and construct a mercury-free high vacuum apparatus.

This requirement of the absence of mercury precluded the use of the conventional mercury manometers and McLeod gauges for pressure measurements, and also the use of Topler pumps for gas transfer.

Mercury cut-offs could not be used for the isolation of the vessel containing the catalyst surface between its preparation and use, and it was expected that the use of a high-vacuum tap would lead to contamination of the catalyst surface by vapours originating from the tap grease. It was therefore necessary to use glass break-seal connections on the catalyst vessels and to use these vessels immediately the seals were broken. Elsewhere high vacuum taps were used in the apparatus. This chapter is concerned with the construction of this vacuum apparatus and the technique



PENNING GAUGE

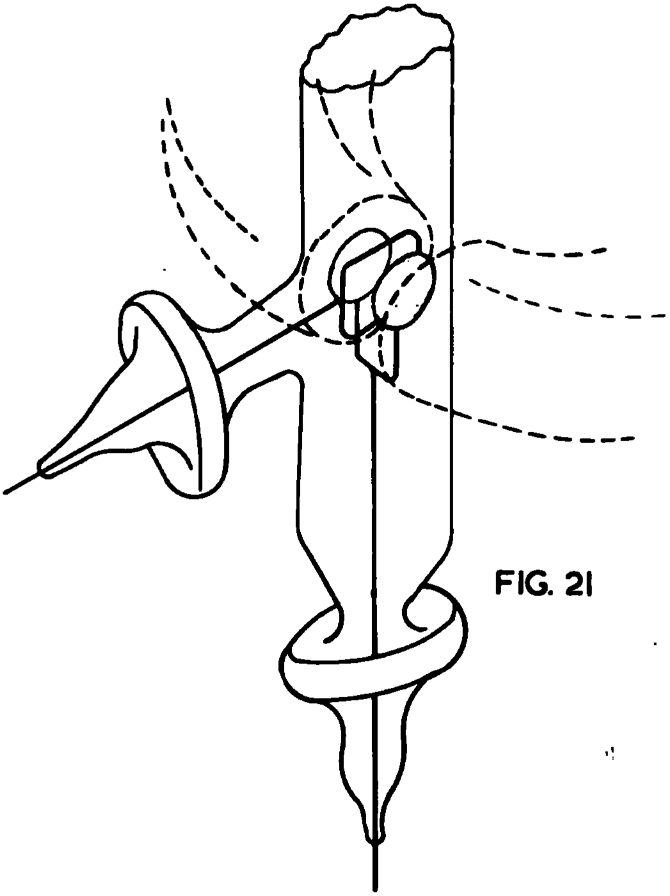


FIG. 21

for the production and standardisation of nickel films.

7.1. The Mercury-free High Vacuum System.

The high vacua necessary for the production of nickel films were obtained as follows. A rotary oil pump was used to back a 'Metrovac' oil diffusion pump filled with Dow-Corning DC 703 silicone oil. Liquid nitrogen traps were situated between the two pumps and between the diffusion pump and the high vacuum line. Pressures as low as 10^{-6}mm of mercury were obtained and these were measured on a Penning ionisation gauge.

7.2. The Penning Gauge.

The Penning gauge (13) consisted basically of a discharge tube attached to the end of the high-vacuum line, and the principle of its operation was that the current carried by the discharge was a function of the gas pressure..

The construction of the gauge was as shown in fig.21. The electrodes between which the discharge was passed were two cathodes of aluminium between which was arranged an anode consisting of a loop of stout nickel wire. These electrodes were mounted on thick tungsten leads which were sealed into a 3cm Pyrex envelope. The lead to the cathodes was taken through the bottom of the tube and that to the anode through a side arm, In each case the glass walls of the tube were blown out above these seals to form rings. These rings prevented the formation of a continuous conducting layer of sputtered metal and decomposed grease vapours from forming between the electrodes after prolonged use of the gauge.

The discharge was produced by the application of a potential of 2000 volts between the electrodes, and this was provided by a 2 KV transformer and diode valve rectifier coupled to a smoothing circuit. In order to maintain this discharge at the low pressures encountered it was necessary to arrange the discharge tube with its electrode axis between the poles of a 2000 gauss magnetron magnet. This caused the accelerating electrons between the electrodes to assume a spiral path and maintain the discharge by secondary ionisation resulting from collisions with gas molecules.

The current passed by the gas was measured by means of a microammeter arranged in the circuit shown in fig.21. Two meter ranges were made available by the use of a shunt, the scale of the higher range being ten times that of the lower, and a neon tube 'striking' at 75 volts was used to protect the meter against overload when the more sensitive range was in use.

PENNING GAUGE

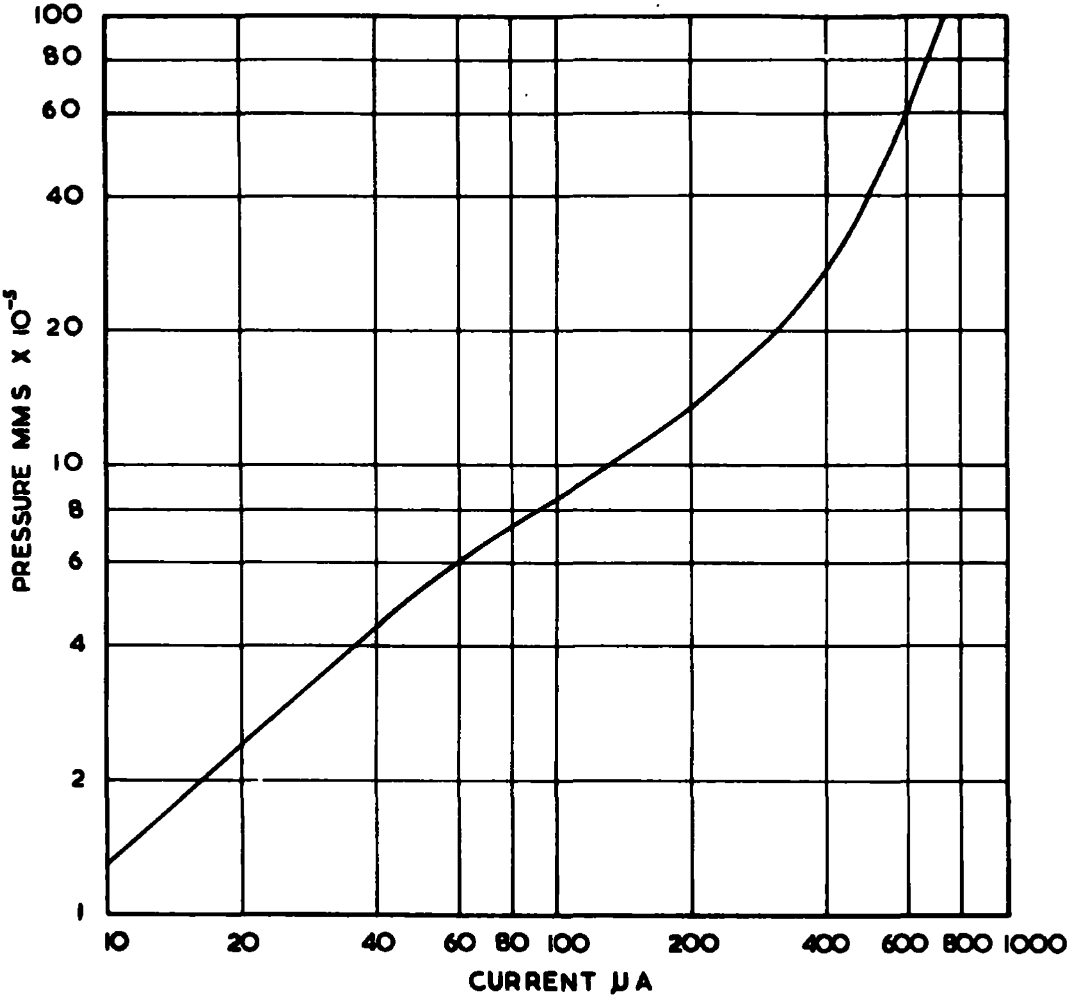


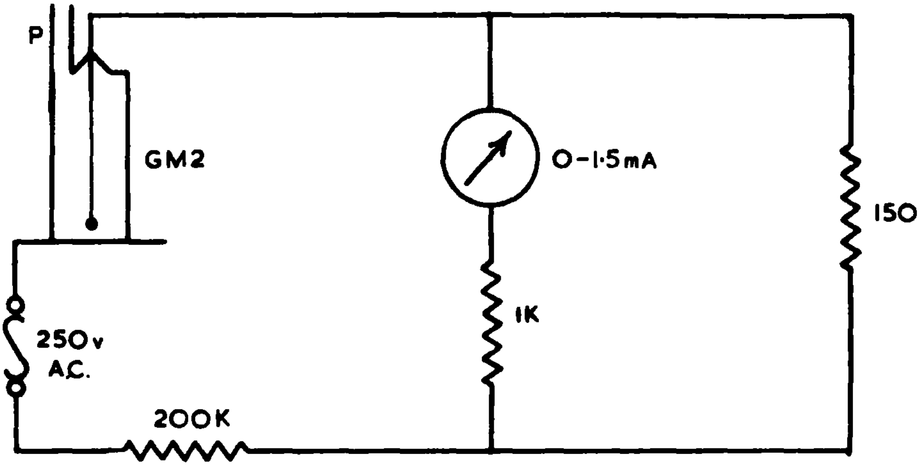
FIG. 22

A powerful gettering action, common to all ionisation gauges, has been observed when the gauge was in use and the main vacuum line tap (to the pumps) closed. In view of the reasonably wide diameter of the tubing used for the high-vacuum line (2.5 cm), pressure gradients set up as a result of this gettering action have been considered to be unimportant. The differences, noted by Penning, in behaviour between different gases have been neglected, and Penning's calibration has been assumed to apply to this gauge as this assumption has been found to be justified by other workers.(74). A graph showing the relationship between the gas pressure and the discharge current is shown in fig.22.

7.3. The Argon Gauge.

In order to obtain orientated films of nickel it was necessary to carry out the evaporation of the metal in argon at 1 mm pressure. A means was therefore sought which would enable this pressure of argon to be measured without introducing any sources of contamination into the apparatus, and it was decided to design an ionisation gauge for this purpose also. The circuit is shown in fig.23. An empty Geiger-Muller counter tube (G.E.C. type GM 2) was used as the discharge tube and this was attached, by means of Everet's wax, to the apparatus so that its internal volume formed part of the section

ARGON PRESSURE GAUGE



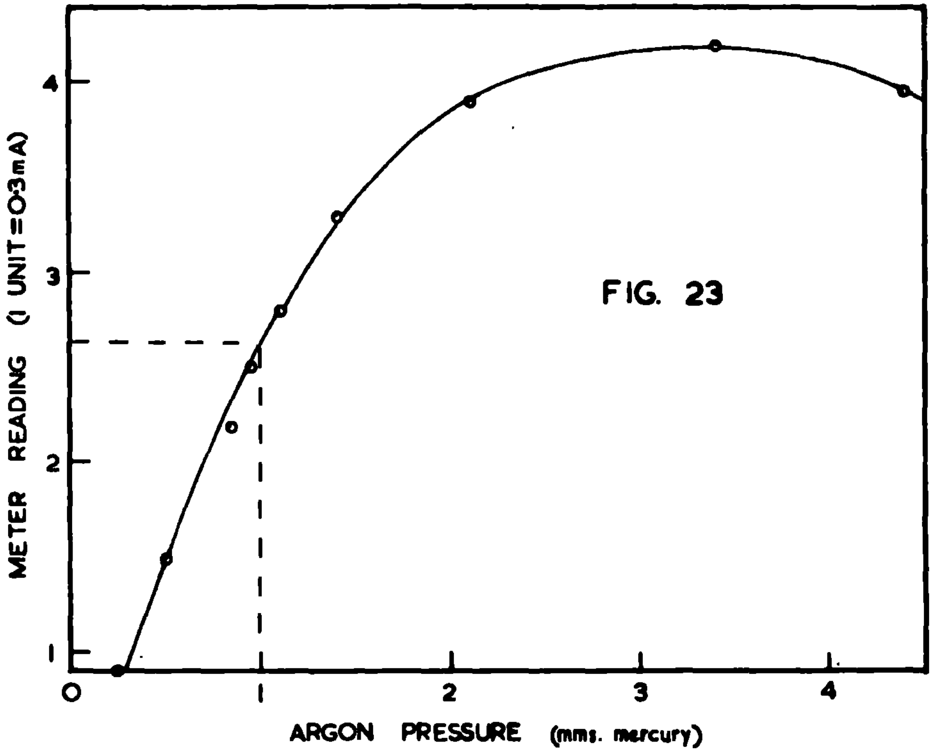


FIG. 23

within which it was desired to measure the argon pressure. A 250 v A.C. supply was used as this was found to be adequate to produce a discharge in the argon, and the current passed by the gas was measured using a moving-coil D.C. milliammeter. This was possible as it was found that efficient rectification occurred because of the large difference in area of the two electrodes in the discharge tube, and this partially rectified and unsmoothed current produced only a barely perceptible oscillation of the meter needle.

The device was initially calibrated against a dibutyl phthalate filled manometer, which gave the relation between argon pressure and meter shown in fig.23. At higher pressures (above 12 mm) a negative deflection was produced, indicating that the rectified current had changed direction. No satisfactory explanation has been obtained for this, but it does not affect the use of the gauge in the present work.

7.4. Construction of the Catalyst Vessel.

Various types of catalyst vessel were used for different purposes, but the essential features were the same and the differences lay only in the design of the side-arms and break-seals. The design of the simplest type, that used for gas adsorption measurements, is shown in fig.24 and its construction is described in

CATALYST VESSEL

FOR ADSORPTION MEASUREMENTS

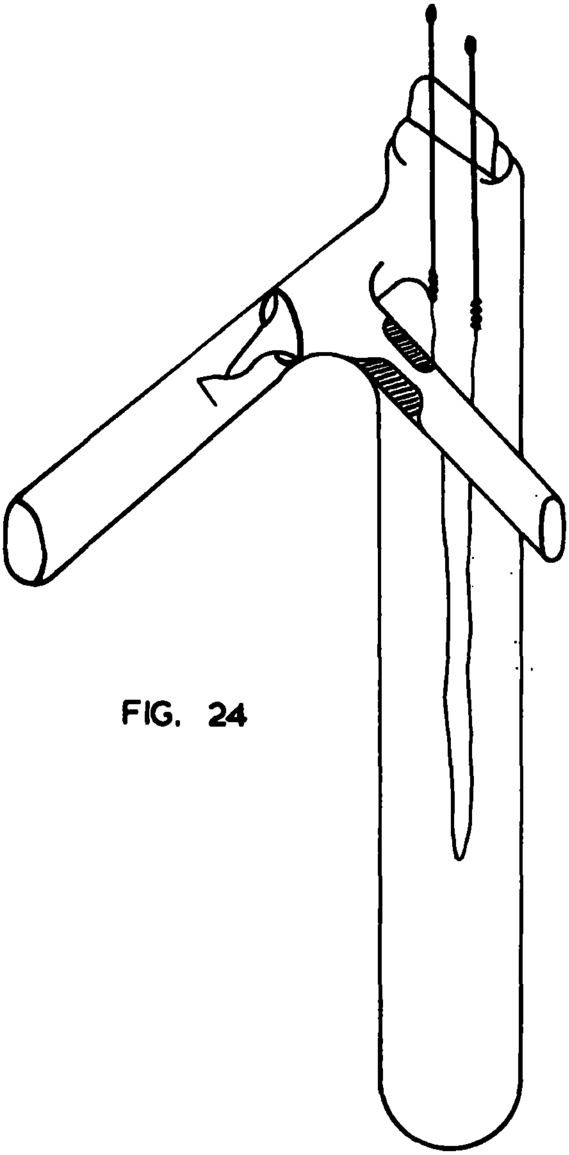


FIG. 24

this section. The catalyst vessel consisted essentially of a 2 cm diameter Pyrex tube which was suspended a nickel filament supported on two tungsten leads. The tungsten leads were prepared from Messrs. Johnson Matthey's 1mm diameter annealed tungsten wire, cut into 7 cm lengths on the edge of a carborundum wheel to avoid splitting the laminae of the wire. These leads were cleaned by being heated to red heat and plunged into solid sodium nitrite, when a rapid exothermic surface reaction occurred. Care was necessary to avoid appreciable loss of tungsten by reaction with the sodium nitrite during this cleaning process. The leads were then washed with distilled water and sleeved with 2½ cm lengths of drawn-out Pyrex tubing. The sleeving was melted on to the tungsten in an oxygen blowpipe flame, when a glass-to-metal seal of characteristic bronze colour was produced if the cleaning process had been thorough. 20 cm lengths of Johnson Matthey pure grade nickel wire 0.02" diameter were used for preparation of the filaments. Each end of the nickel filament was wound spirally around one of the prepared tungsten leads and spot welded using a 2 volt mains transformer capable of producing momentary currents of up to 1000 amps. This process did not appear to result in fusion of the tungsten, but the nickel spiral fused to form a tube around the tungsten, thus making a good electrical contact between the two. Previously silver solder was used to join the nickel to the tungsten. When this was done a bright mirror was produced in the side arm which joined the catalyst vessel to the vacuum system during the baking out process to be described later. This may have been caused by the distillation of zinc from the silver solder. The spot welding method was introduced to obviate this. The prepared filament was bent into a hairpin shape and sealed into a Pyrex tube 20 cm long and 2 cm diameter by making a pinch seal on to the Pyrex coated tungsten leads. Before the pinch seal was annealed, the side arm comprising the seal and break-seal arrangements, having previously been prepared, was joined to the tube below the glass to metal seal, and the whole was annealed for 5 min in a gas flame containing a little oxygen. During this annealing process, a connecting lead of 22 s.w.g. tinned copper wire was silver soldered on to the outer end of each of the tungsten leads. This was done in such a way as to cover completely the ends of the tungsten wires with silver solder, thereby sealing the laminae against gas leakage. The filament was straightened if necessary and centred in the Pyrex tube, and the lower end of the tube closed and rounded off. The completed vessels were sealed in units of three to the section of the apparatus containing the source of argon and argon gauge, to be prepared for the deposition of the film.

7.5. Treatment of Catalyst Vessels before Film Production.

Before a nickel film , free from surface contamination, could be made it was necessary to degas thoroughly the walls of the catalyst vessel and the nickel filament by heating them under high vacuum conditions. Tubular furnaces were used for this purpose. These were wound on a metal former 15 cm long and 3 cm diameter, with nichrome wire to produce a cold resistance of 55 ohms. These furnaces heated the catalyst vessels to 500°C with an applied voltage of 120 volts. Thermocouples constructed either of chromel-alumel or iron-constantan in series with a 2.5 mA meter and 6 ohm resistance were used to monitor the temperature produced by the furnaces. The meter deflections were calibrated against a standard platinum/platinum-10% rhodium thermocouple. One of these furnaces was placed around each of the catalyst vessels, which were heated under high vacuum for a period of at least 12 hours.

During the last two hours of this treatment, the filaments were degassed by raising the filament temperature gradually by means of an electric current to a temperature just below the evaporation temperature. Preliminary tests showed that this condition was achieved with a current of 4.0 amps with the furnace at 500°C. The power supply used for heating the filament consisted of a 70 amp 12 volt mains transformer fed by a Variac transformer, and the filaments of the three catalyst vessels were connected in series to the supply. It was necessary to adjust carefully the heating current, and its magnitude was measured by means of a current transformer and Avo meter. Readings on the Penning gauge showed that considerable gas evolution took place during the degassing process. The vacuum line pressure rose to more than 10^{-3}mm on first heating the filament, but this fell slowly over a period of 2 hours to a pressure of 10^{-5}mm. Raising of the current to 4.4 amps at this stage was found to result in no further gas evolution, and this indicated that the degassing procedure was adequate. It was then necessary to drive off adsorbed gas from the glass of the constriction which was to be used in sealing-off the catalyst vessel. The constriction was heated in the yellow flame of a glassblowing torch until this flame became orange in colour; this indicated that the glass had been heated to the softening point. This was repeated several times until no further gas was liberated, as indicated by the

Penning gauge. Tests with vessels to be used for the production of vacuum deposited films showed that no increase in Penning gauge deflection occurred when the vessel was sealed off using the oxygen flame, indicating that degassing of the constriction had been effective under the conditions used.

In the case of catalyst vessels in which argon deposited films were to be deposited, the argon was admitted at this stage in the preparation. British Oxygen Co. Ltd. spectrally pure argon supplied in glass phials of 1 litre capacity was used for this purpose. Samples of this gas were transferred to smaller break-seal tubes of 4 ml. capacity immediately the original container was opened, in order to reduce the risk of subsequent contamination. One of these argon sample tubes was used for each set of three catalyst vessels. The tap connecting the apparatus to the high vacuum line was closed, and the seal on the argon tube broken with a steel ball and magnet. The argon guuge was switched on, when a 'negative' deflection was produced, and the tap to the vacuum line opened slightly to allow the argon to be slowly pumped away until the meter reading had become 'positive', increased to its maximum and fallen to 2.7: this indicated a pressure of 1 mm. The vessels were then sealed off from the apparatus ready for the nickel deposition to be carried out.

7.6. Deposition of Nickel Films.

In order to prevent undue sintering of the nickel films during the deposition it was necessary to ensure that the walls of the catalyst vessel were kept cool.

The vessels were therefore immersed in a large vessel of water through which was passed a brisk stream of tap water. The deposition was carried out by heating the filament electrically using the same equipment as in the degassing process. Careful control of the heating current was required as high currents resulted in fusion and consequent breakage of the wire before sufficient nickel had evaporated, while low currents resulted in inconveniently slow evaporation rates. Satisfactory results were obtained with a filament current of 7.0 to 7.2 amp for deposition in argon, while for deposition under vacuum conditions the appropriate current was 5.9 to 6.0 amp. Evaporation rates of 15 to 20 mg nickel per hour were obtained under these heating conditions. At the evaporation temperature the filament was at a very bright red, almost white, heat. By this method films of weight 25 to 30 mg were normally produced but they could be prepared with weights up to about 60 mg. The films were a metallic black colour when evaporated in argon but much more mirror-like when deposited under high-vacuum conditions.

7.7. Estimation of Nickel.

Films normally had a weight of 25 to 30 mg, and consequently the gravimetric estimation of nickel with dimethylglyoxime was considered to be inadequate for accurate estimations. The use of a colorimetric method was therefore favoured, and a survey of the literature revealed the existance of several methods (75). It was found that methods based on the solvent extraction of nickel II dimethylglyoxime were unsatisfactory, as cloudy organic layers were produced. The nickel III dimethylglyoxime complex on the other hand was water-soluble and solvent extraction was unnecessary. A method was developed in which this complex was used in conjunction with colorimetry as follows. The following solutions were prepared.

Nitric acid approx. 10N.

Potassium bromate-bromide mixture (3g $KBrO_3$ and 12g KBr per litre, giving 0,1N bromine on acidification).

Dimethylglyoxime 1% in ethanol.

Ammonia solution, 0.88 ammonia diluted 1:10

The nickel film to be estimated was dissolved in 25 ml. warm 10N nitric acid and diluted to 1 litre

COLORIMETRIC ESTIMATION OF NICKEL

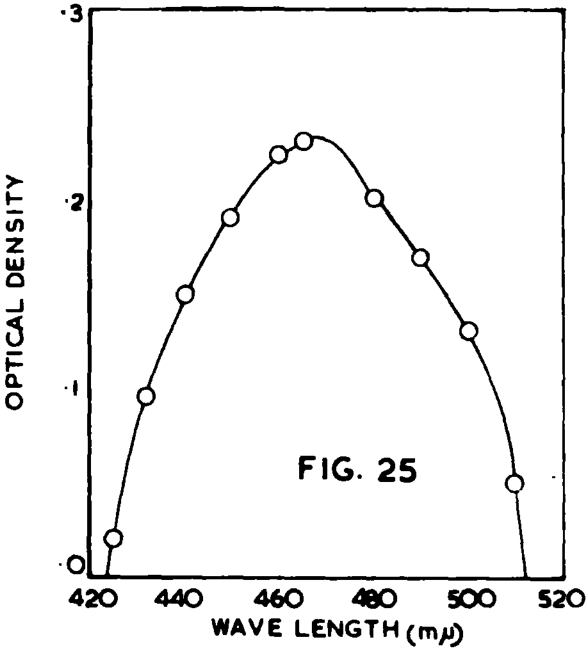


FIG. 25

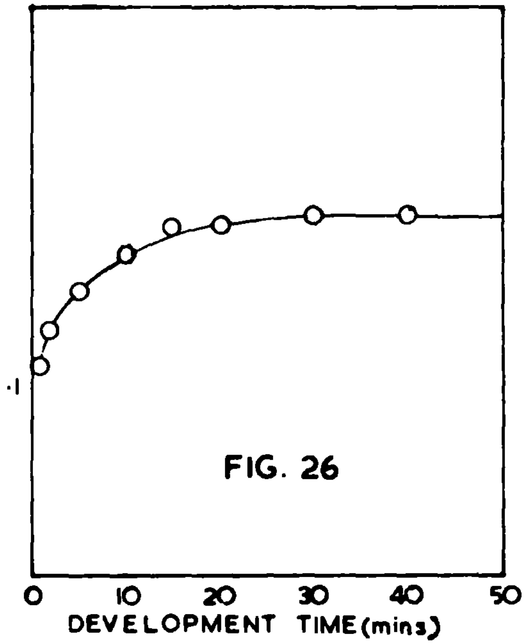


FIG. 26

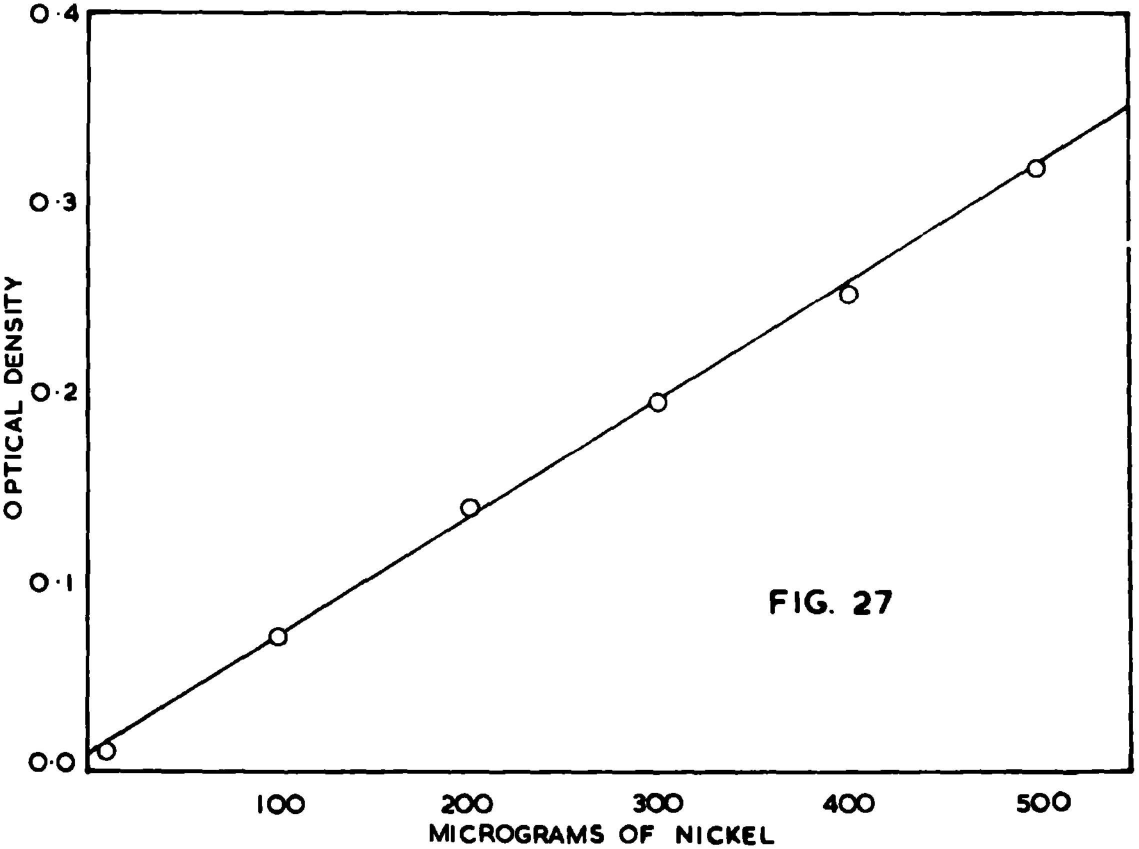


FIG. 27

with distilled water. 10ml. of this solution were measured out with a pipette and transferred to a 50 ml. standard flask. 10 ml. potassium bromate-bromide solution were added to oxidise the nickel to the trivalent state, when the solution gradually became yellow because of the liberation of excess bromine. 1 ml. dimethylglyoxime was then added, followed by 10 ml. ammonia solution. An orange red solution was produced which was diluted to 50 ml. with distilled water.

Preliminary tests were carried out to find the position of the absorbtion maximum and the time of colour development. The results of these tests are shown graphically in fig.25, and accordingly measurements of the optical density were made at a wavelength of 465 μ with a Unicam spectrophotometer; the colour in the solutions was allowed to develop for 30min. Standard nickel solutions were prepared using weighed specimens of the same nickel wire as was used for the preparation of the filaments, dissolved in 25 ml. 10N nitric acid and made up to 1 litre. These standard solutions were used to produce solutions of the coloured complex which enabled the relationship between optical density and weight of nickel shown in fig.25 to be obtained. The weights quoted were those in 50 ml. of the coloured solution, which were derived from 10 ml. of the orig-

CHAPTER 8.

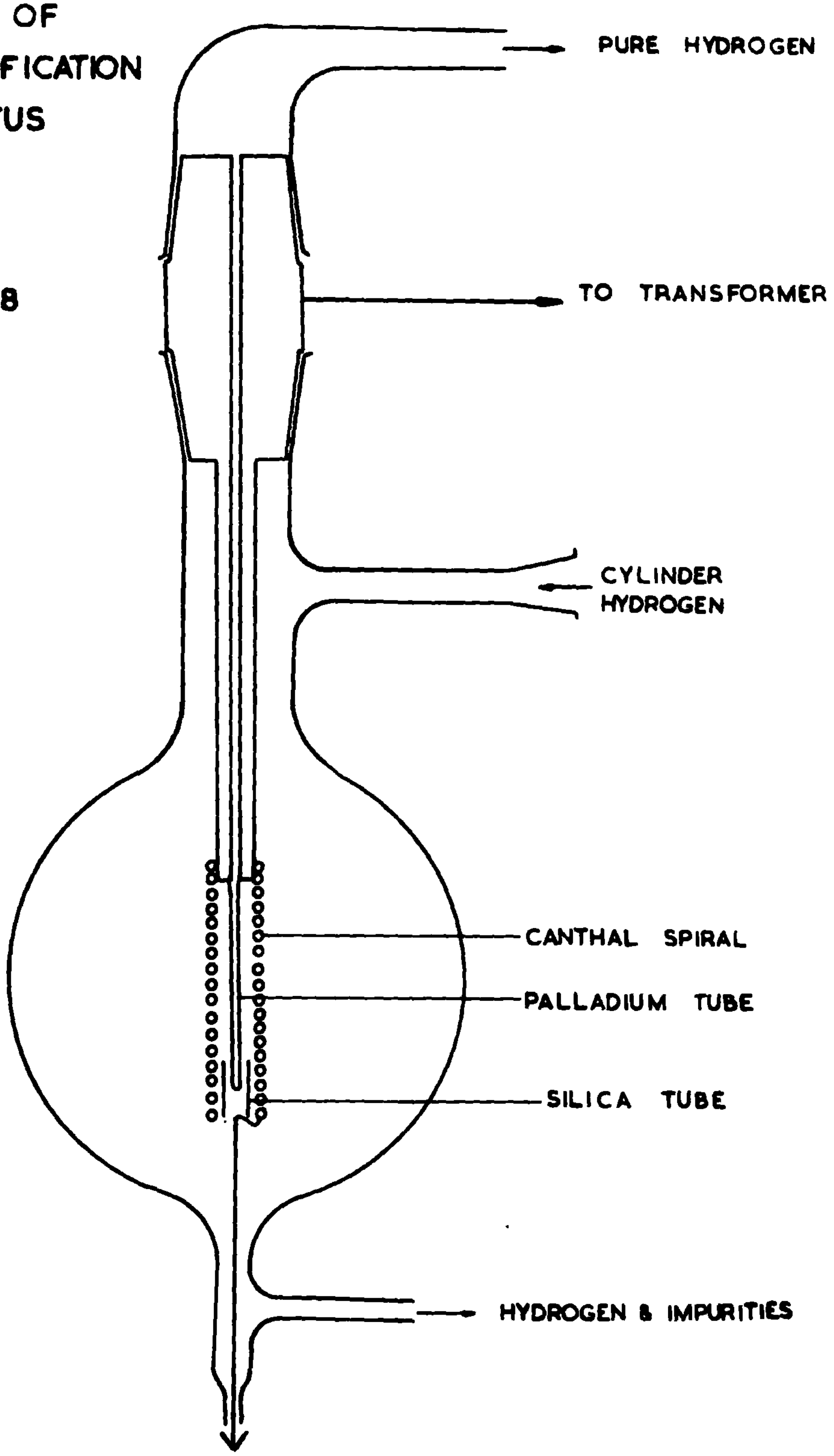
THE MEASUREMENT OF ADSORPTION AND CATALYTIC ACTIVITY.

In order to be able to study adsorption and catalysis on evaporated nickel films it was necessary to have due regard for their extreme sensitivity towards being poisoned. It was therefore essential to purify carefully all the materials to be used to avoid contaminants, and this will be discussed in the first part of the chapter.

The second part of the chapter is devoted to a description of the apparatus used for the study of catalytic hydrogenation rates of propylene and cyclopropane on evaporated nickel films. Provision was made to poison this catalyst progressively by the admission of radioactive mercury between successive measurements. The results obtained from these measurements indicated that mercury selectively poisoned the cyclopropane hydrogenation reaction. To elucidate the mechanism of the poisoning process it was decided to study what was likely to be the fundamental step in the catalysis, that of chemisorption. Accordingly, the third part of this chapter is concerned with the techniques employed for the measurement of chemisorption using a mercury-free vacuum system, the effect of mercury on this adsorption,

SECTION OF HYDROGEN PURIFICATION APPARATUS

FIG. 28



and finally, the adsorption of mercury itself.

8.1. The Preparation and Purification of Materials.

(a) The Purification of Hydrogen.

The ability of palladium to absorb hydrogen, specifically and in large quantities, is well known, and it was decided to make use of this property to purify hydrogen for adsorption and hydrogenation measurements. In practice the hydrogen was allowed to diffuse through a heated palladium tube, and fig.28 shows the apparatus used. The palladium tube, supplied by Messrs. Johnson Matthey and Co., was thin walled 5 cm long × 2.5 mm outside diameter and closed at one end. The open end was joined to a piece of brass tubing, by means of a silver soldered joint. Provision was made for heating the palladium tube by surrounding it with a Kanthal wire spiral which could be heated electrically. This heating element, which was not in contact with the palladium, was supported by the brass tube, which also served as one of the necessary electrical connections, and a small piece of silica tubing ensured the insulation of the lower end of the palladium tube from the heating spiral. The other end of the brass tube was equipped with two B19 brass cones arranged as shown in fig.28. The uppermost of these cones was sealed with black wax into a B19 socket on the apparatus within

which the hydrogen was to be used, and by means of this connection the space inside the palladium tube could be pumped to a high vacuum. The lower of these cones was fitted into a B19 necked flask of 1 litre capacity. The neck of this flask was fitted with a side arm into which a stream of British Oxygen Co. cylinder hydrogen was passed, and a tube joined to the bottom of the flask allowed this to escape. The Kanthal spiral was heated by passing a current of about 4 amp through it, provided by a 14 volt mains transformer. The pure hydrogen which diffused through the palladium tube was collected in the vacuum system at the rate of about 50 cm^3 at 1 cm pressure per min, while the impurities were carried away in the stream of excess hydrogen. A decrease in the rate of production, of course, occurred as pure hydrogen accumulated in the vacuum system, because of diffusion in the opposite direction. Hydrogen produced by this method was found to give consistent results when used for adsorption and hydrogenation studies.

(b) The Preparation and Purification of Propylene.

Propylene was prepared by the debromination of 1.2 dibromopropane with magnesium, using the following method. 1.2 dibromopropane (propylene dibromide), supplied by L. Light and Co., was purified by distillation

PREPARATION OF PROPYLENE

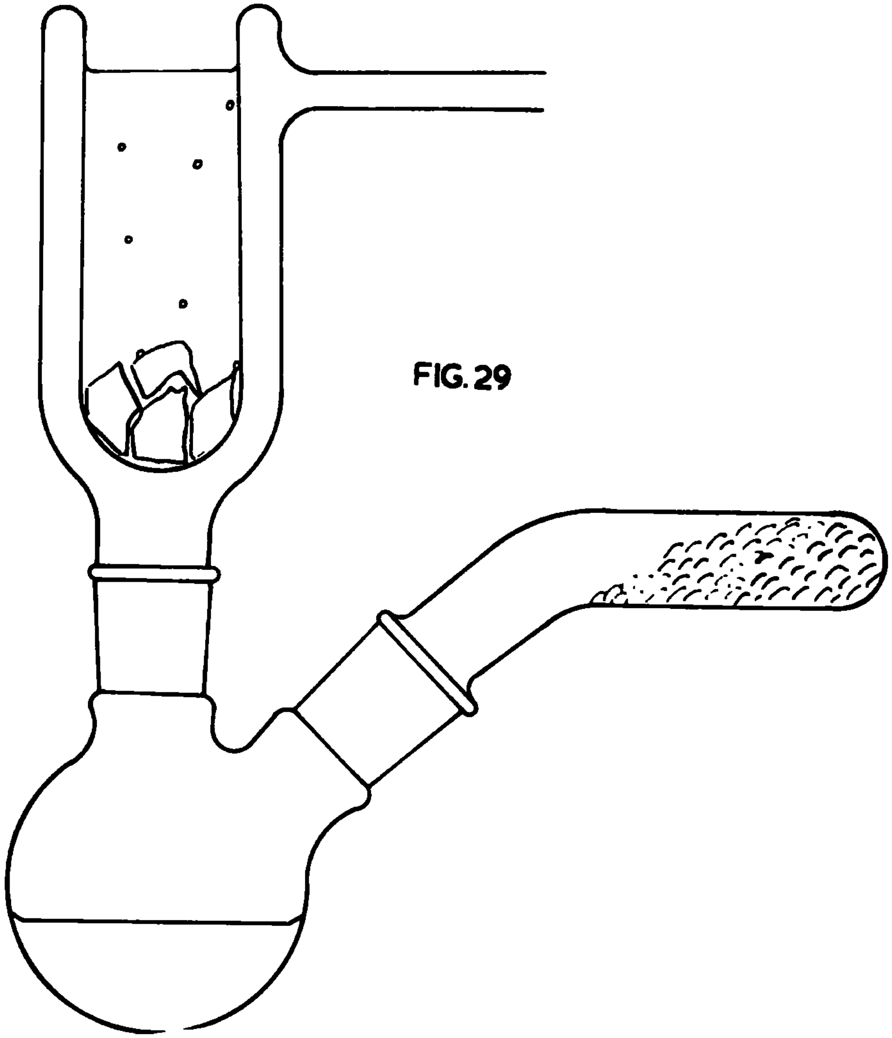


FIG. 29

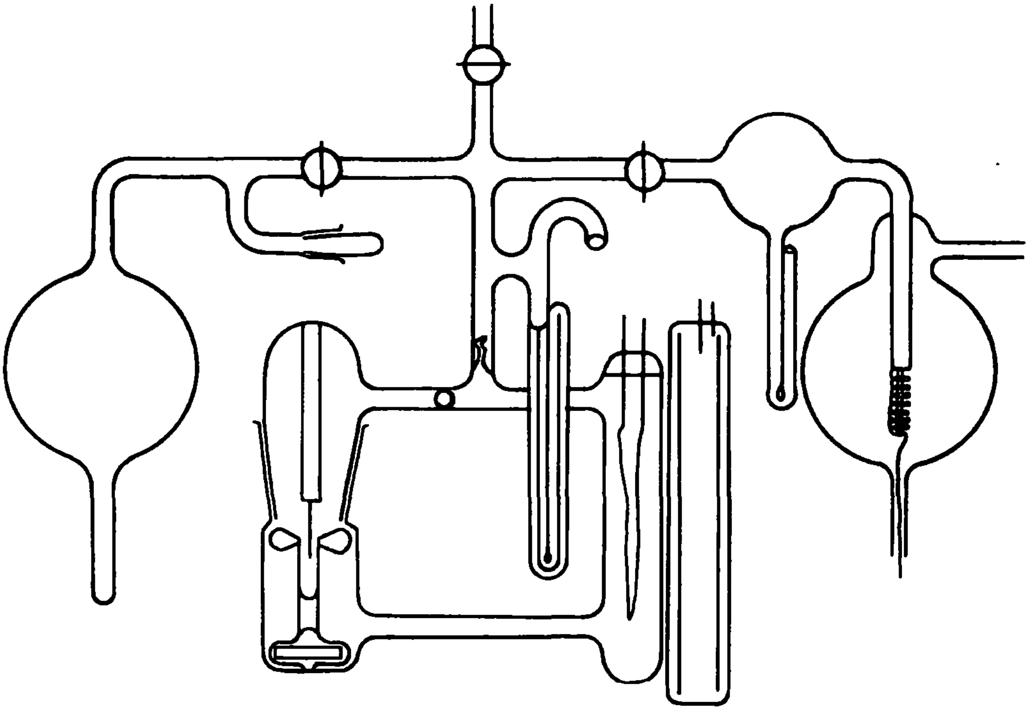
and 10g placed in a 25 ml. two B14 necked flask together with 10 ml. 95 % ethyl alcohol. A B14 side arm was fitted into one of the necks and was bent in such a way as to lie horizontally. 10g magnesium turnings were placed in this side arm. A cold finger trap was fitted into the other neck of the flask. The complete apparatus is shown in fig.29, and it was connected to the appropriate vacuum system through two traps, one of which contained calcium chloride and the other phosphorus pentoxide. Before the reaction was begun the materials were freed from dissolved permanent gases. This was achieved by filling the trap with acetone-solid carbon dioxide mixture and pumping out the air from the apparatus, thereby causing the liquid in the flask to boil and condense on the cold finger. The tap to vacuum was then closed and the trap allowed to become warm to allow frozen propylene dibromide to melt. The side arm was rotated about its joint, and this caused the magnesium turnings to fall into the alcoholic solution of propylene dibromide. A brisk reaction occurred which produced propylene. Gross amounts of alcohol, water and unchanged dibromopropane were removed by the cold trap and the remainder by the calcium chloride and phosphorus pentoxide. The propylene was condensed into another trap cooled in liquid nitrogen and any permanent gas pumped away. About three-quarters of the propylene was allowed to condense into a reservoir fitted with a side arm cooled in liquid nitrogen, and the rest rejected. The liquid propylene was allowed to evaporate in the reservoir, then condensed again with liquid nitrogen. The reservoir was then connected to the pumping system to remove any permanent gas. This procedure was repeated twice more to ensure complete removal of permanent gases.

(c) Purification of Cyclopropane.

Cyclopropane was supplied by L. Light & Co. in the form of liquid stored in a small cylinder under pressure. This cylinder was fitted with a B10 brass cone to enable it to be attached to the reservoir section of the vacuum apparatus. The apparatus was evacuated and a sample transferred to one of the reservoirs by opening the cylinder valve. This reservoir was fitted with a cold-finger tube, which could be cooled in liquid nitrogen to condense and freeze the cyclopropane, and a degassing procedure similar to that described for propylene was carried out.

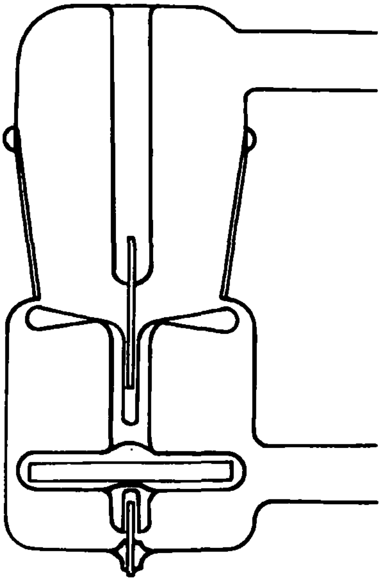
8.2. Apparatus for the Measurement of Hydrogenation Rates.

In the design of an apparatus for measuring rates of hydrogenation on nickel films it was necessary to



HYDROGENATION APPARATUS

FIG. 30



take great care to prevent exposure of the films to mercury vapour and other sources of contamination during the production of the film. These precautions were dealt with in chapter 7. On the other hand, the actual measurements had to be carried out in an environment such that mercury vapour could be admitted at will in order to study its effect on the reaction. The apparatus was therefore designed so that it could be connected to the mercury-free vacuum system for the stages preliminary to the production of the film, after which it was sealed off. After the film had been deposited the apparatus was transferred to a mercury containing vacuum system. The connection to the mercury containing system in which the hydrogenations were to be observed was made by means of a break-seal.

Another essential feature of the design of the apparatus was some provision whereby the gas could be circulated over the catalyst, and a circulating system was used which will now be described.

(a) The circulating system.

For the purpose of circulating the reactants through the catalyst vessel, a glass fan was designed and constructed as shown in fig.30. This consisted of a glass rotor which was mounted on two bearings of 1 mm diameter tungsten wire, which was sealed through the ends of two complementary B34 joints for ease of assembly. The rotor was constructed as follows. A piece of 1½ mm bore Pyrex capillary tubing was taken and joined to a short piece of 8 mm diameter tubing. The end of this 8 mm tube was heated and reamed out to form a flange of 35 mm diameter. This was cut with scissors while the glass was still soft to form eight segments. Each of these segments was reheated at its point of contact and twisted to a pitch of about 35°-45° to make the fan blades. This fan was joined to a rotor, designed as shown in fig.30 and equipped with bearings of thick walled capillary tubing. A 3 cm length of mild steel rod was sealed into the cross piece to enable the rotor to be driven by a rotating magnet external to the system. A Towers' magnetic stirrer was used for this purpose. The rotor was mounted on its bearings between the two B34 joints, which were sealed together with apiezon W wax. The fan was connected to the top and bottom of the catalyst vessel by 1½ cm diameter tubing as shown in fig.30, except that the shape of the vessel and side-arms was such that they could be surrounded by a furnace for degassing the surfaces. The fan was connected to the catalyst vessel before the preparation of the film so as to avoid the use of break-seals within the circulating system, as it was thought that these would unduly impede the flow of gas. A break-seal was provided however for connecting the complete circulating system to the apparatus in which the hydrogenation rate was to be observed.

(b) The Hydrogenation Apparatus.

This apparatus is illustrated in fig.30 and it consisted of a reservoir containing the hydrocarbon under study, the hydrogen purification apparatus described in 8.1. and another storage bulb in which mixtures of hydrocarbon and hydrogen could be stored. Radioactive mercury was used to attempt to poison the catalyst and this was contained in a manometer made from capillary tubing. This gave a convenient method of measuring the pressure change accompanying hydrogenation as well as acting as a source of mercury. The procedure for measuring the hydrogenation rate was as follows.

(c) The Method of Measurement of Hydrogenation Rates.

After the catalyst vessel and circulating system had been attached, the system was pumped to a 'sticking' vacuum. A sample of cyclopropane or propylene was transferred from its reservoir to the storage bulb and condensed in the cold finger with liquid nitrogen. Hydrogen was admitted to the storage bulb from the palladium diffusion apparatus, and the condensed hydrocarbon in the cold finger allowed to evaporate. The mixture was allowed to stand for an hour to become homogeneous. The magnetic stirrer was started, the break-seal broken and a sample of the gas mixture in the storage bulb admitted to the system. Pressure readings were taken at various time intervals for 15 to 20 min. The gas was then pumped away and another hydrogenation measurement immediately made, this time with a sample at the full pressure from the storage bulb. This procedure was adopted so that any effect of change of initial pressure of the reactants could be observed, and corrections applied to the results obtained with partially poisoned films. After this measurement the gas was again pumped away, and the tap to the vacuum main closed. For the study of hydrogenations in the presence of mercury a time interval of 15 min to 1h was allowed to elapse before the next determination in order to allow diffusion of radioactive mercury vapour from the manometer on to the film to take place. Hydrogenation rates were then observed in the presence of the mercury. This procedure was repeated for subsequent determinations until sufficient data were available to show the effect of mercury vapour on the catalytic activity. The results were referred to in chapter 1. It was then necessary to find the amount of mercury which had arrived on the nickel film. The catalyst vessel was therefore removed from the apparatus and the nickel film dissolved in 25 ml. 10N nitric acid. 10 ml. of this solution were placed in a liquid counter and the radioactivity due to the mercury present measured. This activity was used in calculations to obtain the weight of mercury present by comparing it with the activity of 10 ml. of a standard radioactive mercury solution. This standard was prepared by dissolving a weighed quantity (about 10mg) of mercury of the same specific activity in 250 ml. 10N nitric acid. The film solution was then diluted to 1 litre with distilled water for estimation of the nickel as described in 7.7.

A fuller description of the method used for mercury estimation is given in section 8.3(d).

8.3. The Measurement of Adsorption.

The apparatus for the measurement of adsorption was constructed as part of the mercury free vacuum system. This necessitated the use of somewhat unconventional gas handling techniques, including the use of a Bourdon gauge and a specially designed thermal conductivity gauge for pressure measurements. The amount of gas adsorbed on the nickel films was obtained from results of observation of the fall in pressure. In this section the various components of the system are described individually, followed by a description of the procedure for making adsorption measurements.

8.3(a). The Bourdon Gauge.

The Bourdon gauge consisted essentially of a very thin walled glass bulb shaped in such a way that a distortion was produced in the bulb when the pressure inside was different from the external pressure. This movement was magnified using an arm and an optical lever system. The sensitivity obtained varied with different gauges but was of the order of 2 cm scale deflection per mm of mercury pressure change. The gauge was however used as a null instrument and was enclosed in an outer jacket to which dry air could be admitted to balance the internal pressure at the null point. This jacket was connected to the mercury containing vacuum system, so that the pressure could be adjusted by means of a valveless Topler pump. This pressure and hence the pressure in the Bourdon gauge was measured on a mercury manometer. In order to protect the mercury-free system against contamination in the event of the breakage of the gauge under excessive pressures, a trap containing a spiral of sodium wire was fitted into the connecting tubing. A tap was used to prevent mercury vapour from being continuously absorbed by the sodium when the apparatus was not in use. The constructional details of the gauge were as follows. A piece of 8 mm diameter Pyrex tubing was drawn out to form a thin-walled capillary 15 cm long and tapering to 1 mm diameter and the thin end was sealed by heating in a flame. The tubing was reheated at the point where the diameter began to decrease until the glass was soft and a thin-walled oval bulb about 3 cm diameter and 5 cm long was blown. This bulb was then partially rotated in a fierce yellow gas flame in such a way as to cause the wall to collapse all around the circumference except for a region about 1 cm wide. When thus constructed, the distortion of the bulb by a small pressure difference caused a deflection of the long thin capillary pointer. The gauge was mounted by joining the 8 cm tube to a B14 cone, which could be fitted into a B14 socket on the apparatus. This B14 socket was a specially made non-standard component, which had a tube joined above the ground glass joint. To this tube was attached the enclosing jacket of the gauge, and this was designed using B34 joints as shown in fig.31 so that it could be easily removed in the event of the need for the gauge to be renewed. The upper end of the enclosing jacket was connected to the mercury-containing high-vacuum system. The optical lever system comprised a 1 cm square plane mirror attached to a rectangular framework of 1 mm glass rod by means of Apiezon W wax. A stainless steel knife edge was attached to the upper side of this framework, and this rested on two V shaped prongs of 3 mm glass rod attached to the upper B34 cone of the enclosing jacket, whilė the lower side was supported by the long capillary arm of the gauge. This arm was arranged to tilt the mirror to an angle of about 10° to the vertical under equal pressure conditions, so that a change of pressure in either sense caused the mirror angle to alter. This device was used in conjunction with an illuminated cross-wire and lens to give an image by reflection from the mirror at a distance of 1 meter. A side arm W 2cm long and 3 cm diameter was provided in the outer jacket opposite the mirror, and a plane glass disc was fixed to the end of this with Apiezon W wax, to obtain good definition of the image.

8.3(b).The Thermistor Gauge.

In order to be able to measure the uptake of small samples of gas by nickel films, it was necessary to have some means of pressure measurement to cover the range 1 mm to 10^{-3}mm or less. For this purpose a thermal conductivity gauge was designed and constructed, after the style of the Pirani gauge; thermistors (76-8)

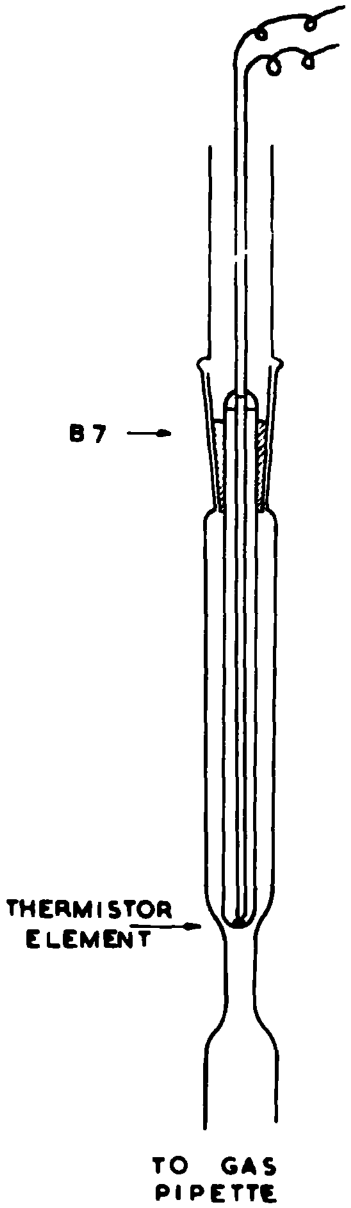

B 7
THERMISTOR ELEMENT
TO GAS PIPETTE

FIG. 32

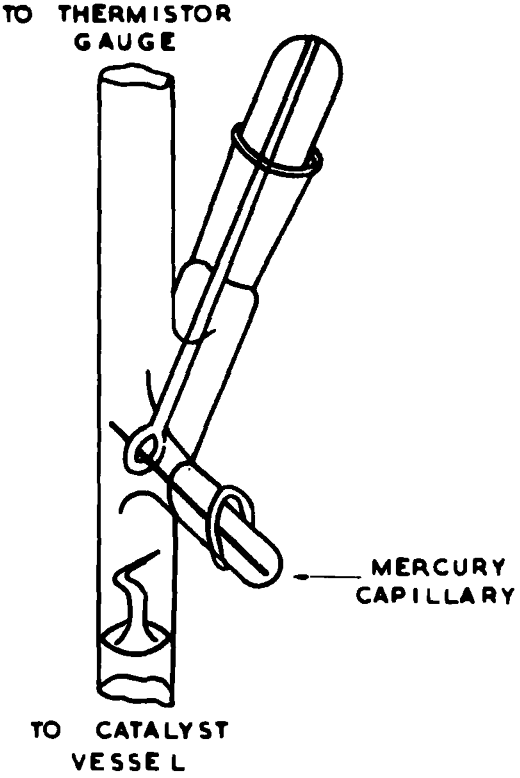

TO THERMISTOR GAUGE
MERCURY CAPILLARY
TO CATALYST VESSEL

FIG. 33

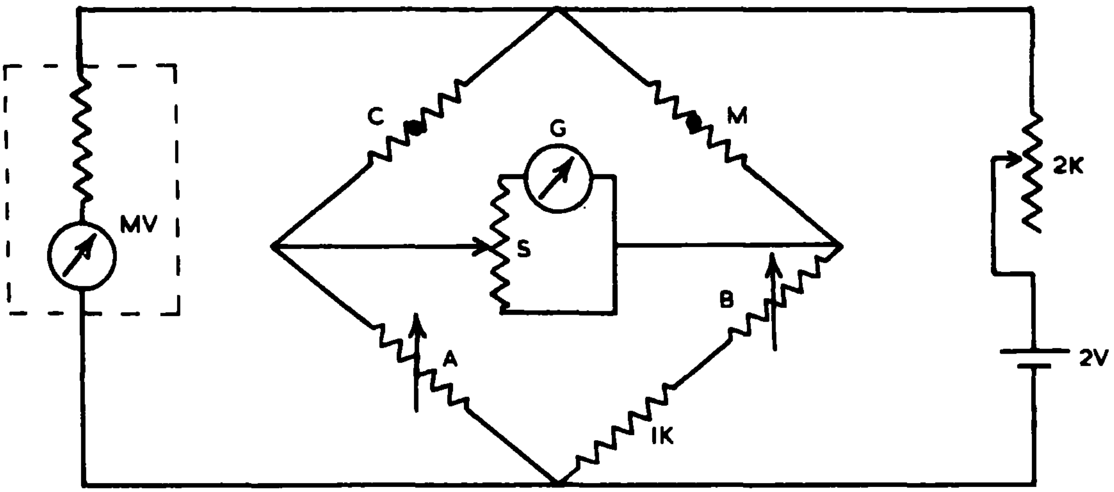
were used in this gauge in place of the usual metal filaments. The advantages of these were that:

(a) the very large temperature coefficient of resistance made possible a large increase in sensitivity, and

(b) as this temperature coefficient was negative and as it varied approximately logarithmically with temperature adequate sensitivity was obtained at much higher pressures than would have been possible with the conventional type of gauge. Theoretical considerations show that the sensitivity of a thermal conductivity gauge varies inversely as the square root of the absolute temperature of the walls of the enclosing tube, and as the gauge was used at 25° C, a much higher temperature than in the case of the conventional Pirani gauge, the sensitivity gained by the use of thermistors was important. Stantel type F2311/300 thermistors were used, in which the semiconductor material was embedded in the tip of a sealed glass tube. This type was favoured as it seemed desirable to have some protection for the elements from contact with hydrogen. The glass tube was 3 mm diameter and 6 cm long and the two leads to the thermistor were brought out through a glass-to-metal seal at the opposite end of the tube to the thermistor bead. One of the thermistors was mounted in a B7 cone as shown in fig.32. This was fitted into section C of

THERMISTOR GAUGE

FIG. 34



THERMOSTAT

FOR THERMISTOR GAUGE

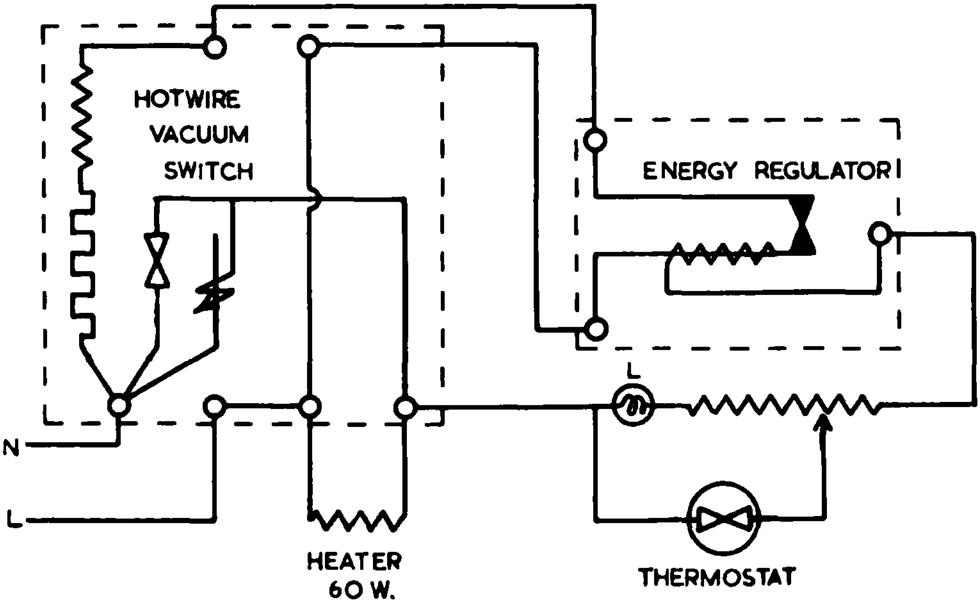


FIG. 35

the gas pipetting system, so that the thermistor bead was enclosed by a constricted tube to reduce the emitter to wall distance. A similar thermistor was sealed into a tube filled to 1 mm pressure with hydrogen. This was used to compensate for small spurious changes in temperature common to both thermistors. Both thermistor units were surrounded by $\frac{1}{2}$" copper tubes, as it was found that they were sensitive to light, and the thermistors, pipetting system and catalyst vessel were placed in a thermostat at $25^{\circ} \pm 0.01^{\circ}$C. A circuit diagram for the gauge is shown in fig.34., and it is essentially that of a Wheatstone bridge. M is the thermistor used for pressure measurement and C its compensator. The other two arms were respectively a 0-999 (×1) ohm decade resistance box B and a 1000 ohm wirewound resistance in series with a 0-99 (×0.1) ohm decade resistance box A. These decade resistances and 1000 ohm resistance were high-stability, low-tolerance Muirhead components. The sum of the resistances in these two arms was kept at about 2000 ohms, but the individual values were adjusted to approximately balance the bridge under high-vacuum conditions. The bridge off-balance current was measured by a Pye mirror galvanometer of 1,800 ohms resistance and having a sensitivity of 5,700 mm per microampere measured on a scale at 1 metre distance.

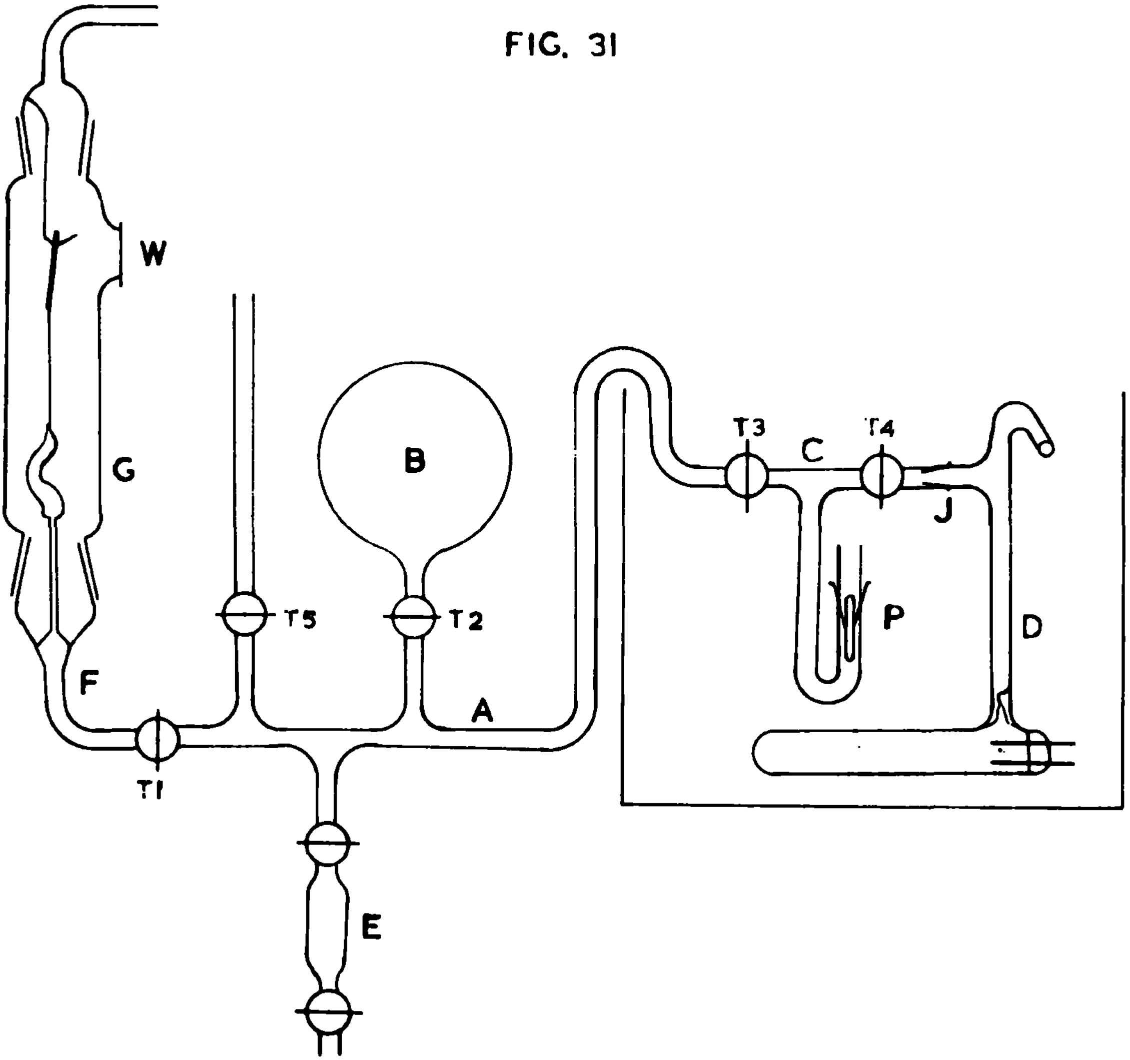
This galvanometer was connected to a Muirhead variable shunt, which also acted as a damping resistance. It was necessary to limit the out-of-balance current by means of a 22K ohm high stability wirewound resistance in series with the shunt. A 2 volt lead accumulator was used as the power supply for the circuit, and was connected through a 2000 ohm wirewound potentiometer with which the applied potential was adjusted to 1.50 v, measured by a Unipivot multi-range millivoltmeter.

The gauge was calibrated for each gas used by lowering the gas pressure in steps until the required range had been covered, and the galvanometer deflection was noted at each stage. This was done by using the same technique as is described in the next section for adsorption measurement, except that a tube of known volume was fitted in place of the catalyst vessel. A 10-times shunt was found to give adequate sensitivity and enabled the full pressure range to be covered without alteration of the decade resistances. The sensitivity varied with the magnitude of the pressure measured, but was 10^{-2}mm pressure per mm scale deflection at 1 mm pressure and 10^{-3}mm pressure per mm scale deflection at 10^{-1}mm. Calibrations for cyclopropane, propylene, and hydrogen are shown in fig. 7,8 and 11 respectively.

The thermostat used in conjunction with the gauge

ADSORPTION APPARATUS

FIG. 31



consisted of a tank of water in which the gauge and compensator, the pipetting system and the catalyst were immersed. The temperature of the water was kept uniform by the use of a stirrer driven by a 24 volt motor, fed by a 20 volt mains transformer. A flexible drive, using picture-cord and brass pulleys mounted on ball-races, was used to enable the motor to be mounted at bench level to reduce vibration. The water was heated to 25°C using a 60 watt gasfilled electric lamp, controlled by the circuit shown in fig.35, using a Sunvic Energy Regulator, Hotwire Vacuum Switch and Thermostat. In order to prevent spurious deflections on the thermistor gauge galvanometer, the thermostat tank was earthed.

8.3(c).Method of Adsorption Measurement.

A diagram of the adsorption apparatus is shown in fig. 31. The volumes of sections A, B and C had been determined by weighing each, empty, and full of water. Likewise the volumes of the catalyst vessels were determined after each experiment.

When the vacuum in the apparatus was 10^{-5}mm, a sample of the gas to be adsorbed was admitted to the calibrated section A and the Bourdon gauge F from the gas pipette E and reservoirs. Sufficient was taken to produce a pressure of 2 - 5 cm, which was measured with the Bourdon gauge. Tap T1 was then closed and T2 opened, to allow the gas to expand into the calibrated bulb B. T2 was then closed and section A pumped out by opening tap T5 to high vacuum. Taps T3 and T4 were also opened and when a vacuum of the order of 10^{-5}mm was obtained the thermistor gauge galvanometer reading was noted, the break-seal on the catalyst vessel D was broken with a glass enclosed steel slug, and the argon pumped away. T4 and T5 were then closed and T2 opened, to allow a sample of gas to enter the thermistor section C. Tap T3 was closed and the galvanometer reading again taken T4 was opened and the fall in pressure due to expansion and adsorption observed on the galvanometer scale. The process was repeated with further samples from the expansion bulb until a residual pressure was obtained. Immediately after the adsorption measurement, a thermistor gauge calibration check was made by the following method. Tap T4 was closed and T3 opened to admit a further sample of gas from the reservoir B. Tap T3 was closed and the section A pumped out by opening T5. The galvanometer reading was taken and T5 closed and T3 opened to allow the gas to expand from C to A, when a further reading was taken. This procedure was repeated to reduce the pressure until an adequate range was covered. The amount of gas adsorbed could be calculated from these results from the known quantity of gas admitted as measured by its volume and pressure, and from the amount remaining in the gas phase from the last sample calculated by Boyle's Law. The volumes of the various calibrated sections are recorded in table 17.

TABLE 17

Section	Volume cm^3
A	60.55
B + T2	2296
C	12.83
C + T3	13.05
D + T4	6.04 + catalyst vessel.

The effect of mercury on the hydrogen adsorption, and also on the cyclopropane and propylene adsorptions, was investigated by admitting mercury before or after the adsorption and allowing time for the vapour to diffuse to the catalyst surface. For this purpose, the mercury was contained in a sealed capillary tube, into which it had been distilled under high-vacuum using the mercury containing vacuum system. This capillary was housed in a side-arm joined above the septum on the catalyst vessel and was held by a small glass ring attached to a B14 cone. When this cone was turned in its socket the capillary was broken. Fig. 33 shows a

APPARATUS FOR THE PREPARATION OF ^{203}Hg-LABELLED MERCURY

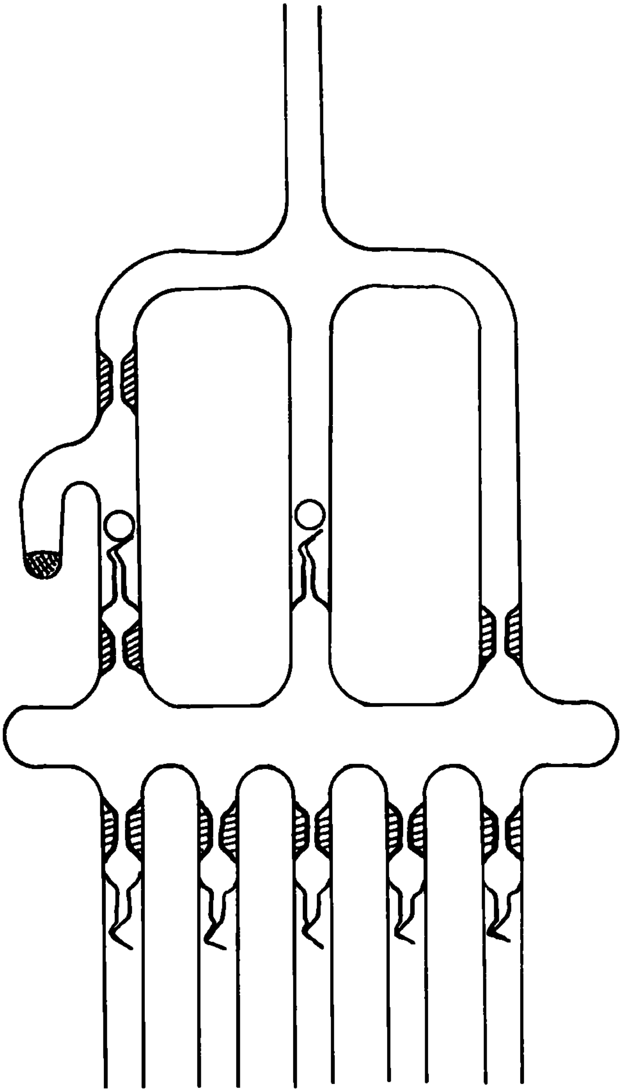


FIG. 36

diagram of the device. Mercury diffusion on to the film was allowed to take place overnight, after which adsorption studies were made. In other experiments where adsorption of gas had been carried out before mercury was admitted, any desorbed gas was measured after exposure of the film to mercury vapour. Between each set of measurements, before a new catalyst vessel was attached, section D was very carefully washed out with nitric acid to remove all traces of mercury.

8.3(d).Adsorption of Mercury in the Absence of Other Gases.

The adsorption of mercury was studied by a radiochemical method. Radioactive mercury was obtained from the Atomic Energy Research Establishment and it contained the active isotopes ^{197}Hg and ^{203}Hg. The initial activities were 800 mC ^{197}Hg and 40 mC ^{203}Hg obtained by irradiation of 2 g mercury for 4 weeks at pile factor 10. These isotopes had half-lives of 65 h and 47 d respectively, and most of the ^{197}Hg was allowed to decay before use. A sample of this mercury was diluted with inactive mercury if necessary, sufficient to give a count of about 3000 counts/min when 10 mg were counted on a nickel tray 4 cm from the window of an end-window counter. The mercury was distilled into break-seal tubes using the apparatus illustrated in fig. 36.
In this apparatus provision was made to seal-off from

ADSORPTION OF MERCURY

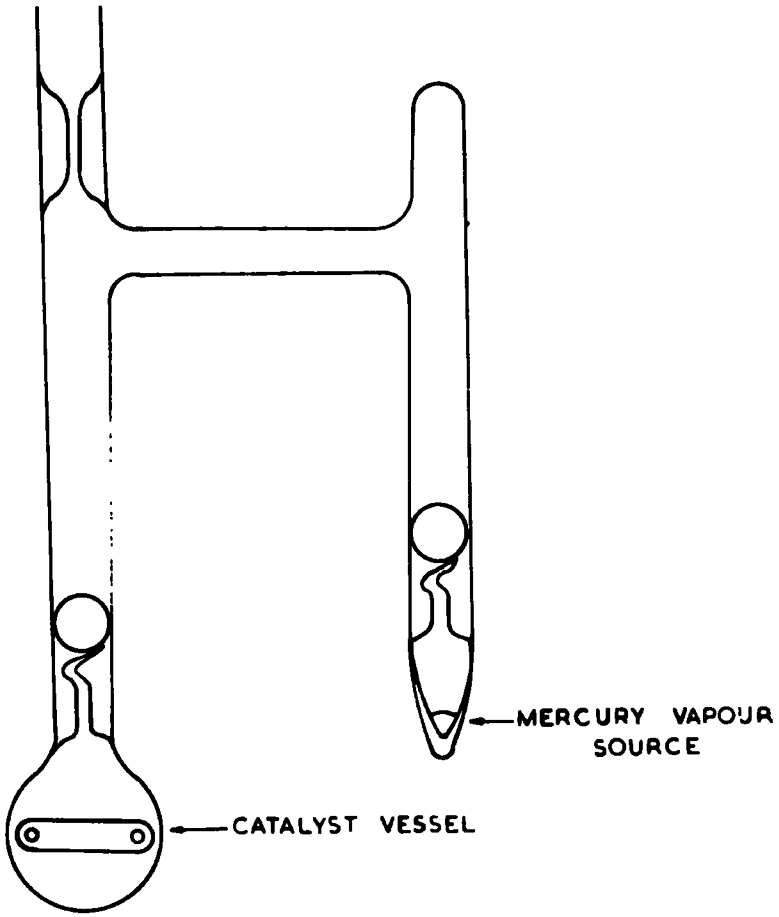


FIG. 37

the high vacuum line after degassing the glass in order to prevent contamination of the vacuum apparatus during the distillation of the radioactive mercury. A break-seal enabled the apparatus to be reconnected to vacuum however after the distillation as a precaution to remove any gas liberated from the mercury during this process. The break-seal tubes were then sealed off.

For each adsorption measurement, one of these break-seal tubes was connected to a catalyst vessel prepared in the usual manner. Provision was made for breaking the two break-seals, as shown in fig. 37 and the dead-space was pumped to a high vacuum (10^{-5}) mm on the mercury-free vacuum system and sealed off. The break seals were then broken to allow radioactive mercury vapour to diffuse into the catalyst vessel. This was allowed to proceed over a period of several weeks, during which time the catalyst vessels were maintained in a thermostat at 25°C, with their mercury sources outside the tank to ensure that transfer of mercury to the catalyst vessel by distillation rather than adsorption did not occur.

At the end of several weeks, the film was assayed for mercury and nickel. It was therefore necessary to develop a method for estimating radioactive mercury. Preliminary trials were made using precipitation methods, but these were considered to be inaccurate in view of the soft nature of the β particles from ^{203}Hg and the property of high density common to all mercury compounds. The reason for this was that, even if the method was made to be comparitive, the difficulty of reproducing back scattering and self-absorption conditions would lead to considerable errors. It was decided instead to use liquid counting, and the following method was developed. The film was dissolved in 25 ml. 10N nitric acid, as for the nickel analysis method, and 10 ml. of this solution counted in a liquid counter. A standard solution was prepared by dissolving about 10 mg (accurately weighed) of the same sample of mercury in 250 ml. 10N nitric acid. 10 ml. of this solution were counted using the same liquid counter, and the count rates compared. The activity measured was mainly that due to γ radiation, but it was thought that there might be a β contribution due to the higher counting efficiency for β particles. Tests were therefore carried out to see if self-absorption was important within the limits of concentration of the solutions used. 10 ml. of a solution of active mercury was counted in a liquid counter. 20 mg nickel chloride and 20 mg mercuric oxide were dissolved in the solution, which was then re-counted. As table 18 shows, the count rates were equal within the statistical accuracy of the counting measurements.

TABLE 18

Background count = 13.1 counts/min

Solution count = 593.7 counts/min

Solution + added nickel and mercury = 597.8 counts/min

Background standard deviation = ±0.2 counts/min

Soln. count standard deviations = ±20.0 counts/min

CHAPTER 9.

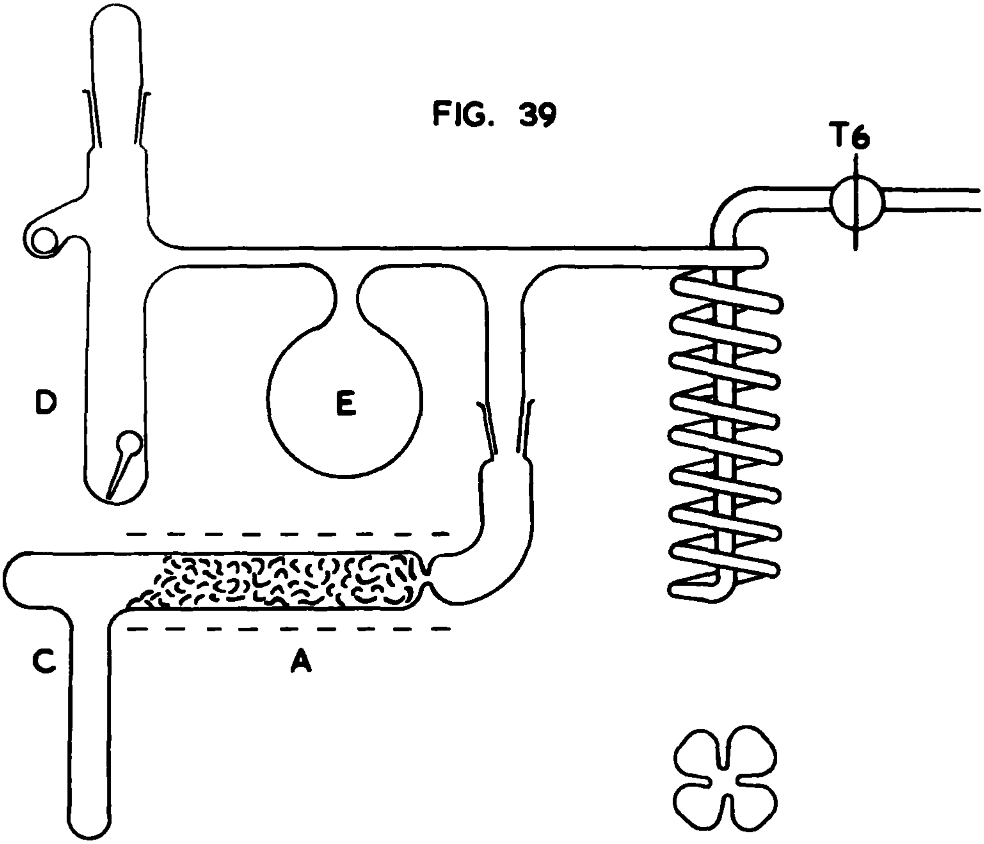
APPARATUS FOR STUDYING HYDROGEN DISPLACEMENT BY MERCURY.

It had been observed that the extent of mercury adsorption on nickel films was much greater than that of hydrogen, and that it was possible to displace hydrogen adsorbed on nickel films by mercury. For the detailed investigation of this phenomenon, information was required about the number of hydrogen atoms displaced by a given number of mercury atoms. This information could have been obtained laboriously from experiments in which such displacements were carried out to various stages of completion. It was realised however that if a technique could be devised whereby the amounts of mercury and hydrogen present on the film at any instant could be found, a single experiment could yield as much information as several using the other technique.

This was achieved by the development of a method making use of mercury and hydrogen labelled with radioactive isotopes: ^{203}Hg and ^{3}H (tritium) respectively. The apparatus was part of the mercury-containing vacuum system, mentioned previously in connection with the hydrogenation measurements. This system was evacuated with a rotary vacuum pump used to back a two-stage mercury diffusion pump, with the usual liquid nitrogen

APPARATUS FOR THE PREPARATION OF TRITIUM

FIG. 39



traps at each side of the diffusion pump. A Vacustat was used to indicate the state of the vacuum, and a secondary vacuum line was provided for working Topler pumps etc.. This chapter is devoted to a description of the apparatus and its method of use, and to the development of the experimental technique.

9.1. The Preparation of Tritium-labelled Hydrogen.

Tritium was obtained from the Atomic Energy Research Establishment in the form of tritiated water. Various methods of reduction have been described in the literature for the production of tritium-hydrogen from tritiated water for the purposes of gas counting (79). These were chosen primararily for their ability to give quantitative yields to avoid isotope effects. For the purposes of the present study, extreme purity of the resultant hydrogen was of prime importance rather than a quantitative yield. Nevertheless, one of these methods. the reduction by magnesium at 500°C (80), was chosen, for it was thought that such a reactive reagent would react with and remove many impurities likely to be present. The apparatus is illustrated in fig. 39. A 2 cm Pyrex tube A was packed with Messrs. B.D.H. magnesium turnings for a distance of 12 cm. This portion of the tube was surrounded by a furnace wound on a core of silica with nichrome wire and lagged with asbestos. One ned of the magnesium tube was attached to the apparatus by means of a B14 joint sealed with Apiezon W wax, while the other end was closed but bore a side-arm C 1 cm diameter and 10 cm long. The sample of tritiated water was contained in a glass phial 4 - 6 mm diameter, the neck of which was sealed. This phial was placed bulb uppermost in the tube D, which was closed with a greased B14 stopper. A small steel ball rested in the side arm of this tube. The 250 cm^3 bulb E was fitted to increase the volume of the apparatus, to accomodate the hydrogen as it was formed, and also to prevent the small amount of air contained in the phial with the tritiated water from blowing the magnesium turnings out of the heated region of the tube when the phial was broken. The apparatus was evacuated through tap T6 (c.f. fig. 40) and the magnesium tube furnace heated to 350°C. This temperature was maintained and pumping continued to produce a 'sticking' vacuum. This usually occurred after not less than 12 hours baking. The furnace was then allowed to cool and the apparatus shut off from the high vacuum line. The tube D was cooled in liquid nitrogen and a steel ball dropped on to the phial to break it. Tube C was cooled in liquid nitrogen and the water sample distilled through the cold magnesium into C. The air released from the sample bulb was then pumped away and the magnesium furnace heated to 500°C. Pumping was continued at this temperature until a 'sticking' vacuum was again obtained, when the apparatus was shut off from the pumps by closing T3 (fig. 39). The tritiated-water was then allowed to evaporate and pass through the heated magnesium. The hydrogen produced was removed and transferred by the Topler pump (fig. 40) to a reservoir fitted to the B10 joint at G in place of the gas counter.

It was necessary to adopt this procedure to condense the tritiated water through the magnesium because the apparatus had been designed to handle water samples for tritium assay. The first part of the degassing procedure was carried out at 350°c to avoid the formation of magnesium mirrors with which the water would subsequently react in the cold. In future designs of apparatus the phial breaking apparatus could be fitted in place of the side arm on the magnesium tube. This would make it unnecessary to condense the water through the magnesium; the degassing procedure could then be carried out at 500°C from the start.

Preliminary tests yielded tritium-hydrogen which adsorbed on nickel films to an extent lower than expected, from which it was concluded that some investigation of the purity of the product was necessary. When the magnesium tube was removed from the apparatus the characteristic smell associated with boron hydrides was noticed. The glass of the tube had become more brittle and had a blue-black or brown coating on the inner surface, which when treated with dilute hydrochloric acid evolved a gas which was spontaneously inflammable. It burned with an orange flame to give a white smoke. It was concluded that reaction had probably occurred between the borosilicate glass and the magnesium to give magnesium boride and silicide. The formation of boron and silicon hydrides by subsequent reaction with the tritiated water was therefore possible. While these gases may not affect the G.M. counting characteristics when the hydrogen is used for counter fillings, it is extremely likely that they would act as catalyst poisons. A spiral which could be cooled in liquid nitrogen was therefore introduced into the system at R to remove condensible substances. Samples of tritium-hydrogen prepared after this precaution had been taken gave reliable results on adsorption.

9.2. Estimation of Tritium-Hydrogen.

The activity of tritium, which was used as a tracer for hydrogen desorbed from nickel films, was determined using standard gas counting techniques. Owing to the small quantity of gas involved, high specific activities were used for the sorption and desorption studies.

The gas counter used for these measurements was constructed from Pyrex tubing 2.5 cm diameter. A polished copper tube 2.2 cm (7/8") diameter and 10 cm long was used as the cathode, and the anode was a 0.1 mm diameter tungsten wire arranged coaxially within the copper tube and attached to the glass at both ends. The electrical connections to these electrodes were taken through the glass by tungsten seals. The complete counter was fitted with a tap and connected to the apparatus (fig. 40) by means of a B10 joint. It was surrounded by lead bricks of thickness 2.5 to 5 cm to reduce the background counting rate.

The gas counter filling used was 8 cm pressure of inactive hydrogen and 2 cm pressure of ethyl alcohol to act as a quenching agent. The hydrogen used was British Oxygen Co. commercial grade hydrogen, purified by passage through a charcoal tube cooled in liquid nitrogen. The small tritiated hydrogen samples were added to this filling by means of the Topler pump. As the addition of the sample for assay would cause an increase in the partial pressure of hydrogen in the counter experiments were made which established that

TRITIUM COUNTING

VARIATION OF COUNTER CHARACTERISTICS WITH HYDROGEN PRESSURE

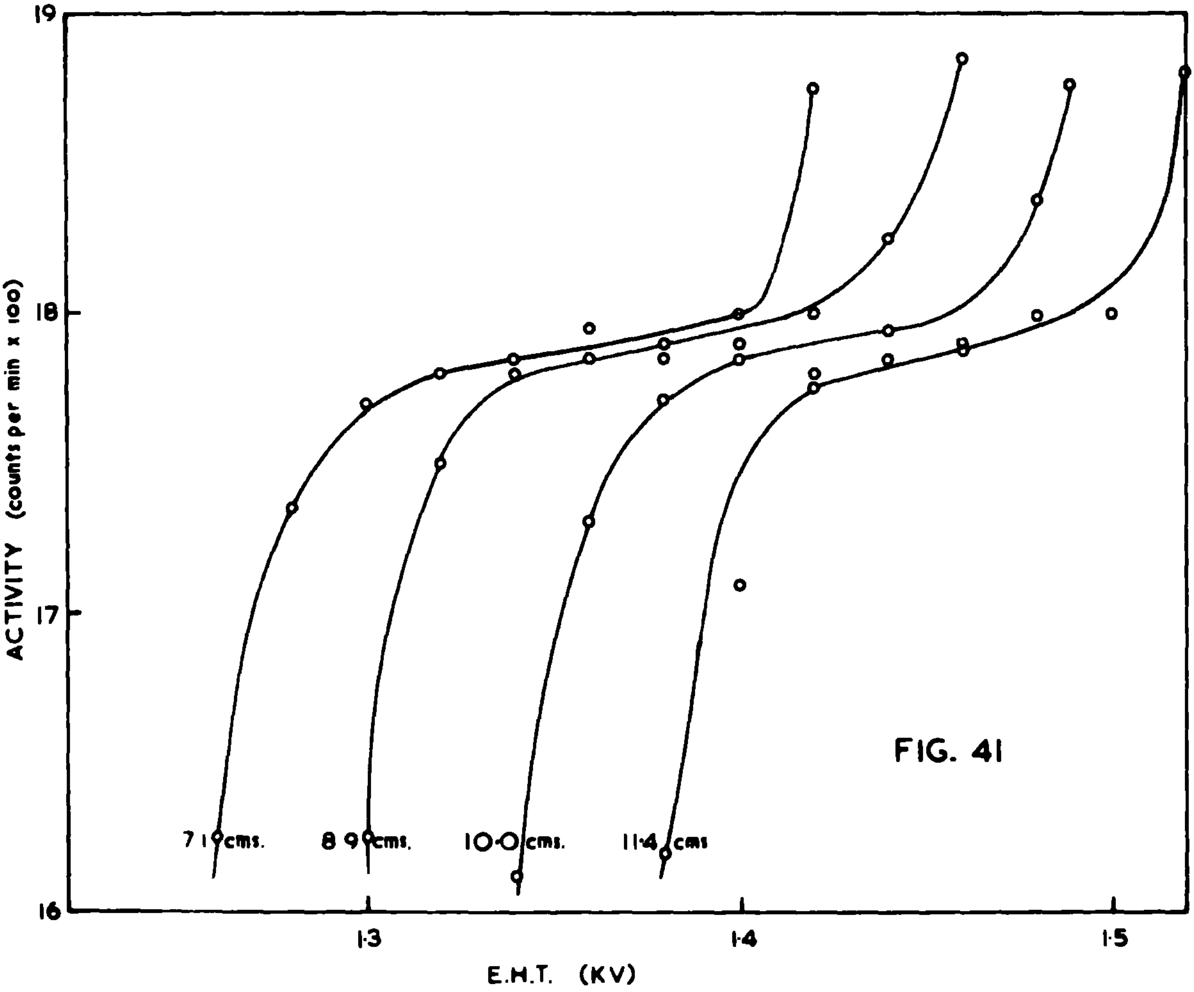


FIG. 41

the count rates were independant of the pressure of the inactive hydrogen over the range 7 cm to 9 cm. This was shown as follows. The counter was filled with ethyl alcohol vapour to a pressure of 2 cm, and hydrogen containing tritium added to produce a partial pressure of 7 cm, when a plateau determination was carried out. The hydrogen pressure was raised by pumping in a small quantity of inactive hydrogen and a second plateau determined. This was repeated until a range had been covered far in excess of the maximum limits of pressure change expected during the actual measurements (about 2 mm). The results are shown in the graph (fig. 41). From this it was seen that although an increase in the partial pressure of hydrogen shifted the plateau to higher voltages, the centres of all plateaux corresponded to the same count rate and occurred at about 120 volts above the starting voltage. This observed plateau shift amounted to less than 20 volts per cm pressure and so the effect was negligible under the experimental conditions. It was therefore unnecessary to redetermine a plateau each time a small tritium sample was added to the counter; consequently the tritium activity couldbe measured at more frequent intervals during displacement experiments. Various counter faults developed from time to time, which are mentioned in appendix D, together with the means whereby they were rectified.

9.3. Continuous Estimation of Adsorbed Mercury.

It was necessary to find some means of determining the extent to which mercury adsorption had taken place on nickel films at any given time. The advantage of the method to be described was that mercury sorption studies could be made while they were in progress without interrupting the catalyst runs in any way. Mercury containing the radioactive isotope ^{203}Hg was again used for this investigation, and this section is concerned with the method which was developed for its continuous estimation.

In outline, the method used was to observe the activity using a counter placed near the film and screened from the source of active mercury by lead bricks. This counter detected the gamma emission of the ^{203}Hg. At the end of a series of measurements, the final count rate under these conditions could be observed and related to a definite amount of mercury. The amount present at any previous time could be found by proportion. This was accomplished by dissolving the film in 10N nitric acid and comparing the acticity of this solution with a standard, as described in section 8.3(d)

GAMMA RAY COUNTING OF ^{203}Hg

NEON-ARGON-BROMINE COUNTER PLATEAU

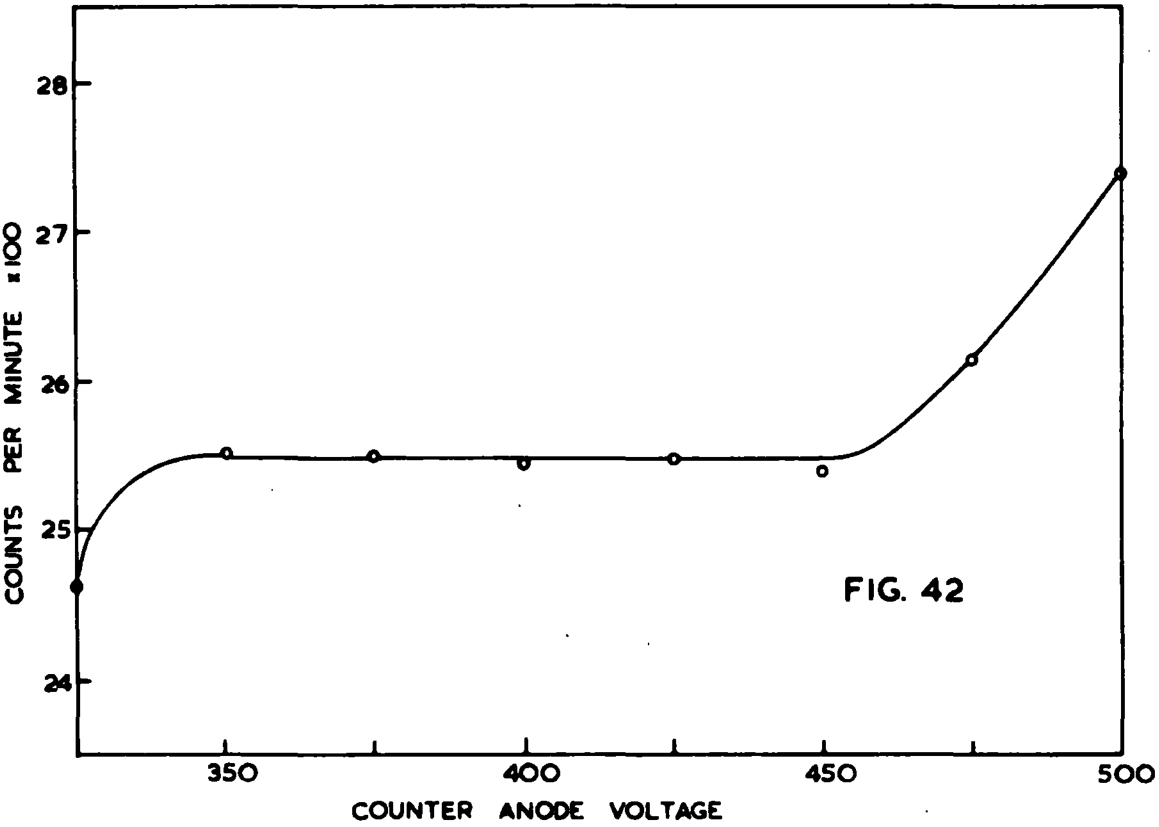


FIG. 42

Precautions had to be taken to ensure that a method was used whereby the measured film activity was proportional to the amount of mercury actually present on the film. The only assumption made in the method was that the radial distribution of mercury was uniform. It was thought likely that the portion of the film nearest to the mercury source would tend to adsorb more mercury in the initial stages than the more distant parts, and therefore that any method whereby a small section of the film was treated as being representative of the whole would lead to quite serious errors. Because it was possible that mercury distribution along the film was not necessarily uniform it was decided that a long counter should be set up in such a way that it was sensitive to mercury on any part of the nickel film.

A halogen-quenched counter was mounted parallel to the catalyst vessel. This counter was 25 cm long and 2.3 cm diameter. The cathode was a passive-iron cylinder 23 cm long and the filling was a neon-argon mixture with bromine as the quenching agent. The counter had a working voltage of only 410 volts and a plateau of length 100 volts with no perceptible slope, as shown in the plateau graph (fig. 42).

Many desirable properties were claimed for this type

GAMMA RAY COUNTING OF ^{203}Hg

VARIATION OF COUNTING RATE WITH DISTRIBUTION OF ACTIVITY

LINEAL DISTRIBUTION

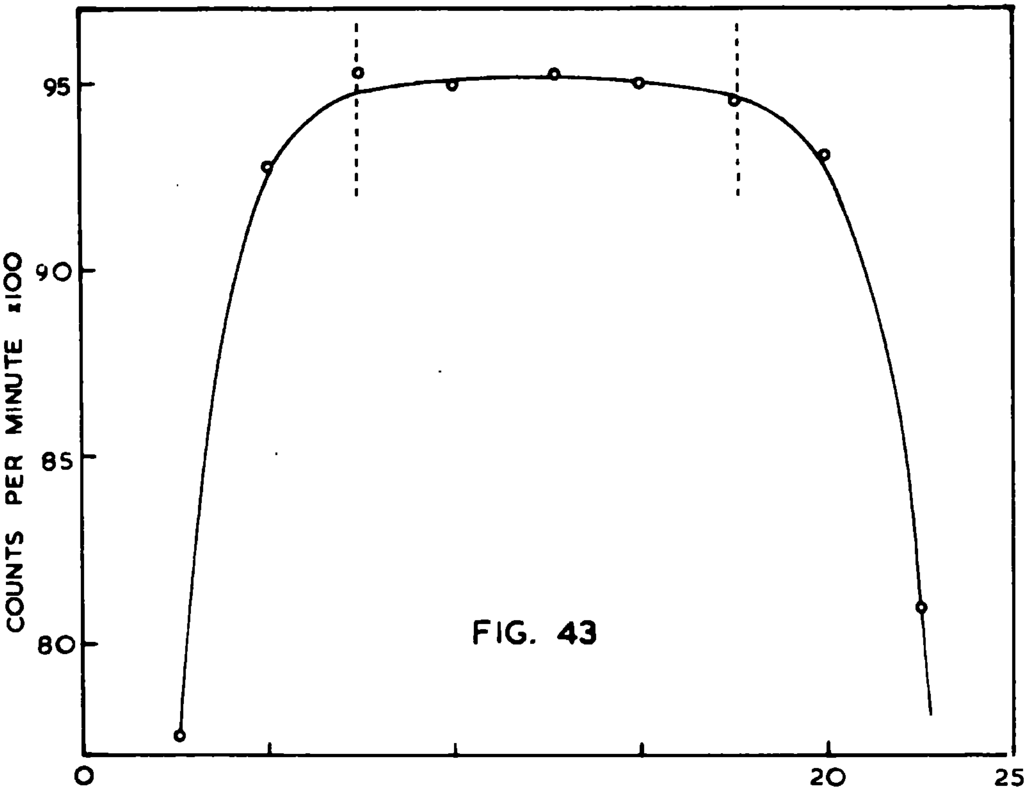


FIG. 43

RADIAL DISTRIBUTION

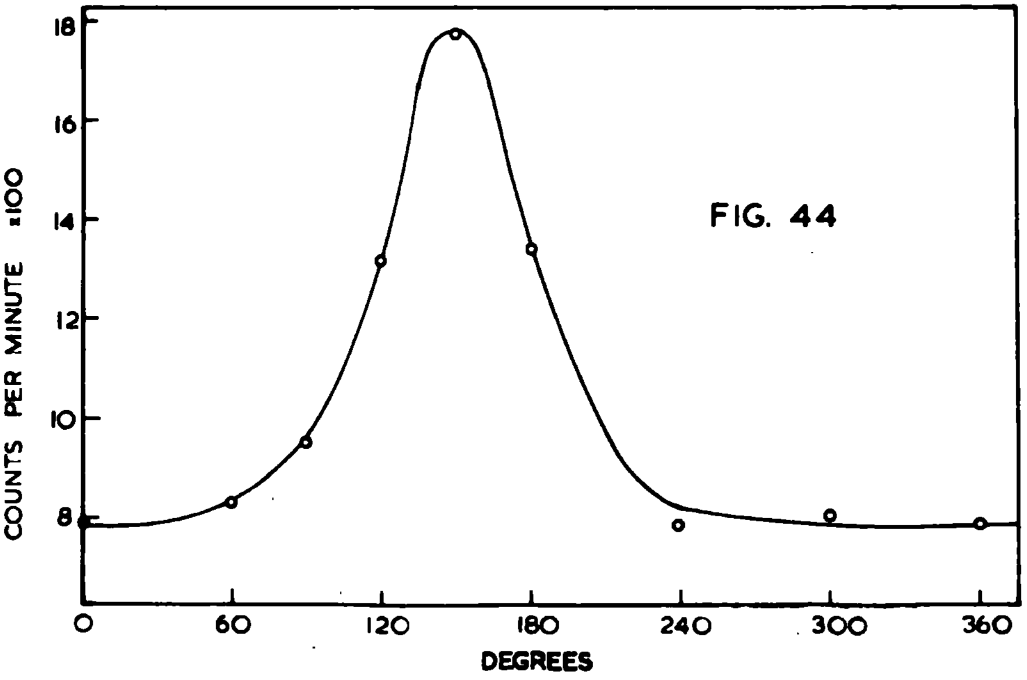


FIG. 44

of counter (81,82).

Preliminary tests were carried out to test the relative response to activity distributed in various positions with respect to the counter. A small compact mercury source was moved along a line parallel to the axis of the counter at a distance of 2 cm from the counter wall. The count rate observed at various distances, measured from one end of the counter, is shown in fig.43. From this graph it was seen that a uniform response was obtained when the source was adjacent to the centre 10 cm region of the counter. In no case was the length of the evaporated nickel film greater than 10 cm, and so it was decided that this counter would be suitable if arranged in such a way that the centres of the film and the counter cathode were adjacent.

A test was next carried out to determine the effect of radial distribution of activity, as follows. A short length of 2 cm diameter Pyrex tubing was taken, and a small globule of radioactive mercury held on the inside surface by a piece of Sellotape. This tube was placed in contact with the counter, and the count rate determined at various stages of rotation of the tube bearing the source. The results are shown graphically in fig. 44, from which it was seen that the maximum and minimum count rates, obtained when the source was at its nearest to the counter and rotated from this position through 180° respectively, were in the ratio 2.25:1.

It seemed reasonable to assume that at any point along the length of the film, the radial distribution of the mercury would be uniform provided that of the nickel was uniform also. Visual observation of the optical density of the films during deposition showed that no non-uniformity of thickness could be detected except at points where the filament was less than about 2 mm from the walls of the tube.

This detection method for mercury was therefore adopted, but care was taken to arrange the filament symmetrically and well clear of the walls during the construction of the vessels for these measurements. Results subsequently obtained supported the validity of this assumption, for final count rates proportional to the count rate on the solution were always found.

The same electronic counting equipment was used with this counter as was used with the gas counter, namely a type 200 scaling unit and a 1014a probe unit having a paralysis time of 500 μsec and a 240 volt quenching pulse.

As previously outlined, the counting rates observed during a tritium displacement experiment were related to quantities of mercury on the film as follows. After the final count rate had been determined the catalyst vessel was removed from the apparatus and immediately seperated from the mercury source. The nickel film was dissolved in 25 ml. 10N nitric acid and 10 ml. of this solution counted in the liquid counter. 10 ml. of a standard solution prepared from a weighed sample of mercury of the same specific activity were counted under the same conditions. From the values obtained, the amount of mercury present on the film at finality could be obtained. The amount present at any given time during the adsorption was calculated by proportion from the counting rate at the given time and that at finality as measured by the halogen-quenched counter. The values obtained were those corresponding to the specific activity of the mercury at the time of the final count on the film. A decay correction was applied if necessary, to the activities determined during the course of the mercury adsorption, using the published value of 47 days for the half life of ^{203}Hg (46.91±0.14) (83).

9.4. The Design of the Catalyst Vessel.

The type of catalyst vessel used for these measurements was essentially similar to those previously described,

CATALYST VESSEL FOR
DISPLACEMENT MEASUREMENTS

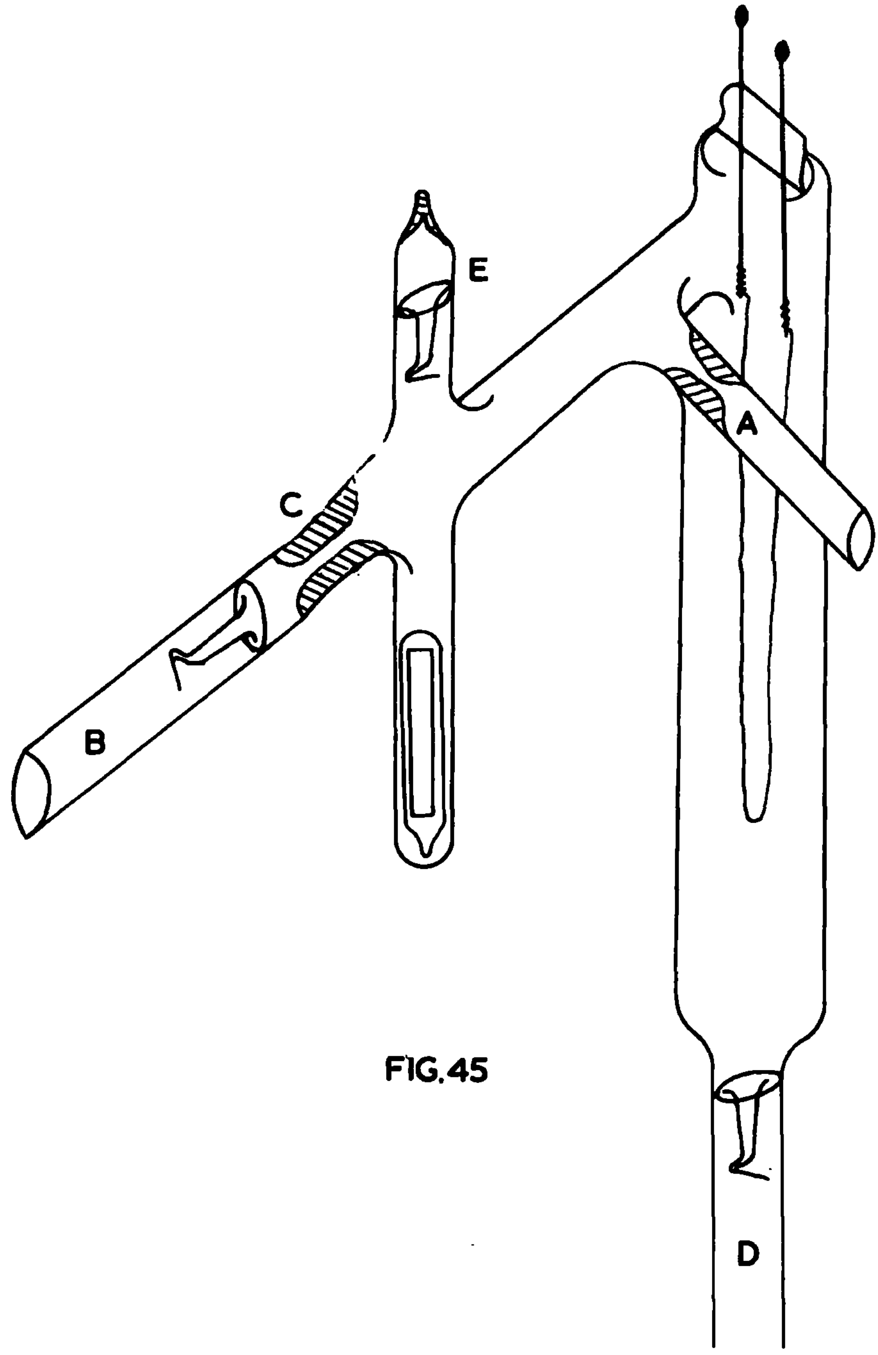


FIG.45

but it was necessary to make provision for transferring it between different sections of the apparatus during the course of the measurements. Fig. 45 shows the design of the vessel, and its method of use was as follows. The vessel was thoroughly outgassed as previously described (chapter 8), paying particular attention to the constrictions A and C, and sealed off at the constriction A. The nickel film was then deposited and the vessel connected by the tube B to the adsorption apparatus. Adsorption of tritium-hydrogen was then carried out in the usual manner and the vessel sealed off at C. Finally, the tube D was used to connect the vessel to the apparatus for studying the displacement, using the radioactive mercury in the break seal tube E prepared as described in section 8.3(d).

9.5. Calibration of the Apparatus.

Calibration of the apparatus was necessary in order to find what pressure of hydrogen in section A would be required to produce a pressure of 8 cm in the gas counter G and dead-space B after transfer by the Topler pump. This calibration was carried out by filling the Topler pump bulb with mercury and taking a convenient condensible gas (cyclopropane was used) at a pressure of 8 cm in the gas counter and sections B and C (fig. 40), measured by the manometer M. Tap T4 was closed and T1

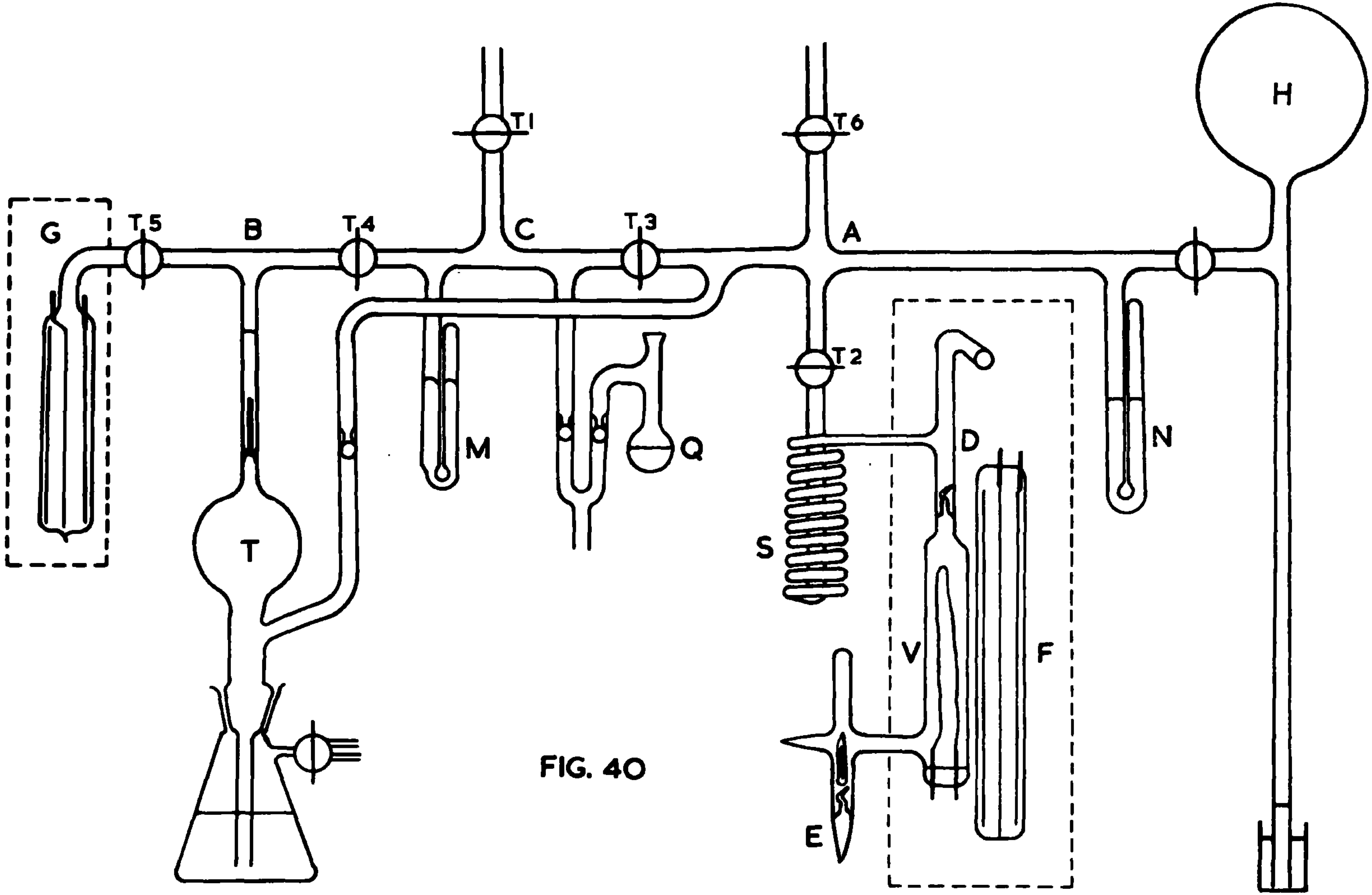


FIG. 40

opened to pump away the gas from section C. T1 was closed and T4 and T3 opened. A piece of cotton wool soaked in liquid nitrogen was applied to the tubing of section A until the pressure indicated by the manometer was zero because of condensation of the cyclopropane. Tap T3 was closed and the coolant removed to allow the solid cyclopropane to melt and evaporate. The pressure indicated by manometer N when room temperature was reached was 9.75 cm, which was therefore the pressure of hydrogen required to be taken in section A to produce a pressure of 8 cm in B and the gas counter.

Beyond this, no calibration of the apparatus was necessary, as the specific activity of the tritium was obtained by counting a sample taken either from a gas pipette or from the expansion bulb on the adsorption apparatus. In this latter method a sample tube of accurately known volume, bearing a tap and B10 cone, was fitted on to the adsorption apparatus in place of the catalyst vessel after an adsorption measurement had been made. This sample tube was pumped to a high vacuum and the taps opened to the expansion bulb B. A sample of the tritium-hydrogen used in the adsorption was thus taken in the sample tube at a pressure of about 1 mm or less. The tap on the sample tube was closed and the tube transferred to the displacement apparatus, again being fitted in place of the catalyst vessel, for the activity of the sample to be determined.

9.6. Experimental Procedure for Measuring Simultaneous Mercury Adsorption and Hydrogen Displacement.

The apparatus comprised the gamma ray counter for mercury, and the gas counter for tritium , together with the catalyst vessel which enclosed a nickel film upon which a measured amount of tritium-hydrogen had been adsorbed using the adsorption apparatus. A hydrogen reservoir, Topler pump, and alcohol reservoir were used in filling the gas counter. A diagram of the apparatus is shown in fig. 40.

The experimental procedure for studying the displacement of the adsorbed tritium-hydrogen was as follows. Taps T1, T2, T3, T4, and T5 were opened and the apparatus pumped to a 'sticking' vacuum, when T1, T2 and T3 were closed. Air was admitted to the mercury reservoir of the Topler pump T by means of the two-way tap, causing the mercury to fill the bulb of the pump. The alcohol reservoir Q was cooled and the mercury lowered in the cut-off. Ethyl alcohol vapour was thus allowed to fill the counter, and the alcohol reservoir was warmed by hand until a pressure of 2 cm was indicated on the manometer M, when tap T4 was closed and the mercury level again raised in the cut-off. A sample of hydrogen was taken in section A from the reservoir H at a pressure of 9.75 cm indicated by manometer N. (Volume calibration showed that this pressure was required to produce a pressure of 8 cm in the counting section). This sample was transferred to the counter using the Topler pump and the last traces cleared from the section by connecting to high vacuum via the taps T1 and T3.

The position of the counter plateau was determined with the aid of an external source of gamma rays, and a background count determined. Section A, the dead-space and spiral connecting the catalyst vessel were pumped to a sticking vacuum and tap T3 closed. A Dewar flask of liquid nitrogen was placed around the spiral trap and the septum on the catalyst vessel broken by a steel ball. Any gas phase tritium-hydrogen was transferred to the gas counter by means of the Topler pump and its activity determined. A background count was determined with the halogen quenched counter and the septum on the mercury source broken.

The displacement was allowed to take place, and the tritium-hydrogen returned to the gas phase was extracted at various times by the Topler pump and transferred to the gas counter. The gas counter filling was renewed when necessary to avoid measuring high tritium activities. Mercury counting was carried out to alternate with the tritium counting, and the counts obtained in each case were plotted with respect to time. The same counting equipment was used for both the tritium and the mercury counting, the change over being effected by changing the coaxial plug on the probe unit.

9.7. The Isotope Effect.

It was realised that the adsorption of tritium-hydrogen, when carried out to completion so that a gas-phase residue remained, might be subject to an isotope effect. Independant experiments were therefore carried out to attempt to measure this isotope effect, by comparing the specific activity of a sample of tritiated hydrogen with that of the residual gas after partial adsorption upon a nickel film.

The type of catalyst vessel used was similar to that used in the displacement measurements except that the mercury source was omitted. This catalyst vessel after preparation was first fitted to the adsorption apparatus, where a quantity of tritium-hydrogen was admitted such that only about half could be adsorbed by the film. The vessel was then sealed off and transferred to the other apparatus for the specific activity of the residual hydrogen to be determined.

A technique was developed to determine this specific activity without the possibility of errors due to incomplete transfer of very small samples of gas to the counting section. This technique was as follows. A small McLeod gauge having a 30 cm^3 bulb and a capillary tube of 2.5 mm bore precision-bore tubing was fitted to the apparatus of fig. 40 to replace the catalyst vessel and its gamma ray counter. A tap was provided in this section whereby the catalyst vessel could be subsequently connected.

After the catalyst vessel had been attached and the apparatus pumped to a 'sticking' vacuum, the septum was broken and a sample of the gas residue was taken in the McLeod gauge section and the tap to the catalyst vessel closed. The mercury was raised in the Mc.Leod gauge and the pressure and volume were read in arbitrary units. After the gas counter had been filled and the section A pumped out, the gas was allowed to expand from the Mc.Leod gauge into section A through the tap T2, which was then closed. The remainder of the gas in the Mc.Leod section was then remeasured. Taps T3, T4 and T5 were opened to allow the counter filling to expand into the tritium sample. T4 was then closed and the gas pumped back into the counter by means of the Topler pump. The count rate was measured and the procedure repeated with further samples expanded from the Mc.Leod gauge. A graph was constructed by plotting the count rate against the pressure-volume reading of the Mc.Leod gauge (in arbitrary units) and the specific activity (also in arbitrary units) obtained from the slope. This value was compared with values for further samples from the catalyst vessel and with the original specimen of tritium-hydrogen. By this means any isotopic enrichment could be detected.

APPENDIX A.

This appendix contains the experimental date which were used to calculate the adsorptoin results reproduced in chapter 2.

Calibration of the Thermistor gauge for Cyclopropane.

Shunt ×3 , Bridge resistances 947 and 53 ohms.

Galvanometer natural zero = 38.65 cm.

Pressure of cyclopropane = 58.7 mm at 21°C.

Pressure after expansion = 1.50 mm

Pressure (mm)	1.50	0.78	0.41	0.21	0.11	0.058	0.030
Deflection (cm)	-4.0	-1.5	+1.0	4.95	10.5	17.0	24.4

Pressure reduced by expansion from section C to section D. Volume of D = 63.8 cm^3.

Pressure (mm)	1.46	0.26	0.046	0.008
Deflection (cm)	-3.6	+3.6	20.5	36.9

This calibration was used for adsorption measurements with film 26.

Film 26. Cyclopropane Adsorption. Vacuum deposited film.

Pressure of cyclopropane sample = 28.70 mm at 20.5°C.

	Initial deflection	Final deflection
Sample 1.	-3.4 cm	35.45 cm
Sample 2.	-3.9 cm	6.90 cm

Catalyst vessel pumped for ½ hour. Penning gauge deflection = 10 μA

Sample 3.	-4.2 cm	8.3 cm

The initial deflections were used to make corrections for zero drift. Volume of catalyst vessel = 53.77 cm^3.

Nickel analysis.

	Standard solns.		Film solns.	
	10.70 mg	20.86 mg	A	B
Optical dens.	0.000	0.357	0.214	0.216

<u>Film 30 Cyclopropane adsorption</u>. Argon deposited.

Pressure of cyclopropane sample = 48.9 mm at 20.0°C.

	Initial deflection	Final deflection
Sample 1.	20.4 cm	36.0 cm
Sample 2.	20.6 cm	27.6 cm

Thermistor gauge deflection on condensing gas at liquid nitrogen temperature after 1 day exposure to mercury. vapour = 26.7 cm.

Thermistor Calibration.

Pressure	1.6	2.58×10^{-1}	5.2×10^{-2}	9.4×10^{-3}
Deflection	20.2	23.1	29.9	36.1

Volume of catalyst vessel = 79.64 cm^3

Nickel Analysis.

	Standard solns. 20.86mg	28.90mg	Film solns. A	B
Optical dens. (average)	0.005	0.385	0.012	0.000

Film weight = 20.73 mg.

Film 32 Cyclopropane Adsorption. Argon deposited.

Pressure of cyclopropane sample = 33.5 mm at 20.1°C.

	Initial deflection	Final deflection
Sample 1.	19.45	37.1
Sample 2.	19.55	29.5

Thermistor gauge deflection on condensing gas at liquid nitrogen temperature after 1 day exposure to mercury vapour = 26.35 cm

Thermistor gauge calibration as in the case of film 30.

Volume of catalyst vessel = 77.15 cm^3

Nickel Analysis.

	Standard solns. 10.70mg	20.86mg	Film solns. A	B
Optical dens. (average)	0.000	0.350	0.166	0.167

Film weight = 15.5 mg.

Film 33. Cyclopropane Adsorption. Argon deposited.

Pressure of cyclopropane sample = 45.1 mm at 20.9°C.

	Initial deflection	Final deflection
Sample 1.	18.90 cm	36.80 cm
Sample 2.	18.90 cm	26.45 cm

Thermistor gauge deflection on condensing gas at liquid nitrogen temperature after 1 day exposure to mercury vapour = 21.50 cm.

Thermistor gauge calibration as in the case of film 30.

Volume of catalyst vessel = 77.15 cm^3.

Nickel Analysis.

	Standard solns.		Film solns.	
	10.70mg	20.86mg	A	B
Optical dens. (average)	0.000	0.348	0.247	0.250

Film weight = 18.5 mg

<u>Film 90</u> <u>Cyclopropane adsorption</u>. Argon deposited.

The results of this adsorption measurement are given in full to show how the amount of gas adsorbed was calculated from the experimental data.

Pressure of cyclopropane sample = 35.5 mm

	Initial deflection	Final deflection
Sample 1.	8.8 cm	33.3 cm
Sample 2.	8.6 cm	29.4 cm
Sample 3.	8.2 cm	20.2 cm
Sample 4.	8.5 cm	13.6 cm

Thermistor gauge calibration.

Initial deflection = 7.7 cm

Pressure reduced in three stages, giving deflections 13.2 cm, 23.2 cm, and 29.8 cm. Volume of catalyst vessel = 64.4 cm^3

Calculation.

Pressure of cyclopropane sample after expansion to

bulb B $= 35.5 \times \frac{(\text{Vol. A})}{(\text{Vol.A+B})}$

$= 35.5 \times \frac{60.55}{2356}$ mm

Thermistor gauge calibration.

Pressure ar beginning of calibration

$$= 35.5 \times \frac{60.55}{2356} \times \frac{(2356)^8}{(2369)} \text{ mm}$$

$$= 0.879 \text{ mm}$$

Pressure reduction factor for each stage

$$= \frac{(\text{Vol. C})}{(\text{Vol.A+C})}$$

$$= 0.1773.$$

From this the following table may be derived

Pressure (mm)	Deflection (cm)
0.879	7.7
0.156	13.2
0.028	23.2
0.005	29.8

The thermistor gauge calibration curve shown in fig.7 was constructed from these data.

Adsorption calculation.

The thermistor gauge galvanometer deflections showed that the first cyclopropane sample was completely adsorbed and the second was adsorbed with negligible residue.

∴ Amount of gas adsorbed in these two samples

$= 12.83 \times 2 \times 35.5 \times \frac{60.55}{2369}$ cm^{3}mm

$= 22.58$ cm^{3}mm at residual pressure 5×10^{-3} mm

Third sample:

Amount of gas admitted

$= 12.83 \times 35.5 \times \frac{60.55}{2369}$ cm^{3}mm

$= 11.29$ cm^{3}mm

Amount remaining, at equilibrium

= (Vol.C+D) × (Pressure corresponding to deflection of 20.2 cm)

$= 77.27 \times 0.05$ cm^{3}mm

$= 3.86$ cm^{3}mm

∴ Amount adsorbed $= 11.29 - 3.86$ cm^{3}mm

$= 7.43$ cm^{3}mm

Total adsorbed $= 30.01$ cm^{3}mm at residual pressure 5×10^{-2} mm.

Fourth sample:

Amount of gas admitted

$= 11.24$ cm^{3}mm

Remainder from third sample

$= \frac{64.4}{77.3} \times 3.86$ cm^{3}mm

$= 3.22$ cm^{3}mm

Total sample $= 14.46$ cm^{3}mm

Amount remaining at equilibrium

$= 77.27 \times 0.18$ cm^{3}mm

$= 13.91$ cm^{3}mm

Amount adsorbed = 0.55 cm^3mm

Total adsorbed = 30.56 cm^3mm at residual pressure 1.8×10^{-1}mm.

Nickel Analysis.

	Standard solns.		Film solns.	
	30.08mg	38.4mg	A	B
Optical dens. (average)	0.142	0.439	0.000	0.014

$$\text{Weight of nickel} = 30.1 - \left(\frac{0.142}{(0.439-0.142)} \times (38.4-30.1) \right)$$

$$= 26.09 \text{ mg.}$$

<u>Film 61</u> <u>Propylene adsorption</u>. Argon deposited.

Pressure of propylene sample = 35.9 mm at 20.8°C.

	Initial deflection	Final deflection
Sample 1.	8.40 cm	23.20 cm
Sample 2.	8.50 cm	13.52 cm
Sample 3.	8.60 cm	11.01 cm

Thermistor gauge calibration.

Pressure (mm)	8.97×10^{-1}	1.59×10^{-1}	2.82×10^{-2}	5.00×10^{-3}	8.87×10^{-4}
Deflection (cm)	8.65	13.15	22.20	29.10	33.91

Volume of catalyst vessel = 56.84 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	10.70mg	20.86mg	A	B
Optical dens. (average)	0.015	0.357	0.011	0.000

Film weight = 10.3 mg.

<u>Film 67</u> <u>Propylene Adsorption</u>. Argon deposited.

Pressure of propylene sample = 38.9 mm at 19.9°C.

	Initial deflection	Final deflection
Sample 1.	9.0 cm	25.0 cm
Sample 2.	8.9 cm	14.1 cm
Sample 3.	9.1 cm	11.5 cm

Thermistor gauge calibration

Pressure	9.7×10^{-1}	1.7×10^{-1}	3.1×10^{-2}	5.4×10^{-3}
Deflection	8.95	13.4	21.7	32.9

Volume of catalyst vessel = 50.34 cm^3

Nickel Analysis.

	Standard solns.		Film soln.	
	20.05mg	30.08mg	A	B
Optical dens. (average)	0.282	0.637	0.000	0.001

Film weight = 12.14 mg

<u>Film 70</u> <u>Propylene Adsorption</u>. Argon deposited.

Pressure of propylene sample = 38.0 mm

	Initial deflection	Final deflection
Sample 1.	9.90 cm	34.81 cm
Sample 2.	9.50 cm	25.13 cm
Sample 3.	9.35 cm	14.79 cm

Thermistor deflection after 2 days exposure to mercury vapour = 12.20 cm

After condensing at liquid nitrogen temperature = 29.8 cm

Thermistor gauge calibration

Pressure	9.5×10^{-1}	1.7×10^{-1}	3.00×10^{-2}	5.3×10^{-3}
Deflection	8.70	13.17	22.70	30.15

Volume of catalyst vessel = 72.5 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	20.05mg	30.08mg	A	B
Optical dens.	0.000	0.421	0.048	0.054

Film weight = 21.27 mg

Film 69 Propylene Adsorption. Argon deposited.

Pressure of propylene sample = 43.2 mm at 20.4°C.

	Initial deflection	Final deflection
Sample 1.	8.45 cm	35.0 cm
Sample 2.	7.75 cm	26.7 cm
Sample 3.	7.72 cm	15.6 cm
Sample 4.	7.70 cm	10.2 cm

Thermistor gauge deflection after 2 days exposure to mercury vapour = 10.15 cm

After condensing gas at liquid nitrigen temperature

= 36.0 cm

Thermistor gauge calibration

Pressure	1.07 mm	1.9×10^{-1}	3.37×10^{-2}	5.98×10^{-3}
Deflection	7.69	11.79	21.30	29.36

Volume of catalyst vessel = 48.54 cm^3

Nickel Analysis.

	Standard solns. 20.05mg	 30.08mg	Film solns. A	 B
Optical dens.	0.000	0.298	0.268	0.270

Film weight = 29.10 mg

Film 68 Propylene Adsorption Vacuum deposited.

Pressure of propylene sample = 35.9 mm at 20.2°C

	Initial deflection	Final deflection
Sample 1.	8.0 cm	26.2 cm
Sample 2.	8.0 cm	13.9 cm
Sample 3.	7.9 cm	10.8 cm

Thermistor gauge calibration

Pressure	8.97×10^{-1}	1.59×10^{-1}	2.82×10^{-2}	5.00×10^{-3}
Deflection	7.9	12.2	21.1	28.1

Volume of catalyst vessel = 50.84 cm^3

Nickel Analysis.

	Standard solns. 10.70mg	 20.05mg	Film solns. A	 B
Optical dens.	0.000	0.338	0.703	0.711

Film weight = 30.7 mg.

APPENDIX B.

The experimental data obtained from the hydrogen and mercury adsorption experiments are recorded in this appendix.

Thermistor gauge calibration.

Initial hydrogen pressure = 75.8 mm

The gas was expanded from 63.02 cm^3 to 2372 cm^3, then pressure reduced in steps with reduction factor

$$\frac{59.01}{122.78} = 0.4807$$

Pressure (mm)	1.98	0.95	0.46	0.22	0.11	0.051	0.025
Deflection (cm)	11.7	15.4	21.4	27.5	34.5	39.8	43.6

Film 7. Hydrogen adsorption Argon deposited.

Hydrogen sample pressure = 69.40 mm at 21.8°C.

First adsorption - thermistor gauge deflections

	Initial deflection	Final deflection
Sample 1.	11.9 cm	52.0 cm
Sample 2.	12.0 cm	52.1 cm
Sample 3.	11.9 cm	51.9 cm
Sample 4.	11.9 cm	52.2 cm
Sample 5.	11.8 cm	51.9 cm
Sample 6.	11.8 cm	39.4 cm
Sample 7.	11.6 cm	24.2 cm

Second adsorption.

Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	11.85 cm	38.7 cm
Sample 2.	12.03 cm	24.8 cm

Volume of catalyst vessel = 52.37 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	28.9mg	38.4mg	A	B
Optical dens.	0.000	0.431	0.229	0.239
	0.000	0.436	0.231	0.239

Film weight = 34.3 mg

Film 8. Hydrogen adsorption. Argon deposited.

Hydrogen sample pressure = 99.7 mm at 21.6°C.

Adsorption. Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	9.6 cm	50.1 cm
Sample 2.	9.0 cm	50.7 cm
Sample 3.	9.0 cm	45.4 cm
Sample 4.	8.9 cm	20.8 cm

Volume of catalyst vessel = 52.88 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	28.9mg	38.4mg	A	B
Optical dens.	0.047	0.269	0.000	0.002

Film weight = 26.9 mg.

Film 12. Hydrogen adsorption. Argon deposited.

Thermistor gauge calibration.

Initial hydsogen pressure = 129.5 mm

Pressure after expansion = 3.09 mm

Pressure reduction factor = 0.5242

Pressure (mm)	3.09	1.62	0.85	0.45	0.23
Deflection (cm)	2.10	5.49	9.59	14.70	20.50
Pressure (mm)	0.12	.065	.034	.018	.009
Deflection (cm)	26.41	32.00	36.70	40.60	43.04

Hydrogen sample pressure = 60.85 mm at 19.0°C.

Adsorption. Thermistor gauge deflection

	Initial deflection	Final deflection
Sample 1.	6.6 cm	47.0 cm
Sample 2.	6.5 cm	46.5 cm
Sample 3.	5.5 cm	46.0 cm
Sample 4.	5.5 cm	41.7 cm

Volume of catalyst vessel = 61.00 cm^3

Nickel analysis.

	Standard solns.		Film solns.	
	LO.7mg	20.86mg	A	B
Optical dens.	0.000	0.392	0.358	0.330
	0.000	0.394	0.362	0.332

Film weight = 19.6 mg

<u>Film 13</u>. <u>Hydrogen Adsorption</u>. Argon deposited.

Hydrogen sample pressure = 50.45 mm at 21.9°C.

First Adsorption. Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	8.6 cm	46.1 cm
Sample 2.	8.2 cm	47.4 cm
Sample 3.	9.0 cm	47.2 cm
Sample 4.	8.3 cm	46.8 cm
Sample 5.	8.2 cm	32.8 cm
Sample 6.	8.2 cm	22.2 cm

Second adsorption, after pumping for 2 hours at 6μA

Penning gauge deflection.

Thermistor gauge deflections

	Initial deflection	Final deflection
Sample 1.	9.78 cm	30.7 cm

Volume of catalyst vessel = 71.99 cm^3

<u>Film 14</u>. <u>Hydrogen Adsorption</u>. Argon deposited.

Hydrogen sample pressure = 49.25 mm at 18.6°C.

Adsorption. Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	8.7 cm	48.7 cm
Sample 2.	8.9 cm	50.0 cm
Sample 3.	8.9 cm	48.1 cm
Sample 4.	8.6 cm	47.2 cm
Sample 5.	10.0 cm	36.1 cm

Deflection after exposure of film to mercury vapour = 13.2 cm

∴Pressure = 0.744 mm

Volume of catalyst = 70.98 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.042	0.379	0.000	0.000
	0.043	0.380	0.000	0.001

Film weight = 19.85 mg.

<u>Film 15</u>. <u>Hydrogen Adsorption</u>. Argon deposited.

Hydrogen sample pressure = 55.35 mm at 20.5°C.

Adsorption. Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	7.5 cm	44.4 cm
Sample 2.	7.7 cm	46.7 cm
Sample 3.	8.2 cm	49.7 cm
Sample 4.	8.5 cm	50.0 cm
Sample 5.	8.9 cm	48.7 cm
Sample 6.	9.0 cm	47.2 cm
Sample 7.	8.8 cm	33.9 cm
Sample 8.	8.8 cm	24.3 cm

Volume of catalyst vessel = 72.70 cm^3.

Nickel Analysis.

	Standard solns.		Film solns.	
	28.90mg	38.41mg	A	B
Optical dens.	0.000	0.425	0.211	0.211

Film 16. **Hydrogen adsorption.** Argon deposited.

Hydrogen sample pressure = 60.90 mm at 21.0°C.

Adsorption. Thermistor gauge deflections.

	Initial deflection	Final deflection
Sample 1.	12.6 cm	50.3 cm
Sample 2.	11.5 cm	50.0 cm

Thermistor gauge deflection after exposure of film to mercury vapour = 22.7 cm

∴ Pressure = 0.391 mm

Volume of catalyst vessel = 66.14 cm^3

Nickel Analysis.

	Standard solns.		Film solns.	
	28.90mg	38.41mg	A	B
Optical dens.	0.000	0.418	0.402	0.407
	0.000	0.417	0.410	0.412

Film weight = 38.2 mg.

Films 65 and 105 - see chapter 5.

Film 46.

1. Tritium-hydrogen recovered from film by displacement.

Observed count = 10861 counts per 15 min (900 sec)

Total dead-time = 10861 millisec

= 11 sec

∴ Activity $= \frac{10861}{889} \times 60$ cts./min, corrected for dead-time.

$= 733$ cts./min $\left(\pm\frac{\sqrt{10861}}{15}\right)$

Background count = 14 cts./min.

Tritium activity = 719 ± 1% cts./min

2. Tritium-hydrogen adsorbed - specific activity

56.98 mm pressure taken in 7.206 cm^3 pipette at 20°C.

Quantity of tritium-hydrogen = 410.60 cm^3mm

Observed count = 10560 cts./3 min

Dead-time = 10560 millisec

= 11 sec

∴ Activity = $\frac{10560}{169} \times 60$ cts./min

= 3727 cts./min

Background count = 14 cts./min

Tritium activity = 3713 cts./min

∴ Specific activity = $\frac{3713}{410.6}$ cts./min cm^3mm

= 9.043 cts/min cm^3mm

3. Quantity of tritium-hydrogen adsorbed at 20°C.

= $\frac{719}{9.04}$ cm^3mm

= 79.5 cm^3mm

Volume at 25°C = 80.9 cm^3mm

Second extraction from catalyst vessel

Count = 42 cts./min

By similar calculation

Total displaced tritium-hydrogen

= 85.6 cm^3mm at 25°C.

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90	A	B
Optical dens.	0.000	0.261	0.191	0.201
	0.000	0.262	0.191	0.200

Film weight = 26.9 mg

Calculated adsorptive capacity

= 26.9 × 3.833 cm^{3}mm at 25°C.

= 103.1 cm^{3}mm

% Hydrogen recovered = $\frac{85.6}{103.1}$ × 100 %

= 83.1 %

Film 43.

1. Tritium-hydrogen recovered from the film by displacement.

Observed count = 12,662 cts./min×13

= 974 cts./min

Background = 28 cts./min

2. Tritium-hydrogen - specific activity

Quantity of gas taken = 67.82 × 7.206 cm^{3}mm at 20°

= 488.7 cm^{3}mm

Observed count = 5340 cts./min

Background = 28 cts./min

Specific Activity = 10.87 cts./min cm^{3}mm at 20°

=

3. Quantity of tritium-hydrogen desorbed at 20°C.

$$= \frac{946}{10.87} \text{ cm}^3\text{mm}$$

$$= 87.07 \text{ cm}^3\text{mm at } 25^\circ\text{C.}$$

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.284	0.258	0.249
	0.000	0.280	0.256	0.246

Film weight = 28.1 mg

Calculated adsorptive capacity = 107.6 cm^{3}mm

<u>Film 49</u>

1. Tritium-hydrogen recovered from film by displacement

Observed count = 10,060 cts./min×15

= 671 cts./min

Background count = 23 cts./min

2. Tritium-hydrogen specific activity as for film 46.

3. Quantity of tritium-hydrogen desorbed at 20°C.

$$= \frac{671}{9.04} \text{ cm}^3\text{mm}$$

$$= 72.9 \text{ cm}^3\text{mm at } 25^\circ\text{C}$$

Nickel Analysis.

	Standard Solns.		Film solns.	
	20.86mg	28.90	A	B
Optical dens.	0.000	0.267	0.083	0.081
	0.000	0.279	0.086	0.082

Film weight = 23.3 mg

Calculated adsorptive capacity
$= 89.3\ cm^3 mm$

Mercury Adsorption Experiments.

Film 54.

Counter background = 18.8 cts./min

Count on 10 ml. film 54 soln., made by dissolving film in 25 ml. nitric acid = 5,205 cts./min

Count on 10 ml. standard soln. - 10.09 mg per 100 ml. nitric acid = 701.1 cts./min

Weight of mercury in 25 ml. standard soln.

$$= 10.09 \times \frac{25}{100}\ mg$$

$$= 2.52\ mg$$

Weight of mercury in 25 ml. film soln.

$$= \frac{(5205-18.8\ )}{(701.1-18.8)} \times 2.52\ mg$$

$$= 19.15\ mg$$

Nickel Analysis

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.284	0.473	0.489
	0.000	0.282	0.470	0.485

Film weight = 34.6 mg

Film 55.

Counter background = 14 cys/min

Count on 10 ml. film soln. = 1730 cts./min

Count on 10 ml. standard = 430 cts./min

Weight of mercury = 10.40 mg

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.303	0.310	0.319
	0.000	0.309	0.318	0.326

Film weight = 29.1 mg

<u>Film 56</u>.

Counter background = 12.2 cts./min

Count on 10 ml. film soln. = 913.2 cts./min

Count on 10 ml. standard (2.52 mg per 25 ml.) = 414.0 cts./min

Weight of mercury = 5.54 mg

Nickel Analysis.

	Standard soln.		Film soln.	
	20.86mg	28.90mg	A	B
Optical density	0.000	0.335	0.081	0.096
	0.000	0.333	0.081	0.096

Film weight = 23.0 mg

<u>Film 57</u>.

Counter background = 12.5 cts./min

Count on 10 ml. film soln. = 3618 cts./min

Count on 10 ml. standard (2.26 mg per 25 ml.) = 267 cts./min

Weight of mercury = 32.08 mg

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.288	0.264	0.271
	0.000	0.286	0.258	0.260

Film weight = 28.2 mg

Film 59.

Counter background = 12.5 cts./min

Count on 10 ml. film soln. = 2902 cts./min

Count on 10 ml. standard (2.26 mg per 25 ml.) = 267 cts./min

Weight of mercury = 25.71 mg

Nickel Analysis.

	Standard solns.		Film solns.	
	20.86mg	28.90mg	A	B
Optical dens.	0.000	0.315	0.294	0.301

Film weight = 28.3 mg

Film 62.

Counter background = 12.5 cts./min

Count on 10 ml. film soln. = 993 cts./min

Count on 10 ml. standard (2.26 mg per 25 ml.) = 267 cts./min

Weight of mercury = 9.06 mg

Nickel Analysis.

	Standard soln. 10.70mg	Standard soln. 20.86mg	Film soln. A	Film soln. B
Optical dens.	0.021	0.000	0.387	0.002
	0.021	0.000	0.392	0.000

Film weight = 10.1 mg

<u>Film 52</u>. (Exposed to air)

Counter background = 16.0 cts./min

Count on 10 ml. film soln. = 15.9 cts./min

No mercury adsorbed.

<u>Film 79</u>. (Exposed to propylene)

Counter background = 14.0 cts./min

Count on 10 ml. film soln. = 285 cts./min

Count on 10 ml. standard (2.57 mg per 25 ml.) = 784 cts./min

Weight of mercury = 0.84 mg

Nickel Analysis.

	Standard solns. 20.86mg	Standard solns. 28.90mg	Film solns. A	Film solns. B
Optical dens.	0.000	0.291	0.016	0.017

Film weight = 21.3 mg

APPENDIX C.

This appendix contains experimental data obtained from the hydrogen displacement by mercury experiments described in chapter 5.

Film 83.

1. Tritium-hydrogen adsorption

Pressure of sample = 20.3 mm

Thermistor gauge deflections

	Initial	Final
Sample 1.	4.0 cm	32.6 cm
Sample 2.	3.3 cm	32.5 cm

Deflection under high-vacuum = 33.0 cm

Quantity of hydrogen adsorbed= 13.3L cm^3mm at 25°C.

2. Tritium specific activity

5.55 mm tritium taken in 6.302 cm^3 pipette

Observed count = 3269 cts./min
Background = 20 cts./min
Dead-time = 99 cts./min
Corrected count = 3348 cts./min
Specific activity = 95.8 cts./min cm^3mm

3. Film weight.

	Standard solns. 20.05mg	Standard solns. 30.08mg	Film solns. A	Film solns. B
Optical dens.	0.067	0.514	0.001	0.000

Film weight = 18.55 mg

Film 85.

1. Tritium-hydrogen adsorption

Pressure of sample = 33.9 mm

Thermistor gauge deflections

	Initial	Final
Sample 1.	-1.2 cm	22.9 cm

Deflection under high-vacuum = 23.1 cm

Quantity of hydrogen adsorbed = 10.83 cm^{3}mm at 25°C.

2. Tritium specific activity = 95.8 cts./cm^{3}mm

(see film 83)

3. Film weight.

	Standard solns.		Film solns.	
	20.05mg	30.08mg	A	B
Optical dens.	0.000	0.382	0.489	0.490

Film weight = 32.9 mg

Film 107.

1. Tritium-hydrogen adsorption

Pressure of sample = 22.6 mm

Thermistor gauge deflections

	Initial	Final
Sample 1.	-1.0 cm	20.0 cm
Sample 2.	-1.0 cm	19.8 cm
Sample 3.	-1.1 cm	21.1 cm

Deflection under high-vacuum = 21.4 cm

Quantity of hydrogen adsorbed= 22.21 cm^{3}mm

2. Tritium specific activity

5.33 mm tritium taken in 6.302 cm^3 pipette

Observed count = 3835 cts./min

Background = 39 cts./min

Dead-time = 133 cts./min

Corrected count = 3929 cts./min

Specific activity = 110.7 cts./min cm^{3}mm

3. Film weight

	Standard solns.		Film solns.	
	20.05 mg	30.08mg	A	B
Optical dens.	0.000	0.374	0.307	0.311

Film weight = 28.33 mg

Film 105

1. Tritium-hydrogen adsorption.

Pressure of sample = 27.3 mm

Thermistor gauge deflections

Sample	1	2	3	4	5	6	7	8
Initial	-3.0	-3.0	-3.0	-3.1	-3.1	-3.0	-3.1	-3.1
Final	19.8	19.5	19.7	19.9	19.9	18.5	18.3	18.8

Sample	9	10	11	12	13	14	15
Initial	-3.1	-3.1	-3.0	-3.0	-3.0	-3.0	-3.1
Final	17.2	19.4	18.9	18.4	18.2	16.5	12.1

Deflection under high vacuum = 19.5 cm

Quantity of hydrogenadsorbed = 118.9 cm^{3}mm

Volume of catalyst vessel = 53.7 cm^3

Volume of catalyst vessel after sealing

= 42.2 cm^3

2. Tritium specific activity

4.24 mm tritium taken in 6.3o2 cm^3 pipette

Observed count = 2927 cts./min

Background = 32 cts./min

Dead-time = 67 cts./min

Corrected count = 2962 cts./min

Specific activity = 110.9 cts./min cm^{3}mm

3. Film weight.

	Standard solns.		Film solns.	
	30.08 mg	38.41mg	A	B
Optical dens.	0.000	0.364	0.037	0.037

Film weight weight = 30.93 mg

<u>Film 108</u>.

1. Tritium-hydrogen adsorption

Pressure of sample = 35.1 mm

Thermistor gauge deflections

Sample	1	2	3	4	5
Initial	0.8cm	0.7cm	0.7cm	0.7cm	0.8cm
Final	20.4cm	20.6cm	20.6cm	19.9cm	16.1cm

Thermistor gauge calibration

Pressure (mm)	0.897	0.159	0.028	HV
Deflection (cm)	0.60	12.21	16.03	21.4

Quantity of hydrogen adsorbed = 54.04 cm^{3}mm

Volume of catalyst vessel = 67.4 cm^3

Volume of catalyst vessel after sealing = 40.1 cm^3

2.Tritium specific activity = 110.7 cts./min cm^{3}mm (see film 107)

3.Film weight

	Standard solns.		Film solns.	
	10.70mg	20.05mg	A	B
Optical dens.	0.000	0.350	0.130	0.131

Film weight = 14.19 mg

Film 113

1.Tritium-hydrogen adsorption

Pressure of sample = 48.6 mm

Thermistor gauge deflections

Sample	1	2	3
Initial	-0.5	-0.6	-0.6
Final	24.5	22.9	18.6

Deflection under high-vacuum = 24.0 cm

Quantity of hydrogen adsorbed= 45.80 cm^{3}mm

Volume of catalyst vessel = 61.1 cm^3

Volume of catalyst vessel after sealing = 40.3 cm^3

2. Tritium specific activity

29.6 cm^3 sample taken from expansion bulb on adsorption apparatus, pressure = 41.5 mm before expansion

Observed count = 3249 cts./min

Background = 34 cts./min

Dead-time = 88 cts./min

Corrected count = 3303 cts./min

Specific activity = 114.8 cts./min cm^{3}mm

3. Film weight =

	Standard solns.		Film solns.	
	20.05mg	30.08mg	A	B
Optical dens.	0.000	0.340	0.127	0.131

Film weight = 23.96 mg

APPENDIX D.

Counter faults in Tritium Counting.

Various counter faults developed from time to time among which the following, with the means whereby they were rectified, may be mentioned.

1.Contamination.

Contamination was indicated by a high background count observed after an activity measurement.. This was observed on one occasion when a catalyst vessel with a slight leak was used, and the contamination was presumed to be caused by tritiated water formed by catalytic oxidation of hydrogen. The counter was filled to a few cm pressure with hydrogen, heated and the hydrogen pumped out. A normal background count rate (30 - 40 counts pre min) was thereby restored.

2.Photosensitivity.

When this occurred, a count rate of about 2000 counts per min was observed with an inactive filling when the counter was in its castle (semi-darkness). This count rate increased with increased illumination. This fault also was remedied by heating the counter with hydrogen.

3. High Background.

High background counts, without photosensitivity or contamination, were often observed in cold weather. The background count rate could be reduced to a normal value by warming the counter to 20°C. It is difficult to attribute this phenomenon to partial condensation of alcohol, as at 2cm pressure the vapour does not become saturated until the temperature is reduced to 9°C, which is below normal room temperatures.

4. Loss of Plateau.

The cause of this phenomenon was not known. It was remedied however by admitting air to the counter at 4 cm pressure and increasing the voltage until a continuous discharge occurred. This discharge was allowed to continue for several minutes, after which the air was pumped away.

An incurable loss of plateau occurred with one counter, and in the absence of any other apparent defect it was concluded that this was caused by amalgamation of the cppperxcathode by exposure to mercury vapour. In later work with a new counter precautions were taken to keep the tap closed when the counter was not in use, and the trouble has not recurred.

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