SURFACE PROCESSES
ON EVAPORATED METAL FILMS

THESIS

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CONTENTS

ABSTRACT

Thin films of nickel, copper, platinum, palladium, and iron have been deposited on to a Pyrex glass substrate at various temperatures in a low pressure of krypton. It has been shown that when the substrate is maintained at 77°K during the evaporation process, quantities of krypton are incorporated in to the growing film. The highest value observed was for nickel; in one case, 5.4% of all the atoms in the complete film were krypton atoms.

The process of krypton incorporation is believed to involve krypton atoms adsorbed at the growing surface of the film. The kinetics of the incorporation process in the region below 40% surface coverage have been interpreted in terms of the Langmuir theory of adsorption. Evidence has been obtained to show that the adsorbed state of krypton on the surface of a growing nickel film differs significantly from the state of classical physical adsorption.

Release of the krypton held by metal films has been conveniently followed by using, in their preparation, krypton containing a proportion of the radioactive isotope ^{85}Kr.

On warming the films, it was found that most of the gas held by them at 77°K was lost in the temperature range 100°K to 150°K, but that appreciable amounts were retained up to the highest temperatures studied (800°K). In terms of the thermal release of krypton, the films were found to behave in a manner similar to that observed for solid kryptonates. At each temperature, a stable concentration of krypton was attained, and no more krypton was lost until the temperature was increased.

The quantity of krypton retained by a series of films prepared under widely different conditions of deposition, after the temperature had been allowed to rise to 295°K, has been shown to be fairly constant for each metal excepting iron, where insufficient data were obtained. The mean value at 295°K ranged from 0.25 atomic % of the film for nickel, to 0.70 atomic % of the film for palladium.

The characteristics of krypton release during dissolution of nickel films in acid, and during oxidation of copper films at 443°K, have been interpreted to show that the retained gas is homogeneously distributed throughout the bulk of the films.

The results which have been obtained for the oxidation of copper show that films produced by this technique are suitable for use as homogeneous kryptonates in chemical analyses.

Films of nickel, palladium and platinum have been used in an investigation of the release of krypton during the processes of adsorption and catalysis. Some krypton was lost in all experiments, showing that the surface must be subject to considerable rearrangement during these processes. While thermal sintering owing to the heat of adsorption and catalysis has been eliminated as a possible explanation of the surface changes observed, the limitations of the data obtained have prevented the formulation of an alternative explanation.

CHAPTER I

THE AIMS OF THE INVESTIGATION

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It is usual for a summary of the existing state of knowledge in a field to precede a statement of the aims of an investigation designed to extend such knowledge.

However the investigation described in this thesis had origins in several fields which are not apparently related to each other. Before these subjects are considered individually in Chapter 2, "THE INTRODUCTION", it is appropriate to deal with the basis for bringing them together.

Studies of surface processes and heterogeneous catalysis generally centre on the alterations in the rates and courses of gas phase reactions which are brought about by the adsorption of the reactants on the surface of a solid catalyst. That such effects are found arises from the effect of adsorption on the bonding structure of reactants and intermediate species. Many attempts have been made to relate the structure and composition of a surface to its catalytic properties.

However the surface of a catalyst is itself effected by the processes of adsorption and catalysis. In general, a catalyst is poisoned, sintered, eroded, or otherwise deactivated during its use. For a proper understanding of the process of catalysis, an understanding of the effect of a reaction on the catalyst must be sought.

One technique which has been rarely applied is the study of the release of radioactive rare gas atoms occluded in the catalyst, during adsorption and catalysis. If the structure is initially stable, then any loss of radioactivity from the substance must be related to changes in its surface structure brought about by these surface processes.

It has been shown that inert gas atoms may be introduced in to many solid substances, being retained stably in the lattice unless the structure of the solid is altered by increase of temperature, corrosion, or physical wear. Substances of this type are called "kryptonates", when the inert gas used is radioactive krypton.

There are two methods of preparing them, both of which have disadvantages as far as heterogeneous catalysis is concerned. Preparation by the first method, ion bombardment, may result in the sputtering of material from the surface, and in the enhancement of catalytic activity by an unknown amount. Preparation by the diffusion method requires that the substance be heated under high krypton pressure for a prolonged period, resulting in extensive sintering and a low specific surface area. An alternative method of kryptonate preparation for the study of surface processes must therefore be sought.

It has been shown that hydrogen adsorption on metal films is enhanced by deposition in the presence of hydrogen at 77°K, as a result of the access of hydrogen to all metal atoms in the film during its deposition, so that hydrogen is retained at sites not subsequently accessible from the gas phase. This process has similarities with that of cryotrapping, which is exemplified by the observation that the admission of water vapour to a vessel containing an inert gas at low temperature,resulted in a reduction of the gas phase pressure as gas molecules were trapped during the process of condensation of water on to the vessel walls.

Evaporated metal films are among the most studied of catalyst systems, having the advantages of cleanliness, high surface area, and ease of investigation by electron microscopy.

Accordingly the aims of this investigation were as follows:

(I) To produce kryptonated metal films by "cryotrapping" of krypton during the deposition of metal films at a suitable temperature, and to compare the properties of such films with these of typical evaporated metal films and of kryptonated solids.

(2) To investigate the applications of the completed films in the understanding of surface processes.

CHAPTER 2

THE INTRODUCTION

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2.I THE SURFACE IN ADSORPTION AND CATALYSIS

An atom within the bulk of a crystalline solid is completely surrounded by and bonded to other atoms;its environment is homogeneous. On the other hand an atom at the surface of a solid is bonded only to atoms within the solid, and it retains the ability to form further bonds to molecules which come into contact with the solid.

The phenomenon of heterogeneous catalysis arises from this property of chemisorption, which was first recognised by Langmuir (I). Where bonds are formed between unsaturated surface atoms and a gas (or liquid) phase species, the properties of such species may be altered, in some way that renders it more reactive (2). First, its bonding structure may be changed. When a number of molecules are adsorbed in close proximity on a two-dimensional surface, the number of possible directions of approach for chemical reaction is limited, and thus the effective concentration of the species is increased. Finally, a normally unstable transition state may be stabilised by the effect of adsorption on its bonding structure.

In summary, it is possible for a surface to decrease the energy barrier to reaction, and to increase the proportion of molecular collisions that lead to reaction.

A catalyst is defined as a substance which increases the rate of attainment of chemical equilibrium by a system, with the general implication that the catalyst itself is not altered. Where an increase is brought about in the rate of a forward reaction, a corresponding increase must of necessity be brought about in the rate of the back reaction, since the same transition state is involved. Although catalysts cannot therefore initiate reactions which are thermodynamically unfeasible, where there are several possible reaction paths the particular catalyst may determine which path is followed.

For example, formic acid is decomposed by alumina to give water and carbon monoxide, and by various metals to give hydrogen and carbon dioxide (3).

Accordingly many attempts have been made to relate the catalytic activity of a substance to its known physical and chemical properties, with a view to the ready selection of a suitable catalyst for any possible reaction.

Studies which are intended to relate the properties of a catalyst to the activity of its surface are complicated by the very factor which makes them of interest, namely that the bulk properties are different from those at the surface of a solid.

The earliest attempts to rationalise catalysis lay in the relation of the activity of a substance to its crystalline lattice spacings. This relation is referred to as the "geometric factor". On a theoretical basis Sherman and Eyring (4) calculated that the activation energy for the adsorption of hydrogen on carbon depended on the distance between the carbon atoms concerned. Where this distance was large, the activation energy was high because the molecule had effectively to be dissociated before adsorption could occur. For decreasing distance between the carbon atoms, the activation energy passed through a minimum and then increased because repulsive forces retarded adsorption. Similarly, Twigg and Rideal (5) considered the adsorption of ethylene on adjacent nickel atoms, and predicted that while adsorption on the 2.47 Å lattice spacing would be strain free, adsorption on a 3.50 Å lattice spacing would involve considerable strain. As strong adsorption is, by definition, an energetically favourable state, it is a general principle of catalysis that very strongly adsorbed species are not reactive (6,7,8). It was therefore predicted that the ethylene adsorbed on 3.50 Å lattice spacings would be more readily hydrogenated. This was confirmed experimentally by Beeck, Smith, and Wheeler (9) who produced oriented nickel films which preferentially exposed the IIO face, with a higher concentration of 3.50 Å lattice spacings, and found that they were more reactive than non-oriented films. Although a considerable amount of evidence for the operation of a geometric factor has been obtained, the concept does not provide a complete explanation of surface processes. On a practical basis, it was found that the existance of an apparently favourable lattice spacing did not necessarily give rise to high catalytic activity. Further, catalysts are rarely perfect crystals, and the distribution of particular lattice spacings at the surface is not generally known. It has also been shown that the interatomic distance at the surface of a solid is not necessarily equal to that of the bulk (I0).

An alternative approach considered the electronic properties of the bulk catalyst in relation to its catalytic activity. According to Pauling's theory of bonding, transition metals posses vacant atomic d-orbitals. Where the amount of d-character in the metallic bond is high, then conversely the availability of electrons in atomic d- orbitals is low. Beeck (7) showed that the catalytic activity of a series of metals for ethylene hydrogenation was related to the % d-character of the metallic bond according to Pauling.

According to the band theory of metals, the valency electrons move freely throughout the crystal, and there are 'bands' of permitted energy levels for these electrons. Transition metals in crystal form possess incomplete d-levels. The possibility that the structure of the d-band might determine the catalytic activity of a substance was investigated by Couper and Eley (II), who studied the parahydrogen conversion on alloys of palladium and gold. The operation of a geometric factor was minimised by the selection of two elements of closely similar atomic radii, one of which had an incomplete d-band, and the other full s- and d-bands. A decrease in catalytic activity was found when sufficient gold was present in the alloy to fill the vacancies in palladium's d-band with s-electrons. Similar results were obtained by Reynolds (I2), who studied ethylene hydrogenation on copper-nickel alloys.

This electronic approach to catalysis, while useful, is not of general validity. In the first place, differently arranged crystal faces of a particular metal with a given d-band structure frequently show greater differences in catalytic activity than would be found between metals with different d-bands (I3). Secondly, bonds can in fact be formed between active species(for example, hydrogen introduced as atoms) and the surfaces of metals which have no d-vacancies (I07), so that a theory of adsorption which requires the presence of d-vacancies is of limited validity.

It may therefore be concluded that the bulk properties of a substance cannot be directly related to its catalytic activity with any degree of consistency. An alternative approach of potentially great value, is to consider the properties of the surface itself in terms of its homogeneity or heterogeneity, the relative exposure of particular crystal planes, and the concentration of defects.

From calorimetric studies it may be shown that surfaces are heterogeneous in nature. The heat of adsorption of a gas is found to fall with increasing surface coverage (I4); this is taken to show that the adsorbate is mobile on the surface so that sites of high adsorption energy are occupied first. A part of this effect may be explained on the basis of increased repulsive forces between adsorbed species in the later stages of adsorption.

That surfaces may be heterogeneous in terms of the exposure of different crystal planes has already been stated; several investigations of catalytic activity in respect of the particular distribution of exposed crystal planes have been reported (I5,I6,I7).

Heterogeneity may also arise from the interaction of the surface with crystal defects such as dislocations, where the lattice spacings are distorted from the normal value, possibly to give particularly favourable sites for adsorption or the stabilisation of a transition state. Uhara et al, and other workers (I8-20, 2I, 22) have shown that the catalytic activity of metals is increased by treatment which increases the defect concentration, such as cold-rolling, physical distortion, or ion bombardment. The activity is reduced by annealing the metal at a temperature where, from other evidence, (23), defects and dislocations are known to be annahilated. This approach is also subject to the criticism that a bulk property is being measured; however in some cases direct estimates of the surface defect concentration have been made (24). It is also difficult to separate the effects of recrystallisation to give different crystal faces,and defect annealing, since both are brought on by heat treatment.

No one of the above explanations provides a complete insight in to catalytic behaviour,but in individual cases each may appear to be valid. The problem is further complicated by the fact that the catalyst is not uneffected by adsorption and catalysis. The simplest example of this is catalyst poisoning, where the surface of a catalyst is completely and irreversibly covered by some species, resulting in the destruction of its catalytic activity. The poison may be an intended reactant, a product of the reaction, or some extraneous species.

The effect of adsorption on the bulk properties of a solid is readily shown, for example by resistance changes induced in metal films owing to the electronic nature of the adsorption bond (8,25).

Surface properties have also been investigated to some extent. The surface potential and work function of the catalyst are changed by adsorption (I4, 25, 26); however it is profitable to consider this in terms of the coverage of the coverage of the surface by adsorbed species, rather than as a change in the surface itself.

The properties of a surface are definitely altered by the presence of adsorbed species. Anderson and Baker have shown that adsorbed hydrogen on a nickel surface reduces the rate of thermal sintering (27). This is explained by the stabilisation of the surface which results from the bonding of each adsorbed hydrogen atom to several surface atoms. Anderson has also suggested that the dissipation of adsorption energy may initiate the migration of surface nickel atoms (28).

Much attention has been paid to changes in surface area brought about in surfaces as a result of the process of adsorption. Surface area is normally measured by the physical adsorption of a supposedly inert species.(Section 2.5)

Early investigations by Dell, Klemperer, and Stone, and by Brennan, Hayward, and Trapnell, which showed reductions in surface area as a consequence of chemisorption, were interpreted in terms of thermal sintering of the surface induced by the heat liberated in adsorption (29,30). A consideration of the amount of heat involved (3I), and of the fact that sintering is both temperature- and time-dependent (32), throws doubt on this hypothesis. It has been shown by Campbell and Duthie that the same apparent decrease in surface area is brought by the chemisorption of oxygen on nickel films, whether directly or by an indirect method involving the decomposition of nitrous oxide on the surface (3I). The more favourable conditions for heat dissipation in the latter case would have resulted in appreciably less thermal sintering if this was the explanation of the surface area change. Likewise the occurence of a necessarily permanent process of thermal sintering can not explain the regeneration on standing, of the surface area of manganese films on which oxygen has been chemisorbed(30), the apparent increase in area of iron films after hydrogen adsorption reported by Roberts(33), or the increase in area found by Muller for the adsorption of oxygen on nickel powder(34). Finally, it was shown by Samaane and Teichner that after an apparent reduction of the surface area of supported nickel oxide caused by the adsorption of oxygen, the area could be increased almost to the initial value by heating to a temperature sufficient to desorb the oxygen (35). If thermal sintering had caused the initial apparent decrease in area, then a further decrease must have been expected on raising the temperature.

While it is thus clear that thermal sintering is not an acceptable explanation of the changes caused by adsorption,one contrary result may be mentioned. Knor and Ponec found that the apparent change in surface area of thermally unstabilised nickel films after hydrogen adsorption at 77°K was related to the size of the doses of hydrogen admitted to the system(36). The total amount of hydrogen adsorbed was the same in each case, so that the results were explained in terms of the greater rise in film temperature resulting from the adsorption of a large quantity of gas.

In view of the problems associated with the determination of surface areas by physical adsorption of an inert gas, (Section 2.5) it is not clear whether the measured changes in surface area represent real changes in the character of the surface. Some results may be explained in terms of the blocking of micropores on the surface by adsorbed species, so as to reduce the area accessible to the inert gas(35,37). Alternatively, various explanations based on the effect of the layer of chemisorbed species on the character or quantity of physical adsorptoon may be acceptable(31,38,39).

Techniques for the direct examination of real changes in surfaces during adsorption and catalysis have been less widely applied.

The techniques of electron diffraction and transmission electron microscopy are particularly powerful for the study of evaporated metal films (Section 2.2). Significant changes in surface structure are found by examining films before and after catalysis(40).

Recrystallisation phenomena occuring during catalysis have been observed by optical microscopy(41,42).

Another technique which permits of the examination of the surface during an adsorption or catalytic process is low-energy electron diffraction. The surface of nickel has been observed to undergo a considerable rearrangement as a result of the adsorption of hydrogen(43). There are problems in the interpretation of the results of this method(44), and Bauer has suggested that the adsorbed species, not the surface, is being observed(45). However the phenomenon of surface reconstruction is now accepted as genuine in many cases. Bauer has stated that a surface on which the atoms have the same position as in the bulk is energetically unfavourable, and that the surface energy may be reduced either by adsorption alone, or by adsorption with reconstruction(46). It may be noted that the possibility of surface reconstruction during catalysis invalidates attempts to relate the known structure of a metal to its catalytic activity(the geometric factor).

Jech demonstrated that the surface rearrangements could be sufficiently extensive as to release inert gas atoms occluded in the solid catalyst(47). The use of radioactive species made it easy to follow the release.

It was hoped in the current investigation to develop the potential of this latter technique.

2.2 VACUUM EVAPORATED METAL FILMS

Since the early work of Beeck et al(9), evaporated metal films have been extensively used in studies of adsorption and catalysis. They are typically produced by electrical heating of a metal filament in vacuum to the point of evaporation, so that a film is deposited on to the inner walls of a cylindrical Pyrex vessel. Although such systems are not used at all in applied catalysis, for basic studies they have considerable advantages over catalysts prepared in the form of powders, wires, or supported metals. When evaporation is carried out in a good vacuum, an uncontaminated surface of high specific area is produced.

The high surface area arises because these films are porous in nature. In Beeck's original study it was shown that the amount of various gases which could be chemisorbed by the films was proportional to film weight, demonstrating that the gas must have access to effectively all of the interior of the film. Later workers have shown that the surface area is only proportional to weight if conditions are kept precisely constant. The effect of radiant heat from the hot filament in sintering the film during deposition has been mentioned by Trapnell(48), and that of variations in the condensation rate by Anderson, Baker, and Sanders(49).

It has also been shown that the temperature of condensation, and the presence of an inert gas in the film vessel during evaporation, may determine the structure of a film. Both observations were first made by Beeck(9). The effect of temperature of condensation has been investigated by Knor and Ponec (36,49). High surface areas result from evaporation at low temperature. This observation is explained by the greater tendency at low temperature for a metal atom to stick at the point where it collides with the film, resulting in the production of a less ordered film. The presence of an inert gas also favours the production of films with high surface area(9,50).

According to Beeck, the presence of inert gas caused orientation of the resulting film; however Sachtler was able to produce oriented films in a vacuum of better than 10^{-7}torr(51), and it is now believed that the particular substrate is more important than the presence of inert gas(52).

Films prepared by this method have considerable stored energy, in terms of a high defect concentration(53). It is accordingly necessary to subject them to thorough annealing before adsorption measurements can be made with any certainty(8). As stated in Section 2.1, the surface and defect structure of films has been shown to determine their catalytic properties, and this factor probably explains the tendency for different workers to disagree in measurements of adsorption and catalysis by films.

Another advantage of evaporated metal films is that they are easily investigated by transmission electron microscopy(54). Prepared mounts, normally covered by a film of carbon or silicon monoxide, are placed in the film vessel before evaporation,or alternatively a replica of the film may be made. Although in some cases the change in substrate may effect the properties of the film(55), in general the use of prepared mounts is a powerful technique which leads to information on crystallite size and distribution, the topography of the surface, and the defect concentration in individual crystallites.

Electron diffraction gives information on the structure and orientation of the crystallites(56), and may point to changes in the chemical composition of the film(49,57).

Although films prepared by evaporation are porous, nevertheless only a small proportion of the atoms in a complete film are accessible to the gas phase, It has been shown by Sheridan and Campbell that the adsorption of hydrogen on metal films is considerably enhanced by evaporation of the films in hydrogen at a low temperature, as a result of the access of gas to all of the interior sites during formation of the film(58). Some hydrogen is held at sites inaccessible to the gas phase after warming the film.

It is not necessary to have a species which is chemisorbed on the film in order to incorporate quantities of gas. Winters and Kay have demonstrated that argon implanted as ions during deposition of a nickel film is stably retained once growth ceases, although in principle the gas can not be chemisorbed in this case(59).

2.3 KRYPTONATES

The study of the trapping of inert gases within solids originated from observations that gas discharge lamps employing inert gases would cease to function after a period of time owing to a drop in gas pressure below a threshold value(60). This effect arises because the inert gas atoms, ionised while the lamp is operating, are impelled in to the cathode and remain there. Diffusion from the cathode back to the gas phase is so slow that eventually the quantity of gas removed to the cathode is sufficiently large to result in failure of the lamp.

It has been shown that neon, argon, krypton, xenon, and radon may all be incorporated in to solids by ionisation in an electric field. The most thorough study of this subject was carried out by Almen and Bruce, who used an electomagnetic isotope separator, which permitted of the selection of the mass, energy, charge and entrance angle of the bombarding species(6I). These authors found that under given conditions the quantity of the inert gas introduced in to the solid reached a saturation value as a result of the attainment of dynamic equilibrium between the processes of ion implantation and the loss of the surface layers of the target by sputtering.

Rimmer and Cottrell have indicated that initially the gas atom is trapped between the planes of the solid crystal, but suggest that owing to the resultant strain in the lattice, the gas atom subsequently takes up a substitutional position by displacing one of the atoms of the target(62). While it is accepted that in many cases the gas is held at lattice points, evidence has been obtained for some substances which relates the incorporated gas to defect structures(63). The amount of krypton which can be introduced in to molecular sieves, clathrate compounds, and boron nitride, has been shown to be particularly large(64,65); this is associated with the presence of voids in the lattices of these substances.

The depth of penetration has been shown by Davies et al(66,67), to be generally in the order of IO^3 A°. The distribution with depth was studied by Thulin, using a target composed of thin stacked sheets of formvar(68). After bombardment these were separated, and it was found that the concentration of gas first increased, passed through a maximum, and then decreased with depth.

Once an inert gas has been introduced in to a solid by this method, the concentration of gas decreases as the temperature is raised. For each temperature a stable concentration is reached, when no further thermal treatment at or below this temperature results in further loss of gas(69). Some gas is held almost to the melting point of the solid.

On the basis of the known character of inert gas diffusion in solids at room temperature, and assuming an exponential increase in the diffusion coefficient with temperature, Chleck has shown that at temperatures over

800°K, most solids should quickly lose all of the gas held within them(69). This is not observed in practice.

After stabilisation at a selected temperature, the incorporated gas is only released by treatment which disrupts the lattice of the host solid, such as physical removal of the surface layers or chemical action. It is this property which has caused the interest in substances of this type. Many applications arise from the relation of the loss of radioactive inert gases to the treatment of the solid concerned(70,71).

Inert gases are used for these studies because they do not enter metabolic systems and are thus very safe, and because it is unlikely that there would be any chemical interaction with the host solid. Most attention has been paid to kryptonates, which name is given to solids which hold krypton; radioactive kryptonates are prepared from krypton containing a proportion of the unstable isotope Kr^{85}. The reason for the general use of krypton lies in the convenience of detection of this isotope owing to the long half-life(10.27 years), and the energy of the β-radiation(almost entirely 0.672 MeV).

The symbol A(^{85}Kr) has been proposed for radioactive kryptonates, where A is the carrier substance(72). This convention will be adopted here.

In general the chemical properties of a kryptonate are identical to those of the host solid. Chleck(69) has shown that the activation energy for the oxidation of Cu(^{85}Kr) is identical to that reported by Dushman(73), and that the rate of oxidation of kryptonated pyrolytic graphite at room temperature is identical to that found by Blum and Pappis(74).

This statement may not be completely true for kryptonates prepared by the techniques of ion-bombardment developed by Chleck and Jech(47,75,76). It is possible for the surface of a solid to be extensively damaged by such treatment. A considerable increase in catalytic activity may result(21). It has also been shown that the loss of krypton from ion-bombarded solids at high temperatures is partly related to annealing out of the defect structures produced by ion-bombardment, showing that the krypton is not all held at substitutional or 'normal' defect structures, but that some is held at new defects created by ion-bombardment(77,78).

Several other methods of kryptonate preparation have been reported. The first preparation of a stable kryptonate by Chleck and Zeigler(65) involved slow crystallisation of hydroquinone from the melt in an atmosphere of high pressure krypton. This is an example of the important class of kryptonates prepared from clathrate compounds, which have the krypton located in the cage structures.

Another method of preparation which has been particularly applied to clathrate compounds is that of sublimation in an atmosphere of krypton(79,80).

The preparative technique which is most widely applied is that of diffusion at high temperature and krypton pressure(70,75). In contrast to the findings for krypton loss, the amount of gas incorporated is in accordance with the predictions of diffusion theory. The quantity of gas taken up is proportional to the krypton pressure and to the square root of exposure time, and exponentially proportional to the temperature. Diffusion kryptonation is normally carried out in a pressure bomb, and the excess krypton is lost when the bomb is opened. However microdiffusion techniques of particular application to powder samples, using small quantities of krypton, have been developed(81).

Kryptonates may be prepared from most solid substances by one or other of these methods, without significant alterations of their properties. Several reviews of their applications have been published(70-72,82).

Most simply, a kryptonate provides a safe and convenient solid source of β-radiation.

Many applications are related to physical changes of the kryptonate. Chleck measured the activity of a previously kryptonated metal turbine blade which had been mounted for a period in an operating engine, and was able to derive a temperature profile under the working conditions(71). Cucchiara and Goodman have shown that frictional wear can be related to the loss of krypton from surfaces in contact(83); this technique can indicate irregularities such as lubricant breakdown or a sudden load increase. Krypton release provides a method for detecting crystalline phase changes and the onset of melting(84). As a final example, the use of kryptonates in stress-strain studies has been demonstrated(85). A nichrome (^{85}Kr) wire lost more activity under stress in an oxygen atmosphere than in a nitrogen atmosphere. This was taken to show the susceptibility to oxidation of the fresh surfaces exposed as a result of metal creep.

The most important range of applications of the kryptonates is in the field of chemical analyses.

A kryptonate may be used as an end-point indicator. Where a kryptonated solid does not react with the solution being titrated, but does react with the titrant, it loses none of its activity until excess titrant appears in the solution. Thus the onset of activity change marks the end-point. By suitable choice of the kryptonate, a wide range of titrations may be studied (72).

Alternatively the kryptonate may itself be used as the analytical reagent. In this case it is particularly important that the kryptonate be stabilised before use with respect to temperature and time under the working conditions. Further, it is desirable that the distribution of krypton throughout the host solid should be homogeneous, in order that the amount of krypton released should be proportional to the extent of reaction, and thus to the amount of the species to be determined. In this respect kryptonates prepared by crystallisation and sublimation are most suitable, owing to the access of krypton to all of the interior sites of the solid during its formation. Kryptonates prepared by ion- bombardment can not be obtained with homogeneous distribution, but in the diffusion method homogeneous kryptonates can be produced by prolonged treatment of small particles(82).

The scope of the analytical method is very wide and the concentrations of many gas-phase and liquid-phase species can be determined by suitable choice of the kryptonate reagent. The method may be used in reaction to completion, to determine the total quantity of the species of interest, or in a flow system to determine a constant concentration. Some examples of substances which have been determined by the use of kryptonates are given in table I.

TABLE I. EXAMPLES OF THE USES OF KRYPTONATES IN CHEMICAL ANALYSES

REAGENT	KRYPTONATE	REPORTED DETECTION RANGE	REFERENCE
H_2O(in organic solvents)	$CaC_2(^{85}Kr)$	0.25%-2.0%	86
HCI (aq)	$Ag(^{85}Kr)$	$IO^{-1}M-IO^{-4}M$	87
O_2 (aq)	$Tl(^{85}Kr)$	to 0.3ppm	88
O_2 (gas)	$Cu(^{85}Kr)$	IO^{5} ppm-IO^{-5} ppm	89
H_2 (gas)	$PtO_2(^{85}Kr)$	to IOppm	64
O_3 ((gas)	$[C_6H_4(OH)_2]_3(^{85}Kr)$	$IO^{-6}-IO^{-10}gI^{-1}$	90
F_2 (gas)	$(C_6H_4(OH)_2)_3(^{85}Kr)$	to 2ppm	9I
SO_2 (gas)	$NaClO_2$/ $(C_6H_4(OH)_2)_3(^{85}Kr)$	to IO ppm	90

The final example in this table is of a two-component system. Sulphur dioxide first releases chlorine dioxide from sodium chlorite. This in turn reacts with the hydroquinone kryptonate to release krypton.

It may be noted that care must be exercised to ensure that only the species of interest will react with the chosen kryptonate.

The use of a kryptonate may of course confirm that a substance is not effected by some treatment. This is exemplified by Jech's investigation of passive films on $Fe(^{85}Kr)$ and $Zn(^{85}Kr)$ (76), and by Chleck's demonstration from a comparison of the activity of painted and unpainted $Fe(^{85}Kr)$, that a paint was protective against oxidation to 700°K.(85)

The rate of loss of krypton has been used to determine the kinetics of oxidation(84), and of corrosion(85). The kinetics of oxidation of $Cu(^{85}Kr)$ have been interpreted to show that there are two distinct stages of reaction: an "open-structure" reaction while an oxide film is being formed, and a "diffusion" reaction once it is complete(89). These two reactions have not been successfully separated by any other technique.

Kryptonates have rarely been applied in catalysis. Chleck observed that

$PtO_2(^{85}Kr)$ did not lose any activity when hydrogen was added to a stream of air passing over it. This was interpreted to show that hydrogen reacted catalytically with oxygen on the oxide surface, and not with the oxide itself(64). However in this case the source activity was monitored, so that the loss of a small proportion of the total activity might not have been observed.

Jech found that Rn, ^{131}Xe, and ^{85}Kr were released from platinum as a result of hydrogen adsorption and the H_2/O_2 reaction at room temperature(47). Here gas release was followed by monitoring the activity of the gas stream leaving the catalyst chamber. Part of the release in this investigation was taken to be caused by a rise in temperature of the catalyst bed, owing to the dissipation of the reaction heat.

2.4 CRYOTRAPPING

Interest in the sorption of gases at low temperatures has centred on its use as a pumping technique(92). The eventual pressure in a system is limited by the vapour pressure of the adsorbate, and the method is therefore not efficient for the pumping of gases such as hydrogen, helium, and neon.

From the point of view of vacuum technique, the discovery that the admission of a large quantity of condensible material to a system at low temperature resulted in a decrease of the pressure of non-condensible species was of considerable importance. The non-condensible species is trapped during condensation within the bulk of the condensate. This phenomenon was first observed by Chuan for the trapping of hydrogen by nitrogen condensing at 20°K(93), and by Brackman and Fite for the same system, and also for the trapping of air by water vapour condensing at 77°K(94). This process of cryotrapping is analogous to that of gettering(95). The utility of cryotrapping as a pumping technique in relation to that of cryosorption has been reviewed by Hengevoss(96).

Although most attention has been paid to this practical aspect of the technique, it has also been shown by Haygood et al(97, 98) and by Schmidlin et al (99), that the technique can be applied to the investigation of the sorption process.

In the limit, where the rate of condensation is very low, the pressure of the non-condensible species tends to that predicted by the equilibrium adsorption isotherm. At higher rates of condensation, a steady-state treatment may be applied to the system.

It is assumed, first that the number of adsorption sites is constant throughout an experiment, and second that the number of adsorbed species is constant throughout an experiment. The first assumption implies that the process of cryotrapping occurs only at the 'growing' surface of a film; a correction may have to be applied for a small amount of cryosorption occuring in to the bulk of the condensate. The second assumption requires that the number of molecules newly adsorbed by the surface is balanced by the sum of those desorbed and those buried by the surface turnover resulting from continual condensation.

For the trapping of nitrogen, argon, and air at 77°K by condensation of water vapour, it has been shown that the results in the region of low surface coverage may be interpreted on the basis of the Langmuir theory of adsorption (98,99,1). Data on the probability of adsorption and the size of the adsorption site have been obtained.

2.5 INERT GAS / SURFACE INTERACTIONS

In section 2.1, the only type of adsorption considered was chemisorption, which results from the formation of chemical bonds between the surface and the adsorbed species. Such adsorption is characterised by a high energy of adsorption, and usually by the existance of an activation energy. It results in the saturation of the surface valencies by a monolayer of the adsorbed species, and is generally irreversible.

The distinction between chemisorption and physical adsorption is not clear-cut. In many cases, physical adsorption may be a necessary precursor to chemisorption. However in principle physical adsorption derives from the action of the much weaker forces of permanent and induced dipole attraction. These are the forces responsible for cohesion in liquids, and indeed a physically adsorbed layer may be considered to resemble the liquid state of the adsorbate. Physical adsorption is characterised by a low heat of adsorption, by the absence of an activation energy, and by ready reversibility.

It is of particular interest in the determination of surface areas. Early measurements of surface area by workers such as Emmett and Brunauer(I00), Beeck (I0I), and Rideal and Trapnell(I02), used the irreversible chemisorption of gases such as carbon monoxide and hydrogen. Apart from the obvious disadvantage that further study of the surface was not possible, the determined area depended to some extent on the location of the adsorbed gas molecules.

Most surface area determinations are now carried out by low temperature physical adsorption of inert gases. In principle this is a reversible process, and there is no possibility of bond formation, so that the technique should not be specific for different surfaces. The main problem, that multilayer adsorption is usually involved, was dealt with by Brunauer, Emmett, and Teller, in their theory of multilayer adsorption(I03).

However, in studies conducted by this method, it became clear that the atoms of a physically adsorbed inert gas frequently interact with the surface to a greater extent than could be accounted for on the basis of the simple picture of physical adsorption. Even the adsorption of argon has been found to be specific for different surfaces(I04). Measurements of surface potentials, in particular of adsorbed xenon, are remarkably high(26). It is clear that there is some electrostatic contribution to the bond. Reference has been made in section 2.I to the ways in which the presence of chemisorbed species on the surface may effect the character of physical adsorption of an inert gas.

The ready reversibility of the physical adsorption of inert gas atoms on surfaces has been questioned by Knor and Ponec, who found that a part of the krypton adsorbed on thermally unstabilised nickel films at 77°K was not removable by pumping(36).

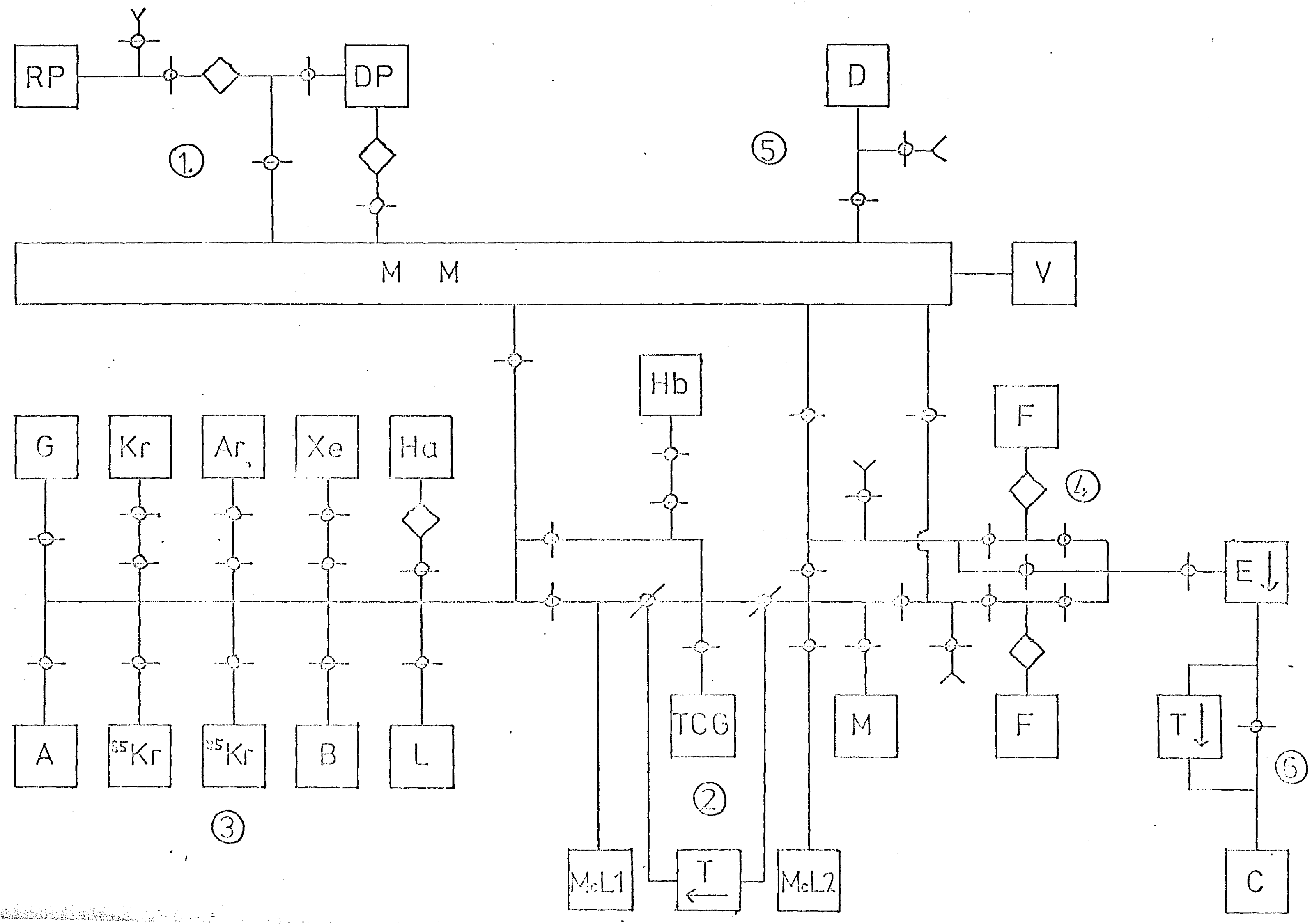
It is not now believed that the inert gases are literally inert; many examples of their compounds have been synthesised(I05). It is probable that the purely physical picture of the association between inert gases and surfaces is also not in accord with reality.

The possibility of the existance of surface compounds of krypton, at least after ion-bombardment(I06), can not be ruled out. Once an atom of an inert gas is introduced in to a surface or solid by whatever means, it may remain there stably in analogy to the stable adsorbed state of hydrogen atoms on gold, where direct molecular adsorption is not possible(I07).

CHAPTER 3

APPARATUS AND EXPERIMENTAL TECHNIQUES

FIGURE 1 THE VACUUM SYSTEM—DIAGRAMMATIC



CHAPTER 3 : APPARATUS AND EXPERIMENTAL TECHNIQUES

3.I THE VACUUM SYSTEM

The vacuum system was constructed throughout from Pyrex glass. The layout of the system in its final form is shown diagrammatically in figure I.

This layout was developed throughout the course of the investigation, so that at earlier stages of the work the capabilities of the system were less; where this fact is important, reference is made to it in the text.

A simplified diagram of the portion of the apparatus used in film deposition is shown in figure I2.

KEY TO FIGURE I.

—○—	Spangham high vacuum taps (various sizes).
—◇—	Liquid nitrogen cooled trap.
—○—<	Air leak (for glass-blowing, etc.)
RP	Speedivac Type IS50 rotary vacuum pump.
DP	Jencons,Ltd. all-glass mercury diffusion pump.
D	Wire degassing vessel.
MM	Main manifold.
V	Edwards,Ltd. 'Vacustat' Type 2-G.
G	Spare gas storage bulb.
Kr	Inactive krypton in I-litre break-seal bulb.
Ar	Argon in I-litre break-seal bulb.
Xe	Xenon in I-litre break-seal bulb.
H(a)	Hydrogen storage bulb (for hydrogen purification).
H(b)	Low pressure hydrogen storage bulb.
A	Break-seal ampoule of radioactive krypton.
^{85}Kr	Charcoal storage trap for active krypton (2, for krypton of different specific activities).
B	Gas burette.
L	Palladium-silver alloy thimble for hydrogen purification.
McLI	McLeod gauge (I59.2 ml bulb).
McL2	McLeod gauge (29.3 ml bulb).
T↓	Toepler pump (showing direction of pumping).
TCG	Thermal conductivity gauge.
M	Mercury manometer.
F	Film vessel.
E	Mercury vapour ejection pump.
C	Gas radioactivity counting chamber.

SECTIONS

I. Pumping section.
2. Gas pressure and quantity measuring section.
3. Gas supply section.
4. Film deposition section.
5. Wire degassing section.
6. Gas counter section.

The purpose of the system was to enable films of various metals to be deposited on to a glass substrate by evaporation either in vacuum or in the presence of measured amounts and pressures of gases, and after deposition to investigate the properties of the resulting films.

The apparatus may conveniently be considered to consist of six sections, as described below.

Number I, the pumping section, served to evacuate the system. Initially pumping was carried out by the rotary pump alone; when a pressure of the order of 0.I torr had been attained, the rotary pump was used as a backing pump for the mercury diffusion pump. The ultimate pressure obtainable in the system was too low to be measurable using the McLeod gauge. No gas space was visible at the top of the closed capillary, and the mercury was observed to 'stick' in the closed capillary when the level in the open capillary was lowered. The ultimate pressure may thus be assumed to be no higher than $I0^{-6}$ torr.

Number 2, the gas quantity and pressure measuring section, consisted of: (a) McLeod gauges, a Toepler pump, a manometer, and sections of calibrated-volume tubing, and (b) a thermal conductivity gauge for continuous monitoring of the pressure. The methods of operation of these two parts are described in sections 3.2 and 3.3 respectively, of this thesis.

Number 3, the gas supply section, consisted of a series of six gas storage bulbs. Three of these were break-seal bulbs containing pure inert gases. The provision of two taps in the length of tubing leading from the main line to these bulbs permitted of the delivery to the system of small quantities of gas. Also in this section was attached a break-seal ampoule of radioactive krypton, and two tubes containing charcoal maintained at 77°K by means of liquid nitrogen, on which krypton of two specific activities, (5% and 0.6% ^{85}Kr), was kept adsorbed before being used. Krypton was desorbed when the charcoal was allowed to warm up to room temperature.

A palladium-silver thimble heated to 520°K was used to purify hydrogen passing from a cylinder to the hydrogen storage bulb Ha. This bulb was connected to a mercury manometer so that the pressure of hydrogen introduced could be read off at a glance; accordingly a cold trap was interposed to protect the palladium-silver thimble from contamination by mercury. Quantities of the hydrogen thus purified were passed to storage bulb Hb. This also was isolated

FIGURE 2 THE FILM VESSEL

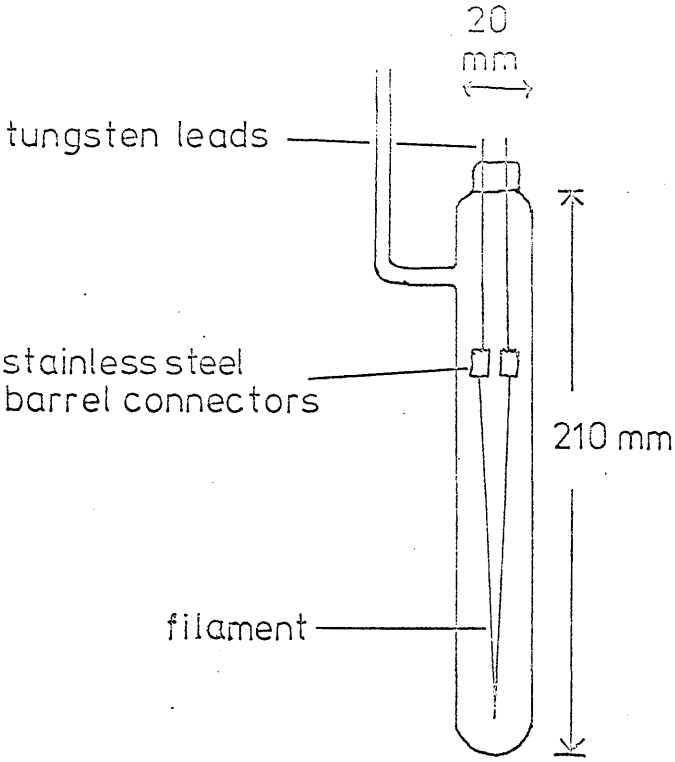


FIGURE 3 THE DEGASSING VESSEL

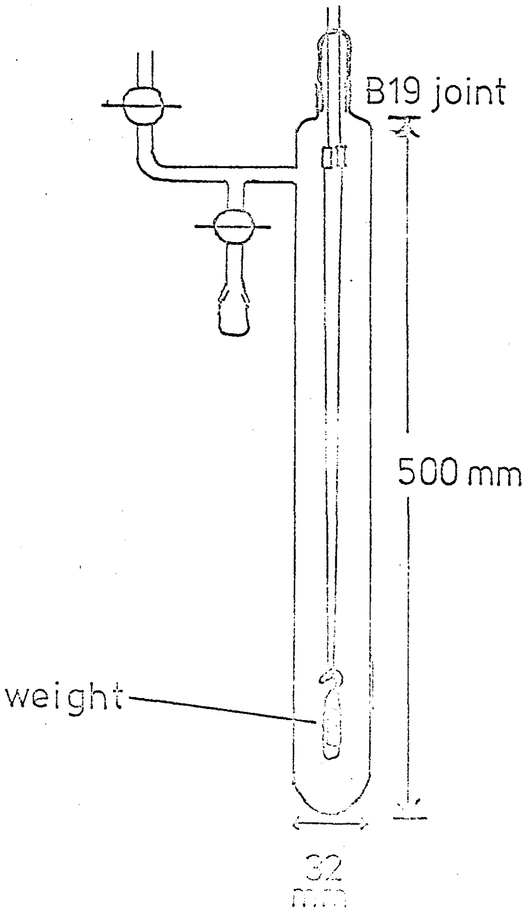
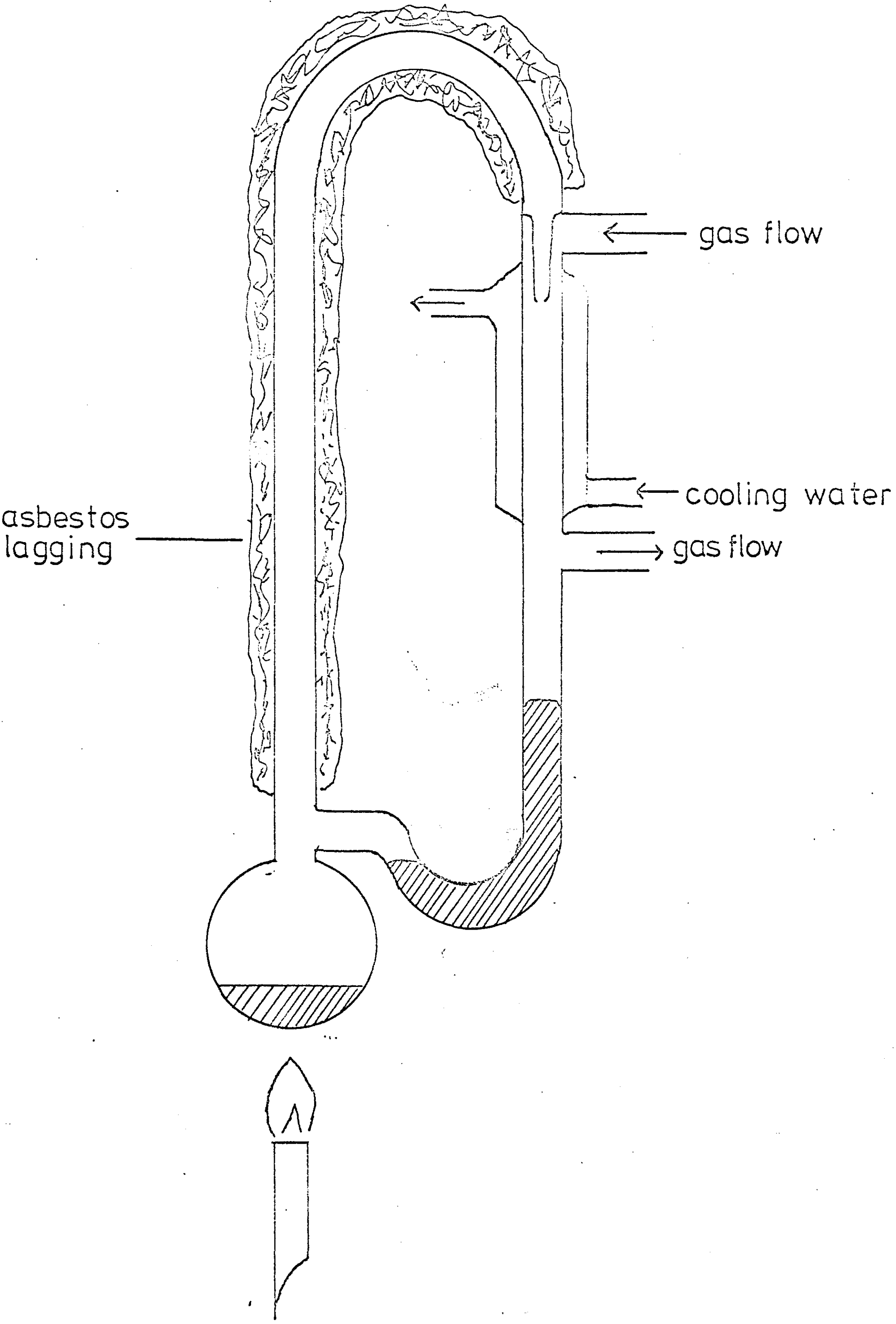


FIGURE 4 THE MERCURY VAPOUR EJECTION PUMP



by two taps so that conveniently small quantities of hydrogen could be delivered for measurement in the McLeod gauge.

Number 4, the film deposition section, comprised two film vessel lines each capable separately of being opened to section 2 or section 6, of being evacuated, or of being opened to the atmosphere. Accordingly glassblowing or degassing could be carried out in one line while a film was being deposited or investigated in the other. A bypass in one line permitted of the direct connection of sections 2 and 6.

Film vessels were constructed from Pyrex tubing of 20 mm internal diameter. They were 210 mm in length, and were connected to the main line by tubing of 4 mm internal diameter. Filaments were supported by means of stainless steel barrel connectors on 110 mm tungsten leads sealed in to the top of the vessel. (see figure 2) Film vessels of modified design were sometimes used. In such cases details appear in the text.

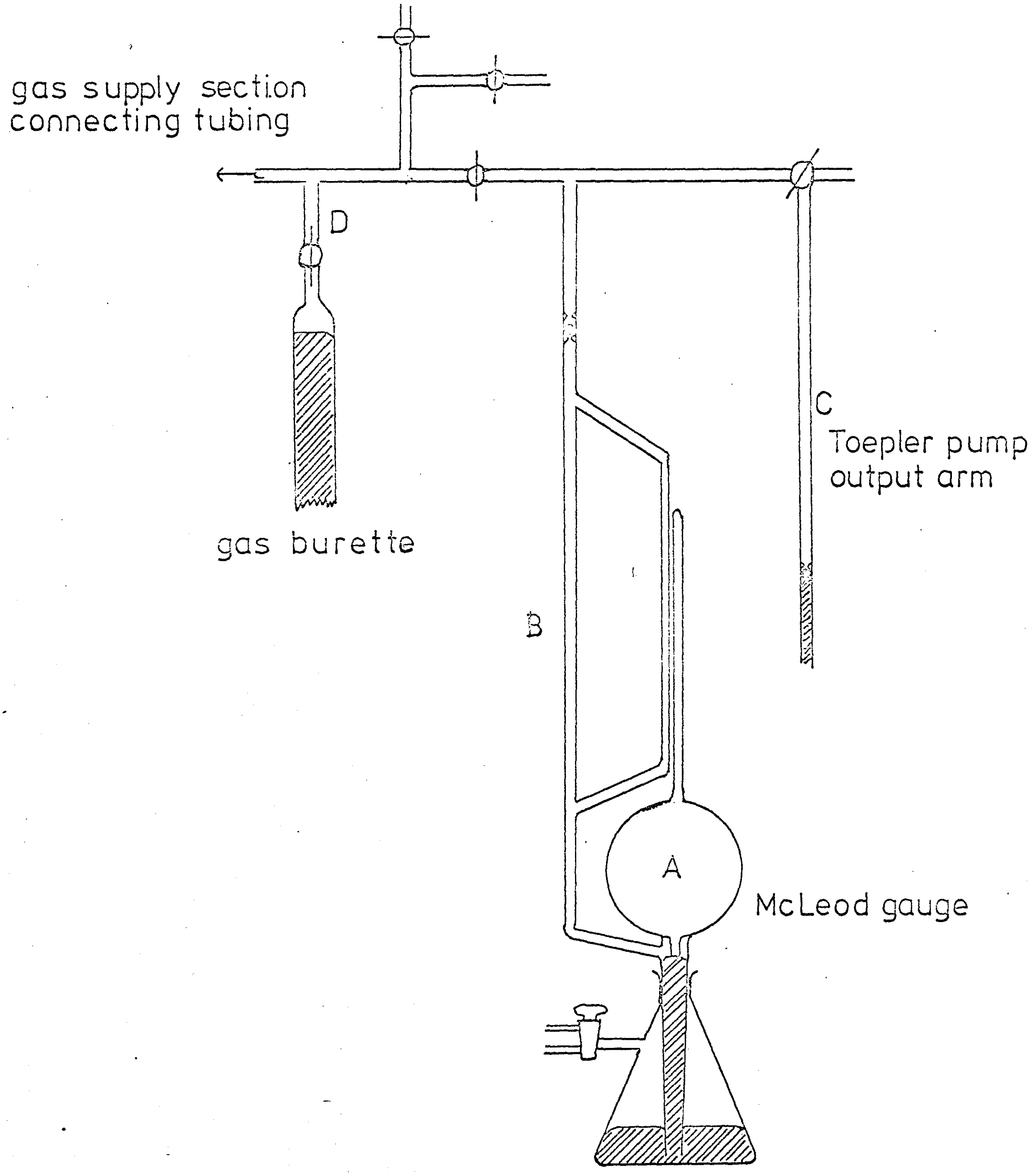
Current for evaporation of the filaments was supplied by a mains transformer of unknown specification, controlled by a Type 200CMH Variac.

Section number 5, the wire degassing section, consisted of a large vessel with a B19 socket at the top. Wires of the appropriate metal, up to 700 mm in length, were joined by stainless steel barrel connectors to tungsten leads sealed in to a B19 cone unit. A steel bar sealed in a length of glass tubing was used to keep the wire under tension and clear of the vessel walls during degassing.(see figure 3) Current for degassing was supplied by the unit used for film evaporation.

Number 6, the gas counting section, was used to measure the radioactivity of gas transferred from the film vessels. Efficient transfer was ensured by the use of a mercury vapour ejection pump. (figure 4) The Toepler pump in this section was employed as a backing pump for the ejection pump. Further details of the radioactivity monitoring arrangements are given in section 3.4 of this thesis.

All vacuum taps in the system were greased with Apiezon N grease, and all cone and socket joints with Apiezon L grease.

FIGURE 5 CALIBRATED PARTS OF APPARATUS



3.2 SECTIONS OF APPARATUS CALIBRATED FOR VOLUME

The apparatus, as described in the previous section, included two McLeod gauges. The larger of these was used for the measurement of pressure in the system, and to detemine the quantity of gas samples; the smaller only for pressure measurement. Before each of these gauges was attached to the system it was calibrated. This was done by inverting the bulb and filling it to the cut-off with mercury, which was then emptied out and weighed to enable its volume to be calculated.

When the dimensions of the bulb and the precision-bore tubing were known, it was possible, from consideration of the gas laws (appendix A) to relate the initial pressure in the system at the instant when mercury rising from the conical flask reservoir isolated the bulb from the rest of the system, to the length of the compressed column of gas in the sealed capillary.

The large McLeod gauge could thus be used for accurate pressure measurement in the range 2.2×10^{-1}torr(enclosed column length 210 mm) to 5×10^{-4}torr(enclosed column length 10 mm). The mercury level was determined with a travelling telescope.

The small McLeod gauge was capable of pressure measurement in the range 2.4 torr(200 mm) to 6×10^{-3}torr(10 mm). The mercury level was determined from graduations on the precision tubing.

It is obvious that the quantity of gas isolated in a McLeod gauge bulb may be determined by compressing the gas in to the capillary and measuring the length and pressure of the gas column. An operation may be carried out elsewhere in the system which alters the quantity of the gas thus measured. The extent of the change could in theory be determined by recovering the gas to the McLeod gauge bulb and measuring as before. In the apparatus used in the present work, the gas could not all be restored to the bulb. It was possible, however, to transfer all of a quantity of gas via the Toepler pump to the McLeod gauge bulb(A in figure 5), its dead space tubing(B in figure 5), and the portion of tubing above the ball-bearing seal on the output side of the Toepler pump(C in figure 5). The total volume of A+B+C was determined by the expansion of gas from the McLeod gauge bulb in to the evacuated tubing B+C. (see appendix A)

In the case of an actual measurement, the known ratio of the total volume A+B+C to the volume of the bulb made possible the calculation of the quantity of gas transferred to the entire calibrated portion of apparatus.

The volume of the bulb and tubing B was determined by a similar expansion experiment. A measured quantity of gas could therefore be delivered to the system without the necessity of pumping down the dead space. Further, quantities of gas 25% larger could be delivered.

In some cases it was required to measure accurately much larger amounts of gas. Accordingly an experiment was carried out to determine the volume of the connecting tubing of the gas supply section. All taps were closed save that to the gas burette. The level of mercury in the gas burette was set to the I50 ml calibration mark, that is, there was 350 ml of calibrated tubing open to the system, plus a dead space of unknown volume. Once the volume of the connecting tubing and the gas burette had been determined by expansion, the total calibrated volume could be varied by changing the mercury level in the gas burette.

The volumes of all the calibrated parts of the apparatus are given in table 2.

TABLE 2 : VOLUMES OF CALIBRATED PARTS OF APPARATUS

SECTION	VOLUME (ml)	MAXIMUM MEASURING CAPACITY (μ Moles at 293°K)
Large McLeod gauge bulb (A)	I59.2	I.86
(A) + dead space tubing(B)	20I.5	2.35
(A)+(B)+ Toepler 'out' arm(C)	207.4	2.42
(A)+(B)+(C)+ Gas supply section dead space tubing + gas burette (gas burette variable by 400 ml)	237.0-637.0	2.76-7.4I
Small McLeod gauge bulb	29.3	-

FIGURE 6 THE THERMAL CONDUCTIVITY GAUGE

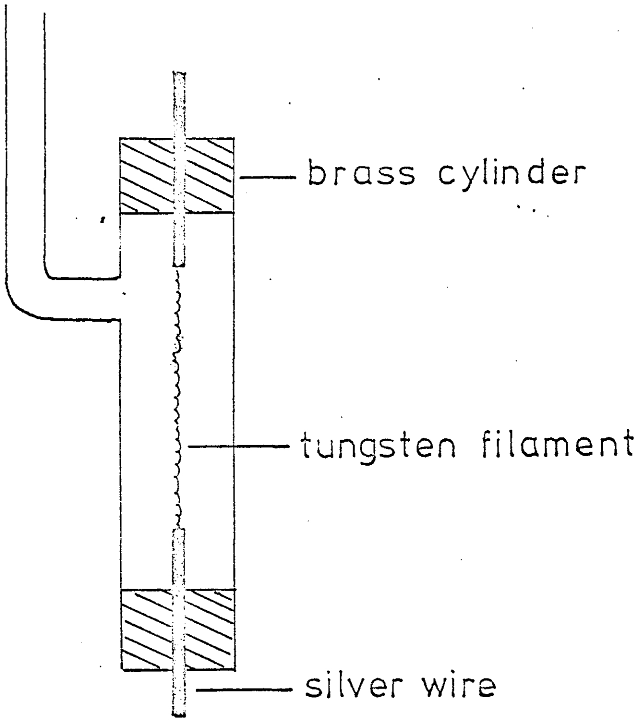
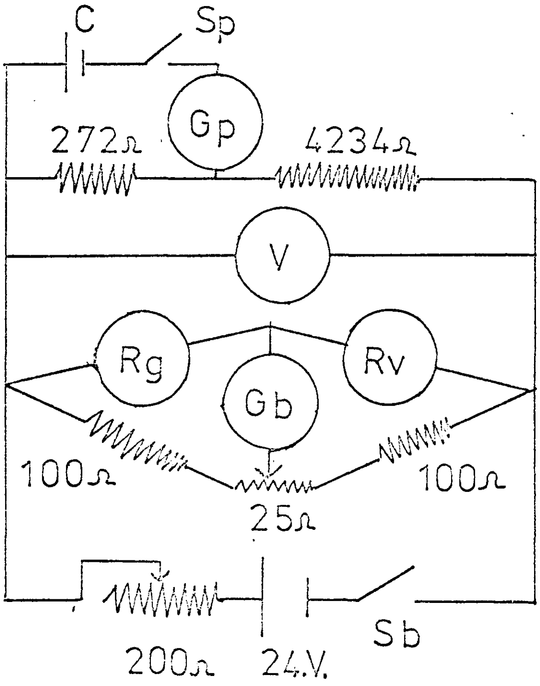


FIGURE 7 THE WHEATSTONE BRIDGE CIRCUIT (key on page 26)



3.3 THE THERMAL CONDUCTIVITY GAUGE

THEORETICAL BASIS

When a wire is heated electrically its resistance rise in relation to its temperature. In a cold environment, its temperature is determined in part by a constant rate of heat loss through its supports by conduction, and in part by the conductive properties of the medium surrounding the wire. Where a constant voltage is applied to the wire, it is therefore possible to relate its resistance to the pressure of a gas surrounding it, or to changes in the composition of the gas to give products of different thermal conductivity.

CONSTRUCTION

The thermal conductivity gauge is shown in figure 6. Its design is based on those described by Farkas (I08).

Two ½-inch glass-to-metal seals were joined together by way of the glass parts, and the ends of the resulting cylinder were sealed off by soldering in two I0 mm brass cylinders. A 50 mm length of I mm diameter silver wire was passed and soldered through the centre of each. The tungsten filament taken from a 25 watt Osram light bulb was silver soldered between the internal ends of the two silver wires.

A Wheatstone Bridge circuit was constructed (figure 7). The external ends of the silver wires were connected in to the circuit at the point Rg.

KEY TO FIGURE 7

C	Muirhead Type D402A standard cell, I.0I859V.
V	Voltmeter 0-30V.
Gp	Potentiometer galvanometer.
Gb	Bridge galvanometer.
Rv	Variable resistor.
TCG	Thermal conductivity gauge.
Sb	Main switch.
Sp	Potentiometer switch.

A potentiometer incorporated in the circuit made it possible for a constant voltage to be delivered to the bridge from two I2 Volt accumulators and a rheostat.

Because the two bridge resistors were only nominally I00 ohms, it was necessary before using the bridge, to vary the 25 ohm resistor until the bridge balanced.

METHOD OF OPERATION

A given gas sample was allowed to equilibrate in a system including the thermal conductivity gauge. The main switch Sb was closed to supply current to the bridge, and the 200 ohm resistor was adjusted until, on closing switch Sp, no current was observed to be passing through galvanometer Gp. At this point the ratio, 272:4234 is equal to the ratio, standard cell voltage: bridge voltage. In this circuit the bridge voltage is I6.86 V. (see appendix B)

The bridge resistor was now adjusted until no current flowed through the galvanometer Gb, during which process it was necessary to readjust the 200 ohm resistor in order to maintain the bridge voltage at I6.86 V.

When no current passes through either galvanometer, then the resistance of the gauge filament is equal to that of the variable resistor at the set potential.

Initially a variable resistor was employed which was graduated in ohms, but for most of the period of the investigation a variable resistor with a IO turn dial, connected in series with a standard resistor, was used. Calibrations were made in terms of the reading of the dial.

APPLICATION

The gauge has been calibrated for measurement of krypton pressure in the range I.8 torr - IO^{-3}torr, and measurement of argon pressure in the range I.8xIO^{-1}torr - IO^{-3}torr. It was also calibrated for ortho/para hydrogen analysis, but use was not made of this in the present work.

The method of calibration and the results obtained are described in appendix B. An experiment has been conducted to show that the effect of thermomolecular flow on krypton and argon pressure measurements may generally be neglected in the range of interest. This is presented in appendix C.

SECOND GAUGE

In the later stages of the investigation the original gauge developed an untraceable leak. It was replaced by a gauge constructed as far as possible to be identical. The second gauge was not calibrated, but was used as a null-zero instrument, in order to detect changes in a set pressure of gas.

FIGURE 8 'TOUCHING' COUNT.

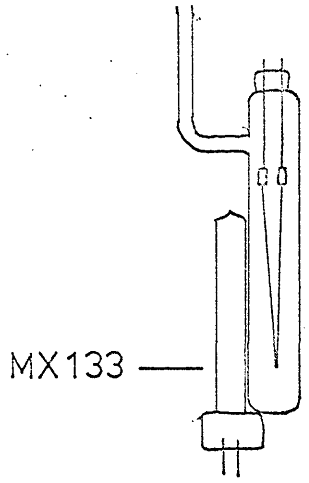
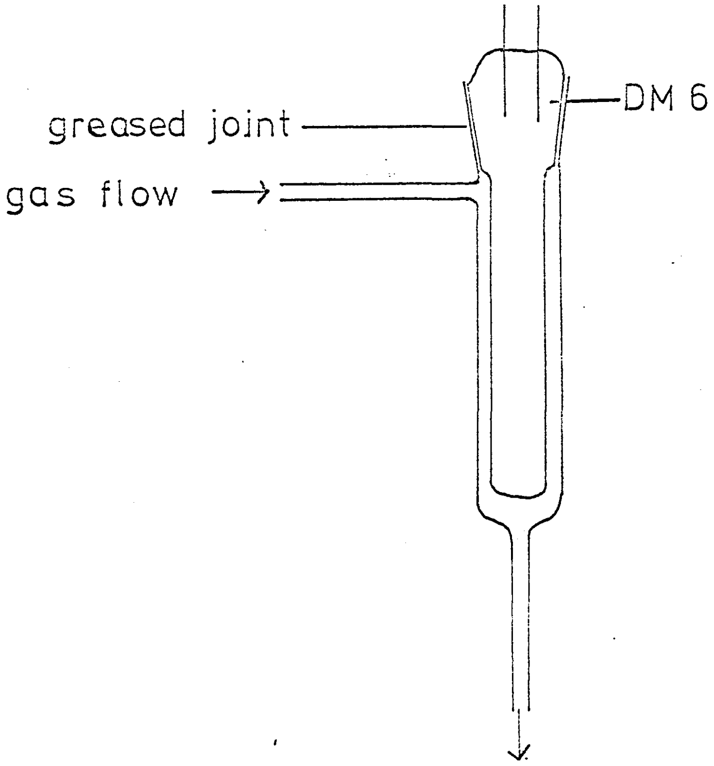


FIGURE 9 THE GAS FLOW COUNTER



3.4 ARRANGEMENTS FOR RADIOACTIVITY MONITORING

In the course of the investigation it was often necessary to determine the quantity of radioactive krypton held by a metal film at a given time, or the quantity of radioactive krypton in the gas phase in the system. Various types and arrangements of Geiger-Muller counters were used. Counts were recorded on either an Ecko Electronics Ltd. Type N529D scaler or a Panax Equipment Ltd Type D657 scaler. Ecko Electronics Ltd Type N558B probe units were used.

The various methods of determining the quantity of radioactive krypton were as follows.

TOUCHING COUNT or PARALLEL COUNT

A Mullard Type MXI33 thin wall counter was arranged parallel to, and normally in contact with, a film vessel containing a film the activity of which was to be measured. (figure 8)

FLOW COUNT

The activity of a gas stream was measured by passing it through the jacket of a 20th Century Electronics Type DM6 liquid counter, which had been modified by the addition of two side arms. (figure 9) The effective counting volume was approximately 9 ml.

All flow experiments were conducted with nitrogen flowing at atmospheric pressure, at 50 ml min^{-1}.

GAS COUNT

The activity of all the gas within a section of the apparatus was measured by transferring it to a chamber of reproducible geometry, and then counting it. Two arrangements were used.

For experiments in thermal release of krypton (section 4.9), gas was transferred by the Toepler pump to the McLeod gauge. The gas isolated in the McLeod gauge bulb was then transferred in to a I00 mm length of the closed capillary. The Mullard MXI33 counter was clamped in contact with this portion of tubing. (figure I0) Measurements of the quantity and activity of gas could

FIGURE 10 GAS COUNT IN McLEOD GAUGE CAPILLARY

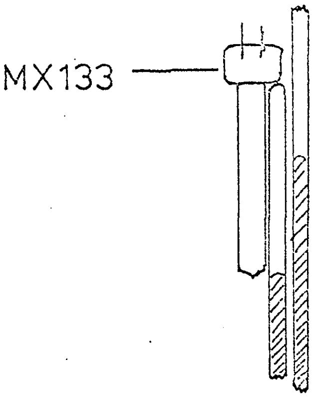
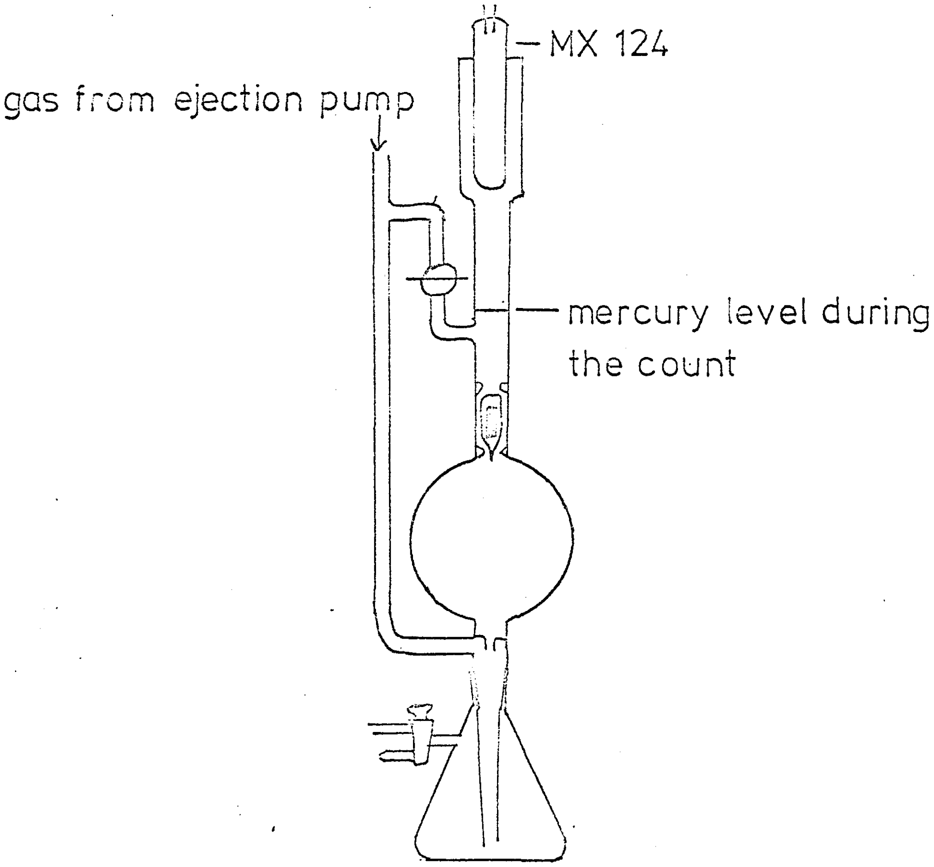


FIGURE 11 THE GAS COUNTING CHAMBER



be made simultaneously by this method, but because of the shielding effect of the thick glass of the capillary wall, the method was only applicable to gas of high specific activity.

Gas of lower specific activity was diluted with inactive krypton and transferred to the gas counting chamber of apparatus section 6, using the mercury vapour ejection pump and the Toepler of this section. It was then compressed by raising the mercury to a set mark. The volume of the gas space during counting was approximately 30 ml. A Mullard MXI24/0I liquid counter was incorporated in the counting chamber. (figure II)

Details of the operating voltages and calibration plots for the counters are given in appendix D.

CHAPTER 4

DEPOSITION OF NICKEL FILMS IN THE PRESENCE OF KRYPTON AND ARGON, AND INVESTIGATION OF THEIR PROPERTIES.

4.I DEPOSITION OF NICKEL FILMS IN THE PRESENCE OF KRYPTON; PRELIMINARY NOTE.

It was decided to conduct preliminary studies using nickel, because of the ease with which films of this metal could be produced by evaporation from an electrically heated filament, and because the properties of nickel films have been widely investigated.

Nickel films were deposited in the presence of a quantity of krypton (5% ^{85}Kr) at various temperatures, in order to find out whether at some temperature, krypton might be stably incorporated in to a film during its growth.

No evidence was found for the incorporation of krypton in to films deposited in film vessels maintained at 273°K(ice/water bath), or at I95°K(solid CO_2 / acetone bath). However when a film was deposited in a film vessel maintained at 77°K(liquid nitrogen bath), there was a rapid decrease in the gas phase krypton pressure. This film was allowed to warm up to room temperature, and it was found that a large proportion of the krypton initially present did not return to the gas phase, but appeared to be stably retained by the film.

Accordingly a series of films was grown in order to investigate the extent and character of the incorporation and retention of krypton by nickel films deposited at 77°K.

4.2 PREPARATION OF NICKEL AND KRYPTON.

Nickel wire (0.50 mm) was supplied by Messrs Johnson, Matthey, and Co.,Ltd. In later experiments, 700 mm lengths of this wire were predegassed in vacuum by passing a current of approximately 4.I A overnight, followed by two hours at 4.7 A. As a result of this treatment a light bake-out film was usually produced in the degassing vessel.

Filaments were cut from the wire thus prepared. They were approximately 220 mm in length, with weights in the range 0.40 g to 0.44 g. When a filament had been connected by means of stainless steel barrel-connectors to the tungsten leads in the top part of the film vessel, and the two parts of the vessel were joined by glassblowing. The vessel was then degassed by heating under vacuum to 770°K for a period of at least eight hours, in order to remove any species adsorbed on the glass walls. During this period, a current of 4.2 A was passed through the filament.

Some of the earlier films were grown before the degassing vessel was added to the system. A slightly less rigorous degassing procedure was used. Since the whole procedure was carried out in the film vessel, there was usually a light bake-out film in the vessel before deposition of the film at 77°K. This bake-out film was normally almost invisible to the eye, and its weight was neglected.

In many cases, deposition was halted before the filament broke. The filament in such a case was frequently used for a subsequent film; the first stage of degassing was then omitted.

Modified film vessels were used in some parts of the work. Reference to this is made in the text, where appropriate.

5% ^{85}Kr was supplied in IO mCi ampoules by the Radiochemical Centre, Amersham. Inactive krypton was supplied in I litre Pyrex bulbs by the British Oxygen Co., Ltd. Krypton containing 0.6% ^{85}Kr was obtained by the mixing of measured amounts of krypton from the above sources.

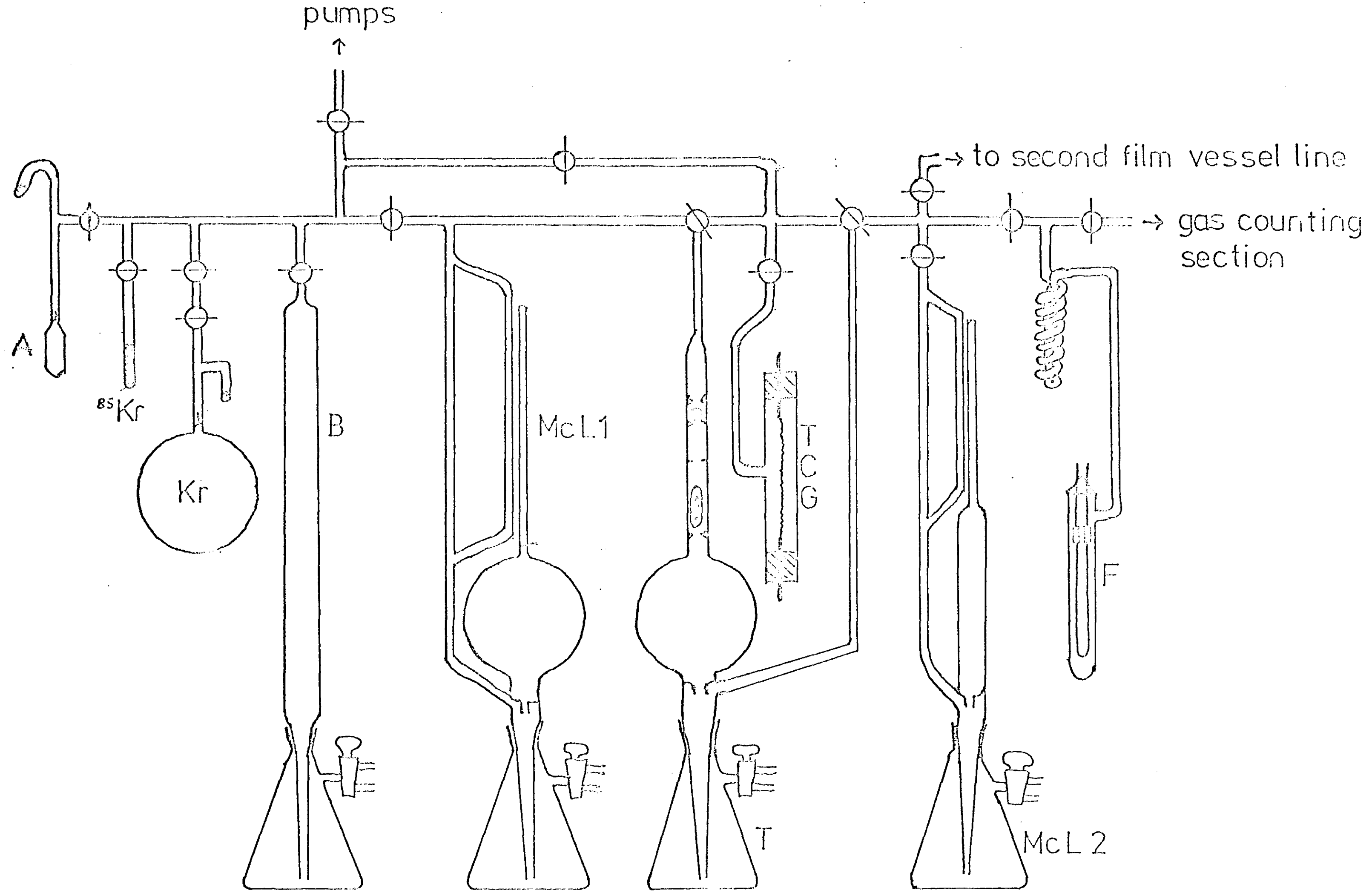
4.3 DEPOSITION OF NICKEL FILMS AT 77°K IN A SYSTEM OF CONSTANT VOLUME; EXPERIMENTAL TECHNIQUE

At first, the rate at which krypton was being incorporated in to a film was measured by occasionally raising the mercury in the McLeod gauge in order to measure the gas phase pressure. This method involved a considerable disturbance of the system on each occasion, and the isolation of its component parts for the time taken to raise and lower the mercury.

For a short time of deposition this technique would therefore be totally unsatisfactory. Accordingly at this point the thermal conductivity gauge was calibrated for measurements of krypton pressure, so that the pressure could be monitored continuously, without disturbing the system.

Films were grown in a system comprising the McLeod gauge, the thermal

FIGURE 12 SIMPLIFIED DIAGRAM OF APPARATUS USED IN FILM DEPOSITION (KEY ON PAGE 21)



conductivity gauge, the cold trap, and the film vessel. (see figure I2) The Toepler pump was evacuated before deposition of a film. A quantity of krypton was measured accurately in the McLeod gauge, and then permitted to expand in to the other parts of the system. When an equilibrium pressure had been attained, the applicability of the thermal conductivity gauge calibration for krypton pressure measurement was checked by balancing the resistance bridge and reading off the dial value for the variable resistor, then immediately measuring the krypton pressure with the McLeod gauge.

The system was now allowed to return to the original equilibrium pressure, which having been attained, the filament current was switched on and adjusted to the chosen value within the range 6.4 A to 7.3 A. This current was maintained constant throughout growth of the film. The time of onset of nickel deposition was decided arbitrarily, a clock being started when the luminosity of the filament appeared to have reached a steady value.

Krypton pressure was first observed to rise because of the increase of the temperature of gas in the film vessel owing to the warming of the filament. Within at most one minute,the pressure began to drop rapidly. Throughout the growth of the film, the resistance bridge was regularly balanced, and readings were taken of the variable resistor dial so that the krypton pressure could be determined.

Usually deposition of nickel continued until the filament broke, but in some cases deposition was halted deliberately.

When deposition ended the rate of decrease of the krypton pressure showed a considerable increase, and the pressure of krypton quickly dropped below the value which would have been predicted on the basis of a simple lowering of the average gas temperature, corresponding to the increase observed at the onset of deposition. A low equilibrium temperature was eventually reached. This behaviour is believed to represent physical adsorption of krypton on to the completed film. (see section 4.I0)

For each film an attempt was made, with the film still at 77°K, to recover krypton which had not been stably and permanently incorporated in to the bulk of the film. The Toepler pump, previously evacuated, was now opened on the one hand to the film vessel, cold trap, and thermal conductivity gauge, and on the other hand to the McLeod gauge.

It was found that no absolute limit to the quantity of recoverable krypton could be reached, even employing up to fifty strokes of the Toepler pump. Each stroke would on the basis of the gas laws be expected to remove approximately half of the gas phase krypton from the film vessel. After an arbitrary number of strokes in excess of ten, the process was halted and the apparent net incorporation of krypton was calculated by subtraction of the quantity recovered from the measured initial quantity.

For a small number of films, krypton was recovered by pumping at 77°K, using the mercury vapour ejection pump, which was added to the system later in the course of the investigation. This pump was capable of maintaining a pressure of less than 10^{-5} torr in the film vessel. More krypton could be recovered by this method. Results of these investigations are presented in section 4.9.

In general a more reliable estimate of the quantity of krypton incorporated in to each film at 77°K was required. This quantity was taken to be the amount of krypton which had disappeared from the gas phase during the period of deposition, while the conditions of deposition prevailed in the system.

From a consideration of the gas laws, the quantity of krypton incorporated in to a film, Q, is given by the formula :

$$Q = \frac{Pi - Pf}{Pi} \times Qo$$

Qo refers to the measured initial quantity of krypton introduced in to the system, and Pf refers to the pressure immediately before deposition of the film ceased (obtained from the continuous monitoring of pressure using the thermal conductivity gauge). In order that Pi, the initial pressure in the system, may be compared to Pf, a value must be obtained for Pi under the conditions of deposition. This value was obtained in each case by back extrapolation of the pressure versus time plot, to zero time, in order to compensate for the fact that at zero time the krypton in the system was cooler, and thus at a relatively lower pressure than during the period of deposition proper.

This calculation will only be valid if the quantity of gas in the system is assumed to be proportional to the pressure. There are a number of factors which might prejudice this assumption. An appreciation of these factors and a justification of the assumption are presented in appendix C.

4.4 DEPOSITION OF NICKEL FILMS AT 77°K IN A CONSTANT PRESSURE OF KRYPTON; EXPERIMENTAL TECHNIQUE

To the constant volume system described in the previous section was added a gas burette of capacity 500 ml. For the first few films in this series, the level of mercury in the gas burette was controlled by raising and lowering a reservoir of mercury connected to the burette by rubber tubing and a tap. This arrangement was found to be unsatisfactory, and the mercury level was controlled throughout most of the investigation by varying the pressure of air in a conical flask. (see figure I2) The alterations required to implement this change in the system necessitated a reduction to 400 ml of the calibrated volume of the gas burette.

Filament weights and other physical particulars were the same as those described for the previous series of films.

Since the total volume of the system was now much increased when the mercury level in the gas burette was lowered, it was found that the McLeod gauge no longer sufficed to measure the quantities of krypton which were required to maintain pressures over $5x10^{-2}$ torr in the system. Thus krypton quantity measurements could not be taken directly for films deposited at higher krypton pressures.

On admitting to the system a quantity of krypton, which was allowed to attain an equilibrium pressure, the resistance bridge was balanced to find the reading of the variable resistor dial corresponding to this pressure. The krypton pressure was then measured immediately with the McLeod gauge.

When deposition was commenced in the manner described previously, the pressure in the system was observed to rise, disturbing the balance of the resistance bridge.,However, within one minute, the pressure began to fall. The volume mark corresponding to the level of mercury in the gas burette was noted at the time when the bridge had just returned to its initial balanced state. The continuing decrease in pressure was then offset by raising the level of mercury in the gas burette, to reduce the volume of the system. The system was disturbed as little as possible, but a pressure was established which was marginally higher than the measured initial pressure. When the resistance bridge again returned to balance, further readings of volume and time were noted.

This process was continued until either the filament broke, or the mercury level reached the limit of the calibrated volume of the gas burette, whereupon deposition was halted.

The quantity of krypton which had disappeared from the gas phase was calculated from the total change in the volume of the system during deposition, measured from the gas burette calibration, and the known constant pressure in the system during deposition. The volume versus time plot was extrapolated back to zero time in order to compensate for the effect of the initial warming up of the system.

Assumptions were made, firstly that the krypton in the gas burette was at the same temperature as the laboratory, and secondly that the temperature gradients throughout the remainder of the system remained constant during the deposition of a film.

It should be noted that the pressure was not precisely constant during deposition of a film. In fact, because of the particular technique used, the pressure was alternately rather higher and rather lower than the initial measured value. These oscillations of pressure were small compared to the total pressure.

The weights of all nickel films were determined from the loss in weight of the filament.

4.5 RESULTS OF PRELIMINARY EXPERIMENTS

Two films were deposited in the presence of krypton, (5% ^{85}Kr), one at 273°K (ice/water bath), and one at I95°K (solid CO_2/acetone bath). In each case, when current was supplied to the filament, the pressure in the system rose, corresponding to the warming of gas in the film vessel by the hot filament, and then remained constant throughout deposition. No evidence for krypton incorporation could be found either from a drop in gas pressure in the system, or from an increase measured above the background activity on bringing the G.M. counter in to contact with the film vessel at 295°K after deposition of the film.

TABLE 3 NICKEL FILMS DEPOSITED IN KRYPTON AT I95°K AND 273°K

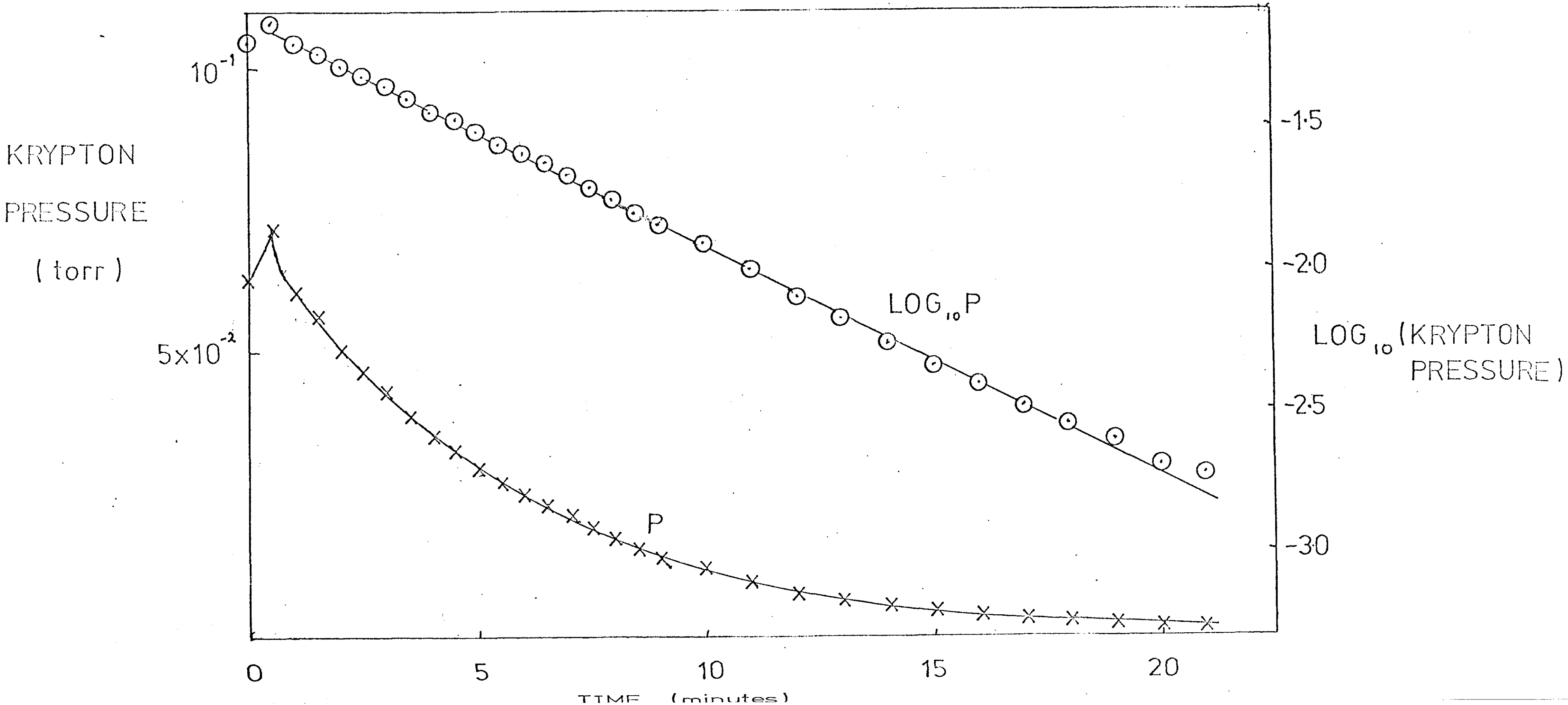
FILM NUMBER	KRYPTON PRESSURE (torr)	WEIGHT OF NICKEL (mg)	RATE OF NICKEL DEPOSITION (mg min^{-1})
I (273°K)	3xIO^{-2}	40.0	0.37
73 (I95°K)	6.9xIO^{-2}	54.9	0.78

A film was now deposited in the system: McLeod gauge, cold trap, and film vessel. The film vessel was cooled to 77°K by means of liquid nitrogen. During deposition there was a rapid fall in krypton pressure. This was followed by measuring the pressure four times with the McLeod gauge. The rate of pressure fall with time was shown to correspond to exponential decrease by the linearity of a plot of logarithm(krypton pressure) against time.

The initial pressure for this film, No 2, was 9xIO^{-2}torr. The total weight was 34.4 mg, and the rate of nickel deposition was 2.5 mg min^{-1}. The slope of the linear plot of logarithm(krypton pressure) against time, was 0.I2I min^{-1}.

When the film was allowed to warm up to room temperature, it was observed that a large proportion of the krypton which had been incorporated in to the film at 77°K, was not released to the gas phase, but appeared to be stably held by the film. Despite further warming for one hour periods to temperatures up to 773°K, and overnight sintering at 800°K, the bulk of the activity measured at room temperature was retained by the film. The results obtained for the thermal release of krypton from a series of nickel films are considered in detail in section 4.9.

FIGURE 13 VARIATION OF KRYPTON PRESSURE DURING DEPOSITION OF A NICKEL FILM (No.17) UNDER CONSTANT VOLUME CONDITIONS.



It was concluded that this deposition technique afforded a means of introducing ^{85}Kr stably in to the lattice of a nickel film. Before the technique could be adopted for purely preparative purposes, it was necessary to assess the factors which influence the incorporation of krypton in to a growing metal film and to explain the mechanism of incorporation.

4.6 INCORPORATION OF KRYPTON AT 77°K BY FILMS DEPOSITED UNDER CONSTANT VOLUME CONDITIONS

A series of films deposited under constant volume conditions, invariably showed an exponential decrease of krypton pressure with time when the krypton pressure was initially below 0.I torr. An example is shown in figure I3.

The results are summarised in table 4. In a number of cases, films were grown to investigate particular aspects of the kinetics of krypton incorporation. Details of these experiments are presented in sections 4.9 and 4.I0. Although in many cases the system was deliberately disturbed, in every case the rate of krypton pressure decrease eventually returned to the exponential behaviour which was observed for a film grown in a system at near equilibrium conditions throughout deposition. The value given for such a film in table 4, for the slope of the plot of logarithm(krypton pressure) against time, refers to the observed linear region.

Films deposited under higher pressure of krypton did not show exponential pressure decrease, at least initially, although when pressure had dropped to a lower value, exponential decrease was then observed in two cases. Such types of behaviour are shown in figure I4.

FIGURE 14 RATE OF KRYPTON PRESSURE FALL FOR TWO FILMS GROWN AT HIGH KRYPTON PRESSURE

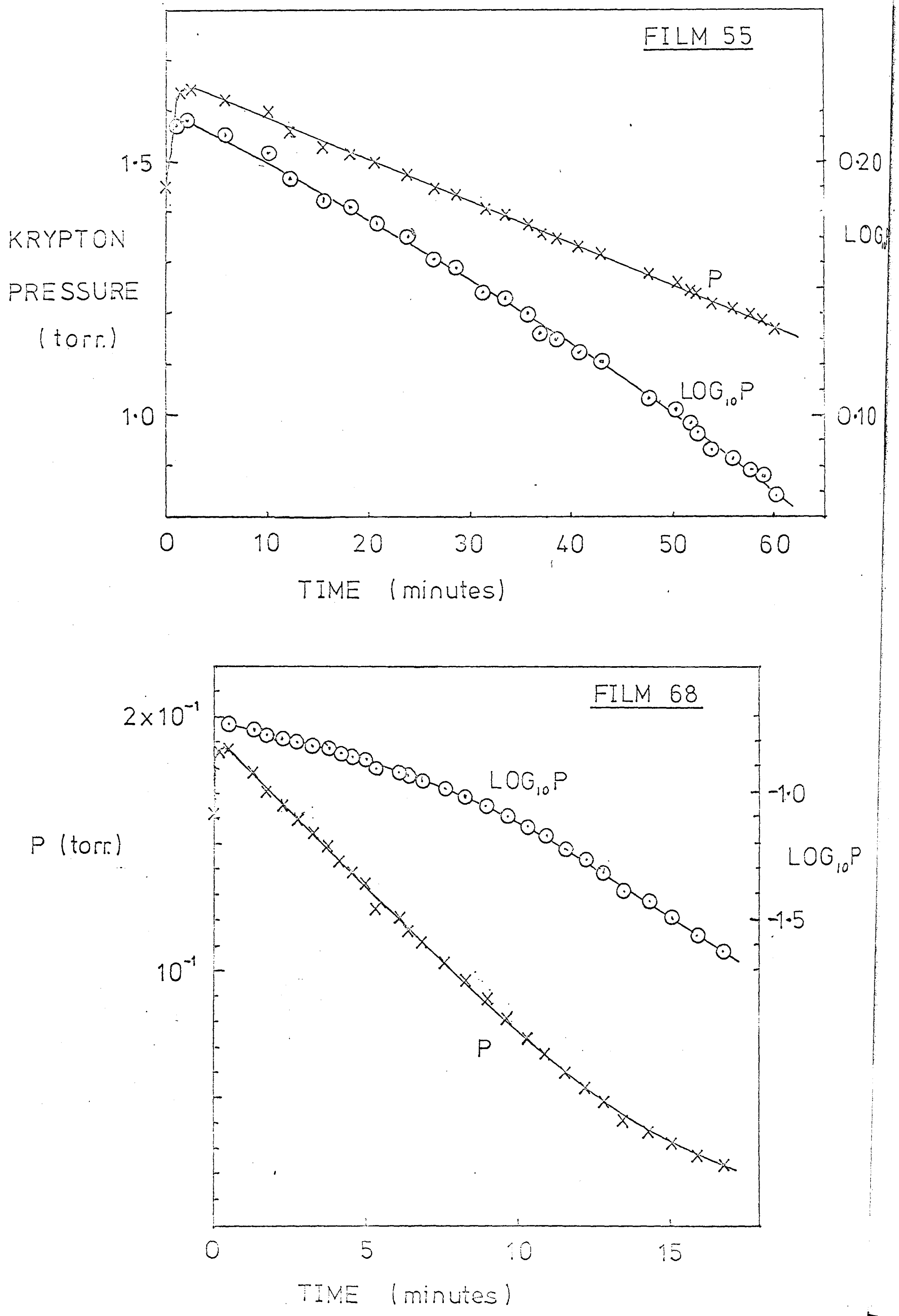


TABLE 4 KRYPTON INCORPORATION BY FILMS OF NICKEL DEPOSITED UNDER CONSTANT VOLUME CONDITIONS

FILM NUMBER	WEIGHT (mg)	RATE OF DEPOSITION OF Ni (mg min^{-1})	PRESSURE RANGE (torr)	SLOPE OF PLOT OF LOG(P) AGAINST TIME (min^{-1})
6	24.5	3.67	3.29xIO^{-2}-7.8xIO^{-3}	9.8xIO^{-2}
I7	38.0	I.8I	7.40xIO^{-2}-I.9xIO^{-3}	7.9xIO^{-2}
I9	I6.9	2.6I	4.98xIO^{-2}-I.20xIO^{-2}	9.8xIO^{-2}
28	7.2	0.67	6.30xIO^{-2}-I.27xIO^{-2}	6.IxIO^{-2}
34	29.7	I.4I	9.35xIO^{-2}-4.0xIO^{-2}	9.3xIO^{-2}
35	8.6	0.66	8.39xIO^{-2}-2.98xIO^{-2}	5.7xIO^{-2}
39	29.2	2.I2	4.45xIO^{-2}-5.0xIO^{-3}	II.IxIO^{-2}
55	2I.8	0.36	I.67-I.I7	not linear
66	29.0	I.I3	4.35xIO^{-1}-6.0IxIO^{-2}	7.9xIO^{-2}(later stages)
68	I7.8	I.06	I.94xIO^{-1}-2.34xIO^{-2}	7.8xIO^{-2}(later stages)

A film deposited in this constant volume system would not be expected to have a homogeneous distribution of krypton in the bulk at 77°K, if each krypton atom was held at the point where it was 'built in' to the film. In the extreme case, the pressure may drop to such a low value that the later-deposited parts of the film may be considered to have been laid down in vacuum.

Therefore the results for the actual quantity of krypton incorporated at 77°K, and the atomic % of krypton in the film are not particularly significant. A comparison with the quantity stably retained at higher temperatures is however of interest, so that the quantity measurements are treated in section 4.9, which deals with the thermal release of krypton from nickel films.

As an example of the magnitude of the quantity of krypton incorporated in to a nickel film, film No I7 took up 2.29 μ moles of krypton, equivalent to 0.35% of all the atoms(nickel and krypton), in the complete film at 77°K.

FIGURE 15 PLOT OF THE RATE OF KRYPTON UPTAKE FOR THREE NICKEL FILMS DEPOSITED UNDER CONSTANT PRESSURE CONDITIONS

(× FILM 38, 0·203 torr. ⊙ FILM 41, 0·201 torr. ○ FILM 43, 0·200 torr.)

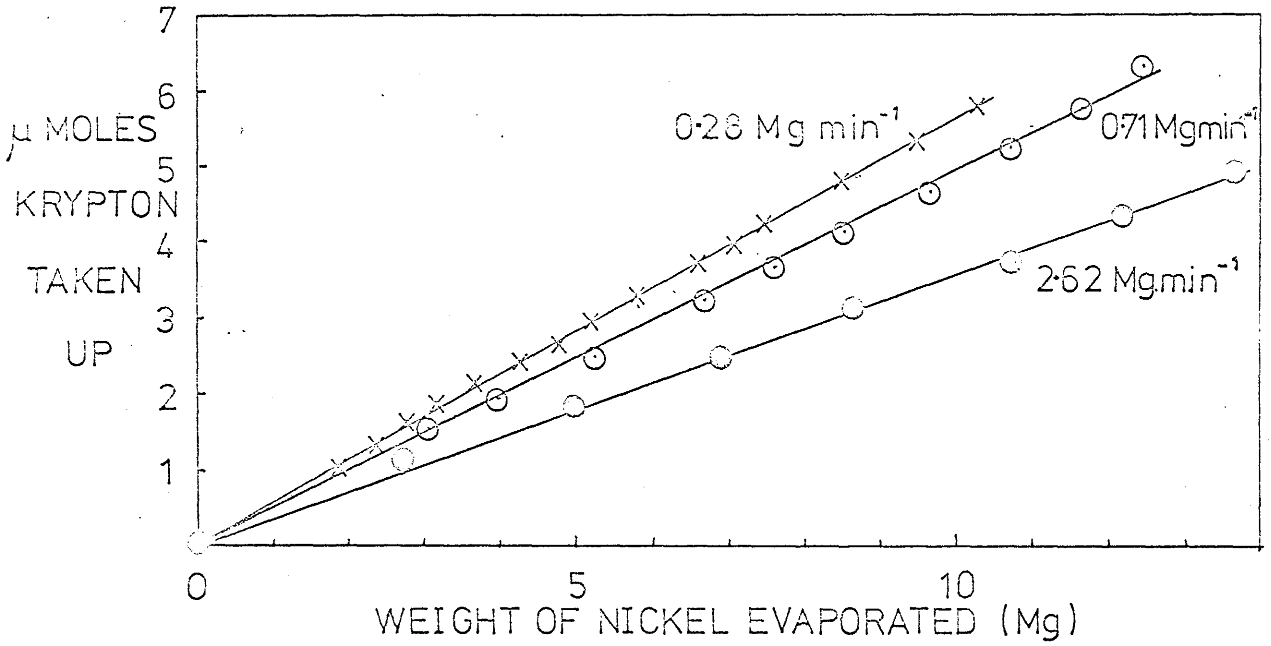
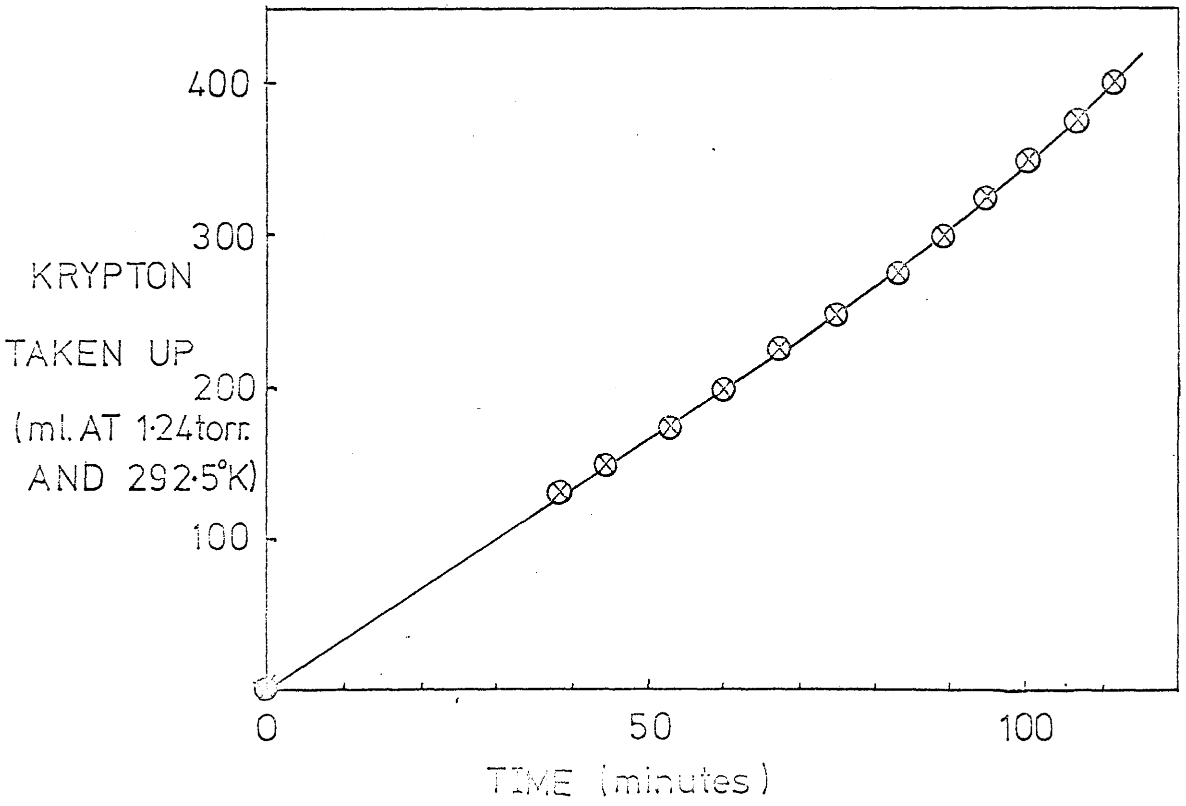


FIGURE 16 VOLUME UPTAKE OF KRYPTON BY FILM 49, DEPOSITED IN KRYPTON AT 1·24 torr.



4.7 INCORPORATION OF KRYPTON AT 77°K BY FILMS DEPOSITED UNDER CONSTANT PRESSURE CONDITIONS

It is more likely that the krypton will be homogeneously distributed throughout the film at 77°K if the conditions of deposition are maintained constant during the period of deposition.

The pressure may be maintained constant during the growth of a film by raising the level of mercury in the gas burette, to compensate for the removal of krypton from the gas phase. For a light film, where the thickness of the filament is not greatly reduced by the quantity of nickel evaporated, it may be assumed that while the current supplied to the filament is held constant, then the rate of evaporation will also be constant. The temperature gradients in the system may be maintained constant by regular topping up of the various liquid nitrogen baths.

Films have been deposited under a wide range of deposition conditions. Constant krypton pressures from 3×10^{-3} torr to 1.3 torr have been employed, and nickel deposition rates in the range 1.3×10^{-2} mg min^{-1} to 4.42 mg min^{-1} have been observed.

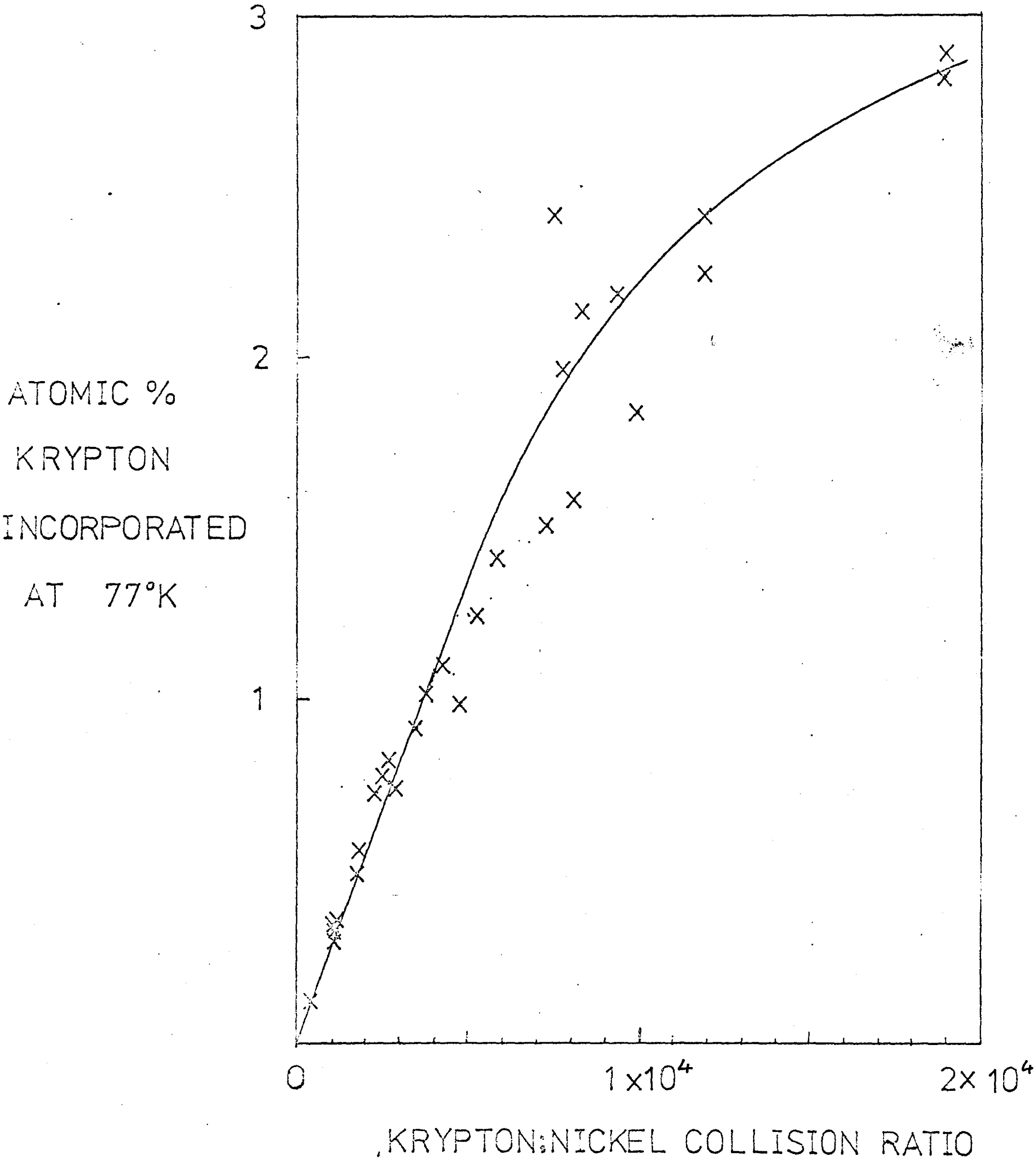
When films were deposited at pressures below 0.3 torr, the rate of uptake of krypton with time was constant throughout the period of deposition. Films grown under higher pressures of krypton, generally showed some degree of acceleration in the rate of krypton uptake during the period of deposition. Examples of linear and accelerated uptakes of krypton with time are presented in figures 15 and 16.

On comparing the results for films grown under the same pressure of krypton, it was found that in general a high rate of nickel deposition resulted in a smaller quantity of krypton being incorporated in to the film. Films evaporated at the same rate, showed a larger amount of incorporation at high krypton pressure.

These statements do not hold for films deposited at particularly low pressure of krypton and high rate of nickel deposition; in such cases the rate of krypton incorporation was rather higher at high nickel deposition rate.

In view of the fact that the quantity of krypton incorporated in to a film

FIGURE 17 PLOT OF ATOMIC % KRYPTON INCORPORATED IN TO NICKEL FILMS DEPOSITED AT 77°K, AGAINST KRYPTON:NICKEL COLLISION RATIO (0–2×10^4)



is dependent both on the krypton pressure and on the rate of nickel evaporation, a relationship may be inferred to the relative rates of collision of the two species with a growing film.

On the basis of a simplified model of the system, it may be shown that under the conditions selected for this series of films, the ratio of the number of collisions of krypton atoms with the film in a given time to the number of collisions of nickel atoms with the film in the same time, is given by the formula:

$$\text{Kr:Ni collision ratio} = \frac{P}{d} \times 1.1 \times 10^{5}$$

Where,

P = The constant krypton pressure in torr.

d = The deposition rate of nickel in mg min^{-1}.

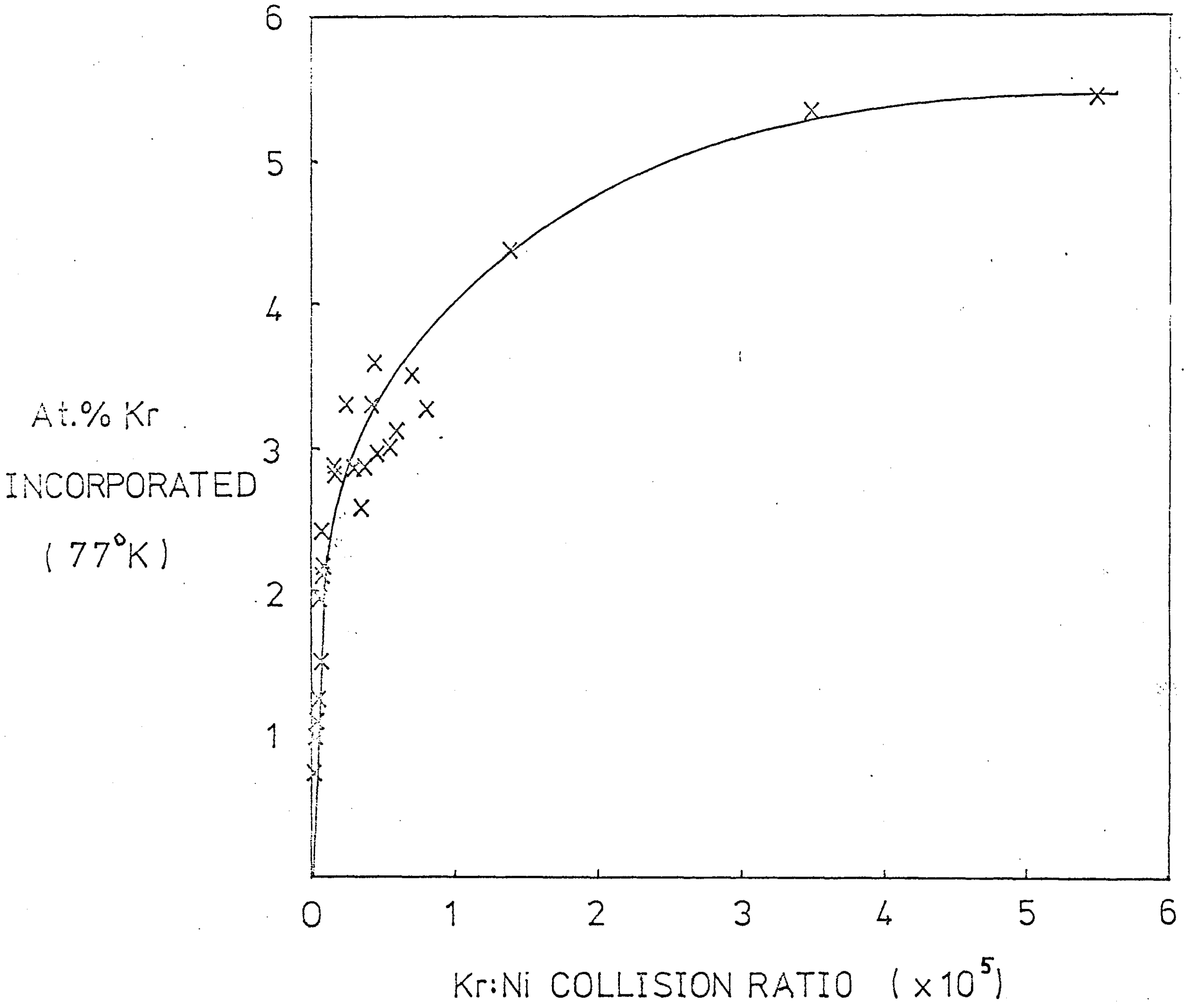
The derivation of this expression is given in appendix H. The assumptions are made: first that the simplified model adopted, and calculations on the basis of the kinetic theory of gases, provide a reasonable representation of the system actually used; second that each nickel atom 'sticks' to the film when it first collides with it; and third that all of the films in the series have the same geometric area.

When a plot was made, (figures 17 and 18), for the series of films grown at constant pressure, of the atomic % krypton incorporated in to each film at 77°K against its Kr:Ni collision ratio, then a linear relationship is found at values of the collision ratio below approximately 10^4. For higher values of the Kr:Ni collision ratio, the quantity of krypton introduced in to the film at 77°K continues to rise but not proportionately.

All values of the atomic % of krypton incorporated in to a film refer to the % of all the atoms(nickel and krypton) in the film.

The scatter of the points may be accounted for by variations in the geometric area of the films, by errors in the quantity of krypton calculated to be incorporated at 77°K (arising from inaccurate back extrapolation to zero time of the krypton uptake plot for each film, or failure to hold the pressure precisely constant during deposition), and by weighing errors in the case of light films.

FIGURE 18 PLOT OF ATOMIC % KRYPTON INCORPORATED IN TO NICKEL FILMS DEPOSITED AT 77°K, AGAINST KRYPTON:NICKEL COLLISION RATIO (0–6x10^5)



Data for all of the films deposited in the constant pressure system are recorded in table 5.

The only film which gave results markedly different from the rest was No 69. In this case , presumably because of a flaw in the filament, the rate of deposition was very low, and deposition resulted in the production of a film over only a 20 mm - 30 mm section of the film vessel. Thus this film had a geometric area appproximately 25% of the average value.

TABLE 5 KRYPTON INCORPORATION BY FILMS OF NICKEL DEPOSITED UNDER CONSTANT PRESSURE CONDITIONS

TABLE HEADINGS: P = constant pressure of krypton in torr.
W = total weight of nickel in mg.
d = rate of nickel deposition in mg min.$^{-1}$
% Kr = atomic % of krypton in the complete film at 77°K.
F = the krypton : nickel collision ratio for each film.

FILM No	P	W	d	% Kr	F
23	3.05xIO^{-2}	5.8	0.70	0.99	4.8xIO^{3}
25	3.30xIO^{-2}	I2.8	I.27	0.74	2.9xIO^{3}
27	7.8xIO^{-3}	I5.3	I.8I	0.I2	4.7xIO^{2}
29	6.80xIO^{-2}	6.2	0.73	I.84	I.0xIO^{4}
38	2.03xIO^{-1}	I0.6	0.28	3.28	8.2xIO^{4}
40	2.00xIO^{-1}	I0.2	0.98	3.3I	2.5xIO^{4}
4I	2.0IxIO^{-1}	I2.4	0.7I	2.86	3.IxIO^{4}
42	I.92xIO^{-1}	I2.3	I.I0	2.82	I.9xIO^{4}
43	2.00xIO^{-1}	I4.2	2.62	2.I4	8.4xIO^{3}
45	3.43xIO^{-1}	I5.0	0.84	3.60	4.5xIO^{4}
46	6.04xIO^{-1}	23.3	0.49	4.37	I.4xIO^{5}
47	I.33xIO^{-1}	9.4	I.92	2.42	7.6xIO^{3}
48	2.99xIO^{-1}	I2.8	0.46	3.5I	7.IxIO^{4}
49	I.24	27.9	0.25	5.44	5.5xIO^{5}
50	I.30	28.4	0.4I	5.35	3.5xIO^{5}
5I	2.09xIO^{-1}	5.0	0.38	3.03	5.6xIO^{4}
57	3.70xIO^{-2}	3.7	0.96	I.II	4.3xIO^{3}
60	4.79xIO^{-2}	2.I	0.56	2.I9	9.4xIO^{3}

TABLE 5 (continued)

FILM No	P	W	d	% Kr	F
6I	8.72xIO^{-2}	3.2	0.23	3.30	4.3xIO^{4}
63	I.57xIO^{-1}	5.9	0.28	3.I3	6.2xIO^{4}
64	I.49xIO^{-1}	6.6	0.42	2.87	3.9xIO^{4}
65	I.I8xIO^{-1}	5.4	0.36	2.57	3.6xIO^{4}
70	4.38xIO^{-2}	2.2	0.4I	2.25	I.2xIO^{4}
72	I.30xIO^{-1}	5.8	0.30	2.97	4.7xIO^{4}
76	3.70xIO^{-2}	3.I	0.55	I.5I	7.4xIO^{3}
85	3.0xIO^{-3}	I.4	0.32	0.28	I.IxIO^{3}
86	4.6IxIO^{-2}	I.5	0.29	2.89	I.9xIO^{4}
87	4.I0xIO^{-2}	2.5	0.58	I.97	7.8xIO^{3}
88	4.49xIO^{-2}	2.3	0.42	2.42	I.2xIO^{4}
89	4.23xIO^{-2}	I.I	0.0I3	4.5	(3.6xIO^{5})
90	4.I7xIO^{-2}	4.0	0.87	I.25	5.3xIO^{3}
9I	3.I6xIO^{-2}	4.I	I.00	0.92	3.5xIO^{3}
93	3.92xIO^{-2}	3.0	0.53	I.59	8.IxIO^{3}
95	3.56xIO^{-2}	I3.8	3.60	0.33	I.IxIO^{3}
96	3.72xIO^{-2}	9.0	2.40	0.49	I.7xIO^{3}
98	4.09xIO^{-2}	6.5	I.80	0.78	2.5xIO^{3}
99	4.0IxIO^{-2}	8.8	2.50	0.56	I.8xIO^{3}
I00	4.20xIO^{-2}	I0.2	4.22	0.35	I.IxIO^{3}
I0I	3.77xIO^{-2}	3.5	0.69	I.42	6.0xIO^{3}
I03	4.00xIO^{-2}	5.2	I.I7	I.02	3.8xIO^{3}
I06	3.65xIO^{-2}	II.8	3.34	0.36	I.2xIO^{3}
I09	3.48xIO^{-2}	5.I	I.70	0.73	2.3xIO^{3}
III	3.76xIO^{-2}	5.8	I.5I	0.83	2.7xIO^{3}

For the films deposited at Kr:Ni collision ratio of less than IO^{4}, the rate of krypton incorporation appeared in the first place to be related only to the krypton pressure. However, a definite tendency for films where the nickel deposition rate was high, to show disproportionately high krypton incorporation rates, was also noted. Additional data for these films are presented in table 6.

TABLE 6 RATE OF KRYPTON INCORPORATION FOR FILMS DEPOSITED AT LOW VALUES OF THE Kr : Ni COLLISION RATIO

TABLE HEADINGS : Q = total quantity of krypton incorporated in to each film at 77°K, in μmoles

RI = rate of krypton incorporation in μmoles min^{-1}

RI÷P = rate of krypton incorporation, divided by the constant pressure of krypton. (μmoles min^{-1} torr^{-1})

FILM No	Q	RI	RI÷P	d(table 5)
23	I.00	0.I2I	3.98	0.70
25	I.64	0.I63	4.93	I.27
27	0.325	0.0348	4.46	I.8I
29	I.95	0.229	3.37	0.73
43	5.28	0.975	4.87	2.62
47	3.96	0.808	6.07	I.92
57	0.690	0.I78	4.82	0.96
60	0.798	0.2I3	4.44	0.56
76	0.806	0.I42	3.84	0.55
85	0.067	0.0I5	5.0	0.32
87	0.837	0.I85	4.50	0.58
90	0.863	0.I88	4.50	0.87
9I	0.645	0.I58	5.0I	I.00
93	0.820	0.I45	3.70	0.53
95	0.703	0.2II	5.93	3.60
96	0.769	0.206	5.54	2.40
98	0.872	0.242	5.93	I.80
99	0.846	0.242	6.04	2.50
I00	0.6I4	0.254	6.05	4.22
I0I	0.86I	0.I69	4.49	0.69
I03	0.9I3	0.205	5.I3	I.I7
I06	0.727	0.206	5.65	3.34
I09	0.642	0.2I4	6.I5	I.70
III	0.823	0.2I5	5.7I	I.5I

4.8 DISCUSSION OF KRYPTON INCORPORATION KINETICS

A steady state treatment, based on the rates of collision of nickel and krypton with the film, was adopted in an attempt to explain the results presented in the two previous sections.

An alternative treatment, based on the adsorption of krypton by nickel at equilibrium, was not believed to be of value. The equilibrium adsorption isotherm for this system at 77°K is not linear in the pressure range of interest (3I). Therefore it would not be possible to explain the exponential decrease of krypton pressure with time for films deposited under constant volume conditions, in terms of the decrease in the amount of krypton adsorbed at equilibrium.

Haygood (98) has investigated the cryotrapping of air by water vapour condensing on to a substrate at 77°K, and has developed a kinetic theory for the steady state sorption of gases during the formation of a condensate. The following theory is based on the principles of his treatment.

It was assumed regarding the incorporation of krypton in to a nickel film during its deposition:

(I) That the geometric area of a film remains constant during its deposition.

(2) That incorporation of krypton occurs when 'adsorbed' krypton is buried by nickel atoms added to the film. The nature of this adsorbed state is discussed in section 4.IO.

(3) That the process of krypton incorporation occurs only at the 'growing' surface of a film.

(4) That sites where krypton atoms are adsorbed are as likely to be buried as free sites.

(5) That a steady state is quickly reached after deposition begins.

Certain terms are defined as follows:

N = The rate of nickel deposition in atoms sec^{-1}.

S = The number of nickel atoms required to produce a site where one krypton atom may be adsorbed.

E = The total number of such sites on the surface of a film at any instant.

X = The proportion of surface sites covered by krypton at any instant.

C = The rate of krypton collisions with the film in atoms sec^{-1}.

p = The probability that a krypton atom which collides with a free site on the surface of the film will enter the adsorbed state.

q = The probability that an adsorbed krypton atom will be desorbed in one second.

From these definitions:-

The number of surface sites buried in one second $= \dfrac{N}{S}$

The number of krypton atoms adsorbed on the surface at any instant $= X.E$

The number of krypton atoms incorporated in to the film in one second $= \dfrac{N.X}{S}$

The ratio of the number of krypton atoms in the film, to the number of nickel atoms in the film $= \dfrac{X}{S}$

At equilibrium, the proportion of sites covered by krypton will be a constant. Since the total number of sites on the surface is a constant, the number of krypton atoms incorporated in to the bulk of the film in one second will be given by the difference between the number of krypton atoms which enter the adsorbed state and the number which desorb in the same time.

$$\therefore \quad \frac{N.X}{S} = C.p\,(1-X) - E.X.q \qquad \underline{\hspace{6cm}}\,(1)$$

Thus when X is small, and p and q are low probabilities, the rate of incorporation of krypton, NX/S, is equal to Cp.

In this case, the rate of incorporation of krypton is proportional to its collision rate, and thus to the pressure of krypton.

From (I), the ratio, Kr atoms : Ni atoms in a film is given by:

$$\frac{X}{S} = \frac{C.p}{N} - X.\left[\frac{C.p}{N} - \frac{E.q}{N}\right] \qquad \underline{\hspace{5cm}}\,(2)$$

Where C/N is the Kr:Ni collision ratio for the particular film.

EVALUATION OF THE PARAMETERS p, q, E, AND S

The equation (2) could be used to predict the quantity of krypton incorporated in to a film if X was eliminated, and if the values of the parameters p, q, E, and S, were known.

To calculate these parameters, it was necessary to assume that all films had identical geometric areas. This assumption was also made in the calculation of the relative rates of collision of nickel and krypton atoms with a film, which appears in appendix H.

The mean length of the portion of the walls of the film vessel over which the films were deposited, was 100 mm. Thus the geometric area of a film was taken to be 62.8 cm^2.

The rates of collision of nickel and krypton ~~and nickel~~ with the film were calculated in terms of the geometric area of the film, that is the portion of the film which would be visible from directly above. The total number of nickel atoms visible from above will depend on the particular planes which are exposed. However, the number of nickel atoms which must be added to the film in order to render the previous surface invisible from above, is the same regardless of the topography of the surface. In all cases it is equivalent to a 'solid sheet' of nickel, one atom thick, and with the same geometric area as the film. In order to allow for the exposure of any possible crystal plane, the number of atoms in such a sheet was calculated from the density of bulk nickel. The result of this calculation was that 1.27×10^{17} atoms of nickel would be required to completely cover the geometric area of the film. It was assumed that the surface of the film would be regenerated by the addition of this number of nickel atoms, and that any krypton adsorbed on the surface would be incorporated in to the film.

It is not implied that the surface of a film is actually regenerated by the addition of a series of such sheets of nickel atoms. Surface turnover may occur more quickly at some parts of the film owing to its topography. The increased number of adsorption sites created and buried at these parts of the film will be compensated by the correspondingly lower rate of surface turnover in other parts of the film.

Although the rate of surface turnover is calculated on the basis of a number of atoms which is calculated from the density of bulk nickel, it is not implied that the film will have the structure of bulk nickel. Reference has been made in chapter 2 to the porosity of evaporated metal films, which would invalidate such an assumption.

An adsorbed krypton atom is taken to be incorporated in to the film when a nickel atom(or atoms) is added to the film at a point vertically above the krypton atom. No assumption is made as to how far above this point might be.

Voids may thus occur in the film, on this picture of surface regeneration.

The total number of surface adsorption sites on a film at any instant is given by:-

$$E = \frac{1{\cdot}27 \times 10^{17}}{S} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_}(3)$$

Let X/S = R, the ratio of the number of krypton atoms in a film, to the number of nickel atoms in the film.

Let C/N = F, the Kr:Ni collision ratio for a film.

Then we may rewrite (2) :-

$$R = F.p - X\left[F.p + \frac{1{\cdot}27 \times 10^{17}.q}{S.N}\right]$$

$$\therefore\ R = \frac{F.p.(1-X)}{1 + \dfrac{1{\cdot}27 \times 10^{17}q}{N}} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_}(4)$$

Thus the proportion of krypton which is incorporated in to a film is shown to vary with F, X, and N. These three terms are of course mutually dependent; it is impossible to change one without effecting the others in an actual experiment. The relationship (4) may however be explained in a physical sense by assuming that the terms can be considered separately.

It is obvious that to increase F, increases the availability of krypton to the film, and that R will increase.

Where X is low then the probability that any one colliding krypton atom will strike a vacant site is high, so that a large number of collisions will result in adsorption and incorporation. Thus a low value of X contributes to a high value of R.

Finally where N, the deposition rate of nickel, is low then a krypton atom may remain on the surface for a considerable time before being incorporated. Since desorption is defined to be a first order process, the effect of desorption in reducing the surface pool of adsorbed krypton will therefore be greater when N is low. Accordingly, when all other factors are held constant, a larger amount of krypton will be incorporated in to a film grown at a high deposition rate.

The number of variables in equation (4) may be further reduced by the substitution of R.S for X.

$$\therefore R = \frac{F.p.(1-R.S)}{1 + \frac{1{\cdot}27\times10^{17}.q}{N}} \quad \underline{\qquad\qquad\qquad} (5)$$

In this equation, R, F, and N are variables, and p, q, and S are unknown constants.

When the surface coverage of krypton is low, and the nickel deposition rate is high, then the rate of krypton incorporation is determined only by the rate of collision C, and the probability of adsorption p. In this limiting case, all krypton atoms strike a vacant site, and all adsorbed atoms are buried immediately.

This is assumed to be the state of affairs for the films deposited at the highest deposition rates within the linear region of the at.% Kr against Kr:Ni collision ratio plots. In this region the highest value observed for the rate of krypton incorporation, divided by the constant pressure of krypton, is 6.I μmoles $min^{-1}torr^{-1}$. This value is assumed to represent the limiting case.

$\therefore$ Limiting rate of krypton incorporation = 6.IxP μ moles min^{-1}, for a film laid down in a pressure of P torr of krypton.

From appendix H, the rate of krypton collisions with a growing film is given as: $I.I3xI0^{24}xP$ atoms min^{-1}.

$\therefore I.I3xI0^{24}xPxp = 6.IxI0^{-6}x6.02xI0^{23}xP$

$$\underline{\underline{p = 3.2xI0^{-6}}}$$

When the value of p is known, the values of R, F, and N may be substituted in to a rearranged form of (5), to yield a linear equation in q and S.

$$R.F.p.S + \frac{R}{N} \times 1{\cdot}27\times10^{17}.q = F.p - R \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (6)$$

The equations obtained for the eight films deposited at the highest values of the Kr:Ni collision ratio, are given in table 7.

TABLE 7 LINEAR EQUATIONS IN q AND S FOR EIGHT NICKEL FILMS

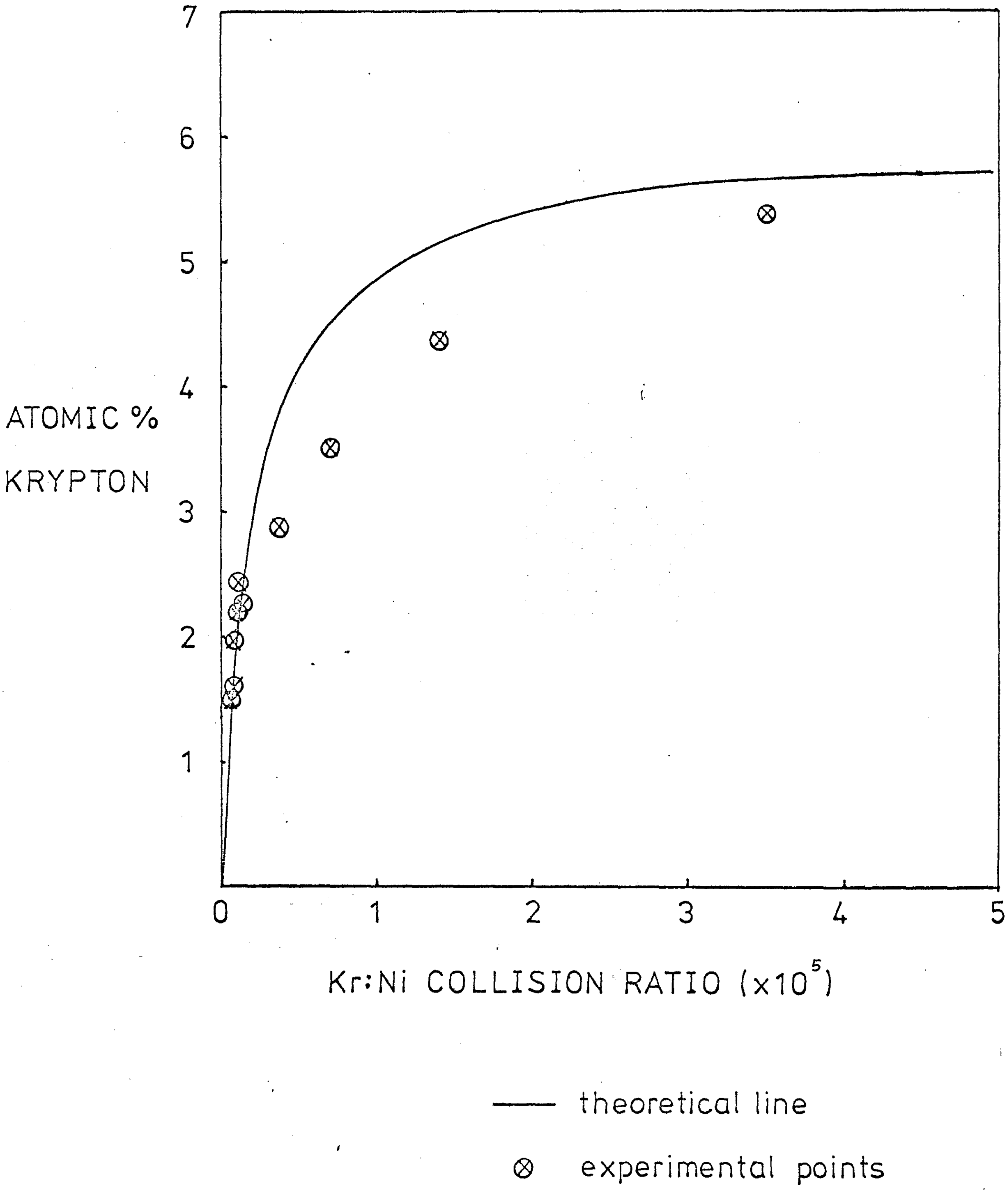
FILM No	F	R	N	EQUATION
49	55000	0.0610	4.3×10^{16}	$0.107S + 0.18q = 1.70$
50	35000	0.0599	7.0×10^{16}	$0.067S + 0.11q = 1.06$
46	14000	0.0459	8.3×10^{16}	$0.021S + 0.070q = 0.40$
38	8200	0.0351	4.8×10^{16}	$0.0092S + 0.093q = 0.23$
63	6200	0.0324	4.8×10^{16}	$0.0064S + 0.086q = 0.17$
51	5600	0.0323	6.5×10^{16}	$0.0058S + 0.063q = 0.15$
72	4700	0.0315	5.1×10^{16}	$0.0047S + 0.078q = 0.12$
45	4500	0.0388	1.43×10^{17}	$0.0056S + 0.034q = 0.11$

When an attempt was made to solve pairs of these equations for the values of S and q, a considerable spread of values was obtained. In part, this is due to the experimental errors which have been mentioned in section 4.7. The mean value found for S was 16 ± 4. The spread of values found for q was in the range 0.25 to 1.3, and it is thus doubtful if this can be claimed to represent a constant value. In the region of high coverage represented by the films of table 7, the equations are not in any case very sensitive to changes in the value of q.

Conversely in the region of low coverage, the equations would not be expected to be very sensitive to the value of S, since effectively all of the surface consists of free sites.

Six equations in q and S were set up for films deposited in the region of low surface coverage (films No 25, 57, 85, 90, 91, and 96). The value of 16 found for S (above) was then substituted in to these equations in order to evaluate q. The mean value found was 0.10 ± 0.04.

FIGURE 19 PLOT OF ATOMIC % KRYPTON INCORPORATED IN TO NICKEL FILMS DEPOSITED AT $8{\cdot}5 \times 10^{16}$ ATOMS SEC^{-1}, CALCULATED FROM EQUATION (6), ASSUMING $p=3{\cdot}2\times10^{-6}$, $q=0{\cdot}10\,sec^{-1}$, $S=16$.



There is clearly a considerable amount of error in the determination of values for q, in the regions (a) of high coverage, and (b) of low coverage. However, if the size of the krypton adsorption site is assumed to be constant over the complete range of coverage from X = 0 to X =I, then the difference between the values of q found in each of these determinations is significant.

The higher value found for q in the region of high coverage may be taken to represent less stable adsorption in this region. If the value of q does in fact increase with surface coverage, then this would explain some of the error in the determination of S. This determination was carried out using data for films which had significantly differing values of the equilibrium surface coverage during deposition.

A finding of less stable adsorption at high surface coverage, would be characteristic of the state of chemisorption, and not of physical adsorption. Reference has been made in section 2.5, to the possibility of a partly chemical bond between an inert gas atom and a surface. These results may be interpreted on this basis.

Alternatively it is possible that the structure of the film at 77°K is effected by the large amount of krypton incorporated in to the film in the region of high coverage, and that the change in the value of q arises from this.

The fact that the value of q or S, or both, may vary with surface coverage, renders a more exact calculation of the values of these parameters, than that presented above, impossible to achieve from the results.

A plot taken from the above theory, of R against F for a series of films, will only be valid for one value of the nickel deposition rate. Figure I9 shows a plot the atomic % of krypton incorporated in to a film (calculated from R), against the Kr:Ni collision ratio, assuming that the parameters have values: S = I6, q = 0.I, and $p = 3.2\times10^{-6}$. This plot is valid for a nickel deposition rate of 8.5×10^{16} atoms sec^{-1}, corresponding to 5.0 mg min^{-1}. Experimental points, for all films deposited at rates of between 4.0 mg min^{-1} and 6.0 mg min^{-1}, are included for purposes of comparison.

For values of F below 2×10^{4}, the experimental points fit well on to the theoretical line. At higher values of F, the fit is not good.

An attempt was made to fit all the experimental points to a theoretical line, by adopting various values of p, q, and S. (It should be noted that the less stable adsorption in the region of high coverage is reflected in different q values, only because both the other terms were assumed to be constant. The characteristics of adsorption will in fact be determined by all three parameters)

It was found impossible to fit all of the experimental points on to a theoretical line. The assumption of various expressions relating q linearly to X, was equally unsuccessful. The reason for this failure may lie in the fact that the experimental at.% Kr against F plot showed a definite sudden decrease in slope at approximately 2.5% krypton. This may imply that there are two types of adsorption site on the surface, one of which is occupied more readily than the other, or that the onset of some structural change in the film occurs when this amount of krypton is being incorporated.

In any case, it is necessary to invoke a considerable degree of interaction between the film and adsorbed krypton in order to explain the results obtained. Such interaction could not be explained by a purely physical picture of the adsorption involved.

Although the precise value is in doubt, the values of q obtained in the region of low coverage (approximately 0.10 sec^{-1}), imply a lifetime of the adsorbed atom on the surface which is in the order of several seconds. This is also in keeping with a partly chemical picture of krypton adsorption under the conditions used.

Various experiments were carried out to investigate the nature of the adsorbed state of krypton. These experiments are described in section 4.10.

KINETICS OF KRYPTON INCORPORATION FOR FILMS GROWN UNDER CONSTANT VOLUME CONDITIONS

It has been shown in the steady state treatment above, that in the limiting case, the amount of krypton incorporated in to a film in a given time is dependent only upon the rate of krypton collisions with the film and the probability of adsorption p. This limiting case is found for films deposited at high deposition rates, and values of F below approximately 10^{4}.

Assuming that the surface conditions during deposition of a film under constant volume conditions are identical at any instant to those found for a film being deposited in the constant pressure system,(with the Kr:Ni collision ratio which corresponds to the instantaneous pressure) then when the Kr:Ni collision ratio is less than approximately 10^4, the rate of krypton incorporation will be linearly related to the pressure throughout the period of deposition. Since the pressure of krypton is determined by the quantity of krypton in the system, a first order decrease in the krypton pressure is predicted in this region. Where the Kr:Ni collision ratio is above 10^4, then a decrease in the amount of krypton in the gas phase, brought about by incorporation in to the film, will produce a less than proportionate decrease in the krypton pressure.

If the films deposited under constant volume conditions are considered in terms of the Kr:Ni collision ratio during the period of deposition, then assuming that the deposition rate of nickel remains constant, the following values are obtained.

TABLE 8 RELATION OF THE KINETICS OF KRYPTON INCORPORATION TO THE Kr:Ni COLLISION RATIO FOR FILMS DEPOSITED UNDER CONSTANT VOLUME CONDITIONS

FILM No	RANGE OF Kr:Ni COLLISION RATIO	OBSERVED KINETICS
6	$9.8\text{x}10^2 - 2.3\text{x}10^2$	FIRST ORDER
17	$4.5\text{x}10^3 - 1.2\text{x}10^2$	FIRST ORDER
19	$2.1\text{x}10^3 - 5.1\text{x}10^2$	FIRST ORDER
28	$1.0\text{x}10^4 - 2.1\text{x}10^3$	FIRST ORDER
34	$7.3\text{x}10^3 - 3.1\text{x}10^3$	FIRST ORDER
35	$1.4\text{x}10^4 - 5.7\text{x}10^3$	FIRST ORDER
39	$2.1\text{x}10^3 - 2.6\text{x}10^2$	FIRST ORDER
55	$5.1\text{x}10^5 - 3.6\text{x}10^5$	APPARENTLY ZERO ORDER
66	$4.2\text{x}10^4 - 5.8\text{x}10^3$	FIRST ORDER BELOW ≈ 15000
68	$1.8\text{x}10^4 - 2.2\text{x}10^3$	FIRST ORDER BELOW ≈ 6000

The results are in reasonable agreement with the prediction of first order pressure decrease at values of the Kr:Ni collision ratio below 10^4.

Variations may be accounted for as follows:

(1) The rate of nickel deposition may not remain constant during the period

FIGURE 20 PLOT OF k_1 AGAINST RATE OF NICKEL DEPOSITION FOR FILMS DEPOSITED UNDER CONSTANT VOLUME CONDITIONS

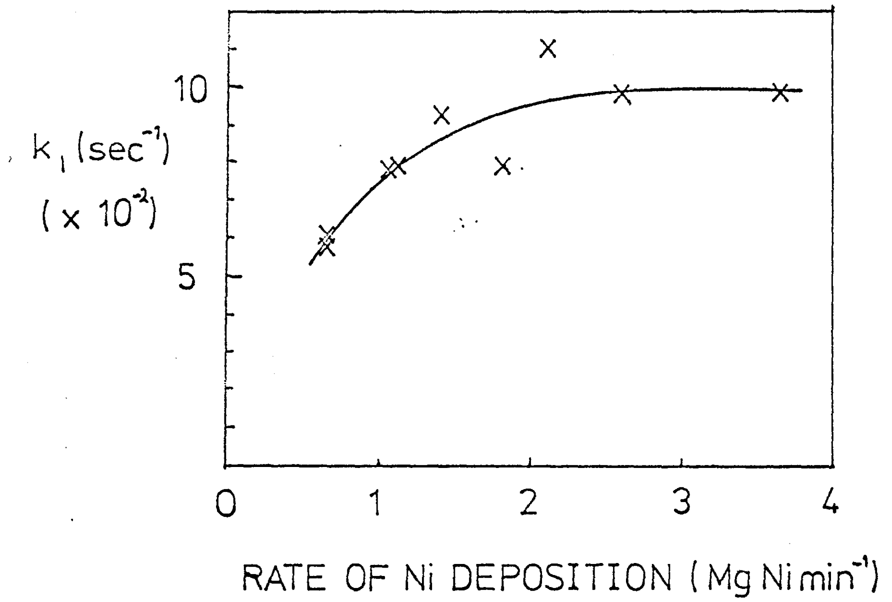
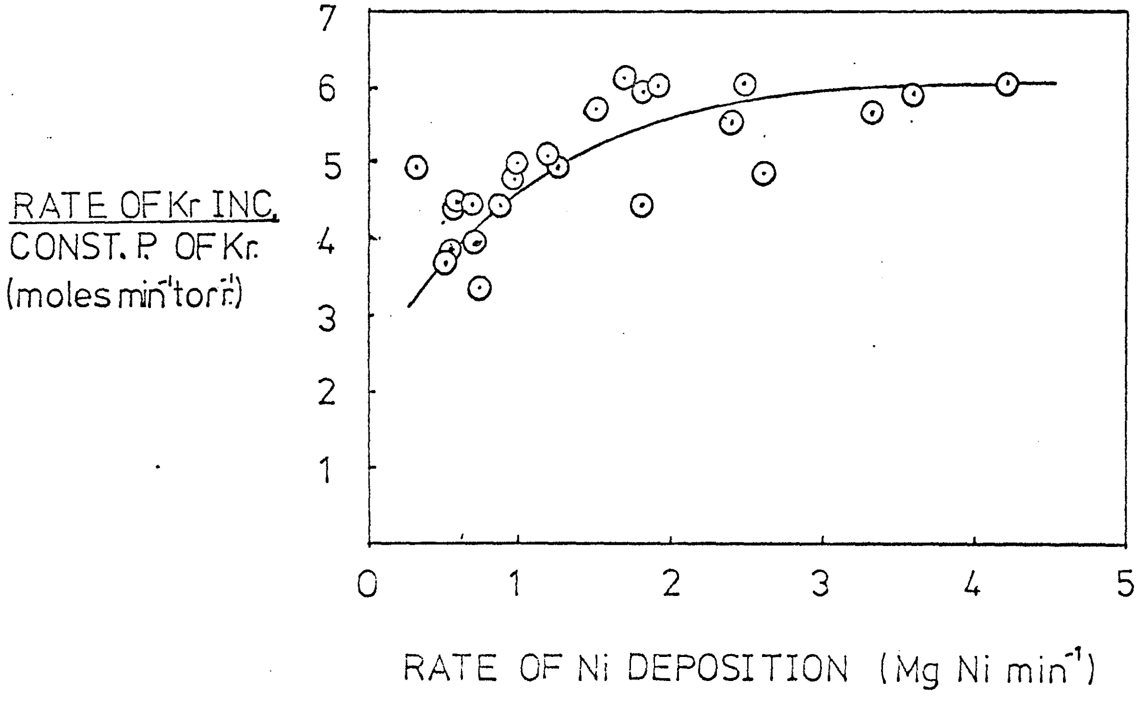


FIGURE 21 PLOT OF (RATE OF KRYPTON INCORPORATION ÷ CONSTANT KRYPTON PRESSURE) FOR FILMS DEPOSITED UNDER CONSTANT PRESSURE CONDITIONS



of deposition. These films are rather heavier than most of the 'constant pressure' films, so that the effect of filament thinning may be more pronounced. Further, the considerable decrease in krypton pressure may effect the filament temperature by variation of the amount of heat lost by conduction.

(2) The rate of krypton incorporation does not in fact vary only with the Kr:Ni collision ratio, but also with the nickel deposition rate, so that a value of 10^4 for the onset of exponential behaviour is approximate.

(3) No precise point of change-over from one type of kinetics to another would be expected to exist ; rather the change would be expected to be gradual, so that the value selected in each case for the point of change-over is somewhat arbitrary.

The apparently linear decrease of krypton pressure with time where the value of the Kr:Ni collision ratio is high, arises because in this region a change in its value produces only a small change in the rate of krypton incorporation.

It may be noted that in table 4, high values of k_1, the gradient of the plot of log(krypton pressure) against time, were found for high rates of nickel deposition. A plot of k_1 against the rate of nickel deposition for this series of films is shown in figure 20. This plot may be compared with a similar plot made for the series of films deposited under constant pressure conditons. In this case, the rate of krypton incorporation , divided by the constant pressure of krypton, is plotted against the rate of nickel deposition. (figure 21)

In order to make a quantitative comparison of the rates of krypton incorporation under both sets of conditions, it is assumed that the level part of each curve represents the limiting case, where each krypton atom strikes a vacant site, and all adsorbed atoms are immediately incorporated in to the film.

It has already been stated that the limiting rate of krypton incorporation under constant pressure conditions, is 6.1 μmoles $\text{min}^{-1}\text{torr}^{-1}$.

The ratio of the initial pressure at zero deposition time, to the quantity of gas present in the constant volume system, has been shown for a series of films deposited in argon, to be equal to $3.66\times10^{-2} \pm 0.16\times10$ torr μmoles^{-1} (see appendix C). For six films deposited in krypton, the mean value obtained was

$3.33\times10 \pm 0.50\times10^{-2}$ torr μmoles^{-1}.

The greater variation for krypton may be accounted for by the greater tendency to physical adsorption on any light bake-out film, and also by the problem of estimating the time of onset of deposition of the film. The initial rates of krypton incorporation were so high that an error of a few seconds could cause a large error in the estimation of the initial pressure. The initial rates of argon incorporation were much less, so that this source of error was less important. (see section 4.II)

The gas laws hold equally for argon and krypton; therefore the more accurate value obtained for argon was used for the purposes of this calculation.

Let P = pressure of krypton in torr

Q = quantity of krypton in μmoles

t = time in minutes

Then,

$$P/Q = 3.7\times10^{-2} \text{ torr } \mu\text{moles}^{-1} \text{ (under deposition conditions)}$$

In the limiting case,

$$dQ/dt = -6.1 \mu\text{moles min}^{-1}\text{torr}^{-1}$$

Thus at pressure P torr,

$$dQ/dt = -6.1\times P \mu\text{moles min}^{-1}$$

$$dP/dt = -2.3\times10^{-1} P$$

Integrating,

$$\ln P = -2.3\times10^{-1}t + \text{constant}$$

$$\log P = -1.0\times10^{-1}t + \text{constant}$$

Therefore k_1, the gradient of the plot of logP against time, is given to be -1.0×10^{-1} in the limiting case for deposition of films in a system of constant volume. This value is in reasonable agreement with the highest observed values of k_1. (figure 20)

4.9 THERMAL RELEASE OF KRYPTON FROM FILMS

Once krypton had been incorporated in to a film at 77°K during deposition, no increase of pressure corresponding to release of krypton was ever noted while the film was maintained at 77°K. However, on warming the film, it was found that a large proportion of the krypton which had been incorporated was released to the gas phase.

EXPERIMENTAL PROCEDURE

In the simplest case, the Dewar flask of liquid nitrogen was removed from round the film vessel. After the film had been left for an hour to reach room temperature, the quantity of krypton released was recovered by the Toepler pump and measured in the McLeod gauge.

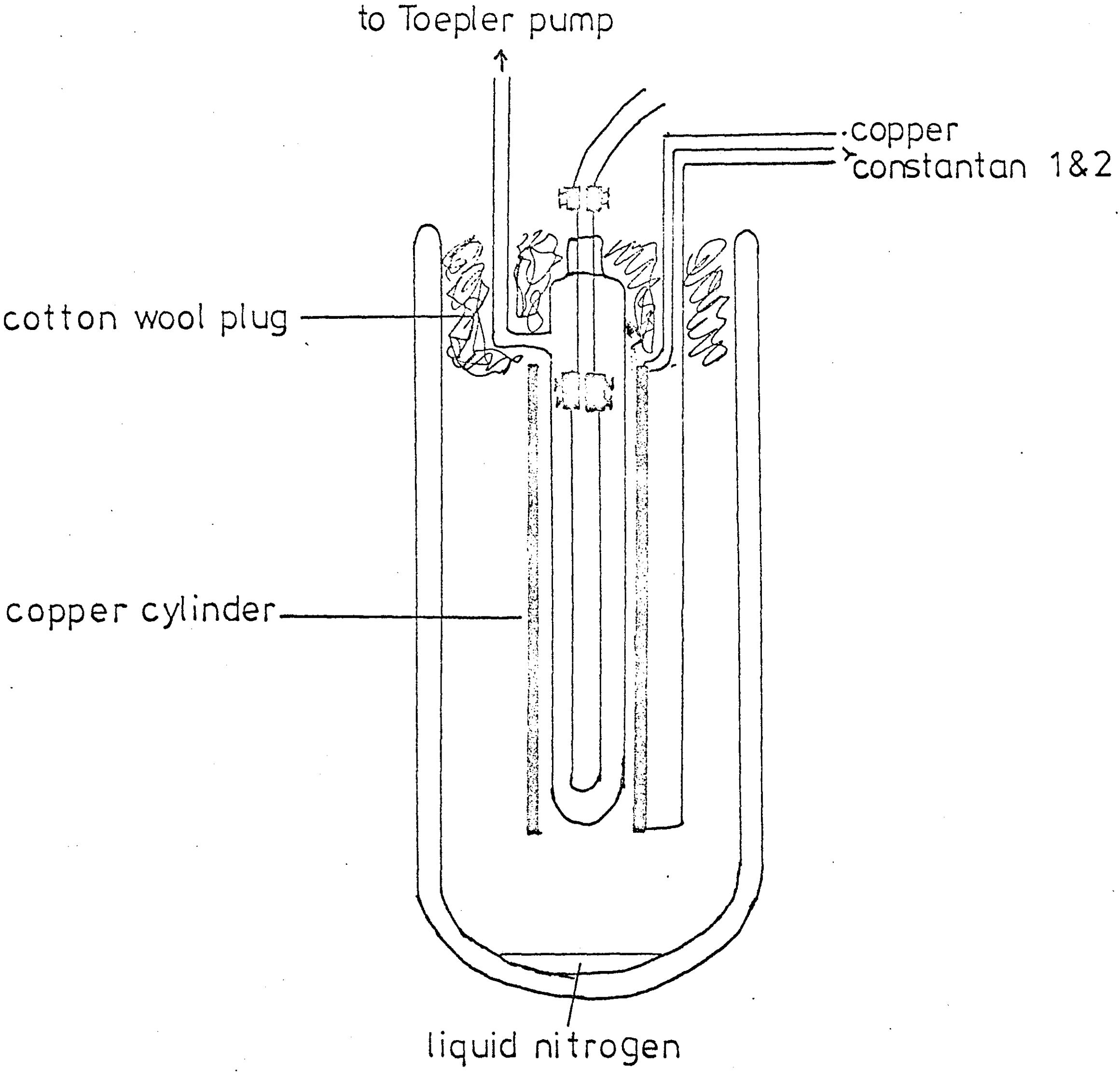
Measurements were taken over a wide range of temperature by one of two techniques. In the first method, the liquid nitrogen bath was removed from the film, and replaced as quickly as possible by baths containing fluids at higher temperatures. After one hour, the quantity of krypton that had released was measured as above. Typically, a film was surrounded successively by liquid argon (87°K), solid CO_2/acetone(193°K), ice/water(273°K), and water at approximately 350°K. Thereafter the film was surrounded by a furnace and heated to higher temperatures for one hour intervals. For temperatures above 470°K it was found that gas was desorbed from the walls of the vessel owing to incomplete degassing. Accordingly the quantity of krypton remaining in the film was measured with the paralled counter, instead of gas-volumetrically.

In the second method, provision was made for continuous monitoring of temperature during a slow rise from 77°K.

A constantan wire was soldered to each end of a heavy copper cylinder and a copper wire to one end. The wires were connected to a Croydon Precision Instrument Type P3 potentiometer. This arrangement was used as a temperature stabiliser and two thermocouples, which were calibrated as described in Appendix E.

The copper tube was placed in position round the film vessel and the whole immersed in liquid nitrogen before deposition commenced. After the film had

FIGURE 22 EXPERIMENTAL ARRANGEMENT FOR MONITORING RELEASE OF KRYPTON FROM A FILM DURING A SLOW RISE IN TEMPERATURE FROM 77°K.



been laid down, and gas phase krypton had been pumped off as far as possible, the Dewar vessel was quickly replaced by one cooled previously to 77°K, and now containing a few drops of liquid nitrogen. (see figure 22) It was found that this could be accomplished sufficiently quickly that no rise in temperature was noted in the thermocouple circuits.

The temperature remained at 77°K for a few minutes until the liquid nitrogen in the Dewar flask had boiled off; then a slow rise in temperature, of approximately I°min^{-1} was observed. The copper cylinder served, by its heat capacity, to slow the rate of temperature rise, and also to maintain an almost constant temperature over the length of the film vessel. The thermocouple at the top of the film vessel normally registered a temperature 5° to I0° above that registered by the lower thermocouple.

Krypton release was measured either by the increase of pressure in the system, or by continuous pumping in to the McLeod gauge using the Toepler pump.

RESULTS: RELEASE OF KRYPTON ON WARMING A SERIES OF NICKEL FILMS TO ≈295°K

The quantity of krypton originally incorporated in to a film at 77°K was calculated from measurements of the pressure, as described previously. For films deposited in the constant volume system, between 22% and 70% of the krypton incorporated at 77°K was stably retained at room temperature (295°K). Films deposited under constant pressure conditions were observed to retain between 6% and 69% of the krypton incorporated at 77°K.

Although there was considerable variation in the proportion of incorporated krypton which, having been incorporated at 77°K, was retained to room temperature, the atomic % of krypton retained in a film was fairly constant.

The results which were obtained for two series of films are shown in tables 9 and I0. All the values of 'atomic % of krypton', refer to the percentage of all the atoms (nickel and krypton) in the film. Thus, for example, a value of 5% represents a ratio of 95 nickel atoms to 5 krypton atoms in the film.

TABLE 9 RETENTION OF KRYPTON BY FILMS DEPOSITED AT 77°K UNDER CONSTANT VOLUME CONDITIONS

FILM No	ATOMIC % OF KRYPTON RETAINED (295°K)
2	0.2I
6	0.2I
I7	0.I3
I9	0.2I

TABLE IO RETENTION OF KRYPTON BY FILMS DEPOSITED AT 77°K UNDER CONSTANT PRESSURE CONDITIONS

FILM No	ATOMIC % OF KRYPTON INCORPORATED (77°K)	ATOMIC % OF KRYPTON RETAINED (295°K)
57	I.II	0.29
60	2.I9	0.32
70	2.25	0.2I
72	2.97	0.I9
76	I.5I	0.24
85	0.28	0.I9
87	I.97	0.36
88	2.42	0.35
90	I.25	0.30
95	0.33	0.I2
98	0.78	0.24
I00	0.35	0.24
I0I	I.42	0.26
I03	I.02	0.23
	MEAN	0.25 ± 0.06

The mean value corresponds to a specific activity of 70 mCi g^{-1} for this series of films.

The value of atomic % at 295°K was very subject to error, as its determination involved the measurement of a small difference between two

FIGURE 23 PRESSURE RISE OWING TO A SUDDEN INCREASE IN TEMPERATURE OF FILM 6 FROM 77°K TO 288°K

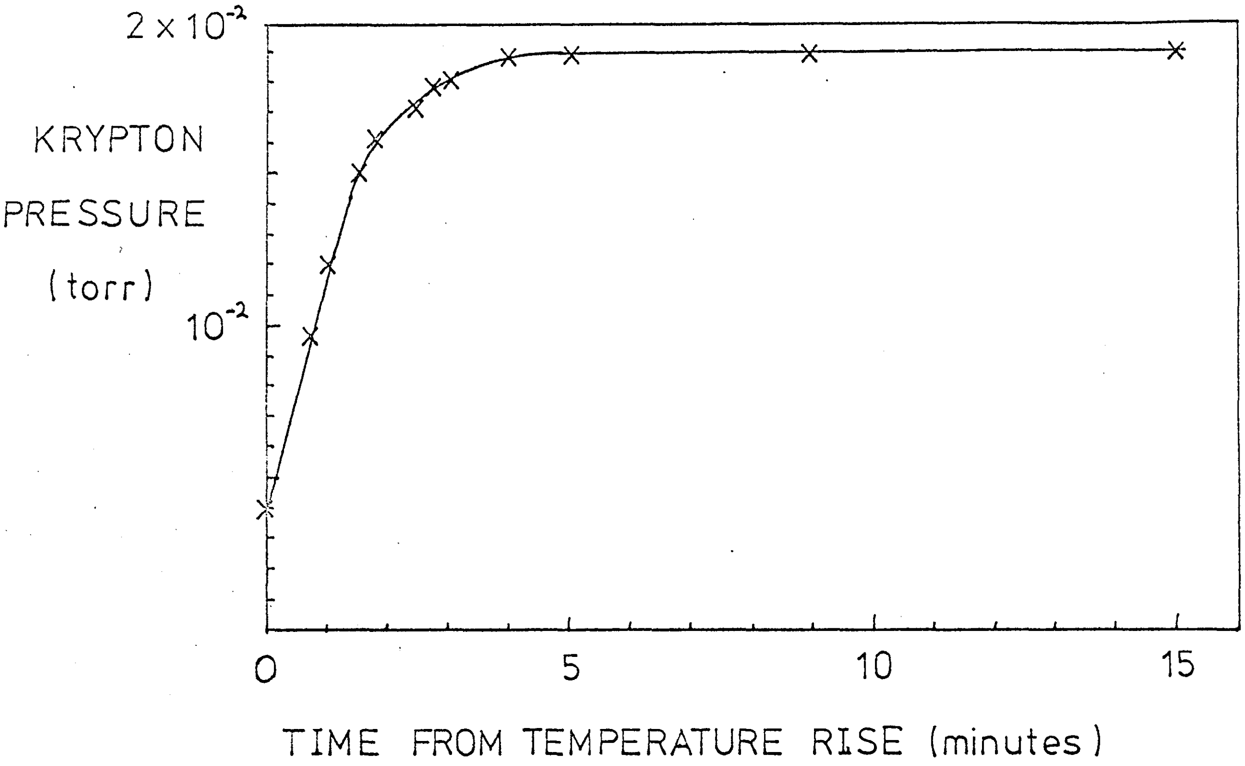
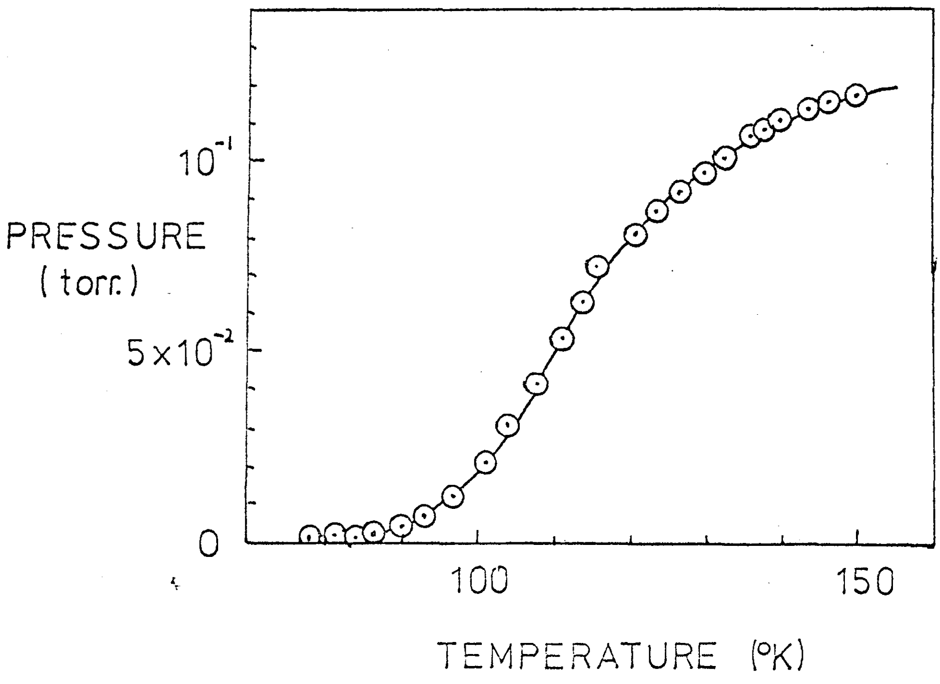


FIGURE 24 PRESSURE OF KRYPTON DURING THE GRADUAL WARMING OF FILM 29 TO 160°K.



relatively large quantities of krypton. Several of the results quoted in table IO were for films with low weights, and the values were therefore subject to weighing errors. In other cases the quantity of krypton was not obtained directly, but by calculation after an exchange experiment. (see section 4.IO)

These factors will contribute to the apparent variation in the mean value observed for the atomic % of krypton at 295°K.

The films deposited under constant volume conditions all showed values of the amount of krypton retained, which were below the mean value observed for the films deposited under constant pressure conditions. The reason for this tendency is that the pressure during the later stages of deposition of these films was so low that a large proportion of the film had very little incorporated krypton at 77°K.

TIME SCALE OF KRYPTON RELEASE

If water at 295°K was substituted for the liquid nitrogen after a film had been deposited, then a rapid release of krypton could be observed by monitoring the krypton pressure. The pressure against time plot obtained for film 6 is shown in figure 23. No further release could be measured after ten minutes. In fact, all films were left for more than ten minutes, in order to be certain that release had terminated.

KRYPTON RELEASE DURING A SLOW RISE IN TEMPERATURE

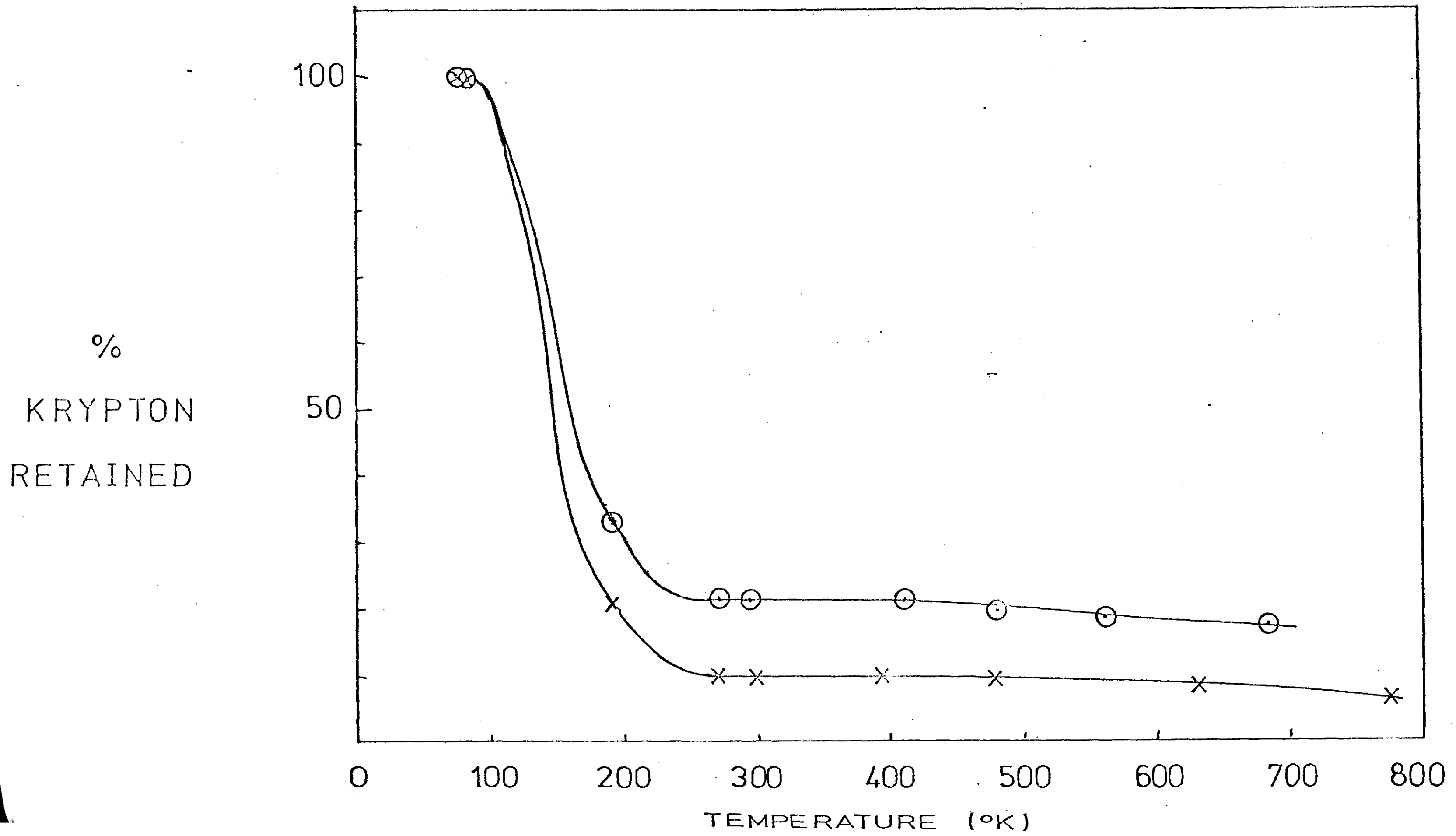
It was found that krypton release could be detected at temperatures below IOO°K, and that the fastest rate of release occurred in the range IOO°K to I40°K.(figure 24) When the release of krypton was followed by pumping it in to the McLeod gauge using the Toepler pump, it appeared that the range of temperature corresponding to the fastest rate of release was rather higher. (figures 27,28) This is explained by the relative inefficiency of pumping with the Toepler pump, so that the quantity measurements were always rather late relative to the temperature reached after a given time.

KRYPTON RELEASE DURING A STEPWISE INCREASE IN TEMPERATURE

This experiment was carried out for two films, numbers 4 and 70. Film 70 was a typical 'constant pressure' film, deposited in 4.38xIO^{-2} torr of krypton. Film 4 was deposited in the constant volume system, with initial pressure of

FIGURE 25 RELEASE OF KRYPTON WITH INCREASE OF TEMPERATURE, FROM TWO NICKEL FILMS.

⊙ FILM 4 (const. Vol.) , x FILM 70 (const. Press.)



3.6×10^{-2} torr. The pressure decrease was not followed accurately in this case.

The quantity of release with increasing temperature is shown in figure 25. Film 70 lost a larger proportion of its krypton, but the atomic % incorporated at 77°K was larger.

The most-prolonged heating employed for any film was a 15 hour period at 800°K for film 2. 79% of the radioactivity which had been measured at room temperature was retained despite this treatment.

In all cases where a film was heated for a period, cooled, and then heated again, the typical 'kryptonate' behaviour (69) was observed. That is, no further release of krypton was detected until the previous maximum temperature was exceeded.

The results obtained for experiments in thermal release of krypton from nickel films are also considered in section 4.10. A general discussion of thermal release for a series of metals appears in section 5(e).

THE APPEARANCE OF THE FILMS

Once films had been allowed to attain room temperature, they appeared black in colour. This was also observed by Beeck (9).

If a bake-out film had been present initially, then the film appeared silver-black.

On sintering at temperatures above 450°K, a progressive silvering was noted. A film sintered at 800°K was silver-grey in colour.

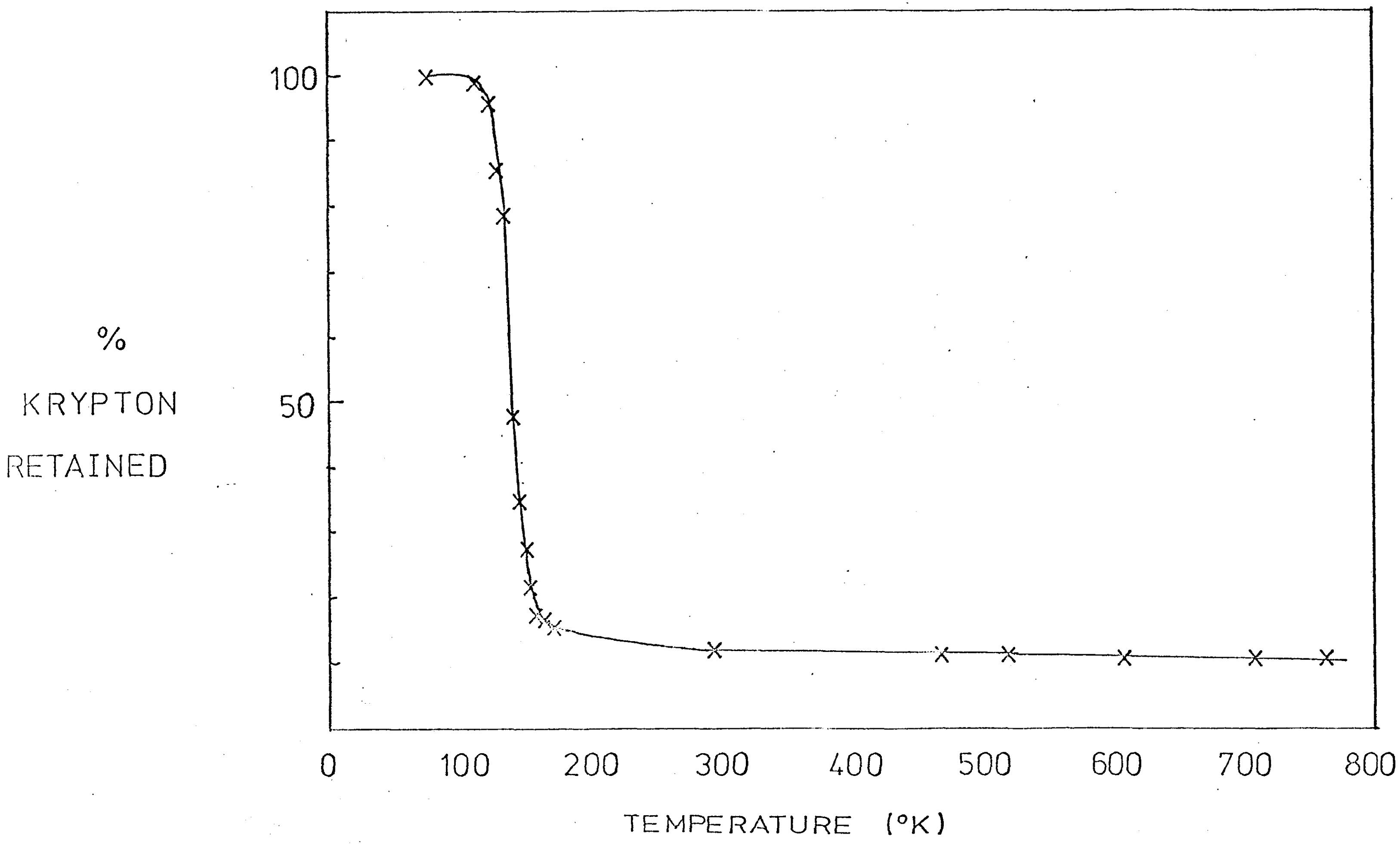
4.10 INVESTIGATION OF THE NATURE OF THE ADSORBED AND INCORPORATED STATES

It was shown in section 4.8 that the kinetics of incorporation of krypton during the deposition of nickel films may be explained by assuming that the incorporation process occurs by the burial of krypton atoms held in some intermediate, adsorbed, state.

The quantity of krypton incorporated during deposition has been defined to be that quantity of krypton which disappeared from the gas phase during the period of deposition, while the conditions of deposition prevailed in the system. It was noted that once deposition ended, more krypton could become

FIGURE 26 THERMAL RELEASE OF KRYPTON IRREVERSIBLY ADSORBED ON FILM 32.

(FILM EVAPORATED IN VACUUM)



associated with the film. This was taken to represent physical adsorption.

In all experiments where attempts were made to remove incorporated krypton from films at 77°K, by pumping for long periods with the Toepler pump, it was found impossible to remove any of the krypton held to be incorporated on the basis of the above definition. However, part of the physically adsorbed krypton could be recovered by this method.

If all the krypton held by the film at this point was in fact physically adsorbed on the film, it might have been expected that such krypton would be readily removed by pumping.

To test this point, two films were laid down at 77°K in vacuum, and were maintained at this temperature. A measured amount of krypton was admitted to the film vessel, and was physically adsorbed by the film. It was also found impossible to remove all of the adsorbed krypton in these cases using the Toepler pump. This is in accord with the findings of Knor and Ponec (36),that the adsorption of krypton on a thermally non-stabilised nickel film is only partly reversible.

When such a film was allowed to attain room temperature and heated to higher temperatures, krypton was released in a similar manner to that observed for films in which krypton had been incorporated. (figure 26) However, the magnitude of the effect was quite different; throughout the temperature range, the retained quantity of krypton represented a much lower proportion of the total film. The atomic % of krypton retained at 295°K is given in table II.

Under similar treatment, a film deposited at 273°K and then cooled to 77°K before exposure to krypton also apparently retained a small quantity of krypton.

TABLE II KRYPTON RETENTION AT 295°K BY VACUUM-EVAPORATED FILMS

FILM No	WEIGHT (mg)	EVAPORATION TEMPERATURE (°K)	ATOMIC % OF KRYPTON (295°K)
32	34.4	77	2.9×10^{-1}
37	34.9	77	2.9×10^{-2}
33	30.5	273	1.1×10^{-2}

It is evident that the quantity of krypton incorporated and retained by films deposited in the presence of krypton at 77°K can not be explained in terms of physical adsorption of krypton on to the exposed surfaces of nickel which develop during the deposition of a film. Nevertheless, it is shown that a process may occur, under conditions where physical adsorption would be expected, which results in the introduction of a smaller quantity of krypton in to the incorporated state.

The addition of the mercury vapour ejection pump to the system enabled gas to be pumped from the film vessel in to the bulb of the Toepler pump in section 6 of the apparatus, and thence to the gas counter. This pump was capable of maintaining a pressure below 10^{-5} torr in the film vessel, so that continuous pumping by this method afforded a much more efficient means of recovering krypton than the use of a Toepler pump alone. A series of films was investigated as follows.

Each film was deposited in the presence of radioactive krypton, and the quantity of krypton which had been incorporated was calculated in the usual manner from the difference in the gas burette levels at constant pressure (a) initially, and (b) immediately before the filament current was switched off. The film was then maintained at 77°K while krypton was pumped in to the gas counter. This was continued until the count rate reached a constant value, normally after 2-3 hours. Pumping was then continued further, to a total of 4-6 hours, to ensure that a limit to the recovery of krypton had been reached. The krypton which had been recovered was then transferred via the by-pass to the McLeod gauge using the main Toepler pump, and was measured in order to determine the quantity retained by the film.

It was found that more krypton could be recovered by this method than by use of the Toepler pump alone. It is not suggested that there is any difference in principle between the two methods; rather the more rigorous conditions resulting from the use of the ejection pump will result in the attainment of a stable state within a reasonable time scale.(Some of the experiments where the Toepler pump alone was used, were abandoned after the raising and lowering of the mercury in the order of fifty times had not resulted in a limit to recovery being reached. Each 'stroke' would be expected, on the basis of the gas laws, to remove approximately half of the gas phase krypton from the film vessel.)

The results which were obtained using the ejection pump to recover krypton from the film vessel are tabulated below.

TABLE I2 MEASUREMENTS OF KRYPTON INCORPORATION, MADE USING THE MERCURY VAPOUR EJECTION PUMP TO RECOVER NON-INCORPORATED KRYPTON AT 77°K

FILM No	WEIGHT(mg)	ATOMIC % OF KRYPTON(77°K)	QUANTITY OF KRYPTON (μmoles) (a) INCORPORATED (DEFINITION)	(b) NOT RECOVERED BY PUMPING
89	I.I	4.5	0.88	0.57
90	4.0	I.25	0.86	0.97
9I	4.I	0.92	0.65	0.62
93	3.0	I.59	0.82	0.86
95	I3.8	0.33	0.70	I.28
96	9.0	0.49	0.77	I.39
99	8.8	0.56	0.85	I.42

The reason that the quantity of krypton which was not recovered by pumping in some cases exceeds the quantity of krypton taken to be incorporated, is that part of the krypton 'physically' adsorbed on to the films after deposition ceased could not subsequently be removed.

When an apparent limit to recovery had been reached in the experiments above, the possibility that non-recoverable krypton might be exchangeable with gas phase krypton was investigated. In four cases, a quantity of inactive krypton was measured with the McLeod gauge and allowed to be adsorbed on to the film under study. After 30 minutes the ejection pump was again switched on to transfer krypton to the gas counter. The quantity of krypton which had been removed from the film was found by counting, and a calculation was made to find the proportion of the krypton held by the film which was exchangeable with a fresh sample of krypton at 77°K. The results of this investigation are given in table I3.

TABLE I3 EXCHANGEABILITY OF THE KRYPTON HELD BY NICKEL FILMS AT 77°K, WHICH COULD NOT BE REMOVED BY PUMPING

FILM No	EXCHANGEABLE KRYPTON (% OF TOTAL RETAINED KRYPTON)
9I	7%
93	I0%
95	I%
96	9%

Considering together the results quoted in tables I2 and I3, it may be noted that even after a fairly rigorous pumping procedure, part of the krypton retained by a film at 77°K is held on sites accessible to the gas phase.

For films where the atomic % of krypton at 77°K, prior to physical adsorption of krypton, was in the range 0.92% to I.59%, the pumping off of gas phase krypton and the krypton held to be physically adsorbed left a quantity of krypton retained by the film which was comparable in magnitude to that which had been calculated to be incorporated.

Where the atomic % of krypton was initially lower, in the range 0.33% to 0.56%, then the films retained part of the krypton which had been adsorbed after deposition ceased.

The film which had an initially much higher atomic % of krypton, 4.5%, released a part of the krypton which had been calculated as incorporated, during the period of pumping.

To explain these observations, it is necessary to recognise that the states described as 'adsorbed' and 'incorporated' are not completely distinct; rather there is a gradation in the strength of adsorption from classical physical adsorption on the one hand, to a totally buried and inaccessible state on the other hand.

During the deposition of a film, adsorption sites will be formed by the arrival of nickel atoms. Some of these sites will be totally buried by nickel which arrives later; others will remain unburied, at internal surfaces within the porous film. The occupancy of sites, buried and unburied, when deposition ceases, will depend on the availability of krypton during film growth.

When deposition ceases, the sites in a film may be taken to fall in to one of three categories:

Type (I) : buried sites,

Type (2) : sites at internal surfaces within the film,

Type (3) : sites at the external, 'growing' surface of the film.

For all practical purposes, vacant type I sites may be taken to have been destroyed. We may associate the krypton held at type I sites with that krypton which is neither recoverable by pumping nor exchangeable with gas phase krypton. From this viewpoint, a site at the internal surface of an isolated void within the film may be described as a type I site.

Up to this point, krypton has been taken to be incorporated by a film when it was removed from the gas phase to sites on the film during the period of deposition. This definition embraces krypton held at sites of type I and type 2, that is, krypton held at sites which are not in dynamic equilibrium with the gas phase at the instant when deposition ceases. Krypton which is held at type 3 sites at this instant has not been included in the definition, since the back-extrapolation of the linear plot of krypton uptake to zero time of deposition compensates for the initial formation of the small steady-state pool of krypton on the surface, which remains constant in quantity until deposition ceases. The quantity in question would in any case be small.

In terms of the character of adsorption, it is not possible to make a sharp distinction between sites of types 2 and 3. The distinction is one of relative accessibility to the gas phase. It is suggested that a proportion of the krypton held at such surface sites is removable by pumping.

If a film is laid down under conditions of ready krypton availability, then sites of type 2 and type 3 will be almost in adsorption equilibrium throughout deposition. On stopping deposition the remainder will be quickly saturated by the krypton which then becomes associated with the film by 'physical' adsorption. Where the strength of adsorption at a large proportion of the sites of types 2 and 3 is such that krypton may be removed from them by pumping, then a proportion of the krypton which disappeared from the gas phase may now be recovered. This corresponds to the observations made for film 89. (see table I2)

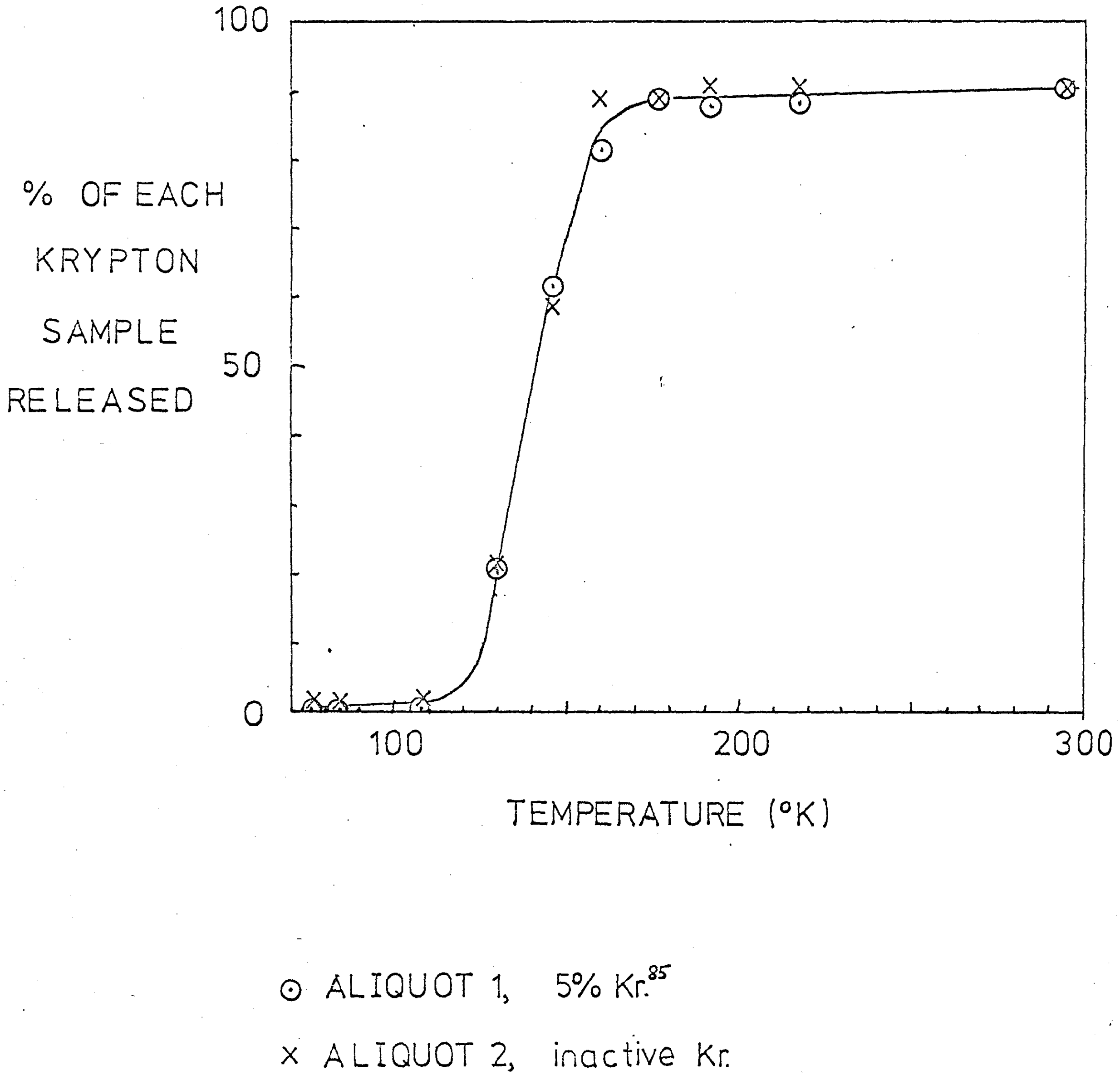
Under conditions where deposition is so fast that krypton is not readily available throughout deposition, sites of types 2 and 3 will be more sparsely occupied at the completion of deposition. Gas phase krypton may now enter sites from which it is not removable by pumping, so that the quantity of krypton retained by the film exeeds that which disappeared from the gas phase during deposition, as observed in the cases of films 95, 96, and 99.

The observations for films 90, 9I, and 93 correspond to cases where the two effects cancel. The occupancy of the sites during deposition is such that none of the krypton which disappears from the gas phase during deposition is removable by pumping, and on ceasing deposition, gas phase krypton enters sites from which it is thereafter readily removable by pumping.

It is not possible to take exact values from the results quoted, in view of experimental error and the possibility of a real variation in the distribution of sites owing to slight variations in the deposition conditions from one film to another. However, values in broad agreement with the data would be obtained by assuming that the numbers of type I and type 2 sites formed during deposition are approximately equal, and that krypton may be irreversibly adsorbed on approximately one fifth of the type 2 sites. The small quantity of krypton taken up by vacuum-evaporated films, which has the properties of incorporated krypton,(see page 6I) is presumably held on such sites. Exchangeable krypton is held less strongly on the remainder of the type 2 sites; the quantity will depend on the particular pumping procedures employed.

A further comparison between adsorbed and incorporated krypton is obtained by considering thermal release of krypton from the two states on allowing the temperature of a film to rise from 77°K to room temperature. The experimental

FIGURE 27 THERMAL RELEASE OF KRYPTON ADSORBED ON TO FILM 37 AT 77°K. (TWO ALIQUOTS, OF DIFFERENT ISOTOPIC COMPOSITION)



method for following the release of krypton was as described in section 4.9. The quantity of krypton released was measured both volumetrically and by monitoring the radioactivity in the McLeod gauge capillary.

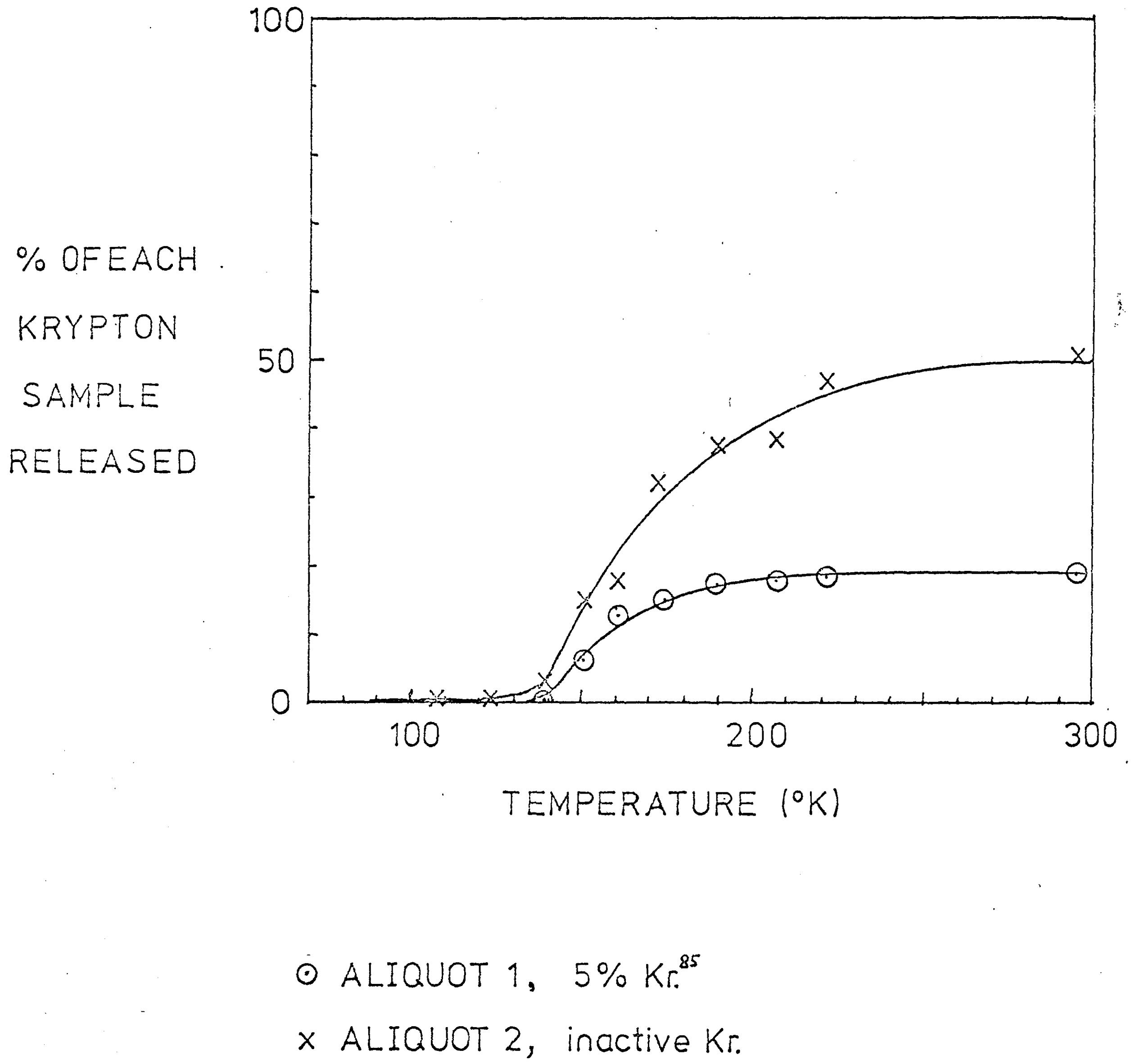
Two experiments were carried out, as follows. In the first, a film (No 37) was deposited in vacuum at 77°K. When deposition was complete, the film was allowed to adsorb a measured quantity of radioactive krypton (5% ^{85}Kr). Once gas phase pressure had fallen to a low value, the film was allowed to adsorb a measured quantity of inactive krypton. The quantity and specific activity of released krypton were now measured during a slow rise in temperature. It was found that the proportion of total ^{85}Kr which had been released up to a given temperature was equal to the proportion of total inactive krypton which had been released, that is, the specific activity of krypton remained constant throughout the release. (see figure 27)

The release of krypton during a rise in temperature may be brought about either by a reduction in the number of adsorption sites as a result of sintering the film, or by changes in the attractive forces which cause adsorption to occur. In either case, all of the krypton introduced on to a film after deposition is effected equally.

In the second experiment, the volume of the gas burette and its connecting tubing was adjusted by varying the mercury level until it was equal to the volume of the McLeod gauge and its dead space. A quantity of inactive krypton, measured with the McLeod gauge, was expanded in to the gas burette. A quantity of krypton containing 5% ^{85}Kr was then measured in the McLeod gauge and was permitted to expand in to the system used for the deposition of films under constant volume conditions. Deposition was commenced normally, but when most of the radioactive krypton had been incorporated in to the film, the taps were quickly turned so as to replace the McLeod gauge in the system by the gas burette. Deposition continued until the filament broke. The plot of pressure against time for the deposition of this film, No 39, appears in figure 46. Other details are noted in table 4.

The quantity and activity of released krypton during a slow rise in temperature were followed as in the previous experiment. Once correction had

FIGURE 28 THERMAL RELEASE OF TWO SAMPLES OF KRYPTON INCORPORATED IN TO FILM 39 DURING ITS DEPOSITION AT 77°K.



been made for the small quantity of radioactive krypton which had been isolated in the McLeod gauge, and that quantity left in the gas phase on exposure to inactive krypton, a plot of the proportion of radioactive and inactive krypton released up to a given temperature could again be made. (see figure 28)

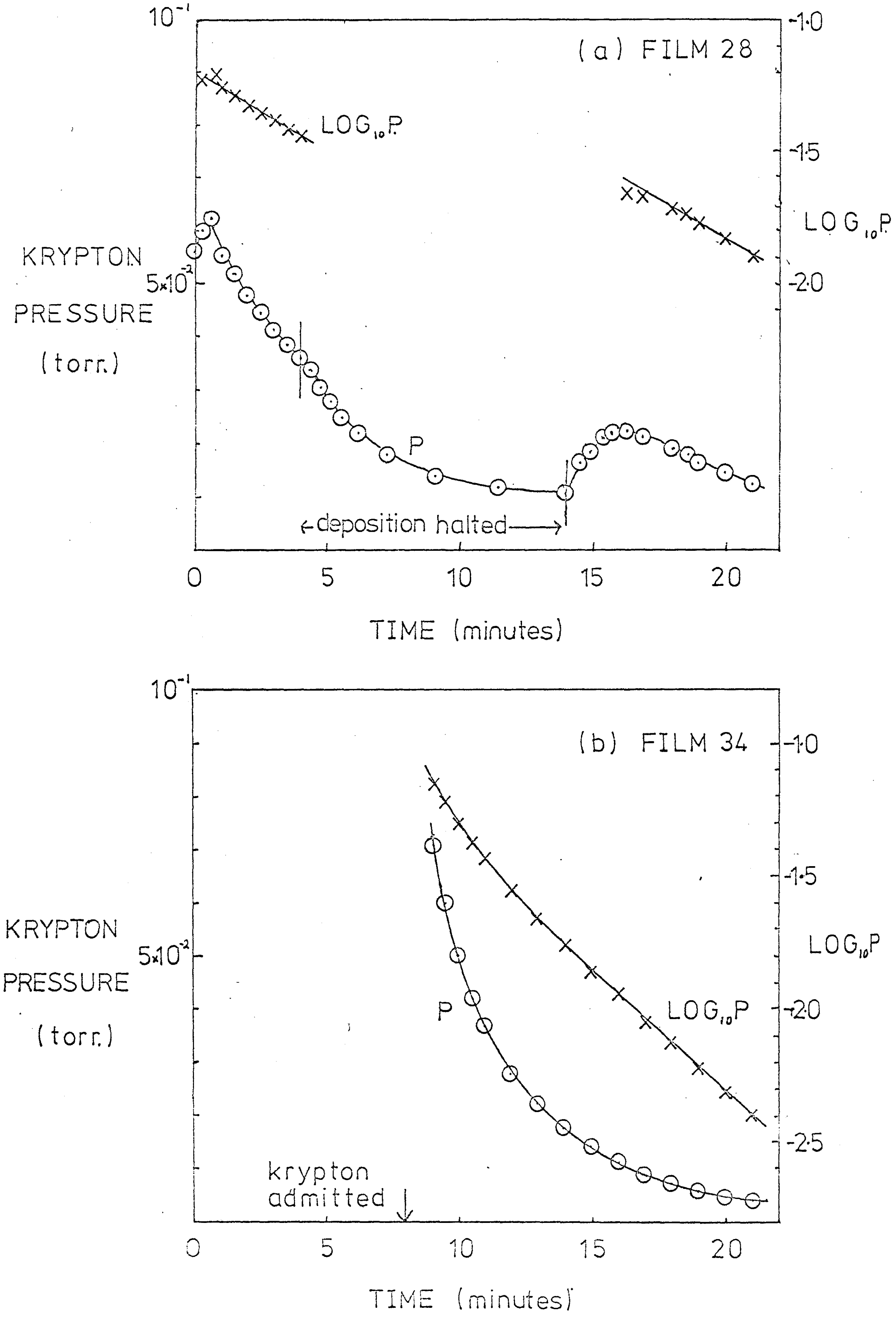
In this case, the proportion of inactive krypton which had been released was higher than the proportion of active krypton released. There are two possible explanations. First, it is possible that krypton incorporated during the later stages of deposition is more readily released. Secondly, it may be noted that the pressure at the time when inactive krypton had just been admitted to the partly grown film was higher than at any other time during deposition, and accordingly the nickel added at this time would have the highest concentration of incorporated krypton. The observations may therefore be explained in terms of a greater tendency to krypton release from those sections of the film where krypton is most concentrated. This latter explanation is believed to be more likely, for reasons stated in section 4.13.

It is thus clear that all of the krypton incorporated during deposition of a film is not equivalent in terms of thermal release.

The apparent equivalence of adsorbed krypton in this respect is surprising because some krypton is sufficiently strongly adsorbed as to be retained up to room temperature. This krypton is presumed to be trapped by the structural changes of the film which result from thermal sintering, as it is unlikely that it could remain stably adsorbed at room temperature. It is possible that as the temperature rises, the krypton atoms which were strongly adsorbed at 77°K become mobile before the onset of these structural changes, so that all the adsorbed krypton atoms have exchanged before a fraction is trapped. This effect would be expected to a lesser extent in the case of deposition-incorporated krypton; it has already been stated that some incorporated krypton is held at surface sites.

At the end of any deposition period, the krypton pressure was observed to fall more rapidly than during deposition. This fast pressure decrease has been associated with physical adsorption, and the saturation of the sites of types 2 and 3. It is not clear why this process should not occur during film

FIGURE 29 VARIATION OF KRYPTON PRESSURE DURING DEPOSITION OF FILMS 28&34 AT 77°K.



deposition. One possibility is that the temperature of a film during deposition is higher than when the filament is not radiating heat, so that the tendency to physical adsorption is less. Alternatively, the access of krypton to sites at interior surfaces within the film may be hindered in some way by the fact that the surface is in a state of flux during deposition of the film.

An experiment was designed to investigate this point. Film 28 was laid down under constant volume conditions. After four minutes of deposition, the current was switched off and the fast pressure decrease was followed. After ten minutes, the current was switched on again, at the same value as before. The pressure rose for two minutes and then began to fall with the same kinetics as in the first period of deposition. (see figure 29a) If the assumption is made that the conditions of deposition had been established within half a minute of recommencing current flow to the filament, then back-extrapolation of the pressure against time plot shows that at least 75% of the krypton taken up during the fast pressure decrease was released again to the gas phase. Certainly the rise in pressure was greatly in excess of that which would be produced as a result of a rise in temperature of the krypton remaining in the gas phase.

From the data presented in section 4.9 regarding the release of krypton adsorbed on vacuum-evaporated films, a temperature rise of at least 20° would be required to produce an effect of this magnitude. It has been estimated from bulk thermal conductivity data(50) that the temperature of a nickel film being deposited at the same current(6.5 A), using a similar nickel filament, and with hydrogen present during deposition, would be approximately 83°K. However, the assumption of the bulk thermal conductivity of nickel for a nickel film is probably not justified. Trapnell(48) has shown that a film may be extensively sintered by radiant heat from the filament. The present observations also indicate that the heat radiated from the filament has a considerable effect on the temperature of the film.

It is not possible to explain the observation that krypton was released from the film when deposition recommenced, on the basis of the surface flux hypothesis.

It was noted that not all of the krypton taken up during the fast pressure decrease was released to the gas phase at this time. The possibility that some krypton might be adsorbed during deposition on to preformed sites, that is, type 2 sites, was investigated by laying down a film initially in vacuum, and then admitting to the system a measured quantity of krypton, without interrupting deposition. It was observed that the rate of disappearance of krypton from the gas phase was higher during the first four minutes after exposure, than subsequently. (see figure 29b) The measured initial first-order rate constant for pressure decrease was 1.35×10^{-1} min^{-1}, which was higher than any other observed value. (see table 4) In the later stages of deposition of this film, No 34, the first-order rate constant was 9.3×10^{-2} min^{-1}. This observation shows that krypton may in fact enter preformed sites during the deposition process. The period of accelerated krypton uptake was about four minutes in length, compared to a time of disturbance which would be expected to be at most two minutes in length on commencing growth of a film in the presence of krypton. However, the weight of the film at the point when krypton was allowed in to the system was approximately 12 mg; relative to the number of vacant type 2 sites which must have been present in the film at this time, a very small amount of krypton was taken up at internal surface sites. Therefore this effect may normally be neglected in a kinetic study such as that presented in section 4.8.

CONCLUSIONS

It is generally accepted that in kryptonates, krypton is held at lattice points (point defects), at other defects such as dislocations, or at voids in the lattice. Metal films evaporated at low temperatures have a high concentration of such defects, which are annealed out on raising the temperature (109). It is reasonable to identify these as the adsorption sites.

Krypton which is held on type I sites in a film is suggested to be not removable by pumping, not exchangeable with krypton in the gas phase, and insensitive to a small rise in temperature. A rise in temperature which is large enough to reduce the number of defect sites, results in the release of some krypton. The implication that structural changes in the film, rather than adsorption characteristics, determine the release of krypton, is supported by the fact that nickel films which had incorporated hydrogen at 77°K released the bulk of their hydrogen in the same temperature range as that observed for krypton release in the present work(58). In this case the characteristics of adsorption would be very much different from those of krypton adsorption.

Krypton which is held at type 2 sites is suggested to be partly removable by pumping, partly exchangeable with the gas phase, and to become mobile on the surface after a small rise in temperature. Some of the krypton is trapped within the film as a consequence of the structural changes caused by raising the temperature. This may involve the sealing off of pores, or the conversion of an individual type 2 site to a type I site as a result of the rearrangement of nickel atoms.

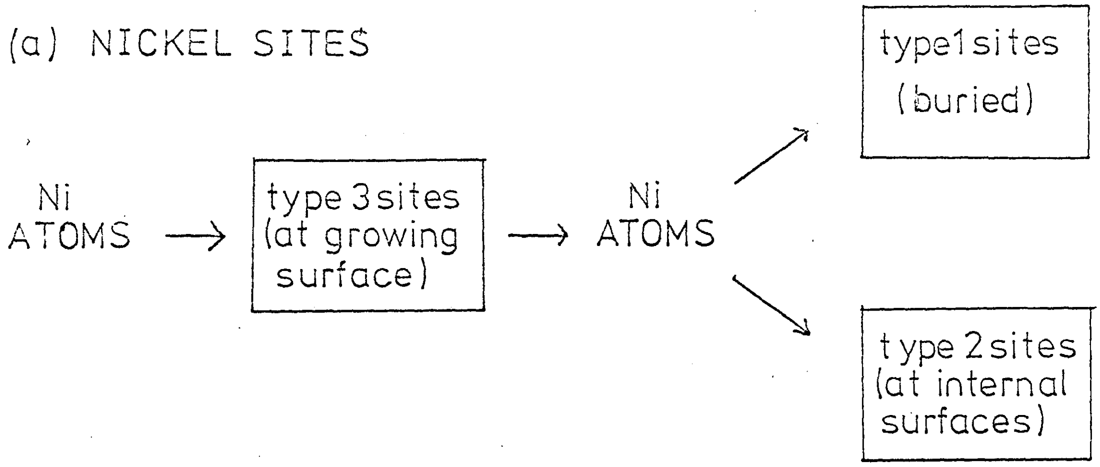
It is difficult to reach any firm conclusions regarding the nature of type 3 sites, or the properties of the krypton adsorbed there.

On the basis of the model which has been adopted, a type 3 site may be considered to be the precursor of sites of type I and 2. If a type 3 surface site is buried by nickel, it becomes a type I site. If nickel is added to the film at other points, the surface grows away from the type 3 site. Eventually it is so far removed from the growing surface that it may considered to be a type 2 site. Thus structurally a type 2 site is identical to a type 3 site, but the location in the film is different. The varying strengths of adsorption at type 2 sites have already been mentioned. In analogy, it was necessary to assume that the growing nickel surface, which contains only type 3 sites, was heterogeneous with respect to krypton adsorption.(section 4.8)

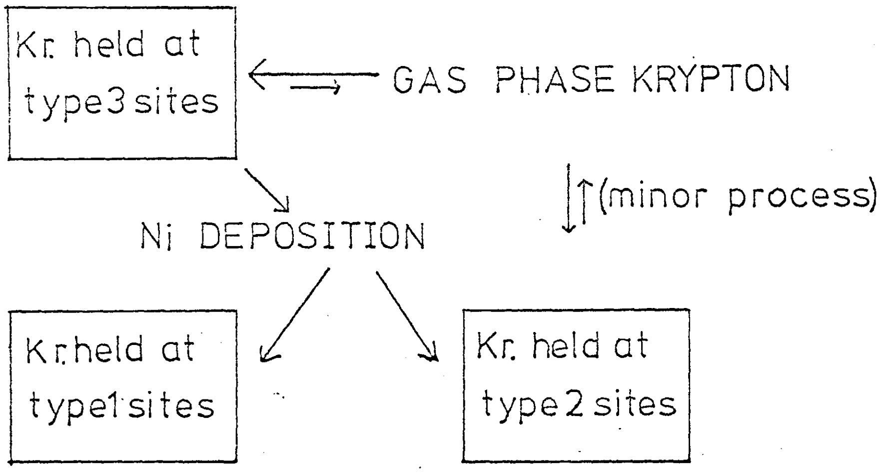
The amount of krypton adsorbed at any instant on type 3 sites will be small, because the growing surface of a film has an area which is small compared to the porous interior. In cases where the krypton pressure during deposition was low, then the formation of the initial surface pool of krypton might be expected to cause a measureable reduction in the pressure when deposition commenced. A tendency to particularly fast rates of incorporation in the first minute of deposition of films at constant pressure below 4×10^{-2} torr was noted. It was

FIGURE 30 PROCESSES OCCURRING DURING DEPOSITION OF NICKEL FILMS AT 77°K IN THE PRESENCE OF KRYPTON

(a) NICKEL SITES



(b) KRYPTON ATOMS



not possible to measure this effect because the system was disturbed in any case, by the onset of deposition.

Figure 30 shows in diagrammatic form the processes which are believed to occur on the surface of a nickel film during its deposition in the presence of krypton at 77°K.

The results obtained up to this point imply that the intermediate adsorbed state has some features of chemisorption. The adsorption is partly irreversible, and surface heterogeneity with respect to krypton adsorption is suggested.

Erlich (II0) has shown that heats of adsorption of krypton obtained experimentally are higher than the values calculated on the basis of a theoretical model which assumes a uniform surface. Preferential adsorption on certain faces of molybdenum and tungsten was observed.

It was decided that a comparison of the krypton results with an investigation of the possibility of the incorporation of argon in to a nickel film during its deposition, might be of value in the interpretation of the data, because the tendency for argon to enter a chemisorbed state would be expected to be much less.

4.II INCORPORATION OF ARGON BY NICKEL FILMS, AND COMPARISON WITH THE RESULTS OBTAINED FOR KRYPTON

A series of nickel films was grown in the presence of argon at 77°K, in order to compare the results with those obtained for krypton under similar conditions.

The experimental technique was identical to that described previously. Films were deposited both under conditions of constant volume and constant pressure.

The thermal conductivity gauge was recalibrated for the measurement of the pressure of argon. (see appendix B)

Argon was supplied in I-litre Pyrex bulbs by the British Oxygen Co, Ltd.

FIGURE 31 EXAMPLES OF THE VARIATION IN ARGON PRESSURE DURING DEPOSITION OF NICKEL FILMS AT 77°K

All vertical axes : ARGON PRESSURE (torr x 10^{-2})

All horizontal axes : TIME (minutes)

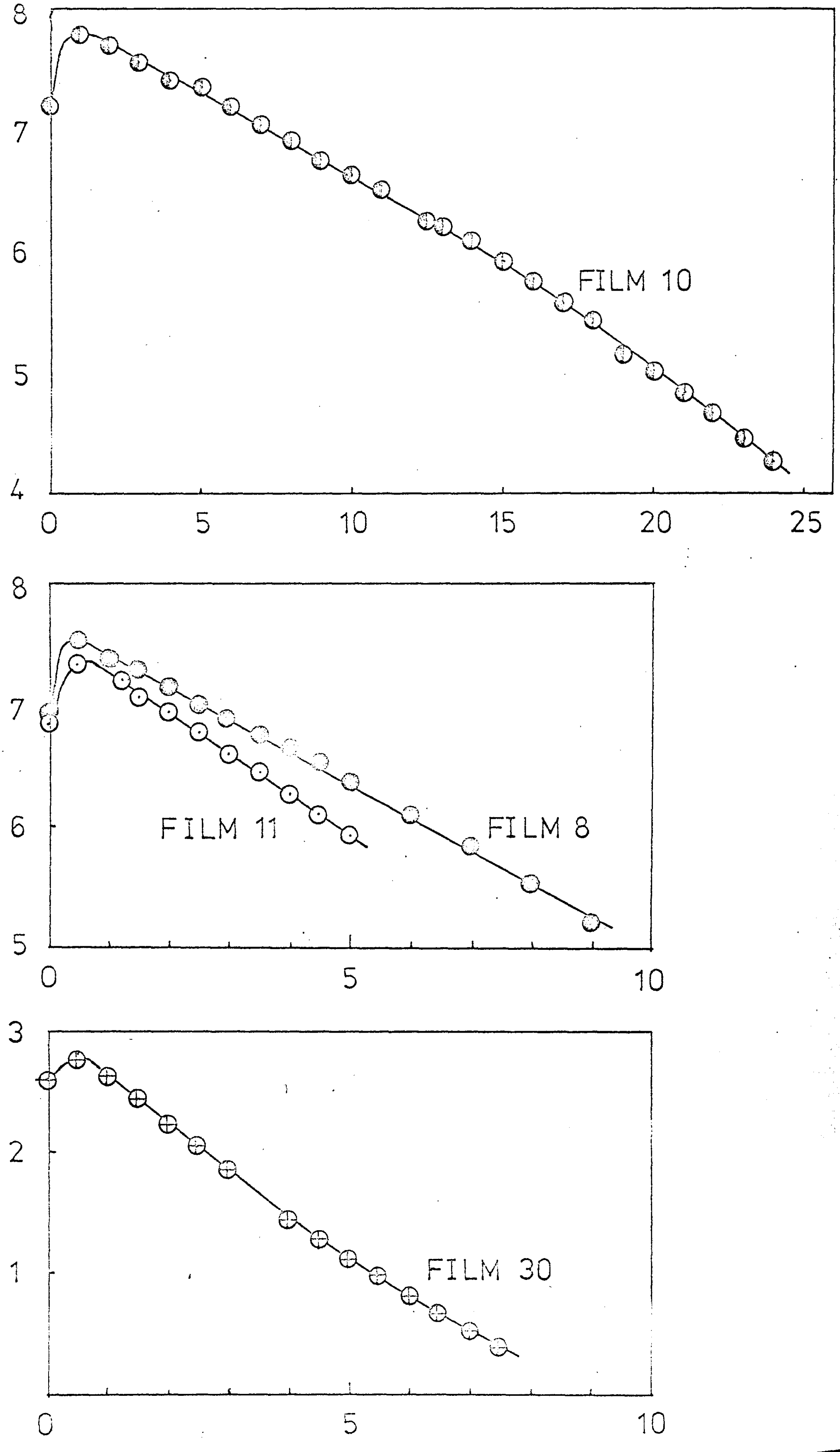
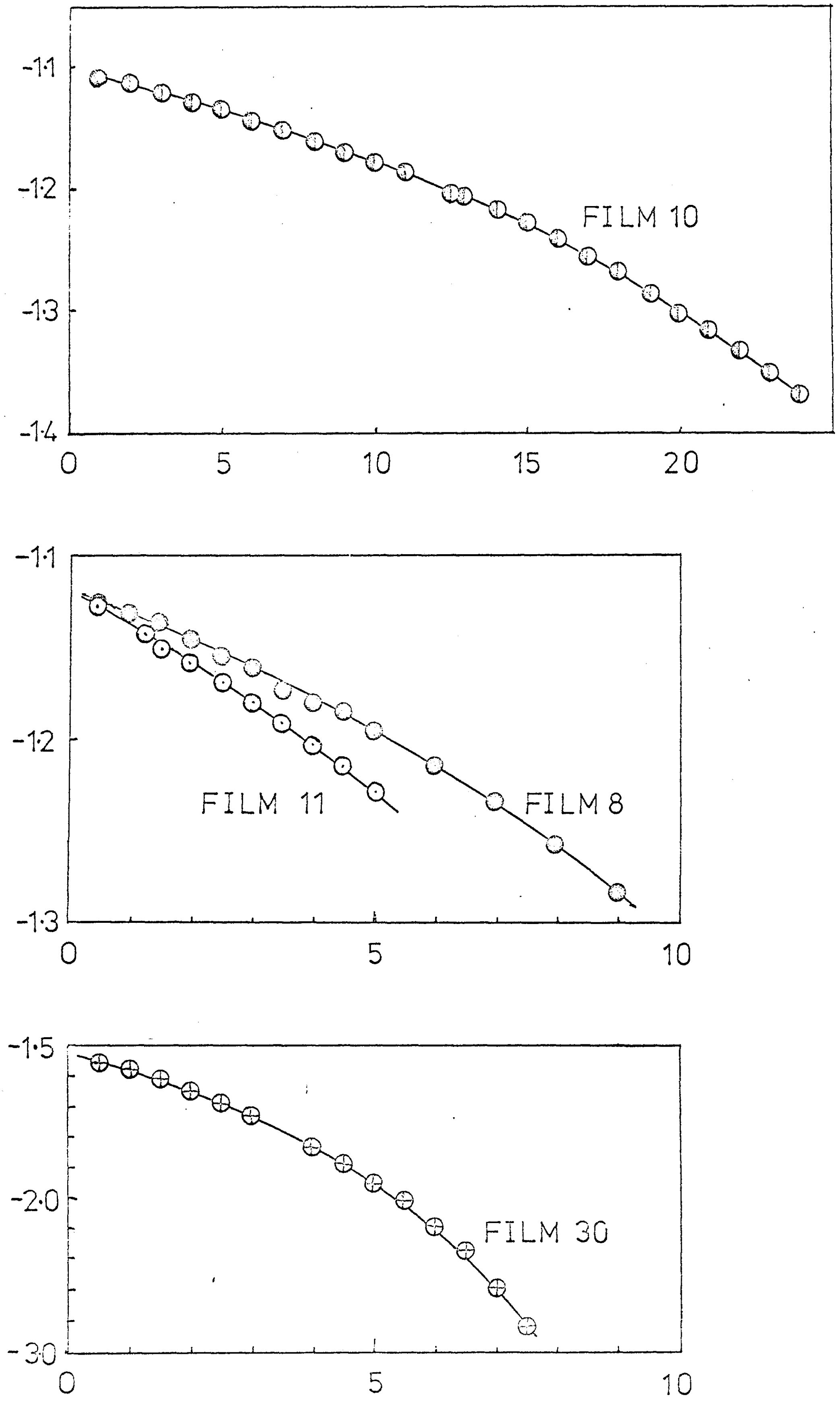


FIGURE 32 PLOTS OF LOG_{10}(ARGON PRESSURE) AGAINST TIME FOR THE FILMS OF FIGURE 31

All vertical axes : LOG_{10}(ARGON PRESSURE)

All horizontal axes : TIME (minutes)



RESULTS (I) FILMS DEPOSITED AT 77°K IN THE PRESENCE OF ARGON, UNDER CONSTANT VOLUME CONDITIONS

All films in this series were deposited at argon pressures initially in the range 2×10^{-2}torr to 9×10^{-2}torr. When the filament current had been adjusted to the chosen value, normally between 6.5 A and 7.5 A, the pressure was observed first to rise because of the raising of the temperature of argon in the film vessel by the hot filament, and then to show an apparently constant rate of fall with time while the filament current was maintained constant.

The various patterns of behaviour which were observed are shown in the pressure against time plots of figure 3I. In the later stages of deposition, some acceleration in the rate of pressure decrease was observed for particularly heavy films, such as film I0. One film, No 30, showed a slowing in the rate of pressure decrease below 10^{-2}torr, but a plot of logarithm(pressure) against time was not linear. The failure of similar plots for the other films of this series, (see figure 32), demonstrates that the linear pressure decrease with time is genuine, as distinct from an exponential decrease observed over an insufficiently long range for the curvature to be apparent.

The rate of argon pressure decrease was invariably much less than the observed initial rate of krypton pressure decrease for a film deposited at the same gas pressure and rate of nickel deposition.

When these films were allowed to attain room temperature, about one half of the argon incorporated at 77°K was released within a few minutes. (see figure 33) No further release could be detected over a period of I2 hours.

All films appeared black at room temperature, and were indistinguishable in appearance from those deposited in krypton.

Data on the films laid down in argon under constant volume conditions are summarised in table I4.

A plot for this series of films, of the rate of argon pressure decrease against the rate of nickel deposition, is shown in figure 34.

FIGURE 33 RELEASE OF ARGON CAUSED BY SUDDENLY RAISING THE TEMPERATURE OF FILM 8 FROM 77°K TO 292°K.

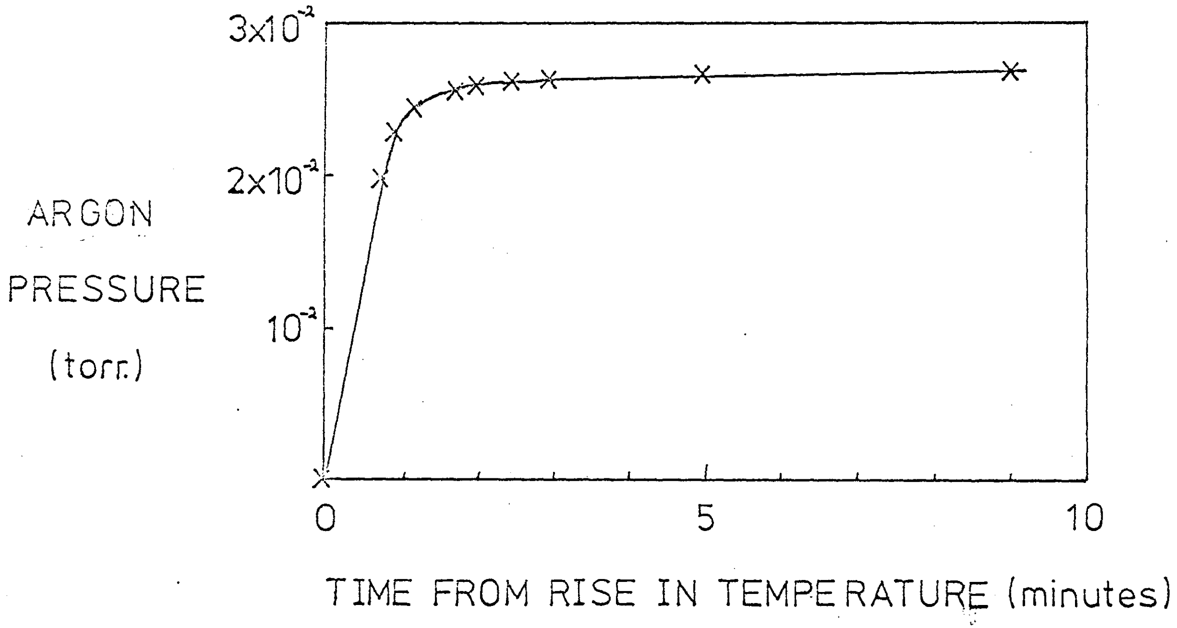


FIGURE 34 RATES OF ARGON INCORPORATION FOR NICKEL FILMS GROWN AT 77°K UNDER CONSTANT VOLUME CONDITIONS

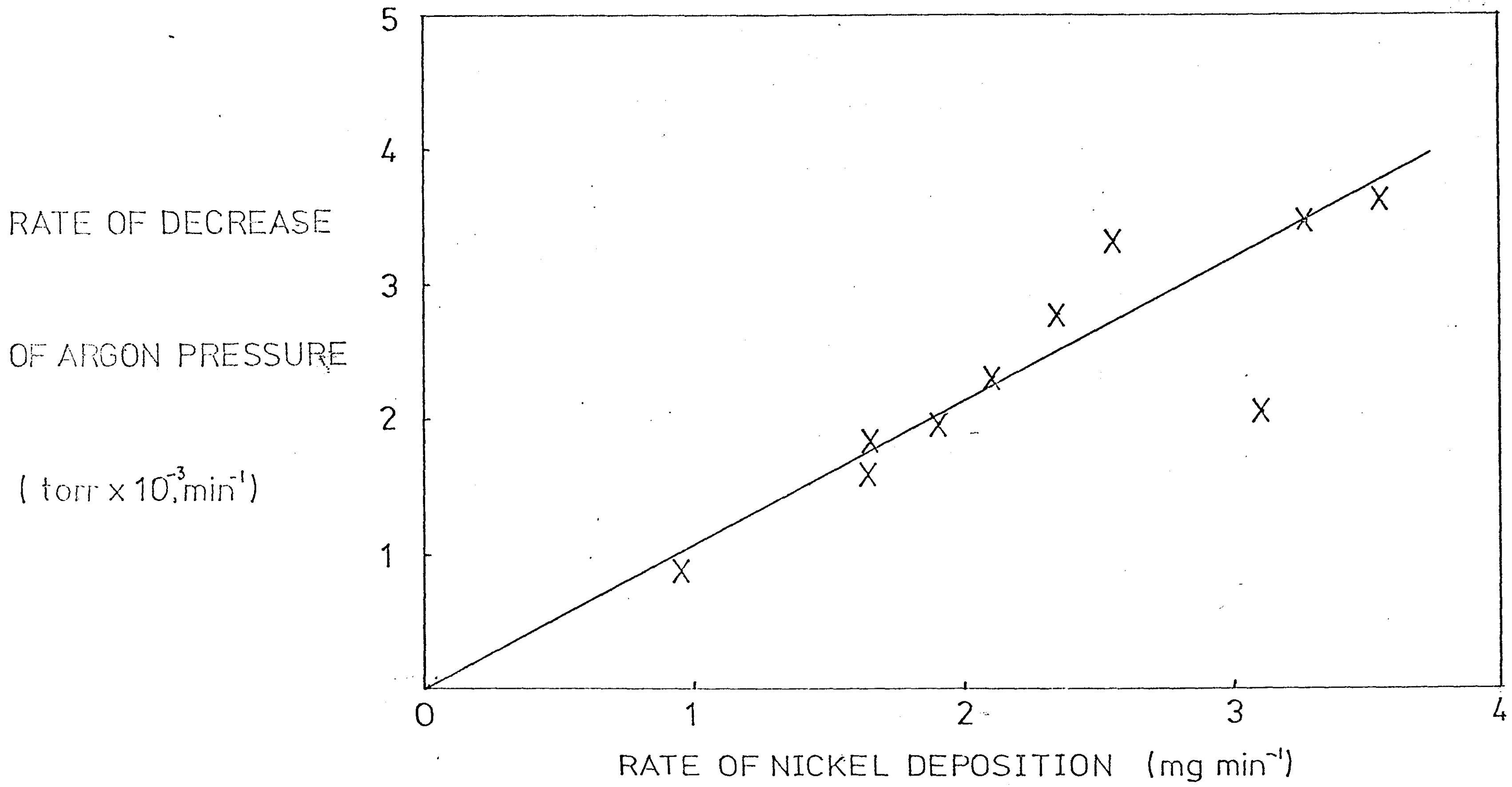


TABLE 14 INCORPORATION OF ARGON BY FILMS DEPOSITED AT 77°K UNDER CONSTANT VOLUME CONDITIONS

TABLE HEADINGS : d = rate of nickel deposition in mg min^{-1}
PR = the pressure range of argon during deposition of the film
k_o = the constant rate of decrease of the argon pressure (torr min^{-1})

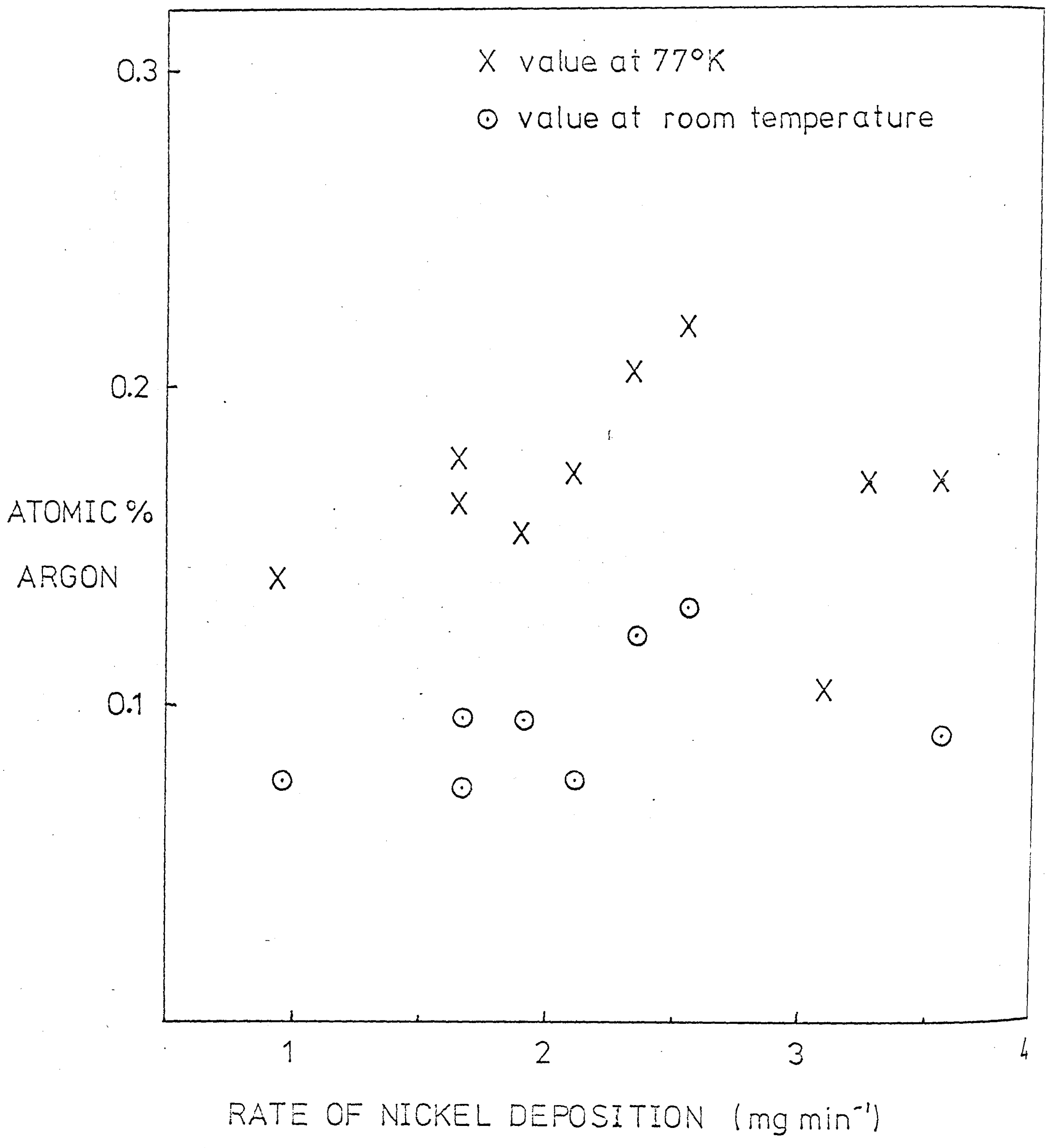
FILM No	WEIGHT(mg)	d	PR (torr)	k_o	LINEARITY
3	33.0	1.67	8.75×10^{-2}–5.05×10^{-2}	1.85×10^{-3}	LINEAR
7	42.9	1.91	7.85×10^{-2}–3.55×10^{-2}	1.96×10^{-3}	ACCELERATION IN LATER STAGES
8	21.6	2.36	7.75×10^{-2}–5.20×10^{-2}	2.78×10^{-3}	LINEAR
9	52.1	0.96	7.55×10^{-2}–2.85×10^{-2}	0.87×10^{-3}	ACCELERATION IN LATER STAGES
10	41.0	1.67	8.00×10^{-2}–4.10×10^{-2}	1.59×10^{-3}	ACCELERATION IN LATER STAGES
11	13.7	2.57	7.60×10^{-2}–5.82×10^{-2}	3.34×10^{-3}	LINEAR
13	18.9	2.12	8.15×10^{-2}–6.10×10^{-2}	2.30×10^{-3}	LINEAR
18	7.5	3.57	6.68×10^{-2}–5.92×10^{-2}	3.62×10^{-3}	LINEAR
30	24.8	3.28	2.96×10^{-1}–3.5×10^{-3}	3.46×10^{-3}	SLOWING IN LATER STAGES
36	26.0	3.12	2.52×10^{-1}–8.2×10^{-3}	2.05×10^{-3}	LINEAR

The plot of figure 34 indicates a linear relationship betwen the rates of argon pressure decrease and nickel deposition. Since all films were grown in systems of the same volume, under reproducible conditions of temperature, this suggests that a fairly constant atomic % of argon atoms was incorporated in to this series of films. The line drawn in figure 34 corresponds to the mean value of 0.171 atomic % of argon.

The scatter of the points may be accounted for by the uncertainty in the time of onset of nickel deposition, the unavoidable variation in film vessel size and temperature gradients, the unknown effect of variable filament geometry, and the adsorption of argon on the light bake-out film present in some cases.

Assuming as in the krypton work that the pressure in the system at any instant is proportional to the amount of argon in the gas phase, it is possible to calculate the quantity of argon incorporated in to the complete film at 77°K from the ratio of the theoretical initial pressure (obtained by back-

FIGURE 35 THE ATOMIC % OF ARGON HELD BY A SERIES OF NICKEL FILMS, (a) AT 77°K.
(b) AT ROOM TEMPERATURE.



extrapolation of the linear pressure plot to time zero) and the pressure at the instant when deposition ceased. The validity of this calculation is assessed in appendix C.

When nickel deposition ceased and the temperature in the film vessel dropped suddenly, the pressure of argon in the system did not become steady. On the contrary it was observed to fall much more rapidly than during the deposition of the film to give a low equilibrium pressure, as in the case of krypton. For example, the filament of film 7 broke when the pressure was 3.55×10^{-2} torr, and within ten minutes a new equilibrium pressure of 4×10^{-3} torr had been established.

Even after 75 Toepler pump strokes, with the film still at 77°K, appreciable quantities of argon could still be recovered from the film vessel and transferred to the McLeod gauge. Because of this effect, the quantity of argon incorporated in the film at 77°K could not be measured directly. As in the case of krypton, the value was obtained from consideration of the pressure at the end of the deposition period.

However, a limit to the quantity of recoverable argon was quickly reached when the film had been allowed to attain room temperature (approximately 295°K). Thus the quantity of argon retained by the film could be calculated by subtraction of the amount recovered from the measured initial quantity of argon.

In two cases, the initial quantity of argon was not measured before deposition commenced, because the films (No 30, No 36) were grown in order to determine whether the rate of decrease of argon pressure with time would be linear in a region of lower pressure. At the time of deposition, only this information was recorded. The quantity of argon incorporated in to these films was calculated from the pressure/quantity relationship presented in appendix C.

The quantity of argon held by this series of films (a) at 77°K, and (b) at 295°K, is given in table I5. A plot of the atomic % of argon in the films at these temperatures, against the rate of nickel deposition, is shown in figure 35.

FIGURE 36 VOLUME OF ARGON TAKEN UP BY NICKEL FILMS DEPOSITED UNDER CONSTANT PRESSURE CONDITIONS

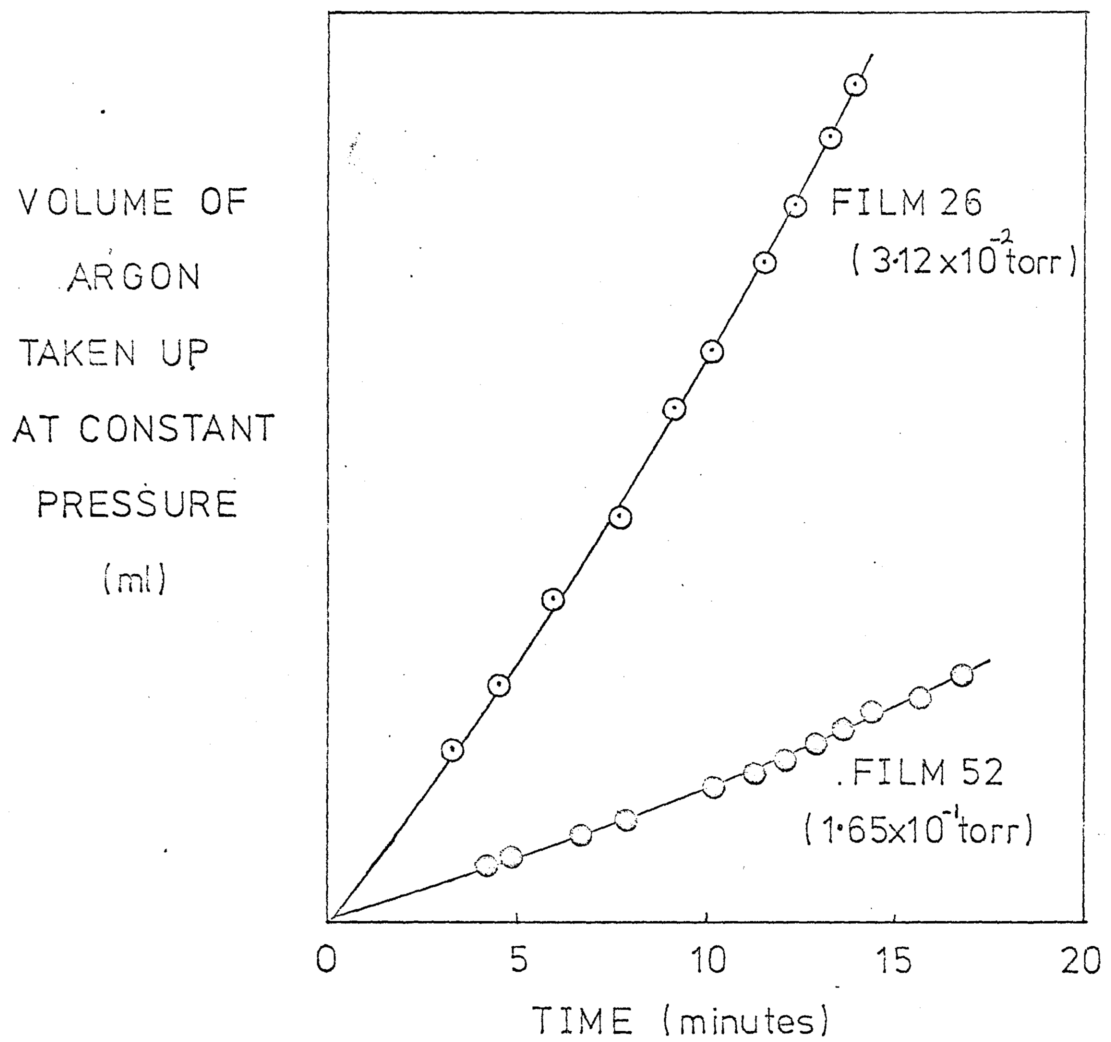


FIGURE 37 PLOT OF ATOMIC % ARGON INCORPORATED AT 77°K, AGAINST Ar:Ni COLLISION RATIO.

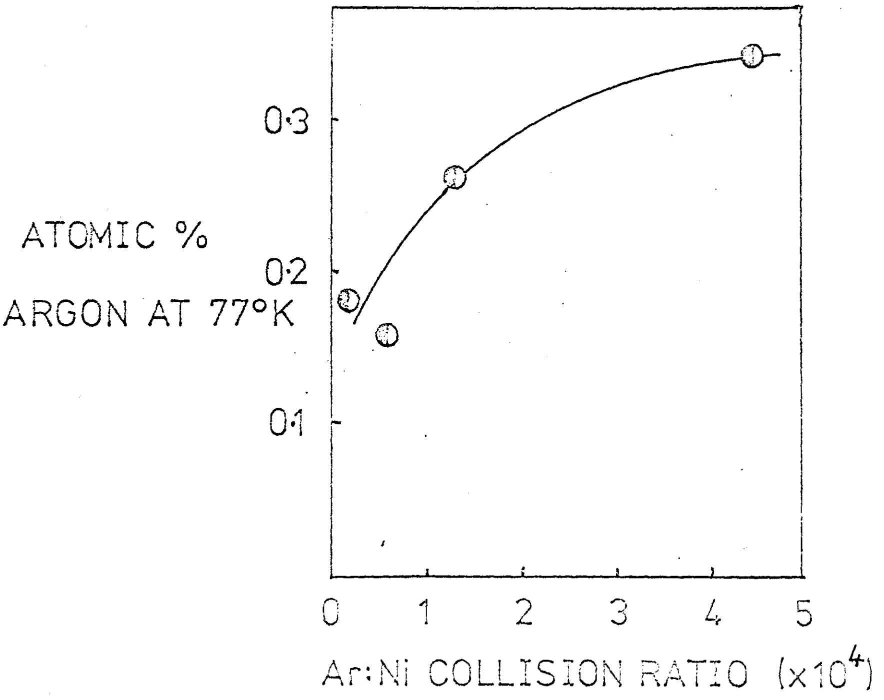


TABLE I5 THE QUANTITY OF ARGON HELD BY NICKEL FILMS DEPOSITED AT 77°K IN THE PRESENCE OF ARGON. (a) AT 77°K (b) AT 295°K

TABLE HEADINGS : INC = the quantity of argon incorporated in to the film during deposition (μmoles)
RET = the quantity of argon retained by the film at 295°K (μmoles)
%RET = the percentage of the argon which, having been incorporated at 77°K, was retained at 295°K
at% 77 = the atomic % of argon in the film at 77°K
at% 295 = the atomic % of argon in the film at 295°K

FILM No	INC	RET	%RET	at% 77	at% 295
3	I.00	0.542	54	0.I78	0.097
7	I.I3	0.700	62	0.I54	0.096
8	0.755	0.454	60	0.206	0.I23
9	I.24	0.678	55	0.I40	0.077
I0	I.I4	0.5I4	45	0.I64	0.074
II	0.5I4	0.309	60	0.220	0.I32
I3	0.558	0.246	44	0.I74	0.077
I8	0.2I7	0.I09	50	0.I7I	0.09I
30	0.7I3	-	-	0.I69	-
36	0.465	-	-	0.I05	-

RESULTS (2) FILMS DEPOSITED AT 77°K IN THE PRESENCE OF ARGON, UNDER CONSTANT PRESSURE CONDITIONS

Four films were deposited in the presence of argon at selected constant pressures in the range 3.12×10^{-2} torr to 1.95×10^{-1} torr. The rate of argon uptake invariably accelerated during the period of film deposition. Two examples of this behaviour are shown in figure 36.

Data obtained from these films are given in table I6. The values of the argon : nickel collision ratio which are quoted in this table, were calculated in the same way as the values quoted previously for the krypton : nickel collision ratio. (see appendix H) In the case of argon the theoretical treatment leads to the expression:

$$\text{Ar:Ni collision ratio} = \frac{P}{d} \times 1.6 \times 10^{5}$$

P is the constant pressure of argon in torr, and d is the nickel deposition rate in mg min^{-1}.

A plot showing the relationship between the Ar:Ni collision ratio and the atomic % of argon incorporated during deposition appears in figure 37.

TABLE I6 INCORPORATION OF ARGON BY FILMS DEPOSITED AT 77°K UNDER CONSTANT PRESSURE CONDITIONS (headings as for table I5)

FILM No	WEIGHT(mg)	d(mg min^{-1})	P(torr)	INC	at% 77	Ar:Ni COLLISION RATIO
24	27.3	0.83	3.I2xI0	0.734	0.I58	6.0xI0^{3}
26	33.7	2.25	3.I2xI0	I.04	0.I82	2.2xI0^{3}
52	36.0	2.02	I.65xI0	I.60	0.26I	I.3xI0^{4}
56	9.0	0.70	I.95xI0	0.525	0.34I	4.5xI0^{4}

COMPARISON WITH THE KRYPTON RESULTS

There are several points of similarity with the krypton series. Incorporation and retention of argon were both observed. The latter observation apparently contradicts the statement made by Beeck (9), that no argon is retained on warming nickel films from 77°K to room temperature. The pressure of argon during deposition in the work of Beeck was in the order of several torr, so that if a quantity of argon of the same magnitude as that observed in the present work had in fact been retained, this would have represented a very small proportion of the total argon in the system, and might not have been detected.

The quantity of argon incorporated at 77°K was approximately an order of magnitude below the quantity of krypton incorporated under similar conditions. However, the quantity of argon retained at room temperature is smaller than the corresponding quantity of krypton, by a factor of only two or three.

The fact that the rate of argon incorporation was observed to increase during deposition for films deposited under constant pressure conditions, and in the later stages of deposition of several films grown under constant volume conditions, is probably related to the thinning of the metal filament caused by the evaporation of nickel. The maintainance of a constant current therefore leads to an increase in the filament temperature, and hence to an increase in the rate of evaporation. The values of the deposition rate which are quoted above for such cases therefore represent mean values.

This effect was also noted for films deposited at high (over $3\text{x}10^{-1}$torr) pressures of krypton. It was only at such, high, krypton pressures that film weights were found which approached those recorded for argon.

In contrast to the krypton results, the atomic % of argon incorporated in to a series of films deposited under constant volume conditions appeared to be substantially independent of the Ar:Ni collision ratio. The value of the Ar:Ni collision ratio for the films of table 14 ranged from $1.3\text{x}10^{4}$ at the commencement of deposition of film 9, to 170 at the end of the deposition period of film 30. Despite this variation, the atomic % of argon incorporated in to these films appeared to be constant. (see figure 34)

The atomic % of argon measured for films 24 and 26, which were deposited under constant pressure conditions, was similar to that for the series of films deposited under constant volume conditions. However the value found for films 52 and 56, which were deposited at higher values of the Ar:Ni collision ratio, was larger in both cases.

These results may be explained if there are present on the surface of the film a limited number of adsorption sites where the sticking probability is very high, and a number of sites where the sticking probability is much lower. Therefore all of the first type of sites would be occupied at the point when they are buried by nickel atoms added to the film, so long as a certain minimum amount of argon is available. Where more argon is available, some of the other sites may be occupied at the time of burial, leading to an enhanced amount of incorporation for high values of the Ar:Ni collision ratio.

No evidence for this effect was found in the case of krypton. This is surprising, because any site capable of adsorbing argon would be expected to adsorb krypton more readily.

It is not clear from the results presented above, whether the atomic % of argon retained by a series of films at 295°K is a constant, or whether it is related to the atomic % of argon incorporated at 77°K. The problem in interpreting the data arises from the relatively small spread of values at

77°K.

In summary, it has been established that argon may also be incorporated in to a nickel film during its deposition; it is possible that the surface of a growing nickel film is more heterogeneous with respect to the adsorption of argon than to the adsorption of krypton. The quantity of argon incorporated is much lower than the corresponding quantity of krypton.

The difference in the quantity of incorporation must be related to the tendecies for the two gases to enter the intermediate adsorbed state. Evidence has been presented to show that this state has features of chemisorption.

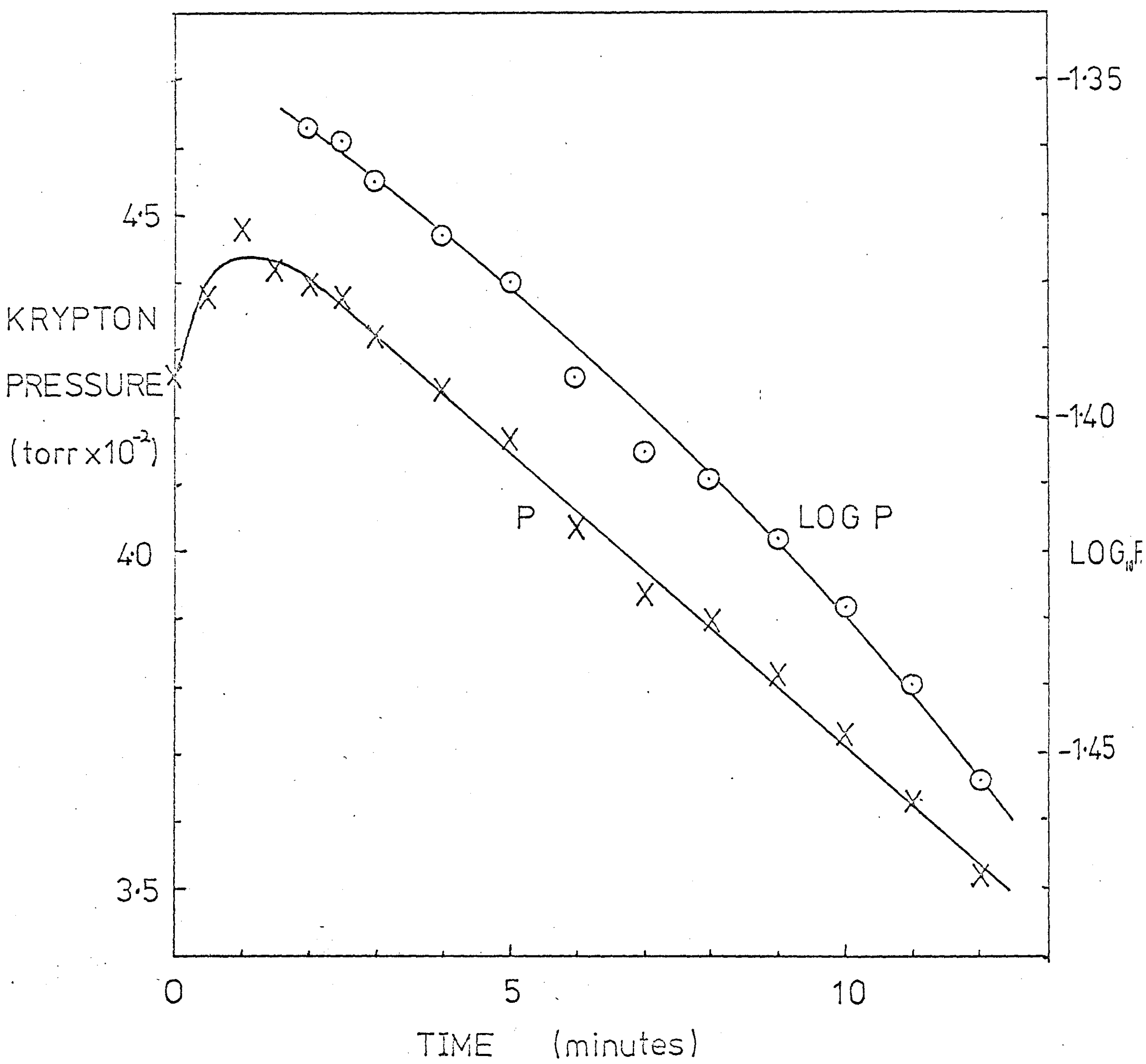
If the nature of the adsorbed state approximates to physical adsorption, then at any given temperature the tendency for krypton to enter it will be greater than the tendency for argon to enter it. The physical adsorption of a gas is akin to its liquefaction; multiple layers of molecules are formed at the surface. The tendency to physical adsorption of a gas is therefore related to the tendency to liquefaction, that is, the vapour pressure. No evidence was found for incorporation of krypton in to nickel films deposited at 195°K or 273°K; this may be due to negligible physical adsorption at these temperatures. Alternatively, the number of adsorption sites may be smaller at higher temperatures, owing to the greater mobility of nickel on the surface, which leads to a film with a lower concentration of defects.

It was therefore decided to attempt to introduce krypton in to nickel films during deposition at a temperature selected so that the vapour pressure of krypton approximated to that of argon at 77°K, to find what changes might be brought about in the incorporation of krypton.

Clausius-Clapeyron plots of vapour pressure against reciprocal absolute temperature were constructed for argon, krypton, and xenon, from literature values of the vapour pressure (III). It was found that the vapour pressure of argon at 77°K is equal to that of krypton at 108°K, and that of xenon at 178°K.

A means of maintaining the substrate temperature at approximately 108°K was now sought; it was found that the melting point of isopentane is 113°K.

FIGURE 38 INCORPORATION OF KRYPTON DURING DEPOSITION OF NICKEL FILM 15 AT 113°K



In view of the approximations involved in relating vapour pressure to physical adsorption, this temperature was held to be close enough to I08°K.

A quantity of isopentane was solidified in a Dewar flask by pouring liquid nitrogen in to a copper tube clamped within the flask. This Dewar flask, containing isopentane slurry, was used to maintain the temperature of the walls of the film vessel at II3°K during the deposition of two nickel films under constant volume conditions. It should be noted that the actual temperature of the film during the deposition process will be higher than II3°K by an unknown amount, as it was previously higher than 77°K.

In both cases incorporation and retention of krypton were observed, but the quantities were very much less than for krypton at 77°K, and also lower than for argon at 77°K. The rate of fall of krypton pressure with time was apparently constant, and a plot of logarithm(pressure) against time was not linear.(see figure 38) Data obtained for these films is presented in table I7.

TABLE I7 INCORPORATION OF KRYPTON DURING DEPOSITION OF NICKEL FILMS AT II3°K

FILM No	WEIGHT(mg)	d(mg min^{-1})	k$_o$(torr min^{-1})	at% II3	at% 295
I5	36.0	2.86	8.69xI0^{-4}	0.063	0.037
I6	20.6	3.69	I2.8xI0^{-4}	0,065	0.03I

The atomic % of krypton incorporated in to these films at II3°K is approximately one third of the value found for argon at 77°K. Considering the uncertainties involved in assuming that physical adsorption at any temperature may be related to the vapour pressure of the adsorbate, and that the theoretical temperature of such equivalence would be I08°K, the agreement with the argon results is striking. Certainly the kinetics and quantity of krypton incorporation at II3°K resemble those of argon at 77°K more closely than those of krypton at 77°K.

However, the actual temperature of the surface of the film during deposition will be higher than II3°K by some amount, and presumably in the range of temperature which corresponds to the fastest release of krypton from a film grown at 77°K. Therefore, the results could be explained by the generation of less adsorption sites at this temperature.

One film, No 113, was deposited under constant pressure conditions, with xenon as the inert gas, and with the film vessel maintained at 185°K by means of a Dewar flask containing solid CO_2, acetone, and some acetone ice. It has previously been stated that the vapour pressure of xenon at 178°K is equal to that of argon at 77°K.

Xenon was supplied in a 1-litre Pyrex bulb by the British Oxygen Co, Ltd. It was found that the thermal conductivity gauge was insensitive for the measurement of xenon pressure, owing to the low thermal conductivity of xenon. The pressure of xenon which could be maintained in the system was low, because a large quantity of xenon was physically adsorbed in the thermal conductivity gauge, which was maintained at 77°K.

The film was deposited at 2.84 mg min , to a weight of 14.2 mg, in xenon at 3.2×10^{-3} torr. Over the five minute period of deposition, approximately 6×10^{-8} moles of xenon was taken up , corresponding to 0.03 atomic % of xenon in the film at 185°K. This value is not inconsistent with the picture of a physically adsorbed intermediate if the approximations involved are taken in to account, and if it is again recognised that less adsorption sites will be generated at the higher temperature.

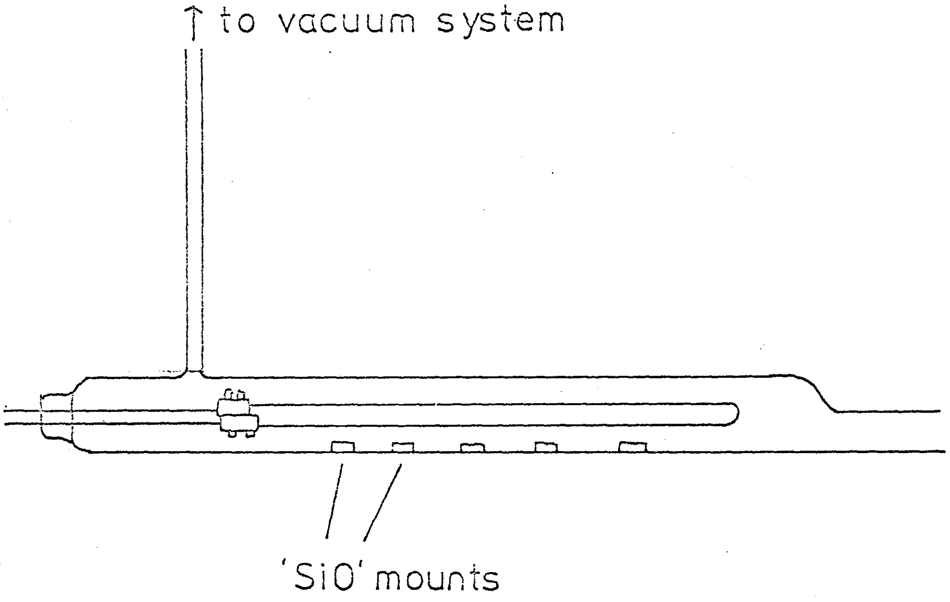
It is not possible to separate the effects of physical adsorption and substrate temperature, but the results approximate to those which would be expected if a physically adsorbed intermediate was involved in all cases.

If a chemisorbed intermediate had been involved, then it is conceivable that the effect of a small rise in substrate temperature in reducing the number of adsorption sites, might be partly offset by the larger proportion of krypton atoms which had sufficient energy to enter the activated adsorption state, because the experiments were not conducted under conditions of adsorption equilibrium.

Assuming that argon adsorption approximates to classical physical adsorption, then clearly the results imply that the krypton adsorption state is similar in nature. However the validity of this assumption is open to question. (see section 2.5)

In conclusion, it is evident that the adsorbed state of krypton on the

FIGURE 39 MODIFIED FILM VESSEL USED FOR THE ELECTRON MICROSCOPY WORK



growing surface of a nickel film at 77°K has several features of chemisorption: the adsorption is partly irreversible, and the surface is heterogeneous with respect to adsorption. A comparison with observations made at higher temperatures is consistent with a physically adsorbed state. It is also suggested that the adsorption of argon shows features of chemisorption.

It was noted that approximately 50% of the incorporated gas was lost when films deposited at 77°K in argon or at II3°K in krypton were allowed to attain room temperature. A speculative explanation is as follows. In section 4.I0, it was concluded that sites of types I and 2 were generated in approximately equal numbers during deposition of a nickel film at 77°K. Gas held at type 2 sites was taken to be trapped by structural changes in the film resulting from a rise in temperature. The higher substrate temperature for the deposition of films in krypton at II3°K, and the lesser tendency to adsorption for argon, may lead to the desorption of all the gas held at type 2 sites before the onset of such structural changes. The initial occupancy of the type I sites is so low as to be little effected by the increase in temperature, and thus roughly half of the incorporated gas is lost in each case, if the site distribution is similar to that for deposition in krypton at 77°K.

4.I2 INVESTIGATION OF NICKEL FILMS BY ELECTRON MICROSCOPY

In view of the observation that nickel films deposited in the presence of inert gas at 77°K appeared black and not silver in colour, it is of interest to examine specimens of these films by electron microscopy and electron diffraction in order to compare their microstructure and lattice spacings to those observed for a nickel film deposited at 273°K.

Films were deposited in a modified film vessel.(see figure 39) This was held horizontal and was sealed on to the system with the narrow section of tubing open.

Platinum/iridium mounts, 2.3 mm in diameter, were covered with a thin film of silicon monoxide by the vacuum evaporation of a powder mixture of silicon and silica.

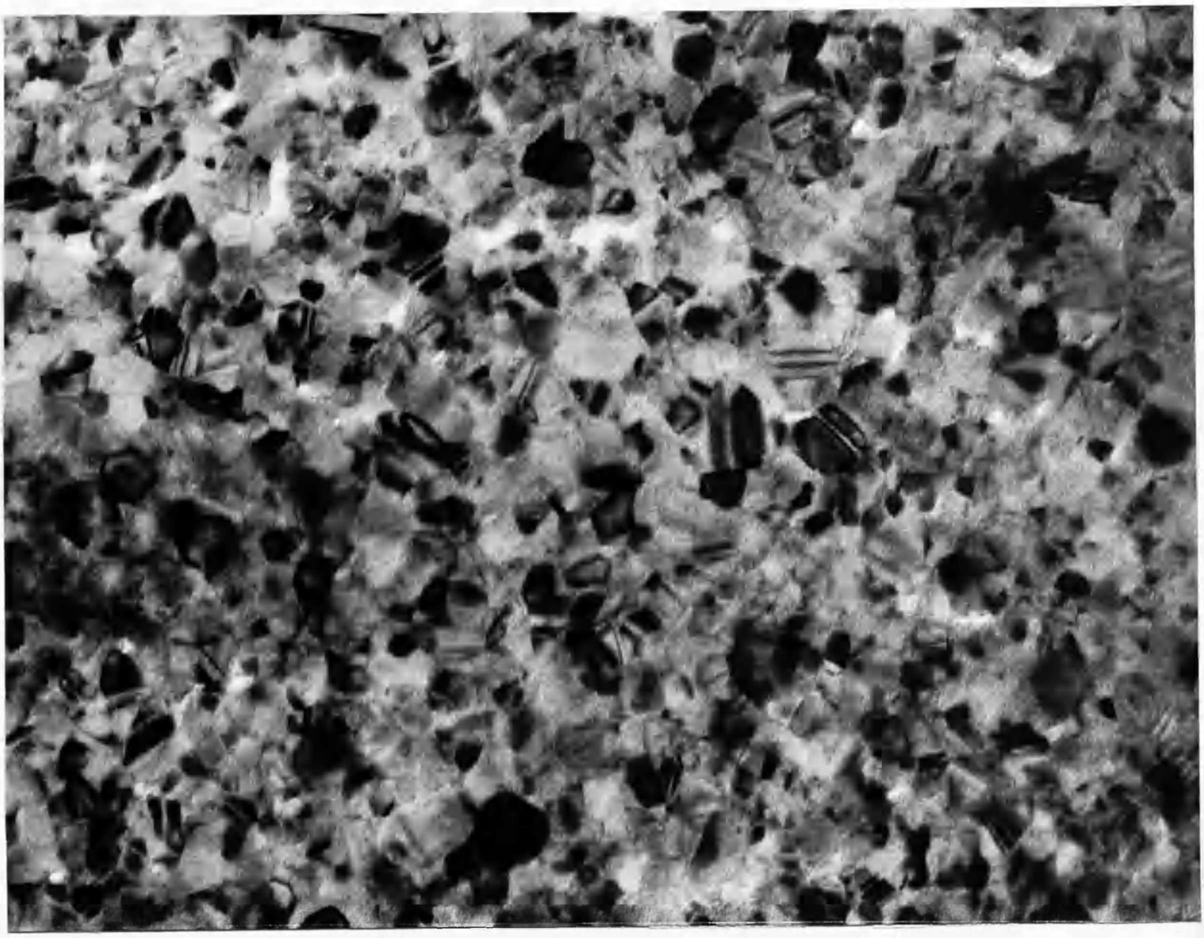


PLATE I A NICKEL FILM DEPOSITED IN 0.2 torr OF KRYPTON AT 77°K (x80,000)

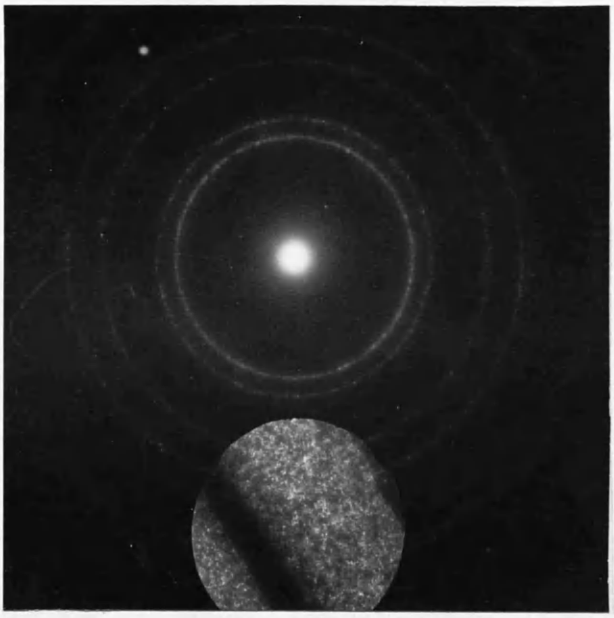


PLATE 2 THE ELECTRON DIFFRACTION PATTERN OBTAINED FROM A NICKEL FILM DEPOSITED IN 0.2 torr OF KRYPTON AT 77°K

The required number of mounts was introduced in to the film vessel through the open tubing, which was then sealed off. The deposition technique was as described previously.

After deposition of the film, the film vessel was allowed to attain room temperature. The section of narrow tubing was cut open and the mounts were extracted.

Electron micrographs and diffraction patterns were obtained using a Siemens Elmiskop I electron microscope, operated at 80,000 V.

Details of the film weights and deposition conditions are given in table I8.

TABLE I8 FILMS STUDIED BY ELECTRON MICROSCOPY

FILM No	WEIGHT(mg)	d(mg min^{-1})	GAS PRESENT	SUBSTRATE TEMPERATURE
5I	5.0	0.38	2.09xI0^{-1}torr of krypton	77°K
53	9.5	I.58	vacuum	77°K
54	3.8	0.55	vacuum	273°K
56	9.0	0.70	I.95xI0^{-1}torr of argon	77°K

An unnumbered film was grown in order to establish the technique, in I.99xI0^{-1}torr of krypton at 77°K. The weight of this film was not taken. Micrographs in this case were identical to those obtained for film 5I.

Variations between the micrographs for films 5I, 53, and 56, were no more significant than variations over different portions of the same film. They differed from those for film 54, in that there appeared to be a higher concentration of dislocations and stacking faults, as evidenced by the lines visible on individual crystallites. This appears to be an effect mainly of the substrate temperature during deposition.

Plate I. shows a micrograph of film 5I, and plate 3 shows a virtually identical area of film 53. The micrographs obtained from film 54 were of low quality, owing to warping and tearing of the SiO support film. Therefore, for purposes of comparison with the low-temperature films, plate 4 shows a micrograph of a nickel film evaporated at 273°K, obtained from another source.

The diffraction patterns for all films showed ring spacings corresponding to the lattice spacings of pure nickel. An example appears in plate 2. Spacing

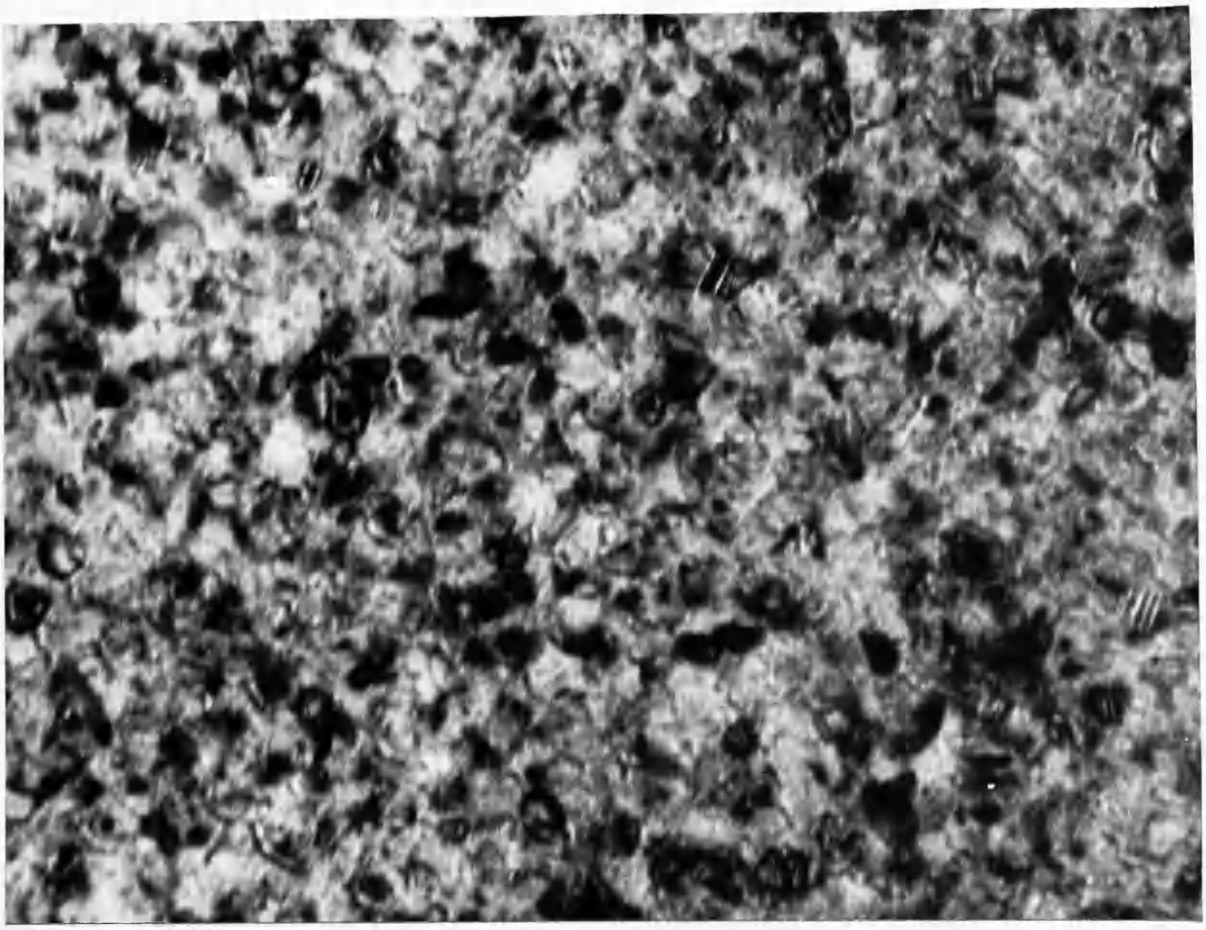
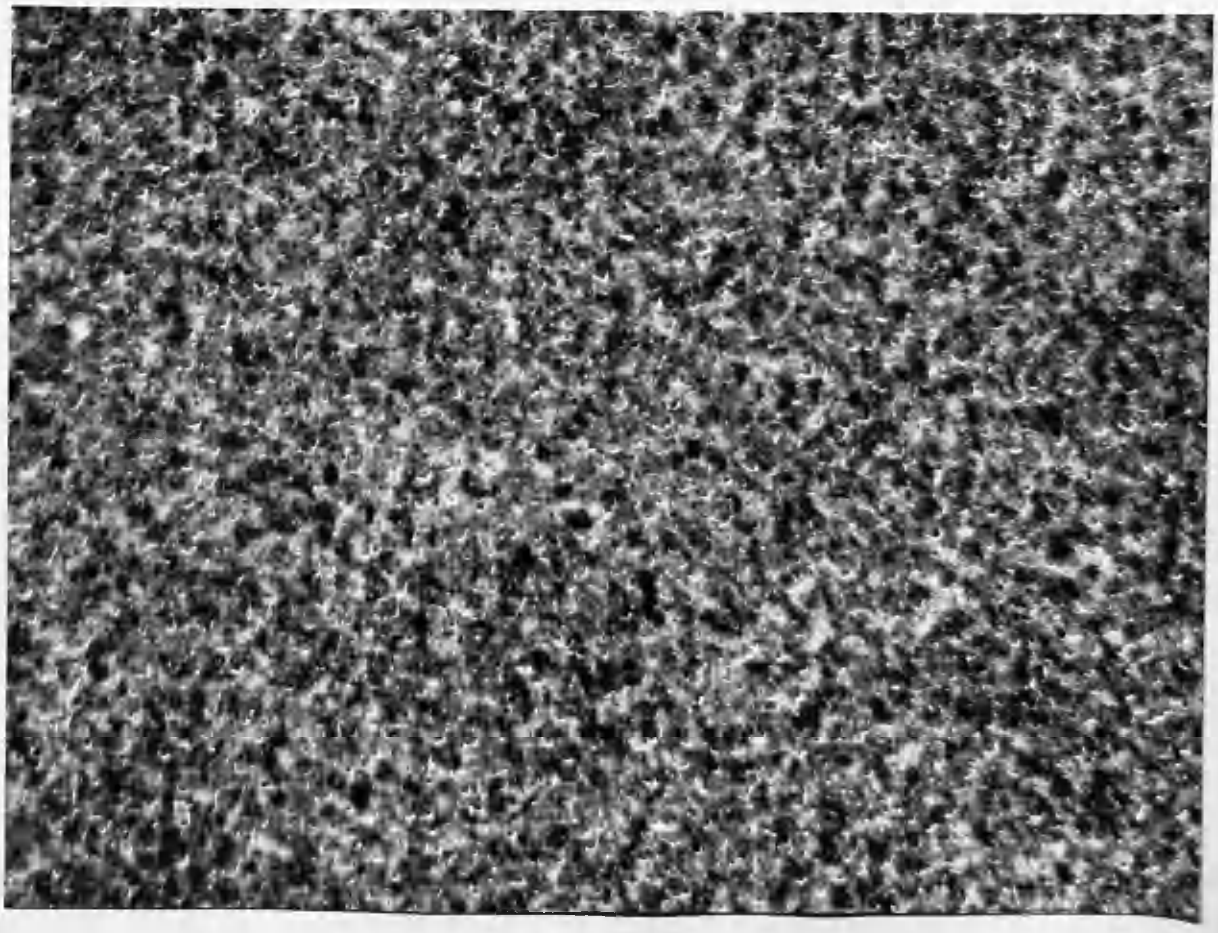


PLATE 3 (above) A NICKEL FILM DEPOSITED IN VACUUM AT 77°K (x80,000)

PLATE 4 (below) A NICKEL FILM DEPOSITED AT 273°K (x80,000)



data were calculated by comparison with a thallium chloride standard.

TABLE I9 ELECTRON DIFFRACTION DATA FOR PLATE 2

RING DIAMETER (mm)	DERIVED LATTICE SPACING (A°)	NICKEL LATTICE SPACING (A°)
20.0	2.03	2.034
23.I	I.76	I.762
32.8	I.24	I.246
38.3	I.06	I.062
39.8	I.02	I.0I7
50.5	0.80	0.808

A faint ring of diameter 28 mm, corresponding to lattice spacing I.45 A°, may derive from the presence of traces of nickel oxide, which has a lattice spacing of I.476 A°. This probably resulted from oxidation between the time of deposition and the examination of the films.

In no case was evidence found for orientation of the films. It may be concluded that the crystal structure of a nickel film deposited at 77°K in the presence of a small pressure of inert gas does not differ significantly from that of a film produced in vacuum at 273°K. The nickel lattice is not measurably strained by the presence of some incorporated gas.

The black appearance of the films does not seem to arise because of variation in crystallite size, and must be at least partly related to the presence of inert gas during deposition. Film 53, which was evaporated in vacuum at 77°K, was blackish-silver in appearance, and obviously different from the black appearance of films evaporated in the presence of gas at 77°K and the silver appearance of films evaporated at 273°K.

It is not believed that the time lapse between producing these films and their examination by electron microscopy could have resulted in significant changes in their microstructure, except for a small amount of oxidation.

Films stored in air remained black and unchanged in appearance for at least six months.

FIGURE 40 QUANTITY OF KRYPTON HELD AT 77°K BY A SERIES OF NICKEL FILMS

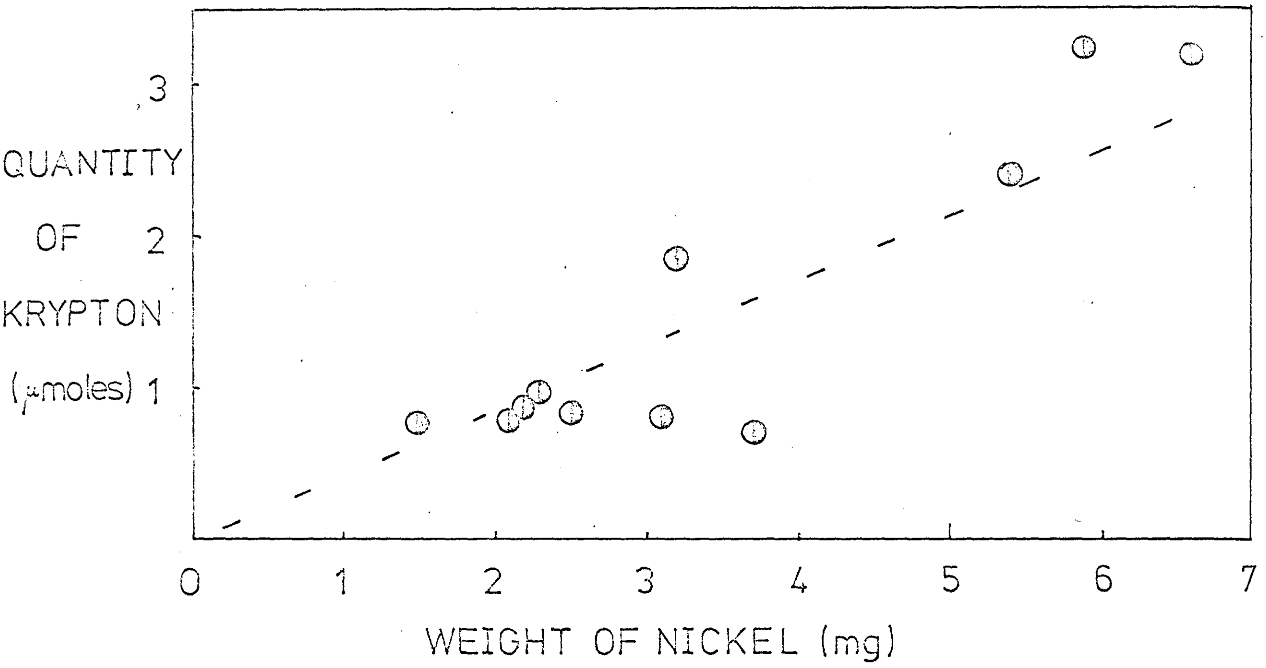
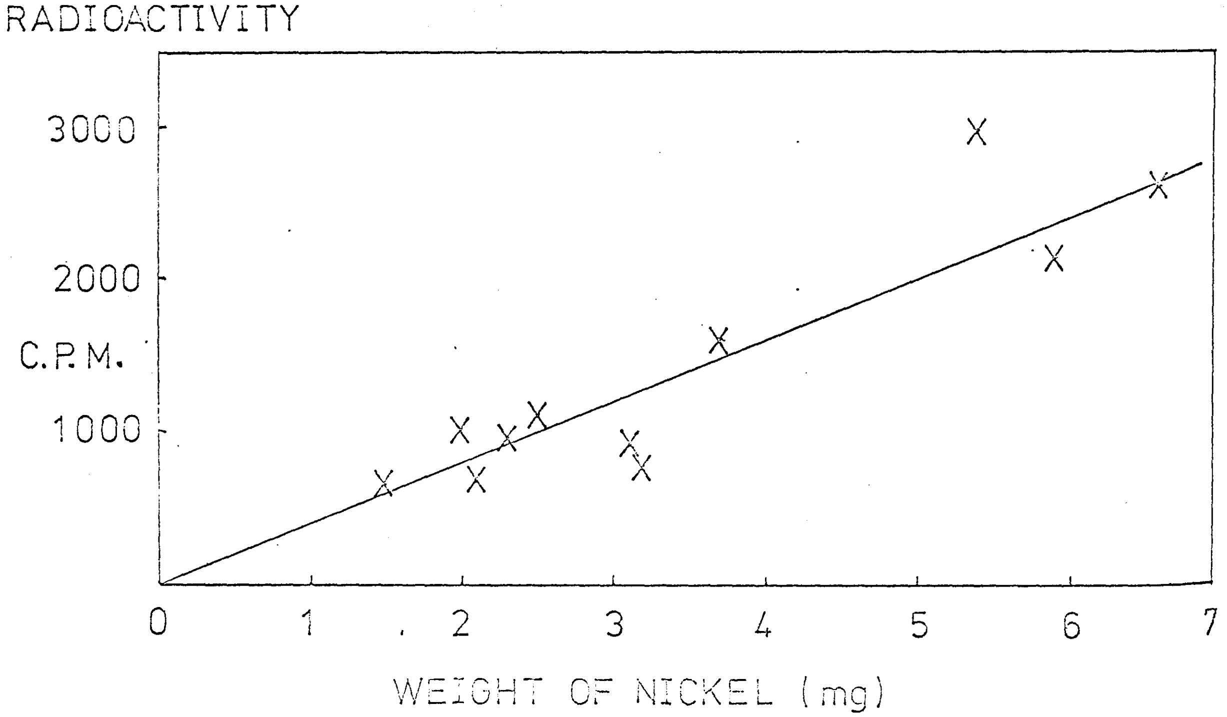


FIGURE 41 RADIOACTIVITY OF THE SERIES OF FILMS ABOVE, MEASURED BY 'TOUCHING COUNT' AT ROOM TEMPERATURE



4.13 EVIDENCE FOR THE HOMOGENEOUS DISTRIBUTION OF KRYPTON THROUGHOUT NICKEL FILMS DEPOSITED IN KRYPTON AT 77°K

It was stated in section 4.9 that for a series of nickel films deposited under constant pressure conditions, which showed a variation in atomic % of krypton at 77°K from 0.33% to 2.97%, the atomic % of krypton retained on warming the films to room temperature was 0.25% ± 0.06%. In view of the considerable possibility of experimental error, it was suggested that the actual variance might be rather less.

One of the aims of this investigation was to produce nickel films in which krypton was held homogeneously throughout the bulk of the film. The quantity measurements quoted above suggest that all films retain a similar quantity of krypton at room temperature, regardless of the deposition conditions. If this is true then it is also reasonable to infer that separate portions of the same film will retain similar quantities of krypton, that is, the krypton is in fact distributed homogeneously.

The quantity measurements were prone to error because it was necessary to evaluate a small difference between two relatively large quantities of gas. Another method of looking at this problem is to deposit films in krypton of a particular specific activity, and to permit them to attain room temperature while pumping off gas phase krypton. The net count rate recorded by a Geiger-Muller counter in contact with the film vessel will then be proportional to the quantity of krypton retained by the film, and may be compared to the film weight.

Data was obtained in this way for eleven films, including six of the fourteen on which the quantity measurements were based. All were laid down in 5% ^{85}Kr. A plot of the quantity of krypton incorporated in to these films at 77°K against film weight is shown in figure 40, and a plot of the measured film radioactivity at 295°K against film weight is shown in figure 41.

Table 20 contains the relevant data.

TABLE 20 RADIOACTIVITY MEASUREMENTS OF NICKEL FILMS

FILM No	at% 77	WEIGHT(mg)	RADIOACTIVITY AT 295°K(cpm)	SPECIFIC ACTIVITY AT 295°K(cpm mg^{-1})
57	1.11	3.7	1605	434
60	2.19	2.1	680	324
61	3.30	3.2	780	244
63	3.13	5.9	2144	364
64	2.87	6.6	2629	398
65	2.57	5.4	2998	555
70	2.25	2.2	1020	464
76	1.51	3.1	923	298
86	2.89	1.5	666	444
87	1.97	2.5	1112	445
88	2.42	2.3	960	417
			MEAN	399 ± 83

The principal error in the measurement of radioactivity by the 'touching count' method was likely to be variation in the counting geometry.

It is apparent from figures 40 and 41 that the scatter of the points is less for the plot of the radioactivity measurements at room temperature. The lines drawn on each plot represent mean values for the plots. That there is an apparent relationship between the quantity of krypton incorporated at 77°K and the weight of a film, arises from the relatively small spread of atomic % of krypton at 77°K for the films considered. The standard deviation of 83 on the mean value of specific activity, 399, represents 22% of the mean value. If a relation actually existed between the quantity of krypton incorporated at 77°K and the weight of nickel in a film, then the standard deviation from the mean value would be 28%, which is appreciably larger.

Thus the conclusions made from measurements of the quantity of krypton retained at room temperature by nickel films are supported by measurements of the radioactivity of a series of films.

It is of interest to note that the activity values for two films deposited

FIGURE 42

MODIFIED FILM VESSEL
FOR STUDIES OF
FILM DISSOLUTION

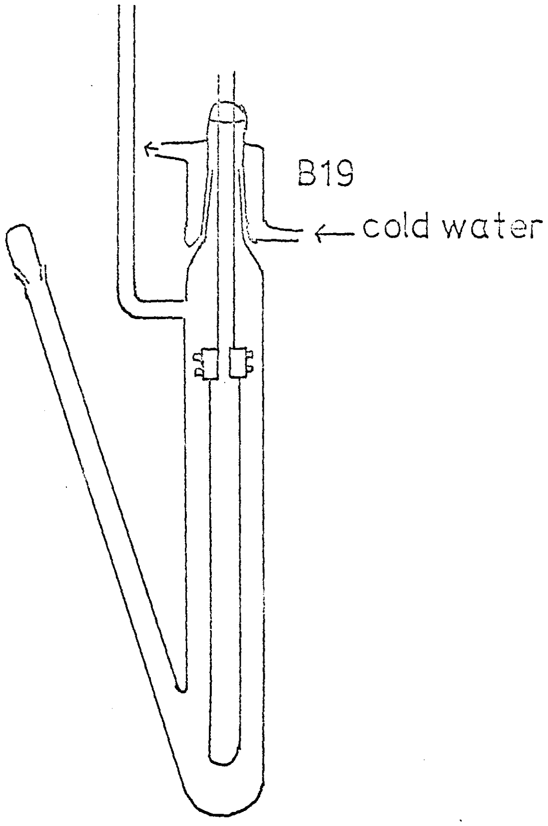
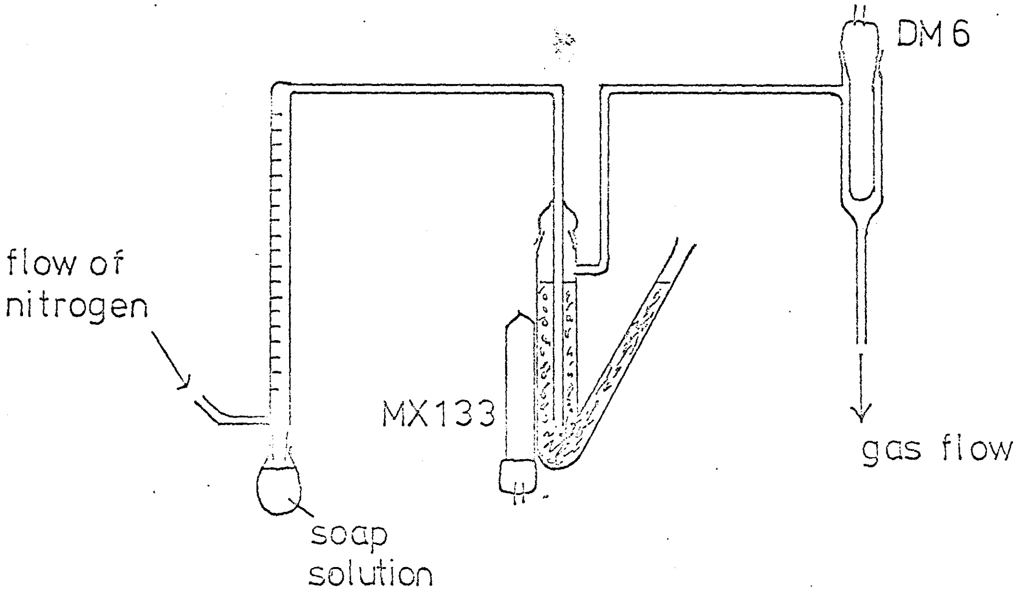


FIGURE 43 FLOW SYSTEM FOR STUDIES OF FILM DISSOLUTION



under constant volume conditions, where the pressure dropped to a low value during the period of deposition, are less than the mean value of specific activity obtained above. These values are given in table 2I.

TABLE 2I RADIOACTIVITY MEASUREMENTS FOR TWO FILMS WHERE THE AVAILABILITY OF KRYPTON DECREASED DUING DEPOSITION

KRYPTON DECREASED DUING DEPOSITION

FILM No	WEIGHT(mg)	RADIOACTIVITY(cpm)	SPECIFIC ACTIVITY(cpm mg^{-1})
2	34.4	I3,057	379
4	40.4	5,864	I46

The initial pressure for film 2 was $9\mathrm{xIO}^{-1}$torr, and that for film 4 was $3.6\mathrm{xIO}^{-2}$torr. It is reasonable to suppose that the lower specific activity registered for film 4 arose because a larger proportion of the film was laid down under a very low krypton pressure.

A more direct method of investigating the distribution of krypton within films was now sought. It was decided to dissolve films slowly in acid, while monitoring the quantiy of krypton released, the film activity, and the concentration of dissolved nickel.

APPARATUS AND EXPERIMENTAL TECHNIQUE FOR DISSOLUTION EXPERIMENTS

It was necessary to redesign the film vessel for these experiments. Vessels were made with a BI9 cone at the top. Filaments were attached to tungsten leads in a BI9 socket unit which was jacketed so that water could be passed through it to cool this section during the high-temperature degassing procedure. The two sections were assembled as shown in figure 42, the joint being greased with Apiezon L grease, and the whole unit was glassblown on to the vacuum system in the usual manner via the narrow side-arm tubing. The wide side-arm was closed with a greased stopper, and the degassing procedure was carried out as usual.

The volume of the vessel was not significantly different from those used previously. The kinetics of deposition were not altered by the use of this type of vessel.

On completing treatment of the film, the two parts of the vessel were separated, and the film vessel was joined in to the simple flow system shown in figure 43.

Nitrogen was passed through this system at a rate of 50 ml min^{-1}. The rate of flow was measured by the time taken for a soap bubble to pass between two marks on the calibrated tubing.

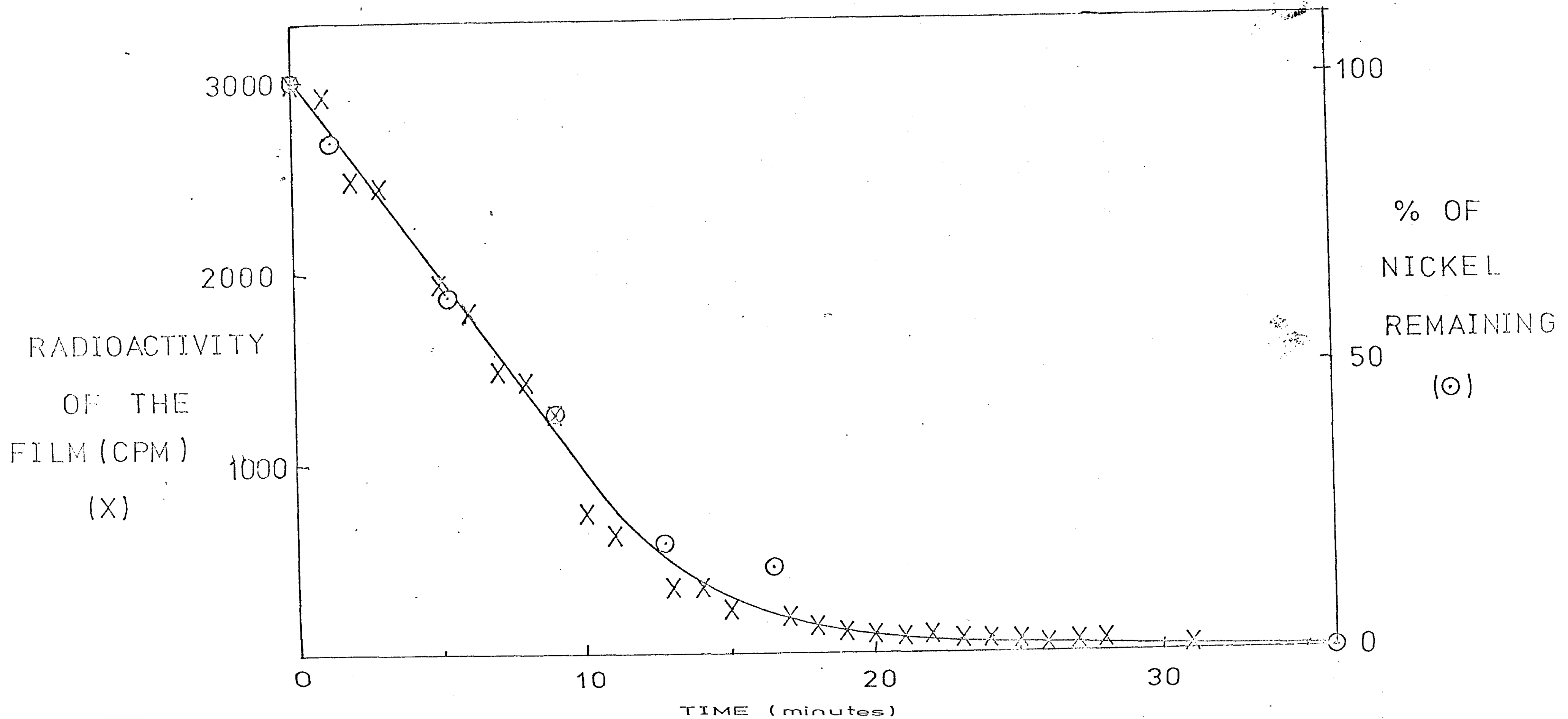
It was found that filling the film vessel with distilled water by way of the side arm produced no effect on the background activity registered by the flow counter, but produced a slight decrease in the activity registered by the parallel counter. This was probably caused by the shielding effect of the water.

However when the distilled water was removed, to be replaced quickly by 0.125 M or 0.25 M nitric acid, the radioactivity of the film began to drop and after a few minutes a corresponding rise in the activity of the gas stream was noted. In two cases, I ml samples of the acid solution were taken during dissolution by inserting a pippette through the side-arm in to the bottom of the film vessel. I ml portions of acid were immediately added in order to maintain the volume of solution. The continuous flow of gas bubbles through the solution had the effect of stirring it and maintaining its homogeneity.

The portions of acid solution which had been withdrawn from the film vessel were neutralised with ammonia. Bromine water and a saturated solution of dimethylglyoxime were added, in order to form the red-brown Ni^{3+}-dimethylglyoxime complex. The samples were made up to 20 ml, and the optical density was measured after allowing 10 minutes for the colour to develop. An Eel colorimeter with a blue filter was used.

No calibration plot was made for the nickel estimation. The final value of optical density, corresponding to the dissolution of all the nickel in the film, was calculated from the measured optical density at this stage, which was corrected to compensate for the removal of a small quantity of nickel in each of the earlier samples. It was assumed that, at the concentrations used, the optical density of the solution was proportional to the concentration of nickel (50). Thus the % nickel dissolved could be calculated from the optical density if allowance was made for the removal of earlier samples.

FIGURE 44 DECREASE OF RADIOACTIVITY DURING DISSOLUTION OF FILM 65 BY 0·25M NITRIC ACID



In cases where solution samples were not required, a film vessel without the wide side arm was used. Here the measured quantity of acid was poured in to the film vessel immediately before the B19 cone was pushed home in to the B19 socket of the flow system.

RESULTS OF THE DISSOLUTION EXPERIMENTS

Films 60 and 65 were dissolved in 0.25 M nitric acid. Samples of solution were withdrawn and analysed colorimetrically. The results of the analyses were consistent.(table 22)

TABLE 22 COLORIMETRIC ANALYSES FOR NICKEL

FILM No	WEIGHT(mg)	CORRECTED O.D. (COMPLETE DISSOLUTION)	$\frac{\text{OPTICAL DENSITY}}{\text{WEIGHT}}$
60	2.1	0.069	0.033
65	5.4	0.169	0.031

The small discrepancy may arise from weighing errors, or from the fact that the optical density values are themselves low and error-prone.

The results for film 65 throughout the period of dissolution are given in table 23.

TABLE 23 DISSOLUTION OF FILM 65 BY 0.25 M NITRIC ACID

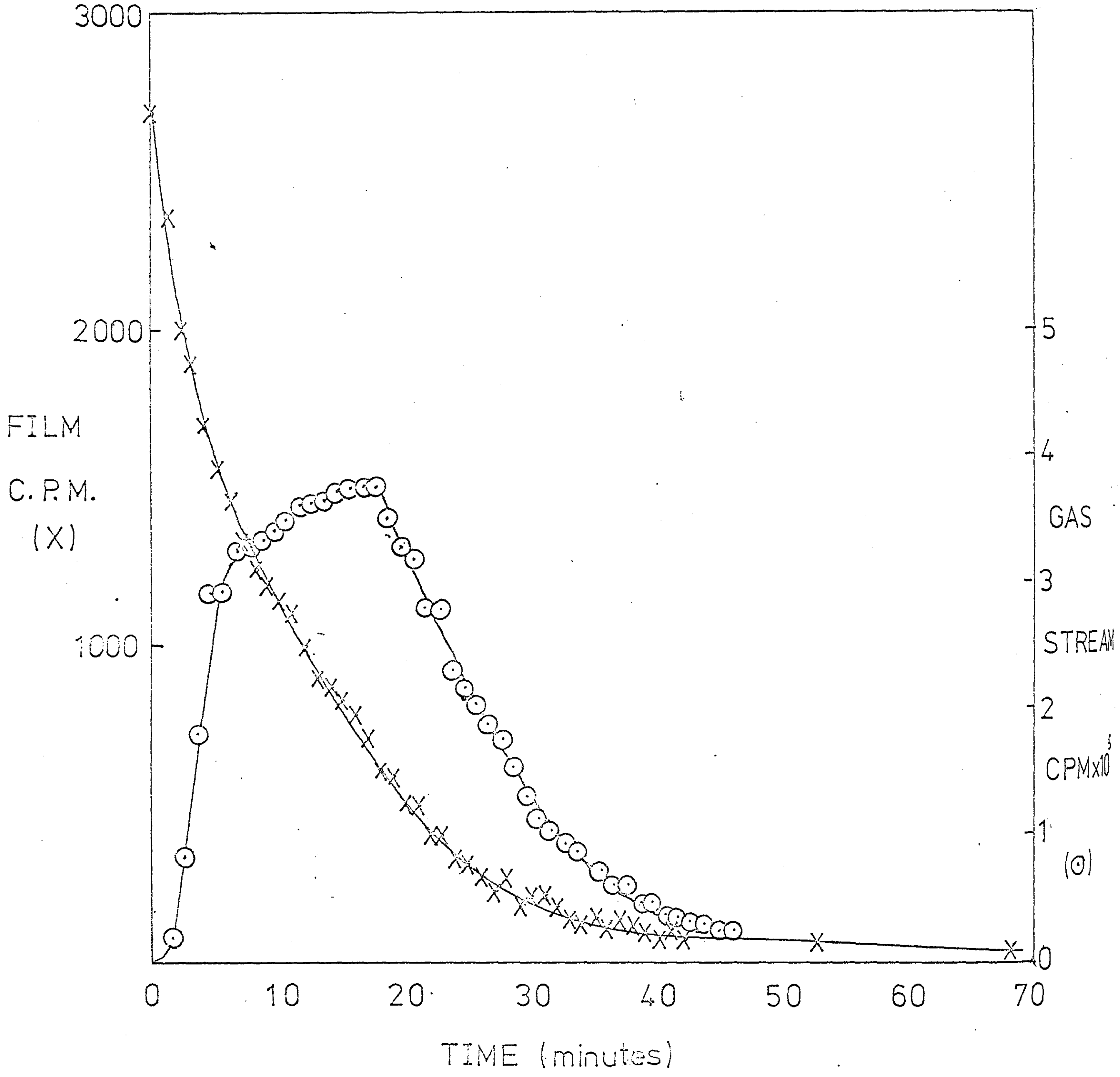
SAMPLE No	TIME WITHDRAWN	MEASURED O.D.	CORRECTED O.D.	% Ni DISSOLVED
A	1 min 20 sec	0.018	0.018	11
B	5 min 20 sec	0.063	0.064	38
C	9 min 00 sec	0.095	0.098	58
D	12 min 45 sec	0.129	0.136	81
E	16 min 30 sec	0.131	0.143	85
F,G	40 min 00 sec	0.152	0.169	100

(The two samples F and G were of optical density 0.151 and 0.153 respectively.)

All sign of the film had disappeared after approximately 25 minutes.

The early samples for film 60 showed the same trend as these results, but it was not possible to corroborate the findings over the whole range. In this

FIGURE 45 FILM AND GAS STREAM RADIOACTIVITY DURING DISSOLUTION OF FILM 64 BY 0·125 M NITRIC ACID



case it was found that only sufficient dimethylglyoxime solution was being added to the samples to complex nickel corresponding to approximately 30% dissolution of the film. This became obvious in time to add excess dimethylglyoxime to the last sample.

During the dissolution of film 65, the radioactivity of the film vessel was measured by the parallel counter, and showed a rate of decrease which was almost identical to the rate of dissolution of the film. (see figure 44) Latterly the film stripped from the walls of the vessel, so that some undissolved film became more shielded by the solution. This may account for the discrepancy in the readings for sample E.

The activity of the gas stream rose for six minutes, remained apparently steady for five minutes, and then declined.

When nitric acid of lower strength (0.125 M) was used to dissolve film 64, which was somewhat heavier (6.6 mg), the gas stream activity showed a pronounced plateau from six minutes to twenty minutes after dissolution commenced. Over one hour was required to dissolve this film completely. The film remained on the walls of the vessel throughout dissolution. Figure 45 shows the variation in the radioactivity of the film and the effluent gas stream. The presence of the plateau, showing an approximately constant rate of krypton release with time during dissolution, also supports the idea that krypton is homogeneously distributed throughout the film.

Assuming that there is a delay of some seven minutes between krypton release during dissolution and its arrival at the gas counter, it is possible to relate the radioactivity of the film at given time to the total quantity of krypton (accumulated gas flow counts) which has passed through the gas counter seven minutes later. This time lag shows that after release from the film, krypton is dissolved first in the solution, and is then swept out by the flow of nitrogen. While the krypton is held in the solution, it is effectively totally shielded by the solution.

The data obtained during the dissolution of film 64 are given in table 24.

TABLE 24 RELATION OF THE FILM RADIOACTIVITY TO THE TOTAL RADIOACTIVITY OF THE EFFLUENT GAS STREAM DURING THE DISSOLUTION OF FILM 64

TABLE HEADINGS : FC = the radioactivity of the film in cpm
%F = the % decrease in the film radioactivity at given time
GC = the total accumulated gas stream count in cpm x IO^3, seven minutes later in time
%G = the % of the accumulated gas count, corresponding to all of the krypton in the film, which is represented by GC

TIME(min)	FC	%F	GC	%G
0	2678	0	I5I5	I6
3	20I0	25	2480	27
6	I552	42	3605	39
9	II96	55	4730	5I
I2	990	62	5755	62
I5	826	69	6535	70
I8	6I2	75	7I80	77
2I	498	8I	7682	82
24	328	87	8030	86
27	224	9I	8294	89
30	208	92	8486	9I
36	I24	96	8748	94

These results may all be summarised as follows: during dissolution of a nickel film in acid, the amount of krypton released by the film is proportional to the amount of nickel dissolved. This is derived from the observation in the case of film 65 that the amount of krypton retained by the film is proportional to the quantity of nickel remaining undissolved. Both of these facts show that krypton is homogeneously distributed throughout the film.

The major error in the measurement of the total accumulated gas counts was likely to be the dead time correction, since for a dead time of 500 μs, the counter would be 'dead' for up to 45 seconds of a minute in some cases. This problem could be overcome by using diluted ^{85}Kr of lower specific activity, but this would make it impossible to monitor the radioactivity of the film through the walls of the film vessel using the parallel counter.

The total amount of accumulated gas stream counts over the whole period of dissolution represents all of the krypton held by a film. The results of this measurement for four films are given in table 25. They are consistent with the observations made by quantity measurements and the parallel count method, in that the quantity of krypton held at room temperature by a series of films is proportional to the weight of nickel.

present at room temperature than did film 70, which was deposited under constant
pressure conditions. Since the amount of krypton within film 4 varied with

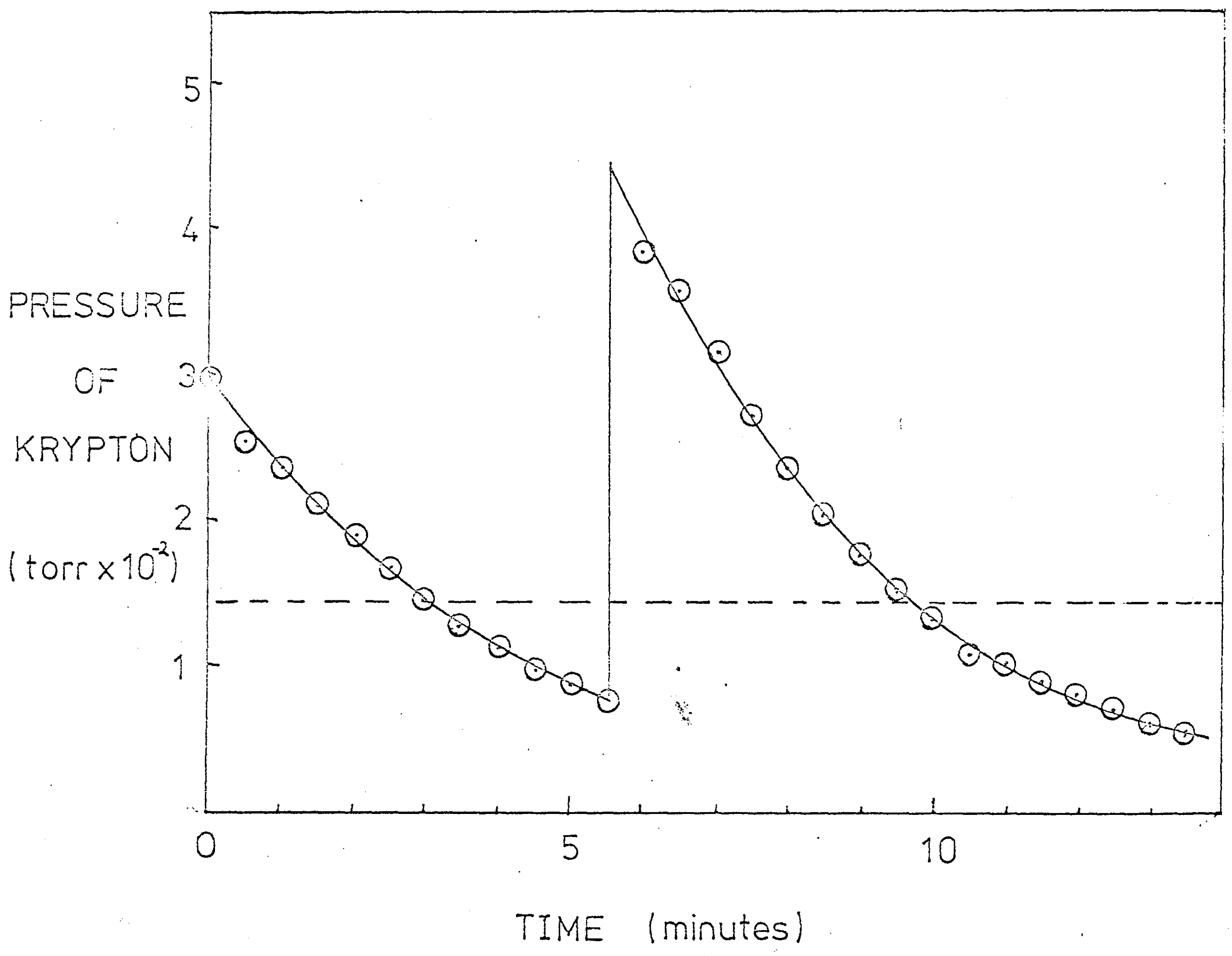
TABLE 25 TOTAL ACTIVITY OF FOUR NICKEL FILMS

FILM No.	WEIGHT (mg)	TOTAL COUNTS	SPECIFIC ACTIVITY (counts mg^{-1})
6I	3.2	$4.04 x I0^{6}$	$I.26 x I0^{6}$
63	5.9	$8.66 x I0^{6}$	$I.47 x I0^{6}$
64	6.6	$9.33 x I0^{6}$	$I.4I x I0^{6}$
65	5.4	$9.I8 x I0^{6}$	$I.70 x I0^{6}$
		MEAN	$I.46 x I0^{6} \pm 0.I6 x I0^{6}$

It is accepted that the experimental errors involved in each of the techniques described in this section are quite large. Nevertheless, the evidence for the homogeneous distribution of krypton throughout these nickel films is consistent.

The exceptions to this general rule arise because the lower availability of krypton throughout part of the deposition process may result in most of the adsorption sites in the later-deposited portion of the film being vacant when deposition ceases. It must therefore be concluded that during the warming of a film, migration of krypton from a site which has been destroyed, owing to the rise in temperature, to a vacant site, is not favoured. Otherwise, krypton expelled from those portions of a film where the concentration exceeds the equilibrium value for the particular temperature, might migrate to portions of the film where the concentration is lower. In fact such krypton is released to the gas phase. This finding is supported by the observation that on further heating above room temperature, film 4, which was deposited under constant volume conditions, invariably retained a higher proportion of the krypton present at room temperature than did film 70, which was deposited under constant pressure conditions. Since the amount of krypton within film 4 varied with

FIGURE 46 PLOT OF CORRECTED PRESSURE AGAINST TIME FOR THE DEPOSITION OF FILM 39



depth, at any temperature the concentration of krypton initially present in an appreciable fraction of the film was below the equilibrium concentration of krypton at that temperature, so that no krypton was lost from this fraction of the film.

Another illustration of this point is provided by a more detailed consideration of the thermal release of krypton from film 39.(see section 4.9) This film was laid down initially in 5%^{85}Kr, and later in inactive krypton. The first period of decreasing pressure in figure 46 represents the incorporation of 5%^{85}Kr; at 5½ minutes after deposition commenced, the reservoir of 5%^{85}Kr was replaced in the system by a reservoir containing inactive krypton. The second period of decreasing pressure corresponds to the incorporation of inactive krypton, plus a small amount of 5%^{85}Kr which was left in the film vessel. Both parts of the plot have been back-extrapolated to compensate for the initial temperature changes in the system.

Figure 28 shows the proportion of the krypton which was incorporated (a) before, and (b) after, the time of changeover, that was subequently released during a slow rise in temperature. Approximately twice as much inactive krypton as active krypton was released up to room temperature.(A total of 32% of all the krypton incorporated at 77°K, was released up to room temperature)

It has already been stated that under the conditions of deposition used for this film, the quantity of krypton incorporated in to the film will be proportional to the pressure of krypton.(section 4.8) Thus the area below a plot of pressure against time will be proportional to the total amount of krypton incorporated. The total area above the dotted line in figure 46 thus corresponds to approximately 32% of all the krypton in the film. This area is divided in to two parts, one corresponding to active krypton and one to inactive krypton. The ratio of these areas is also approximately I : 2. Therefore the release of krypton from this film is explained as the release of krypton from the parts of the film in which it is most concentrated. A more exact calculation, is not presented because it is not certain how much the system was actually disturbed by the substitution of one reservoir for another during deposition.

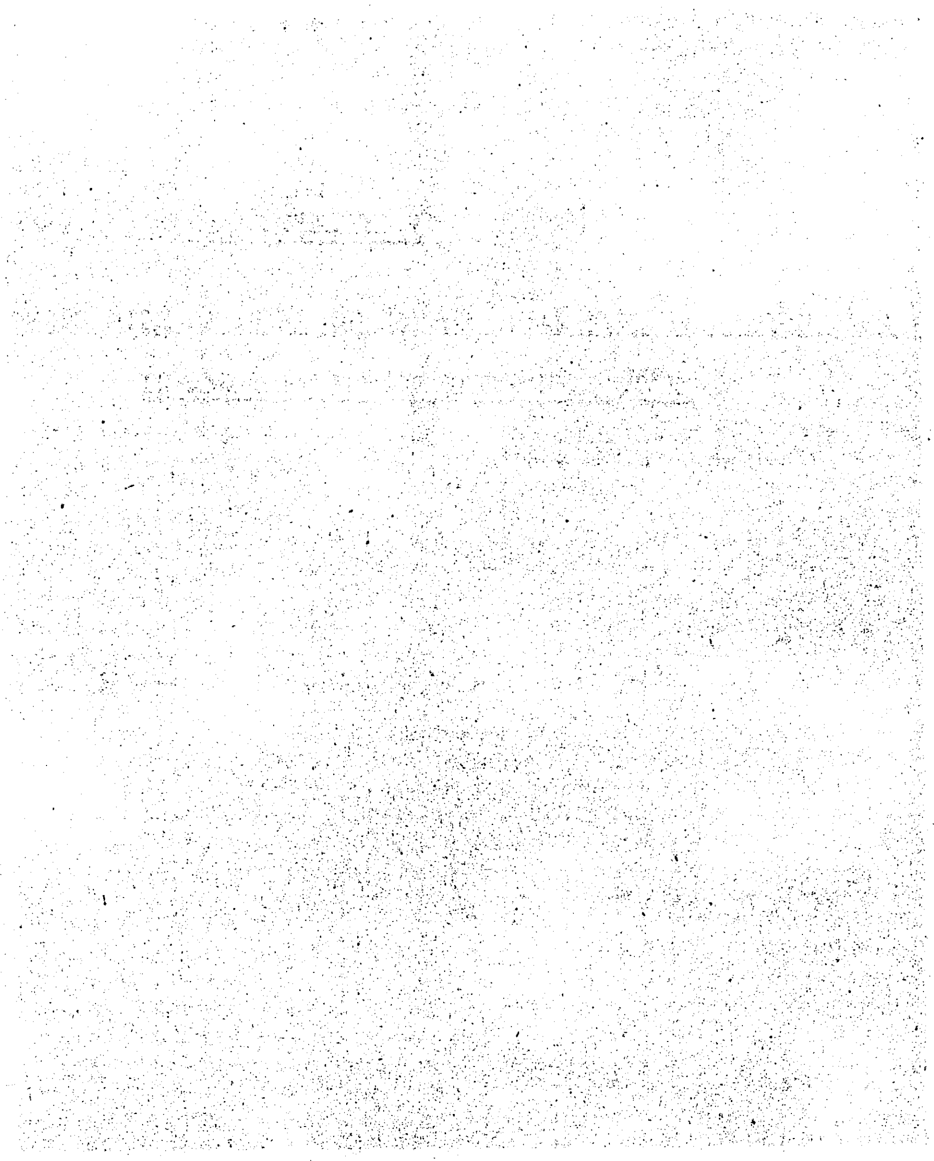
It is possible that a variation in the quantity of krypton which, having been adsorbed on type 2 sites before the onset of warming, is subsequently trapped within the film owing to structural changes during warming, may lead to a genuine variation in the atomic % of krypton at room temperature. It has been suggested that the particular quantity trapped will be determined by the respective rates of thermal desorption of krypton, and of structural changes in the film. At different rates of warming these processes may be effected unequally. If this effect was present, it was not detectable within the limits of the techniques used. However, the effect may contribute to the scatter of the points in the various plots in this section.

4.I4 GENERAL CONCLUSIONS ON THE INCORPORATION OF KRYPTON BY NICKEL FILMS

When nickel films are deposited in the presence of krypton at 77°K, krypton enters sites in the growing film by way of an intermediate adsorbed state which has features of chemisorption. The adsorption is partly irreversible and the surface is apparently heterogeneous with respect to it. However, a comparison with results obtained at a higher substrate temperature, shows differences which may be interpreted in terms of the effect of temperature on a physically adsorbed state. Assuming that the kinetics can be interpreted on the basis of the chemisorbed intermediate, it has been shown that the sticking probability of krypton on the growing surface is approximately $3.2\text{x}IO^{-6}$. The lifetime of the adsorbed state on the surface is in the order of seconds. Approximately I6 nickel atoms are required to produce one krypton adsorption site.

On warming the film, much of the krypton is lost; nevertheless appreciable quantities of krypton are retained even at 800°K. The thermal release process operates in such a way that krypton is lost preferentially from these sections of the film where it is most concentrated. This results in a levelling out of the concentration of krypton throughout the film. Eventually at each temperature a stable concentration is reached, and there is no further release of krypton until the temperature is increased further. In this respect the films resemble solid kryptonates. At room temperature, the atomic % of krypton in nickel films is a constant at 0.25%, within the limits of experimental error.

The lattice structure of the films prepared by this method is not significantly different from that of films deposited in vacuum at 273°K.



CHAPTER 5

DEPOSITION OF FILMS OF COPPER, PLATINUM, PALLADIUM, AND IRON, IN THE PRESENCE OF KRYPTON AT 77°K

CHAPTER 5(a) DEPOSITION OF COPPER FILMS IN THE PRESENCE OF KRYPTON AT 77°K

5(a).I COPPER FILMS; EXPERIMENTAL DETAILS

Copper films were evaporated from filaments cut from 0.57 mm diameter copper wire. Lengths of this wire were predegassed in vacuum by passing a current of 5.7 A for three hours, followed by a current of 6.2 A for one hour, which treatment resulted in a light film being thrown in the degassing vessel. Filaments were approximately 220 mm in length, as in the nickel work.

All copper films were deposited in a modified vessel similar to that used for the nickel dissolution studies, but with no liquid-sampling side-arm. The use of a water-cooled greased joint made it possible to remove a completed film from the vacuum system, and to locate it in a gas-flow system. (see chapter 6)

The assembled vessel was joined to the vacuum system, and evacuated. It was then degassed at 770°K, with a current of 5.5 A passing through the filament.

Films were deposited at 77°K, using filament currents in the range 8.3 A to 9.5 A .

It was found that current control was much more difficult to achieve than in the case of nickel; both slow drifts and sudden jumps occured, so that continuous monitoring was necessary.

Quantities of incorporated krypton were calculated as previously. Film weights were generally very low compared with those of nickel films, resulting in large weighing errors. Accordingly film weights were normally taken colorimetrically. Copper was converted to its complex with biscyclohexanone oxalyldihydrazone. A calibration of the optical density of the resulting solution, against its copper concentration, was prepared using an Eel colorimeter with a red filter. Details appear in appendix F.

5(a).2 DEPOSITION OF COPPER FILMS

All films were deposited under constant pressure conditions. Plots of the quantity of krypton incorporated against the quantity of copper deposited

FIGURE 47 VOLUME UPTAKE OF KRYPTON AT CONSTANT PRESSURE DURING DEPOSITION OF COPPER FILMS 69 & 78

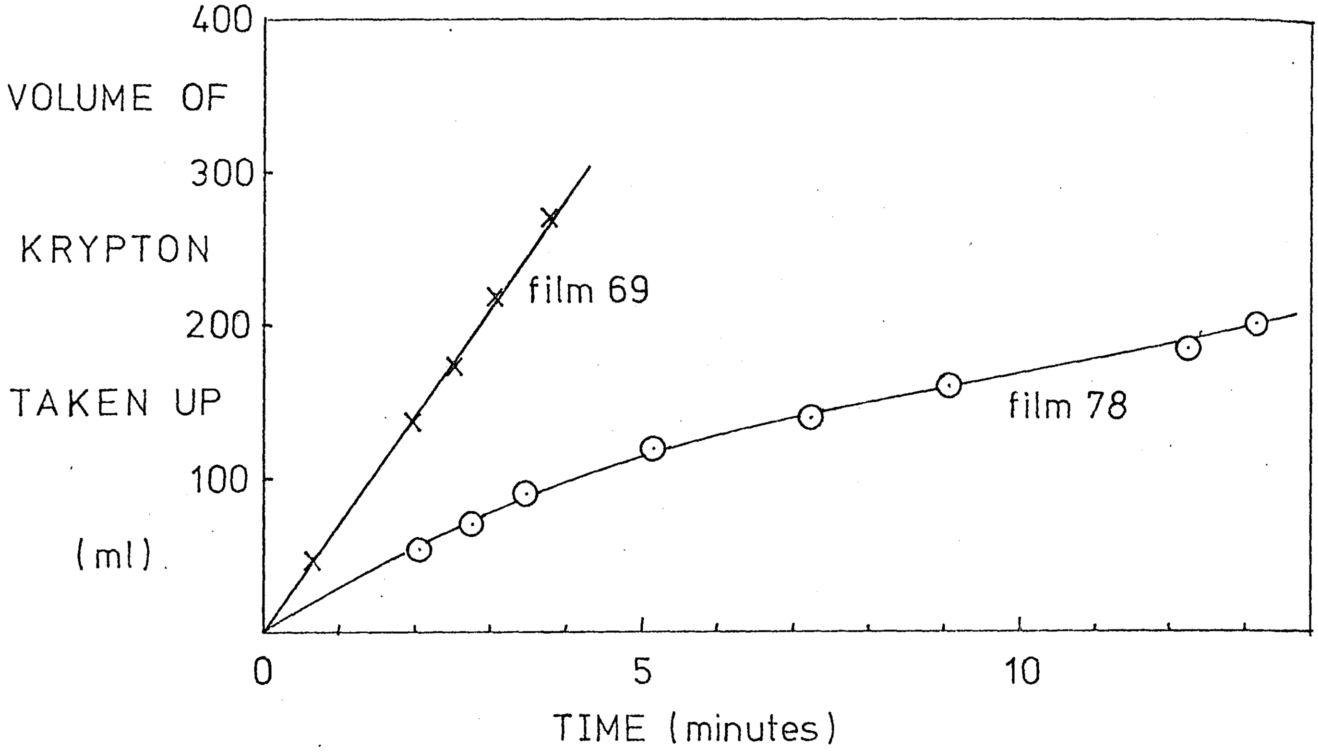
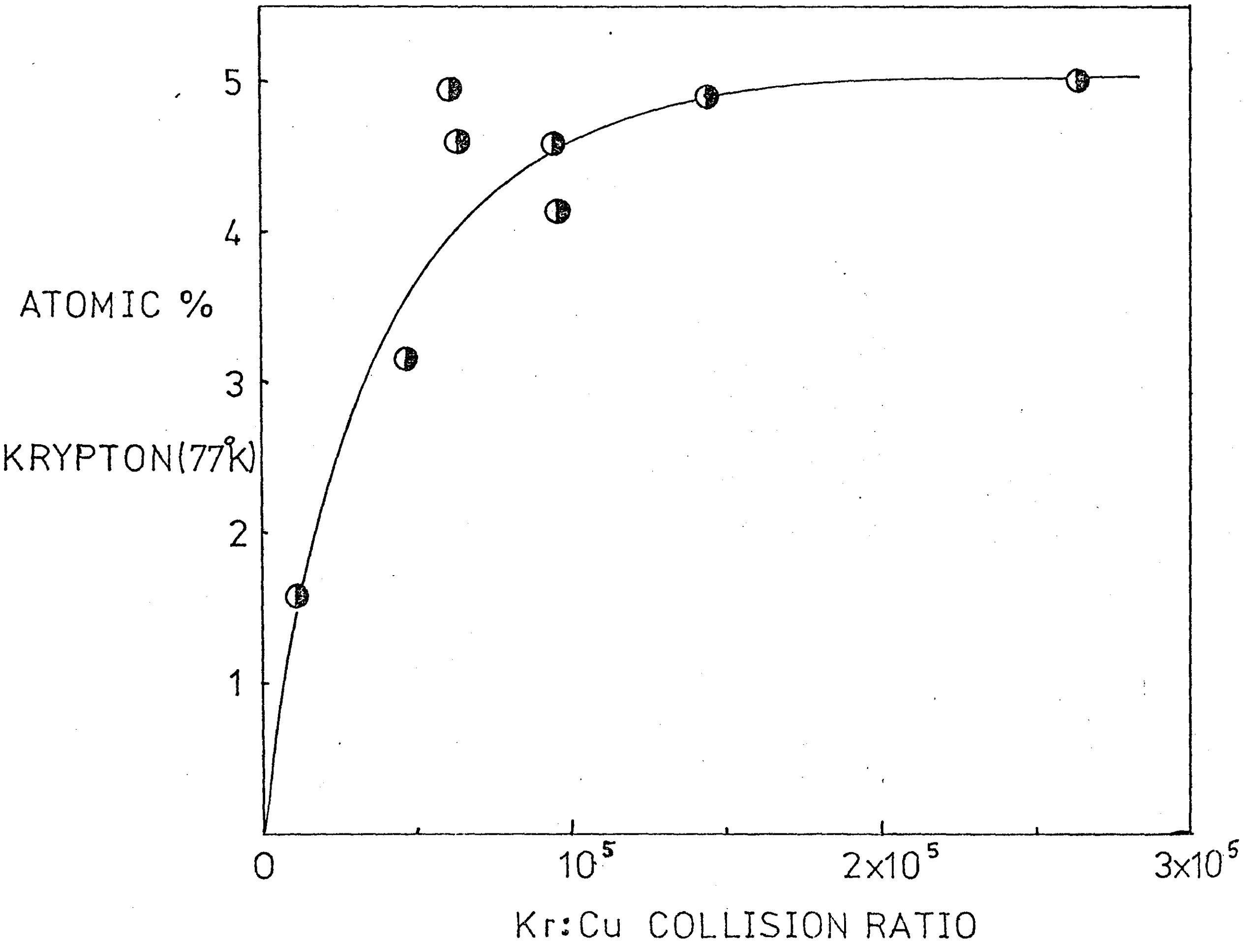


FIGURE 48 ATOMIC % KRYPTON AGAINST Kr:Cu COLLISION RATIO



were usually but not always linear. Figure 47 shows the volume uptake of krypton by films 69 and 70. The cases where non-linear uptake was observed, may be explained by the difficulty in controlling the current, mentioned in the previous section. It is believed that the non-linearity arose because of a genuine variation in the rate of copper deposition. Data recorded for this series of films appears in table 26.

TABLE 26 RESULTS OF KRYPTON INCORPORATION DURING DEPOSITION OF COPPER FILMS IN A CONSTANT PRESSURE OF KRYPTON AT 77°K

FILM No	WEIGHT(mg)	d(mg min^{-1})	P(torr)	at% 77	Kr:Cu COLLISION RATIO
67	0.40	0.8	4.60xIO^{-2}	not measurable	
69	uncertain	-	4.25xIO^{-2}	-	-
7I	0.87	0.063	3.46xIO^{-2}	4.60	6.4xIO^{4}
74	0.90	0.073	3.75xIO^{-2}	4.95	6.IxIO^{4}
75	uncertain	-	4.50xIO^{-2}	-	-
77	0.9*	0.05	4.00xIO^{-2}	4.I4	9.6xIO^{4}
78	I.IO	0.032	3.85xIO^{-2}	4.90	I.4xIO^{5}
79	I.30	0.057	4.50xIO^{-2}	4.6I	9.5xIO^{4}
80	0.75	0.II5	4.45xIO^{-2}	3.I5	4.7xIO^{4}
8I	0.I6	0.0I8	4.I2xIO^{-2}	5.0	2.8xIO^{5}
82	0.I9	0.0I6	2.45xIO^{-2}	not measurable	
83	3.38	0.440	4.24xIO^{-2}	I.58	I.2xIO^{4}

*determined from the loss of weight of the filament

The Kr:Cu collision ratios were calculated on the basis of the method outlined in appendix H. It was assumed that the temperature of gas in the film vessel was similar to that for the nickel films. The theoretical treatment for copper leads to the expression below.

$$\text{Kr:Cu collision ratio} = \frac{P}{d} \times I.2 \times IO^{5}$$

P is the constant pressure of krypton in torr, and d is the deposition rate of copper in mg min^{-1}.

The deposition periods for films 67 and 82 were too short for the quantity of krypton which was incorporated to be measured. The filament broke in each case before the end of the short period corresponding to the warming of gas in the system by the hot filament.

The weights of films 69 and 75, as determined by colorimetry, were inconsistent with the loss in weight of the filmaments. The values were:

FILM No	WEIGHT(filament loss)	WEIGHT(colorimetry)	ATOMIC % KRYPTON (77°K)
69	I.0 mg	0.6 mg	6.9
75	I.5 mg	0.4 mg	8.7

The weights determined for all the other films were reasonably consistent for the two methods. The values for films 69 and 75 are ascribed to experimental errors.

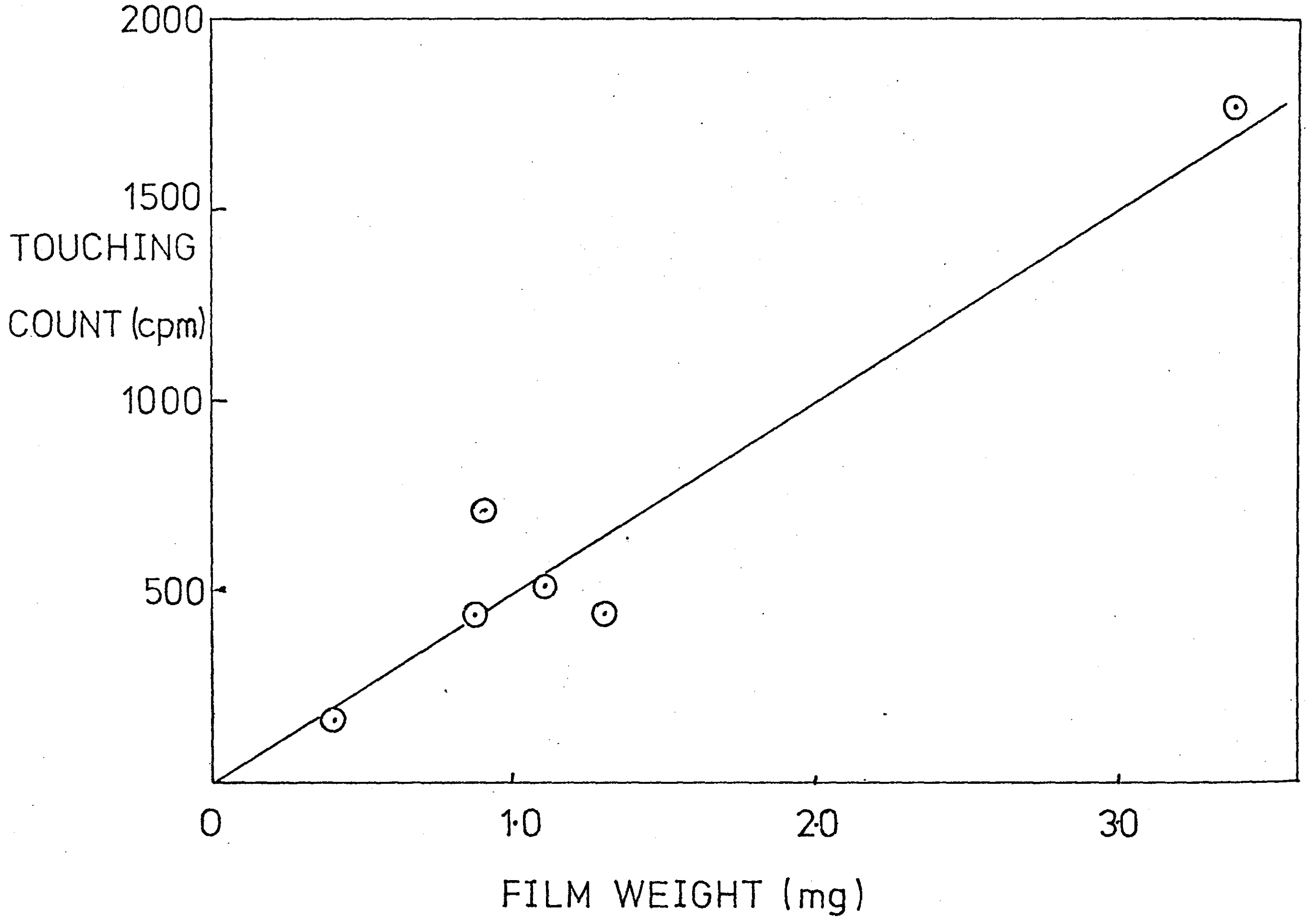
The plot of the atomic % of krypton incorporated during deposition at 77°K in to this series of films, against the Kr:Cu collision ratio, is shown in figure 48. This plot is very similar to that for nickel (figure I8). The values for copper are somewhat higher in the region of Kr:Cu collision ratio = IO^5, but in view of the experimental errors, this is not believed to be significant.

No attempt has been made to evaluate the parameters p, q, and S for copper.

5(a).3 THERMAL RELEASE OF KRYPTON FROM COPPER FILMS

On warming these copper films to room temperature (approximately 295°K), most of the incorporated krypton was released. It was not possible to obtain reliable measurements of the quantity of krypton retained at room temperature by the gas-volumetric method. This may have arisen because the quantity of krypton retained was very small. It is also believed that the copper wire was not degassed completely before deposition of the films. Even after two hours at a current of over six amps, resulting in the deposition of a fairly heavy bake-out film in the degassing vessel, it was found that gas was still being released from the wire in some cases. The degassing treatment had to be curtailled in order to leave a sufficient thickness of filament from which to evaporate the film. Any gas which is left behind in the filament, and which is released during film deposition, will contribute to the errors in quantity

FIGURE 49 PLOT OF RADIOACTIVITY AGAINST WEIGHT, FOR COPPER FILMS AT ROOM TEMPERATURE



measurements.

An atomic % of 0.33% krypton was found for the heaviest film, No 83. The filament of this film had been pretreated in hydrogen in order to aid in removing any occluded oxygen.

This problem was also tackled by measurements of the radioactivity of the series of films. Touching counts were taken at room temperature, as for the nickel films of table 20, using the same type MXI33 Geiger-Muller counter. The results are given in table 27.

TABLE 27 RADIOACTIVITY MEASUREMENTS OF COPPER FILMS

FILM No	WEIGHT(mg)	RADIOACTIVITY(cpm)	$\frac{\text{RADIOACTIVITY}}{\text{WEIGHT}}$ (cpm mg^{-1})
67	0.40	I60	400
7I	0.87	440	5I0
74	0.90	7I0	790
78	I.I0	5I0	460
79	I.30	440	340
83	3.38	I770	520
		MEAN	500 ± I40

Taking the value of 399 cpm mg^{-1} for nickel, and allowing for the difference in atomic weights, a value of 0.34 atomic % of krypton is suggested as the mean for the copper films, compared with 0.25% for nickel.

A plot of the radioactivity of these films against their weight is shown in figure 49. The scatter of the points arises partly from the low film weights, and partly because the copper films were not all evenly distributed over the walls of the film vessel; evaporation from some parts of the filament appeared to be favoured. This may lead to more or less efficient counting depending on the particular distribution of the films over the walls of the vessel.

Nevertheless it is clear that copper retains a somewhat larger quantity of krypton at room temperature than does nickel.

One film, No 7I, was heated to higher temperatures in vacuum for one hour periods. A plot of the radioactivity of the film against the temperature reached is shown in figure 57. During the heat treatment the colour of the film changed. At room temperature, all copper films were blackish-bronze in colour, analagous to the black colour of nickel films.

Full details of the heat treatment of film 7I are given in table 28.

TABLE 28 HEAT TREATMENT OF FILM 7I

TEMPERATURE (°K)	PERIOD OF TIME	RADIOACTIVITY(cpm)	APPEARANCE OF FILM
295	I hour	440	black-bronze
295	3 days	392	"
303	I hour	372	signs of 'copperyness'
423	I hour	300	"
483	I hour	I76	'coppery'
560	I hour	I33	natural copper
295	2 days	I29	"
478	I hour	I25	"
478	I hour	I35	"

All counts were taken at room temperature over ten minutes, the mean of two counts being taken. It should be noted that some krypton was lost on standing at room temperature for a period of days. This effect was not noted for nickel, and if present, is much less significant. On warming to higher temperatures, relatively more krypton was lost than from nickel. After the film had been treated at 560°K, neither standing for two days at room temperature nor heating to 478°K produced any further release of krypton. Small fluctuations in this period are explained by the difficulty of reproducing the counting geometry precisely, after removing the furnace.

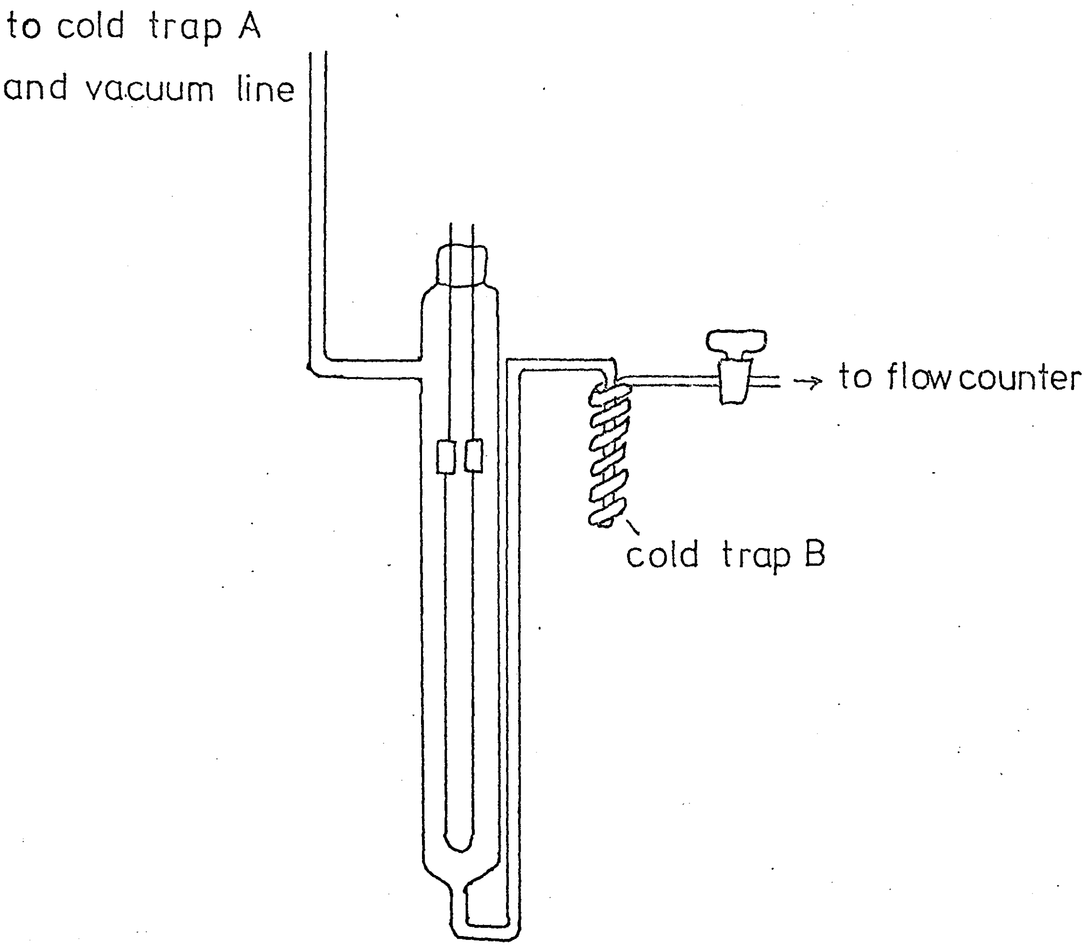
These results show the behaviour which has been reported on heating solid kryptonates (69).

The thermal release of krypton from a series of metals is considered in chapter 5(e).

Precise values were difficult to obtain for this investigation of copper films because the method of evaporation from an electrically heated filament is not suitable for the controlled production of thick copper films.

An alternative method, which would be more suitable, involves evaporation of a bead of copper mounted on an electrically heated filament of a metal such as molybdenum, which has a much higher temperature of evaporation (II2).

FIGURE 50 MODIFIED FILM VESSEL USED FOR PLATINUM FILMS



CHAPTER 5(b) DEPOSITION OF PLATINUM FILMS IN THE PRESENCE OF KRYPTON AT 77°K

5(b).I PLATINUM FILMS; EXPERIMENTAL DETAILS

Platinum films were evaporated from 220 mm filaments of 0.5 mm platinum wire supplied by Messrs Johnson, Matthey, and Co, Ltd. Wires were predegassed in vacuum for four hours at 7.0 A, followed by one hour at 7.6 A. This treatment resulted in a light bake-out film being thrown in the degassing vessel.

Films were deposited in a modified film vessel which was designed so that after deposition, a gas stream could be flowed through the film vessel without prior exposure of the film to the atmosphere. (see figure 50) The dimensions of the vessel itself were identical to those of the standard film vessels. The purpose of this modification was to examine the release of krypton during adsorption and reaction of species injected in to a stream of nitrogen passing over the film. This investigation is described in section 7.3.

Before deposition of a film, the film vessel was sealed on to the system and all parts of the flow system were evacuated. The tap leading to the flow counter was then closed, and the vessel was degassed overnight, with a current of 7.3 A passing through the filament, at a temperature of 770°K.

During deposition and subsequently, the film was protected from contamination by the cold traps, which were filled with liquid nitrogen.

All platinum films were deposited under constant volume conditions, using filament currents in the range 9.7 A to IO.0 A.

Film weights were calculated from the loss in weight of the filament during the evaporation process.

5(b).2 DEPOSITION OF PLATINUM FILMS

Plots of the quantity of krypton taken up at constant pressure, against deposition time, were all linear. Assuming a constant rate of platinum deposition, plots of the quantity of krypton incorporated against the quantity of platinum deposited, were constructed. Three examples are shown in figure 5I.

Data for the series of platinum films are given in table 29.

FIGURE 51 PLOTS OF THE QUANTITY OF KRYPTON INCORPORATED DURING DEPOSITION OF THREE PLATINUM FILMS

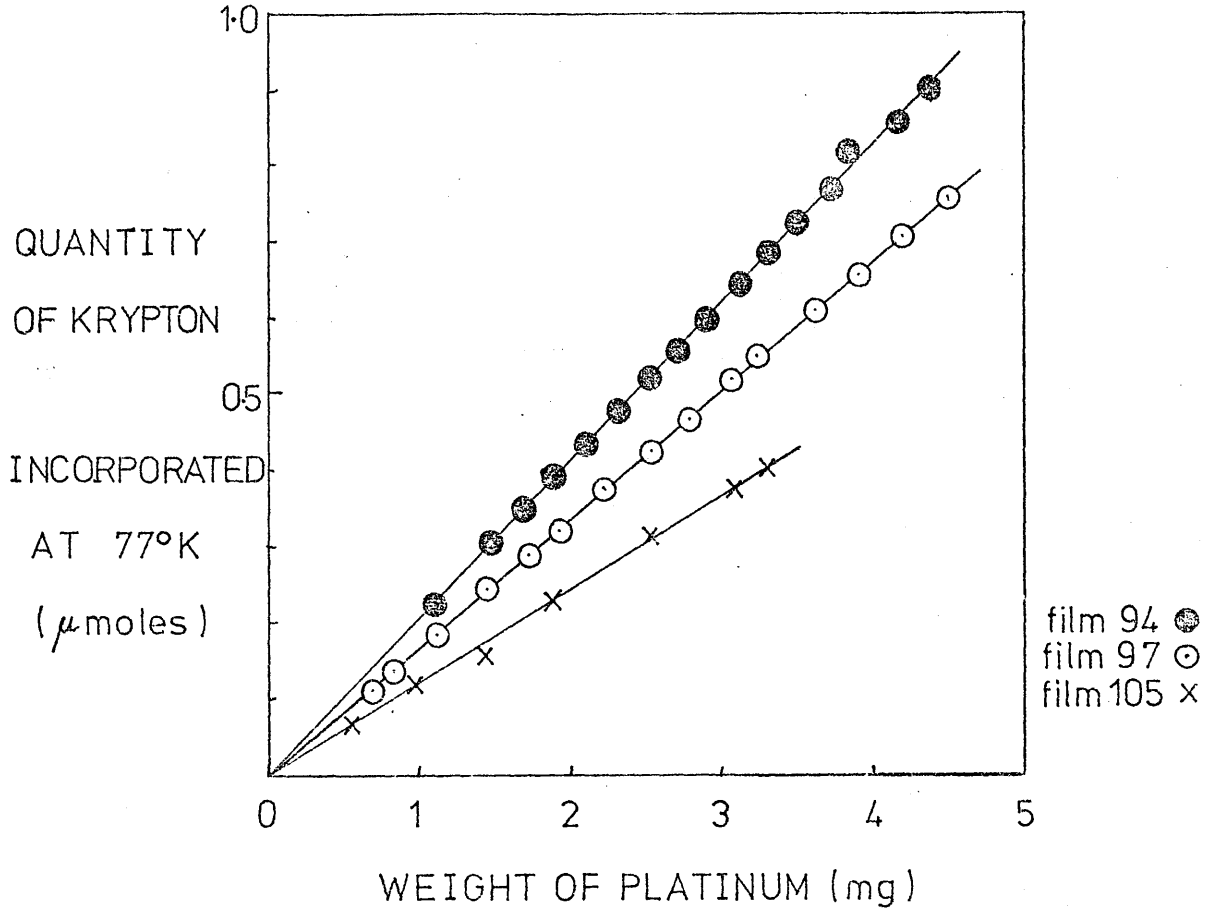


FIGURE 52 ATOMIC % KRYPTON AGAINST Kr:Pt COLLISION RATIO

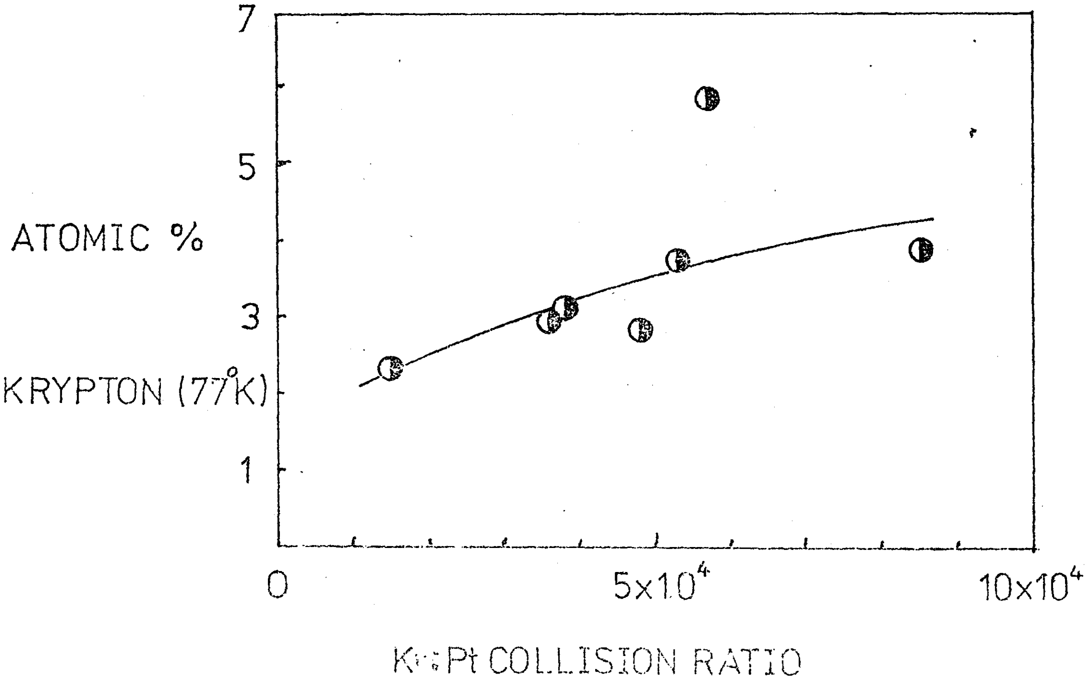


TABLE 29 RESULTS OF KRYPTON INCORPORATION DURING DEPOSITION OF PLATINUM FILMS IN A CONSTANT PRESSURE OF KRYPTON AT 77°K

FILM No	WEIGHT(mg)	d(mg min^{-1})	P(torr)	at% 77	Kr:Pt COLLISION RATIO
94	5.0	0.I7	3.99×10^{-2}	3.90	8.5×10^{4}
97	4.5	0.33	3.50×10^{-2}	3.I6	3.5×10^{4}
I02	6.0	0.37	3.74×10^{-2}	2.95	3.6×10^{4}
I05	3.3	0.73	3.15×10^{-2}	2.32	1.5×10^{4}
I08	3.0	0.22	3.30×10^{-2}	3.7I	5.3×10^{4}
II0	5.5	0.29	3.84×10^{-2}	2.8I	4.8×10^{4}
II2	2.0	0.23	3.61×10^{-2}	5.90	5.7×10^{4}

The krypton : platinum collision ratios were calculated on the basis of the method outlined in appendix H. It was assumed that the temperature of the gas in the film vessel during deposition was the same as for nickel films. This assumption is probably not valid in view of the much higher currents being used, but the theoretical derivation is dependent on the square root of the absolute temperature, and not much error will arise if the temperatures are fairly close. The theoretical treatment leads to the expression:

$$\text{Kr:Pt collision ratio} = \frac{P}{d} \times 3.6 \times 10^{5}$$

A plot of the atomic % of krypton incorporated in to this series of films during deposition at 77°K, against the Kr:Pt collision ratio, is shown in figure 52. The spread of values of the Kr:Pt collision ratio is not very large, but there is again a remarkable similarity to the corresponding plot for nickel (figure I8). The exceptional value recorded for film II2 is assumed to have resulted from a weighing error; this was the lightest film.

5(b).2 THERMAL RELEASE OF KRYPTON FROM PLATINUM FILMS

The films were permitted to attain room temperature (approximately 295°K) and the quantity of retained krypton was measured gas-volumetrically, as for the nickel films. (see section 4.9) The films were left for one hour at room temperature before the quantity of krypton released was measured using the

FIGURE 53 TOUCHING COUNT GEOMETRY FOR THE 'FLOW TYPE' FILM VESSELS

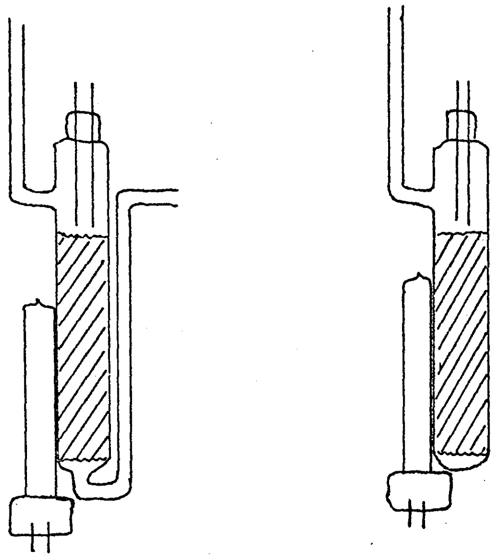
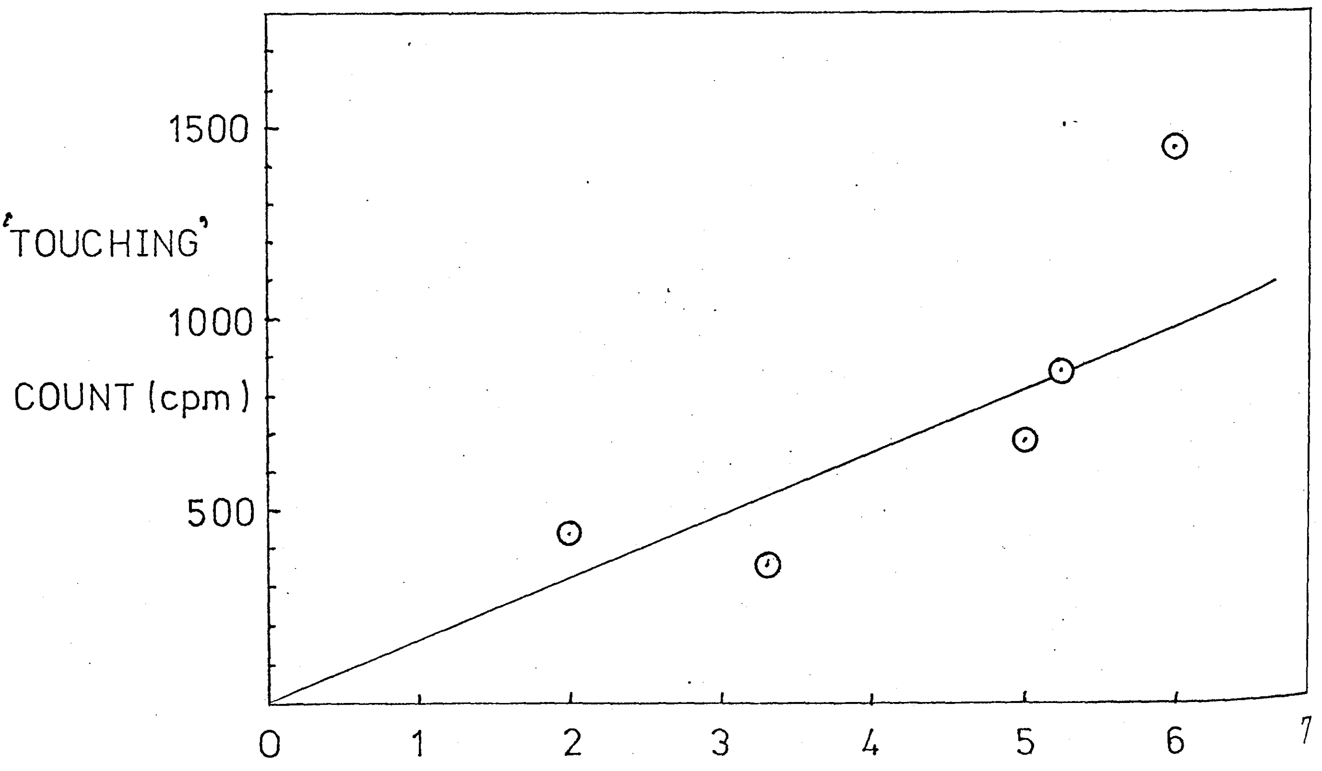

'flow type' film vessel standard film vessel

FIGURE 54 PLOT OF RADIOACTIVITY AGAINST WEIGHT FOR PLATINUM FILMS DEPOSITED IN 5% ^{85}Kr



McLeod gauge. The results are given in table 30.

At room temperature all platinum films were black in colour.

TABLE 30 THE ATOMIC % OF KRYPTON RETAINED AT ROOM TEMPERATURE BY PLATINUM FILMS

FILM No	ATOMIC % OF KRYPTON (295°K)
97	0.65
I02	0.78
I05	I.39
I08	0.87
II0	0.75
II2	0.95

After the measurement for film I05 was taken, the radioactivity of the film, measured by a touching count, fell over a period of 30 minutes from a net value of 432 cpm to 354 cpm. It is possible that the release of krypton from platinum films is slower than for nickel or copper; some of the other values in table 30 may be subject to this effect. The value for film II2 may also be artificially high because of a weighing error.

It is only possible to conclude that the atomic % of krypton retained by platinum films is approximately twice or three times the value for nickel.

Radioactivity measurements were made on a series of five films by the touching count method. These measurements could not be compared to those for nickel and copper because an MXI33 counter of higher efficiency was used, owing to breakage of the original. Another inconsistency arose because the exit tube at the bottom of the film vessel prevented the whole length of the counter from contacting the portion of the vessel where the film was deposited. (see figure 53) Accordingly the errors of counting geometry were larger.

This is reflected in the scatter of the points in figure 54, where the radioactivity of the films is plotted against their weight. The results are given in detail in table 3I.

Another factor which explains the somewhat inconsistent data for these platinum films is that the absolute quantity of krypton which was being measured was smaller than for most of the nickel films of tables I0 and 20, and thus more difficult to measure accurately.

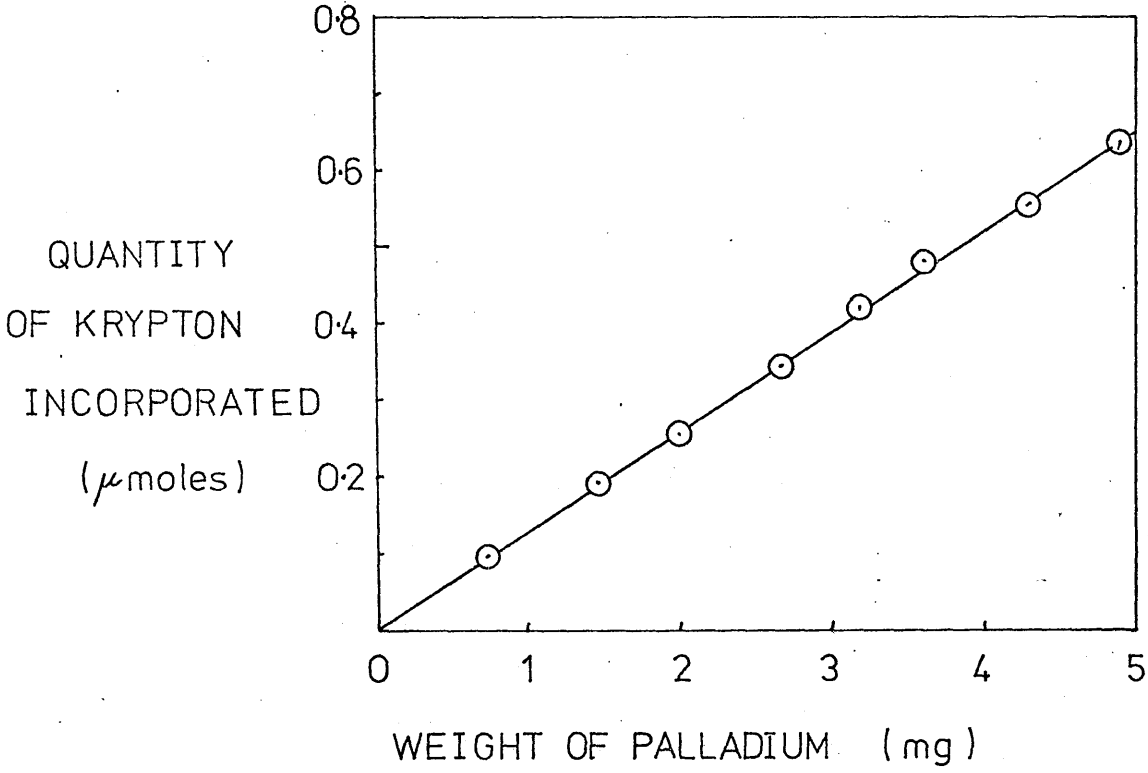
TABLE 3I RADIOACTIVITY MEASUREMENTS OF PLATINUM FILMS AT ROOM TEMPERATURE

FILM No	WEIGHT(mg)	RADIOACTIVITY(cpm)	$\frac{\text{ACTIVITY}}{\text{WEIGHT}}$ (cpm mg^{-1})
94	5.0	682	I36
I02	6.0	I444	240
I05	3.3	354	I07
II0	5.5	86I	I57
II2	2.0	432	2I6
		MEAN	I7I ± 50

One film, No II2, was heated in vacuum by means of a furnace to higher temperatures for one hour periods. The fall in radioactivity of the film above room temperature is shown in figure 57.

Further comment on the atomic % of krypton and activity values at room temperature for these films is made in section 5(c).3.

FIGURE 55 INCORPORATION OF KRYPTON DURING DEPOSITION OF PALLADIUM FILM I07 AT 77°K



CHAPTER 5(c) DEPOSITION OF PALLADIUM FILMS IN THE PRESENCE OF KRYPTON AT 77°K

5(c).1 PALLADIUM FILMS; EXPERIMENTAL DETAILS

Two palladium films were evaporated from 220 mm filaments of 0.5 mm diameter palladium wire, supplied by Messrs Johnson, Matthey and Co, Ltd. The wire was predegassed in vacuum for four hours at 4.0 A.

The films were deposited in a film vessel of the type used for nickel films. This was sealed on to the system and degassed overnight at 770°K, with a current [illegible] A

This was sealed on to the system and degassed overnight at 770°K, with a current

for one hour.

Currents of 6.3 A and 6.5 A were used for evaporation of the films. Both films were grown under constant pressure conditions.

The film weights were calculated from the loss in weight of the filaments during deposition.

5(c).2 DEPOSITION OF PALLADIUM FILMS

The plots of the quantity of krypton taken up at constant pressure, against deposition time, were linear. Assuming a constant rate of palladium deposition, plots of the quantity of krypton incorporated during deposition against the quantity of palladium deposited, were constructed. They were virtually identical for the two films; that for film 107 is shown in figure 55.

Data for the two films are given in table 32.

TABLE 32 RESULTS OF KRYPTON INCORPORATION DURING THE DEPOSITION OF PALLADIUM FILMS IN THE PRESENCE OF KRYPTON AT 77°K

FILM No	WEIGHT(mg)	d(mg min^{-1})	P(torr)	at% 77	Kr:Pd COLLISION RATIO
104	6.4	1.92	3.64×10^{-2}	1.18	3.8×10^{3}
107	4.9	1.59	3.50×10^{-2}	1.36	4.4×10^{3}

The Kr:Pd collision ratio was calculated on the same basis as previously. The theoretical treatment leads to the expression:

$$\text{Kr:Pd collision ratio} = \frac{p}{d} \times 2.0 \times 10^{5}$$

The atomic % of krypton incorporated in to these palladium films is comparable to that for nickel films deposited at the same krypton : metal collision ratio. However, on a per atom basis, the measured rates of palladium deposition are equivalent to a nickel deposition rate of approximately 1 mg min^{-1}. From figure 21, it is apparent that a larger rate of nickel atom deposition would be required to give rise to the rate of krypton incorporation measured in the case of palladium. (see table 33)

TABLE 33 RATE OF KRYPTON INCORPORATION BY PALLADIUM FILMS

TABLE HEADINGS : INC = the total quantity of krypton incorporated during deposition at 77°K (μmoles)
RI = the rate of krypton incorporation in moles min^{-1}
RI÷P = the rate of krypton incorporation, divided by the constant pressure of krypton, in μmoles min^{-1} $torr^{-1}$

FILM No	INC	RI	RI÷P
104	0.715	0.214	5.88
107	0.632	0.205	5.85

5(c).3 THERMAL RELEASE OF KRYPTON FROM PALLADIUM FILMS

The films were allowed to attain room temperature, and the quantities of krypton retained were measured by the gas-volumetric method. Both films were deposited in 0.6% ^{85}Kr, and activity measurements were made at room temperature by the touching count method, using the same MX133 counter employed for the platinum films. The results of these measurements are given in table 34.

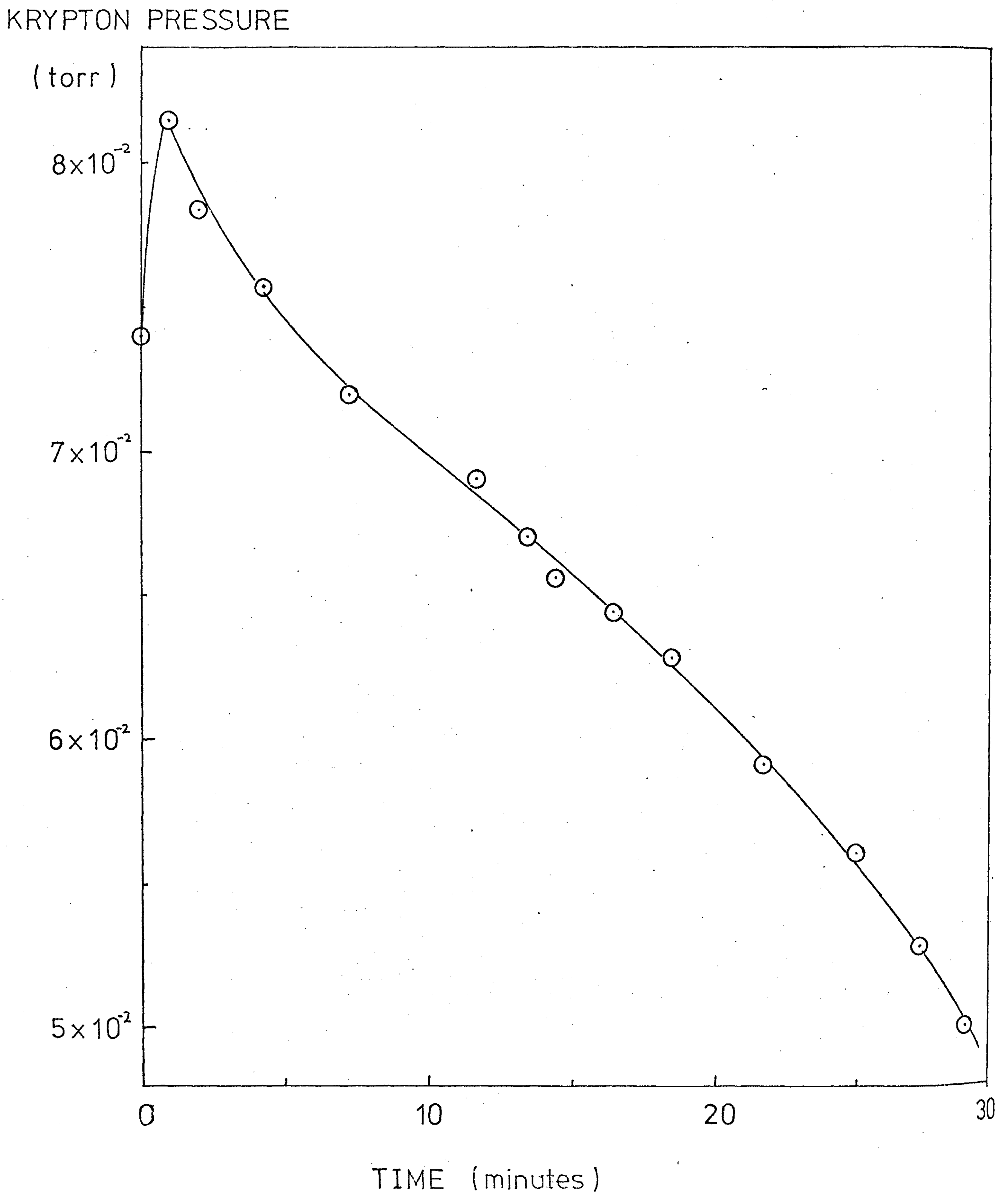
TABLE 34 MEASUREMENTS OF THE QUANTITY OF KRYPTON RETAINED AT ROOM TEMPERATURE BY PALLADIUM FILMS

FILM No	WEIGHT(mg)	at% 295	RADIOACTIVITY(cpm)	ACTIVITY / WEIGHT (cpm mg^{-1})
104	6.4	0.69	453	71
107	4.9	0.71	326	67

Allowing for the lower specific activity of krypton used, and for the difference in atomic weight between platinum and palladium, these values suggest an atomic % of krypton retained by platinum films of approximately 0.43%. The difference in counting geometry (see figure 53) in fact leads to a lower efficiency of counting for the platinum films, so that the final atomic % of krypton retained at room temperature by platinum films is probably only marginally lower than that for palladium. A value of 0.6% is suggested.

The measurements made for the palladium films are believed to be reliable; after 30 minutes at room temperature no further loss of krypton was detected.

FIGURE 56 DECREASE OF KRYPTON PRESSURE DURING DEPOSITION OF IRON FILM 62 AT 77°K



CHAPTER 5(d) DEPOSITION OF IRON FILMS IN THE PRESENCE OF KRYPTON AT 77°K

At a stage in the investigation when only nickel films had been studied, two iron films were deposited in order to check that incorporation of krypton during film deposition could occur for metals other than nickel. Iron wire (0.5 mm) was predegassed at 4.4 A, resulting in a light bake-out film being thrown in the degassing vessel. Filament lengths and film vessels were identical to those used for nickel.

In the case of the first film, No 59, which was laid down under constant volume conditions at an initial pressure of $I.4xI0^{-1}$torr of krypton, a slow fall in pressure of krypton was observed. When the film vessel had been allowed to attain room temperature, more gas was found to be present in the gas phase than the initial measured quantity of krypton. This was believed to result from inadequate degassing or the decomposition of iron oxide in the filament during deposition. Accordingly the filament of the second film, No 62, was treated with hydrogen for 30 minutes at 770°K, with a current of 3.8 A passing through the filament, followed by a further period of degassing in vacuum.

The decrease in krypton pressure during the deposition of this film at 6.7 A was neither exponential nor linear. (see figure 56) The amount of krypton incorporated during deposition corresponded to a mean atomic % of 0.9I% krypton at 77°K. On warming to room temperature, the quantity of krypton retained represented 0.09 atomic % of the film. The weight of the film was 5.8 mg and the rate of deposition was 0.2 mg min^{-1}.

These observations are in marked contrast to those for nickel. A nickel film deposited under similar conditions would be expected to have an atomic % of approximately 3% krypton at 77°K. Although the results for film 59 were not reliable, the rate of pressure decrease during deposition was similar to that for film 62.

It was concluded that the behaviour of iron was genuinely different from that of all the other metals studied, but no detailed investigation was carried out.

CHAPTER 5(e) GENERAL DISCUSSION ON THE INCORPORATION OF KRYPTON DURING THE DEPOSITION OF METAL FILMS AT 77°K

It has been shown that krypton is stably incorporated in to films of nickel, copper, platinum, palladium, and iron during the evaporation of these metals at 77°K in the presence of krypton. Evidence has been put forward to show that the distribution of krypton throughout the resulting films at room temperature is homogeneous. While a detailed investigation of this point has been conducted for nickel only, the results for platinum, copper, and palladium suggest that krypton is homogeneously distributed throughout these metals also.

The following values have been advanced for the equilibrium concentrations of krypton in the metals at room temperature:

TABLE 35 EQUILIBRIUM CONCENTRATION OF KRYPTON IN FILMS OF FOUR METALS AT 295°K

METAL	ATOMIC % OF KRYPTON (% OF ALL ATOMS IN THE FILM)
nickel	0.25%
copper	0.34%
platinum	≈0.6%
palladium	0.70%

The quantity of krypton incorporated in to films of nickel, copper, platinum, and palladium during deposition at 77°K is remarkable for its consistency.

The points taken from the plots of the atomic % of krypton incorporated at 77°K against the krypton : metal collision ratio, for all the metals, could be added to the plot made for nickel (figure 18), without greatly increasing the scatter of the points.

The data for these plots was taken from the measured weights of the films. Allowance was then made for the differences in atomic weight for the various metals. Thus the characteristics of the intermediate adsorbed state must be similar, on a per atom basis, for all of the metals. Since these are all metals which have the face-centred cubic structure, it is possible that the particular adorption site is peculiar to this system. At low temperatures it is likely that metal atoms stick at the point where they collide with the film, and a similar disordered structure may result for all the metals. In support of this speculation, only iron appeared to be distinctly different in terms of the amount of krypton incorporated, and it is a body-centred cubic metal. The results for iron were however very limited, and this is probably too much to read in to them.

Before definite conclusions could be made, a wider range of metals would have to be studied, and some method of examining the structures of the films at 77°K would have to be found. It is likely that the structure of the films at 77°K is different from the structure at 295°K; assuming the known atomic radii of nickel and krypton, it may be shown that in the limit, approximately 20% of the volume of a film at 77°K is composed of krypton atoms.

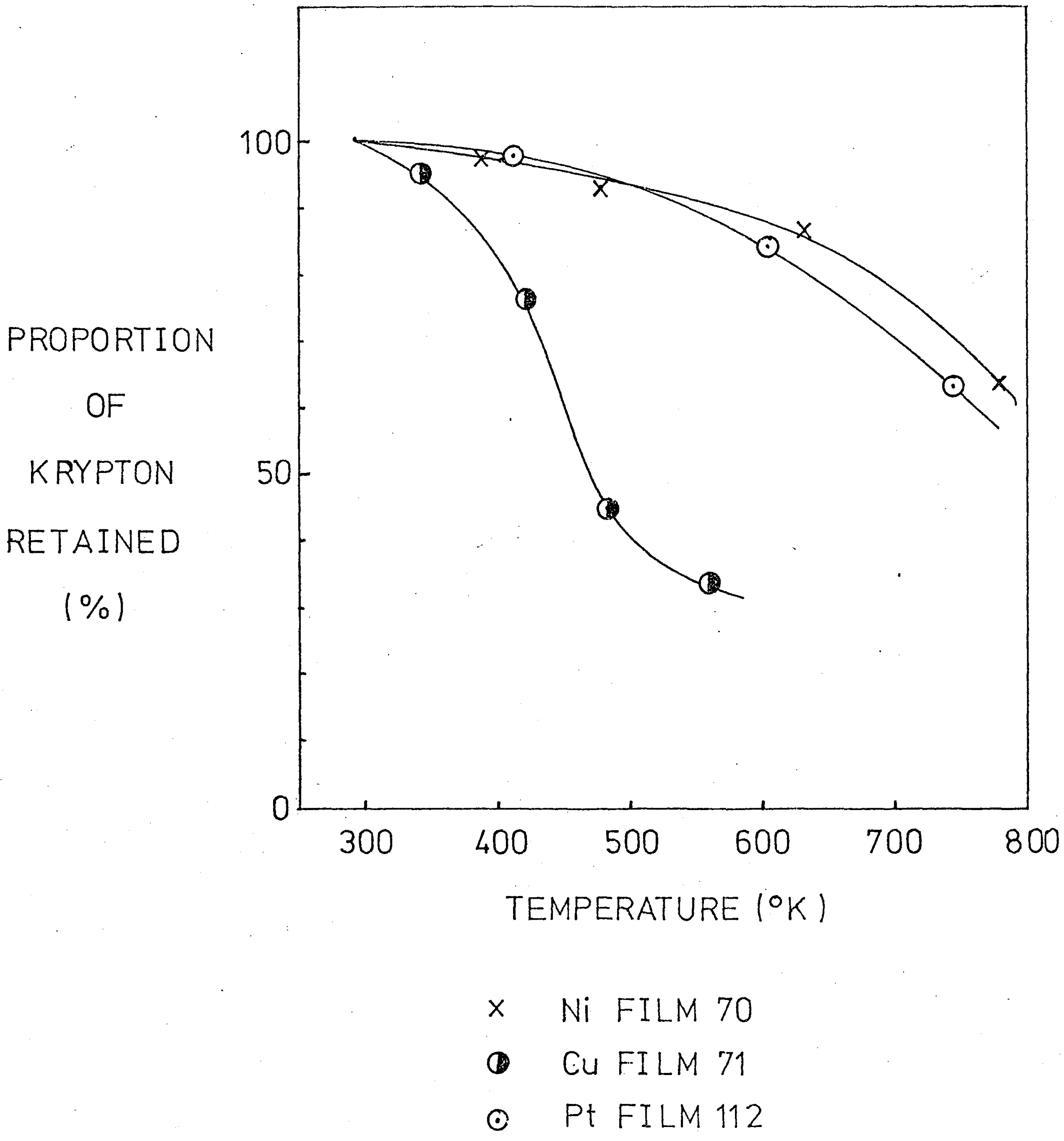
Minor differences in the plots of atomic % krypton at 77°K, against the krypton : metal collision ratio, for copper and palladium, may be interpreted as follows. The higher values of atomic % krypton, in the region of Kr:Cu collision ratio = $I0^5$ for copper, may represent a lesser tendency to surface heterogeneity, or a smaller number of metal atoms required to produce one adsorption site, than for nickel. The higher values for the rate of krypton incorporation for palladium, may represent a higher probability of krypton adsorption than for nickel.

It has been shown that the characteristics of krypton release from the completed films are similar to the characteristics of krypton release from solid kryptonates (69). After any rise in temperature, some krypton is lost. Once a film has been stabilised at a particular temperature, no more krypton is lost until this temperature is exceeded. The time required for stabilisation at room temperature is different for the various metals.

An attempt has been made in the case of nickel to describe the processes which result in krypton loss below room temperature, in terms of thermal desorption of krypton and changes in film structure resulting from sintering. However, throughout the range of temperature up to 800°K, the behaviour of the metals studied is best described in terms of a stable concentration of krypton being reached at each temperature.

Figure 57 shows the proportion of the radioactivity resulting from the

FIGURE 57 PLOT OF THE PROPORTION OF THE KRYPTON HELD BY METAL FILMS STABILISED AT 295°K, WHICH WAS RETAINED AFTER TREATMENT AT HIGHER TEMPERATURES



presence of krypton at room temperature, which was retained on further heating of films of nickel, copper, and platinum to various temperatures for one hour periods.

The known structural changes of these metals in the temperature range of interest may be summarised as follows.

In the temperature range 500°K to 600°K, a recystallisation process results in the disappearance of dislocations from copper (23).

Nickel shows structural changes in two temperature ranges. In the range 470°K to 570°K, changes are ascribed to the disappearance of vacancies (23), or to the combination of vacancies to give larger groups (II3). Dislocations are rearranged and annealed out in the range 850°K to 950°K (23).

Dislocations are annealed out in platinum at temperatures in the region of II00°K (2I).

It has been shown that these processes may occur at lower temperatures for metal films (II3).

Finally, it has been shown that defects induced by radiation may be annealed out at temperatures as low as II0°K, for a series of metals including copper and nickel (II4).

From the experimental results, it is clear that krypton is released by copper after moderate treatment at temperatures above room temperature. This would be expected from the low temperature of recrystallisation of copper.

However, the plots for nickel and platinum are very similar, although nickel would be expected to be effected more by a rise in temperature to 800°K. It should be noted that the quantity of krypton held by platinum throughout the temperature range was twice that held by nickel, on a per atom basis. Possibly the higher concentration of krypton enhances the thermal release of krypton from platinum, so that it is comparable to the thermal release of krypton from nickel.

The two effects of krypton concentration and of changes in metal structure could not be separated in the present work. Certain aspects of the thermal release of krypton may be usefully related to changes in metal structure, and changes in metal structure occur throughout the entire range of temperature over which thermal release of krypton has been observed from films laid down at 77°K.

Accordingly it is suggested that krypton incorporated during the deposition of metal films at 77°K, is located at defect sites in these films, at least initially.

As in the case of solid kryptonates, an explanation of the thermal release of krypton, which is valid throughout the range of temperature studied, remains obscure.

CHAPTER 6

OXIDATION OF COPPER FILMS

CHAPTER 6 OXIDATION OF COPPER FILMS

6.1 THE REACTION OF COPPER FILMS WITH OZONE

Evidence has been presented in chapter 4 to show that krypton is homogeneously distributed throughout nickel films at room temperature, and in chapter 5 to show the similarity in properties of the copper and nickel films in terms of krypton incorporation. Insufficient data is available to show with certainty that krypton is homogeneously distributed at room temperature throughout copper films laid down in krypton at 77°K, but it is reasonable to infer that this is the case.

If this is true, then films prepared by this method should be particularly suitable for analytical chemical applications. It was decided to test this postulate using copper films, because a comprehensive investigation of the oxidation of copper kryptonates prepared by other methods has been reported by Chleck and Cucchiara (89). According to these authors, there is little release of krypton owing to reaction with oxygen at temperatures below 570°K. However, using a flow system with a quartz tube irradiated with an ultraviolet lamp located before the film vessel as an ozone generator, they observed release of krypton at temperatures as low as 370°K owing to reaction with ozone.

In view of the relatively large proportion of krypton which is released from copper films on heating to a high temperature (section 5(a).3), it was decided first to investigate whether copper films could be used as ozone detectors at low temperatures.

After preparation in the vacuum system, copper films were exposed to the atmosphere and transferred to the flow system shown in figure 58. Oxygen, supplied by the British Oxygen Co, Ltd., was passed through this system at 50 ml min^{-1}. Ozone was produced by switching on an ultraviolet lamp which was in contact with a length of ultraviolet-transparent quartz tubing in the system. The rate of ozone production in this system was determined by passing the oxygen/ozone stream in to a solution of potassium iodide. The quantity of iodine produced in a measured time was found by titration of the solution against a known solution of sodium thiosulphate using starch indicator. The

FIGURE 58 FLOW SYSTEM FOR STUDIES OF THE REACTION BETWEEN COPPER FILMS AND OZONE

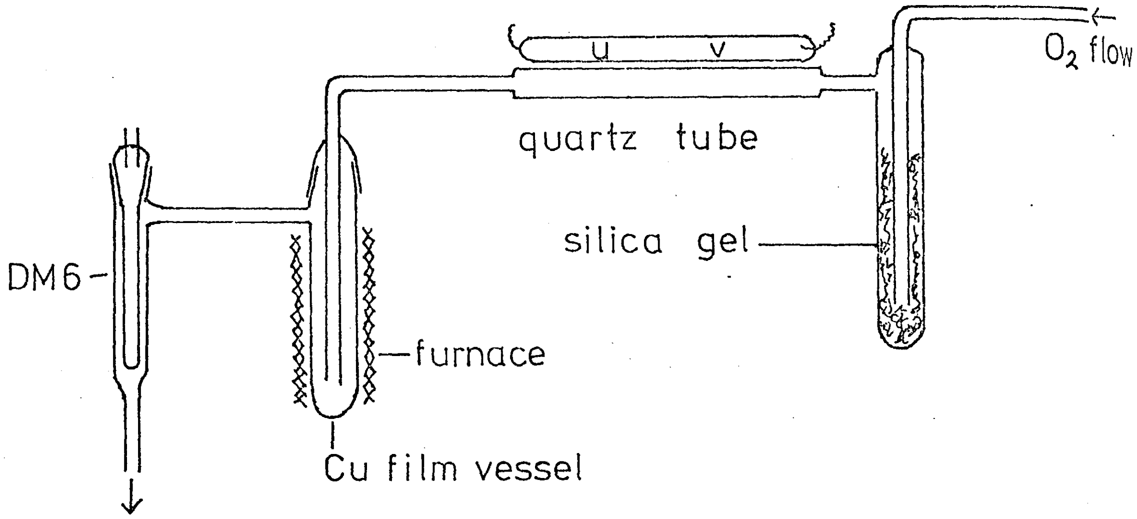
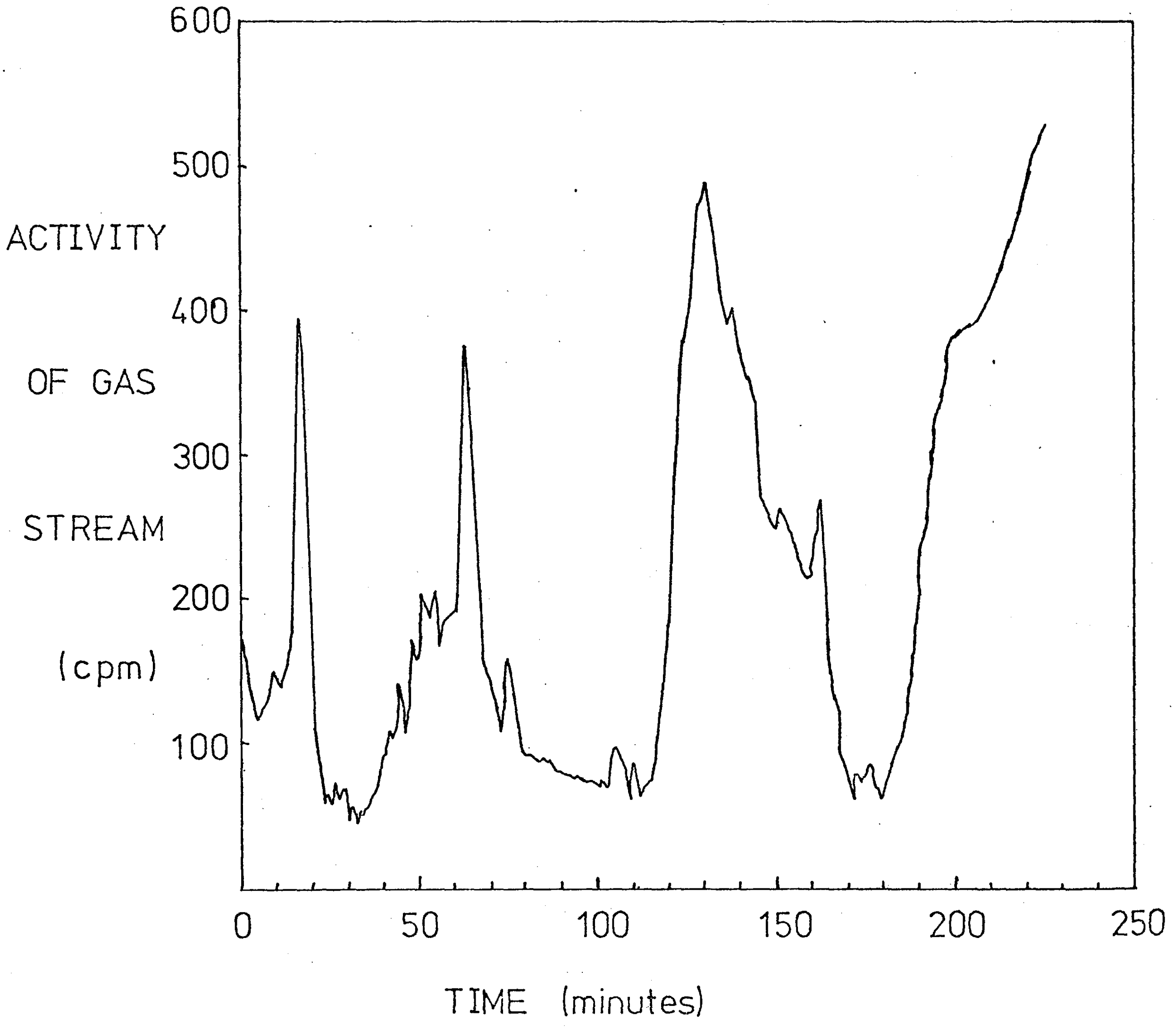


FIGURE 59 RELEASE OF KRYPTON BY FILM 74 (SEE TEXT)



rate of production of ozone was found to be 0.93 μmoles min^{-1}. No ozone was detected in the cylinder oxygen.

It was found that an all-glass system had to be employed, because otherwise the ozone produced by switching on the ultraviolet lamp reacted quickly with rubber or plastic connecting tubing.

Films 69, 71, and 74 were each sintered in vacuum for one hour at 553°K before transfer to the flow system. Despite this treatment, some krypton was released in to the flow of oxygen alone at low temperatures. The rate of release increased when the temperature was raised. Some further release of krypton was observed on switching on the ultraviolet lamp, but in view of the high, variable background activity this was difficult to assess.

The results obtained for film 74 are shown in figure 59. The treatment to which this film was subjected is given in table 36.

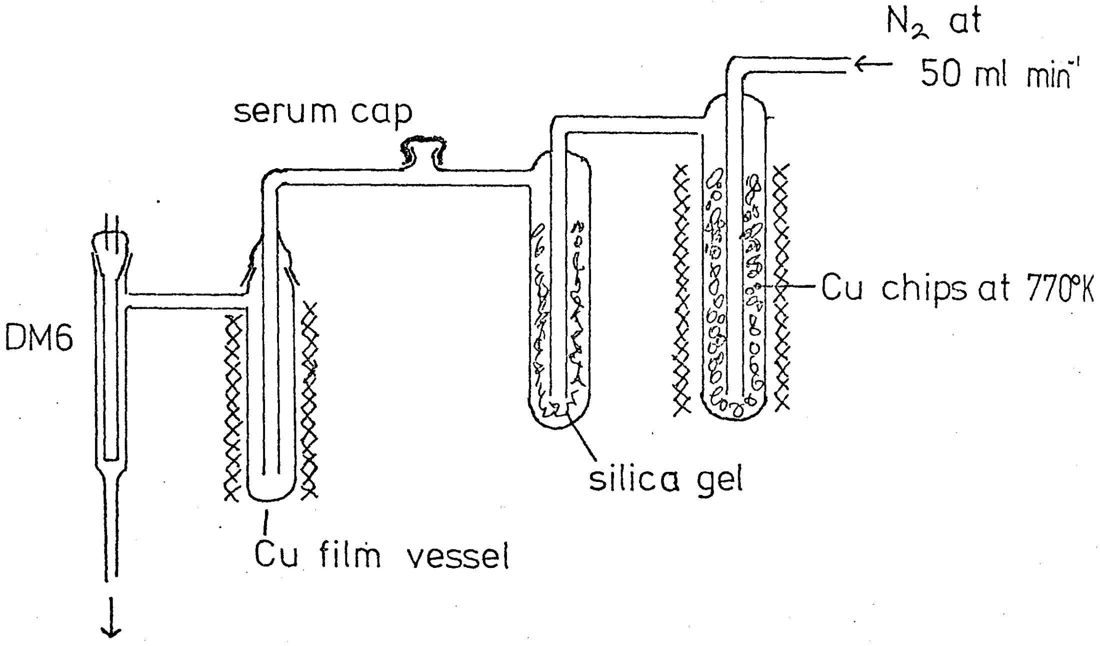
TABLE 36 TREATMENT OF FILM 74 WITH OZONE

TIME(minutes)	TREATMENT OF FILM
0	film at 292°K
16 - 22	U.V. lamp on
26 - 30	U.V. lamp on
31 - 60	temperature raised to 324°K
61 - 68	U.V. lamp on
72 - 78	U.V. lamp on
103 - 109	U.V. lamp on
110 - 150	temperature raised to 375°K
160 - 167	U.V. lamp on
172 - 176	U.V. lamp on
179 -	temperature increase; eventually reached 443°K

(When the temperature of the film reached 443°K, the count rate was over 9000 cpm)

With the film maintained at 292°K and at 324°K, a large peak of radioactivity in the gas stream resulted from the switching on of the ultraviolet lamp for the first time. The radioactivity of the gas stream began to fall in each case

FIGURE 60 FLOW SYSTEM FOR STUDIES OF THE REACTION BETWEEN COPPER FILMS AND OXYGEN



before the lamp was switched off. Subsequent switching on of the lamp produced smaller peaks.

With the film at 375°K, the corresponding peaks could only just be discerned above the background activity, and at 443°K, there was no observable increase in the activity of the gas stream when ozone was being produced.

At the end of this treatment, the film had changed colour from that of near-natural copper, to a golden-yellow. It was also more transparent than before.

It may be concluded that copper films are not suitable for use as ozone detectors in a stream of oxygen. This may be the result of the predominance of the reaction with oxygen, even at low temperatures.

It was decided to investigate whether, if this was the case, copper films might be suitable for use as oxygen-detectors in a stream of inert gas.

6.2 THE REACTION OF COPPER FILMS WITH OXYGEN; EXPERIMENTAL TECHNIQUE

After preparation by the method outlined in section 5(a).I, the films were sintered in vacuum for one hour at 553°K. As a result of this, the activity recorded by the touching counter showed a drop corresponding to the loss of 60%-80% of the krypton held at room temperature.

Each film was allowed to cool in vacuum, then air was admitted to the system, and the film vessel was detached. The film vessel was then joined in to a flow system, shown in figure 60. A flow of dry oxygen-free nitrogen was obtained by passing nitrogen (British Oxygen Co, Ltd.) at 50 ml min^{-1} through a tube packed with copper chips at 770°K, then through a tube of blue silica gel.

When the system had been flushed with nitrogen for several minutes, the temperature of the film vessel was raised to the selected value.

Oxygen and hydrogen were added to the nitrogen flow in measured amounts by means of a Hamilton syringe inserted through a serum cap before the film vessel. Small injections of oxygen were made by injecting air and assuming that the injection contained 21% oxygen. Results obtained from such injections were consistent with those obtained using pure oxygen.

Counts were accumulated by the scaler throughout an experiment. The response to a gas injection was taken to be the sum of the amounts by which the number of counts recorded in each minute exceeded the background value, over the total time that the count rate remained above the background value following the injection.

There was a delay of approximately one minute between the injection of a quantity of gas and the registering of any increase in the activity of the gas stream by the flow counter.

For experiments involving the use of electron microscopy, the film vessels used were of the design described in section 4.12. (see figure 39) The required number of mounts was introduced in to the film vessel before the deposition of the film. After exposure of such films to the atmosphere, a gas flow was established with the film vessel still attached to the vacuum system. The gas flow passed in to the system by way of the film line air leak tap, and out by way of a break in the narrow section of tubing at the end of the film vessel. The film vessel was cooled to room temperature before each removal of mounts. Other details of the electron microscopy procedures were similar to those described in section 4.12.

6.3 THE REACTION OF COPPER FILMS WITH OXYGEN; QUANTITATIVE AND DESCRIPTIVE RESULTS

Some krypton was lost in to the stream of nitrogen while each film was being heated to the working temperature in a stream of nitrogen. The quantity was much smaller than the amount lost on heating the films in a stream of oxygen. The gas phase activity reached the absolute background value of approximately 30 cpm within one hour in all cases.

It was found that some films contained traces of cuprous oxide. (see section 6.4) Accordingly films were normally pretreated with hydrogen at the working temperature. The gas stream activity at this stage was not significantly increased by injections of 10 ml hydrogen, but in some cases there was an appreciable loss of krypton when pure hydrogen was flowed through the system. As an example, the gas stream activity recorded for film 82 reached a peak of

FIGURE 61 INITIAL DECREASING RESPONSE AND INCREASING RESPONSE PERIODS FOR FILM 80

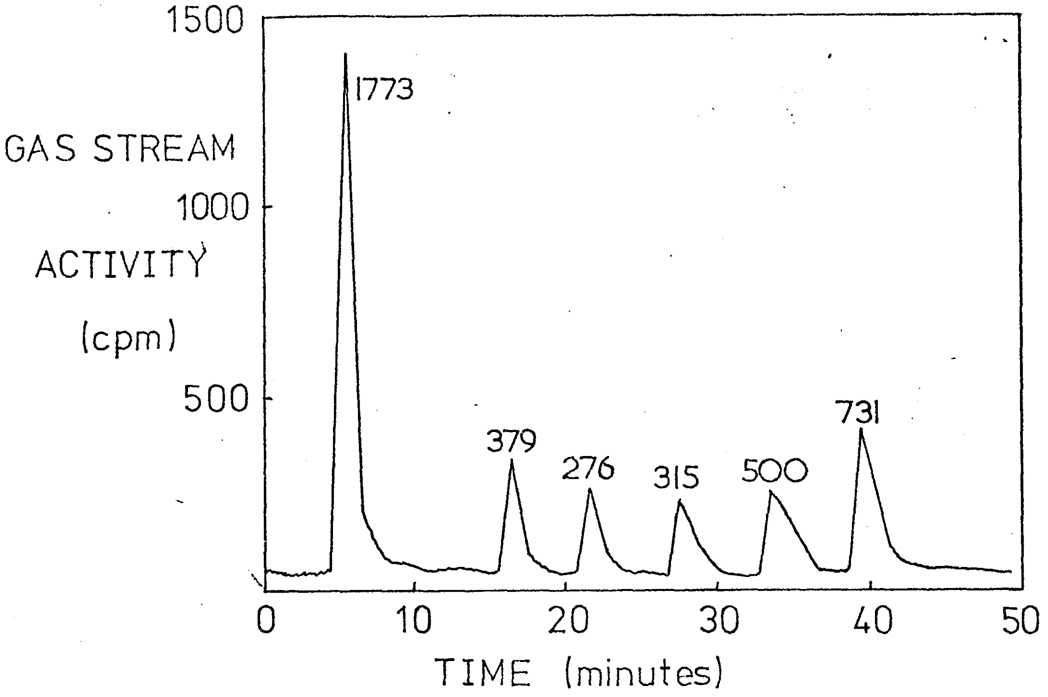
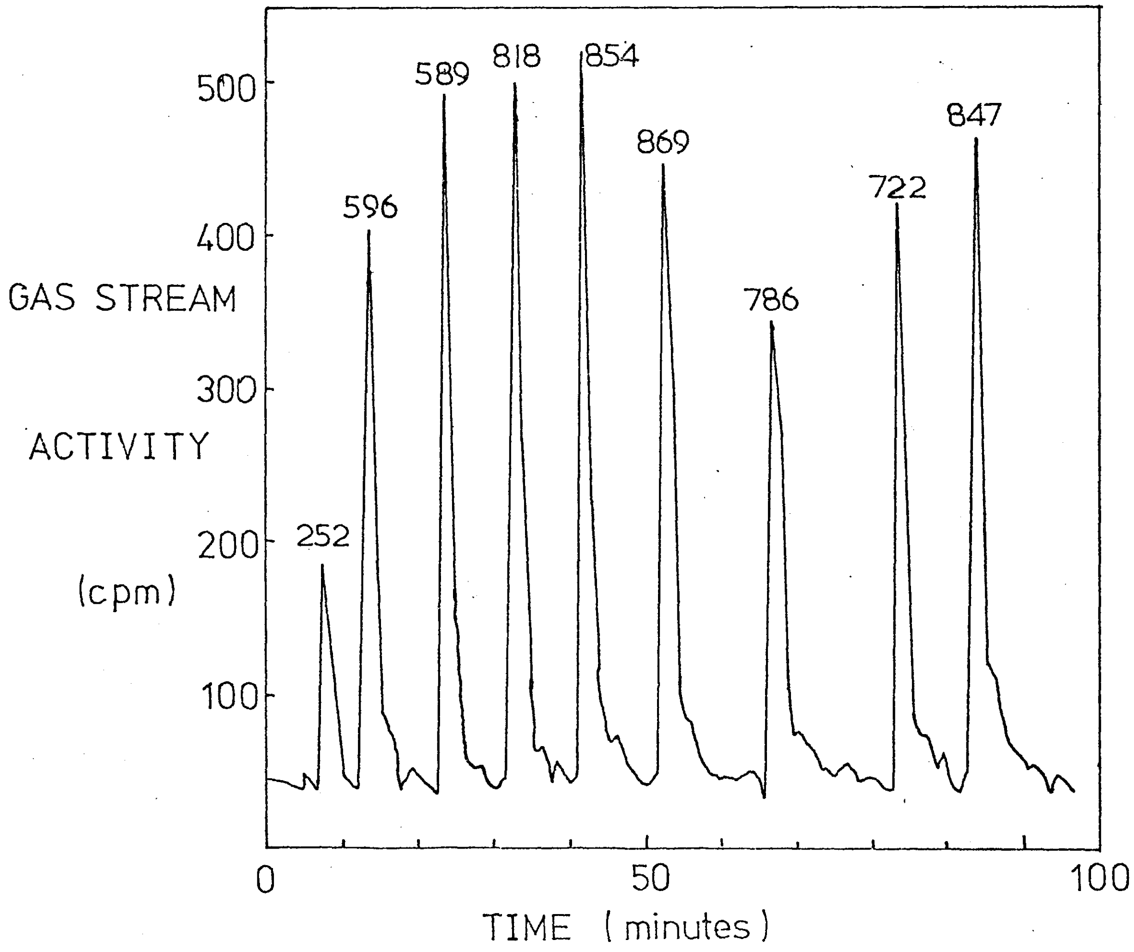


FIGURE 62 PERIODS OF INCREASING AND STEADY RESPONSE AFTER INTERRUPTING THE WORKING PERIOD OF FILM 78, AND LEAVING IN A FLOW OF NITROGEN FOR 3 HOURS AT 443°K



200 cpm, and returned to the background value within two hours. Normally, this effect was less significant.

Some evidence was found for the release of krypton owing to the reaction of copper with oxygen at 343°K, but most experiments were conducted with the films maintained at 443°K in the flow of nitrogen at 50 ml min^{-1}.

On commencing injections of oxygen to a film at 443°K, (I0 ml of air or 2 ml of oxygen) it was noted that the responses to identical, successive injections were not constant at first. However, the variation in responses followed a pattern which had similar features for all films. Three distinct phases of behaviour were noted. These were, in order:

(I) A period of decreasing responses

(2) A period of increasing responses

(3) A period of constant responses -- The working period

The decreasing response period was observed to encompass between 3 and 20 injections of 2 ml oxygen. The magnitude of the responses, and the number of injections, were not related to the weight of the film.

The increasing response period was observed to comprise between 3 and 4 injections of 2 ml oxygen. In two cases it was completely absent.

In the working period, the responses to successive oxygen injections remained constant over long periods, and proportionate responses were produced by varying the quantity of oxygen injected.

The value of the background activity, against which the response to each injection was measured, was found to be important. It was found that if the background activity was allowed to return to the absolute value of 30 cpm, after an oxygen injection, then the response to the next oxygen injection was reduced. Proportionate responses for successive injections were found when the background activity was kept in the region of 40 - 70 cpm. If the background activity was much higher than this, it was found that the response was related not only to the quantity of oxygen injected, but also to the background activity.

In other words, consistent behaviour was only observed when oxygen injections were made during the time when the peak in gas stream activity resulting from the previous injection had almost, but not quite, returned to the natural

FIGURE 63 INCREASING RESPONSE TO SUCCESSIVE OXYGEN INJECTIONS ASSOCIATED WITH RISING BACKGROUND ACTIVITY (FILM 75)

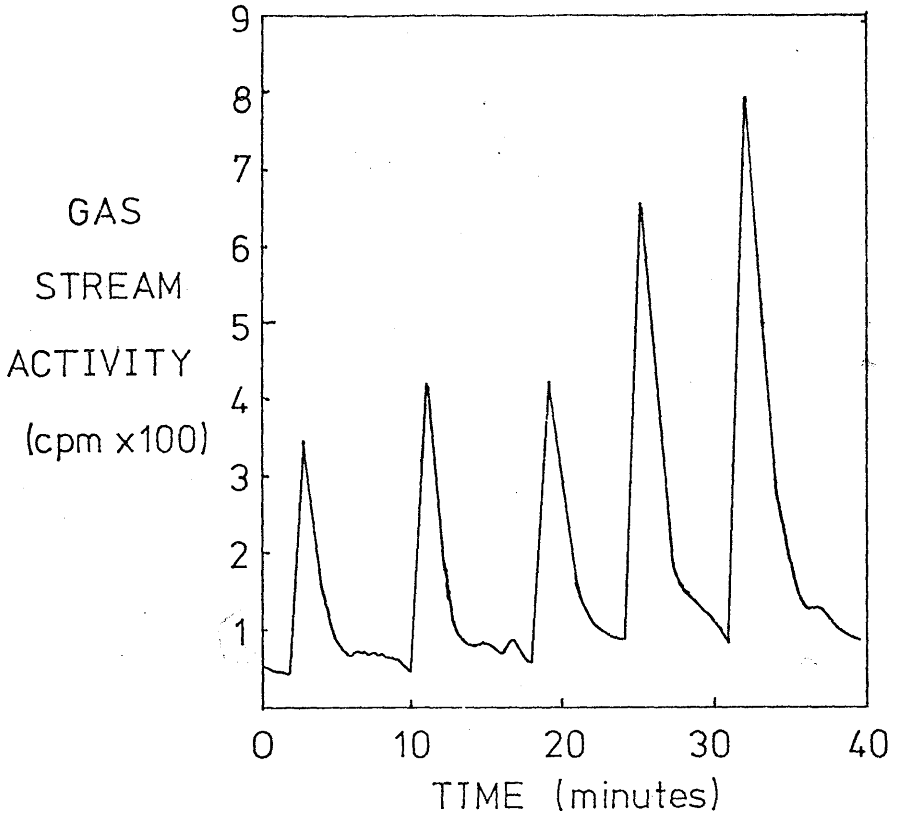
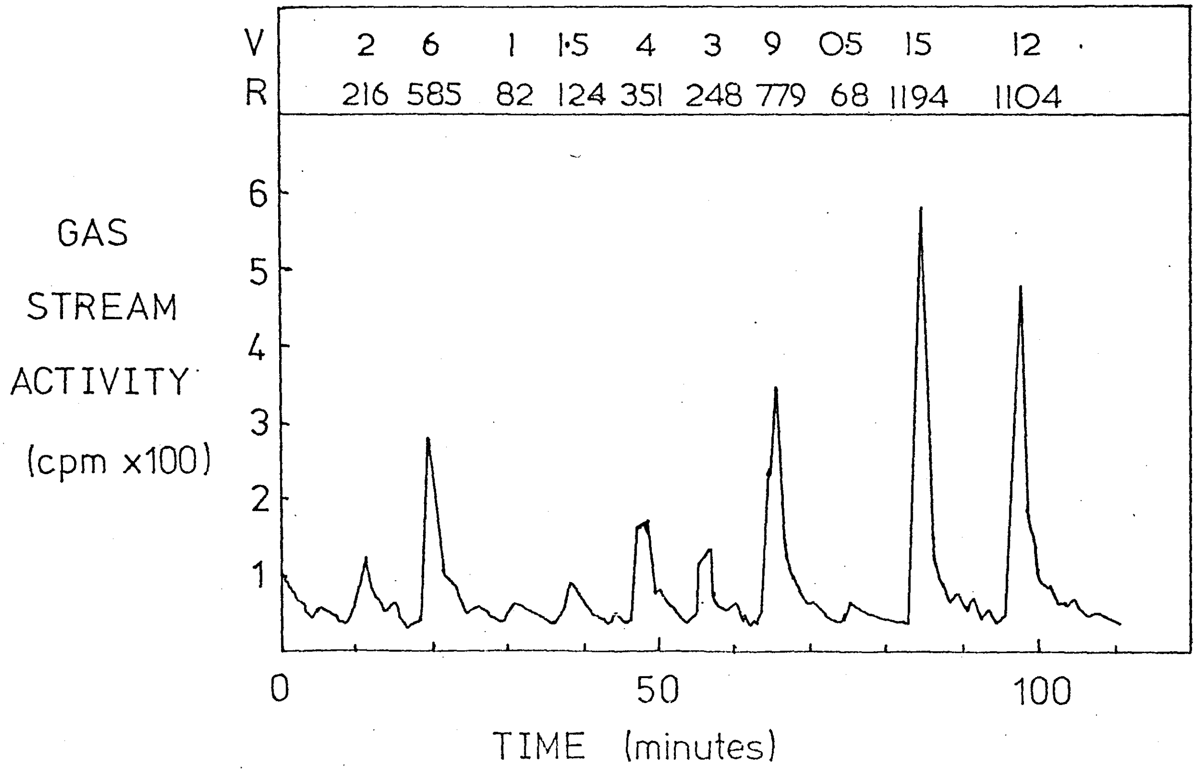


FIGURE 64 PROPORTIONATE RESPONSES OF FILM 78 TO INJECTIONS OF VARIOUS AMOUNTS OF AIR

V = volume of air injected (ml)
R = number of counts released



V	2	6	1	1·5	4	3	9	05	15	12
R	216	585	82	124	351	248	779	68	1194	1104

background value.

If a film was left in the flow of nitrogen for some hours at 443°K during the working period, a short period of increasing responses was again observed before proportionate responses were obtained.

Examples of the various types of behaviour described above are shown in figures 61 - 64. It should be noted that the area of a peak, not its height, is significant. The figure above each peak represents the number of counts released by the particular injection of oxygen.

General details of the results obtained for the six films studied are given in table 37.

TABLE 37 INITIAL RESPONSES OF COPPER FILMS TO INJECTIONS OF 2 ml OXYGEN AT 443°K

FILM No	DECREASING RESPONSE PERIOD	INCREASING RESPONSE PERIOD
75	6 injections: 2000 - 200 counts	4 injections
78	3 injections: 690 - 400 counts	4 injections
79	3 injections: 400 - 100 counts	4 injections
80	3 injections: 1770 - 280 counts	3 injections
82	4 injections: 190 - 70 counts	none
83	20 injections: 13000 - 600 counts	none

NOTES: (1) Film 82 was inadvertently opened to the atmosphere during sintering at 553°K. This is believed to have resulted in extensive oxidation of this light film.

(2) Film 83 was partly broken, and some sections became detached from the walls of the film vessel, during sintering. It was also much heavier than the other films.

The working period of a film, during which time consistent responses to oxygen injections were obtained, could extend over a period of several days.

Figure 65 shows the responses of film 78 to injections containing up to 4 ml of oxygen (measured at atmospheric pressure and at 295°K), in two operating sessions separated by a time of fourteen hours.

Figure 66 shows the responses of film 83 to injections containing up to 10 ml of oxygen, in five operating sessions separated by periods of 2, 12, 2.5,

FIGURE 65 RESPONSES OF FILM 78 TO SMALL INJECTIONS OF OXYGEN

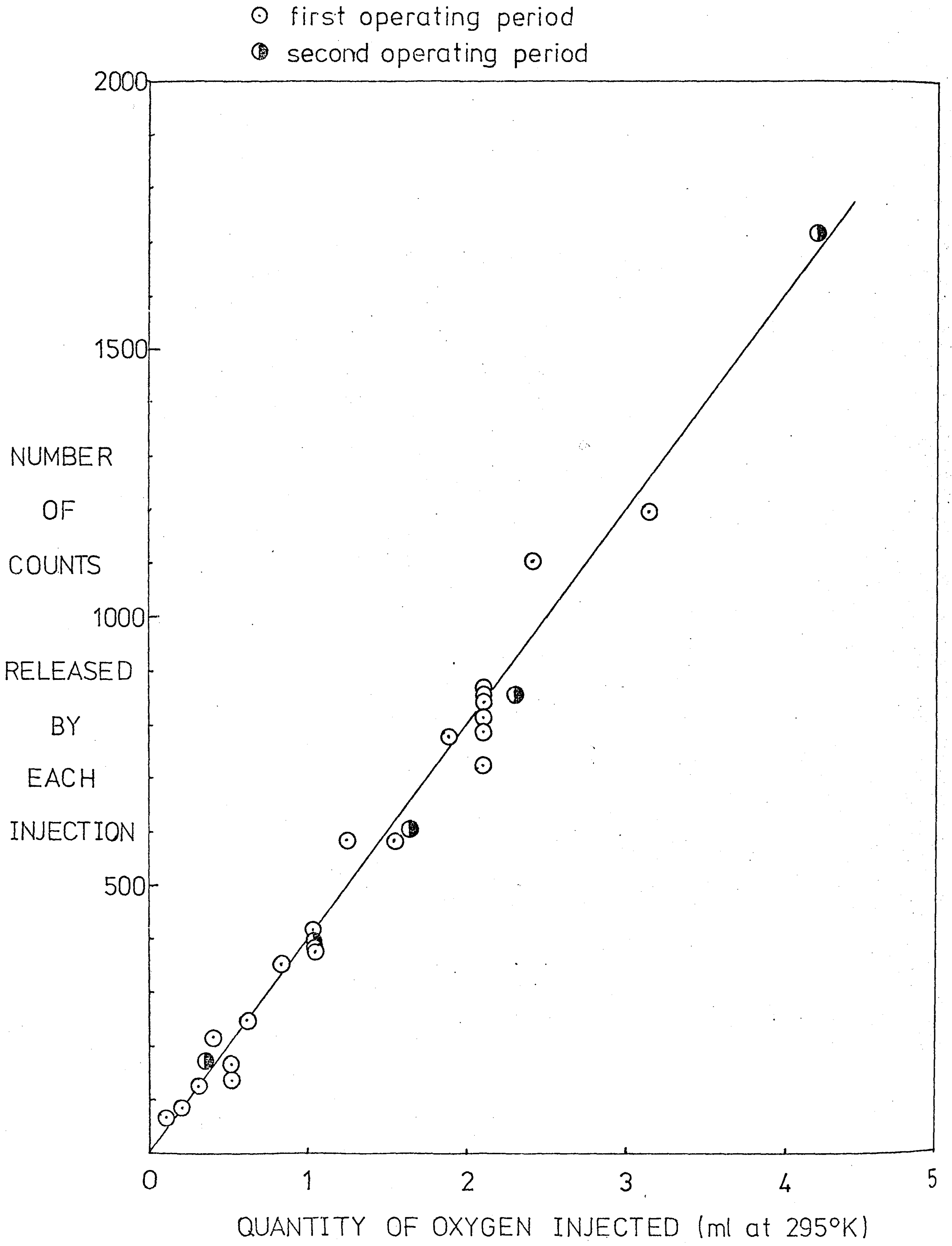
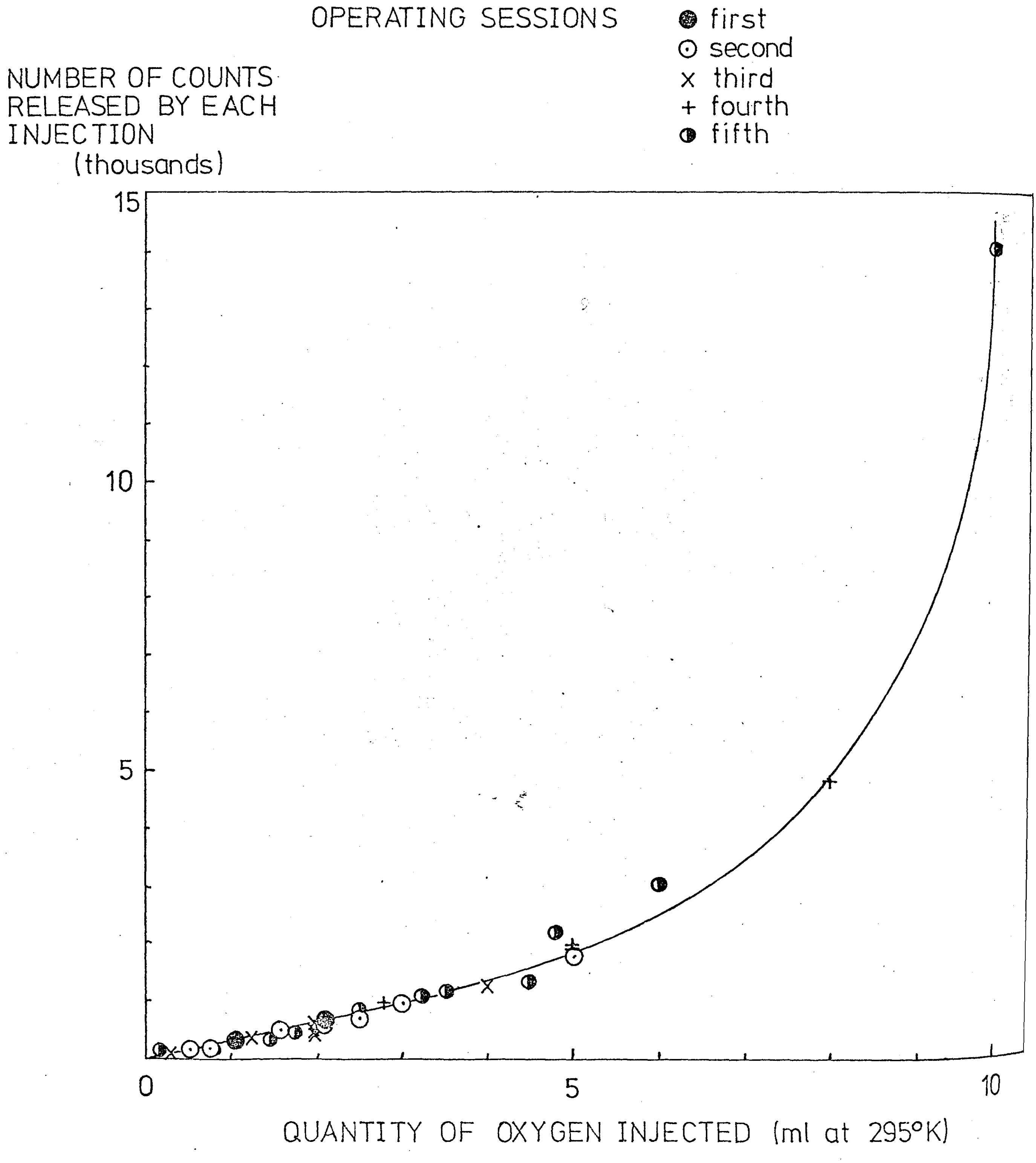


FIGURE 66 RESPONSES OF FILM 83 TO INJECTIONS CONTAINING UP TO 10ml OF OXYGEN



and 17 hours.

It was invariably found that small injections of oxygen produced proportionate increases in the activity of the gas stream, but large injections (over 4 ml) produced disproportionately large responses.

The slopes of the linear region of the plot of response against the size of the injection of oxygen, for five films, are given in table 38.

TABLE 38 MEAN RESPONSE OF COPPER FILMS TO SMALL INJECTIONS OF OXYGEN AT 443°K

FILM No	SLOPE OF LINEAR REGION OF THE RESPONSE PLOT (counts ml^{-1})
75	$\approx$ 400
78	433
79	320
80	309
83	307

For the purposes of compiling this table, the slopes have been referred to doses of oxygen at S.T.P. (figures 65 and 66 show the experimental values for injections of oxygen under laboratory conditions).

The value for film 75 is not known with certainty, because the necessity of controlling the approach to background activity was not then understood.

It was found that when a steady flow of oxygen was added to the nitrogen stream, by means of regular injections of oxygen spaced thirty seconds or one minute apart, the total response was greatly in excess of what would have been predicted for the sum of the individual injections. From the results of table 38, the response to a single injection of 6 ml oxygen would be expected to be approximately 2000 counts. However, when the same quantity of oxygen was added to the gas stream passing over film 75, as 54 injections of 0.5 ml air spaced thirty seconds apart, the gas phase activity rose to 300 cpm above the background within 15 minutes of starting injections, and then remained approximately constant until injections ceased, when it returned slowly to the background value. (see figure 67) The total response to the series of injections was therefore approximately 9000 counts. Where the continual injections were larger, this effect was still more pronounced. The injection of air to film 75 at a

FIGURE 67 RESPONSE OF FILM 75 TO A FLOW OF OXYGEN EQUIVALENT TO 0·21 ml min^{-1}

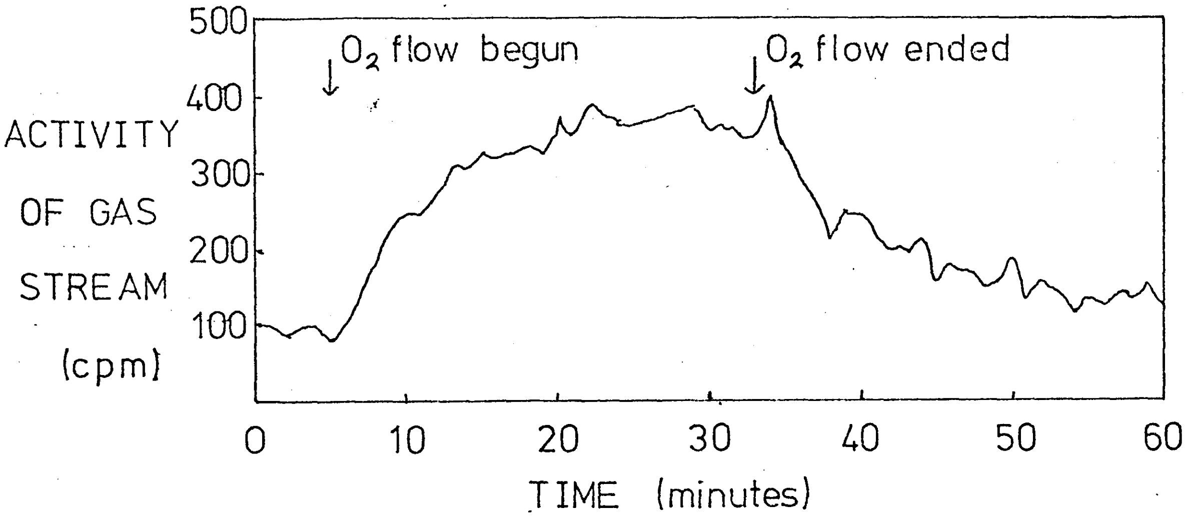
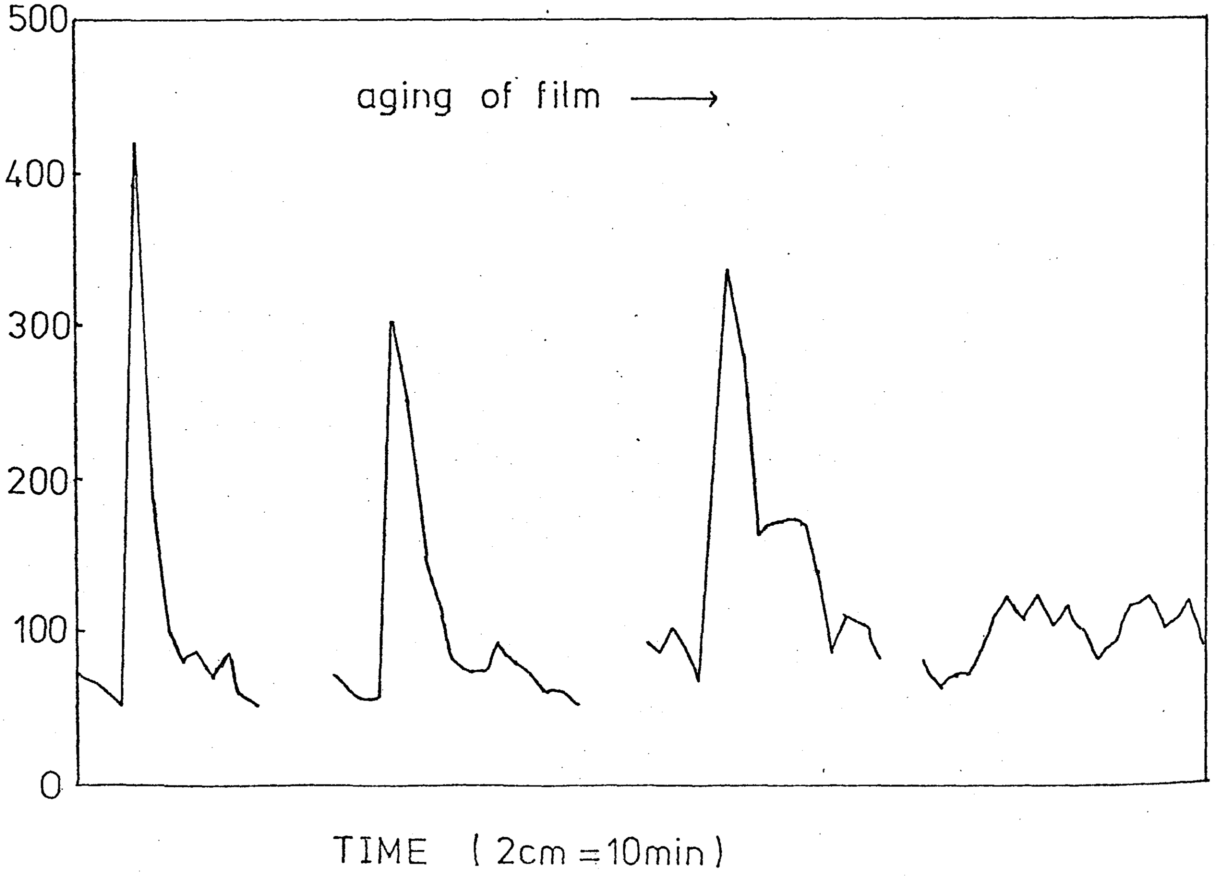


FIGURE 68 CHANGE OF PEAK SHAPE DURING WORKING PERIODS OF FILM 75 (10 ml air injections)



rate amounting to 2.5 ml $\min^{-1}$, resulted in a count rate of 5000 cpm.

Although the total response in terms of counts released was consistent for small injections of oxygen during the working period, the shape of the peaks changed during the working period. For a fresh film, the peaks were sharp, and the activity of the gas stream returned to the background value within six to seven minutes. As the film grew 'older', the peaks became less sharp, and lengthened to twenty minutes or more. The change in peak shape during the working periods of film 75 is illustrated in figure 68.

Eventually peaks became so indistinct that it was not possible to evaluate the total activity released above the background.

There was some evidence to suggest that the peaks were in fact double, consisting of a fast response followed by a slower process, and that the quantity of krypton released by the slow process became more significant as the film was progressively oxidised.

An experiment was conducted using a film vessel with no copper film, but with all other characteristics of the flow system identical to the normal working conditions. The purpose of this experiment was to assess how much variation of responses might be caused by purely random factors such as the time taken to make an injection, variation in the flow rate, etc. A mixture of air and ^{85}Kr, of convenient activity, was prepared. 10 ml portions of this mixture were injected by way of the serum cap, and the gas stream activity was monitored in the usual way.

The peaks observed were sharp. The time by which the response was delayed appeared to be rather less than for an experimental injection, but the experimental method did not permit of an estimation of the actual difference. The gas stream activity returned to the background value in approximately four minutes. The mean response to six 10 ml injections of the standard mixture was 996 counts. The standard deviation from this value was 69 counts, or 7%.

It is apparent that much of the observed variation in responses to equal injections of oxygen to a copper film at 443°K, may be explained by physical variations in the system. The response is shown not to be instantaneous, but to be partly time-controlled, as the gas stream activity remained above the

FIGURE 69 RESPONSES OF OXIDISED FILM 75 TO 10ml INJECTIONS OF HYDROGEN

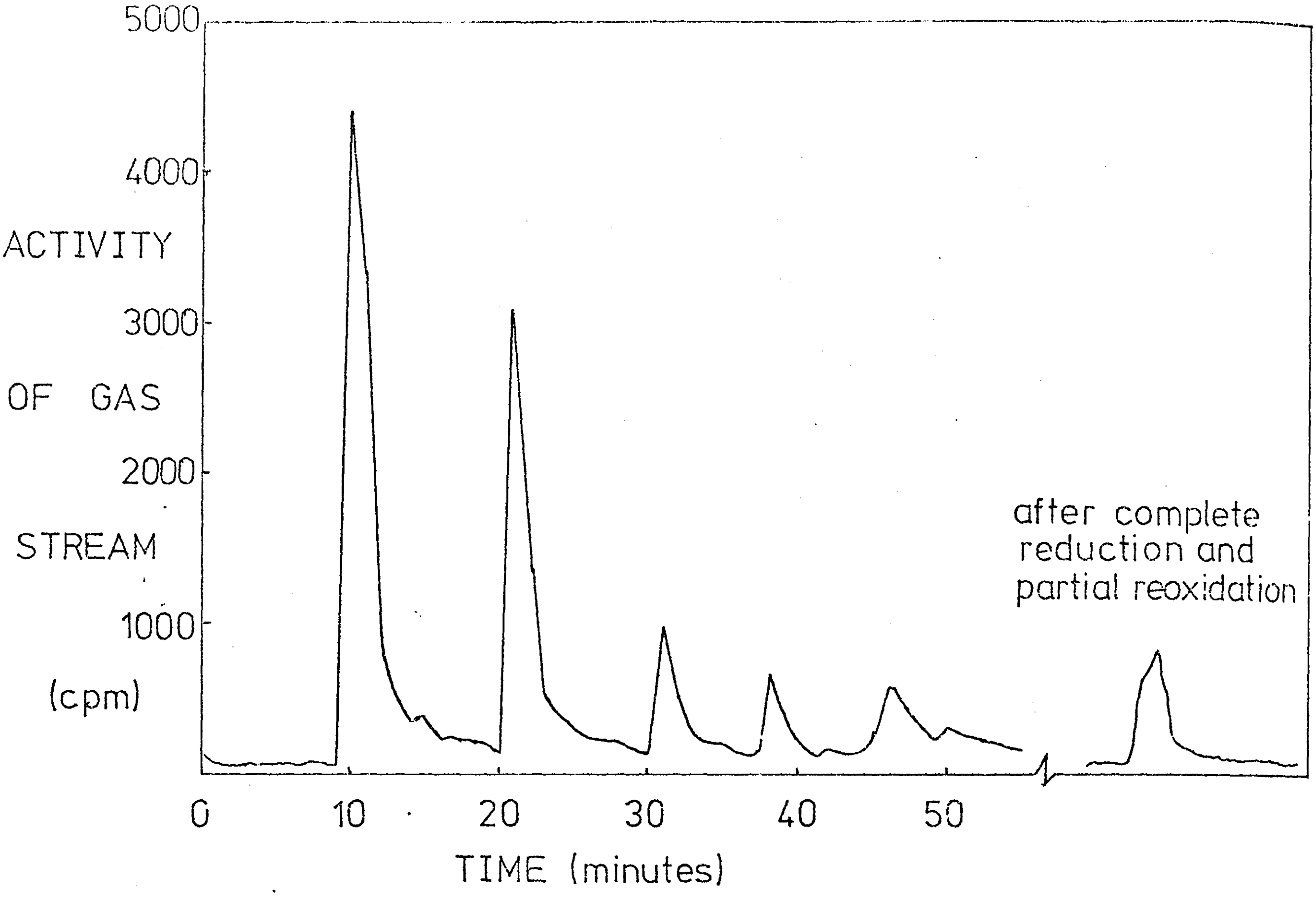
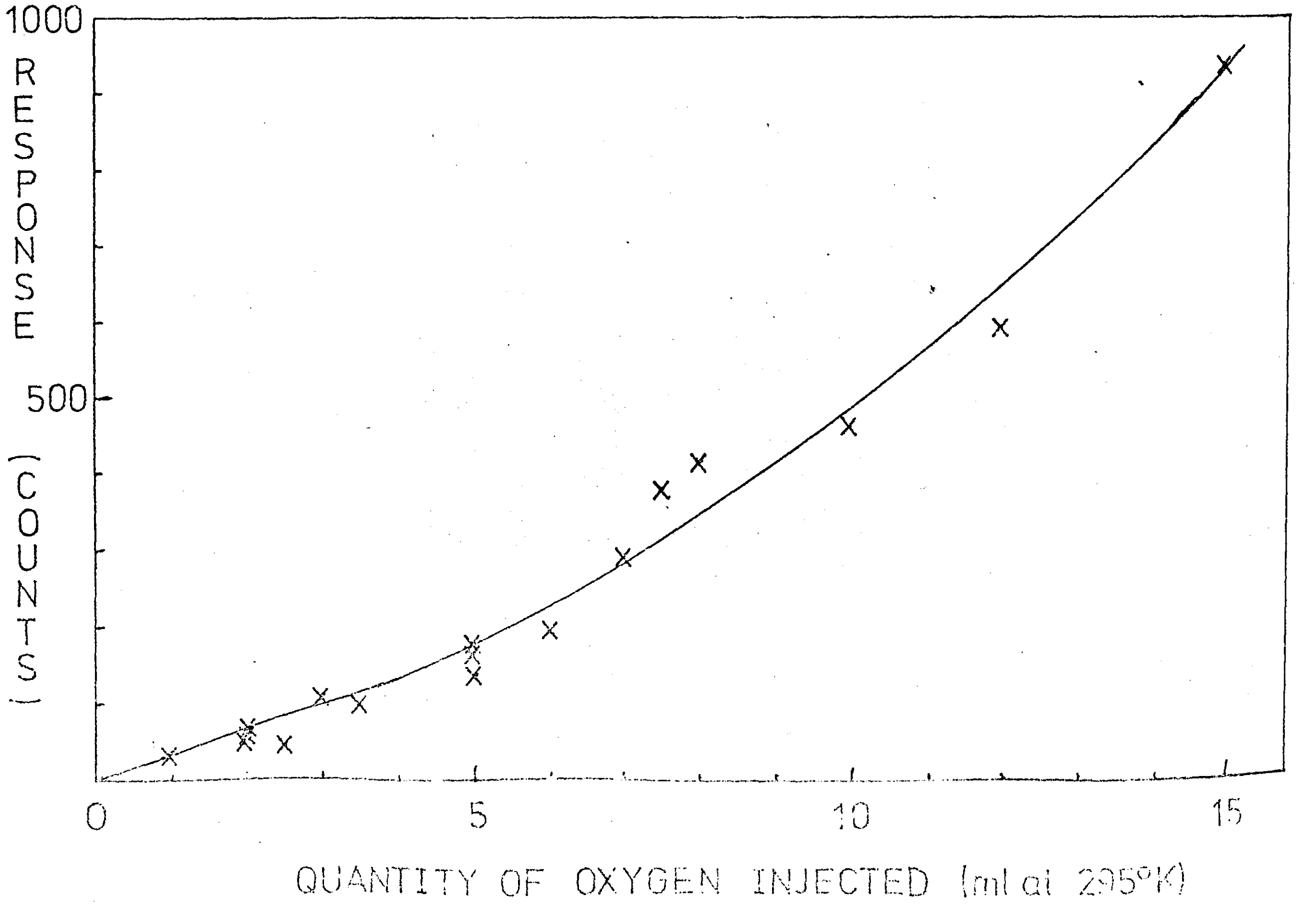


FIGURE 70 RESPONSES OF FILM 83 TO OXYGEN INJECTIONS AFTER REDUCTION BY HYDROGEN



background value for at least six minutes for all experimental peaks.

After a film had been extensively oxidised, it was found that injections of hydrogen produced responses of increased gas stream activity.

Film 75 was oxidised more than any other film in the working period, so that the responses to oxygen injections were very indistinct. The responses to five injections of 10 ml of hydrogen to the film at 443°K, are shown in figure 69. After this treatment, the injection of 10 ml of hydrogen each minute resulted in a rise in the activity of the gas stream to 600 cpm for ten minutes, followed by a drop to the background value over some thirty minutes. Thereafter, injections of hydrogen produced no significant response.

However, injections of oxygen now produced a series of consistent peaks which were quite sharp, but of smaller magnitude than before. After a series of injections amounting to approximately 30 ml of oxygen, it was again found that the film responded to an injection of hydrogen. (see figure 69)

For other films which were initially less extensively oxidised, the response to individual injections of hydrogen was much less; however, in all cases there was an appreciable response to a flow of hydrogen. Once reduction was complete, the responses to oxygen injections were consistent but smaller than before, and the peaks were sharper than those observed immediately before reduction.

Figure 70 shows the plot of response against the quantity of oxygen injected to film 83 after reduction, and may be compared to figure 66.

No attempt was made to relate the decrease in response to the degree of oxidation and reduction of the films studied. For films 75 and 79, the responses after reduction were approximately 50% of those observed in the earlier working period. For film 83, the value was approximately 10%, but in this case a second long decreasing response period was observed, commencing with a response of approximately 4000 counts to an injection of 2 ml of oxygen.

One film, No 78, responded neither to hydrogen nor oxygen after being left in the gas stream over three days. During this time, the silica gel in the flow system had turned completely pink, and it is believed that exposure to water vapour may have desensitised the film in some way. A similar poisoning effect may account for the low level of responses found for film 83 after reduction, described above. In this case also, the responses eventually stopped, although a considerable quantity of krypton was found still to be held by the film when a count with the parallel counter was made at room temperature.

In all cases, the film was found to retain some krypton at the end of the oxidation-reduction treatment. The quantity was uncertain because the final activity was low. Approximate values are given in table 39.

TABLE 39 RETENTION OF KRYPTON BY COPPER FILMS AFTER OXIDATION-REDUCTION TREATMENT

FILM No	% OF INITIAL QUANTITY OF KRYPTON (AFTER SINTERING IN VACUUM), RETAINED BY EACH FILM.
75	28%
78	I2%
79	29%
83	46%

The initial atomic % of krypton held by these films after sintering in vacuum for one hour at 553°K, was approximately 0.I%.

After oxidation, all films were golden-yellow in colour. Reduction restored the colour of natural copper.

When the films were dissolved in acid for the determination of their weights by colorimetry, the colour appeared to revert to that of natural copper before complete dissolution. This is taken to show that oxidation was not complete, but that the colour of the film was derived mainly from the oxide, which dissolved more quickly in acid than did unreacted copper.

The details of the determination of film weights by colorimetry are given in appendix F.

In view of the complexity of the phenomena observed, it was decided to investigate the morphological changes in the films during oxidation and reduction by means of electron microscopy, and to attempt to identify the oxide formed by electron diffraction.

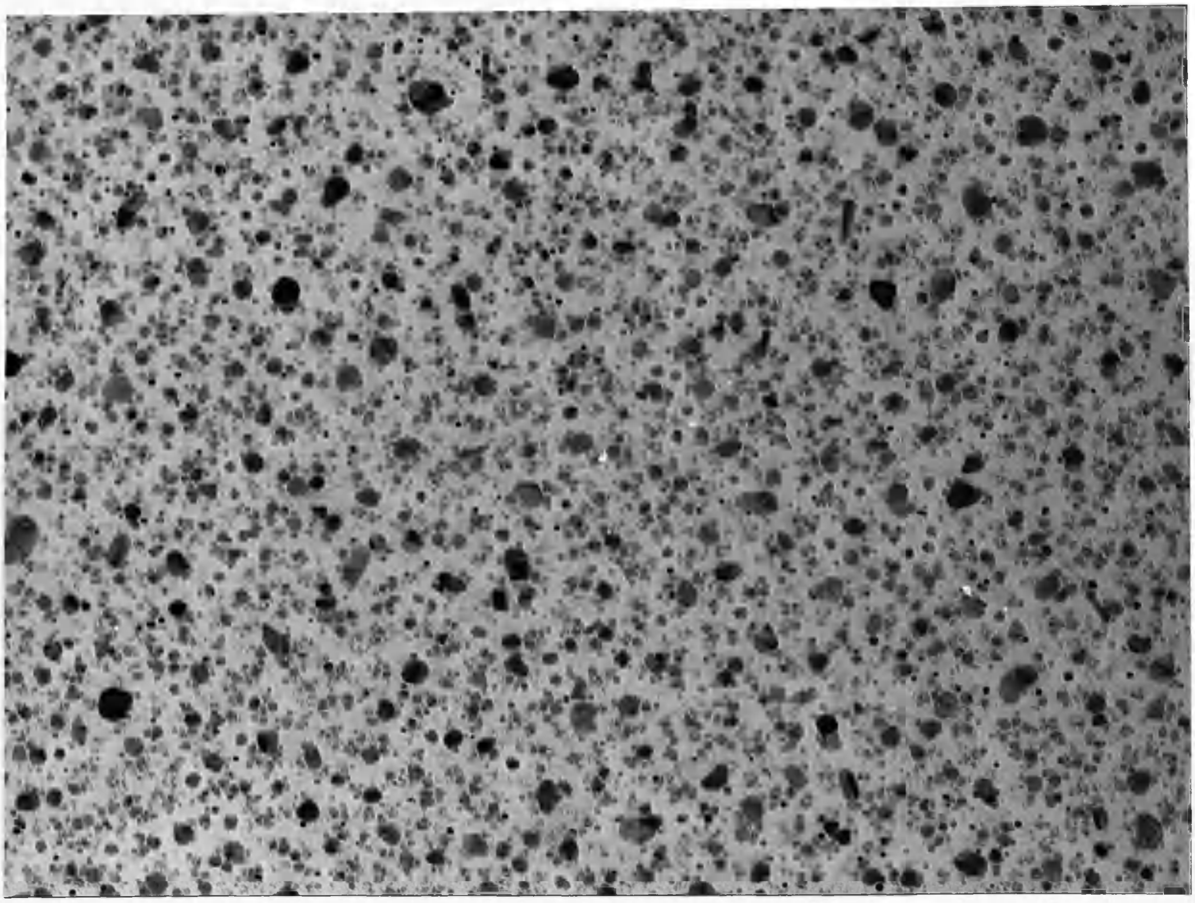


PLATE 5 A COPPER FILM DEPOSITED IN 4xI0^{-2} torr OF KRYPTON AT 77°K, AND SINTERED AT 550°K FOR I HOUR (x80,000)

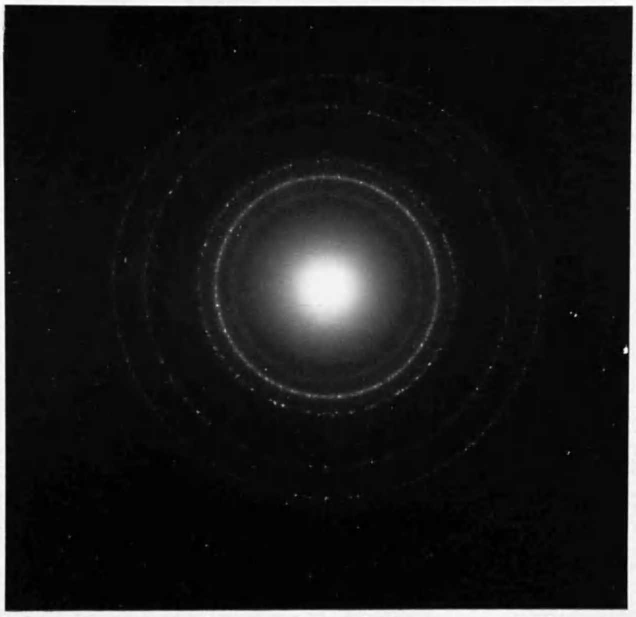


PLATE 6 THE ELECTRON DIFFRACTION PATTERN OBTAINED FROM THE FILM ABOVE

6.4 THE REACTION OF COPPER FILMS WITH OXYGEN; RESULTS OF INVESTIGATION BY ELECTRON MICROSCOPY

Oxidation and reduction were effected by passing streams of pure oxygen or hydrogen respectively through the film vessel at 443°K. Two films were studied.

The appearance of a copper film sintered in vacuum at 553°K for one hour is shown in plate 5. The film consisted of isolated crystallites, up to 1000 A° in diameter. This plate shows a thin portion of film 77; micrographs of film 81 were identical. Other portions of film 77 were thicker, and the crystallites were not completely isolated from each other. The electron diffraction patterns for these films showed the structure of pure copper, with traces of cuprous oxide. The diffraction data for film 77 are given in table 40; the lattice spacings were calculated by comparison with a thallium chloride standard. Plate 6 shows the diffraction pattern obtained for this film.

TABLE 40 ELECTRON DIFFRACTION DATA FOR FILM 77 BEFORE OXIDATION

RING DIAMETER ON PLATE (mm)	DERIVED LATTICE SPACING (A°)	COPPER LATTICE SPACING (A°)
18.5	2.09	2.088
21.3	1.81	1.808
30.2	1.28	1.278
35.5	1.09	1.090
37.2	1.04	1.044
43.0	0.90	0.904
47.1	0.82	0.829
48.5	0.80	0.808

Weak, diffuse rings of diameter 12.8 mm, 15.6 mm, and 25.6 mm, are assigned to the presence of traces of cuprous oxide. This may arise because of oxidation during handling in air, or because of inefficient degassing before deposition of the film. Oxidation during exposure to the atmosphere for a few minutes at room temperature has been reported by Bachmann, Sawyer, and Siegel (55), and this is believed to be the likely explanation of the present observation.

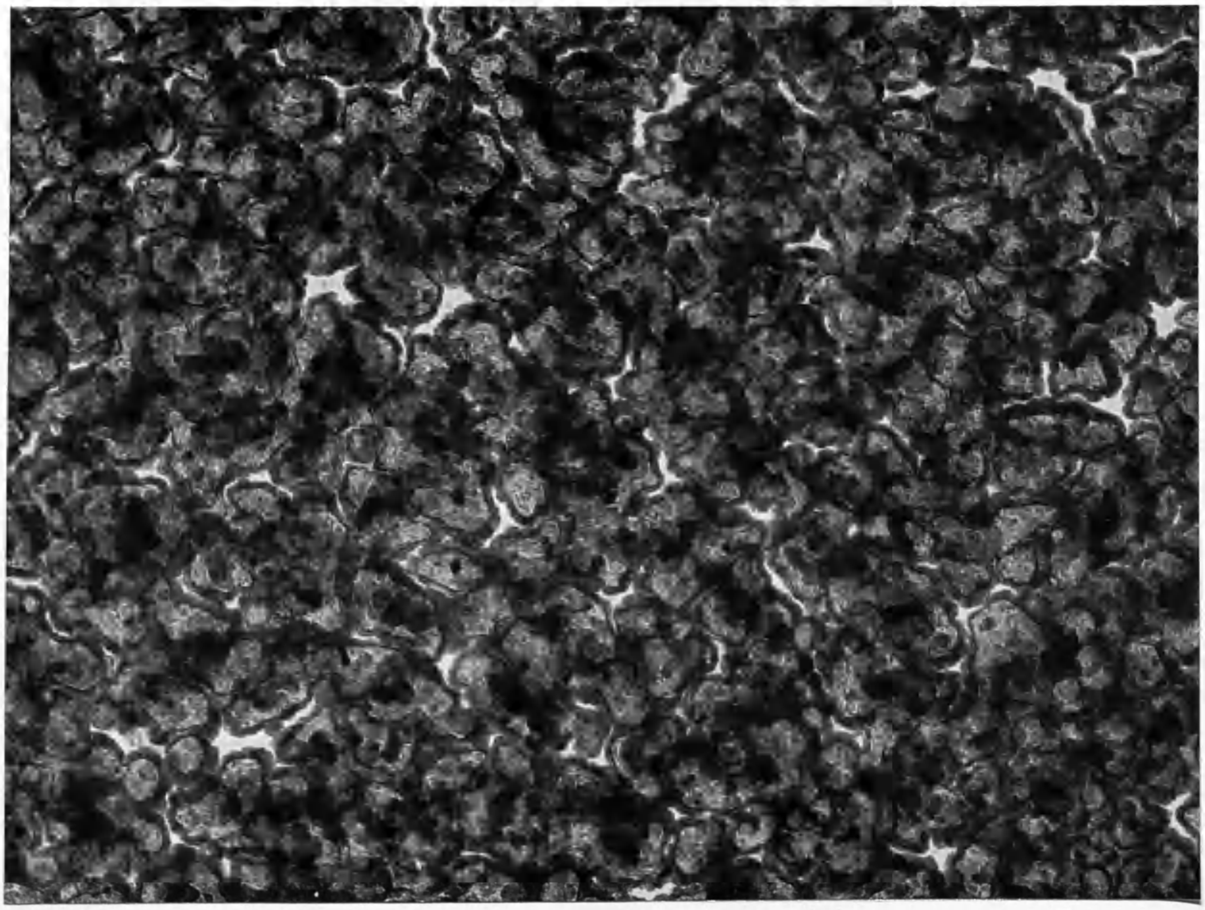


PLATE 7 A PARTIALLY OXIDISED COPPER FILM (x80,000)

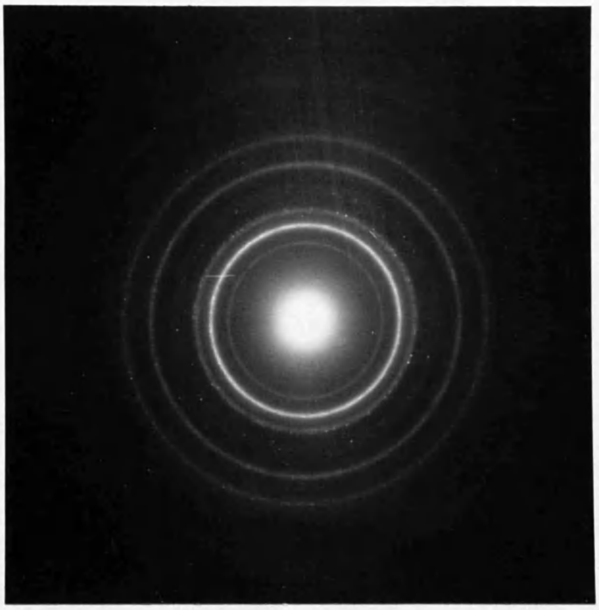


PLATE 8 THE ELECTRON DIFFRACTION PATTERN OBTAINED FROM THE FILM ABOVE

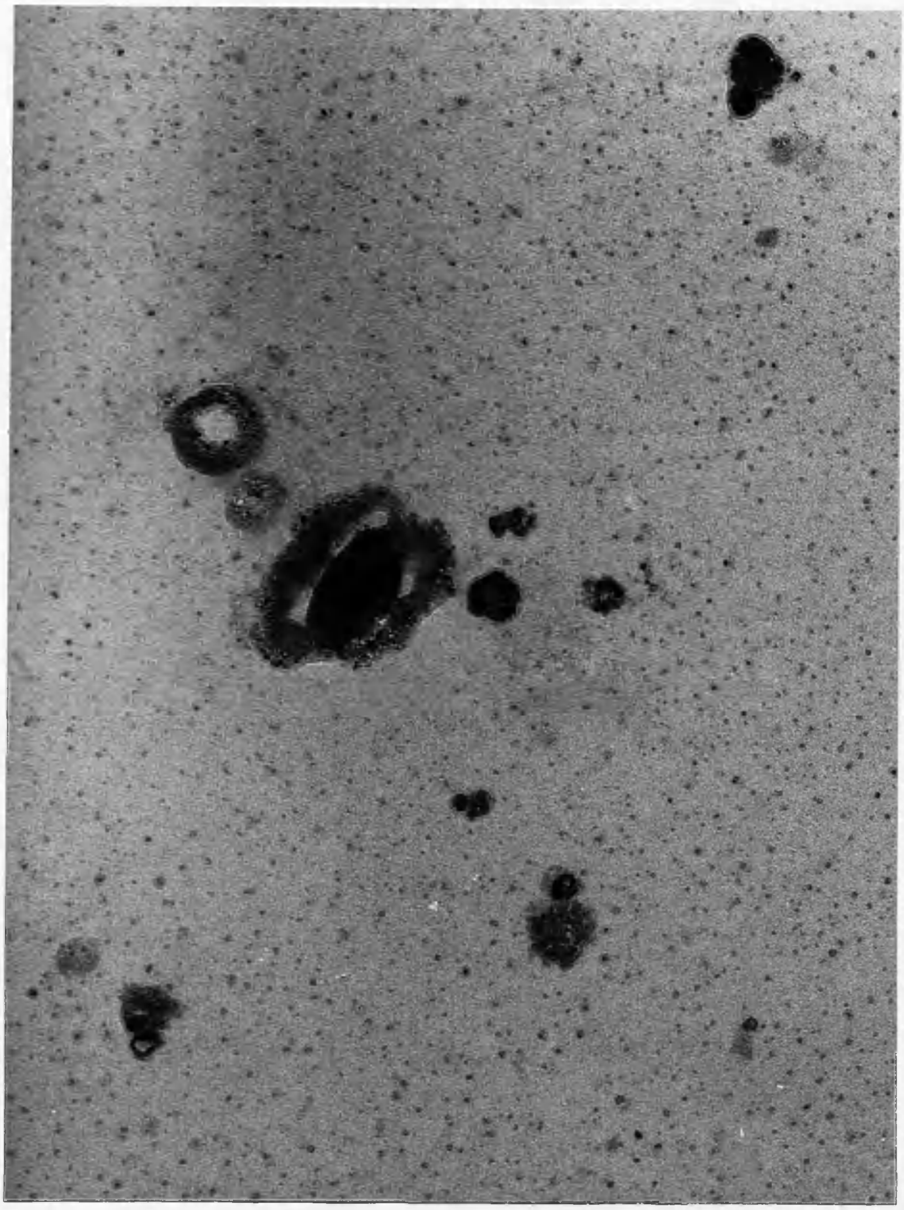


PLATE 9 A PARTLY OXIDISED COPPER FILM, SHOWING THE FORMATION OF AN ANNULAR OXIDE PARTICLE FROM A COPPER CRYSTALLITE (x80,000)

After one hour in a stream of oxygen at 443°K, the appearance of the film had changed considerably (plate 7), and the diffraction pattern was that of cuprous oxide, with traces of copper present (plate 8). The micrograph was taken from a thicker portion of the film than that of plate 5.

Further treatment in an oxygen stream at 443°K, to a total of 23 hours, changed the appearance of the film to that shown in plate I0. The diffraction pattern (plate II) was that of cuprous oxide, with traces of cupric oxide and copper. The diffraction data for this sample are given in table 4I.

TABLE 4I DIFFRACTION DATA FOR FILM 77 AFTER OXIDATION

RING DIAMETER ON PLATE (mm)	DERIVED LATTICE SPACING (A°)	LATTICE SPACING OF CUPROUS OXIDE (A°)
I2.8	3.02	3.020
I5.7	2.46	2.465
I8.2	2.I2	2.I35
22.3	I.73	I.74I
25.9	I.49	I.5I0
30.0	I.29	I.297

The weak ring of diameter 24.5 mm is attributed to copper, and very weak rings of diameter I5.2 mm, I6.5 mm, and 27.5 mm, are attributed to the 2.530 A°, 2.320 A°, and I.4I0 A° lattice spacings of cupric oxide.

However, the film was almost entirely cuprous oxide. The electron diffraction pattern obtained after one hour, represents an intermediate phase, when conversion to cuprous oxide was less complete.

It has thus been shown that at 443°K in a flow of pure oxygen, copper films react with oxygen to give cuprous oxide. The time required in a flow of pure oxygen to produce even trace amounts of cupric oxide precludes its formation under the experimental conditions, where less oxygen was available.

The particles of oxide formed during this process were annular in appearance. This shows that copper migrates from the crystallite which is being oxidised, in to the oxide layer. This process had been completed by the time that the micrograph of plate I0 had been taken; that of plate 7 shows an intermediate

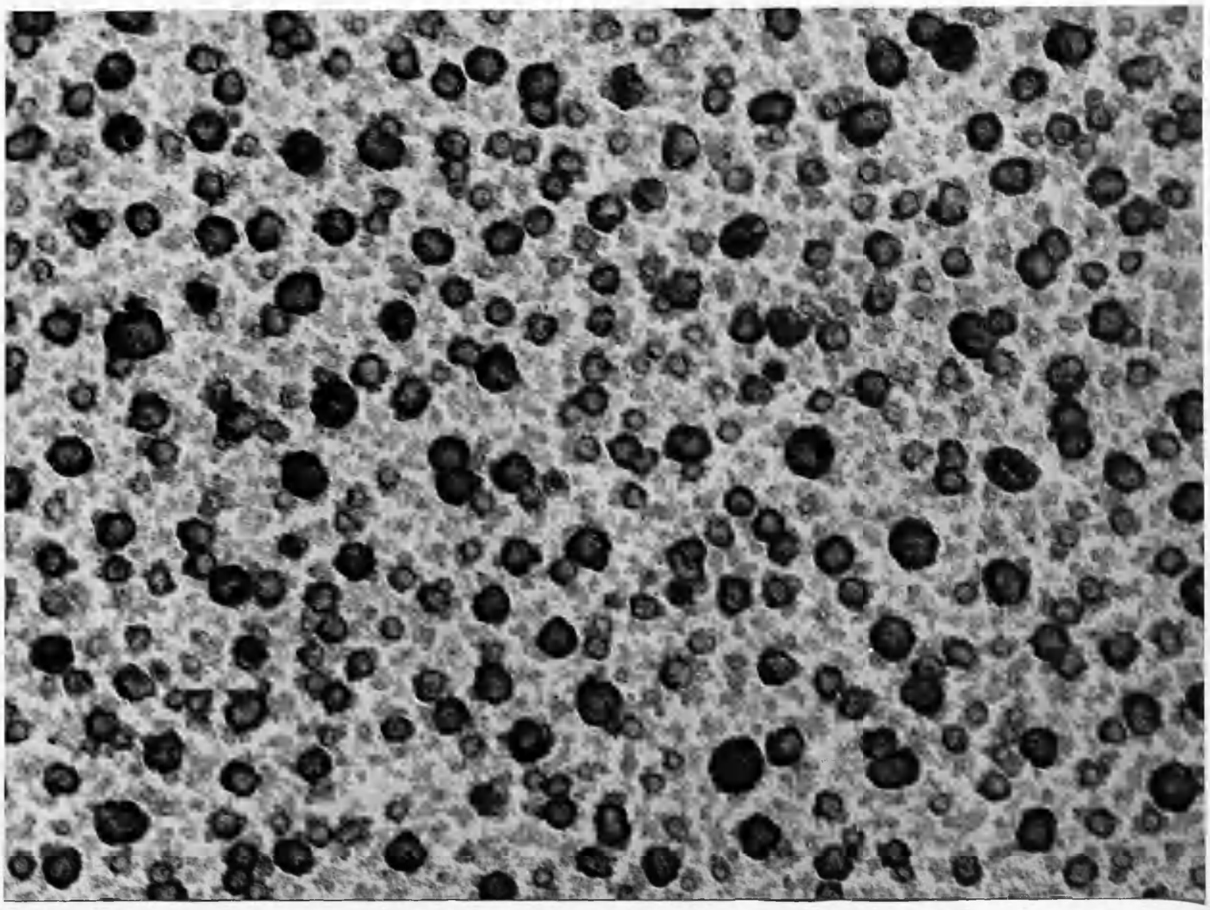


PLATE IO A COMPLETELY OXIDISED COPPER FILM (x80,000)

PLATE II THE ELECTRON DIFFRACTION PATTERN OBTAINED FROM THE FILM ABOVE

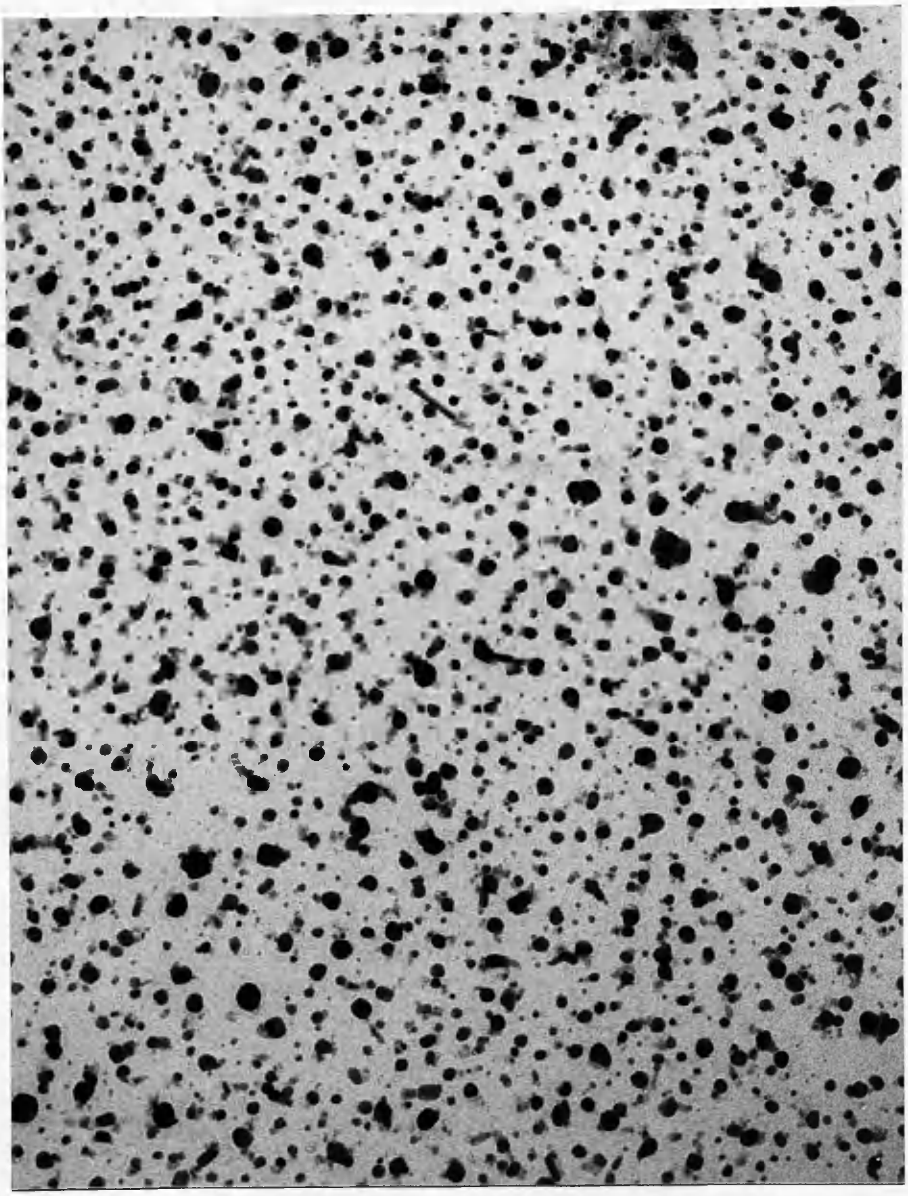


PLATE I2 A COPPER FILM, COMPLETELY OXIDISED AND THEN REDUCED IN HYDROGEN (x80,000) stage.

Film 81 was first treated with hydrogen at 443°K in order to remove any oxide present. There were no significant differences between the micrographs obtained before and after this treatment; both were virtually identical to plate 5.

This film was then progressively oxidised. Plate 9 shows a thin section of the film during an intermediate stage in the formation of cuprous oxide loops. It may be noted that a crystallite which is being oxidised does not necessarily contact the oxide layer over all of its surface. After oxidation for two hours, the diffraction pattern showed only traces of copper remaining, and micrographs showed complete loops, as in plate 10. The film was then reduced for one hour at 443°K in a flow of pure hydrogen. The diffraction pattern obtained after this treatment was that of copper alone. Plate 12 shows a micrograph of the reduced film. It should be noted that while one oxide particle was formed from each copper crystallite as a result of oxidation, during reduction a process of recrystallisation destroys the oxide loops and several copper particles may be formed from one oxide particle.

32% of the krypton initially held by film 77 was retained after complete oxidation. Film 81 was so light that no attempt was made to measure the final activity, which would not have been significant with respect to the background.

While the terms 'loops' and 'annular' have been used to describe the appearance of oxide particles in the micrographs, it should be noted that the particles are in fact three-dimensional, hollow structures. The annular appearance is an effect of contrast. In all micrographs, the dark sharp-edged particles are copper, and the lighter, more diffuse particles are cuprous oxide (115).

6.5 THE REACTION OF COPPER FILMS WITH OXYGEN: DISCUSSION

It may be concluded from the results which have been presented that copper films incorporating krypton are suitable for use as oxygen detectors in a stream of nitrogen. The consistency of responses throughout the working life of a film verifies the postulate that krypton is homogeneously distributed throughout such films.

No attempt has been made to optimise the conditions for the estimation of oxygen by this method.

Certain procedures have been shown to be necessary before consistent responses to oxygen injections are obtained. It is necessary first to pretreat the film with oxygen. During this phase, the response to identical injections is observed to fall. In some cases, this trend stabilises to give consistent responses, but in other cases the response reaches a minimum and then increases to give the consistent value. Consistent responses are only obtained when injections are made at the end of the tailing-off period of the activity peak from a previous injection. If injections are made earlier than this, the response is increased; if injections are made later, then the response is reduced. (In practice, under the conditions used in the present investigation, there was a period of at least fifteen minutes between the two extremes, when a consistent response could be obtained.) In the limit, when the film is left in a flow of nitrogen for several hours at 443°K, the film must be reactivated by means of two or three injections of oxygen. Thereafter consistent responses are again found.

In order to explain this procedure which must be adopted, it is necessary to develop an understanding of the process of oxidation of these films.

The formation of particles giving annular images on electron micrographs has been reported at 420°K - 470°K and higher oxygen pressures, of approximately 5 torr (55). Presumably these particles have a hollow-shell structure. This phenomenon has been observed for other metals, such as tin (116). At 5×10^{-4} torr of oxygen, homogeneous particles of oxide were formed from copper, and at 5×10^{-2} torr, the particles were a mixture of annular and homogeneous types.

The electron microscopy investigation in the present work was conducted in pure oxygen, resulting in the annular particles characteristic of higher oxygen pressures. Under the experimental conditions for oxygen estimation, the smallest injection of oxygen to the system contained approximately 0.2 ml of oxygen under laboratory conditions. If it is assumed that this oxygen enters and leaves the film vessel as a pulse five minutes in length, then with a flow rate of 50 ml min^{-1} of nitrogen, the oxygen may be taken to be associated with 250 ml of nitrogen.

The pressure of oxygen during the time of the pulse is thus in the order of I torr. Even assuming that more mixing in fact takes place, it is evident that for all injections of oxygen under experimental conditions, the high-pressure process is operative. Therefore the morphological changes observed for films oxidised in pure oxygen will represent the processes occurring during the reaction of a film with individual injections of oxygen.

Copper is a classical model for oxide growth by cation transport (II7). The motivation for cation movement arises from the difference in electrical potential between pure copper at the metal/oxide interface, and adsorbed oxygen at the oxide/gas interface. This fact explains the observation that oxidation ceases once a thick oxide film has been built up, in that the potential gradient decreases as the thickness of oxide increases. Eventually the potential gradient is so low that cation movement is negligible. At room temperature the limiting thickness is I30 Å; at higher temperatures, the value is higher (II7). The thickness of the films studied in the current investigation was in the order of I00 Å, assuming the density of bulk copper. It is therefore evident that during most if not all of the time of oxidation, the thickness of the oxide film will be much less than a limiting value at 443°K.

Various mechanisms have been proposed to explain the kinetics of oxidation in terms of copper transport through the oxide layer(II8). The rate of metal ion transport may be controlled either by electrical factors alone, or by the rate of the surface reaction. Most kinetic studies have centred on the oxidation of thicker copper specimens, to give thicker oxide films, in a static system at constant oxygen pressure. The rate of oxide formation is normally observed to fall with time, although a theoretical treatment where the oxide surface is assumed to be saturated with oxygen may lead to a linear law of oxidation. However, it has been shown that the surface of copper is likely to be saturated with oxygen under the conditions used in most investigations of the oxidation of copper, and it has been suggested that the rate of cation transport is determined by the amount of dissociation of 'neutral pairs', consisting of an O^- ion and a positive hole, which are formed by the adsorption of oxygen. The larger the amount of dissociation, the greater is the separation of charge in the oxide layer, and the higher is the potential gradient (II8). Observations of the electrical conductivity of cuprous oxide films during reduction by hydrogen may also be explained in terms of the concentration of positive holes in the oxide (II9).

It is not possible to relate the quantitative results obtained by previous workers in studies of oxidation in a static system, to the quantitative results of the pulse treatment used in the present work. In particular, the time required for formation of a chemisorbed oxygen layer on copper or cuprous oxide may be important in the pulse method. The following theory is presented to explain the results in qualitative terms. It is first assumed that the residence time of oxygen in the film vessel is insufficient for all of the oxygen to react with copper. A calculation is presented in appendix J to show that only a small fraction of the available oxygen reacts. Second, it is assumed that there is present sufficient oxygen to form a chemisorbed monolayer on copper or cuprous oxide under equilibrium conditions. In view of the quantities of metal and gas involved, this is a reasonable assumption.

The decreasing response period arises because krypton is released during the reaction of copper with adsorbed oxygen to initiate a complete layer of cuprous oxide. Although sufficient oxygen is in fact available from one injection to produce a complete oxide layer, the rate of formation of the layer is limited by the time of nucleation or of oxygen adsorption, so that several oxygen injections are necessary to complete the layer. The responses fall because less bare copper surface is available to later injections, and thus less actual reaction of copper occurs. Assuming that the copper film is continuous, no migration of copper ions through the oxide layer is possible until a complete oxide layer has been formed, isolating the copper crystallites from oxygen in the gas phase. No potential difference may be established between the metal/oxide and oxide/gas faces of the oxide film while the film surface consists of portions of copper and cuprous oxide, since both faces of the oxide film are in contact with copper. Once copper has been isolated from the gas phase, copper ions begin to migrate through the oxide film owing to the potential difference which has been established between its faces. Krypton release now occurs where copper ions leave the original crystallite. Since an effectively continuous oxide film now exists, not all of the krypton released escapes to the gas phase, some being trapped at lattice imperfections in the oxide.

In fact, the films are not continuous, so that a complete oxide film may be formed over some crystallites more quickly than others. Therefore the two processes of krypton release may occur simultaneously in different parts of the film. Depending on the morphology of the film and the respective rates of the two processes, either a minimum response may be reached before a rise to the working period, or the responses may simply decline until the working period is reached.

The observation that a particularly high response may be found to the first oxygen injection may arise from the reaction of a larger proportion of oxygen during the formation of the initial layer of oxide, owing to the fact that the reaction is occurring in a part of the film in contact with the gas phase.

The proportionate responses of krypton loss to various injections of oxygen in the working period, and the disproportionately large responses to large injections of oxygen, are difficult to relate to the results reported for the oxidation of copper kryptonate in a continuous-flow system (89). The two mechanisms leading to the release of krypton, referred to as the "open-structure" and "diffusion" reactions, have been separated under conditions of oxygen flow at constant pressure. The adsorption and dissociation of oxygen molecules has been shown to be rate-determining for both reactions from the fact that a half-order dependence on the oxygen pressure is found, resulting in a decrease in specific response at higher oxygen pressures. In contrast to this, it may be concluded that the adsorption of oxygen is not rate-determining in the current investigation, since this would predict the opposite of the observed increase in response to large injections of oxygen.

However, the work of Chleck and Cucchiara (89) was not directly comparable to the current invesigation. Bulk copper was used as the source, and all measurements were made at high temperatures (670°K - 1170°K). Further, the activity remaining in the source was measured during the reaction, not the gas phase activity. It is stated in this paper that "copper does not appreciably react with oxygen at temperatures below 570°K." While it may be the case that at temperatures below 570°K, the actual rate of decrease of source activity is small, nevertheless the increase in gas phase activity has been shown to be readily measurable. Also, thin films may be intrinsically more reactive than the bulk of a substance.

The character of the reponses may therefore be determined by the rate of the surface reaction, by the rate of diffusion of copper, or by physical factors in the system. The lengthening of response peaks during the ageing of a film is consistent with the increasing thickness of the oxide film, through which krypton, released by copper, must diffuse to reach the gas phase. During oxidation, some quantity of copper is in the process of migration through the oxide film; if the surface reaction is slow, then copper atoms may be present at the oxide/gas interface. The quantity of copper oxidised by a typical injection of oxygen is less than 1% of all the copper in the entire film (appendix J). Therefore it must be recognised that the particular copper atoms oxidised by an oxygen injection are not necessarily those which are involved in the release of krypton. An assessment of the physical factors of gas flow in the film vessel is complicated by the simultaneous processes of flow, mixing/diffusion, temperature change, and adsorption/reaction which are occurring.

It is not possible from the data collected in this investigation to make a definite statement of the factors leading to the release of krypton during the oxidation of copper. It is believed that physical factors may be important, as it is difficult to conceive of a purely chemical effect which could lead to enhanced responses for large oxygen injections. One answer may be that increasing the dosage size increases the time span of a reaction which is in fact zero order. If a fast reaction only occurs when a complete adsorbed monolayer of oxygen exists at the oxide surface, then the effect of larger doses may be to lengthen the time during which the partial pressure of oxygen is sufficient to maintain the monolayer. This theory would account for the relatively larger responses when oxygen was flowed continuously, and depending on physical factors it could explain the enhancement of the response to individual large doses. However, it does not explain all of the facts, for example the widely different responses to different flows of oxygen.

The facts that re-sensitisation of the film is necessary after no oxygen has been available for some time, and that enhanced responses are obtained when injections are made before the effect of the previous injection has ended, point to the participation of oxygen in the process other than in the reaction itself. It is likely that when a film is left in a stream of nitrogen for some hours at 443°K, all the adsorbed oxygen will react with copper, or possibly desorb. The adsorbed oxygen layer has been observed to disappear from cuprous oxide on heating for three hours in vacuum at 443°K (120).

A similar effect has been observed by Siegel and Peterson (115). These authors state that " a lower limit of exposure to oxygen was required to produce a displacement of the copper atoms at a measurable rate", but give no further details.

The effect is probably related to the dependence of copper migration on the potential difference between copper metal and the adsorbed oxygen layer. In essence, catalysis by the reactant, oxygen, is implied, possibly in terms of maintaining the concentration of dissolved, migrating copper in the oxide layer. This could explain the enhancement of responses for large injections of oxygen.

A better understanding of the processes involved could be taken from studies of the oxidation of copper films in a continuous flow of oxygen, and by studies of the resistance of the film during the oxidation process.

The process of reduction of an oxidised film is apparently less complex. Responses to successive injections of hydrogen decrease with the lesser availability of the cuprous oxide kryptonate film.

It is surprising that some krypton is retained by a film after the cycle of oxidation-reduction-oxidation, but a small response to a second reduction has been observed (figure 69), although the first oxidation and reduction were carried to the stage where no responses could be detected. Since copper migration is involved in the oxidation process, and recrystallisation in the reduction process, this may imply that the retained state of krypton is more than a passive trapped state; migration of krypton must be involved if it is to be held in the new crystallites. This is certainly necessary to explain the release of krypton when the film of cuprous oxide is reduced. However it is possible that the results of the second oxidation and reduction arise from the exposure of unoxidised copper during the recrystallisation of the first oxide layer associated with its reduction. This could be best investigated by conducting studies of working films by electron microscopy; in the present investigation the electron microscopy studies were undertaken only to show morphological changes in the films during oxidation and reduction, and the structures of working films were not determined by this method.

CHAPTER 7

ADSORPTION AND CATALYSIS ON FILMS OF NICKEL, PALLADIUM, AND PLATINUM.

CHAPTER 7 ADSORPTION AND CATALYSIS ON FILMS OF NICKEL, PALLADIUM, AND PLATINUM

7.I THE ADSORPTION OF HYDROGEN BY NICKEL FILMS AT 273°K

A simple description of the working of a catalyst is that it alters the rate of a chemical reaction without entering the reaction. Although catalysts do not actually react, nevertheless changes in their structure may be brought about by adsorption and catalysis on their surface, showing that at least the outer layers of atoms are disrupted by these processes. (see section 2.I) This is exemplified by the release of the krypton label from ion-bombarded platinum during surface processes involving adsorption and reaction of hydrogen and oxygen (47).

It was decided to investigate the well-characterised adsorption of hydrogen on nickel films in order to find whether the release of krypton owing to adsorption is a general phenomenon, and to quantify any such release for the nickel/hydrogen system.

Nickel films were deposited at 77°K, in krypton, using the techniques described in chapter 4. They were allowed to attain room temperature, and krypton released was recovered using the Toepler pump over a period of one hour, and was measured with the McLeod gauge. This process always left a low residual pressure of krypton in the film vessel because the Toepler pump was not 100% efficient. While this was not significant in terms of total quantity measurements, it was found that the radioactivity of the residual krypton was large enough to introduce errors in to the measurement of the quantity of krypton released by a film owing to adsorption. Accordingly, film vessels were flushed with a large quantity (approximately 5 μmoles) of inactive krypton, and were pumped down with the main pumps, before adsorption measurements were made.

Adsorption measurements were made with the film vessel maintained at 273°K. The sintering process for the films was the period of approximately one hour at room temperature, referred to above. While this treatment is much less rigorous than other sintering techniques which have been employed in order to obtain reproducible results for adsorption on metal films (8), it was found in practice that any release of krypton during standing at 273°K in the course of an experiment was negligible compared to release induced by adsorption. The sintering process was therefore considered to be adequate, at least for studies of krypton release.

Small quantities of hydrogen were measured using the McLeod gauge, and were allowed successively to expand in to the film vessel. For the earlier doses, the pressure dropped to a very low value; the surface was taken to be saturated with hydrogen when an appreciable residual pressure was found. Since all earlier samples were completely adsorbed, the total quantity of adsorbed hydrogen was determined by the quantity of the last aliquot which had been adsorbed. This was determined in one of two ways. The Toepler pump was used in some cases to recover unadsorbed hydrogen for measurement in the McLeod gauge. Alternatively, after all adsorption studies had been completed on a particular film, the volume of the system was found by expansion of a measured quantity of argon. (see appendix A) Then the fraction of the last aliquot which had been adsorbed could be calculated from a measurement of the quantity of hydrogen in the McLeod gauge bulb at equilibrium.

After each aliquot of hydrogen had been allowed to come to equilibrium with a nickel film, the activity of the krypton released was measured. A standard amount of approximately 3 μmoles of inactive krypton was admitted to the system used for the adsorption studies, and was left for ten minutes in order to ensure complete mixing with the small quantity of released krypton. All of the gas in the film system, including any unadsorbed hydrogen, was then transferred to the counting chamber using the mercury ejection pump and the Toepler. After a count had been taken, the counting chamber was evacuated by the main pumps.

At first, 5% ^{85}Kr was used for these studies. However, the activity resulting in the counting chamber was frequently so high that the dead time correction time exceeded the counting time. The effective counting volume was 9 ml at this stage, and it was found that small alterations in the mercury level in the counting chamber produced large changes in the observed count rate. For these reasons, the early results were unreliable, and will not be dealt with in detail.

The results which are quoted in this section were obtained using films deposited in 0.6% ^{85}Kr, which was obtained by dilution, and counts were made in a chamber of volume approximately 30 ml. Under these conditions, convenient and reproducible count rates, in the order of hundreds or thousands of counts per minute, were produced.

Various tests were carried out to investigate possible sources of error in this experimental arrangement. It was found that the krypton held by the films at 273°K was not exchangeable with gas phase krypton, and that krypton release on standing was usually negligible. There was no radioactive contamination of the hydrogen used, but the inactive krypton supplied by the British Oxygen Co, Ltd, was found to be slightly radioactive. The activity corresponding to the natural background, plus the effect of 3μ moles of the supposedly inactive krypton, was found to be 270 cpm. This value was deducted from all measured count rates when inactive krypton was added to dilute the krypton released by a film.

From the gas counter calibration (see appendix D), it can be shown that this level of activity results from the presence of approximately 10^{-5}% of ^{85}Kr in the 'inactive' krypton.

One of the first measurements made with the vacuum system was of the adsorption of hydrogen by a nickel film deposited at 273°K, in order to check that the results would be comparable to those of previous workers. The measurement was made at 295°K, and the results which were obtained are given below.

Weight of nickel in film I = 40.0 mg

Quantity of hydrogen adsorbed = 8.50×10^{18} atoms

Specific adsorptive capacity = 2.12×10^{17} atoms mg

The value obtained for the specific adsorptive capacity of the film is higher than those normally found for films deposited in vacuum at 273°K (9, 50, I2I, I22), but lower than the value obtained for the adsorption of hydrogen by films deposited in a pressure of a few torr of argon (9, I22). Film I was laid down in 3×10^{-2} torr of krypton, and the intermediate value of the specific adsorptive capacity probably arises from the lower value of the gas pressure during deposition.

It was concluded that adsorption measurements in the present system would be consistent with previous work.

The results which were obtained for the adsorption of hydrogen on a series of six nickel films deposited in the presence of krypton at 77°K, are shown in table 42.

TABLE 42 THE ADSORPTION OF HYDROGEN AT 273°K BY FILMS DEPOSITED IN THE PRESENCE OF APPROXIMATELY 4xI0^{-2} torr OF KRYPTON AT 77°K

FILM No	WEIGHT (mg)	QUANTITY OF HYDROGEN ADSORBED (atoms)	SPECIFIC ADSORPTIVE CAPACITY (atoms of H, per mg of Ni)
98	6.5	I.58xI0^{18}	2.44xI0^{17}
I0I	3.5	I.05xI0^{18}	3.00xI0^{17}
I03	5.2	I.38xI0^{18}	2.67xI0^{17}
I06	II.8	2.25xI0^{18}	I.9IxI0^{17}
I09	5.I	8.57xI0^{17}	I.68xI0^{17}
III	5.8	I.43xI0^{18}	2.46xI0^{17}
		MEAN	2.36xI0^{17} ± 0·44xI0^{17}

The agreement between these values is not very good. Variation from one film to another may be explained in part by incomplete annealing of the films during the rise to room temperature after deposition. The necessity for complete and reproducible annealing procedures has been pointed out by Singleton (8). Although in the present work annealing appeared to be complete, in the sense that no ^{85}Kr was released on standing at room temperature, nevertheless it is possible that variations in surface area may have arisen as a result, for example, of different rates of warming. The effect of small variations in the deposition conditions may also be important. Another source of error may lie in the possibility of reversible adsorption of hydrogen by nickel. In this investigation, the surface was taken to be saturated by hydrogen when a measurable pressure of hydrogen was found in the film vessel. The quantity of hydrogen adsorbed to saturate the surface was calculated from the quantity of krypton which could be recovered from the film vessel using the Toepler pump. However, when further aliquots of hydrogen were admitted to the film, it was found that sorption of hydrogen could occur beyond the point of saturation. The results obtained for film I06 are given in table 43.

TABLE 43 HYDROGEN ADSORPTION BY FILM 106 AT 273°K

HYDROGEN ALIQUOT No	INITIAL QUANTITY OF HYDROGEN (μmoles)	QUANTITY OF HYDROGEN NOT RECOVERED BY TOEPLER (μmoles)
1	0.156	0.156
2	0.400	0.400
3	0.394	0.394
4	0.187	0.187
5	0.392	0.392
6	0.398	0.339
7	0.386	0.189
8	0.386	0.143
9	0.386	0.130
10	1.400	0.394
11	1.379	0.268
12	2.409	0.553
13	2.021	0.424
14	2.015	0.277
15	1.995	0.255
16	2.166	0.379

It is not possible for the sum of the quantities of hydrogen apparently adsorbed from each aliquot of hydrogen to have been associated with the film at the end of the experiment. The only possible explanation of the observations is that a quantity of hydrogen which was not recovered by Toepler pumping, was desorbed by the more rigorous pumping with the mercury ejection pump, during transfer to the gas counting section. In each case, a part of the surface would thus be left bare before exposure to the next aliquot of hydrogen. It was not possible to test this postulate while measurements of the amount of krypton release were being made, because the quantity of hydrogen not adsorbed, together with the inactive krypton added as a carrier, was too large for measurement by the McLeod gauge. It is surprising that such hydrogen was not recoverable using the Toepler pump. A possible explanation of the variation in the quantity of hydrogen apparently adsorbed from successive aliquots, is that the efficiency of hydrogen recovery using the Toepler was variable. In all cases, I0 - I2 strokes of the Toepler pump were carried out; this would normally be sufficient to recover effectively all of the gas phase species from a system of the same volume as the film vessel used. However, if the reversible desorption was time-controlled, part or all of the sorbed gas might be left in the film vessel.

This postulate is supported by the results obtained for film III, where measurements were made at equilibrium pressure in a system of known volume. In this case, the quantity of hydrogen apparently sorbed from successive aliquots after the point of saturation was much more constant. (see table 44)

TABLE 44 HYDROGEN ADSORPTION BY FILM III AT 273°K

HYDROGEN ALIQUOT No	INITIAL QUANTITY OF HYDROGEN (μmoles)		QUANTITY OF HYDROGEN ADSORBED (μmoles)
I - 5			I.I02 (saturation)
6	0.354		0.I67
7	0.34I		0.I9I
8	0.355		0.I64
9	0.355		0.I62
I0	I.342		0.I82
II	I.295		0.207
		MEAN OF SIX	0.I80 ± 0.0I7

It has been observed that adsorption of hydrogen is possible beyond the supposed point of saturation of the surface. The phenomenon was first reported by Beeck (I0I), who ascribed it to solution of hydrogen by nickel; later workers (I23, I24, I25) have shown that it is a surface phenomenon. Solution of hydrogen by nickel is observable only at temperatures over 333°K (I24).

This adsorption is a time-controlled process; it is referred to as "slow sorption". The adsorbed state has been shown to be the active intermediate in the catalysis of the parahydrogen conversion by nickel (8). Hydrogen slowly sorbed by nickel may be desorbed by pumping for thirty minutes (I25). Various sites such as lattice defects, spaces between macrocrystals, and particular crystal planes, have been suggested as the particular adsorption sites involved (I25, I26, I27).

Values of between I3% and 22% of the saturation quantity have been found in the studies cited above. In the present work, the highest values represent 25% of the saturation quantity for film I06, and I6% of the saturation quantity for film III. These values are fairly high, but it has been shown that the slow sorption process is favoured on porous films, and it is probable that films laid down at low temperatures are highly porous.

These results demonstrate that for the experimental technique used in this investigation, it is difficult to evaluate the point of saturation with certainty, as in each case a portion of the hydrogen, reversibly sorbed from the aliquot of hydrogen which saturates the surface, may not be removed by the Toepler pump. The spread of values in table 42 is sufficiently large that the effect of incomplete sintering must also be important.

The mean value for the films of table 42, of 2.36xI0^{17} atoms of hydrogen per mg of nickel adsorbed, represents an enhancement of the adsorptive capacity over the values reported for films evaporated in vacuum at 273°K. Typical values for the specific adsorptive capacity of such films fall in the range I.25xI0^{17} atoms mg^{-1} to 2.00xI0^{17} atoms mg^{-1} (9, 50, I2I, I22).

Hydrogen adsorption measurements were made at 295°K on four films (numbers 2, 88, 90, 93), which were deposited in 5% ^{85}Kr. The mean value of the specific adsorptive capacity was 2.45xI0^{17} ± 0.68xI0^{17} atoms mg, which is not significantly different from the value found at 273°K.

The quantity of krypton which was released as a result of adsorption was calculated from the observed count in the 30 ml counting chamber, using the relation 8.5 cpm ≘ I0^{-14} moles of ^{85}Kr. (see appendix D) The total quantity of krypton released up to the saturation point for the six films considered previously is given in table 45. Film 98 was deposited in 5% ^{85}Kr, and the values have been adjusted by a factor of 0.6 ÷ 5.0, in order to compare them with the results for the other films.

TABLE 45 KRYPTON RELEASE DURING SATURATION OF NICKEL FILMS WITH HYDROGEN.

TABLE HEADINGS : ALIQUOTS = the total number of aliquots of hydrogen required to saturate the film.

^{85}Kr RELEASED = the total number of moles of the isotope ^{85}Kr released by the film

(Ni) RELEASE = the total number of moles of the isotope ^{85}Kr released by the film, divided by its weight in mg

SPECIFIC RELEASE = the total number of moles of the isotope ^{85}Kr released by the film, divided by the number of μmoles of hydrogen adsorbed at saturation

FILM No	ALIQUOTS	^{85}Kr RELEASED (moles x 10^{-12})	(Ni) RELEASE (moles x 10^{-12})	SPECIFIC RELEASE (moles x 10^{-12})
98	2	50.0	-	-
98(corr.)	2	6.0	0.92	4.6
101	4	4.9	1.40	5.6
103	4	7.5	1.44	6.5
106	6	9.8	0.83	5.2
109	2	4.6	0.90	6.5
111	5	34.4	5.93	31.1

The values were fairly consistent for all of the films with the exception of film 111. The only distinguishing feature of this film was that the atomic % of krypton retained at room temperature, before the adsorption measurements were begun, was unusually high (0.39%). The adsorptive capacity for hydrogen was typical.

Table 46 shows that proportion of the total incorporated krypton which was released owing to adsorption of hydrogen to the point of saturation, for the films above. It is evident that there is no general relationship between the quantity of krypton initially held by a film at 273°K, and the proportion lost owing to adsorption. The values for film 111 are anomalous in both tables.

TABLE 46 THE PROPORTION OF INCORPORATED KRYPTON LOST OWING TO ADSORPTION OF HYDROGEN TO THE POINT OF SATURATION

FILM No	ATOMIC % OF KRYPTON (273°K)	PROPORTION OF INCORPORATED KRYPTON LOST OWING TO ADSORPTION (%)
98	0.24	0.38
101	0.26	0.53
103	0.23	0.53
106	0.36	0.19
109	0.27	0.32
111	0.39	1.47

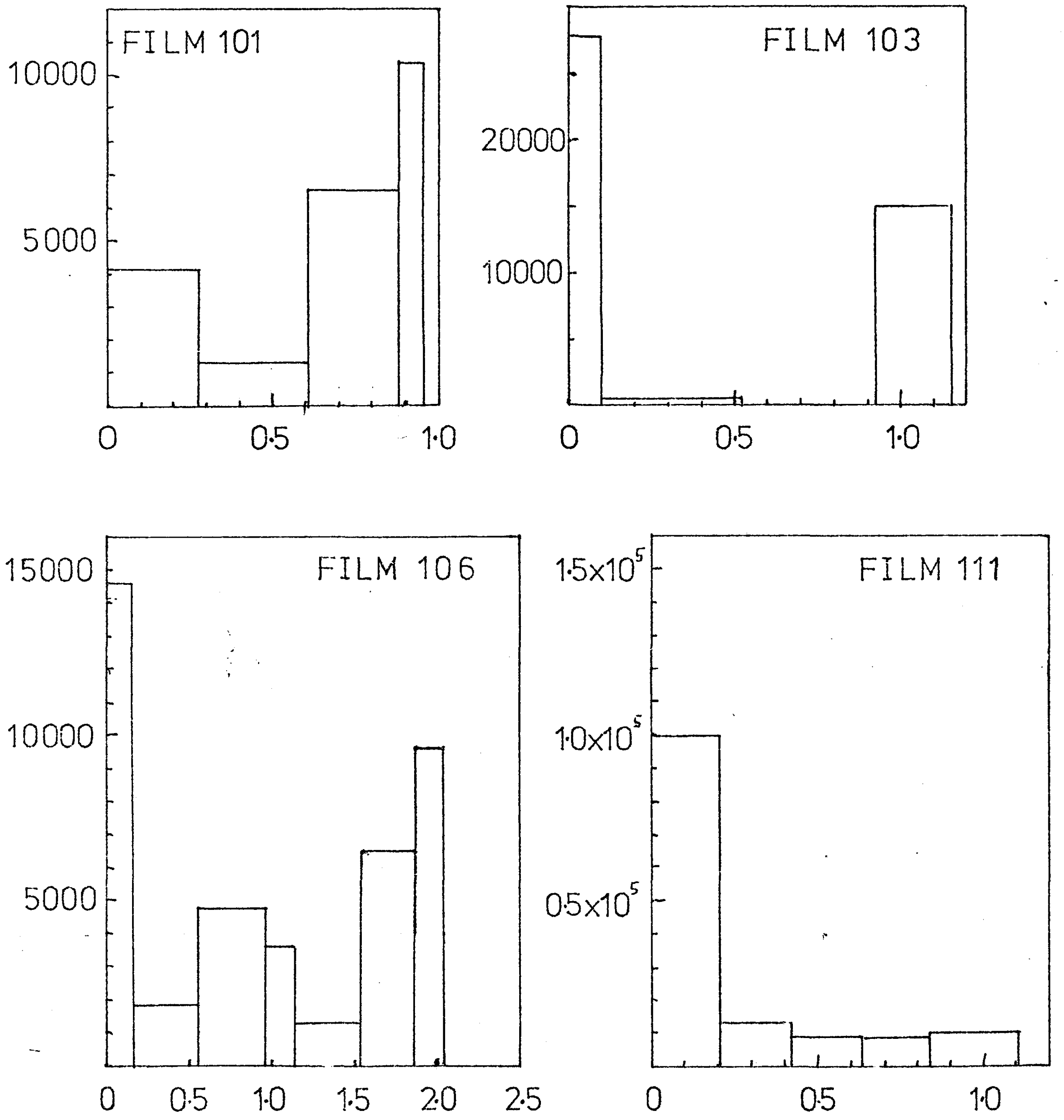
Excluding the data for film 111, the best relationship is obtained by a comparison of the quantity of krypton released with the quantity of hydrogen adsorbed, that is, the "specific release" of krypton, quoted in table 45. The determination of the quantity of krypton held by a film at room temperature is subject to error, and from the results presented for the quantity of hydrogen adsorbed on to these films, it appears that there is a genuine variation in surface area. Assuming that the atomic % of krypton in the films is in fact almost constant, then the quantity of krypton released might be expected to be related to the surface area effected by adsorption, and thus to the quantity of hydrogen adsorbed. The data are sufficiently incosistent that this conclusion cannot be stated with certainty; more rigorous and reproducible sintering procedures would have to be employed before definite conclusions could be reached.

Another difference between the results for film 111 and values for all the other films studied was in the distribution of krypton release between successive aliquots of hydrogen.

For the films which were saturated with two aliquots of hydrogen, it was found that, although less hydrogen was adsorbed from the second aliquot, a relatively greater amount of krypton release was associated with it. This was also observed for the four films laid down in 5% ^{85}Kr, although for reasons stated previously, exact values could not be obtained for these films.

When the size of aliquots was reduced in order that release of krypton during

FIGURE 71 KRYPTON RELEASE DURING PROGRESSIVE COVERAGE OF NICKEL FILMS BY HYDROGEN



ALL x-axes μmoles of hydrogen adsorbed

All y-axes specific release of krypton (cpm per μmole hydrogen adsorbed) progressive coverage of the surface by hydrogen could be investigated, a standard pattern emerged. The results for film 101 are given as an example in table 47.

TABLE 47 KRYPTON RELEASE DURING PROGRESSIVE COVERAGE OF FILM 101 BY HYDROGEN

TABLE HEADINGS : Q ads = the quantity of hydrogen adsorbed in μmoles
RADIOACTIVITY = the observed count rate resulting from krypton released, measured in the gas counter and corrected for background
SPECIFIC ACTIVITY = the observed count rate as above, divided by the quantity of hydrogen adsorbed

HYDROGEN ALIQUOT No	Q ads	RADIOACTIVITY (cpm)	SPECIFIC ACTIVITY (cpm per μmole of H_2)
1	0.275	1150	4180
2	0.336	460	1370
3	0.270	1750	6480
4	0.074	760	10300

It was found that the amount of krypton release was initially high, decreased, and then increased near the saturation point. Although this pattern was found in all cases, the quantity of release was not consistent for all the films. In particular, the first aliquot of hydrogen admitted to film 111 caused the release of a particularly large quantity of krypton. The experimental results for four films are shown in figure 71.

It may be concluded that the mechanism of krypton release is not related to thermal sintering induced by the dissipation of the heat of adsorption of hydrogen. The heat of adsorption is invariably found to decrease with surface coverage (14), so that the increase in specific release near the point of complete surface coverage can not be explained on this basis.

It was further found that the slow sorption process caused the release of considerable quantities of krypton, although for a readily reversible process, very little heat of adsorption could be involved. In the histogram presented for film 106 in figure 71, the seventh block represents krypton released wholly by the slow sorption process. Because of the difficulty in identifying the point of saturation, it is not possible to state how much of the krypton release in the last block of each of the other histograms represents slow sorption.

It is suggested that the increase in the specific release of krypton near the point of complete coverage corresponds to the onset of occupation of the slow-sorption sites on the film.

In the case of film 106, approximately four times as much krypton was lost owing to slow sorption as had been lost as a result of the formation of the initial chemisorbed layer of hydrogen. This was the result of the repetition ten times of the cycle slow sorption/desorption. Krypton release persisted as far as the film was studied, although the quantity of krypton released was lower for later aliquots of hydrogen. Successive aliquots occasionally caused very different amounts of release, probably because of differing physical factors such as adsorption time, pumping time, and the rate of pumping.

Films 109 and 111 were treated less rigorously. Release of krypton owing to slow sorption was followed until amounts of krypton corresponding to 28% and 42% of the saturation quantity had been released; in neither case was a limit to release observed.

This phenomenon is not the result of the release of krypton from the film for some other reason over the time of the experiment. In the cases of films 106 and 111, a quantity of inactive krypton was left exposed to the film for a period of time much longer than the time of an adsorption measurement; little activity was acquired by the inactive krypton. For example, the net activity for one sample left for twelve hours over film 106 was 400 cpm, which was less than a quarter of the lowest activity release measured for an aliquot of hydrogen after the point of saturation. Krypton release therefore arises because of the interaction of hydrogen with the film.

No krypton appeared to be released by films 101 and 103 after the point of saturation. This was probably the result of a difference in the experimental technique. It was assumed at first that the krypton released by a film would immediately mix with gas phase hydrogen. Accordingly, once the point of saturation had been reached, when it was known that a large quantity of hydrogen would remain in the gas phase, inactive krypton was not added prior to counting. At this stage the phenomenon of slow sorption had not been observed, and after the point of saturation the quantity of hydrogen in each aliquot was measured only before introduction to the film vessel.

The assumption that released krypton mixes immediately with gas phase hydrogen does not seem to be justified by the results for films IOI and IO3. Krypton that is released owing to the slow-sorption process may be loosely held by the film, and may only enter the gas phase as a result of exchange with gas phase krypton. This possibility reveals another source of possible error in the results presented in this section.

A short investigation of the release of krypton from palladium films was now carried out. It was hoped that any differences found might aid in the interpretation of the nickel results, in terms of the different modes of interaction of hydrogen with the two metals (I29).

7.2 THE ADSORPTION OF HYDROGEN BY PALLADIUM FILMS AT 273°K

The techniques employed for the investigation of hydrogen adsorption by palladium films at 273°K were identical to those used for study of the nickel films described in section 7.I. Hydrogen aliquots were left to equilibrate over the film for at least thirty minutes. Two films were studied; in each case, the surface appeared to be saturated by the second aliquot of hydrogen.

When measurements of the uptake of hydrogen were made, first from the pressure in the system at equilibrium, and subsequently by Toepler pump recovery of gas phase hydrogen for measurement in the McLeod gauge, it was found that part of the hydrogen which had disappeared from the gas phase at equilibrium could be readily recovered by Toepler pumping. The results are given in table 48. As in the case of the nickel results, the values quoted for irreversible adsorption are subject to error because it is not certain that a limit to hydrogen recovery could be reached using the Toepler pump.

TABLE 48 THE ADSORPTION OF HYDROGEN AT 273°K BY PALLADIUM FILMS DEPOSITED IN THE PRESENCE OF APPROXIMATELY 4×10^{-2} torr OF KRYPTON AT 77°K

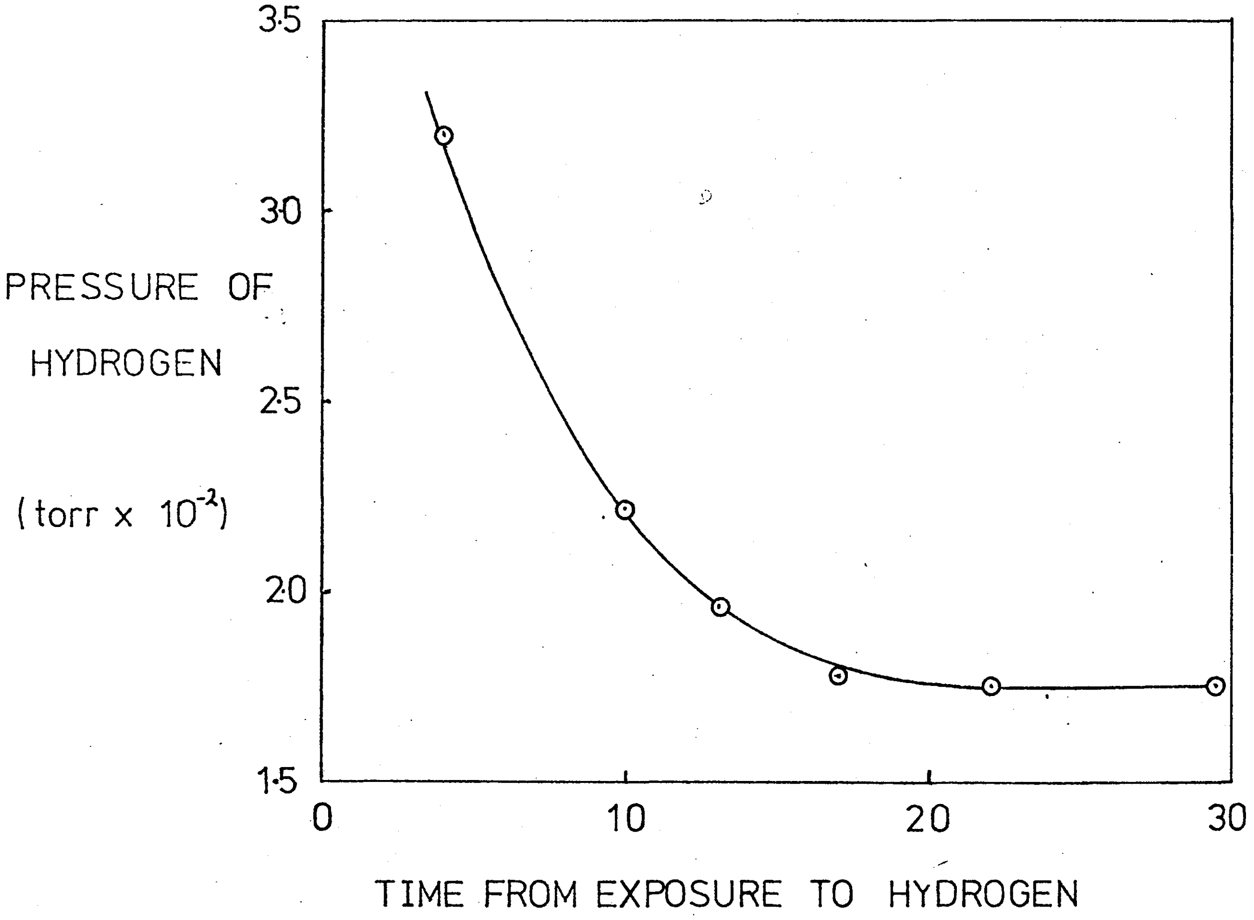
FILM No	WEIGHT (mg)	SPECIFIC ADSORPTIVE CAPACITY (atoms of H, per mg of Pd)		% REVERSIBLE ADSORPTION
		TOTAL	IRREVERSIBLE	
I04	6.4	5.80×10^{17}	4.32×10^{17}	25
I07	4.9	4.66×10^{17}	3.58×10^{17}	23

It is evident that hydrogen is adsorbed in larger quantities by palladium than by nickel. The value found for the total amount of adsorption is larger than that found by Stephens (I29) for palladium films deposited in vacuum at 273°K (1.48×10^{17} atoms mg^{-1}) Of the quantity measured by Stephens, some 40% was readily desorbed by pumping.

The quantity of hydrogen irreversibly adsorbed by these films represents an atomic ratio of approximately I H : I4 Pd, compared to an atomic ratio of I H : 43 Ni under identical conditions for the nickel films.

The hydrogen was taken up quite slowly by the two palladium films. The

FIGURE 72 DECREASE IN PRESSURE OF HYDROGEN EXPOSED TO PALLADIUM FILM I07



process appeared to be complete some twenty minutes after hydrogen was admitted to the film. Figure 72 shows the decrease in pressure of the second aliquot of hydrogen admitted to film I07.

In both cases, the quantity of krypton released by the second aliquot of hydrogen exceeded that released by the first aliquot, although a smaller amount of hydrogen was actually adsorbed by the film. The proportion of the total quantity of krypton held by the films at 273°K, which was released owing to adsorption of the two aliquots of hydrogen in each case, is given in the table below.

TABLE 49 THE PROPORTION OF INCORPORATED KRYPTON LOST FROM PALLADIUM FILMS OWING TO THE ADSORPTION OF HYDROGEN TO THE POINT OF SATURATION

FILM No	ATOMIC % OF KRYPTON (273°K)	PROPORTION OF INCORPORATED KRYPTON LOST OWING TO ADSORPTION (%)
I04	0.69	0.67
I07	0.7I	0.34

These results are comparable with those obtained for nickel, despite the relatively larger quantity of krypton taken up by palladium. If the effect of hydrogen solution had been a factor contributing to the release of krypton, then more krypton would have been expected to be released by palladium than by nickel. However, the tendency to release of krypton is probably related to the manner by which a film holds krypton; it has been shown that palladium retains more krypton at room temperature than does nickel. It is possible that the release of krypton owing to adsorption of hydrogen is also less favoured for palladium than for nickel.

In view of the spread of results for the two metals, no definite conclusions can be drawn from the data.

No study of the release of krypton owing to sorption of hydrogen past the point of saturation was attempted for palladium. However the higher specific release of krypton from the film owing to adsorption of the second aliquot, which saturated the film, indicates that the behaviour of the metals is probably similar.

7.3 CATALYSIS OF THE HYDROGEN/OXYGEN REACTION BY PLATINUM FILMS AT 295°K

The measurement of total gas phase activity by a process involving quantitative transfer of gas from the film vessel to the counting chamber was a somewhat laborious process. The investigation of krypton release during catalysis was not attempted by this method, in view of the difficulty of obtaining reproducibility in the adsorption measurements, and the added complexity of handling two reactant gases. Instead, it was decided to inject the reactants in to a stream of an inert carrier gas passing through the film vessel, under conditions where a surface reaction would be expected, and to measure the release of krypton by a downstream flow counter.

Because of its high catalytic activity at low temperature, platinum was the metal selected; catalysis of the hydrogen/oxygen reaction by platinum has been observed at room temperature (47).

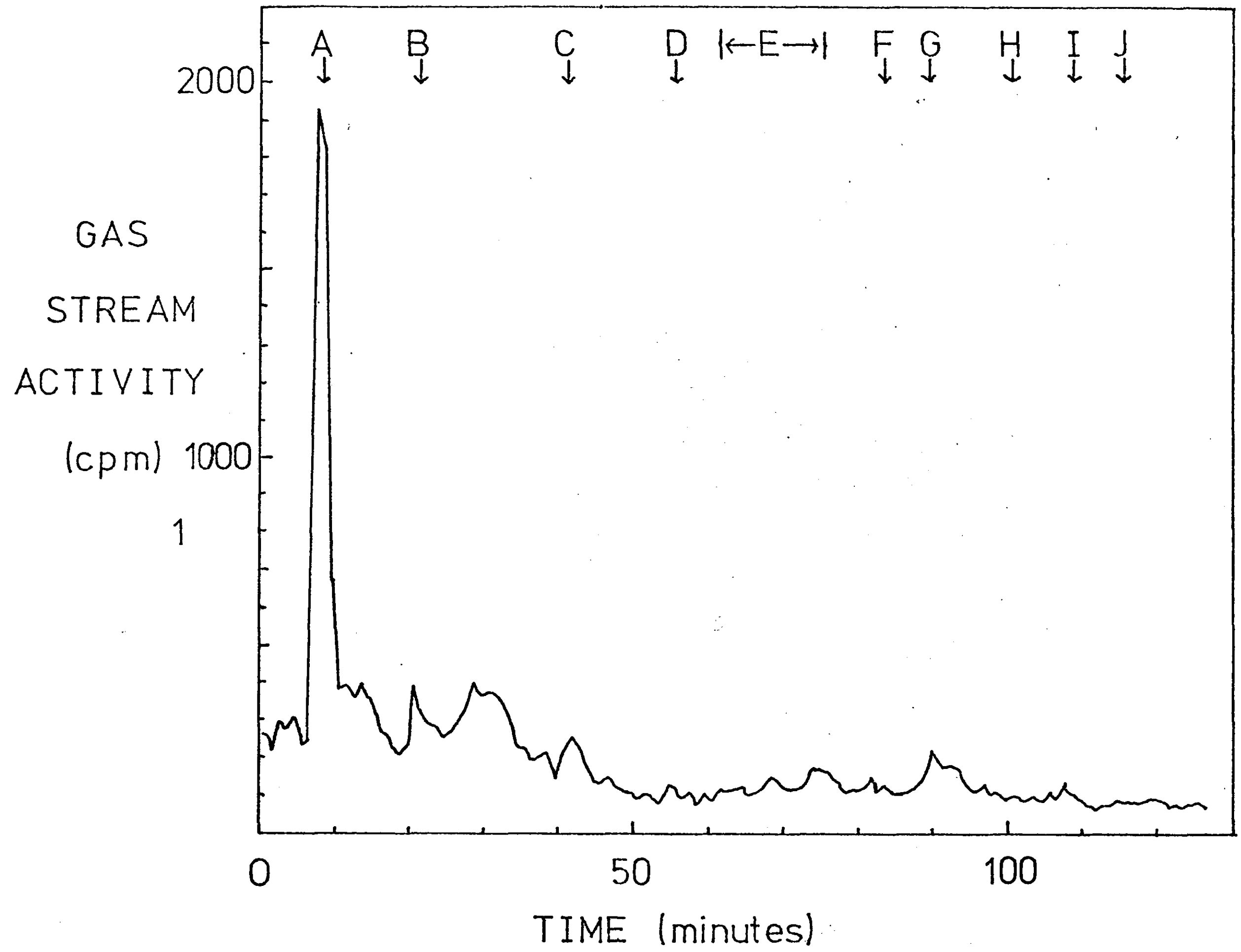
The platinum films were deposited in 5% ^{85}Kr by the techniques described in section 5(b). Details of the modified film vessels used in these experiments also appear in this section. (see figure 50)

Once the films had been allowed to attain room temperature, a flow of dry oxygen-free nitrogen, prepared as in the copper oxidation studies, was passed through the cold trap A to the film vessel, and thence to the flow counter. The flow of nitrogen entered the film line by way of the air leak tap, and injections of gas were made through a serum cap in a section of glass tubing located in the B9 socket of the air leak. Films were at no time exposed to the atmosphere. The rate of flow of nitrogen was 50 ml min^{-1}.

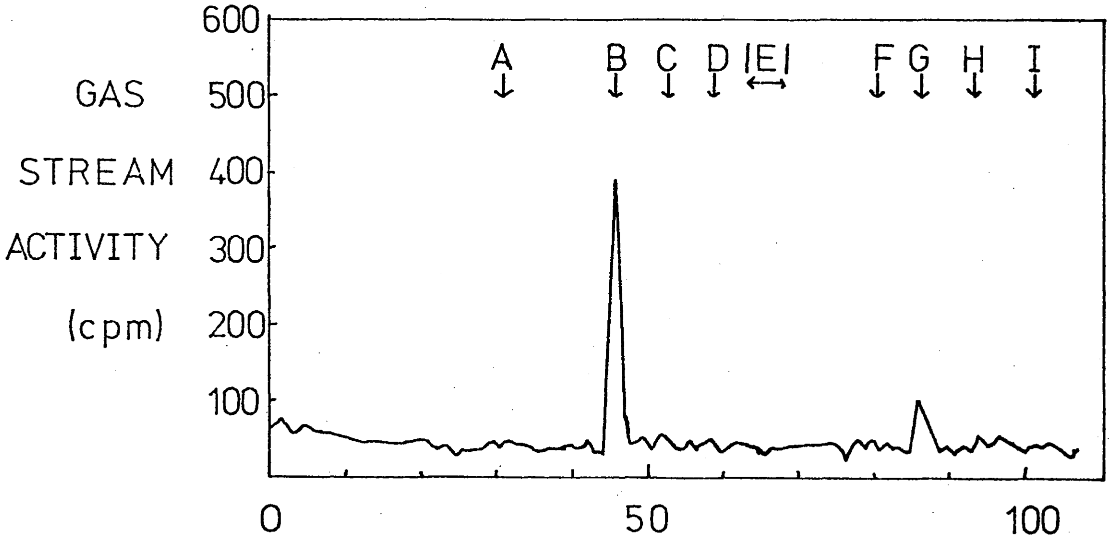
On commencing a flow of nitrogen through a film vessel containing a platinum film, a quite high count rate was registered by the flow counter. This effect was more pronounced than that found when a flow of nitrogen was begun over copper films (chapter 6); however copper films had previously been exposed to the atmosphere. The effect may arise first from the sweeping out of a low pressure of gas phase krypton, and second from a slow process of removal of krypton physically adsorbed in the cold traps. It was necessary to maintain the level of the liquid nitrogen in cold trap A, upstream from the film vessel, throughout a run. A peak of activity in the gas stream resulted from lowering the Dewar vessel. This may

FIGURE 73 GAS STREAM ACTIVITY DURING TREATMENT OF PLATINUM FILMS 105 AND 110

FILM 105



FILM 110



have been caused either by sintering of a condensed mercury film which incorporates some krypton, or by desorption of physically adsorbed krypton.

The downstream cold trap B was permitted to warm up to room temperature once the nitrogen flow had been established. Any contaminants condensed in this trap prior to and during deposition, including physically adsorbed krypton, were swept away from the film by the nitrogen stream.

Two runs were carried out with the films at room temperature (approximately 295°K). In the first experiment the film was not pretreated above room temperature. Gas injections commenced one hour after the nitrogen flow was begun. At this time the count rate was approximately 240 cpm, considerably in excess of the natural background. The activity release peaks were therefore measured against a falling background. During the experiment, counts were accumulated and a reading was made each minute, as in the copper oxidation work. Details of the injections of gas to this film, No 105, are tabulated below. A hydrogen-oxygen mixture was made by withdrawing first pure oxygen (3.3 ml), and then pure hydrogen (6.7 ml), from streams of the respective gases, using a 10 ml Hamilton syringe.

TABLE 50 INJECTIONS OF HYDROGEN AND OXYGEN TO FILM 105

TIME (min.sec)	GAS INJECTED	QUANTITY OF GAS INJECTED (ml)	REFERENCE TO FIG.73
5.45	hydrogen	5	A
18.45	hydrogen	5	B
38.45	hydrogen	5	C
52.45	hydrogen	5	D
58.45 - 72.45	hydrogen flow	10 ml min	E
80.45	oxygen	2	F
86.45	hydrogen/oxygen mix	10(6.7 ml H_2, 3.3 ml O_2)	G
97.45	oxygen	2	H
105.45	hydrogen	10	I
112.45	hydrogen/oxygen mix	10(6.7 ml H_2, 3.3 ml O_2)	J

The release of activity from this film is shown in figure 73.

In the second experiment, the film was first heated to 503°K for 150 minutes in the nitrogen flow, after which treatment a count rate of 60 cpm was found. The temperature of the film was also changed during the run. Details of the treatment of this film, number 110, are tabulated below.

TABLE 51 DETAILS OF THE TREATMENT OF FILM 110

TIME (min.sec)	TEMPERATURE OF FILM (°K)	GAS INJECTED	QUANTITY OF GAS INJECTED (ml)	REFERENCE TO FIGURE 73
0 - 6 min	503	-	-	-
6 - 21 min	cooling to 295	-	-	-
25.00	'jump' to 363	-	-	A
31 - 40 min	cooling to 295	-	-	-
42.45	295	hydrogen	2	B
49.45	"	hydrogen	2	C
55.45	"	hydrogen	2	D
60.15 - 65.15	"	hydrogen flow	10 ml min^{-1}	E
77.15	"	oxygen	2	F
83.00	"	hydrogen/oxygen mix	10	G
90.00	"	hydrogen/oxygen mix	10	H
98.00	"	hydrogen/oxygen mix	10	I

The release of activity by this film is also shown in figure 73. The jump in temperature to 363°K after 25 minutes was brought about by suddenly immersing the film vessel in a Dewar vessel containing water at 367°K.

It should be noted that the time between making an injection to the system and the detection by the gas counter of the activity released was approximately three minutes. A delay of three minutes has therefore been taken in to account in making the reference marks on figure 73.

The two plots of activity loss during treatment of the films are very similar. In each case, the first hydrogen injection produced a large peak, and much smaller effects were produced by later hydrogen injections. Once each film had stopped responding to hydrogen injections, there was no significant response to an injection of oxygen alone. However, a significant peak was observed when a mixture of hydrogen and oxygen, in the approximate proportion for reaction, was injected. Thereafter, only minor effects were noted.

The observation that the size of the initial peak was greater for the film which had not been preheated, may have arisen by an acceleration of the process of thermal stabilisation, owing to adsorption of hydrogen. From the length and shape of the first two hydrogen peaks for this film, some evidence may be taken for a slower secondary process of krypton release in this case.

The most important observation, however, is of parallel behaviour for two films of vastly different thermal history. It may first be concluded that the krypton lost owing to adsorption can not be identified with the krypton which is lost owing to a small rise in temperature. Also, from the fact that there was no response to a sudden temperature rise for film 110, it is clear that release of krypton from a film does not arise from thermal sintering induced by the dissipation of the heat of adsorption and reaction.

Some observations were made at 403°K, of hydrogen injections to films 94 and 97, which had been sintered at 433°K. It was noted that the release of krypton was not as much concentrated in the peak corresponding to the first hydrogen injection, but that a series of falling peaks was found for successive injections of hydrogen.

7.4 DISCUSSION OF KRYPTON RELEASE DURING ADSORPTION AND CATALYSIS

From the results which have been presented in this chapter, it may be concluded that the changes induced in the surface of a metal film as a result of adsorption and catalysis can not be associated directly with the dissipation of heat during these processes.

If the changes in the surface which resulted in the release of krypton had arisen through thermal sintering, then a steady decrease in krypton release throughout progressive surface coverage of a nickel film by hydrogen would have been expected, little or no krypton release would have been expected to be associated with the process of slow sorption of hydrogen, and krypton release would not have been expected at 295°K, using a platinum film presintered to equilibrium at 503°K.

Conflicting results have been presented on this subject. It has been shown that the surface area changes observed for nickel films after chemisorption by oxygen are substantially independent of the energetics of the method whereby the oxygen monolayer is produced (31). Since thermal sintering is both a temperature-controlled and time-controlled process (32), it is not believed that a momentary rise in temperature could in any case result in extensive sintering. On the other hand, it has been reported that the surface area of thermally unstabilised nickel films on which hydrogen has been chemisorbed at 77°K is related to the dose size of hydrogen (36). This is explained in terms of the greater rise in temperature, and hence greater degree of sintering, resulting from each of a small number of large doses of hydrogen. A fuller discussion of this point is presented in section 2.1.

The possibility of surface migration of nickel being assisted by the liberation of adsorption energy has also been suggested (28). Thus sintering could result from direct conversion of adsorption energy. While this could explain the platinum results, the results for hydrogen adsorption on nickel indicate a substantial amount of krypton release under conditions where the energy changes are minimal. One interpretation of the results is that the onset of occupation of the sites for the slow-sorption process produces atom movements which are at least as great as in the early stages of chemisorption.

However, the interpretation of the present results is complicated by the problem of precisely how krypton is held by a film. It has generally been suggested that in solid kryptonates, the krypton is held at defects in the lattice. The release of krypton in the near-saturation and post-saturation stages of an adsorption experiment, might therefore be explained in terms of hydrogen entering defect sites which are thermodynamically less favourable for adsorption (or less accessible to the gas phase) resulting in the release of krypton held at such sites. Although it is normal to consider that adsorption is favoured at defect sites, this assumption is based on the distortion of the lattice at such sites, and there is no reason to believe that unfavourably distorted defect sites can not exist.

It has been shown that hydrogen adsorbed by slow-sorption on nickel is highly catalytically active, at least for the parahydrogen conversion (8). And it is also believed that such hydrogen is held at defect sites (123). It is thus evident that strong adsorption is not invariably found at defect sites. Indeed, many studies have been reported (see section 2.1), relating the defect concentration of metals to their catalytic activity, and it is a general principle of catalysis that too strong adsorption of a species depresses its catalytic activity.

However, even assuming the existance of unfavourable defects, it is not possible to explain how the process of slow sorption supplies any energy, by whatever means, to disrupt the nickel lattice and cause the release of krypton. We must also invoke krypton migration induced by the slow sorption of hydrogen in order to explain the continuing release of krypton by sorption of hydrogen. Accordingly, while it is clear that thermal sintering can not explain the results, no alternative explanation can be advanced. Another problem is the necessity for the presence of krypton in the gas phase in order to sweep out the inert gas after its release from a nickel film. This involves krypton atoms being held at 273°K in some state which is accessible to and exchangeable with krypton in the gas phase, but which they are unable to leave spontaneously. While krypton adsorption at low temperatures shows features of chemisorption, it is difficult to believe that this is the case at 273°K.

It is evident that a much wider investigation would be required to clarify the situation. Many of the answers probably lie in deficiencies of the experimental techniques.

First, controlled, reproducible, and thorough sintering techniques would be necessary.

Second, the apparatus would have to be redesigned in order to make possible simultaneous measurements of quantities of inactive krypton and hydrogen, and to permit of the direct transfer of large quantities of gas from the film vessel for measurement and counting in one operation. In the present investigation, the requirement that inactive krypton be allowed access to all parts of the system necessitated the re-opening to the film vessel of the measured amount of non-adsorbed or desorbed hydrogen. Therefore the slow-sorption process was therefore repeated to some extent with all samples, and the time factors could not be reproduced.

In general, no attempt was made to reproduce time factors precisely, in any case. Pumping was normally halted when the radioactivity of the gas recovered from the film vessel reached a steady value, regardless of the time required. If the process of surface reconstruction is time-controlled, this could introduce errors. A time-controlled surface reconstruction has been observed for the adsorption of oxygen on nickel (I30), but this at least partly caused by the penetration of adsorbed oxygen in to the bulk to form an oxide layer (I3I), and no such possibility exists for hydrogen.

In this section, it has been assumed that there were only two distinct adsorbed states of hydrogen on nickel; however it is likely that the real state of affairs is more complex (I32). Up to four distinct phases have been identified, but no physical picture of the various states has been developed.

CHAPTER 8

GENERAL CONCLUSIONS AND SUGGESTED FUTURE DEVELOPMENTS

CHAPTER 8 GENERAL CONCLUSIONS AND SUGGESTED FUTURE DEVELOPMENTS

It has been shown that krypton may readily be incorporated in to metal films during deposition on to a substrate at 77°K. The properties of the films are not significantly altered by the presence of krypton in the lattice, and the krypton has the properties reported for krypton held by solid kryptonates. The homogeneous distribution of krypton throughout the films makes them particularly suitable for use as homogeneous kryptonates in chemical analyses. By variation of the technique, it is likely that any substance capable of being evaporated and condensed could be kryptonated by this method, using simple vacuum apparatus. There is no reason why a perfectly homogeneous solid kryptonate could not be prepared by the method if an adequate source of metal vapour was available.

The use of the films in the study of surface processes has been demonstrated. In particular, the combination of krypton release and electron microscopy has been shown to be a powerful technique for the study of reactions of films.

While it has not been possible to reach definite conclusions as to the mechanism which results in the release of krypton during the processes of adsorption and catalysis, it is believed that most of the problems resulted from deficiencies in the experimental technique. With improvements the method should prove to be an interesting tool for the investigation of surface changes of typical metal films during adsorption and catalysis.

Three possibilities for future work may be suggested. First, the investigation of adsorption and catalysis by films evaporated partly in krypton and partly in vacuum, might reveal the distribution of sites for adsorption and catalysis at various depths in the film. Second, if a non-continuous film could be evaporated in krypton on to a stirred catalyst support powder at 77°K, the product might be expected to show properties similar to those of supported catalysts prepared by other methods. Then the influence of the support could be investigated, as only processes effecting the metal component would result in the release of krypton. A similar but contrasting experiment could be attempted using a support kryptonated by ion-bombardment or diffusion. Third, the problem of whether an input of energy is required to result in surface rearrangement could be tackled using a palladium thimble kryptonated only on the exterior. If the experimental arrangement was such that a monolayer of hydrogen could be formed on the exterior surface of the thimble at approximately 500°K either by direct adsorption from the gas phase or by diffusion from within, then a direct comparison of the release of krypton in each case would be interesting. In one case, all of the heat of adsorption would be dissipated at the kryptonated surface; in the other case, none of the heat of adsorption would be dissipated there. It is envisaged that a thin film of kryptonated palladium could be thrown on to the original thimble by having it in a film vessel during evaporation of a film at 77°K. There is the disadvantage that the thimble would have then to be transferred through the atmosphere. Possibly in this case kryptonation by ion bombardment of the thimble in situ would be simpler and less subject to contamination. Unfortunately, with palladium, there is the complicating factor of absorption (which makes the experiment possible). The thimble could however supply adsorbed hydrogen to a non-continuous film of some other metal deposited on its surface.

As an indirect consequence of the investigation, it has been shown that the adsorption of krypton by a growing nickel film shows features of chemisorption. Even argon adsorption can not be explained on the basis of the classical picture of physical adsorption. These facts may be added to the growing body of evidence which suggests that the interaction of inert gases with solids at low temperatures is not purely physical.

The properties of growing films, and of thermally non-stabilised complete films, are worthy of further investigation. It should be noted that as a technique for investigation of the sorption process, adsorption on to a growing film provides a surface which is effectively clean, without recourse to ultra-high vacuum. However, more work would have to be done in order to determine the structures of the films during and after deposition, if the results were to be generally applicable.

APPENDICES

FIGURE A1
A McLEOD GAUGE
(not to scale)

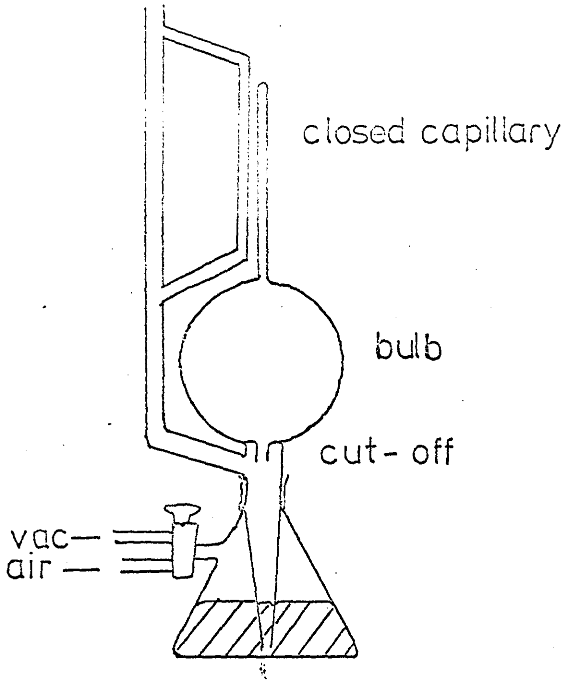
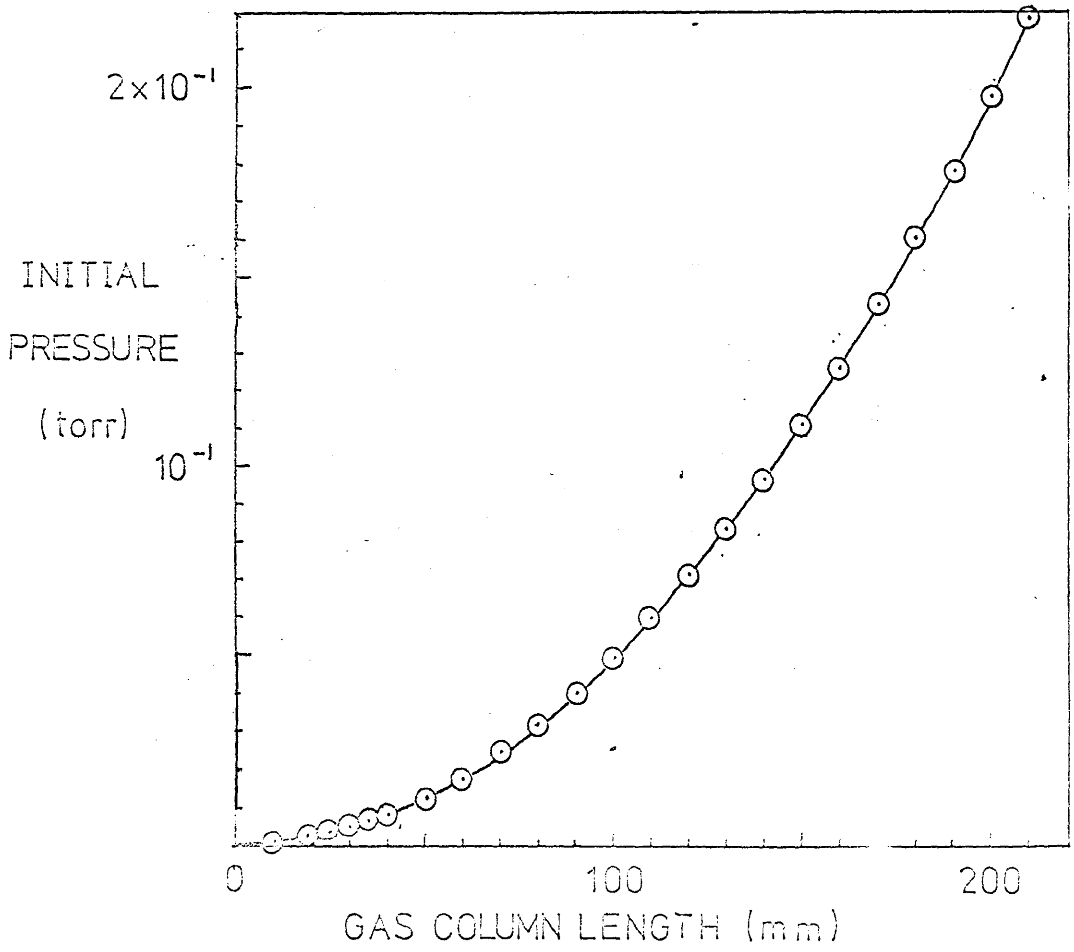


FIGURE A2
PLOT OF ENCLOSED GAS COLUMN LENGTH AGAINST INITIAL PRESSURE IN SYSTEM (LARGE McLEOD GAUGE)



APPENDIX A PRESSURE AND VOLUME MEASUREMENT BY McLEOD GAUGE IN THE VACUUM SYSTEM

The component parts of a McLeod gauge are shown in figure AI. They comprise a large bulb of known volume which may be isolated from the rest of the system by mercury rising from a reservoir, a sealed precision-bore capillary tube in to which any gas thus trapped may be compressed, a matched capillary (not sealed) in order that the effects of capillary depression may be compensated, and a large bore tube to facilitate evacuation of the bulb.

To measure the pressure in a system which includes the McLeod gauge bulb, air is admitted to the enclosed space in the mercury reservoir, causing the mercury to rise in to the gauge and to isolate the bulb at the cut-off. The mercury is permitted to rise until it reaches that point in the open capillary which is at the level of the end of the sealed capillary. At this stage, assuming that all of the gas isolated in the McLeod gauge bulb has been compressed in to the closed capillary, then the length of the enclosed gas column will be equivalent to its pressure expressed in millimetres of mercury. The initial pressure P, at the instant when mercury rising in to the gauge isolated the bulb, may be calculated from the expression:

$$P = \frac{l^2 A}{V} \text{ torr}$$

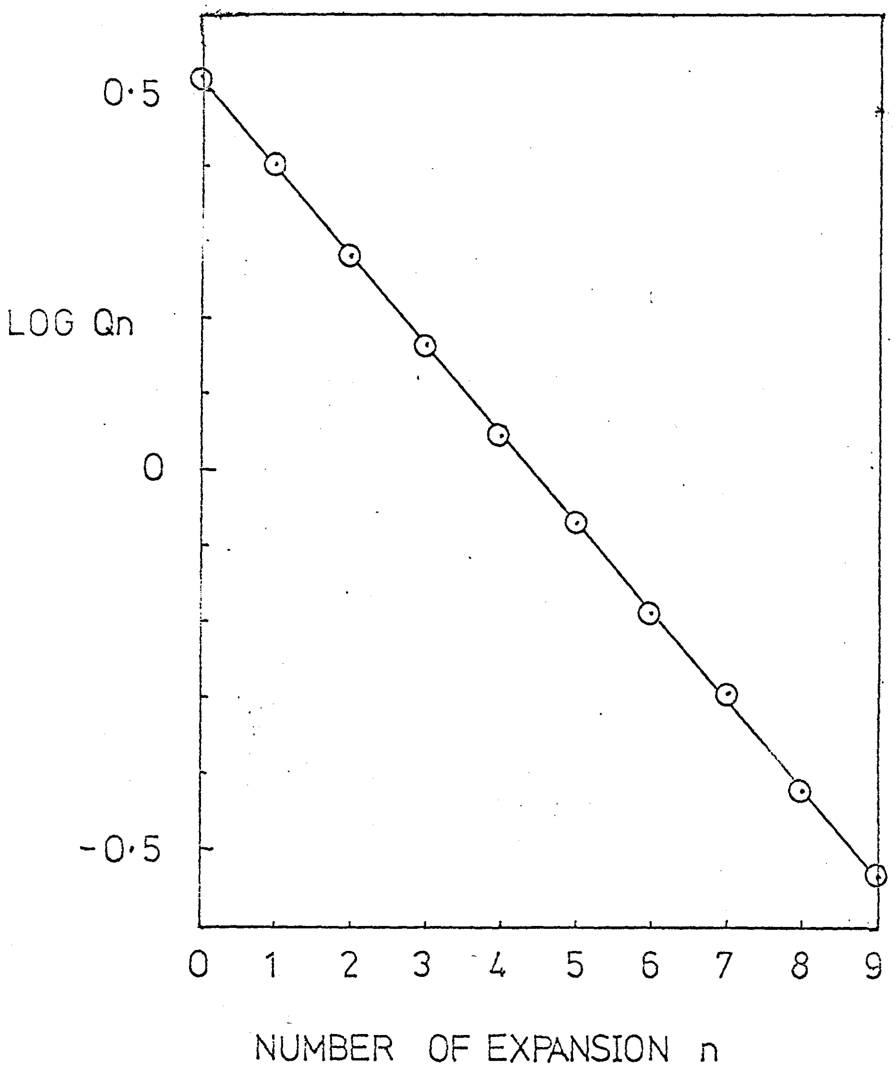
In this expression, V is the volume of the McLeod gauge bulb in mm^3, l is the length of the enclosed gas column in mm, and A is the cross-sectional area of the capillary in mm^2.

Rather than to calculate the pressure on each occasion, it was found convenient to construct for each gauge a plot relating the length of the gas column to the initial pressure, and to read off the pressure from this plot. The plot for the larger gauge is shown in figure A2.

The known volume of a McLeod gauge bulb may be used to find the volumes of other parts of an apparatus.

Consider a space of volume S, evacuated and isolated from the McLeod gauge bulb, which has a volume V, by mercury raised to the cut-off. It is now possible to measure a quantity of gas Q_0 trapped in the bulb, by further raising the level of mercury so that all of the gas is compressed in to the capillary.

FIGURE A3 LOG Qn VERSUS n PLOT FOR DETERMINATION OF VOLUME OF McLEOD GAUGE DEAD SPACE + TOEPLER PUMP OUTPUT ARM



The quantity of gas may be calculated from the length and pressure of the gas column.

If the mercury is now lowered in to the reservoir, then the gas will expand in to the space S. At equilibrium, the quantity of gas remaining in the bulb, Q_1, is given by consideration of the gas laws to be:

$$Q_1 = Q_0 x \frac{V}{V + S}$$

On raising the mercury to isolate the bulb again, pumping out the space S, and repeating the process:

$$Q_2 = Q_0 x \left[\frac{V}{V + S}\right]^2$$

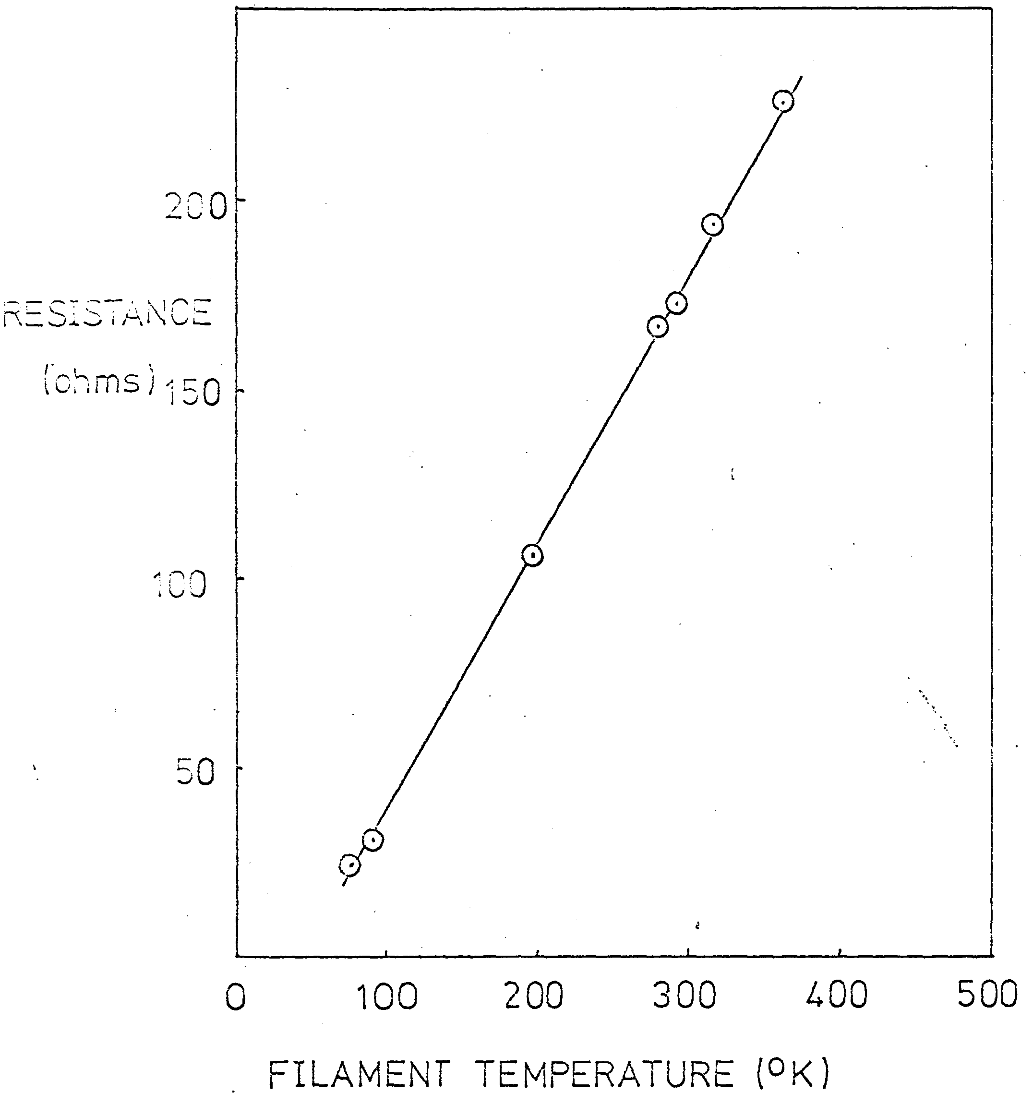
and $$Q_n = Q_0 x \left[\frac{V}{V + S}\right]^n$$

Taking logarithms, $\text{Log } Q_n = \text{Log } Q_0 + n.\text{Log}\left[\frac{V}{V + S}\right]$

A plot of Log Q_n against n for successive expansions will yield a straight line of slope $\text{Log}\left[V \div (V + S)\right]$.

As outlined in chapter 3, such expansion experiments were carried out for various sections of the apparutus. An example is shown in figure A3. This plot was obtained for the expansion of gas from the McLeod gauge bulb in to the McLeod gauge dead space and the portion of the Toepler pump output arm above the ball-bearing seal.

FIGURE B1 TEMPERATURE DEPENDANCE OF RESISTANCE OF THERMAL CONDUCTIVITY GAUGE FILAMENT



APPENDIX B: CALIBRATION OF THERMAL CONDUCTIVITY GAUGE

This gauge was originally included in the system to provide a means for measuring the % of para-hydrogen in a given sample of hydrogen, as it was proposed to study catalysis of the parahydrogen conversion by nickel films.

It was subsequently found that the gauge was also applicable to pressure measurement of argon and krypton in the range of interest.

Since the gauge had to be suitable in the first place for ortho-para hydrogen analysis, it was necessary to select a filament operating temperature such that the difference in thermal conductivity between ortho- and para-hydrogen would be at the maximum. The temperature corresponding to the greatest difference in thermal conductivity has been given by Farkas(108) as 140-160°K.

The temperature of the hydrogen, conducting heat from a hot filament to the cold (77°K) walls of the gauge, will be intermediate between the temperature of the filament and that of the gauge walls.

To provide an estimate of the filament temperature when the gauge was operating, the effect of temperature on filament resistance was investigated. The gauge was filled with hydrogen at $\frac{1}{4}$ atmospheric pressure and surrounded in turn by baths maintained at temperatures between 77°K and 361°K. A decade resistor was coupled to the Wheatstone bridge circuit at the point marked Rv in figure 7. A voltage of only 0.5V was applied to the bridge in order to minimise heating effects, and the decade resistor was adjusted until no current flowed through the bridge galvanometer Gb. The resistance of the gauge filament was then equal to that of the decade resistor.

The assumption that no appreciable heating effect was contributing to the temperature and resistance of the filament at the applied potential of 0.5V was checked by raising the voltage to 1.0V, and the resistance of the gauge filament remained equal to that of the decade resistor. Further increases in voltage disturbed the balance of the bridge. It was concluded that the filament was nearly enough at the temperature of its surroundings at both 0.5V and 1.0V. The results of this experiment are depicted in figure B1.

FIGURE B2 PLOT OF T.C.G. RESISTANCE AGAINST
APPLIED VOLTAGE (a) 25% para-HYDROGEN
(b) 50% para-HYDROGEN

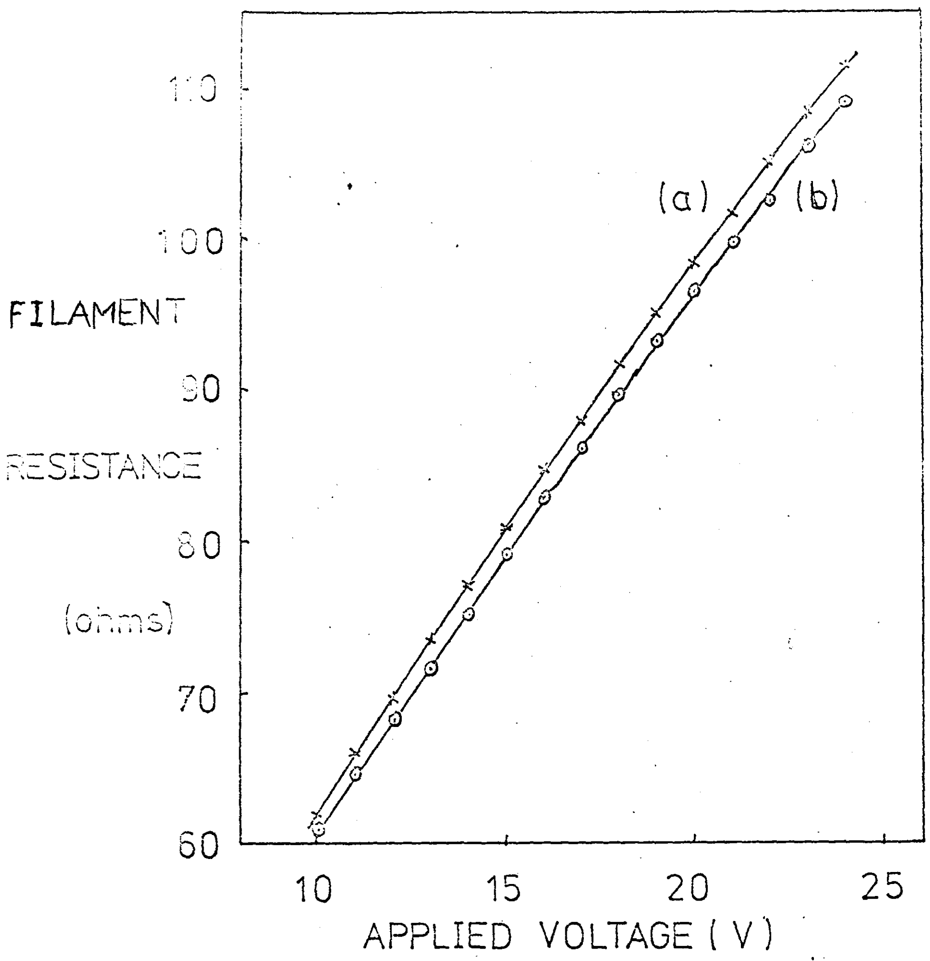
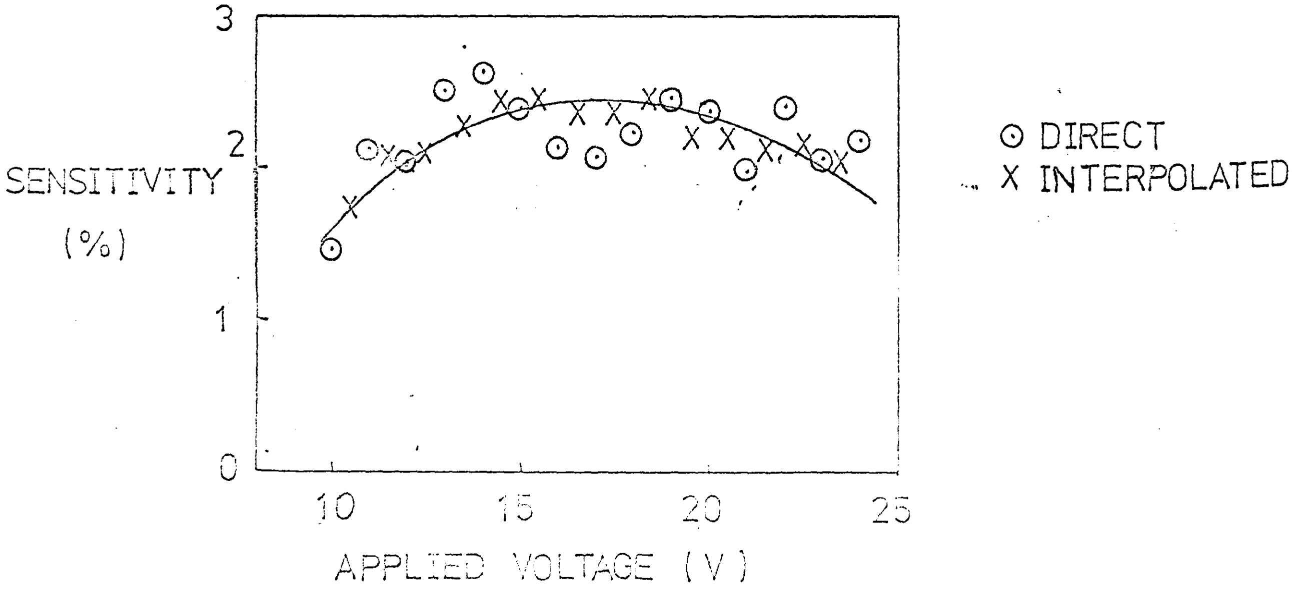


FIGURE B3 SENSITIVITY OF T.C.G. FOR HYDROGEN ANALYSIS



DETERMINATION OF APPLIED VOLTAGE TO GIVE MAXIMUM SENSTIVITY OF GAUGE.

For practical reasons, it was required to use a pressure of hydrogen between 30 and 35 torr.of hydrogen

Two experiments were carried out. In the first, the gauge was filled to a pressure of 33.5 torr of hydrogen which had been purified by passing it through a palladium-silver thimble at 600°K. Such treatment ensured that the hydrogen had the thermodynamic equilibrium concentration of 25% para-hydrogen. In the second experiment, the gauge was filled to the same pressure with hydrogen which had been first purified and then permitted to equilibrate over activated charcoal at 77°K, so that a concentration of 50.4% para-hydrogen was established.

In each case, the main switch was closed and the voltage was raised in steps of one volt. The Wheatstone bridge was balanced as previously, and the resistance of the gauge filament was measured when it was equal to that of a decade resistor.

It was found that when the applied voltage was below ten volts there was little difference in the resistances measured in the two cases.

Plots were made of the measured resistance of the gauge filament against the applied voltage in the range IOV to 24V. These plots are shown in figure B2. It was found that the difference in resistance at a given voltage was small compared to the total resistance of the gauge. Thus the difference between the two readings at a particular applied voltage was subject to error. Accordingly, the best lines were drawn through the experimental points, and the difference in resistance at a particular voltage was interpolated from these lines.

As the voltage was increased, the difference in resistance also rose throughout the range of voltage studied. A measure of the sensitivity of the gauge for hydrogen analysis was taken from the expression:

$$\text{SENSITIVITY} = \frac{2.(R_1 - R_2)}{R_1 + R_2} \times 100\ \%$$

In this expression, R_1 is the resistance of the gauge at given voltage when it contains 25% para-hydrogen. R_2 is the resistance of the gauge at the

FIGURE B4 PLOT OF T.C.G. RESISTANCE AGAINST HYDROGEN PRESSURE (a) 25% para (b) 50% para

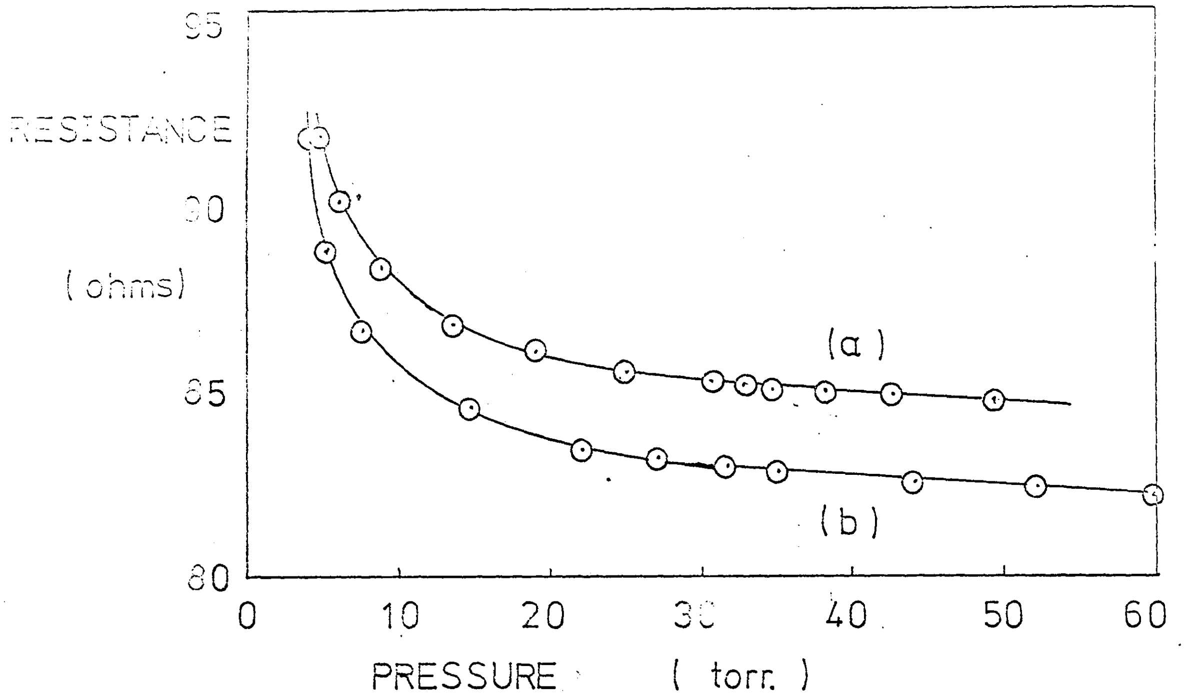
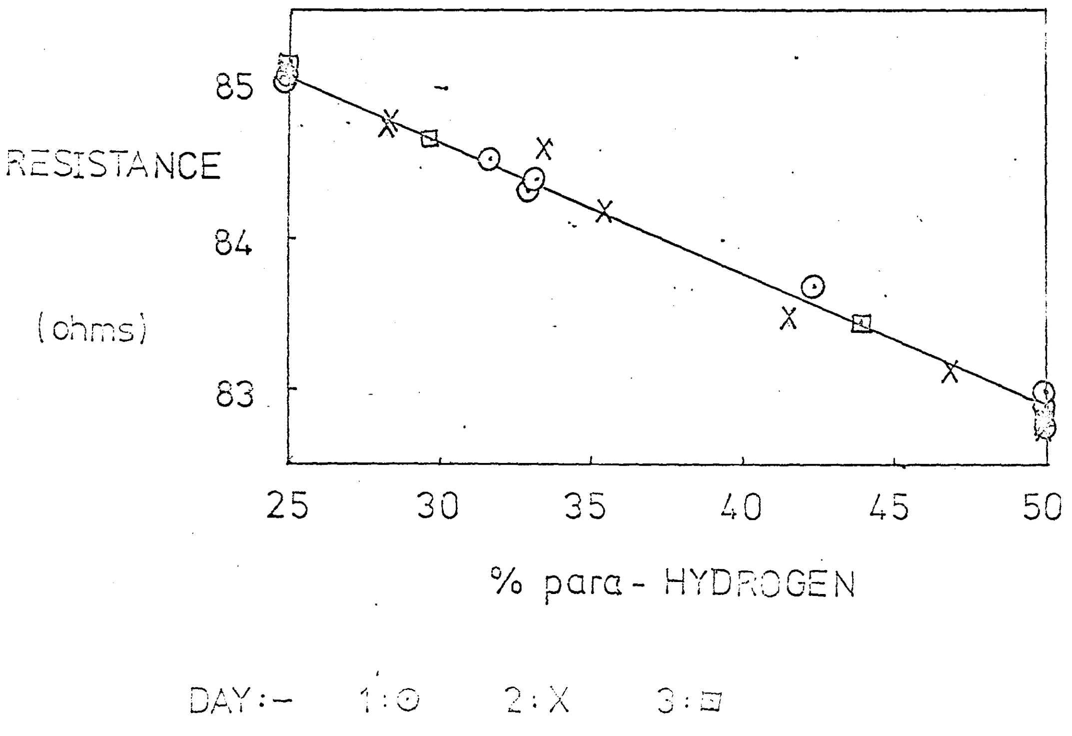


FIGURE B5 CALIBRATION FOR HYDROGEN ANALYSIS



same voltage when it contains 50.4% para-hydrogen. A plot of the sensitivity of the gauge against the applied voltage is shown in figure B3. The line is drawn from values interpolated as above, and the experimental points are included for purposes of comparison.

The sensitivity was found to reach a maximum at approximately 17V, corresponding to a filament resistance of 87 ohms and a filament temperature of 168°K. This may be compared with the findings of Farkas, who showed that in a gauge of this type, the gas temperature should be in the range of 140°K to 160°K, to make use of the greatest possible difference in thermal conductivity between ortho- and para-hydrogen, and thus to achieve maximum sensitivity (108).

Separate batches of 25% and 50.4% para-hydrogen were introduced in to the gauge and the resistance was checked over a two hour period. No change was found. Thus there was no possibility that re-equilibration of hydrogen could have interfered with the results of the experiment above.

A one-setting potentiometer was incorporated in the Wheatstone bridge circuit so that a reproducible voltage of 16.86V could be supplied to the bridge This particular value resulted from the resistances of the precision resistors which were available.

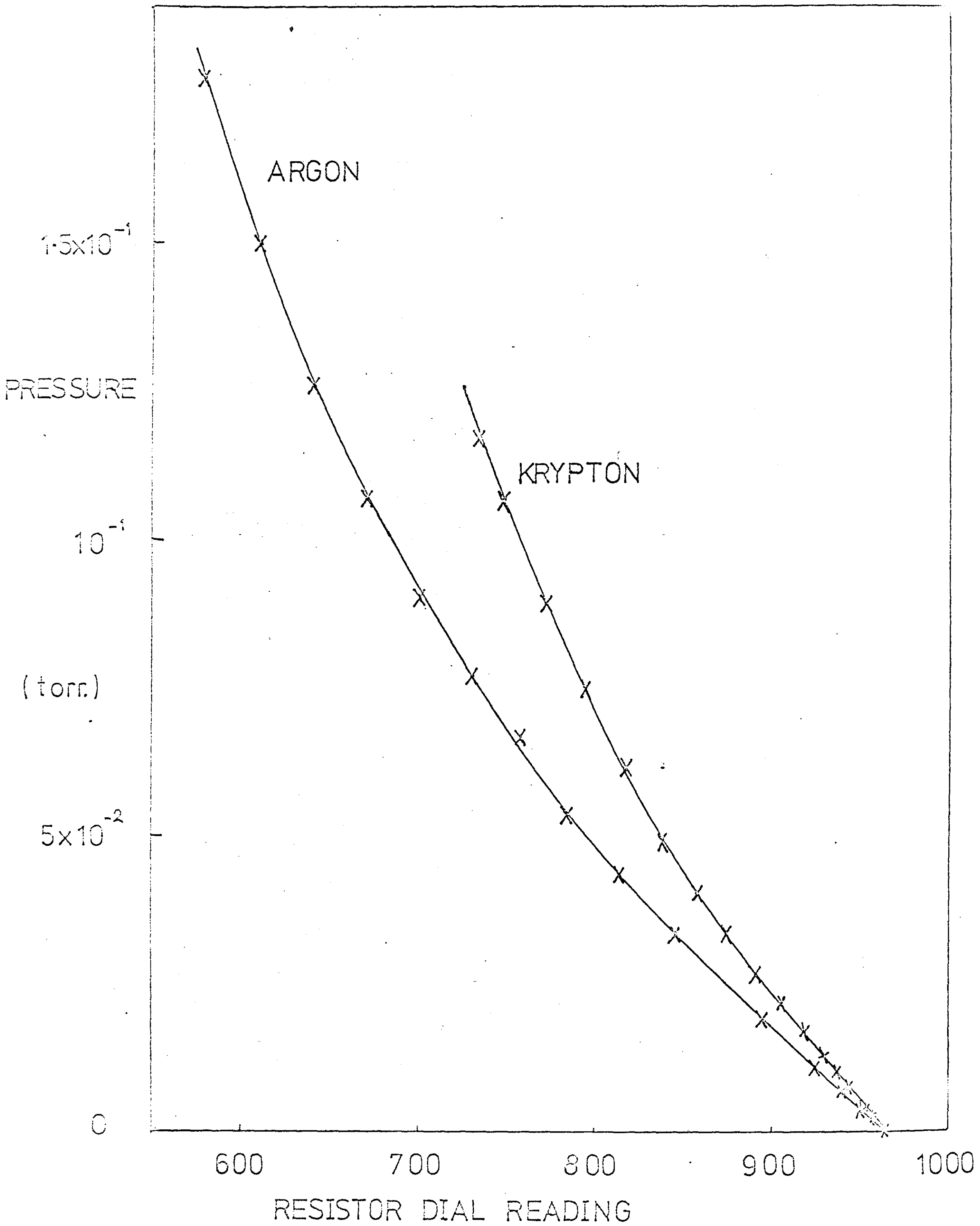
Some idea of the pressure sensitivity of the gauge was sought, in order to be able to correct the measured resistance in cases where it was impossible to adjust the pressure of hydrogen to exactly 33.5 torr. The gauge was filled with 50.4% para-hydrogen to a pressure of 60 torr, and the resistance of the filament was measured with the standard voltage of 16.86V applied to the bridge. Some of the hydrogen was pumped out, and a second reading was taken. This process was continued until the pressure was below 10 torr. The process was then repeated for 25% para-hydrogen.

The results are plotted in figure B4. Between 30 and 40 torr, the relationship may be taken to be linear, and a correction factor of 2.7×10^{-1} ohms torr^{-1} could be applied.

CALIBRATION OF THE GAUGE FOR HYDROGEN ANALYSIS

Batches of 25% para-hydrogen and 50.4% para-hydrogen were prepared, and were mixed in the system. The final % of para-hydrogen in the mixture was

FIGURE B6 CALIBRATION OF T.C.G. FOR DETERMINATION OF KRYPTON AND ARGON PRESSURE



calculated from the partial pressures of the two batches. The resistance of the filament at an applied potential of I6.86V was then measured, and was corrected to the value expected at 33.5 torr. A plot was made of the results, and a linear relationship was found. However, the readings tended to vary a little from day to day (see figure B5). This effect was minimised by keeping the gauge permanently at 77°K, but it was still necessary on a given day to determine the resistance for 25% and50.4% para-hydrogen at 33.5 torr, and then to assume a linear relationship.

CALIBRATION OF THE GAUGE FOR KRYPTON AND ARGON PRESSURE MEASUREMENT

When the need arose in the course of the project to have a continuous measurement of the pressure of argon or krypton on the system, without disturbing the system by raising the level of mercury in a McLeod gauge, it was found that the thermal conductivity gauge was sensitive to changes in the pressure of these gases.

The system was filled with krypton at a pressure of approximately I.5xIO^{-1} torr, the mercury in the McLeod gauge being held just below the cut-off. The resistance of the gauge filament was taken and the pressure was measured immediately by raising the level of mercury in the McLeod gauge. Some krypton was then pumped out of the system. A range of values of pressure down to IO^{-3} torr was covered. The process was then repeated using argon.

A 500 ohm variable resistor with a ten turn dial was connected in series with a resistance nominally of eighty ohms. The filament resistance was balanced against this arrangement; the reading was taken not in ohms, but in the units of the dial calibration. The results of the calibration for the two gases at low pressures are shown in figure B6. A further experiment was carried out to calibrate the gauge for the measurement of higher krypton pressures up to I.8 torr, when a McLeod gauge capable of measuring pressures in this range was added to the system.

Over a period of months it was found that the system had drifted from the values found for the calibrations, possibly because of the condensation of quantities of mercury on the filament. Accordingly, each time that the gauge was to be used for the measurement of variable pressures, the readings of the resistor dial corresponding to (a) vacuum, and (b) a pressure measured with the McLeod gauge, were noted. The amount of drift was sufficiently small that a simple linear correction factor was applied to the experimental readings.

The readings were found to be consistent over a period of hours or days.

Frequently the gauge was used to check that a pressure remained constant for a period of time in the system. In this case, the initial pressure was measured with the McLeod gauge, and a note was made of the reading of the resistor dial. This reading was left unaltered throughout the experiment; if the galvanometer showed that the system was moving out of balance, then the pressure in the system was varied until the bridge balanced again.

APPENDIX C EXPERIMENTAL JUSTIFICATION OF PRESSURE/QUANTITY ASSUMPTIONS

In view of the difficulty of desorbing physically adsorbed argon or krypton from a freshly deposited film (chapter 4), the quantity of inert gas incorporated in to each film was calculated from the expression below.

$$Q = \frac{Pi - Pf}{Pi} \times Qo$$

In this expression, Q is the quantity of gas incorporated by the film during deposition, Qo is the known quantity of gas initially present in the gas phase, Pf is the pressure in the system at the instant when deposition ceased, and Pi is the theoretical initial pressure at the instant of commencing deposition of the film. Pi was evaluated by back extrapolation to zero time of the pressure against time plot, or the Log(pressure) against time plot, whichever was linear for the film in question, in order to allow for the initial warming of gas in the film vessel by the hot filament.

This calculation will only be valid if the pressure of gas in the system is proportional to the quantity in the gas phase. There are a number of factors which could invalidate this assumption: adsorption of gas by a light bake-out film, failure to reproduce temperature gradients exactly, slight differences in the area of the films, variation in the volumes of the film vessels or dead space for the two film lines.

A further problem is that the pressure may not be consistent throughout parts of the system which are at different temperatures, because of the phenomenon of thermal transpiration.

CONSISTENCY OF EXPERIMENTAL CONDITIONS

The data presented below have been taken from the results for the series of films deposited in the presence of a measured quantity of argon.

The term Pe refers to the equilibrium pressure of argon in the system at 77°K, before current was supplied to the filament in order to evaporate the film.

The pressure/quantity ratios found for this series of films are consistent over a range of values of initial pressure, and it may be concluded that it is possible to reproduce the experimental conditions accurately from one film to another, and to maintain them constant during deposition of a film.

TABLE CI PRESSURE/QUANTITY DATA FOR ARGON FILM SYSTEMS

FILM No	Qo (μmoles)	Pe (torr)	Pi (torr)	Pe/Pi	Pe/Qo	Pi/Qo
3	2.40	7.05xIO^{-2}	8.75xIO^{-2}	0.806	2.94xIO^{-2}	3.65xIO^{-2}
7	I.94	6.82xIO^{-2}	7.85xIO^{-2}	0.870	3.52xIO^{-2}	4.05xIO^{-2}
8	2.I4	6.93xIO^{-2}	7.75xIO^{-2}	0.894	3.24xIO^{-2}	3.62xIO^{-2}
9	2.I3	6.70xIO^{-2}	7.55xIO^{-2}	0.9I8	3.I5xIO^{-2}	3.55xIO^{-2}
IO	2.I8	7.20xIO^{-2}	8.00xIO^{-2}	0.902	3.30xIO^{-2}	3.67xIO^{-2}
II	2.I8	6.85xIO^{-2}	7.60xIO^{-2}	0.902	3.I4xIO^{-2}	3.49xIO^{-2}
I3	2.20	7.20xIO^{-2}	8.I5xIO^{-2}	0.883	3.27xIO^{-2}	3.70xIO^{-2}
I8	I.88	5.90xIO^{-2}	6.68xIO^{-2}	0.883	3.I4xIO^{-2}	3.56xIO^{-2}
			MEAN	0.882	3.2IxIO^{-2}	3.66xIO^{-2}
			±	0.032	0.I9xIO^{-2}	0.I6xIO^{-2}

Pe was normally measured with the McLeod gauge, Pi with the thermal conductivity gauge. These results were sufficiently consistent that the mean values were used to calculate the quantity of argon initially present and incorporated in to two films, numbers 30 and 36. (see table I5) These two films were grown specifically to investigate the kinetics of argon incorporation at low pressures and the actual quantity of argon used was not measured at the time of deposition. The assumption that the results for these two films will be consistent with those presented above, is supported by the fact that from the pressure measurements which were made, the value of Pe/Pi is in good agreement with the mean value of table C.I.

TABLE C2 PRESSURE MEASUREMENTS FOR FILMS 30 and 36, AND QUANTITIES Qo and Q DERIVED FROM THE PRESSURE/QUANTITY RELATIONS OF TABLE DI

FILM No	Pe(torr)	Pi(torr)	Pe/Pi	Qo(μmoles)	Q(μmoles)
30	2.60xIO	2.96xIO	0.879	0.809	0.7I3
36	2.20xIO	2.52xIO	0.873	0.688	0.465

THERMAL TRANSPIRATION

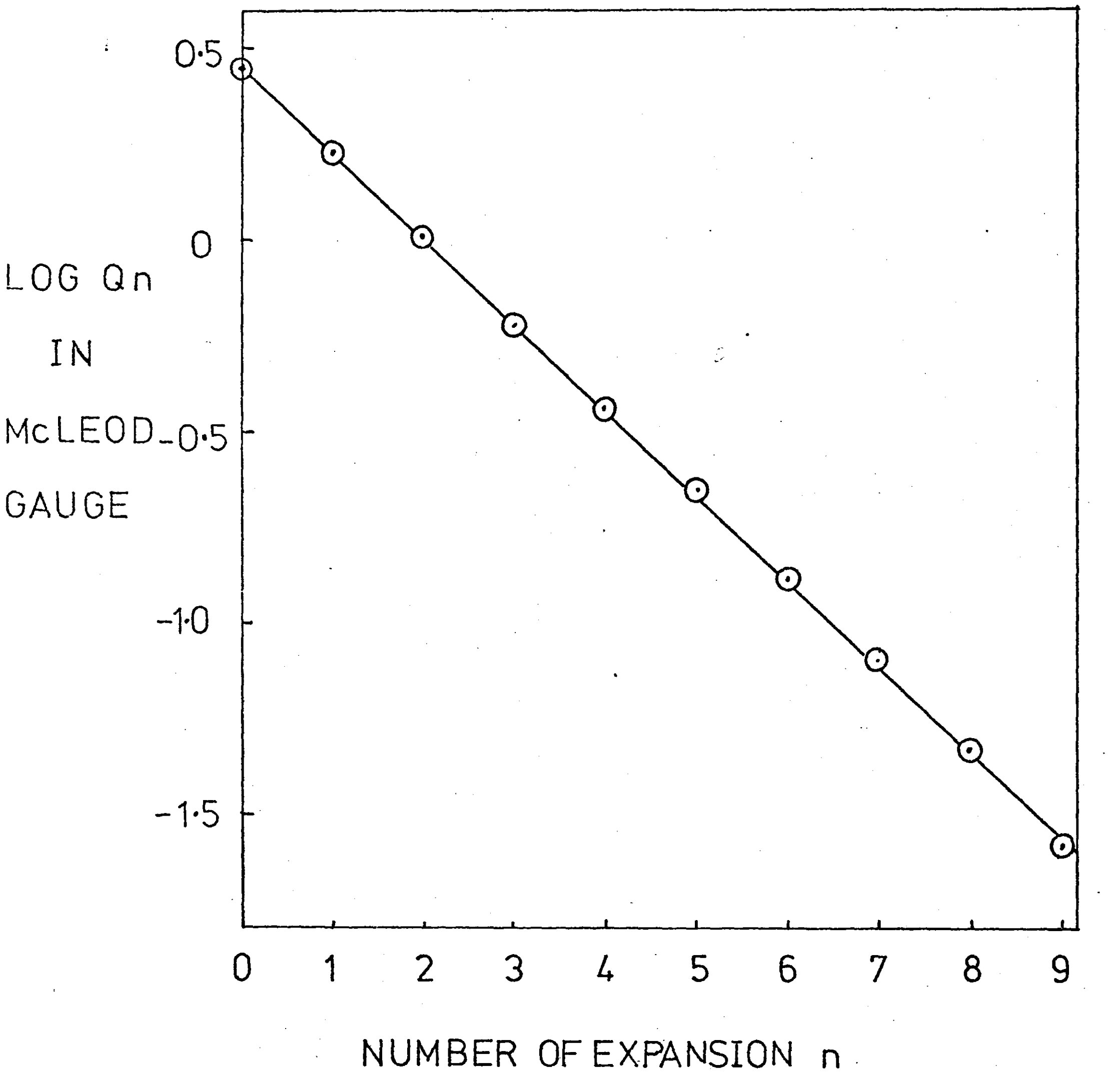
If at low pressures, two parts of a system are maintained at different temperatures, then a pressure gradient is associated with the temperature gradient along the connecting tube. This effect is known as thermal transpiration or thermomolecular flow. Various theoretical (133, 134) and empirical (135) methods of correction have been proposed. However, in any particular case, it is advisable to make an experimental assessment of the magnitude of the effect. The magnitude of the effect is increased by increasing the temperature difference, by decreasing the bore of the connecting tubing, or by lowering the gas pressure.

During deposition of a metal film by the method described in chapters 4 and 5, the system may be considered to consist of three parts: the gas reservoirs (at room temperature), the thermal conductivity gauge (in a liquid nitrogen bath, with the gas temperature raised to some higher value by the heated tungsten filament), and the film vessel (also in a liquid nitrogen bath, where again the gas is warmed to some higher value by the filament used to evaporate the film — see appendix G).

Supposing that the pressures of the gas in the various parts of the system fall in a region where the effects of thermal transpiration are significant, as the inert gas is incorporated in to the film and the pressure falls, then the magnitude of the effects will become greater, and the pressures will become more disparate. The quantity of gas required to maintain a proportionate pressure, measured in the part of the system at room temperature, will thus change during deposition of the film. Therefore the calculation described previously will give an incorrect estimate of the quantity of incorporated gas. Since the temperatures of the various parts of the system are not precisely known, an experimental assessment of the effect is desirable. For a system containing vessels at three different temperatures, in a dynamic experiment, a calculated correction would be difficult to apply in any case.

An experiment was therefore designed to directly evaluate the effect of thermal transpiration under conditions similar to those encountered during

FIGURE C1 CHECK. FOR EFFECT OF THERMAL TRANSPIRATION ON KRYPTON PRESSURE MEASUREMENTS



deposition of a film. The McLeod gauge was taken as the warm (295°K) vessel, and the thermal conductivity gauge, because of its conveniently small volume, was taken as the cold (77°K) vessel. The tubing joining the thermal conductivity gauge to the system was of the same bore as that used for the film vessels (4 mm). The gauge was maintained at 77°K throughout, no current being applied to its filament.

A quantity of krypton was measured in the McLeod gauge, while the thermal conductivity gauge and the short section of connecting tubing were evacuated. It was then permitted to expand to reach an equilibrium pressure in the thermal conductivity gauge. The McLeod gauge was now isolated and the quantity of krypton remaining in it was again measured, while the thermal conductivity gauge and connecting tubing were re-evacuated. This process was continued to a total of nine expansions, as if the volume of the thermal conductivity gauge was to be determined by the method outlined in appendix A. During this experiment, the pressure of krypton in the McLeod gauge fell from 1.75×10^{-1} torr to 2×10^{-3} torr.

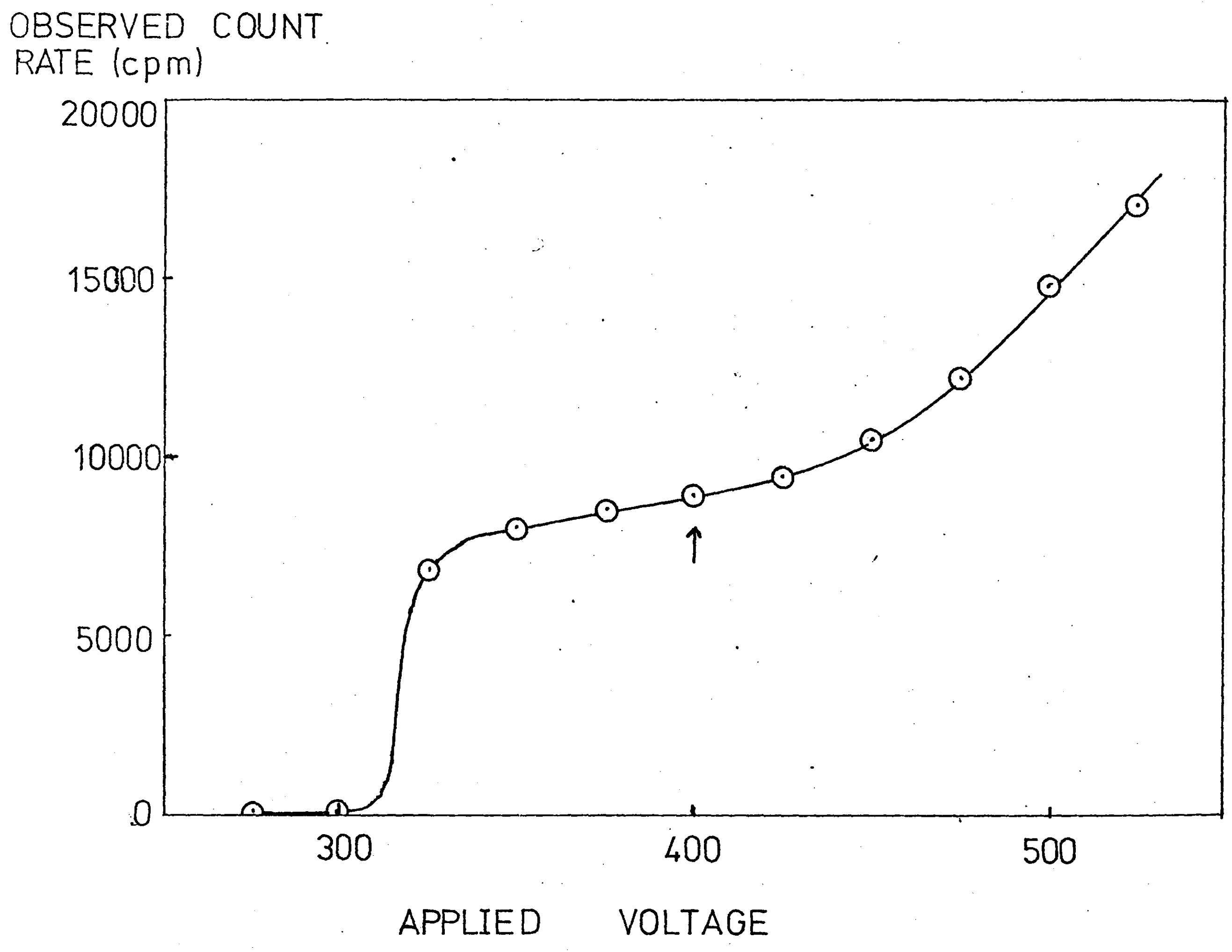
A plot of the logarithm of the quantity of krypton in the McLeod gauge after successive expansions, against the number of the expansion, yielded a straight line (figure C1). This is only possible if the ratio of the quantities of krypton in the two parts of the system at equilibrium is constant over the range of pressures covered by this experiment. It may thus be concluded that thermal transpiration is not a significant factor in the system, to pressures as low as 2×10^{3} torr, which is about the limit of accurate pressure measurement using the thermal conductivity gauge under experimental conditions.

Even if it becomes a more significant factor at lower pressures, this will not interfere in practice with calculations of the quantity of gas incorporated. By the time that a pressure of 10^{-3} torr is reached during the deposition of a film, some 99% of the available gas will have been incorporated already. The error on the remaining 1% may be neglected.

The effect, being negligible for krypton at temperatures 295°K/77°K, may be ignored for the higher temperatures encountered in the film vessel during deposition of a film. It is also assumed that it may be neglected for argon.

From the pressure/quantity data presented for argon, it is evident that the experimental conditions during deposition of a series of films are consistent. Since the effect of thermal transpiration may be ignored, the assumption that the pressure supported by a quantity of gas is proportional to that quantity, is verified for the experimental conditions in the present work.

FIGURE D1 SELECTION OF OPERATING VOLTAGE FOR MX133 GEIGER-MULLER TUBE



APPENDIX D CALIBRATIONS FOR RADIOACTIVITY MONITORING

In order that measurements of radioactivity in the experimental system could be related to the distribution of ^{85}Kr in the system, it was necessary first to determine the optimum conditions for operation of the Geiger-Muller counters, and second to determine relationships between the quantity of ^{85}Kr and the observed count rate.

The operating voltage for each of the counters was found by clamping it a convenient distance from an unopened ampoule of radioactive krypton, and taking one minute counts at various values of the applied voltage. The operating voltage was selected to be close to the centre of the 'plateau' of the plot of count rate against applied voltage.

Details of the results for all three counters are given in table D. As an example, the plot of count rate against applied voltage for the Mullard MXI33 counter is shown in figure DI.

TABLE D OPERATING VOLTAGES OF GEIGER-MULLER COUNTERS

G.M. TUBE TYPE	USAGE	PLATEAU REGION	OPERATING VOLTAGE
MULLARD MXI33	'touching count'	300 V - 450 V	400 V
20th CENTURY ELECTRONICS DM6	'gas flow count'	950 V - II00 V	I050 V
MULLARD MXI24	'gas count'	325 V - 425 V	375 V

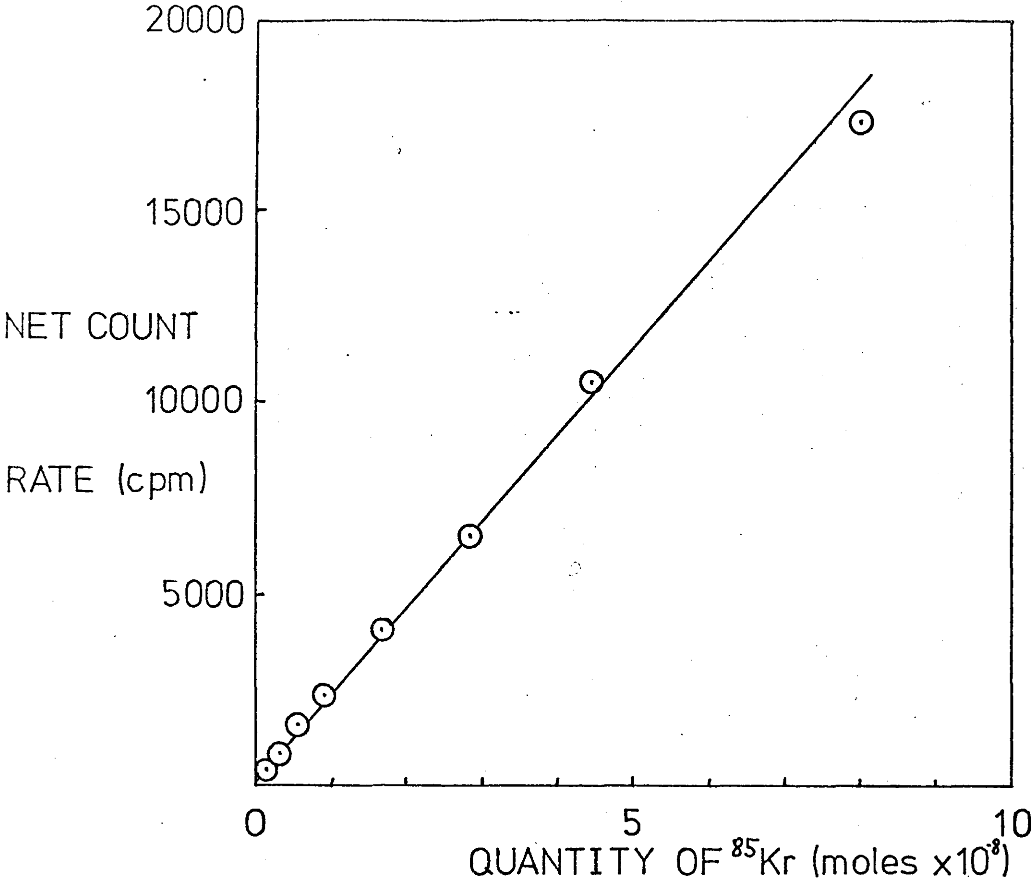
Calibration plots, relating the quantity of ^{85}Kr in a counting chamber to the observed count rate, were constructed for two experimental arrangements, which were selected to have different sensitivity.

The first arrangement, which was relatively insensitive, was used for experiments in the thermal release of krypton during warming of films from 77°K to room temperature. The second, more sensitive, arrangement was used to determine the much smaller quantities of krypton released during experiments involving adsorption and catalysis by the films.

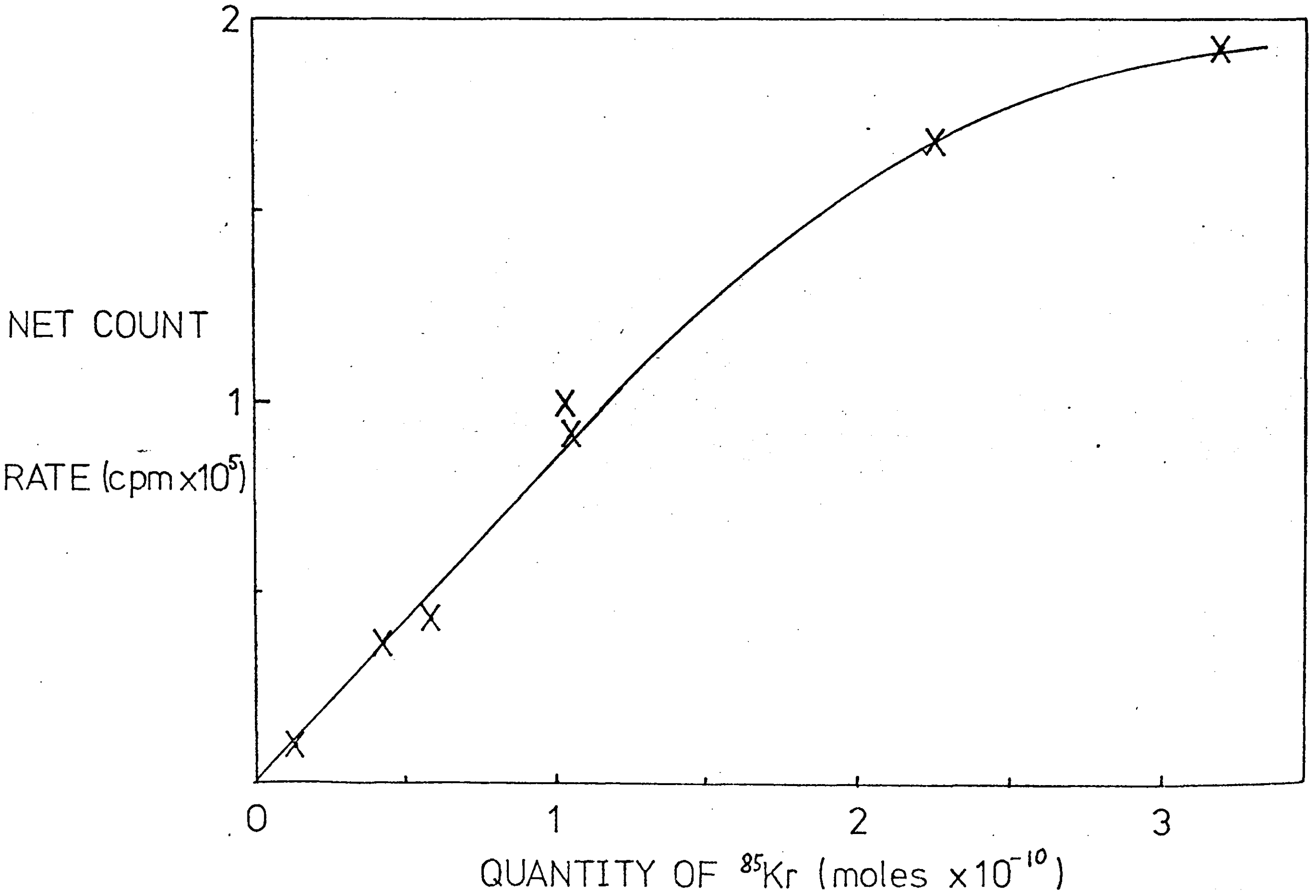
In the first method, the MXI33 counter was clamped in contact with the closed capillary arm of the McLeod gauge. (see figure I0) A quantity of krypton was

FIGURE D2 GAS COUNTER CALIBRATION PLOTS

(a) KRYPTON IN McLEOD GAUGE CAPILLARY



(b) KRYPTON IN GAS COUNTING CHAMBER



transferred to the McLeod gauge and the upper part of the Toepler pump output arm. The krypton in the McLeod gauge bulb was then compressed in to a 100 mm length of the capillary, and a count was taken. In the second method, krypton was transferred in to the counting chamber of section 6 of the vacuum system. (see figure II)

The method of calibration of the two arrangements was the same. Small quantities of krypton of known specific activity were measured accurately and were transferred to the counting chamber. Plots were constructed relating the observed count rate to the known quantity of the isotope ^{85}Kr. A small correction was made for the additional activity of the supposedly inactive krypton used for dilution in some cases.

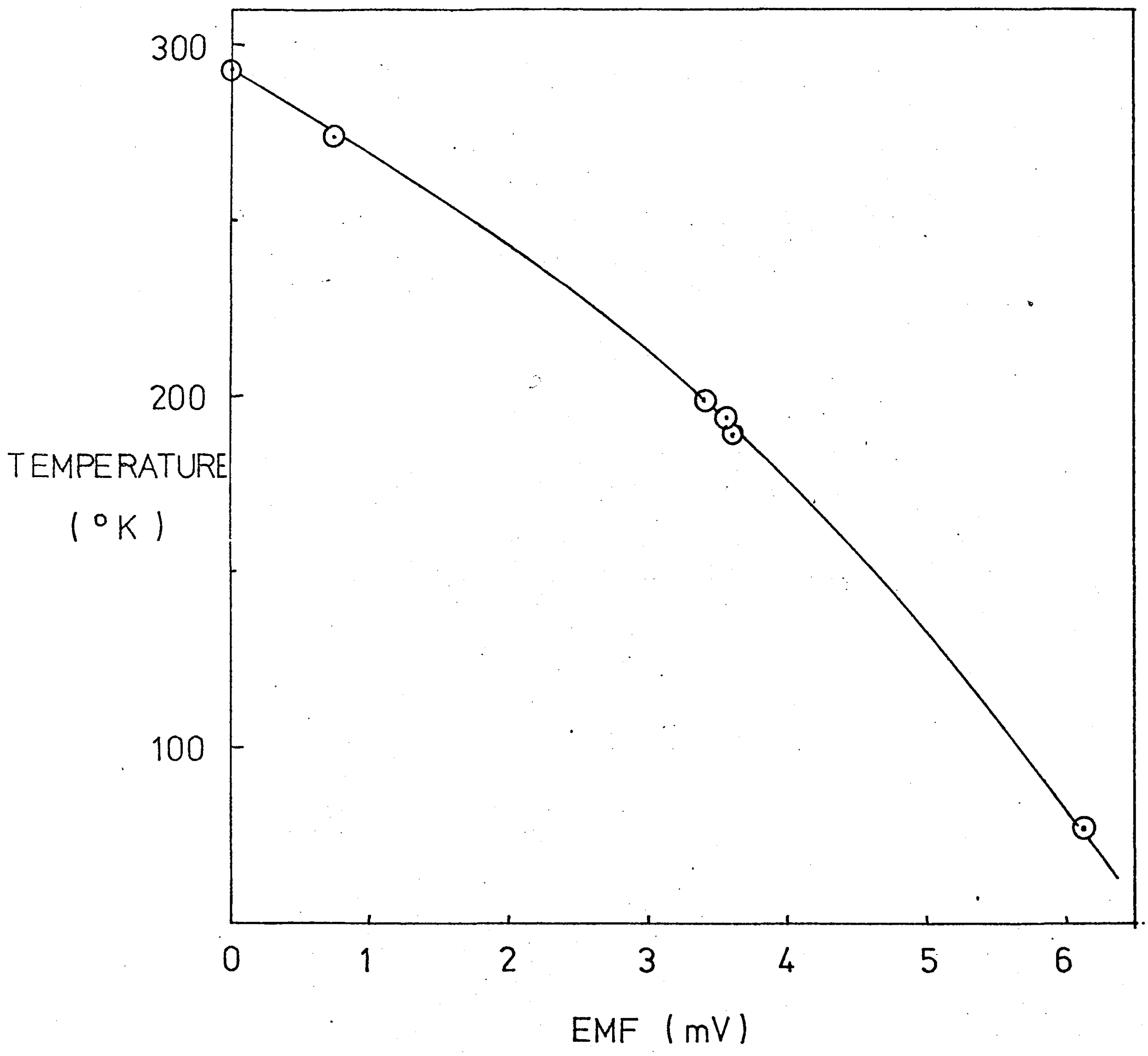
The resulting plots are shown in figure D2. Both were linear for small amounts of krypton, and usually in the case of an experimental measurement, the results were calculated from the gradients of these plots.

The expressions used were:

(a) 10^{-11} moles of ^{85}Kr $\equiv$ 2.34 cpm

(b) 10^{-14} moles of ^{85}Kr $\equiv$ 8.50 cpm

FIGURE E1 CALIBRATION CURVE FOR COPPER-CONSTANTAN THERMOCOUPLES



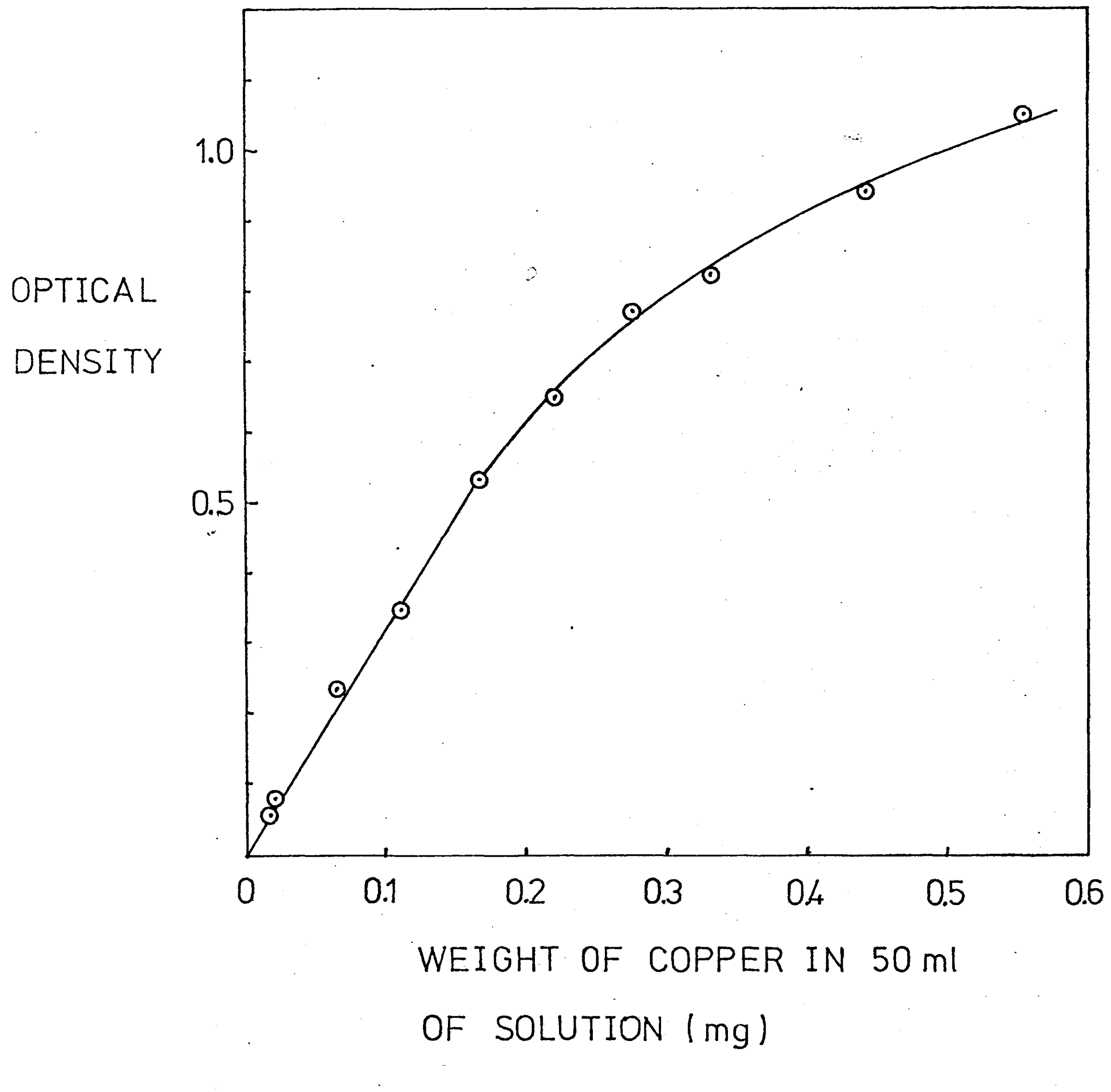
APPENDIX E : CALIBRATION OF COPPER-CONSTANTAN THERMOCOUPLES

For the experiments on thermal release of krypton incorporated within nickel films it was necessary to have a means of monitoring the temperature of a heavy copper cylinder surrounding the film vessel. Two copper-constantan thermocouples were connected to this cylinder and formed part of a potentiometer circuit with a Croydon Precision Instruments Co, Ltd. Type P3 potentiometer.

The calibration was carried out by immersing the copper cylinder in liquid nitrogen, in several CO_2/acetone baths of various temperatures (measured by an alcohol thermometer), in an ice/water bath, and in water at 294°K. In each case the input voltage was balanced against that of the standard cell and the thermocouple EMF was read off. It was found to be equal for the two thermocouples and consistent from day to day. The values were in good agreement with the values of potential quoted in the literature.(III).

The calibration curve is shown in figure EI.

FIGURE F1 CALIBRATION PLOT FOR THE DETERMINATION OF THE WEIGHTS OF COPPER FILMS BY COLORIMETRY



APPENDIX F COLORIMETRIC ESTIMATION OF COPPER

Because of the low weights of copper films, it was necessary to have a method of estimating the weight, which was more accurate than measuring the loss in weight of the filament during film deposition. Accordingly, the copper in a complete film was dissolved by nitric acid and was converted to its complex with biscyclohexanone oxalyldihydrazone. The optical density of the resulting solution with respect to red light was measured using an Eel colorimeter. The method used was that of Somers and Garraway (136), and the following reagents were used.

10% aqueous ammonium citrate.

Borate buffer solution, made up by mixing 400 ml of 0.5M boric acid and 60 ml 0.5M sodium hydroxide solution. (pH 8.3 - 8.9)

0.5% biscylohexanone oxalyldihydrazone in 50% aqueous ethanol.

A calibration plot was made as follows. A known weight of copper wire, part of a filament which had been used for evaporation of a film, was dissolved in nitric acid. When dissolution was complete, the solution was made up to 500 ml with distilled water. Small measured portions of this solution were made just alkaline with ammonia, and to each was added first 1 ml of the ammonium citrate solution, then 20 ml of the borate buffer solution and finally 2 ml of the solution of biscyclohexanone oxalyldihydrazone. Water was added to make up the volume to 50 ml. A blank solution was made up using water in place of the standard copper solution, but with all other quantities as above. The optical density of this solution was set at zero on the colorimeter scale, and the optical density of the other samples was measured using a red filter.

The plot of figure F1 shows the relation between the measured optical density and the quantity of copper in each final 50 ml solution.

To make an experimental measurement, the film was dissolved in nitric acid, and the solution was made just alkaline with ammonia. A measured fraction was made up to 50 ml as above. All readings of the optical density were taken within five minutes of the time of preparation of the 50 ml Cu^{2+}-biscyclohexanone oxalyldihydrazone solution, because the colour intensity was observed to lessen with time.

APPENDIX G CALCULATION OF THE TEMPERATURE OF GAS IN A FILM VESSEL DURING DEPOSITION OF NICKEL FILMS AT 77°K

When current was supplied to each filament in order to evaporate a film, there was an immediate rise in pressure in the system, owing to the warming of the gas in the film vessel. In the constant volume system this rise in pressure amounted to approximately 13% of the initial pressure for both argon and krypton.

From this measurement an approximate estimate of the temperature of gas under deposition conditions may be obtained by consideration of a simplified model of the system.

A volume of the thermal conductivity gauge and its attendant tubing, equivalent to 136 ml at 295°K, was derived from the slope of the plot carried out in order to investigate the effects of thermomolecular flow. An equivalent volume of 340 ml at 295°K may therefore be taken for the McLeod gauge, its dead space, the thermal conductivity gauge, and all connecting tubing. The film vessels all had volumes of approximately 60 ml.

An equilibrium pressure P was established in the system with the film vessel and the gas in it at 77°K, and all other parts of the system equivalent to 340 ml at 295°K. From the general gas law, $P.V = n.R.T$, we may write:

The quantity of gas in the film vessel $= \frac{P}{R} \times \frac{60}{77}$ moles. (Qa)

The quantity of gas in the remainder of the system $= \frac{P}{R} \times \frac{340}{295}$ moles (Qb)

On warming the gas in the film vessel to a new temperature t, the pressure in the system rises to $1.13 \times P$.

The quantity of gas now in the film vessel $= \frac{1.13 \times P \times 60}{R \times t}$ moles (Qc)

The quantity of gas now in the remainder of the system $= \frac{1.13 \times P \times 340}{R \times t}$ moles (Qd)

Since the total quantity of gas in the system is unchanged, we may equate:

$$Qa + Qb = Qc + Qd$$

On solving for t, a value of 108°K is obtained.

APPENDIX H CALCULATION OF THE RELATIVE COLLISION RATES OF INERT GAS ATOMS AND METAL ATOMS WITH A GROWING FILM

All films were deposited on to the walls of a vessel whose inside diameter was 2 cm. Consider a number of inert gas atoms N, contained within an undetermined length of such tubing. Let all the atoms be moving with the mean speed u cm sec^{-1}, one third in the x-direction, one third in the y-direction, and one third in the z-direction, at any instant.

Since the vessel had a circular cross-section, all of the atoms moving in the x-direction or the y-direction may be considered to be moving along chords of a circle. The mean length for a series of chords spaced the same distance apart may be calculated by geometry.

Considering first the atoms moving in the x-direction, then assuming that the gas is homogeneously distributed throughout the vessel, it is obvious that the number of atoms moving along a particular chord at any instant is proportional to the length of that chord. The mean length of a chord, weighted by the number of atoms on each chord, will be the average distance between successive collisions with the walls for an individual atom. This distance, the root mean square length of a chord, may be shown to be I.64 cm for a 2 cm diameter circle.

Then the number of collisions with the walls in one second, for an atom moving in the x-direction or the y-direction, is given by $u \div 1.64\ sec^{-1}$.

It is assumed that collisions of the gas atoms with the top or bottom of the vessel, that is, collisions with the vessel for atoms moving in the z-direction, simply result in restoring the atom to the system.

Now two-thirds of all atoms are moving in the x-direction and the y-direction at any instant.

$$\text{Total rate of collisions with the side walls} = \frac{2}{3} \times N \times \frac{u}{1.64}\ sec^{-1}$$

$$= 0.407 \times N \times u\ sec^{-1} \quad \text{(I)}$$

The mean speed of the molecules of a gas whose molecular weight is M, at absolute temperature T, is given by $u = \left[\frac{8 \times R \times T}{\pi \times M}\right]^{\frac{1}{2}}$

The temperature of argon or krypton in a film vessel during nickel film deposition has been shown to be approximately 108°K. (see appendix G) At 108°K, the mean speed of krypton atoms is 1.65×10^{4} cm sec^{-1}.

Substituting this value in to (I), the total rate of collisions with the side walls is given as $4.03 \times N \times 10^{5}\ min^{-1}$.

The quantity N is identified with the gas in the section of tubing of length L cm where the film is laid down. Thus the volume of gas interacting with a film is $3.14 \times L\ cm^{3}$. At a pressure of P torr, and a temperature of 108°K, the number of atoms will be: $N = 2.81 \times 10^{17} \times L \times P$.

Therefore the total rate of collisions of krypton atoms with the growing film, being laid down in a 10 cm section of the film vessel, is given by:

$$\text{Collision rate for krypton atoms} = 1.13 \times 10^{24} \times P\ min^{-1} \qquad (2)$$

All absolute rates of collision quoted in chapter 4 are derived from this formula.

Assuming that all nickel atoms stick to the film on the first occasion that they collide with it, then the rate of nickel collisions with the growing film is equal to the rate of evaporation. If d is the rate of evaporation in mg min^{-1},

$$\begin{aligned}\text{Collision rate for nickel atoms} &= \frac{d \times 10^{-3}}{58.7} \times 6.02 \times 10^{23}\ min^{-1} \\ &= 1.02 \times 10^{19} \times d\ min^{-1} \qquad (3)\end{aligned}$$

Therefore the ratio of the number of collisions of krypton atoms with the growing film in unit time, to the number of collisions of nickel atoms with the growing film in the same time, abbreviated to 'Kr:Ni collision ratio', is given by:

$$\begin{aligned}\text{Kr:Ni collision ratio} &= (2) \div (3) \\ &\doteqdot 1.1 \times 10^{5} \times \frac{P}{d}\end{aligned}$$

Assuming that the temperature in the film vessel is the same in each case as for nickel films, and allowing for the difference in atomic weights, it can be shown that:

Ar:Ni collision ratio = $1.6 \times 10^{5} \times (P \div d)$

Kr:Cu collision ratio = $1.2 \times 10^{5} \times (P \div d)$

Kr:Pt collision ratio = $3.6 \times 10^{5} \times (P \div d)$

Kr:Pd collision ratio = $2.0 \times 10^{5} \times (P \div d)$

APPENDIX J ESTIMATION OF THE FRACTION OF AN OXYGEN INJECTION WHICH REACTS WITH A COPPER FILM AT 443°K

The atomic % of krypton in copper films at room temperature has been estimated to be 0.34 %.(See chapter 5(a)) Sintering in vacuum for one hour at 553°K reduced this value to 0.I % approximately.

From the experiments in dissolution of nickel films described in section 4.I3, approximately $I.5\times I0^{6}$ counts were released in to a flow of 50 ml of nitrogen per minute, when I mg of a nickel film containing 0.25 % of krypton was dissolved by acid.

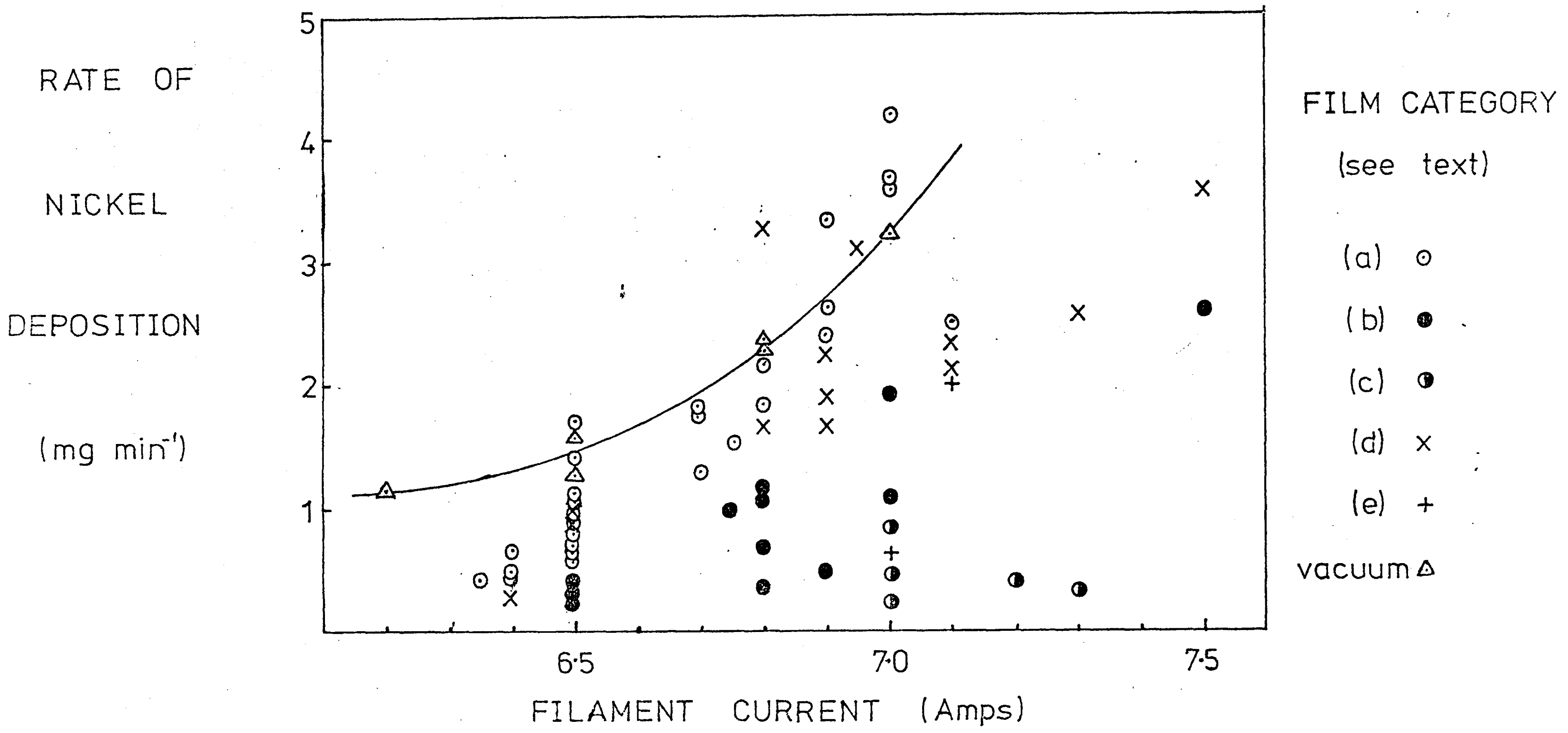
By proportion, the quantity of krypton retained by a I mg copper film after sintering represents $6\times I0^{5}$ counts. Therefore the total quantity of krypton retained by one mole of copper represents $4\times I0^{10}$ counts, in a flow of 50 ml min^{-1} of nitrogen.

An injection containing 2 ml of oxygen is equivalent to approximately $I0^{-4}$ moles of oxygen, and releases some 600 counts from a copper film. (see table 38) Two-thirds of the krypton held by film 77 was lost owing to complete oxidation. This was the only film characterised both by electron diffraction and radioactivity measurements at this stage, but values for other films are in reasonable agreement.

Assuming that two-thirds of the krypton held by a film is released owing to complete oxidation, then the oxidation of one mole of copper will release approximately $2.7\times I0^{10}$ counts in to the gas stream. Therefore 600 counts will be released in to the gas stream by the oxidation of approximately $2\times I0^{-8}$ moles of copper. The product is cuprous oxide, so that the quantity of oxygen used will be less than $I0^{-8}$ moles, or less than 0.0I% of the oxygen injected. For a typical I.0 mg copper film, rather less than I% of the copper in the film is oxidised as a result of the injection of 2 ml oxygen.

In view of the approximations involved in this estimation, the quantities quoted should be taken only to give the order of magnitude of the amounts of copper and oxygen reacting.

FIGURE K1 PLOT OF THE RATES OF NICKEL DEPOSITION AGAINST THE FILAMENT CURRENTS FOR FILMS DEPOSITED IN THE PRESENCE OF INERT GAS, AND IN VACUUM



APPENDIX K THE EFFECT OF THE PRESENCE OF INERT GAS ON THE RATE OF EVAPORATION OF NICKEL FILMS AT 77°K.

APPENDIX K THE EFFECT OF THE PRESENCE OF INERT GAS ON THE RATE OF EVAPORATION

In the sections of this thesis dealing with the evaporation of nickel films in the presence of an inert gas under constant volume conditions, (sections 4.3, 4.6, 4.8, 4.10, 4.11), it has been assumed that the rate of nickel deposition remained constant throughout, although the pressure of gas in the film vessel decreased as gas was incorporated in to the film.

This assumption will be valid if heat loss from the filament occurs mainly by radiation, and the amount of conduction is minimal. It can be tested by a comparison with the rates of evaporation of films in vacuum at 77°K. Six films were laid down in vacuum in the course of the project; details of the currents used and the rates of deposition are given in table K.

TABLE K RATES OF EVAPORATION FOR NICKEL FILMS DEPOSITED AT VARIOUS FILAMENT CURRENTS IN VACUUM AT 77°K

FILM No	FILAMENT CURRENT (A)	RATE OF DEPOSITION (mg min^{-1})
20	6.5	1.28
21	7.0	3.22
32	6.8	2.29
37	6.8	2.36
44	6.3	1.14
53	6.5	1.59

For purposes of comparison, all other films have been classified as follows.

(a) Films deposited in krypton at pressure below 0.1 torr.
(b) Films deposited in krypton at pressures between 0.1 torr and 0.3 torr.
(c) Films deposited in krypton at pressure above 0.3 torr.
(d) Films deposited in argon at pressure below 0.1 torr.
(e) Films deposited in argon at pressure above 0.1 torr.

The observed values for all films are plotted in figure K1; the line drawn is the best line for the films deposited in vacuum.

It is clear that when the filament current was high (6.7 A or above), the rates of evaporation of films laid down in a pressure of less than 0.I torr of krypton were not significantly different from those of films laid down in vacuum. (It is not surprising that at higher currents, a larger proportion of heat loss occurred by radiation) For such films, the initial assumption is valid.

For all other films, the rates of deposition were appreciably lower than those of films deposited in vacuum at the same current, showing that the effect of conduction in reducing the temperature of the filament was significant. Therefore, as the pressure of gas decreased, it would be expected that the rate of evaporation would rise, and as a consequence, the rate of gas incorporation would tend to increase.

In cases where the rate of pressure decrease is tending to exponential behaviour, that is, tending to become slower, the effect of an increased rate of evaporation is to oppose this tendency, so that the rate of incorporation may remain almost steady or may actually increase. This factor probably contributes to the apparently linear pressure decrease observed for films laid down in argon, and at high pressures of krypton.

The effect of filament thinning has previously been invoked to explain these results. It is believed that both effects contribute to the phenomena observed, but no attempt has been made to separate them.

REFERENCES

REFERENCES

I. I. Langmuir, J. Am. Chem. Soc. 38, 222I (I9I6).

2. G. C. Bond, "Catalysis by metals," Academic Press, London and New York, I962, Chapter I.

3. J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, London and New York, I967, p.9.

4. A. Sherman and H. Eyring, J. Am. Chem. Soc. 54, 266I (I932).

5. G. H. Twigg and E. K. Rideal, Trans. Faraday Soc. 36, 533 (I940).

6. S. J. Thomson and J. Wishlade, J. Chem. Soc. 4278 (I963).

7. O. Beeck, Disc. Faraday Soc. 8, II8 (I950).

8. J. H. Singleton, J. Phys. Chem. 60, I606 (I956).

9. O. Beeck, A. E. Smith, and A. Wheeler, Proc. Roy. Soc. AI77, 62 (I940).

I0. L. H. Germer, A. U. MacRae, and C. D. Hartman, J. Appl. Phys. 32, 2432 (I96I).

II. A. Couper and D. D. Eley, Disc. Faraday Soc. 8, I72 (I950).

I2. P. W. Reynolds, J. Chem. Soc. 265 (I950).

I3. J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, London and New York, I967, p.3I4.

I4. F. Sweett and E. K. Rideal, Actes du Deuxième Congrès International de Catalyse (Paris, I960), I, I75.

I5. H. Jaeger, J. Catalysis 9, 237 (I967).

I6. D. D. Eley and D. M. MacMahon, J. Catalysis I4, I93 (I969).

I7. G. Bliznakov and D. Lazarov, J. Catalysis I4, I87 (I969).

I8. I. Uhara, S. Yanagimoto, K. Tani, and G. Adachi, Nature I92, 867 (I96I).

I9. I. Uhara, S. Kishimoto, T. Hikino, Y Kageyama, H. Hamada, and Y. Numata, J. Phys. Chem. 67, 996 (I963).

20. I. Uhara, J. Phys. Chem. 69, 880 (I965).

2I. H. E. Farnsworth and R. F. Woodcock, Adv. Catalysis 9, I23 (I957).

22. K. B. Keating, A. G. Rozner, and J. L. Youngblood, J. Catalysis 4, 608 (I965).

23. L. M. Clareborough, A. E. Hargreaves, and G. W. West, Proc. Roy. Soc. A232, 252 (I955).

24. J. W. Hall and F. H. Rase, Ind. and Eng. Fundamentals 3, I58 (I964).

25. D. D. Eley, Disc. Faraday Soc. 8, 34 (1950).

26. J. P. C. Mignolet, Disc. Faraday Soc., 8, 105 (1950).

27. J. R. Anderson and B. G. Baker, J. Phys. Chem., 66, 482 (1962).

28. J. R. Anderson, Phys. Chem. Solids 16, 291 (1960).

29. R. M. Dell, D. F. Klemperer, and F. S. Stone, J. Phys. Chem. 60, 1586 (1956).

30. D. Brennan, D. D. Hayward, and B. M. W. Trapnell, Proc. Roy. Soc. A256, 81 (1960).

31. K. C. Campbell and D. T. Duthie, Trans. Faraday Soc. 61, 558 (1965).

32. E. Crawford, M. W. Roberts, and C. Kemball, Trans. Faraday Soc. 58, 1761 (1962).

33. M. W. Roberts, Trans Faraday Soc. 56, 128 (1960).

34. J. Muller, Disc. Faraday Soc. 41, 186 (1966).

35. M. Samaane and S. J. Teichner, Bull. Soc. Chim. Fr. 1927 (1968).

36. Z. Knor and V. Ponec, Coll. Czech. Chem. Commun. 28, 942 (1963).

37. G. A. Nicolaon and S. J. Teichner, J. Coll. Interface Sci. 38, 172 (1972).

38. M. V. C. Sastri, T. S. Viswanathan, and T. S. Nagarjunan, J. Phys. Chem. 63, 518 (1959).

39. F. S. Stone and P. F. Tiley, Nature 167, 654 (1951).

40. J. Bagg, H. Jaeger, and J. V. Sanders, J. Catalysis 2, 449 (1963).

41. J. B. Wagner and A. T. Gwathmey, J. Am. Chem. Soc. 76, 390 (1954).

42. R. E. Cunningham and A. T. Gwathmey, J. Am. Chem Soc. 76, 391 (1954).

43. L. H. Germer and A. U. MacRae, J. Chem. Phys. 37, 1382 (1962).

44. L. H. Germer, Surface Sci. 5, 147 (1966).

45. E. Bauer, Surface Sci. 5, 152 (1966).

46. E. Bauer, Colloq. Int. Cert. Nat. Rech. Sci. 187, 111 (1969).

47. C. Jech, Actes du Deuxième Congrès International de Catalyse (Paris, 1960) 2, 2285 (1960).

48. M. W. Trapnell, Trans. Faraday Soc. 51, 368 (1955).

49. Z. Knor and V. Ponec, Coll. Czech. Chem. Commun. 26, 29 (1961).

50. M. H. Sheridan, Ph.D. Thesis, Glasgow, 1966.

51. W. M. H. Sachtler, J. Chim. Phys. 51, 491 (1954).

52. G. A. Bassett, J. W. Menter, and D. W. Pashley, "Structure and Properties of Thin Films," Wiley, New York and London, 1959, p.11.

53. J. S. Anderson, Disc. Faraday Soc. 8, 362 (1950).

54. G. A. Bassett, "Techniques for Electron Microscopy," Blackwell Scientific Publications, Oxford, 1965, Chapter 13.

55. L. Bachmann, D. L. Sawyer, and R. M. Siegel, J. Appl. Phys. 36, 304 (1965).

56. R. H. Anderson and J. S. Halliday, "Techniques for Electron Microscopy," Blackwell Scientific Publications, Oxford, 1965, Chapter 15.

57. K. C. Campbell, J. Catalysis 17, 7 (1972).

58. M. H. Sheridan and K. C. Campbell, J. Catalysis 13, 245 (1969).

59. H. F. Winters and E. Kay, J. Appl. Phys. 38, 3928 (1967).

60. L. B. Loeb, "Processes of Electrical Discharge in Gases," Wiley, New York, (1939).

61. D. Almen and G. Bruce, Nucl. Instrum. Meth. 11, 257 (1961).

62. D. E. Rimmer and A. M. Cottrell, Phil. Mag. 8, 1345 (1957).

63. D. Chleck, R. Maehl, and O. Cucchiara, USAEC Report NYO-2757-5, Parametrics, Inc. (1963).

64. D. Chleck, R. Maehl, and O. Cucchiara, USAEC Report NYO-2757-3, Parametrics, Inc. (1963).

65. D. J. Chleck and C. A. Ziegler, Internat. J. Appl. Radiation Isotopes 7, 141, (1959).

66. J. A. Davies, J. Friesen, and J. D. McIntyre, Canad. J. Chem. 38, 1526 (1960).

67. J. A. Davies and G. A. Sims, Canad. J. Chem. 39, 601 (1961).

68. S. Thulin, Ark. Fys. 9, 107 (1955).

69. D. Chleck and R. Maehl, Internat. J. Appl. Radiation Isotopes 14, 593 (1963).

70. J. E. Carden, Isotopes and Radiation Technology 3, 206 (1966).

71. J. E. Carden, Isotopes and Radiation Technology 3, 318 (1966).

72. J. Tolgyessy and S. Varga, Talanta 17, 659 (1970).

73. S. Dushman, "Vacuum Technique," Wiley, New York, 1949.

74. S. L. Blum and J. Pappis, J. Electectronic Progr. 4, 1 (1960).

75. D. Chleck, R. Maehl, O Cucchiara, and E Carnevale, Internat J. Appl. Radiation Isotopes 14, 593 (1963).

76. C. Jech, Jaderna Energie 4, 390 (1958).

77. H. Matzke and C. Jech, J. Phys. Chem. Solids 31, 753 (1970).

78. C. Jech, Phys. Status Solidi 4, 499 (1964).

79. V. Jesenak, J. Tolgyessy, S. Varga and M. Hradil, Sb. Ved. Prac. Chemickotechn. Fak. SVST, Bratislava, I966, p.II7.

80. V. Jesenak, J. Tolgyessy, S. Varga and M. Hradil, Sb. Ved. Prac. Chemickotechn. Fak. SVST, Bratislava, I967, p.89.

8I. V. Jesenak, S. Varga, and J. Tolgyessy, Atompraxis I4, 204 (I968).

82. P. Goodman, International Laboratory Nov/Dec I97I, p.32.

83. O. Cucchiara and P. Goodman, Mater. Eval. 25, I09 (I967).

84. P. Goodman and M. R. Ronayne, Air Force Avionics Lab. Report AFMC-7R-65-66, Parametrics, Inc. (I965).

85. Chleck, cited in reference 7I.

86. D. J. Chleck, R. Maehl and O. Cucchiara, Chemist-Analyst 54, 84 (I965).

87. J. Tolgyessy, V. Jesenak, and E. Koval, J. Radioanal. Chem 4, I3 (I970).

88. J. Tolgyessy and S. Varga, Talanta I6, 625 (I969).

89. D. Chleck and O. Cucchiara, Internat. J. Appl. Radiation Isotopes I4, 599 (I963)

90. D. J. Chleck and C. A. Ziegler, "Radioisotopes in the Physical Sciences and Industry", IAEA, Vienna, I962, p.35I.

9I. L. O. Hommell, F. J. Brousaides, and R. L. Bersin, Anal. Chem. 34, I608 (I962).

92. W. Guthrie, "Vacuum Technique", Wiley, New York and London, I965, p.I32.

93. R. L. Chuan, University of Southern California Engineering Centre Report No 56-I0I (I960).

94. R. T. Brackman and W. T. Fite, J. Chem. Phys. 34, I579 (I96I).

95. W. Guthrie, "Vacuum Technique", Wiley, New York and London, I965, p.II7.

96. J. Hengevoss, Trans. Int. Vac. Congr. 3rd, Stuttgart, I, 5I (I965).

97. F. S. J. Wang, J. A. Collins and J. D. Haygood, Adv Cryogen. Eng. 7, 44 (I96I).

98. J. D. Haygood, J. Phys. Chem. 67, 206I (I963).

99. F. W. Schmidlin, L. O. Heflinger, and E. L. Garwin, Trans. 9th Vac. Symposium MacMillan, New York, I962, p.I97.

I00. P. H. Emmett and S. Brunauer, J. Am. Chem. Soc. 59, I553 (I937).

I0I. O. Beeck, Adv. Catalysis 2, I5I (I950).

I02. E. K. Rideal and B. M. W. Trapnell, Proc. Roy. Soc. A205, 409 (I95I).

I03. S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (I938).

104. G. A. Nicolaon, Bull. Soc. Chim. Fr. 91 (1969).

105. N. Barlett, International Science and Technology, Sept 1964, p.56.

106. S. J. Thomson and M. Stenhouse, unpublished work.

107. R. S. Yolles, B. J. Wood, and H. Wise, J. Catalysis 21, 66 (1971).

108. A. Farkas, "Light and Heavy Hydrogen," Cambridge University Press, 1935.

109. J. W. Mitchell, "Structure and Properties of Thin Films," Wiley, New York and London, 1959, p.3.

110. G. Ehrlich, "Structure and Properties of Thin Films," Wiley, New York and London, 1959, p.423.

111. The Chemical Rubber Company Handbook of Chemistry and Physics, 50th Edition, 1970.

112. J. A. Allen, C. C. Evans and J. W. Mitchell, "Structure and Properties of Thin Films," Wiley, New York and London, 1959, p.46.

113. R. W. Hoffman, F. J. Anders and E. C. Crittenden, Jr. J. Appl. Phys. 24, 231 (1953).

114. J. W. Marx, H. G. Cooper and J. W. Henderson, Phys. Rev. 88, 106 (1952).

115. B. M. Siegel and C. C. Peterson. "Structure and Properties of Thin Films," Wiley, New York and London, 1959, p.97.

116. T. Baird, J. R. Fryer, and E. V. Riddell, Surface Sci. 28, 525 (1971).

117. N. Cabrera and N. F. Mott, Rept. Progr. Phys. 12, 163 (1949).

118. T. B. Grinley and B. M. W. Trapnell, Proc. Roy. Soc. A234, 405 (1956).

119. W. E. Garner, T. J. Gray and F. S. Stone, Proc. Roy. Soc. A197, 294 (1949).

120. W. E. Garner, T. J. Gray and P. F. Tiley, Proc. Roy. Soc. A211, 472 (1952).

121. D. F. Klemperer and F. S. Stone, Proc. Roy, Soc. A243, 375 (1957).

122. G. K. L. Cranstoun, Ph.D. Thesis, Glasgow, 1962.

123. P. M. Gundry and F. C. Tompkins, Trans. Faraday Soc. 52, 1609 (1956).

124. P. M. Gundry and F. C. Tompkins, Trans. Faraday Soc. 53, 218 (1957).

125. M. M. Baker, G. I. Jenkins and E. K. Rideal, Trans. Faraday Soc. 51, 1592 (1955).

126. D. O. Hayward, P. J. Herley and F. C. Tompkins, Surface Sci. 2, 156 (1964).

127. W. M. H. Sachtler and G. J. H. Dorgelo, Bull. Soc. Chim. Belges 67, 465 (1958).

I28. V. Ponec, Z. Knor and S. Cerny, Disc. Faraday Soc. 4I, I49 (I966).

I29. S. J. Stephens, J. Phys. Chem. 63, I88 (I959).

I30. A. M. Horgan and D. A. King, Surface Sci. 23, 259 (I970).

I3I. M. W. Roberts and B. R. Wells, Trans. Faraday Soc. 62, I608 (I966).

I32. G. Rienacker, Proc. 4th Int. Conf. Catalysis, Moscow I968, I, 537.

I33. M. Knudsen, Ann. Physik. 3I, 205 (I9I0).

I34. A. S. Porter, Disc. Faraday Soc. 8, 358 (I950).

I35. S. Chu Liang, J. Phys. Chem. 57, 9I0 (I953).

I36. E. Somers and J. C. Garraway, Chem. and Ind., 395 (I957).