THE APPLICATION OF TRACER MOLECULES TO THE STUDY OF SURFACE PROCESSES

THESIS

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ABSTRACT

Ethylene-D_4, ^{14}C-ethylene and tritium have been used as tracer molecules in a study of the nature and reactivity of adsorbed species on several different nickel catalysts. Reactions have been carried out on alumina- and silica-supported metal catalysts at nickel concentrations of 0.1 and 5%, a nickel powder catalyst, and a nickel catalyst partially poisoned by nickel phosphide in an attempt to determine the effect of the form of the metal on the catalyst reactivity. As well as the metal catalysts, the support materials themselves have formed part of the study.

The catalysts were contained in a microcatalytic reactor which formed part of a flow system and the reaction gases were injected onto the catalysts after reduction. Catalyst temperatures ranged from 20°C to 400°C and after separation of the products by gas chromatography, reaction components were either detected by a gas proportional counter or analysed by mass spectrometry, as appropriate.

Using tritium, it has been found that at the temperature of reduction of the supported catalysts the alumina support is itself active in exchange with gas phase hydrogen (at 400°C) whereas the silica support is not. The presence of nickel was found to initiate the exchange reaction on silica at the same temperature but to decrease the amount of exchange observed with alumina. A smaller extent of reaction of

tritium with the nickel catalyst is interpretated in terms of the absence of participation of a support medium.

The reactivity of the catalysts tritiated after reduction, towards gas phase ethylene has been investigated. In general, tritium did not appear in the ethylene component of the reaction products although as the catalyst temperature was raised the activity of the ethane and methane fractions was found to increase. In contrast to the reaction of hydrogen with the alumina support, the presence of metal was necessary for the reaction of ethylene with preadsorbed tritium.

The reactions of two ethylene tracer molecules, labelled in different halves of the molecule, have shown that the carbonaceous part of initially adsorbed ethylene is retained by the catalyst as an unreactive and strongly adsorbed species, whereas the hydrogen from dissociated ethylene exchanges more readily with further ethylene injections. The partially poisoned nickel catalyst has behaved differently from the other catalysts in that molecular exchange of preadsorbed ethylene with gas phase ethylene was observed to take place readily at room temperature. The results are discussed in terms of the likely surface species formed by ethylene chemisorption at different temperatures and the possibility of the formation of a different type of surface species on the nickel/nickel phosphide catalyst is proposed.

CHAPTER 1. INTRODUCTION

Section 1.1 Principles of Catalysis.

It is found by experiment that some substances increase the rate at which a chemical reaction attains equilibrium and yet do not appear in the stoichometric equation of the reaction. Such substances are known as catalysts, and their action as catalysis.

There are many reactions whose velocities are immeasureably slow in gaseous or liquid solutions, but which go quite swiftly if a suitable solid surface is available. Heterogeneous catalysis describes the enhancement in the rate of a chemical reaction brought about by the presence of an interface between two phases. For example, when hydrogen gas escapes from a cylinder into the air, no change is observed. If the escaping hydrogen is directed at finely divided platinum it is observed that the platinum glows and eventually ignites the hydrogen. In the absence of platinum the reaction rate is too small to observe.

When catalyst and reactants are present in the same phase the process is known as homogeneous catalysis. Examples of gaseous catalysed homogeneous reactions are not very common; one of the best known is the decomposition of ethers and aldehydes in the presence of iodine as a catalyst. The catalyst acts by providing a mechanism for the decomposition that has a considerably lower activation energy than the uncatalysed reaction. Most examples of homogeneous catalysis have been studied in liquid solutions and perhaps the most important of these are those generally included under the title acid-base catalysis. The rates of a great number of organic reactions and many of the processes of physiological chemistry are governed by acid-base catalysts.

The success of catalysts devised by man to accelerate chemical reaction rates appear insignificant compared with the catalytic activity of enzymes in biological systems. Enzymes are specific, colloidal catalysts and have particle diameters in the range, 100 to 1000Å. Enzyme catalysis is therefore midway between homogeneous and heterogeneous catalysis and is sometimes called microheterogeneous. Pepsin in the gastric juice and ptyalin in the saliva are examples. Ptyalin is the catalyst which accelerates the conversion of starch to sugar. Although starch will react with water to form sugar, it takes several weeks for the conversion to occur. A trace of ptyalin is enough to make the reaction proceed at a biologically useful rate.

Since Berzelius[1] in 1836 coined the word 'catalysis' and used it to describe a number of observations already recorded in the literature, it has become recognised that the reacting components in catalytic reactions are held to the surface or adsorbed during the period in which they are reacting.

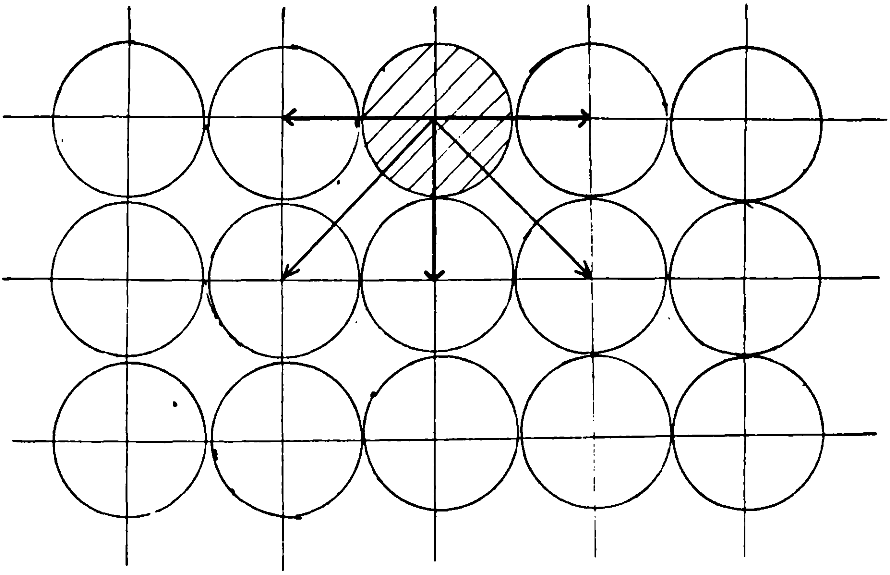


FIG. 1

As the process of attachment is of great importance in catalysis, it is imperative that the characteristics of adsorption are fully appreciated.

Section 1.2 Adsorption.

The activity of a heterogeneous catalyst resides at the interface of the solid and the less dense phase. An atom at the surface of a solid is bound to other atoms in the same plane and below it, but there are of course no atoms above it; there is therefore a net resultant force acting in the direction of the bulk (see Fig. 1). When a fresh surface is exposed to a gas a higher concentration of gas molecules will result on the surface compared with that in the gas phase. This preferential concentration of gas molecules at the surface is termed adsorption. The existence of two types of adsorption of gases on solids has been recognised for many years.[2,3] Langmuir[2] proposed that the forces by which molecules or atoms may be held on a surface should show, for different substances, 'as great a range of intensity as is observed in the case of forces acting inside of solid bodies.' He considered the adsorption of gases by active adsorbents, such as metals, due to primary valence forces. It is now established that although the strength and extent of adsorption may vary widely from system to system, it is possible to divide all adsorptions into two main types; physical adsorption and chemical adsorption. The latter is termed chemisorption.

Section 1.3 Thermodynamics of Adsorption.

In adsorption the free energy of the system decreases as the surface valencies become saturated. The enthalpy change for the process is $\Delta H = \Delta G - T\Delta S$. In all cases of physical adsorption, where only weak molecular forces are involved, the process is similar to simple condensation: the molecules have less freedom on the surface, and ΔS is negative. In the case of chemisorption, chemical bonds are involved, and an adsorbed molecule can become dissociated. In all but a very small number of cases such dissociation is insufficient to render the overall entropy change positive. It can thus be stated that all adsorptions with negative entropy change, which comprise all physical and the great majority of chemical adsorptions are exothermic.

Section 1.4 Physical Adsorption and Chemisorption.

There are differences in the properties of the two kinds of adsorption, which can be used as experimental criteria for deciding the adsorption type. Probably the best single criterion is the magnitude of the heat of adsorption. During physical adsorption the heat liberated per mole of gas adsorbed is generally in the region of 2 - 6 kcal, [4,5] and seldom does the heat of physical adsorption exceed the heat of liquefaction of the gas in question by more than a factor of two or three. During chemisorption larger values for the heat of adsorption are generally encountered and are rarely less than 20 kcal[6,7] mole^{-1}.

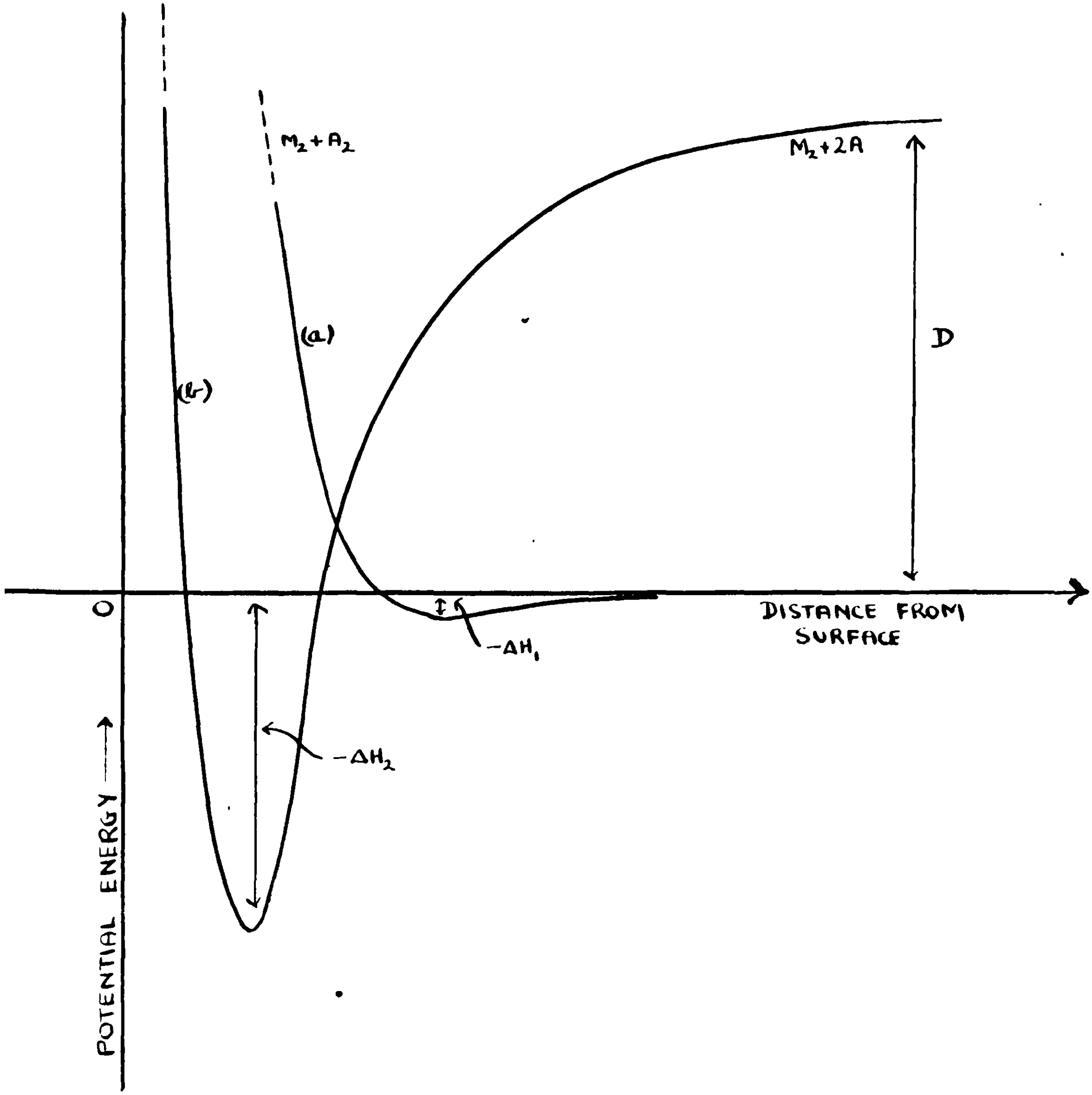

M₂ + A₂
M₂ + 2A
(a)
(b)
D
O
DISTANCE FROM SURFACE
−ΔH₁
−ΔH₂
POTENTIAL ENERGY →

FIG. 2

Chemisorption, like other chemical reactions, is often an activated process. As physical adsorption simulates liquefaction, then it should, like liquefaction, require no activation and therefore occur very rapidly. In general this distinction proves a useful quide although there are exceptions such as the adsorption of hydrogen on a tungsten filament[8] at a low temperature.

Another contrast between physical adsorption and chemisorption is provided by the thickness of the adsorbed layer; chemisorption is confined to a single atomic or molecular layer whereas in physical adsorption the layer becomes multimolecular at higher relative pressures.

A final distinguishing feature of chemisorption is that it is highly specific; hydrogen, for example, is chemisorbed by tungsten or nickel but not by gold or copper. Physical adsorption on the other hand is essentially non specific and the amount of gas which is adsorbed is a function of condensibility and not of its chemical properties.

Section 1.5 Potential Energy Diagram for Adsorption.

Lennard-Jones made a clear distinction between physical adsorption and chemisorption with the help of potential energy curves. The diagram (see Fig. 2) shows the variation of potential energy with distance from the surface for the interaction of a diatomic molecule A_2 with a metal M. Curve (a) is observed with physical adsorption. The potential energy shows a broad and shallow minimum at a distance of about 4Å away from the surface. $-\Delta H_1$ is the heat of physical adsorption and the value is small as only weak forces are involved. The minimum energy distance from the surface is approximately the sum of the covalent radii of the metal and A plus the additional thickness of the two van der Waals envelopes.

The potential energy curve for chemisorption (curve (b) in Fig. 1.2) differs from that for physical adsorption in that a deep and narrow minimum is observed quite close to the surface. The minimum energy distance from the surface is approximately 2Å and corresponds to the sum of the covalent radii of the metal and A. The depth of the trough is a measure of $-\Delta H_2$, the heat of chemisorption, and D is the dissociation energy of the molecule A_2 into atoms.

Section 1.6 Adsorption Isotherms.

Adsorption is most generally described in terms of isotherms which show the relationship between the pressure of the adsorbate gas and the amount adsorbed at a constant temperature.

(i) Langmuir Isotherm. In 1916 Langmuir[2] applied a simple kinetic theory to the adsorption equilibria. Three important assumptions were made in the derivation of the Langmuir adsorption isotherm. These were as follows:
a) the adsorbed entities are attached on the surface of the adsorbent at definite, localised sites. b) each site can accommodate only one adsorbed entity. c) the energy of

the adsorbed entity is the same at all sites on the surface, and is independent of the presence or absence of other adsorbed entities at neighbouring sites. If we consider a gas at pressure p in equilibrium with a surface then the number of collisions of gas molecules with unit area of the surface is proportional to p, by the kinetic theory of gases. If this number in unit time is k_1p and θ is the fraction of the surface which is covered by adsorbed molecules then the rate of condensation of the gas on the crystal is $\alpha(1-\theta)\,k_1p$ where α is the probability that a molecule will adsorb when it strikes a bare site. If the rate of desorption is k_{-1} then at equilibrium the two rates must be equal. Hence $(1-\theta)\,k_1p = k_{-1}\theta$ whence, if $b = k_1/k_{-1}$, $\theta = bp/(1+bp)$ At low gas pressure the adsorption is proportional to the gas pressure, and at high pressures a limit is reached when the surface becomes saturated with $\theta = 1$. The full kinetic derivation is discussed by Trapnell.[11] The Langmuir isotherm, given by the above equation when molecular adsorption occurs takes a different form when the adsorbed molecule is dissociated, as with hydrogen adsorbed on tungsten. Langmuir[12] treated the problem as follows. Let θ be the fraction of the surface covered by adsorbed atoms. For a molecule approaching the surface to become adsorbed, two adjacent spaces must be vacant. The chance of one being vacant is $(1-\theta)$ and of both being vacant $(1-\theta)^2$. The rate of adsorption is therefore $(1-\theta)^2 k_2 p$, where $k_2 p$ again gives the number of molecules colliding with unit area of surface in unit time, and α is now the probability of adsorption at a collision of a molecule with a vacant space having an appropriate neighbouring vacant space. Evaporation only occurs when adsorbed atoms are in adjacent spaces, and the probability that a given space is occupied by an atom is θ. Therefore the chance that atoms shall be in adjacent spaces is proportional to θ^2 and the rate of evaporation of molecules from the surface is $k_{-2}\theta^2$, where k_{-2} is the rate of evaporation from a completely covered surface. For equilibrium

$$(1-\theta)^2 k_2 p = k_{-2}\theta^2 \text{ whence, if } a = \alpha k_2/k_{-2}$$

$$= (ap)^{\frac{1}{2}}/[1+(ap)^{\frac{1}{2}}]$$

This equation is the Langmuir adsorption equation for a dissociative chemisorption in which two similar fragments are formed, and the equation is often used in this form.

(ii) Change in heat of adsorption with coverage. If the Langmuir theory were universally valid, we should expect the heat of adsorption to remain constant with increasing values of the coverage θ. However, in many cases, the heat of adsorption is observed to decrease with increasing surface coverage and the possible explanations have been discussed by Gundry and Tomkins.[13] First, the decrease may be due to

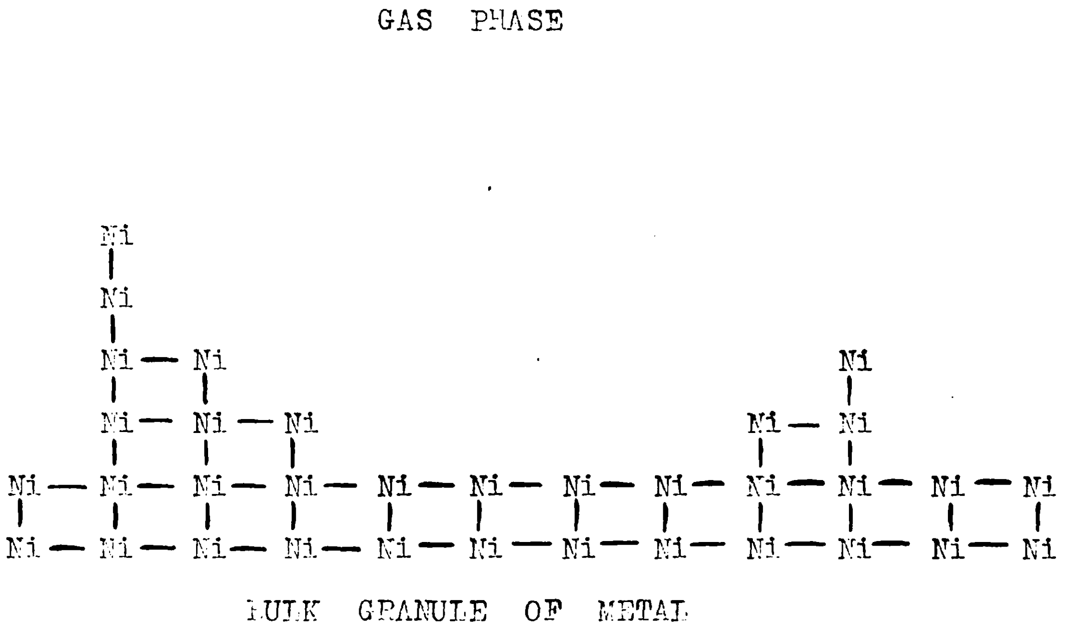


Fig. 3

surface heterogeneity. H. S. Taylor[14] in 1925 advanced the hypothesis that on the surface of a metallic catalyst there would be occasional groups of atoms fixed in metastable positions associated with high energy and chemical unsaturation relative to the atoms in the regular lattice below (see Fig. 3). The first addition of gas to such a surface will result in a preferential adsorption on the "active" sites either because the rate of adsorption on such sites is greater than on less "active" sites or if the adsorption is mobile because the adsorbed species will migrate to the sites of highest energy. Subsequent gas additions will be adsorbed on sites of progressively lower activity and the heat of adsorption will decrease. Regions of the surface where the heat of chemisorption is likely to be different from that at smooth parts of the surface are: (i) the points of emergence of screw and edge dislocations (ii) point defects, such as Frenkel and Schottky defects, situated in the outermost layers of the solid (iii) metallic and non metallic impurity centres.

A second explanation, due to Roberts[15], is that falling heats of adsorption are due to forces of repulsion between oriented dipoles of molecules in the adsorbed layer. Quantitative calculations have shown that the size of the heat decrease to be expected on the basis of dipole moments of the kind normally found is quite insufficient to fit the observations.

The third explanation, due to Eley[16] and Schwab[17], is based on the concept of work function. If it is assumed that in the formation of a chemisorbed layer, electrons are extracted from the solid, then, as coverage increases, more energy will be expended in forming the chemical bond since extra work will have to be done against the progressively increasing work function. If on the other hand an electron is donated by the gas or a covalency is formed, electrons from the gas enter the solid. Since in crystals these are bands of permitted electron energies, the first electron will enter the lowest unoccupied level of the band system and then higher and higher levels will be used as adsorption proceeds. Again the heat will fall. Although this effect may be significant in hydrogen-metal systems, the correlation between calculated and observed falls is frequently poor.

(iii) Freundlich Isotherm. In early studies of adsorption it became clear that many experimental data did not obey the Langmuir isotherm. An alternative isotherm, which was empiric at the time of its proposal, was suggested by Freundlich[18]. Titoff[19] had found that the amount of gas, x, adsorbed by charcoal varied with the equilibrium gas pressure p according to the equation $x = kp^{1/n}$ where k and n are constants; usually n is between 1 and ∞ and is characteristic of the particular system which is studied. Since the amount of gas adsorbed is proportional to a fractional power of the pressure, the Freundlich isotherm is often obeyed over wide ranges of adsorbed amount, and also by systems which do not obey the Langmuir isotherm. In spite of its original empiricism, the Freundlich equation may be derived if the following assumptions are made: (a) the heat of adsorption falls exponentially as the coverage is increased. (b) the decrease in heat is due to heterogeneity rather than to repulsive forces between adjacently adsorbed species. Two such derivations have been made, one of which uses a thermodynamic approach[20], the other a kinetic approach.[21]

(1V) The Tempkin Isotherm. A third form of adsorption isotherm was derived theoretically by Slygin and Frumkin[22] and popularised by Tempkin and Pyzhev[23] in their interpretation of the decomposition of ammonia on platinium and tungsten. This isotherm is based on the assumption that the heat of adsorption falls linearly with surface coverage. The equation may be written simply as $\theta = (\frac{1}{f})$ ln $(a_o p)$ where f and a_o are both constant at a given temperature. This expression is expected only to hold in the middle range of coverage (θ from 0.2 to 0.8) owing to the simplifying assumptions made in its derivation.

Section 1.7 Metal Catalysts.

Catalysts can be divided into two main categories (a) forms containing only one component, the metal, and (b) forms containing one or more components in addition to the metal. Into category (a) come unsupported metal powders, colloidal metals, evaporated metal films, wires and foils; into category (b) come a variety of supported and promoted metal catalysts. Metals which chemisorb molecules and also display catalytic activity are prone to contamination and metal surfaces which are exposed to air are covered either by a layer of adsorbed oxygen or a thin layer of metal oxide, and these may render the surfaces ineffective as catalysts. The nature and extent of any catalyst cleaning process depends on the use to which the material will subsequently be put. A distinction can be made between (a) the preparation and cleaning of surfaces to be used in fundamental studies of adsorption (b) the cleaning of surfaces to be used as catalysts. In the study of chemisorption and its role in catalysis two extreme approaches are possible. One is to take the solid surface in the condition known to be catalytically active and study gas adsorptions on such a surface. The approach is essentially empirical and the dangers are that outgassed, clean and reproducible surfaces are not employed. The other extreme is to strive to produce stringently clean surfaces and to study the interaction of simple molecules with such surfaces. The limitation here is that there is a tendency to recede farther away from the problems of primary concern in heterogeneous catalysis and move towards ever more simple systems.

(i) Films. The advent of ultra high vacuum techniques has made it possible to keep metal surfaces clean for a reasonable time and much work has been done in recent years on the preparation of clean metal surfaces. The metal is evaporated in vacuum from a wire, which is electrically heated, on to a substrate, which is usually glass, but sometimes another metal, or the cleaved face of a crystal. The wire is at first outgassed by heating in vacuum with continuous pumping, at as high a temperature as possible without significant evaporation of the metal. After outgassing, the metal is more strongly heated to evaporate it on to the inner wall of its containing vessel. This produces an evaporated metal film. Chemically significant work with such films was carried out as early as 1935 by O. I. Leypunsky but the widespread use of these films in catalytic research followed a paper by O. Beek, A. E. Smith and A. Wheeler.[25]

(ii) Powders. Whilst evaporation yields a film almost completely free from contaminants, metal powders can only be obtained in a 'clean' form with considerable difficulty. Metal powders may be prepared by the reduction of suitable compounds, usually oxides or chlorides in a stream of reducing gas. Hydrogen is the gas generally used and leaves no undesirable residues on the surface as do, for example, carbon monoxide and formic acid. It has been shown by Roberts and Sykes[26] that by subjecting nickel powder to prolonged reduction in purified hydrogen that surfaces were produced which in part simulated the behaviour of evaporated nickel films as judged by the activity with which the surface chemisorbed hydrogen at - 183°C. Another method of preparing nickel powders is the thermal decomposition of metal salts of organic acids; very often the formate is used. Nickel powders have been prepared by the decomposition of nickel carbonyl but the catalytic activity is limited by traces of adsorbed carbon monoxide which remain.[27]

(iii) Supported Metals. Supported metal catalysts are examples of catalysts containing a component other than the metal itself. Usually supported catalysts contain less than 20 per cent by weight of the metal. It has generally been thought that there is no chemical interaction between the metal and the carrier in supported metals. However, there is a growing body of evidence to suggest that some of the differences between supported and unsupported metals may be attributed to the support. Three methods of preparation are available for the production of supported catalysts (i) impregnation (ii) co-precipitation and (iii) deposition. The first of these is the most commonly used and involves soaking the carrier in a solution of the metal salt. The material is then dried and reduced to the metal by hydrogen at the appropriate temperature. In the co-precipitation method the simultaneous precipitation of metal and carrier from solution is induced. For example, with nickel, silica supported catalysts are obtained from a solution of the metal nitrate and sodium meta-silicate. In the deposition method the metal, or one of its compounds, is deposited from suspension onto a suspension of the carrier. For example, when hydrogen is passed through a solution of palladium nitrate in which activated charcoal is suspended the reduced metal deposits on the charcoal. Catalysts produced by the impregnation or deposition method have the active component available at the surface of the carrier. In co-precipitated catalysts some of the active material may be embedded within the carrier. Nickel-silica catalyst systems have been studied[28,29] in relation to catalyst preparation and the results have shown that some revision of the role of the carriers may be called for. The effect of the nature of the support and of crystallite size on specific activity has been found for nickel supported on silica-alumina. The hydrogenolysis of ethane to methane falls as the crystallite size increases.[30] The specific activity for this reaction of nickel supported on silica, alumina and silica-alumina changes as the support changes, being highest for silica and lowest for silica-alumina.[31]

Section 1.8 Bifunctional Catalysts.

When the metal is supported on a second component which is also catalytically active a dual-function or bifunctional catalyst is formed. For example, platinum on silica-alumina can be a bifunctional catalyst for hydrocarbon reactions. The platinum acts as a dehydrogenating catalyst, and an olefin formed can be converted by proton addition to a carbonium ion at an acid site on the silica-alumina surface. The carbonium ion can then isomerise by rearrangement of the carbon skeleton, after which a proton is released. In this way methyl cyclopentane can be converted to cyclohexene which may be further dehydrogenated on a platinum site to benzene. These catalysts have been reviewed by J. H. Sinfelt.[32]

Section 1.9 Experimental Aspects of Adsorption.

(i) Measurement of heats of adsorption. The strength of an adsorption bond is reflected in the magnitude of the heat of adsorption: the greater the amount of heat liberated per mole adsorbed, the stronger is the bond. If the heat of adsorption, Q, is large for a given species, catalysis may be hindered precisely because that species is too tightly held at the surface. If, on the other hand, Q is low, the species may not be adsorbed on the catalyst surface for a time long enough to facilitate reaction. It appears that catalysis requires a situation where the heat of adsorption is not too large to cause desorption problems and not too small to hinder rearrangement in the adsorbed phase.

Heats of adsorption may be determined experimentally by direct calorimetric measurement. Calorimetric measurements are of two kinds. First the heat liberated by adsorption may be used to cause a phase change in a surrounding

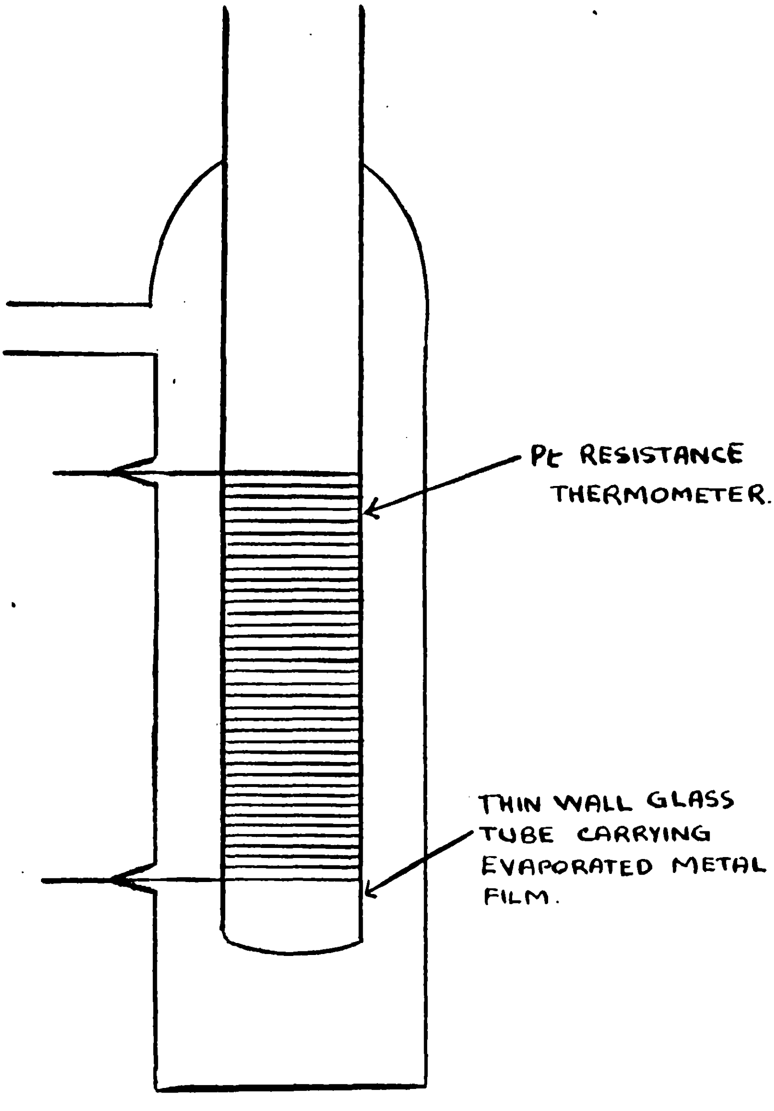

Pt RESISTANCE THERMOMETER.
THIN WALL GLASS TUBE CARRYING EVAPORATED METAL FILM.

Fig. 4

solid or liquid and as the heat causes the volume change in the surrounding substance the measurement is isothermal. Second, the escape of heat from the adsorbent may be prevented, and the heat determined from the rise in the adsorbent temperature. These measurements are adabiatic. Both methods may be used when the adsorbent is in powder form although the low surface area of evaporated metal films requires the use of an adabiatic calorimeter. The calorimeter of Beeck[33] and co-workers is shown in Fig. 4 and a similar type of calorimeter has been used by Brennan[34,35] et al. and Stone[36] for measuring the heats of adsorption of oxygen and hydrogen on a variety of evaporated metal films. Essentially the apparatus consists of two concentric tubes. The calorimeter proper is the lower portion of the inner tube and is made from very thin glass; above it is a constriction to minimise heat losses to the upper part of the system. Fine platinum wire is wound around the calorimeter to form a resistance thermometer. The metal filament is deposited on the inside of the eggshell tube from a heated filament and during the process cooling water is circulated through the outer jacket to prevent softening and collapse of the thin glass. The outer jacket is evacuated to produce a vacuum calorimeter and the temperature rise accompanying the admission of very small quantities of gas is then obtained.

(ii) Measurements of work function changes. The electron work function of a solid, $e\phi$, is defined as the energy required to remove an electron from the highest occupied level inside the solid into a vacuum outside its surface. Since, in general, the electronegativities of the adsorbate and adsorbent are different, adsorption involves electron donation to or from the adsorbent surface and dipoles are thus formed in the adsorbed layer. If the negative end of the dipole in the adsorbed layer points away from the surface, then the potential barrier through which the electrons escaping from the solid must pass will be increased, so that $e\phi$ is increased. Conversely, if the negative end of the dipole is directed towards the surface the value of the electron work function of the solid will be decreased. When the electronegativity difference between the adsorbate and adsorbent is small the dipole moment created will be small and the bond can then be described as essentially covalent; if the electronegativity difference is large, the dipole moment will correspondingly be large and the bond is then essentially ionic. The determination of the dipole moment of a chemisorption bond can therefore establish its nature.

If the adsorbed layer is treated as a parallel plate condenser, the capacity of such a condenser is given by $C = \frac{A}{4\pi d}$ where A is the area of the plate and d is the distance of separation. The voltage across the condenser

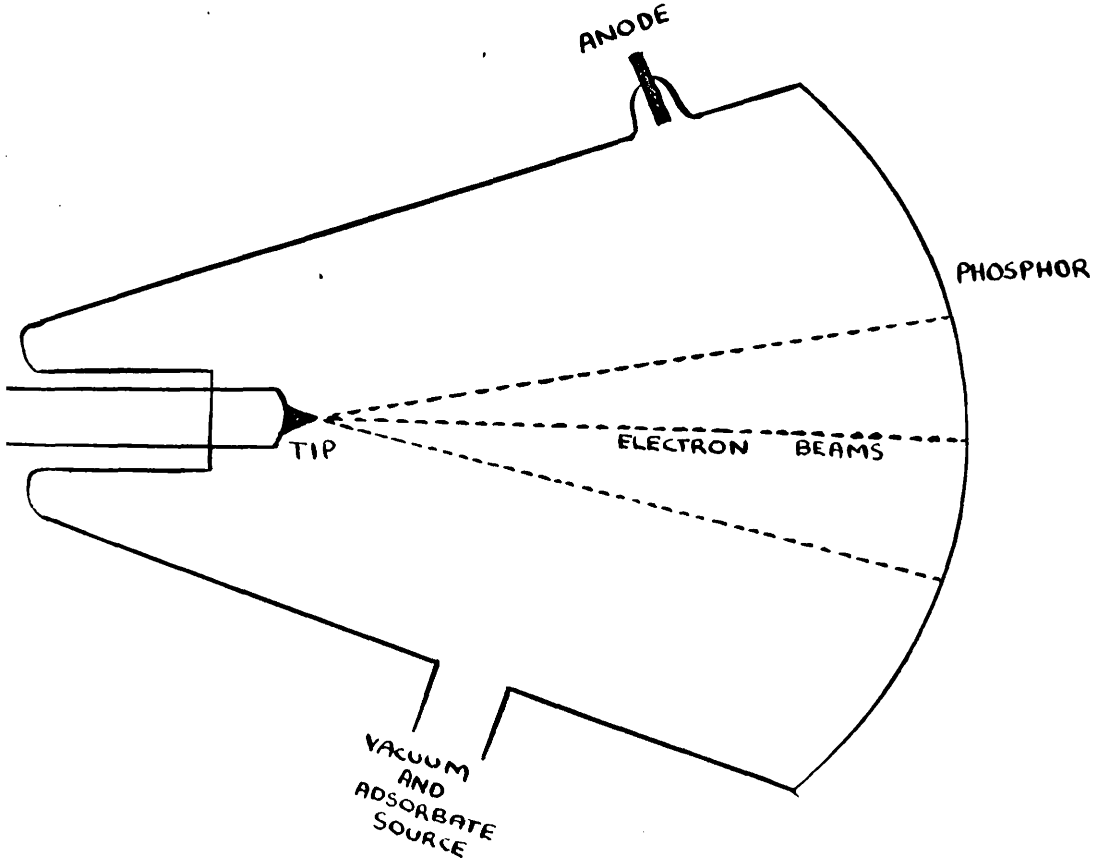

ANODE
PHOSPHOR
TIP
ELECTRON BEAMS
VACUUM AND ADSORBATE SOURCE

FIG. 5

is therefore: $V = \frac{4\pi dQ}{A}$. For the adsorbed layer $\left(\frac{dQ}{A}\right)$ equals the product of the dipole moment (μ) and the number of adsorbed species ($n_s\,\theta$), where n is the number of sites per cm^2. The potential drop across the adsorbed layer is therefore

$$\Delta V = 4\pi n_s \theta \mu$$

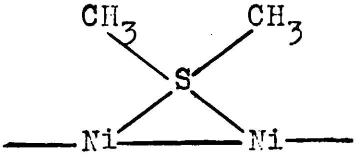
e ΔV is a measure of the change of energy required to remove an electron from the solid after adsorption and thus e $\Delta V =$ e $\Delta\phi$ and therefore $\Delta\phi = 4\pi n_s \theta \mu$ where $\Delta\phi$ is the change in work function on adsorption. $-\Delta\phi$ is termed the surface potential of the layer. The significance of this equation is that it enables the dipole moment of the adsorption bond to be calculated from measurement of the surface potential. From the value of μ it is possible to deduce whether the surface bonding is predominantly covalent, ionic or physical.

An important application of changes in work function following adsorption is the field emission microscope. The microscope was first developed by E. W. Muller[37] and lately it has been used by Gomer[38,39] and Becker[40] not only for the purpose of measuring work function changes but to observe the surface diffusion of adsorbed species. The surface under study is in the form of a minute tip (see Fig. 5) the radius of curvature of which is around 1,000Å and is surrounded by a conducting fluorescent screen. Since the radius of the tip is extremely small compared with the radius of the spherical anode field strengths of the order of 10^7- 10^8 V cm^{-1} are readily attained. The presence of a high external field can reduce the width of the potential barrier at a metal surface to such an extent that electrons approaching the surface may tunnel through the barrier and be emitted. The emitted electrons have very little kinetic energy and therefore follow the lines of force which diverge radially from the tip. The resulting fluorescent pattern displayed on the screen gives a magnified image of the emission from the solid and as the intensity of fluorescence at any point depends on the number of impinging electrons at that point a measure of the work function at the corresponding point on the solid surface is obtained. The etched tip used in the microscope is usually a single crystal and since the sharp end is hemispherical many different crystal planes are exposed. Changes in the work function of the various crystal faces when a gas is admitted can then be followed visually. The changes in intensity with time permit the calculation of the relative rates of adsorption on different crystal faces and, by heating the metal tip, rates of desorption can be studied. The resolution of the field emission microscope is limited to about 20Å. The field ion microscope was developed from the field emission microscope by E. W. Müller[41] and may be discussed at this point, not because of its relevance to the measurement of work function, but because of the similarity of the technique to field emission microscopy. The general experimental set up is very much the same in both techniques except that in field ion microscopy a large positive potential is applied to the fine tip and an imaging gas, usually heluim, is present at a pressure of around 10^{-3} torr. When a field of about 10^{8} V cm^{-1} is applied helium atoms are attracted to the tip by polarisation forces and ionisation takes place.[42] The ions are then accelerated radially outwards and impinge upon the phosphor where they form a projection image of the end of the tip. The pattern produced is similar to that obtained in field emission microscopy, but with the advantage that the resolution is increased to 3Å. As the probability of ionization of the helium depends upon the local geography of the surface of the end of the tip, the image on the screen reflects the fine details of this atomic structure. An important feature which arises from field emission adsorption studies is that the free energy of adsorption differs according to the plane on which adsorption takes place. Becker[40] has found for the tungsten oxygen system that (211) faces take up oxygen first, followed by (111), then (100).

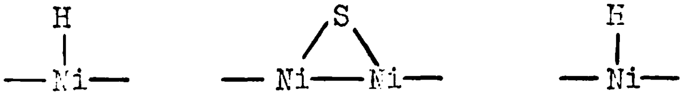
(iii) Electrical measurements. Another method which is used to study the nature of the bonding between adsorbent and adsorbate determines the change in resistance of a metal film deposited in vacuum when a gas is adsorbed onto the film surface. The underlying principle is that if conduction electrons are drawn from the metal and an electronegative layer is formed then the conductivity decreases. Similarly entry of electrons into the metal should increase the conductivity if the added electrons contribute to electrical conduction. The metal is evaporated onto the walls of a vessel containing two platinum contacts and the film resistance between them is measured. The film should be annealed above the adsorption temperature as their resistance may otherwise slowly alter with time. In calculating the change in the number of electrons per adsorbed atom the doubtful assumption is made that grain boundary resistance is negligible and that the only effect of chemisorption is to change the number of conduction electrons. Gases with high heats of adsorption, such as oxygen, are known to cause film sintering even after annealing[43] and this could well have an effect on the conduction properties of the film. Sachtler[44] has shown that the variation in conductivity when hydrogen is adsorbed by a nickel film is dependent on the initial cleanliness of the surface. Conductivity decreases are found when nickel films are prepared under rigorous vacuum conditions and an opposite effect results when a vacuum of 10^{-6} mm Hg is employed.

(iv) Magnetic measurements. Chemisorption often involves the unpaired electrons in solids, with a consequent change in their magnetic properties. Substances which possess unpaired electrons have a positive value of magnetic susceptibility and are, by definition, paramagnetic. As the magnetic properties are bulk and not surface properties the surface/volume ratio must be high, otherwise the effect of adsorption is not detectable; magnetic measurements are therefore usually carried out on fine powder samples. An experimental measurement of susceptibility can be made with a magnetic balance. The specimen is suspended from a balance beam so that it is half inside and half outside the region between the poles of a strong magnet (about 5000 gauss). When the field is applied a paramagnetic sample is drawn into the region and the force necessary to restore the original balance point is given by $mg = \frac{(X_1 - X_2)}{2} AH^2$, where A is the cross sectional area of the specimen, X_1 is its susceptibility and X_2 is the susceptibility of the surrounding atmosphere. When a ferromagnetic material, such as nickel, is being studied, it is best to measure the specific magnetisation, XH (where H is the field strength) because, for ferromagnetics, the susceptibility is large and dependent upon field strength. Difficulties in measurement arise when ferromagnetic materials are studied in a fine state of subdivision. When the particle size is in the region 100 - 300Å, the magnetic behaviour of ferromagnetic substances differs from that of ferromagnetic substances in bulk in that, with small particles, magnetisation is dependent on field strength and temperature in a similar manner to paramagnetic substances. As supported catalysts have the metal in a fine state of subdivision a low frequency a.c. permeater method of measuring susceptibility is employed.[45]

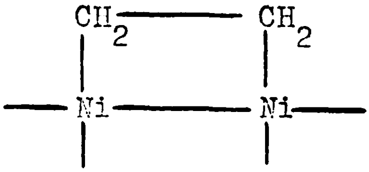
The results of Selwood[46] and his co-workers are most significant in this field in relation to catalytic studies. One of the best known examples of the use of the technique concerns the action of the catalyst poison, dimethyl sulphide, on nickel. When a plot of $\frac{\Delta M}{M}$ (where M is the intensity of magnetisation) is made against the volume of dimethyl sulphide chemisorbed a slope equal to that in the hydrogen on nickel case is obtained. This would suggest that sulphur is bonded to two nickel atoms as follows:



For hydrogen sulphide on nickel the $\frac{\Delta M}{M}$ plot gives a slope twice that of hydrogen; this is consistent with the following surface fragments:



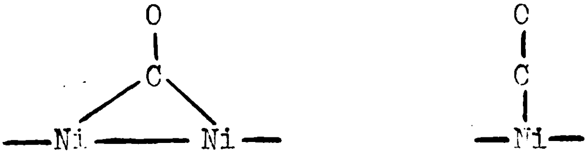
Ethylene behaviour on supported nickel has been found to vary significantly with temperature. At 0°C the magnetisation change caused by one molecule of ethylene is the same as that caused by one molecule of hydrogen. This can be interpretated in terms of associative bonding:



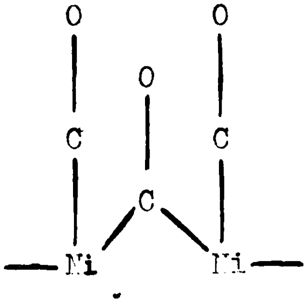
As the temperature of adsorption is increased to 28°C the number of bonds formed per molecule increases to 3, then to 8.4 at 100°C. This means that dissociation is taking place and this is verified by recovery of methane from the system.

(v) The infrared spectra of adsorbed gases. Interest in the study of adsorbed molecules and adsorption complexes on metals by infrared spectroscopy has increased steadily since about 1950. Eischens[47,48] and his co-workers have contributed greatly to the development of the technique and have studied several important gas-metal systems of interest in the field of catalysis.

Most of the experimental work has been carried out on supported metal catalysts; silica and alumina have been used as carriers, with particle sizes preferably in the range 150-200Å to reduce radiation losses by scattering. Metal particles of size $\leqslant$ 100Å are necessary to obtain measurable adsorption by transmission through the adsorbent. The infrared spectrum of the gas adsorbed on the silica or alumina support is observed and compared with that of the same system with the



Frequency (cm^{-1}) 1915 (strong) 2035 (strong)



Frequency (cm^{-1}) 1963 (medium)

Frequency (cm^{-1}) 2057 (medium) 2082 (weak)

Fig. 6

addition of metal particles.

Ethylene adsorption has been extensively studied on supported nickel. Eischens and Pliskin[48] have shown that the type of chemisorption depends on the pretreatment of the catalyst surface. The adsorption is associative or dissociative according to the temperature of the adsorption and the presence or absence of preadsorbed hydrogen. The associative type of adsorption is favoured when the olefin is adsorbed on nickel which has a preadsorbed layer of hydrogen. When the hydrogen is removed from the catalyst surface, by outgassing, before admitting the olefin, dissociative adsorption predominates. Admission of hydrogen to the associatively bonded species produces spectra indicative of ethyl group formation on the surface; these are likely intermediates in ethylene hydrogenation.

One of the most detailed studies has been on the adsorption of carbon monoxide on metal catalysts. In the case of nickel, Yates and Garland[49] have concluded that there are five distinct species of carbon monoxide adsorbed (see Fig. 6). The effect of the support on the infrared spectra of carbon monoxide adsorbed on platinum[48] and nickel[50] has been found to be significant. Eischens and Pliskin[48] found that the ratio of the concentrations of bridged to linear forms was much larger when platinum was supported on silica than when it was supported on alumina. O'Neill and Yates[50] showed that not only did the relative numbers of the two surface species differ but also the strength of the two types of adsorption varied with the nature of the support.

The infrared technique has also been applied to metal films. Harrod, Roberts and Rissmann[51] have observed the spectrum of carbon monoxide adsorbed on evaporated thin films of rhodium, platinum and iridium by transmission of infrared rays through several very thin films in series. The films were prepared in ultra high vacuum and considered to be atomically clean. Differences between the spectra of carbon monoxide on clean and contaminated surfaces were attributed to the unusual stricture of the clean films, which were unsintered.

Infrared spectrometry is proving to be a very useful tool in obtaining detailed information as to the nature of chemisorbed species. It must be remembered, however, that the species which this technique, and the other experimental methods too, identifies may not be one of importance in a catalytic process. The species may be present in large amount but be unreactive, whereas an important reactive catalytic intermediate may be present in too small an amount to be detected.

Section 1.10 The Application of Tracer Molecules to Studies of Adsorption and Catalysis.

(i) Radioactive isotopes.

Emmett and his co-workers[52,53,54,55] have applied the radiochemical technique to their investigations of the mechanism of the Fischer-Tropsch synthesis of hydrocarbons from hydrogen and carbon monoxide. Iron or cobalt catalysts are used at 200 to 300°C to produce hydrocarbons ranging from C_1 to C_{40}. A mechanism which appeared plausible involved a metallic carbide as an intermediate;

$$2Fe + 2CO \longrightarrow Fe_2C + CO_2$$

and

$$2Fe_2C + 2H_2 \longrightarrow C_2H_4 + Fe$$

This mechanism was examined[52] by forming $Fe_2{}^{14}C$ on the surface of an iron catalyst by exposing it to radioactive carbon monoxide. The labelled iron catalyst was then exposed to a mixture of inactive carbon monoxide and hydrogen. Emmett found that only about 10% of the radioactivity had been transferred from the surface to the gas phase. This showed that a carbide mechanism was not the principal path. Another possible pathway was through the formation of carbon-hydrogen-oxygen complexes on the catalyst. These complexes could act as nuclei for the construction of higher hydrocarbons by the addition of further molecules of carbon monoxide. Further investigations[53,54] with ^{14}C led to the conclusion that primary and secondary alcohols were involved as principal intermediates over Fischer-Tropsch catalysts. By labelling different carbon atoms of the alcohol it was shown that the growth of chains occured at the carbon atom to which the hydroxyl group was attached.

Another possible intermediate which has been examined is ketene, $CH_2=C=O$. When ketene was labelled in the methylene position and added to the synthesis gas it was observed that on cobalt or iron catalysts CH_2 groups from ketene did not build extensively into the higher hydrocarbons. It was deduced that ketene acts as an initiator in a similar manner to alcohols as the radioactivity per molecule of the synthesis products was independent of the number of carbon atoms per molecule.

The work of Campbell and Thomson[56,57] provides an example of the application of radioactive isotopes to the question of catalyst poisoning. Mercury poisons the activity of a nickel catalyst surface and, once deposited, the atoms of mercury are virtually impossible to remove. Campbell and Thomson, by using tritiated hydrogen and the mercury isotope ^{203}Hg, found that mercury readily displaced hydrogen from nickel surfaces at 20°C but that total displacement was not observed even after multilayer mercury adsorption. With films covered to extents less than 50% of their adsorptive capacity, hydrogen corresponding to 7% of that capacity could not be displaced. For fully covered films, 16.5% was retained. Cyclopropane and propylene were adsorbed on Ni films and the catalysts exposed to mercury vapour. The ability of mercury to displace cyclopropane as well as hydrogen, but not propylene, corresponded to the ability of mercury to poison the hydrogenation of cyclopropane but not that of propylene.

(ii) Use of stable isotopes.

In 1933 deuterium became available for catalytic studies. Early investigatons followed hydrogen exchange reactions by measuring the dilution of deuterium by hydrogen by means of thermal conductivity. Farkas and Farkas[58] and Farkas[59] studied the exchange of hydrocarbons with deuterium on Pt catalysts in this way. Three major points were established by this early work (i) the exchange of hydrocarbons with deuterium occurs more readily than the cracking of hydrocarbons despite the fact that C-H bonds are stronger than C-C bonds (ii) a dissociative mechanism is probably involved (iii) the ease of exchange depends on the hydrocarbon and the order of reactivity is roughly

$$\text{cyclo} - C_6H_{12} \cong C_6H_{14} \cong C_4H_{10} > C_3H_8 > C_2H_6 \gg CH_4$$

The advent of the mass spectrometer as an analytical tool has enabled the incorporation of deuterium into hydrocarbons to be observed and a wealth of detail about the nature of reactions taking place on the catalysts has been obtained. One of the first reactions studied[60] by this technique was the exchange between CH_4 and CD_4 on a silica-alumina caralyst. In 1950, Turkevitch et al.[61] examined the exchange and deuteration of ethylene on a nickel wire and found that the ethane which was produced initially contained a substantial amount of C_2H_6. Since then much work has been done in this field, especially by Bond,[62] Burwell,[63] Kemball[64] and their co-workers.

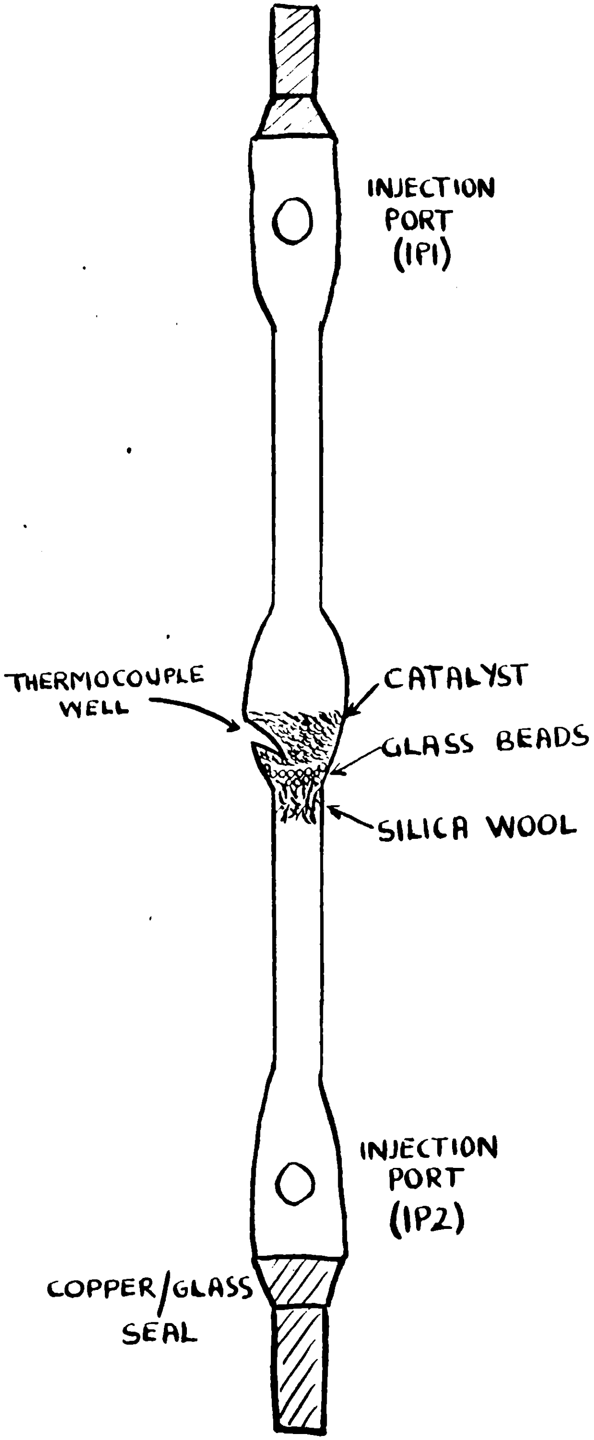
Some studies have been made of the exchange reactions between deuterated and non deuterated olefins in the absence of hydrogen or deuterium. In early experiments, no exchange was found between ethylene and ethylene - D_4 over a nickel wire at 76° in times much longer than those required to effect hydrogenation.[65] The failure in this system was at least partly due to the small surface area used, for exchange between ethylene - D_4 and propylene and butenes[66] has been detected using nickel powder at 45°. Exchange between ethylene and deuterated 1 - butene and 2 - butene has also been found using Raney nickel and palladium charcoal catalysts at 110°.[67] Ethylene has been found to exchange with ethylene - D_4 over nickel wire and nickel-kieselguhr at room temperature.[68]

The application of tracer techniques has been accepted as a well established and elegant method of approach to the problems involved in the study of adsorption and catalysis.

In the present study the radioactive hydrogen isotope, tritium, has been used to study the reactivity of hydrogen retained on a variety of nickel catalysts after reduction. In particular, its behaviour in hydrogen and ethylene exchange has been observed. Different types of nickel catalyst have been used to investigate the effect of the catalyst form and composition on the reactivity of the metal.

The state and reactivity of the surface species after ethylene adsorption has been studied by allowing the nickel catalysts to adsorb labelled ethylene and then determining the exchange with gas phase ethylene. By using $^{14}C_2H_4$ and C_2D_4 the reactivity of both the hydrogen and carbon of the ethylene molecule in the exchange reaction has been studied separately to give an insight into the exchange mechanism.

Fig. 7


INJECTION PORT (IP1)
THERMOCOUPLE WELL
CATALYST
GLASS BEADS
SILICA WOOL
INJECTION PORT (IP2)
COPPER/GLASS SEAL

CHAPTER 2. THE EXPERIMENTAL SYSTEM

The apparatus consisted of a gas flow system which contained the catalyst reactor and into which injections of sample gases could be made. A chromatography system separated and detected the reaction products and was linked to a gas proportional counter which analysed the radioactive samples in the tracer experiments. The design of the flow system was based on the design of a microcatalytic reactor developed by Kokes, Tobin and Emmett.[69]

Section 2.1 The Catalytic Reactor.

The vessel (see Fig. 7) was made of 'Pyrex' glass with copper-'Pyrex' seals at each end. The metal of the seals had been turned down to ¼" to accommodate 'Swagelok' couplings which united the reaction vessel to the rest of the metal system. A small piece of nylon tubing was inserted between the hydrogen inlet and the switch valve (SV1) to minimise the stress at the glass to metal seals when the couplings were tightened. A pipette shaped vessel had been chosen to keep the dead space to a minimum while allowing the required quantities of catalyst to be used without the catalyst bed being deep enough to act as a chromatographic column. The catalyst was supported by small glass beads resting on a plug of silica wool. The wool had to be packed in such a way that particles of catalyst were not carried through it,

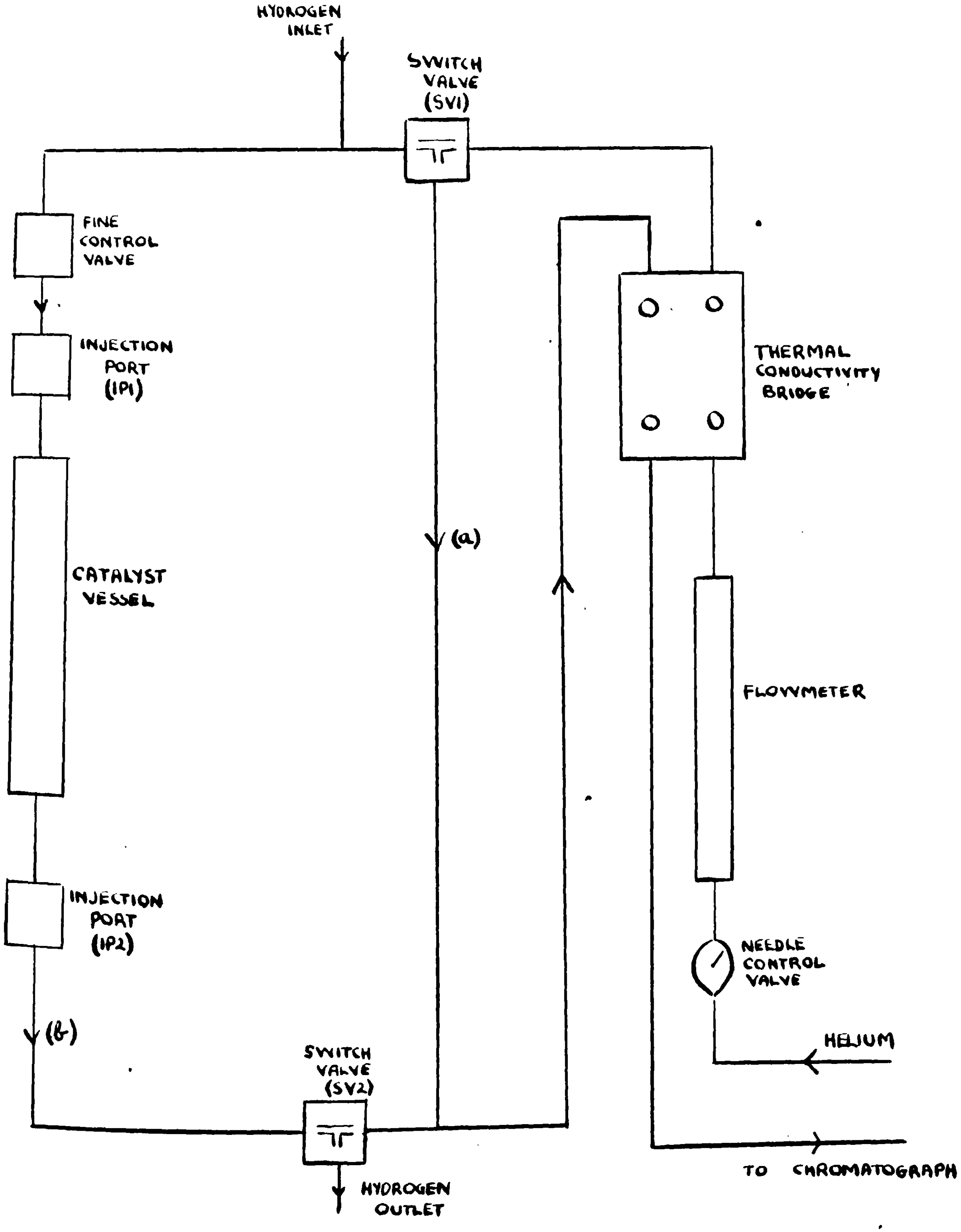

HYDROGEN INLET
SWITCH VALVE (SV1)
FINE CONTROL VALVE
INJECTION PORT (IP1)
CATALYST VESSEL
INJECTION PORT (IP2)
(b)
(a)
THERMAL CONDUCTIVITY BRIDGE
FLOWMETER
NEEDLE CONTROL VALVE
HELIUM
SWITCH VALVE (SV2)
HYDROGEN OUTLET
TO CHROMATOGRAPH

FIG. 8

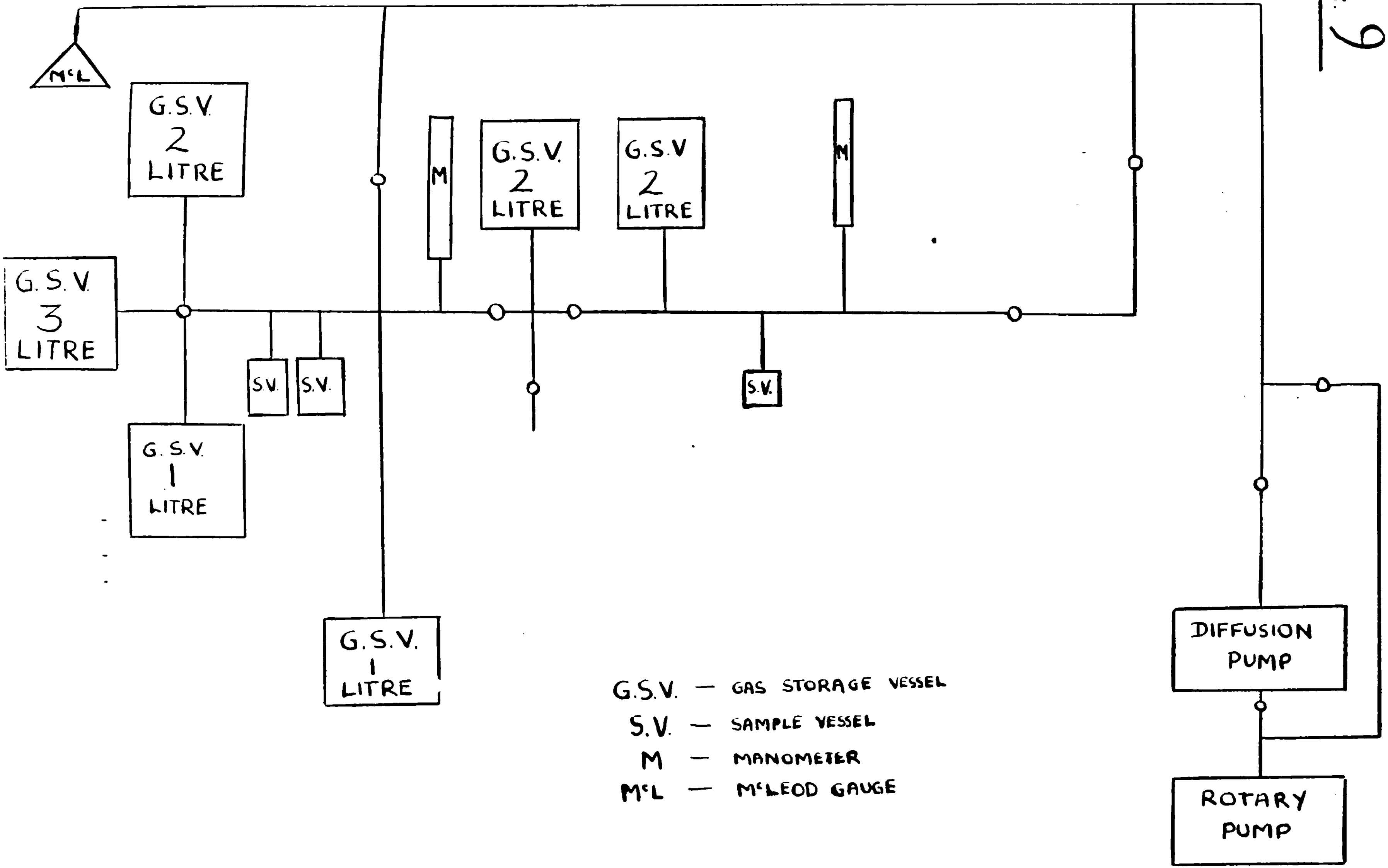
while at the same time allowing an unrestricted flow of the helium carrier gas. Injection ports IP1 and IP2, for reaction and calibration injections respectively, were situated above and below the catalyst bulb. Their diameter was such that a tight seal was obtained with ¼" serum caps (SUBASEAL, ESCO RUBBER CO.) which had both internal and external sealing edges.

The temperature of the catalyst was varied by a cylindrical electric furnace surrounding the catalyst vessel. The current to the furnace was controlled by a 'Variac' variable transformer and the temperature of the catalyst was recorded by a 'Comark' electronic thermometer (Type 1602). The thermocouple lead (chromel/alumel) was inserted into the well in the reactor and bound with asbestos string. A heat shield, in the form of an aluminium plate, covered the top of the furnace and deflected the rising hot air from the subaseal cap in IP1.

Section 2.2 The Catalyst Section.

The construction of the catalyst section is shown in Fig. 8. The flow of the carrier gas, helium, was regulated by a needle valve (EDWARDS HIGH VACUUM LTD.) and measured by a 'Rotameter' gas flowmeter which had been calibrated against a soap bubble flowmeter at the outlet of the system. From the 'Rotameter' the helium passed through the reference side

FIG. 9


M'L
G.S.V. 2 LITRE
G.S.V. 3 LITRE
G.S.V. 1 LITRE
S.V.
S.V.
G.S.V. 1 LITRE
M
G.S.V. 2 LITRE
G.S.V 2 LITRE
M
S.V.
DIFFUSION PUMP
ROTARY PUMP
G.S.V. — GAS STORAGE VESSEL
S.V. — SAMPLE VESSEL
M — MANOMETER
M'L — M'LEOD GAUGE

of the thermal conductivity cell associated with the chromatographic system (section 2.5). The rotary switch valve (SV1) led the gas either directly back through the chromatograph and counter via line (a), the by-pass circuit, or through a Nupro fine control valve over the catalyst section (b) and through a second switch valve (SV2). The hydrogen used for the in situ reduction of the catalysts entered the section through a T-piece after SV1 and passed out to the atmosphere through SV2. A second bubble flowmeter was attached to this outlet to measure the rate of hydrogen flow during reduction. In the meantime the carrier gas could flow through the rest of the system via the by-pass circuit.

Section 2.3 The Vacuum System.

A vacuum apparatus (Fig. 9) was used to store and prepare the gases for the reaction studies. The pumping system consisted of a mercury diffusion pump backed by a rotary oil pump and included the appropriate traps. Large amounts of gas could be removed from the system via a by-pass without interfering with the operation of the diffusion pump. Two connections were made from the main (25 mm) line to a secondary manifold (12 mm) which was divided by 2 mm traps and connected to six gas storage reservoirs and three sample vessels fitted with injection ports and serum caps. An outlet to atmosphere was used to fill the reservoirs with the required gases and their pressures, relative to atmospheric pressure, were read on two open ended manometers. All taps and joints were lubricated with 'Apiezon N' vacuum grease.

A M^{c}Leod gauge was fitted to the system to measure the pressure in the evacuated system and the residual pressure over condensed hydrocarbons. The volume of the gauge bulb and capillary (158.9cc) was calculated from the amount of mercury required to fill the gauge to that point. When the mercury in the open capillary was level with the top of the closed limb, the pressure was given by $\frac{a \times h_c^2}{158.9}$cm where a (the cross sectional area of the precision bore capillary) = $(3.142)(0.075)^2\text{cm}^2 = 0.01767\text{cm}^2$ and h_c is the difference in mercury levels in cm. The pressure in the system at any time was thus given by $1.11 \times 10^{-4} \times h_c^2$cm.

Section 2.4 The Gas Syringes.

Gas tight syringes (HAMILTON COMPANY) were used to transfer samples from the vacuum storage system to the flow system. When Chaney adaptors are fitted to the syringes a reproducibility of the injection size of 0.01% is claimed. Syringes of 1.0ml, 2.5ml and 10ml capacity were used in the present studies. 'Cold flow' of the teflon tip occured after prolonged use resulting in a loss of their gas-tightness. This was remedied by suspending the tips of the plungers over boiling water for one hour.

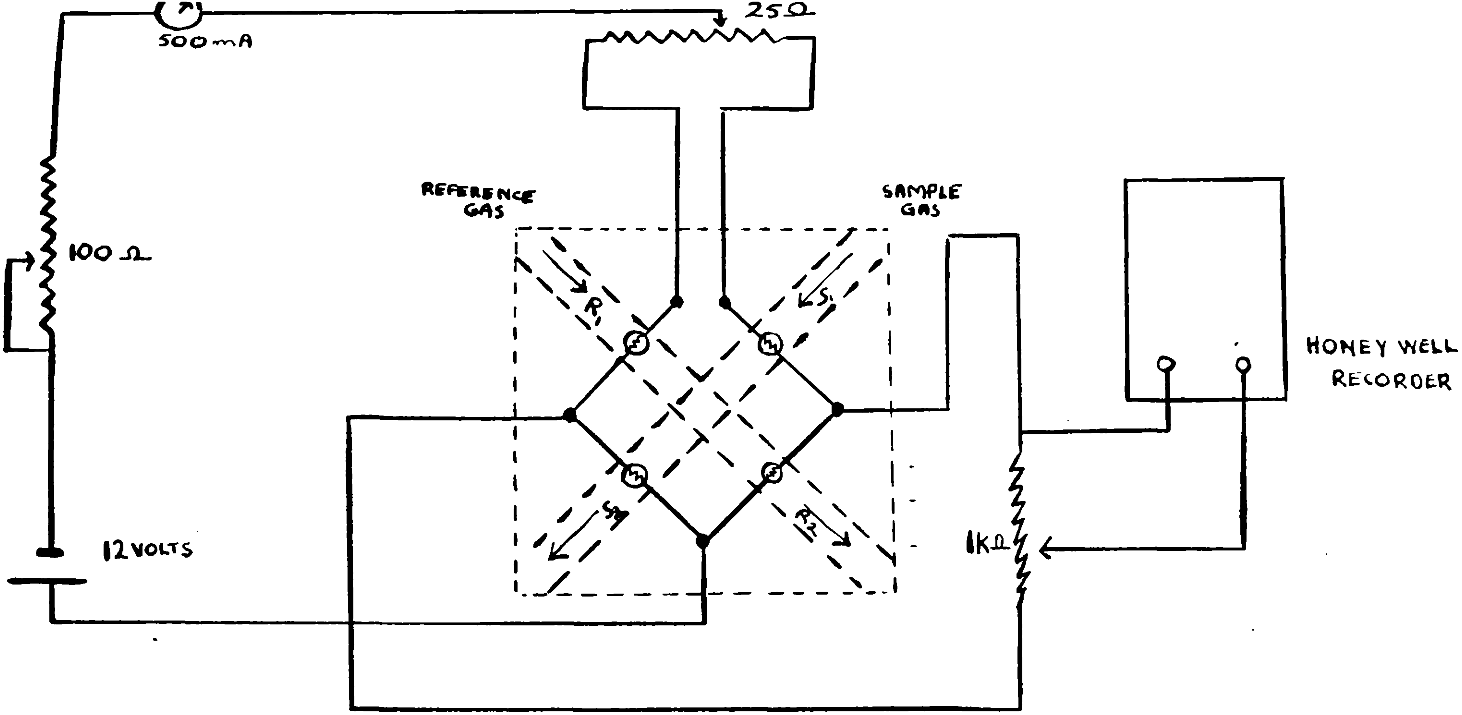
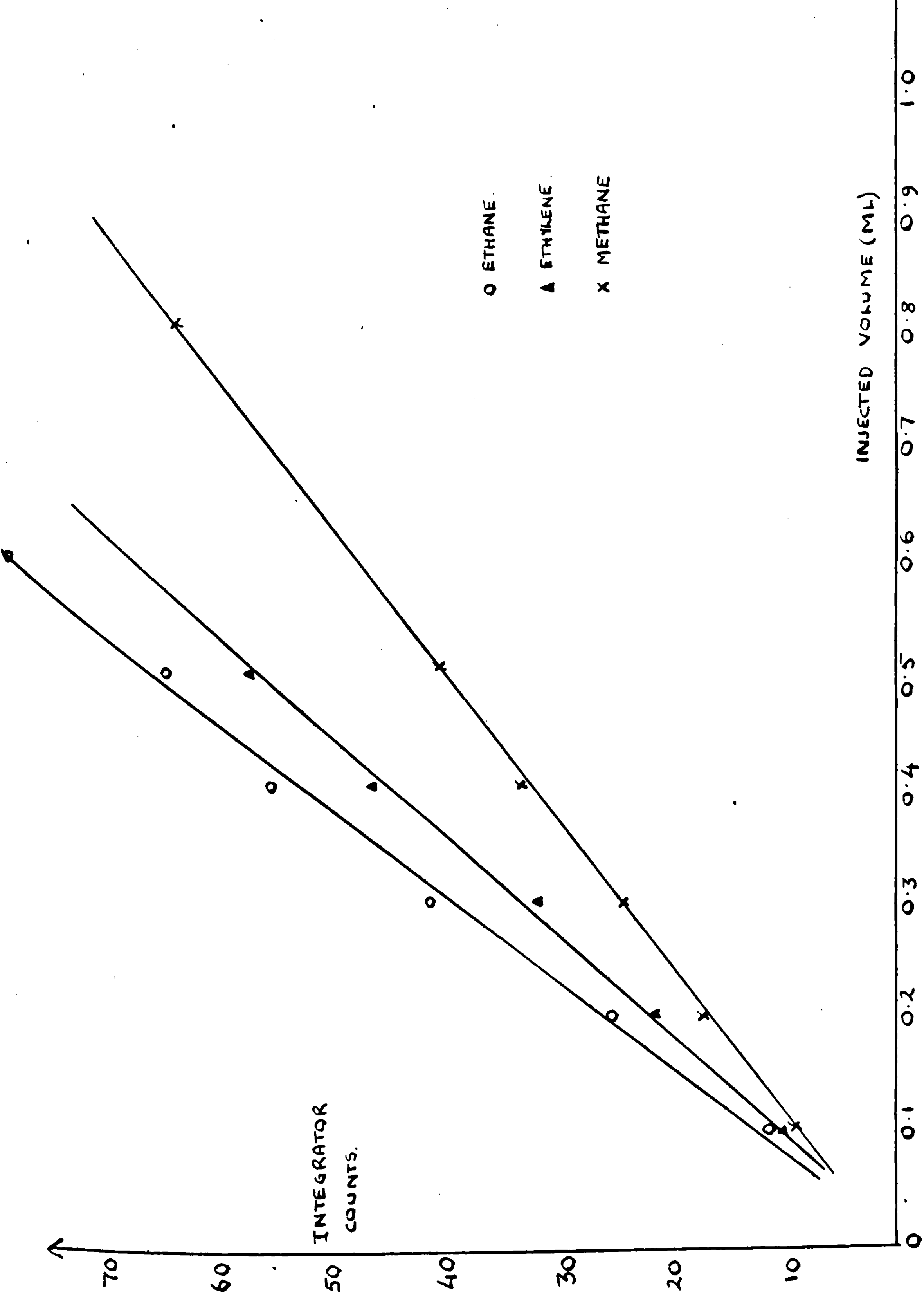

500mA
25Ω
100 Ω
12 VOLTS
REFERENCE GAS
SAMPLE GAS
R1
S1
S2
R2
1KΩ
HONEY WELL RECORDER

FIG. 10

Section 2.5 The Chromatograph.

For all the hydrocarbon analyses, a 4' long, ¼" o.d. copper column filled with 40/60 silica gel was used. The furnace for the column was constructed from a 14" length of 'Pyrex' tubing of diameter 3". 30 yards of nichrome tape (11.3ohms/yard) were wound onto the tube and enclosed in asbestos paper. The tube was housed in an asbestos pipe using 'vermiculite' packing as a thermal insulator. The W-shaped copper column, was packed into the heating tube with steel wool to improve thermal conductivity. A thermometer in the steel wool recorded the temperature which was regulated by a 'Variac' variable transformer. A previous worker[70] had found that a column temperature of 80°C and a flow rate of 60ml min^{-1} for the helium carrier gas provided the best operating conditions for the separation of methane, ethane and ethylene. However as the column was run for long periods at 80°C, accummulation of water in the silica gel reduced the resolving power. Baking the column out at 160°C in a slow flow of helium overnight restored the activity of the silica. The components of the reaction eluant separated by the chromatography column were detected by a thermal conductivity bridge (GOW MAC INSTRUMENT CO.) containing four Rhenium-Tungsten filaments arranged in the form of a Wheatstone bridge (see Fig. 10). Helium carrier gas was passed through two of the bridge filaments (R_1 and R_2) before entering the catalyst vessel section and through the other pair of filaments (S_1 and S_2) at the exit of the column. When the column was being baked out the 'Swagelok' connections to the detector unit were removed to avoid damage to the filaments by desorbed water. The chromatograph was used with a filament current of 200ma and the power supply to the bridge was a 12 volt battery which was kept on constant charge when not in use. The bridge was coupled to a Honeywell -0.25 to 2.5 mV recorder fitted with an electromechanical continuous integrator unit. It had been previously found[71] that the integrator was not perfectly linear in response throughout the range of the recorder, deviations being greatest at outputs less than 2% full scale deflection. As the output was continuous the integrator had to be read and zeroed after every peak. The greatest inaccuracies in peak area determination by the integrator were obtained with very small quantities of reaction product. At the start of each experiment, calibration injections of the volume of gases to be used were made to test the sensitivity and reproducibility of the experimental conditions. Day to day fluctuations in retention times and integrator readings for calibration doses were observed and if an experiment was particularly long the calibration procedure was repeated at frequent

Fig. 11


INTEGRATOR COUNTS.
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
INJECTED VOLUME (ML)
o ETHANE
▲ ETHYLENE
x METHANE

intervals. To relate the areas of reaction eluant peaks with hydrocarbon volumes, integrator readings were taken for different volumes of methane, ethane and ethylene. When plotted, these gave a good linear relationship (see Fig. 11). These data were used to obtain the relative sensitivity of the detector system to the different hydrocarbons. From the gradients of the graphs sensitivity factors were obtained for methane and ethane relative to ethylene. When these factors were multiplied by the integrator counts for methane and ethane in reactor eluant, product quantities could be calculated in ml.

The average retention times and sensitivity factors for the hydrocarbons on the silica solumn are shown in Table 1. The difference in retention times for injections made above and below the catalyst may be attributed to a slight 'chromatographic effect' by the catalyst. This was most noticeable at a catalyst temperature of 23°C.

TABLE 1

RETENTION TIMES ON SILICA COLUMN

He Flow Rate of 60ml min^{-1}. Column Temperature Of 80°C.

GAS	SENSITIVITY FACTOR	RETENTION TIME (CALIBRATION)	RETENTION TIME (REACTION) 20°C
METHANE	1.23	1 min 15 sec	1 min 20 sec
ETHANE	0.80	2 min 50 sec	3 min
ETHYLENE	1.00	4 min 35 sec	4 min 45 sec
HYDROGEN	-	1 min	1 min 10 sec

Section 2.6 Materials.

(i) Various nickel catalyst preparations were used in the investigations.

(a) The metal was supported on 'Aerosil' silica and 'γ' alumina (both from DEGUSSA LTD.) at concentrations of 0.1 and 5% by the impregnation of Analar nickel nitrate hexahydrate onto a aqueous slurry of the support material. The catalysts were first dried at 110°C overnight, calcined at 450°C for 3 hours and then reduced in situ, usually overnight at a temperature of 400°C and a hydrogen flow rate of 30ml min^{-1}. For support studies samples of alumina and silica were treated in the same way.

(b) Nickel powder was prepared in situ by the thermal decomposition of nickel formate with continual removal of the products formed by means of a stream of pure hydrogen. A previous worker[72] had found that the nickel formate supplied by the BRITISH DRUG HOUSES COMPANY was contaminated with NH_4^+ salts. To avoid the possibility of reaction poisoning the formate was produced from Analar reagents as described by Csuros, Geizy and Szabo.[73]

(c) A nickel phosphorus alloy catalyst was prepared as described by Morikawa.[74] Nickel hydroxide dispersed in water was reduced with a sodium hypophosphite solution and heated to 90-100°C. A black precipitate was formed and hydrogen was evolved. The powdery precipitate was washed with water at first, then with alcohol and finally with ether, and allowed to dry in air at room temperature.

Surface area determination of the supported metal catalysts by nitrogen absorption were made by JOHNSON, MATTHEY AND COMPANY, LTD. These results and the surface area figures supplied by DEGUSSA LTD. for the supports are shown in Table 2.

TABLE 2.

SAMPLE	NITROGEN SURFACE AREA (m^2g^{-1})
Al_2O_3	100
0.1% Ni on Al_2O_3	124
5% Ni on Al_2O_3	69
SiO_2	380 ± 40
0.1% Ni on SiO_2	453
5% Ni on SiO_2	462

(ii) The carrier gas, helium, was obtained from AIR PRODUCTS LTD; a purity of 99.995% was claimed. The gas was passed through a 5A molecular sieve maintained at -195°C to remove any trace of water vapour that might upset the operation of the proportional counter. As chromatographic detection in the system depended on the difference in thermal conductivities of the gases used a comparison of the conductivity values relative to the flow gas, helium, had to be made. It can be seen from Table 3 that because of the similarity in values for helium and hydrogen accurate quantitave measurements of hydrogen volumes were not possible. Good response was obtained for methane, ethane and ethylene.

TABLE 3.

GAS	THERMAL CONDUCTIVITY cal/(sec)(cm^2)($^\circ$C/cm) x 10^{-6}
Helium	36.03
Hydrogen	44.63
Methane	8.18
Ethane	5.12
Ethylene	4.92
Nitrogen	6.24

(iii) Hydrogen was obtained from the BRITISH OXYGEN COMPANY, LTD., and before use was passed through an Engelhard Deoxo Hydrogen Purifier and a 5A molecular sieve maintained at -195°C.

(iv) The methane used to form a counting mixture with helium was obtained from AIR PRODUCTS LTD. and was the CP grade. The gas flow was regulated with a needle valve (EDWARDS HIGH VACUUM LTD.) and before entering the counter passed through a slow flow bubble meter containing concentrated sulphuric acid; this removed any water vapour present in the gas. The meter was calibrated against the bubble flowmeter at the outlet of the system and a good linear relationship between the number of bubbles and the flow rate was obtained. Calibration was thus in terms of gas at atmospheric pressure.

(v) Ethylene and ethane were obtained from the BRITISH OXYGEN COMPANY LTD., and were purified by condensing and degassing until no impurity was recorded on the chromatograph when a gas sample was injected into the flow system.

(vi) ^{14}C- ethylene was supplied by the RADIOCHEMICAL CENTRE, AMERSHAM. The ampoules contained 0.5mCi of ethylene of specific activity 47.9mCi/mM and were attached to the gas inlet on the vacuum system. After evacuation the seal was broken and the radioactive gas diluted to the required activity by the transfer of inactive ethylene from a storage bulb.

(vii) The tritium was also obtained from the RADIOCHEMICAL CENTRE. A one curie sample, 0.4cc at S.T.P. and of 98% isotopic abundance was diluted to one litre with purified hydrogen. The activity was further diminished by diluting samples at 1cm pressure in a 3 litre bulb to atmospheric pressure. As calibration injections were incorporated in each series of reaction injections, no attempt was made to reproduce exactly dilutions of labelled hydrogen or hydrocarbon from one run to the next.

(viii) Ethylene-D_4 was obtained from MERCK, SHARP and DOHME LTD., Montreal, Canada who claimed an isotopic purity of 99%.

(ix) The carbon monoxide used was grade X from the BRITISH OXYGEN COMPANY LTD.

Section 2.7 The Proportional Counter.

The proportional counter takes its name from the proportionality between the output pulse and the initial ionisation. The absolute pulse size produced in the proportional region is smaller than in the Geiger plateau region and in contrast to pulses from G.M. tubes require several stages of valve amplification. Stable and reproducible measurements and short dead times after each pulse are characteristic of proportional counters. The design of the counter and the voltage applied are such that a very high voltage gradient exists in the vicinity of the positive electrode. Under this voltage gradient the liberated electrons undergo a high acceleration, and are capable of producing further ionisation by collision with gas molecules. Under suitable conditions gas multiplications of 1,000 or more are possible, the total ionisation (and hence pulse size) being proportional to the initial ionisation.

In order to obtain the high electric fields required to produce gas amplification, the proportional counter usually takes the form of a metal cylinder, having a fine wire, insulated at its ends, stretched along its length.

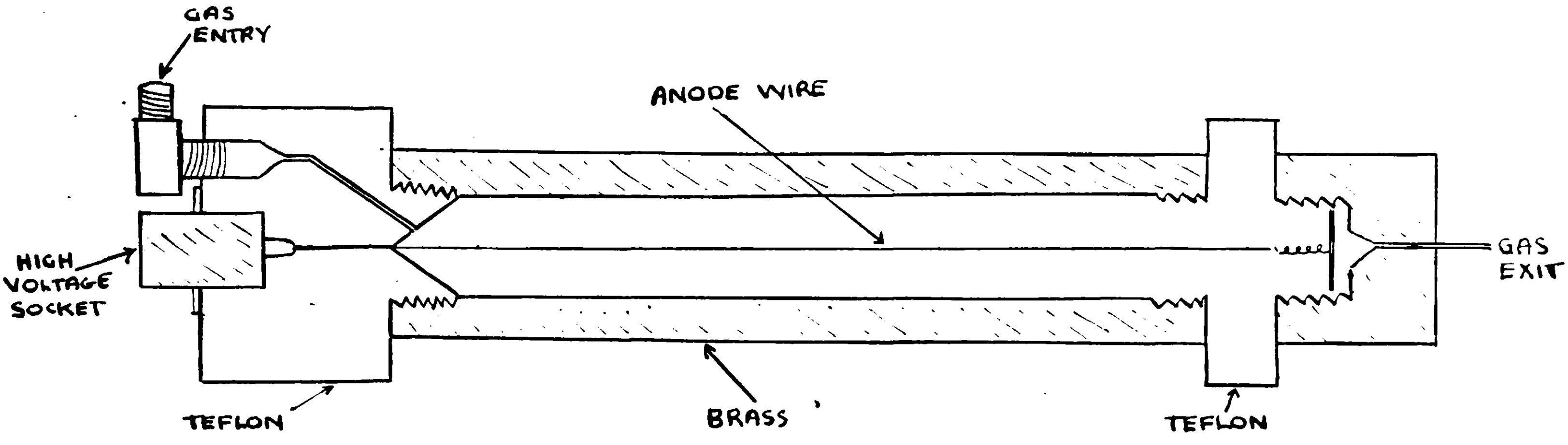
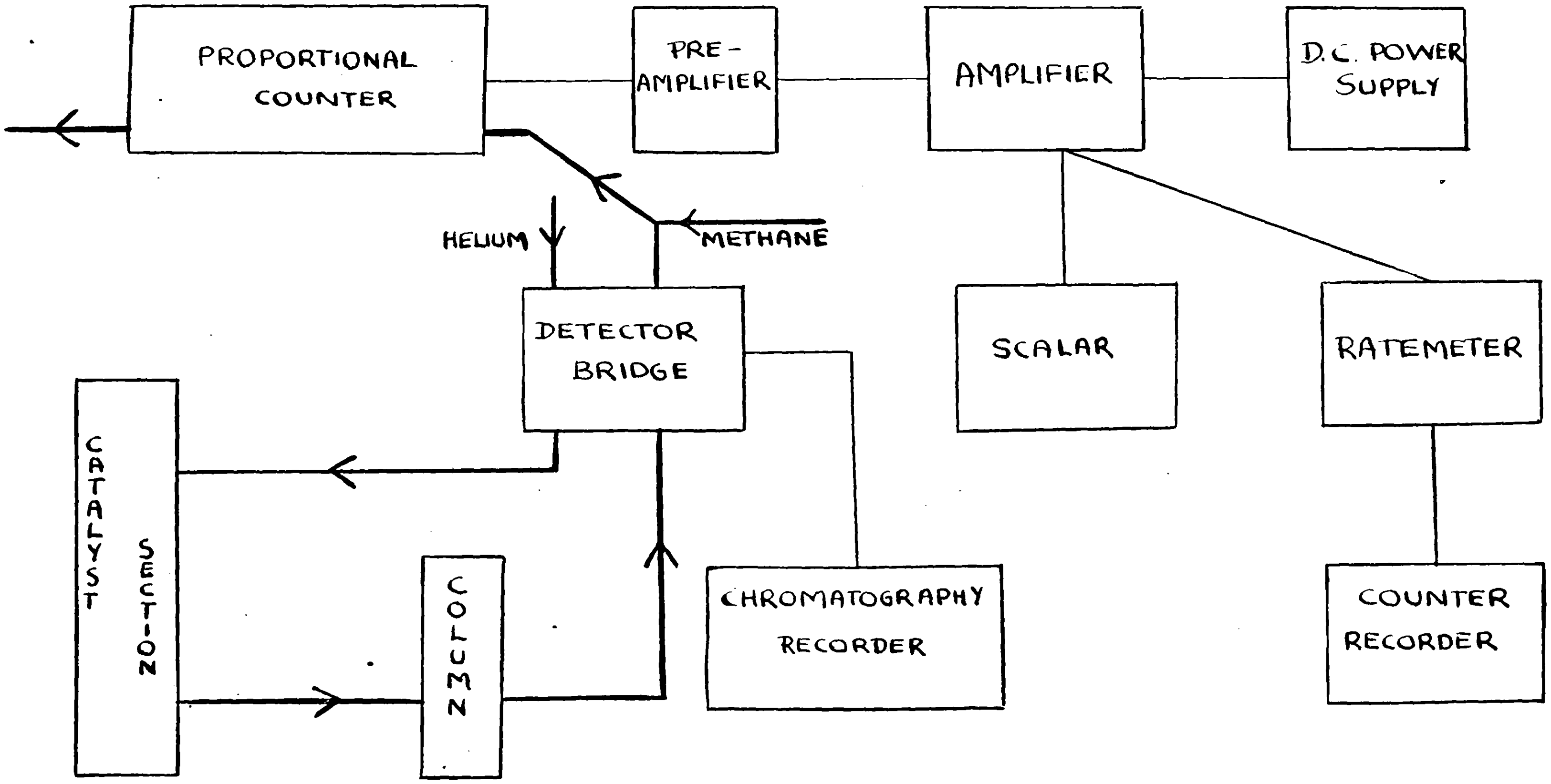

GAS ENTRY
ANODE WIRE
HIGH VOLTAGE SOCKET
GAS EXIT
TEFLON
BRASS
TEFLON

FIG. 12

FIG. 1


PROPORTIONAL COUNTER
PRE-AMPLIFIER
AMPLIFIER
D.C. POWER SUPPLY
HELIUM
METHANE
DETECTOR BRIDGE
SCALAR
RATEMETER
CATALYST SECTION
COLUMN
CHROMATOGRAPHY RECORDER
COUNTER RECORDER

As the samples are completely enclosed within the counting chamber, the counter is very sensitive to slightly radioactive samples.

Carbon -14 and tritium (a very weak β emitter, E max 0.018 MeV) were used in the present work. The counter design (fig. 12) follows that of Schmidt-Bleck and Rowland[75] modified to accommodate different connectors for the gas inlet and high voltage supply. A schematic diagram of the electronic instrumentation associated with the counter is shown in Fig. 13. The reproducibility of proportional counter measurements is dependent on a stable high voltage supply and this was supplied by a Dynatron (type N103) unit, the output from which was variable from 300 to 3300 volts. The amplification was through a Dynatron (type 50D) pulse amplifier, consisting of high gain preamplifier connected to the counter and a main amplifier in which the gain could be altered in 2 db steps in the range 0 - 40db. The output from the amplifier was fed to an EKCO High speed scalar (type 530D), with a dead time of 5 μsec, and to an EKCO N522C ratemeter which integrated arriving pulses into a direct current and recorded this on a microammeter calibrated directly in pulses per second. A 'Servoscribe' potentiometric recorder was coupled to the ratemeter and displayed the observations of the counter as peaks. This continuous record acted as an aid in determining when to start and stop the scalar counts.

FIG. 14

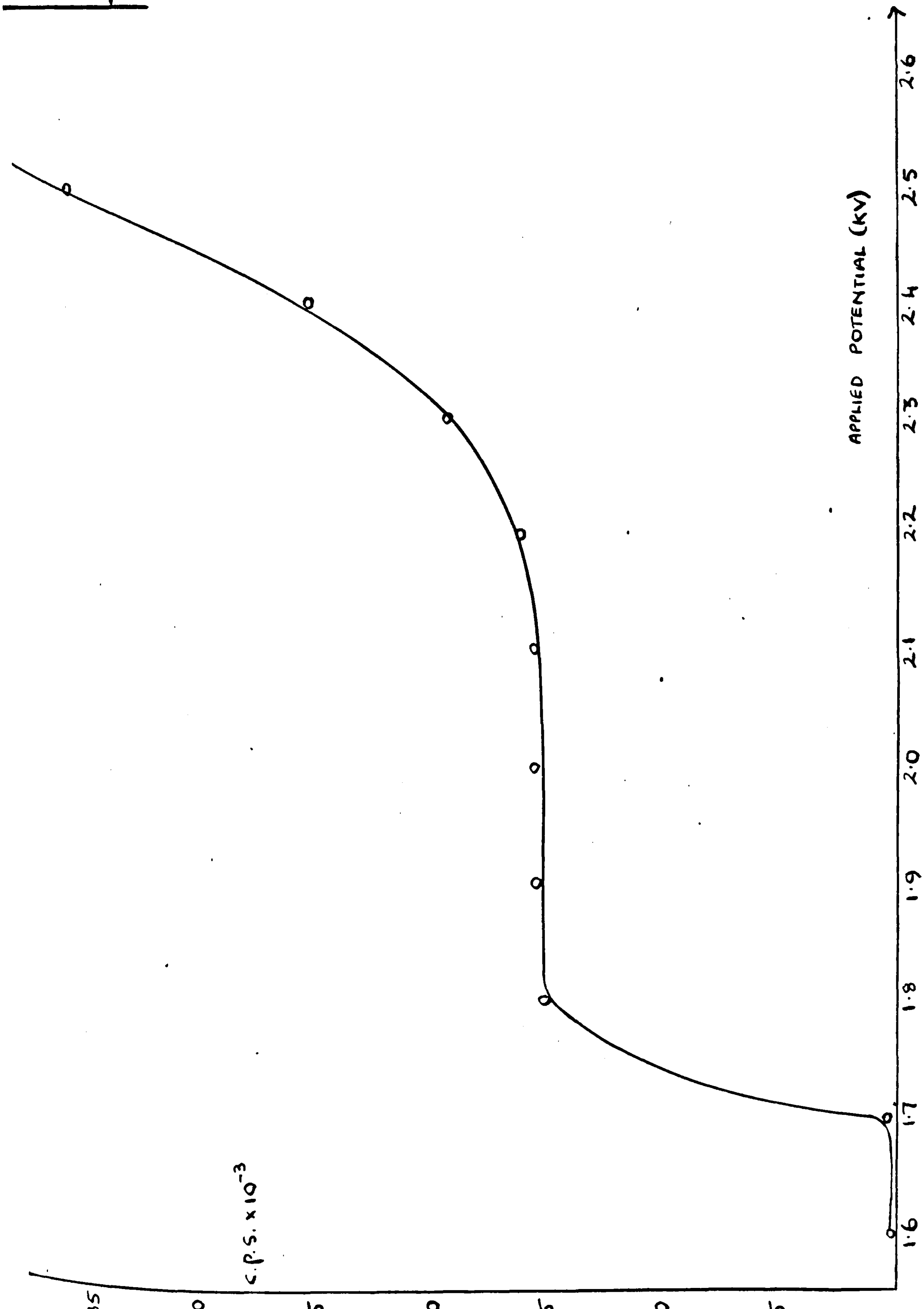
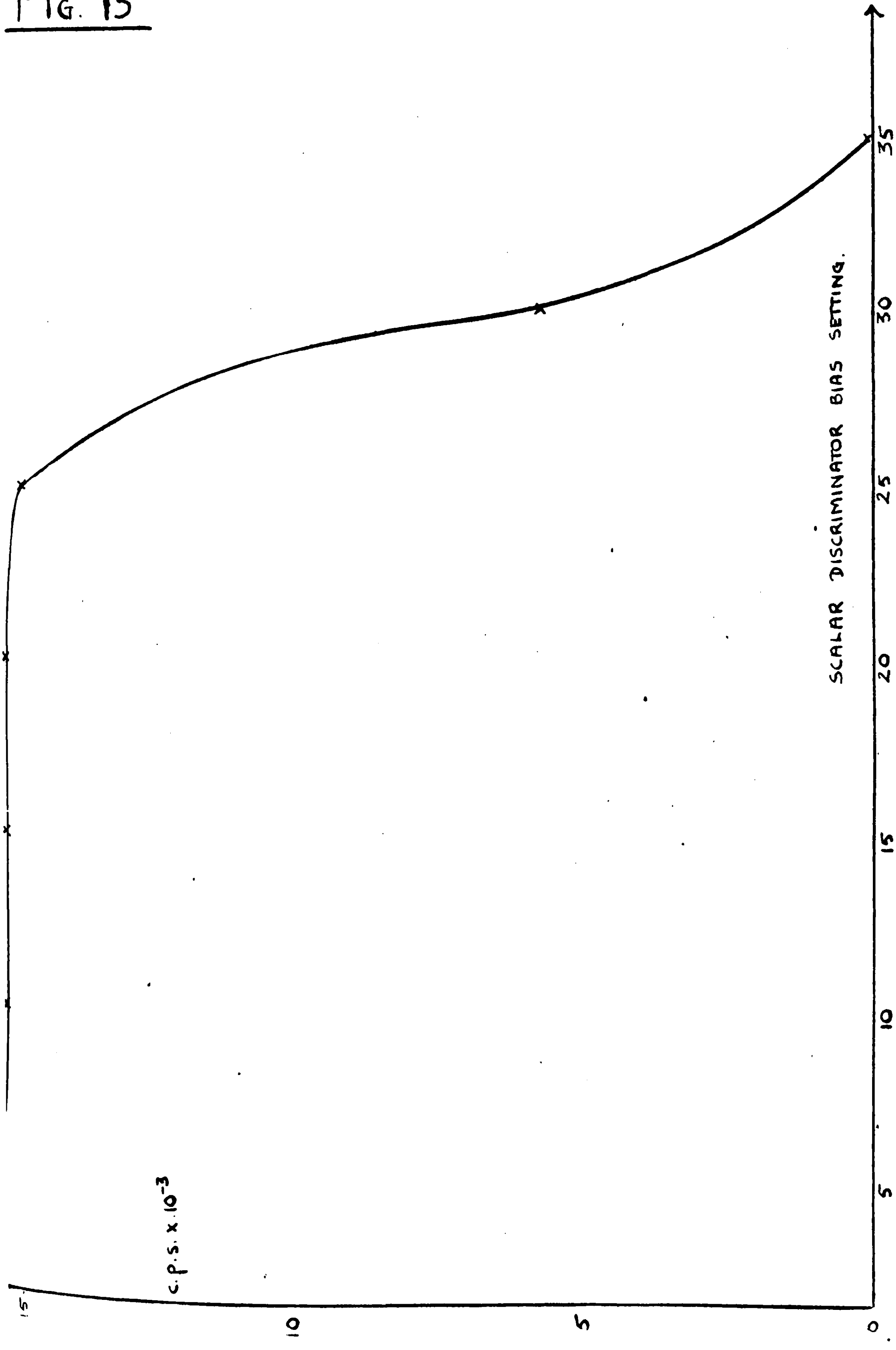

APPLIED POTENTIAL (KV)
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
2·5
2·6
c.p.s. × 10^{-3}
5
10
15
20
25
30
35

FIG. 15


SCALAR DISCRIMINATOR BIAS SETTING.
c.p.s. x 10^{-3}
0
5
10
15
20
25
30
35
5
10
15

Section 2.8 Operation of the Counter.

It had been found[71] that the best counting conditions, in terms of plateau length and slope, were achieved with a helium to methane ratio of 11:1. As a helium flow rate of 60ml/minute had to be maintained for chromatographic separations the methane flow was fixed at 6ml/minute. The gases were blended at a T-piece junction of the gas lines (⅛" O.D. copper tubing) at the entrance to the counter. The amplifier was set at maximum attenuation of 40 db., i.e. minimum gain. The pulse shaping controls of differentiation and integration were set at 6.4 and 0.1 μ sec respectively. With these settings and using a Cs^{137} external source the variation of count rate against applied voltage was investigated for a helium to methane ratio of 11:1. The plateau is shown in Fig. 14. With this counting mixture a plateau of negligible slope and length greater than 300 volts was regularly achieved.

The scalar and ratemeter were both fitted with variable discriminators which when set to a given value would allow pulses of amplitude greater than the set value to pass. After the plateau had been determined the effect of varying the discriminator bias potential was found for both the ratemeter and the scalar using the Cs^{137} source. With the applied voltage set at the centre of the plateau the counting rate was measured against the bias potential (Fig. 15). It was found that for both the scalar and the ratemeter the

FIG. 16

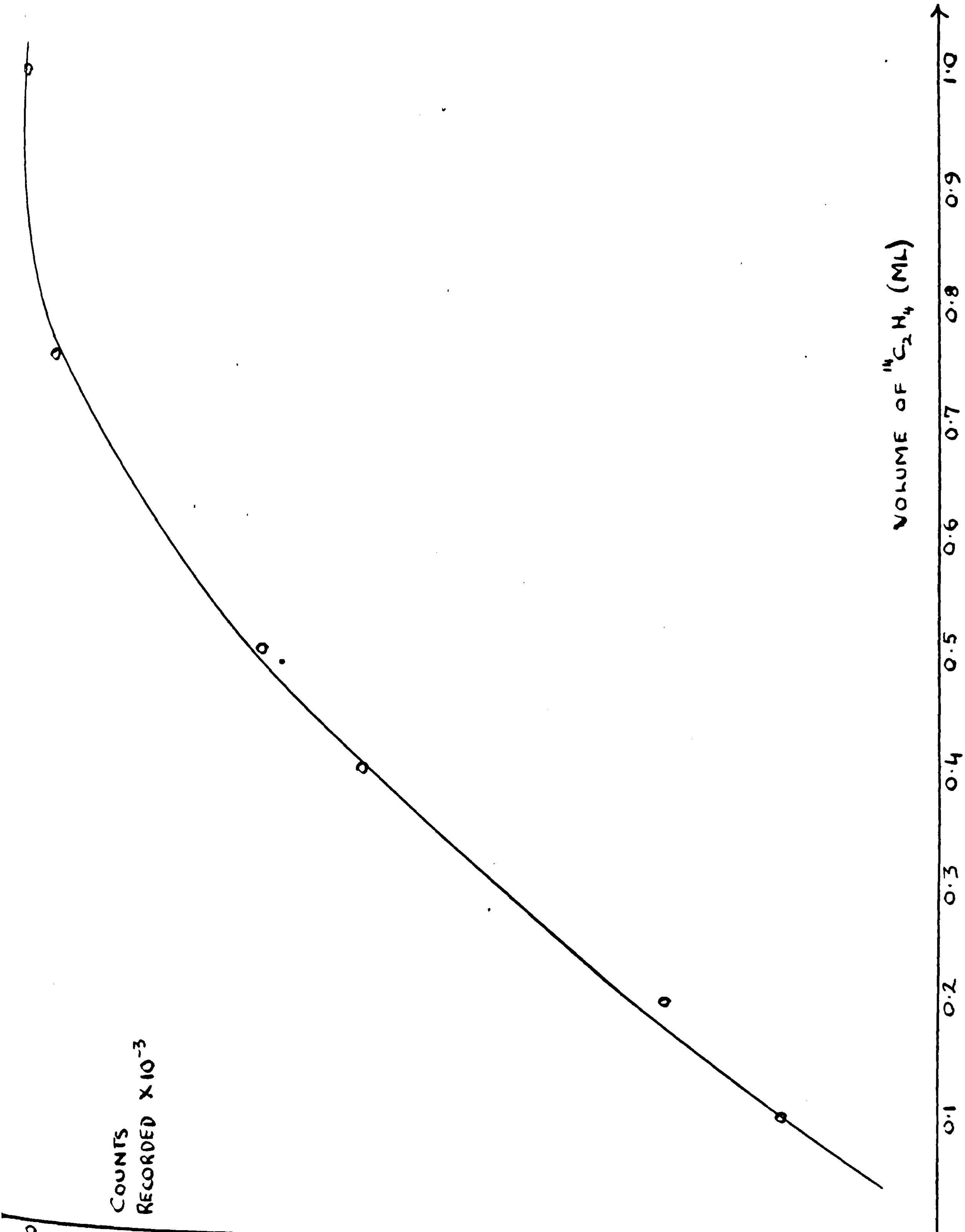
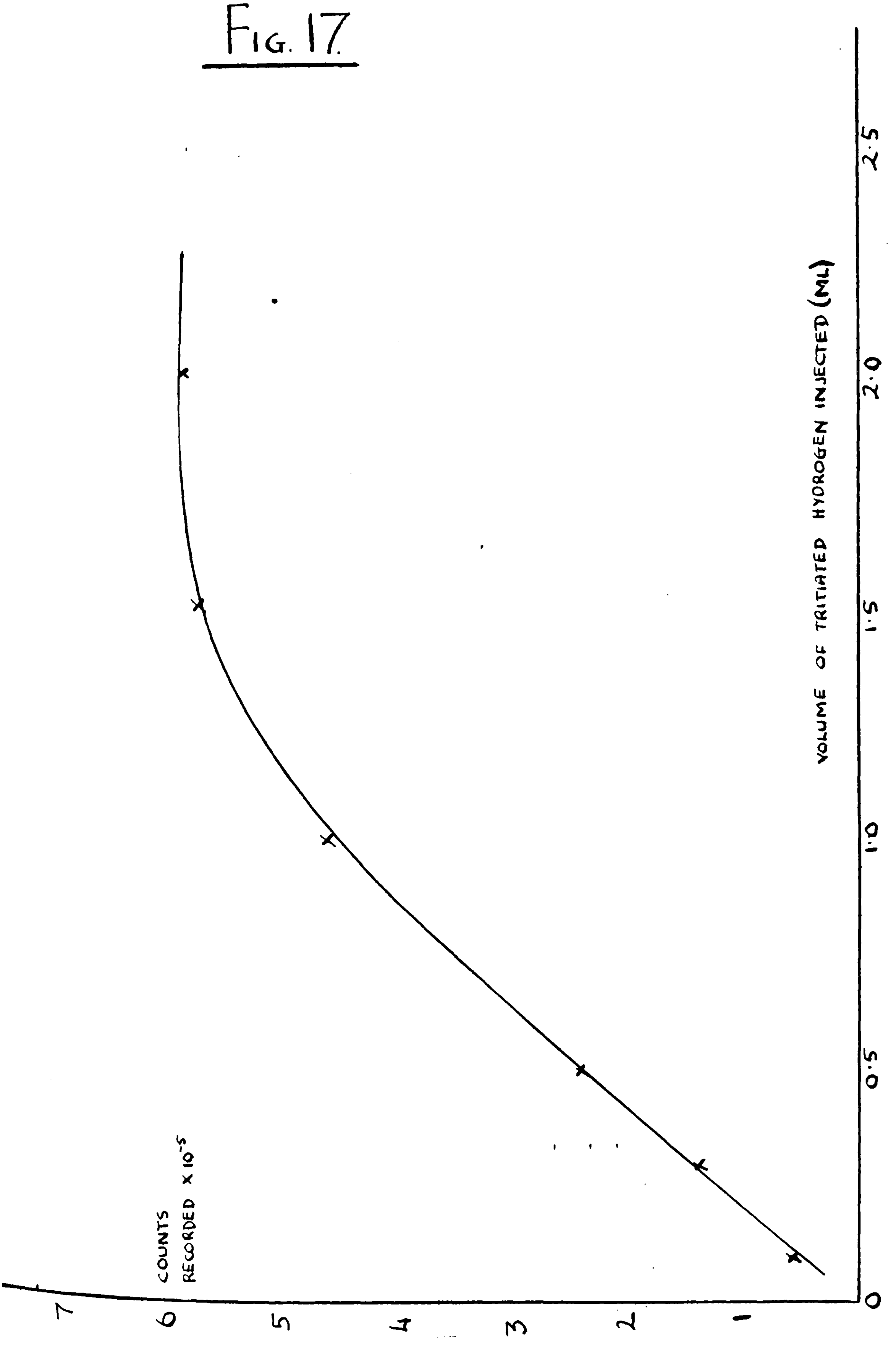

COUNTS RECORDED X 10^{-3}
80
70
60
50
40
30
20
10
VOLUME OF $^{14}C_2H_4$ (ML)
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0

Fig. 17.



COUNTS RECORDED × 10⁻⁵
7
6
5
4
3
2
1
0
0·5
1·0
1·5
2·0
2·5
VOLUME OF TRITIATED HYDROGEN INJECTED (ML)

plateau had negligible slope and extended over 15mV. The bias potentials were set at 15mV. The counter was shielded with lead bricks and a background of 1-2c.p.s. was normally achieved with this arrangement.

Section 2.9 Initial Counting Experiments.

Before beginning the injection of labelled compounds it was necessary to investigate the effect on the efficiency of the counter of the passage of gas quantities expected in the course of an experiment. Since 0.5ml of ethylene and 1.0ml of hydrogen were almost always used, these quantities were injected into the flow stream with the external source in position. With the applied potential set at the mid-plateau value a slight lowering in the count rate was observed for ethylene but there was no reduction in the count rate as the hydrogen passed through the counter. Different volumes of the radioactive gases were injected into the flow system and the total counts recorded on the scalar. The results for ethylene and tritium are shown in Fig. 16 and Fig. 17. Satisfactory quantitative calibrations were obtained for the amounts used in the catalytic experiments. When 2ml of tritium were injected, however, two peaks were observed on the ratemeter trace and the total count was less than that expected from a linear relationship between amount injected and the count recorded. The question of peak twinning is discussed in detail in the next section.

Section 2.10 Experimental Procedure.

The reaction vessel was removed form the flow system at the 'Swagelok' connections, cleaned with a 'Pyroneg' solution, rinsed in distilled water and thoroughly dried. A plug of silica wool was inserted into the bulb of the vessel. Some glass beads and 0.50g of the catalyst were placed on top of the plug and compacted by tapping the vessel. The furnace was slipped over the vessel and the thermocouple inserted into the well and bound in position with asbestos string. New serum caps were put into the injection ports, the section reassembled into the flow system and the heat shield arranged above the top of the furnace.

The hydrogen line was connected to the catalyst side of the switch valves and hydrogen was passed over the catalyst at 30ml min^{-1}. A gas bubbler was connected to the exhaust from SV2 and the flow rate was regulated by the fine control valve in the section. After hydrogen had been allowed to flow for fifteen minutes to displace air from the system the temperature of the catalyst was raised to 400°C. At this temperature the reduction was carried out overnight.

Towards the end of the reduction period the flow rates of helium and methane were set at 60ml min^{-1} and 6ml min^{-1}

respectively. With the helium flowing round the by-pass circuit, the battery was connected to the conductivity bridge and the bridge current set at 200 ma. The temperature of the chromatographic column was adjusted to 80°C.

The counter plateau and stability were checked using the Cs^{137} source and a background determination was made.

The serum caps on the sample vessels of the vacuum apparatus were renewed and the system evacuated. Gases were admitted to the sampling vessels form the storage vessels and condensed or contracted to a pressure of 1.2 atmospheres. A super-atmospheric pressure was required to ensure that during the gas transfer from the sample vessel to the flow system no air entered the syringe. Before making injections the syringe was flushed twice with the appropriate gas.

(i) The C^{14}- ethylene Experiments.

At the end of the reduction period the flow of hydrogen was stopped and the switch valve (SV1) turned to direct the He flow over the catalyst. To remove the bulk of the gas phase hydrogen from the system the helium and hydrogen were allowed to exit through the exhaust for a few seconds. SV2 was then turned to divert the helium flow into the chromatograph. As the flow of gas returned and the hydrogen content in the helium dropped the chromatographic recorder pen returned to the baseline. A steady baseline was always achieved within one minute of this operation. As the catalyst was cooling to the required temperature calibration injections of 0.5ml were made into 1P2, the calibration port. Usually three injections were sufficient to illustrate the reproducibility of the injection technique and the detection system. In the case of an injection of radioactive material counter calibrations could also be made. Successive injections were then made over the catalyst at a variety of temperatures, and calibration injections were repeated periodically below the catalyst.

(ii) The Ethylene - D_4 Experiments.

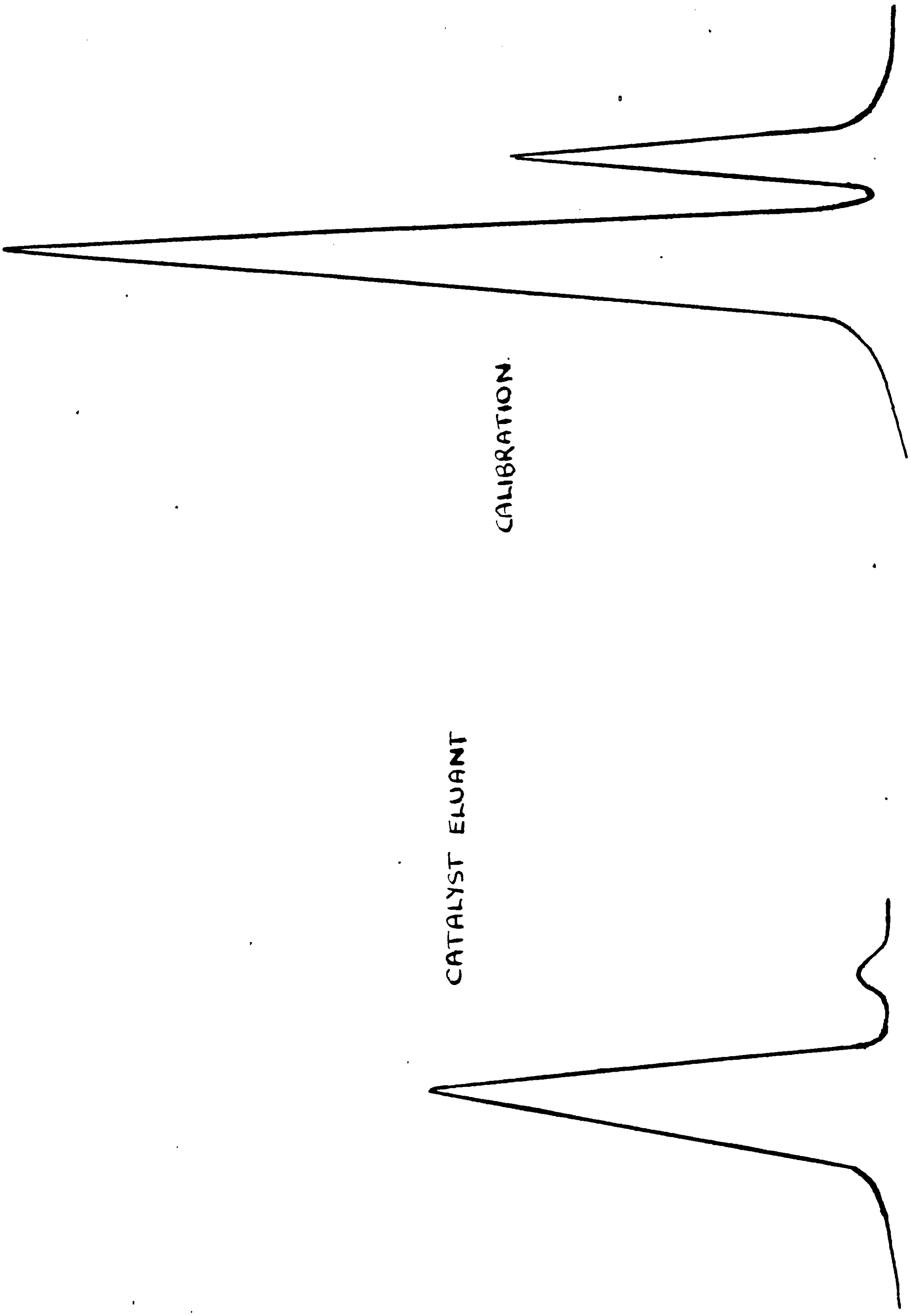
The activity of ethylene hydrogen towards ethylene exchange was examined by using fully deuterated ethylene as the labelled molecule. A procedure similar to that used in the ^{14}C - ethylene exchange experiments was followed. Once again, injections of the labelled ethylene (0.5ml of C_2D_4) were made over the catalyst first.

A mass spectrometric analysis was made of the products obtained from a subsequent injection of C_2H_4. To enable separate collection of the reaction products as they emerged from the chromatographic column, the gas proportional counter was replaced by a series of U-tubes into which the product components were condensed.

(iii) The Tritium Experiments.

The activity of the catalyst hydrogen, retained after

Fig. 18



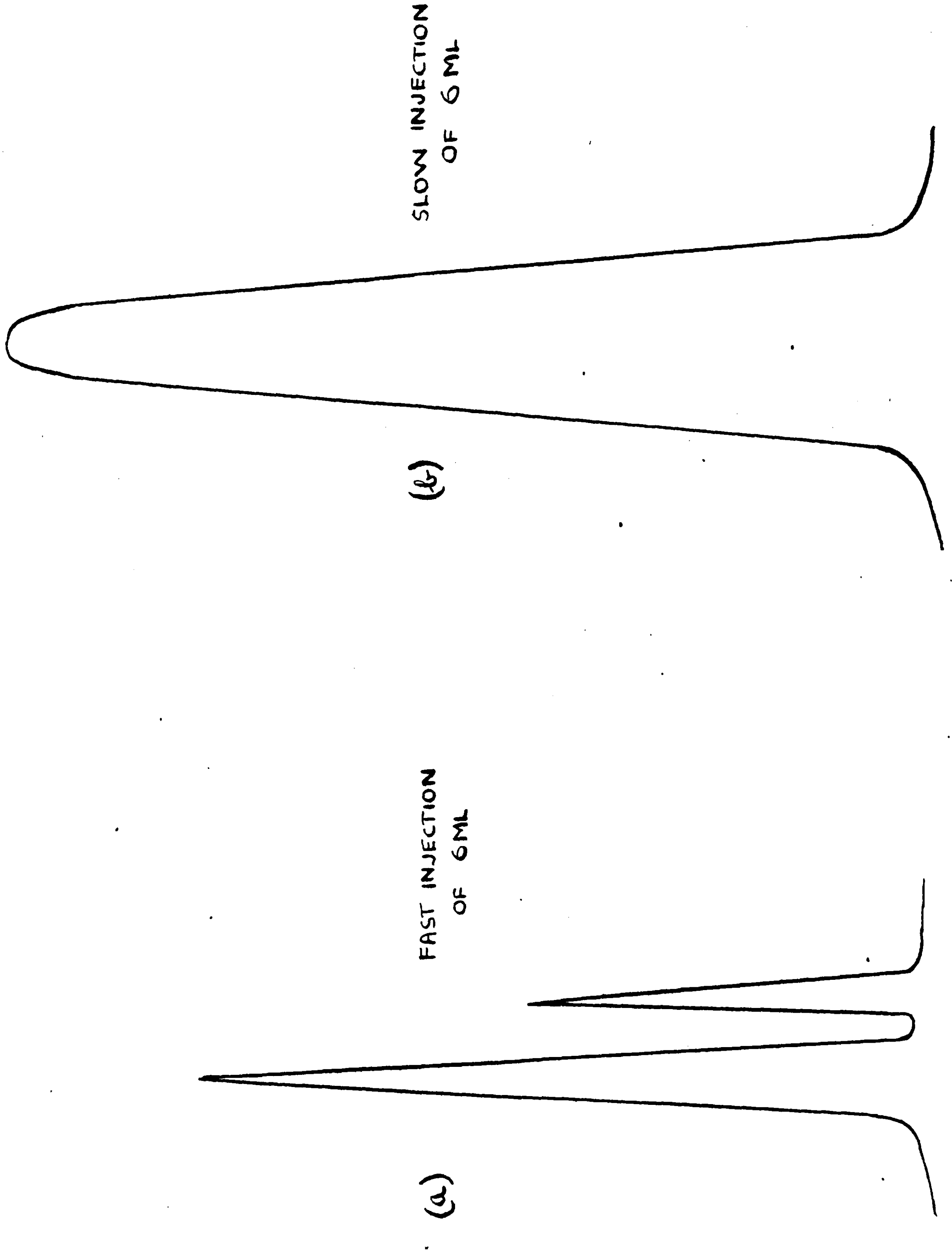
the reduction process, towards hydrogen and ethylene was investigated with the aid of tritium as a tracer. Initially a static method of exchange was employed to label the surface hydrogen with tritium. At the end of the reduction period, the hydrogen flow rate was reduced to about 5ml min^{-1} and 6ml of tritium were injected over the catalyst. The hydrogen flow was immediately stopped and the catalyst allowed to exchange with the tritium for 30 minutes at the reduction temperature. At the end of this period the helium flow was directed over the catalyst and the entire gaseous content of the reaction vessel section was blown through the counter. Two peaks appeared on the ratemeter trace and the total count was recorded. For all the nickel catalysts investigated, background counting was achieved within a few minutes of the appearance of the second peak. It has been shown that in the case of palladium,[71] tritium continued to desorb from the catalyst for periods of up to 11 hours.

To determine the amount of tritium retained by the catalyst after the exchange procedure, it was necessary to obtain a calibration count for 6mls of tritium. Two peaks were obtained from the calibration injection in 1P2 and the total count was recorded. The calibration count and the catalyst eluant count were in the ratio of 7:1 (Fig. 18). Before making the assumption that the difference in count was entirely due to retention by the catalyst the possibility of tritium adsorption on the inner surfaces of the reaction vessel was investigated in the following way. A plug of silica wool and some glass beads were placed in the reaction vessel, without the catalyst, and the reduction procedure carried out in the normal way. After the hydrogen flow had been stopped the helium was directed through the catalyst vessel displacing the hydrogen contained in that section through the column and counter. As the hydrogen passed through the counter a trace of activity, in the form of a small peak after one minute and a second similar peak after a further minute, appeared on the ratemeter chart. The switch valves were turned to their former positions so that helium was once again flowing around the by-pass circuit and hydrogen was passing through the reaction vessel which was maintained at 400°C. After 30 minutes when all the helium had been displaced from the reaction vessel section, the hydrogen flow rate was reduced and 6ml of tritium were injected into 1Pl over the glass beads and silica plug. The hydrogen flow was immediately stopped and the section isolated and left for 30 minutes. The helium flow was then directed into the section and the hydrogen and tritium blown through the counter. Two peaks were again observed; one after one minute and a larger peak after two minutes. The peaks were very similar to those obtained from the eluant when a catalyst was present (Fig. 18).

The switch valves were turned to their former positions allowing hydrogen to blow through the reaction vessel and helium to flow around the by-pass. After the helium had been displaced from the reaction vessel section, the section was isolated and the temperature raised to 430°C. After 30 minutes the gas in the section was carried through the counter by the helium stream. Once again, two very small peaks were recorded on the ratemeter chart and as there was no significant difference between these peaks and those obtained from the previous hydrogen displacement it was concluded that the large difference between the reaction eluant counts after the static exchange and the calibration count could not be attributed to a reversible adsorption of tritium on the interior of the reaction vessel section.

When a static method of exchange was used to determine the amount of tritium adsorbed onto the catalyst at the end of the reduction period the assumption had been made that the gas proportional counter would view the tritium displaced from the reaction vessel section after the exchange in the same way as a calibration injection. In the former case the tritium injected for exchange purposes was considerably diluted with the hydrogen remaining in the section after reduction whereas a calibration count of the tritium was a direct injection into the helium flow. From the result of

Fig 19

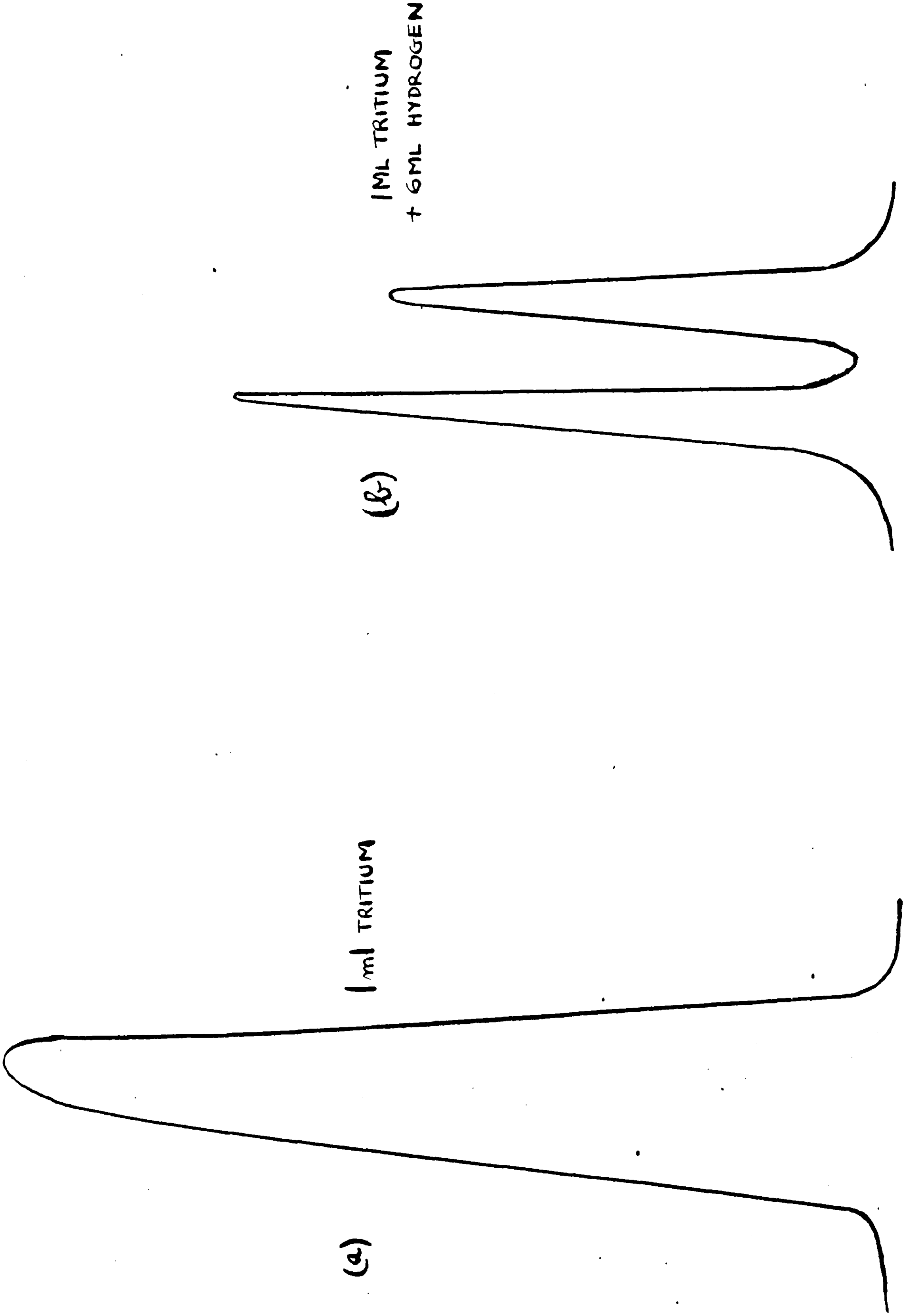


the experiment in which the catalyst was not used it was evident that the assumption was invalid and that the large difference between reaction and calibration counts was a function of the system.

In an attempt to explain the splitting of the tritium peaks, injections were made into the flow system at different rates. Helium gas was passed over the silica plug and glass beads, maintained at 400°C, and 6ml of tritium were injected quickly into 1Pl. The injection time was 10 seconds. As the tritium passed through the counter a split peak was recorded on the ratemeter trace (Fig. 19). 6ml of tritium were then injected into the helium stream over a 2 minute period and a single, but wider, peak was obtained on the recorder (Fig 19). From this result it became apparent that the dilution of the tritium in the carrier gas stream was very significant. The speed at which the radioactive material passed through the counter was the same for both injections as the flow rate was the same. However, in the case of the slow injection a much longer 'slug' of active gas was present in the helium flow. Thus for large injections, the time taken to inject the tritium into the helium was proportional to the total count.

A further experiment was carried out to determine the effect on the counter of adding hydrogen to a sample of known activity. 1ml of tritium was injected from a 10ml syringe into the helium stream and a single peak was recorded by the

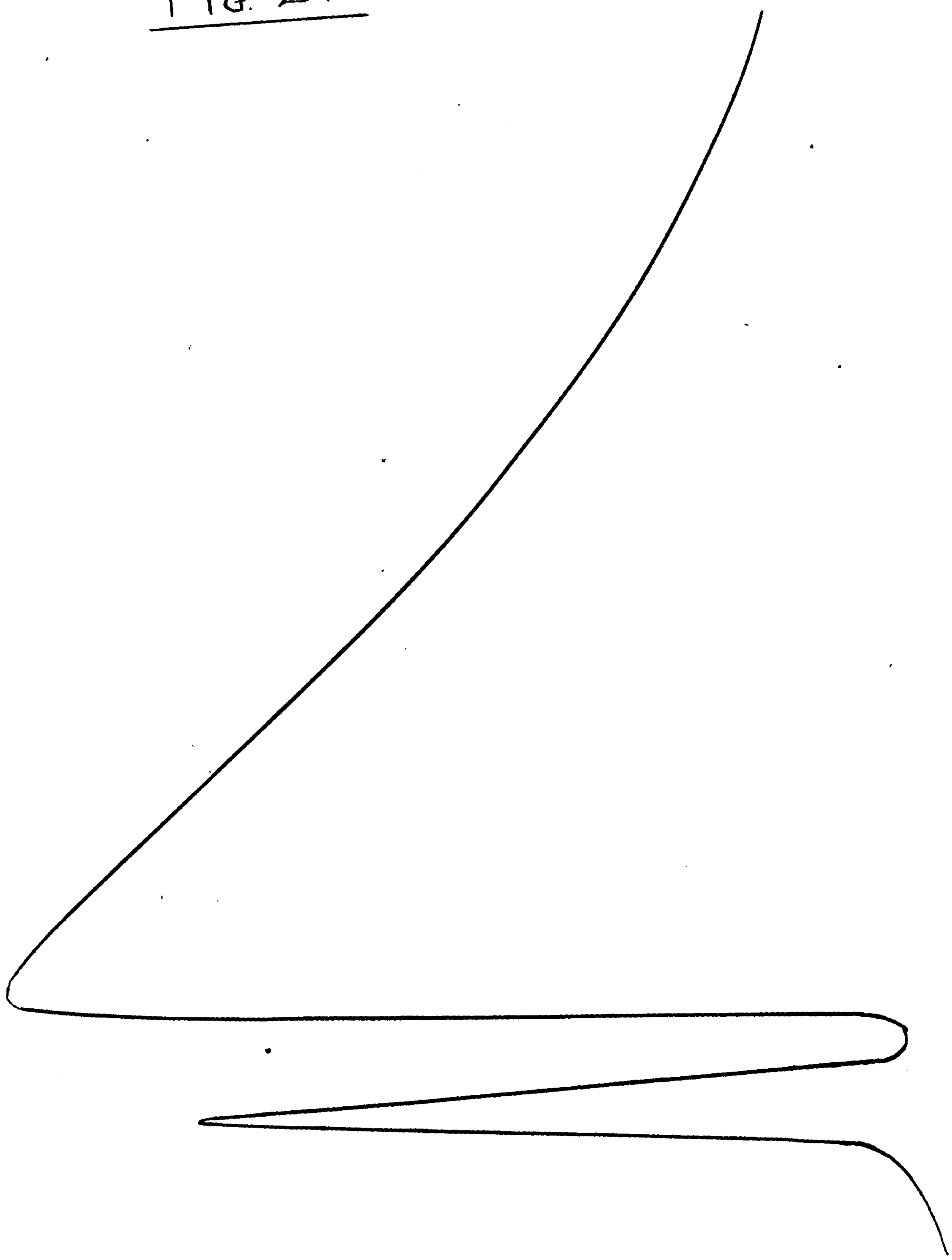
IG. 20



counter (see Fig. 20). A second 1ml sample of the same tritium was withdrawn and a further 5ml of hydrogen withdrawn into the same syringe. The mixture was injected into the helium flow and two peaks were recorded (Fig. 20). The count was much smaller for the 6ml sample although the overall width of the recordings for both injections was the same. This led to the conclusion that the addition of hydrogen had significantly changed the counting characteristics of the counter and that the two peaks observed corresponded to the beginning and the end of the active slug. When the bulk of the hydrogen tritium passed through the counter the counting mixture was disturbed to such an extent that counting stopped completely. If, as had been shown, the injection was made slowly enough, sufficient dilution of the hydrogen/tritium was made to provide a good counting response. Alternatively, a rapid injection reduced the efficiency of the counter and produced a split peak of much smaller total count.

An estimate of the volume of hydrogen necessary to disturb the counting conditions within the counter was made in the following way. The Cs^{137} was placed next to the counter and the plateau determined in the usual way. With the voltage set mid-way along the plateau injections of hydrogen were made into the helium flow. It was found that as little as 3ml of hydrogen were sufficient to reduce the count rate to zero for a few seconds, although as stated earlier an injection

Fig. 21



of 1ml did not reduce the plateau count rate (~200 c.p.s.) at all.

Further 3ml injections were made with ethane, ethylene, oxygen and nitrogen and in each case the quantity proved sufficient to stop the counter functioning for a short period.

An attempt was made to eliminate the splitting of the hydrogen/tritium peaks by inserting a mixing chamber into the helium flow line. The chamber had a volume of 250ml and was located at the junction with the methane flow line. The result of displacing 6ml of tritium in hydrogen from the empty reaction vessel is shown in Fig. 21. Although dilution of the hydrogen/tritium in the helium was indicated by a much longer time for background to be reached the overall effect on the counter was the same.

A second method of examining the exchange of the hydrogen associated with the catalyst after reduction was adopted. After the helium flow had been directed over the catalyst and as soon as the counter had been calibrated, 1ml injections of tritium were made over the catalyst and the eluant counts recorded. Calibration injections were made into IP2 at frequent intervals. A sample size of 1ml did not significantly upset the counting conditions and splitting of the ratemeter peak did not occur for any of the injections.

The reactivity of tritium, retained by the catalysts during static and flow exchange procedures, towards ethylene, was analysed over a range of temperatures.

Section 2.11 Presentation of Results.

The nature and quantity of reaction products were determined from their chromatographic retention times and from the integrator count. In the case of hydrocarbon injections the integrator count was related to the calibration value for ethylene and in the eluted gases corrections were made to the counts recorded for methane and ethane to account for the difference in detector sensitivity. In this way the volumes of the eluted gases were converted into millilitres. An estimate of the volume retained by the catalyst was made by subtracting the total volume eluted from the amount injected.

At the higher injection temperatures ethylene was cracked by the catalysts and methane appeared as a reaction product. As two molecules of methane may be derived from one molecule of ethylene, the volume of methane eluted was halved before subtraction from the injected volume.

In the tables of results the radioactive content of the hydrocarbons was expressed as counts per millilitre (cpml). This activity was obtained by dividing the total integrated counts from the proportional counter by the volume of hydrocarbon as determined by the gas chromatograph.

CHAPTER 3 THE RESULTS

Section 3.1 The Exchange of Hydrogen Retained by the Catalyst with Tritium.

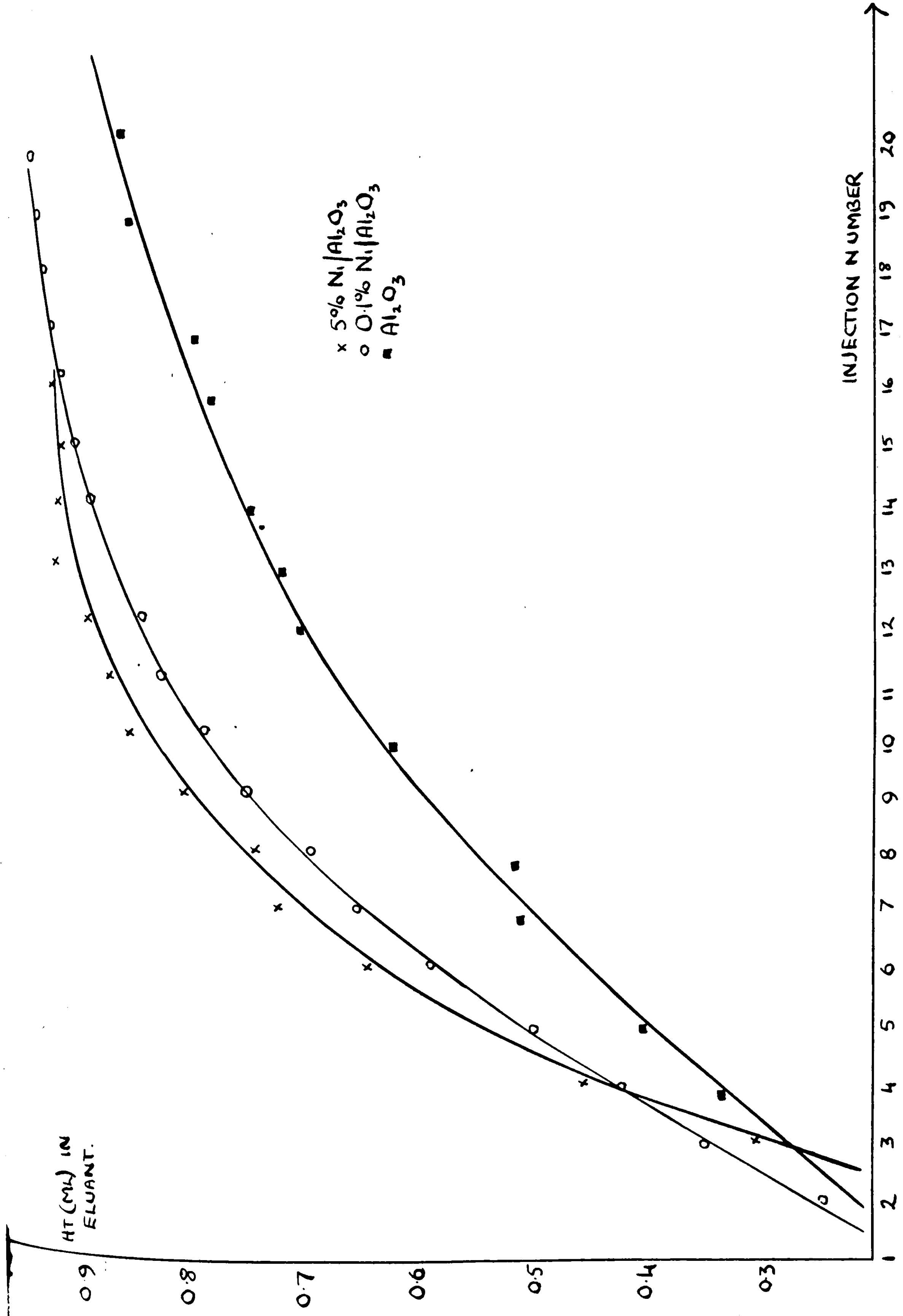
(i) Static exchange reactions on 5%Ni/Al_2O_3 and 5%Ni/SiO_2.

The nickel catalysts were treated with tritium as described previously. [See section 2.10 (iii)]. From the difference between the count obtained for tritium displaced when a catalyst was present within the catalyst vessel and the calibration count obtained when there was no catalyst present, the volume retained by the catalyst could be determined. At the reduction temperature of 400°C, 1.0×10^{19} molecules of tritium were retained per gram of 5% Ni/Al_2O_3 catalyst. 0.6×10^{19} molecules were retained by 1g of the 5% Ni/SiO_2 catalyst.

(ii) Flow-exchange reactions on various catalysts and supports.

Flow-exchange reactions were studied using Al_2O_3, SiO_2, 0.1% Ni/Al_2O_3 and 0.1% Ni/SiO_2, 5% Ni/Al_2O_3 and 5% Ni/SiO_2, Ni powder and Ni/P alloy. The experimental technique used in these experiments has been described previously [See section 2.10 (iii)]. 0.5g of the catalyst, or a sample of support material, was reduced in hydrogen overnight at 400°C and injections of tritiated hydrogen commenced as soon as possible after the helium flow had been directed through the

FIG. 22


HT (ML) IN ELUANT.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
INJECTION NUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
× 5% Ni/Al2O3
o 0.1% Ni/Al2O3
■ Al2O3

catalyst vessel. In the initial flow exchange experiments the catalyst was maintained at the reduction temperature of 400°C throughout the series of injections. The quantity of tritiated hydrogen which had exchanged with surface hydrogen and thus been retained by the catalyst was obtained by subtracting the reaction eluant count from the calibration count. Calibration injections were made at frequent intervals during the course of an experiment, to confirm stable performance of the counting system. Injections of tritiated hydrogen were usually continued until eluant count corresponded to the calibration count. In the case of lengthy experiments, however, the run was stopped when the eluant count had risen to within 10% of the calibration value.

Experimental results were plotted as the quantity (ml at 20°C and 760mm)of labelled hydrogen in the reaction eluant against the appropriate injection number. It was found that a plot of the log (activity retained in the nth injection / activity injected) against the injection number produced a straight line, the gradient of which could be related to the amount of exchangeable hydrogen on the catalyst surface. The derivation of this relationship is shown in Appendix I. Fig. 22 illustrates the rise in the activity of the eluant hydrogen during a series of injections onto 0.5g samples of Al_2O_3, 0.1%Ni/Al_2O_3 and 5%Ni/Al_2O_3 at 400°C. A plot of

FIG. 23.

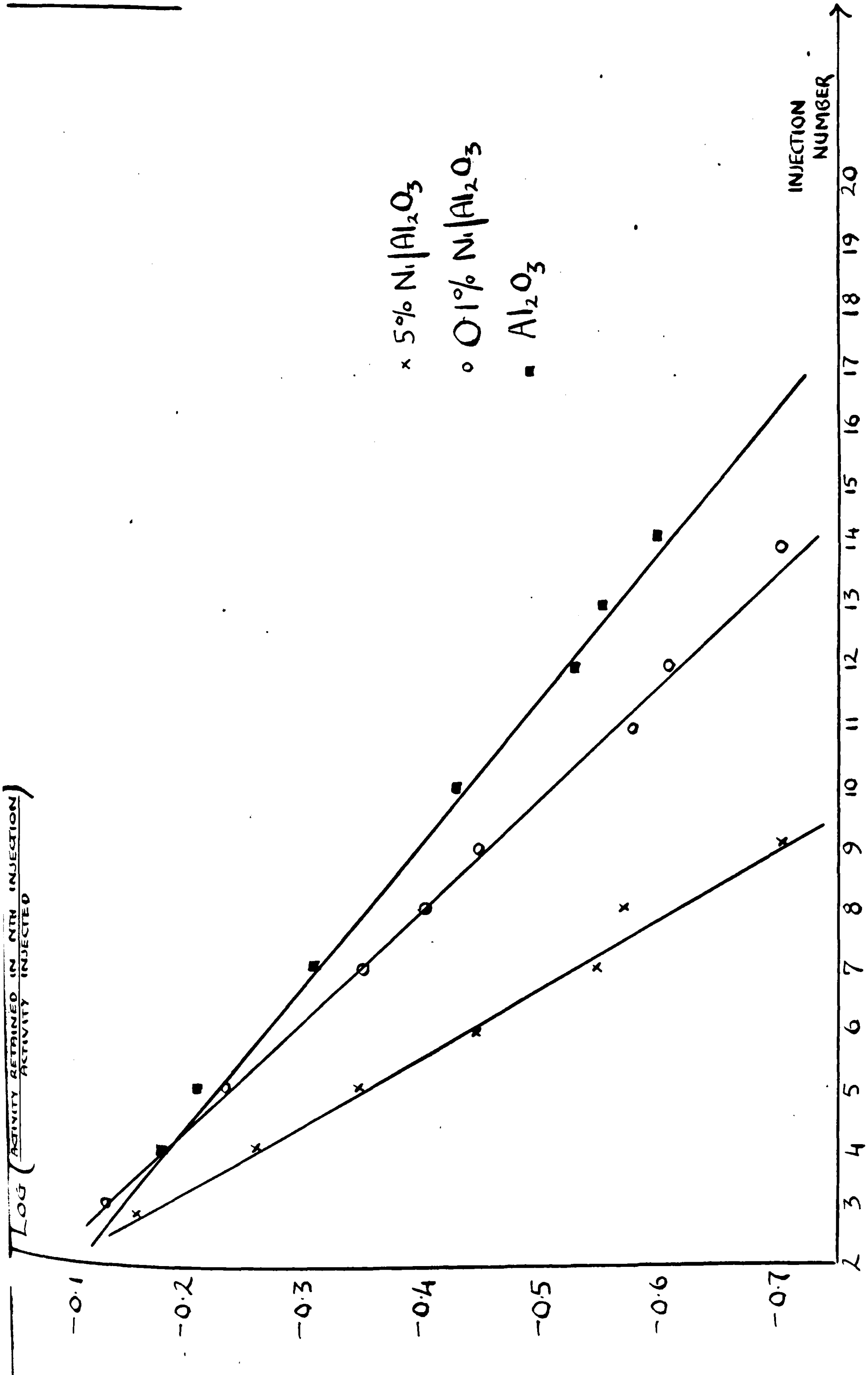

LOG (ACTIVITY RETAINED IN NTH INJECTION / ACTIVITY INJECTED)
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
INJECTION NUMBER
× 5% Ni|Al$_2$O$_3$
○ 0.1% Ni|Al$_2$O$_3$
■ Al$_2$O$_3$

FIG. 24

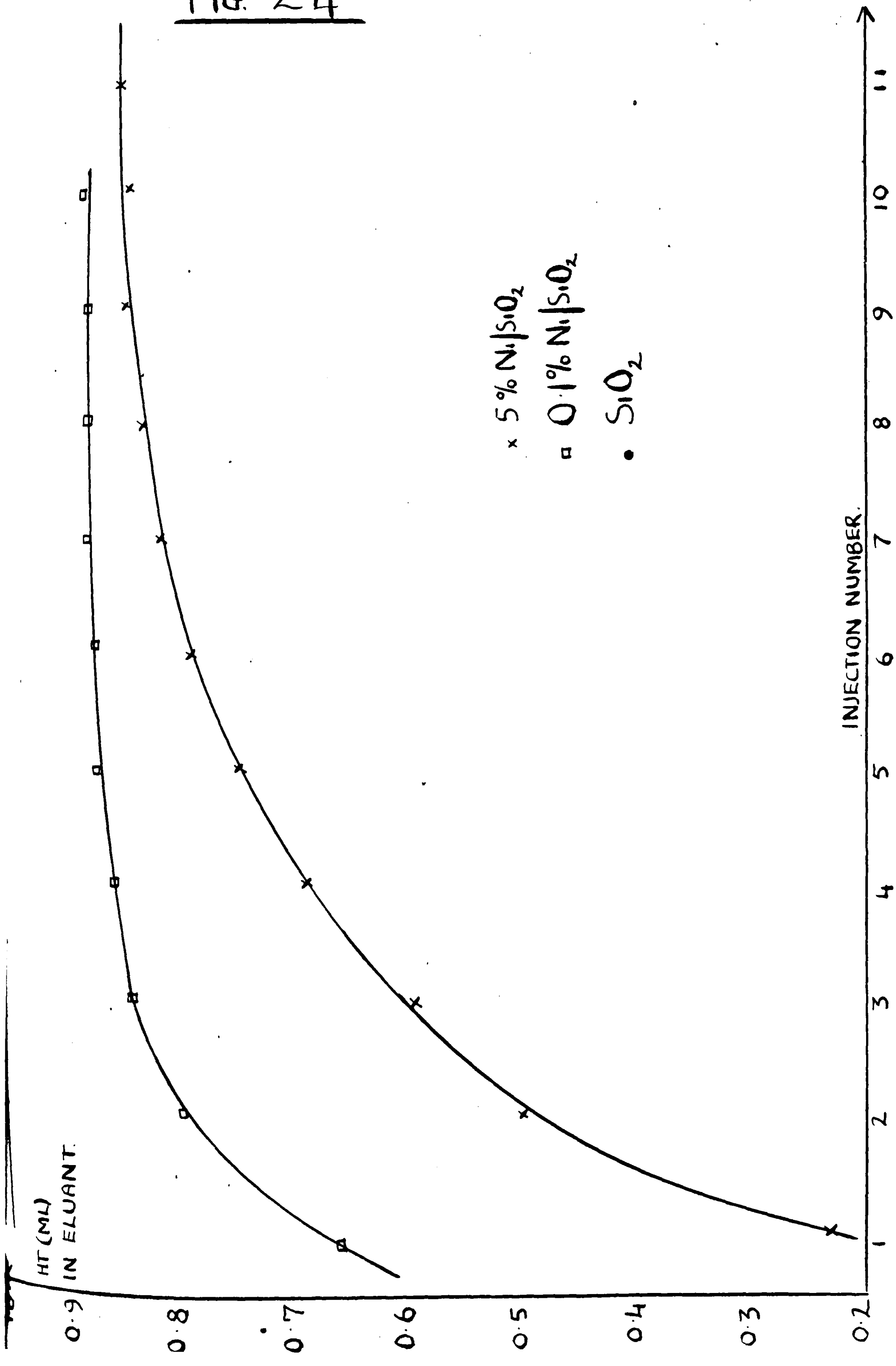
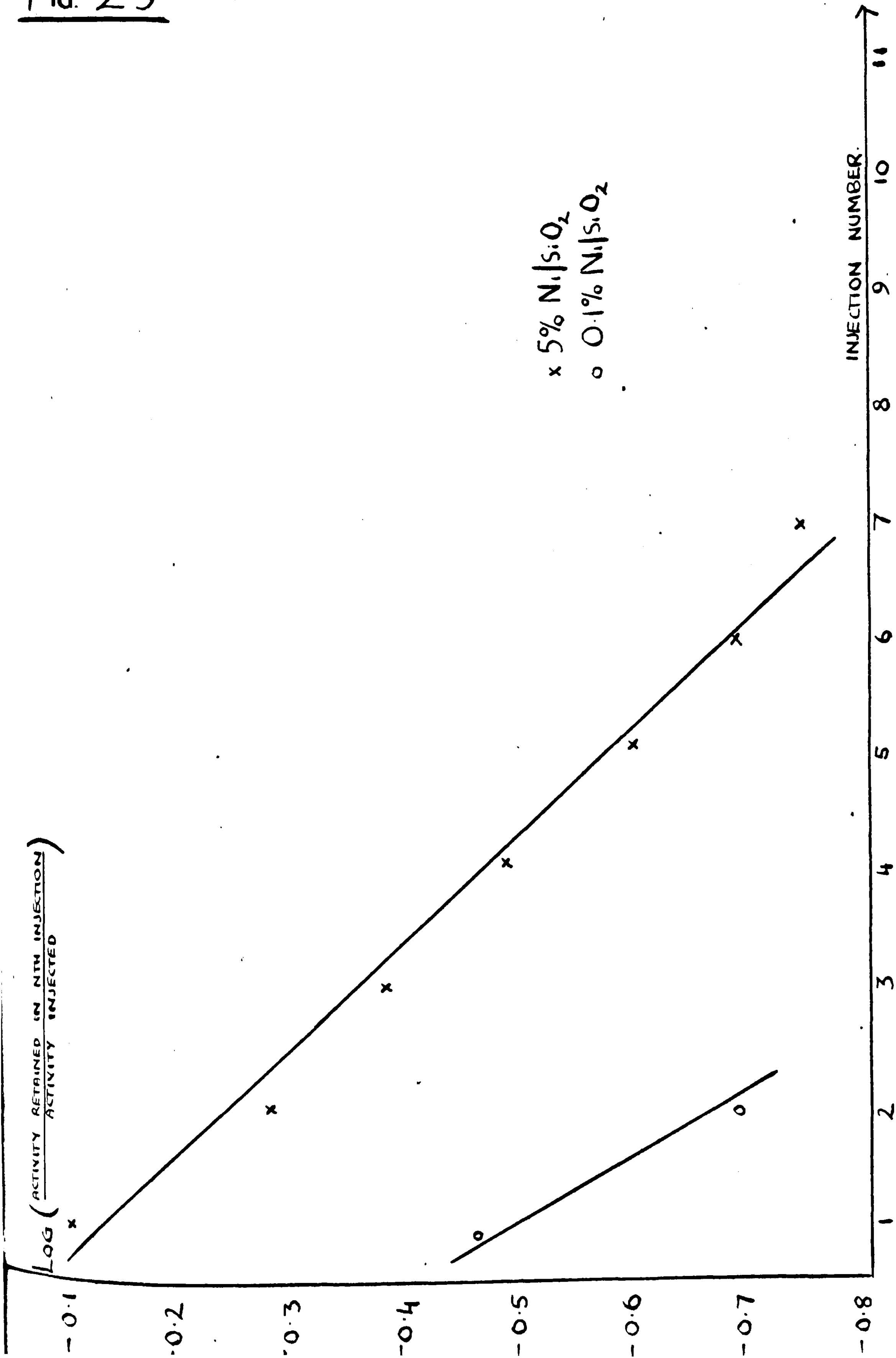

HT (ML) IN ELUANT
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
INJECTION NUMBER
1
2
3
4
5
6
7
8
9
10
11
× 5% Ni|SiO₂
□ 0·1% Ni|SiO₂
● SiO₂

FIG. 25


LOG (ACTIVITY RETAINED IN NTH INJECTION / ACTIVITY INJECTED)
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
1
2
3
4
5
6
7
8
9
10
11
INJECTION NUMBER.
× 5% Ni/SiO$_2$
o 0.1% Ni/SiO$_2$

the log function against injection number for each case is shown in Fig. 23. The amount of exchangeable hydrogen on each sample was calculated from gradient measurements.

Similar flow exchange experiments were carried out with SiO_2 and Ni supported on SiO_2 (0.1% and 5%). The variations in eluant activity are shown in Fig. 24. SiO_2 showed no detectable exchange with the tritiated hydrogen, the first eluant count being very close to the calibration value. Exchange was observed, however, with the 0.1%Ni/SiO_2 catalyst and, to a greater extent, with the 5%Ni/SiO_2 catalyst. The exponential treatment was applied to the metal on silica catalysts. The results are shown in Fig. 25.

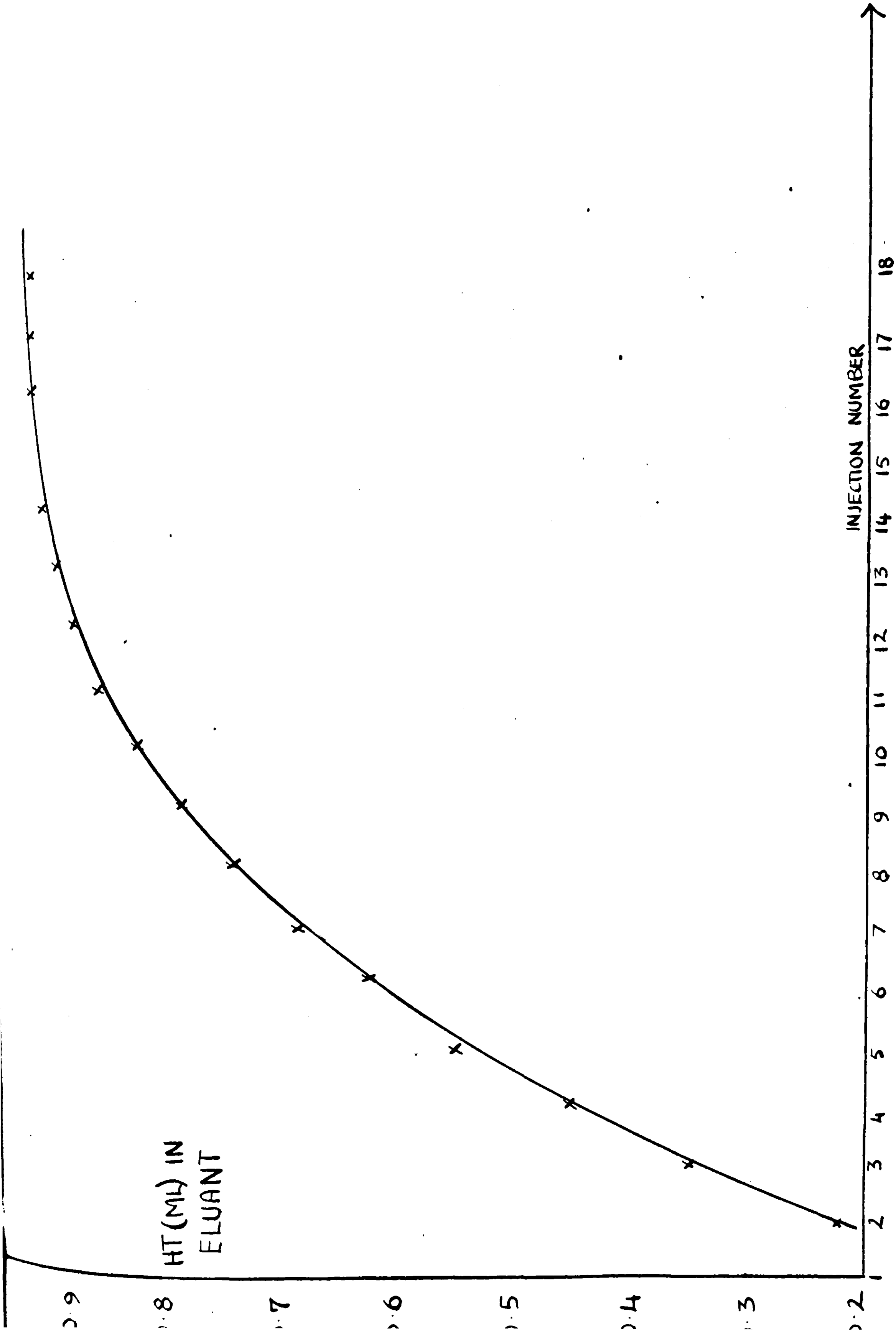
Samples of Ni powder, prepared by the 'in situ' decomposition and reduction of the formate, and Ni/P alloy exchanged to a lesser degree with labelled hydrogen at 400°C. The results of the flow exchange experiments are summarised in Table 4.

TABLE 4.

The Volume (ml at 20°C and 760mm) of Exchangeable Hydrogen Determined by Flow Exchange at 400°C.

Al_2O_3	0.1%Ni/Al_2O_3	5%Ni/Al_2O_3
9.9	9.65	4.4
SiO_2	0.1%Ni/SiO_2	5%Ni/SiO_2
0.0	1.0	3.0
Ni powder	Ni/P	
0.45	0.39	

FIG. 26


HT (ML) IN
ELUANT
INJECTION NUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9

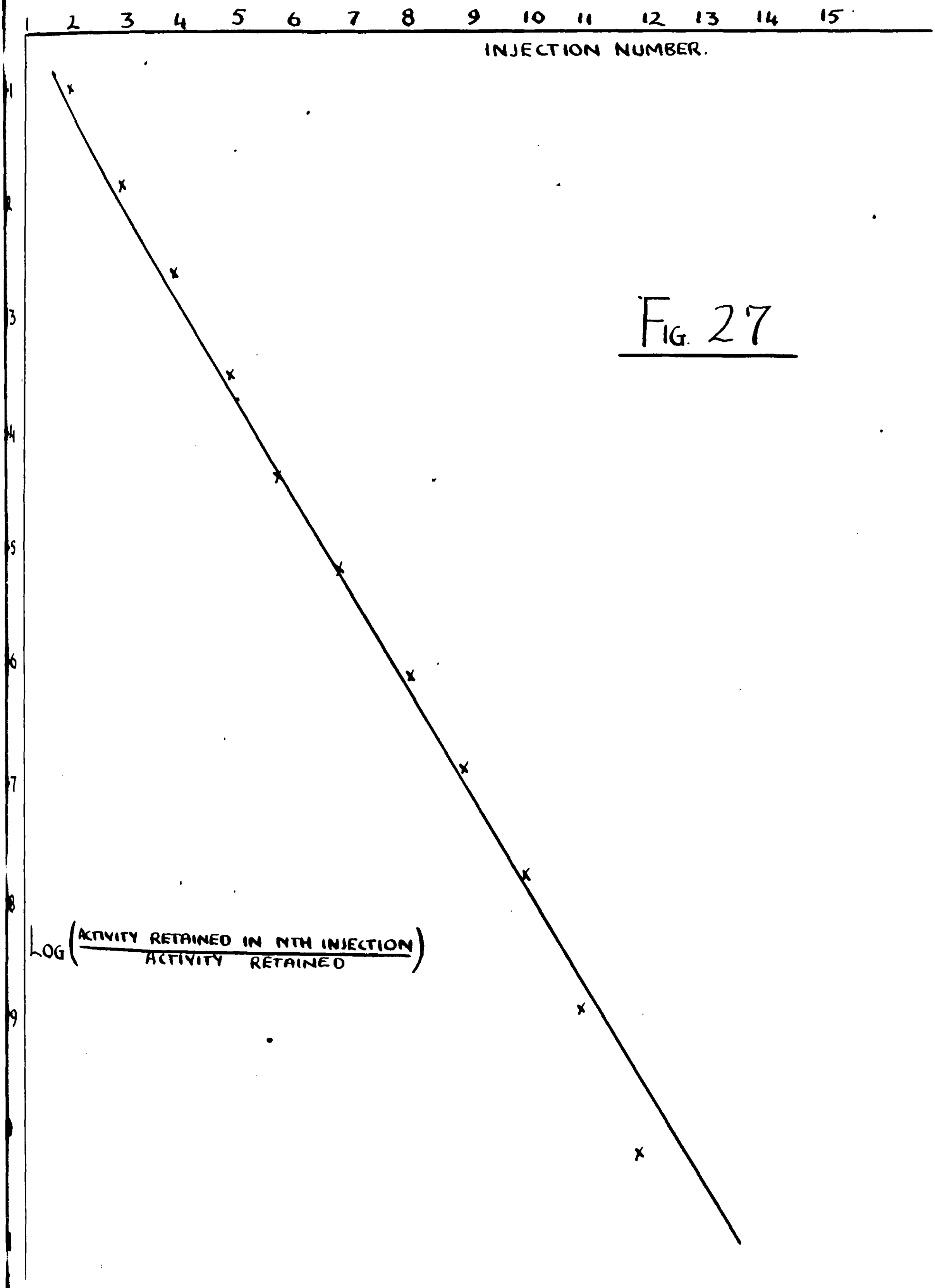

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
INJECTION NUMBER.
1
2
3
4
5
6
7
8
9
LOG (ACTIVITY RETAINED IN NTH INJECTION / ACTIVITY RETAINED)

FIG. 27

It was found that, in the case of alumina, the presence of Ni reduced the amount of hydrogen capable of exchange at 400°C. The reverse effect was found in the case of silica catalysts and the exchange tended to be less on the silica supported catalysts than on the alumina-supported catalysts.

(iii) The effect of flow rate on the exchange reaction.

A helium flow rate of 60ml min^{-1} and a methane flow rate of 6ml min^{-1} were used in the above experiments. To determine whether or not complete equilibrium was being attained in the exchange reaction the flow rates of helium and methane were reduced to 30ml min^{-1} and 3ml min^{-1} respectively. With these flow rates a counting mixture of the same composition as before was obtained. By reducing the flow rate and maintaining the temperature at 400°C the effect of a longer time of interaction of the labelled hydrogen slug with the catalyst could be observed. The presence of more exchange at the slower flow rate would imply incomplete equilibrium at the higher flow rate.

The catalyst used was 0.5g of 5%Ni/Al_2O_3 and Fig. 26 shows the plot of eluant gas activity against injection number, while the straight line graph of the log function is shown in Fig. 27. The amount of exchangeable hydrogen was found to be 4.9ml and was comparable to that calculated from the results of the experiment at twice the flow rate (4.4ml).

(iv) The effect of temperature on the flow exchange reaction.

In a further series of flow exchange experiments the temperature of the alumina catalysts was varied. The results already presented for silica and alumina catalysts were obtained at a temperature of 400°C. However, the exchange activity of the hydrogen associated with each catalyst may vary independently with temperature. To investigate this, exchange reactions were carried out with the alumina catalysts at the following temperatures; 20°C, 150°C, 250°C and 400°C. The catalyst was first reduced overnight at 400°C and injections of labelled hydrogen started at this temperature. The catalyst was then reduced once again at 400°C for 2 hours and a further series of injections of tritiated hydrogen made at 400°C. In this way the reproducibility of the reduction procedure was examined. After a further reduction of the catalyst at 400°C for 2 hours the temperature was lowered to 250°C and the exchange reaction repeated at this temperature, then at 150°C, and finally room temperature. Between each series of injections the catalyst was reduced for 2 hours at 400°C in a stream of hydrogen and throughout the experiments frequent calibration injections were made.

As an illustration of the results, the data obtained with the 5%Ni/Al_2O_3 catalyst are presented in Table 5. As before, the activity of the eluant hydrogen was plotted

TABLE 5

5% Ni/Al_2O_3

400°C. Injection No.	Eluant count	Corrected Count	HT (ml)	Log Function
1	2568	1433	0.026	-0.011
2	7947	6709	0.12	-0.056
3	14079	12841	0.23	-0.114
4	20073	18835	0.34	-0.180
5	25392	24154	0.44	-0.248
6	29929	28691	0.52	-0.316
7	33523	32285	0.58	-0.378
8	37521	36283	0.65	-0.460
9	40146	38908	0.70	-0.524
10	42272	41034	0.74	-0.584
11	45093	43855	0.79	-0.678
12	47450	46212	0.83	-0.776
13	48142	46904	0.85	-0.809
14	49885	48647	0.88	-0.908
15	50818	49580	0.89	-0.971
16	52041	50803	0.92	-1.071
17	52738	51500	0.93	-1.141

Catalyst reduced for 2 hours at 400°C.

Injection No. 400°C.	Eluant count	Corrected Count	HT (ml)	Log Function
1	8254	7222	0.130	-0.061
2	14166	12928	0.23	-0.115
3	20483	19245	0.35	-0.185
4	24414	23176	0.42	-0.235
5	28189	26951	0.49	-0.289
6	31851	30613	0.55	-0.348
7	34031	32793	0.59	-0.388
8	35940	34650	0.62	-0.425
9	40437	38199	0.71	-0.506
10	42977	41739	0.75	-0.605
11	44851	43561	0.78	-0.667

TABLE 5 CONTD.

Catalyst reduced for 2 hours at 400°C.

Injection No. 250°C.	Eluant Count	Corrected Count	HT(ml)	Log Function
1	2063	1689	0.020	-0.009
2	6302	5928	0.070	-0.031
3	12518	12144	0.14	-0.067
4	19023	18648	0.22	-0.107
5	26104	25696	0.30	-0.156
6	32135	31745	0.37	-0.203
7	38180	37772	0.44	-0.255
8	42190	41782	0.49	-0.293
9.	45094	44686	0.53	-0.323
10	49586	49178	0.58	-0.374
11	52746	52338	0.62	-0.414
12	53925	53517	0.71	-0.537
13	57190	56728	0.75	-0.607
14	59790	59382	0.79	-0.674
15	60470	60062	0.80	-0.692
16	64155	63747	0.85	-0.812
17	64677	64252	0.85	-0.831
18	65338	64913	0.86	-0.858
19	67993	67568	0.90	-0.985

Catalyst reduced at 400°C for 2 hours.

Injection No. 150°C	Eluant Count	Corrected Count	HT(ml)	Log Function
1	6131	5761	0.083	-0.038
2	11508	11138	0.16	-0.076
3	14947	14577	0.21	-0.102
4	25200	24830	0.36	-0.192
5	29583	29213	0.42	-0.236
6	29499	29129	0.42	-0.235
7	37901	37531	0.54	-0.336
8	41010	40640	0.58	-0.380
9	46073	45703	0.66	-0.474
10	47213	46843	0.67	-0.485
11	50759	50389	0.72	-0.558
12	52418	52048	0.75	-0.597
13	54307	53937	0.77	-0.646
14	56381	56011	0.80	-0.708
15	57012	56642	0.81	-0.728
16	57960	57590	0.83	-0.761
17	57751	57381	0.82	-0.754

TABLE 5 CONTD.

Catalyst reduced at 400°C for 2 hours.

Injection No. 20°C.	Eluant Count	Corrected Count	RT(ml)	Log Function
1	40070	39684	0.465	-0.272
2	55070	54649	0.641	-0.445
3	59712	59291	0.695	-0.516
4	64783	64362	0.755	-0.610
5	66444	66023	0.774	-0.646
6	61933	61512	0.721	-0.555
7	76999	76578	0.898	-0.992
8	77129	76708	0.900	-0.998
9	77869	77448	0.908	-1.038
10	79876	79455	0.932	-1.166
11	78160	77739	0.912	-1.054
12	78100	77679	0.911	-1.051
13	81743	81322	0.954	-1.335

Fig. 28

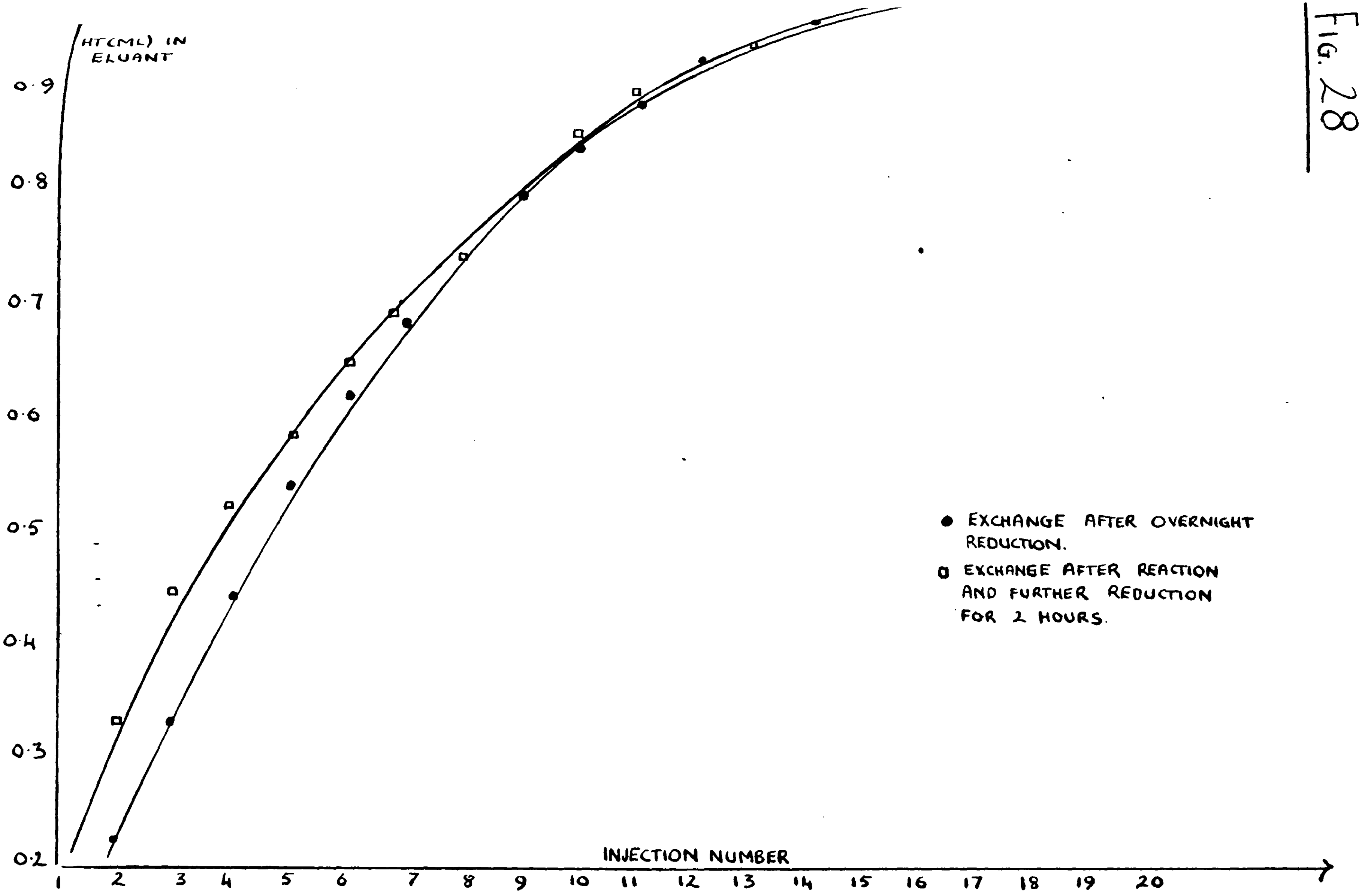
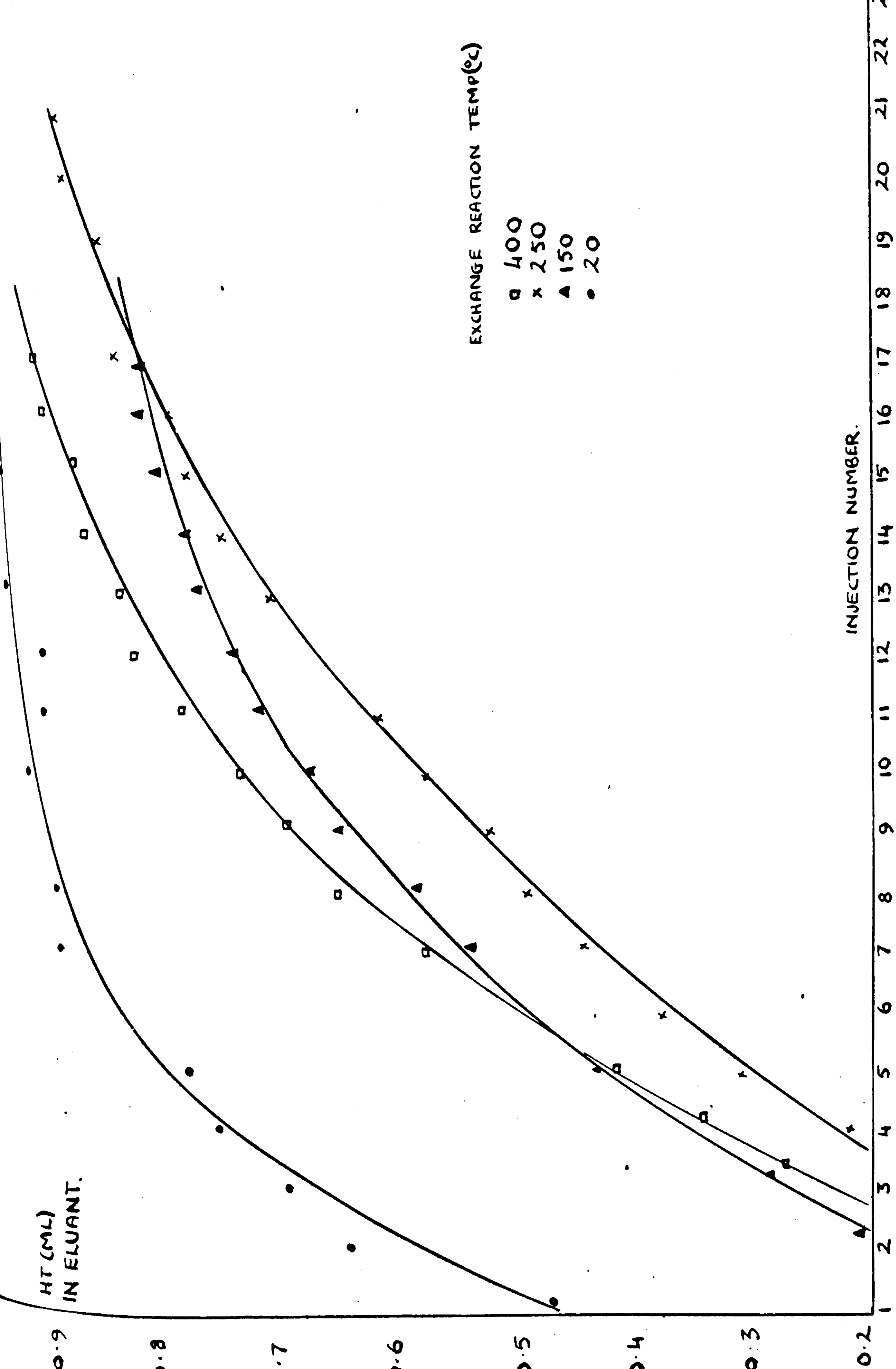

HT(ML) IN ELUANT
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
INJECTION NUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
● EXCHANGE AFTER OVERNIGHT REDUCTION.
□ EXCHANGE AFTER REACTION AND FURTHER REDUCTION FOR 2 HOURS.

FIG. 29


HT (ML) IN ELUANT.
INJECTION NUMBER.
EXCHANGE REACTION TEMP(°C)
▫ 400
× 250
▲ 150
● 20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
0·9
·8
·7
·6
·5
·4
0·3
0·2

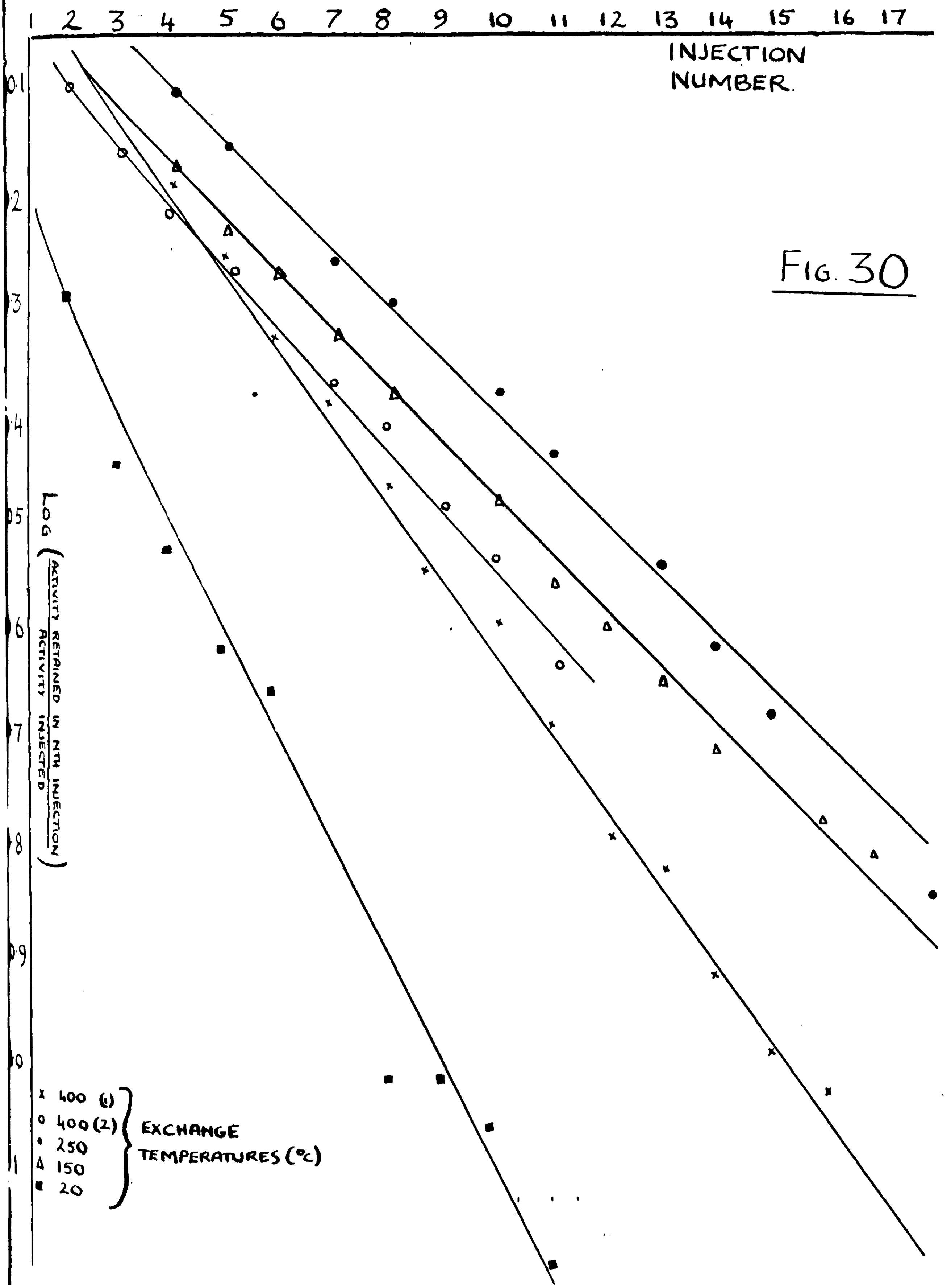
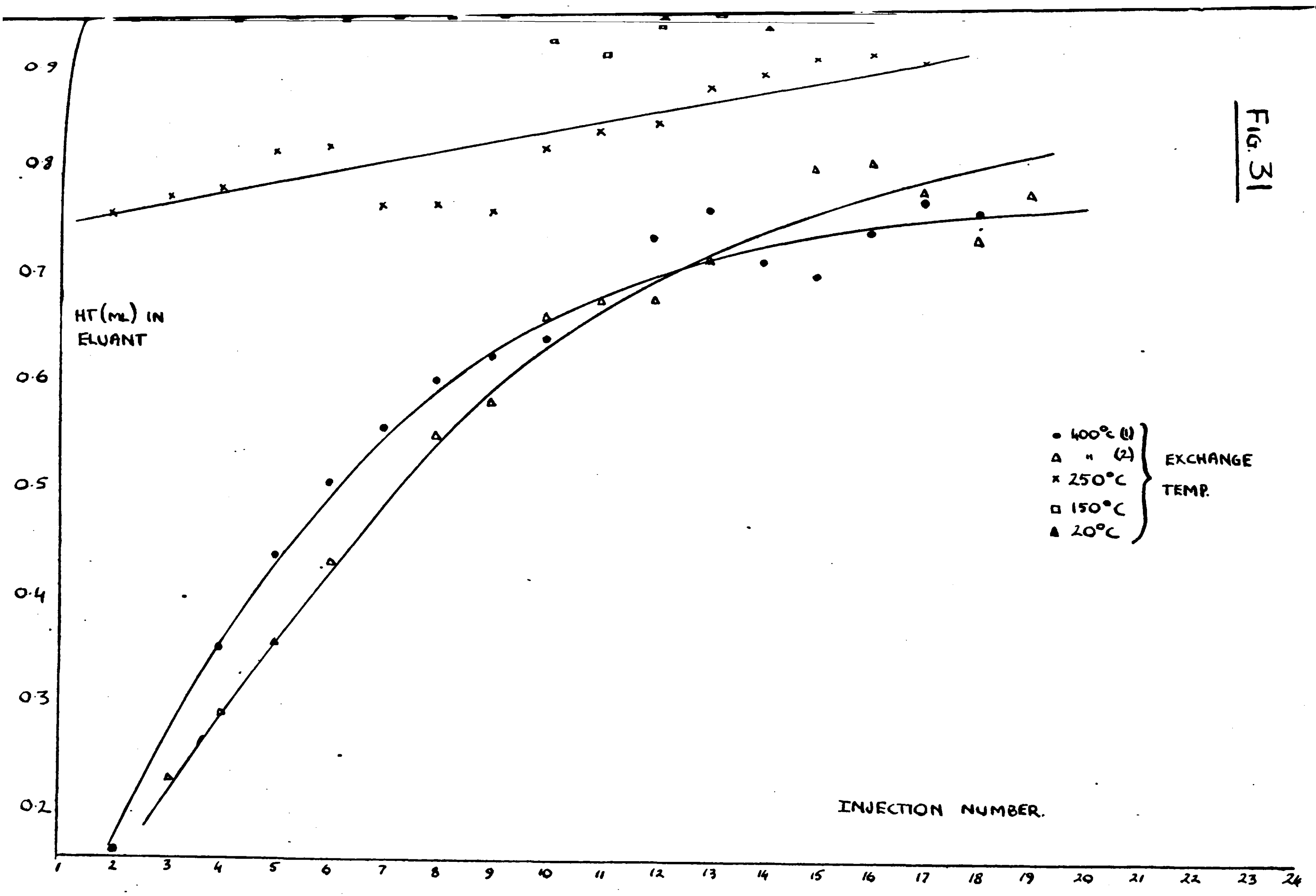

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
INJECTION NUMBER.
0·1
·2
·3
·4
0·5
·6
·7
·8
0·9
0
1
LOG (ACTIVITY RETAINED IN NTH INJECTION / ACTIVITY INJECTED)
x 400 (1)
o 400 (2)
• 250
Δ 150
■ 20
EXCHANGE TEMPERATURES (°C)

FIG. 30

FIG. 31



HT (ML) IN ELUANT
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
INJECTION NUMBER.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
● 400°C (1)
△ " (2)
× 250°C
□ 150°C
▲ 20°C
EXCHANGE TEMP.

FIG. 32

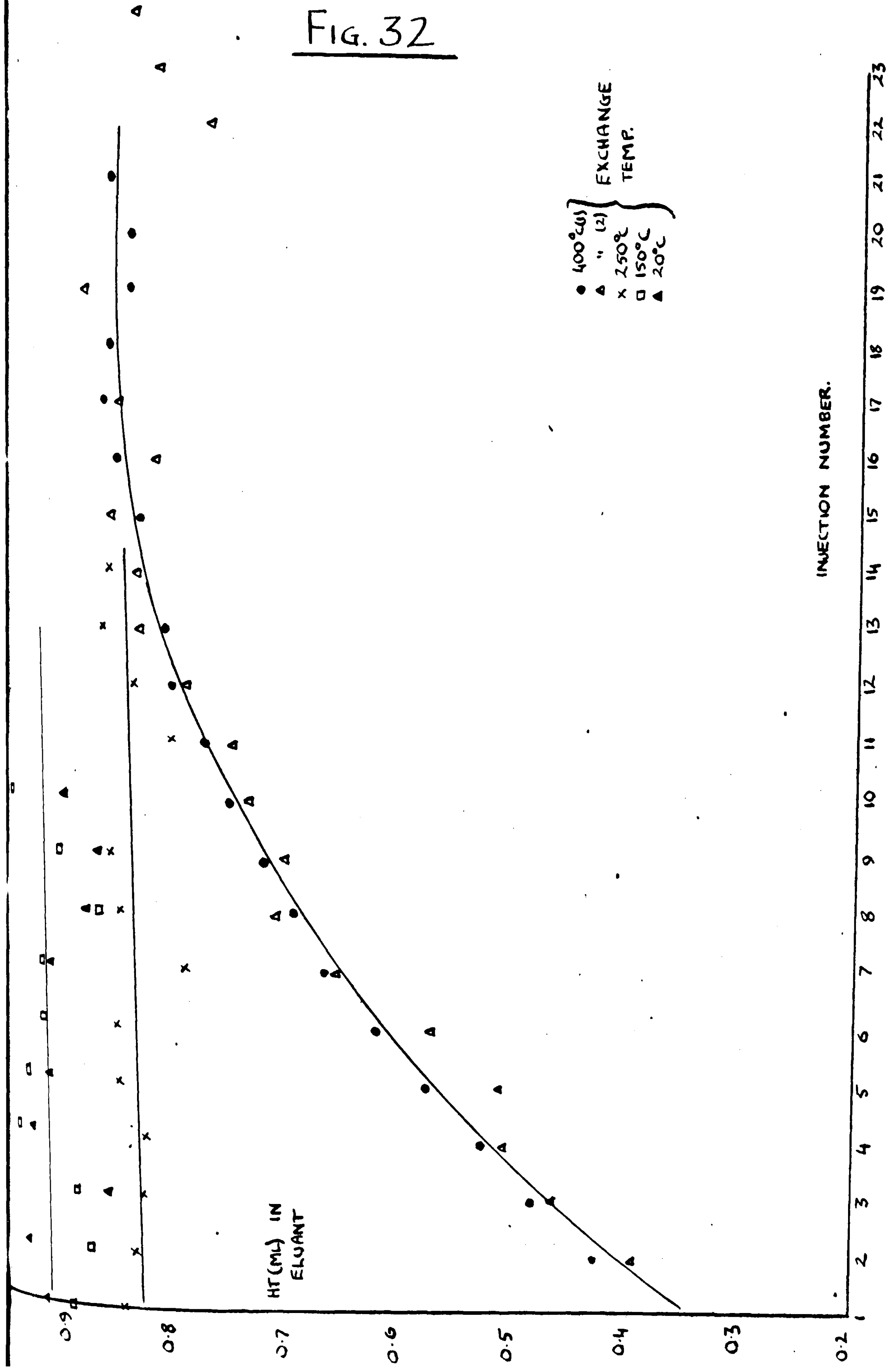

HT(ML) IN ELUANT
INJECTION NUMBER.
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
● 400°C(1)
△ " (2)
× 250°C
□ 150°C
▲ 20°C
EXCHANGE TEMP.

FIG. 33.

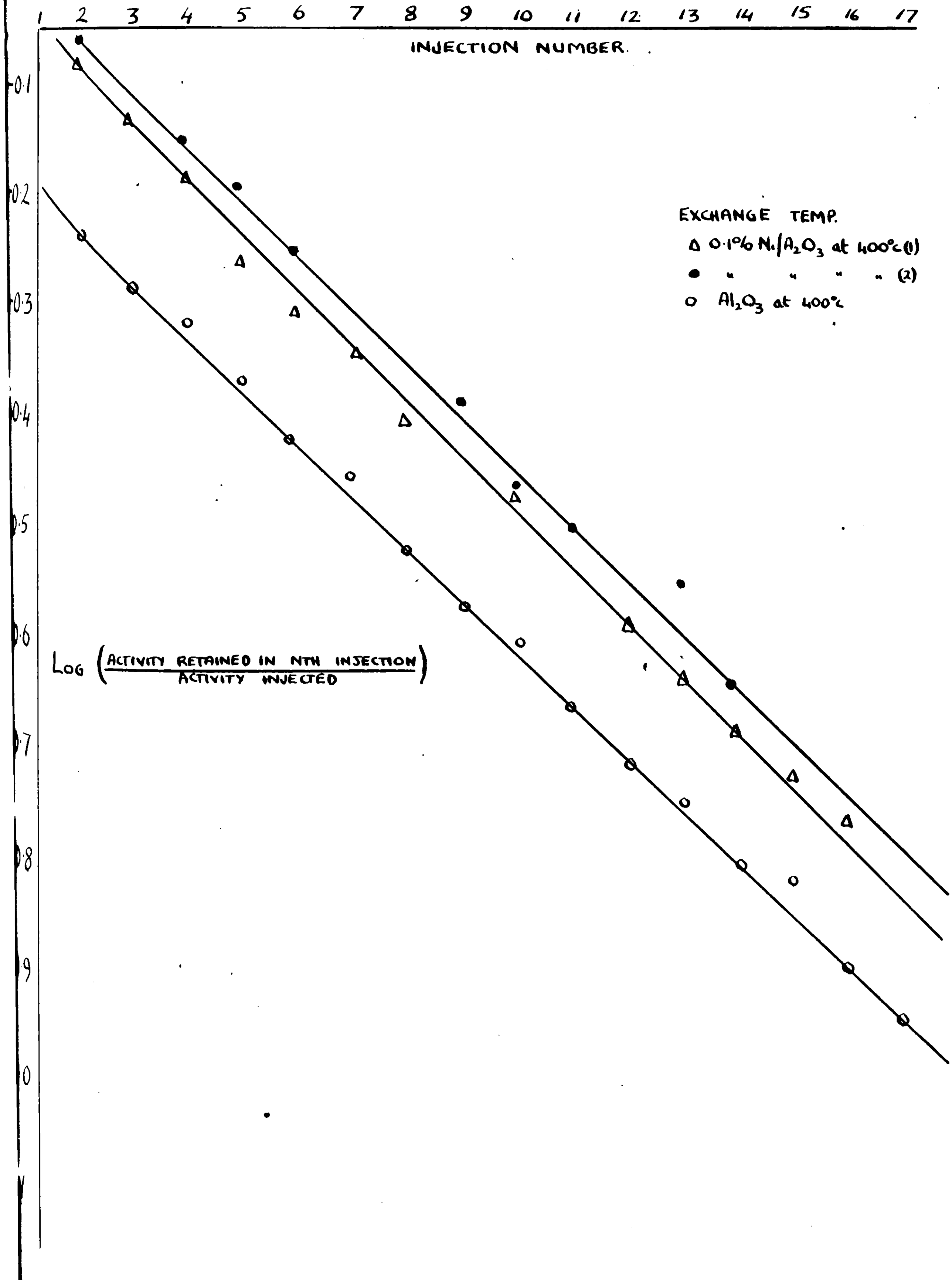
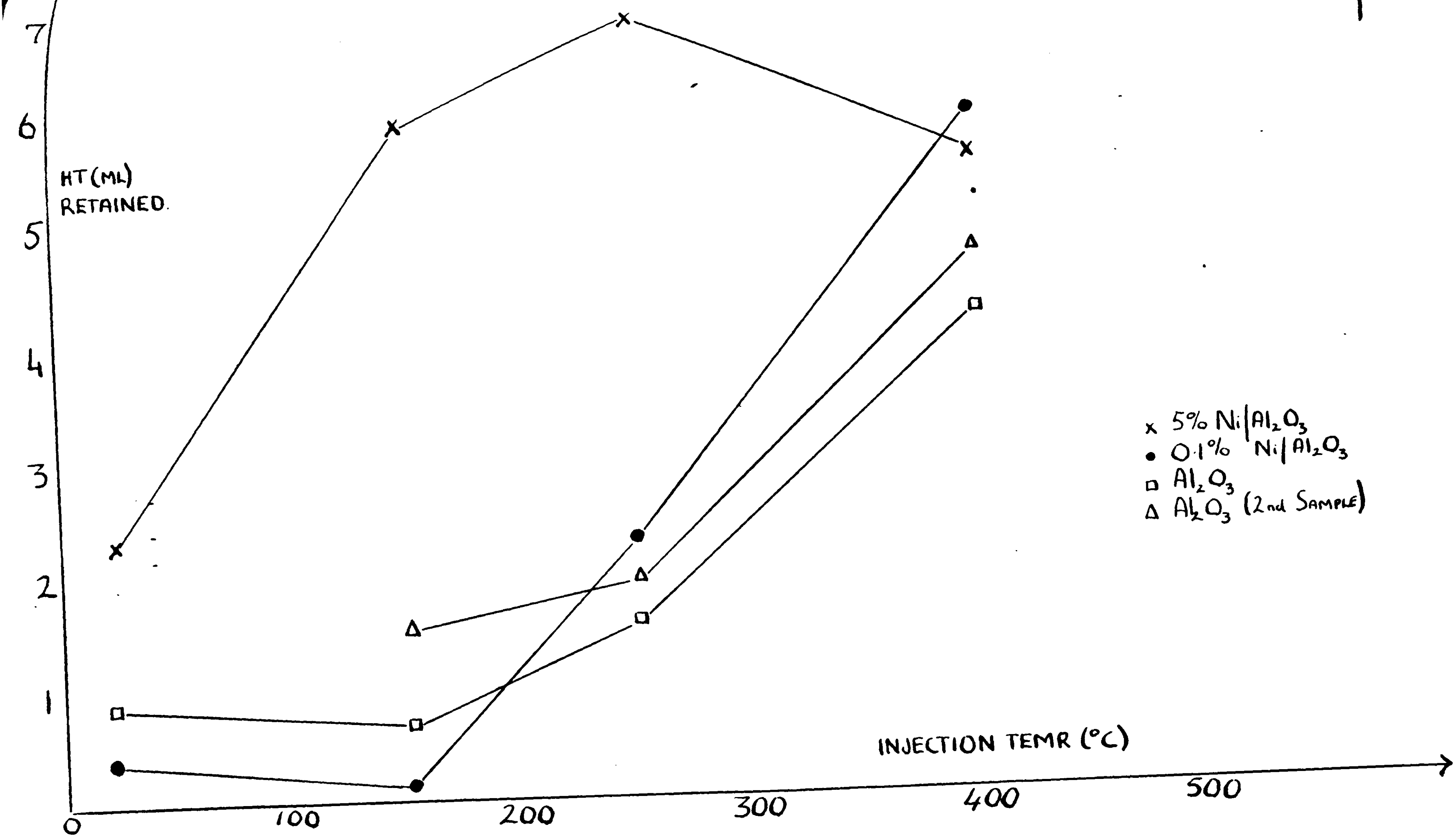

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
INJECTION NUMBER.
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
EXCHANGE TEMP.
Δ 0·1% Ni/Al₂O₃ at 400°c (1)
● " " " " (2)
○ Al₂O₃ at 400°c
Log (Activity retained in Nth injection / Activity injected)

FIG. 34



HT (ML) RETAINED.
7
6
5
4
3
2
1
0
100
200
300
400
500
INJECTION TEMR (°C)
× 5% Ni|Al₂O₃
● 0.1% Ni|Al₂O₃
□ Al₂O₃
Δ Al₂O₃ (2nd SAMPLE)

against the injection number. In Fig. 28 the set of results obtained at 400°C after overnight reduction, and after a further 2 hour reduction are compared. Slightly lower exchange was found with the catalyst after the second and shorter reduction.

The variety of exchange patterns with the 5%Ni/Al_2O_3 catalyst at the four reaction temperatures is shown in Fig. 29. By applying the exponential treatment to these results straight line plots were again obtained (see Fig. 30). A maximum value (8.3ml) of exchangeable hydrogen for the 5% catalyst was found at 250°C and the minimum exchange was observed at room temperature (3.5ml).

Results for the exchange reaction with 0.1%Ni/Al_2O_3 and Al_2O_3, treated as a catalyst, are plotted in Figs. 31 and 32 respectively. In each case the figures for both exchange reactions at 400°C are shown. Logarithmic plots (see Fig. 33) of the results at 400°C for the latter catalysts yield the following amounts of exchangeable hydrogen; 8.5ml for the 0.1% catalyst and 8.9ml for the Al_2O_3. These results compare favourably with those obtained in the exchange reactions conducted only at the reduction temperature.

The volumes of labelled hydrogen retained in the first 12 injections by the alumina catalysts at the different exchange temperatures were calculated. The amount retained was plotted against the exchange temperature (see Fig. 34).

It can be seen that a maximum value is obtained for the 5% catalyst at 250°C, while retention by the 0.1% and Al_2O_3 catalysts continues to increase as the temperature is raised.

Section 3.2 The Reactivity of the Retained Tritium Towards Ethylene.

Catalysts were treated with tritium by both the static and flow methods of exchange, [see Section 2.10 (iii)]. Injections of ethylene (0.5ml) were then made onto the catalyst at the following temperatures; 20°C, 50°C, 150°C, 250°C and 350°C. Hydrogenation of the ethylene to ethane and incorporation of tritium into ethylene and ethane were observed.

As the temperature of the catalyst was being raised, peaks were sometimes observed on the counter recorder although the chromatograph recorder remained at the base line level, even when set at the highest sensitivity. In the flow exchange experiments using tritium there was always a rapid return to background counts after an injection was made over the catalyst, and the desorption of radioactive material was not observed as the temperature of the catalyst was raised. This would suggest that tritium labelled carbonaceous species were being desorbed from the catalyst after the surface had been dosed with ethylene, rather than tritium labelled hydrogen.

(i) The reaction of ethylene on catalysts treated by the static method of tritium exchange.

Catalysts studied were 0.1% and 5%Ni/Al_2O_3, and 0.1%

and 5%Ni/SiO_2. The results for the first injection of ethylene onto the catalysts at each temperature are shown in Table 6.

With the 5% catalysts ethylene and ethane appeared at the lower temperatures, while cracking commenced at 250°C to produce methane. The production of ethane, termed the hydrogenation activity, was greater with the alumina catalyst than the silica catalyst. Both catalysts showed maximum hydrogenation activity at 250°C, the temperature at which methane appeared. The Ni/Al_2O_3 catalyst also showed a higher cracking activity.

The exchange of ethylene with tritium, called the exchange activity, was not significant although incorporation of tritium into ethane was greater with the alumina-supported catalyst than the silica-supported catalyst.

Ethylene injections onto 0.1% catalysts produced no hydrogenation activity and no cracking activity. A small amount of ethylene exchange was observed at the higher temperatures. It would appear that the metal concentration has a greater effect on the hydrogenation and cracking activity than it does on the exchange activity.

(ii) The reaction of ethylene on catalysts treated by the flow method of tritium exchange.

Al_2O_3, 0.1%Ni/Al_2O_3, 5%Ni/Al_2O_3, 0.1%Ni/SiO_2, 5%Ni/SiO_2, Ni/P and Ni powder catalysts were used.

TABLE 6

Ethylene on Tritiated Ni catalysts (Static Exchange)

(Results for the First Injection at each Temperature)

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
5%Ni/SiO$_2$	20	0.15	-	-	0.10	0.00	0.25	0.00
	50	0.08	-	-	0.01	0.00	0.41	0.00
	150	0.14	-	-	0.17	0.11	0.19	0.03
	250	0.15	0.02	0.91	0.34	0.23	-	-
	350	0.28	0.14	0.86	0.15	0.63	-	-
	450	0.43	0.14	1.3	-	-	-	-
5%Ni/Al$_2$O$_3$	20	0.25	-	-	0.22	0.00	0.03	0.00
	50	0.17	-	-	0.22	0.00	0.11	0.00
	150	0.13	-	-	0.36	0.06	0.01	0.00
	250	0.20	0.14	0.60	0.23	0.92	-	-
	350	0.37	0.24	0.42	0.01	1.5	-	-

TABLE 6 CONTD.

Catalyst	Catalyst Temp(^{o}C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpml$\times 10^{-5}$	ml	cpml$\times 10^{-5}$	ml	cpml$\times 10^{-5}$
0.1%Ni/SiO$_2$	20	0.03	-	-	-	-	0.47	0.00
	50	0.01	-	-	-	-	0.49	0.00
	150	0.02	-	-	-	-	0.48	0.00
	250	0.04	-	-	-	-	0.46	0.00
	350	0.04	-	-	-	-	0.46	0.004
0.1%Ni/Al$_2$O$_3$	20	0.06	-	-	-	-	0.44	0.00
	50	0.02	-	-	-	-	0.48	0.00
	150	0.06	-	-	-	-	0.44	0.00
	250	0.02	-	-	-	-	0.48	0.006
	350	0.05	-	-	-	-	0.45	0.02

A procedure similar to that above was adopted in these experiments. Injections of ethylene (0.5ml) were made onto the catalysts over the same range of temperature after a tritium flow exchange experiment had been completed at 400°C. The catalysts were then cooled to room temperature and in the case of the 5% catalysts 4 injections of ethylene were made at each temperature. The results for the alumina and silica-supported catalysts are shown in Tables 7 and 8 respectively.

The hydrogenation activity of the 5% catalysts decreased with successive injections at the lower temperatures. As the temperature was raised from 20°C to 50°C the production of ethane diminished but was restored by raising the catalyst temperature to 150°C. At 250°C and 350°C hydrogenation was greater with the silica catalyst than the alumina catalyst although this was compensated by the greater cracking activity of the latter. Similar patterns had been observed with the 5% catalysts treated by the static method of tritium exchange.

On both the alumina-supported and the silica-supported catalysts the activity of the ethane was considerably greater than that of the ethylene. The activity of the ethane produced was greater on catalysts supported on alumina than on silica. The extent of ethylene retention was also greater with the alumina catalyst.

TABLE 7

Ethylene on Tritiated Ni Alumina Catalysts

(Flow Exchange of Tritium)

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
Al_2O_3	20°C	-	-	-	-	-	0.50	0.00
	50°C	-	-	-	-	-	0.50	0.00
	150°C	-	-	-	-	-	0.50	0.00
	250°C	0.02	-	-	-	-	0.48	0.00
	350°C	0.06	-	-	-	-	0.44	0.00
0.1%Ni/Al_2O_3	20°C	0.01	-	-	-	-	0.49	0.00
	50°C	0.02	-	-	-	-	0.48	0.00
	150°C	0.00	-	-	-	-	0.50	0.00
	250°C	0.00	-	-	-	-	0.50	0.05
	350°C	0.01	-	-	-	-	0.49	0.07

TABLE 7 CONTD.

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
5%Ni/Al$_2$O$_3$	20°C(1)	0.23	-	-	0.25	0.00	0.02	0.00
	" (2)	0.15	-	-	0.12	0.00	0.23	0.00
	" (3)	0.11	-	-	0.02	0.00	0.37	0.00
	" (4)	0.10	-	-	-	-	0.40	0.00
	50°C(1)	0.11	-	-	0.04	0.00	0.35	0.00
	" (2)	0.10	-	-	0.04	0.00	0.36	0.00
	" (3)	0.09	-	-	0.01	0.00	0.40	0.00
	" (4)	0.09	-	-	0.01	0.00	0.40	0.00
	150°C(1)	0.14	-	-	0.36	0.12	-	-
	" (2)	0.16	-	-	0.34	0.18	-	-
	" (3)	0.20	-	-	0.30	0.21	-	-
	" (4)	0.18	-	-	0.26	0.23	0.06	0.22

TABLE 7 CONTD.

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpml x 10^{-5}	ml	cpml x 10^{-5}	ml	cpml x 10^{-5}
5%Ni/Al_2O_3	250°C(1)	0.21	0.05	2.22	0.27	0.54	-	-
	" (2)	0.20	0.05	2.08	0.28	0.56	-	-
	" (3)	0.18	0.04	1.81	0.30	0.52	-	-
	" (4)	0.22	0.03	2.31	0.27	0.59	-	-
	350°C(1)	0.38	0.22	1.45	0.02	1.13	-	-
	" (2)	0.38	0.22	1.34	0.02	1.02	-	-
	" (3)	0.39	0.20	1.25	0.02	0.75	-	-
	" (4)	0.39	0.20	1.20	0.02	0.46	-	-

TABLE 8

Ethylene on Tritiated Ni/SiO$_2$ Catalysts (Flow Exchange of Tritium)

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
0.1%Ni/SiO$_2$	20	0.03	-	-	-	-	0.47	0.00
	50	0.01	-	-	-	-	0.49	0.00
	150	0.05	-	-	-	-	0.45	0.00
	250	0.05	-	-	-	-	0.45	0.00
	350	0.03	-	-	-	-	0.47	0.00
5%Ni/SiO$_2$	20(1)	0.10	-	-	0.12	0.00	0.28	0.00
	"(2)	0.03	-	-	0.07	0.00	0.40	0.00
	"(3)	0.03	-	-	0.02	0.00	0.45	0.00
	"(4)	0.03	-	-	-	-	0.47	0.00
	50(1)	0.03	-	-	0.03	0.00	0.44	0.004
	"(2)	0.03	-	-	0.03	0.00	0.45	0.006
	"(3)	0.02	-	-	-	-	0.48	0.006
	"(4)	0.03	-	-	-	-	0.47	0.005

TABLE 8 CONTD.

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
5%Ni/SiO$_2$	150(1)	0.09	-	-	0.11	0.09	0.30	0.014
	" (2)	0.04	-	-	0.04	0.08	0.42	0.014
	" (3)	0.04	-	-	0.02	0.04	0.44	0.012
	" (4)	0.03	-	-	0.01	0.05	0.46	0.012
	250(1)	0.17	0.01	2.5	0.33	0.26	-	-
	" (2)	0.12	0.01	2.5	0.38	0.12	-	-
	" (3)	0.14	0.01	2.0	0.36	0.12	-	-
	" (4)	0.13	0.01	1.6	0.37	0.13	-	-
	350(1)	0.24	0.12	2.4	0.20	0.26	-	-
	" (2)	0.27	0.10	2.2	0.18	0.20	-	-
	" (3)	0.28	0.10	1.8	0.17	0.16	-	-
	" (4)	0.28	0.08	1.7	0.18	0.14	-	-

TABLE 9

Ethylene on Tritiated Ni and Ni/P Catalysts.

Catalyst	Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpm $\times 10^{-5}$	ml	cpm $\times 10^{-5}$	ml	cpm $\times 10^{-5}$
Ni	20°C	0.04	-	-	0.02	0.03	0.44	0.00
	50°C	0.01	-	-	0.01	0.00	0.48	0.00
	150°C	0.03	-	-	0.02	0.00	0.45	0.00
	250°C	0.05	-	-	0.20	0.006	0.25	0.002
	350°C	0.31	0.06	0.04	0.16	0.01	-	-
Ni/P	20°C	0.02	-	-	-	-	0.48	0.00
	50°C	0.02	-	-	-	-	0.48	0.00
	150°C	0.02	-	-	-	-	0.48	0.00
	250°C	0.03	-	-	0.01	0.00	0.46	0.009
	350°C	0.05	-	-	0.02	0.06	0.43	0.008

0.5g samples of Ni powder and the alloy of Ni and P were also treated with tritium by flow exchange. The results of the first ethylene injection at each temperature are shown in Table 9.

The extent of retention and hydrogenation on these catalysts was found to be low. The Ni powder catalyst exhibited slight cracking activity at 350°C. Although ethylene exchange was greater with the Ni/P catalyst at 250°C, the hydrogenation activity was less than that of the Ni catalyst.

Section 3.3 Ethylene Exchange Reactions.

Two forms of isotopically labelled ethylene were used in the exchange experiments: $^{14}C_2H_4$ and C_2D_4. As before, injections of labelled material were made over the catalysts after reduction, first at room temperature, then at a range of higher temperatures. An injection of inactive ethylene was made after the labelling process at each temperature. The products were separated by gas chromatography and analysed for exchange by gas proportional counting or mass spectrometry as appropriate.

(i) $C_2H_4/^{14}C_2H_4$ (preadsorbed) exchange. 0.1%Ni/Al_2O_3, 5%Ni/Al_2O_3, 5%Ni/SiO_2, Ni powder and Ni/P alloy catalysts were used. Four injections of $^{14}C_2H_4$ were made at each temperature over the 5% Ni catalysts. The reactivity of the retained ethylene was studied by injecting 0.5ml of inactive ethylene onto the $^{14}C_2H_4$ treated surface and determining the radioactivity of the products. The results are shown in Table 10 and 11. The extent of retention with successive injections tended to decrease more rapidly at the lower temperatures. The Ni/Al_2O_3 catalyst retained more than the Ni/SiO_2 catalyst and this was again more evident at the lower temperatures. Molecular exchange of ethylene was not observed for either catalyst at any temperature. Methane appeared in the exchange products at 250°C and 350°C with the Al_2O_3 supported catalyst but only at the higher temperature in the case of the SiO_2 supported Ni.

As in the tritium experiments, trace amounts of radioactive species were again desorbed from the catalysts as the temperature was increased. The quantities involved were too small to be detected by the chromatograph. It was observed that desorption was considerably greater from the 5%Ni/Al_2O_3 catalyst than it was from the 0.1%Ni/Al_2O_3 catalyst. Desorption from 5%Ni/SiO_2 was similar to that from the alumina catalyst of the of the same metal content. It would therefore appear that this effect is more dependent on the metal concentration than on the nature of the catalyst support.

There is, therefore, no ethylene retained on the catalyst surface in a form that will undergo simple molecular exchange. Carbonaceous species are, however removed as the temperature is raised and, furthermore, at higher temperatures surface species

The Exchange of C_2H_4 with Preadsorbed $^{14}C_2H_4$ on 5%Ni/Al_2O_3

		Catalyst Temp(°C)	Retention (ml)	Methane ml	Methane cpml×10^{-5}	Ethane ml	Ethane cpml×10^{-5}	Ethylene ml	Ethylene cpml×10^{-5}
		20°C							
$^{14}C_2H_4$	(1)		0.33	–	–	0.17	0.66	–	–
	(2)		0.21	–	–	0.13	0.71	0.16	0.97
	(3)		0.13	–	–	0.08	0.72	0.29	0.91
	(4)		0.10	–	–	0.02	0.96	0.38	0.92
C_2H_4		50°C	0.06	–	–	–	–	0.44	0.00
$^{14}C_2H_4$	(1)		0.09	–	–	0.06	0.80	0.35	0.87
	(2)		0.05	–	–	0.03	0.88	0.42	0.79
	(3)		0.03	–	–	0.02	1.3	0.45	0.80
	(4)		0.03	–	–	0.01	1.6	0.46	0.81
C_2H_4		150°C	0.03	–	–	–	–	0.47	0.00
$^{14}C_2H_4$	(1)		0.25	–	–	0.23	0.65	0.02	2.0
	(2)		0.20	–	–	0.17	0.70	0.13	1.1
	(3)		0.17	–	–	0.13	0.77	0.20	1.0
	(4)		0.15	–	–	0.09	0.80	0.26	1.0

TABLE 10 CONTD.

		Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpml$\times10^{-5}$	ml	cpml$\times10^{-5}$	ml	cpml$\times10^{-5}$
C_2H_4		150°C 250°C	0.12	-	-	0.06	0.00	0.32	0.00
$^{14}C_2H_4$	(1)		0.30	0.04	1.2	0.18	0.71	-	-
	(2)		0.27	0.02	1.5	0.22	0.67	-	-
	(3)		0.26	0.02	1.2	0.23	0.66	-	-
	(4)		0.26	0.02	1.1	0.23	0.66	-	-
C_2H_4			0.26	0.02	0.2	0.23	0.00	-	-
$^{14}C_2H_4$	(1)	350°C	0.31	0.27	0.62	0.05	1.0	-	-
	(2)		0.32	0.23	0.71	0.06	1.0	-	-
	(3)		0.32	0.23	0.75	0.06	1.0	-	-
	(4)		0.32	0.23	0.77	0.06	0.90	-	-
C_2H_4			0.31	0.25	0.50	0.06	0.00	-	-

The Exchange of C_2H_4 with $^{14}C_2H_4$ Preadsorbed on 5%Ni/SiO$_2$

		Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
		20°C							
$^{14}C_2H_4$	(1)		0.15	-	-	0.1	0.6	0.25	0.76
	(2)		0.03	-	-	0.02	0.7	0.45	0.71
	(3)		0.04	-	-	-	-	0.46	0.73
	(4)		0.03	-	-	-	-	0.47	0.74
C_2H_4		50°C	0.02	-	-	-	-	0.48	0.00
$^{14}C_2H_4$	(1)		0.04	-	-	0.03	0.61	0.43	0.73
	(2)		0.02	-	-	-	-	0.48	0.71
	(3)		0.02	-	-	-	-	0.48	0.72
	(4)		0.02	-	-	-	-	0.48	0.72
C_2H_4		150°C	-	-	-	-	-	0.50	0.00
$^{14}C_2H_4$	(1)		0.01	-	-	-	-	0.49	0.72
	(2)		-	-	-	-	-	0.50	0.72
	(3)		-	-	-	-	-	0.50	0.71
	(4)		-	-	-	-	-	0.50	0.00

TABLE 11 CONTD.

		Catalyst Temp(^{o}C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpm1x10^{-5}	ml	cpm1x10^{-5}	ml	cpm1x10^{-5}
C_2H_4		150°C 250°C	-	-	-	-	-	0.50	0.00
$^{14}C_2H_4$	(1)		Faulty Injection						
	(2)		0.27	0.03	1.2	0.21	0.66	-	-
	(3)		0.27	0.02	1.8	0.22	0.64	-	-
	(4)		0.26	0.01	1.4	0.21	0.66	0.02	1.0
C_2H_4			0.21	-	-	0.18	0.00	0.11	0.00
$^{14}C_2H_4$	(1)	350°C	0.34	0.11	0.92	0.10	0.73	-	-
	(2)		0.34	0.06	0.91	0.13	0.72	-	-
	(3)		0.34	0.04	1.2	0.14	0.70	-	-
	(4)		0.33	0.04	1.0	0.15	0.72	-	-
C_2H_4			0.33	0.03	1.6	0.15	0.00	-	-

appear as part of the methane fraction from ethylene cracking.

The results of the exchange reaction on the Ni powder and Ni-P alloy catalysts are shown in Tables 12 and 13.

The Ni powder catalyst showed hydrogenation activity at the higher temperatures and, to a lesser degree, some cracking activity. Only traces of ethane were observed with the Ni/P catalyst. Molecular ethylene exchange was found, however, on the Ni/P catalyst at room temperature. It appears that, in some way, the presence of phosphorus poisons the nickel towards hydrogenation or cracking but does not prohibit the exchange reaction.

(ii) C_2H_4/C_2D_4 (preadsorbed) exchange on 5%Ni/Al_2O_3 5%Ni/SiO_2 and Ni powder.

The experimental procedure used was similar to the radiochemically labelled ethylene exchange reaction discussed in the last section. The gas proportional counter was not, of course, used in these experiments and was replaced by a series of three capillary U-tube traps into which products from the 'light' ethylene injections onto the pretreated catalysts could be condensed using liquid nitrogen. Once again, reactions were studied at five temperatures, the sequence of injections being four doses (0.5ml) of C_2D_4 followed by one of C_2H_4 (0.5ml). To illustrate the comparability of the catalytic conditions with those employed in the $^{14}C_2H_4$ (preadsorbed)/C_2H_4 exchange reaction the products from the C_2D_4 pretreatment injections were analysed and compared with those obtained in the radiochemical pretreatment with $^{14}C_2H_4$. Very similar results were obtained in both cases. The distribution of products obtained from the C_2D_4 injections onto 5%Ni/Al_2O_3 is shown in Table 14.

Depending on availability of the instruments, either an A.E.I. 'M.S. 10' or 'M.S. 12' was used to analyse the products of the 'light' ethylene injections. In each case an electron energy of 15ev was used. With this low energy only two or three fragment ions were formed and subsequent calculations were made relatively simple. Product compounds were distinguishable by the different fragment ions to which they gave rise and it is therefore necessary to estimate and subtract from the observed total ion current at each mass the contributions of all fragment ions to that mass, in order to derive the contribution of the parent ion. The mass spectrum of each individual species was not known but was obtained by purely statistical reasoning. This method ignored the differences which exist between the various isomers of a particular mass and made the approximation that the removal of a hydrogen atom and a deuterium atom was equally easy and that the probability of loss was not dependent on isotopic composition. This model proved satisfactory in that the calculated ion currents at masses less than that of the lightest parent ion compared favourably with those observed.

TABLE 12

Ethylene Exchange with Labelled Ethylene Residues on Ni Powder.

	Catalyst Temp(^{o}C)	Retention (ml)	Methane		Ethane		Ethylene	
			ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
	$20^{o}C$							
$^{14}C_2H_4(1)$		0.03	-	-	0.01	0.67	0.46	0.40
$^{14}C_2H_4(2)$		0.02	-	-	-	-	0.48	0.38
C_2H_4		0.04	-	-	-	-	0.46	0.00
	$50^{o}C$							
$^{14}C_2H_4(1)$		0.02	-	-	-	-	0.48	0.40
$^{14}C_2H_4(2)$		0.02	-	-	-	-	0.48	0.39
C_2H_4		0.03	-	-	-	-	0.47	0.00
	$150^{o}C$							
$^{14}C_2H_4(1)$		0.02	-	-	0.04	0.4	0.44	0.4
$^{14}C_2H_4(2)$		0.00	-	-	0.02	0.5	0.48	0.38
C_2H_4		0.00	-	-	0.01	0.00	0.49	0.00

TABLE 12 CONTD.

		Catalyst Temp(°C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpmlx10^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
		250°C							
$^{14}C_2H_4$	(1)		0.22	0.02	1.6	0.23	0.35	0.04	0.50
	(2)		0.07	-	-	0.10	0.34	0.33	0.41
	(3)		0.08	-	-	0.10	0.33	0.32	0.43
C_2H_4			0.05	-	-	0.10	0.00	0.35	0.00
		350°C							
$^{14}C_2H_4$	(1)		0.34	0.03	0.3	0.15	0.32	-	-
	(2)		0.30	0.02	0.3	0.18	0.30	0.01	0.40
	(3)		0.25	0.01	0.4	0.15	0.31	0.09	0.50
C_2H_4			0.22	-	-	0.11	0.00	0.17	0.00

Ethylene Exchange with Labelled Ethylene Residues on Ni/P Alloy.

		Catalyst Temp(^{o}C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpmlx16^{-5}	ml	cpmlx10^{-5}	ml	cpmlx10^{-5}
		20^{o}C							
$^{14}C_2H_4$	(1)		0.07	-	-	-	-	0.43	0.90
	(2)		0.01	-	-	-	-	0.49	0.93
	(3)		-	-	-	-	-	0.50	0.93
	(4)		-	-	-	-	-	0.50	0.91
C_2H_4			-	-	-	-	-	0.50	0.11
		50^{o}C							
$^{14}C_2H_4$	(1)		-	-	-	-	-	0.50	0.87
	(2)		-	-	-	-	-	0.50	0.88
	(3)		-	-	-	-	-	0.50	0.92
	(4)		-	-	-	-	-	0.50	0.89
C_2H_4			-	-	-	-	-	0.50	0.04
		150^{o}C							
$^{14}C_2H_4$	(1)		0.04	-	-	0.05	2.8	0.41	0.94
	(2)		0.03	-	-	-	-	0.47	0.93
	(3)		0.02	-	-	-	-	0.48	0.91
	(4)		0.02	-	-	-	-	0.48	0.93

TABLE 13 CONTD.

		Catalyst Temp(^{o}C)	Retention (ml)	Methane		Ethane		Ethylene	
				ml	cpml$\times$10^{-5}	ml	cpml$\times$10^{-5}	ml	cpml$\times$10^{-5}
		150^{o}C							
C_2H_4			0.02	-	-	-	-	0.48	0.00
		250^{o}C							
$^{14}C_2H_4$	(1)		0.08	-	-	0.03	1.0	0.39	1.0
	(2)		0.06	-	-	0.02	1.0	0.42	0.98
	(3)		0.05	-	-	0.01	2.4	0.44	0.97
	(4)		-	-	-	-	-	0.50	0.87
C_2H_4			-	-	-	-	-	0.50	0.00
		350^{o}C							
$^{14}C_2H_4$	(1)		0.04	-	-	0.01	1.2	0.45	0.95
	(2)		0.03	-	-	-	-	0.47	0.93
	(3)		0.02	-	-	-	-	0.48	0.91
	(4)		0.02	-	-	-	-	0.48	0.91
C_2H_4			0.02	-	-	-	-	0.48	0.00

TABLE 14

The Exchange of C_2H_4 With Preadsorbed C_2D_4 on 5% Ni/Al_2O_3

		Catalyst Temp (C°)	Retention (ml)	METHANE Deuterium		ETHANE Deuterium		ETHYLENE Deuterium	
				ml	No.	ml	No.	ml	No.
C_2D_4	(1)	20	0.33	-	-	0.17	-	-	-
	(2)		0.26	-	-	0.13	-	0.11	-
	(3)		0.15	-	-	0.07	-	0.28	-
	(4)		0.06	-	-	0.01	-	0.43	-
C_2H_4			0.03	-	-	-	-	0.47	0.28
C_2D_4	(5)	50	0.07	-	-	0.02	-	0.41	-
	(6)		0.06	-	-	0.02	-	0.42	-
	(7)		0.05	-	-	0.01	-	0.44	-
	(8)		0.03	-	-	0.01	-	0.46	-
C_2H_4			0.05	-	-	-	-	0.45	0.23
C_2D_4	(9)	150	0.24	-	-	0.23	-	0.03	-
	(10)		0.20	-	-	0.18	-	0.12	-
	(11)		0.21	-	-	0.12	-	0.17	-
	(12)		0.13	-	-	0.11	-	0.26	-
C_2H_4			0.18	-	-	0.11	0.40	0.21	0.17

TABLE 14 CONTD.

		Catalyst Temp (°C)	Retention (ml)	METHANE Deuterium		ETHANE Deuterium		ETHYLENE Deuterium	
				ml	No.	ml	No.	ml	No.
C_2D_4	(13)	250	0.30	0.02	-	0.19	-	-	-
	(14)		0.27	0.02	-	0.22	-	-	-
	(15)		0.28	0.01	-	0.22	-	-	-
	(16)		0.28	0.01	-	0.22	-	-	-
C_2H_4			0.29	0.01	-	0.21	1.44	-	-
C_2D_4	(17)	350	0.30	0.26	-	0.07	-	-	-
	(18)		0.31	0.24	-	0.07	-	-	-
	(19)		0.30	0.25	-	0.08	-	-	-
	(20)		0.29	0.24	-	0.09	-	-	-
C_2H_4			0.32	0.26	-	0.05	1.88	-	-

With ethylene samples ion currents were calculated at masses 26 and 27 and with ethanes at masses 28 and 29. The breakdown pattern of reservoir C_2H_4, C_2D_4 and C_2H_6 was measured with each lot of samples so that accurate fragmentation factors could be applied to the computation of the parent ion currents. The presence of naturally occurring ^{13}C in the hydrocarbons was also taken into account in the calculations.

Sets of equations were used to calculate parent ion currents from the measured ion intensities of the ethylene and ethane products of the C_2H_4 injection. These equations are derived in Appendix II.

For the ethylenes,

Ion Mass	Measured Ion Intensity (Corrected For ^{13}C)	Parent Ion
32	A	a
31	B	b
30	C	c
29	D	d
28	E	e
27	G	
26	H	

then $a = A$

$b = B$

$c = C - f_1(0.25b + a)$

$d = D - f_1(0.75b + 0.5c)$

$e = E - f_1(0.5c + 0.75d) - f_2(a + 0.5b + 0.17c)$

$G = f_1(e + 0.25d) + f_2(0.5d + 0.67c + 0.5b)$

$H = f_2(e + 0.5d + 0.17c)$

where f_1 = height of $C_2H_3^+$ /height of $C_2H_4^+$, and f_2 = height of $C_2H_2^+$ /height of $C_2H_4^+$.

For the ethanes,

Ion Mass	Measured Ion Intensity (Corrected For ^{13}C)	Parent Ion
36	A	a
35	B	b
34	C	c
33	D	d
32	E	e
31	G	g
30	H	h
29	J	
28	K	

the equations are

36 $a = A$

35 $b = B$

34 $c = C - f_1(a + 1/6b)$

33 $d = D - f_1(5/6b + 1/3c)$

32 $e = E - f_1(2/3c + 1/2d) - f_2(a + 1/3b + 1/15c)$

31 $g = G - f_1(1/2d + 2/3e) - f_2(2/3b + 8/15c + 1/5d)$

30 $h = H - f_1(1/3e + 5/6g) - f_2(3/5c + 3/5d + 2/5e)$

29 $J = f_1(1/6g + h) + f_2(1/5d + 8/15e + 4/6g)$

28 $K = f_2(1/15e + 2/6g + h)$

where $f_1 =$ height of $C_2H_5^+$/height of $C_2H_6^+$, and $f_2 =$ height of $C_2H_4^+$ /height of $C_2H_6^+$.

The fragmentation ratios, for ethylene, f_1 and f_2, were almost identical at 0.17 and 0.18 respectively. The ratios for the ethanes were found to be 0.5 and 2.36 respectively. Ethane is a special case in that the process

$$C_2H_6 \longrightarrow C_2H_4^+ + H_2 + e^-$$

is particularly favoured, the appearance potential of $C_2H_4^+$ (12.7eV) being only very slightly greater than the ionisation potential of ethane (11.6eV).

Once calculated, the parent ion currents were converted into a percentage composition and from these values the mean number of deuterium atoms per ethylene molecule - the deuterium number - was derived. The fully deuterated ethylene used in the experiments was known to contain 4% of C_2D_3H (i.e. a deuterium number of 3.96) and consequently the products from the 'light' ethylene injections contained less deuterium than if this impurity had been absent. The appropriate correction was made to the apparent deuterium numbers.

The results of the exchange reaction over the catalysts, 5%Ni/Al_2O_3, 5%Ni/SiO_2 and Ni powder are shown in Tables 14, 15 and 16. The products of the pretreatment injections of C_2D_4 onto the Ni/Al_2O_3 catalyst are included in Table 14.

TABLE 15

C_2H_4/C_2D_4 (Preadsorbed) Exchange Reaction on 5% Ni/SiO_2

	Catalyst Temp (°C)	Retention (ml)	METHANE ml	METHANE Deuterium No.	ETHANE ml	ETHANE Deuterium No.	ETHYLENE ml	ETHYLENE Deuterium No.
C_2H_4	20	0.01	–	–	–	–	0.49	0.09
C_2H_4	50	0.01	–	–	–	–	0.49	0.10
C_2H_4	150	0.04	–	–	0.02	–	0.44	0.09
C_2H_4	250	0.21	–	–	0.15	0.21	0.14	0.16
C_2H_4	350	0.37	0.03	–	0.12	0.68	–	–

TABLE 16

C_2D_4 (Preadsorbed)/C_2H_4 Exchange Reaction on Ni Powder

	Catalyst Temp (°C)	Retention (ml)	METHANE		ETHANE		ETHYLENE	
			ml	Deuterium No.	ml	Deuterium No.	ml	Deuterium No.
C_2H_4	20	0.02	–	–	–	–	0.48	–
C_2H_4	50	0.02	–	–	–	–	0.48	–
C_2H_4	150	0.02	–	–	–	–	0.48	–
C_2H_4	250	0.08	–	–	0.03	–	0.39	0.06
C_2H_4	350	0.26	–	–	0.01	–	0.23	–

With the 5% Ni/Al_2O_3 catalyst, deuterium incorporation into the 'light' ethylene was found at the lower temperatures. A higher deuterium content was observed in the ethanes produced at the higher temperatures. A similar pattern was observed with the 5% Ni/SiO_2 catalyst although the deuterium numbers were lower. Apart from a slight incorporation of deuterium into ethylene at 250°C the nickel powder catalyst produced no exchange. At every temperature the supported metal catalysts predominantly yielded the mono-deuterated product. This is illustrated in Table 17.

The significance of the results is greatest when considered in conjunction with the results of the $^{14}C_2H_4$ (preadsorbed)/ C_2H_4 exchange reactions [see section 3.3(i)]. For the same three catalysts labelled carbon atoms were not observed in the products of the C_2H_4 injections other than in the form of methane. Ethylene and ethane products of the C_2H_4 injections contained none of the activity of the surface carbon atoms over the entire temperature range. By labelling the 'hydrogen part' of the ethylene molecule with deuterium it has been shown that over the same temperature range and under reproducible catalytic conditions the same factors which govern exchange do not apply to both parts of the ethylene molecule.

Section 3:4 The Reaction of Carbon Monoxide with the Catalysts.

Injections of carbon monoxide (0.45ml) were made over each of the catalysts previously studied. The same weight (0.5g) of each catalyst 5%Ni/Al_2O_3, 0.1%Ni/Al_2O_3, Al_2O_3, 5%Ni/SiO_2 0.1%Ni/SiO_2, SiO_2, Ni powder and Ni/P alloy was used. After the normal reduction procedure injections of CO were made over the catalysts at 20°C until no further retention was observed, after which the catalyst was raised to 150°C and the process repeated. The quantity of CO retained by the catalyst was calculated from the difference in chromatographic counts between a calibration injection and an injection over the catalyst.

The results are shown in table 18 which also gives the ratio of the total number of CO molecules retained at 20°C to the total number of Ni atoms present.

Injections of CO were also made over the catalyst at 250°C and 350°C. At these temperatures the 5%Ni/Al_2O_3, 5%Ni/SiO_2 and Ni powder catalysts produced a product aluant mixture of carbon monoxide and carbon dioxide. The production of carbon dioxide increased in the following catalyst order; Ni powder, 5%Ni/SiO_2 and 5%Ni/Al_2O_3. The disproportionation was also found to be greater at the higher temperature.

TABLE 17

Percentage Distribution of Deuterated Products from the Reaction of C_2H_4 with C_2D_4 (Preadsorbed) on 5%Ni/Al_2O_3 and 5%Ni/SiO_2

	Catalyst Temp(°C)	Product	d_6	d_5	d_4	d_3	d_2	d_1	d_0
5%Ni/Al_2O_3	20	C_2X_4	-	-	-	-	3.3	14.2	82.5
	50	C_2X_4	-	-	-	-	-	17.7	82.3
	150	C_2X_6	-	-	-	-	8.7	17.9	73.4
		C_2X_4	-	-	-	-	1.3	9.8	88.9
	250	C_2X_6	-	-	5.6	10.1	22.9	40.5	20.9
	350	C_2X_6	-	5.3	9.9	19.8	17.4	22.4	25.2
5%Ni/SiO_2	20	C_2X_4	-	-	-	-	-	3.7	96.3
	50	C_2X_4	-	-	-	-	-	5.5	94.5
	150	C_2X_6	-	-	-	-	-	-	-
		C_2X_4	-	-	-	-	-	3.5	96.5
	250	C_2X_6	-	-	-	-	-	15.6	84.4
		C_2X_4	-	-	-	-	-	10.7	89.3
	350	C_2X_6	-	-	-	-	17.1	28.4	54.5

TABLE 18

The Retention of CO (ml at 760mm) by the Catalysts.

	20°C	150°C	CO/Ni at 20°C
5%Ni/Al_2O_3	0.52	0.12	0.051
0.1%Ni/Al_2O_3	0.05	0.00	0.25
Al_2O_3	0.00	0.00	-
5%Ni/SiO_2	0.23	0.02	0.022
0.1%Ni/SiO_2	0.03	0.00	0.15
SiO_2	0.00	0.00	-
Ni powder	0.05	0.00	0.25×10^{-3}
Ni/P	0.08	0.00	0.56×10^{-3}

CHAPTER 4. DISCUSSION

Section 4.1 The Reaction of Ethylene with the Catalysts.

In the reactions of ethylene with tritiated catalysts retention data and product analyses were obtained for a variety of nickel catalysts over a range of temperatures. Six different nickel catalysts were used so that the effect of the catalyst form on the activity of the metal could be studied.

The extent of tritium incorporation into the products of the ethylene injection will be considered in a later section.

At temperatures below 250°C ethylene and ethane were the only products found. Cracking of ethylene to methane and hydrogenation to ethane were observed at 250°C and 350°C with the 5% catalysts and Ni powder. With metal concentrations of 0.1% hydrocarbon retention was greatly reduced and neither cracking or hydrogenation was observed. The alumina support was completely inert except for a small amount of ethylene retention.

The production of alkanes was always accompanied by olefin retention; a high retention generally corresponded to a relatively high alkane yield while little or no alkane products were found when hydrocarbon retention was low.

At the lower temperatures alkane yield and retention from the first injection was greater than for subsequent injections. As the temperature of the catalyst reached 250°C and 350°C, however, hydrocarbon retention and the yields of ethane and methane tended to remain constant.

These results would suggest that, at the lower temperatures, retention of olefin causes a decrease in the catalytic activity. If the participation of hydrogen associated with the catalysts after reduction is ignored (until discussed later with the tritium results) the adsorbed species may provide a source of hydrogen to yield alkane. Ethylene first is chemisorbed dissociatively freeing hydrogen atoms which remain adsorbed

$$C_2H_4 \longrightarrow C_2H_2(a) + 2H(a) \text{ —— } (1)$$

The adsorbed hydrogen then reacts either with gaseous ethylene

$$C_2H_4 + 2H(a) \longrightarrow C_2H_6 \text{ —— } (2)$$

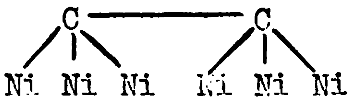
or with the adsorbed complex

$$C_2H_2(a) + 4H(a) \longrightarrow C_2H_6 \text{ —— } (3)$$

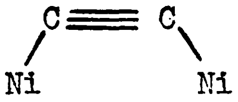
The results of the present system do not indicate whether reaction (2) or reaction (3) leads to alkane production. Jenkins and Rideal[76] have shown that, over nickel films, reaction (2) proceeds rapidly and (3) only relatively slowly.

The decrease in the amount of hydrogenated product over a series of injections corresponds to the reduction in reactive surface area in bulk hydrogenation reactions when ethylene, rather than hydrogen, is admitted to the catalyst first. Beeck[77] has estimated that when ethylene is preadsorbed on nickel, the initial rate of hydrogenation at 0°C is decreased by 60%. The pretreatment of the catalyst with olefin results in the formation of complexes which participate in the bulk reaction to a varying degree depending on the metal. Cormack et al.[78] have shown that in the case of Ni, 24% of the initially adsorbed ethylene was retained after hydrogenation, while the percentage retained by Pt was 6.5%

The extent of ethylene cracking to methane on the catalysts at 350°C was found to be greatest with the 5% Ni/Al_2O_3 and 5% Ni/SiO_2 catalysts. No evidence of methane formation was found with the 0.1% catalysts or the Al_2O_3 support. The fairly constant cracking activity of the 5% catalysts can be attributed to the extensive dissociation of the ethylene molecules and the formation of surface nickel carbide i.e.



or



The exposure of nickel crystals to ethylene at high temperatures is known to result in carbon deposition.[79]

More self hydrogenation, but less cracking, was observed with 5% Ni/SiO_2 than the 5% Ni/Al_2O_3 catalyst. Morrow and

Sheppard[80] have shown that with a 9.2% silica supported catalyst self hydrogenation of ethylene takes place at 150°C. At this temperature the infra-red spectrum of the adsorbed species was extremely weak although addition of hydrogen led to intense bands. They concluded that a hydrogen deficient surface carbide was formed on the nickel.

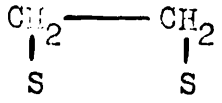
Altham and Webb[81] found that ethylene cracking only becomes appreciable on 5%Pt/Al_2O_3 at 300°C. This result implies that higher temperatures are required to break carbon - carbon bonds on Pt than on Ni and this is confirmed in Sheppard's[80] work. He observed that the products of ethylene chemisorption on Ni at -78°C were similar to those on Pt at +95°C and that the same products are found to occur on both metals but over a different range of temperatures.

Using the technique of magnetisation changes, Selwood[82] has shown that when ethylene is chemisorbed on nickel-silica the extent of dissociation increases as the temperature is raised. A treatment of the catalyst with flowing ethylene at 130°C converted the nickel to a non-magnetic carbide, which liberated virtually pure methane on the addition of hydrogen.

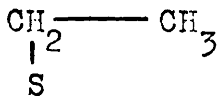
At temperatures of 250°C and 350°C the reactivity of the 5% catalysts over a series of injections was more constant than at the lower temperatures. Extensive carbon-carbon bond rupture was evident from the large methane yields and the formation of surface carbide was indicated by the large quantities retained by the catalyst. The reactivity of the nickel is not markedly affected by the formation of carbide as it is by the presence of surface complexes at the lower temperatures.

Carbide formation at an elevated temperature has also been observed in the reaction of nickel with benzene vapour.[83] M. Hofer et al.[84] have shown that the carbide has considerable stability at 350°C; an induction period of approx. 9 hours precedes the decomposition and no detectable change is observed in the carbide structure during the induction period. However it is clear from the infra red studies[48] and the magnetic measurements[82] that the addition of hydrogen can liberate the surface carbon as methane. The mechanism of methane production copiously observed in the present work will be examined in the discussion of the results of ethylene injections onto tritium labelled catalysts and onto catalysts preadsorbed with $^{14}C_2H_4$.

Apart from slight olefin retention at 250°C and 350°C (see table 7) the δ-alumina support was inert towards injections of ethylene. However, chemisorption of ethylene has been observed by other workers at room temperature. Lucchesi et al.[85], who studied η-alumina, observed that the intensity of the infra red spectrum of the chemisorbed ethylene increased slowly over a period of 8 days. Different forms of surface species were observed with different samples of η-alumina.

(i) 

CH_2-CH_2 (each CH₂ bonded to S)

(ii) 

CH_2-CH_3 (CH₂ bonded to S)

(where S denotes a surface site)

The reason for the absence of detectable ethylene adsorption in the present work at temperatures used by other workers could be a consequence of the reaction system employed here. Under flow system conditions the time of contact of ethylene with alumina may not be long enough to allow detectable adsorption to occur. The presence of nickel at concentrations 0.1% and 5% has been shown to enhance the adsorption of ethylene on alumina to the extent that the adsorption can be measured under flow system conditions. The use of steady state conditions, as used in the infra red studies, may be necessary to allow appreciable adsorption on alumina itself.

The activities of the Ni powder catalyst and the Ni/P alloy were considerably less than those of the supported metal catalysts (5%). Ethane was observed as a reaction product at each temperature with the Ni catalyst, but was only produced in small amounts at 250°C and 350°C when Ni/P was used. The latter catalyst was also incapable of cracking ethylene, even at the highest temperature. This is consistent with the reduction in catalytic activity observed by Morikawa[74] who found that the catalyst could promote the reduction of benzaldehyde to benzyl alcohol in good yield in contrast to other reduced nickel catalysts which give mainly toluene and benzene under similar reaction conditions.

Section 4.2. The Reaction of Tritium with the Catalysts.

The results presented in Table 4 show the variation in catalyst activity towards hydrogen exchange at the reduction temperature (400°C). The presence of nickel tended to decrease the ease of the exchange reaction on Al_2O_3 but to increase the rate on SiO_2.

Greater quantities of exchangeable hydrogen were found when the catalysts were subjected to flow exchange; the static method of labelling the surface hydrogen did not give such a high surface activity as a series of injections flowing through the catalyst.

A comparison of the total number of tritium atoms retained with the number of metal atoms present is shown in Table 19. An estimate of the total number of surface atoms present on the supported metals has been made by determining the volume of carbon monoxide retained by the catalysts. The ratio of carbon monoxide molecules adsorbed to the number of Ni atoms was found to be less than 1. However, the number of tritium atoms retained per carbon monoxide molecule adsorbed is considerably in excess of unity. Quantities of hydrogen very much greater than those required for monolayer coverage of the metal are therefore retained by exchange on some of the catalysts and these results lead to the conclusion that some of the retained tritium is associated with the support rather more than the metal.

TABLE 19

Catalyst	No. of Ni Atoms ($\times 10^{-19}$)	Molecules of Tritiated Hydrogen Retained ($\times 10^{-19}$)	$\frac{\text{T Atoms}}{\text{Ni Atoms}}$	No. of Surface Atoms (Co Measurement; $\times 10^{-19}$)	$\frac{\text{T Atoms}}{\text{Surface Atoms}}$
5%Ni/Al_2O_3	25.6	11.0	0.86	1.3	16.9
0.1%Ni/Al_2O_3	0.51	24.2	94.9	0.13	372
Al_2O_3	0.00	24.8	∞	–	∞
5%Ni/SiO_2	25.6	7.5	0.59	0.58	25.9
0.1%Ni/SiO_2	0.51	2.5	10.0	0.08	62.5
SiO_2	0.00	0	–	–	–

The existence of hydroxyl groups on the surface of alumina and silica has been shown by infra red spectroscopy.[86,87,88] The concentrations of the hydroxyl groups have been estimated by Hall et al.[89,90] using a technique based on the exchange of the hydroxyl hydrogen with deuterium as the temperature is slowly and continuously increased. Concentration values of 4.4 x 10^{14}cm^{-2} and 2.6 x 10^{14}cm^{-2} were obtained for alumina and silica respectively.

From the retention measurements and from the BET area of the alumina (100m^2/g) used in the present work the number of tritium atoms retained at the reduction temperature is calculated to be 9.8 x 10^{14}cm^{-2}. This result would suggest that the retained tritium is located at the hydroxyl groups of the alumina support.

The hydroxyls of the silica (in the absence of metal) were not so readily exchanged and at 400°C no significant incorporation of tritium was observed over a series of injections. This is consistent with the results of Hall et al.[89] who observed that exchange did not take place on their silica samples until a temperature of 500°C had been reached. Exchange of the surface groups of silica has, however, been observed at room temperature with D_2O.[88] In a previous study[81] similar amounts of tritium were retained by both the alumina and silica supports, as well as platinum supported catalysts. These results were obtained, however, by a static method of tritium exchange and the similarity in the data of the previous work may have been a consequence of the recurring error which this technique introduces. [see section 2.10 (iii)]

The case of hydrogen exchange on alumina has been shown to vary with temperature (see Fig. 34), the quantity of exchangeable hydrogen available increasing sharply towards 400°C. This is in accordance with the work of Carter et al.[87] who found that the rate of exchange increased as the temperature was raised from 75°C to 250°C. They also observed that the ratio of OD appearance on the alumina surface to OH disappearance was essentially unity, indicating that the reaction with deuterium was limited to the exchange, there being no evidence for the additional formation of OD groups beyond those formed by exchange.

By plotting the present exchange results as a logarithmic function against injection number estimates of the amount of hydrogen capable of exchange have been made. The validity of the original assumption (see Appendix I) that the quantity eluted from the catalyst was equal to the amount of hydrogen injected, i.e. 1ml, has been proved by the emergence of straight line graphs for most catalysts; these relationships would not have been found if a further reaction, involving adsorption, had been taking place on the catalysts.

Further evidence of the exchange of alumina hydroxyl groups with deuterium gas has been produced by Periand Hannan.[86]

These workers, like Carter et al.[87] observed the existence of different types of surface hydroxyl groups and found that between 250°C and 500°C the rate of exchange of hydroxyl groups occured at a convenient rate.

The variation in the rate of exchange with temperature is an indication of the non uniformity of the alumina surface. If it can be assumed that the strength of the OH bond determines the rate of exchange, the absence of silica exchange at 400°C indicates that the terminal hydroxyl groups of alumina are more acidic at this temperature. Rapid equilibration of alumina hydrogen may therefore occur at temperatures where only a small portion of the hydrogen on a silica catalyst has been exchanged.

The presence of nickel has been found to increase the rate of hydrogen exchange over silica at 400°C. Although the same enhancement is observed with nickel on alumina (5%) at temperatures up to 250°C a change in the order of exchange activity is observed at 400°C (see Fig. 34). At this temperature more exchange is observed with the Al_2O_3 than the 5%Ni/Al_2O_3 catalyst. Similar reduction conditions were used before reaction at 400°C as at the lower temperatures when the presence of Ni increased the amount of exchange. It is therefore unlikely that the decrease can be attributed to incomplete reduction of the catalyst.

The graphical representation of the hydrogen exchange results of Hall et al.[89,90] would, at first sight, appear to exhibit similar features to the variation in exchange rates with temperature observed in this work (see Fig. 34). In the exchange reactions of deuterium with supports and supported catalysts studied by Hall the temperature of the catalyst was gradually increased during the course of the reaction. In the present study reaction temperatures were maintained constant during the course of an exchange reaction. As a result of this difference in the experimental conditions a closer comparison of the results cannot be made.

Supporting platinum on alumina does not materially lower the concentration of surface hydroxyl groups.[90] The maximum in rate of hydrogen exchange has been found to occur at a higher temperature with a reduced platinum catalyst than an unreduced one although this result has been attributed to the presence of chloride on the catalyst introduced during its preparation.

Carter et al.[87] have shown that in the temperature range 75°C to 150°C the rate of exchange of deuterium with surface hydrogen has been increased by the impregnation of platinum. The extent of exchange was however, not significantly greater on a 2% Pt catalyst than it was on 0.6% Pt at 150°C.

The influence of Ni on the exchange reaction of the alumina hydroxyls is temperature dependent, the presence of the metal effectively reducing the temperature required for exchange. At the reduction temperature of 400°C the alumina support itself is capable of significant exchange.

A significant difference in the exchange activity of 0.1% and 5%Ni/Al_2O_3 can be seen in the present results. The enhancement of the exchange rate with tritium when nickel is present on silica is also evidence of a cooperative effect of nickel on the reaction. One possibility is that the metal may activate neighbouring hydroxyl groups of the support by increasing their acidity e.g. the hydroxyl bond may be weakened by the interaction of the nickel atom with the oxygen of the hydroxyl group.

On this basis one would expect that the greater the metal content of the catalyst, the greater would be the exchange.

A second possibility is that the nickel activates gas phase hydrogen to exchange with the hydroxyl groups. It may be that the exchange effect involves transport of active species between nickel sites and sites on the support surface. The increase in exchange observed on 5%Ni/Al_2O_3 up to 250°C implies that the exchange is an activated process and that in some way the metal reduces the activation energy of the reaction leading to exchange. Perhaps dissociation of hydrogen occurs on nickel sites and subsequently migrates to hydroxyl groups on the support to exchange.

i.e. $2Ni + H_2 \longrightarrow 2NiH$

$NiH \longrightarrow \text{support } H$

$\text{support } H + OT \longrightarrow \text{support } T + OH$

$\text{support } T \longrightarrow NiT$

$NiT + NiH \longrightarrow 2Ni + HT$

The probability that metal centres on supported metal catalysts can activate hydrogen in some way, which then migrates to centres on the support where further reaction takes place has been postulated by other workers.[91,92,93] Perhaps the best example of this effect, known as 'spillover' is that described by Sinfelt and Lucchesi.[91] Their work showed that, under comparable conditions, the rate of ethylene hydrogenation was much greater when Pt/SiO_2 was mixed with Al_2O_3 than when the supported metal was used alone. As both supports are inert for the reaction under similar conditions it has been concluded that the enhanced activity of the mixture is due to spillover of active hydrogen from platinum to the alumina surface where it reacts with chemisorbed ethylene.

Most examples have been observed in the presence of the noble metal platinum where the important criterion appears to be the degree to which the metal is in contact with the support component in that the greater the interface between the two the greater is the acceleration of the process. Reduction in the degree of dispersion of the metal on the support would therefore retard the migratory process. This is a possible explanation of the decline in exchange activity on 5%Ni/Al_2O_3 at 400°C; at this temperature some sintering of the metal may be occurring which could reduce the interface between metal and support.

The exchange of gas phase tritium with the Ni powder and Ni/P alloy catalysts resulted in a much smaller retention of activity than had been observed with the alumina support or the supported metal catalysts. In the case of the unsupported metal catalysts only hydrogen chemisorbed on the metal after reduction and the helium treatment could participate in the reaction with tritium. Thus in the absence of a support medium, exchange precesses, which might occur as a result of 'spillover' of hydrogen from metal onto a support, cannot take place.

The possibility of incomplete reduction of the nickel oxide formed by the decomposition of the formate cannot be ruled out. Analysis by electron microscopy found that oxide was present to a small extent although oxidation could have occured in transit to the microscope.

Section 4.3 The Tritium Content of the Hydrocarbons.

The results of ethylene injections onto tritiated catalysts (see Tables 7,8, and 9) show that catalyst 'hydrogen' was active in the formation of hydrogenation and cracking products and to a much lesser extent in ethylene exchange.

The results on alumina and nickel-alumina contrast with those observed for hydrogen exchange in that the presence of metal was necessary for the incorporation of tritium into the hydrocarbon products. Ethylene reaction on the silica support was not investigated as this had been shown to be inert for hydrogen exchange at 400°C. The extent of tritium participation in the production of ethane and methane was found to increase with the concentration of metal for both silica and alumina catalysts. The same trend was observed in the hydrogen exchange reaction with SiO_2 supported catalysts although, in contrast, the reactivity of tritium on alumina towards gas phase hydrogen at the reduction temperature was found to decrease in the presence of nickel.

Injections of ethylene were made over the catalysts at a constant temperature after treatment of the catalysts with tritium by static or flow exchange at the reduction temperature. Greater activity was again found for the 5% catalysts. Although the maximum amount of tritium was present on the catalysts after cooling to room temperature, the ethane produced from the first injections at 20°C and 50°C included none of the surface activity. Not until the catalyst temperature had been increased to 150°C did the tritium associated with the catalyst participate in ethylene hydrogenation. The observation that the ethane was not radioactive indicated that at temperatures $\leqslant 50°C$ the hydrogenation process takes place via a dissociative mechanism on the metal. As a result of hydrogen exchange with the 5%Ni/Al_2O_3 catalyst at room temperature (see Fig. 34) it can be concluded that the absence of activity in the products of ethylene injections at this temperature arose from a higher activation energy for the reaction of catalyst 'hydrogen' with ethylene.

Injections of tritium onto the nickel powder catalyst resulted in a smaller uptake than with the supported catalysts. However, in contrast to this the results on supported nickel with ethylene showed some activity in the ethane produced by the powder at room temperature. Ethylene self hydrogenation on this catalyst therefore involved hydrogen, labelled by flow exchange with tritium, retained on the metal after reduction. Greater quantities of ethane appeared at 250°C and 350°C but contained much less activity than either the 5%Ni/SiO_2 or 5%Ni/Al_2O_3 catalysts.

These results lead to the conclusion that in the absence of a support the reaction of ethylene with nickel involves hydrogen sited on the metal after reduction. When the metal is supported considerable quantities of support hydrogen are made available to the reaction as the temperature is raised. No evidence has been found for the reaction of ethylene with hydrogen retained by the metal or support of the supported catalysts at room temperature.

Some of the ethane produced at higher temperatures may, of course, proceed by the addition of hydrogen from dissociated olefin to other ethylene molecules but the extent of this reaction is obscured by the presence of tritiated alkane in the product.

Only slight ethylene exchange was observed with the catalysts, most of the surface activity appearing in the ethane and methane fractions of reaction. It would appear, therefore that if olefin exchange and hydrogenation with tritium proceed through a common intermediate, i.e. adsorbed alkyl, then the probability of addition of hydrogen to yield alkane must be considerably in excess of the probability of alkyl reversal. Any adsorbed alkyl which is produced on nickel must rapidly react with hydrogen/tritium to form ethane rather than undergoing alkyl reversal to yield exchanged olefin.

The absence of reaction between the tritiated alumina support and ethylene would suggest that the reaction of tritium with ethylene takes place on the metal of the supported catalysts rather than on the support.

The hydrogen released by the dissociative adsorption of ethylene may exchange with the retained tritium as the catalyst temperature is raised,

i.e. $C_2H_4(g) \longrightarrow C_2H_{4-n}(a) + nH(a)$

$H(a) + OT \longrightarrow T(a) + OH$

and the tritium can then react with adsorbed olefin to yield tritiated alkane, the reaction occurring on the metal

$$C_2H_4(a) + T(a) \rightleftarrows C_2H_4T(a) \xrightarrow{T(a)} C_2H_4T_2$$

The increase in the amount of dissociated hydrogen, [nH(a)], as the temperature is raised would explain the observed increase in activity of ethane and methane with temperature. With the present system it has not been possible to determine whether the rise in specific activity with increasing temperature can be attributed to an increase in the number of molecules participating in exchange or an increased number of tritium atoms in the exchange product. The results obtained with the supported Ni catalysts (5%) differs from those with supported Pt in one important aspect. Altham and Webb[81] found that in the reaction of ethylene with supported Pt preadsorbed tritium was present in both the ethylene and ethane product fractions at room temperature. Tritium did not appear in the products from supported nickel until the catalyst temperature had been raised to 150°C although in other respects (amounts of catalyst retention, self hydrogenation etc.), the reactions of ethylene with supported Ni and Pt appear comparable. The absence of tritium in the ethylene and ethane products on Ni at room temperature would suggest that the activity of catalyst tritium in the reaction is greater on Pt than on Ni at this temperature. A possible explanation is that, on supported Pt, hydrogen which is released in ethylene dissociation may rapidly exchange with retained tritium,

i.e. $$H(a) + OT(a) \xrightarrow{k} T(a) + OH(a)$$

where k is larger on supported Pt than on supported Ni. The retained tritium may then react with adsorbed hydrocarbon leading to tritiated ethylene or ethane,

i.e. $$C_2H_4(a) + T(a) \rightleftharpoons C_2H_4T(a) \xrightarrow{T(a)} C_2H_4T_2$$

On supported Ni (at 23°C) adsorbed ethylene reacts only with the hydrogen of dissociated ethylene.

i.e. $$C_2H_4(a) + H(a) \rightleftharpoons C_2H_5(a) \xrightarrow{H(a)} C_2H_6$$

The absence of ethylene exchange at higher temperatures indicated that it is an unlikely reaction at room temperature.

The results of the hydrogen exchange experiments have shown that the reaction on alumina alone occurs at a convenient rate if the temperature is raised to 400°C. It is probable therefore that most of the hydrogen exchanged is produced by direct reaction on the support, the extent being determined chiefly by the temperature. In the presence of nickel, dissociation of hydrogen can take place on the metal and migrate to the support and exchange, then desorb from the support or migrate back to the metal. At temperatures up to 250°C where the exchange rate is considerably higher with 5%Ni/Al_2O_3 than 0.1%Ni/Al_2O_3 or Al_2O_3 increased desorption from the metal can account for the rise in exchange but at 400°C increased strengths of metal-hydrogen chemisorption would lead to a reduction in the number of metal sites for hydrogen desorption.

Most of the tritium liberated from the catalysts appeared in methane at temperatures above 150°C. When ethylene reacts with unsupported nickel in a static system[94] methane has been observed at 60°C, the concentration rising rapidly until at 200°C it was the sole reaction product. The pressure over the catalyst remained constant at this temperature which indicated the following disproportionation reaction.

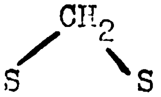
$$C_2H_4 \longrightarrow CH_4 + C$$

The high activity of the methane produced with the 5% Ni catalysts indicates that this is not the sole reaction on supported nickel and that reaction of catalyst tritium with products of ethylene dissociation takes place.

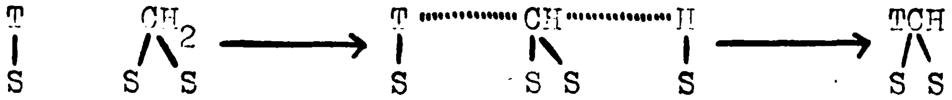
Kemball[95] has shown that the relative strength of methane adsorption decreases along the series

Pd, Pt, W, Rh, Ni

and that the reactive species in methane exchange is the methylene group i.e.



Incorporation of tritium may therefore be occurring via this intermediate in the following way:



The marked increase in retention by the catalysts as the temperature was raised can be explained by the formation of hydrocarbon polymers on the surface. Selwood[82] has shown that ethylene dissociation on adsorption increases with temperature and that ~~at~~ 100°C each molecule requires six sites for adsorption. These results and those of the IR studies[48] have shown that processes such as the following can be envisaged;

This mechanism of olefin polymerisation involves the elimination of hydrogen and it is of interest to note that during the series of ethylene injections onto tritiated 5%Ni/Al_2O_3 considerable quantities of tritium labelled species were detected by the proportional counter as the temperature was raised from 150°C to 250°C and again, to a greater extent, between 250°C and 350°C. As similar desorptions were not observed in the hydrogen exchange experiments with the same catalyst at different temperatures, it was originally believed that the hydrocarbon material consisted entirely of tritium labelled hydrocarbons, rather than tritium labelled hydrogen. However, it is probable that at least some of the desorbed material, which was not detected by the chromatographic system is in fact labelled hydrogen which originated from a polymerisation or dissociation process. During each temperature increment adsorbed species can further polymerise or dissociate releasing hydrogen for exchange and desorption. Ethylene injections onto tritiated alumina did not produce these desorptions.

From the previous discussion, it seems probable that the enhancement of the hydrogen exchange by the nickel on silica and alumina ($<$400°C) is due to migration of hydrogen between the metal and support. Tritium is incorporated into the products of reaction of ethylene with the catalysts only when metal is present and occurs to a much greater extent with the 5% supported catalysts than the powder catalyst. The effect of supporting the metal is therefore much greater than would be expected from the combination of results on the support and those on the powder. 'Spillover' of the reaction products of ethylene with nickel onto the support would account for the larger quantities of ethylene retained, than could be accommodated on the available metal sites if the CO adsorption measurements are taken as a valid measure of the metal area.

The possibility of direct reaction of adsorbed ethylene on the support and tritium on the support must be considered as some ethylene retention was observed on Al_2O_3 at 250°C and 350°C. However, the reaction was observed to take place only in the presence of metal and perhaps only the hydrogen migrating between the metal and support is active in the reaction with ethylene on the support.

Section 4.4 The Reaction of Inactive Gas Phase Ethylene with Preadsorbed ^{14}C-Ethylene.

The results in Tables 10-13 show that only one catalyst - Ni/P - is active in molecular exchange. On the other catalysts used the retained species are thus, for the most part, present in a form incapable of reacting with ethylene from the gas phase; this is a further indication that the surface species are hydrogen deficient.

The injection of inactive ethylene onto the 5% catalysts which had been exposed to $^{14}C_2H_4$ led to the recovery of inactive ethylene and ethane. This is in agreement with a radiochemical study[96] of the exchange reaction on nickel films at room temperature where exchange between gas-phase ethylene and chemisorbed ethylene was negligible. Radioactive methane was produced by the alumina catalyst at 250°C and 350°C but only on the silica catalyst at the latter temperature.

The absence of carbon-14 in the product ethanes, when formed, is an indication that the formation of ethane did not involve the wholesale participation of preadsorbed ethylene. Ethane production must, therefore, result from freshly adsorbed ethylene, the extent of hydrogenation being determined by the availability of surface hydrogen. i.e. the mechanism followed is

$$^{14}C_2H_4(g) \longrightarrow {}^{14}C_2H_2(a) + 2H(a)$$

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

rather than

$$^{14}C_2H_4(g) \longrightarrow {}^{14}C_2H_4(a) \xrightarrow{H} {}^{14}C_2H_5(a)$$

$$^{14}C_2H_5(a) + C_2H_4(a) \longrightarrow {}^{14}C_2H_6(g) + C_2H_3(a)$$

Ethylene exchange reaction on supported Pt[81] catalysts have indicated a slightly greater participation of preadsorbed ethylene in the ethylene exchange and hydrogenation reactions.

On the other hand, more cracking and a higher activity in the methane fraction from the unlabelled ethylene injection has been evident for supported Ni.

Surface hydrogen may arise from the dissociation of adsorbed ethylene or from hydrogen remaining on the catalyst after reduction. The results of the tritium experiments have shown that catalyst 'hydrogen' does not become involved in the process of self hydrogenation until 150°C and that at room temperature hydrogenation is a result of ethylene dissociation.

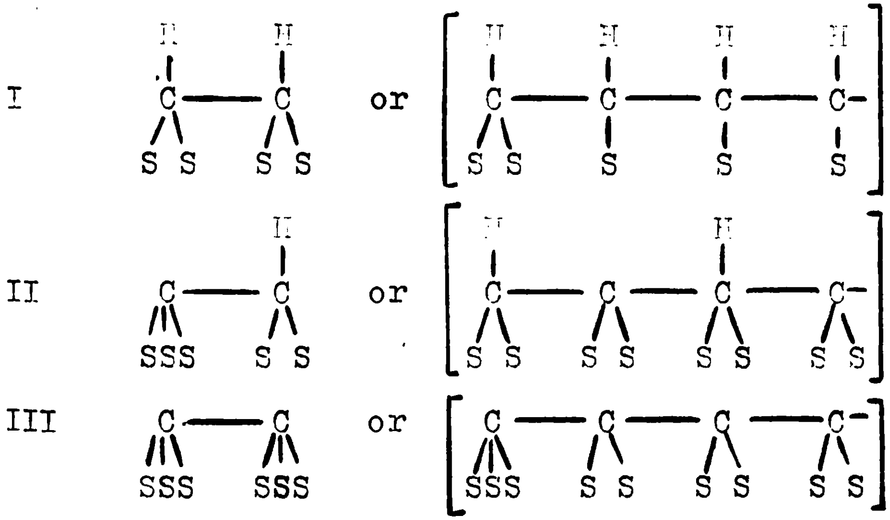
A common factor of these exchange results and those of ethylene on tritiated catalysts is that the maximum amount of surface activity appears in the methane fraction. The lack of activity in the ethane fractions suggests that the methane is not formed by hydro-cracking of the saturated hydrocarbon although this reaction is known to occur over nickel.[97] There is evidence[95,98] to show that nickel is highly active in breaking carbon-carbon bonds and the temperature dependence of surface residues of ethylene on nickel has been investigated.[99] M^c^Kee has calculated the overall composition of the adsorbed residues on the surface in the form $(CH_n)_x$ and observed that the valus of n decreased rapidly with increasing temperature until at 200°C the metal surface was observed to be free of hydrogen. Sabatier[83] found that complete carbonisation of nickel occurred at 300°C.

A possible reaction sequence leading to the formation of surface carbide is as follows;

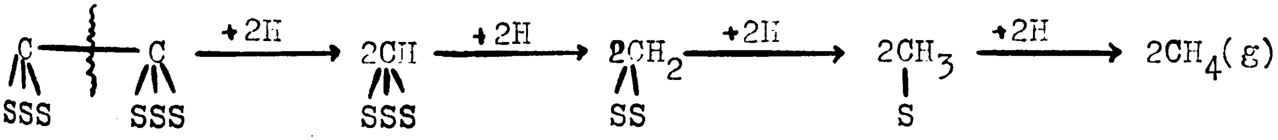
$$C_2H_4(g) \longrightarrow C_2H_4(a) \xrightarrow{-H} C_2H_3(a) \xrightarrow{-H} \underset{I}{C_2H_2(a)}$$

$$\xrightarrow{-H} \underset{II}{C_2H(a)} \xrightarrow{-H} \underset{III}{C_2(a)}$$

Possible structures of the dissociated species are;



The scission of carbon-carbon bonds leads to the production of methane.



Preadsorbed carbon atoms can therefore appear in the gas phase as methane, which is readily desorbed from nickel, and some of the hydrogen required for the formation of methane arises from the support as discussed earlier.

The exchange results on the nickel catalyst poisoned by phosphide point to the presence of different surface species on ethylene adsorption. Molecular exchange was observed with this catalyst at room temperature and again to a lesser extent at 50°C. It is likely that the decrease in molecular exchange activity with temperature is due to an increase in the extent of dissociation of the adsorbed species.

Methane was not produced on the catalyst at any temperature and only traces of ethane were observed as the temperature was raised. The absence of self hydrogenation at room temperature makes dissociative adsorption unlikely. The exchange evidence is therefore indicative of a reactive type of adsorbed ethylene, perhaps in the associated form, which can exchange readily with ethylene from the gas phase.

The selective activity of the catalyst for the exchange reaction may be compared to its mild action in the reduction of benzaldehyde to benzyl alcohol observed by Morikawa.[74] If the action of the phosphide can be ascribed to the blocking of specific crystal faces of nickel then the heterogeneity of the catalyst surface is modified and the mechanism of ethylene chemisorption may well be governed by the geometry of the available crystal faces of the nickel.

Work on phosphorus interaction with hydrogen-covered nickel films[100] has indicated at least two different types of hydrogenation reactions. The presence of phosphorus prevented the adsorption of hydrogen on the sites of higher reactivity. The type of ethylene adsorption which would therefore appear most likely on a phosphide poisoned nickel catalyst would not readily involve hydrogen bond formation. The dissociative adsorption of ethylene (which itself produces adsorbed hydrogen) would be expected to be discriminated against in favour of associative adsorption. The blocking action of the poison would also limit the number of sites available for chemisorption reducing the possibility of dissociative adsorption. The exchange of gas phase ethylene with associatively adsorbed ethylene would be expected to take place more readily than with the dissociative form, because it can take place by simple place exchange rather than the rearrangement of several fragments.

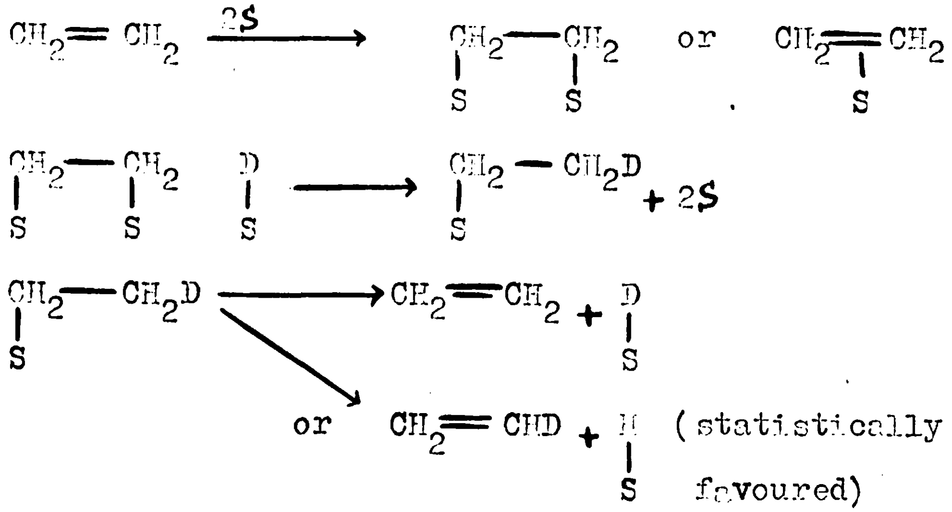
Section 4.5 The Reaction of Gas Phase Ethylene, C_2H_4, with Preadsorbed C_2D_4

In the reaction of ethylene with preadsorbed C_2D_4 surface hydrogen in the form of deuterium was found to be more active in the exchange with gas phase ethylene than carbon atoms deposited by the same injection process. A difference in the reactivity of the carbon and hydrogen components of adsorbed ethylene and an increase in the deuterium incorporation with temperature are further evidence for a dissociative mechanism of olefin adsorptions on supported catalysts.

From the $^{14}C_2H_4/C_2H_4$ exchange results it was deduced that ethane production involved the carbon atoms of freshly adsorbed ethylene. At room temperature the source of hydrogen has been shown not to be the support and the C_2D_4/C_2H_4 results confirm that the hydrogen arises from dissociated olefin and also that, unlike preadsorbed carbon, hydrogen already present on the catalyst is active in the self hydrogenation process.

Injections of ethylene onto the 5% tritiated Ni catalysts at room temperature did not lead to the incorporation of activity into the ethylene and ethane products. When the same catalysts were pretreated with deuterated ethylene, the deuterium made available was observed to exchange with light ethylene and to participate in the hydrogenation reaction. This evidence suggests that the catalyst hydrogen (tritium) and the ethylene hydrogen (deuterium) occupy sites of different reactivities on the catalysts. On the one hand, deuterium produced by dissociative adsorption of ethylene can react readily with light ethylene because it is present on the metal whereas higher temperatures are required to activate the reaction of ethylene with tritium which is associated with the catalyst support.

The question arises as to the mechanism of the addition of adsorbed deuterium into freshly added ethylene. The most likely explanation is that the exchange is a result of associative adsorption on sites adjacent to dissociated ethylene from the initial injections thereby allowing the formation and reversal of alkyl groups. i.e.

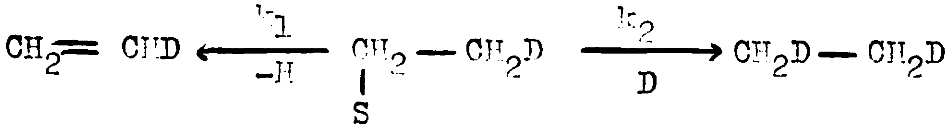


(statistically favoured)

The associative adsorption of ethylene and evidence for ethyl group formation, the 'half hydrogenated state', on nickel known to contain surface hydrogen have been observed elsewhere.[48]

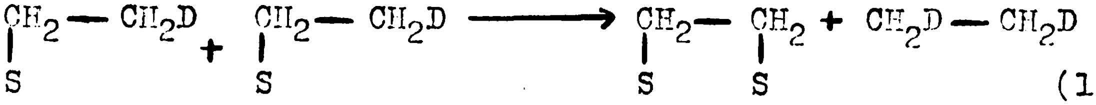
The hydrogenation activity of the catalysts was, once again, observed to increase with temperature as a result of increased dissociation of adsorbed ethylene. The amount of deuterium rose to a maximum with the 5%Ni/Al_2O_3 catalyst at 350°C where only 25% of the ethane was free of deuterium. Smaller concentrations of deuterium were found in the ethylene exchange fractions than in the ethane and it would appear that as the temperature is raised the increased availability of surface deuterium increases the tendency of alkane formation rather than alkyl reversal. That is to say, k_2

becomes larger compared with k_1.

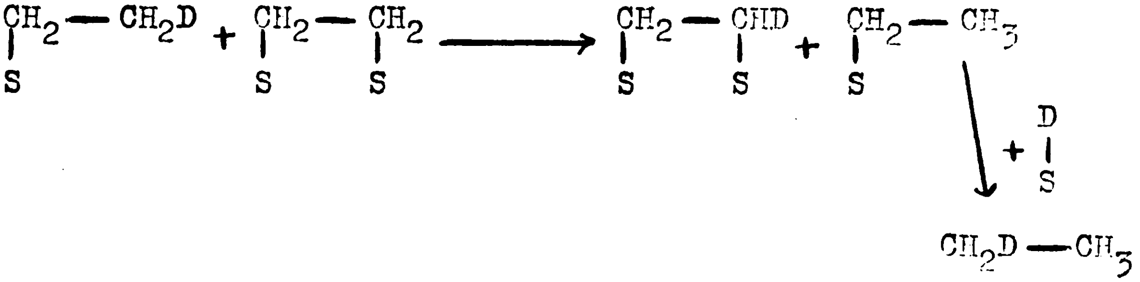


$$CH_2{=}CHD \xleftarrow[-H]{k_1} \underset{\overset{|}{S}}{CH_2}-CH_2D \xrightarrow[D]{k_2} CH_2D-CH_2D$$

In addition to this mechanism there are other ways in which the surface deuterium can add to the light ethylene to produce labelled ethane.



$$\underset{\overset{|}{S}}{CH_2}-CH_2D + \underset{\overset{|}{S}}{CH_2}-CH_2D \longrightarrow \underset{\overset{|}{S}}{CH_2}-\underset{\overset{|}{S}}{CH_2} + CH_2D-CH_2D \qquad (1)$$



$$\underset{\overset{|}{S}}{CH_2}-CH_2D + \underset{\overset{|}{S}}{CH_2}-\underset{\overset{|}{S}}{CH_2} \longrightarrow \underset{\overset{|}{S}}{CH_2}-\underset{\overset{|}{S}}{CHD} + \underset{\overset{|}{S}}{CH_2}-CH_3 \xrightarrow{+\ \underset{S}{\overset{D}{|}}} CH_2D-CH_3 \qquad (2)$$

Some dissociative adsorption of the light ethylene injection occurs at the higher temperatures as evidenced by the presence of light ethane although part of this may be due to the increasing role played in the hydrogenation by the support hydrogen.

Studies of the exchange reaction between light and heavy ethylene have in the past been conducted with a simultaneous addition of the ethylenes to the catalyst. In the experiments of Conn and Twigg[65], who used a nickel wire catalyst, exchange between the ethylenes was not observed even at temperatures as high as 300°C and the results were taken[101] as a strong argument in favour of the associative mechanism of ethylene chemisorption. More recent work has, however, been in agreement with the present findings and evidence has been presented for exchange on supported nickel[68] and nickel film[102] catalysts and interpreted in terms of the dissociative mechanism of Farkas.[103]

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APPENDIX I

The amount of tritium injected onto the catalysts was 1ml.

Let the amount of exchangeable hydrogen on the catalyst be xml. If the activity of 1ml tritium is '1 unit' and there is complete equilibration between gas phase and surface hydrogen (including tritium), $x/1+x$ units will be retained on first injection. For convenience call $x/1+x = r$.

1st injection	1 unit of activity
	r units retained $(1-r)$ units eluted
2nd injection	$1+r$ units
	$r(1+r)$ retained $(1-r)(1+r)$ eluted
3rd injection	$1+r(1+r) = 1+r+r^2$ units
	$r(1+r+r^2)$ retained $(1-r)(1+r+r^2)$ eluted
4th injection	$1+r(1+r+r^2) = 1+r+r^2+r^3$
	$r(1+r+r^2+r^3)$ retained
	$(1-r)(1+r+r^2+r^3)$ eluted

Thus in general for the nth injection

amount eluted $= (1-r)(1+r+r^2 \text{-----} r^{n-1})$

$= (1-r^n)$

amount retained $= r^n = y$ (say)

$$y = r^n \therefore \log y = n \log r$$

A plot of log y [i.e. log (activity retained/activity injected)] against n gives a straight line of slope log r where $r = x/1+x$ as defined.

APPENDIX II

The various isotopic ethylenes possible are:-

C_2D_4	C_2D_3H	$C_2D_2H_2$	C_2H_3D	C_2H_4
32	31	30	29	28

Let the measured ion currents be:-

C_2D_4	C_2D_3H	$C_2D_2H_2$	C_2H_3D	C_2H_4		
32	31	30	29	28	27	26
A	B	C	D	E	G	H

and the parent ion currents be:-

a	b	c	d	e	g	h

On a statistical basis the breakdown pattern from each parent ion is as follows:-

	ION	m/e	INTENSITY
a.	$C_2D_4^+$	32	1
	$C_2D_3^+$	30	f_1
	$C_2D_2^+$	28	f_2
b.	$C_2HD_3^+$	31	1
	$C_2D_3^+$	30	$f_1/4 = 0.25f_1$
	$C_2HD_2^+$	29	$3f_1/4 = 0.75f_1$
	$C_2D_2^+$	28	$2/3.3/4f_2 = 0.5f_2$
	C_2DH^+	27	$3/4.2/3f_2 = 0.5f_2$
c.	$C_2H_2D_2^+$	30	1
	$C_2HD_2^+$	29	$f_1/2 = 0.5f_1$
	$C_2H_2D^+$	28	$f_1/2 = 0.5f_1$
	$C_2D_2^+$		$f_2/6 = 0.17f_2$
	C_2DH^+	27	$2/3f_2 = 0.67f_2$

	ION	m/e	INTENSITY
c. contd.	$C_2H_2^+$	26	$1/6f_2 = 0.17f_2$
d.	$C_2H_3D^+$	29	1
	$C_2H_2D^+$	28	$3/4f_1 = 0.75f_1$
	C_2DH^+	27	$f_2/2 = 0.5f_2$
	$C_2H_3^+$		$f_1/4 = 0.25f_1$
	$C_2H_2^+$	26	$0.25f_2$
	C_2D^+	26	$0.25f_2$
e.	$C_2H_4^+$	28	1
	$C_2H_3^+$	27	f_1
	$C_2H_2^+$	26	f_2

The contribution of the parent ion to each peak can therefore be calculated from the following equations:-

32 $a = A$

31 $b = B$

30 $c = C - f_1(0.25b + a)$

29 $d = D - f_1(0.75b + 0.5c)$

28 $e = E - f_1(0.5c + 0.75d) - f_2(a + 0.5b + 0.17c)$

27 $G = f_1(e + 0.25d) + f_2(0.5d + 0.67c + 0.5b)$

26 $H = f_2(e + 0.5d + 0.17c)$

The various isotopic ethanes possible are:-

C_2D_6	C_2HD_5	$C_2H_2D_4$	$C_2H_3D_3$	$C_2H_4D_2$	C_2H_5D	C_2H_6
36	35	34	33	32	31	30

Let the measured ion currents be:-

A	B	C	D	E	G	H	J	K
36	35	34	33	32	31	30	29	28

and the parent ion currents be:-

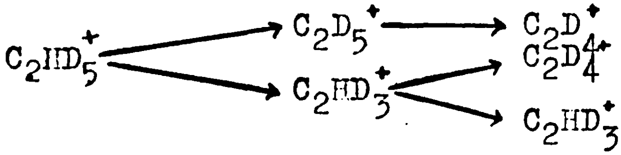
a b c d e g h j k

On a statistical basis the breakdown pattern from each parent ion is as follows:-

a.

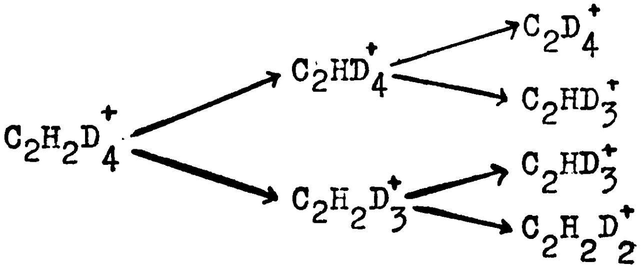
$$\begin{array}{ccccc} C_2D_6^+ & \longrightarrow & C_2D_5^+ & \longrightarrow & C_2D_4^+ \\ 36 & & 34 & & 32 \\ 1 & & f_1 & & f_2 \end{array}$$

b.



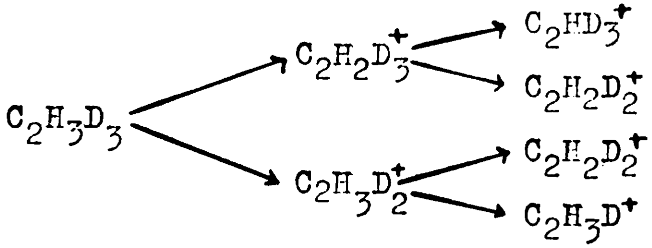
$C_2HD_5^+$	35	1
$C_2D_5^+$	34	$1/6f_1$
$C_2HD_4^+$	33	$5/6f_1$
$C_2D_4^+$	32	$5/6.1/6f_2 = 1/5.5/6f_2 = 1/3f_2$
$C_2HD_3^+$	31	$4/5.5/6f_2 = 2/3f_2$

c.



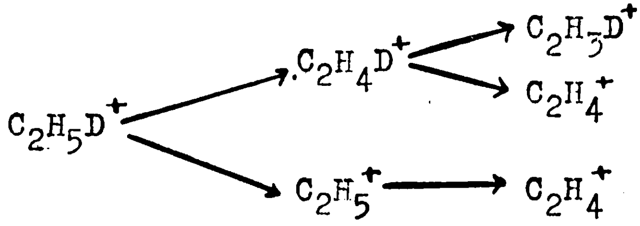
c. contd.	$C_2H_2D_4^+$	34	1
	$C_2HD_4^+$	33	$1/3f_1$
	$C_2H_2D_3^+$	32	$2/3f_1$
	$C_2D_4^+$	32	$1/5.1/3f_2 = 1/15f_2$
	$C_2HD_3^+$	31	$(4/5.1/3 + 2/5.2/3)f_2 = 8/15f_2$
	$C_2H_2D_2^+$	30	$3/5f_2$

d.



$C_2H_4D_2^+$	32	1
$C_2H_3D_2^+$	31	$2/3f_1$
$C_2H_4D^+$	30	$1/3f_1$
$C_2H_2D_2^+$	30	$3/5.2/3f_2 = 2/5f_2$
$C_2H_3D^+$	29	$(2/5.2/3 + 4/5.1/3)f_2 = 8/15f_2$
$C_2H_4^+$	28	$1/5.1/3f_2 = 1/15f_2$

g.



$C_2H_5D^+$	31	1
$C_2H_4D^+$	30	$5/6f_1$
$C_2H_5^+$	29	$1/6f_1$
$C_2H_3D^+$	29	$4/5.5/6f_2 = 4/6f_2$
$C_2H_4^+$	28	$(1/5.5/6 + 5/6.1/6) = 2/6f_2$

h. $C_2H_6^+ \longrightarrow C_2H_5^+ \longrightarrow C_2H_4^+$

$C_2H_6^+$	30	1
$C_2H_5^+$	29	f_1
$C_2H_4^+$	28	f_2

36 $a = A$

35 $b = B$

34 $c = C - f_1(a + 1/6b)$

33 $d = D - f_1(5/6b + 1/3c)$

32 $e = E - f_1(2/3c + 1/2d) - f_2(a + 1/3b + 1/15c)$

31 $g = G - f_1(1/2d + 2/3e) - f_2(2/3b + 8/15c + 1/5d)$

30 $h = H - f_1(1/3e + 5/6g) - f_2(3/5c + 3/5d + 2/5e)$

29 $J = f_1(1/6g + h) + f_2(1/5d + 8/15e + 4/6g)$

28 $K = f_2(1/15e + 2/6g + h)$