CHEMISORPTION OF GASEOUS MIXTURES ON METALS

A thesis submitted for the
Degree of Doctor of Philosophy
of the University of London

by

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November,1966.

ABSTRACT.

The mixed adsorption of oxygen and hydrogen has been investigated on platinum, nickel and copper films. The interaction of hydrogen with adsorbed oxygen atoms takes place in different temperature ranges on different metals. About 70% of a monolayer of hydrogen can be sorbed on oxygen saturated platinum at 77°K by a slow process which is described by the Elovich model. On warming the film to 195°K more oxygen and hydrogen are taken up in the ratio of 1:3 to form a stable complex layer on the surface. Water can be produced by alternate treatment of an oxygen-hydrogen (1:3) saturated film with oxygen and hydrogen at 195°K. A model is suggested for water formation which involves gaseous oxygen and weakly chemisorbed hydrogen atoms. On increasing the ratio of oxygen to hydrogen the rate of water formation is increased, reaching a peak value near an oxygen -hydrogen ratio of 2:1, after which the rate falls slowly. This behaviour is discussed qualitatively.

Nickel saturated with oxygen sorbes only a negligible amount of hydrogen below 273°K. The slow sorption of hydrogen above 273°K on an oxygen preadsorbed surface

can be described by the Elovich equation. The inability of producing water from an oxygen saturated nickel film in the temperature range 77°K to 325°K is probably due to the influence of the oxygen which is incorporated in the lattice. Oxygen saturated copper films can sorb hydrogen above 373°K and produce water at higher temperatures.

The study of hydrogen interaction with oxygen saturated platinum, nickel and copper films suggests that the dissociation of hydrogen molecules is one of the pre-requisites for the interaction of hydrogen with oxygen adatoms on these metals.

ACKNOWLEDGMENTS

I wish to thank Professor R.M.Barrer F.R.S. for the provision of laboratory facilities in the Department of Physical Chemistry,Imperial College,and to thank the Government of East Pakistan for the award of a scholarship for three years.

To Professor F.C. Tompkins F.R.S. I wish to express my sincere thanks and gratitude for his patience during the early stages of this work, and his valuable help and guidance during many discussions.

I also like to thank the technical staff of the Department.

Finally I wish to thank all my colleagues in Room 124 for their friendly gesture and help.

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INTRODUCTION

Some General Aspects of Adsorption on Metals.

The elementary process whereby gases interact with clean metal surfaces , that is of adsorption, poses complex problems. Despite considerable progress, the mechanism of interaction is far from clear. The difficulties in defining metal surfaces have in part greatly hindered progress in the understanding of the mechanism of the gas-metel interaction. It is well known that it is very difficult to generate and,to maintain atomically clean surfaces. Since some of the metals of the transition series can be cleaned by "flashing" at a high temperature,the greater amount of reliable work has been done on such metals. Coupled with this,of course, is the catalytic importance of the group as a whole. The use of ultra high vacuum technique and evaporated metal films plus the availability of single crystal planes[1] have helped in the more precise elucidation of results of a complicated nature .

It is generally accepted that the adsorption of gases by solids can be divided into two main domains- physical or Van der Waal's adsorption and chemisorption. The former is non-specific

and can take place on all surfaces. It is caused by physical forces, comparable with those responsible for liquefaction of gases. The molecules are bound to the surface of the adsorbent by Van der Waal's cohesion forces which include permanent and induced dipole attractions. It is generally appreciable in a low temperature range when non-dissociated molecular species may be reversibly adsorbed and multilayers formed.

On the other hand, chemisorption involves the formation of ionic(2) and covalent[28] bonds and thus involves transference or sharing of electrons. In many systems, dissociation of the adsorbate molecule occurs and the adsorption is mostly highly localised. Mobility in the chemisorbed layer then reduces to a series of migrations from site to site, each requring an activation energy. The advent of improved techniques to measure the sticking probabilities(4,5,6) have proved the existence of weakly chemisorbed species and there is often a spectrum of bonding energies lying between those formally attributed to physisorption and chemisorption.

Adsorption is accompanied by an entropy decrease since prior to interaction with the surface the gas molecules move freely in three dimensions. The change in heat content of the system is given by

$$\Delta H = \Delta G + T\Delta S \quad \ldots \ldots \ldots \ldots \quad 1.1$$

and as both ΔG and ΔS are negative, ΔH must be negative i.e. the process is exothermic. So one of the basic macroscopic studies carried out on gas-metal systems has been the measurement of differential heats of adsorption. The heat is generally found to fall with increasing coverage[3,7,8,9] and three main explanations have been proposed. The earliest one, due initially to Constable[10] and Taylor[11], is that the fall is due to surface heterogeneity. The second one, by Roberts[12], is that falling heats are due to the force of repulsion between molecules in the adsorbed layer. Finally Eley[13] and Schwab[14] consider the energy of electron-transfer taking place in the formation of the surface bond. If the electron is either donated by the gas or a covalent bond is formed, electrons from the gas enter the solid. Since in metals there are bands of permitted electron energies, the first electron will go to the lowest unoccupied level of the band system and then higher and higher levels will be engaged as adsorption proceeds. If on the other hand electrons are donated by the solid to the gas, the first electron will come from the highest occupied state, and then deeper levels will be used. Consequently, in either cases, the heat will fall. Although Temkin[15] developed the idea of heat decrease due to electron-transfer involving a surface band system, Gundry and Tompkins[16] criticised it on the ground that electrons in a surface electron band of metals would be in equilibrium with those

in the bulk metal,which during chemisorption would act as an almost infinite reservoir for replenishment or depletion of the surface band. The magnitude of the heat of adsorption in a gas-metal system depends both on the metal and on the gas,but it is possible to place a number of gaseous adsorbates in sequence such that one is more strongly adsorbed by a metal than the one succeeding it[17]. Comparison of heats extrapolated to zero coverage yields a scale of values descending in the order[17,18].

$$Ti,Ta > Nb > W,Cr > Mo > Fe > Mn > Ni,Co > Rh > Pt,Pd > Cu,Au \ .$$

This order can not be considered to be very precise since ΔH values vary from one worker to another. For example,the maximum heat of adsorption measured for the oxygen-nickel system varies from 105 Kcal[19] to 150 Kcal[20] . A similar wide variation is also observed in oxygen-iron system[19,21]. These ,of course, are extreme cases. Attempts have been made to relate the heats to the electronic structure of metals as measured by the percentage d-character of the metallic bond[18, 22,23]. According to the theory of Mott and Jones[24], transition metal crystals possess incomplete d-bands,and Pauling[25] suggested they possess vacant atomic d-orbitals. This interpretation requires that the bond between metal and adatom be essentially covalent[26,27,28,29] which is in

accord with the experimental investigations, excepting for some alkali metals on tungsten[30,31,32], where the interaction is more ionic in character.

The importance of the d-band in gas-metal interactions is illustrated by the work of Couper and Eley[27] on the activation energy for the ortho-para hydrogen conversion on palladium-gold alloys. The activation energy undergoes a sharp change as the d-band is filled by alloying with gold. Again Trapnell[33] studied several gases on a large number of metal films and concluded that metals with vacancies in the d-band are much more active adsorbents than other metals in the periodic table.

The detailed nature of the adsorption bond in chemisorption is still not clear. Single participation of d-band character in bond formation of transition metals is criticised by different workers[34,35]. Thus, in the dissociative chemisorption of a diatomic gas, the chemical potential of atoms, bound together as molecules in the gas phase, must exceed that of atoms bound to the solid in order for chemisorption to occur[36,37]. If the entropic contribution to the chemical potential is excluded, chemisorption can occur only if the binding energy of an adaton, χ, exceeds one half the dissociation energy D of the diatomic molecules in the gas phase. Among the transition elements the thermodynamic requirement is met as shown by the fact that adsorption energies are higher

on these elements than on non-transition metals.
To define a unique dependence of bonding upon electronic structure of the solid it is necessary to examine the adsorption of gaseous atoms. Semi quantitative data on the bond energies of hydrogen atoms for a variety of surfaces, suggest that there is no particularly dependence upon band structure[38]. Thus atoms can be bound to typical non-transition metals like mercury[39], aluminium[40], potassium[41] and nitrogen atoms, for example, can be chemisorbed on noble metals[42]. Such chemisorbed hydrogen bonds may sometimes involve a surface rearrangement towards a hydride phase and involve complex changes in the hybridization of the metallic orbitals, affecting several atoms as each adsorbate is chemisorbed, rather than a simple bonding with a vacant orbital[16].

The strongly bound hydrogen atoms on tungsten with heats of adsorption from 20 to 46 Kcal depending on the crystal face, desorb above 280^{0}K . Carbon monoxide on tungsten does not differ greatly from hydrogen on tungsten [43] . The heat fall in carbon monoxide-tungsten system from 100 Kcal β_3-state, 70Kcal β_2-state, 52 Kcal β_1-state to 20 Kcal α-state gives a spectrum of heats of adsorption accompanying surface specificity. The adsorption of nitrogen on tungsten proceeds through a simultaneous filling of different binding states; once again there is a sprectrum of binding states from 2 Kcal for a physi-

sorbed state, to 9 Kcal for γ-state, 20 Kcal for α-state and 87 Kcal for β-state.

The mobility of adsorbed gas layers on metals has been demonstrated by Gomer[44], Ehrlich and Hudda[45] and Klein(46) using field emission microscopy. Activation energies for diffusion were measured from the direct observation of the movement of boundaries on field emission tips. A minimum of three types of diffusion was observed. For deposits in excess of a monolayer, a sharp boundary moving over the field emission tip, was observed at ca 27°K for oxygen and 20°K for hydrogen. The layer formed in this way was not mobile if the deposit was insufficient for complete spreading. The sharp boundary remained constant to much higher temperatures unless more gas was added. This type of diffusion showed an upper limit above which it did not occur. According to Gomer the physically adsorbed gas on the top of an immobile chemisorbed layer, can wander to the edge of the primary layer and be chemisorbed on the bare surface. A second type of diffusion occured involving the chemisorbed adatom layer. Atoms could migrate over planes as 110, but were trapped on the rough surface at its edge. The trap sites were presumed to consist of surface configurations offering more near neighbours to a diffusing atom. A low coverage diffusion from trap to trap becomes rate controlling when there is insufficient adsorbate to saturate the traps.

This was found with hydrogen on tungsten.

Measurement of the ratio of the activation energy for diffusion to the heat of adsorption, E_d/E_{ad} [44], showed that the ratio increases with roughness of the surface. On a perfectly smooth surface diffusion would require little activation energy and be independent of the energy of adsorption. A similar increase in ratio was demonstrated on going fron hydrogen to carbon monoxide on tungsten. This is probably connected with the number of formal bonds made with the surface. The small size of an hydrogen atom permits it to be in contact with almost its full quota of tungsten atoms even during diffusion. Studies[47] of γ- and α-state of nitrogen did not show any appreciable diffusion process in the temperature range of their stability. The activation energy for conversion to more stable state or evaporation, must be comparable to the barrier that prevented hopping from one site to another.

Roberts[48] discussed the weak binding state of molecular adsorption on an immobile layer, where a random distribution of pair of sites rather than single sites ϕ was obtained. In such a situation a number of single sites will be completely surrounded by occupied sites, and will therefore be available for weak molecular adsorption only. About eight percent vacant sites are available on an immobile adsorbed layer. Roberts as well as Langmuir and Tonks[49], have considered a slightly different model in which adsorption on a given lattice

site precludes adsorption on neighbouring sites and,accordingly found thirty seven percent are filled.Roberts' original model is a little difficult to make reasonable since even if at equilibrium the adsorbed layer is immobile, the two adatoms formed by dissociation of a single molecule need not go into adjacent sites on the surface.

Ehrlich[50] showed that a model based on the excluded sites can be used for nitrogen-tungsten system. If each nitrogen adatom prevents occupation of an adjacent site by another adatom and each adatom is restricted to one hop, about 36% of the surface sites on the 100 plane can be filled with adatoms. This model fits reasonably with the experimental results; the γ-state can be identified with unavailable pair sites and the concentration of the γ-state is reduced when the film is annealed at high temperatures following the removal of domain boundaries . This filling of the surface depends on the crystal planes involved, with some surface specificity. The observation of weak binding states does not essentially depend on the presence of singular sites,since different crystal faces have a varying ability to bind molecules and this may be relatively important with some systems.

Evidence from surface potential and field emission investigations shows that most of the weakly held states results in a decrease of the metal work function i.e. they have a dipole

with the positive end pointing away from the surface. This type of dipole arrangement is generally characteristic of the interaction of a molecule with a metal surface, rather than an atom or ion. High surface potential changes have been observed for the interaction of rare gases with transition metals at $77^{o}K$[45,51,52]. The positive dipole has been interpreted in terms of induced polarisation[53], charge transfer of donor acceptor type or surface defects. Molecules on the surface are incorporated partly in the metal double layer, which is accepted as having its negative end out from the surface[55,56,57] so that the polarised molecule will have a positive dipole outward from the surface.

This postulation is acceptable for large, easily polarisable rare gas molecules, but quite inadequate for small molecules such as hydrogen. This may be explained in terms of donor-acceptor interaction for transition metals which possess low energy d-orbitals, and they will be good acceptors and yield high surface potentials in agreement with the experimental results. For molecules this type of interaction may also be relevant. For example, the high heats of adsorption of molecular hydrogen on hydrogen covered platinum and tungsten surfaces are 15 and 9 Kcal $mole^{-1}$ respectively, and difficult to explain by polarisation effects alone.

Ehrlich[58] and Kisliuk[5] discussed the available literature

and pointed out the importance of weakly bound, particularly physically adsorbed molecules in the kinetics of chemisorption. Ehrlich concludes that with perhaps the exception of hydrogen, molecules physically adsorbed on the surface form a reservoir from which chemisorption can occur. Delchar[59] showed in his study of the hydrogen-nickel system at 77^{o}or 90^{o}K that after a critical coverage of hydrogen, the subsequent hydrogen adsorption can be ascribed to the formation and dispersion of a second layer of a weakly bound species resting for a while on the chemisorbate, before migrating to the clean part of the film where it becomes chemisorbed. If the sticking probability is less than one and the condensation co-efficient is equal to one, any chemisorption process must involve the participation of weakly bound precursor state. If the probability factor is low, the molecules in the precursor state-probably a physically adsorbed weak species- desorb rather than migrate to vacant sites. However, if the precursor is a weakly bound chemisorbed state, the probability factor for desorption may be low, and in this case the precursor state may play an important role even in an activated process.

Metal Films- Structure and Properties.

Metal films produced by thermal evaporation behave in some respects differently from metal filaments and foil. They are very unstable due to their high surface energy and consist of aggregates of micro-crystallites. They tend to change spontaneously to a more stable form. Their surface areas are irreversibly changed by the formation of larger crystallites at temperatures far below the melting point[1].

X-ray and electron diffraction studies indicate that there is a great similarity between the bulk and surface structure of the metals. Germanium films evaporated onto glass have diamond structure without any preferential orientation[2].Under certain conditions germanium films may have an amorphous structure when deposited at temperature below 380° ,but are crystalline at higher temperature[3,4,5,6]. Nickel and aluminium films condensed in a hydrogen atmosphere have structure and lattice parameters similar to those of the bulk materials[7].

Films deposited at 78°K are composed of small crystallites; the size may be as small as 30 A°[8](linear dimension) and the film is porous. When these films are heated at room temperature, the number of spherulites increases and grows quickly in size with temperature. For example, the average crystal width of nickel deposited at 273°K is about 260 A°

and on heating it to 670°K, the size increases to 2000 Å to 3000 A°[8]. Anderson et al. made a detail study of nickel and tungsten films by electron microscopy. From the transmission electron micrographs the presence of gaps up to 20A° between the crystals have been established for nickel film examined when deposition was carried at 273°K . On sintering, the first stage is the removal of intercrystalline gaps while in later stages surface asperities are removed and crystal growth occurs and, at the same time surface atoms rearrange so that low index planes are exposed. High temperature sintering produces a crystalline structure almost the same as that in the bulk phase, and the original film area is considerably reduced[8,9].

From the surface area measurement it is found that the surface area is a linear function of film weight for nickel and tungsten. Copper film deposited at 90°K is bronze in colour and the large area is also proportional to the film weight[10]. On warming to room temperature, the film turns red and the area reduces to the geometric value. Silver and gold films on sintering at room temperature behave similarly[11,12,13]. Mignolet[14] has shown that work function of films increases with sintering and approaches that of normal metal. Beecks' reports regarding the enhanced catalytic activity of oriented nickel films also seems to be exceptional and this effect has been disproved by Sachtler[15] who used similar films produced

by different method. There is some indication of slow ageing on sintering even at as low a temperature as 173°K[16], as shown by electrical resistivity for films deposited at low temperature, indicating that the atoms of the metals have high surface mobility. Investigation on the mobility of cadmium[17] and on platinum and palladium[16] atoms gives substantial support to this contention.

Direct inveatigations by a number of complementary techniques have shown the role of surface structure in affecting chemisorption. The importance of atomic arrangement of the surface has been realised for many years, but the use of the field emission microscope[18] has demonstrated the variation in surface migration rates over heterogeneous surfaces. For the interaction of nitrogen and carbon monoxide with tungsten , a variety of microscopic and macroscopic observations are now available to prove that a large number of equilibrium and kinetic phenomena is dependant upon the atomic arrangement of the surface.

In the nitrogen -tungsten system nitrogen is chemisorbed in three different states designated γ,α,and β in order of increasing stability. Kinetic studies show the adsorption of nitrogen at low temperature($T \sim 115^{\circ}K$) occurs at a higher rate, with a sticking probability of 0.5 compared to 0.3 at room temperature[21]. This due to the presence of the α-state. Probably nitrogen is first trapped on the (110) plane after

collision from the gas phase and then it migrates to the kinked sites of high activity. So,it is concluded that adsorption takes place through a precursor state, which had been postulated to fit the rate data obtained by macroscopic method. Even though the (110)[22] planes do not directly participate in chemisorption phenomena, it appears that they do influence the overall kinetics of the rate process. The results of Trapnell,Kembell and Eley who used evaporated metal films,together with others[13], also established that the extent of chemisorption was different on different crystal planes, . Later work on single crystal planes has confirmed this specificity of rate on different crystal planes[19,20].

Adsorption of Hydrogen :

In the middle of 1930 s some important work on hydrogen-metal systems was initiated by Roberts[1,2]. His investigation has led to the view that hydrogen is rapidly chemisorbed by clean metal surfaces at room temperature. The chemisorbed layer of hydrogen on tungsten, for example, only starts to evaporate in a good vacuum at 500°. The slow process of hydrogen adsorption observed on tungsten powder, outgassed at 750°[3], may be attributed to a diffusion process, e.g. of oxygen present as a contaminant on the external surface into the interior, thus setting surface sites free for adsorption[1].
Suhrmann[4] in 1929 pointed out from his photoelectric investigation that two types of hydrogen were present on the surface of platinum during chemisorption, and the existence of multiple states of binding was proved by Hickmott[12] from flash filament studies of hydrogen tungsten system. More than two peaks have at various times been claimed[18], suggesting the presence of further binding states, but later work showed that these were from impurity in the system[19].
Mignolet[5] from his surface potential measurements reported the formation of a second layer of hydrogen on top of the primary chemisorbed layer on nickel. Such a second layer has been found for hydrogen on tungsten[7,8]. More recently, however, hydrogen has been reported[6] to be chemisorbed in

three different binding states. It is possible, but not demonstrated, that one of these may be chemisorbed slowly and this state may play a role in catalytic synthesis. Investigations of nickel films by resistance measurements[9,10,11] showed, when plotted against the hydrogen coverage, two peaks which were interpreted as indicating surface complexes. However, one should not rely too much on resistance values which refer to a bulk property as evidence for a surface process. Further evidence which throws considerable light on the complex nature of chemisorption and the existence and behaviour of weakly bound states have been obtained by Sachtler et al.[13], using the field emission microscope. Their results indicate the presence of four adsorbed entities in the temperature range 77°K to 800°K as follows:

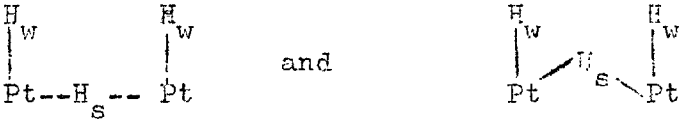
Strongly chemisorbed hydrogen atoms with heat of adsorption 20 to 46 Kcal depending on crystal faces, desorb above 280°K. The second type with a positive dipole outwards, had a heat of adsorption, 15 to 20 Kcal. The third, with a negative dipole outwards, had a heat of adsorption of 8 to 14 Kcal. The last two species showed a preference for the 411 plane. Lastly a weakly bound positively polarised state, of heat of adsorption 6 to 10 Kcal, was found mainly on the 411, 111 and 320 faces. These results have been interpreted by Sachtler in terms of a topographic dependence of heat of adsorption.

The bond strengths have been correlated with the number of surface atoms simultaneously contacted, and with their degree of unsaturation. At low coverages the adsorbate is concentrated on the faces with the highest heats of adsorption, these faces becoming populated mainly by surface diffusion from faces with less heats of adsorption. Only at very low temperatures where diffusion is restricted, will there be uniform coverage over the crystal faces. While the importance of surface heterogeneity is pronounced, some species are the result of induced or polarisation effects, since they are only seen on faces covered with the adsorbate.

Adsorption of hydrogen on tungsten at 100°K shows similar behaviour[7]. However, once the primary process is completed, additional hydrogen goes into a second weakly binding state; this behaviour is confirmed by Mignolet's[14] contact potential investigations.

To explain the observation[6] of two types of hydrogen on an iron catalyst it has been suggested[15] that hydrogen can exist polarised with either a negative or a positive charge outward. Each of them, probably operate in different temperature ranges. Siddiqi and Tompkins[16] also pointed out from their surface potential measurements of adsorbed hydrogen, carbon monoxide and a mixture of these two gases on evaporated nickel films that chemisorbed hydrogen may exist in two

forms. The first one, weakly bound and reactive, has a positive dipole outwards from the metal, and is formed when two adjacent metal atoms carry chemisorbed carbon monoxide molecules; the hydrogen species is postulated as carrying a positive charge of magnitude about half of an electronic charge and is situated about 1 A° unit from the surface.The other exists when the adjacent metal atoms are free and is strongly bounded with the negative dipole outwards. The I.R. investigation of Pliskin and Eischens[17] has confirmed that both species of hydrogen are atomic,the suggestions that in the later stages a weak molecular chemisorption is taking place through a Mulliken charge transfer bond having been discarded. They found bands at 4.86 and 4.76 microns respectively for strong and weak chemisorption of hydrogen. The results confirm that there are two mechanisms of atomic chemisorption; if the weak process, even molecular, a band should appear at about 5.4 microns when HD is adsorbed. However, when an equilibrated H_2/D_2 mixture was placed in contact with the platinum sample, no adsorption occurred at this weave length. Both strong and weak adsorptions must therefore be atomic; representing the species as H_s and H_w Pliskin and Eischens suggest two possible structures , namely



i.e. the two chemisorptions are associated with different topographical positions on the surface, the strong adsorption being part way towards solution in the metal. Mizushima[20] claimed that his results show three hydrogen species on nickel (i) negatively charged atom, (ii) positively charged atom and (iii) molecular hydrogen.

Adsorption of Oxygen

The study of oxygen chemisorption on metals is often complicated by the occurrence of oxidation, even at low temperatures. However, adsorption of oxygen on clean metal surfaces at around 78°K shows that two kinds of sorption can be distinguished: an " irreversible" chemisorption and a "reversible" one. The kinetics of the irreversible one were not affected by interrupting the reaction, a result which is in contrast to the restoration observed when the diffusion controlled oxidation at high temperatures is interrupted[1]. In some cases the reversible adsorption was shows to follow a modified Langmuir type isotherm[2].

$$N_{rev} = N_o \; P^c/[\beta+P^c] \quad \ldots \quad \ldots \; 1.2$$

where N_{rev} is the no. of reversibly adsorbed oxygen molecules per unit area, N_o, no. of oxygen molecules(atoms) in a monolayer of adsorbed oxygen, P, the ambient pressure, and β is an empirical const. Rosenberg et al.[2] from their study of oxygen-germanium suggest that reversible adsorption may be physical in nature and the value of c which is less than unity ($\neq$ 0.5), is attributed to strong repulsion between the adatoms. But it is likely that the molecules of the reversible process may be one of the weakly chemisorbed species on a heterogeneous

surface with a spectrum of adsorption energies. The value of $\underline{c}$ as small as 0.5 may suggest the process is a dissociated one, but the study of krypton adsorption on oxygenated germanium[4] at low coverage(10% to 50%) indicates that a fractional pressure exponent of equation 1.2 may not imply that a dissociation of the adsorbed species has taken place.

At high temperature (195°K) reversible adsorption ceases, but incorporation and oxidation is pronounced. From the photoelectric investigation of Quinn and Roberts[5] and surface potential measurement of Delchar[6] there emerges an"incorporation process" for oxygen on some of the transition metals. The ease of incorporation lies in the order Cr > Fe > Ni > Cu .

Delchar calculated the apparent activation energy of incorporation of oxygen and found it was 1-2 Kcal for nickel and 6 Kcal for copper and for chromium and iron even less than one Kcal. He developed an equation, where the energy term was split into two components.

$$\text{rate} = n \exp -(Q-qaF)/RT \quad \ldots \ldots \ldots \quad 1.3$$

where Q is activation energy for transfer of an oxygen ion from the surface into the metal lattice and qaF, where q is the charge on the ion situated at a distance (a) from the metal, and F is the electric field at the metal surface.

From this equation the value of Q for nickel was found to be 32 to 31 Kcal from 100° to400°K and for copper 28 to 29 Kcal . Grimley and Trapnell[7] have estimated that Q for the transfer of a copper atom into a thin oxide layer is 26.5 Kcal.One would expect that an anion such as O^- would require a greater energy.The agreement is reasonable and probably the surface field controls the rate during incorporation process. Bennett[8] also observed the incorporation process in his investigation of germanium-oxygen system.

Although marked incorporation was observed above 146°K in the case of nickel- oxygen system, there must be some incorporation at 77° or 90°K. This follows from the observation that 2.4×10^{18} molecules are required to reach the surface potential maximum, while 2.0×10^{18} molecules of carbon monoxide or 1.0×10^{18} molecules of hydrogen were sufficient on films prepared in a strictly comparable fashion, and having similar weight. Hopkins et al.[9] also found that at 0.5 monolayer coverage in the oxygen-tungsten system the diffraction patterns of LEED indicated a tungsten -oxygen place exchange, with oxygen buried, but at higher coverages, surprisingly enough, the pattern requires that the tungsten atoms' return to their normal lattice positions[10].

There are some cases where oxygen is chemisorbed without being dissociated into atoms. The molecular adsorption in the

form of O_2^- ions may be the first step of atomic adsorption. Oxygen molecules have a positive electron affinity of 2 to3 Kcal/ mole[11] . O_2^- ions are found in the normal oxidation of the alkali metals,like potassium, when lattices of superoxides result from the reaction of metal with oxygen(KO_2). A cesium metal surface, when exposed to oxygen at 77^oK, is spontaneously covered with a chemisorbed layer of oxygen probably as O_2^- species. From the surface potential investigations the relatively small surface potential due to adsorbed oxygen was originally interpreted[12] to mean that adsorbed oxygen was essentially atomic in character.MacRae[13] has argued that the surface potential data can also be used in support of considerable charge transfer to the adsorbed oxygen. Magnetic studies yield conflicting evidence[14]. Park and Farnworth[15] consider agreement of photoelectric data with the Fowler curve for metals as strong evidence for adsorbed oxygen being mainly atomic in character.

Boreskov[16] used isotopic exchange technique to investigate the character of the oxygen bond on the metal surfaces of platinum, silver, palladium and nickel. He observed that it is probable that the sorbed oxygen penetrates into the surface layers of metal to some depth. A study of the exchange with the chemisorbed oxygen provides evidence for the non-uniformity of oxygen on platinum film.

The heat of sorption varies between 13 and 24 Kcal/mole over

25% of the monolayer, while the activation energy increases by 5 Kcal/mole. The rate of a homomolecular exchange is close to the initial rate of the isotopic exchange with adsorbed oxygen measured at insignificant degrees of exchange. Hence, one may conclude that the homomolecular exchange reaction proceeds on a small area, only 3% of the overall platinum surface[17]. The rate of homomolecular exchange of oxygen on silver films is one order of magnitude less than that of platinum[18]. The studies indicate that the surface oxygen is uniform over most of the surface. PdO is formed on the palladium surface from the adsorbed oxygen and the rate of heterogeneous exchange rapidly decreases with the extent of exchange which indicates that oxygen on the surface is non-uniform. Initial exchange rate on freshly prepared nickel film exceeds that of platinum but in an hour it is reduced to one sixth of the original value. After a large amount of oxygen adsorption, the specific activity of the film approaches the character of an oxide film. From the above results of the isotopic exchange of oxygen there emerges a definite indication that there are various forms of oxygen bonding on the surface of the films and some of them probably do take part a passive role in simple catalytic reactions. Tikhomirova[19] et al. showed by their various pulse methods that at the moment of anode polarisation to $\phi \pm 1.2$ V(i.e. before the formation of oxide phases on the platinum surface) various

types of oxygen(chemisorbed) are formed, differing in bond strength. However, when the same techniques were used on the cathode side (i.e. during reduction of chemisorbed oxygen), at least, two types were detected. Morrison and Roberts[20] using the accommodation co-efficient method, observed two different chemisorbed species of oxygen on tungsten; one evaporating at 800° which is belived to be molecular and the other, evaporating at 1400°, an atomic type. Some eight percent of single sites are in fact left over when an immobile layer formed by dissociation of diatomic molecules to atoms, and it was suggested that on these a strong molecular chemisorption might result. Any way, high temperature evaporation data are even more difficult to interpret with oxygen than with hydrogen, because of the fact that the desorption may be from oxides.

Adsorption of Water Vapour

Water molecules adsorb on metal films in the right temperature range and , chemisorption is effected generally by donation of a lone pair of electrons from oxygen to metal resulting in co-ordination type bond[21].
Law et al. studied the adsorption of water molecules on germanium at very low pressures using mass-spectrometry. It was found that n_L monolayer was completed at a pressure less than one tenth of the saturation vapour pressure. At the saturation pressure about eight to ten layers were reversibly adsorbed with heats of adsorption comparable to that of condensation as would be expected in the multilayer region. By comaring the experimental entropy values with those calculated from various models, it was shown that first layer was localised but that succeeding layers were mobile, having effectively the similar properties as liquid water. Reversibly adsorbed water molecules could be removed by pumping until the monolayer region was reached. Further desorption was observed, however, on heating to about 350° indicating that the monolayer was chemisorbed. Analysis showed that the desorbed products were a mixture of hydrogen and water molecules; hydrogen was produced by dissociation and surface oxide layers were formed. On the other hand water molecules desorb from the platinum films at room temperature.

Experimental evidence showed that monolayer of water molecules was stable upto 195°K and at room temperature(300°K) almost all of it was desorbed.

Suhrmann et al.[23] studies the adsorption of water on nickel films by recording surface potential and electrical resistance change at 77° to 90°K and 195° to 273°K. Between 77°to 90°K resistance R increased and potential ϕ decreased on adsorption of water. In this temperature range, the positive pole of the dipole of adsorbed water molecule points away from the nickel surface. Schaaff[24] observed an increase of the photoelectric emission of platinum in presence of water vapour as a result of donation of the lone electrons of oxygen atoms in the water molecules to the electron gas of the metal.The water molecules decompose on the nickel films at 195°K and especially at 273°K, resulting in an additional increase of ϕ. The fragments are bound to the surface and affect the electronic interaction between the successively adsorbed water molecules and the metal surfaec in such a way that the adsorption of water molecules at 273°K,90° and 77°K is accompanied by a decrease in R which at 273°K can be reversed by desorption.

The conversion of the surface layers of many oxides into surface hydroxide layers is the result of the chemisorption of water molecules on oxides[25].

Mixed Adsorption

Adsorption of mixed gases or one gas after another may result in a number of processes ,such as, surface displacement,the formation of complexes, acceleration or retardation of sorption of different components, or individual adsorption of different gases on different planes of a polycrystalline metal surface.

The displacement of an adsorbed species,A, from a complete covered surface (i.e. monolayer or more) by a second species, B,from the gas phase is possible provided the free energy change is negative. From the thermodynamical considerations, if the bond strength D(M-A) is much less than that of D(M-B), it may be expected that the displacement process may occur. Displacement of hydrogen by nitrogen[1] and hydrogen by oxygen on molybdenum[2] shows that partial displacement is possible. Roberts et al.[1] pointed out that surface diffusion of displaced atoms are essential before molecular desorption. If the surface is not fully covered i.e. $\theta_H < 1$, the rate of hydrogen desorption by nitrogen is negligible up to 60°. Clearly, the smaller are the values of θ_H and T the more likely will displaced hydrogen adatoms be successfully retained by the surface. Probably heterogeneity of the surface controls the partial and stepwise displacement of

hydrogen[3].

Lambert and Heaven[4] found that the adsorbed phase contained three times as much oxygen as argon if oxygen was admitted first, but only halh as much if argon was given priority. A similarity was found with oxygen -nitrogen mixtures, in agreement with the earlier findings of Lemon and Blodgett[5] for these mixtures on charcoal.The probable explanation[6] is that molecules of the component first admitted are adsorbed in cracks and capillaries from which displacement by the added second component is a very slow process. White and Schneider[7] repeated Lambert and Heaven's work with a variation of experimental techniques(continuous gas circulation) and found that adsorption of a particular component depended . solely on the partial pressure, whether it was adsorbed alone or from a mixture. This latter result although in sharp contrast to the findings of Lambert and Heavens that oxygen and argon mutually enhance each other's adsorption , is reasonable in view of the very low coverage of the surface. The process of selectivity of adsorption and its degree for a particular component from a mixture such as adsorption of nitrogen-argon on silica gel and charcoal at low temperatures[8],has been interpreted by Brunauer[6] on the basis of multilayer formation. In the first layer nitrogen is more strongly adsorbed than argon, whereas in the second and higher layers argon is preferen-

tially adsorbed on account of its greater heat of condensation.

Different components of a mixture may lead to a chemical reaction and there has been and continues to be much dispute about the mechanism of the bimolecular reactions. However, the whole field can be broadly divided into two schools of thoughts. According to the original hypothesis of Langmuir[10], accepted by Hinshelwood[9] and Bonhoeffer[11], such reactions proceed through the adsorption of the two species on adjacent sites, followed by their interaction and desorption of the product or products. Most of the reactions to which the Langmuir-Hinshelwood mechanism were applied, whether unimolecular or bimolecular, took place at high temperatures where it is reasonable to expect the rate of desorption of reactants and products to be fast in spite of the high activation energy of such a process.

The reaction may be considered as occurring between the molecules of the reactants, A and B, and a dual site S_2 on the surface; thus[12]

$$A+B+S_2 \rightleftharpoons [A\text{-}B\text{-}S_2] \longrightarrow \text{Products} \quad \ldots \quad \ldots \quad 1.4$$

If the fraction of the surface covered by reactant A is θ and that covered by B, θ_1, then the no. of bare sites adjacent to any given site will be $S(1-\theta-\theta_1)$, where S is the total no. of possible sites adjacent to any given site.

So, the no. of dual sites per cm^2 is $1/2\ C_s S[1-\theta - \theta_1]$. The fraction θ and θ_1 may be expressed in terms of concentration of the adsorbed molecules . C_a for atoms of A and C_{a1} for that of B as follows,

$$\theta = C_a/[C_a + C_{a1} + C_s] \quad \ldots \quad \ldots \quad 1.5$$

and

$$\theta = C_{a1}/[C_a+C_{a1}+C_s] \quad \ldots \quad \ldots \quad 1.6$$

and concentration of dual sites $= [1/2\ S\ C_s^2]/L$ ...1.7

where $L = C_a+C_{a1}+C_s$

The velocity of reaction rate by the theory of absolute reaction rate is

$$v = \frac{1}{2} S \frac{C_g C_{g1} C_s^2}{L} \cdot \frac{kT}{h} \cdot \frac{f_+}{F_g F_{g1} f_s} e^{-E_o/(kT)} \quad \ldots 1.8$$

where C_g s are conc. terms in gas phase, F_g s are partition functions and f_+ and f_s ,the partition functions for activated complex and for the reaction sites, respectively.

An alternative formulation, due to Rideal[13] and Eley[14] which involves interaction between a chemisorbed species and a second molecule either in the gas phase or held briefly in a physically adsorbed layer. There are several variants

of this mechanism, and it is not easy to distinguish between them and the Langmuir- Hinshelwood adjacent adsorption mechanism on the basis of kinetic measurements alone.

In the Rideal-Eley mechanism, if one reactant is strongly chemisorbed and mobile and the second one is physically adsorbed, the reaction must take place within the mean residence time t, where

$$t = t_o \exp [-\Delta H_p / RT] \quad \ldots\ldots \quad 1.9$$

where t_o is time of one vibration in the adsorbed state, $-\Delta H_p$, heat of physical adsorption.
It has been calculated[15] that for hydrogen at 273°K, t will correspond to only about fifteen vibrations if $-\Delta H_p$ is 1.5 Kcal $mole^{-1}$, and this process can not be significant above this temperature when the second reactant is hydrogen. If one reactant is strongly adsorbed but mobile and the second one colliding from the gas phase, the situation is similar as the last one. But if the first component is strongly adsorbed, and immobile, originally envisaged by Rideal, there will be about eight percent single sites vacant in a complete layer and the second one may adsorb, perhaps " end on" over such sites. The chief virtue of this mechanism is to provide a means of bringing the second species into intimate contact with the surface under circumstances where the second

species cannot chemisorb in competition with the first one sufficiently to bring about efficient reaction. The heat of adsorption over such vacant sites could be considerably greater than the normal heat of physical adsorption, and the objection referred to above is thereby obviated.

In the catalysed oxidation[16] of ammonia a gas-phase ammonia molecule reacted with oxygen adsorbed on the platinum surface and Tenkin and Mikhailova proposed that gaseous carbon dioxide molecules removed adsorbed hydrogen atoms in the reaction $H_2 + CO_2 \longrightarrow H_2O + CO$ over platinum.

Nitrogen adsorption on tungsten at room temperature occupies only half of the surface and the remainder can be filled up by a second gas, such as, hydrogen, oxygen or carbon monoxide, as was established by the work of Beeck[18], Trapnell[19], and Wagner[20]. Wagner, in his studies, demonstrated that when nitrogen was first adsorbed on a tungsten film, an equal amount of carbon monoxide could still be adsorbed thereafter. If the order of adsorption was reversed, however, and carbon monoxide was adsorbed first, no further nitrogen uptake was found, This can be explained from the view that carbon monoxide layers completely cover the surface.

Nasini and Ricca[21] studied the extent of adsorption of carbon monoxide on a varying amount of nitrogen preadsorbed on tungsten foil. They found that total amount of nitrogen

plus carbon monoxide remained constant; the addition of one molecule of nitrogen reduces by one carbon monoxide molecule that could be taken up later. The sticking co-efficient for carbon monoxide was affected by the preadsorbed nitrogen in the same way as had been carbon monoxide itself. It proves that nitrogen occupies the sites which were also available to carbon monoxide. Their findings of displacement of one carbon monoxide molecule by one nitrogen molecule indicate that α-CO occupies the excluded sites around the nitrogen atoms and also sites on the (110) planes where nitrogen does not adsorb at room temperature. The equivalence of nitrogen and carbon monoxide sites implies that nitrogen occupy sites on high index planes that would otherwise be available to the β_2 and β_3 states of carbon monoxide. In Rigby's[22] experiments it is found that carbon monoxide does not displace nitrogen; on the contrary, nitrogen does slowly displace carbon monoxide from the adsorbed state at room temperature, with one nitrogen molecule for a single carbon monoxide molecule. This displacement results in the almost complete disappearance of the α-state of carbon monoxide.

CHAPTER 2.
EXPERIMENTAL.

2.1 Materials.

Gases.

Pure water was obtained by double distillation from a solution of potassium permanganate in commercially distilled water. About 30 mls were introduced into a glass bulb which was then sealed to the vacuum apparatus. After a preliminary outgassing with the bulb immersed in a solid cardice-acetone bath at 195°K, the water was subjected to a melting-freezing procedure during which time it was being evacuated by the pumps. It was finally purified by low temperature distillation in vacuum and stored in a vessel containing purified glass wool to increase the surface area from which evaporation could proceed.

Hydrogen was obtained from British Oxygen Company in sealed glass ampoules and purified in situ for each experiment by diffusion through an electrically heated (325°) silver-palladium thimble.

Oxygen was prepared by heating B.D.H. analar potassium permanganate crystals, which had been outgassed and flushed with oxygen and stored in a litre flask with a U-tube manometer. Helium, krypton were similarly obtained.

Metals

Spectroscopically pure metals were supplied by Johnson, Matthey and Co.Ltd. Nickel(grade I), and copper, and platinum wires were used for film deposition.Tungsten wire was supplied by Murex Ltd.

Analysis of the metals :

Metal	% purity	Impurities(p.p.m.)
Nickel	spec. pure	Si:7,Fe:5,Mg:2,Al:2, Ca,Cu: 1 each.
Copper	99.99(gr.1)	not quoted.
Platinum	spec.pure	not quoted

2.2 The Vacuum Apparatus

The vacuum system (fig.1) was housed in a movable, rectangular box on wheels; it was constructed from Dexion angle 225 and measured 4 ft. by 2 ft. by 2ft. 6 ins. The top of this framework was covered with Sandenyo. Holes were cut in this sheet to allow the passage through of the vacuum line and insulated electrical wires and to allow Dewars to be raised around the cell. The section sited above the Sandenyo sheet was that which it was necessary to bake out at high temperature. For this purpose a furnace, 2 ft. high and 13 ins. diameter was constructed which could be lowered over the vacuum line to rest on the insulating top sheet of the

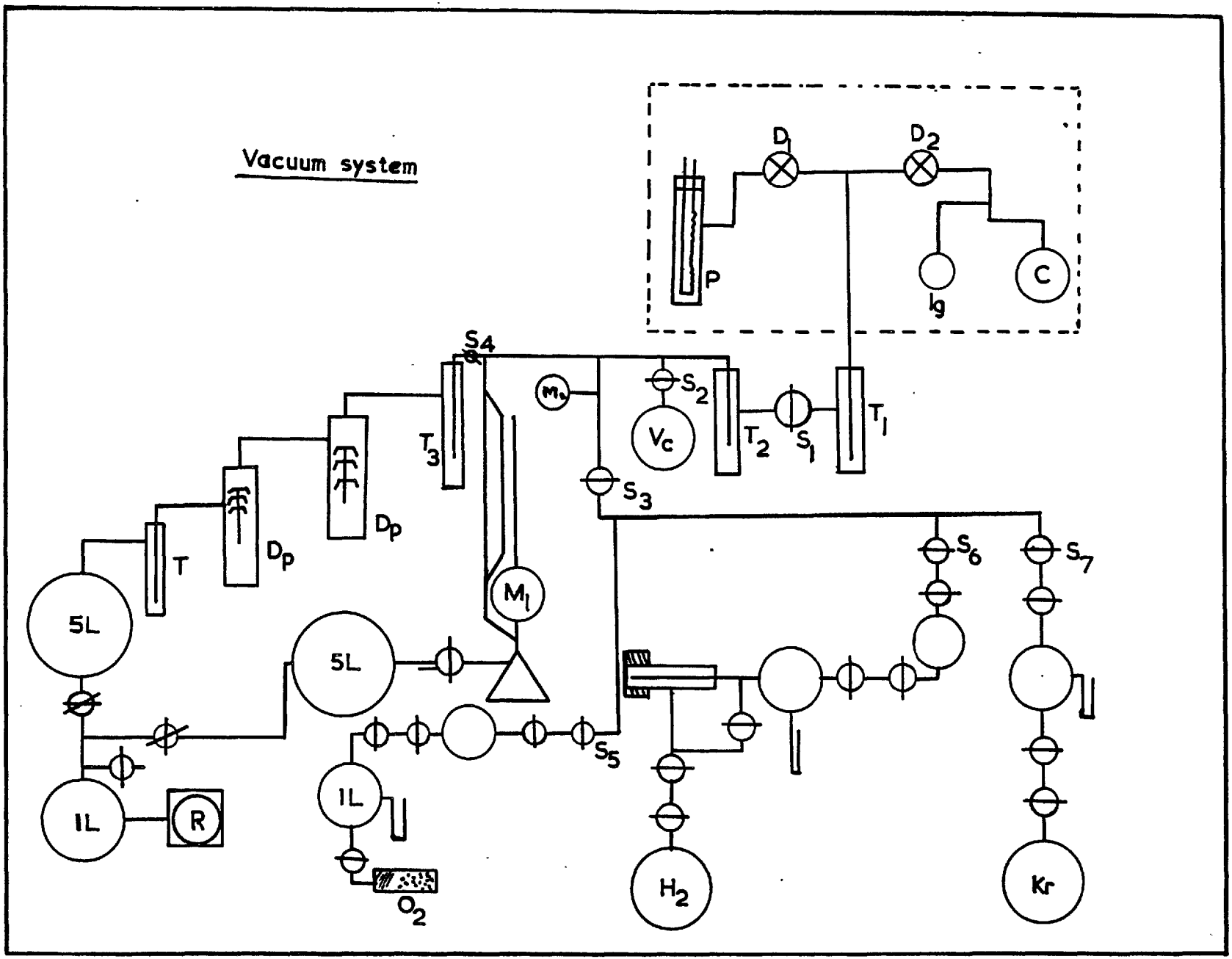

Vacuum system
D1
D2
P
lg
C
S4
M2
S2
Vc
T3
T2
S1
T1
S3
Dp
Dp
T
5L
M1
5L
S6
S7
S5
1L
R
1L
O2
H2
Kr

Fig 1

Dexion frame. The furnace consisted of a innermost cylindrical steel former and two co-axial asbestos cylinders. 16S.W.G. nichrome wire was wound uniformly round the inner cylinder and permanently cemented by a paste of magnesium oxide in asbestos wool. It was finally covered by aluminium foil. The top of the furnace could be lifted when necessary. The temperature of the furnace could be raised to 450°. The apparatus was constructed mainly of pyrex glass; the tungsten/glass seals were of W-1 glass. The main pumping leads were of 25 mm diameter to facilitate rapid evacuation and the rest of the apparatus was made from 6to 12 mm internal diameter tubings.

The Pumping System

The design of the pumping system followed usual high vacuum practice and was found capable of an ultimate vacuum of 5×10^{-10} torr . The ultra high vacuum section consisting of the cell, ion-gauge, Pirani gauge, glass valves, was on top of the Sandenyo sheet, was evacuated by two three stage high speed annular-jet mercury-diffusion pumps, backed by a two-stage rotary oil pump. The cell could be isolated from the pumping system by a system of magnetically operated glass ball-joint valve, D_1, D_2 (Decker valves), and protected against condensable vapours by a system of conventional cold traps (T_1, T_2) situated in the dosing line, all of which were

baked out at 200° by passage of electrical current through heating tapes.

The Gas Metering System

The dosing system comprised four glass stopcocks joined end to end, the first two being separated from the last two by a glass bulb(200 cm^3) . The pressure of the gas in the volume defined by the first two taps was roughly measured on a mercury manometer. Gas in this volume was expanded into the large bulb and a small volume(2.9 cm^3) isolated between the last two taps. This dose was then admitted to the vacuum system(the section defined by the stopcocks $S_1S_2S_4S_5$ S_6 and S_7) and accurately measured by the Mcleod gauge(M_1) and then further expanded upto the Dekker D_1 by opening the stopcock S_1. Doses of different sizes from 4.5 $x10^{-6}$ mole to as small as $x10^{-9}$mole could be accurately measured.

The Pressure Measurement

The pressure in the system could be measured by two Mcleod gauges, a Pirani gauge, and an ion-gauge, the latter being incorporated at a later stage of the work.

One mm diameter precision capillary tubing was used for one gauge for the pressure range 10^{-6} to 10^{-1} torr and three mm diameter capillary in the other for measuring higher pressure (10^{-2} to 6 torr).

The Pirani gauge contained a 120 mm long tungsten filament of 0.01 mm diameter and 155 ohms resistance uniformly stretched between and spot welded to nickel clips which in turn were welded to a pair of tungsten rods of 1.5 mm diameter. Since the sensitivity of the gauge is proportional to the temperature difference between the wall and the wire, the gauge was immersed in liquid nitrogen; the refrigerant was always kept at a constant level well above the top of the filament. In the water vapour experiments the gauge and trap T_1 were immersed in ice. In operation the resistance of the Pirani filament was measured by a Wheatstone bridge(fig.3). The stabilized power supply to the bridge, which was stepped down by high resistors in two of the ratio arms, had a constant output of 40 mA at 300 V. The ratio of the fixed arms was 20 to 1; a Pye Scalamp galvanometer(Cat.no.7893/5) of 210 mm/ μA sensitivity was found sufficiently sensitive for use in the measuring circuit.

The Pirani zero, R_o, was the resistance of the filament at sticking vacuum of the Mcleod gauge(10^{-7} torr) and 78°K. Equilibrium was established in half an hour after switching on the current supply. No fluctuation in the zero value was evident during the experiments, but a change of R_o of about $\pm$ 10 ohms occurred over a few weeks. To avoid this change, tungsten tips were silver soldered with sleeved(insulated) 1 mm nickel wires which were connected to the Pirani

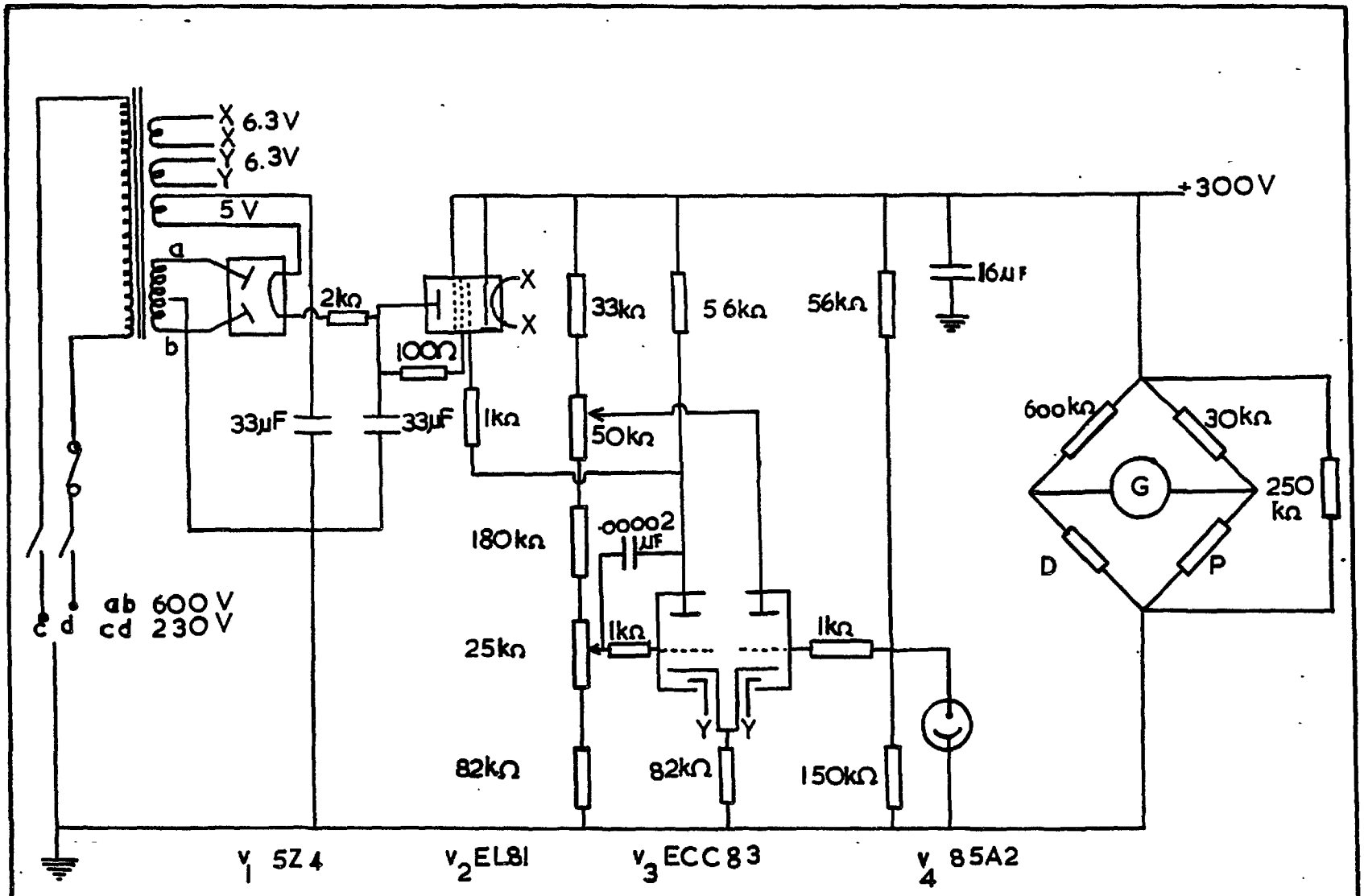


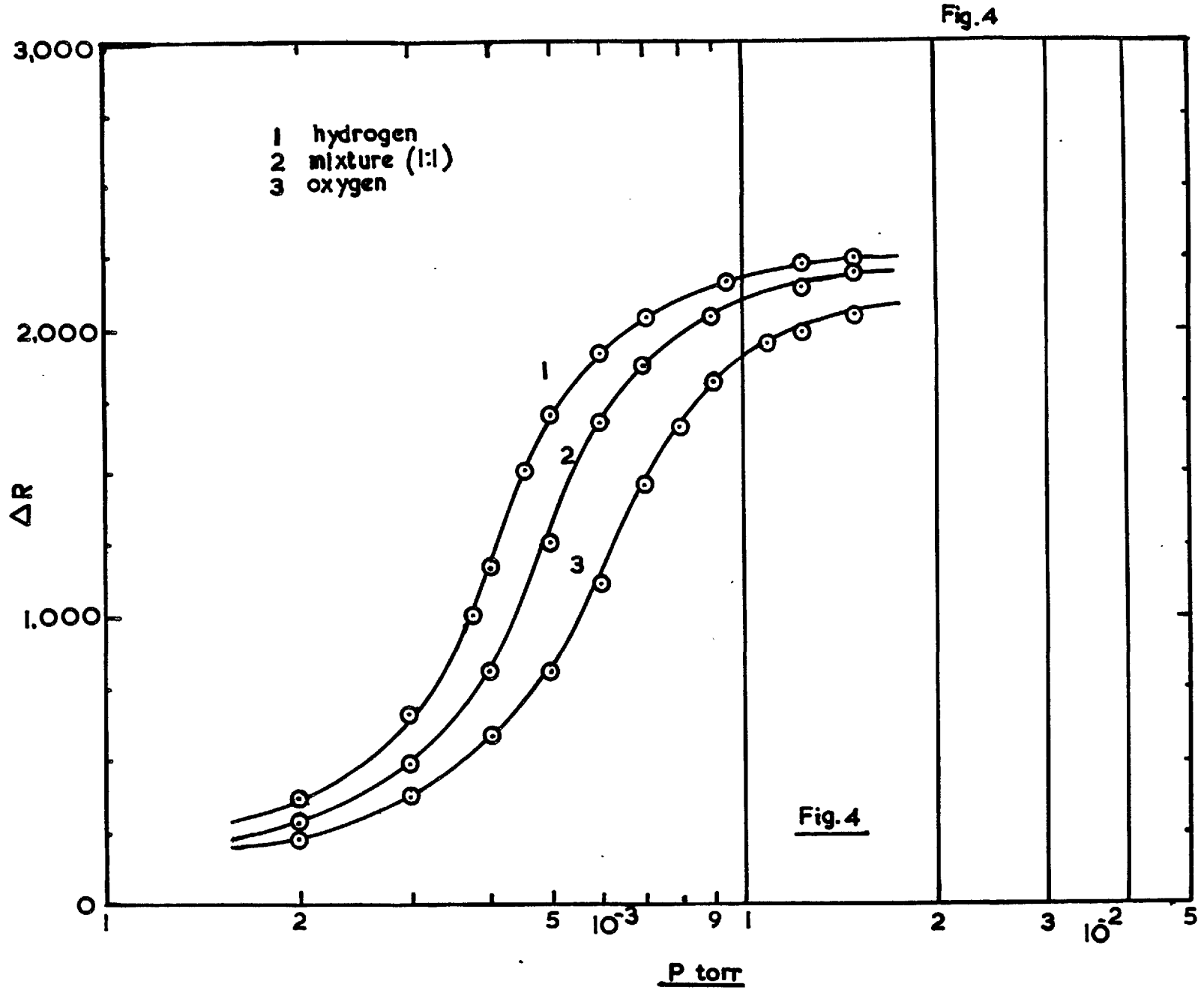
Fig. 3 Pirani Circuit

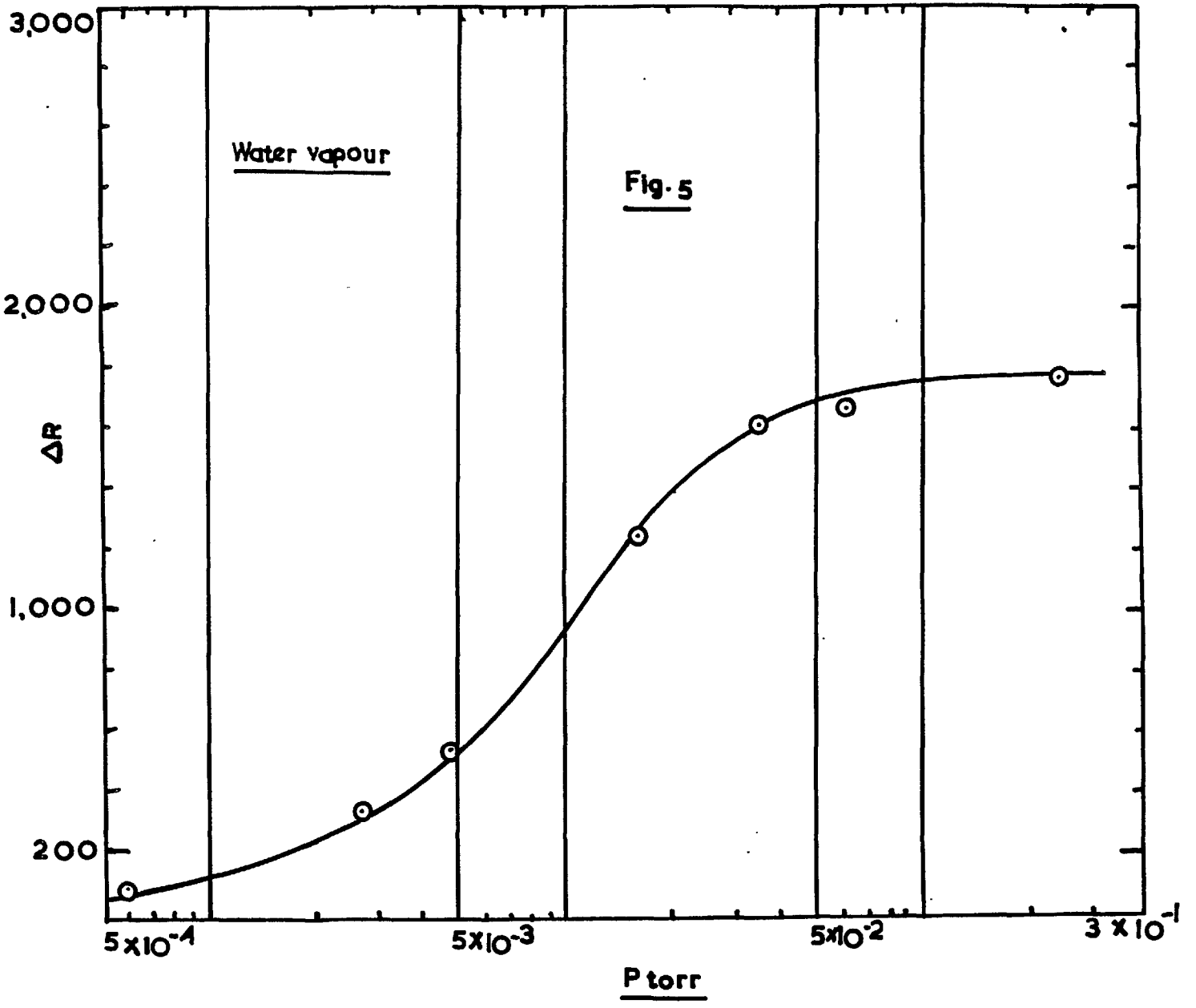
circuit. Overheating of the gauge($<450^{\circ}$) was always avoided. In calibration

$\Delta R[= (R_o - R_1)$ where R_1 is the resistance corresponding to a gas pressure $P_1]$ was plotted against the Mcleod pressure. During every run sufficient Mcleod readings were taken to check the calibration. The sensitivity of the gauge decreased rapidly above 9 $x10^{-3}$ torr, above which press. all measurements were taken by the Mcleod. The Pirani gauge was also used as analyser of oxygen-hydrogen mixture(fig.4). It was calibrated for different oxygen and hydrogen mixtures of known composition of gases against Mcleod readings at different pressures; any gas sample could be analysed by taking simultaneously Pirani reading and a Mcleod reading and, comparing them with known calibration curves either directly or by intrapolation.The gauge was also calibrated(fig.5) for water vapour(at $273^{\circ}K$) and krypton.

Ion-Gauge

The Mullard ion-gauge control WPS-3 and high sensitivity ion-gauge IOG 12 situated near to the cell gave stable measurements of low pressure from 10^{-3} to 10^{-11} torr. The ion-gauge was only used to monitor the initial vacuum conditions and the pressure when the films were deposited. Only 100 μA and 1mA emission current range were used to minimize the gauge ion pumping.


Fig.4
3,000
2,000
1,000
0
ΔR
1 hydrogen
2 mixture (1:1)
3 oxygen
1
2
3
1
2
5
10⁻³
9
1
2
3
10⁻²
5
P torr
Fig.4


3,000
2,000
1,000
200
ΔR
Water vapour
Fig. 5
5x10⁻⁴
5x10⁻³
5x10⁻²
3 x 10⁻¹
P torr

The Reaction Cell

Fig.2 shows details of the cell for all metals used;it consists of a cylindrical neck with a side arm of 12mm diameter and a bulb of 200 cm^3. Two tungsten rods of 2 mm diameter that would safely carry 10 amp. current were used. To replace the filament, the neck cut above the side arm and the film removed by nitric acid (for platinum hydrofluoric acid was used) ;then it was thoroughly washed and dried and a weighed filament, previously cleaned by an A.C. electrolysis in sodium hydroxide, was spot welded on tungsten rods via nickel clips and finally the cell was sealed to the system. Nickel films were deposited directly from 0.5 mm wire but for copper and platinum the throwing filament was a spiral of the metal wire mounted via nickel stips to 2 mm tungsten rods. The evaporation current was supplied from a heavy duty step-down transformer feed by a variac transformer. In this way it was possible to have a fine control on the current through the filament. An ammeter in series with the filament measured the film deposition current.

Calibration of Mcleod gauge and volume calibration constants

Mcleod gauge (M_1): cross-section of the capillary:$7.84 \times 10^{-3} cm^2$,
volume of the bulb:202.5 cm^3,

(M_2): capillary cross-section:$7.1 \times 10^{-2} cm^2$

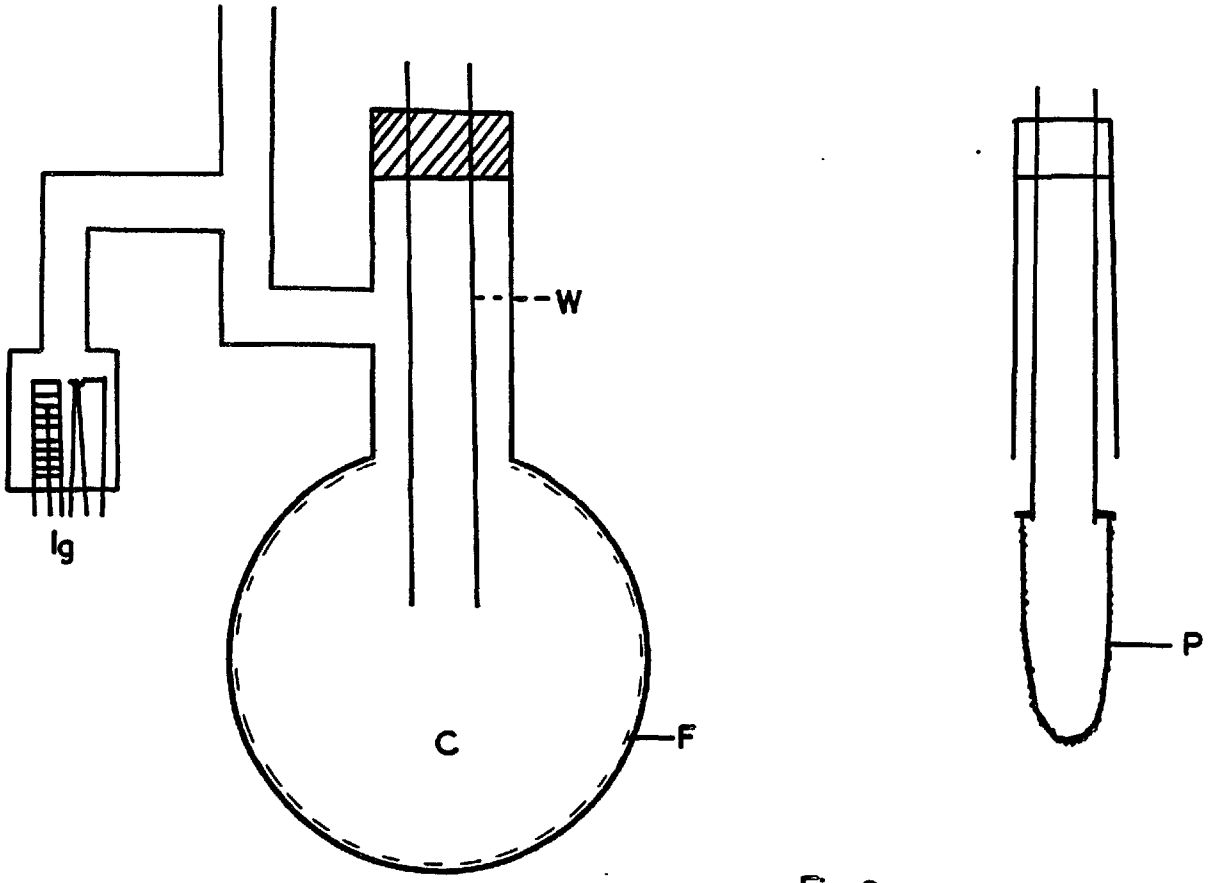


Fig.2

volume of the bulb(M_2): 46.82 cm^3,

$K_{M_1} = 3.877 \times 10^{-6}$

$K_{M_2} = 1.517 \times 10^{-4}$

The pressure $P = h_1 h_2 K$ mm.

where h_1(mm) is the height of the enclosed gas in the capillary and h_2(mm), the difference in the height between the level of mercury columns in the closed and the open capillary and, they were measured with sufficient accuracy by a cathetometer. At 10^{-4} mm and below the pressure reproducibility was within 5% and at higher pressure, within 1%.

The volumes of the different sections of the system were measured by gas expansion from a bulb (544.7 cm^3) which had been calibrated with water. Section I was defined by the stopcocks $S_1 S_2 S_4 S_5 S_6$ and S_7, with the Mcleod gauge(M_1) and trap T_2 in liquid nitrogen and section II was from stopcock S_1 upto the cell with Pirani (P) and Dekkers, $D_1 D_2$. The apparent volumes of these two sections immersed in the cold traps were measured in the working pressure range.

To calculate the number of moles in the gas phase at any pressure the following constants have to be multiplied by equilibrium pressures. The subscript indicates the temperature of the cold bath around the cell .

$C_{(I)78^{o}K} = 3.6 \times 10^{-5}$

$C_{(I+II)\ 78^{o}K} = 11.63 \times 10^{-5}$

$C_{(I+II)\ 195^{o}K} = 8.96 \times 10^{-5}$

$C_{(I+II)\ 273^{o}K} = 8.25 \times 10^{-5}$

$C_{(I+II)\ 328^{o}K} = 7.89 \times 10^{5}$

when the cell at 195°K and traps T_1, T_2 were at 273°K

$$C_{(II)} = 4.53 \times 10^{-5}$$

and for the section between D_1 and S_1

$$C_{D_1S_1} = 1.77 \times 10^{-5}$$

Temperature baths

The following organic liquids cooled to their melting points by liquid nitrogen were used to obtain temperature below 273°K

Table 1

Temperature Baths

Baths	Temperatures ^{o}K
boiling nitrogen	77.3
boiling oxygen	90.0
melting isopentane	113.5
melting n-pentane	141.7
melting methyl cyclohexane	146.6
melting ether	160.0
melting toluene	177.0
solid CO_2 slurry in alcohol	195.0
melting chloroform	210.0
melting di-ethyl malonate	223.2
melting methyl benzoate	260.6
melting ice	273.0

A conventional thermostatted bath was used for temperatures above room temperature.

2.3 Procedure

Evaporated films from the previous experiments were normally removed by dissolution in moderately concentrated nitric acid. However, platinum adhered strongly to the glass; consequently the cell was rinsed with dilute hydrofluoric acid. The acid did not appear to dissolve the platinum but merely lifted it from the glass substrate. Then the cell was repeatedly washed with distilled water. The filament to be evaporated was prpared by winding a spiral of the wire, generally three turns of diameter about 5 mm. Copper, having a low melting point, was evaporated from a filament of tungsten wire(0.3 mm) around which was wound the copper wire. Details of the filaments used are given in the table 2.

Table 2

Filaments

Metal	Diameter in mm	Current to	
		Outgass	throw
Platinum	0.1(0.3mm W)	5.4	7.5
Copper	0.5(0.3mm W)	5.0	6.4
Nickel	0.5	4.6	6.4

For copper and nickel enough care was taken to reduce the filaments in hydrogen atmosphere at one torr for removing oxide films which were formed during cell preparation.

The Outgassing Technique

With the cell attached, the apparatus was pumped out to pressure less than 10^{-5} mm. The system was then baked out with the aid of the furnace placed over the cell, Pirani, ion-gauge and greaseless Dekkers valves. Sections outside the furnace were at the same time heated with tapes. The temperature of the entire system, starting at the throat of the diffusion pumps was raised slowly. All the greased stopcocks were protected against higher temperature by circulating cold water through polythene tubing and, by aluminium foil. The furnace temperature was about 450°. Sections outside the furnace were maintained at about 300°. In the first baking after four hours the current to the heating tapes of traps T_2 and T_3 near diffusion pumps was switched off; cooling with liquid nitrogen was started about half an hour later. At that point the furnace was allowed to cool slowly and current to all heating tapes was turned off and all traps were cool down to 78°K. When the temperature of the furnace was sufficiently low(100°), the furnace was removed and the vacuum was checked with the Pirani and the ion-gauge. When the pressure was less than 10^{-9}

torr, the filament was switched on for twenty four hours in order to outgass it. When the filament was thoroughly outgassed, the system was again baked out for a second time for twelve hours.

The Preparation of Films

Prior to evaporation of the film the Pirani was immersed in a liquid nitrogen bath . The current to the gauge was switched on to allow to reach a steady state. The ion-gauge was also used to check the vacuum. The cell was immersed in the suitable bath (either 78°K or 325°K) and the current of the filament was slowly increased until evaporation proceeded while the cell still open to the pumping system. The duration of evaporation and current were carefully controlled so that similar films could be deposited every time.

Films which were deposited at 78°K(Ni and Cu), were sintered by raising the temperature of the cell to 25° and after 10 mts. the bath-temperature was again changed to 78°K. The temperature cycle was repeated four times in order to stabilise the film. When the film was deposited at 325°K, it was immediately brought down to the desired temperature after switching off the depositing current. Film weight,calculated from the loss of the weight of the wire,varied from 15 to 20 mgs. Evaporation of copper films was effected from 0.5 mm spec.pure wire wound closely around ø0.3mm tungsten core, all adjacent turns touching.Unless the evaporation was conducted extremely slowly,the wire melted into

globule and dropped off the wire, sometimes causing damage to the cell. If the degassing was not carried out for sufficiently long time, it was extremely difficult to maintain a good vacuo during evaporation. The vacuo obtained during evaporation of nickel was 10^{-9} torr, but in the case of copper it was never better than 10^{-8} torr. For platinum, however, the vacuo was in the order of 10^{-10} torr.

2.4 Thermal Transpiration Correction

It was necessary to apply thermal transpiration correction to obtain the true equilibrium pressure in the cell when it was immersed in a bath at 77°K or at 195°K which was different from the rest of the system. The necessity of such corrections has been demonstrated by Tompkins and Wheeler[1], and Porter[2] and other workers[3,4]. Various theoretical approaches have been made, of those that due to Liang[5,6,7,8,] is simple and easy to compute as compared with the derivation of Webers and Keesom[9], which was later developed[10]. Finally Bennett and Tompkins[11] suggested some modifications to Liang's empirical equation.

$$\frac{P_1}{P_2} = R = \frac{\alpha_{He}(f\phi_g\, x)^2 + \beta_{He}(f\phi_g\, x) + R_m}{\alpha_{He}(f\phi_g\, x)^2 + \beta_{He}(f\phi_g\, x) + 1}$$

where R = the ratio of the pressures in the two regions at temperatures, T_1 and T_2,

$R_m = (T_1/T_2)^{1/2}$

$f =$ 1 for connecting tubes of internal diameter, d 1cm

1.22 " " " " " , d 1cm

$x = P_2 d$

$\alpha_{He} = 3.70(1.70-2.6.10^{-3} T)^{-2}$ ($T = T_2-T_1$)

$\beta_{He} = 7.88(1-R_m)$ for R_m 1

and values of $\phi_{g(H_2)} = 1.44$

$\phi_{g(O_2)} = 2.87$

$\phi_{g(Kr)} = 3.90$

Bennett and Tompkins also point out that ϕ_g values may be calculated from the collision diameter, r_o, given by Hirschfelder, Bird and Spotz[12], by making use of the equation

$$\log r_o = 0.43 + 0.24 \log \phi_g$$

The calculated values for P_1/P_2 are plotted in fig. 6,7,8, against log P_2 for oxygen, hydrogen and krypton respectively for various pressures and temperatures.

2.5 Surface area measurements

Since physical adsorption is non-specific it can be used to measure the total surface area exposed to the gas phase. The method used for surface area measurements employs the well known B.E.T. isotherm for multilayer physical adsorption[13]

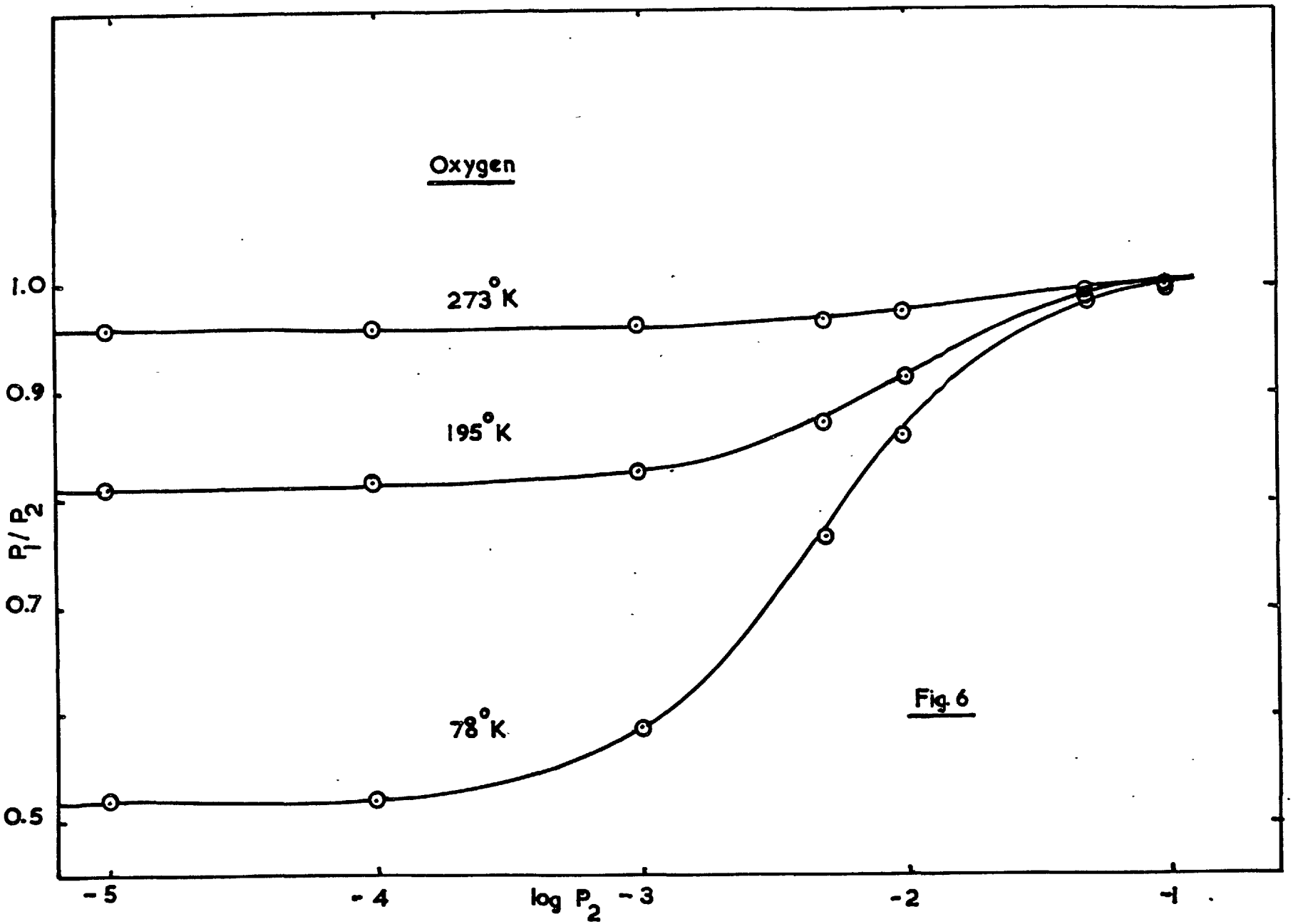


Fig. 6

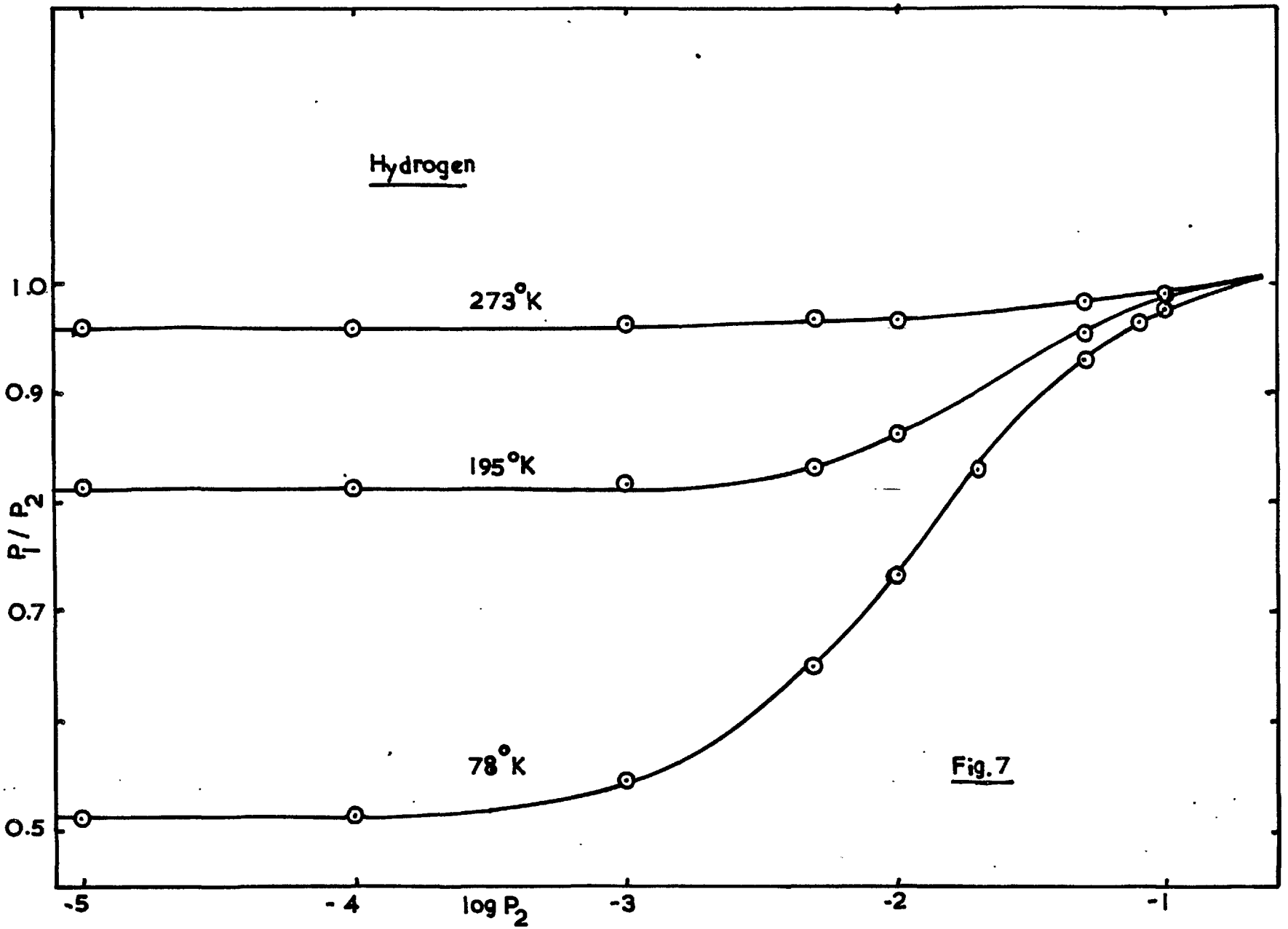


Fig. 7

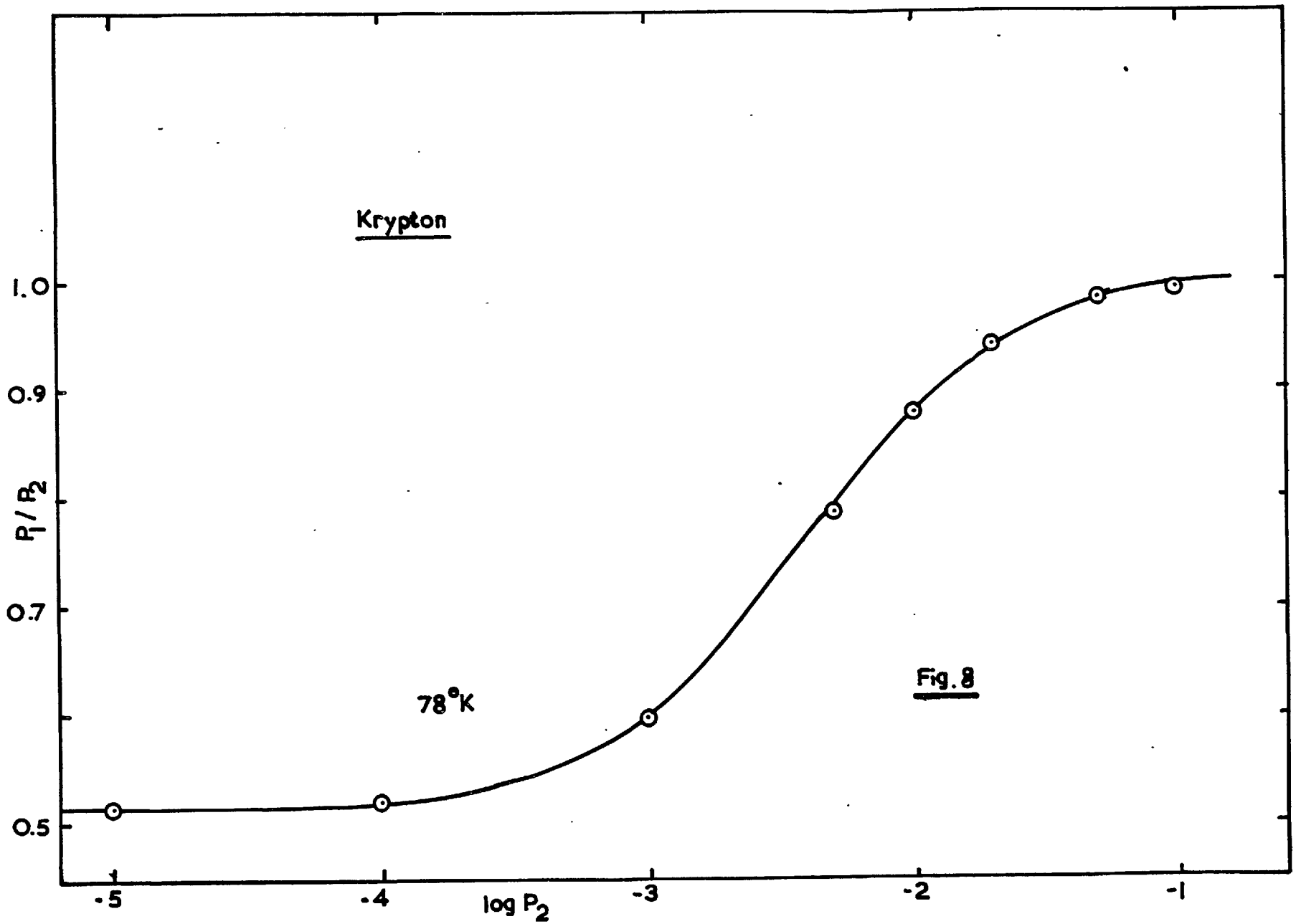


Fig. 8

$$P/V(P_o-P) = 1/V_mC + (C-1)/V_mC\ (P/P_o)$$

where V_m = volume necessary to form a monolayer,

V = volume adsorbed at a pressure P,

P_o = vapour pressure of the adsorbate at the temperature of the experiment,

C = a constant, which depends on the nature of the adsorbate-adsorbent system.

By plotting $P/V(P_o-P)$ against P/P_o, the volume V_m can be calculated. One typical B.E.T. isotherm for platinum film is shown in fig. 10.

While the basic assumptions of the isotherm have been critised by Hill[14] as crude, there is considerable evidence that the values of V_m obtained by Harkin and Jura[15] with weakly physisorbed molecules on heterogenous surfaces are acceptable.

The krypton adsorption at liquid nitrogen temperature was used for determination of small surface areas[17,18,19] (by B.E.T.) which are comparable with those of Keely[20], and Lincoln & Carnevale[21] by a rapid x-ray line broadening technique.

The cross-section of a krypton molecule has been determined by various workers[16,17,22] based on the accepted cross-section of nitrogen molecules as 16.2 $A^{o\ 2}$. Beebe, Beckwith and Honig[16] have determined the surface area of

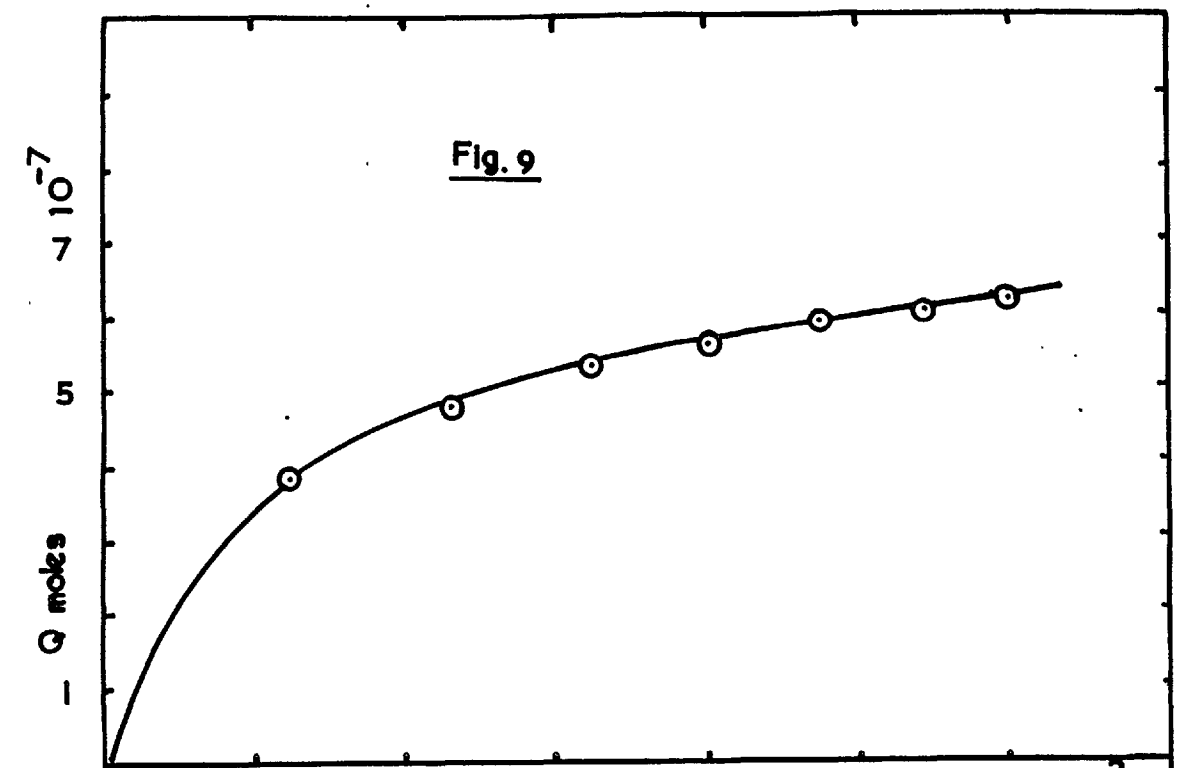
an anatose sample obtained from Harkins' and found the cross-section of a krypton molecule as 19.5 ± .4 $A^{o\,2}$.

Beebe[16] found that the temperature of liquid nitrogen varies from 77.5°K to 79.1°K and in this temperature range the vapour pressure of solid krypton varies from 1.8 to 2.62 torr and extrapolated values for liquid krypton ranged from 2.63 to 3.72 torr.A value of 1.73 torr has been found by Kingston and Holmes[23]. However, due to the low values (10^{-2} torr) of the working pressures, the values of P_o has little effect[24] on the values of the surface area measurements. The values of V_m by B.E.T. method was always found higher than those of " point B" method which can be calculated from fig. 9.

V_m was obtained in units of moles, and transformed to surface areas using 19.5 A^{o2} for the cross-sectional area of the Kr atom. The number of sites on each metal film was found by dividing the B.E.T. area by the average area of the site.The number of sites depends on the crystal structure of the metal[25] and was calculated as follows:

No. of sites per cm^2 for f.c.c metal $\frac{1.91}{a^2} \times 10^{16}$

The calculated values are given in the table 3 .


Fig. 9
7 10^-7
5
1
Q moles
2
4
6
8
10
12 X10^-3
P torr

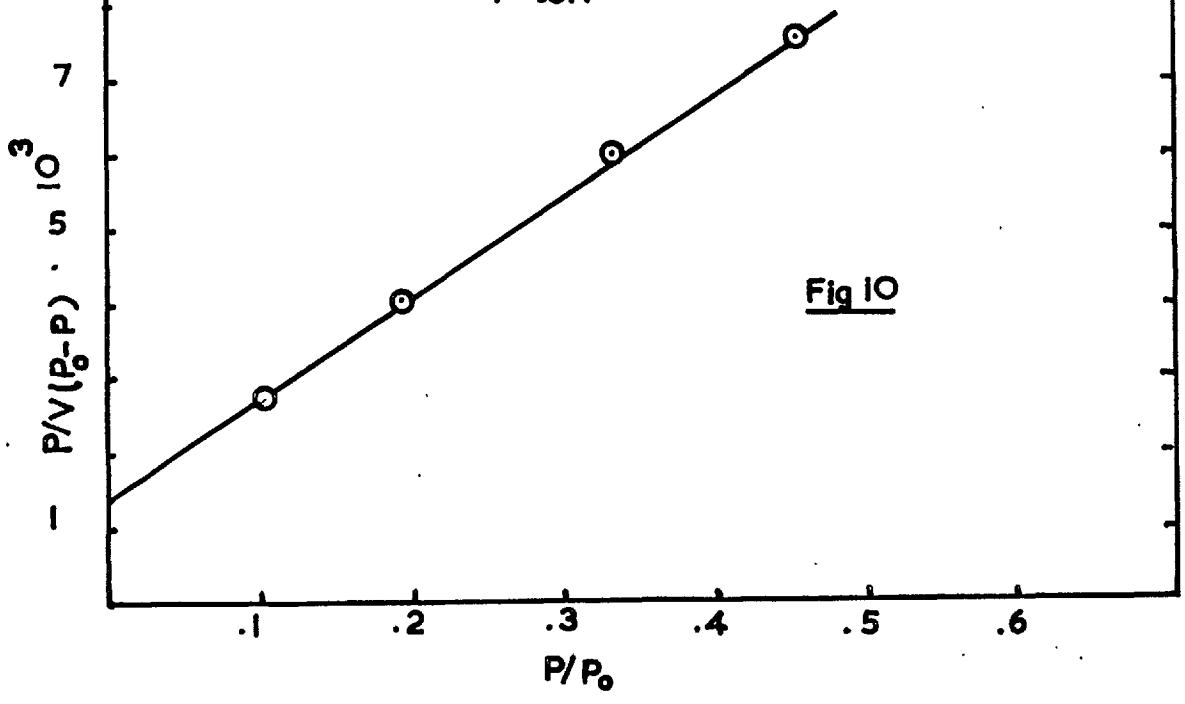

7
5
1
- P/V(P_o-P) · 5 10^3
.1
.2
.3
.4
.5
.6
P/P_o

Fig 10

table 3

metal	crystal type	a	sites/ cm^2 $x10^{15}$
Copper	f.c.c.	3.61	1.47
Nickel	f.c.c.	3.52	1.54
Platinum	f.c.c.	3.91	1.25

[Lattice parameters are taken from F. Seitz , "Modern theory of solids",McGraw Hill,N.Y.,1940]

CHAPTER 3

RESULTS AND DISCUSSION.

3.1 System: Oxygen+Platinum+Hydrogen.

The interaction of hydrogen and oxygen on platinum films has been studied at 77°K and 195°K. The films were deposited from a clean tungsten core at a bath temperature between 325°K and 345°K. The duration of deposition of the films was approximately one hour and the current through the filament was 7.5 amps.; this current was much less the current needed to evaporate tungsten(11 amps.). The weight varied from 17 to 20 mgs. on different films.The geometric area of the cell was approximately 200 cm^2 and the roughness factor of the film was around five. The surface area which in the order of 10^3 cm^2, was measured by Kr-isotherm at 77°K. The surface area by "Point B" method was found about 75% of the B.E.T. area derived from the analytical expression. In this investigation B.E.T. analytical area was used for computation. The results which varied within experimental limits,were the mean values and the agreement between the similar type of experiments was within ±5%.

After evaporation the film was brought down to liquid nitrogen temperature and measured doses of oxygen($Q \sim 10^{-7}$mole) were admitted to the cell . In run Pt 22 a total amount of 100×10^{-8} mole of oxygen(equivalent to 95% surface coverage) was adsorbed at an equilibrium pressure of 1.3×10^{-3} torr.

When the slow adsorption process became negligible, the gas phase oxygen was pumped off.After rapid evacuation of the gas phase oxygen in less than a minute, a small dose of 25 $x10^{-8}$ mole of hydrogen was introduced. 14 $x10^{-8}$ mole was taken up instantaneously followed by a slow process. When the whole dose had been taken up, another dose was introduced and the fall of pressure against time was recorded.A third dose led to saturation of the surface corresponding to 70% of a monolayer. The results are shown in fig.11 and fig. 12.

The slow decay of hydrogen pressure which corresponds to the amount sorbed, may be the result of an activated interaction with preadsorbed oxygen adatoms on a heterogeneous platinum surface. The slow activated process can be described by the Elovich equation[1]. If the non-uniform surface is divided into a number of elements of areas $\underline{ds}$, each of which is an uniform patch, and the activation energy for interaction is assumed to vary as follows with s

$$E = E_o + \alpha s \quad \ldots \quad \ldots \quad \ldots \quad 3.1$$

the rate process becomes

$$r_a = P\, y\, \sigma \int_0^1 (1-\theta)\, e^{-(E_o+\alpha s)/RT}\, ds \quad \ldots\ldots \quad 3.2$$

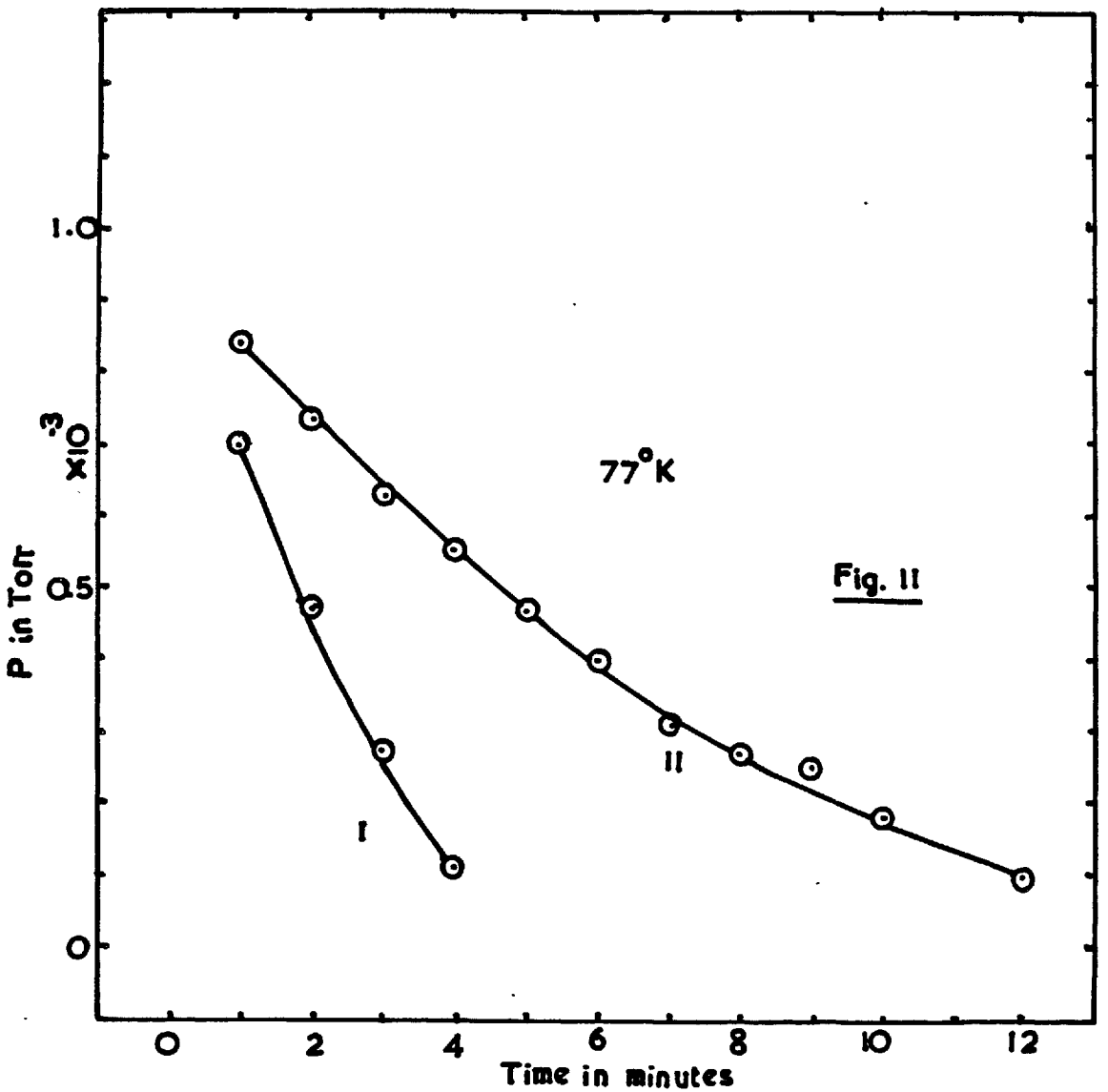


Fig. 11

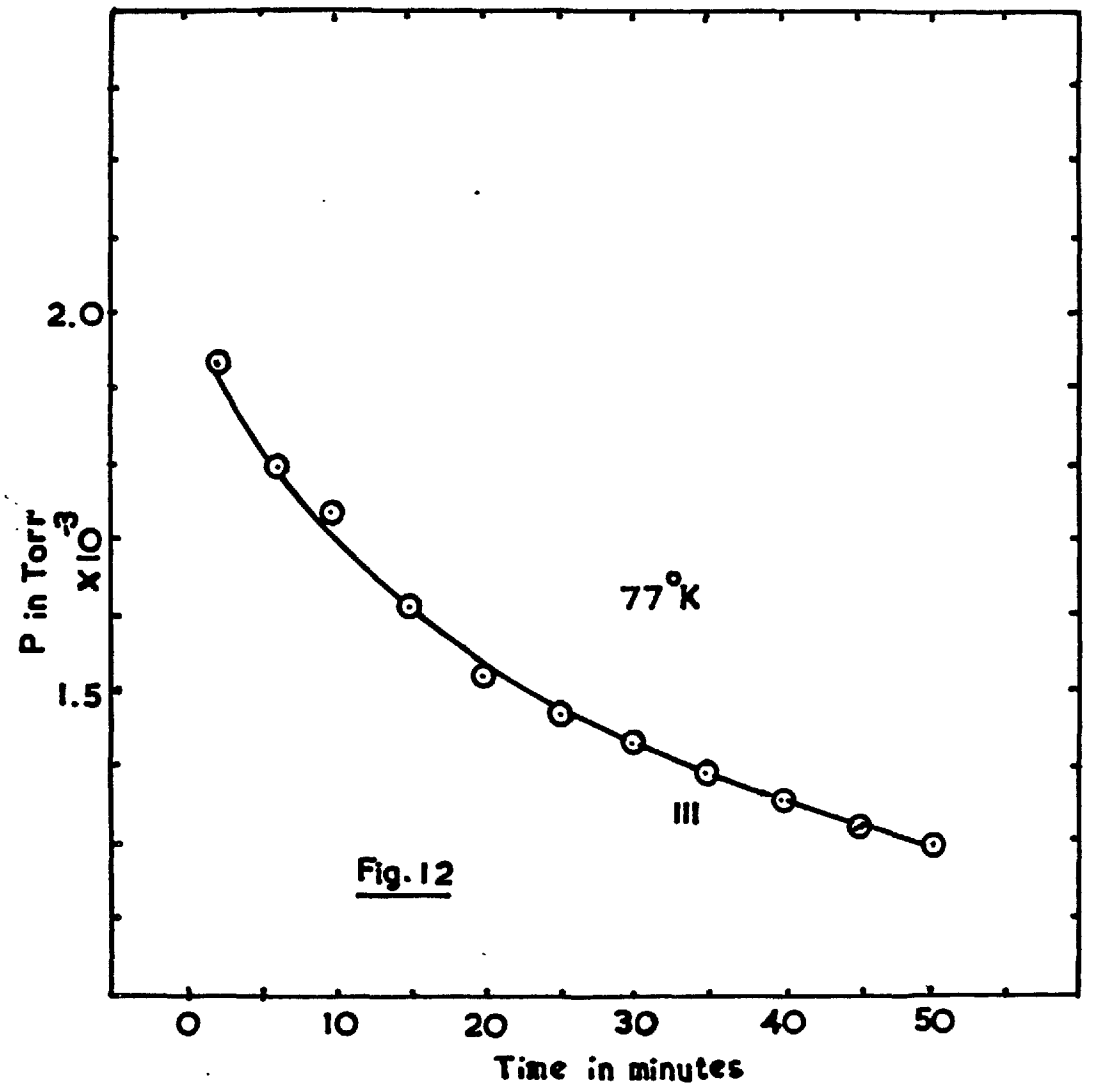


Fig. 12

where γ = frequency factor ,

σ = sticking probability ;

For integration of the equation 3.2 the following assumptions are made: If the variation of E is significant, the sites on the surface with the lower E values will be covered far more quickly than the parts of the surface on which E is high. So, at a given instant, the surface will consist of two parts- an almost covered part(low E), and almost a bare part (high E) . In this case the integral of the equation 3.2 may be replaced by an integral carried out simply over that part of the surface which is bare, for which $1 - \theta_s = 1$. The limits of integration are $s = \theta$, the fraction of the surface covered and $s = 1$;

then

$$r_a = \gamma \sigma \int_{\theta}^{1} e^{-(E_o + \alpha s)/RT} \, ds \quad \ldots \quad \ldots . \; 3.3$$

On integration

$$r_a = \gamma \sigma \frac{RT}{\alpha} e^{-E_o/RT} \left[e^{-\alpha\theta/RT} - e^{-\alpha/RT} \right] \ldots \quad \ldots \quad 3.4$$

If θ does not approach unity, $e^{-\alpha\theta/RT} \gg e^{-\alpha/RT}$

The rate takes the form

$$r_a \propto e^{-\alpha\theta/RT} \quad \ldots \quad \ldots \quad \ldots \quad 3.5$$

or, the velocity equation is

$$\frac{d\theta}{dt} = a\, e^{-\alpha\theta/RT} \quad \ldots \quad \ldots \quad \ldots \quad 3.6$$

and on integration of 3.6

$$\theta = \frac{RT}{\alpha} \ln [(t + t_o)/t_o] \quad \ldots \quad \ldots \quad \ldots \quad 3.7$$

where $t_o = RT/a\alpha$

The equation 3.7 predicts a plot of q against $\log(t+t_o)$ should give a straight line. In fig.13 q from different doses against time is shown. The plot shows that two processes are operative within the range of data and their α's are 2.07×10^{-15} cal mole^{-1} molecule^{-1}(I) and 3.0×10^{-15} cal mole^{-1} molecule^{-1} (II) .

This type of multiple stages of interaction may be supported by the observation of Low and Taylor[2]. The linear q-log t plots were found with the carbon monoxide-ruthenium system whereas the plot was discontinuous when hydrogen was pre-

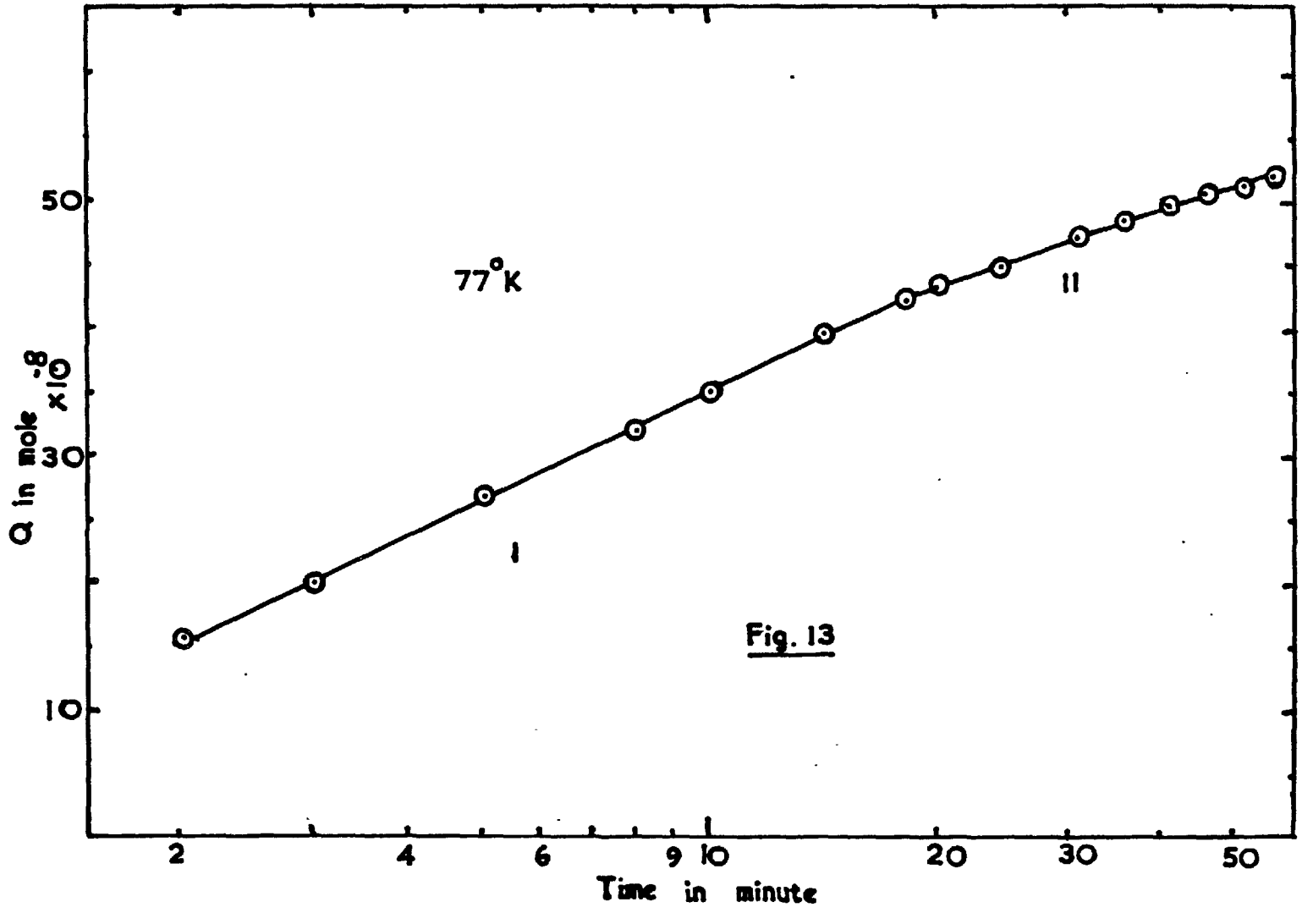


Fig. 13

adsorbed by the solid. The Elovich plot of pure hydrogen (fig.34) or oxygen (fig.35) does not show any break for their slow interaction with clean platinum either at 77°K or 195°K.

In an attempt to measure the extent of interaction of oxygen and hydrogen at higher temperature platinum films first saturated with oxygen and then, with hydrogen, were warmed to 195°K. At this temperature the process became quite different. The gas phase hydrogen was taken up instantaneously and additional doses were sorbed in the similar fashion until the oxygen - hydrogen ratio became 1:3. In a particular run (run Pt 23) the amount of hydrogen adsorbed was 62×10^{-8} mole at an equilibrium pressure of 2×10^{-3} torr on the top of 99.5×10^{-8} mole of oxygen preadsorbed film at 77°K. Then the film temperature was raised to 195°K. A total of $(231 \times 10^{-8} + 62 \times 10^{-8})$ or 293×10^{-8} mole of hydrogen was taken up to give a ratio of 1:3 for oxygen to hydrogen. The residual hydrogen was evacuated and the cell was isolated by Decker valves. The condensable product likely to be water was frozen out in a trap and in the Pirani gauge both immersed in liquid nitrogen baths. In order to measure the water vapour the cell was isolated, the cold baths around the Pirani and trap T_1 were removed; the vapour measured by a Mcleod was found to be less than 1% water calculated in terms of the number of oxygen atoms

originaly adsorbed. This indicated that water did not desorb (heat of desorption $\Delta H \pm 11$ Kcal[3]) from the film at 195°K [vapour pressure of water at 195°K is 5.6×10^{-4} torr[4]], since at room temperature water desorbed completely[5,6] along with hydrogen which was about 20% of a monolayer.

If the temperature of the film was maintained at 195°K with 1:3 oxygen and hydrogen composition, it was found that it could sorb or react with further oxygen . Thus when oxygen doses were introduced at that stage, an average of 72×10^{-8} mole(run Pt 23) was apparently taken up. After evacuating the gas phase oxygen ($P \simeq 3 \times 10^{-3}$ torr) water was measured and found to be 25% of oxygen atoms sorbed in the second time.Hydrogen gas was then introduced to the oxygen treated surface. About 146×10^{-8} mole of hydrogen, which is twice the amount of oxygen sorbed in the previous treatment,was taken up. No evidence of water formation was obtained after hydrogen sorption. The alternate oxygen and hydrogen treatment or the oxygen-hydrogen cycle could be repeated and the reproducibility was within $\pm$ 5% . In run Pt 22 an average of 86×10^{-8} mole of oxygen took part in oxygen-hydrogen cycle. The amount of oxygen reacted in oxygen-hydrogen cycles varied from cycle to cycle within 5%, but the quantity of hydrogen was always twice the amount of oxygen. In run Pt 23, the film saturated with oxygen and hydrogen(1:3) at 195°K,

was subjected to four oxygen-hydrogen cycles. Water which was found to be 65%, was measured by a heated Mcleod[7].It was observed that variation of ambient pressure (one order of magnitude) had negligible effect on the total quantity of oxygen or hydrogen taken up in the oxygen-hydrogen cycle.

The differences of yield of water obtained by the Mcleod measurement clearly illustrate the difficulty of measuring condensable vapour in a Mcleod gauge. Armbruster[7] as well as Frazer et al.[8] found that the danger of condensation of water vapour could be avoided at higher pressure, by warming the capillary to higher temperature during pressure measurements.In the present investigation the capillary and the bulb of the Mcleod were heated to 50°C ,but the measurement still showed less than 100% production of water. This was probably due to adsorption of water vapour on the glass and mercury surface. Later on, the yield of water was measured by a calibrated Pirani gauge and the yield was found to be nearly quantitative (93%)

3.2 System: Hydrogen+Platinum+Oxygen.

Hydrogen was adsorbed on a clean platinum film at 77°K and the quantity adsorbed was 106 $x10^{-8}$ mole(an average of run Pt 18 , 20,21) corresponding to 90 % of surface coverage at an equilibrium pressure P~6.5 $x10^{-4}$ torr. After rapid evacuation of the gas phase hydrogen, oxygen was introduced. 16 $x10^{-8}$ mole of oxygen removed instantaneously followed by a slow process in which 5 $x10^{-8}$ mole was in sixty minutes(fig.14).Analysis of the gas phase during sorption of oxygen on a hydrogen covered surface showed that it was always pure oxygen and no evidence was obtained for hydrogen displacement . The total amount of oxygen sorbed on a hydrogen covered surface varied from 15 to 25 % of a monolayer on different films. When oxygen at higher pressure(P~2 $x10^{-2}$ torr) was allowed to react with a monolayer of hydrogen adatoms on platinum film at 77°K ,a portion of oxygen adsorbed reversibly on the film. For film Pt 9 oxygen at 1.6 $x10^{-2}$ torr was allowed to react with 200$x10^{-8}$ mole of preadsorbed hydrogen at 77°K . 101$x10^{-8}$ mole of oxygen was taken up, a portion of which was reversibly sorbed. To isolate the reversible part the pressure of oxygen in the gas phase was reduced step wise, by expansion of the gas in the cell into another vessel of accurately known volume, and the amount of oxygen released from the film was measured. The quantity released is given in the table 4.

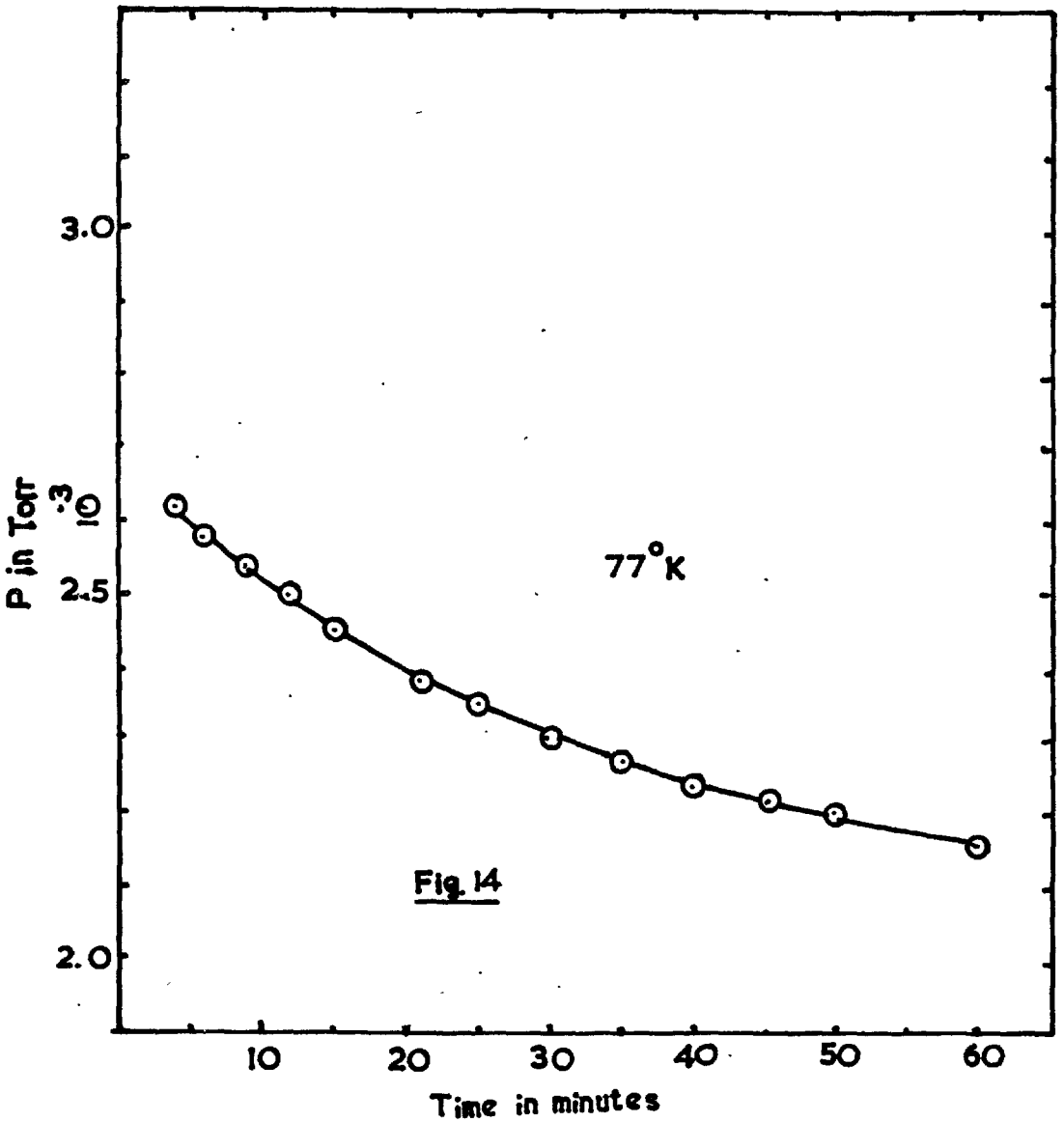


Fig. 14

Table 4

Press. of O_2 ($P \times 10^{-3}$ torr)	$Q \times 10^{-8}$ mole
11.8	11.6
8.8	10.1
6.5	6.9
4.9	6.6
3.6	4.1
2.7	3.1

The reversible isotherm obeyed a logarthmic equation.In fig.19 Langmuir's type of plot of $\log[(N_o/N_r)-1]$ vs log P of equation 1.2 is shown. The value of pressure exponent C is found to be 1.05 which probably means that the reversible sorption of oxygen on the top of a hydrogen adatom layer is molecular,and that the Langmuir equation is a reasonable approximation. On warming a film first saturated with hydrogen and then, with oxygen at $77^{o}K$ to $195^{o}K$, 65.7×10^{-8} mole of oxygen was taken up to make the total quantity 85.8×10^{-8} mole. The oxygen from the gas phase was rapidly evacuated and the bath temperature again changed to $77^{o}K$. Only 7×10^{-8} mole

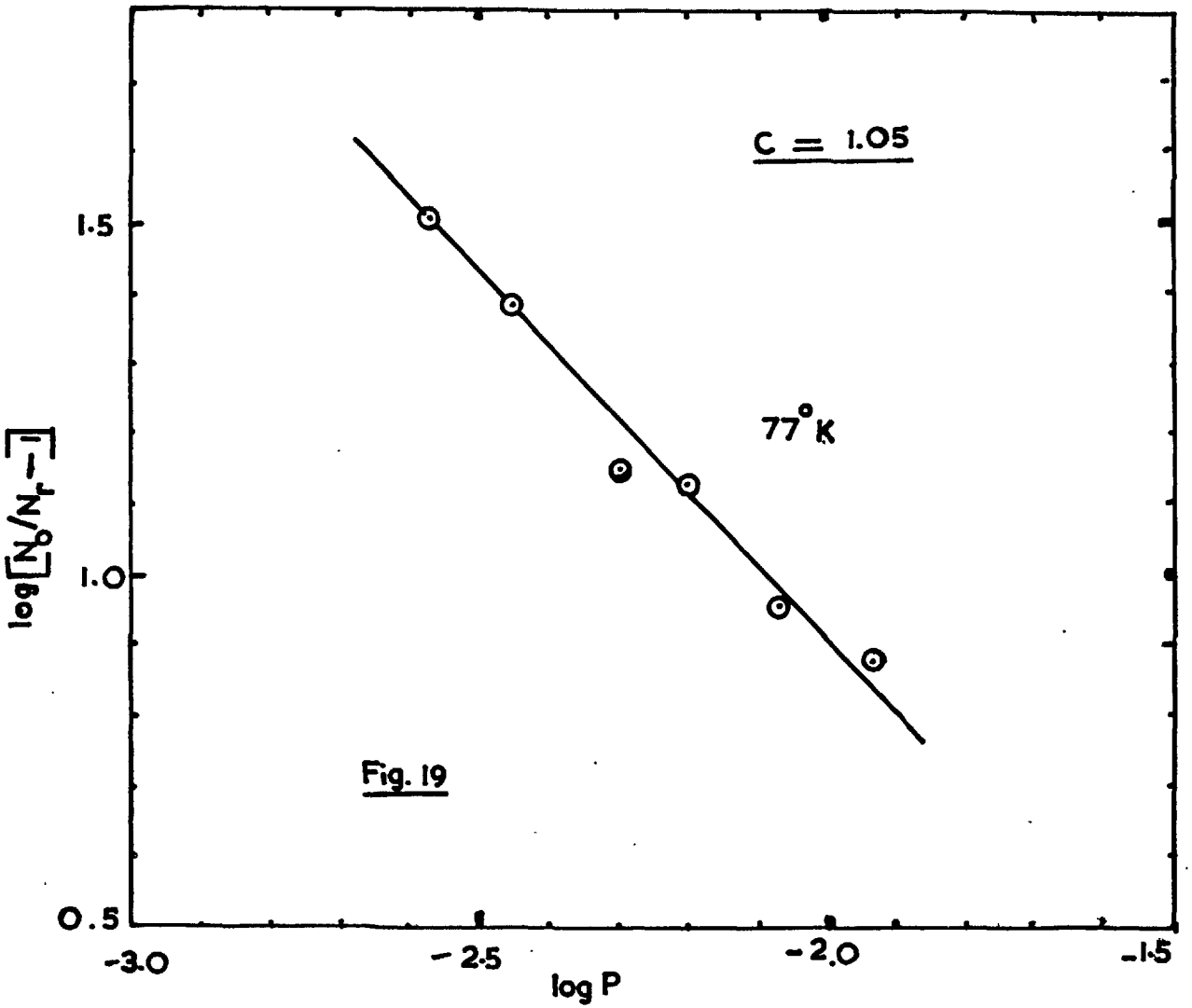


Fig. 19

of hydrogen was sorbed on introduction of a hydrogen dose. When the film was warmed up to 195°K, 138 $x10^{-8}$ mole of hydrogen was taken up to give a 1:3 oxygen-hydrogen ratio. The film was isolated and the condensed product in the traps was measured; again the quantity was very small,less than 1 %. If the film was warmed to room temperature,similar behaviour of water and hydrogen desorption was observed similar to the Oxygen+Platinum+Hydrogen system.

Instead of warming to the room temperature if the film was allowed to stay at 195°K with oxygen-hydrogen ratio 1:3, the film could be subjected to alternate oxygen and hydrogen treatments. In such runs(run Pt 20,21) 252.7 $x10^{-8}$ and 78.5 $x10^{-8}$ mole of hydrogen and oxygen were on the surface at 195°K. When the oxygen-hydrogen cycles were repeated on such a film, $55x10^{-8}$ mole of oxygen and $110x10^{-8}$ mole of hydrogen participated in oxygen-hydrogen cycles.

Both of the oxygen and hydrogen sorption were rapid and 90 to 95 % of them could be taken up in a couple of minutes.The rapid processes were always followed by slow ones. Typical plots of slow oxygen intercation with hydrogen preadsorbed film and hydrogen interaction with oxygen preadsorbed film at 195°K are shown in fig. 15 and fig. 16. The slow processes of hydrogen and oxygen of oxygen-hydrogen cycles were similar in different cycles.

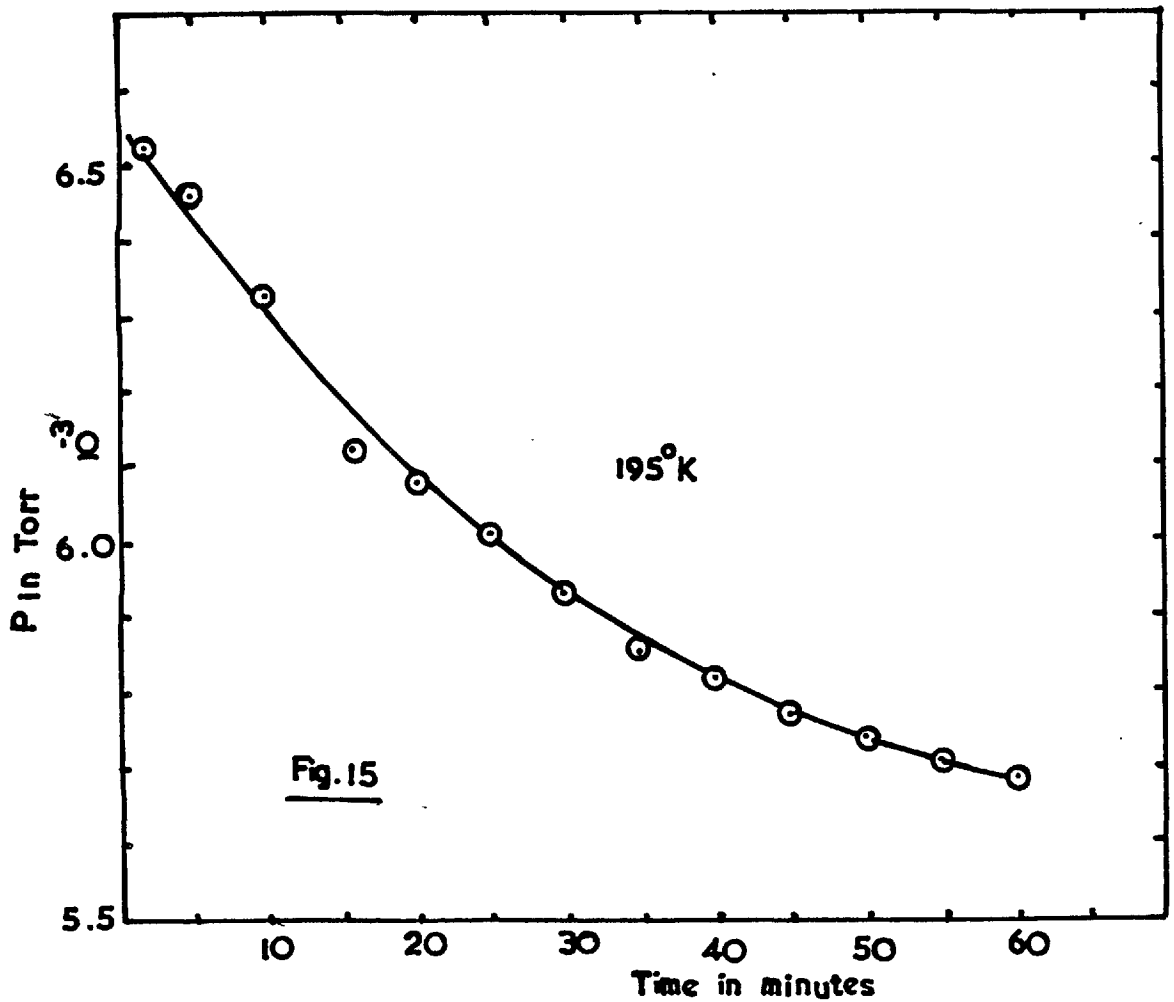


Fig.15

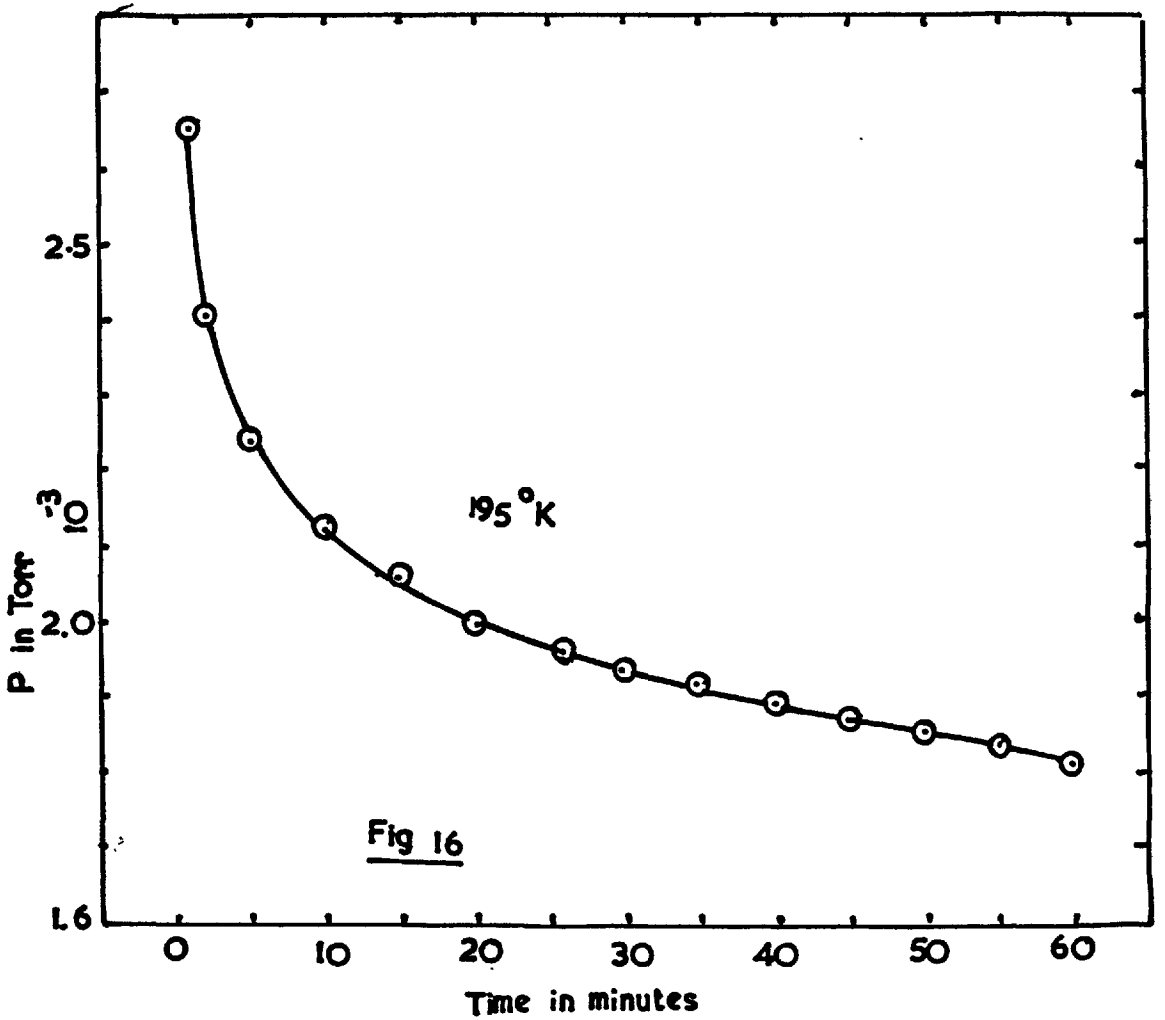


Fig 16

These slow processes obeyed the Elovich plot of equation

$\theta = \frac{RT}{\alpha} \ln \frac{(t + t_o)}{t_o}$ and they are shown in fig.17 and 18.

The values of α i.e. dE/dq are 1.35×10^{-14} cal mole^{-1} molecule^{-1} for oxygen and 4.1×10^{-14} cal mole^{-1} molecule^{-1} for hydrogen.

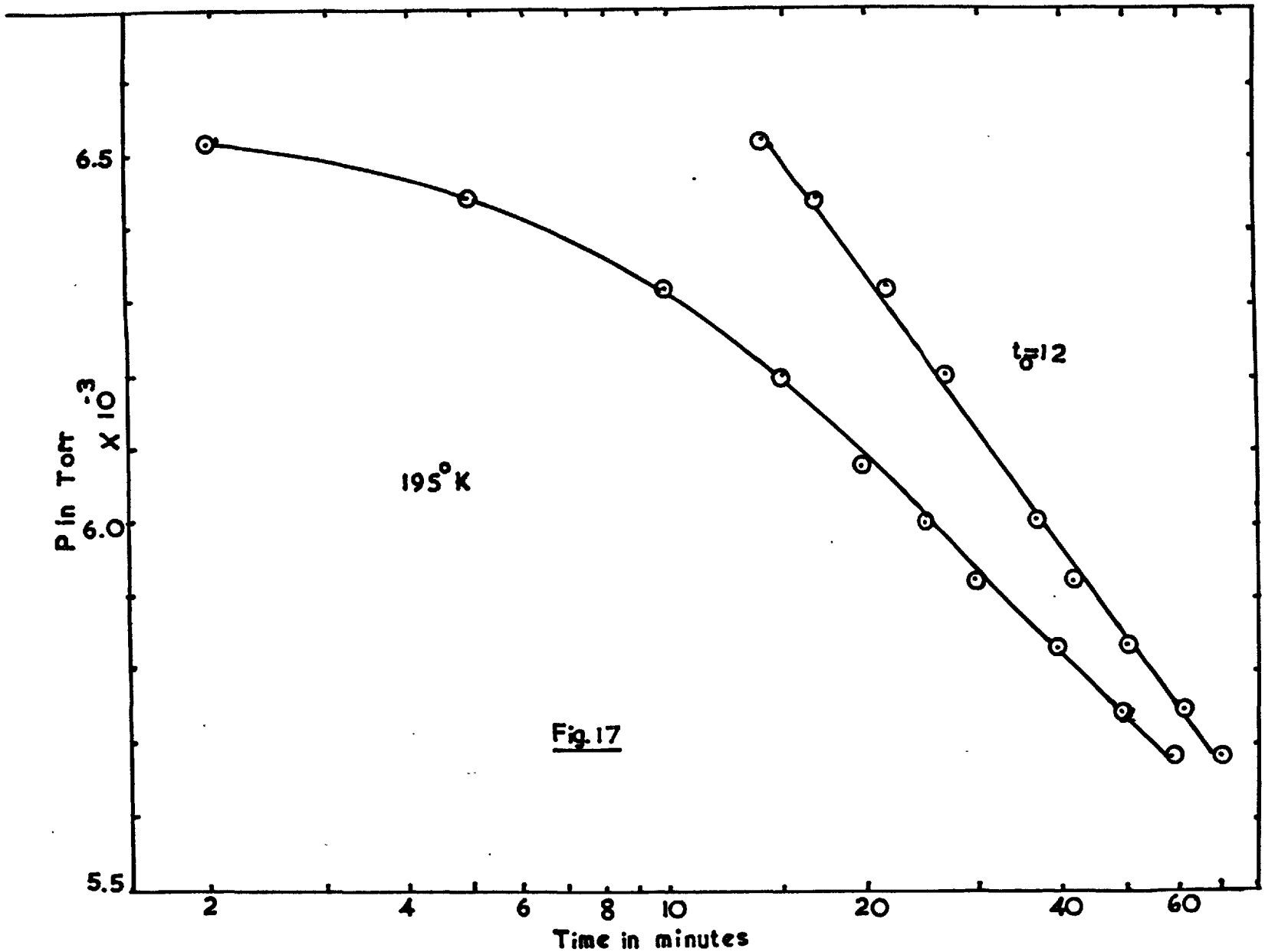


Fig. 17

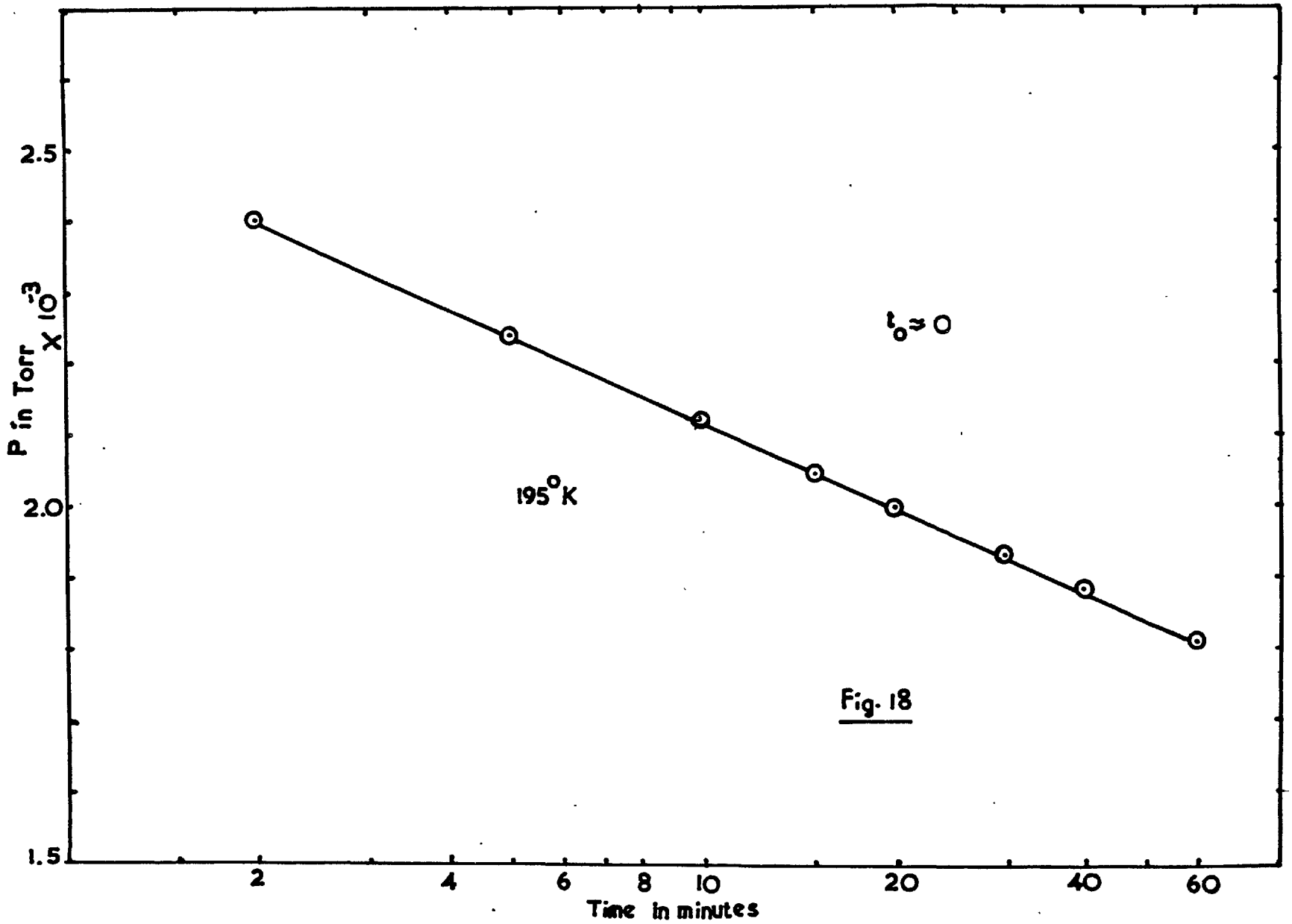

2.5
2.0
1.5
P in Torr X 10^{-3}
$t_o \approx 0$
195°K
2
4
6
8
10
20
40
60
Time in minutes

Fig. 18

3.3 System: Water + Platinum + Hydrogen.

The study of water adsorption on platinum films at 195°K revealed that if water was dosed on a clean film, the quantity of water molecules adsorbed was twice the number of molecules of oxygen that could have been adsorbed on a similar clean film. Hence water adsorbed molecularly, the bond being a coordinated one. Further equal amount of hydrogen could be sorbed on water preadsorbed film to give an identical pattern of hydrogen and oxygen arrangement as was found with pure oxygen and hydrogen. In run Pt30 200×10^{-8} mole of water was adsorbed at an equilibrium pressure of 5×10^{-4} torr followed by 60.2×10^{-8} mole of hydrogen at 1.1×10^{-3} torr. In the reverse case i.e. if hydrogen was adsorbed first and then the film exposed to water vapour, the sorption of water was 20% less in the similar range of pressure (3×10^{-4} torr). The water and hydrogen (1:1) treated film could be subjected to oxygen -hydrogen cycles to produce water in the similar way as it could be done by a surface with 3:1 hydrogen and oxygen at 195°K.

Attempts were also made to measure the interaction of oxygen with the adatoms of water only on platinum surface. In run Pt 44, 166×10^{-8} mole of water was adsorbed on the platinum surface. After rapid evacuation of any gas phase

water vapour, oxygen was introduced. Only 35.5×10^{-8} mole of oxygen reacted with adatoms of water molecules on the surface. This interaction might be a partial displacement of water molecules by oxygen or an interaction with hydrogen to form water provided the water molecules adsorbed on the surface were dissociated. Then 80×10^{-8} mole of hydrogen was introduced to the cell after the evacuation of oxygen. The cell was isolated and the cold bath was removed to ensure that the added hydrogen was utilised to form water. After a few minutes the cell was immersed in a cardice- alcohol bath and oxygen was introduced to the cell. The whole cycle was repeated for a number of times and the average amount of oxygen was taken up for interaction was found to be 34.2×10^{-8} mole (an average of four: 35.5×10^{-8}; 32.6×10^{-8}; 34.6×10^{-8} and 34.2×10^{-8} mole) in good agreement with the subsequent measured water vapour.

High Temperature Treatment.

On warming the film above 195°K, weakly adsorbed hydrogen species was desorbed from a platinum which was saturated with oxygen and hydrogen (1:3) at 195°K. The quantity of the desorbed hydrogen species increased with the increase of temperature. This desorbed hydrogen was quantitatively readsorbed when the temperature was lowered to 195°K. In an attempt to measure the desorbed quantity of hydrogen the film was subjected to slow temperature increase (1.8 minutes per degree °C rise) and the quantity of hydrogen desorbed against temperature was noted. Such a plot is shown in fig. 20.

The plot of dq/dt vs. temperature is shown in fig. 21. The plot of dq/dt vs. T qualitatively illustrate the energy distribution of the sites on which hydrogen atoms are adsorbed and, that the distribution of site energies is continuous and no specific energy sub-states are distinguishable.

When the subsequent operations of oxygen- hydrogen cycle were stopped after oxygen treatment and all the water produced was pumped out, more water could be formed from the oxygen treated film by raising the temperature alone. The yield varied from 50% to 70% of a monolayer of hydroxyl groups on different films at a temperature around 350°K.

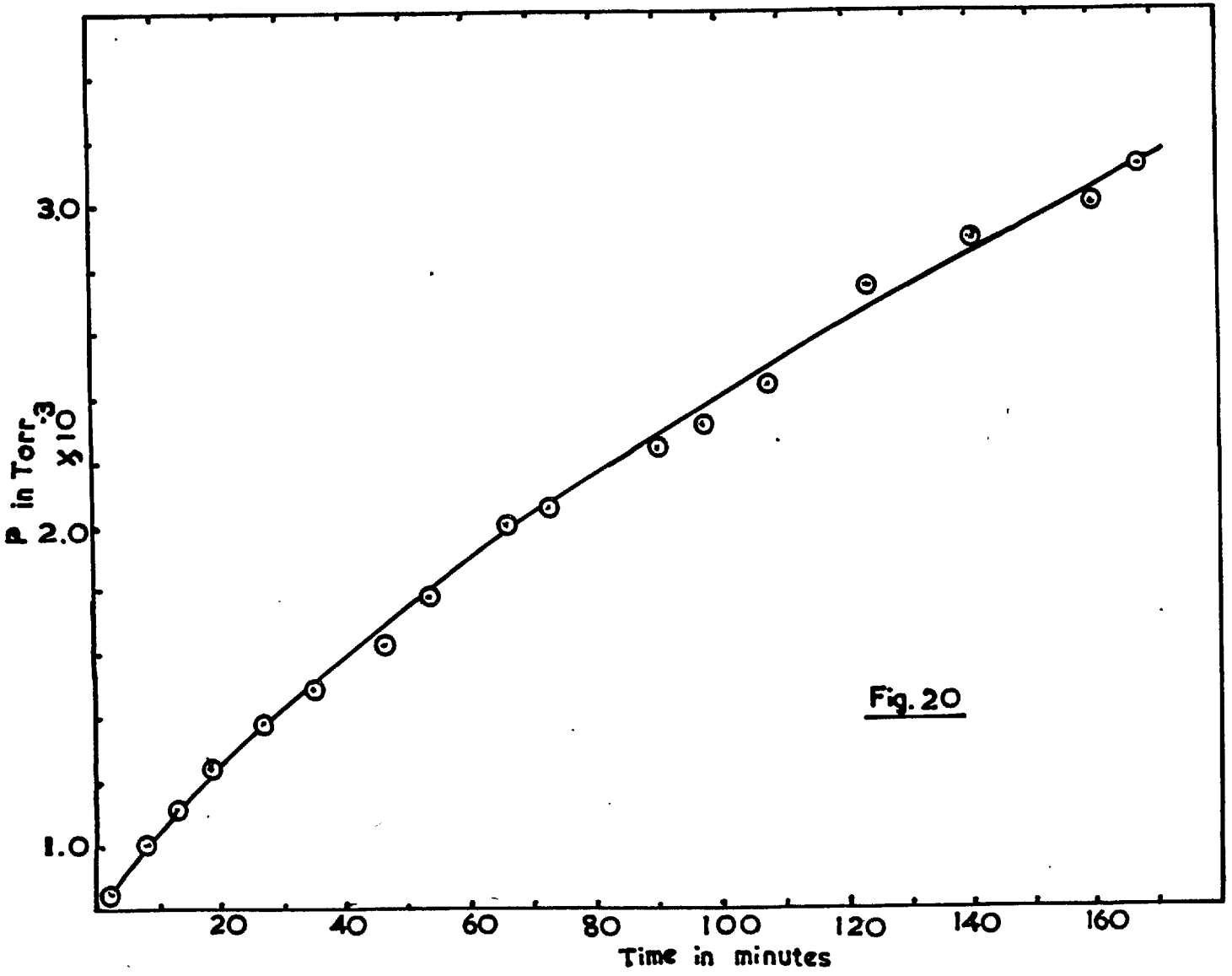

P in Torr. x 10^-3
3.0
2.0
1.0
20
40
60
80
100
120
140
160
Time in minutes

Fig. 20

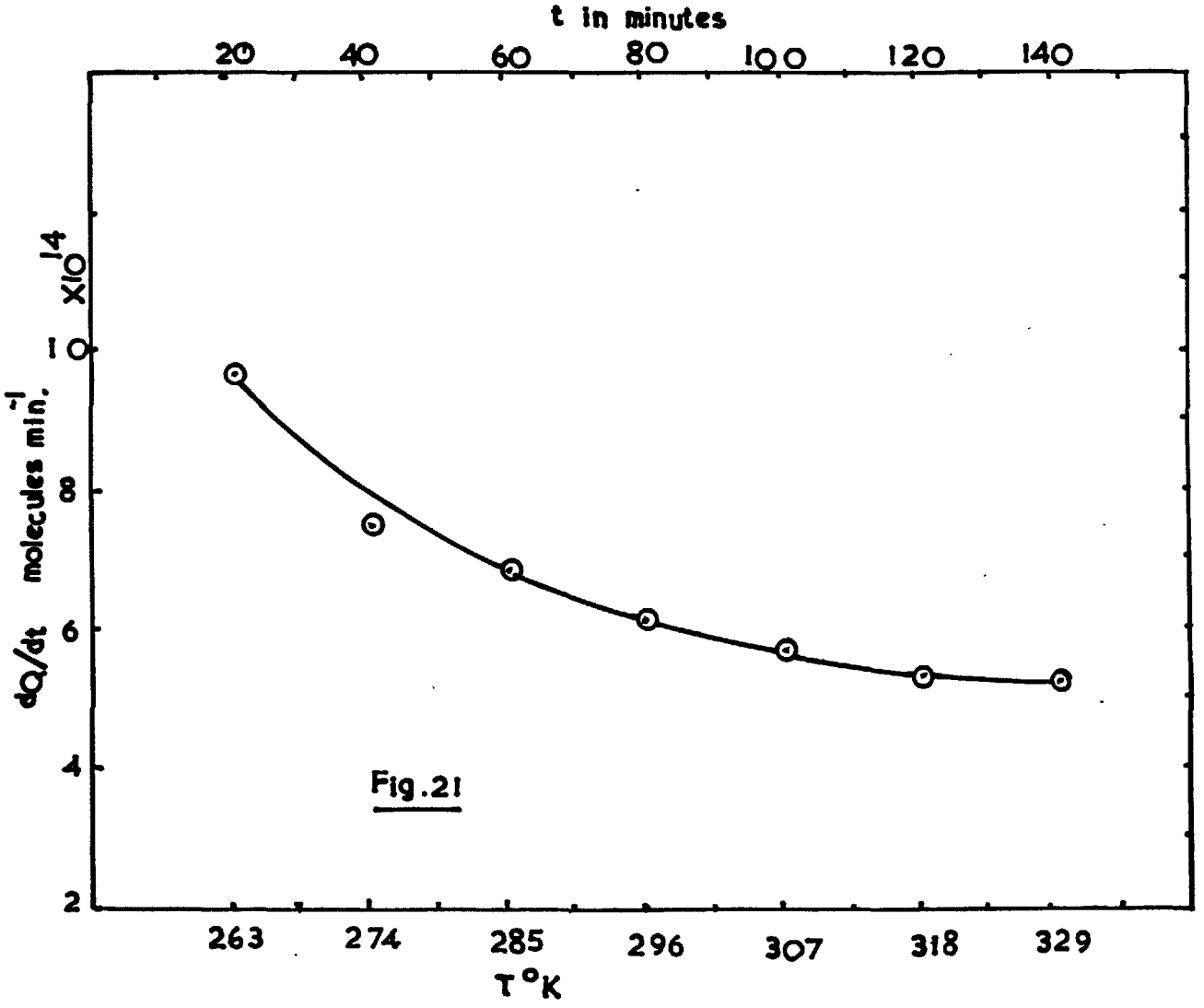

t in minutes
20
40
60
80
100
120
140
dQ/dt molecules min.$^{-1}$ X10^{14}
10
8
6
4
2
263
274
285
296
307
318
329
T°K

Fig.21

This process reduced the subsequent activity of adsorption of oxygen or hydrogen of oxygen-hydrogen cycle.

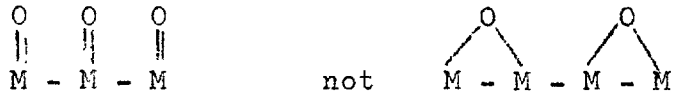
After a high temperature treatment at 350°K, the film would adsorb less amount of oxygen at 195°K. In run Pt 42 the film was heated for 30 minutes at 373°K after oxygen treatment. Then the temperature was lowered to 195°K and, subjected to oxygen-hydrogen cycles. The quantity of oxygen taken up in the cycle was found to be 61.2×10^{-8} mole instead of 74×10^{-8} mole adsorbed before the high temperature treatment.

This decrease in activity might be due to the poisoning effect of hydrogen or oxygen or both at high temperature. . To study such a poisoning effect clean films were saturated with a single gas, i.e. either oxygen or hydrogen. Then the residual gas was pumped off and the film was warmed to 373°K for half an hour. In run Pt 39 the film adsorbed an additional amount of 23×10^{-8} mole of hydrogen at 195°K after high temperature treatment at 373°K. This amount corresponds to 28% of initial oxygen (82.8×10^{-8} mole) on the surface and formed water molecules when hydrogen was added. All oxygen ($82.8 \times 10^{-8} + 23 \times 10^{-8}$) or 105.8×10^{-8} mole react with hydrogen to give a ratio of 1· 3 oxygen-hydrogen. This indicated that probably no oxygen was incorporated in the film. Similarly the effect of pure hydrogen on platinum film was examined at 373°K.

No poisoning effect was observed. An additional 54.5% of a monolayer of hydrogen was adsorbed after the high temperature treatment. About 35% of hydrogen (37×10^{-8} mole) of a monolayer became unavailable for oxygen-hydrogen cycle and probably diffused in the bulk to form a species like bulk hydride.

Discussion.

Almost a monolayer adsorption of oxygen on platinum film at 77°K suggests that the chemisorbed oxygen atoms form a linear structure (A) at high coverage, not a bridged two site adsorption (B) i.e.,



A B

On adding hydrogen to such an oxygen preadsorbed film at 77°K there was an instantaneous process (20%)followed by a slow adsorption until the number of hydrogen atoms adsorbed was equal to 70% to 80% of the number of the oxygen atoms on the surface. This hydrogen dissociated to atoms on bare metal surface and probably react with oxygen linear structured adatoms to form hydroxyl group layer on the surface rather than forming a negative dipole layer in the interstitial position in the surface at the centre of an array of platinum atoms. On the otherhand when hydrogen was adsorbed first, only 25% of oxygen was adsorbed irreversibly and the rest 25% (at a pressure of 1.6×10^{-2} torr in run 9) formed a

physically adsorbed molecular species. If initially adsorbed hydrogen adsorb in the interstitial position and subsequently added oxygen adsorb on the metal sites, the amount of chemisorbed oxygen should be equivalent to a monolayer. But experimentally it was found that only 25% of the surface could be covered irreversibly. This inability of chemisorbing further oxygen molecules by the film may be attributed to the considerable decrease of the heat of chemisorption of oxygen due to hydrogen preadsorption. As the adsorption heat of the surface is decreased by the adsorption of hydrogen and 25% of a monolayer of oxygen, the dissociation of oxygen molecules to atoms may not be able to occur so that further chemisorption of oxygen adatoms does not take place.

In an analogous case of hydrogen + nickel + oxygen system Siddiqi and Tompkins [9] suggested a bridged oxygen structure for hydrogen to oxygen ratio of 2:1,; no water was formed at room temperature. The hydrogen + platinum + oxygen or oxygen + platinum + hydrogen system behave identically to oxygen -hydrogen cycle to form water, which suggests that in both the cases the oxygen form linear structure. The structural representation may be as follows:-



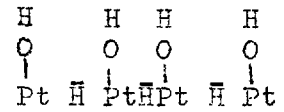
C D

The negative sign indicates that the dipole has its negative end pointing outwards from the metal surface and, not that an ionised state has been formed.

On warming a film with either hydrogen+ platinum + oxygen or oxygen + platinum + hydrogen system to 195°K further oxygen and hydrogen were taken up to give a stable layer of oxygen and hydrogen of ratio 1:3. Water could be desorbed almost quantitatively at room temperature from the film saturated with oxygen and hydrogen (1:3) at 195°K .

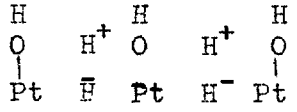
The desorption of water and hydrogen at room temperature from the film saturated with oxygen and hydrogen at 195°K suggests that complexes leading to water molecules are formed on the surface from the adsorbed oxygen and hydrogen. The weakly chemisorbed hydrogen, a portion of which can be desorbed at room temperature and readsorbed at 195°K, may be a pseudo protonic situated on the top of the interstitial hydrogen on the surface. Similar type of pseudo protonic hydrogen species was also observed by Siddiqi & Tompkins[9] in their carbon-monoxide + nickel + hydrogen system. At 195°K hydrogen reacts with oxygen to form hydroxyl groups which

may desorb as water at room temperature. The probable atomic arrangement of oxygen - hydrogen complexes may be represented by



E

which is capable of adsorbing more hydrogen to give the structure

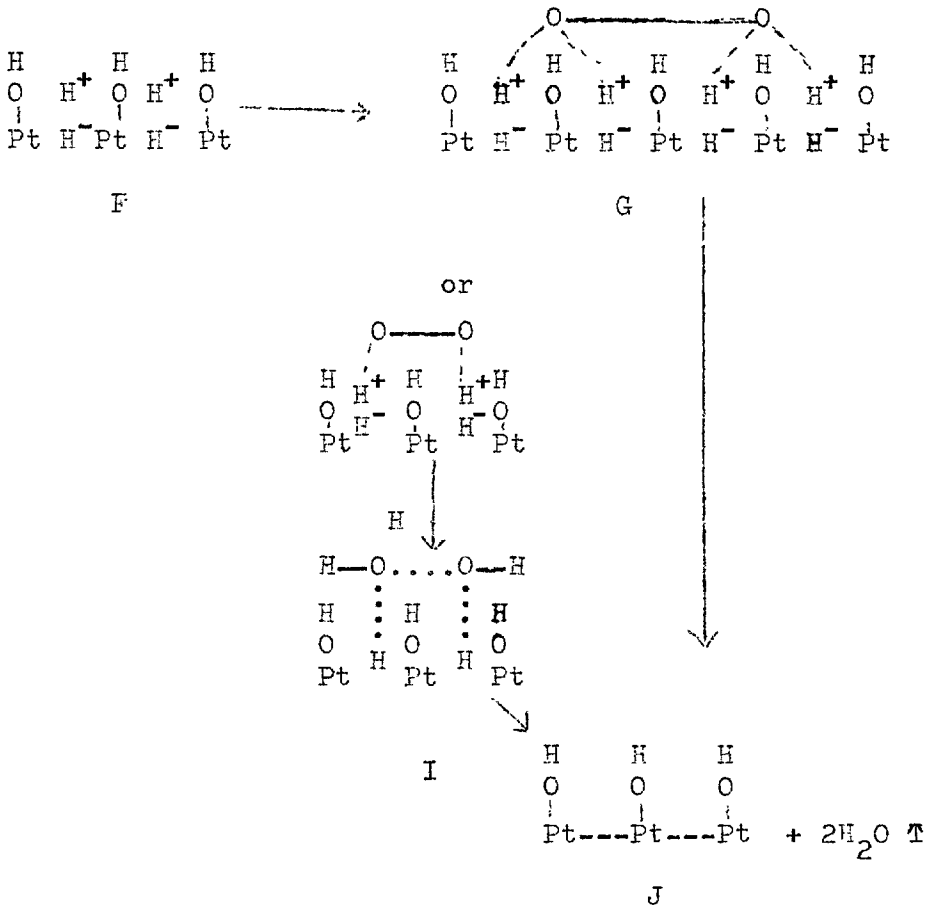


F

This process is an example of the production of different hydrogen adatoms at 195°K. The adsorption of pseudo protonic hydrogen atoms is enhanced by the presence of adjacent hydroxyl groups. This conclusion may be compared with the infrared spectrometric results of Eischens and Plaskin[10], who found the chemisorption of hydrogen was effected by the presence of a preadsorbed layer of carbon monoxide.

If oxygen is added to a film saturated with hydrogen and oxygen (3:1) (probable structure F) at 195°K, there is a probability of formation of water as a result of interaction of weakly chemisorbed hydrogen and gas phase oxygen. Experimental evidence suggests that weakly chemisorbed

pseudo-protonic hydrogen atoms do react with gas phase oxygen to form water. As the oxygen molecules are either in the gas phase or physically adsorbed on the primary oxygen-hydrogen layer, water molecules require small energy to desorb from the surface. On the other hand relatively higher desorption energy (11 Kcal [16]) prevent the water molecules from desorbing at the same temperature. The reaction of protonic hydrogen and oxygen may be brought about by the collision of oxygen from the gas phase. In the first stage oxygen molecule may react with pseudo protonic hydrogen atoms to form a peroxide like structure.At the same time interstitial hydrogen probably takes the position of protonic hydrogen. At this stage oxygen-oxygen bond became very weak (Ca 33 Kcal whereas hydrogen-oxygen bond is 110.6 Kcal). The weak oxygen-oxygen (x- O - O- x) bond eventually breaks and the free "OH" groups collide with the second hydrogen atoms to form water molecules or the reaction may proceed by the formation of a complex with four pseudo-protonic hydrogen with a molecule of oxygen at the first stage and weak oxygen-oxygen bond (-O- O-) breaks to form water molecules. Then the second oxygen molecule collides with the interstitial hydrogen in the similar way to produce water. The sequence of the events may be as follows:-

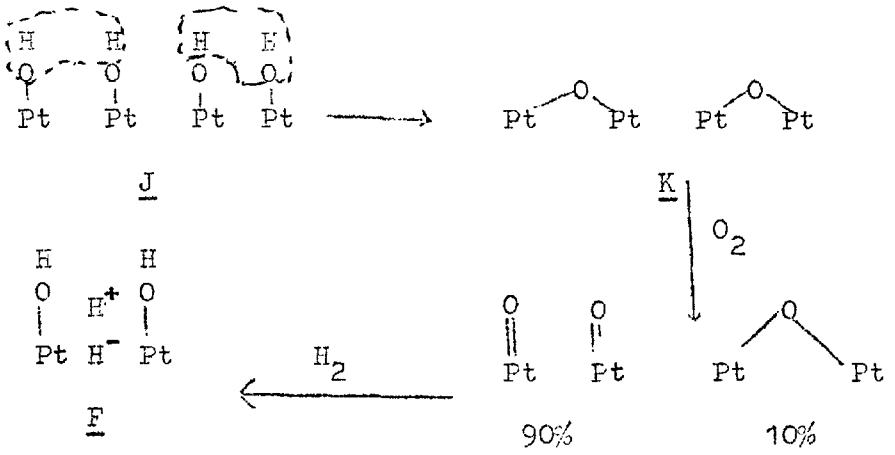


It is expected that there should be no hydrogen for desorption at higher temperature after complete oxidation of structure F and the experimental evidence confirms the structure J. The total consumpton of the weakly chemisorbed hydrogen suggests that pseudo-protonic weakly chemisorbed hydrogen atoms are essential for such type of reaction mechanism at 195°K. Participation of 60% to 80% of initially

chemisorbed or hydrogen indicates that some hydrogen atoms are strongly bound on the heterogeneous surface and are not available for interaction. When hydrogen was added to an oxygen treated surface (structure J), twice the amount of oxygen was taken up to form the initial hydrogen-oxygen arrangement which was ready for the next oxygen-hydrogen cycle to be repeated.

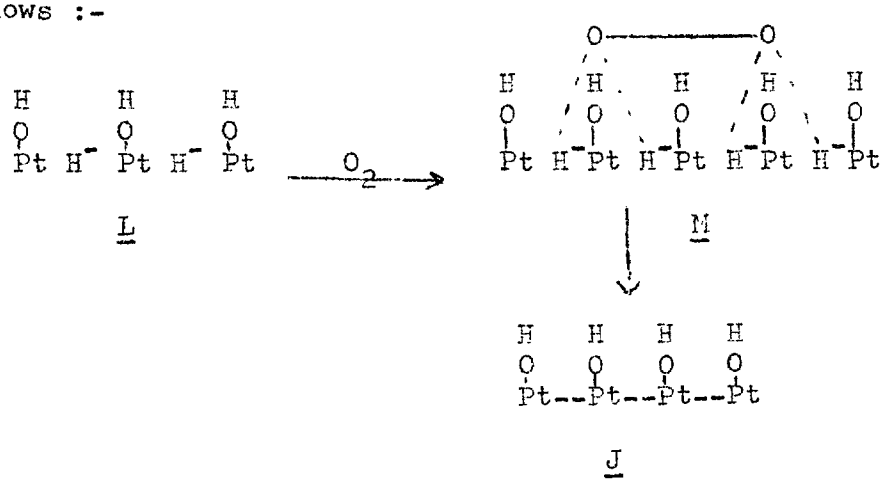
If the film was heated at the stage J, water could be formed from the two adjacent hydroxyl groups. Experimental results shows that water could be produced on warming the film to 273°K. The maximum production of water was 80% of the surface hydroxyl groups at 373°K and the yield corresponds to 40% of the surface monolayer of oxygen. When oxygen was introduced to the film at 195°K after high temperature treatment about 15% of oxygen of a monolayer was adsorbed. On addition of hydrogen to such a film only 90% of the surface assumes the original structure F and the whole cycle could be repeated from the beginning.The observation of the reduced activity of the film for water formation may be attributed to the formation of "Oxide" at higher temperature. This oxide would not be reduced at lower temperature (at 195°K). As the higher temperature treatment is repeated, the oxide patches increased in size and hence the passivity became larger. Similar behaviour of reduced activity as a

result of higher temperature treatment of oxygen-platinum system was also observed by Langmuir[11]. The structural representation of water production from J may be as follows:-



If the film is saturated with water at 195°K, chemisorption probably first involve a coordination bond by the donation of lone pair of electrons from oxygen atom of the water molecule to the surface. This is followed by the dissociation of the water molecule to hydroxyl group and hydrogen. A similar dissociation was observed in water-nickel system [12]. The water saturated platinum surfaces can produce 50% of water corresponding to a monolayer by the addition of oxygen. The weakly chemisorbed hydrogen species is effective in water production. As only one hydrogen atom is available from each water molecule, every two hydrogen from two water molecules are used for the production of a molecule of water, which

may account for the 50% production of water. After addition of an oxygen dose the film can be treated with hydrogen to produce a similar structure as found with oxygen-hydrogen saturated film (F). If a film saturated with chemisorbed water is treated with hydrogen, the film can be subjected to the oxygen-hydrogen cycles which suggest that hydrogen and water treated film essentially has the similar structure as with oxygen and hydrogen at 195°K. The water production by a water saturated film by oxygen may be shown as follows :-



Simultaneous Adsorption:

To study the simultaneous adsorption the film was saturated with oxygen and hydrogen (1:3) at 195°K and a mixture of oxygen and hydrogen (1: 1) was introduced to the cell at a total pressure of 10^{-2} torr. The dose was taken up in less than two minutes. It is interesting to note that the concentration of oxygen or hydrogen on the surface could be varied if the ratio of oxygen to hydrogen of the mixture was varied. When oxygen was in considerable excess in the mixture, the surface was left with a ratio of 1:1 oxygen to hydrogen and the reverse case i.e. if hydrogen was in excess in the mixture, the surface had oxygen and hydrogen of 1: 3 ratio.

In order to study the influence of the concentration of oxygen or hydrogen on the reaction rate different mixtures of oxygen and hydrogen in different ratios were introduced to a platinum film at 195°K. The whole investigation was divided into two series. In one series, the pressure of hydrogen was constant at an arbitrary value of 3.4×10^{-2} torr and the ratio of oxygen to hydrogen varied from 0.3 to 3.4. The surface was always saturated with hydrogen and oxygen (3: 1) before the mixtures were introduced. The fall of pressure which corresponds to the rate of reaction is plotted against

time in fig. 22. As the gas analysis was not accurate in the pressure range of 10^{-2} torr, the initial readings which compositions were accurately known, were taken for calculations. The initial rate (- dP/dt) against composition is shown in fig. 23. The values are subject to an error in drawing of the tangents. Fig. 23 shows that the rate of reaction increases with the increase of concentration of oxygen in the mixtures and it increased upto oxygen to hydrogen ratio of about two and then very slowly decreased. Similarly the initial rate of reaction was studied with variation of hydrogen of the mixture from 0.3 to 3.7 with constant oxygen pressure at 3.2×10^{-2} torr (fig.24 and fig. 25). The reaction rate did not vary within the range of the experimental data. The temperature effect on the reaction rate was also investigated. In run Pt 44 the film was exposed to a mixture of 1 : 1 ratio of oxygen and hydrogen at a pressure of 10^{-1} torr at 195°K and at 300°K. The fall of pressures with time are shown in fig.26. The initial reaction rate at 195°K and 300°K are 1.59×10^{-2} torr min^{-1} and 1.62×10^{-2} torr min^{-1} respectively;if the same mechanism is operative, this means that the apparent activation energy is approximately zero.

The essential primary steps of the interaction of oxygen

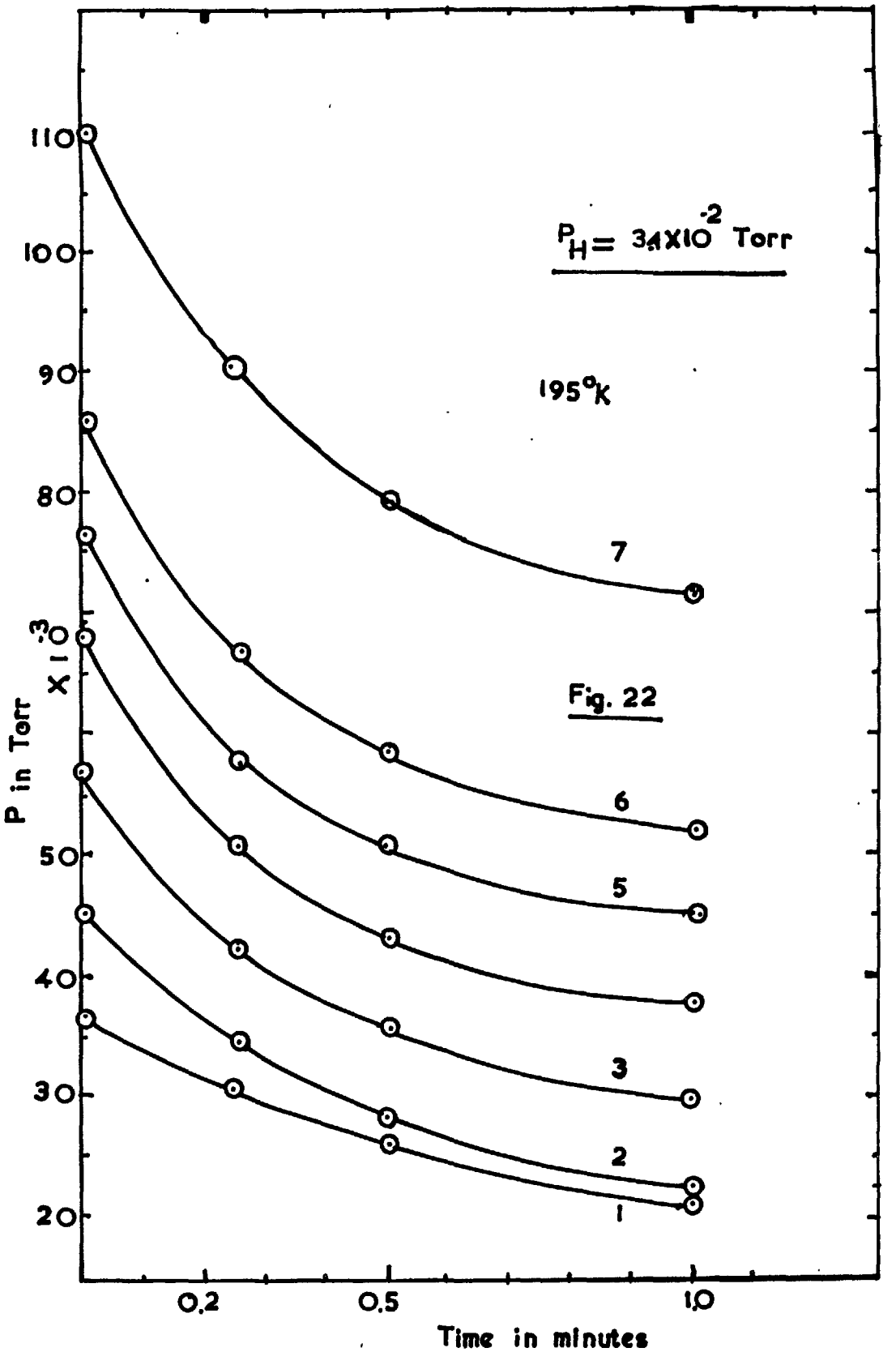

$P_H = 3.4 \times 10^{-2}$ Torr
195°K
7
6
5
3
2
1
110
100
90
80
50
40
30
20
P in Torr $\times 10^{-3}$
0.2
0.5
1.0
Time in minutes

Fig. 22

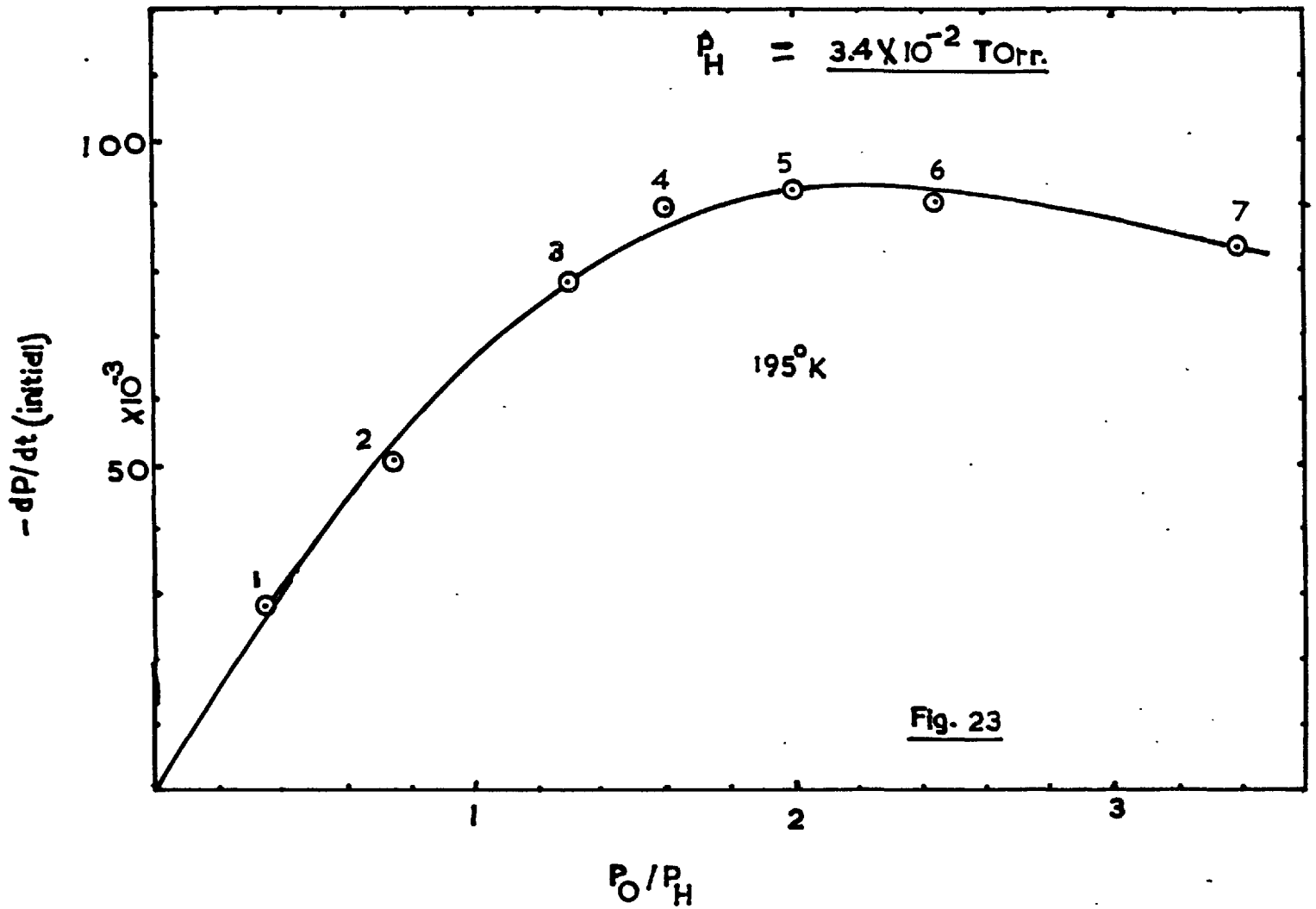
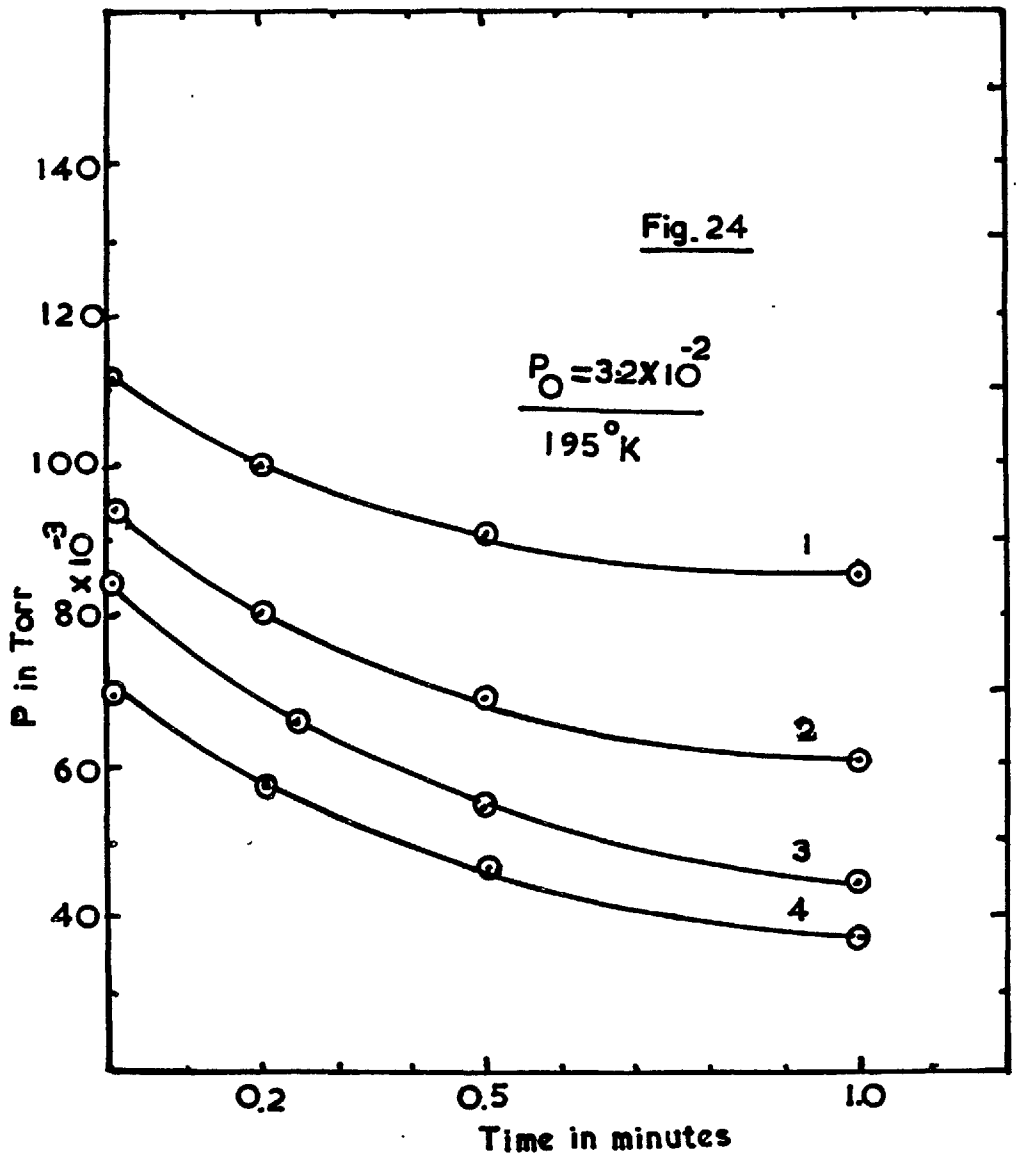

P_H = 3.4 X 10^{-2} Torr.
100
50
$-dP/dt$ (initial) X10^{-3}
1
2
3
4
5
6
7
195°K
1
2
3
P_O/P_H

Fig. 23


Fig. 24
$P_O = 3.2 \times 10^{-2}$
195°K
140
120
100
80
60
40
P in Torr
$\times 10^{-3}$
1
2
3
4
0.2
0.5
1.0
Time in minutes

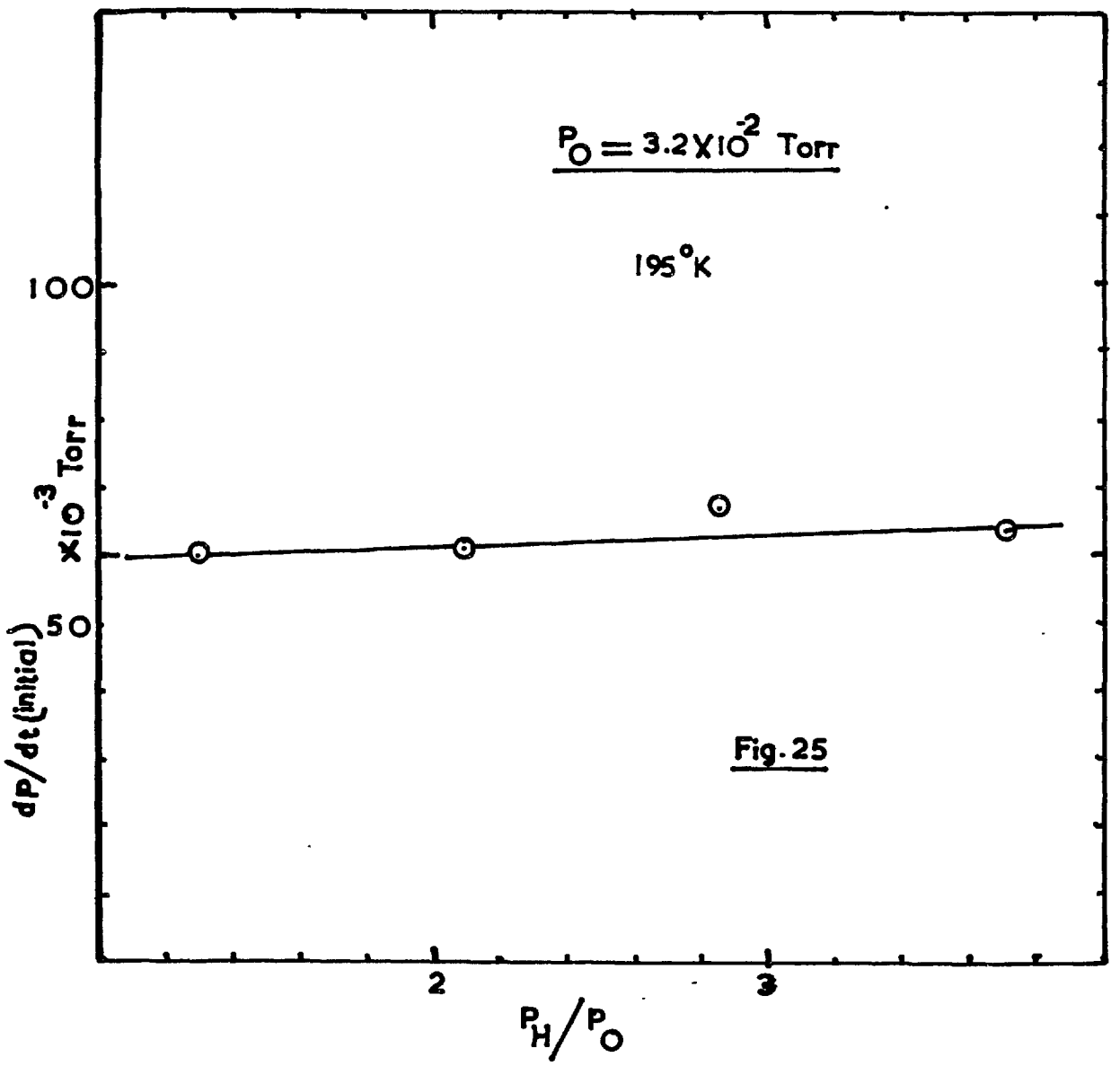

$P_O = 3.2 \times 10^{-2}$ Torr
195°K
100
50
$\times 10^{-3}$ Torr
dP/dt (initial)
2
3
P_H/P_O

Fig. 25

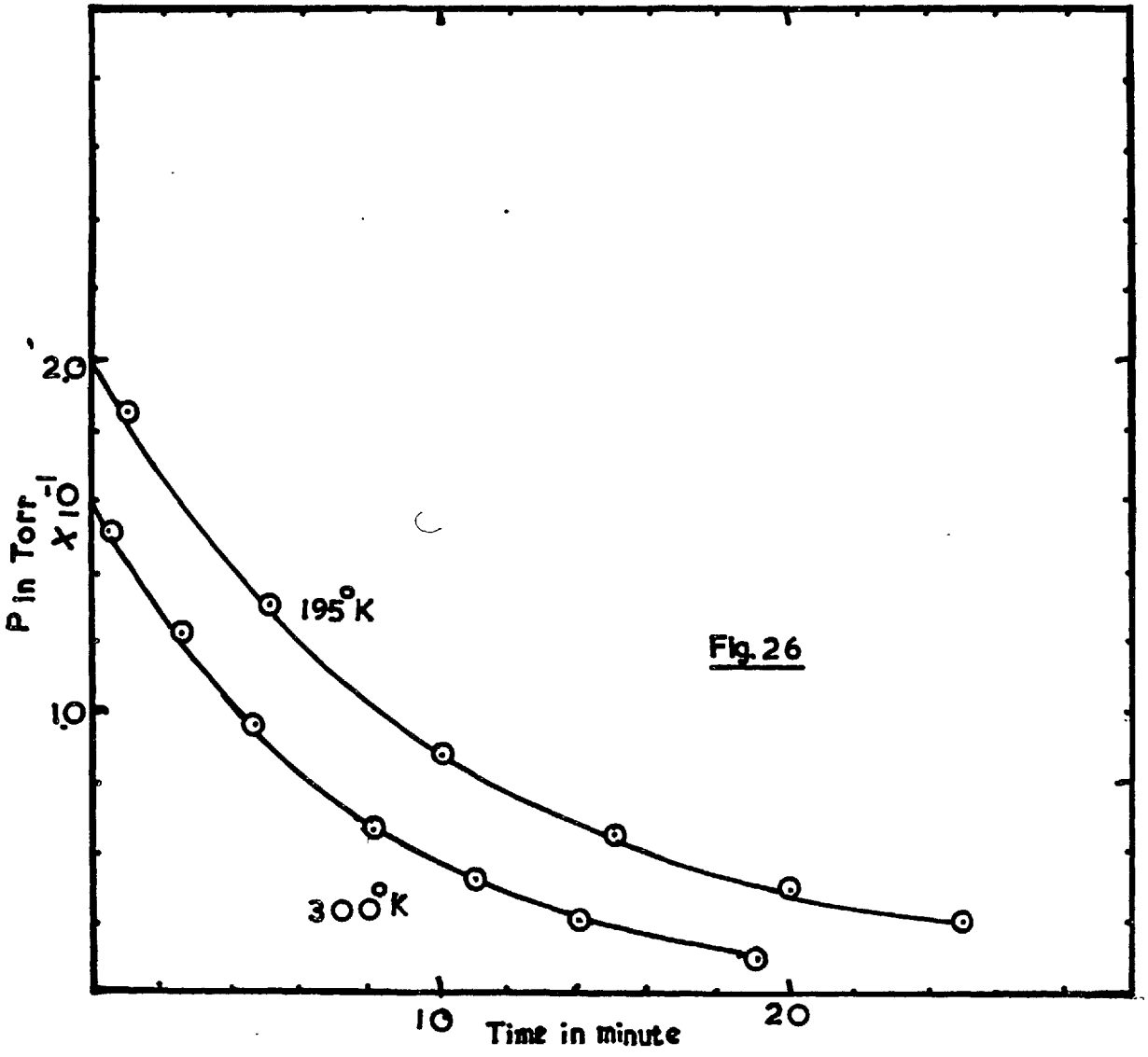


Fig. 26

and hydrogen may be

at 78°K

$$H_{2(g)} \longrightarrow 2H_{(a)}$$

$$O_{2(g)} \longrightarrow 2O_{(a)}$$

and a small proportion of

$$O_{(a)} + H_{(a)} \longrightarrow OH_{(a)}$$

and at 195°K

$$2H_{(a)} \longrightarrow H_{2(g)}$$

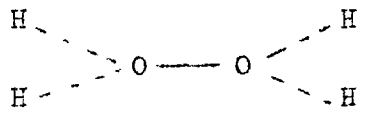
$$O_{(a)} + H_{(a)} \longrightarrow (OH)_{(a)}$$

$$OH_{(a)} + 2H_{(a)} \longrightarrow (HOH.H)_{(a)}$$

followed by

$$(HOH.H)_a + 1/2\ O_{2(g)} \longrightarrow HO_{(a)} + H_2O\uparrow$$

with the intermediate transition state



(transition complex).

Experimental evidence shows that weakly chemisorbed hydrogen

is essential to form water at low temperature range (195°K) on platinum films. The oxygen molecule from the gas phase may be physically adsorbed on the primary chemisorbed oxygen-hydrogen layer with a heat of adsorption of 2-3 Kcal $mole^{-1}$ (13) .

The life time of the physically adsorbed oxygen molecule may be evaluated from the following equation(14)

$$t = to\, e^{-\Delta H/RT} \quad \ldots \quad 3.8$$

where to is the time of oscillation of the molecule in the adsorbed state and it is equal to 10^{-13}sec. ΔH is the heat of physical adsorption and T is 195°K.

The life time of a physically adsorbed oxygen molecule is found to be approximately 2×10^{-10} Sec. during which time it should react with pseudo-protonic hydrogen to form a peroxide like structure followed by the transition complex. The bond between - O- O- becomes very weak and consequently is broken to form water molecules. The reaction rate depends on how quickly the transition state leads to the formation of water molecules and how quickly the replenishment of weakly bound hydrogen from the gas phase takes place. The model predicts that the reaction rate is controlled by the concentration of oxygen in the gas

phase, and that, after a certain limit, the concentration of gaseous hydrogen has little effect on the reaction rate, as the concentration of weakly chemisorbed hydrogen has reached a steady state. The experimental evidence (fig. 25) confirms this behaviour. This behaviour suggests that the reaction rate should reach its maximum when the collision frequencies of oxygen and hydrogen are equal. At an arbitrary pressure P torr and 195°K the ratio of the collision frequencies of hydrogen and oxygen is 4:1. It follows that the reaction rate should attain its maximum at oxygen to hydrogen ratio of 4: 1 , but experimentally the peak rate was found at oxygen to hydrogen ratio of about 2. This experimental observation can be treated qualitatively as follows:

$$H_2 \underset{K_1'}{\overset{K_1}{\rightleftharpoons}} 2H_{(a)}$$

$$2H_{(a)} + 1/2\ O_2 \xrightarrow{K_2} H_2O$$

θ = Concentration of hydrogen.

at equilibrium

$$K_1 P_{H_2} (1 - \theta) = K_1' + K_2 P_{O_2} \theta \quad .... \quad 3.9$$

$$\theta = K_1 P_{H_2} / [K_1 P_{H_2} + K_1' + K_2 P_{O_2}] \quad \ldots \quad 3.10$$

$$\text{or} \quad d(H_2O)/dt = [K_1 K_2 P_{H_2} P_{O_2}] / [K_1 P_{H_2} + K_1' + K_2 P_{O_2}] \quad \ldots \quad 3.11$$

The equation 3.11 can qualitalively explain the experimental observations.

When both the gases compete for the sites the rate expression becomes

$$d(H_2O)/dt = K\theta_{H_2}\theta_{O_2} = K K_1 K_2 P_{H_2} P_{O_2} / [1 + K_1 P_{H_2} + K_1' + K_2 P_{O_2}]^2 \quad \ldots \quad 3.12.$$

The expression 3.12 predicts that the rate will pass through a maximum .

Roginskii[15] et al., postulated the equation

$$\text{Rate} = [K a_{O_2} \cdot a_{H_2} Z] / [a_{O_2} Z + a_{H_2}]^3 \quad \ldots \quad \ldots \quad 3.13$$

$$\text{where} \quad Z = P_{O_2} / P_{H_2}$$

to show that the reaction depends on the ratio of the partial pressure of the components ,not on their absolute values.Their investigation shows that the reaction rate passes through a maximum at a oxygen-hydrogen ratio of three at 293°K. The difference of ratio between 2 at 195°K and three at 293°K for maximum rate may be

attributed to the different mechanisms involved at low and high temperature range. At 293°K the reaction does not follow only one mechanism but a mixture of two- one associated with weakly chemisorbed hydrogen and the other involving in the formation of water from the two adjacent hydroxyl groups.

The initial reaction rates at 195°K and 300°K were more or less the same (1.59×10^{-2} torr $min.^{-1}$ and $1.62 \times 10^{?2}$ torr $min.^{-1}$ respectively). This may be explained with the assumption that at 195°K only one process is operative for producing water and it is only by the interaction of gas phase oxygen molecules with the weakly chemisorbed hydrogen. At 300°K the population of weakly chemisorbed hydrogen becomes less on the surface by the formation of hydrogen molecules from such atomic species and, its subsequent desorption. Consequently the reaction rate should fall.

The rate of water production reduction, if it has a non-zero E, should, other conditions being the same, increase with temperature. If, however, the heat of adsorption of "protonic" hydrogen $-\Delta H$ is about the same as E, then although the rate of water production per protonic hydrogen increase, with increase of temperature(T), the number of such hydrogen atoms decreases. Consequently the two effects, reduction of

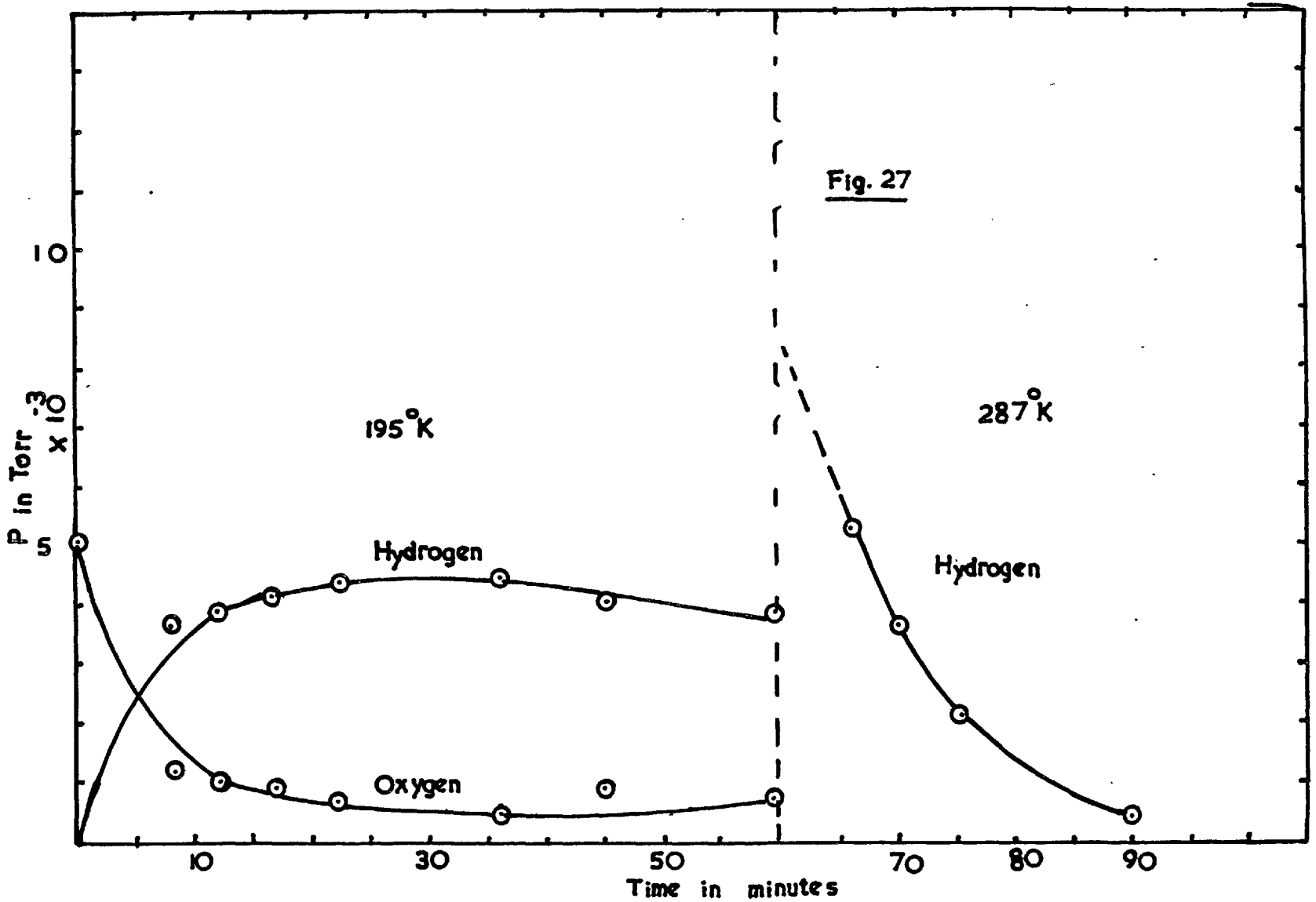
concentration of reactive hydrogen causing a decrease rate proportional to exp $-\Delta H/RT$, and, thermal acceleration of the rate of reaction of gaseous oxygen with active adsorbed hydrogen according to a term exp $-E/RT$ more or less compensates i.e. $E \approx -\Delta H$.

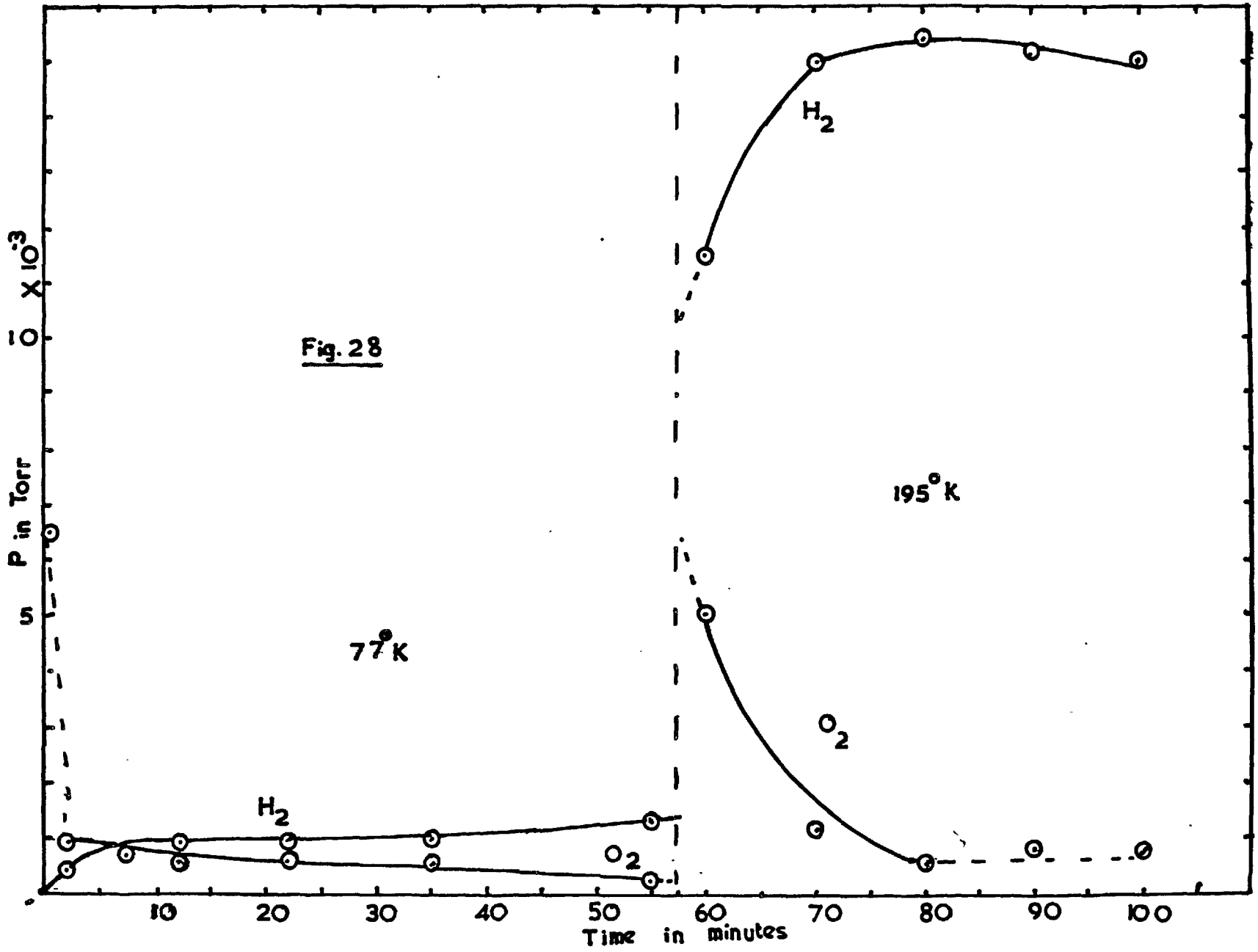
System: Hydrogen+Nickel+Oxygen .

The interaction of hydrogen and oxygen has been investigated on nickel films from 77°K to 325°K. The films were deposited under high vacuum conditions(10^{-9} torr) at 77°K. The duration of deposition was normally 45 minutes at 6.4 amps. and the weight varied from 14 mgs. to 18 mgs. with roughness factor between 13 to 20 on different films. After the evaporation the film was stabilised by alternate heating and cooling for a number of times(generally four times and ten minutes halt at each temperature) between 298°K and 77°K. After the thermal cyclings the temperature of the film was lowered to 77°K and the film was saturated with measured doses of hydrogen . In run Ni 9 the film adsorbed 221 $x10^{-8}$ mole of hydrogen at a pressure of 6.15 $x10^{-3}$torr corresponding to 70 % surface coverage. After rapid evacuation of gas phase hydrogen 100 $x10^{-8}$mole of oxygen was introduced at a pressure of 7.2 $x10^{-3}$torr. The pressure dropped instantaneously to 1.2 $x10^{-3}$ torr indicating that much of oxygen (90 $x10^{-8}$mole) was taken up by the surface. Analysis of the gas phase during interaction of oxygen with adatoms of hydrogen showed that hydrogen was partially displaced by oxygen. The displaced hydrogen was monitered by a calibrated Pirani gauge. The amount of displaced

hydrogen varied from 4% to 8 % on different films. When such a film was warmed to 195°K , a burst of pressure was observed initially followed by a negligibly slow readsorption. During this time the pressure rose to 1.6×10^{-2} torr corresponding to 140×10^{-8} mole of mixed oxygen & hydrogen of which 130×10^{-8} mole was hydrogen. In another set of runs (run 6 & 7) the film was saturated with hydrogen at 195°K and then the film was exposed to oxygen. About 33% of hydrogen was displaced as a result of interaction. On warming the film to room temperature the gas phase hydrogen was rapidly taken up by the film. In fig (27) the interaction of oxygen with hydrogen preadsorbed nickel film is shown at 195°K and 287°K.

The preliminary investigation of interaction of oxygen on hydrogen preadsorbed nickel film (fig.27 & 28) showed that the study can be divided into three parts- reactions at 77°K, at 195°K and 298°K. For the reaction at 273°K to onwards a rapid fall of pressure of gas phase hydrogen was observed. The fall of pressure due to adsorption of hydrogen on vacant sites created by the incorporation process of oxygen into lattice and interaction of adsorbed hydrogen with chemisorbed oxygen. For a detail study the surface was saturated with oxygen at 77°K and any residual gas was rapidly pumped out. The temperature was raised to


Fig. 27
10
5
P in Torr x 10^-3
195°K
287°K
Hydrogen
Hydrogen
Oxygen
10
30
50
70
80
90
Time in minutes


Fig. 28
P in Torr X 10^{-3}
77°K
195°K
H_2
O_2
H_2
O_2
10
20
30
40
50
60
70
80
90
100
Time in minutes

325°K for a few minutes[16] and then the temperature was again lowered to 77°K. The film was dosed with oxygen until saturation was reached. The procedure of temperature cycling was repeated until no appreciable adsorption of oxygen was observed at 77°K. The excess amount of oxygen which adsorbed due to thermal cyclings was due to "incorporation" of oxygen into the metal lattice. The incorporated amount of oxygen varied from 60% to 70% of a monolayer on different films. When the film was saturated with oxygen after high temperature cyclings, the gas phase oxygen was evacuated and a measured dose of hydrogen was introduced at 77°K. No reaction was observed until the temperature was raised to 273°K. At 273°K the film started to take up hydrogen due to interaction with preadsorbed hydrogen. The rate of reaction was slow and a typical fall of pressure against time is shown in fig (29). In run 19 the film adsorbed 917 x 10^{-8} mole of oxygen and the quantity incorporated was 70% of the monolayer. The film adsorbed 61.6 x 10^{-8} mole of hydrogen in six doses in 140 minutes. The slow process is described by the Elovich plot which is shown in fig (30). The linearity of the plot breaks at point B to show that the slow process involves two different processes, each with different value of dE/dq; the values of dE/dq are 1.11 x 10^{-14} cal $mole^{-1}$ $molecule^{-1}$

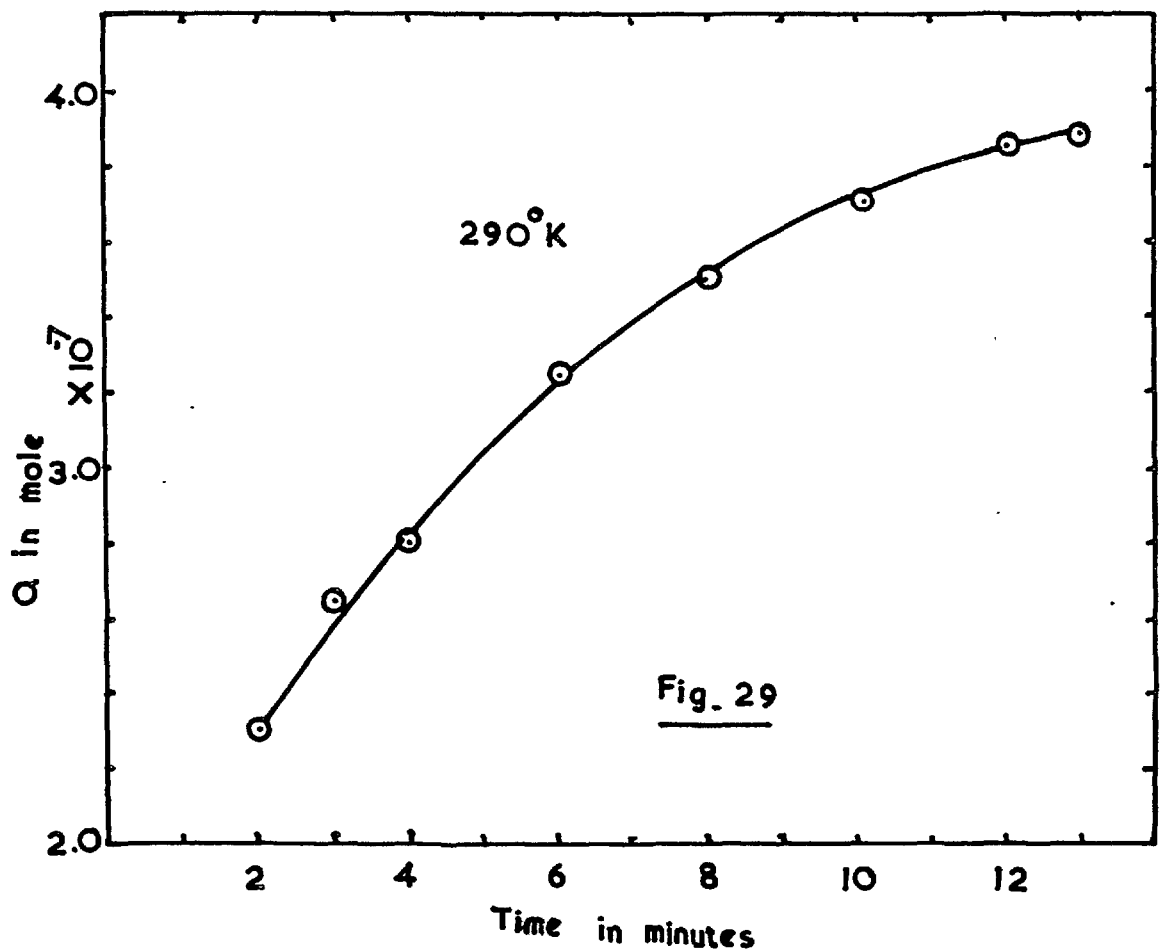


Fig. 29

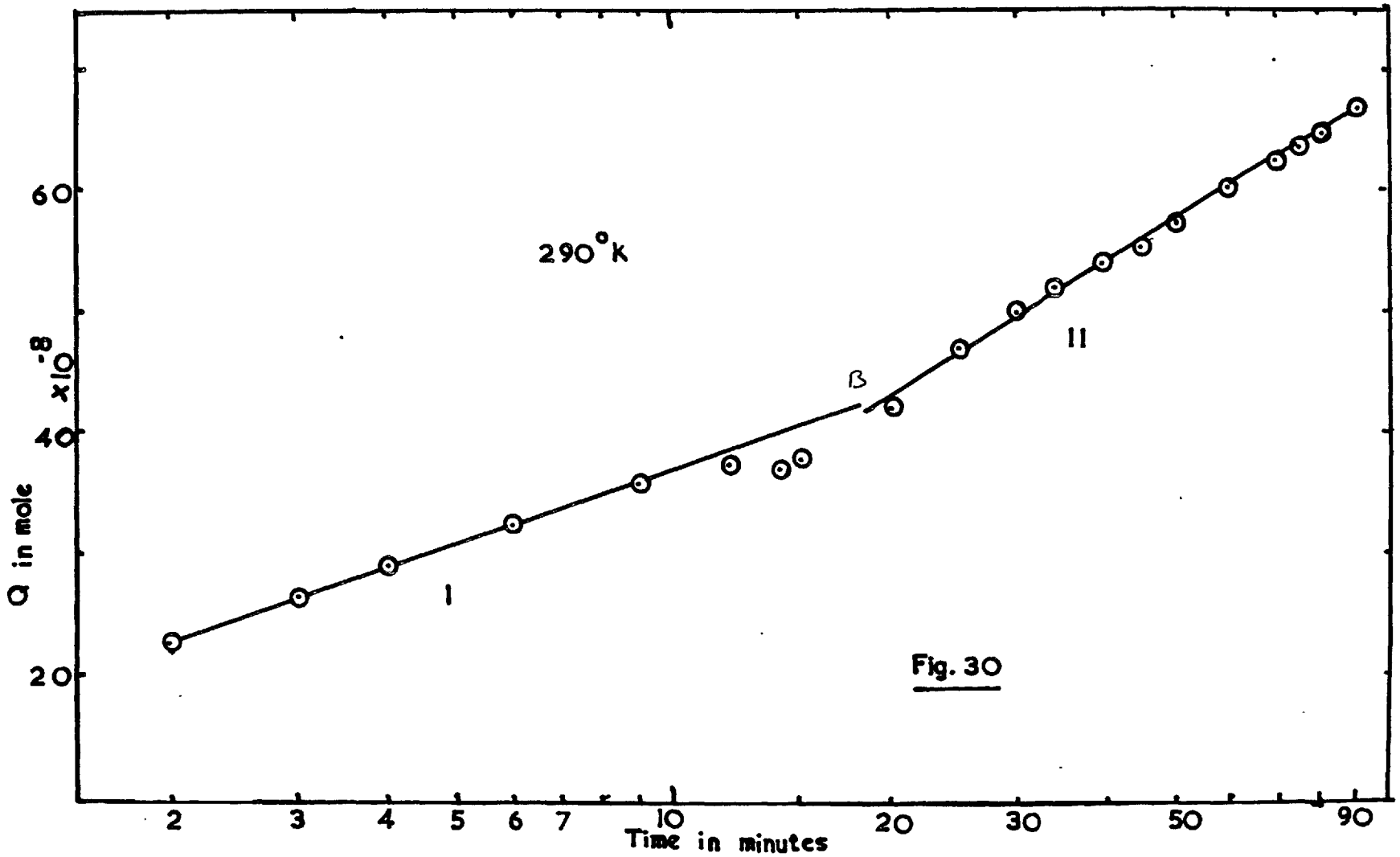

290°K
I
B
II
Q in mole
x10^-8
60
40
20
2
3
4
5
6
7
10
20
30
50
90
Time in minutes

Fig. 30

and 6.47×10^{-15} cal mole^{-1} molecule^{-1} for stage I and stage II respectively. The stage I represent the chemisorption of hydrogen on bare surface and after a certain stage those molecules have energy equal to $E_o + E_1^o$ (where E_o is activation energy of chemisorption and E_1^o that of reaction), may enter into reaction to form "OH". The stage II probably represent that section.

Effect of Pressure.

Variation of r_s with pressure at constant T (temperature and q (amount adsorbed).

The rate of sorption of hydrogen on a oxygen preadsorbed nickel film is influenced by the pressure (P) in contact with the film and the amount of hydrogen adsorbed.The doses of hydrogen were selected so that the pressure in in the system was 10^{-3} torr a few second after admission. All rate measurements reported here are concerned therefore with films which were covered ($\theta \approx 1$) with a monolayer of oxygen. Since the rate was largely controlled by the amount (q_1) already adsorbed,the following method was adopted to find the effect of pressure on the rate of sorption(r_s) . A small dose of gas was admitted and a pressure-time plot(fig.31 was recorded in the lower pressure range(P_L) for a period of few minutes; than a further large dose was introduced and a new , faster rate of uptake

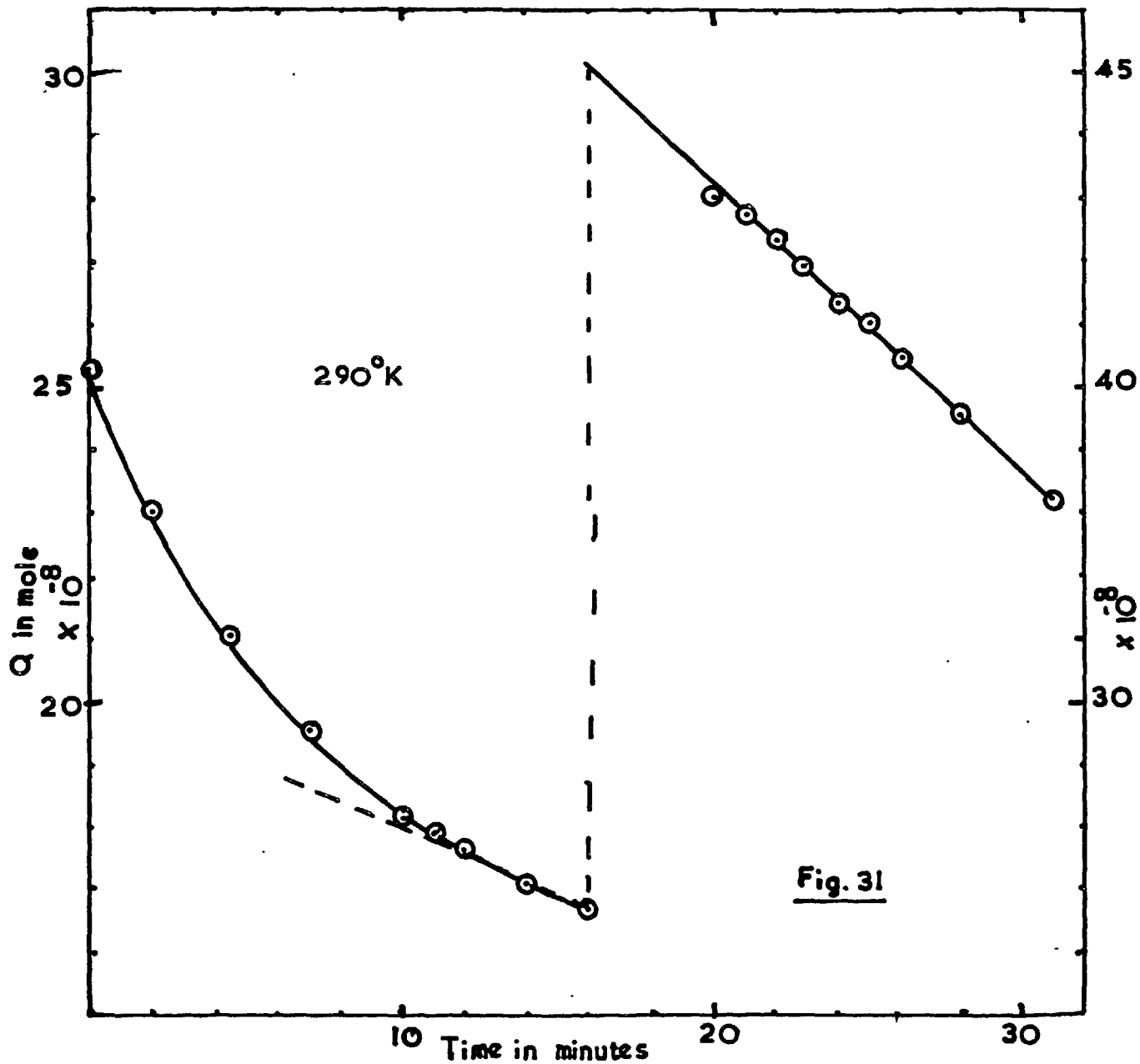

30
25
20
45
40
30
290°K
Q in mole x 10⁻⁸
x 10⁻⁸
10
20
30
Time in minutes

Fig. 31

in this higher pressure region (P_H) was measured. Both the plots in the high and low-pressure regions could than be extrapolated to the same time (t_A) of admission of the second dose and the two rates r_L & r_H at two pressures P_L, P_H were obtained. Using these values of P_L, P_H and the volume of the system, it was proved that the amount adsorbed /q, at t_A both pressures P_L & P_H was the same within the experimental error, indicating negligible instantaneous adsorption. The value of the exponent n, calculated from the expression

$$\left(r_H / r_L \right)_{\text{Constant } Q} = \left(P_H / P_L \right)^n$$

are given in the table 5. It is concluded that the rate of hydrogen sorption varies as the pressure for constant q and temperature.

Table 5 .

Approximate values of n

(Run 19)

r_H x10^{-8} mole min^{-1}	r_H x10^{-8} mole min^{-1}	r_H/r_L	P_H/P_L	n
0.425	0.722	1.7	2.44	1.6
0.288	0.476	1.66	1.62	1.06
0.38	0.426	1.12	1.135	0.92
0.203	0.56	2.73	2.76	0.99
0.232	0.62	2.71	2.86	0.96

Variation of r_s with q at constant temperature and pressure.

Both the r_S and q were calculated from the pressure readings, and hence the r_S - q plot records the simultaneous variation of r_S with P and q. However, the decrease due to P is alone is negligible to that of r_S; consequently little error is made in assuming constancy of pressure. The rate curve shown in fig (32) is well expressed by the equation

$$\ln r_S = \ln a - bq/RT,$$

a form of Elovich equation. The value of b i.e. of dE/dq is found to be 4.4×10^{-15} cal mole^{-1}molecule^{-1} compared to similar value of 6.47×10^{-15} cal mole^{-1} molecule^{-1} from the plot of Elovich in fig (30).

Activation Energies:

The activation energy may be calculated by comparing the rate of adsorption (-dp/dt)at equal coverage but at different temperature. Using the different rates r_1 and r_2 at T_1 and T_2 at constant coverage the activation energy was calculated by the equation

$$\log (r_1 / r_2)_q = \text{constant} = \Delta E/2.3R(1/T_1 - 1/t_2)$$

In fig (33) activation energy against Θ is plotted. The linearity of the plot proves ΔE increase linearly with q which is a basic assumption for Elovich type

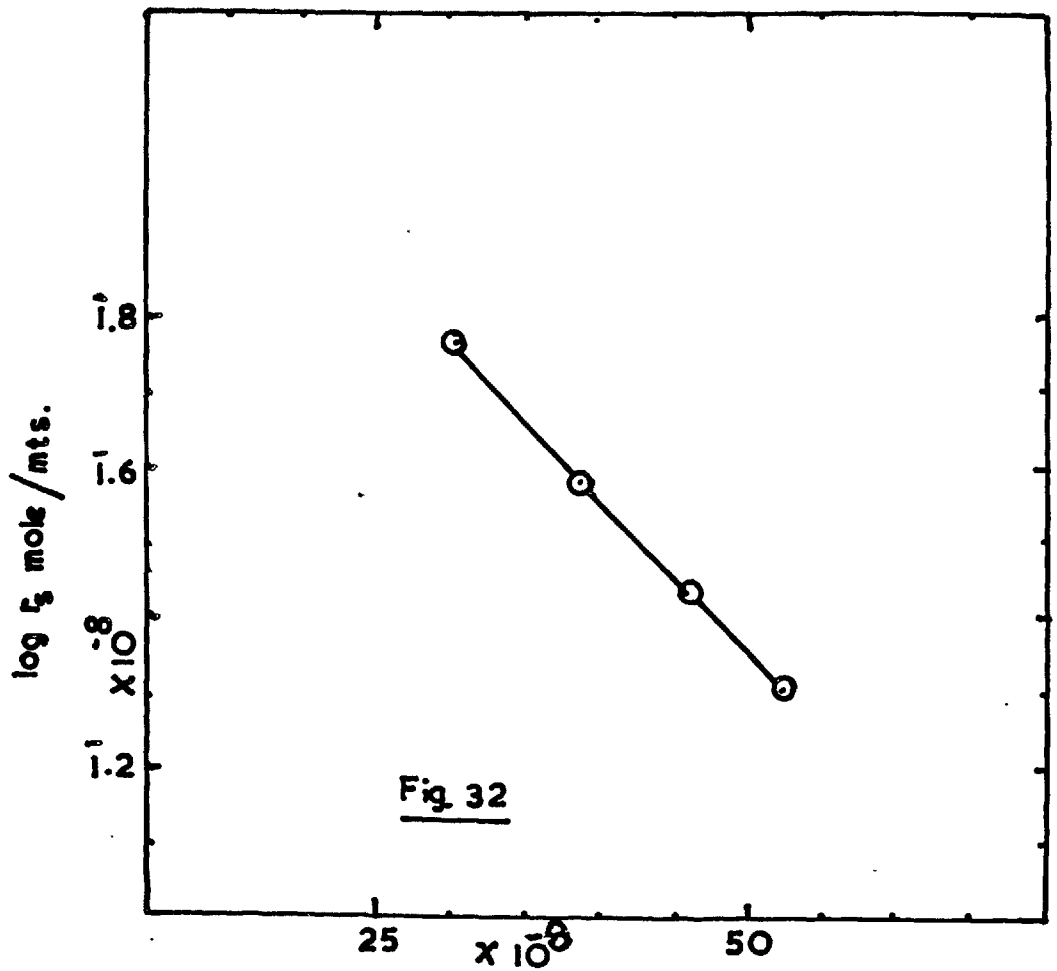


Fig. 32

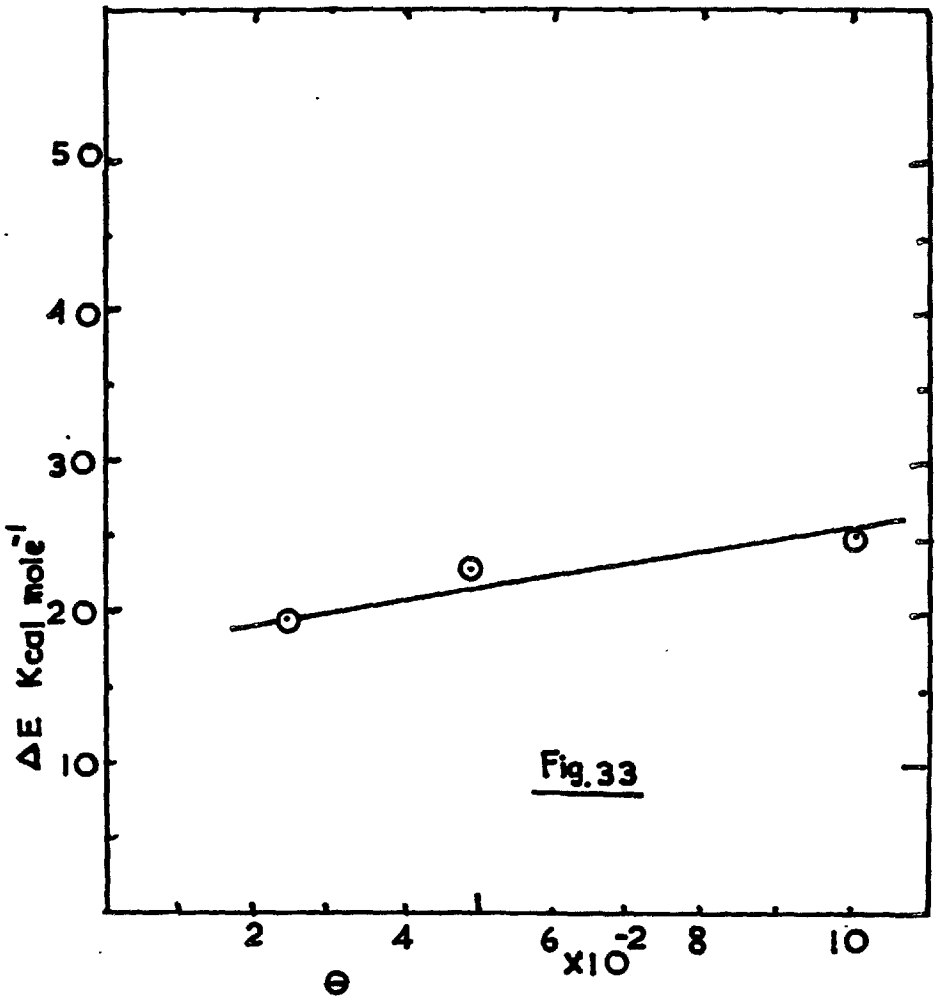


Fig. 33

model for slow process.

Discussion:

Addition of oxygen to a hydrogen preadsorbed nickel surface is accompanied by a displacement of hydrogen from 4% to 8% at 77°K and about 20% to 30% at 195°K on different films. This partial displacement may have occured from the weakly chemisorbed hydrogen. In an analogous case of oxygen treatment with hydrogen covered molybdenum film resulted in a partial displacement of hydrogen (34-40%)[17]. After warming the film to room temperature the surface was partially covered with hydrogen and oxygen. Some of the oxygen was on the surface, some was incorporated. The hydrogen either sitting in the interstitial positions among the nickel atoms or on top of the chemisorbed oxygen, or both. The fast sorption of hydrogen may be due to adsorption on the sites left vacant by the partially incorporated oxygen atoms. This type of fast adsorption of hydrogen was also observed by Delchar[16] in an identical case. A similar behaviour was also displayed by a partially incorporated oxygen on iron film[19]. When the film was saturated with incorporated oxygen, the fast adsorption of hydrogen was stopped. The adsorption of hydrogen was controlled by a slow activated process and

the uptake was 20% to 30% hydrogen of a monolayer in four to five hours time.

The reduced activity of oxygen incorporated nickel film for hydrogen sorption may be attributed to the loss of original metallic character of nickel atoms by incorporated oxygen in the lattice. Roberts et al.[12] suggested from their work function, and photoelectric measurements that different types of oxygen species may be formed on the nickel surface by controlling the temperature and oxygen pressure and they are chemisorbed oxygen ($Ni\text{-}O^{\partial-}$), low work function oxide (Ni_mO) by incorporation and high work function oxide (Ni_nO) which is not distinguishable from ($Ni_mO + O^{\partial-}$ chemi). The inertness of the chemical reactivity of some of these oxygen species may be due to their oxide like character.

The interaction of hydrogen with the oxygenated nickel surface can conceiveably have two forms.

1) Nondissociative interaction of the hydrogen molecule with surface oxygen leading to a species, such as a surface water complex bonded to the surface by oxygen.

2). Dissociative interaction with hydrogen bonded to a nickel atom and a surface oxygen, both of these hydrogen being protonic in character. Since some oxygen has become incorporated in the nickel lattice (Ni_mO) the surface

nickel atoms will not have quite their original metallic character so that the dissociation of hydrogen is not possible at the investigated temperature range. If the first mechanism is operative, chemisorbed oxygen (Ni - $O^{\delta-}$) would form water which could be measured at room temperature. Addition of hydrogen to an oxygen treated nickel surface produced negligible amount of water ($< 3\%$) which means that the mechanism (1) is not operative and mechanism (2) can not be favoured due to the influence of incorporated oxygen. Consequently the yield of water production is very low in the temperature range 273°K to 325°K.

General Discussion

The interaction of oxygen and hydrogen has been studied on platinum, nickel and copper films in the temperature range 77°K to 325°K. Although some adsorbed species(e.g. hydrogen) can be displaced by another species (e.g. oxygen or nitrogen), it is not often observed experimentally. When oxygen was introduced to a film of Pt, Rh, Pd preadsorbed with hydrogen, no hydrogen was detected in the gas phase. This may be due to the adsorption of displaced atoms on a vacant site in an incompletely covered surface, or the adsorption of small displaced hydrogen atoms in the interstitial positions. But in an analogous case on nickel film only a few percent of hydrogen (4% to 8%) was displaced at 77°K and at 195°K the displaced amount rose to 30%. This displacement may be effected from the weakly chemisorbed hydrogen.

The slow process of hydrogen interaction with preadsorbed oxygen on platinum can take place at 77°K whereas in a similar case on nickel the slow process starts only at 273°K. This observation is in agreement with the oxygen-hydrogen interaction study by Ponece at al.[20]. Roberts et al.[18] reported that oxygen chemisorbed at 77°K can react with hydrogen at 295°K and the θ_H value was found to be 0.64. One should be careful about this

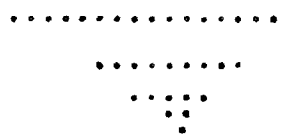
interaction because our experimental evidence shows that at 295°K 60 % to 70 % of oxygen can be incorporated from the surface . If the surface is not saturated by subsequent addition of oxygen at 77°K, equivalent amount of hydrogen to incorporated oxygen is taken up rapidly at 295°K . When hydrogen is allowed to interact with preadsorbed oxygen on copper film, the reaction only starts at 373°K. This suggests that dissociative adsorption of hydrogen is an essential step before the interaction of oxygen and hydrogen starts. This condition is probably satisfied at 77°K for platinum film, at 273°K for nickel film and at 373°K for copper film ,all being presaturated with oxygen. The kinetic analysis of the slow process favours some type of interaction between oxygen and hydrogen on the surface. The slow process on clean platinum and nickel [21] can be described by the Elovich model and only one process is observed in the linear plot of data in the experimental range . But when hydrogen was allowed to interact with an oxygen preadsorbed nickel or platinum surface, the linearity of the Elovich plot breaks after sometime and a second process becomes operative. The adsorption of carbon monoxide on clean ruthenium[2] shows that the rate decline monotonically, whereas it was discontinuous when hydrogen is preadsorbed by the solid suggesting that there might be some interaction taken place between the reactants on the surface.

This may be concluded that the first stage is due to chemisorption of hydrogen on clean bare surface of the low energy sites and the second stage is due to interaction with the preadsorbed oxygen atoms.

Hydrogen molecules react with oxygen on a platinum film to form water molecules at 195°K and can be desorbed at 273°K but hydrogen does not react with preadsorbed oxygen on nickel even at 273°K. The incorporated oxygen hinder the step $H + OH \longrightarrow H_2O$ for water formation on nickel surface.However, the water production on nickel film is due to some other mechanism at higher temperature. Therefore, it may be concluded that water can be produced on platinum films at 195°K because no incorporation of oxygen takes place in the lattice and it also can dissociate hydrogen at the same temperature. Nickel can not produec water in such a temperature range because the incorporated oxygen obstructs the final step ($H_a + OH_a \longrightarrow H_2O$) and as copper can not dissociate hydrogen molecules, the interaction of hydrogen and oxygen does not take place in the similar temperature range.

The interaction of oxygen-hydrogen on nickel and other transition metals has been studied by Ponece et al.[22]. They observed that no interaction of gaseous hydrogen is possible with completely oxygen covered metal surface.But the reaction can proceed on Pt,Rh,Pd surface if the gas phase hydrogen

is atomized and the reaction poduct(water) desorbs at 273°K from the surface and the continuation of the process is possible. Copper films can also produce water if the hydrogen molecules in the gas phase is atomized. Their observation of more or less 1:1 ratio of oxygen to hydrogen on oxygen preadsorbed nickel films is also in good agreement with the present investigation.



Appendix 1.

System: Oxygen +Copper + Hydrogen.

Copper films were deposited at a bath-temperature 77°K with the object of investigating the interaction of hydrogen with adsorbed oxygen on the surface. After the deposition the film was stabilised by thermal cyclings between 77°K and 300°K as was done in the nickel systems. The analytical values of surface area measurements showed that the roughness factor varied from 1.5 to 2.5 on different films.

In run Ni 4 the film was saturated with 62 x 10^{-8} mole of oxygen at a pressure 3 x10^{-3} torr. On warming the film the incorporation of oxygen was observed. When the film was warmed to 325°K and then recooled to 77°K, further 18.5 x10^{-8} mole of oxygen, corresponding to 30% of a monolayer, was incorporated in the film. This incorporated quantity in copper was less than that incorporated in nickel in the same temperature range.

When hydrogen was added to an oxygen saturated copper film, no sorption of hydrogen was observed at 77°K. On slowly increasing the temperature, sorption of hydrogen stated near 373°K.

Water could be produced on copper films at higher temperature.

In run Ni 4 only 10.4 $x10^{-8}$ mole of water was measured corresponding to 8 % of oxygen adsorbed on the surface at 400°K. The experiments on copper suggest, that hydrogen fron the gas phase does not interact with oxygen adatoms, but that hydrogen molecules may : dissociate at higher temperature on copper films to produce hydrogen atoms which can react with the adsorbed oxygen to produce water.

2. Adsorption of Hydrogen and Oxygen on Platinum Films.

The interaction of hydrogen or oxygen with platinum has been studied at 77°K and 195°K. After evaporation the temperature of the film was lowered to 77°K and measured doses of hydrogen were introduced. The initial adsorption was rapid, followed by a slow process. About 100^{-8} mole of hydrogen was adsorbed to cover 80% to 90 % of the surface at P~10^{-3} torr. About 10 % of the gas was adsorbed reversibly at 77°K. When thet temperature of oxygen or hydrogen saturated film was increased from 77°K to 195°K , more gas was adsorbed irreversibly. This is probably due to the redistribution of gas to the sites which are inaccessible at lower temperature

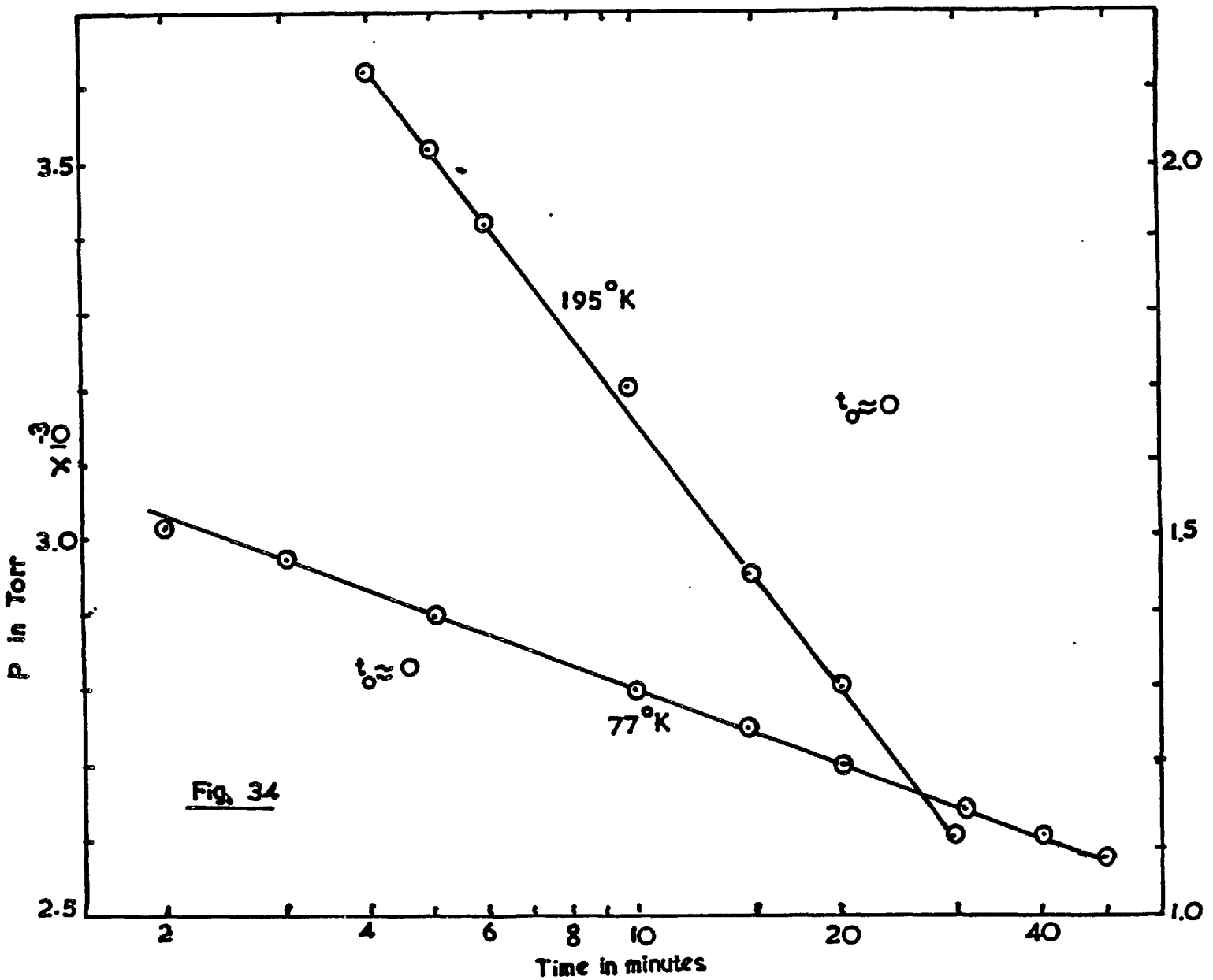

3.5
3.0
2.5
P in Torr
X 10^-3
2.0
1.5
1.0
195°K
77°K
t₀≈0
t₀≈0
2
4
6
8
10
20
40
Time in minutes

Fig. 34

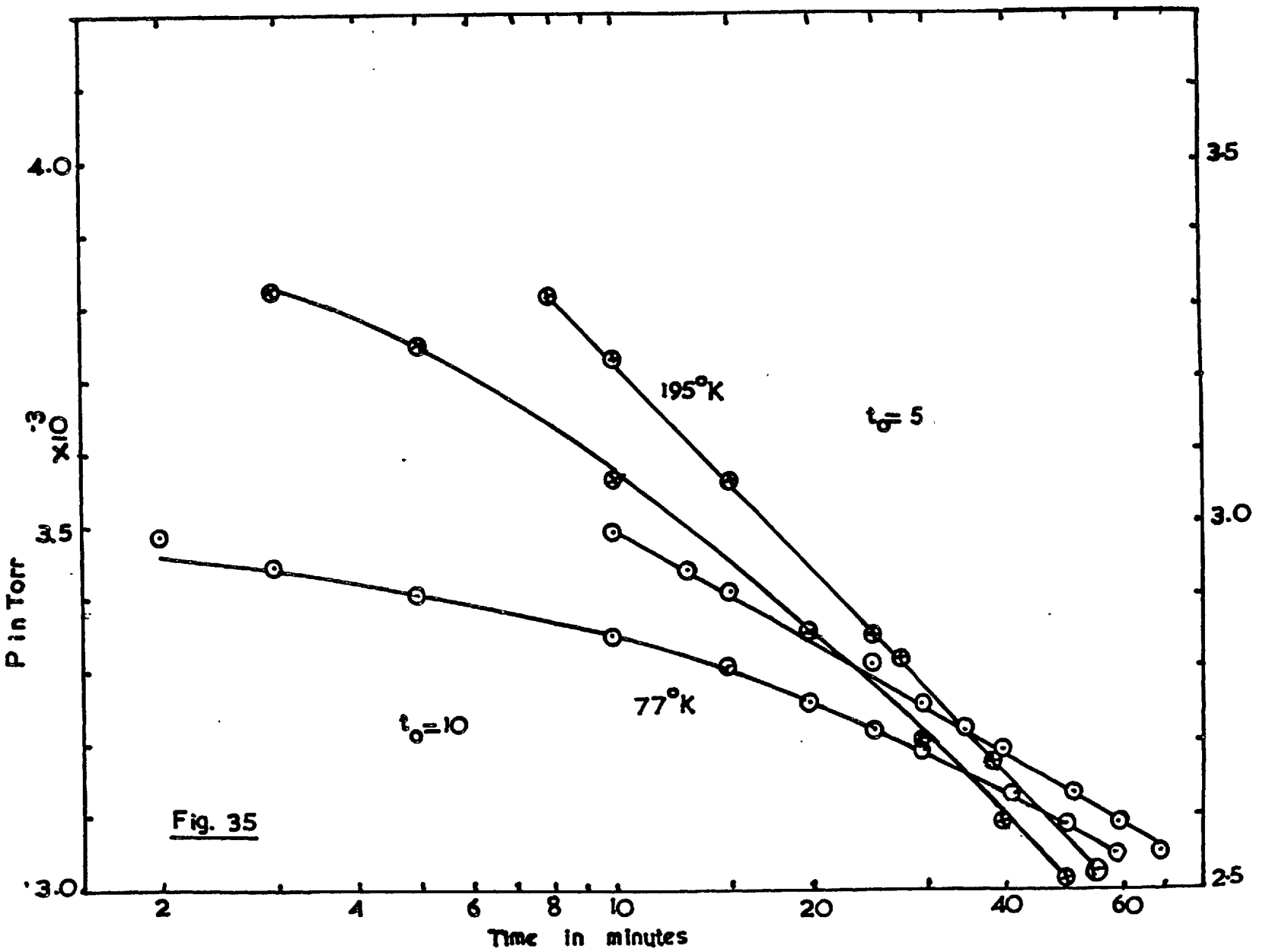

4.0
3.5
3.0
·3
X10
P in Torr
3.5
3.0
2.5
195°K
t_o= 5
77°K
t_o=10
2
4
6
8
10
20
40
60
Time in minutes

Fig. 35

($77^{o}K$).

The slow adsorption of oxygen or hydrogen on platinum film at $77^{o}K$ and $195^{o}K$ can be described by the Elovich equation. The plot of P aganist $\ln(t+ t_{o})$ of equation 3.7 are shown in fig.34 for hydrogen and fig.35 for oxygen.The plots for hydrogen shows that the values of t_{o} are approximately zero. The slope of the plots is $2.3\ RT/\ (\partial E/\partial q)$ and K_a values are 1.75×10^{-14} cal $mole^{-1}$ $molecule^{-1}$ and 1.66×10^{-14} cal $mole^{-1}$ $molecule^{-1}$ at $77^{o}K$ and $195^{o}K$ respectively for hydrogen and the corresponding values for oxygen are 1.0×10^{-14} cal $mole^{-1}$ $molecule^{-1}$ and 1.6×10^{-14} cal $mole^{-1}$ $molecule^{-1}$.

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