INTERACTION OF GASES WITH METAL SURFACES

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by

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ABSTRACT

The mixed adsorption of the following groups of gases O_2 + H_2; H_2 + O_2; H_2O + H_2 + O_2; H_2 + H_2O + O_2; O_2 + H_2 + O_2 + CO; NH_3 + H_2 + O_2 and CH_3OH + H_2 + O_2 have been investigated on platinum at 195°k and iridium at 195 and 273°k. In general in all these systems both metals catalyse the formation of water by the same mechanism. Both oxygen and hydrogen are dissociatively chemisorbed on the clean metal films at 195°k (for Pt) and 273°k (for Ir); there is no evidence for incorporation of these atoms into the bulk metal. At higher temperatures ($>$100°C), however, the uptake of oxygen corresponds to two monolayers; nevertheless, all these oxygen atoms are removed by treatment with gaseous hydrogen at 195°k and there is little loss of area or reactivity of the film at 70°C. At 300°C, a third oxygen layer is found but the additional oxygen uptake is unreactive and there is now evidence of marked sintering.

On platinum, when oxygen is the first adsorbate on the clean film, water is catalytically produced at 195°k when the surface is subsequently treated with gaseous hydrogen and an equivalent amount of chemisorbed hydrogen atoms remain on the surface. Treatment with oxygen now regenerates the oxygen adatom surface; this oxygen/hydrogen cycle with formation of water may be repeated indefinitely. Calculations of the number of surface sites occupied by hydrogen and oxygen adatoms during the cycles confirm

this conclusion. The utilization of this oxygen/hydrogen process for the determination of the reactive area of the platinum catalyst is discussed.

When hydrogen is chemisorbed as the first adsorbate on clean platinum, the process is complicated by the occurrence of molecularly adsorbed hydrogen molecules over the primary adlayer. These molecules are rapidly oxidised by oxygen to give water and simultaneously the primary hydrogen adatoms react but more slowly. Similarly, when water, or ammonia, or methyl alcohol, are added to a clean film, dissociative chemisorption (Pt-OH, Pt-H; Pt-NH_2, Pt-H; Pt-CH_3, Pt-OH) has probably taken place and again the primary hydrogen adatoms are only slowly oxidised; the main formation of water here proceeds via the molecularly adsorbed hydrogen molecules adsorbed on top of the primary layer. The other ad-radicals present are in general stable towards gaseous oxygen and hydrogen. Finally, experiments, in which treatment with carbon monoxide following a first cycle with oxygen and hydrogen were performed, showed that this had little effect on subsequent oxygen/hydrogen cycling to form water; the monoxide is quantitatively oxidised to the dioxide and the oxygen adatom layer is recovered by treatment with this gas at 70°C. The results and conclusions with iridium films were similar at 273°k.

A separate series of experiments were performed in which water was chemisorbed on platinum, iridium and on tungsten at 273°k (the

latter being used since it is not a catalyst for water formation at these low temperatures), followed by subsequent decomposition at higher temperatures. There were marked differences in behaviour, e.g., hydrogen was evolved at 273°k using tungsten films and the hydrogen evolved could not be readsorbed at room temperature after a previous higher temperature decomposition. With platinum and iridium, however, hydrogen evolution only occurred above 200°C and most of this hydrogen would be re-adsorbed at room temperature. These differences are discussed in terms of a possible associative chemisorption of water on platinum and iridium at 273°k, followed by the decomposition at the higher temperatures to produce hydrogen.

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CHAPTER I

INTRODUCTION

1. General Aspects of Chemisorption

When a gas or vapour is allowed to come to equilibrium with a solid or liquid surface, the concentration of gas molecules is always found to be greater in the immediate vicinity of the surface than in the free gas phase, regardless of the nature of the gas or surface. The process by which this surface excess is formed is termed adsorption.

Adsorption of gases by solids generally can be divided into two main domains, Physical or Van der Waal's adsorption and chemisorption. Van der Waal's adsorption is non-specific and takes place on all surfaces. It is caused by physical forces comparable with those responsible for the liquefaction of gases. The molecules are bound to the surface of the adsorbent by dispersive forces and those due to permanent and induced dipole attraction. It is generally appreciable in a low temperature range when molecular species may be reversibly adsorbed and multilayers formed. Chemisorption on the other hand involves the formation of chemical bonds and involves at least partially transference or sharing of electrons. The magnitude of the work function of the adsorbent affects the formation and the strength of such bonds. Covalent bonds are formed if the adsorbent possesses orbitals with unpaired electrons capable of entering into covalence. Co-ordinate bonds require the latter to have vacant orbitals capable of receiving the pair.

Adsorption takes place with decrease in surface free energy, G, and generally with decrease in entropy, S, because by confining an adsorbed molecule to a thin surface layer, some degrees of freedom are lost. Use of the equation

$$\Delta G = \Delta H - T.\Delta S \qquad (1)$$

then shows that ΔH is also negative, that is, adsorption is in general 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 (1,2,3,4,) and three main explanations have been proposed. The earliest one, due initially to Constable(5) and Taylor(6), is that the fall is owing to the surface hetrogeneity. The second is that falling heats are due to the force of repulsion between molecules in the adsorbed layer, by Roberts.(7) Finally Eley(8) and Schwale(9) 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 the 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 subsequently deeper levels will be used. Consequently in either case, the heat will fall, although Temkin(10) developed the idea of heat decrease due to electron transfer involving a surface band system. Gundry and Tompkins(11) 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.(12) Comparison of heats extrapolated to zero coverage yields a scale of values decreasing in the order(13) Ti, Ta > Nb > W, Cr > Mo > Fe > Mn > Ni, CO > Rh > Pt, Pd > Cu, Au.

This trend cannot be considered as precise since there is a considerable variation from one worker to another. For example the variation of maximum heats measured for oxygen on Ni ranges from 105 k cal(14) to 150 k cal(15). A similar wide variation occurs for iron and oxygen, namely 100 k cal(16), to 130 k cal(14), though these are some extreme examples. The general trend of heats of adsorption has been correlated with the d character of the metallic bonds(20). This interpretation requires that the bond between metal and adatom be essentially co-valent(21,22,23) which is in accord with all the experimental observations excepting some alkali metals on tungsten(24,25,26) where the interaction is more ionic in character.

The importance of the d-bond in gas-metal interaction is brought out quite neatly by the work of Couper and Eley$^{(22)}$ on the activation energy for the ortho-para hydrogen conversion on palladium. The activation energy undergoes a sharp rise as the d-band is filled by alloying with gold. Again Trapnell$^{(27)}$ concluded from studies of the chemisorption of several gases on a large number of metal films, that metals with vacancies in the d-band are much more active adsorbents than other metals.

The detailed nature of the adsorption band in chemisorption is still not clear. Single participation of d-band character in bond formation of transition metals is criticised by different workers.$^{(28,29)}$ 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.$^{(30,31)}$ If the entropic contribution to the chemical potential is excluded, chemisorption can occur only if the binding energy of an adatom, x, 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. Semiquantitative data on the bond energies of hydrogen atoms for a variety of surfaces suggest that there is no particular dependence upon band structure.(32) Thus H atoms can be bound to typical non-transition metals like mercury(33), aluminium(34), potassium(35); and nitrogen atoms, for example, can be chemisorbed on noble metals.(36) Such chemisorbed hydrogen bonds may sometimes involve a surface rearrangement towards a hydride phase and involve complex changes in the hydridization of the metallic orbitals, affecting several atoms as each adsorbate is chemisorbed, rather that a simple bonding with a vacant orbital.(21)

Different bonding may occur on different crystal faces of the same adsorbent. Thus there are strongly bound H atoms with heats of adsorption of 20-46 k cal and these desorb above 280°k; another species has a positive dipole outwards, and a heat of adsorption of 15-20 k cal. A species with a negative dipole outwards and heat of adsorption 8-14 k cal also exists. Both these latter species showing a preference for the 411 face. Lastly a weakly bound positively polarised state, with a heat of adsorption of 6-10 k cal is found mainly on the 411,111 and 320 faces. These results have been interpreted by Sachtler in terms of a topographic dependence of the heat of adsorption. The bond strengths have been correlated with the number of surface atoms contacted simultaneously, 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 less attractive faces. 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 formed as a result of induced or polarisation effects since they are only obtained on faces covered with the adsorbate. The heats for carbon-monoxide on tungsten do not differ greatly from hydrogen on tungsten.(37) The heats fall in carbon-monoxide tungsten system from 100 k cal β_3-state, 70 k cal β_2-state, 52 k cal, β-state to 20 k cal α-state, thus giving a spectrum of heats of adsorption accompanying surface specificity.

The adsorption of nitrogen on tungsten proceeds through a simultaneous filling of different binding states; again there is a spectrum of binding states from 2 k cal for a physi-sorbed state, to 9 k cal for the γ-state, 20 k cal for the α-state and 87 k cal for the β-state. The mobility of adsorbed gas layers on metals has been demonstrated by Gomer(38), Ehrlich and Hudda(40) and Klein(40) 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 monolayer, a sharp boundary moving over the field emission tip, was observed at about 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 base surface. A second type of diffusion occurred involving the chemisorbed adatom layer. Atoms could migrate over such planes as the (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 shows that the ratio increases with surface roughness.(38) The potential structure of the surface imitates to some extent its physical one. On a perfectly smooth substrate, diffusion would require zero activation energy, regardless of the energy of adsorption. A similar increase in ratio is demonstrated in going from 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 H atom permits it to be in contact with almost its full quota of W atoms even during diffusion. Studies on nitrogen(41) of the γ and α-state did not show any appreciable diffusion process in the temperature range of their stability. The activation energy for conversion to more stable state or for evaporation, must be comparable to the barrier that prevented hopping from one site to another. Roberts(42) discussed the weak binding state of molecular adsorption on an immobile layer, where a random distribution of pairs of sites rather than single sites 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 Tanks,(43) have considered a slightly different model in which adsorption on a given lattice site and accordingly found thirty-seven percent are filled. Roberts original model may be incorrect 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.

However, Ehrlich(44) showed that a model based on the notion of excluded sites can be used for the 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, and the γ-state can be identified with unavailable pair of sites; 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, i.e. displays surface specificity. The observation of weak binding states does not essentially depend on the presence of singular sites, since the same molecules would be bound more tightly to some crystal faces than to others. This may be relatively important with the same system.

The nature of the binding of weakly held layers is not yet resolved. Evidence from surface potential and field emission investigations shows that most of the weakly held states results in a decrease of the metal work functioning;for example, 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°k.(39,45,46) The positive dipole has been interpreted in terms of induced polarisation,(47) charge transfer of donar acceptor type or surface defects. Molecules on the surface are incorporated partly in the metal double layer, which has its negative end out from the surface(48,49,50) so that the polarised molecule will have a positive dipole outwards from the surface.

The explanation is most acceptable for large, easily polarisable molecules, such as the rare gases, but for a small molecule such as hydrogen there are objections. The second explanation in terms of donor-acceptor interactions, proposes that since the transition metals possess d-orbitals of low energy, they will accordingly be good acceptors and yield high surface potentials in agreement with the experimental results. For molecules, the donor acceptor interaction may also be relevant. For example, the high heats of adsorption of hydrogen molecules on hydrogen covered tungsten and platinum surfaces are 9 and 15 k cal/mole respectively, are difficult to explain by polarisation effects alone. The importance of weakly bound, particularly physisorbed, molecules in the kinetics of chemisorption has been discussed by Ehrlich(51) and Kisluik(52). Ehrlich has discussed the available data on the adsorption of diatomic molecules on bare metal surfaces. He concluded that with perhaps the exception of H_2, molecules physically adsorbed on the surface form a reservoir from which chemisorption can occur. Delchar(53) showed in his study of hydrogen-nickel system at 78° k or 90° 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 chemisorption, before migrating to the clear part of the film where it becomes chemisorbed. If the sticking probability is less than one, and the condensation coefficient is equal to one, any chemisorption process must involve the participation of physically adsorbed precursors. In view of the variety of binding energies found for surface states, the precursor to chemisorption does not necessarily need to be physisorbed in the strict sense; one of the weakly bound states could doubtless function as a precursor.

2. Structure and Properties of Metal Films:

The films produced by thermal evaporation or cathodic sputtering behave differently from metal filaments or foils. These are very unstable and consist of aggregates of micro-crystallites having high surface energy; they tend to change spontaneously to more stable forms. Their surface areas are irreversibly changed by the formation of larger crystallites at temperature far below the melting point.(1) Their properties are also greatly dependent upon the nature and the temperature of the substrate, the presence of the adsorbed gas and purity of the metal.

X-ray and electron diffraction studies of metallic films have done much to elucidate the structure of films, and it is now emphasised that there are great similarities between the structure of films and that of the bulk metals. Germanium films evaporated on the 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 30Å (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 to 3000°A.(8) Anderson made a detailed study of nickel and tungsten films by electron microscopy. From the transmission electron micrographs the presence of gaps up to 20°A between the crystals have been established for Ni films examined when deposition was carried out 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 reduced considerably.(8,9)

Normally it is found by chemisorption studies that the surface area of the refractory metal films is a linear function of film weight; this is conclusively proved in the case of Ni and W. Cu films thrown at -183°C are bronze in colour and the large areas are also proportional to film weight;(10) on warming to room temperature films, red in colour having an area close to the geometric area, are formed. Silver and gold films on sintering at room temperature behave similarly.(11,12,13) Mignolet(14) has shown that the work function of the film increases with sintering and approaches that of the normal metal.

Beeck's reports regarding the enhanced catalytic activity of oriented Ni films also seems to be exceptional and this effect has been disproved by Sachlter(15) who used similar films produced by different methods. There is some indication of slow aging 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 Pt and Pd(16) atoms gives substantial support to this contention. Direct investigations 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 surface. 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.

Kinetic studies show the adsorption of nitrogen at low temperature (115°k) occurs at a high rate, with a sticking probability of 0.5 compared to 0.3 at room temperature.(19) This is due to the presence of the α-state. Nitrogen probably 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)(20) 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 Kley(12) who used evaporated metal films also established that the extent of chemisorption was different on different crystal planes.

3. Adsorption of Oxygen

The study of oxygen chemisorption on metals is complicated by the occurrence of oxidation even at low temperatures. Brennan, Hayward and Trapnell(1) have compared the volume of Krypton physically adsorbed on evaporated films with the extent of oxygen chemisorption at room temperature on the same film. The adsorption of oxygen at 78°k shows that two kinds of sorption occur, (i) an "irreversible" and the (ii) reversible one. The kinetics of the irreversible one were not affected by interrupting the reaction.

In some cases the reversible adsorption was shown to follow a Langmuir type isotherm.(2)

$$N_{rev} = No \frac{p^c}{\left[\beta + p^c\right]} \qquad (1)$$

where N_{rev} = 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.

β = an empirical constant.

A study of the oxygen-Germanium system by Rosenberg et al(2) suggest that reversible adsorption may be physical in nature and the value of c which is less than one (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 system of adsorption energies. The value of c suggests that the process is a dissociative one, but the study of Kr adsorption on oxygenated Germanium(3) at low coverage (10% to 50%) indicates that a fractional pressure exponent of equation (1) may not imply that a dissociation of the adsorbed species has taken place. The reversible adsorption of oxygen takes place at (195°k) but incorporation and oxidation is pronounced. Quinn and Roberts,(4) in a photoelectric investigation and Delchar$^{(5)}$ by surface potential measurements showed an "incorporation process" for oxygen on some of the transition metals. The incorporation lies in the order Cr > Fe > Ni > Cu. The apparent activation energy of incorporation of oxygen by Delchar shows that it was 1-2 k cal for Ni and 6 k cal for copper and for Cr and Fe even less than one k cal. The results obeyed an equation where the energy term was split into two components.

$$\text{Rate} = n \exp - (Q - qaF)/_{RT} \qquad (2)$$

where Q = activation energy for transfer of an oxygen ion from the surface into the metal latices.

q = is the charge on the ion situated at a distance (a) from the metal.

F = the electric field at the metal surface.

The value of Q for Ni from this equation was found to be 32 to 31 k cal from 100° to 400° k and for Cu 28 to 29 k cal. Grimley and Trapnell$^{(6)}$ have estimated that Q for the transfer of a copper atom into a thin oxide layer is 26.5 k cal. 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. In the Germanium-oxygen system Bennett$^{(7)}$ also observed the incorporation process.

In some cases, the 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 to 3 k cal/mol.(8) In the normal oxidation of alkali metals, like potassium, the O_2^- ions are found when lattices of superoxides result from the reaction of metal with oxygen (KO_2). When a Caesium metal surface was exposed to oxygen at 77°K, it is spontaneously covered with a chemisorbed layer of oxygen as O_2^- species. The surface potential investigation shows that the relatively small surface potential due to adsorbed oxygen was originally interpreted(9) to mean that adsorbed oxygen was essentially atomic in character. It was found by Macrac(10) that the surface potential data can also be used in support of considerable charge transfer to the adsorbed oxygen. Magnetic studies yield conflicting evidence.(11) Park and Farnworth(12) consider agreement of photoelectric data with the Fowler curve for metals as strong evidence for adsorbed oxygen being mainly atomic in character. Boreskov(13) used isotopic exchange technique to investigate the character of the oxygen bond on the metal surfaces of Pt, Ag, Pd and Ni. 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 Pt film.

The heat of chemisorption varies between 13 and 24 k cal/mol over 25% of the monolayer, while the activation energy increases by 5 k cal/mol. The rate of a homo-molecular 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 Pt surface.(14) This rate of homomolecular exchange of oxygen on silver films is one order of magnitude less than that of Pt.(15) The studies indicate that the surface oxygen is uniform over most of the surface. PtO is formed on Pt 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.

On freshly prepared Ni films the initial exchange exceeds that of Pt 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 a passive role in simple catalytic reactions. Tikhomirover et al(16) showed by their various pulse methods that at the moment of anode polarisation to $\theta = 1.2$v (i.e. before the formation of oxide planes on the Pt surface) various types of O_2 (chemisorbed) are formed, differing in bond strength. However, when the same techniques were used on the cathode side (i.e. during reduction of chemisorbed O_2) at least, two types were detected. Morrison and Roberts,(17) using the accommodation coefficient techniques, found oxygen layers on a tungsten filament to evaporate in two different temperature ranges. The less stable portion, evaporating at 800°C was believed to be a molecular film, and the more stable portion, evaporating at 1,400°C, an atomic film. Some 8% of single sites are in fact left over when an immobile layer is formed by dissociation of diatomic molecules to atoms, and it was suggested that on these a strong molecular chemisorption might take place. Evaporation data are however even more difficult to interpret with oxygen than with hydrogen owing to the possibility of desorption as oxide.

4. Adsorption of Hydrogen

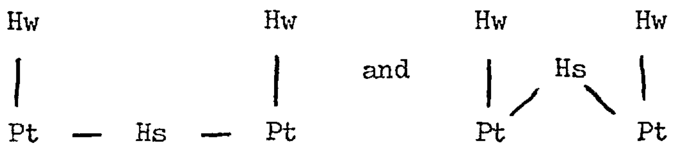
Some important work on hydrogen metal systems was initiated by Roberts(1,2) in the middle of 1930. He showed that hydrogen was chemisorbed rapidly by clean metal surfaces at room temperature. The chemisorbed layer of hydrogen on tungsten, for example, only starts to evaporate in a good vacuum at 500°C. When tungsten powder was outgassed at 750°C,(3) hydrogen was adsorbed only slowly; this may be attributed to a diffusion process; for example, oxygen present as a contaminant on the external surface may diffuse into the interior and thus set surface sites free for adsorption.(1) Beeck and Ritchie(4) have compared the volume of hydrogen chemisorbed by an evaporated nickel film with the volumes, Vm of various gases physically adsorbed into a monolayer. These volumes were obtained from adsorption isotherms by application of the Brunauer-Emmett-Teller equation for multilayer adsorption.(5) From this, the volume of gas Vm, physically adsorbed into a monolayer can be obtained. Then if each physically adsorbed molecule occupies an area a_1($\mathrm{\AA}^2$) on the surface, and v_2 cms^3 of hydrogen are chemisorbed, the area a_2($\mathrm{\AA}^2$) occupied by each chemisorbed molecule is

$$a_2 = \frac{a_1 Vm}{V_2} \qquad (3)$$

Hence a_2 may be obtained provided a_1 is known. For simple molecules such as Krypton, methane and nitrogen it may be assumed that there is close packing in physically adsorbed monolayers, with a_1 equal to the cross-sectional area in the liquid phase. For more complex molecules it is necessary to assume some definite configuration on the surface. With n-butane, it has proved valid to assume that the molecule lies flat, in the form of a cylinder of diameter 4.75A° and length 5.16A°.

The value of a_2 obtained by Beeck and Ritchie are independent of the gas used in physical adsorption. V_2 was measured as the volume chemisorbed at (-196°C) and 0.1 mm pressure. The nickel films were randomly oriented, and are likely to have exposed in their surfaces the low index planes (100), (110) and (111) to roughly equal extents. The areas per site in these three planes are respectively 6.15, 8.70 and $5.32\text{A}^{\text{o}2}$, the mean being $6.72\text{A}^{\text{o}2}$. If in the saturated layer one hydrogen atom is present per nickel atom, the area covered by each hydrogen molecule would be 2 x 6.72 = $13.44\text{A}^{\text{o}2}$. This is good agreement with the experimental value, and suggests 1:1 bonding.

More recent work has been concerned to discover whether more than one mechanism of chemisorption may be operating within the monolayer. This was first suggested by Mignolet(6,7) as a result of studies of the change in work function (μ) on coverage (θ). Often μ-θ curves are non-linear, showing an apparent decrease in the surface dipole as an adsorption proceeds. Hitherto this had been ascribed to mutual depolarization, but the case of platinum is more extreme.(8) The work function initially increases on adsorption, but then decreases, eventually giving an electro-positive layer. Clearly, mutual depolarization cannot explain the result, and Mignolet suggested that in the later stages a weak molecular chemisorption is taking place through a Mulliken charge transfer bond. However, infra-red work by Pliskin and Eischens(9) shows that this cannot be the case. These workers found bands at 4.86 and 4.76 microns respectively for the strong and weak chemisorption of hydrogen, and at 6.8 and 6.7 microns in the case of deuterium. The results confirm that there are two mechanisms of chemisorption, but if the weak adsorption is molecular, a band should appear at about 5.4 microns when HD is adsorbed. However when an equilibrated H_2/D_2 mixture was contacted with the platinum sample no adsorption occurred at this wavelength. Both strong and weak adsorptions must therefore be atomic, and representing the species as Hs and Hw, Pliskin and Eischens suggest two possible structures, namely,



That is, the two chemisorptions are associated with different topographical positions on the surface, the strong adsorption being part way towards solution in the metal. In the case of tungsten, there is no reversal of the dipole as adsorption proceeds,(7) simply a decrease. However, if a filament is covered with gas at liquid air temperatures and then flashed the curve relating the rise in pressure due to desorption with rise in temperature shows two peaks.(10) Other peaks have at various times been claimed,(11) suggesting the presence of further binding states, but later work showed that these arise from impurity in the system.(12) The weak chemisorption of hydrogen on tungsten is small in extent and pressure dependent, and is confined to temperatures below 200°k. It may well be molecular and take place in gaps in the strongly adsorbed layer, though as yet this must be regarded as unproven.

Certainly the balance of evidence supports the existence of two mechanisms, and this is confirmed by the effect hydrogen chemisorption has on the conductivity of metal films.(13) In the case of iron films, the resistance first increases on admission of hydrogen but then decreases, eventually reaching almost the initial value for the clean surface. Those who have used the resistance method tend to agree with those who have used infra-red spectra, not only that two mechanisms exist, but also that these are due to adsorption at different lattice points.(14) The alternative possibility, namely, that the second weak adsorption takes place in the gaps in an immobile atomic layer, does not at present find favour.

5. Adsorption of Water Vapour

When metal films are treated with water molecules, adsorption occurs in the right temperature range, and chemisorption is effected generally by donation of a lone pair of electrons from oxygen to metal and a co-ordination type bond(1) is formed. The adsorption of water molecules on Germanium at very low pressures using mass spectrometry were studied by Law et al.(2) It was found that the 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 a heat of adsorption comparable to that of condensation as would be expected in the multilayer region.

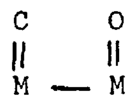
By comparing the experimental entropy values with those calculated from various models, it was found that the higher layers were mobile, having effectively properties similar to liquid water. Water molecules adsorbed reversibly could be removed by pumping until the monolayer region was reached. On heating to about 350°C further desorption was observed, indicating that the monolayer was chemisorbed. It was found by analysis 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, for water molecules, desorbed from Pt films at room temperatures, experimental evidence showed that monolayer of water molecules was stable up to 195°k and at room temperature (300°k) almost all of it was desorbed.

Adsorption of water on nickel films, by recording the surface potential and electrical resistance change at 77° to 90°k, caused the potential to decrease. In this temperature range, the positive pole of the dipole of adsorbed water molecule points away from the nickel surface. An increase of the photoelectric emission of Pt in the 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 was observed by Schaaff.(4) On nickel films the water molecules decompose at 195°k and especially at 273°k, resulting in an additional increase of ϕ. The fragments are bound to the surface and effect the electronic interaction between the successively adsorbed water molecules and the metal surface, in such a way that the adsorption of water molecules at 273°k, 90°k and 77°k is accompanied by a decrease in resistance which at 273°k can be reversed by adsorption. In the chemisorption of water molecules on oxides,(5) the surface layers of these oxides were converted into the surface hydroxide layers.

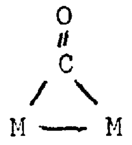
6. Adsorption of Carbon-monoxide

The volumetric work has been carried out on carbon-monoxide layers with the aim of obtaining the ratio of adsorbed molecules to surface metal atoms. Brunauer and Emmett,(1) for example, compared the low temperature adsorption of nitrogen on iron powders with the extent of carbon-monoxide chemisorption. Unfortunately their work is difficult to interpret as some low temperature nitrogen chemisorption was almost certainly taking place in addition to physical adsorption. However, similar work by Beeck et al.(2) on evaporated nickel films suggested that a single site chemisorption of carbon-monoxide was taking place indicating a surface complex NiCO analagous to the bonding in nickel carbonyl. He studied mostly nickel film, but also studied films of iron, cobalt, Pd, Pt and Cu; with the exception of Cu similar results were obtained.

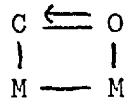
On Molybdenim and Rhodium films, on the other hand, Lanyon and Trapnell(3) found the carbon-monoxide and hydrogen chemisorption to be almost equal in extent, suggesting a two-site mechanism, while on iron and tungsten films, the carbon-monoxide chemisorption was respectively 1.23 and 1.40 times the hydrogen chemisorption, suggesting mixed one; and two-sites mechanisms. Only on Pt and Pd films did the CO chemisorption correspond to a single site mechanism. The carbon-monoxide molecules can cover two sites in one of three ways, namely



(i)



(ii)



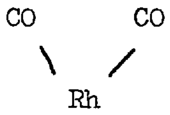
(iii)

and no final decision between these is possible on volumetric grounds. This question and others have, however, been resolved by Eischens and his co-worker;(4,5) they obtained infra-red spectra of carbon-monoxide adsorbed on a number of metals, normally supported on silica or alumina. Some pertinent information can be obtained from the number of bands in the spectra at a single stage of surface coverage as shown in the original spectra of chemisorbed carbon-monoxide. However, these single stage spectra do not reveal the relative strength of bonding for the chemisorbed CO contributing to each band or the effect of interaction on the band position. To obtain this information the spectra of chemisorbed CO were studied as a function of surface coverage over silica-supported Pt, Pd and Ni. Their most important results are the following:-

1. Both one and two site adsorption occur.
2. One site adsorption involves a single bond between metal and carbon atoms, and should therefore be represented as M-C≡O.
3. The relative amounts of one and two sites chemisorption vary (a) with the metal (b) with the nature of the support and (c) with the surface coverage.

In the case of palladium at room temperature both one and two site adsorption occur. The initial adsorption takes place primarily by a two site mechanism, single site adsorption clearly becomes important as the surface coverage increases. Probably the effect is due to surface hetrogeneity rather than to adjacent pairs of sites being filled and leaving only single sites. On nickel, mixed one and two site adsorption was also observed, but both on supported Pt and on evaporated films single site adsorption predominated.(5) However, the relative proportions of the two types of adsorption varies with the nature of the support. Two site chemisorption is rather more extensive on alumina supported than on silica supported platinum.(6) This result may show that the nature of the support influences the electronic structure of the metal, since a relatively greater donation of electrons by the metal is required for two site than one site adsorption.

Yang and Garland(7) find one and two site adsorption on rhodium, together with a third mechanism in which one rhodium atom adsorbs two molecules of CO.



Their relative proportions of the various types of adsorption again depend on the coverage and on the concentration of rhodium on the support.

Desorption studies on tungsten filaments by Ehrlich(8) and by Redhead(9) confirm the existence of two mechanisms. Redhead finds that two-site chemisorption takes place first and to a greater extent and concluded that the small amount of single-site chemisorption (some 10% of the total) is a gap-filling process. Both Ehrlich and Redhead agree that there are three sub-phases within the two-site mechanism. These have different heats of chemisorption, and may arise from adsorption on different lattice spacings. An unexplained result which relates to CO chemisorption is that isotopic exchange between CO molecules takes place on iron powders at temperature as low as -35°C.(10)

$$^{13}CO + C^{18}O \rightleftharpoons {}^{13}C^{18}O + CO$$

At face value the result is difficult to explain. However, iron powders are undoubtedly contaminated, presumably with oxygen, and exchange might take place through association of the chemisorbed CO with this oxygen.

7. Adsorption of Ammonia

With ammonia, adsorption involves dissociation of hydrogen, the extent of which increases with rising temperature. At very high temperatures, many metals decompose ammonia to nitrogen and hydrogen, and this suggests that the ammonia molecule is completely dissociated in chemisorption. Confirmatory evidence that nitrogen atoms are present on the surface is that on tungsten,(11) ammonia decomposition and the nitrogen exchange reaction both commence at similar temperatures.

$$^{14}N_2 + {}^{15}N_2 \longrightarrow 2\,{}^{14}N^{15}N$$

At room temperature Wahba and Kemball(12) have studied NH_3 chemisorption on tungsten, iron and nickel films, and found that with Nickel and iron the ammonia chemisorption at room temperatures and low pressures on a given film area is roughly equal to the hydrogen chemisorption. Under these conditions the surfaces will not have been completely covered, but the Θ values for both gases will have been high, and not greatly different from one another; since the hydrogen molecule covers two sites in chemisorption, the ammonia molecules must cover roughly two sites also.

With tungsten and iron, when more than a certain quantity of ammonia has been admitted, hydrogen appears in the gas phase. Some hydrogen is liberated in the absence of excess ammonia in the gas phase, but the extent and velocity of hydrogen evolution is increased if ammonia is present. The volume of hydrogen liberated after exposure to 0.1 mm pressure of ammonia for 24 hours is about 1.5 times the initial ammonia chemisorption. With nickel there is almost no liberation of hydrogen. The most reasonable explanation of these results is that with these metals there is an initial two site chemisorption, according to the equation

$$2M + NH_3 \longrightarrow MNH_2 + MH$$

When this layer is exposed to excess ammonia, there will be a tendency for the chemisorbed hydrogen to be displaced by amine radicals, provided the heat of NH_3 chemisorption somewhat exceeds the heat of hydrogen chemisorption. With tungsten and iron this state of affairs holds but with nickel it does not, and so very little hydrogen is liberated. The mechanism of displacement is probably through desorption of hydrogen followed

$$2MH \longrightarrow 2M + H_2$$

by ammonia chemisorption on the resulting vacant sites. The overall equation for displacement is then

$$MH + NH_3 \longrightarrow MNH_2 + H_2$$

If chemisorption as amide and displacement of hydrogen were the only processes, the volume of hydrogen liberated would be equal to the initial NH_3 chemisorption. However, with both iron and tungsten the volume approaches 1.5 times the ammonia chemisorption and the most likely reason for this is a further slow breakdown of amide radicals to imide radicals, or possibly to nitrogen. The fact that some hydrogen is slowly liberated in the absence of gaseous ammonia offers some support for this idea.

8. Mixed Adsorption

The investigation of the adsorption of mixed gases or one gas after another was reported by Smith(1) as early as 1863. In the adsorption of a pure gas on a given surface of fixed area there are three variables, temperature, pressure, and amount adsorbed. For a binary gas mixture the composition of the adsorbed and gas phases at equilibrium must also be known. Thus five variables must be evaluated in order fully to characterize experimental point. At constant temperature, three of these variables may be unambiguously depicted on a three dimensional plot. In other words a mixed isotherm is properly represented not by a line but by a surface.(2,3) Tompkins and Young(4) depicted a mixed adsorption isotherm.

In mixed adsorption a number of processes may occur such as the formation of complexes, surface displacement, acceleration or retardation of sorption of different components, or individual adsorption of different gases on different planes of a polycrystalline metal surface. According to Robert et al(5) partial displacement is possible, e.g., the displacement of hydrogen by nitrogen(5) and hydrogen by oxygen on Molybdenum.(6) He also stated that surface diffusion of displaced atoms are essential before molecular desorption. If the surface is not covered completely, e.g., Θ is less than one, the rate of hydrogen desorption by nitrogen is negligible up to 60°. The smaller the value of Θ and T the more likely will displaced hydrogen adatoms be successfully retained by the surface.

It appears that many surface reactions between two substances involve interaction between two adsorbed molecules, the adsorption occurring on neighbouring surface sites; this is conveniently known as a Langmuir-Hinshelwood mechanism. The rate of a reaction between A and B is then proportional to the probability that A and B molecules are adsorbed on neighbouring sites, and this is proportional to the product of the fractions covered by A and by B. Let the fraction of surface covered by molecules of the type A be θ, and the fraction covered by B be θ'. The rate of adsorption of A is given by

$$\mathcal{V}_1 = k_1 P(1-\Theta-\Theta') \qquad (1)$$

where P is the partial pressure of A; $(1-\Theta-\Theta')$ is the fraction of surface that is bare. The rate of desorption of A is $k_{-1}\theta$, and equating these rates gives

$$\frac{\theta}{(1-\theta-\theta^1)} = kP \qquad (2)$$

where k is equal to k_{1}/k_{-1}. In a similar way it can be shown that for the equilibrium of the gas B,

$$\frac{\theta^1}{(1-\theta-\theta^1)} = k^1P^1 \qquad (3)$$

where P^1 is the partial pressure of B and k^1 is equal to the ratio of the rate contents for the adsorption and desorption of B. Solution of equations (2) and (3) gives

$$\theta = \frac{kP}{1+kP+k^1P^1} \qquad (4)$$

and

$$\theta^1 = \frac{k^1P^1}{1+kP+k^1P^1} \qquad (5)$$

for the fractions covered by A and B respectively.

The rate of the reaction, being proportional to the product of these two fractions, may thus be written as

$$= k_2\theta\theta^1 \qquad (6)$$

$$= \frac{k_2kk^1PP^1}{(1+kP+k^1P^1)^2} \qquad (7)$$

If the pressure P^1 is kept constant and P is varied the rate first increases, passes through a maximum and then decreases. A similar variation with P^1 is also found. The physical explanation of the falling off of the rate at high pressure is that the more strongly adsorbed reactant displaces the other from the surface as its pressure is increased. It is most convenient to consider a number of special cases of the general equation (7).

Case (i) Sparsely covered surface:- If the pressure P and P^1 are sufficiently low, the terms kP and k^1P^1 may both be neglected in comparison with unity, and the rate equation is

$$\upsilon = k_2kk^1PP^1 \qquad (8)$$

The rate is thus proportional to the product of the two partial pressures, and the reaction can be said to be of the first order with respect of both A and B, and is of the second over-all order. If both reactants are present at the initial pressure Po, and the pressure at time t is P, the rate equation is

$$-\frac{dP}{dt} = kP^2 \qquad (9)$$

and this integrates to

$$P = \frac{Po}{1+Pokt} \qquad (10)$$

A number of reactions obey laws of this type; examples are the reaction between nitric acid and oxygen on glass(7) and the reaction between ethylene and hydrogen on copper(8,9) under certain conditions of temperature.

Case (ii):- One reactant very weakly adsorbed:- If reactant A is weakly adsorbed, the term kP is the denominator of eq.(7) may be neglected in comparison with $1+k^1P^1$ and the rate equation becomes

$$\mathcal{V} = \frac{k_2 k k^1 P P^1}{(1+k^1 P^1)^2} \qquad (11)$$

The rate is now proportional to the pressure of A, but as the pressure B increases the rate first increases, passes through a maximum and then decreases. Such a maximum in the rate has been observed in the reaction between hydrogen and carbon-dioxide on Pt,(10,11,12) and in the exchange reaction between deuterium and NH_3 on an iron surface.(13)

If reactant B is sufficiently strongly adsorbed so that k^1P^1 is much greater than unity, the rate equation becomes

$$\mathcal{V} = \frac{k_2 k P}{k^1 P^1} \qquad (12)$$

This rate is now inversely proportional to the pressure of the strongly adsorbed reactant B. For example under certain conditions, the rate of the reaction between carbon-monoxide and oxygen on the surface of quartz and Pt(14,15,16) is directly proportional to the pressure of oxygen and inversely proportional to that of CO; the latter is therefore strongly adsorbed and as its pressure is increased it displaces the oxygen from the surface. Another example is the reaction between hydrogen and oxygen on Pt,(15) the rate of which, under certain conditions is inversely proportional to the hydrogen pressure.

Calorimetric measurements are reported by D. Brennan and M.J. Graham,(17) which show that oxygen adsorbed to saturation on Mo and W at 78°k, has the same energy as oxygen adsorbed on these metals at 273°k to the same coverage. The additional coverage at 273°k, either for a surface initially saturated at 77°k/or for a surface maintained at 273°k throughout the adsorption is effectively the same in both cases and is associated with the same energy which is lower than that of the initial state and falls with increasing coverage. It is argued that the final state of the adsorbed layer on these metals at 273°k is independent of the temperature path.

Ponec studied that hydrogen displaced by oxygen from Mo surface;(18) adsorption of H_2 on iron precludes the slow chemisorption of nitrogen(19) etc. Oxygen was pre-adsorbed on Ni;(20,21) hydrogen subsequently admitted at 78°k did not react with the pre-adsorbed oxygen; it merely restricted subsequent adsorption of H_2 to an extent roughly proportional to the part of the surface which had been left unoccupied by oxygen. At room temperature an extensive interaction took place with the pre-adsorbed oxygen,(20,21) but only if some part of the surface had been left uncovered by oxygen adsorption. Interaction at 298°k and its absence at 78°k, is evidenced by two facts (a) change of the film resistance and of the work function at 298°k, which is after admission of hydrogen to surface with pre-adsorbed oxygen, the reverse of the normal change with clean surfaces. The extent of H_2 consumption was several times greater on surface with pre-adsorbed oxygen (if the extent of oxygen preadsorption was sufficiently great) than on clean surface of the same area. If no part of the surface is left free, consumption of the hydrogen decreases almost to zero, and no interaction can be detected by measuring the film resistance.

However, under analogous conditions, Quinn and Roberts(22) found a certain interaction by the work function measurement. If the surface of Ni is completely covered by oxygen, reaction of hydrogen with pre-adsorbed oxygen can take place at 273°k if hydrogen is atomized in the gas phase.(23) Platinum behaves in the same way, the only difference being that the reaction can be detected at 78°k. The extent of H_2 with pre-adsorbed oxygen at 273°k differs for various metals. On iron and Mo the extent is small, on Ni(20,21) and Mo(19) reaction stops after the pre-adsorbed oxygen had reacted to a degree, corresponding to a ratio H/O not much greater than unity. On Pt,(24) Pd,(25) oxygen and hydrogen can mutually react at 273°k without limitation and the product of reaction desorbs from their surface. On Cu(26) no adsorption of gaseous hydrogen takes place when H_2 had been atomized in the gaseous phase, it reacted easily with pre-adsorbed oxygen. This reaction can be repeated without restriction which means that, as with Pt and Pd, the product desorbs at 273°k from the surface and makes the continuation of the reaction possible.

Metals clearly differ in the products of interaction at 273°k

Where reaction can be repeated without limitation i.e. on Pd, Pt, Rh and Cu, the most probable product is desorbable water. With other metals, the reaction proceeds probably only to the stage of formation of the OH group. This is indicated by Fschlier(27) and C. Thompson.(28) The formation of the OH group at 273°k also agrees well with the fact that H_2O on the surface of Ni and Fe decomposes at 273°k with the formation of H_2 which is liberated into the gaseous phase.(29) The fact that even with atomized H_2 desorbable products do not form on Ni, Fe, and Mo at 273°k, shows that the addition of further H_2 to the OH group, which is the most probable product of interaction, is a difficult process and that water, which can be produced under suitable conditions, (e.g., Ni catalysts are used in industry for removal of traces of O_2 at low temperature), is probably formed by a mechanism other than that of the mere addition of H+OH.

The over-all order of the activity of metals Pt, Pd, Rh, Cu (H atoms) Ni, Mo, Fe, Cu, as derived from the temperature and other conditions under which H_2 and oxygen interaction takes place, is generally in good agreement with catalytic experience. There is no direct connection between the catalytic activity and the presence or absence of the positive effect on the film resistance against coverage plots, i.e. between catalytic activity and the various kinds of chemisorption bonds of hydrogen. The same conclusion holds also for other catalytic reactions of hydrogen.(30)

A homo-molecular exchange and the exchange with sorbed oxygen was studied on Pt, Ag, Pd, and Ni films by G.H. Boreskov(31) and he found that there is sorbed an amount of oxygen on Pt and Ag corresponding to several monolayers at 200°C.(32) The over-all amount exceeds the solubility of oxygen in the metal and it is probable that the sorbed oxygen penetrates into the surface layers of metal to some depth. The homo-molecular exchange of oxygen on Pt films proceeds with an observable rate at 200°C. The activation energy is 16 ± 2k cal/mole, and the order with respect to oxygen pressure is close to 0.5. A study of the exchange with the sorbed oxygen provides evidence for the non-uniformity of oxygen on Pt surface. The sorption heat varies between 13 and 24 k cal/mole over 25% of the monolayer, while the activation energy increases by 5 k cal/mole. The rate of a homo-molecular 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 homo-molecular exchange reaction proceeds on a small area, which is only 3% of the over-all Pt surface.(33) The rate of a homo-molecular exchange of O_2 on Ag films is one order of magnitude less than on Pt.(34) The study of the exchange with sorbed oxygen indicated that, in contrast to Pt, the surface is uniform at least over most of the surface.

The adsorption of oxygen, hydrogen and carbon-monoxide on evaporated Pd films was studied by S.J. Stephens.(35) The method used was to allow a monolayer of adsorbed gas to react with a second gas, added in small doses and to follow the reaction volumetrically and by analysis of the gas phase. He found in the Pd + O_2 +CO system that CO was found to react readily with a Pd-O_2 surface at 0°, forming CO_2 gas and adsorbed carbon-monoxide. Reaction continued until about 90% of the adsorbed oxygen had been removed from the surface as CO_2, after which further addition of CO resulted in an increase in CO pressure but little or no adsorption or reaction. The amount of CO_2 formed was directly proportional to the amount of CO added over the entire range of reaction. Some 86-92% of the adsorbed oxygen was removed from the surface as CO_2 during the course of the reaction. The O_2 which did not react may be held on the surface at sites of high binding energy, or may have penetrated beneath the surface of the metal and so be inaccessible for reaction. In the Pd + O_2 + H_2 system, S.J. Stephen(35) found that the uptake of H_2 by a Pd-O_2 surface was similar in some respects to that of H_2 by clean Pd. Hydrogen was taken up rapidly and both strong and weak adsorption were found. However, the amount of hydrogen taken up by a Pd-O_2 surface was considerably greater than that by a clean Pd surface, and is directly related to the amount of oxygen in the adsorbed layer.

J.G. Aston(36) has studied the chemisorption of hydrogen and oxygen on Pt black at low temperature by the titration method. The heat of adsorption of H_2 at 60, 120 and 273°k was measured as a function of coverage on Pt. Strong chemisorption of hydrogen takes place at low coverages even at very low temperatures. Between 90 and 100°k physically adsorbed hydrogen undergo a transition to weak chemisorption. Weak chemisorption takes place on bare Pt-sites where strong chemisorption can no longer proceed. At sufficient high temperatures, weakly chemisorbed H_2 can transform into strongly chemisorbed hydrogen.

According to Eley, Moran and C.H. Rochester(37) hydrogen adsorbed on Pt silica gives infra-red bands at 2040 and 2120 cm^{-1}, and on Pt - alumina at 2040 and 2110 cm^{-1}. The 2110-2120 band is much enhanced by treatment by oxygen, and adsorption-desorption behaviour together with deuterium shift establish the band as due to weakly adsorbed H_2. It is proposed that the hydrogen is adsorbed on Pt oxide patches, possibly on Pt (38) surface ions. The effect of oxygen pretreatment is to reduce or remove the 2040 band, which however, slowly appears in the presence of water, more quickly for H_2 plus water, in either order, for Pt-silica. On Pt alumina the addition of water is not necessary to observe this band. It is suggested that the 2040 band is due to H atoms chemisorbed on Pt and H bonded to an adjacent OH . This may be formed by dissociative chemisorption of water, or even by OH ions diffusing from the adjacent support for alumina. Experiments on CO rule out any possible impurity effects due to this gas. The bands observed agree with the observations of Eischens and Pliskin.(39) These workers have measured the infra-red spectra of the chemisorbed species when hydrogen and deuterium are adsorbed on Pt, and concluded that weakly bonded H_2 is adsorbed as atoms on the top of, and essentially covalently bonded to the surface Pt atoms. The infra-red data gave no information about the polarity of the Pt-H bond.

Eley and Rochester(37) confined discussion to the Pt-H interface in the absence of other chemical species. However, the infra-red data were obtained for metal samples in which the Pt (9% by weight) was distributed in a α-alumina support. Pliskin and Eischens reported that, with silica-supported Pt samples, absorption peaks due to adsorbed hydrogen were observed at the same frequencies but at lower intensities than for the alumina supported samples. This suggests a possible involvement of the support in the chemisorption process. During the course of measurements of the infra-red absorption bands attributed to chemisorbed H_2 it became clear that pre-adsorbed oxygen or water were having some effect which was therefore also quantitatively investigated.

The adsorption of hydrogen, oxygen and CO on Pt-on-alumina re-forming catalysts and on the alumina base was investigated by Gruber.(40) By means of hydrogen adsorption the Pt surface area of freshly prepared samples was found to be 200 to 270 cms^2/g. of Pt. The decrease of Pt dispersion due to heat treatment of catalysts is shown. Several catalysts were subjected to complete oxidation-reduction cycles and the amounts of hydrogen and oxygen taken up in the different steps of such a cycle were measured. A probable mechanism for the oxidation-reduction cycles was established. The mechanism of CO adsorption on supported Pt was found to depend not only on the nature of the support but also on the degree of dispersion of the metal. The fraction of CO adsorbed in the bridged structure decreases with decreasing metal dispersion.

The reaction of hydrogen at room temperature with oxygen adsorbed on supported and unsupported Pt catalysts has also been studied by Boudart,(41) and used to measure the surface area of the metal. His work shows that the volumetric titration can be performed with Pt supported on alumina, which absorbs the water formed. Since three hydrogen atoms are consumed for each accessible Pt atoms, there is a threefold increase in sensitivity over direct hydrogen chemisorption and more than a 50% increase over CO chemisorption. Because the sample is deliberately exposed to oxygen there is no need to exclude oxygen from the sample, and the sample need not be completely reduced prior to measurement. Because of the small blank on the alumina support, the method used by Boudart offers a distinct advantage over conventional adsorption techniques with hydrogen and carbon-monoxide on pre-reduced samples. The advantages appear decisive in the case of samples containing small amounts of platinum.

CHAPTER 2

APPARATUS AND EXPERIMENTAL PROCEDURE

1. Materials

Gases:

Oxygen

Oxygen was prepared by heating B.D.H. analar potassium permanganate crystals, which had been outgassed; after flushing with oxygen, it was stored in a litre flask connected to U-tube manometer.

Krypton, Carbon-monoxide and Hydrogen

These were obtained from British Oxygen Company in sealed glass ampoules. Hydrogen was purified for each experiment by diffusion through an electrically heated (325°) silver-palladium thimble. The other gases were used without further purification except to pass through a liquid nitrogen-cooled trap before being closed into the system. The supplier gives the purities of these "Grade X" gases as:

H_2 not less than 99.9995% pure
CO not less than 99.9% pure
K_r not less than 99.99% pure

Ammonia

Ammonia was purified on a separate apparatus; it was obtained from a cylinder of gas supplied by Imperial Chemical Industries. About 700 ml of gas were transferred to a litre bulb by freezing out by liquid nitrogen in a side arm of a storage bulb. Before being dosed on the film, it was passed through a trap cooled to 195°k, after low-temperature vacuum distillation.

Water

Pure water was obtained by distillation from a solution of potassium permanganate in distilled water. About 50 ml were introduced into a 150 ml flask which was then joined to the vacuum apparatus. After a preliminary outgassing with cardice bath around the water flask, the water was subjected to a melting-freezing procedure during which time it was being evacuated by the pump. It was stored in a bulb containing purified glass wool to increase the surface area from which evaporation could proceed.

Methyl Alcohol

Pure A.R. methyl alcohol was provided by James Burrough Ltd. It was purified by freezing in a liquid nitrogen bath, and then using melting-freezing procedure with evacuation. This operation was repeated three times.

Metals

Spectroscopically pure metals were supplied by Johnson, Matthey and Company Limited. Platinum and iridium wires were used for film deposition. Tungsten wire was supplied by Murex Limited.

2. Description of the Apparatus

The apparatus used for the subsequent experiment was constructed of pyrex glass and it is shown diagrammatically in (Fig. 1). It was housed in a movable, rectangular box on wheels; it was constructed from Dexion angle 225 and measured 4 feet, by 2 feet, by 2 feet 6 inches. The top of this frame-work 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 feet high and 13 inches diameter was constructed which could be lowered over the vacuum line to rest on the insulating top sheet of the Dexion frame.

The furnace consisted of an innermost cylindrical steel former and two co-axial asbestos cylinders. 16 S.W.G. michrome 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 main pumping leads were of 25 mm diameter to facilitate rapid evacuation and the rest of the apparatus was made from 6 to 12 mm internal diameter tubings.

The Pumping System

The vacuum system comprised the cell, Pirani gauge and glass valves. It was evacuated by two high speed annular-jet mercury-diffusion pumps, backed by a two stage rotary oil pump.

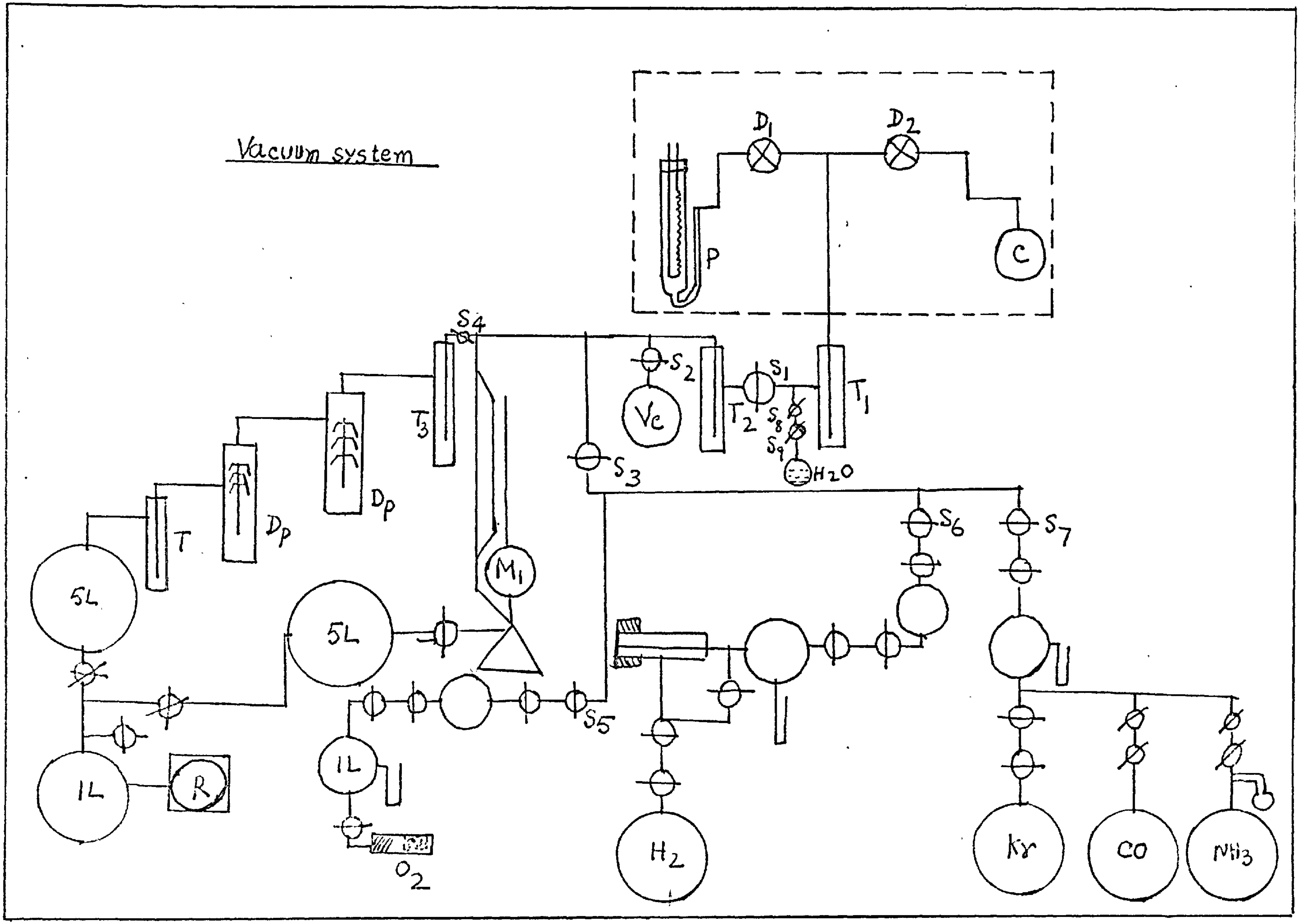

Vacuum system
D1
D2
P
C
S4
S2
S1
T1
T2
T3
Vc
S8
S9
H2O
S3
T
Dp
Dp
S6
S7
5L
5L
M1
S5
1L
1L
R
O2
H2
Kr
CO
NH3

Fig 1.

The cell could be isolated from the pumping system by a system of magnetically operated glass ball-joined valves D_1 and D_2 (Dekker 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 300° by means of electrical heating taps.

The Gas Dosing System

The dosing system consisted of four glass stopcocks joined end to end; the first two being separated from the last two by a glass bulb (200 cms^3). The pressure of the gas in the volume defined by the first two taps was roughly measured on a mercury monometer. Gas in this volume was expanded into the large bulb and a small volume (2.9 cms^3) isolated between the last two taps. This dose was then admitted to the vacuum system (the section defined by the stopcocks S_1, S_2, S_4, S_5, S_6, and S_7) and accurately measured by the McLeod gauge (M_1) and then further expanded up to the Dekker D_1 by opening the stopcock S_1. Doses of different sizes from 4.5×10^{-6} mole could be accurately introduced.

The Pressure Measurements

McLeod Gauge

The McLeod gauge and Pirani gauge were used for the measurement of pressure in the system. One mm diameter precision capillary tubing was used for the McLeod gauge for the pressure range 10^{-6} to 10^{-1} torr.

Pirani Gauge

The Pirani gauge was primarily intended for use in rate measurements (Fig. 2). It 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 (1.5 mm diameter), care being taken to avoid twisting of the wire during the stretching of the filament. The tungsten support rods were glass coated as far as possible and were held in pinched or button glass metal seals. 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. For use with water vapour, the gauge and trap T_1 were immersed in ice bath and for CO_2 calibration the gauge and all the traps were at cardice bath (195^{o}k) except the trap T_3 which was at liquid nitrogen temperature and was out of the system (near the diffusion pump).

The measuring circuit was a simple 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 300v. The ratio of the fixed arms was 20 to 1; a Pye scalamp galvanometer (cat. no. 7893/5) of 210 mm/uA sensitivity was found sufficiently sensitive for use in the measuring circuit.

The Pirani zero, Ro was the resistance of the filament at

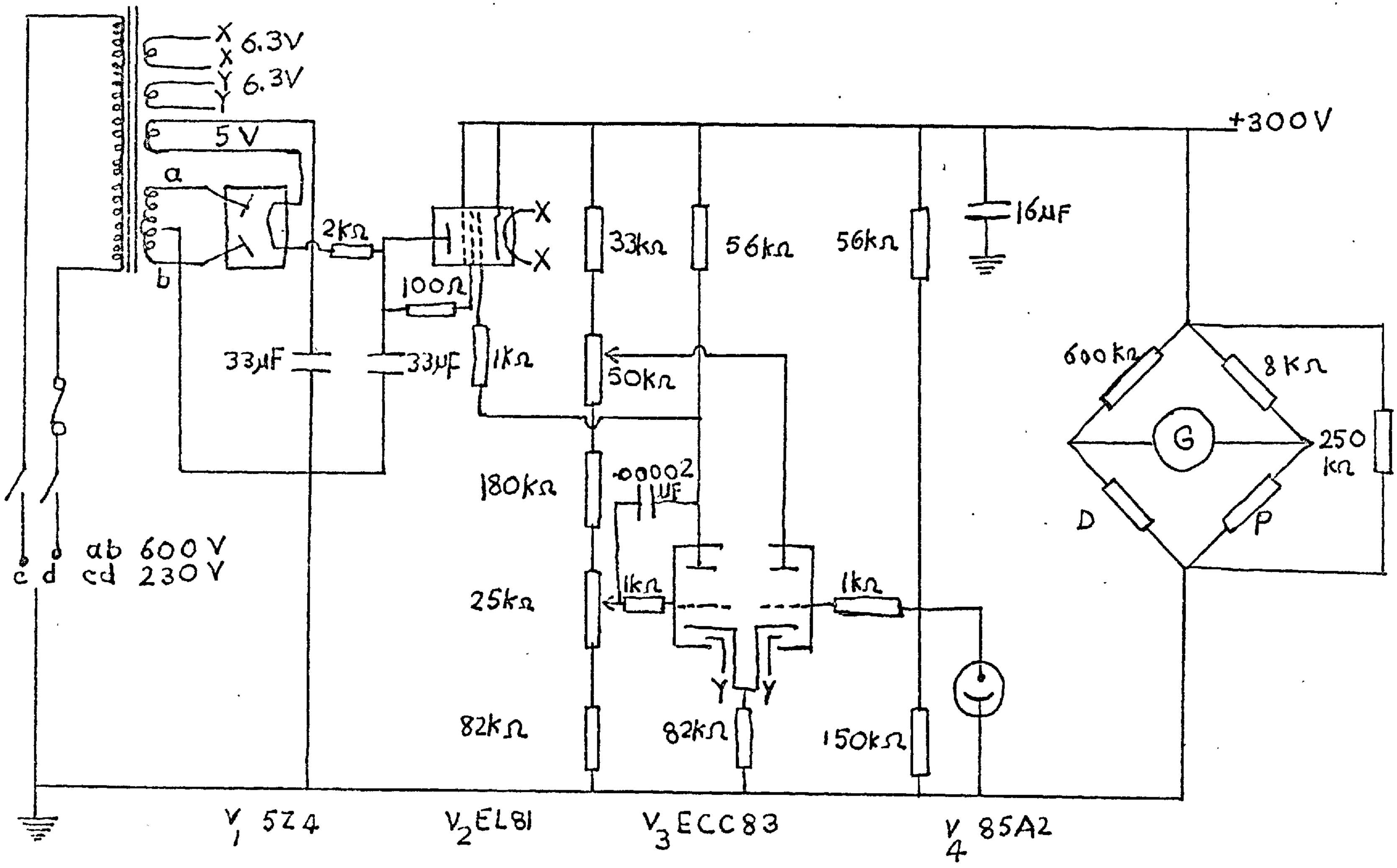


Fig. 3 Pirani circuit.

sticking vacuum of the McLeod gauge (10^{-6} torr) and 78°k. Equilibrium and stability were established after about 45 minutes, after switching on the current supply. No fluctuation in the zero value was evident during the experiments, but a change of Ro of about ±10 ohms occurred over a few weeks. It could be returned to its original value by suitable outgassing of the tungsten filament. Overheating of the gauge ($>450^{\circ}$) was always avoided.

In calibration $\Delta R = (Ro - R_1)$ where R_1 is the resistance corresponding to a gas pressure (P_1) measured on the McLeod pressure. During every run sufficient McLeod readings were taken to check the calibration. The sensitivity of the gauge decreased rapidly above 9×10^{-3} torr, above which pressure all measurements were taken by the McLeod. The Pirani gauge was also used as an analyser of oxygen-hydrogen mixtures (Fig. 4). It was calibrated for different oxygen and hydrogen mixtures of known composition against McLeod readings at different pressures; any gas sample could be analysed by taking simultaneous Pirani readings and a McLeod readings and, comparing them with known calibration curves either directly or by intrapolation. The gauge was also calibrated for water (Fig. 5) by putting different temperature baths around the cell (containing H_2O) and an ice bath around the Pirani and trap T_1 (273°k). It was also calibrated for carbon-dioxide (Fig. 6).

The Reaction Cell

The reaction cell consisted of a cylindrical neck with a

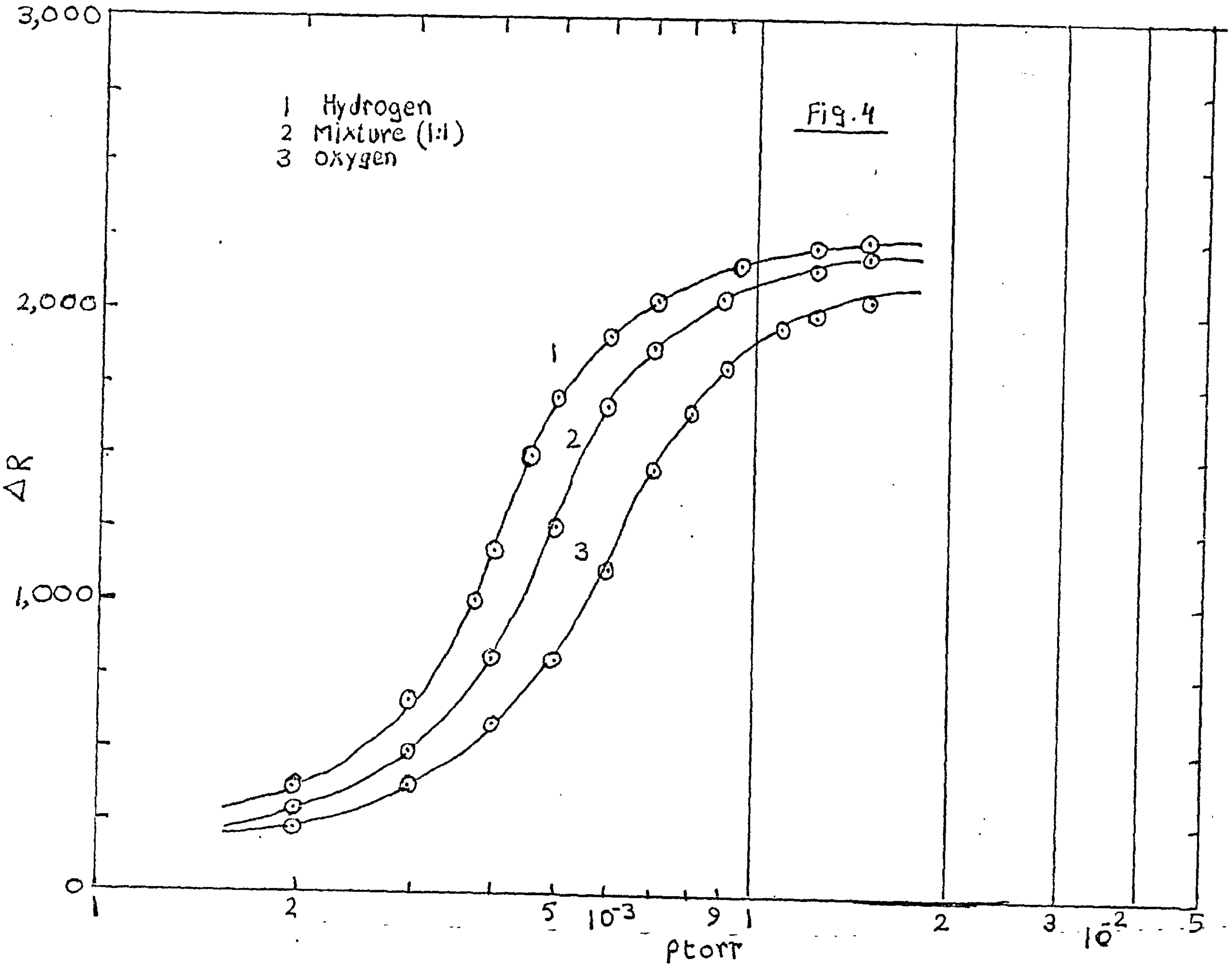

3,000
2,000
1,000
0
ΔR
1 Hydrogen
2 Mixture (1:1)
3 oxygen
1
2
3
1
2
5
10^{-3}
9
1
2
3
10^{-2}
5
ptorr

Fig. 4

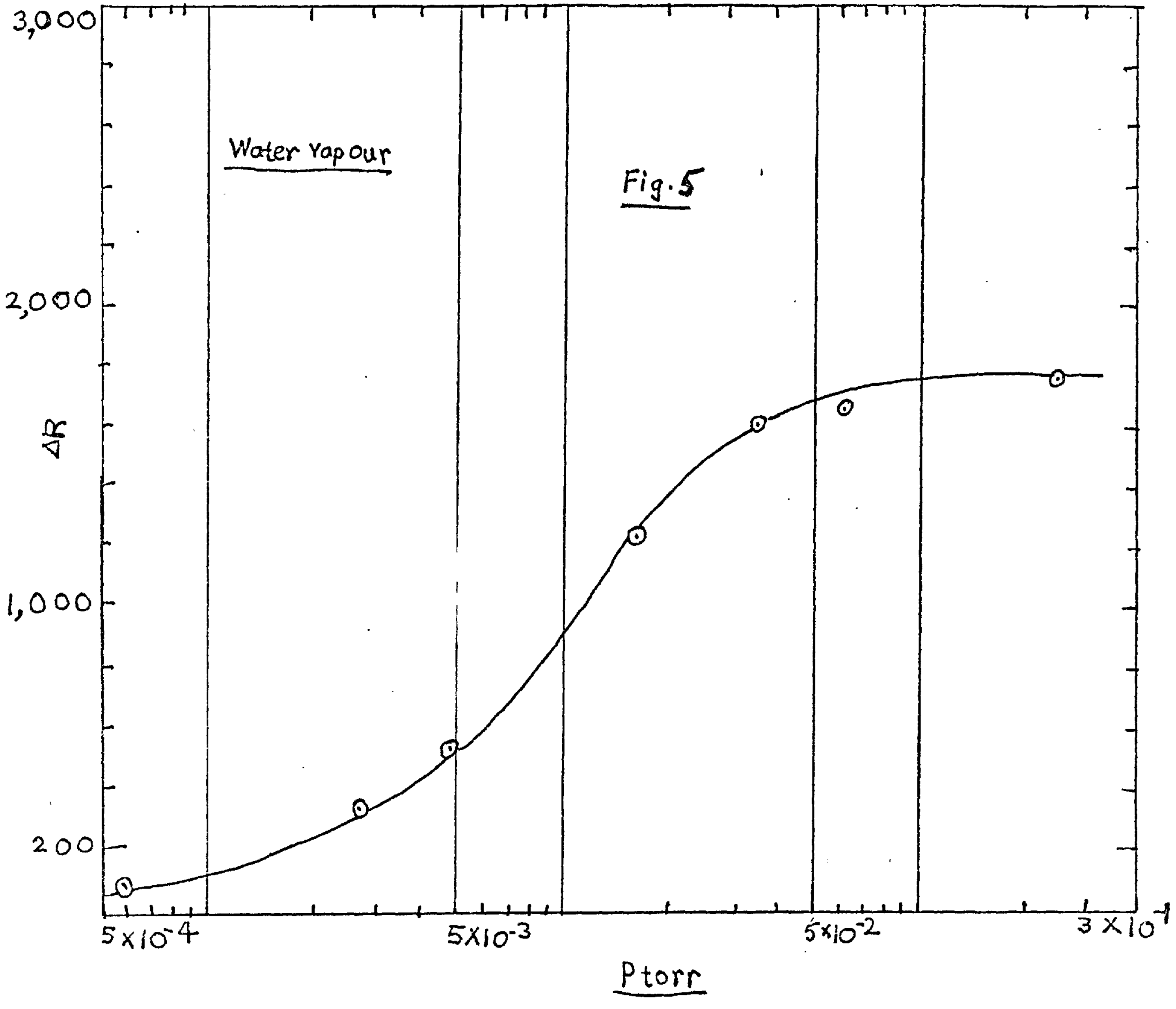
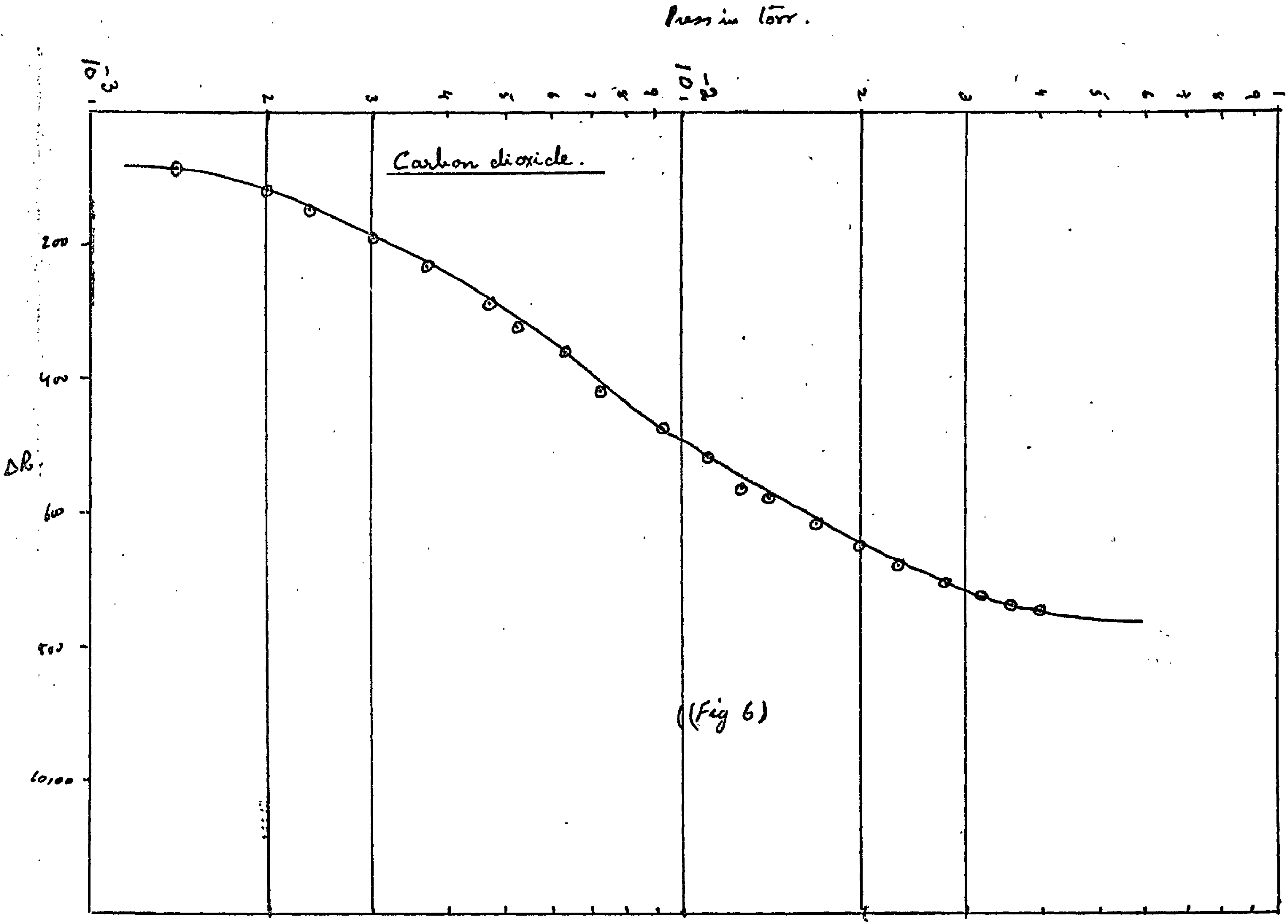


Fig. 5


Press in torr.
10⁻³
2
3
4
5
6
7
8
9
10⁻²
2
3
4
5
6
7
8
9
1
Carbon dioxide.
ΔR.
200
400
600
800
10,000

((Fig 6)

side arm of 12 mm diameter and a bulb of 250 cms^3 (Fig. 2). Two tungsten rods of 2 mm diameter that would safely carry 10 amps current were used. To replace the filament, the neck was cut and the film was removed by hydrofluoric acid; then it was thoroughly washed and dried and a filament, previously cleaned by A.C. electrolysis in sodium hydroxide, was spot welded to the tungsten rods via nickel clips and finally the cell was sealed to the system. Iridium and tungsten films were deposited directly (0.5 mm and 0.25 mm respectively diameter), but for platinum the throwing filament was spiral of the metal wire mounted via nickel strips to 2 mm tungsten rods. The evaporation current was supplied from a heavy duty stepdown 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 recorded the film deposition current.

3. Calibration of the Volumes of the System

McLeod Gauge

Cross-section of the capillary of McLeod Gauge (M_1) = $7.84 \times 10^{-3} cms^2$

Volume of the bulb = 202.5 cms^3

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

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

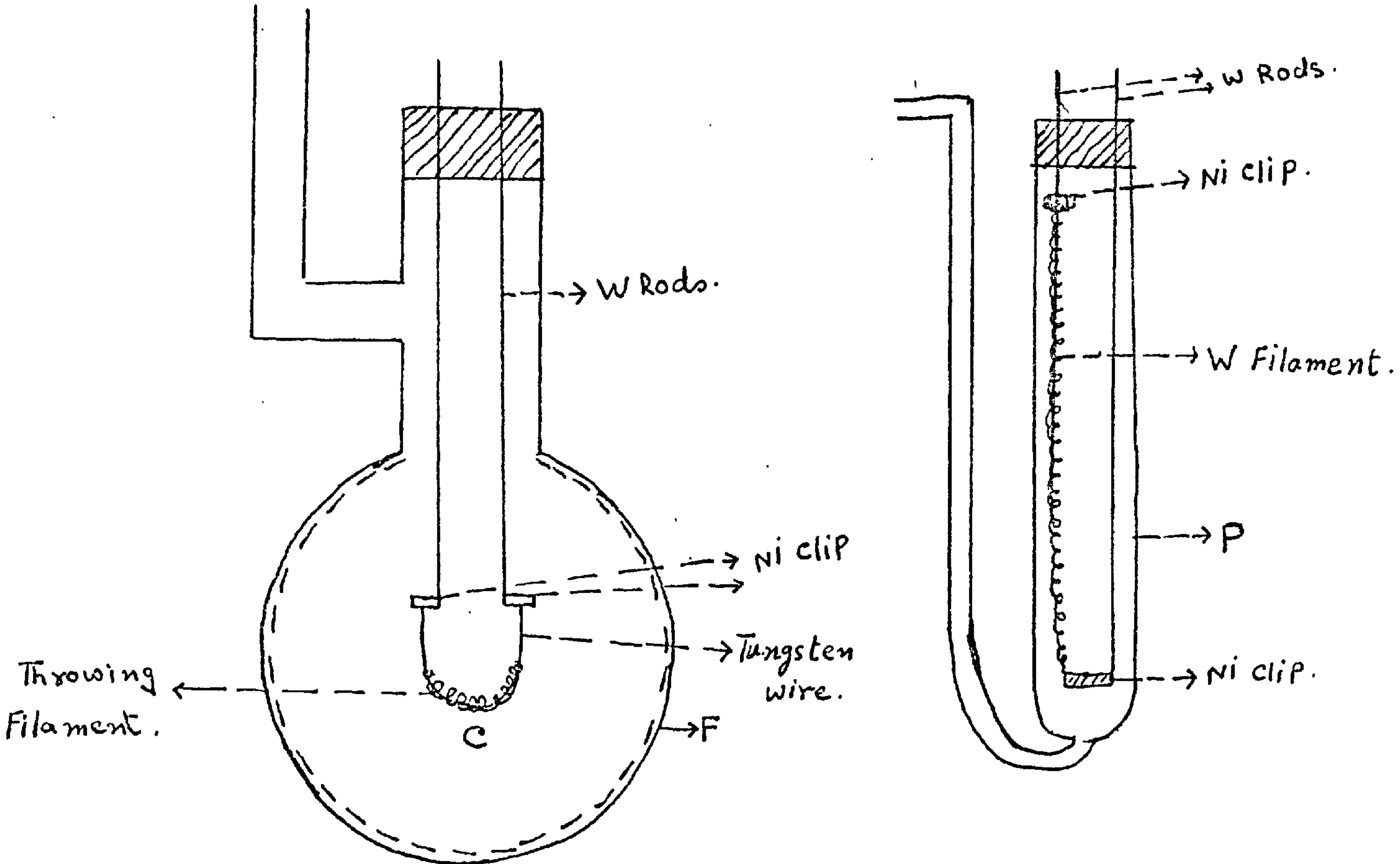

W Rods.
Ni clip
Tungsten wire.
Throwing Filament.
C
F
W Rods.
Ni clip.
W Filament.
P
Ni clip.

Fig. 2

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 up to within one percent.

Volume Calibration of the System

The volume of different sections of the system were measured by gas expansion from a bulb (544.7 cms^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 up to the cell with Pirani (P) and Dekkers D_1, D_2 and the water vessel with two stopcocks (S_8 and S_9).

For volume calibration hydrogen gas was used. It was allowed to enter the system with the stopcock of the calibrated bulb (C) open and the pressure was measured by the McLeod (P_1). The stopcock of the bulb (C) was closed and the rest of the apparatus (whose volume was to be calibrated was evacuated. The pressure was recorded on the McLeod (P_2). Now the stopcock of the bulb (C) was opened and the pressure recorded on McLeod (P_f). The relevant data were obtained and the volume V_2 calculated from

$$V_2 = \frac{V_1(P_1 - P_f)}{(P_f - P_2)}$$

where V_1 = the volume of the calibrated bulb (544.7 cms^3).

The apparent volumes of different sections of the system immersed in cold traps were measured by the above method.

To calculate the number of moles in the gas phase at any pressure the following constants have to multiply by equilibrium pressures units.

$C_{(I)}$ 78°k = 3.78×10^{-5}

$C_{(I + II)}$ when cell and Pirani was at 78°k = 9.91×10^{-5}

$C_{(I + II)}$ when cell was at 195°k and Pirani was at 78°k = 9.00×10^{-5}

$C_{(I + II)}$ when cell was at 273°k and Pirani was at 78°k = 8.2×10^{-5}

$C_{(I + II)}$ when cell was at 328°k and Pirani was at 78°k = $8{,}094 \times 10^{-5}$

$C_{(II)}$ when cell and Pirani both were at 195°k = 5.063×10^{-5}

Temperature Baths

The following organic liquid cooled to their melting points by liquid nitrogen were used to obtain temperatures below 273°k.

TABLE 1

Cold Temperature Baths

Baths	Temperature °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 Diethyl Molonate	223.2
Melting Methyl Benzoate	260.6
Melting Ice	273.0

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

4. Experimental Procedure

The cell used for a previous experiment was cut off and the evaporated film removed by dissolution in moderately concentrated nitric acid. Platinum, and iridium adhered strongly to the glass, consequently the cell was rinsed with dilute hydrofluoric acid. The acid did not appear to dissolve these metals but merely lifted them from the glass substrate. Then the cell was repeatedly washed with distilled water. The filament to be evaporated was prepared by winding a spiral of the wire, generally three turns of diameter about 5 mm. Pt was evaporated from a filament of tungsten wire (0.3 mm) around which was wound the Pt wire. The tungsten wire used for this purpose was electrolysed in a dilute caustic solution to remove any surface impurities. It was then rinsed in distilled water, dried on absorbent paper. This filament was spot welded between a pair of nickel clips on the tungsten rods as shown in the (Fig. 2). Details of the filaments used are given in the Table 2.

TABLE 2

Metal	Diameter in mm	Current in A	
		Outgassing	Throwing
Platinum	0.1 (on 0.3W)	6.4	8.0
Iridium	0.5	11.0	14.5
Tungsten	0.25	6.9	9.0

Outgassing

After fitting a weighed filament on the nickel sleeves and sealing the cell, the system was evacuated to 10^{-5} mm Hg, and the outgassing heaters were switched on. The cell, Pirani and greaseless Dekkers values were baked out with the aid of the furnace. Sections outside the furnace were at the same time heated with heating taps. The temperature of the entire system starting at the throat of the diffusion pump was raised slowly. All the greased stopcocks were protected against the 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 taps of traps T_2 and T_3 near the diffusion pump 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 the current to all heating taps was turned off and all traps were cooled 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 gauge. When the pressure was less than 10^{-6} 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.

Film Throwing

Prior to throwing the film, traps T_2 and T_3 near the difusion pumps were cooled in liquid nitrogen. At that point the furnace was allowed to cool slowly after baking the system for twelve hours, so that the mercury vapour was condensed from the reaction section. Liquid nitrogen was placed around the third trap T_1, and the furnace removed and the Pirani was immersed in liquid nitrogen bath. The current to the gauge was switched on to allow a steady state to be attained. The cell was immersed in the cooling bath (either 78^{o}k or 325^{o}k) and the current of the filament was slowly increased until evaporation proceeded with the cell still open to the pumping system. For platinum and tungsten the temperature of the bath used for throwing film was 325^{o}k and for iridium was 300^{o}k. The duration of evaporation and current was carefully controlled so that similar films could be deposited every time.

5. 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 78^{o}k or at 195^{o}k which was different from the rest of the system. The necessity of such correction has been demonstrated by Tompkins and Wheelar(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 Keeson,(9) which was later developed.(10)

Finally Bennett and Tompkins(11) suggested some modifications to Liang's empirical equation.

$$\frac{P_1}{P_2} = R = \frac{\overset{\alpha}{He}\, g^{(f\phi x)^2} + \overset{\beta}{He}\, g^{(f\phi x)} + Rm}{\overset{\alpha}{He}\, g^{(f\phi x)^2} + \overset{\beta}{He}\, g^{(f\phi x)} + 1}$$

where R = the ratio of the pressures in the two regions at temperature T_1 and T_2.

$Rm = ({}^{T_1}/T_2)^{\frac{1}{2}}$

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

$X = P_2 d$

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

$\overset{\beta}{He} = 7.88(1 - Rm)$

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 ϕg values may be calculated from the collision diameter, ro, given by Hirschfelder, Bird and Spotz$^{(12)}$, by making use of the equation.

$$\log ro = 0.43 + 0.24 \log \phi g$$

The calculated values for P_1/P_2 are plotted in (Fig. 7, 8, 9) against $\log P_2$ for oxygen, hydrogen and krypton respectively for various pressure and temperatures.

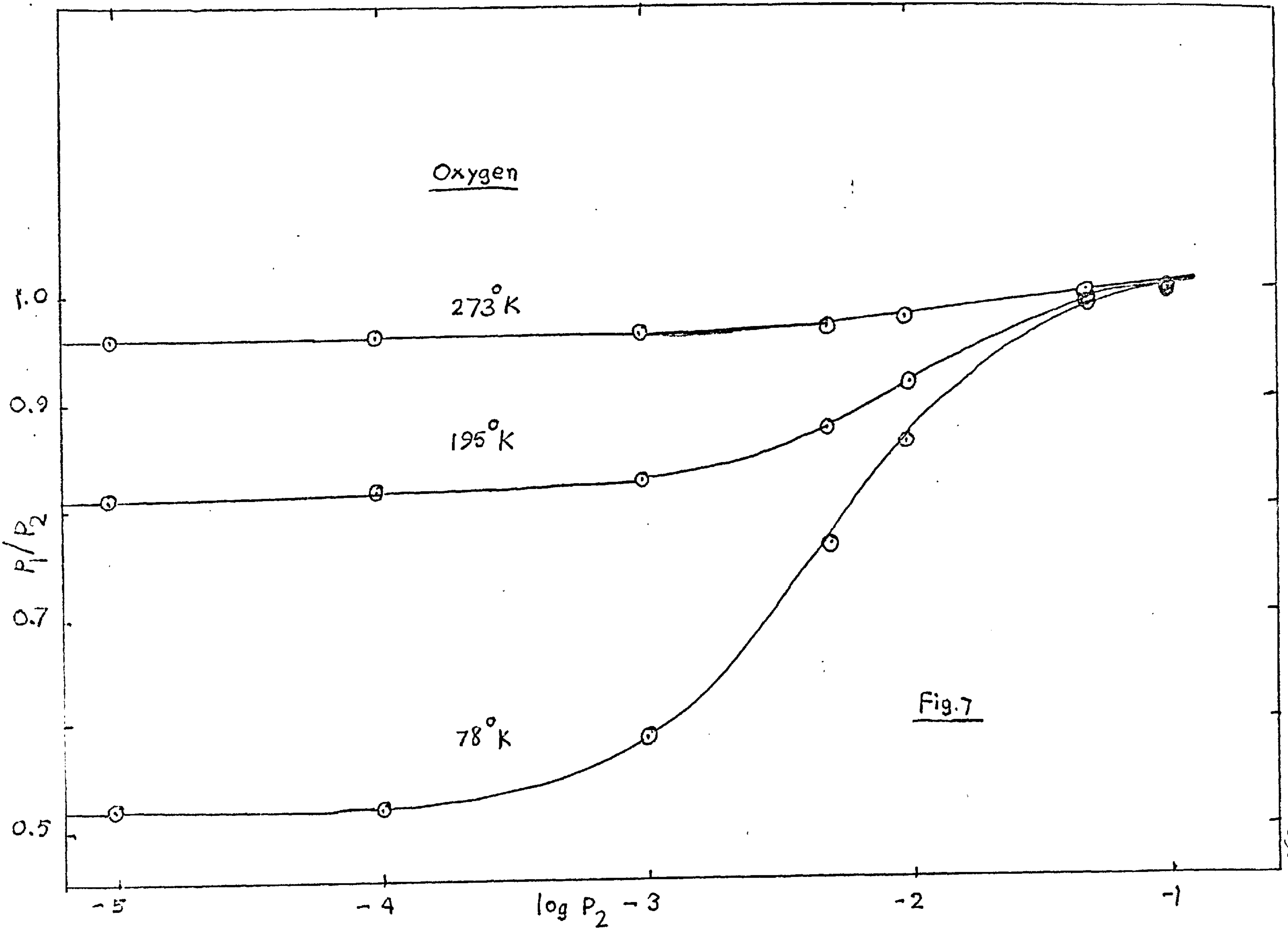


Fig. 7

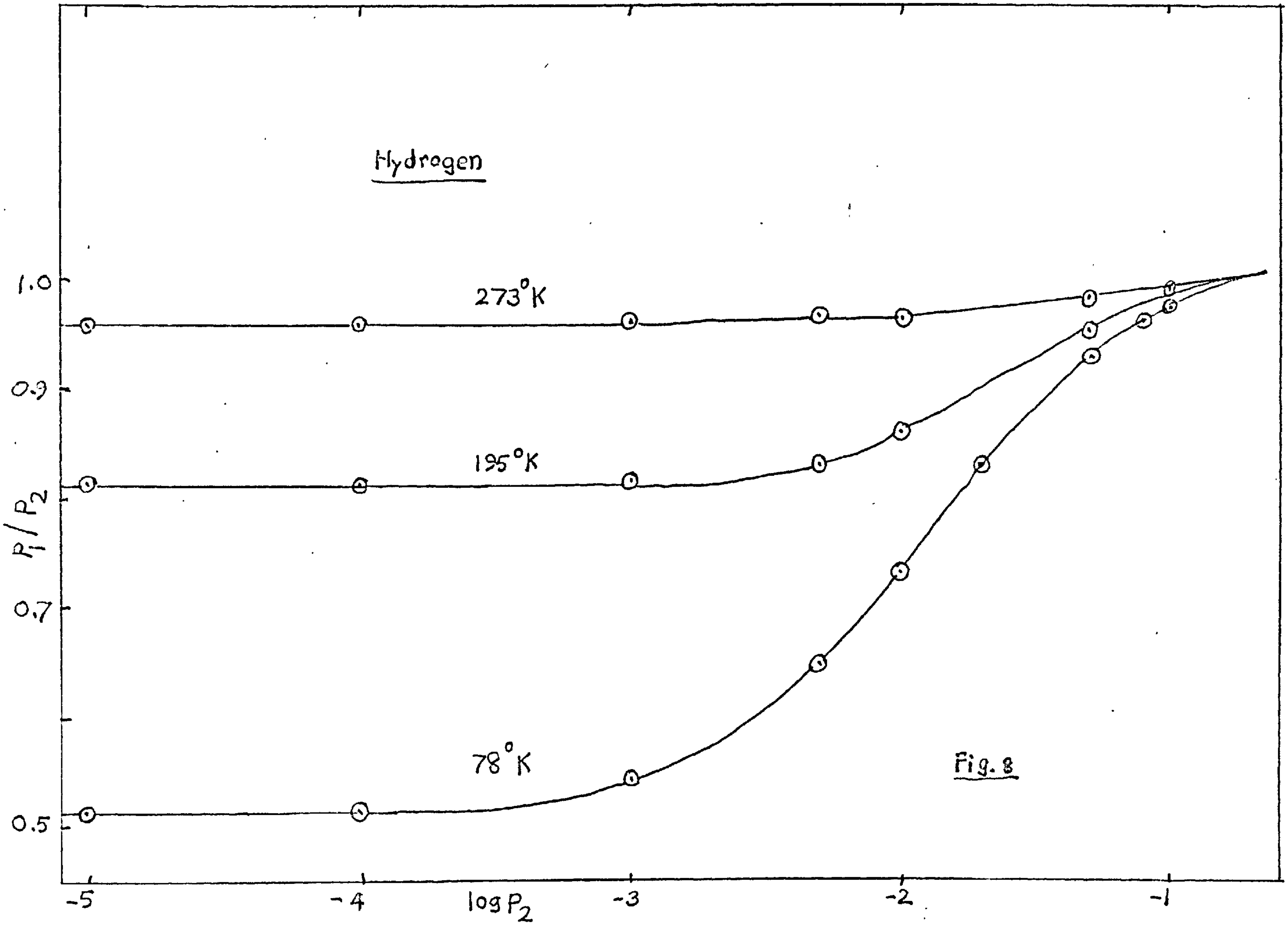
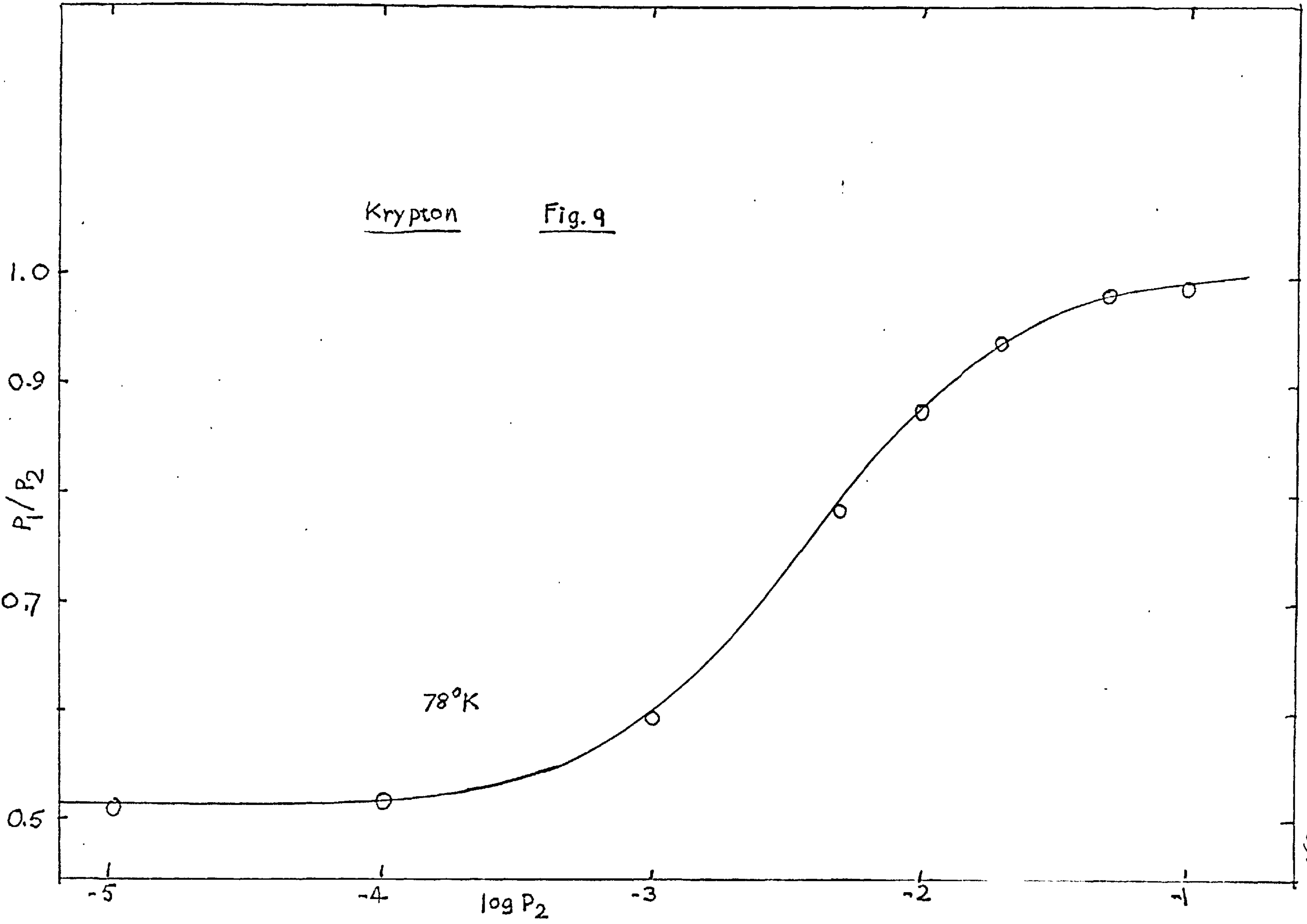


Fig. 8



Krypton Fig. 9

6. Surface Area Measurements

The surface area of the metal was determined using the B.E.T. equation for multilayer adsorption,(13) the equation is

$$\frac{P}{V(Po-P)} = \frac{1}{VmC} + \frac{(C-1)P}{VmC(Po)}$$

where V = Volume adsorbed at a pressure P

Vm = Volume necessary to form a monolayer

Po = 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 $P/_{V(Po-P)}$ against $P/_{Po}$, the volume Vm can be calculated. One typical B.E.T. isotherm for Pt and Ir is shown in (Fig. 10,11). While the basic assumptions of the isotherm have been criticised by Hill,(14) there is considerable evidence that the values of Vm obtained by Harkins and Jura(15) with weakly physisorbed molecules on hetrogeneous surface are acceptable.

The Krypton adsorption at liquid nitrogen temperature was used for determination of small surface areas(16,17,18) (by B.E.T.) which was comparable with those of Keely(19) and Lincoln and Carnevale(20) by a rapid X-ray line broadening technique.

The cross-section of a Krypton molecule has been determined by various workers(16,20,22) based on the accepted cross-section of nitrogen molecules as $16.2A^{o2}$. Beebe, Beckwith and Honing(21) have

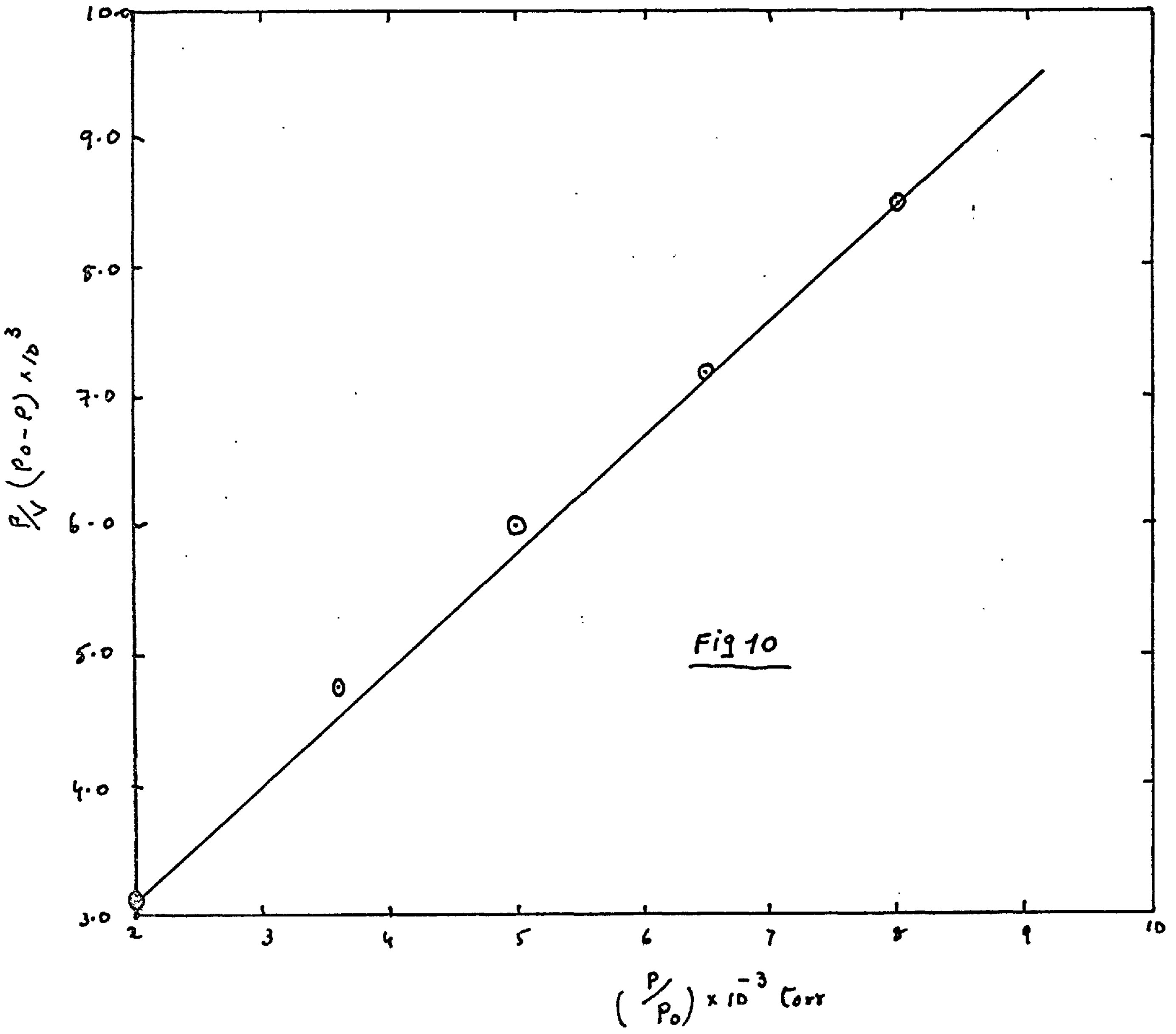


Fig 10

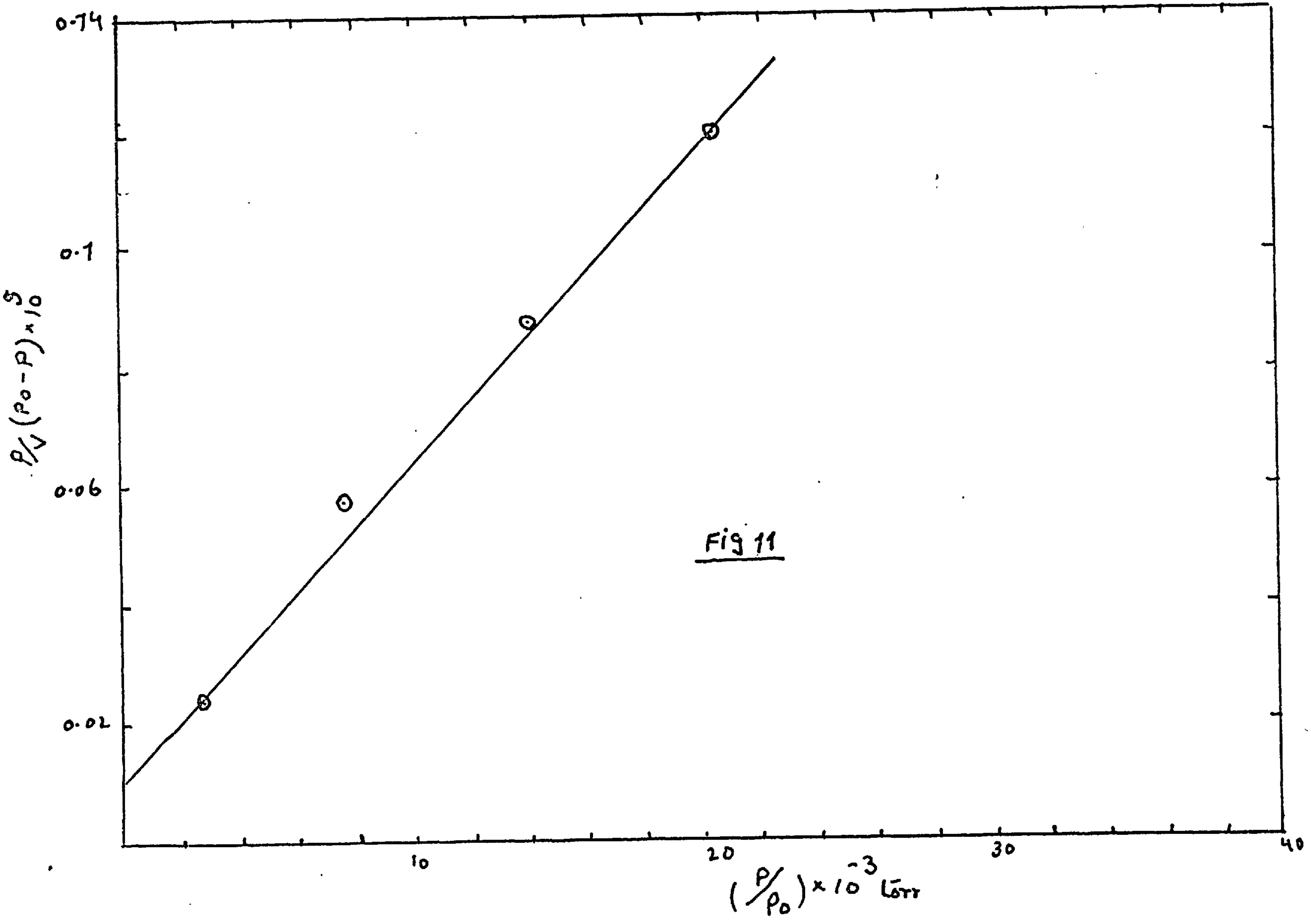


Fig 11

determined the surface area of an anatase sample obtained from Harkins and found the cross-section of a krypton molecule as $19.5 \pm .4 A^{O2}$.

Beebe$^{(21)}$ 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 Kr ranged from 2.63 to 3.72 torr. A value of 1.75 torr has been found by Kingston and Holmes.$^{(23)}$ However, due to the low values (10^{-2} torr) of the working pressures, the value of Po has little effect$^{(24)}$ on the values of the surface area measurements. The values of Vm by B.E.T. methodwere always found higher than those of "point B" method.

Vm was obtained in units of moles and transformed to surface areas using $19.5 A^{O2}$ for the cross-section 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 and was calculated as follows:

No. of sites per cms^2 for f.c.c. metal $\frac{1.91}{a^2} \times 10^{16}$. The calculated values are given in the table below.

Metal	Crystal type	a	$[\text{sites/cms}^2] \times 10^{15}$
Pt	f.c.c.	3.92	1.24
Ir	f.c.c.	3.83	1.30
W	b.c.c.	3.16	1.91

The lattice parameters are taken from F. Seitz "Modern Theory of Solids" McGraw Hill, N.Y. (1940).

CHAPTER 3

RESULTS AND DISCUSSION

PLATINUM

1. System: Oxygen + Platinum + Hydrogen

The interaction between oxygen and hydrogen on evaporated platinum films has been studied mainly at 195°k. The film was deposited from a clean tungsten core at a bath temperature (50-55°C). The deposition time was approximately one hour and the current through the filament was eight amperes. This current was much less than that needed to evaporate tungsten (11 amperes).

After evaporation the film was cooled to cardice bath temperature (195°k) and measured doses of oxygen were admitted to the cell until the rate of the slow process became negligible (time $\sim$ 20 minutes); it was then assumed that the film was saturated with oxygen and the remaining gas-phase was removed by rapid evacuation in less than two minutes. A measured dose of hydrogen was then introduced; some 95% of the final amount was taken up instantaneously and the remainder in the subsequent slow process. At that stage the uptake of hydrogen was approximately three times the amount of oxygen on the film. The residual hydrogen was evacuated and the cell was heated at 60°C with the pump isolated. Any water produced was condensed in the Pirani gauge and trap T_1 and later vapourized. The amount of water vapour was first measured on the McLeod gauge but the amount obtained was very small due to its adsorption on the glass surface of the apparatus, whose volume was approximately 1500 ml. Consequently the water produced was vapourised at (60-65°C) into the Pirani and trap T_1 only and its vapour pressure measured by a Pirani gauge which had been calibrated for water vapour with the cell in the temperature range (60-65°C). In this case the volume of the system was reduced to 850 ml after isolating the section I.

Run 5

Bath temperature = 195°k

Oxygen Adsorbed		Hydrogen Adsorbed	
moles	atoms	moles	atoms
45.5×10^{-8}	91	132.0×10^{-8}	264
58.0	116	115.5	231
53.5	107	113.0	226
54.4	109	110.0	220
56.3	113	108.0	216
53.8	108	106.0	212
49.5	99		
371.0×10^{-8}		684.5×10^{-8}	

Total water formed at the end of all cycles = 520 x 10^{-8} moles.

Run 6

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
59.0 x 10^{-8}	118	166.8 x 10^{-8}	234
72.9	146	134.0	268
68.5	137	143.0	286
70.4	141	142.6	285
69.0	138	134.8	270
65.5	131		
405 x 10^{-8}		721.2 x 10^{-8}	

Total water formed at the end of all cycles = 520 x 10^{-8} moles.

In run 5 oxygen was adsorbed on a fresh Pt film at 195°K. After the evacuation of the residual oxygen, hydrogen was adsorbed on the oxygen-treated surface. This O_2/H_2 treatment is called an O_2/H_2 cycle. In run 5, six O_2/H_2 cycles were done and the sixth cycle was finished with hydrogen treatment. Water was measured at the end of all cycles. Similarly in run 6, oxygen was chemisorbed on a fresh Pt film at 195°K and 5

O_2/H_2 cycles were done at that temperature. The last cycle was finished with oxygen treatment. The water was measured at the end of all these cycles.

Explanation

In run 5 the amount of oxygen adsorbed on a fresh Pt film at 195^{o}k was 45.5×10^{-8} moles. It is assumed that the O_2 is dissociative adsorbed as chemisorbed atoms, so that there are 91 x N sites on the Pt surface, where N is Avogadro's number. We shall therefore abbreviate the description of the site number to 91 (i.e. by omitting N throughout). The surface was assumed to be covered completely with O atoms. The amount of H_2 on the oxygen-treated surface was 132×10^{-8} moles. According to Gruber(1) and Boudart(2) the uptake of H_2 by a Pt surface is greatly increased by the pre-adsorption of a O_2 monolayer. This is attributed to the reaction,

$$Pt - O + 3/2\ H_2 \longrightarrow Pt - H + H_2O$$

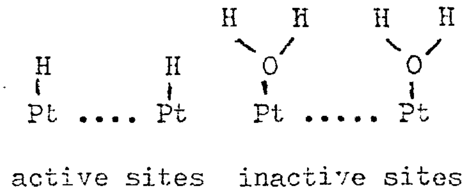
The water was adsorbed on the support in their work but condensed out in liquid nitrogen in the present work. From this reaction the ratio of hydrogen "adsorbed" to that of the pre-adsorbed oxygen should be 1:3, leaving a surface saturated with hydrogen atoms. In the second adsorption of oxygen we assume that these were oxidised to water and the surface to be then saturated with oxygen atoms. After each dose of hydrogen the surface may be represented as

H   H   H   O   O   O
| | | | | |
Pt Pt Pt, and Pt Pt Pt after each oxygen treatment.

Hence the oxygen taken up in the first two doses should be equal to ½ (total hydrogen taken up in these two doses minus that left on the surface, which represented ⅓ ratio of the first dose) e.g., in run 5, oxygen taken up in first two doses is equal to $45.5 + 58 = 103.5 \times 10^{-8}$ mol. This value should be therefore equal to $\frac{1}{2}\left[132 + 115.5 - 132/3\right] = 103.0 \times 10^{-8}$ mol (that is, a good agreement). In run 6 the comparitive figures were 131.9×10^{-8} mol and 123.0×10^{-8} mol. In run 5 the amount of oxygen adsorbed on a fresh film was 45.5×10^{-8} mol and the amount of hydrogen adsorbed subsequently was 132.0×10^{-8} mol, so the ratio between that oxygen and hydrogen doses was 1:2.9 in run 5 and 1:2.82 in run 6. Finally, the ratio between oxygen and hydrogen was always approximately 1:2 in all H_2/O_2 cycles except for the first cycle. The total amount of oxygen used in forming water will be the total number of oxygen atoms taken up during the whole process minus the amount of chemisorbed atoms left on the surface, when the cycle is completed by an oxygen treatment. When the cycle was completed by a hydrogen treatment, all the oxygen has been used to form water. In run 5, therefore, $(371 - 45.5) = 325.5 \times 10^{-8}$ mol were used in water formation. The total amount of hydrogen used is calculated similarly, noting that if the final treatment is with hydrogen, the surface is covered with chemisorbed H atoms and has to be subtracted from the total amount. In run 5 this is 648.5×10^{-8} mol. The ratio between the total amount of oxygen and hydrogen used in forming water is $684.5/325.5$ = 1:2.1. In run 6 the oxygen and the H_2 used in water formation was 346.3×10^{-8} mol and 721.2×10^{-8} mol respectively, a ration of $721.2/346.3$ = 1:2.08.

Similarly, the ratio of oxygen taken up in the second dose of oxygen to that adsorbed in the 1st dose should be 3:2. This follows from the fact that the first oxygen, when adsorbed on fresh Pt film, covered the whole surface of Pt. The first hydrogen dose reacted with this chemisorbed oxygen to form water and then covered the surface with chemisorbed hydrogen. The second dose of oxygen reacted with the chemisorbed hydrogen to form water, and then covered the surface with chemisorbed oxygen. Hence, additional oxygen was used in the 2nd dose to remove the chemisorbed hydrogen and this required half the amount of oxygen necessary to cover the surface with chemisorbed oxygen atoms. So the ratio between the oxygen adsorbed in the 1st dose and the O_2 adsorbed in the 2nd dose was 1.67. In run 5 and 6 the actual figures are $58/45.5$ = 1.27 and $72.9/59$ = 1.24 respectively. The probable explanation for these low values is that some of the chemisorbed oxygen atoms, formed from the first dose of O_2, when treated with H_2 remained on the surface and took no further part in the catalytic production of water.

The number of active oxygen atoms that took part in water formation may be deduced from $\frac{2}{3}$ the number of oxygen atoms taken up in the second dose, whereas the total number of all sites (active and inactive) is obtained from the first dose of oxygen. Thus in run 6 the total number of sites is 118, of which 97 are active and 21 inactive. In order to obtain a mass balance, H_2 must have reacted with inactive oxygen atoms; two obvious possibilities are $\overset{OH}{Pt}$' or $\overset{H\ \ H}{\underset{Pt}{O}}$ since separate experiments (see later) prove that water is chemisorbed on Pt at 195°k and is still present, at least in part, at 200°C. The water complex gives a much better balance than does a $\overset{OH}{Pt}$ complex. Thus in run 6 the H_2 uptake should be $3 \times 97 + 2 \times 21 = 333$ H atoms compared with the experimental figures 334. In run 5, corresponding figures: total number of sites 91 of which 77 are active and 14 inactive hence H_2 uptake should be $3 \times 77 + 2 \times 14 = 259$ H atoms, and 264 was the experimental figures. The percentage of inactive sites are in run 5, 15.4% and in run 6, 17.7%; the closeness of these figures probably reflect the fact that the films were prepared under as identical conditions as possible. After the 1st H_2 treatment the surface structure has the form:



and only the active sites take part in the cycles.

Benson and Boudart(9) have used the titration method to measure the surface area of the supported Pt. This method is obviously applicable to surface films, so we calculated the number of sites for H_2 and O_2 left on the surface in each oxygen-hydrogen treatment in the cycle. In run 6 the first oxygen dose adsorbed on a fresh Pt film was 118 "atoms" from which only 97 "atoms" ($\frac{2}{3}$rd of 2nd O_2 dose) were reactive throughout the cycling process. After 1st hydrogen dose 97 hydrogen "atoms" were left on the surface for reaction. In second oxygen dose of 146 "atoms", 48 react with 97 hydrogen "atoms" to give H_2O leaving (146-48) = 98 oxygen "atoms" on the surface. In the next H_2 dose of 268 "atoms" only 2 x 98 = 196 "atoms" were used to form water leaving (268-196) = 72 H "atoms" on the surface. The other oxygen and H_2 doses are treated in the same way, and the values for run 5 and 6 are given in the following tables.

Run 5

1st oxygen = 91 atoms

2nd oxygen = 116 atoms

Active sites = $\frac{2}{3}$ (2nd dose of O_2) = $\frac{2}{3}$ x 116 = 77

Inactive sites = 91 - 77 = 14

so total sites = 91 active = 77 inactive = 14

Measurement of doses as "atoms"	No. of "atoms" used to form H_2O	No. of sites occupied
		77 H
116 O	38 O	78 O
231 H	156 H	75 H
107 O	37 O	70 O
226 H	140 H	86 H
109 O	43 O	66 O

220 H	132 H	88 H
113 O	44 O	69 O
216 H	138 H	78 H
108 O	39 O	69 O
212 H	138 H	74 H
99 O	37 O	62 O

$$\left.\begin{array}{ll}\text{No. of } O_2 \text{ sites} = 78\quad 70\quad 66\quad 69\quad 69\quad 62 & \text{Mean} = 70 \\ \text{No. of } H_2 \text{ sites} = 77\quad 75\quad 86\quad 88\quad 78\quad 74 & \text{Mean} = 80\end{array}\right\rangle \text{Mean} = 75$$

Active sites = 77 and inactive = 14

Active H_2 = 77 x 3 = 231 H atoms

Inactive H_2 = 14 x 2 = 28 H atoms

Total H_2 uptake = 231 + 28 = 259 H "atoms"

Total H_2 uptake in first dose is equal to 264 "atoms" and from calculation it is equal to 259 "atoms".

Run 6

1st Oxygen = 118 atoms

2nd Oxygen = 146 atoms

Active sites = $\frac{2}{3}$(2nd dose of O_2) = $\frac{2}{3}$ x 146 = 97

Inactive = 118 - 97 = 21

Total sites = 118 Active = 97 Inactive = 21

Measurement of doses as "atoms"	No. of "atoms" used to form H_2O	No. of Sites Occupied
		97 H
146 O	48 O	98 O
268 H	196 H	72 H
137 O	36 O	101 O
286 H	202 H	84 H
141 O	42 O	99 O
285 H	198 H	87 H
138 O	43 O	95 O
270 H	190 H	80 H
131 O	40 O	91 O

No. of O_2 sites = 98 101 99 95 91 Mean = 97

No. of H_2 sites = 97 72 84 87 80 Mean = 84

Mean = 90

Active sites = 97 and inactive = 21

Active hydrogen = 97 x 3 = 291 H atoms

Inactive H_2 = 21 x 2 = 42 H atoms

Total H_2 uptake = 291 + 42 = 333 H "atoms"

Total H_2 uptake in first dose is = 334 "atoms" and from calculation it is 333"atoms".

The total water formed is equal to the sum of the number of oxygen "atoms" used (column 2 in Table) + $\frac{1}{2}$ sum of hydrogen "atoms" used (column 2 in Table); in figures for run 5 the amount of water formed is equal to 253 + $\frac{1}{2}$(781) = 643.5 x 10^{-8} moles.

It may also be calculated from (i) the total hydrogen uptake minus that left on the surface if cycle is completed with H_2, the value in run 5 is equal to 684.5 x 10^{-8} mole; and (ii) from the total oxygen uptake in terms of oxygen atoms minus that left on the surface if cycle is completed with oxygen. The value for run 5 is (371 - 45.5) x 2 = 651 x 10^{-8} moles. So mean of water produced in these three cases is equal to 662.0 x 10^{-8} mole. The amount of water produced experimentally is equal to 520 x 10^{-8} mol, that is, $\frac{520 \times 100}{662}$ = 78.5% only. In run 6 the total amount of water formed from the sum of the number of oxygen atoms + $\frac{1}{2}$ sum of number of hydrogen atoms is equal to 215 + $\frac{1}{2}$ 883 = 656.5 x 10^{-8} mole. The amount produced from total hydrogen uptake is equal to 721 x 10^{-8}mol, and from total oxygen uptake is (405 - 59) x 2 = 692 x 10^{-8} mol. The mean value is equal to 690 x 10^{-8} mol. The amount of water produced experimentally is equal to 520 x 10^{-8} moles, that is 75.5%. The low experimental values are to be expected because of the adsorption of water on the walls of the Pirani and trap T_1.

The calculation for the number of active sites in run 6 and 5 shown in the Table was done by taking $\frac{2}{3}$ of second oxygen dose used as water formation. An alternative method is as follows, using the hydrogen uptake in the 1st dose. Of the first dose, 91 atoms left on the surface (in run 5), x are inactive and from chemisorbed water on the surface with the first hydrogen dose, the remainder (91 - x) react to form water and leaves (91 - x) on the surface; these latter require 3 hydrogen atoms per site where as the complex only requires 2 hydrogen atoms per site,.

Hence $3(91 - x) + 2x = 264$

or $273 - 3x + 2x = 264$

or $x = 9$

i.e. 82 active, 9 inactive, compared with 14 derived from first and second oxygen doses. Similarly in run 6,

$3(118 - x) + 2x = 334$

or $x = 20$

Here there are 77 active, 20 inactive as compared with 21 derived from first and second oxygen doses. The calculated number of sites for oxygen and hydrogen for both cases are given below, since the site-number values are very sensitive to the number of active sites taken.

Run 5

No. of oxygen and hydrogen sites when 77 sites active (from $\frac{2}{3}$ of 2nd O_2):

No. of O_2 sites	=	78	70	66	69	69	62	Mean = 70	Mean = 75
No. of H_2 sites	=	77	75	86	88	78	74	Mean = 80	

No. of oxygen and hydrogen sites when 82 sites active (from 1st hydrogen).

No. of O_2 sites = 75 67 63 66 66 59 Mean = 66
No. of H_2 sites = 82 81 92 94 84 80 Mean = 86
Mean = 76

Run 6

No. of oxygen and hydrogen sites when 97 sites active (from $\frac{2}{3}$ of 2nd O_2).

No. of O_2 sites = 98 101 99 95 91 Mean = 97
No. of H_2 sites = 97 72 84 87 80 Mean = 84
Mean = 90

No. of oxygen and hydrogen sites when 77 sites active (from $\frac{1}{3}$ of 1st H_2).

No. of O_2 sites = 108 111 109 105 101 Mean = 107
No. of H_2 sites = 77 52 64 67 60 Mean = 64
Mean = 86

The mean of the number of sites from oxygen, hydrogen sites in both cases are close to each other (as shown above) but separately as oxygen or hydrogen sites they are different particularly in run 6, thereby showing how sensitive these calculations are to the actual number of active sites. In fact the oxygen or hydrogen figures can be brought close together by a slight adjustment of this number.

From a viewpoint of surface area determination there are five possible values. They are: (i) from first oxygen, (ii) from $\frac{2}{3}$ of 2nd oxygen, (iii) from 1st hydrogen, (iv) from the oxygen site number

(v) from the hydrogen site number.

	(i)	(ii)	(iii)	(iv)	(v)	Mean of (iv) + (v)
Run 5	91	77	82	70	80	75
Run 6	118	97	77	97	84	90

The "true" surface area should be given by (i) since this includes all sites (active and inactive). The usual titration method is based on (iii), and should there be inactive sites, this figure will be low. The mean of (iv) and (v) is still lower since they should theoretically both be 77 in run 5 and 97 in run 6. This is largely due to the fact that in both oxygen and hydrogen uptake, the initial rapid pressure decrease is followed by a slower uptake of gases. In the first oxygen dose to approach saturation, 20 minutes were allowed and a similar time was given for the first hydrogen dose, but in the subsequent cycling process, 6-8 minutes was the normal uptake time. It would therefore appear that saturation with oxygen or with hydrogen requires a period of at least $\frac{1}{2}$ hour, so the cycle results would have to be multiplied by a factor of 1.22 in run 5 and 1.31 for run 6 to obtain the total number of all sites i.e. for a measurement of surface area.

It is therefore suggested that oxygen adsorption may give a greater accuracy for surface area determination. However, the advantage of the titration method is that, titration with hydrogen requires little care in cleaning the Pt surface from oxygen, but is largely a measure of the active surface; the fraction of the total number of sites that are active will clearly be dependent on the conditions of evaporation, annealing and subsequent treatment. For a catalytic process, the surface area of the active portion is obviously the more useful value.

2. System: Hydrogen + Platinum + Oxygen

In the preceeding oxygen-hydrogen adsorptions on Pt we adsorbed oxygen first on the fresh film but in this system, hydrogen was adsorbed first on the fresh film, followed by oxygen and then by H_2/O_2 cycles.

Run 26

Bath Temperature = 195°k

Hydrogen Adsorbed		Oxygen Adsorbed	
moles	atoms	moles	atoms
21.4×10^{-8}	43	16.5×10^{-8}	33
43.0	86	19.5	39
53.2	106	23.1	46
62.1	124	27.0	54
70.2	140	30.0	60
76.4	153	30.7	61
326.3×10^{-8}	652	146.8×10^{-8}	293

In run 26 hydrogen was adsorbed on a fresh Pt film at 195°k and the amount adsorbed was 21.4×10^{-8} moles. After the evacuation of the gas phase H_2, oxygen was introduced and the amount adsorbed was 16.5×10^{-8} moles. Excess was pumped out. Five more H_2/O_2 cycles were done and the last cycle was finished with oxygen adsorption. The amount of O_2 and H_2 varied from cycle to cycle. Analysis of the gas phase during the sorption of oxygen on hydrogen covered surface showed that the oxygen displaced some H_2 preadsorbed, the amount being about 20-10%.

Explanation

When H_2 is adsorbed first on a Pt film followed by adsorption of oxygen, the catalytic formation of water is partly inhibited i.e. the bonding and reactivity of such chemisorbed atoms are different from those which remain after oxygen is first chemisorbed followed by hydrogen. If one assumes that the last H_2 uptake 76.4×10^{-8} moles has been utilized in producing water by the usual process then there are $\frac{1}{3}(2 \times 76.4) = 51$ active sites. The total H_2 uptake throughout the cycles (326 x 2) = 652 atoms and of oxygen there are 293 atoms hence, excess of H_2 corresponding to (652 - 586) = 66 H atoms, if no oxygen is left on surface after final oxygen treatment (see NH_3 run later), hence there are hydrogen atoms originally chemisorbed on surface still present. There were in fact only 43 adsorbed from the 1st dose, so there is a slight discrepancy of (66 - 43) = 23 H atoms which is not large. In the NH_3 run, we assumed H_2 molecular adsorption when NH_3 chemisorbed first, hence we assume the same effect here.

Hence we assume 43 H atoms in first layer and label these with star to denote differences from later hydrogen in cycle.

Assume 43 H* atoms (which do not cover all sites) followed by 33 oxygen atoms in primary layer (with no formation of water) so that the total site number is 43 + 33 = 76. We assume that all the oxygen atoms are active so these require 66 H atoms for formation of water. Now the second dose of hydrogen comprises 86 H atoms; the 33 oxygen atoms need 66 H atoms to form water leaving 86 - 66 = 20 H atoms as $10H_2$ on top of 43 H* atoms on the surface. So the total hydrogen on the surface is now $43H^* + 10H_2$.

There is experimental evidence that about 20% of the hydrogen adsorbed is desorbed without oxidation. The first desorption possible with the second oxygen dose of 39 atoms. When it is introduced 20% molecularly adsorbed H_2 is desorbed leaving $8H_2$ in the second layer. The amount of oxygen adsorbed therefore is 39 + 2 = 41 O atoms since H_2 evolution into the gas-phase makes the measured uptake of O_2 too low.

Now of these 41 O atoms, 8 are used for water production leaving 33 O atoms on the surface. Of the second dose of 106 H atoms, 66 H atoms are used for water formation leaving 40H or $20H_2$ molecularly adsorbed hydrogen. Due to the desorption this hydrogen is reduced to $18H_2$ moles, and the oxygen dose must be increased to 50 O atoms. So from 50 O atoms, 18 are used for water formation leaving 32 on the surface. By this method the rest of the calculation was done and the sequence obtained as below.

Sequence

Oxygen left on the surface as atoms = 33 32 33 34 31

Hydrogen left on the surface as moles = 8 18 27 33 38

Summary

If H_2 is adsorbed first it reacts like NH_3 (see NH_3 run later) i.e., it remains on the surface as unreactive primary adatoms and take no part in water production but hydrogen is adsorbed as molecules above these chemisorbed H atoms. The first oxygen dose fills the remaining sites on the surface (assumed in the calculation to be all active). The next hydrogen dose reacts with the active oxygen to give H_2O, the remainder being adsorbed as H_2 over the H atoms with the primary layer; these are oxidised to water when the next dose of oxygen is added. These figures have been corrected for 20% H_2 desorbed without reaction from the 2nd layer as each dose of oxygen is added. Then a consistent set of values are obtained.

Oxidation here proceeds (i) via the originally adsorbed oxygen atoms in the normal way and (ii) by oxidation of H_2 adsorption on top of the H atoms in the primary layer.

The difference with NH_3 is that the hydrogen is less strongly held over the H atoms surface than is NH_3, hence there is some desorption of molecularly adsorbed H_2 by oxygen but not from an NH_3 surface, where good agreement is obtained without desorption.

3. System: Water + Platinum + Hydrogen

Water is adsorbed on a Pt film (see later) and decomposition with evolution of hydrogen does not occur until a temperature of 200°C is attained. It is assumed that H_2O is dissociatively adsorbed to give $\overset{OH}{\overset{|}{Pt}}$ and $\overset{H}{\overset{|}{Pt}}$ on a clean Pt film. Unfortunately there is no means of measuring the amount of adsorption of H_2O in the present apparatus because of the large adsorption on the glass walls. Adsorption of hydrogen at 195°k proceeds on top of this primary layer and we presume that this is in the form of chemisorbed hydrogen molecules; such molecules are oxidised by oxygen rapidly but the primary chemisorbed H atoms from the water are oxidised slowly. Such a sequence of events gives a sequence of primary H atoms on the surface which is reduced to zero after five cycles. There is a fairly constant concentration of chemisorbed O atoms on the surface after O_2 uptake, and a small increase of H_2 molecular adsorption as primary H atoms are removed.

Run 38

Adsorption of H_2O on fresh Pt film at 273°k

Bath temperature = 195°k

Oxygen Adsorbed		Hydrogen Adsorbed	
moles	atoms	moles	atoms
		56.0×10^{-8}	112
40.6×10^{-8}	81	84.0	168

54.0	108	92.0	184
62.8	126	99.0	198
54.2	108	93.0	186
53.2	106	96.0	192
265.0×10^{-8}		520×10^{-8}	

In run 38, water was adsorbed on a fresh Pt film at 273°k when the Pirani gauge and trap T_1 was also at 273°k temperature. After 5 minutes the excess of water was evacuated for 20 minutes and then the temperature of the cell was changed to 195°k and Pirani and trap T_1 to 78° k and a measured dose of hydrogen was adsorbed on the water treated film. The amount adsorbed was 56×10^{-8} moles. The residual H_2 was pumped out and a measured dose of oxygen was introduced. The amount adsorbed was 40.6×10^{-8} moles. Four more H_2/O_2 cycles were done at 195°k and the last cycle was finished with a H_2 uptake. The total amount of H_2 and O_2 in these 5 cycles was 520×10^{-8} moles and 265×10^{-8} moles respectively.

Explanation

In absence of information of the extent of water adsorption we assume the site number is given by the first hydrogen adsorption X . Hence one starts with 112 OH and 112 H, i.e. $\overset{OH}{Pt} - H$ $\overset{OH}{Pt}\ H$, and then the first H_2 does go on top as 56 moles hydrogen. This is oxidised by the second dose of oxygen, and the remaining oxygen oxidises some of the 112 H atoms, this number being $\frac{2}{3}$ oxygen available to leave O atoms in like number on the surface.

Hence of 81 oxygen atoms, we require 56 to oxidise 56 moles hydrogen leaving 81 - 56 = 25 oxygen atoms; $\frac{2}{3}$(25 x $\frac{2}{3}$) = 17 go on the surface to take the place of H atoms; the remainder (25 - 17) = 8 oxidise 16 of the primary hydrogen atoms leaving (112 - 16) = 96 H on the surface + 17 oxygen atoms.

The second hydrogen dose is 168 atoms; 34 are used for the 17 oxygen atoms, but H atoms are not adsorbed on the surface so that (168 - 34) = 134 H atoms go on top as 67 H_2 moles.

The second oxygen dose is 108 requiring 67 for 67 moles hydrogen in 2nd layer leaving 41; $\frac{2}{3}$ of 41 are deposited on the surface and 27 H are removed, so there are now 69 H and 27 oxygen and so on.

<u>Sequence of H atoms on surface</u>

112 96 69 41 20 0

<u>Sequence of Chemisorbed oxygen</u>

17 27 27 20 23

<u>Sequence of molecular H_2 adsorption</u>

67 65 73 72 73 10 oxygen atoms are in excess which are unaccounted for

Total hydrogen used for water (520 - 73) = 447 x 10^{-8} moles; to this add $112/2$ = 56 moles H_2 from dissociation of water. So that the total equals 447 + 56 = 503 x 10^{-8} mole.

Total oxygen used for water is 265×10^{-8} moles i.e. still slight excess of oxygen as requires $503/2 = 252 \times 10^{-8}$ moles by calculation. So 13 oxygen are in excess.

Summary

Water is dissociatively adsorbed as OH and H. Thus hydrogen is slowly oxidised but not replaced on the surface by hydrogen adsorption from the gas phase. The main formation of water is oxidation of molecular H_2 adsorbed in the second layer.

Only part of surface, about 20% is utilized for water via oxygen chemisorbed on the surface as the rest is blocked by OH radicals.

4. System: Hydrogen + Platinum + Water

In this system hydrogen was adsorbed on a fresh Pt film at 273°k and then on the hydrogen-treated surface, water was adsorbed at 273°k. After evacuation of excess of water, the temperature of film was changed to 195°k and O_2/H_2 cycles were done in the normal way.

Run 20

Adsorption of H_2 at 273°k = 275×10^{-8} moles or 550 atoms

Water was then adsorbed at 273°k

Bath temperature = 195°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
180.8×10^{-8}	362	265×10^{-8}	530
107.0	214	220	440
107.4	215	207	414
105.2	210	211	422
99.5	199	204.2	408
99.5	199	193	386
699.4		1300	

In run 20 hydrogen was adsorbed on a fresh film at 273°k; the amount adsorbed was 275×10^{-8} moles. Excess of gas was pumped out and the temperature of the Pirani gauge and trap T_1 was changed to 273^{o}k and water was introduced to the H_2 treated film with S_1 closed. After 5 minutes the tap S_1 was opened and excess of water was pumped out for 20 minutes. Then the temperature of the cell was changed to 195^{o}k and the Pirani and trap T_1 was immersed in liquid nitrogen baths and a measured dose of oxygen was introduced. The amount adsorbed was 180.8×10^{-8} moles. Then, after the evacuation of the residual oxygen, H_2 was introduced and the amount adsorbed was 265×10^{-8} moles. After that, 5 more O_2/H_2 cycles were done and the last cycle was finished with H_2 adsorption. The total amount of oxygen and hydrogen adsorbed in these 6 cycles was 699.4×10^{-8} moles and 1300×10^{-8} moles respectively.

Explanation

In this run the film was apparently very thick. After the adsorption of 275×10^{-8} moles of hydrogen, water was adsorbed. After the chemisorption of water, adsorption of oxygen but not of hydrogen may take place directly on the platinum i.e. all the hydrogen is adsorbed on top of the primary layer as molecular hydrogen and is later oxidised by the next dose of oxygen to form water. The site number calculation is shown below.

Site no. calculation

275×10^{-8} moles of H_2 are oxidised by the first oxygen dose which was 362 O atoms leaving$(362 - 275) = 87$ O atoms on the surface.

Doses of Oxygen & Hydrogen in atoms	Oxygen-hydrogen used for H_2O	Oxygen-hydrogen left on surface	
530 H	174 H_2O	178 H_2	(moles)
214 O	178 H_2O	36 O	(atoms)
440 H	72 H_2O	184 H_2	(moles)
215 O	184 H_2O	31 O	(atoms)
414 H	62 H_2O	176 H_2	(moles)
210 O	176 H_2O	34 O	(atoms)
422 H	68 H_2O	177 H_2	(moles)
199 O	177 H_2O	22 O	(atoms)
408 H	44 H_2O	182 H_2	(moles)
199 O	182 H_2O	17 O	(atoms)
386 H	34 H_2O	176 H_2	(moles)

Oxygen sequence

36 31 34 22 17

Hydrogen sequence

178 184 176 177 182 176

Conclusion

The constant values for molecular hydrogen adsorption suggests that the general mechanism is correct; the decreasing oxygen values suggests that there is some small desorption of this molecularly adsorbed hydrogen without oxidation when the next oxygen dose is added. Thus, the measured uptake of oxygen will be slightly low since hydrogen is being added to the gas-phase i.e. the measured pressure drop changes are slightly too small.

5. System: High temperature treatment of chemisorbed oxygen layer

The effect of heating a Pt film with a chemisorbed oxygen layer may cause:

(i) incorporation of the oxygen thereby freeing surface area,

(ii) sintering and loss of effective surface area,

(iii) active chemisorbed oxygen atoms to be made inactive.

Run 24

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
	46.8×10^{-8}	94		
Oxygen treated surface is heated at 100°C for 1 hour				
	40.4×10^{-8}	81	126×10^{-8}	252
set (i)	55.7	111	149	298
	56.4	113	126	252
	57.0	114		
		513		802
Oxygen treated surface is heated at 300°C for 1 hour				
			$51\ 2 \times 10^{-8}$	102
	31.6×10^{-8}	63	55.0	110
set (ii)	31.0	62	62.6	125
	30.0	60	56.3	113
	292	185	626.0	450

In run 24, oxygen was adsorbed on a fresh Pt film at 195°k and the amount adsorbed was 46.8×10^{-8} moles; after the evacuation of the residual gas, the temperature of the film was raised to 100°C and heated for one hour. After heating the temperature was again changed to 195°k and a second dose of oxygen was adsorbed; this time the amount adsorbed was 40.4×10^{-8} moles. After evacuation of the residual gas a measured dose of hydrogen was introduced and the amount adsorbed was 126×10^{-8} moles. Two more O_2/H_2 cycles were done at 195°k and the last (3rd cycle) was finished with oxygen adsorption. These three O_2/H_2 cycles are called the 1st set. The 1st set finished with O_2 adsorption. Now the film was again heated at 300°C for one hour; after one hour the temperature was dropped to 195°k and hydrogen was adsorbed first. The amount adsorbed was 51.2×10^{-8} moles. Then three O_2/H_2 cycles were done and the last cycle was finished with H_2 adsorption. The cycles which were done after heating at 300°C are called the second set. The total amount of hydrogen and oxygen adsorbed in the two sets was 626×10^{-8} moles and 292×10^{-8} moles respectively.

Explanation

In the present experiment (run 24), 46.8×10^{-8} moles of oxygen were initially adsorbed at 195°k corresponding to 94 sites; after evacuation of the residual oxygen, the film was heated at 100°C for one hour. There was no desorption of oxygen but 40.4×10^{-8}

moles of oxygen could be adsorbed at 195°k. Since no desorption of oxygen, then presume that these 81 O atoms are incorporated.

In set (i), total oxygen adsorbed (before and after heating) was 513 atoms of which 81 incorporated (when heated at 100°C). So oxygen available on surface was (513 - 81) = 432 atoms. Total H_2 was 802 atoms. However, from $\frac{2}{3}$ of mean C_2(in set (i)) 75 sites were active and 14 inactive. Since the 1st set (after 100°C treatment) finished with oxygen, then presume 75 O atoms left on surface. Hence should reduce 432 O atoms to (432 -75) = 357 which would require 714 H atoms, this means remainder (802 - 714) = 88 H atoms. These 88 H atoms can reduce 44 O atoms (of incorporated O_2) leaving 81 - 44 = 37 O atoms. Of these 37 oxygen atoms, 19 are probably inactive on the surface, so that H_2/O_2 cycling at 195°k can remove virtually all incorporated oxygen.

Now 195°k treatment (after heating at 100°C) in set (i) leaves 112 oxygen atoms, of which 75 are reactive surface oxygen atoms, and the remainder 37 oxygen atoms are either surface inactive or incorporated. This surface now heated to 300°C for 1 hour and further incorporation of surface oxygen takes place (no O_2 is desorbed). The first hydrogen dose of 2nd set (102 atoms) can reduce 51 oxygen atoms, so we presume these are surface active oxygen atoms, the remainder (112 - 51) = 61 oxygen atoms are probably all incorporated. These cannot be removed by hydrogen treatment at 195°k as shown in the second set.

The first oxygen dose (63 atoms) of 2nd set goes on the surface to occupy 63 sites. The H_2 (110 atoms) oxidises 55 oxygen leaving 63 - 55 = 8 oxygen atoms on the surface, presumably on inactive sites. Hydrogen is apparently not adsorbed on this 300°C surface, but oxygen is. The second dose of oxygen comprises 62 O atoms and the 2nd H_2 dose is 125 atoms hence all oxygen atoms are removed. The third oxygen dose is 60 atoms and these are largely oxidised by 113 H atoms again leaving an apparent excess of 7 oxygen.

In the 2nd set 185 oxygen atoms are used and 348 H; the excess oxygen (11 O atoms) are probably present on surface as inactive sites or this may be an accumulated experimental error.

This suggests that 60 oxygen atoms are active (after 300°C treatment) compared with 75 after 100°C treatment, the decrease being due to sintering.

Conclusion

(i) Oxygen atoms is incorporated at 100°C almost to give two monolayers.

(ii) All oxygen was active for H_2 treatment at 195°k.

(iii) Oxygen incorporated at 300°C (61 atoms) cannot be removed by H_2 treatment at 195°k.

Run 36

This run in the 1st two sets is similar to run 24, and in the third set to carbon-monoxide runs (see CO runs later), but without carbon-monoxide adsorption.

It is expected that oxygen will be incorporated at the high temperature of 70°C. In the first set, a chemisorbed oxygen layer was heated at 70°C and then uptake at 195°k of oxygen was measured. In the second set, a chemisorbed hydrogen-layer was heated at 70°C to find whether H_2 desorption took place, and then heated at 70°C in the presence of gas-phase oxygen; this was followed by normal H_2/O_2 treatment at 195°k.

Run 36

Bath Temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (i)	50.5×10^{-8}	101	152.0×10^{-8}	304
	75.5	141	140.0	280
	69.5	139	141.0	282
	70.0	140		

Oxygen treated surface is then heated at 70°C for ½ hour

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (ii)	21.0×10^{-8}	42	176.0×10^{-8}	352
	70.8	142	160.0	320
	81.0	162	155.4	311
	70.2	140	151.0	302

Desorption of H_2 at 70°C = 25.6×10^{-8} mol.

H_2 left on surface = $(151 - 25.6) = 125.4 \times 10^{-8}$ moles

Adsorption of Oxygen at 70°C = 78×10^{-8} moles or 156 atoms

Bath Temperature

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			187.0×10^{-8}	374
set (iii)	63.5×10^{-8}	127	152.4	305
	67.5	135	148.6	297

In run 36, three O_2/H_2 cycles were done at 195°k starting with adsorption of oxygen. This 1st set of three O_2/H_2 cycles was finished with oxygen adsorption. Then the film was heated at 70°C for $\frac{1}{2}$ hour. After heating, the temperature was again dropped to 195°k and four O_2/H_2 cycles were done as shown in the table (set ii). This set was finished with H_2 adsorption; the amount was 151×10^{-8} moles; The film was again heated at 70°C. 25.6×10^{-8} moles of H_2 desorbed at 70°C; after evacuation of this H_2, oxygen was adsorbed at 70°C and the amount adsorbed was 78.0×10^{-8} moles. Then the temperature of the film was again changed to 195°k and three H_2/O_2 cycles were done with 1st adsorption of hydrogen.

Explanation

From first oxygen there are 101 sites and from $\frac{2}{3}$ of (second oxygen($141 \times \frac{2}{3}$) there are 94 sites active and 7 inactive. So hydrogen sequences should be $3 \times 94 + 2 \times 7 =$ 296 H atoms; hydrogen used experimentally is equal to 304 atoms (in good agreement).

Site no. check for set (i)

	94 H
141 O - 47	94 O
280 H - 188	92 H
139 O - 46	93 O
282 H - 186	96 H
140 O - 48	92 O

Site number is in good agreement.

Set (i) was finished with an oxygen treatment. The film was now heated at 70°C for 30 minutes and after cooling to 195°k, 42 o oxygen atoms were adsorbed so we conclude that an equal number of oxygen atoms had been incorporated in the heat treatment. This surface was then subjected to 4 H_2/O_2 cycles, starting and ending with a hydrogen treatment. The total amount of oxygen used in these cycles was 222×10^{-8} moles and there are an additional 21 $\times 10^{-8}$ moles incorporated and 47×10^{-8} moles on the surface. The total amount of hydrogen used in these cycles was 642×10^{-8} moles but since the cycle ends with a hydrogen treatment, we assume that 94 H atoms still remain on the surface (i.e. as in set (i), assuming no sintering); hence $642 - 47 = 595 \times 10^{-8}$ moles of hydrogen are oxidised. These would require 298 x 10^{-8} moles of oxygen whereas 222 + 21 + 47 = 290 x 10^{-8} moles are available. Hence, if all incorporated O atoms are used for oxidation, good agreement is found.

In the third set, the total amount of hydrogen added was 488 x 10^{-8} moles and the total amount of oxygen was 131 x 10^{-8} moles + 78 x 10^{-8} moles used at 70°C, i.e. a total of 209 x 10^{-8} moles. If we assume that the amount of hydrogen left of the surface at the end of set (iii) is 26 x 10^{-8} moles more that that present at the beginning of this set (the 26 x 10^{-8} moles were desorbed at 70°C and are undoubtedly re-adsorbed at 195°k) then 488 - 26 = 462 x 10^{-8} moles of hydrogen are oxidised, requiring 231 x 10^{-8} moles of oxygen compared with the total of 209 x 10^{-8} moles above. This discrepancy is either experimental error or as is more likely, there is desorption of adsorbed hydrogen (without reaction) when an oxygen dose is added since the circumstances are similar to a film when it is treated first with hydrogen.

6. System: Oxygen + Platinum + Hydrogen + Oxygen + Carbon-monoxide

Preliminary Run: (30)

Run 30 was a preliminary run in this system. Oxygen was adsorbed on a fresh Pt film at 195°k. On the oxygen-treated surface hydrogen was adsorbed. After the evacuation of residual H_2, a second dose of oxygen was introduced. Now after the adsorption of oxygen, carbon-monoxide was introduced. This CO was oxidised by preadsorbed oxygen and formed carbon-dioxide. The CO_2 formed was measured in this run by putting an ice bath around the Pirani and with the cell and trap T_1 at room temperature. The CO_2 was pumped out and the temperature of the cell was again changed to 195°k and the Pirani and trap placed in the 78°k baths and a measured dose of oxygen was introduced. Two O_2/H_2 cyclewere done but it was found that there was no further adsorption of H_2/O_2 after the adsorption of CO as shown in the Table below.

Run 30

Bath temperature = 195°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
19.4×10^{-8}	39	63.0×10^{-8}	126
27.1	54		

Adsorption of CO at 195°k = 80×10^{-8} moles

After the evacuation of CO_2 formed

Bath temperature = 195°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
0.2×10^{-8}	0.4	0.6×10^{-8}	1.2
0.2	0.4	0.8	1.6

Explanation

The first oxygen uptake on a fresh Pt film at 195°k was 39 atoms and the second was 54 atoms. From the 1st oxygen dose 36 sites are active ($\frac{2}{3}$ of second oxygen, $\frac{2}{3}$ x 54) and 3 are inactive. So amount of hydrogen required should be 3 x 36 + 2 x 3 = 114 H atoms whereas hydrogen used experimentally was 126 atoms, so there are possibly 6 sites on the surface contaminated during preparation. The total oxygen is now 39 + 6 = 45 of which 36 is reactive.

If we assume that the 36 active oxygen atoms oxidise CO to CO_2, then there are 80 -36 = 44 sites left on surface. Since there are 45 sites, then CO remains on surface as $\overset{\text{CO}}{\overset{|}{\text{Pt}}}$ (36 in number) and as $\begin{matrix}\text{CO}\\|\\\text{O}\\|\\\text{Pt}\end{matrix}$ (19 in number) hence requiring 45 CO molecules, of which 44 are available. Since reaction of gas phase oxygen at 195°k with $\overset{\text{CO}}{\overset{|}{\text{Pt}}}$ is slow, no further adsorption of oxygen or hydrogen is expected as is found experimentally.

Run 32

In run 30, an inactive surface was produced after CO treatment. In the following three runs, the amount of CO_2 produced was measured. It was necessary to raise the temperature to 70°C in order to react all the CO with gas-phase oxygen; in this process all the CO was quantitatively oxidised to CO_2. However, as found previously, at 70°C, oxygen is incorporated into the bulk, and it was of value to see whether this was then available for oxidation in a H_2/O_2 cycle at 195°k. It was also of interest to find whether CO adsorption on an oxygenated surface at 195°k would be a measure of surface area. Thus in run 32, we calculate 81 sites are available and 88 CO molecules can be adsorbed, the higher value reflects some oxidation by chemisorbed oxygen at 195°k. It is of interest also that CO treatment cleans up contaminated sites (see below).

Run 32

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (i)	34.3×10^{-8}	69	110.2×10^{-8}	220
	43.3	87		

Adsorption of CO at 195°k = 88.0×10^{-8} moles

CO_2 formed = 16.5×10^{-8} moles

Adsorption of oxygen at 70°C = 137×10^{-8} moles or 274 atoms

CO_2 formed = 73.9×10^{-8} moles

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			194.7×10^{-8}	390
	69×10^{-8}	138	146.6	293
set (ii)	64.2	128	139.1	278
	63.3	126	138.0	276
	196.5		618.4	

H_2 used to form H_2O = 618.4 - 194.7

$= 423.7 \times 10^{-8}$ moles

Run 32 was similar in the beginning to run 30. After the adsorption of the second O_2 dose, CO was introduced; the amount adsorbed was 88.0×10^{-8} moles. After the evacuation of the residual CO, the amount of CO_2 formed was measured by the calibrated Pirani gauge. The temperature of the Pirani and trap T_1 was then changed to 195°k. The cell was already at 195°k. Both Dekker D_1 + D_2 were opened while S_1 was closed. The amount of CO_2 formed was 16.5×10^{-8} moles only. This CO_2 was evacuated and the temperature of the cell was changed to 70°C while the Pirani and traps was maintained at liquid nitrogen temperature and a measured dose of oxygen was introduced. The amount adsorbed was 137.0×10^{-8} moles. Again CO_2 formed was measured by the method described above; the amount was 73.9×10^{-8} moles. Now again the temperature of the cell was changed to 195°k and hydrogen was introduced first. The amount adsorbed was 194.7 x 10^{-8} moles. After this H_2 adsorption, three O_2/H_2 cycles were done. The total oxygen and hydrogen adsorbed in these three cycles was 196.5 x 10^{-8} moles and 618.4 x 10^{-8} moles respectively.

Explanation

From the first oxygen dose there are 69 sites and from ⅔ of 2nd oxygen (⅔ x 87) there are 58 sites active and 11 inactive. Hence hydrogen required should be 3 x 58 + 2 x 11 = 196 H atoms. The experimental value is higher at 220 hence it would appear that the film was contaminated with chemisorbed oxygen over $(220 - 196)/2$ = 12 sites; hence total sites are 69 + 12 = 81 of which 23 are inactive. After the first H_2 dose, 58 active H atoms are left; the second oxygen dose is (87 - 29) = 58 oxygen sites (active).

The surface was treated at 70°C later with 274 oxygen atoms, hence the total oxygen is 274 + 58 = 332, of which 88 were used for CO oxidation leaving (332 - 88) = 244 oxygen atoms, and since the site number has not been changed at 87, there are three layers of oxygen atoms (compare two previously) with 70 in the third layer.

Active sites in final set(ii)87 (⅔ x 131 mean oxygen in three cycles) hence the CO treatment apparently "cleans up" inactive sites.

Hence with 390 H atoms (1st H_2 after 70°C treatment) added, we assume as before nearly two layers of oxygen are used for oxidation; actual number is 390 - 87 (surface hydrogen) = 303 accounting for 152 oxygen, leaving 244 - 152 = 92 oxygen atoms, or 92- 70 = 22 oxygen atoms in second layer. The second set finishes with a hydrogen layer, hence total hydrogen (in three cycles) is equal to 423.7×10^{-8} mole and total oxygen (in three cycles) is 196×10^{-8} moles. If 22 atoms or 11×10^{-8} moles of oxygen in second layer are reduced, total oxygen is then $196 + 11 = 207 \times 10^{-8}$ moles which require 414×10^{-8} moles of hydrogen, whereas total hydrogen uptake experimentally is 423.7×10^{-8} moles.

Summary

(1) This film is partly contaminated with oxygen (inactive).

(2) 70°C treatment gives three layers but only two react with H_2 at 195°k.

(3) CO apparently increases active site number (by cleaning surface i.e. removing inactive oxygen).

(4) Neither H_2 nor CO react with oxygen atoms in third layer.

Run 34

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (i)	33.2×10^{-8}	66	100×10^{-8}	200
	42.4	85	92.6	185

Desorption of H_2 at 70°C = 10.2×10^{-8} moles

H_2 left on the surface = $92.6 - 10.2 = 82.4 \times 10^{-8}$ moles

or 165 atoms

Adsorption of oxygen at $70^{o}C = 90 \times 10^{-8}$ moles or 180 atoms

Bath - temperature = $195^{o}k$

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			180×10^{-8}	360
	62×10^{-8}	124	135	270
set (ii)	61.3	122	134	268
	61.0	122		

Adsorption of CO at $195^{o}k = 92.5 \times 10^{-8}$ moles

CO_2 formed = 25.82×10^{-8} moles

Adsorption of oxygen at $70^{o}C = 78 \times 10^{-8}$ moles or 156 atoms

CO_2 formed = 66.07×10^{-8} moles

Bath temperature = $195^{o}k$

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			160.65×10^{-8}	321
	49×10^{-8}	98	123.0	246
set (iii)	51.3	102	119.0	238
	53.0	106	118.2	236
	153		520.8	

In run 34, first, two oxygen-hydrogen cycles were done in the normal way at $195^{o}k$. The second cycle was finished with H_2 adsorption ;

the amount adsorbed was 92.6 x 10^{-8} moles. After H_2 adsorption the film was heated at 70°C for ½ hour. Some H_2 was desorbed; the amount was 10.2 x 10^{-8} moles. So the H_2 left on surface after desorption at 70°C was 92.6 - 10.2 = 82.4 x 10^{-8} moles. The temperature of the cell was again dropped to 195°k and H_2 was introduced first; the amount adsorbed was 180 x 10^{-8} moles. Three H_2/O_2 cycles were done in this set (after heating) and the third cycle was finished with an oxygen adsorption; the amount adsorbed was 61 x 10^{-8} moles. On that oxygen treated surface carbon-monoxide was adsorbed at 195°k. Some of it was oxidised by preadsorbed oxygen to CO_2 but the amount was only 25.8 x 10^{-8} moles. Now the CO_2 was evacuated and the film was heated again at 70°C and oxygen was introduced; the amount of oxygen adsorbed at 70°C was 78 x 10^{-8} moles. This oxygen oxidised all the CO present on the surface to CO_2; the amount was measured and was equal to 66 x 10^{-8} moles. This CO_2 was pumped out and the temperature of the film again changed to 195°k and H_2 was introduced first. The amount adsorbed was 160.6 x 10^{-8} moles. After that, three O_2/H_2 cycles were done in this set and the third cycle was finished with H_2 adsorption; the amount was 118.2 x 10^{-8} moles.

Explanation

This run should display some similar features to those found after heat treatment in run 24.

From first oxygen uptake there are 66 sites but from ⅔ of second oxygen uptake there are only (85 x $\frac{2}{3}$) = 57 active, leaving 9 inactive. Hence first H_2 uptake should be 3 x 57 + 2 x 9 = 189 atoms but experimental value is 200 atoms, hence there may have been some contamination e.g. 5 inactive oxygen covered sites. Total sites are now 66 + 5 = 71 (cp.run 24 where there are 75).

The second oxygen uptake is 85 atoms, from which 28 are used for 57 active H_2 leaving 85 - 28 = 57 oxygen atoms; the second H_2 dose is 185 atoms of which 114 go to water leaving 71 H atoms, of which 20 desorbed giving 71 - 20 = 51 H atoms on surface. At 70°C, the oxygen uptake is 180 atoms of which 25 are used for water leaving 180 - 25 = 155 oxygen atoms.

From set (ii), $\frac{2}{3}$ oxygen uptake (mean O_2 in three cycles) gives 82 active sites (whereas 71 above), so leaves 82 on surface and 155 - 82 = 73 incorporated. (cp. with heat treatment in run 24 after heating at 100°C; 81 atoms of O_2 were incorporated).

Now in set (ii) the total oxygen uptake is (in three cycles) 368 atoms + 73 incorporated = 441 atoms. Total H_2 uptake is 898 atoms or 449 molecules used to form water. Hence 441 is good agreement with 449. All incorporated oxygen is removed in set (ii).

Carbon-monoxide adsorption starts with 82 oxygen atoms on surface and 156 are added at 70°C, so total oxygen is 156 + 82 = 238 atoms.

Of 238 oxygen atoms, 93 used for CO oxidation leaving 238 - 93 = 145 oxygen atoms.

In third set, active oxygen (from $\frac{2}{3}$ of 2nd dose) correspond to 68 sites, hence (145 - 68) = 77 incorporated at this stage and 68 on the surface. The oxygen which was incorporated after first treatment at 70°C above was 73 (and in run 24,81).

Total H_2 used in set (iii) is 1040 atoms - 68 left on surface = 972 H atoms hence could oxidise 486 atoms of oxygen. Total oxygen in set (iii) is 306 atoms; other oxygen available is 68 + 77 (incorporated). So total oxygen available is = 306 + 68 + 77 = 451 atoms in reasonable agreement with 486. All incorporated oxygen is removed in the last set.

Summary

- (i) First set is "normal", leaving H_2 covered surface.
- (ii) Heating in oxygen leaves 73 incorporated (roughly two layers).
- (iii) All incorporated O_2 removed in set (ii).
- (iv) Oxygen treatment after CO adsorption leaves 77 (incorporated).
- (v) All incorporated O_2 removed in the final set or (set iii) leaving hydrogen surface.

Run 35

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (i)	29×10^{-8}	58	108×10^{-8}	216
	45.0	90	101.9	204

Desorption of H_2 at 70°C = 11.0×10^{-8} moles

H_2 left on the surface = 90.9×10^{-8} moles

Adsorption of oxygen at 70°C = 75×10^{-8} moles or 150 atoms

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			165×10^{-8}	330
set (ii)	59.6×10^{-8}	119	128.9	258
	60.6	121	130.8	262
	59.0	118		

Adsorption of CO at 195°k = 98×10^{-8} moles

CO_2 formed = 50×10^{-8} moles

Adsorption of oxygen at 70°C = 70×10^{-8} moles or 140 atoms

CO_2 formed = 50×10^{-8} moles

Bath temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			154×10^{-8}	308
set (iii)	57×10^{-8}	114	121.4	243
	54.0	108	121.4	243

Run 35 was done exactly with similar procedure as run 34. It was done in order to confirm the results of run 34, therefore all steps were similar in both runs.

Explanation

From the first oxygen there are 58 sites and from $\frac{2}{3}$ of the second oxygen (9 x $\frac{2}{3}$) = 60 sites are active, hence all sites are active. But this requires only 3 x 60 = 180 H atoms whereas 216 H atoms used experimentally, i.e., excess of 36; similarly $\frac{1}{3}$ (1st hydrogen) gives $216/_3$ = 73 sites; hence there must have been contamination. If contaminated sites are inactive then there are 18 of them (i.e. $36/_2$) and the total site number is 60 + 18 = 78 sites.

60 H atoms are left on the surface from the first hydrogen dose and there are 90 O atoms adsorbed from second oxygen dose, of which 30 oxidise 60 H atoms leaving 90 - 30 = 60 O atoms on the surface. The second dose of hydrogen was 204 H atoms of which 120 H atoms are used for the 60 O atoms leaving 204 - 120 = 84 surface H atoms, of which 22 were lost on desorption so the amount of hydrogen left on the surface was 84 - 22 = 62 H atoms.

Oxygen adsorption at 70°C requires 150 oxygen atoms of which 31 are used (i.e. $62/_2$) for water leaving 150 - 31 = 119 O atoms; hence if the site number is 78 there are (119 - 78) = 41 oxygen atoms incorporated.

The $\frac{2}{3}$ of oxygen in the 2nd set (mean O_2 of three cycles = 120 x $\frac{2}{3}$) gives 80 sites in good agreement with the original site number of 78 sites above.

Hence oxygen treatment leaves 78 oxygen atoms on the surface +41 oxygen inrorporated; total is equal to 78 + 41 = 119 atoms.

The first H_2 dose in set (ii) is 330 atoms but leaves 80 atoms on surface i.e. (330 - 80) = 250 H atoms left which would oxidise 125 oxygen atoms but actually only 119 available; that is, in reasonable agreement, and means as before that all incorporated oxygen is removed.

Site no. check

119 - 40 = 79 O
258 - 158 = 100 H
121 - 50 = 71 O
262 - 142 = 120 H
118 - 60 = 58 O

hence fair check with O site number of 80, but H is always high because it reacts with incorporated oxygen.

Before CO treatment have 80 oxygen atoms on surface and 140 oxygen atoms taken up at 70°C, so the total is 80 + 140 = 220 oxygen atoms of which 98 used for CO_2 leaving 220 - 98 = 122 oxygen atoms (cp with previously 119) hence 42 oxygen atoms incorporated if 80 sites (i.e. 122 - 80).

The $\frac{2}{3}$ of second oxygen (108 x $\frac{2}{3}$ in set (iii)) gives 72 sites which is good agreement with 78.

$\frac{1}{3}$ of first hydrogen would give 103 sites (first H_2 from set (iii) i.e. $308/3$) hence some incorporated oxygen atoms are being oxidised.

First H_2 is 308 atoms (in set (iii)) of which 72 H atoms left on surface leaving 308 - 72 = 236 atoms which could react with 118 oxygen atoms; since 122 are available. This is good agreement; alternatively 4 oxygen atoms may remain inside.

Total oxygen is 111 x 10^{-8} moles (57 + 54 in set (iii)) + 2 moles inside = 113 x 10^{-8} moles. Total H_2 is equal to 243 x 10^{-8} moles (121.4 + 121.4) which oxidised 121 x 10^{-8} moles oxygen and we have 113 x 10^{-8} moles available; so again there is reasonable agreement.

7. System: Ammonia + Platinum + Hydrogen

A series of runs were performed in which ammonia was adsorbed first, followed by H_2/O_2 cycles. It seemed likely from the work of Siddiqui and Tompkins(4) that hydrogen would be adsorbed "on top" of NH_3 and this would be oxidised leaving $\overset{NH_3}{\text{Pt}}$ or $\overset{NH}{\text{Pt}}$ depending on whether NH_3 was dissociativeadsorbed or not. The details of the runs and the various conditions used are given in the tables.

Run 41

Adsorption of NH_3 at 195°k = 200 x 10^{-8} moles

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
	74 x 10^{-8}	148	42 x 10^{-8}	84
set (i)	77.0	154	40.0	80
	82.0	164	38	76
	78.0	156	42	84
	311		162	

Adsorption of NH_3 at 195°k = 46.5 x 10^{-8} moles

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
26 x 10^{-8}	52	26 x 10^{-8}	52

set (ii)	48	96	28	56
	59	118	33	66
	133		87	

The NH_3 gas was purified by putting a liquid nitrogen bath around the side arm bulb (which was connected with the NH_3 storage bulb). The condensed NH_3 was pumped free of gaseous impurities with all traps at cardice bath (195^{o}k) temperature. After evacuation the pump was isolated and a 195^{o}k bath placed around the NH_3 bulb. Then a measured dose of NH_3 was introduced to the fresh film at 195^{o}k. The temperature of the Pirani and all traps was also at 195^{o}k. The amount adsorbed was 200×10^{-8} moles. The residual NH_3 was pumped out in three minutes and the baths around the Pirani gauge and traps changed to liquid nitrogen and a measured dose of hydrogen was introduced. The amount adsorbed was 74×10^{-8} moles. The residual H_2 was pumped out and oxygen was adsorbed, the amount being 42×10^{-8} moles. After this adsorption of oxygen, three more H_2/O_2 cycles were done in set (i). The last cycle was finished with an oxygen adsorption. Again the temperature of all traps and Pirani was changed to 195^{o}k and NH_3 was adsorbed. The amount adsorbed this time was 46.5×10^{-8} moles. The residual NH_3 was pumped out in 1½ minutes, and the temperature of the Pirani and traps was changed to 195°k and H_2 was adsorbed. Three H_2/O_2 cycles were done in set (ii) and the third cycle was finished with an oxygen adsorption. The total oxygen and H_2 adsorbed in set (i) was 162×10^{-8} moles and 311×10^{-8} moles respectively and in set (ii), 87×10^{-8} moles and 133×10^{-8} moles respectively.

Run 42

Adsorption of NH_3 at 195°k = 182.3×10^{-8} moles

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
Set (i)	60×10^{-8}	120	31×10^{-8}	62
	57	114	30	60
	55	110	29	58
	66	132	30	60
	238		120	

Adsorption of NH_3 at 195°k = 40.0×10^{-8} moles

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
Set (ii)	22×10^{-8}	44	17.5×10^{-8}	35
	34.5	69	24.0	48
	44.5	89	25.5	51
	101		67	

Run 42 was done similarly to run 41.

Run 43

Adsorption of NH_3 at 195°k

(i) Dose = 228×10^{-8} moles

(ii) Dose = 124×10^{-8} moles

Actual NH_3 adsorbed = 228 - 124 = 104×10^{-8} moles

Bath temperature = 195°k

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
	90×10^{-8}	180	52×10^{-8}	104
set (i)	84	168	49	98
	91	182	51	102
	94	188	56	112
	359		208	

Adsorption of NH_3 at 195°k = 34×10^{-8} moles

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
	50×10^{-8}	100	35×10^{-8}	70
set (ii)	66	132	39	78
	76	152	42	84
	192		116	

In run 43, 228×10^{-8} moles NH_3 were adsorbed and should have saturated the surface. However when a 2nd dose was added a further 124 x 10^{-8} moles were adsorbed. It thus appears that when the excess gas-phase NH_3 in the first dose was evacuated, with a liquid nitrogen trap around trap T_3 close to the diffusion pump, 124 x 10^{-8} moles were desorbed. This was probably physically adsorbed on top of chemisorbed NH_3 on the film. Hence the total amount of chemisorbed NH_3 was (228 - 124) = 104 x 10^{-8} moles. After that the procedure was same as in run 41 and 42.

Run 44

Adsorption of NH_3 at 195°k = 208 x 10^{-8} moles

Desorption of NH_3 at 195°k (with L.N trap) = 90 x 10^{-8} moles

NH_3 left on surface = 208 - 90 = 118 x 10^{-8} moles

Bath temperature = 195°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
86 x 10^{-8}	172	53 x 10^{-8}	106
100	200	46	92
98	196	49	98
102	204	50	100
97	194	49	98
483		247	

In run 44 we tried to confirm that some of the initially adsorbed NH_3 was desorbed. A measured dose of NH_3 was introduced to a fresh Pt film at $195^{o}k$. The amount adsorbed was 208×10^{-8} moles and the amount of residual NH_3 left in the gas-phase was 214×10^{-8} moles. So the total amount of NH_3 in the system was $214 + 208 = 422 \times 10^{-8}$ moles. Now a liquid nitrogen bath was placed around trap T_2 and the residual NH_3 condensed out. After some time when the pressure of NH_3 in the gas phase was very small (checked with McLeod), the cell was isolated and the liquid nitrogen around the trap T_2 was removed and the ammonia allowed to expand. The amount was 304×10^{-8} moles. So the actual amount of NH_3 which was left on the surface was therefore $422 - 304 = 118 \times 10^{-8}$ moles. A measured dose of H_2 was then introduced; the amount adsorbed was 86×10^{-8} moles. The residual H_2 was evacuated and oxygen was introduced; the amount adsorbed was 53×10^{-8} moles. After that, 4 more H_2/O_2 cycles were done and the last cycle was finished with the adsorption of oxygen. In this run only set (i) of the H_2/O_2 cycles was done. The total amount of H_2 and O_2 adsorbed in this set (in all 5 cycles) was equal to 483×10^{-8} moles and 247×10^{-8} moles respectively.

Various General Conclusions were evident from runs 41-44

In set (i) of all runs (41-44), a good 2/1 ratio was obtained for the total hydrogen and oxygen in the set. This would be meaningful if the surface was free of oxygen after the final oxygen dose.

Total H_2/O_2 in set (i)

Run 41

$$\left.\begin{array}{l}\text{Total } H_2 = 311 \times 10^{-8} \text{ moles}\\ \text{Total } O_2 = 162 \times 10^{-8} \text{ moles}\end{array}\right]$$ good 2/1 ratio if no O_2 on surface

Run 42

$$\left.\begin{array}{l}\text{Total } H_2 = 238 \times 10^{-8} \text{ moles}\\ \text{Total } O_2 = 120 \times 10^{-8} \text{ moles}\end{array}\right]$$ good 2/1 ratio

Run 44

$$\left.\begin{array}{l}\text{Total } H_2 = 483 \times 10^{-8} \text{ moles}\\ \text{Total } O_2 = 247 \times 10^{-8} \text{ moles}\end{array}\right]$$ good 2/1 ratio

In the second set, after further NH_3 adsorption, the 2/1 ratio was poor, there being always an excess of oxygen. However, there was a good general agreement of additional NH_3 adsorbed (as molecules) and excess oxygen (as atoms) suggesting oxidation of NH_3 possibly to NH_2OH (hydroxylamine). Unfortunately no chemical tests were made to confirm its presence.

Total H_2/O_2 in set (ii)

Run 41

$$\left.\begin{array}{l}\text{Total } H_2 = 133 \times 10^{-8} \text{ moles}\\ \text{Total } O_2 = 87 \times 10^{-8} \text{ moles}\end{array}\right]$$ Poor 2/1 ratio, too much oxygen = (174-133) = 42 and NH_3 readsorbed is 46.5×10^{-8} moles.

Run 42

$$\left.\begin{array}{l}\text{Total } H_2 = 101 \times 10^{-8} \text{ moles} \\ \text{Total } O_2 = 67 \times 10^{-8} \text{ moles}\end{array}\right]$$

Poor 2/1 ratio, too much O_2 = 134-100 = 33 and NH_3 readsorbed = 40 x 10^{-8} moles

Run 43

$$\left.\begin{array}{l}\text{Total } H_2 = 192 \times 10^{-8} \text{ moles} \\ \text{Total } O_2 = 116 \times 10^{-8} \text{ moles}\end{array}\right]$$

Poor 2/1 ratio, too much O_2 = 232-194 = 38 and NH_3 readsorbed = 34 x 10^{-8} moles

Run 44

No second set.

Furthermore, the second NH_3 adsorption and the next hydrogen adsorption was equal to the amount of the first H_2 adsorption in the first set. This suggested that the NH_3 competed for hydrogen sites available in the last cycle (see the table below).

Coverage of NH_3 - then H_2

Runs 2nd NH_3 + 1st H_2 (from 2nd set) $\equiv$ 1st H_2 (from 1st set).

(41) 46.5 x 10^{-8} moles + 26 x 10^{-8} moles = 72.5 x 10^{-8} $\equiv$ 74 x 10^{-8} moles.

(42) 40 + 22 = 62 $\equiv$ 60

(43) 34 + 50 = 84 $\equiv$ 90

(44) no figures

Conclusion

NH_3 + H_2 compete for sites of 1st molecular hydrogen.

Other obvious dependent relationships are given in the tables below.

Correspondence of NH_3 and H_2

(43) 104 NH_3, 90 H_2 (mean) 24 NH_3 in excess
(44) 118 NH_3, 97 H_2 (mean) 21 NH_3 in excess

Conclusion

Equal amounts of H_2 and NH_3 originally adsorbed but site number only approximately equal if hydrogen adsorbed as H_2.

Correspondence of NH_3 and O_2

(43) 104 NH_3, 2 x 52 = 104 oxygen atoms
(44) 118 NH_3, 2 x 50 = 100 oxygen atoms

Correspondence of H_2 and O_2

(43) 104 atoms of O_2, 90 moles of H_2
(44) 100 atoms of O_2, 97 moles of H_2

In the second NH_3 adsorption, the NH_3 excludes H_2 adsorption in part but both are oxidised by the oxygen to give H_2O or NH_2OH. The calculations are as follows:

Check H_2 + NH_3 for oxygen

(41) 133 H_2 + 46.5 NH_3 requires 179.5 oxygen - found 87 x 2 = 174
(42) 101 H_2 + 40 NH_3 requires 141 oxygen - found 67 x 2 = 134
(43) 192 H_2 + 34 NH_3 requires 226 oxygen - found 116 x 2 = 232

$\overline{546.5}$ = (calculated) (fd)= $\overline{540}$

In general the results of all runs in the first set could be interpreted as follows; NH_3 is dissociatively adsorbed as NH_2 and H so all primary H atom sites are occupied. Consequently H_2 was molecularly adsorbed, the amount adsorbed being roughly equal to the amount of NH_3 adsorbed. This hydrogen was oxidised by the next dose of oxygen but no oxygen atoms (or few on vacant sites) left on surface. The calculations for the runs are shown below.

Site number assuming molecular H_2 adsorbed

Run 41

74 H_2 42 O_2 leaving 5 O_2
77 H_2 45 O_2 leaving 6 O_2
82 H_2 44 O_2 leaving 3 O_2
78 H_2 45 O_2 leaving 6 O_2

i.e. 6 O_2 left on surface after 1st set.

Run 42

60 H_2 31 O_2 leaving 1 O_2
57 H_2 31 O_2 leaving 2 O_2
55 H_2 31 O_2 leaving 3 O_2
66 H_2 33 O_2 leaving 0 O_2

no oxygen left on surface

Run 44

86 H_2 53 O_2 leaving 10 O_2
100 H_2 56 O_2 leaving 6 O_2
98 H_2 55 O_2 leaving 6 O_2] 6 O_2 left on surface
102 H_2 56 O_2 leaving 5 O_2
97 H_2 54 O_2 leaving 6 O_2

General Conclusions

(i) Hydrogen is adsorbed molecularly on surface covered with NH_3.

(ii) Oxygen oxidises this to water; some small amount of oxygen may be physically adsorbed.

(iii) NH_3 blocks sites for oxygen adsorption on the Pt.

(iv) The molecularly adsorbed hydrogen may be partly replaced by NH_3 which is oxidised to NH_2OH.

Hence we can explain the good 2/1 ratio in the first set and the good agreement of (NH_3 + H_2) oxidised in the second set.

The sum of 2nd NH_3 + 1st hydrogen of second set equals the first H_2 of set (i) indicating that molecular adsorption of H_2 and NH_3 occur on the same "sites". Original NH_3 covers surface as chemisorbed molecules and remains unchanged througout; second dose of NH_3 largely remains on surface as molecularly adsorbed, whereas there appears to be little molecularly adsorbed NH_3 initially. This is probably due to the fact that the evacuation time to remove gas-phase NH_3 was appreciably longer than that used to remove excess NH_3 added after the first H_2/O_2 cycle.

8. System: Methyl alcohol + Platinum + Hydrogen

Methyl alcohol is expected to behave similarly to water i.e. is dissociatively adsorbed on the clean film but CH_3-Pt will probably be not oxidised or only very slowly. Again, hydrogen is always adsorbed as molecules.

Run 47

Adsorption of methyl alcohol at 273°k

Bath temperature = 195°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
52×10^{-8}	104	27×10^{-8}	54
56	112	33	66
67	134	37	74
70	140	39	78
81	162	38	76
82	164		
408		174	

In run 47, methyl alcohol was adsorbed on a fresh Pt film at 273°k, and after 5 minutes it was evacuated for 10 minutes. Then the temperature of the film was changed to 195°k and the Pirani and trap T_1 to 78°k, and a measured dose of hydrogen was introduced. The amount adsorbed was 52 x 10^{-8} moles. The residual gas was evacuated and a measured dose of oxygen was adsorbed. The amount adsorbed was 27 x 10^{-8} moles. After that, 4 more H_2/O_2 cycles were done and the last cycle was finished with hydrogen adsorption. The total amount of hydrogen and oxygen adsorbed in these cycles was 408 x 10^{-8} moles and 174 x 10^{-8} moles respectively.

Explanation

In this run hydrogen is always adsorbed as molecules hence 52 H_2 molecules (1st H_2 after CH_3OH) are adsorbed; the 54 oxygen atoms in the first oxygen dose oxidises 52 H_2O leaving 54 - 52 = 2 O atoms on the surface; which are used to form water in the next hydrogen treatment but no primary H atom adsorption occurs i.e. oxygen may be chemisorbed in the primary layer and be used for water production but H atoms are not chemisorbed in the primary layer, but only as molecular H_2 in the second layer. These can be completely oxidised in the next oxygen treatment as shown in the site number calculation below.

Site number calculation

112 H	atoms	4 H	atoms	used	for	H_2O	leaving	54 H_2 moles
66 O	"	54 O	"	"	"	"	"	12 O atoms
134 H	"	24 H	"	"	"	"	"	55 H_2 moles
74 O	"	55 O	"	"	"	"	"	19 O atoms
140 H	"	38 H	"	"	"	"	"	51 H_2 moles

78 O atoms 51 O atoms used for H_2O leaving 27 O atoms

162 H " 54 H " " " " " 54 H_2 moles

76 O " 54 O " " " " " 22 O atoms

164 H " 44 H " " " " " 60 H_2 atoms

Hence the Sequence

H_2 molecularly adsorbed = 54 55 51 54 60

O atoms left in primary layer = 2 12 19 27 22

Conclusion

(i) Increase of oxygen site number probably means some oxidation of CH_3OH or gradually replacement of CH_3OH by oxygen atoms on the surface to build up to a limit of around 24 (Mean of 27 + 22), then no further change.

(ii) Hydrogen is not adsorbed as H atoms but always as hydrogen molecules.

(iii) Total H_2 is 408 - 55(on surface at end) = 353 and total oxygen is 174 requiring 348 H_2 (in good agreement with 353).

IRIDIUM

1. System: Oxygen + Iridium + Hydrogen

The interaction of oxygen and hydrogen on evaporated iridium film has been studied at 195°k and 273°k. The film was deposited at a bath temperature ($50-55^{\circ}$C). The deposition time was approximately one hour and the current through the filament was 14 amperes.

Run 5

Bath Temperature = 195°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
set (i)	234×10^{-8}	468	634×10^{-8}	1269
	201	402	515	1030
	215	430	424	848
	217.7	434	448	896
	214.5	429		
	1083		2021	

Bath Temperature = 273°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
		441×10^{-8}	882
236.5×10^{-8}	473	506.6	1013
254.8	510	481	962
224	448	489	980
240	480		
955		1918	

After evaporation the film was cooled to cardice bath temperature (195°k) and a measured dose of oxygen was introduced; the amount adsorbed was 234×10^{-8} moles. The rest of the gas was pumped out and a measured dose of hydrogen was introduced; the amount adsorbed was 634.5×10^{-8} moles. After that, four more O_2/H_2 cycles were done and the last cycle was finished with oxygen adsorption. The total amount of oxygen and hydrogen adsorbed in all five cycles was 1083×10^{-8} moles and 2021×10^{-8} moles respectively.

After the 5th cycle the temperature of the film was changed to 273°k. There was no desorption of pre-adsorbed oxygen. Then a measured dose of hydrogen was introduced and the amount adsorbed was 441×10^{-8} moles. Four more O_2/H_2 cycles were done at 273°k and the last cycle was finished with oxygen adsorption. The total amount of oxygen and hydrogen adsorbed in these five cycles was 955×10^{-8} moles and 1918×10^{-8} moles respectively.

Explanation

In run 5 at 195°k, the general mechanism is similar to that on platinum but there appears to be two main differences (i) the primary adsorbed oxygen is reduced in subsequent H_2 treatment and is gradually completely removed from the surface;(ii) at this lower temperature some of the hydrogen is molecularly adsorbed over the primary H-atom layer and is oxidised by the next oxygen.treatment. We do not know how many oxygen atoms are reactive at any stage but since there are about 282 atoms of oxygen reactive at the end, if we assume the $\frac{2}{3}$rd oxygen rule, i.e. 468-282 = 186 oxygen atoms are left after the first hydrogen treatment and all these react during the second treatment (although probably some are left and react in 3rd and 4th treatment) The site number calculation is given in the table. The H value is much in excess of the oxygen value since considerable H_2 adsorption takes place; thus if 210 moles H_2 go into 2nd layer (after 1st adsorption where there is a higher amount adsorbed molecularly) the site numbers are as follows:

Site no. Calculation for set (i)

1st oxygen $\equiv$ 468 atoms

Active oxygen ($\frac{2}{3} \times 424$) = 282 atoms

1st H_2 = 1269 atoms of which 564 used for 282 oxygen leaving

1269 - 564 = 705 H atoms.

Now the surface is 186 O atoms 705 H atoms

402 O - 352	50(+186 O) = 236 O
1030 H - 472	568 H
430 O - 284	146 O
848 H - 292	556 H
434 O - 278	156 O
896 H - 312	584 H
429 O - 292	137 O

Sequence

	O :	268	236	146	156	137	Mean = 146
total	H :	705	568	556	584		
	H :	150	148	136	164		Mean = 150
	H_2:	277	210	210	210		

The figure of 277 represents the higher molecular hydrogen adsorption on an oxygenated surface.

Site no. calculation for second set

Before 2nd set starts there are 150 oxygen atoms on the surface.

	150 O atoms
882 H - 300	582 H
473 O - 291	182 O
1013 H - 364	649 H

510 O - 325	185 O
962 H - 370	592 H
448 O - 296	152 O
980 H - 304	676 H
480 - 338	142 O

Hence the sequence:

	O :	150	182	185	152	142
Total	H :	582	649	592	676	
	H_2:	230	230	230	230	
	H :	122	189	132	216	

As expected, slightly more oxygen atoms are reactive at the higher temperature; but the higher H_2 molecular at higher temperature is unexpected. It is possible that this molecular adsorption may be an activated process, the activation energy being acquired more easily at the higher temperature.

2. System: High temperature treatment of Chemisorbed Oxygen Layer

The effect of heating an Iridium film with a chemisorbed oxygen layer may cause incorporation of the oxygen or sintering and loss of effective surface area.

Run 14

Bath temperature = 273°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
	112×10^{-8}	224	304×10^{-8}	608
set (i)	118	236	250.2	500
	118	236	244.2	488
	115.8	232		

Oxygen treated surface is heated at 90°C for $\frac{1}{2}$ hour

Bath temperature = 273°k

	25×10^{-8}	50	258.5×10^{-8}	517
set (ii)	115.8	232	245.3	491
	112.5	225	252.7	505

Desorption of H_2 at 90°C = 14.7×10^{-8} moles

Hydrogen left on the surface = $252.7 - 14.7 = 238 \times 10^{-8}$ moles

Adsorption of oxygen at 90°C = 118.6×10^{-8} moles

Bath temperature = 273°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			259×10^{-8}	518
set (iii)	108.6×10^{-8}	217	233.2	466
	107.4	215	232.3	464

In run (14), three oxygen-hydrogen cycles were done at 273°k starting with the adsorption of oxygen. The first set of three O_2/H_2 cycles was finished with oxygen adsorption and the final amount adsorbed was 115.8×10^{-8} moles of oxygen. Then the film was heated at 90°C for 30 minutes. After heating the temperature was again changed to 273°k and a measured dose of oxygen was introduced first; the amount adsorbed was 25×10^{-8} moles. After the evacuation of residual oxygen, hydrogen was adsorbed; the amount adsorbed was 258.5×10^{-8} moles. Then two more O_2/H_2 cycles were done in set (ii) and the last cycle was finished with H_2 adsorption. Again the film was heated at 90°C for $\frac{1}{2}$ hour; 14.7×10^{-8} moles of H_2 were desorbed on heating. Now the desorbed H_2 was pumped out and a measured dose of O_2 was introduced. The amount adsorbed was 118.6×10^{-8} moles. After the evacuation of the residual gas, the temperature of the cell was again changed to 273°k and H_2 was adsorbed first. The amount adsorbed was 259×10^{-8} moles. The residual H_2 was evacuated and two more O_2/H_2 cycles were done at 273°k. The last cycle was finished with H_2 adsorption.

Explanation

From first oxygen dose there are 224 sites and from $\frac{2}{3}$ of second oxygen dose there are 157 active sites and 67 inactive.

Now the total amount of hydrogen adsorbed in set (i) was 1596 atoms and of oxygen was 928 atoms, of which 798 used for water formation leaving 928 - 798 = 130 O atoms in excess.

Site no.-calculation for set (i)

If we assume that 150 oxygen atoms are active so 300 H used leaving 224 - 150 = 74 O on surface and 608 - 300 = 308 H atoms.

Now	236 O	154	82(+ 74 O) =	156 O
	500 H	312		188 H
	236 O	94		142 O
	488 H	284		204 H
	232 O	102		131 O

Hence the sequence:

O:	224	156	142	131
H:	308	188	204	

Now at this stage the film was heated at 90°C for $\frac{1}{2}$ hour and after that heating the temperature was again changed to 273°k and oxygen was introduced; the amount adsorbed was 50 atoms but we assume that there are still 131 O atoms on the surface. So the total oxygen is 131 + 50 = 181 O atoms, because there was no desorption of oxygen at 90°C, and the film still adsorbed 50 oxygen atoms so that 50 oxygen was incorporated.

Site no. calculation for set (ii)

(a) When incorporated oxygen is used in first cycle.

Now total oxygen with incorporated oxygen was 181 atoms.

517 H - 362 155 H
232 O - 78 154 O
491 H - 308 183 H
225 O - 92 133 O
505 H - 266 239 H

Hence the sequence:

O: 181 154 133
H: 155 183 239

In the above site no. calculation all incorporated oxygen (50 atoms) used was removed by the first hydrogen dose.

Site no. calculation for set (ii)

(b) When some of incorporated oxygen used in 2nd and 3rd cycle of set (ii), i.e. reaction with O is slow and only reacts in later cycles.

Total oxygen on surface = 131 atoms.

517 H - 262	255 H
232 O - 128	104 (+20) = 124 O
491 H - 248	243 H
225 O - 122	103 (+30) = 133 O
505 H - 266	239 H

Sequence

O:	131	124	133
H:	255	243	239

Here all the incorporated oxygen was used in the 2nd and 3rd cycle.

There are 239 H atoms left on the surface at the end of second set. Now the film was heated at 90°C for ½ hour at this stage and 29 atoms of hydrogen were desorbed. So the H_2 left on the surface after desorption was 239 - 29 = 210 H atoms. Now 237 atoms of oxygen were adsorbed at 90°C of which 105 oxidised 210 hydrogen leaving 237 - 105 = 132 O atoms on surface.

Site no. calculation for set (iii)

Now before 3rd set starts there are 132 O atoms on the surface. Let us assume that no oxygen was incorporated when the film was heated at 90°C for the second time.

then 132 O

518 H - 264	244 H

217 O - 122	95 O
466 H - 190	276 H
215 O - 138	77 O
464 H - 154	310 H

Hence the sequence:

H:	244	276	310
O:	132	95	77

These sequence of values (oxygen decreasing, hydrogen increasing) suggests that some of 132 oxygen atoms are partly incorporated.

Thus if we assume here that of 132 O atoms and 32 go inside on heating at 90°C, then 100 are left on the surface. We now use the incorporated oxygen in the 2nd H_2 treatment in the calculation.

	100 O
518 H - 200	318 H
217 O - 159	58 (+32) = 90 O
466 H - 180	286 H
215 O - 143	72 O
464 H - 144	320 H

Sequence:

H:	318	286	320
O:	100	90	72

The sequence then becomes more consistent but the available data do not allow us to state how much oxygen is incorporated and how much of this reacts in each subsequent H_2 treatment. It seems evident, however, that (i) incorporation has taken place and (ii) with sufficient number of H_2 cycles, all the oxygen can be removed.

3. System: Oxygen + Iridium + Hydrogen + Oxygen + Carbon-monoxide

In this system after the adsorption of oxygen on a fresh Iridium film, hydrogen was adsorbed; and after that a second oxygen dose was introduced; the Carbon-monoxide was then adsorbed as shown in the Table below.

Run 13

Bath temperature = 273°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
	99.4×10^{-8}	199	252×10^{-8}	504
set (i)	111.0	222		

CO adsorbed at 273°k = 117×10^{-8} moles

CO_2 formed = 76×10^{-8} moles

Adsorption of oxygen at 90°C = 73.8×10^{-8} moles

CO_2 formed = 42.6×10^{-8} moles

Bath temperature = 273°k

	Oxygen adsorbed		Hydrogen adsorbed	
	moles	atoms	moles	atoms
			238×10^{-8}	476
	91.3×10^{-8}	183	197.3	395
set (ii)	89.8	180	194.5	389
	87.4	175	192.2	384

In run (13), oxygen was adsorbed on a fresh iridium film at 273°k and the amount adsorbed was 99.4×10^{-8} moles. After the evacuation of the residual oxygen, a measured dose of H_2 was introduced and the amount adsorbed was 252×10^{-8} moles. Then a second oxygen dose was adsorbed; the amount was 111×10^{-8} moles. After the evacuation of residual oxygen, carbon-monoxide was adsorbed on the oxygen-treated surface; the amount of CO adsorbed was 117×10^{-8} moles. Some of this CO formed CO_2 with pre-adsorbed oxygen and the amount was 76×10^{-8} moles. This CO_2 formed was pumped out and the temperature of the cell was changed to 90°C and a measured dose of O_2 was introduced; the amount adsorbed was 73.8×10^{-8} moles. Now this oxygen formed CO_2 with the rest of the CO which was left on the surface and the amount of CO_2 was 42.6×10^{-8} moles. This CO_2 was pumped out and the temperature of the cell was again changed to 273°k and hydrogen was introduced first. The amount adsorbed was 238×10^{-8} moles. After this H_2 dose, three O_2/H_2 cycles were done and the last cycle was finished with hydrogen adsorption.

Explanation

The total amount of oxygen adsorbed in the two sets was 552×10^{-8} moles and the total amount of H_2 was 1074×10^{-8} moles. Since the last cycle in the second set was finished with H_2 adsorption, H_2 should be left on the surface at the end. The amount of CO adsorbed was 117×10^{-8} moles. Now oxygen required for the oxidation of

117 x 10^{-8} moles of CO to CO_2 was 58 x 10^{-8} moles. So oxygen left for oxidation of H_2 was 552 - 58 = 494 x 10^{-8} moles. This can reduce 988 x 10^{-8} moles of O_2 to water leaving 1074 - 988 = 86 x 10^{-8} moles of H_2 or 172 atoms at the end.

Now after CO_2 formation, oxygen is left on the surface. The total amount of oxygen adsorbed in set (i) was 284 x 10^{-8} moles (i.e. 99 + 111 + 74) and H_2 adsorbed was 252 x 10^{-8} moles. Now CO adsorbed was 117 x 10^{-8} moles so from 284 x 10^{-8} moles of oxygen 58 were used for CO_2 formation leaving 284 - 58 = 226 x 10^{-8} moles for H_2 oxidation and of these 126 oxidise 252 x 10^{-8} moles of H_2 leaving 226 - 126 = 100 x 10^{-8} moles of oxygen on the surface.

Now 100 x 10^{-8} moles or 200 atoms of oxygen are left on the surface at the end of the first set. Of these 200 atoms of oxygen we assume that only 160 are used for H_2O formation and 40 are left on the surface which react slowly in subsequent hydrogen treatments.

Now the first H_2 adsorbed in set (ii) was 476 atoms of which 320 were used for 160 oxygen atoms leaving 476 - 320 = 156 H atoms.

The 1st O_2 dose was 183 atoms of which 78 were used for 156 H atoms leaving 183 - 78 = 105 O atoms +40 already there on the surface, so the total oxygen available was 105 + 40 = 145 O atoms.

Now 395 H atoms were added which oxidised ($395/3$) = 132 O atoms leaving 145 - 132 = 13 oxygen atoms and 132 H atoms on the surface.

Then 180 O atoms were adsorbed of which 66 were used for 132 H leaving 180 - 66 = 114 O atoms + 13 already present there, so the total oxygen now on the surface was 114 + 13 = 127 atoms.

389 H atoms were now added which oxidised $(389/3)$ = 130 O atoms leaving 130 H atoms on the surface (no oxygen left at this stage on the surface).

175 oxygen atoms were then added of which 65 were used for 130 H atoms leaving 175 - 65 = 110 O atoms.

Finally 384 H atoms were added of which 220 were used for 110 oxygen atoms leaving 384 - 220 = 164 H atoms.

Hence the sequence:

O:	200	145	127	110	Mean = 145
H:	156	132	130	164	Mean = 145

Run 15

Bath Temperature = 273°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
109×10^{-8}	218	302×10^{-8}	604
128.8	258		

CO adsorbed at 273°k = 186×10^{-8} moles

CO_2 formed = 103×10^{-8} moles

Adsorption of oxygen at 90°C = 112.5×10^{-8} moles

CO_2 formed = 88×10^{-8} moles

Bath temperature = 273°k

Oxygen adsorbed		Hydrogen adsorbed	
moles	atoms	moles	atoms
		305×10^{-8}	610
120×10^{-8}	240	275	550
116	232	258	516

Run (15) was done in order to confirm the results of run (13), so all the steps were the same as in run (13).

The results in run 15 show the same general pattern as run 13.

Difference of Iridium and Platinum

The reactions were essentially the same for both metals but the reaction of H_2 with chemisorbed oxygen is slow and does not go to completion i.e., some oxygen is left on the surface after the first H_2 treatment but this gradually oxidised by subsequent H_2 treatments. Oxygen, however, completely reacts with chemisorbed H atoms on the surface at each stage.

4. System: Ammonia + Iridium + Hydrogen + Oxygen

In this system there appears to be two acceptable alternative mechanisms.

I. Mechanism

At the high temperature of 273°k, NH_3 is assumed to be dissociatively adsorbed to give Ir-NH_2 and Ir-H so that all primary sites for dissociative adsorption of the first dose of hydrogen are blocked. Hence the subsequent hydrogen adsorption is always adsorbed on top as molecular H_2 and this is rapidly oxidised when oxygen is added. Additionally, some of the primary hydrogen atom layer is also oxidised slowly.

Run 19

Adsorption of NH_3 at 195°k

$255.5 \times 10^{-8} \times 10^{-8}$ moles

Desorption of NH_3 at 273°k = 3.5×10^{-8} moles

NH_3 left on surface = $(255.5 - 3.5) = 252 \times 10^{-8}$ moles

According to run (21) only 72% of 1st dose NH_3 was left on the surface (the rest being desorbed by evacuation and liquid nitrogen trap). We therefore assume that 181×10^{-8} moles of NH_3 are adsorbed in the primary layer.

Bath temperature = 273°k

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
	74×10^{-8}	148	84.5×10^{-8}	169
set (i)	164.0	328	98.0	196
	187.8	376	96.5	193
	204.7	409	97.4	195

Adsorption of NH_3 at 195°k = 20×10^{-8} moles

Desorption of NH_3 at 273°k = 2.8×10^{-8} moles

NH_3 left on surface = $(20 - 2.8) = 17.2 \times 10^{-8}$ moles

Bath temperature = 273°k

	Hydrogen adsorbed		Oxygen adsorbed	
	moles	atoms	moles	atoms
	122×10^{-8}	244	66×10^{-8}	132
set (ii)	124	248	66	132
	131	262	65	130

In run 19, NH_3 was adsorbed on a fresh iridium film at 195°k; the Pirani gauge and all traps (except T_3 which was not in the system) was also at 195°k. The amount adsorbed was 255.5×10^{-8} moles. After the evacuation of the residual NH_3, the temperature of the cell was changed to 273°k and that of the Pirani and all traps to liquid nitrogen temperature. Some NH_3 was desorbed at 273°k and the amount was 3.5 x 10^{-8} moles.

A measured dose of hydrogen was introduced on the NH_3-treated surface. The amount adsorbed was 74 x 10^{-8} moles. The residual gas was pumped out and oxygen was introduced. The amount adsorbed was 84.5 x 10^{-8} moles. After that, three more H_2/O_2 cycles were done and the last cycle was finished with oxygen adsorption. Now again the temperature of the cell and traps was changed to cardice bath (195°k) temperature and a measured dose of NH_3 was introduced. The amount adsorbed this time was 20 x 10^{-8} moles. The temperature of the cell was again changed to 273°k and the Pirani and traps to 78°k temperature. 2.8 x 10^{-8} moles of NH_3 was desorbed at 273°k, so the amount left on the surface after desorption was (20 - 2.8) x 10^{-8} moles = 17.2 x 10^{-8} moles. After the evacuation of the residual NH_3, hydrogen was introduced at 273°k and the amount adsorbed was 122 x 10^{-8} moles. The residual gas was pumped out and a measured dose of oxygen was introduced; the amount adsorbed was 66 x 10^{-8} moles. Two more H_2/O_2 cycles were done and the last cycle was finished with oxygen adsorption.

Run 20

Adsorption of NH_3 at 195°k

290.8 x 10^{-8} moles

Desorption of NH_3 at 273°k = 4.8 x 10^{-8} moles

NH_3 left on surface = 290.8 - 4.8 = 286 x 10^{-8} moles

According to run 21 only 72% of 1st dose of NH_3 is left on the surface (the rest being desorbed); we therefore assume that 206 x 10^{-8} moles of NH_3 are adsorbed in the primary layer.

Bath temperature = 273°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
123 x 10^{-8}	246	159.8 x 10^{-8}	320
310	620	161	322
322.5	645	161	322
325.5	651	159.5	319

Adsorption of NH_3 at 195°k = 25 x 10^{-8} moles

Desorption at 273°k = 2.82 x 10^{-8} moles

NH_3 left on surface = (25 - 2.8) = 22.2 x 10^{-8} moles

Bath temperature = 273°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
164 x 10^{-8}	328	107 x 10^{-8}	214
191	382	104	208
202	404	106	212

Run 20 was done in a similar way to run 19, to confirm the results of that, so all the steps were the same as in run 19.

Run 21

Adsorption of NH_3 at 195°k = 297 x 10^{-8} moles

Desorption of NH_3 at 195°k (with liq. N_2 trap) = 84 x 10^{-8} moles

NH_3 left on surface = (297 - 84 = 213 x 10^{-8} moles

Desorption of NH_3 at 273°k = 5.4 x 10^{-8} moles

NH_3 left on surface = (213 - 5.4) = 207.6 x 10^{-8} moles

Bath temperature = 273°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
133 x 10^{-8}	266	169.6 x 10^{-8}	340
324.4	649	162.5	325
334.8	670	165.6	332
337.4	675	165.0	330
331.0	662	159.5	320

In run (21) NH_3 was adsorbed on a fresh Ir film at 195°k . The amount adsorbed was 297 x 10^{-8} moles, of which 84 x 10^{-8} moles were desorbed by condensation in the liquid nitrogen trap and 5.4 x 10^{-8} moles were desorbed at 273°k. So the total amount of NH_3 left after desorption was 207.6 x 10^{-8} moles (i.e. 72% of 1st dose). After the adsorption of ammonia, hydrogen was adsorbed at 273°k, the amount adsorbed being 133 x 10^{-8} moles. The rest of the gas was evacuated and a measured dose of oxygen was introduced, the amount adsorbed was 169.6×10^{-8} moles. After this oxygen adsorption four more H_2/O_2 cycles were done and the last cycle was finished with oxygen adsorption.

Explanation

I Mechanism

Run 19

From run 21 we assume that only 70% of NH_3 was left on the surface from the first dose; the rest was desorbed by evacuation and condensation in the liquid nitrogen trap. The actual adsorption of NH_3 is therefore $\frac{72 \times 252}{100} = 181 \times 10^{-8}$ moles, occupying 181 Ir-NH_2 and 181 Ir-H sites.

In this mechanism NH_3 is assumed to be adsorbed dissociatively, so it blocked all sites for the dissociative adsorption of hydrogen which is always adsorbed on top as molecular H_2. Hence after the adsorption of NH_3, the first dose of hydrogen goes on top as 74×10^{-8} moles. The first oxygen dose adsorbed was 169 O atoms; it oxidised all the 74×10^{-8} moles of molecularly adsorbed hydrogen to water leaving $(169 - 74) = 95$ O atoms on the surface. Of these 95 O atoms $(\frac{2}{3} \times 95) = 64$ O atoms are left on the surface and 32 atoms are used for the oxidation of the 64 primary hydrogen atoms. Now the second dose of hydrogen adsorbed was 328 H atoms of which 128 H atoms were used for the 64 surface oxygen atoms and produced water leaving $328 - 128 = 200$ H atoms; of these 64 go back to the primary layer leaving 200 - 64 = 136 H atoms or 68 H_2 on top. The rest of the oxygen-hydrogen doses were calculated in a similar way and the sequences as shown below were obtained.

Sequence

H_2 molecularly adsorbed = 74 68 59 70 Mean = 68

O atoms left on surface = 63 86 90 84 Mean = 81

It would appear that of 181 primary H atoms only 81 are "active" i.e. react with oxygen, and these are then rendered unreactive by the second NH_3 adsorption, taken to be 17 x 10^{-8} moles in all. Now before the 2nd NH_3 adsorption, the surface is covered with oxygen atoms and we assume that no H_2 goes on top of these oxygen atoms, since these react with hydrogen and leave H atoms in the primary layer. If NH_3 converts these oxygen atoms to OH radicals this could account for 51 O $\rightarrow$ 51 OH. In this process N_2 is evolved so that the amount of NH_3 adsorbed as measured is low; this may account for the discrepancy. In the first set, the 81 reactive sites (alternatively covered with O and H atoms) are not sites for H_2 molecular adsorption; but after the second NH_3 treatment, the oxygen atoms are converted to OH radicals on which H_2 adsorption can take place. Hence for the second set H_2 adsorption, more H_2 sites are available in the proportion of $^{181}/_{100} \times 68 = 123$, compared with the amount of H_2 adsorbed experimentally which was 122 x 10^{-8} moles. Oxygen then oxidises these H_2 molecules to H_2O

leaving no oxygen behind in the primary layer. The total amount of oxygen in set (ii) was 197 x 10^{-8} moles which can oxidise 394 x 10^{-8} moles of H_2, whereas the total amount of H_2 adsorbed experimentally in set (ii) was 377 x 10^{-8} moles in good agreement with 394 x 10^{-8} moles.

Run 20

According to run 21, 72% of the first dose of NH_3 was adsorbed on the fresh iridium film and the rest was desorbed by evacuation and condensation in the liquid nitrogen trap; the adsorption of NH_3 was therefore 206 x 10^{-8} moles. These occupied 206 NH_2 and 206 H sites. The calculation in this run proceeds as in run (19).

Hence the sequence is:

O atoms left on surface =	131	139	139	135	Mean = 136
H_2 molecularly adsorbed =	123	114	114	117	Mean = 117

Of the 206 primary H atoms only 136 react and (206 - 136) = 70 H atoms remain on the surface throughout.

In the second set of this run (20), the amount of H_2 taken up is increasing with each cycle but that of oxygen is constant (see table of run 20); this is similar to the effect always found (run 19-21) after the first NH_3 treatment. It suggests that not all the oxygen sites are poisoned by the second NH_3 treatment, and some primary hydrogen is being oxidised.

Run 21

In this run the adsorption of NH_3 gives 208 NH_2 and 208 primary hydrogen atoms. The calculation was done similarly as in run (19 and 20) and found the sequence as:

O atoms left on surface =	138	139	137	132	125	Mean = 134
H_2 molecularly adsorbed =	133	117	126	132	132	Mean = 128

Of 208 primary hydrogen atoms, 134 reacted leaving 74 throughout.

Summary

(i) NH_3 is adsorbed on iridium dissociatively giving Ir-NH_2 and Ir-H sites.

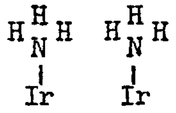
(ii) H_2 is adsorbed molecularly on the primary layer and is oxidised by oxygen.

(iii) The primary H atoms were 181, 206 and 208 in run (19, 20 and 21) respectively. Out of these only 81, 136 and 134 were oxidised by oxygen and 100, 70 and 74 H atoms were left on the surface at the end of cycles in run (19, 20 and 21) respectively.

(iv) After the second NH_3 treatment, molecularly adsorbed hydrogen is oxidised and no oxygen goes into the primary layer.

II Mechanism

Run 19

In this mechanism we assumed that NH_3 is adsorbed molecularly as  $\mathrm{H}\overset{\mathrm{H}}{\underset{\substack{|\\ \mathrm{Ir}}}{\mathrm{N}}}\mathrm{H}\quad \mathrm{H}\overset{\mathrm{H}}{\underset{\substack{|\\ \mathrm{Ir}}}{\mathrm{N}}}\mathrm{H}$; and that the first hydrogen dose goes into the primary layer as H atoms. This is oxidised slowly as primary hydrogen atoms were in mechanism (i).

The first dose of hydrogen was 148 atoms and goes into the primary layer. Now 169 O atoms were added which oxidise ($\frac{2}{3}$ x 169) = 112 H atoms leaving (148 - 112) = 36 H and 112 O atoms on the surface.

In the second hydrogen dose 328 H atoms were adsorbed +36 already on the surface, so the total was (328 + 36) = 364 H atoms which can oxidise all 112 oxygen atoms leaving (364 - 336) = 28 H; hence the total hydrogen left on the surface was 112 + 28 = 140 H atoms. Now 196 O atoms were adsorbed of which ($\frac{2}{3}$ x 196) = 130 react with the primary H atoms leaving (140 - 130) = 10 H atoms and 130 O atoms on the surface.

Now 376 H atoms were added +10 already on the surface, so the sotal was 376 + 10 = 386 H atoms which removed all the oxygen adatoms (130 x 3 = 393) and 130 H atoms are left on the surface. After that 193 O atoms were added of which ($\frac{2}{3}$ x 193) = 129 were used for primary H atoms and 129 O atoms were left on the surface.

Now 409 H atoms were added, of which 387 react with 129 oxygen atoms leaving 409 - 387 = 22 H extra, so the total H atoms left on the surface was 129 + 22 = 151 H atoms. Now finally in set (i) 195 O atoms were added of which 75 were used for the 151 H atoms leaving (195 - 75) = 120 O atoms on the surface.

Hence the sequence

H atoms left on the surface which were unreactive after an oxygen treatment.

36 28 10 22 Mean = 24

Reactive H atoms on the surface.

148 140 130 151 Mean = 142

Reactive O atoms on the surface.

112 130 129 120 Mean = 123

The first set was finished with oxygen adsorption leaving 120 oxygen atoms on the surface. When the second set starts there are 120 O atoms and all are assumed to be active, but from the first hydrogen uptake in set (ii) only ($\frac{1}{3}$ x 244) = 81 sites are active, so that (120 - 81) = 39 oxygen are "deactivated" by NH_3.

Now 81 O atoms (active)

244 H atoms	162 H atoms	used	for	H_2O	leaving	82 H atoms
132 O atoms	41 O	"	"	"	"	"	91 O atoms
248 H atoms	182 H	"	"	"	"	"	66 H atoms
132 O atoms	33 O	"	"	"	"	"	99 O atoms
262 H atoms	198 H	"	"	"	"	"	64 H atoms
130 O atoms	32 O	"	"	"	"	"	98 O atoms

Sequence

H atoms left on surface = 82 66 64 Mean = 71

O atoms left on surface = 91 99 98 Mean = 96

The proportion of oxygen sites is now $96/122$ of those formerly available, so 122 - 96 = 26 oxygen sites are rendered inactive by 17 NH_3, probably by H-bonding to these oxygen sites. The discrepancy is within the error of these calculations.

Run 20

The calculations in run (20) were done in similar way to run (19). The sequence found is given below.

H atoms left on the surface = 246 214 214 214

O atoms left on the surface = 214 214 214 214

In this run, this mechanism seems better than mechanism (i).

Run 21

NH_3 is adsorbed molecularly, so that the first hydrogen dose of 266 atoms goes into the primary layer.

					266 H	atoms	on	surface
340 O atoms	133	used	for H_2O	leaving	207 O	"	"	"
649 H atoms	414	"	for H_2O	"	235 H	"	"	"
325 O atoms	118	"	for H_2O	"	207 O	"	"	"
670 H atoms	414	"	for H_2O	"	256 H	"	"	"
332 O atoms	128	"	for H_2O	"	204 O	"	"	"
675 H atoms	408	"	for H_2O	"	267 H	"	"	"
330 O atoms	134	"	for H_2O	"	196 O	"	"	"
662 H atoms	392	"	for H_2O	"	270 H	"	"	"
320 O atoms	135	"	for H_2O	"	185 O	"	"	"

Hence the sequence

O atoms left on the surface = 207 207 204 196 185

H atoms left on the surface = 235 256 267 270

General Conclusion

Both mechanisms give reasonable explanation but in general the first one seems to give more consistent results.

5. System: Methyl Alcohol + Iridium + Hydrogen

Methyl alcohol was adsorbed dissociatively on fresh iridium film in the primary layer as $\overset{CH_3}{\overset{|}{Ir}}$, $\overset{OH}{\overset{|}{Ir}}$ and then further adsorbed molecularly on the top. When H_2 was molecularly adsorbed on a methyl-alcohol-treated surface, it partly replaced molecularly adsorbed CH_3OH and the oxygen then oxidised this H_2 and some of the molecularly adsorbed CH_3OH.

Run 22

Adsorption of methyl alcohol at 273°k

Bath temperature = 273°k

Hydrogen adsorbed		Oxygen adsorbed	
moles	atoms	moles	atoms
47×10^{-8}	94	125×10^{-8}	250
258.0	516	164.0	328
340.9	682	184.7	370
399.8	800	194.6	389
409.2	818	204.4	409
423.5	847	204.4	409
1878.4		1077.1	

Methyl alcohol was adsorbed on a fresh iridium film at 273°k in run 22, and after five minutes the residual methyl alcohol was evacuated for 10-12 minutes. After the evacuation of residual CH_3OH, a measured dose of hydrogen was introduced; the amount adsorbed was 47 x 10^{-8} moles. The residual H_2 was evacuated and oxygen was adsorbed; the amount adsorbed was 125 x 10^{-8} moles. Then five more H_2/O_2 cycles were done and the last cycle was finished with oxygen adsorption. The total amount of oxygen and hydrogen adsorbed in six cycles was 1077 x 10^{-8} moles and 1878 x 10^{-8} moles respectively.

Explanation

In this run CH_3OH was adsorbed dissociatively in the primary layer and some of it further adsorbed molecularly on top.

When H_2 was introduced, it in part replaced molecularly adsorbed CH_3OH, and oxygen then oxidised this H_2 and some molecularly adsorbed CH_3OH.

Now the first H_2 dose was 47 x 10^{-8} moles, so 23 moles of oxygen were used for that leaving 125 - 23 = 102 x 10^{-8} moles of oxygen. This 102 x 10^{-8} moles of oxygen probably oxidised CH_3OH to form aldehyde (HCHO) and H_2O using one oxygen atom per mole CH_3OH i.e. 204 moles of CH_3OH were oxidised.

$$O + CH_3OH \longrightarrow HCHO + H_2O$$

Hence the second H_2 dose can be adsorbed on the molecular sites of CH_3OH, so that we expect 204 + 47 = 251 x 10^{-8} moles of H_2 to be adsorbed, whereas in the second adsorption of H_2 258×10^{-8} moles were taken up in good agreement. This required 129×10^{-8} moles of O_2 leaving $164 - 129 = 35 \times 10^{-8}$ moles of oxygen for CH_3OH (m) oxidation.

Hence the amount of molecularly adsorbed H should be $258 + 70 = 328 \times 10^{-8}$ moles whereas the experimental value was 341×10^{-8} moles.

After this effect, in cycle 3 there was largely oxidation of molecular H_2 by oxygen, no oxygen being left on the primary layer. Since both the H_2 and O_2 figures still show some increase, further small replacements (without oxidation) of remaining CH_3OH (m) probably take place.

Now the total amount of oxygen in the four cycles was 788×10^{-8} moles and the total amount of H_2 was 1573×10^{-8} moles which is a good 2/1 ratio. Hence here H_2 is molecularly adsorbed and this is oxidised by oxygen but no oxygen goes into the second layer.

Conclusion

(i) CH_3OH is adsorbed dissociatively in the primary layer and then adsorbed molecularly on the top.

(ii) H_2 partly replaced this molecularly adsorbed CH_3OH and then oxygen oxidised this H_2 and some CH_3OH (m).

(iii) H_2 adsorbed molecularly and oxidised by oxygen but no oxygen goes into the second layer.

Some other experiments were done with the sequences (i) H_2/O_2 (ii) $H_2O/H_2/O_2$ (iii) $H_2/H_2O/H_2/O_2$ on iridium but in all cases, no definite conclusions could be drawn. There was considerable non-reproducibility which was associated (i) with the slow rates of reaction at various stages and (ii) the probable desorption (without reaction) of molecular hydrogen over the primary H atoms layer on addition of oxygen. It seemed probable from the general trend of results that had higher temperatures being used, similar effects as found with the platinum film would have been obtained.

System: Adsorption of H_2O vapour on Pt, Ir and W film

Kemball(3) has published some interesting results of the chemisorption and decomposition of water on tungsten films, either clean, or on which presorption of oxygen and hydrogen had taken place. Since tungsten is not an efficient catalyst for the combination of H_2 and O_2 to form water, similar experiments were undertaken using Pt and Ir films to find out whether there were significant differences in behaviour.

Water was introduced to a fresh Pt, (W and Ir) film at 273°k with Pirani gauge, trap T_1 and water bulb at 273°k. After five minutes the water bulb was isolated and the excess water was evacuated from the cell for 20 minutes. Then the temperature of the Pirani and trap T_1 was reduced to 78°k and the film was heated at different temperatures in order to follow the possible production of hydrogen.

With Pt, no hydrogen was detected below 200°C; however, with increasing temperature evolution took place, the total pressures of hydrogen produced being 0.10, 0.4, 1.49 and 2.11 ($\times 10^{-3}$ torr) at 230, 280, 350 and 400°C respectively (Fig. 12).

These results show that water is strongly chemisorbed on a Pt film at 273°k and since H_2 is not evolved till 500°k has been attained, it suggests that the chemisorption may be associative at 273°k but becomes dissociative at the higher temperatures.

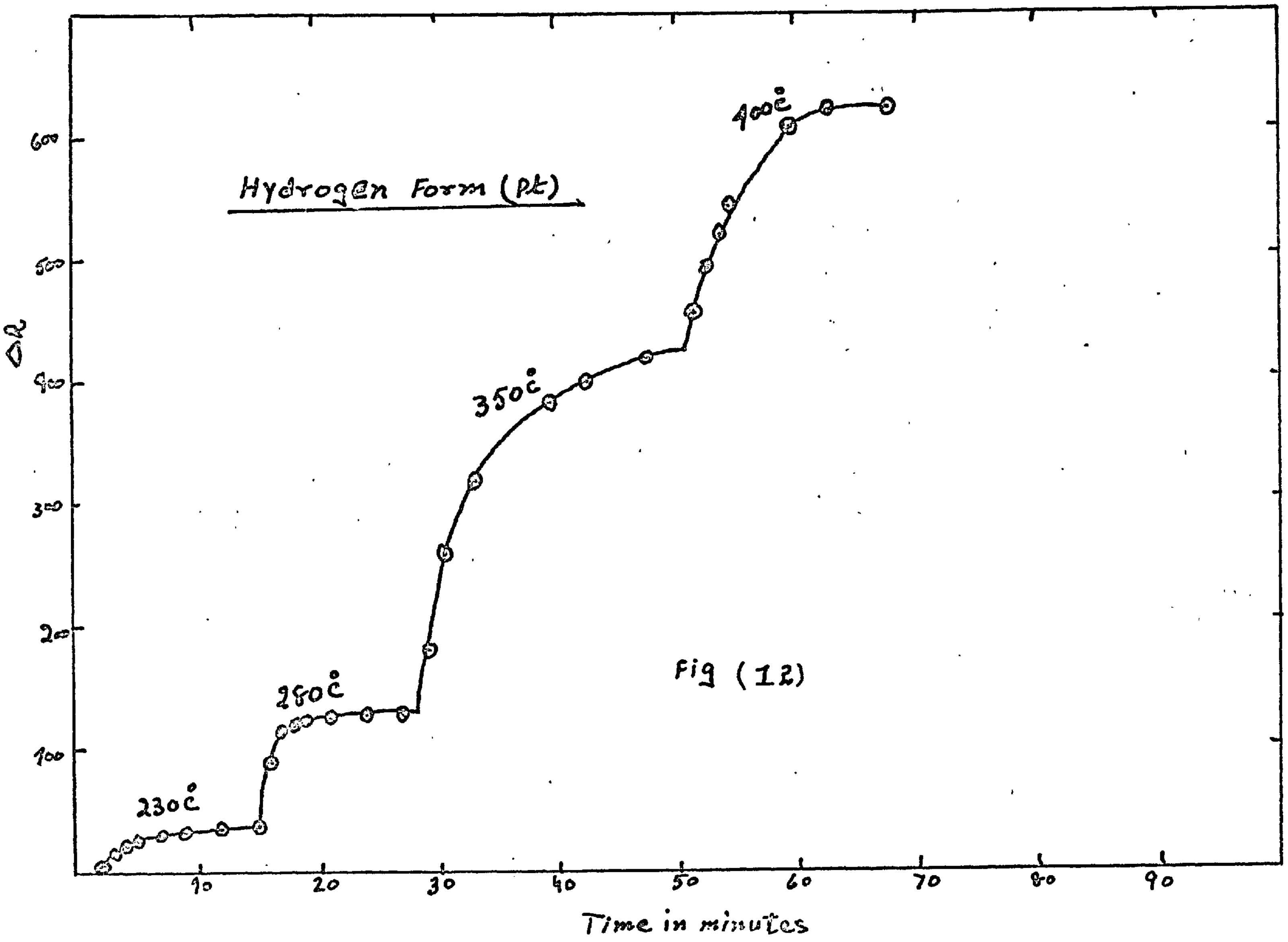

Hydrogen Form (pt)
ΔR
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
Time in minutes
230°C
280°C
350°C
400°C

Fig (12)

Iridium reacts similarly at 212, 300 and 400°C, the total pressure of hydrogen produced was 0.47, 0.72, 0.88 (x 10^{-3} torr).

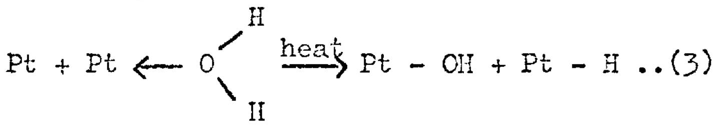
With tungsten, hydrogen was however evolved at as low a temperature as 273°k, The total pressure being 0.86, 6.69, 9.00, 9.73 (x 10^{-3} torr) at 0, 100, 200 and 300°C respectively (Fig. 13). The mechanism suggested by Kemball (3) was

$$2W + H_2O \longrightarrow WOH + WH \qquad \ldots\ldots\ldots\ldots(1)$$

i.e. dissociative chemisorption of water followed by reaction of WH with a further dose of H_2O:

$$WH + H_2O \longrightarrow WOH + H_2 \qquad \ldots\ldots\ldots\ldots(2)$$

With Pt and Ir, a possible mechanism is



$$Pt + Pt \longleftarrow H_2O \xrightarrow{\text{heat}} Pt - OH + Pt - H \quad ..(3)$$

followed by $2Pt - H \longrightarrow 2Pt + H_2 \qquad \ldots\ldots\ldots\ldots(4)$

(and possibly at higher temperatures,

$$2Pt - OH \longrightarrow Pt + Pt\,O + H_2O\ ).$$

There is no evidence for reaction (2) with Pt and Ir.

A further major difference between Ir and Pt on the one hand and W on the other hand, is that with the former when the temperature is lowered to room temperature in presence of the evolved hydrogen, all the hydrogen was re-adsorbed (as would be expected from equation (4)) where Pt sites previously occupied by chemisorbed

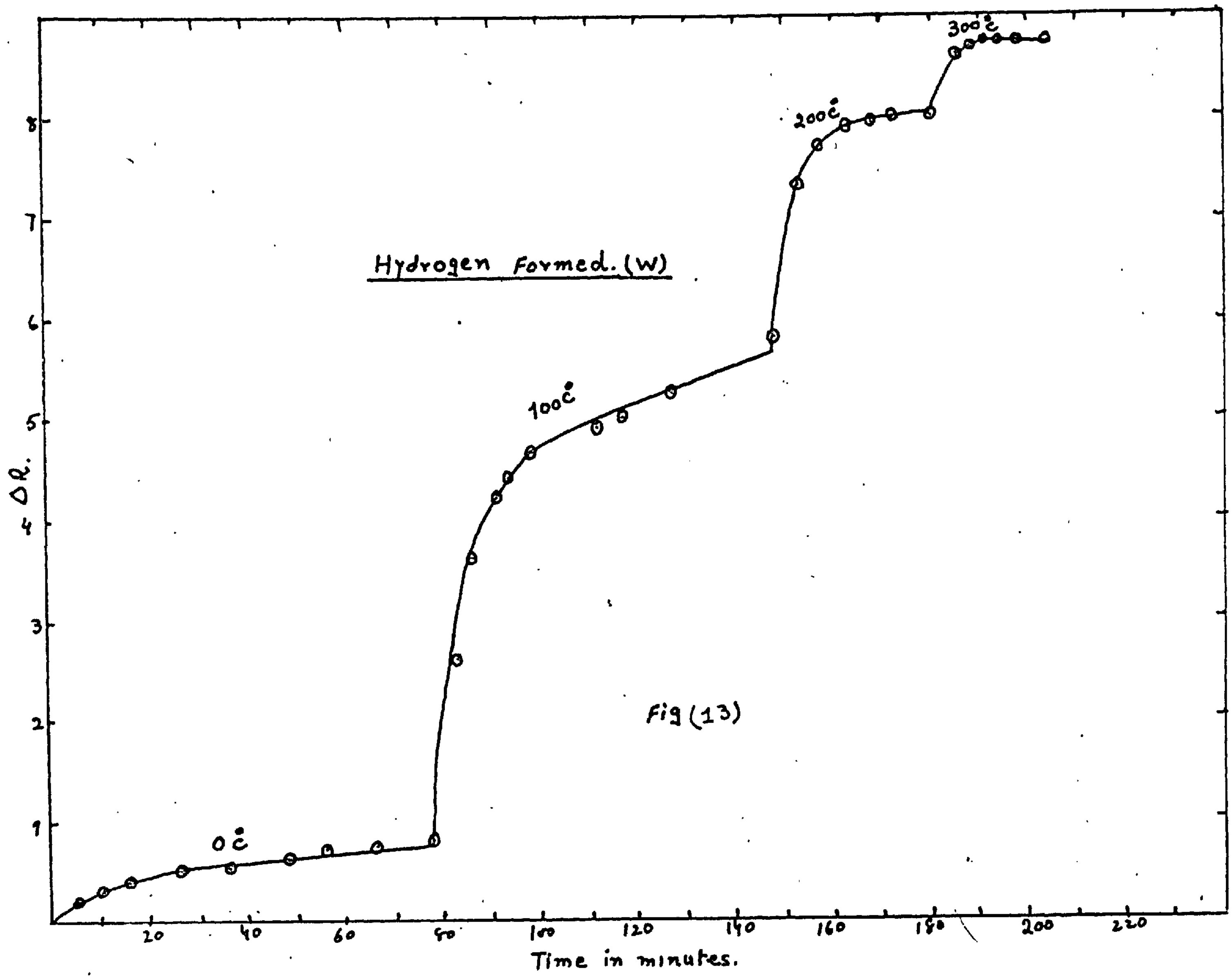
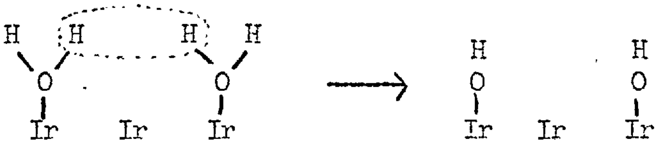

Hydrogen Formed. (W)
ΔQ.
1
2
3
4
5
6
7
8
20
40
60
80
100
120
140
160
180
200
220
Time in minutes.
0°C
100°C
200°C
300°C

Fig (13)

hydrogen are free for re-adsorption (Fig. 14).

With W, there was no re-adsorption of hydrogen, suggesting that possible free metal sites are not available. With iridium, the hydrogen was re-adsorbed to a small extent at the actual temperature of the decomposition . This may mean that H_2O was associatively adsorbed on alternate sites (because of steric difficulties) and H_2 was produced at least in part as in equation (5).



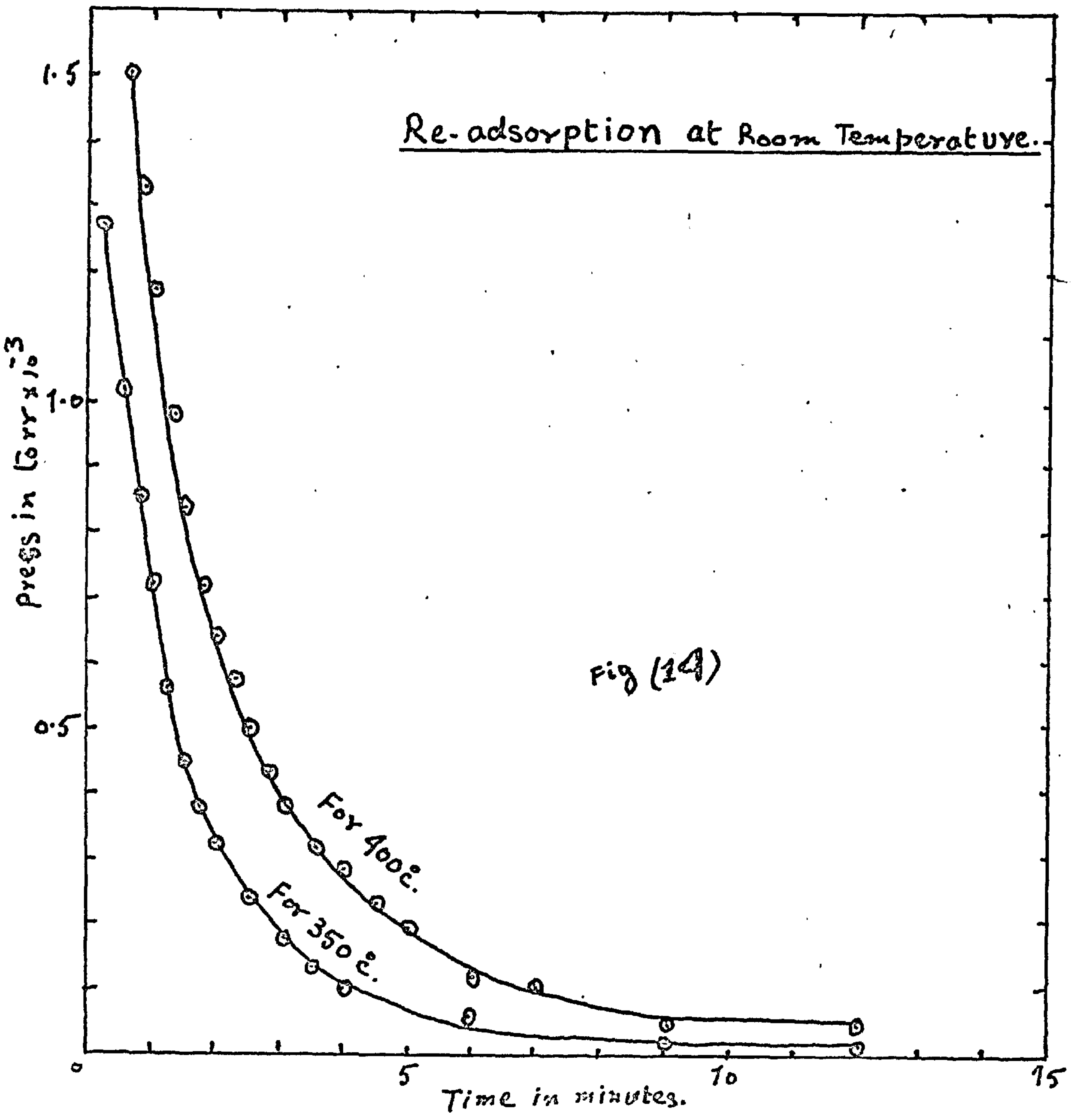
$+ H_2$ .....(5)

The hydrogen is then re-adsorbed on the accessible free Ir sites. Indeed, this may form part of the mechanism on Pt instead of equation (3), (4), the bond Pt-H being less strong than the Ir-H bond, so that no re-adsorption of H_2 occurs at the temperature of decomposition. With W, because of the lower temperature for evolution of hydrogen, we may assume that after dissociative adsorption of H_2O in the primary layer (equation (1)), there is further molecular water adsorption on top of this layer, with probable hydrogen bonding of this molecule to the OH and H radicals on the surface.

Thus equation (2) should probably be written as

$$\mathrm{WOH} + \mathrm{WH} + \mathrm{H_2O}\ (\mathrm{ads}) \longrightarrow 2\mathrm{WOH} + \mathrm{H_2}$$

so that free W sites are not available after hydrogen evolution and



Re-adsorption at Room Temperature.

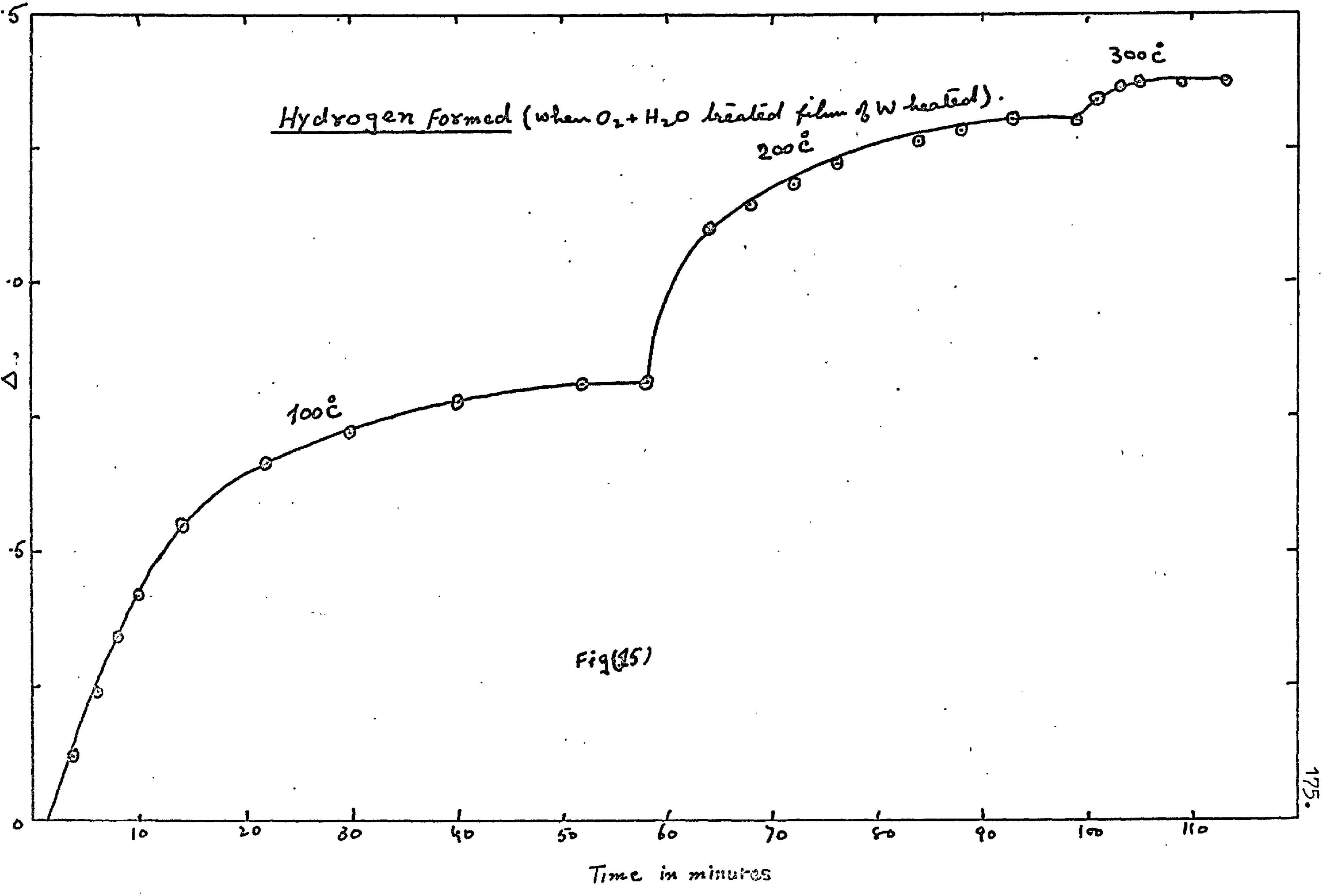
Fig (14)

hence there is no re-adsorption of this gas when the system is cooled down to room temperature.

There is further difference in the reactivity of W and Pt surfaces. After chemisorption of oxygen on the W surface, addition of H_2O (g) and heating to 100, 200 and 300°C causes H_2 to be evolved (Fig 15), whereas with Pt and Ir this does not occur, at least upto 400°C. For W, the surface structure postulated by Kemball was WO_2 and WO_2H-analogous surface compounds with Pt are evidently unstable.

When a water-treated surface of W was treated with oxygen, there was a small rapid adsorption followed by a slow uptake over the next 30 minutes. Very little hydrogen was evolved during this latter process at 0°C.

Similar results were found with Pt-little oxygen was adsorbed on top of the water-treated surface at 273°k indicating strong chemisorption of H_2O, not replaceable by O_2. No hydrogen was evolved on raising the temperature to 373°k and little further oxygen was taken up at this temperature when an oxygen dose was added. Further heat to 230°C gave no evolution of H_2, although a detectable amount would have been expected. Presumably this was evolved as water, formed by oxidation with the small amount of chemisorbed oxygen on the film. On cooling to 273°k, a "normal" dose of H_2 was taken up, i.e., corresponding to that taken up by a comparable film at 273°k which had been treated with H_2O and then

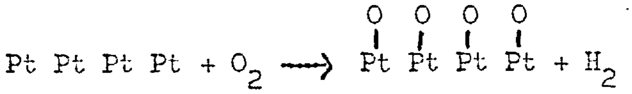

Hydrogen Formed (when $O_2 + H_2O$ treated film of W heated).
·5
·0
Δ
·5
0
10
20
30
40
50
60
70
80
90
100
110
Time in minutes
100°C
200°C
300°C

Fig(15)

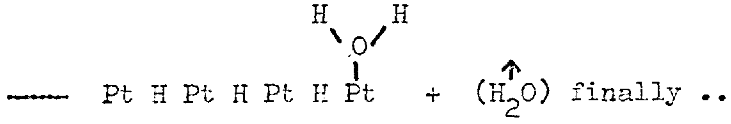
immediately with H_2 at 273°k. These experiments give evidence of the strong chemisorption of water on a Pt film.

General Discussion

There is a rapid reaction between hydrogen and oxygen at 195°k in the presence of a Pt film. The general mechanism, when oxygen is used as the first adsorbent, is the production of an oxygen adatom layer by dissociative adsorption. Most of these adatoms are catalytically active and reactive with hydrogen to form water leaving an equivalent layer of hydrogen atoms on the surface. Some of the oxygen adatoms appear to be inactive but, to preserve a mass balance, these must be hydrogenated to form a stable chemisorbed water molecule, which only decomposes to give hydrogen at temperatures above 200°C. Hence we may write

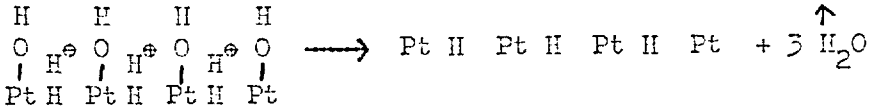


$$\mathrm{Pt\ Pt\ Pt\ Pt} + O_2 \longrightarrow \overset{\overset{O}{|}}{\mathrm{Pt}}\ \overset{\overset{O}{|}}{\mathrm{Pt}}\ \overset{\overset{O}{|}}{\mathrm{Pt}}\ \overset{\overset{O}{|}}{\mathrm{Pt}} + H_2 \quad \ldots\ldots\ldots\ldots\ldots(1)$$



$$\longrightarrow \mathrm{Pt\ H\ Pt\ H\ Pt\ H}\ \overset{\overset{H\diagdown O \diagup H}{|}}{\mathrm{Pt}} + (\overset{\uparrow}{H_2O})\ \text{finally} \quad \ldots\ldots\ldots\ldots(2)$$

A possible intermediate transition surface complex may be



$$\overset{\overset{H}{O}}{\overset{|}{\mathrm{Pt}}}\ \underset{H}{H^{\oplus}}\ \overset{\overset{H}{O}}{\overset{|}{\mathrm{Pt}}}\ \underset{H}{H^{\oplus}}\ \overset{\overset{H}{O}}{\overset{|}{\mathrm{Pt}}}\ \underset{H}{H^{\oplus}}\ \overset{\overset{H}{O}}{\overset{|}{\mathrm{Pt}}} \longrightarrow \mathrm{Pt\ H\ \ Pt\ H\ \ Pt\ H\ \ Pt} + 3\,\overset{\uparrow}{H_2O}\ ..(3)$$

i.e. oxygen adatoms are covalently linked directly to surface Pt atoms; on addition of hydrogen, H adatoms may go into the primary layer in superficial insterstitial sites, the O adatoms are transformed to -OH radicals and the second H adatom is one carrying a high dipole positive outwards - the so-called protonic adatom as found by Siddiqui and Tompkins (4) for CO + H_2, O_2 + H_2 on Ni, and possibly NH_3 + H_2 from the surface potential measurements. This protonic H is highly reactive and not directly bonded to the metal. Water evolution leads to Pt H Pt H Pt H Pt. Treatment of this surface with oxygen definitely produces H_2O and the agreement of oxygen-site and hydrogen-site number suggests that the surface is transferred back to an O-adatom layer. In contrast, tungsten, Roberts (5) found that a molecule of hydrogen was desorbed for each molecule of oxygen chemisorbed i.e.;

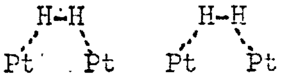
$$O_2 + 2WH \longrightarrow 2WO + H_2,$$

whereas with platinum the equation is

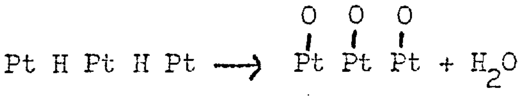
$$\tfrac{3}{2}\, O_2 + 2Pt\ H \longrightarrow 2Pt\ O + H_2O$$

showing the high reactivity of the chemisorbed H adatoms.

A better comparison is for Pt films on which H_2 was adsorbed first, followed by oxygen treatment. In this series, it appeared that about 20% of the hydrogen is desorbed as H_2 molecules and 80% react to give H_2O. With continued cycling, the H_2/O_2 results became "normal" i.e., as if oxygen had been adsorbed first on the clean film. It would appear that there are two types of chemisorbed H adatoms, those produced during cycling being of one form, and those (or part of them) formed by H_2 adsorption on a clean film. There is considerable evidence that two chemisorbed H-species exist which differ in bonding characteristics. Thus, the difference may well be a different site location on the Pt surface for the two different forms. There is, in fact, no evidence that would deny the existence of a chemisorbed H_2 molecule formed during the cycling process, provided two Pt sites were engaged thus :



Such H-species are oxidised by (gaseous) oxygen freeing the Pt sites for the final act of dissociative O adatom adsorption. Similarly in the complex (equation(3)), a process involving the chemisorption of H_2 molecule is not excluded. During oxygen treatment in a H_2/O_2 cycle, water is formed so that the reaction in



$$\mathrm{Pt\ H\ Pt\ H\ Pt} \longrightarrow \overset{\mathrm{O}}{\underset{|}{\mathrm{Pt}}}\ \overset{\mathrm{O}}{\underset{|}{\mathrm{Pt}}}\ \overset{\mathrm{O}}{\underset{|}{\mathrm{Pt}}} + H_2O$$

The agreement of H- and O- site numbers at each step in the H_2/O_2 confirms that no hydrogen is left in the chemisorbed layer.

This oxygen-hydrogen treatment leads to a good method of determining the surface area of a Pt surface, whether as a film or as a supported metal (in this latter case, corrections for adsorption on the support material must be applied where necessary) With a film, where under good conditions, we may assume negligible total contamination of the film, we may distinguish between total area, and reactive area for the H_2/C_2 reaction; this area may well be different than the reactive area for another catalytic reaction, say, CO + O_2 reaction; the present results show however, that such differences are probably slight. For supported metal, the reactive area only may be obtained since the extent of the original contamination and its possible removal by H_2/O_2 cycling is unknown. The advantage of the method of using the extent of H_2 uptake after an initial low temperature treatment with oxygen is that by removal of H_2O produced (e.g. by the support or/and liquid nitrogen trap); the uptake is three times that necessary for a monolayer of H adatoms. The site calculation generally shows that the degree of monolayer coverage is essentially the same for H and O adatoms; this agreement could mean that a value of $\theta = 1$ is being closely approached in the present experiments, where the conditions are $195^{o}k$ and about $3\text{-}5 \times 10^{-3}$ torr. In certain cases, there is evidence of molecular H_2 adsorption in the second layer and is shown by the discrepancy in O and H adatoms site numbers.

As mentioned above, there appears to be some difference in the H_2 bonding in the primary layer depending on the order of the adsorption. If H_2 is first adsorbed on the clean metal, or is formed by dissociative adsorption, e.g. of H_2O, or NH_3 on the clean metal, it appears to react less quickly in the subsequent H_2/O_2 cycles, but finally, after sufficient cycling, the "normal" behaviour found when O_2 is the first adsorbent is usually obtained;

this result indicates that all the initial primary H adatoms have reacted, or further reaction of the most tightly bound atoms does not take place.

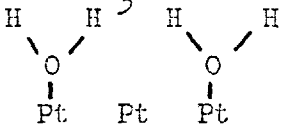
When oxygen adsorption on the clean metal is done at higher temperature (usually adsorption at 195°k, raising the temperature, say to 365°k and subsequent further adsorption of oxygen at 195°k), there is some incorporation of some of the O atoms into the bulk (2nd layer; and at higher temperature, 3rd layer incorporation). It appears that second layer incorporated oxygen can be removed fairly readily and completely by the H_2 in the H_2/O_2 cycling, or by treatment with CO at 70°C, but 3rd layer incorporation seems to be unreactive under the mild conditions of temperature used here. Sintering of an O-adatom layer is not evident at 70°C but at a 100°C some loss of "area" or "reactivity" of the surface O-layer is found.

After O_2-treatment in a H_2/O_2 cycle, the surface is covered with O-adatoms. From the work of Heine, these should be removed by carbon-monoxide. Thus Heyne (6) found that some 20-30% of an O-layer was reduced to CO_2 virtually instantaneously at 78°k. Ahuja (7) showed that more could react at higher temperatures. In the present experiments about a ⅓rd of the O-layer above was converted to CO_2 and all could be removed at 70°C with oxygen. The original H_2/O_2 cycle could then be repeated at 195°k without much change. This particular process (production of CO_2 at 70°C after uptake of CO) could also be used as a means of determining a surface area, if convenient.

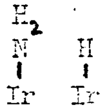
Evidently at lower temperatures some surface complex, e.g.;

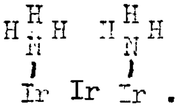
$$O=C=O\cdots Pt$$

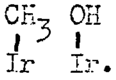
is formed but the "desorption" energy is not sufficiently rapidly acquired at $195^{o}k$ whereas it is at $70^{o}C$. Ahuja(7) has also found evidence for the chemisorption of CO on an oxygenated Pt surface (without production of CO_2 at the lower temperature).

Preadsorption of water vapour and ammonia were undertaken with the assumption that these are dissociatively adsorbed. The former would lead to $\underset{Pt}{\overset{H}{O}}\ \underset{Pt}{H}$ or some similar structure so that by further H_2, and later O_2 treatment, a normal H_2/O_2 cycling series could be induced. With NH_3 however, the surface, possibly $\underset{Pt}{\overset{H_2}{N}}\ \underset{Pt}{H}$, does not have the necessary basic structure and a likely mechanism based on the structure of the transition complex is weak chemisorption of H_2 on top of this primary layer and oxidation of this by the next dose of oxygen. At the same time the oxidation of some primary H-adatoms from the initial dissociation would proceed more slowly. Indeed when H_2 is adsorbed first on a clean Pt surface, it seems that weak decomposition of H_2 molecules proceeds on top of such H adatoms; these are less strongly held than over the ammoniated layer and hence some are probably physically displaced (without oxidation) when O_2 is introduced. It may be noted that in both the presorption of H_2O and NH_3 an associative adsorption on alternative Pt sites, e.g;  on which weak molecular H_2 adsorption proceeds would be reasonably consistent with the experimental results. With water, some slow desorption of the water proceeds during H_2/O_2 cycling thereby freeing some Pt sites; and with NH_3 one would assume some oxidation of the adsorbed NH_3 by oxygen (not necessary with complete removal of all the H atoms, or the N-atoms).

In the case of iridium the general mechanism was similar to that of platinum but there are a few differences. When oxygen is used as the first adsorbent, there is production of an O-adatom layer by dissociative adsorption like Pt but there are two main differences (i) the primary adsorbed oxygen-adatoms are reduced to H_2O more slowly and some of these remain on the surface but are slowly reduced in subsequent H_2 treatment and are gradually removed from the surface; (ii) at lower temperature H_2 is molecularly adsorbed over the primary H-atom layer and is oxidised to water by the next oxygen treatment.

When NH_3 is adsorbed on iridium there appears to be two acceptable alternative mechanisms (i) is similar to that of Pt in which NH_3 is assumed to be adsorbed dissociatively as  $\underset{\mathrm{Ir}}{\overset{\mathrm{H_2}}{\mathrm{N}}}\ \ \underset{\mathrm{Ir}}{\mathrm{H}}$ and in (ii) NH_3

is assumed to be adsorbed molecularly and the surface possibly comprises

$\overset{\mathrm{H}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{H}}{\overset{|}{\mathrm{Ir}}}\ \mathrm{Ir}\ \overset{\mathrm{H}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{H}}{\overset{|}{\mathrm{Ir}}}$. In this case the hydrogen does go into the primary layer as H-adatoms. These H-adatoms oxidised slowly as primary hydrogen did in mechanism (i).

For carbon-monoxide and CH_3OH the mechanism on iridium is the same as on platinum; oxygen was incorporated when the film was heated at 90°C and this could be later used for carbon-dioxide formation as in the case of Pt. Similarly, CH_3OH is adsorbed on iridium dissociatively as for Pt and the surface structure is probably

$\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{Ir}}}\ \overset{\mathrm{OH}}{\overset{|}{\mathrm{Ir}}}$. The only difference is that in the case of iridium some CH_3OH was also adsorbed molecularly on top of the dissociatively adsorbed CH_3OH. These are partly replaced by H_2 admolecules; then oxygen oxidised these to water but no oxygen goes into the second layer.

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