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THE ADSORPTION OF SOME SMALL MOLECULES ON NOBLE METALS AND ITS RELEVANCE TO ADHESION

A thesis submitted for the degree of Doctor of Philosophy in the City University, London

by

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The City University

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PREFACE

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D.R.L.

ABSTRACT

This project represents a study of the effect of water on the adhesive bond between a polymer and a metal. After a review of previous work it contains a description of the setting up and testing of a vacuum line containing an electronic microbalance for the determination of adsorption isotherms for water, nitrogen and ethanol on finely divided palladium. The isotherms are treated to give information regarding the metal surface including heats of adsorption, and the entropy changes on adsorption. These are treated to give the state of mobility of the adsorbed layer.

The choice of an adhesive is then discussed together with the design of an apparatus for the manufacture and testing of bonds which have been made and stored under known conditions of relative humidity. The adhesive finally chosen was a polyester cross-linked with styrene and polymerised at room temperature using benzoyl peroxide initiator together with N N Dimethyl toluidine accelerator. The test pieces were of the pull through type.

The work continues with an examination of the surface properties of the adhesive by measurement of liquid contact angles and surface free energies for water, ethanol/water mixtures and tricresyl phosphate, the last named providing information as to the solid surface free energy with respect to dispersion interactions only.

The last chapter brings together the preceeding work and shows how the observations of the adhesion tests may be justified by considering the free energy change for displacement by water. Some suggestions for further work are included.

CHAPTER I

INTRODUCTION

It has been known empirically for some time that when a polymer is attached to a metal adhesion is frequently weakened by exposure to a high humidity environment either before or after bond formation. This phenomenon has been investigated by several workers (e.g. Falconer, MacDonald and Walker, 1964; Kerr, MacDonald and Orman, 1967; Delollis and Montoya, 1967; Scott; 1966; Carter, 1966; and Wake, James, and Stone, 1965) The main objective of the present work is to find the relationship between the properties of the bond and the interaction between water and the metal and/or the polymer.

Clearly the system is one of considerable complexity and for the present study a noble metal was chosen as the substrate since this should reduce to a minimum any effects due to metal oxidation and facilitate the achievement of a relatively clean, or at least reproducible, surface.

Much of the initial work was carried out using gold as the substrate, but due to the fact that even the finest gold particles have a rather low specific surface area and tend to contain traces of explosive compounds, gold was abandoned in favour of palladium which is obtainable as a black of high specific surface area.

The adhesive chosen was a polymer of styrene cross-linked with a maleic ester. This could easily be polymerised using benzoyl peroxide initiator and N.N Dimethyl toluidine accelerator.

When a polymer forms an adhesive bond with a metal three types of interaction are possible: mechanical, chemical

and physical. Many authors have maintained that mechanical bonding is unimportant in this type of adhesion although some recent work by Packham (1970) has shown that keying is important in the polyethylene/aluminium system. Others maintain that Van der Waals forces are more than sufficient to account for the strength of any adhesive bond provided that good interfacial contact is achieved (e.g. Bikermann 1961; Patrick, Doede and Vaughan Jr., 1957; and Sharpe and Schonhorn, 1964), and it can be shown thermodynamically that close contact alone should yield an adhesive bond strong enough to break cohesively rather than at the interface. However, adhesive bonds are always complex. They do not represent thermodynamic equilibrium and in any case contain cracks and other flaws which result in the stress at which the bond breaks being much less than the stress inside the material at the actual site of bond failure. Moreover, the bond must be held together by forces acting on a molecular scale and a study of the system at the molecular level must either give positive information as to the mode of bond failure or show that mechanical factors always predominate.

Thus, the present study attempts to answer the following questions:

a)Under what conditions does bond disruption occur, and how does water interact with the bond components separately under the same conditions?

b)What particular types of force are important in the case being studied and how are they affected by the presence of water?

It was aimed to answer these questions by the following types of experiment:

a)Adsorption experiments to characterise the metal and to give information as to the nature of the metal/water interaction.

b)Contact angle measurements to give information as to the water/polymer interaction.

c)Adhesion measurements to show how the bond strength is affected by water or by the polymer formulation used.

The work consists, therefore, of a description of the gas adsorption experiments using nitrogen, water, and ethanol as the adsorbates; some contact angle measurements of water and ethanol/water mixtures on the various adhesives used and a descpiption of the making and testing of the adhesive bonds. In addition it contains a review of previous work in this field and a chapter in which an attempt is made to bring together the results from the different types of experiment.

CHAPTER II

REVIEW OF PREVIOUS WORK

Adhesives made from natural products have been used from the earliest times and even today the use of fish glues, blood glues and other natural materials is common place in certain applications. There is considerable archeological evidence that pitches and other natural resins were used by early man to fasten arrows and spearheads to their shafts. Later, adhesives were manufactured by the addition of a liquid phase and/or an inorganic salt; fish and blood glues, casein and starch being typical of this group.

Up to the beginning of this century it appears that little progress was made in fundamental knowledge of the subject nor had there been any great advance in the type of adhesives in general use although a considerable store of practical knowledge had been built up.

Since 1900, advances in colloid science have permitted a much better understanding of the laws governing adhesion, the first systematic study of the subject being made in 1922 by the adhesives committee of the DSIR. Since that time much theoretical and practical work has been done but there is no doubt that much more information is needed before we can understand the adhesive joint. Useful review articles and books have been written by Tabor (1951), Eley (1961), Weiss (1962), Houwink and Salomon (1965), and Patrick (1967).

2.1 Mechanisms of Adhesion

2.11 Mechanical Adhesion This type of adhesion involves the microscopic interlocking of the adhering surfaces and is

important in the adhesion of rubber to textiles (Borroff and Wake 1949), the gluing of paper and cardboard (Bikermann 1961), and the adhesion of polyethylene to aluminium (Packham 1970). Even in these cases intermolecular forces must still operate at the interface and to say that keying is the explanation of the adhesion is simply to say that the combination of intermolecular forces and the mechanical properties of the material embedded in the substrate is stronger than the bulk adhesive.

2.12 Physico-chemical Interactions Where mechanical keying is known to be absent it is clear that the force that tends to hold two adherends together must stem from interactions between molecules of the two materials and any fundamental study of adhesion must involve a study of these forces. There are several types which may be present in many combinations, and although many books have been written on the subject (e.g. Berry and Beuche 1962, Beuche 1962, and Good 1967), there is, as yet, very little correlation between submicroscopic forces which may be calculated (but not normally measured directly), and the strength of a real adhesive joint. However, the study of intermolecular forces is fundamental to the study of wetting which is the prerequisite for the formation of a good adhesive bond. The types of intermolecular forces have been reviewed exhaustively by Hirschfelder (1967). In the following summary chemical interactions will be taken as those involving specific ionic, covalent, or co-ordinate interactions; and physical interactions as all other types.

2.121 Chemical Interactions. These may be classified broadly into ionic and covalent types according to the degree of electron transfer between the participants.

2.1211 Ionic Interactions A pure ionic bond is one in which a positive ion and a negative ion attract one another, the force being given by:

$$F = q_1 q_2 / r^2$$

and the energy by:

$$U = \int q_1 q_2 / r.$$

The bonds are potentially of great strength (1000 ergs./cm^{-2}). However, even when conditions are favourable, an oxide surface is highly irregular on a molecular scale and contains only one suitable hydroxyl group per 50 - 100 A^2. Thus only a small proportion of the active sites in the polyelectrolyte will actually form bonds which may be regarded as convenient anchoring points rather than the main sites of adhesion. Furthermore, those polymers containing ionizable sites are those which interact most strongly with water giving high permeation rates and much swelling.

2.1212 Covalent Interactions

a)General Treatment A covalent bond between two atoms is one in which there is no great excess charge on one atom over the other and there is an accumulation of electrons between the two atoms. The interaction is represented quite well by a Lennard-Jones potential:

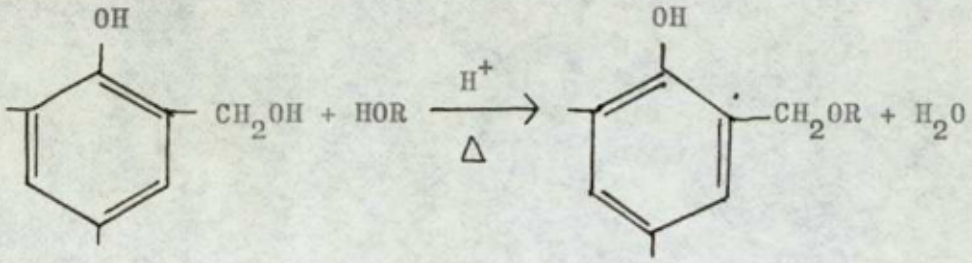
$$F = 6A\left(\frac{1}{r^7} - \frac{r_o^6}{r^{13}}\right)$$

where A is a constant and r_o the equilibrium inter distance.

Whilst this type of bonding is undoubtedly important for the bonding of textiles to water repellent coatings (Baird 1963), it is much less important for bonding to metals. This is because the electronegativity of carbon is much greater than

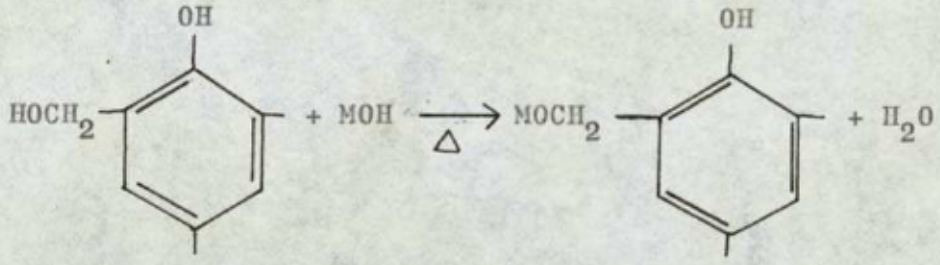
that of all metals and metaloids, giving rise to a polar bond readily susceptible to hydrolytic attack.

b)Bonds involving epoxy resins, alkyd resins, and polyvinyl acetals. A possible exception is the case of high molecular weight bisphenol-A epoxy resins, alkyd resins and polyvinyl acetals. For these, the severe cure conditions in the presence of strong acid catalysts leads to the evolution of water, the following example being taken from Bolger and Michaels (1967).



R is the epoxy, alkyd, or acetyl group.

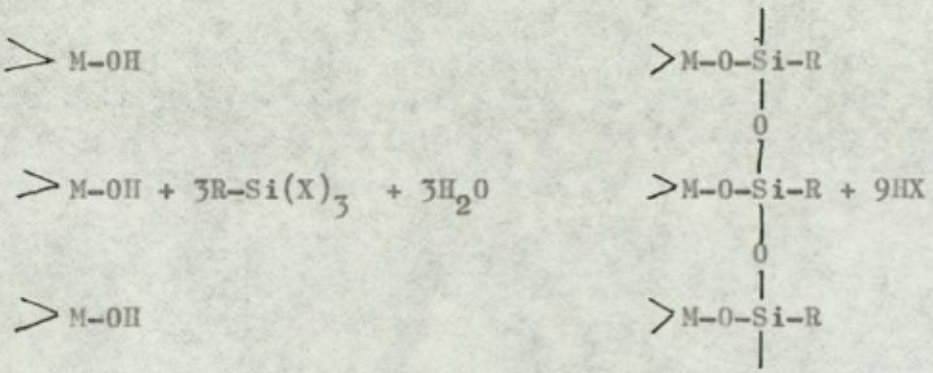
Under these conditions condensation can occur readily between the MOH groups of the substrate and, for example, $-CH_2OH$ groups as shown below.



Whilst this bond may be susceptible to hydrolytic attack, the highly cross linked nature of the adhesive makes the ingress of water a very slow process so that the bonds formed are usually resistant to attack for very long periods.

c)Coupling agents Another exception is exemplified by the silane and titanate coupling agents in which a group IV metal is bonded to a highly electronegative atom such as chlorine.

The following is an idealized surface reaction:



where M is a non-hydrolyzable group which reacts with functional groups in the adhesive phase, and X is hydrolyzable. It is significant that these coupling agents improve the adhesive strength after prolonged immersion in water rather than the initial strength.

2.122 Physical Interactions Physical interactions are of the utmost importance in adhesive bonding since in many cases there is no possibility of the specific interactions detailed in the previous section. This may be because the functional groups are unsuitable or because they do not match geometrically between the two surfaces.

2.1221 Keesom (Dipole-dipole) forces Where a covalent bond has some ionic character the molecule will have a dipole moment defined by:

$$\mu = ql$$

where q is the charge and l is the distance between charge centres. The general expression for the potential energy

is:

$$U = -\frac{\mu_1\mu_2}{r^3}\left[2\cos\theta_1.\cos\theta_2 - \sin\theta_1.\sin\theta_2.\cos(\phi_1+\phi_2)\right]$$

where θ, ϕ are the angles in polar co-ordinates giving the orientations of the dipoles and r is the distance between them.

If the two dipoles are free to rotate they will take up the position of lowest energy in which:

$$U = -2\mu_1\mu_2/r^3$$

2.1222 Debye (Dipole - Induced dipole) forces. If an atom which has no permanent dipole moment approaches one which has, a dipole moment will be induced in the first molecule and the two will then attract one another. The induced moment is given by:

$$\mu = \alpha F$$

where F is the field strength and α the polarizability. The energy of the interaction is then given by:

$$U = -\mu_1^2\alpha/r^6.$$

If both molecules have permanent moments the relation is:

$$U_{12} = -\frac{\mu_1^2\alpha_2 + \mu_2^2\alpha_1}{r^6}$$

or, for similar molecules:

$$U_{11} = -2\mu_1^2\alpha_1/r^6.$$

2.1223 London Dispersion Forces These forces were first proposed by Eisenshitz and London (1930), and London (1930), and have been reviewed by Pitzer (1959). They arise from instantaneous dipole moments which occur in all atoms due to the electron clouds not always being symmetrical. This would not, in itself, give rise to an attraction between

atoms since the moments would, on average, cancel out. However, the instantaneous moments induce moments in adjacent atoms and these interact giving a net attraction. The quantum mechanical treatment gives the results:

$$U = -\frac{3\alpha_1\alpha_2}{4r_{12}^6}\cdot\frac{2C_1C_2}{C_1+C_2}$$

where the α's are the polarizabilities and the C's are constants which have been put equal to the ionization energies. This proceedure has the advantage of simplicity since the ionization energies can readily be evaluated, but other treatments have suggested alternative interpretations for C (Pitzer 1959).

This type of force is of the greatest importance in adhesion since in many applications there cannot be any other interaction across the interface, e.g. non-polar polymers to metals or metal oxides.

2.1224 Hydrogen Bonding This type of interaction was first reported by Rhodebush and Latymer (1920), and has been reviewed by Pimental and McLellan (1960). Here a hydrogen atom forms a bridge between two electronegative atoms, one of which carries a lone pair of electrons and the other the formal bond to the hydrogen. Typical hydrogen bond energies are given below:

HF - HF	6.3 kcal mol^{-1}
H_2O - H_2O	4.0 kcal mol^{-1}
RNH_2 - RNH_2	3.1 - 4.5 kcal mol^{-1}

The bond can achieve considerable strength because of the small size of the hydrogen atom which allows the close approach of the two electronegative members. The strength of the bond thus depends on the electronegativity of one of the

components and on the ability of the other to donate an unshared pair of electrons. In the limit the bond becomes ionic giving:

$$A - H \cdots\cdots B \longrightarrow A^{-}H^{+} - B.$$

Thus strong bonds may be formed between adhesives containing -CO-, NR_3, or strongly anionic groups such as $NaO(SO_2)R$. In all these cases a liquid adhesive interacts strongly with the predominantly OH containing surface and, once set, the separation involves the separation of two charges or, in the presence of water, the production of free acid and free base - both thermodynamically highly unfavourable processes.

2.1225 Metallic Forces A metal may be regarded as an array of ion cores embedded in an electron gas which obeys Fermi-Dirac statistics. The ion cores repel one another since they are all positively charged. There is also a dispersion force of attraction which falls off as the seventh power of the distance. Whilst this type of force is of importance only for bonds between metals (i.e. welding) it is relevant in that it contributes a large amount to the surface free energy of metals and it is important to note that interactions with non-metals can be by dispersion forces only.

2.2 Wetting

Since the good interfacial contact required for good adhesion cannot be obtained between two solids, adhesives are normally applied in the form of liquids and the interaction between solids and liquids is thus of the greatest importance.

The first important investigation of the subject was that of Laplace (1805), who explained liquid to solid adhesion

in terms of force fields between the volume elements of a continuous medium. This was later shown to be unable to explain some simple phenomena, and the fundamental quantity, the force field, was not experimentally obtainable.

2.21 The Young Equation and Work of Adhesion. The next important developement was due to Young (1806), who proposed the famous equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta$$

where the γ's are the interfacial tensions and θ the contact angle at the interface. Although there are conceptual and experimental difficulties it has been shown that the equation is valid so long as the surface is not too deformable. If it is assumed that the work of adhesion is given by:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

it is easily shown (Lester 1961), that the equation is

$$W_a = (\gamma_S{}^o - \gamma_{SV}{}^o) + \gamma_{LV}\theta(1 + \cos\theta)$$

where:

$$\gamma_S{}^o - \gamma_{SV}{}^o = RT\int_o^{p_o} \Gamma\, d(\ln p)$$

in which p_o is the saturation vapour pressure and Γ the Gibbs adsorption excess per unit area.

2.22 The Critical Surface Tension More recently, studies of wetting have taken on a new dimension with the work of Zisman, and of Good, Girafalco and Fowkes. Zisman (1964) has defined the critical surface tension of a solid as that point at which a plot of $\cos\theta$ vs γ cuts the line $\cos\theta = 1$. This quantity, γ_c, has been identified with the surface free energy of the solid, a quantity very difficult to measure directly. Zisman shows how γ_c may be related to the chemical constitution of the surface layer, and suggests that where the experimental points representing $\cos\theta$ vs γ lie in a

band, the lowest intercept corresponds to γ_c. The higher values correspond to cases where forces other than dispersion forces are operative.

2.23 The Relation Between Interfacial Forces and Critical Surface Tension Girafalco and Good (1957), and Fowkes (1965) have developed a theoretical approach giving the interaction of forces across the interface in terms of the contact angle. Their equation is:

$$\cos\theta = \frac{-\gamma_L + 2\sqrt{\gamma_S^D \cdot \gamma_L^D} - \pi_S}{\gamma_L - \pi_L}$$

where the γ^D's are the contributions due to dispersion forces only and the π's, often neglected, are the spreading pressures. Of course, where the liquid molecules interact with one another by dispersion forces only, $\gamma_L = \gamma_L^D$. Where this condition is not fulfilled the work of adhesion, W_a, is given by:

$$W_a = \Phi\sqrt{W_{c1} \cdot W_{c2}}$$

where the W_c's are the works of cohesion of the two phases separately, and Φ is a constant which has been evaluated theoretically by Good (1964). It is the variability of Φ for different liquid/solid combinations which has caused much dispute as to whether Zisman's concept of critical surface tension is applicable to cases where the value of γ_c depends on the series of liquids used to determine it. Dann (1970a and 1970b) collects a large amount of data from the literature and adds some of his own to show that we not only do, but should, obtain different values of γ_c depending on the liquid series. He also demonstrates that the plot of $\cos\theta$ vs γ is not necessarily a straight line and that long extrapolations

are to be avoided.

2.24 The calculation of Interfacial Free Energy It is also possible to calculate the surface free energy at the interface between two slabs of material (subscripts a and s) and if σ_{max} is the maximum force an interface can support, the result:

$$\sigma_{max} = 1.64 \times 10^{8} W_a / (V_a^{\frac{1}{3}} + V_s^{\frac{1}{3}})$$

is obtained. The V's are the molar or unit volumes and W_a the thermodynamic work of adhesion. For a single material for which the cohesive energy density is known, W_a can be eliminated and by making a series of approximations the result

$$\sigma_{max} = 1.025 \delta^2$$

where δ^2 is the cohesive energy density, is obtained. The agreement with experiment is good for materials such as metal whiskers which are likely to be fairly free from flaws.

2.25 The Calculation of the Maximum Stress an Interface can Support The theory of Girafalco and Good (1957) can be used to derive a similar expression for the maximum force an interface can support and the result:

$$\sigma_{max} = 1.025 I_I I_v^{1.5} \delta_a \delta_s$$

is obtained where the I's are the interaction parameters as above. It is also shown that the failure will be interfacial if the following condition is fulfilled.

$$\delta_a / \delta_s \geq I_I I_v^{1.5}$$

If the contact is not perfect the failure may be interfacial for mechanical reasons even though this condition is not

fulfilled and for this reason adhesives should be chosen which will give the best possible wetting. Unfortunately these will, by definition, have low cohesive energy densities. This dilemma is overcome by making joints at high temperatures or in the presence of a solvent which will lower the surface free energy of the adhesive.

2.3 The Interaction between Metals and Polymers

2.31 Additivity of Forces across an Interface It has been shown (Feynmann 1939) that for molecules for which several types of interaction force are important, the forces are additive, and it is useful to consider the types of interaction which will be important for the metal/polymer systems used in the present study.

A piece of palladium will consist of palladium atoms covered by a thin layer of oxide. This will normally be covered by a layer of strongly bound water molecules and these will attract a greater or lesser number of more loosely bound water molecules depending on the relative humidity.

If an adhesive bond is to be made to such a material, the hydrated oxide layer must either be removed or the bond must be made on top of it. It has been suggested that since virtually all metal oxides have a similar hydrated structure, adhesives should behave in the same manner towards all such surfaces. Thus Wade and Hackermann (1964) found that the heats of immersion of silicon dioxide, titanium dioxide, and aluminium oxide depended much more on the particle size than on the nature of the metal atom. However, since, in general, different materials behave differently in this respect, we must consider the differences between these surfaces, the most

important being geometric factors, rate of hydration, and the activity of surface hydroxyl groups.

2.32 Magnitude of Interactions between Polymers and Metals For pure dispersion forces between a polar polymer and a metal oxide, the interaction energies are about 100 dynes.cm^{-2}; about the same value as the total interaction between the same metal and a non polar polymer. For water on metal oxides, however, the interaction is much greater being about 500 dyne.cm^{-2}. Thus a bond between a metal oxide and a non polar polymer cannot normally retain adhesion after prolonged immersion in water, a typical free energy change being -300 erg.cm^{-2}.

2.4 The Destruction of Bonds by Water

2.41 Experimental Studies The destruction of bonds by water was first studied in detail by Falconer, MacDonald and Walker (1964) who investigated the reduction at high relative humidity in the adhesion of two types of adhesive (Heat Resistant Phenolic, and an Aromatic Amine Epoxide) bonded to stainless steel and tested both in tension and in shear.

They found that the bonds failed cohesively during the early stages of the tests but later the failure changed to adhesive. The authors postulated solvation of the adhesive close to the interface leading to movement of the chain segments and the production of weak boundary layers.

Kerr, MacDonald and Ormann (1967) improved on the experimental technique and worked with aluminium. Their results show that exposure to ethanol or oxygen at 90°C causes no deterioration in the bond strength. They measured

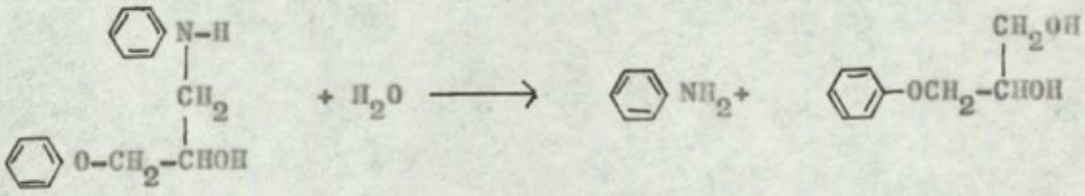
the fall in the tensile strength of the polymer on uptake of water and of ethanol. They found that, with water, equilibrium was reached in about ten days, (with about 8% loss in strength) whereas ethanol took much longer to reach equilibrium, giving about 30% loss after about 50 days during which time the polymer swelled appreciably.

2.411 Conclusions Careful examination of the results suggests that the adhesive weakening is a function of the boundary layer rather than of the bulk polymer. The authors also conclude that the interaction is chemical rather than physical and suggest that numerous hydrogen bonds close to the interface will be greatly weakened by the ingress of water, which will tend to congregate at hydrophilic centres.

2.412 Recovery on Drying More recent work by the same authors (1970a and 1970b) has shown that the bonds recover part, but not all, of their strength on drying. Further studies with grossly undercured polymers (to reduce the crosslink density) shows that the authors' earlier theory was in error since the undercured polymer was less affected than the normally cured specimen. (The undercured polymer would be expected to have a larger number of unoccupied H-bond sites and therefore to be more affected.)

2.42 A New Theory The authors then suggest that their work supports the theory of Kwei (1966) that the rupture of covalent bonds is involved. This was confirmed by further experiments in which bonds were exposed to environments rich in formaldehyde, ammonia, and methanol, none of which was detrimental to the bond strength. This, together with the fact that the bonds show a slight initial increase in strength before reverting to their original value, suggests that some plasticising action is involved. It is possible that

water also acts as a plasticiser, but the ingress of water is so rapid that it masks the effect. The following hydrolysis reaction is postulated:



Other examples of this type of reaction have already been given, (2.1212).

2.43 Ionic Interactions Ionic reactions have also been postulated by Bolger and Michaels (1967) who classify reactions into the following types:

A 1 Dipole interactions with organic acids

A 2 Ionic Interactions with organic acids

B 1 Dipole interactions with organic base

B 2 Ionic interactions with organic base

They then distinguish between the types by deriving the relations:

$$\Delta_A = IEPS - pK_{A(A)}$$

$$\Delta_B = pK_{A(B)} - IEPS$$

were IEPS is the isoelectric point and the Δ's are the logarithms of the respective equilibrium constants for the surface reactions.

Then if Δ_A or $\Delta_B > 0$ the ionic reaction should predominate and if Δ_A or $\Delta_B < 0$ the dipole interaction should predominate.

The strongest bonds should occur at large positive values of Δ_A or Δ_B. The authors tabulate a large number of values of Δ_A and Δ_B for different adherend/

adhesive combinations, and give typical surface reactions. They then use their theory to show that water resistance should increase where ionic attractions for the organic-substrate interface are large relative to the attraction for the water-solid interface in neutral systems - i.e. with no additional ions such as OH^- or H^+ to shift the equilibria. It is then shown that for strong ionic interactions either

$$pK_{A(A)} < pH < IEPS$$

for type A interactions, or

$$IEPS < pH < pK_{A(B)}$$

for type B interactions.

The theory is then confirmed by experimental measurements of the underwater adhesion of a large number of air dried, solvent based, primer coatings, containing alkylated phenolic resins with polyvinyl butyrol or nitrile rubbers.

Of course, the foregoing should not be taken to indicate that the polymer should contain large numbers of ionizable or hydroxyl groups since these polymers exhibit high water solubility, swelling etc., and in any case a very small number of active groups is normally suitably placed for adhesion.

2.44 Glass fibre/resin composites This type of treatment has been taken up by Bascom (1970), and applied to glass fibre/resin composites.

Bascom also gives a treatment of the way in which cracks might propogate in the presence of water vapour, saying that the presence of water must alter the cohesive strength of the material at the crack tip.

It is also possible that water condensing in the crack

tip can exert some capillary action tending to open the crack, but this mechanism will be important only at high relative humidities. Some experimental evidence is presented to support each of these possibilities but the author concludes, by saying that most workers tend to study particular systems with a view to finding the conditions under which the bond is stable rather than formulating a more general treatment of its failure.

2.5 Mechanical Factors Affecting Adhesion

When an adhesive is tested to destruction the failure may occur in several ways and which of them is important depends on the mode of formation of the bond, rate of application and direction of the applied stress, the presence or absence of cracks, and the bulk properties of the adhesive.

2.51 Properties of Polymers When a stress is applied to a polymer below its glass transition temperature the polymer cannot elongate to any great extent and normally breaks at a few percent extension. Above the glass transition temperature the polymer may extend several hundred percent before breaking.

The ultimate breaking strength of the polymer, σ_{max}, is strongly dependant on the geometry of the sample since as the cross section decreases the probability of finding flaws decreases (Anderegg 1939). Furthermore, even in uniaxial tension, shear stresses will develop in the sample and it has been found that a notched specimen has a much larger ultimate tensile strength due to the fact that interior material is inhibited by the material outside, (Orowan, Nye, and Cairns, 1945).

2.52 Crack Propagation and Limiting Crack Size If the material contains cracks, the stress at the edge of the crack will be greater than average. According to the theory of Griffith (1924), the crack will propagate if the energy required to increase the free surface of the material is less than the energy released by the release of strain at the crack boundary. This leads to the equation:

$$\sigma_{max} = K(E\gamma/c)^{\frac{1}{2}}$$

where γ is the surface free energy, E the elastic modulus, and c the crack size.

Barenblatt (1962) proposed that a system of crack closure forces should be imagined as acting on the crack surface near the border in such a manner as to remove the infinite stress there. Three mutually perpendicular directions were considered for the action of the crack closure forces and it is possible to calculate the limiting crack size for catastrophic failure of the sample. It is clear from the results that, other things being equal, a tiny crack or unwetted region of the adhesive is of great importance in a sample to be loaded in tension, but not for one to be loaded in shear.

2.53 Dependence of Bond Strength on Adhesive Thickness In most applications, the adhesive is weaker than the substrate to which it is attached, and for a butt joint the strength increases with decreasing thickness of the adhesive layer. It has been shown (Meissner and Merrill 1948) that in some cases the strength of the joint may exceed that of the adhesive. This is because the presence of a rigid substrate reduces the values of the shear stresses in the adhesive to values much lower than those present when a bulk sample is tested.

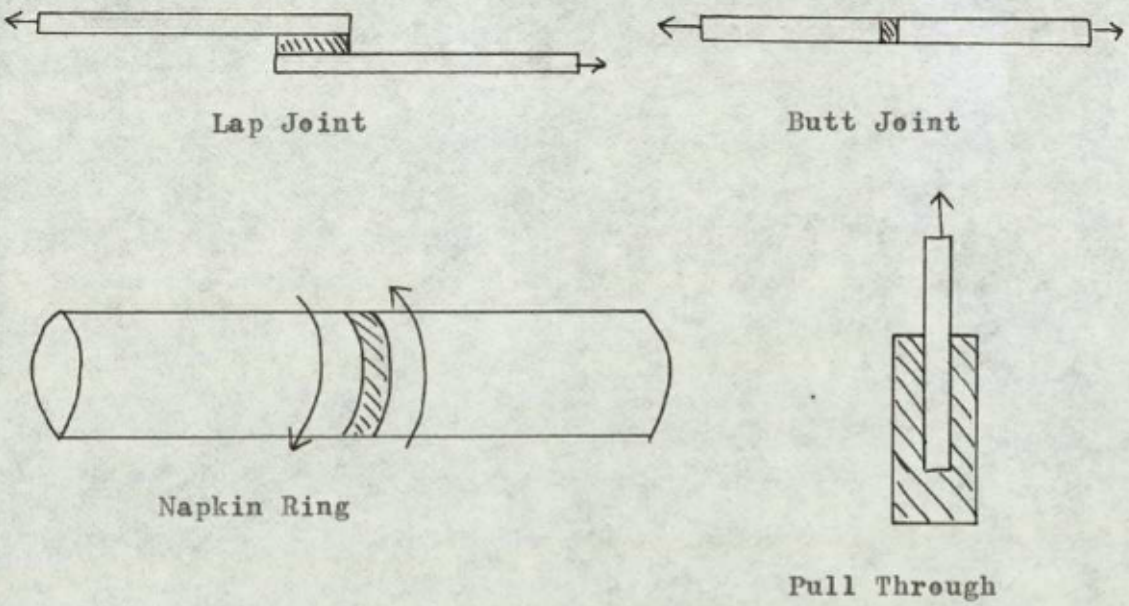
Bikermann (1941) suggested that the effect is due to the fact that the probability of there being a flaw in the adhesive increases with increasing thickness, although this cannot be the case if the failure is adhesive as stated in Gardon (1963).

2.6 The Geometry of Adhesive Joints

In view of all the factors mentioned in the previous section, it is clear that the geometry of an adhesive joint will have a large effect on the measured strength so that it is important to consider the stresses set up in the various types of joint. The subject has been treated by Mylonas and de Bruyne (1951) and reviewed by Sneddon (1961).

2.61 The Different Types of Joint

The basic types of joint are illustrated below.



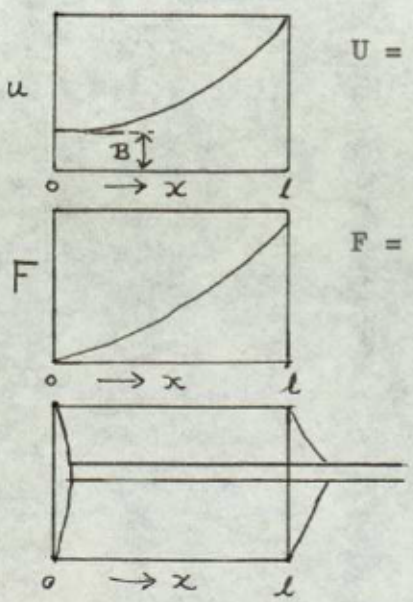
Within each type there are several variations (e.g. scarf joints, double lap joints, etc.) and for each of these the distribution of stresses will be different.

When an adhesive joint is tested to destruction, above

average stresses may arise in two ways: from the geometrical form of the joint, and from irregularities in the joint or the adherends. Whilst the first can be allowed for or even eliminated by a suitable choice of joint geometry, the second cannot easily be eliminated or even measured and it is thus necessary for a study of adhesion on a molecular scale to choose a joint in which the stress is not only as pure as possible (in magnitude and in direction) but also in which stress concentrations due to joint imperfections have the minimum effect.

2.62 Stress Analysis of the Pull Through Joint For the present study the pull through type of joint was chosen as described in section 7.2 The stress analysis has been carried out by Wood (1956).

His theory depends on the consideration of the equilibrium of substrate embedded in rubber. Subsequent integration of the force over the length embedded enables the total pull through force to be calculated as a function of the embedded length. His results are summarised in the graphs shown below.



U = Bcoshnx U = Displacement

n = 2c/Er

F = Enutanh n x F = force/unit area

2.7 The Adsorption of Gases

As described in section 2.44, the adsorption of gases at the interface may well influence the propogation of a crack during bond failure and for this reason and also because of the general information which may be obtained concerning the interface between adhesive and adherend it is instructive to consider gas adsorption on either or both surfaces.

When a gas or vapour exists in contact with a solid surface, forces between the molecules of the two phases will cause an excess of gas molecules to be present close to the interface. This process is known as adsorption. Since it is governed by the equation:

$$\Delta G = \Delta H - T\Delta S$$

and since ΔS is negative (because the molecules lose at least one degree of freedom on adsorption) it follows that the process is normally exothermic. If it is not, the phenomenon is known as negative adsorption.

Adsorption may be classified as physisorption or chemisorption depending on the nature of the interaction. It is usual to characterise chemisorption as involving specific electronic interactions and a large heat change, and physisorption as that which involves only weak Van der Waals or dipole forces and a heat change comparable with the heat of liquefaction of the gas.

2.61 The Langmuir Theory The first successful theory of gas adsorption was that due to Langmuir (1915) who dealt with monolayer coverage only, and assumed localized identical sites and the absence of lateral interaction. His equation is:

$$\theta = \frac{k_1 p}{k_2 + k_1 p}$$

Although it is sometimes used for elucidating reaction mechanisms it is not nowadays of great importance.

2.72 The BET Theory A significant extension to the Langmuir theory was not made until Brunauer, Emmett, and Teller (1937, 1938, and 1940) proposed their famous equation which was based on the following assumptions:

2.721 The Assumptions of the BET Theory

1)The adsorption sites are fixed.

2)The adsorbed molecules do not interact.

3)The layers are adsorbed successively.

4) Heat of adsorption is constant for each layer.

5)The heat of adsorption into the second and subsequent layers is constant and equal to the heat of Liquefaction.

6)As the pressure approaches the saturation value the adsorption approaches infinity.

2.722 Derivation of the BET Equation The derivation of the equation depends on the sum to infinity of equations such as:

$$a_i p s_{i-1} = b_i e^{-E_i/RT} s_i$$

where s_i is the coverage in the i'th layer and E_i is the heat of adsorption. The final result is:

$$\frac{p}{x(p_o - p)} = \frac{1}{x_m c} + \frac{c - 1}{x_m c} \cdot \frac{p}{p_o}$$

where x_m is the amount of gas adsorption at monolayer coverage and c is given by:

$$C = \frac{a_1 b_2}{a_2 b_1} . e^{(E_1 - E_L)/RT}$$

where E_1 is the heat of adsorption into the first layer and E_L is the latent heat of evaporation.

2.723 Limitations of the BET theory The assumptions of the BET theory are invalid on several counts:

1) Lateral interactions must be considerable (except possibly for noble gases at low pressures.
2) The heats of adsorption are by no means constant, either between layers or within each layer.
3) The layers are not adsorbed successively, and even if they were the molecules in the second layer would not adsorb directly above those in the first layer as implied by the BET theory.
4) No gas is critically pure and a very little strongly adsorbed impurity will soon saturate the surface.

2.724 Calculation of the statistical monolayer capacity and specific surface area Despite these objections the BET equation is of considerable value since from a plot of

$$p/x(p_o - p) \quad \text{vs} \quad p/p_o$$

It is possible to calculate the statistical monolayer capacity. Then if the area occupied by one molecule of the adsorbate is known, the specific surface area of the substrate can be found.

2.725 The Molecular Area The surface area occupied by different molecules is still the subject of much dispute, only the value for nitrogen (obtained from the liquid density and confirmed by a wealth of adsorption experimental data) being generally accepted at $16.2A^2$. Values for other, more

readily condensible, vapours are of much more doubtful validity since they are based on particular crystal packings which are certainly not found on the the surface.
Values for some simple molecules were first calculated by Brunauer and Emmett and Teller (1937b) using the equation:

$$\sigma = 3.464 \times 10^{16} \left(\frac{M}{4\sqrt{2}\, N \rho} \right)^{\frac{2}{3}}$$

where ρ is the density of whichever phase is appropriate at the temperature of the experiment, N is Avogadro's number, and M is the molecular weight of the adsorbate. Some authors (e.g. Nay and Morrison 1949) have produced sets of corrected areas based on the nitrogen value for some standard solid, or based on the absolute method of Harkins and Jura (1944). However, all these methods depend on the doubtful assumption that the area occupied by one adsorbate molecule is independant of the solid used. As illustrated by Dzisko and Krasnopdskaya (1952) this assumption may be grossly in error.

2.73 Other Isotherm Equations Other isotherms have been derived to take into account the variation of the heat of adsorption with coverage. The isotherm due to Zeldovitsch (1934) genarally known as the Freundlich isotherm, assuming an exponential decrease in ΔH with coverage gives:

$$\theta = kp^{1/n}$$

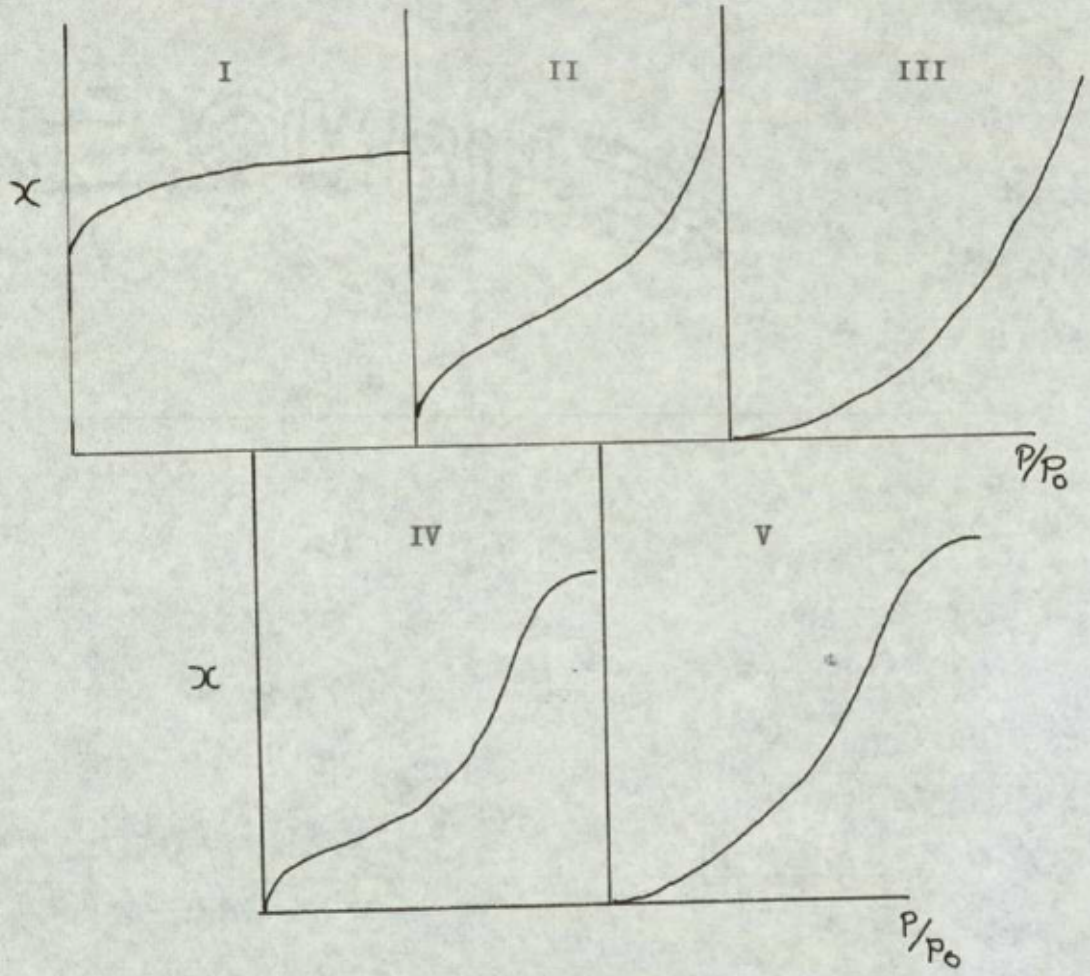
whilst Temkins and Pyzhev (1940) assumed a linear decrease and derived the relation:

$$\theta = a.\ln(bp).$$

Numerous other treatments have been given and are reviewed by Young and Crowell (1962), but whilst some of them have

achieved limited popularity, many involve so many constants, with or without physical significance, that it is impossible to test the theories as opposed to simply fitting data.

2.74 Classification of Isotherms A considerable amount of information may be obtained from the shape of the isotherms themselves. Brunauer, Emmett, and Teller (1945) classified the isotherms into five types which are shown below.



Type I is found where no adsorption is found above monolayer coverage and types II and III represent multilayer adsorption, the second corresponding to two dimensional condensation. Types IV and V are analogous to II and III except that here the presence of capillaries restricts adsorption to a certain

number of layers. Where the molecules interact with the surface much less strongly than with one another we expect two dimensional condensation to be evident from the adsorption isotherms, (types II and IV). A detailed treatment has been given by de Boer (1968).

2.75 Calculation of Thermodynamic Quantities from the Isotherm

If a series of isotherms is measured at different temperatures it is possible to calculate various thermodynamic quantities, of which the most important are the heat of adsorption and the entropy.

2.751 Heat of Adsorption There are two types of adsorption which may take place: isothermal and adiabatic. For an isothermal process the adsorbate is placed in a constant temperature bath and the term 'heat of adsorption' refers to the heat transferred to the bath during the adsorption process. For adiabatic adsorption the adsorbate is placed inaa calorimeter and the heat of adsorption is the temperature rise of the calorimeter and contents multiplied by its heat capacity. There are two types of isothermal process; in one the pressure is allowed to decrease as the gas is taken up giving rise to a quantity known as the differential heat of adsorption. In the other, the system is visualised as containing a piston so that the pressure is kept constant and the adsorption is also isobaric. It can be shown that this corresponds to the isosteric heat of adsorption (i.e. at constant coverage) determined from the isotherms by means of the Clapeyron-Clausius Equation, (de Boer 1968 page 70).

2.752 The Entropy of Adsorption Entropies of adsorption may also be obtained from the isotherms at different temperatures using the equations:

$\Delta G = -RT\ln(p_o/p)$ and $\Delta G = \Delta H - T\Delta S$

Thus if the coverage at different temperatures and pressures is known it is possible to calculate the entropy of adsorption at any given coverage. These experimental entropies of adsorption can then be compared with theoretical ones evaluated using the Sakur-Tetrode equation. In order for the campaŗison to be valid the experimental values must be converted to some standard state. A discussion of the choice of standard state has been given by de Boer (1968).

Calculations of this type have been carried out by Kemball and Rideal (1946), and Everett (1950 & 1957) Has analysed several sets of data.

CHAPTER III

ADSORPTION STUDIES - APPARATUS AND PRELIMINARY EXPERIMENTS

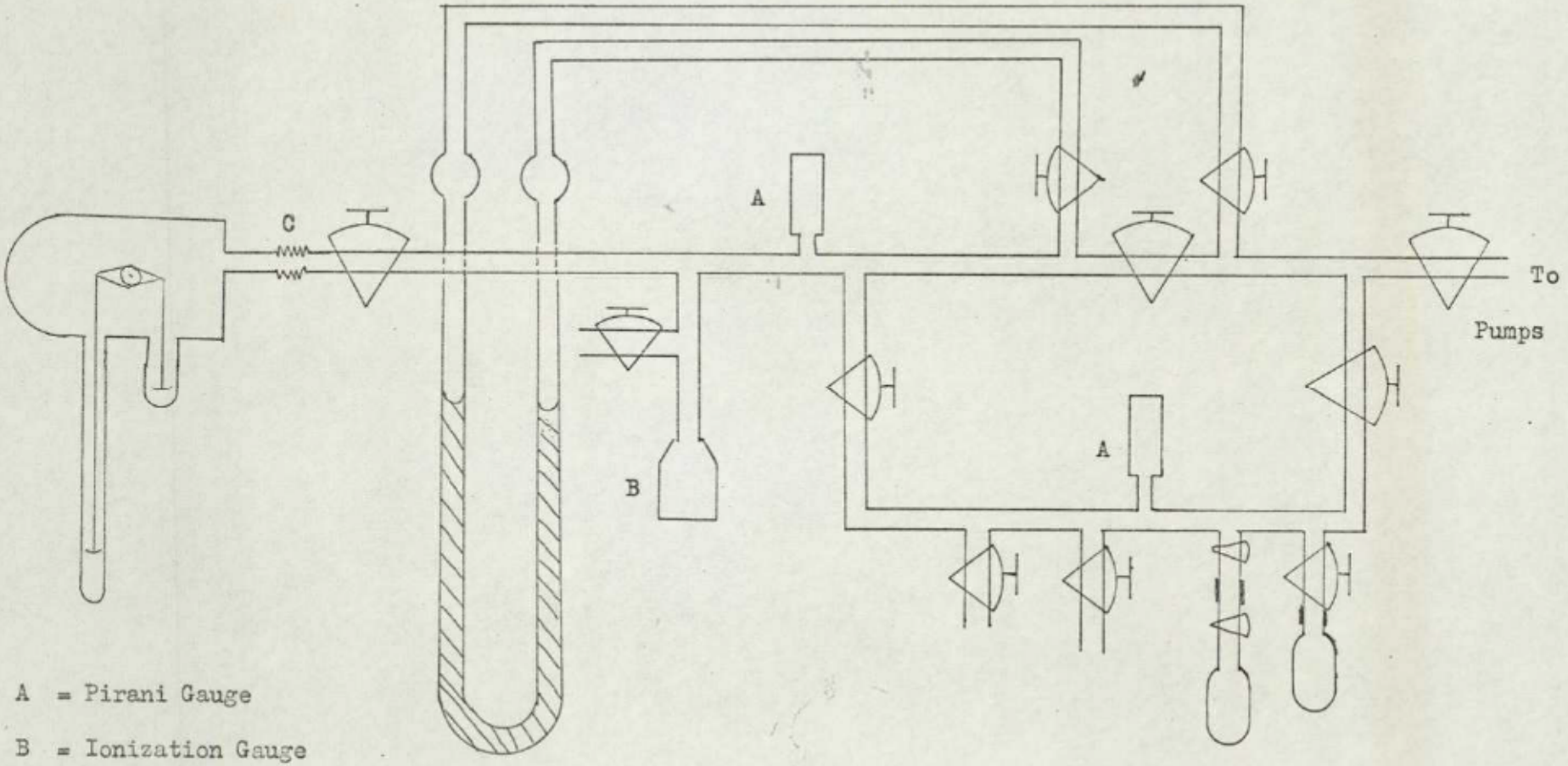
3.1 Apparatus For the determination of adsorption isotherms a vacuum line containing a C.I. Mk. II microbalance was set up and is shown in fig. 1. The balance was an electronic instrument similar to that designed by Gregg (1955) and had a capacity of 1g and a sensitivity of 10^{-6}g.

3.11 The Vacuum System The vacuum system consisted of a two stage mercury diffusion pump backed by a two stage rotary pump to give a minimum pressure of 4×10^{-6}mm. The pumps were connected to a vacuum line leading to the balance and contained a loop in which the adsorbate gases could be purified and stored before being admitted to the balance.

3.12 The Measurement of Pressure Pressure was measured by an Edwards Ionization Gauge at the lowest pressures ($< 10^{-4}$mm), by two Pirani Gauges in the next pressure range (10^{-4} - 10^{-1}mm), and by a manometer containing diffusion pump oil for pressures up to about 40mm. The oil had a vapour pressure of about 10^{-8}mm at room temperature and 10mm of oil corresponded to 0.6414mm of mercury. Provision was also made for the insertion of a mercury manometer close to the liquid nitrogen cold trap but due to the danger of contamination of the sample by mercury this was used in very few series of experiments.

3.2 Outgassing the Apparatus

The apparatus was set up initially as shown in Plate I. The initial outgassing took a considerable time as the system could not be baked due to the presence of greased taps and joints. Thus, when the system had been pumped for about five days and



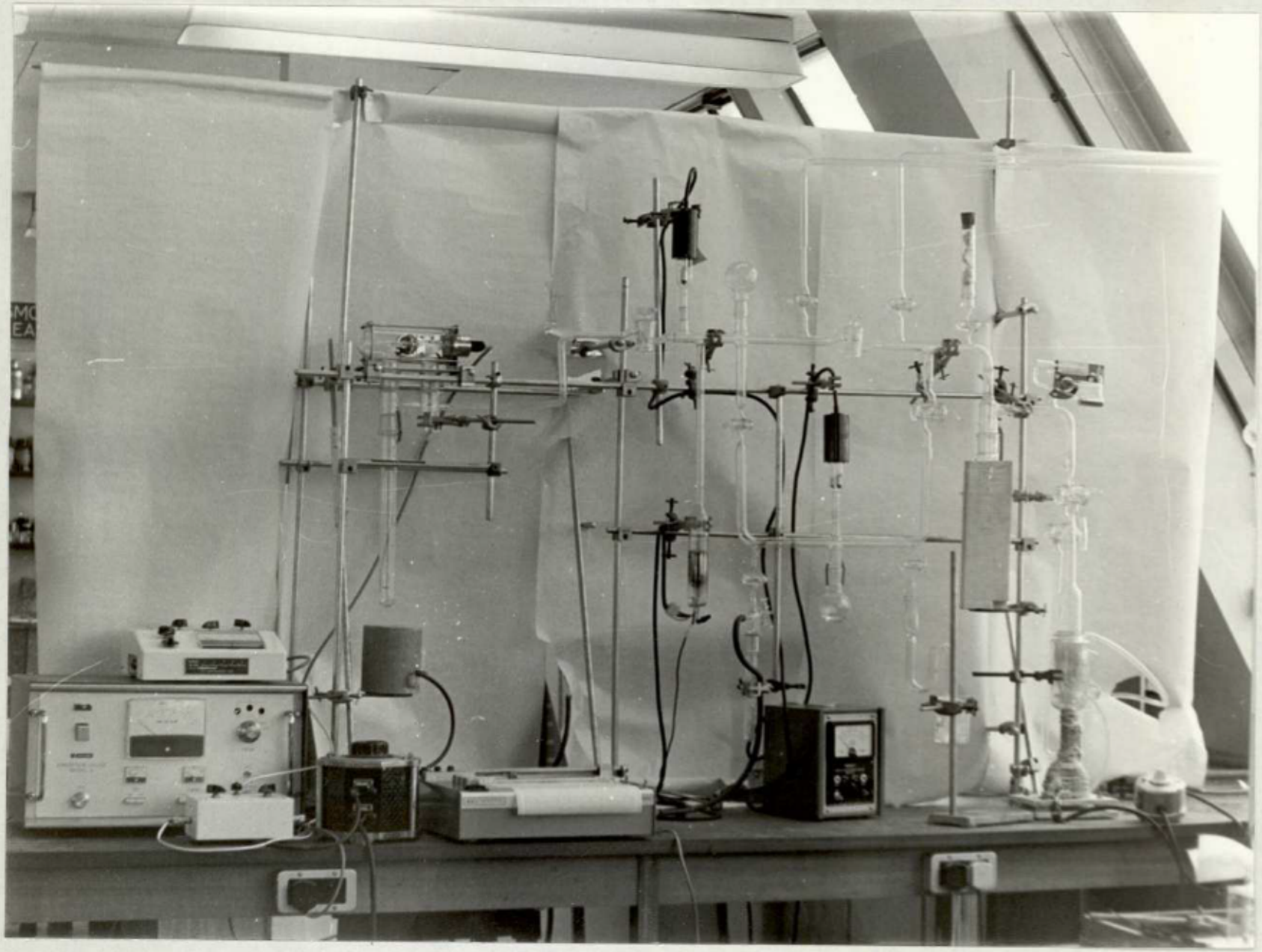
A = Pirani Gauge

B = Ionization Gauge

C = Flexible Tubing

Figure 1.

The Adsorption Apparatus



the pressure was about 10^{-4}mm, if the balance was isolated, the pressure rose to about 10^{-3}mm in about one minute and to about 0.1mm in about one hour. To accelerate the outgassing a hot air blast was directed onto all possible parts of the apparatus. This caused a considerable evolution of gas and, in particular, large quantities of gas were pumped out of the grease on the taps. An attempt was also made to heat the balance itself by means of an infra red lamp, but this appears to have had little effect.

In all, the outgassing was continued for about four weeks, the ultimate pressure attained being $1x10^{-5}$mm. The system was then able to hold a vacuum of 10^{-4}mm for about 30mins and 10^{-3}mm for several hours.

3.3 The Adsorption of Nitrogen on Carbon

In order to test the apparatus, the first sample used was a sample af carbon black obtained from the Cabot Carbon Company and with a published surface area of $65m^2g^{-1}$. This value was obtained by iodine adsorption from solution, and graphs are provided in the manufacturer's literature which show the relationship between these measurements and the BET method used here.

3.31 Blank Runs The adsorbate gas was BOC White Spot nitrogen which was used without further purification. Blank runs were carried out at 77°K with a 200mg weight on each scale pan. These runs, over the range 10^{-3} - 300mm were identical to within the experimental error, and contained apparent weight changes of up to +150 and -30μg. These changes are thought to be due largely to thermomolecular flow arising from the difference in temperature between the sample at 77°K and

the balance at 300°K. The readings were added to or subtracted from the readings taken with the sample in place.

3.32 The Sample The carbon sample used was of about 200mg and was balanced by an equal weight in the right hand scale pan. It was found that whilst the balance could be read to better than 1μg, the useful precision was only ± 4μg due to vibrations reaching the balance from the environment. However, this figure was somwhat variable and in one case (when a pneumatic drill was started on an adjacent building site) the oscillations were so severe (20 - 30μg) that a run had to be abandoned. Some improvement was obtained by using a damped recorder, and the final readings are reproducible to ± 2μg.

3.33 Outgassing the Carbon Sample The sample was outgassed by pumping overnight (after which the pressure was about 10^{-4}mm) and then heating for 1hour at 550°C to give an ultimate pressure of 8×10^{-5}mm. Although no detailed measurements were taken it appears that prolonged heating drastically reduces the surface area, since after heating overnight the BET nitrogen adsorption indicated a surface area of only $20 m^2 g^{-1}$.

A fresh sample was then taken and the following standard procedure adopted: pump down to 5×10^{-4}mm (normally overnight) heat to 550°C for one hour, and finally cool and pump until the pressure ceases to fall. In this way the minimum pressure attained with the sample at liquid nitrogen temperature was 4×10^{-6}mm.

3.34 The Adsorption Measurements Nitrogen was let into the system to fill the lower part at just below atmospheric pressure. The pressure was reduced to a suitable value

before allowing the gas to expand into the balance.

The adsorption of nitrogen consisted of an initial rapid uptake of gas, followed by a slow build up to equilibrium over a period of about 15mins. It was possible to follow the adsorption by watching the decrease in pressure, the method used by Brunauer, Emmett, and Teller (1938) in their original work on adsorption. The measurements were made over the range 10^{-3} - 300mm using the same sample for successive isotherms. The adsorption appears to be completely reversible since virtually all the gas was removed by pumping for 30mins. The remaining gas (about 10μg) was removed by heating to 550°C for about 15mins. This probably consisted of traces of water which had desorbed from the walls of the apparatus during the run.

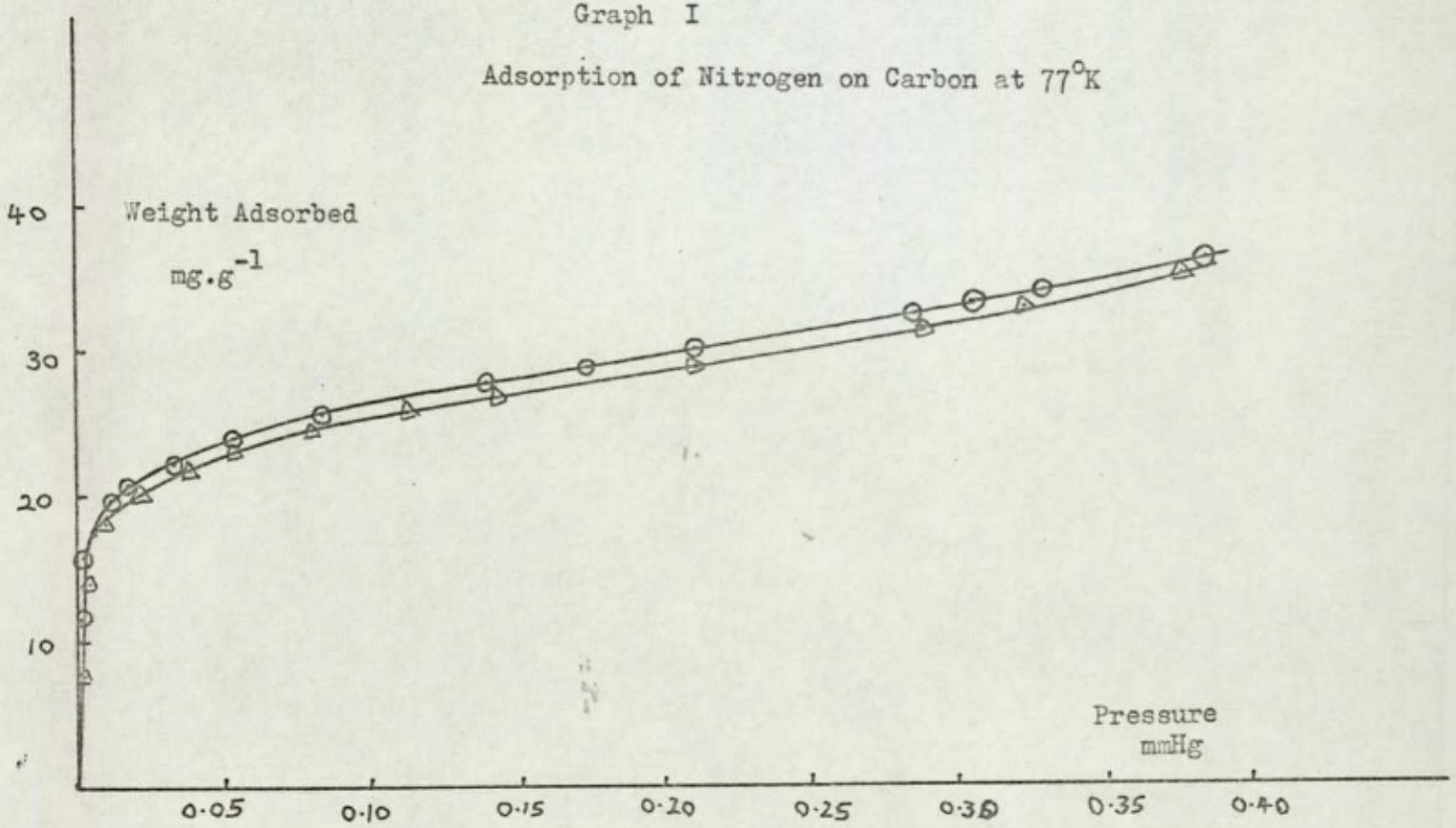
Two runs were made and whilst they were not identical they differed by no more than 10% over the BET range ($0.05 < p/p_o < 0.35$). The isotherms are shown in Graph I. The BET plots were also drawn (Graph II) and gave surface areas of 81.2 ± 0.5 and 79.9 ± 0.5 m^2g^{-1}. The reduction in the surface area, which is just outside the experimental uncertainty, is probably due to the heat treatment between the runs. While this result is somewhat higher than the best result obtained by iodine adsorption, inspection of the published graphs comparing the two methods indicated that this discrepancy is well within the random variations shown.

3.4 The Adsorption of Nitrogen on Gold

The first metallic sample used was a 315mg sample of gold powder of 99.99% purity, obtained from BDH and used as received. The sample was outgassed by heating and pumping

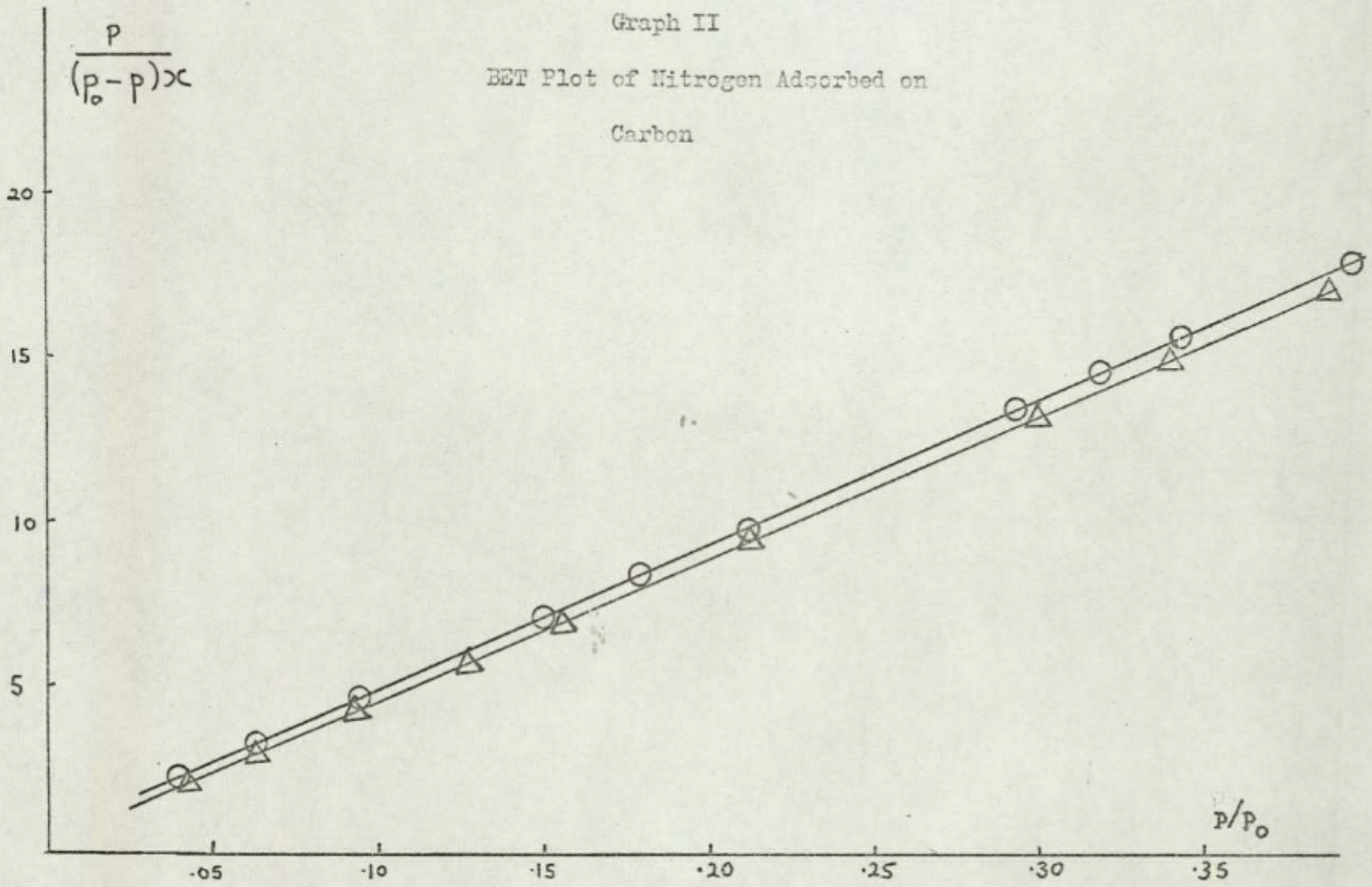
Graph I

Adsorption of Nitrogen on Carbon at 77°K



Graph II

BET Plot of Nitrogen Adsorbed on Carbon



for a total period of two hours. No loss in weight occurred until the sample reached 450°C and although this temperature was maintained for two hours all the weight loss (about 10μg) took place during the first 15 minutes and was assumed to be chemisorbed water.

It has been reported by Sarakhov (1957) that nitrogen does not adsorb on gold. To test this, nitrogen was admitted to the outgassed gold sample, cooled in liquid nitrogen, at a pressure of 760mm, and left overnight. No increase in weight was recorded after 24 hours and, following Sarakhov, the adsorption of benzene was attempted.

3.5 The Adsorption of Benzene on Gold

As benzene dissolves readily in hydrocarbon tap grease all the stopcocks were lubricated with sugar grease (Meloche and Frederick 1952 and Appendix I).

3.51 The Temperature of the Adsorption The temperature for the adsorption was rather critical as the pressure range used had to be entirely within the range of the Pirani gauge and this had to be within the range of benzene relative vapour pressure 0.05 - 0.35. In addition, the pressure of the first point had to be high compared to the miminum outgassing pressure (10^{-3}mm). This meant that the sample temperature had to be maintained at around -65°C, and a bath made by pouring liquid nitrogen onto chloroform to form a slush was found to be suitable. Two blank runs and several adsorption runs were made.

3.52 Results On addition of the first sample of vapour (at 5×10^{-3}mm) an immediate uptake of gas amounting to about 10μg was observed. Subsequent additions of gas resulted

in no further weight increases. This result was unsatisfactory because the uncertainty in the reading of the balance was at least $\pm 5\mu g$, but a value for the specific surface area was calculated on the assumption that the initial uptake represented the filling of a monolayer and was found to be about $0.4 m^2 g^{-1}$.

3.6 The Unsatisfactory Nature of the Apparatus

At this stage a new reference cell was put into the balance and was found to increase the sensitivity at least tenfold. However, the improved sensitivity merely served to indicate the inadequacy of the experimental measurements and, in particular, it was suspected that the equipment was very sensitive to temperature. This affects the adsorption in two ways, by altering the temperature of the adsorption itself, and by altering the saturation vapour pressure of the gas in the bulk of the system.

Where the adsorption of nitrogen is carried out at the temperature of liquid nitrogen these effects should not be observed since the saturation vapour pressure of nitrogen at liquid nitrogen temperature will always be atmospheric pressure on the day of the experiment, and an adsorbent immersed in liquid nitrogen will be maintained at fairly constant temperature. However, for adsorbates whose saturation vapour pressures are less than atmospheric pressure, the relative vapour pressure of the gas in the system will vary appreciably for very small changes in ambient temperature although the sample may be at constant temperature.

To confirm this, a thermistor was connected to a recorder to act as a sensitive recording thermometer and left overnight so that a detailed comparison could be made

between temperature variations and variations in the weight which was also recorded. It was found that the variations in weight closely followed the temperature fluctuations, and it became clear that the balance should be maintained at constant temperature if meaningful results were to be obtained.

3.61 Modifications to the Apparatus To overcome the effect of temperature fluctuations, the whole apparatus was surrounded by a wooden enclosure with a removable perspex front containing a small door for access to taps etc., and fitted with an air thermostat. The opportunity was also taken to reduce the amount of dead space in the apparatus considerably. Three methods of heating were tried for the enclosure, the aim being to maintain the temperature at 25 $\pm$ 0.1°C. First, a 500 Watt i.r. heater was found to maintain a constant temperature very well but was not sufficiently powerful to keep the temperature more than 7°C above room temperature. It was found however, that a length of heating tape rated at 100 Watts and arranged to cover as much of the bottom of the enclosure as possible was ideal and held a constant temperature to better than $\pm$0.1°C. In very cold weather this was supplemented by a 100 Watt electric fire element contained in a glass tube near the front of the enclosure.

In addition to the air thermostat the sample tube was surrounded by a copper coil which was in turn immersed in a dewar flask containing water. Water circulated through the copper coil and maintained the temperature to better than $\pm$0.02°C.

For outgassing the sample could be heated by means of a furnace which surrounded the sample tube and which could give temperatures up to 600°C.

3.62 Difficulties Experienced due to Volatile Materials

With the balance maintained at constant temperature it became clear that consistent results were still not being obtained as illustrated by the following experimental results.

3.621 Experimental After the system had been out of use for several days the pumps were started and the pressure fell to 10^{-3}mm an about 15 minutes, and to about 10^{-4}mm in about one hour. When the balance was isolated from the pumps the pressure rose to 10^{-3}mm in about 2 minutes. Throughout these experiments there was no sample on the balance pan but the weight was continuously recorded. It was found that the weight appeared to vary in anrandom fashion during the first hour's pumping but then settled down to a steady value. However, at irregular intervals sudden weight changes of up to 30µg were noted. These were eliminated by surrounding the hangdown tube with aluminium foil connected to earth so as to prevent charge building up on the walls of the apparatus. After 24 hours the pressure was less than 10^{-4}mm and on isolating the balance from the pumps the pressure rose to 10^{-3}mm in 3minutes. However, with the pumps isolated but with a liquid nitrogen cold trap in the system the pressure rose more slowly and the weight rose much more slowly, (about 10µg.hr^{-1}). Furthermore, when the pumps were switched on the decrease in weight was much more rapid than previously observed and followed the decrease in pressure with little or no time lag.

3.622 Conclusions The foregoing experiments show that whilst a vacuum of 10^{-4}mm may be attained fairly rapidly, the pressure resulting is a dynamic equilibrium resulting from the desorption of gas from the balance and the glassware.

Secondly, unless the pumping is continuous, at least part of the gas leaving the walls of the apparatus is readsorbed by the balance giving rise to an unsteady base line. Thirdly, the very slow rise in pressure in the presence of a cold trap indicates that most of the gas leaving the walls is readily condensible. Finally it is clear that after short pumping times the gas is being readsorbed onto the balance since there is a considerable delay between any sudden pressure variations and the attainment of weight equilibrium. However, after pumping for 48 hours or longer the attainment of equilibrium was a very rapid process when the pressure was suddenly altered and this was taken to indicate that the variations were now due mainly to thermomolecular flow. It was also noted that when the balance had been opened to the atmosphere for as little as 5 minutes the whole sequence was repeated and at least two days were required to obtain a stable balance reading and a satisfactory vacuum.

3.7 Electron Micrographs of the Gold Powder

3.71 Experimental and Results As the results of all the experiments to determine the specific surface of the gold powder were indeterminate it was decided to take some electron micrographs of the gold powder and those at 900x magnification are shown in plate II.

The following facts may be noted. Although most of the particles appear to be spherical, about 3% are in the form of hexagonal plates of about 2μm radius and about 0.2μm thick. Two calculations of the specific surface were made, (a) corresponding to spheres and (b) corresponding to platelets.

The results are tabulated below:

	Spherical	Platelets
Radius	2μm	2μm
Specific Surface Area	$0.025 m^2 g^{-1}$	$0.5 m^2 g^{-1}$
Expected Weight Change (N_2)	^{2}2μg	40μg

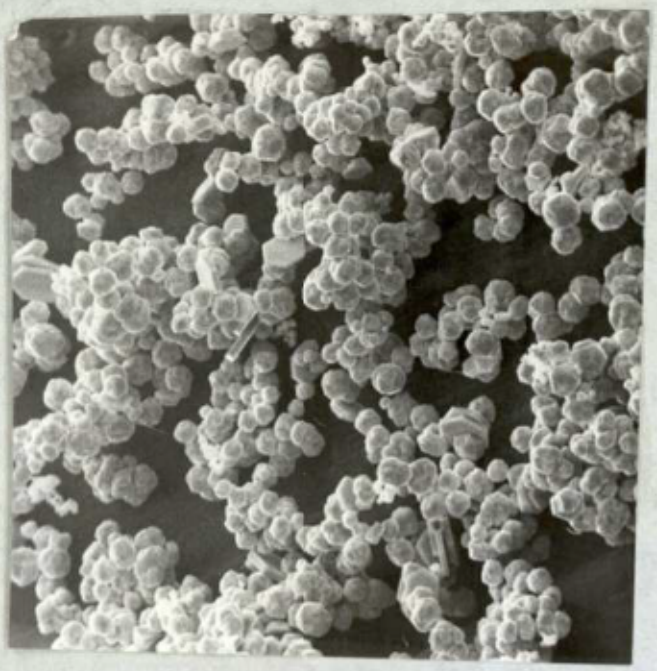


Plate II

Gold Powder 900X Magnification

The quantity "expected weight change for N_2" is the monolayer uptake of nitrogen on a sample of 0.25g. The value for disc shaped particles is in order of magnitude agreement with that obtained from benzene adsorption. However, as the uncertainty in the area occupied by one benzene molecule is about ±25% and the experimental uncertainty is of the same order of magnitude little confidence can be placed in the results.

3.8 The Adsorption of Krypton on Gold

As the results indicated a very low specific surface area for

the gold powder it was decided to attempt the adsorption of krypton which has been reported by Genot and Duval (1967) to adsorb on gold.

3.81 The Advantages of Using Krypton The use of krypton has several advantages. It has a saturation vapour pressure of about 1.72 mmHg at the temperature of liquid nitrogen so that the use of a mercury manometer is unnecessary. (It was desired to avoid the use of a mercury manometer as far as possible to reduce sample contamination to a minimum.) Secondly, the krypton molecule is spherical and the area occupied by it, although not as well known as that of nitrogen, is considerably more certain than that of other inert gases or of more complex molecules. The generally accepted value for krypton adsorbed on metals is $14.2A^2$. Furthermore, krypton is a fairly heavy molecule so that with a surface area less than that of nitrogen the weight increases expected are about twice those for the lighter gas.

3.82 The Interpretation of the Isotherms However, the interpretation of the isotherms is more difficult than for nitrogen. Firstly, there is some uncertainty as to the appropriate value for the saturation vapour pressure, p_o, which has to be inserted into the BET equation. The temperature 77K is well below the triple point of krypton and it might seem logical to take p_o as the vapour pressure of solid krypton. Now the BET equation is:

$$\frac{p}{x(p_o-p)} = \frac{1}{c.x_m} + \frac{c-1.p}{x_m c\ p_o}$$

where x_m is the mass of one monolayer per gram, p_o is the

saturation vapour pressure, and c is a constant which is normally greater than 100 for permanent gases. When c is large this equation reduces to:

$$\frac{p \cdot p_o}{x \cdot (p_o - p)} = \frac{p_o}{c x_m} + \frac{p}{x_m}$$

It can thus be seen that the value for the specific surface area obtained does not depend greatly on the value chosen for the saturation vapour pressure. However, it is noted that in many cases the BET plot is noticeably less non-linear when p_o is referred to the supercooled liquid rather than to the solid. Furthermore, it is doubtful whether the BET procedure is applicable to noble gases below their triple points since it is often found that the thickness of the adsorbed layer approaches a finite value as the pressure approaches the saturation vapour pressure. It should, however, be possible to determine the specific surface area using the 'point B' method.

3.83 Experimental and Results When the adsorption experiments were tried, it was found that any weight increases were much less than the corrections due to thermomolecular flow which were, unfortunately, at a maximum in the pressure region of most interest. The results did, however, confirm those from the electron micrographs; namely, that the surface area of the gold powder was too small to measure reliably using the apparatus and experimental technique as described.

3.9 The Stability of the Balance

During these experiments the stability of the balance deteriorated considerably, and as the manufacturers seemed

unable to offer any useful advice, some intensive efforts were made to reduce the effects of environmental vibrations on the balance.

To this end, a new mounting of $\frac{1}{4}$" aluminium plate was made to a design similar to that of the Cahn balance operated with success on the same bench. A piece of flexible metal tubing about 3" long was inserted between the balance and the main vacuum line to cut down any vibrations which may have been transmitted from the pumps to the balance. It was found, however, after some two months had been spent in investigating the causes of the vibrations that rather than the accuracy of the measurements improving, the readings could not now be obtained to better than $\pm$ 1mg.

Accordingly, the manufacturers were contacted again and they finally admitted that this behaviour was uncharacteristic and replaced the balance head. It appears that on the original head the coil insulation had broken down, causing leakage between one turn and the next, thus producing a very unsteady base-line. It was found that the new head was capable of giving readings to better than $\pm$ 1µg.

With the balance now working, it was decided to try the adsorption of nitrogen and water on palladium since this metal can be obtained as a finer powder and should thus be easier to work with.

CHAPTER IV

ADSORPTION EXPERIMENTS - NITROGEN ON PALLADIUM

4.1 Preliminary Experiments

4.11 Blank Runs Two blank adsorption runs for nitrogen were made and these were in agreement to about $\pm 5\mu g$ over the whole range.

4.12 The Sample The palladium black sample was obtained from Johnson Matthey and was used as received. It was outgassed by heating to 100°C overnight at a pressure of 1×10^{-5} mm by which time the weight loss was less than $1\mu g.hr^{-1}$.

4.13 Results After each run at 77°K the sample was warmed to room temperature and outgassed at 100°C until no further weight loss was noted. Three full runs were made, and in addition, nitrogen was admitted to the apparatus and pumped away twice between the first and second runs. It was found that the amount of gas taken up increased throughout the series and that after each run the amount of gas desorbed was greater than the amount taken up.

4.14 Conclusions Three possible reasons for these phenomena were considered:

1)The surface of the powder is actually increasing due to the successive breaking down of spongy particles and with the release of air which may have been trapped in pockets in the metal.

2)The apparent surface may have increased due to the successive vacation of active sites.

3)The changes could have been due to zero shifts on the balance.

the balance.

Since the discrepancies decrease with increasing run number it appears that alternatives 1 or 2 are most likely to be correct. This conclusion was bourne out by some later experiments in which no gas other than dry nitrogen was admitted to the apparatus for about six weeks. Apart from periods of 6 - 7 hours when nitrogen adsorption runs were being carried out and during weekends, the system was pumped continuously. The nitrogen gas was always dried over phosphorus pentoxide for at least six hours before being admitted to the balance. It was found that even after such intensive drying the ultimate pressure attainable was still decreasing appreciably and that volatile material was still being desorbed from the walls of the glassware. In addition, when a fresh sample was taken, the results obtained were in only approximate agreement with those obtained initially and it was decided to carry out some tests to find out where the errors were arising.

4.2 Efforts to Obtain Reproducible Results

Before this new series of experiments with nitrogen the aluminium counterbalance scale pan was replaced with a platinum pan and platinum weights. Outgassing was at 100°C and 10^{-5} mm pressure until the weight loss was less than $2\mu g.hr^{-1}$. All the blank runs contained a peak of height about 75µg at relative vapour pressure $\sim 5\times10^{-4}$ and levelled out to a value constant to $\pm$ 4µg at higher pressures. The "constant" to which all runs levelled out varied from -5µg to +18µg but was reproducible to $\pm$ 2µg if the liquid nitrogen refrigerant was not removed between runs.

In one case the constant dropped by about 10μg over a period of about one hour.

4.21 Variations in Temperature

These variations in weight occurred over a relatively long period and consideration was given to the possibility of their being due to variations in the temperature of the hangdown tube. This was refrigerated in liquid nitrogen during the nitrogen adsorption runs and it was thought possible that the refrigerant was taking up oxygen or water from the atmosphere, thus causing a rise in temperature. To test this, a thermocouple was placed in a dewar of liquid nitrogen and left for several hours. If the mouth of the flask was plugged with tissue paper any temperature rise was less than $1^{\circ}K$ per day. If, however, the mouth of the dewar was left open to the atmosphere the temperature rose by about $1^{\circ}K$ per hour. From this point onwards care was taken to ensure not only that the vacuum flask around the hangdown tube was kept covered at all times, but also that the refrigerant was topped up only with fresh nitrogen from the stock bottle.

It also seemed to be important to keep the nitrogen level well above the level of the scale pan, not only to maintain the temperature of the pan as close to $77^{\circ}K$ as possible, but also to keep any water condensing on the pan to a minimum. It is interesting to note that even at 10^{-5}mmHg about 10^{15} molecules strike every square centimetre of surface every second, and that the mean free path is about 8 metres so that gaseous water molecules in the system have a fairly high chance of striking the palladium surface in any reasonably short time interval. However,

since the total number of molecules present in the system is only of the order of 10^{14} and since any molecule striking the cold surface of the balance or of the hangdown tube will almost certainly stay there indefinitely, any molecule desorbed from the walls of the warm part of the system and straying into the cold part will be removed from the system almost immediately. It should be noted that no provision has been made in the system for measurement of the sample temperature and this is certain to be higher than the temperature of the boiling liquid nitrogen due to conduction from the warm balance head. However, all the deductions made from the nitrogen isotherms have come from the weight readings and from their shape and should therefore not be significantly affected by inaccuracies in the measurement of temperature.

4.22 The Measurement of Pressure Another source of uncertainty arises from the fact that the pressure is measured in the warm part of the system and the pressure near the sample will be different from that measured. To find the magnitude of this effect consider the interface between a region at temperature T_1 and pressure P_1 and a region at temperature T_2 where T_1 is greater than T_2. At equilibrium the number of molecules passing the interface in each direction must be the same, hence:

$$\frac{NP_1}{(2MRT_1)^{\frac{1}{2}}} = \frac{NP_2}{(2MRT_2)^{\frac{1}{2}}}$$

Thus when the sample is at 77°K the pressure near it is about 0.51 times that measured by the manometer at 300°K.

This theory is applicable at low pressures at which the mean free path is much greater than the length of the tube in which the temperature is varying. At higher pressures the measured pressure is the same as the actual pressure. Between these extremes (i.e. at about 0.1mm in the present case) there is no simple relation between the measured pressure and the actual pressure. It is in this region too that the effects of thermomolecular flow are greatest. Fortunately, for the nitrogen isotherms, this part of the pressure range is not of great quantitative importance.

Provision for the insertion of a mercury manometer was made in these experiments so that the measurements could be extended up to atmospheric pressure. It was placed close to the cold trap and could be isolated by means of a tap, when required, to reduce any contamination of the balance pan or the sample by mercury. Work by N. G. Adams (unpublished) has shown that for platinum, large quantities of mercury are taken up in relatively short time intervals.

4.3 The Adsorption Experiments

Some adsorption runs of nitrogen were then carried out as blank runs reproducible to $\pm 2\mu g$ had been obtained. The sample was outgassed at 100°C to constant weight. Five independent runs were made and each run was duplicated by simply pumping off the nitrogen at 77°K and repeating the experiment. The nitrogen was all removed by pumping at 77° K for 20 minutes. In every case the duplicates

obtained in this way were identical to better than $\pm 5\mu g$ over the whole range.

4.4 Results

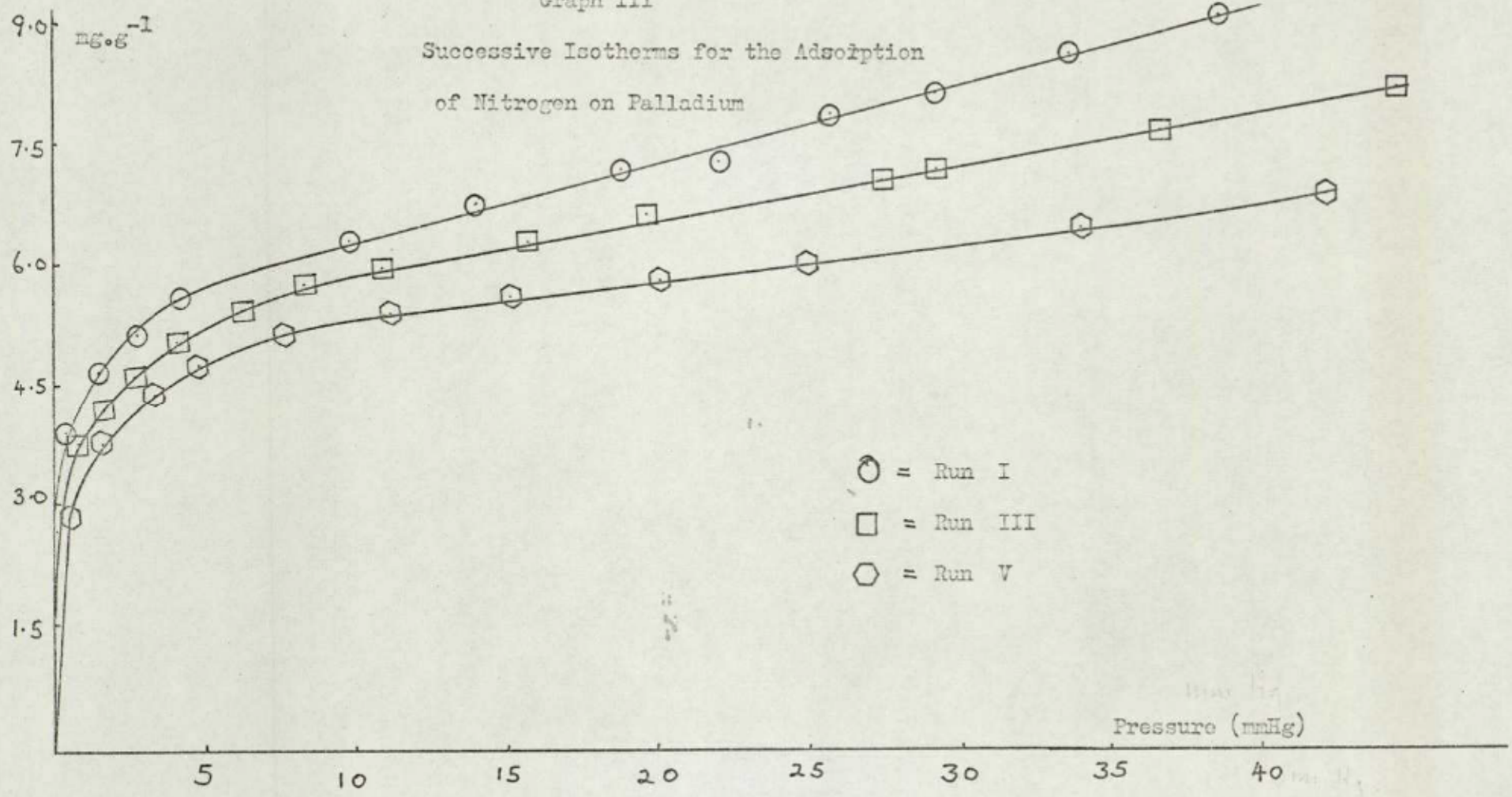
The results were treated in two ways. Firstly, it was assumed that when the initial zero of weight had been set at the beginning of the series this should remain for all runs. This gave rise to differences of up to 20% in the measured surface area, the order of the runs being (in decreasing order of surface area) I, III, IV, II, V.
If, however, the zero was set separately for each run, the surface area decreased each time the sample was heated, the total decrease being about 10% in this case. At the same time, the gradient of the flat portion of the graph decreased in the same order, indicating that the surface area decreased on heating due to sintering, but that monolayer coverage is achieved at progressively lower pressures and that there is less tendency for multilayer adsorption to occur. The results, reproduced in graph III for runs I, III, and V, suggest that the increase in surface area found earlier (section 4.13) was due to incomplete outgassing.

In one experiment, the sample was outgassed by heating to 150°C and whilst this accelerated the process considerably, it was found that after heating to this temperature for about 6 hours the surface area of the sample had decreased by about 30%.

4.41 The Outgassing Process and The Low Pressure Isotherm. On reducing the pressure above the powder samples a loss in weight was noted almost instantly due to the loss of atmospheric gases. This represented the loss of about

Graph III

Successive Isotherms for the Adsorption of Nitrogen on Palladium



1 - 2 monolayers of gas of molecular weight 20 - 30 and surface area 10 - 15 $m^2 g^{-1}$. On prolonged heating at 100°C and 10^{-5}mm one more monolayer was removed. Heating to 150°C after equilibration removed little more gas. On cooling the sample to room temperature no uptake of gas was noted provided the sample had been outgassed for several days prior to the experiment. On cooling to 77°K a considerable weight increase was noted and some consideration was given as to whether the initial zero of weight should be taken as the lowest weight reached or the weight after cooling to the experimental temperature. It was found that for nitrogen the beginning of the isotherm was a straight line and that the intercept on the weight axis occurred at the lowest point reached at high temperature and this point was taken as the starting point for all the isotherms.

The isotherms consisted of a steeply rising portion followed by a much flatter part. The earliest part of the graph (up to $p = 4 \times 10^{-3}$mm) was a straight line. Deviations from linearity occur when the weight uptake exceeds about 0.3 monolayers. The BET plots for two pressure ranges are shown in graphs VII and VIII. All graphs shown are taken from typical single isotherms. Other isotherms taken over the same range did not always reproduce the same numerical values precisely due to changes taking place in the surface due to heating. However, repeated isotherms reproduced the same qualitative features at the same pressures to well within the experimental uncertainty. No hysteresis was observed in any of these experiments.

4.3 Discussion

4.31 The Time of Lingering and Heat of Adsorption Now consider

the adsorption of a gas on a metal. When a gaseous molecule of nitrogen strikes the surface of a metal it may either bounce off elastically or it may remain on the surface for a finite time before flying off in a direction unrelated to its original direction of motion. Now if n is the number of molecules striking the surface per second and t is the average time of lingering, then the number of molecules occupying one square centimetre of the surface at any time is: $\sigma = nt$.

t is given by:

$$t = t_o e^{Q/RT}$$

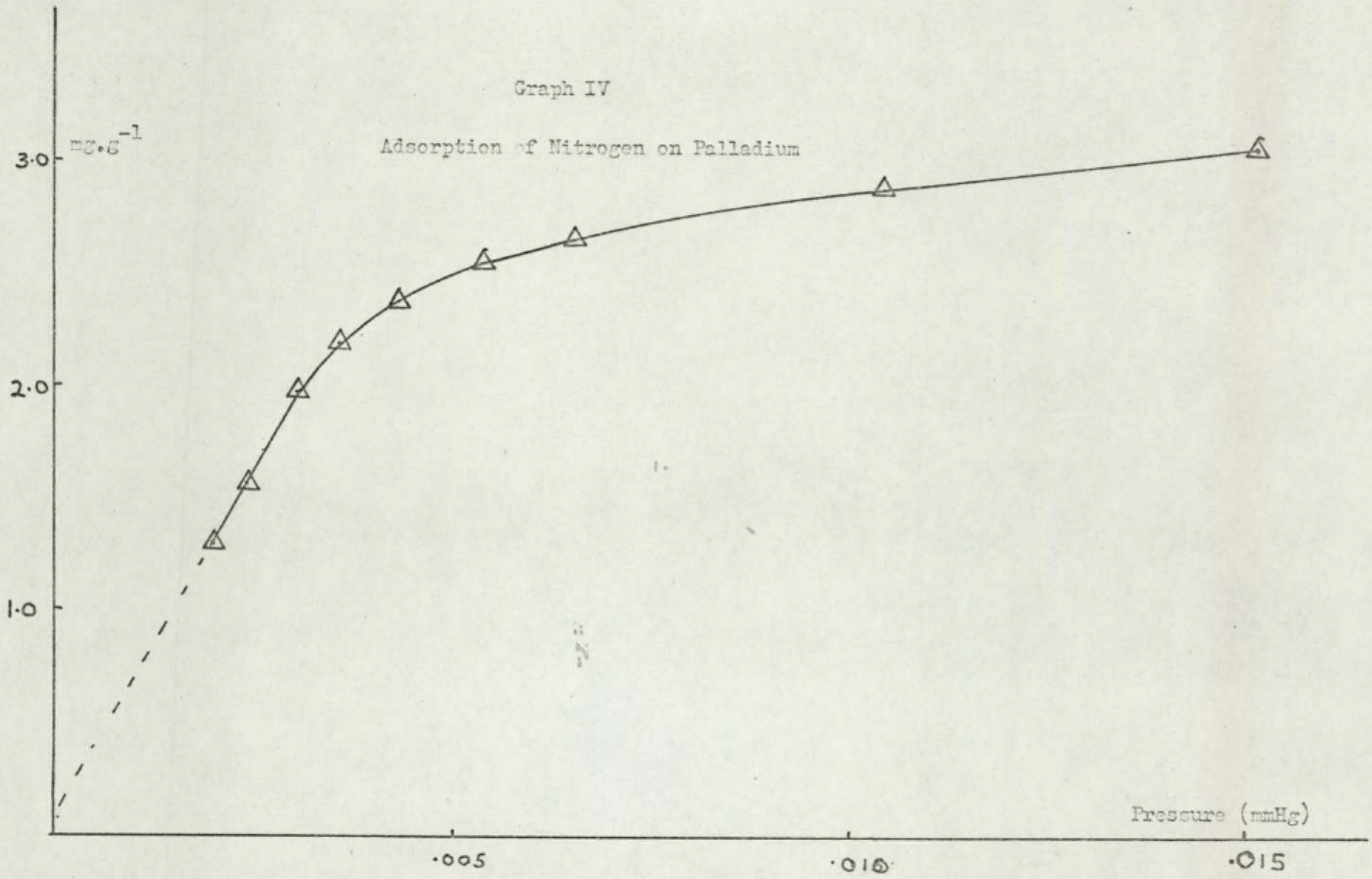
where t_o is the time of oscillation of the molecule in the adsorbed state, and Q is the heat liberated when the molecule is brought from the gaseous state to the adsorbed state.

Now at a pressure of 10^{-3}mm kinetic theory shows that $n = 2.2 \times 10^{18}$ molecules $cm^{-2} sec^{-1}$ and $\sigma = 1.17 \times 10^{14}$ molecules cm^{-2}(from the experimental data). Hence the average time of lingering on the surface (t) equals 0.53×10^{-4} secs. Substitution in the above expresion for Q gives an initial heat of adsorption of 3.2kcals mol^{-1}. This value is obviously somewhat approximate since it is based on the assumption that the surface is smooth, that $t_o = 10^{-13}$sec, and that no entropy is lost on adsorption. Whilst these assumptions are not always strictly justified, they do not have a great effect on the value of Q which is probably accurate to $\pm$200 cals mol^{-1}.

The latent heat of evaporation of nitrogen at $77^{\circ}K$ is 1.45kcals.mol^{-1}. It may be noted that the linear part of the graph extends to very high values of the coverage

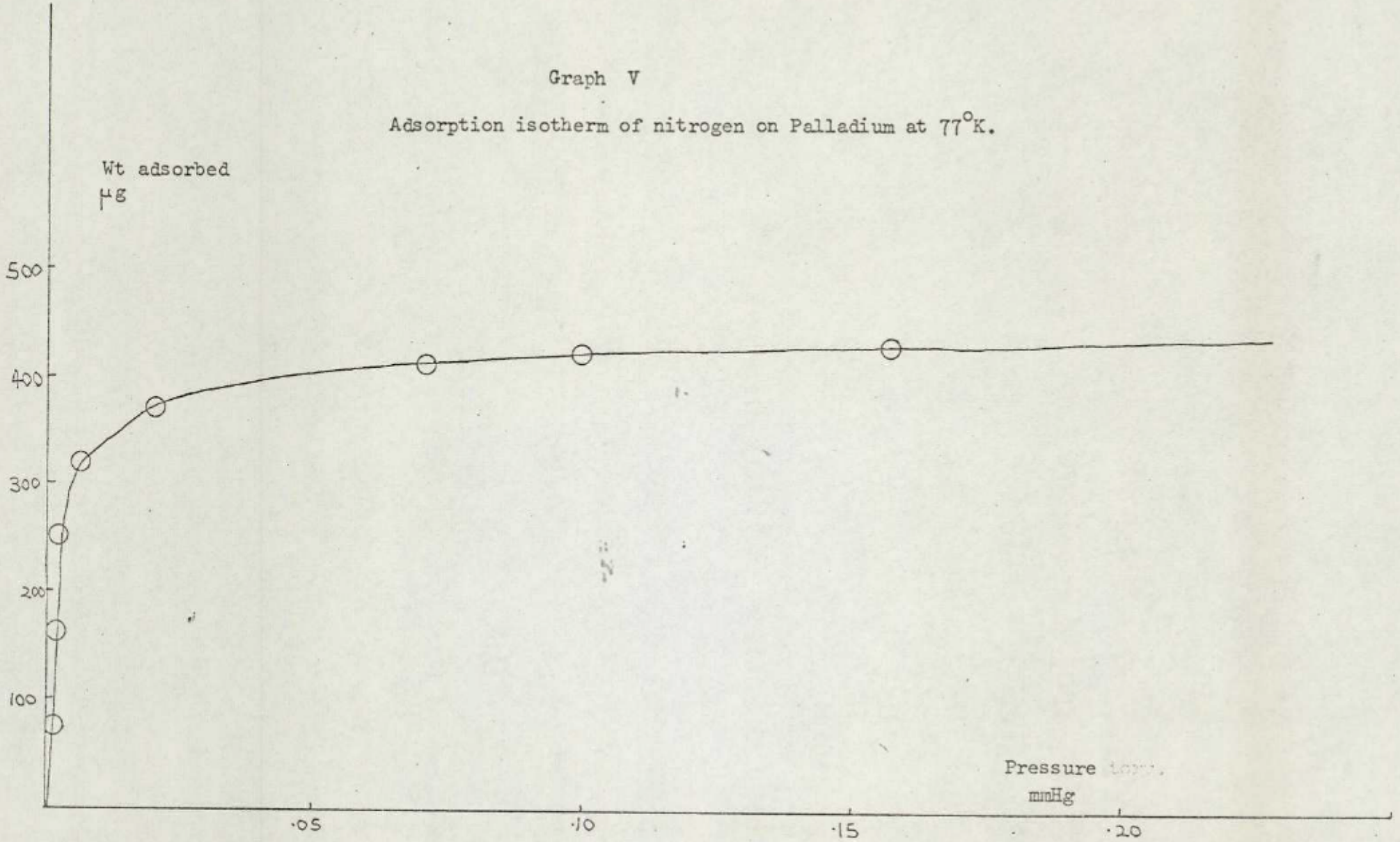
Graph IV

Adsorption of Nitrogen on Palladium



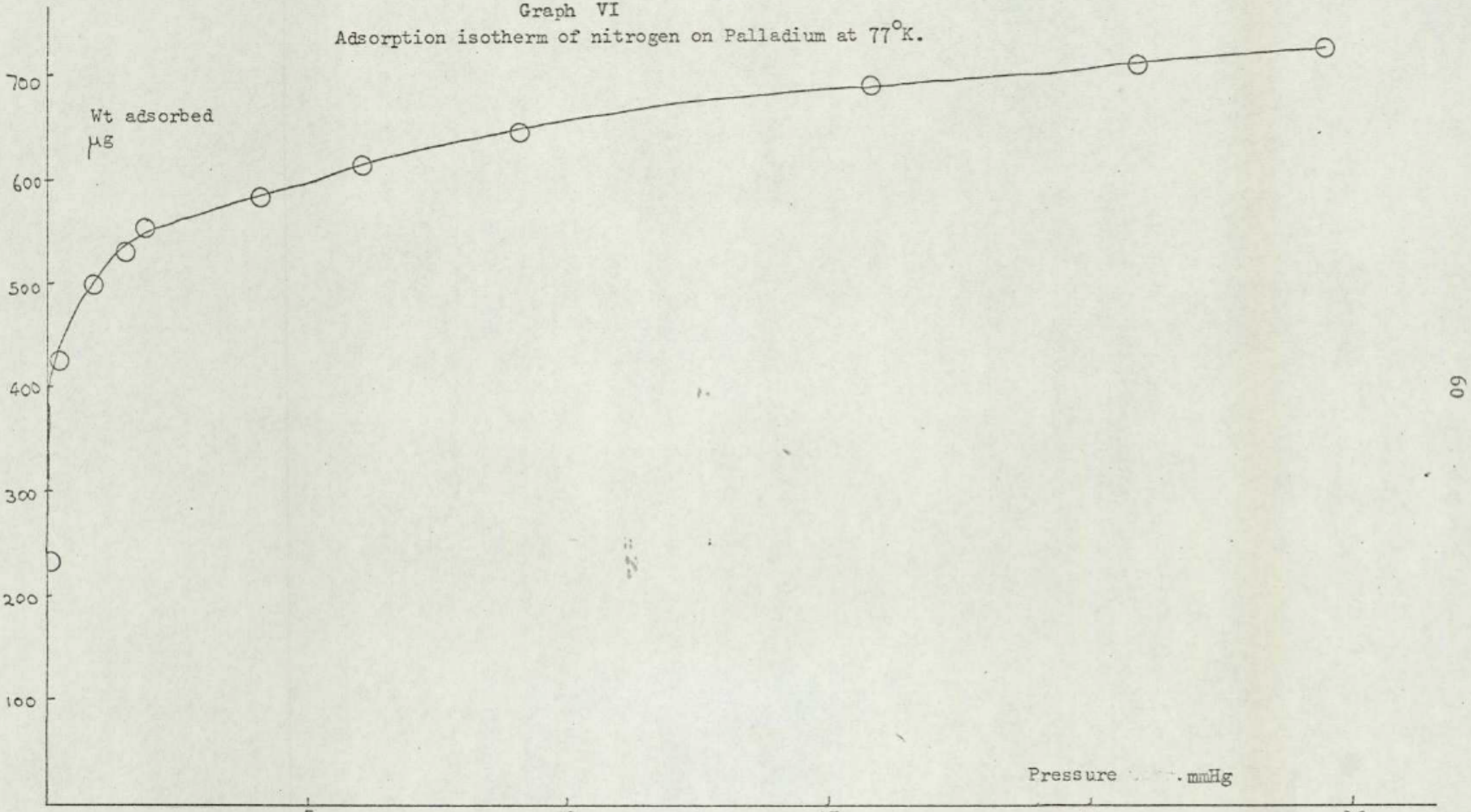
Graph V

Adsorption isotherm of nitrogen on Palladium at 77°K.



Graph VI

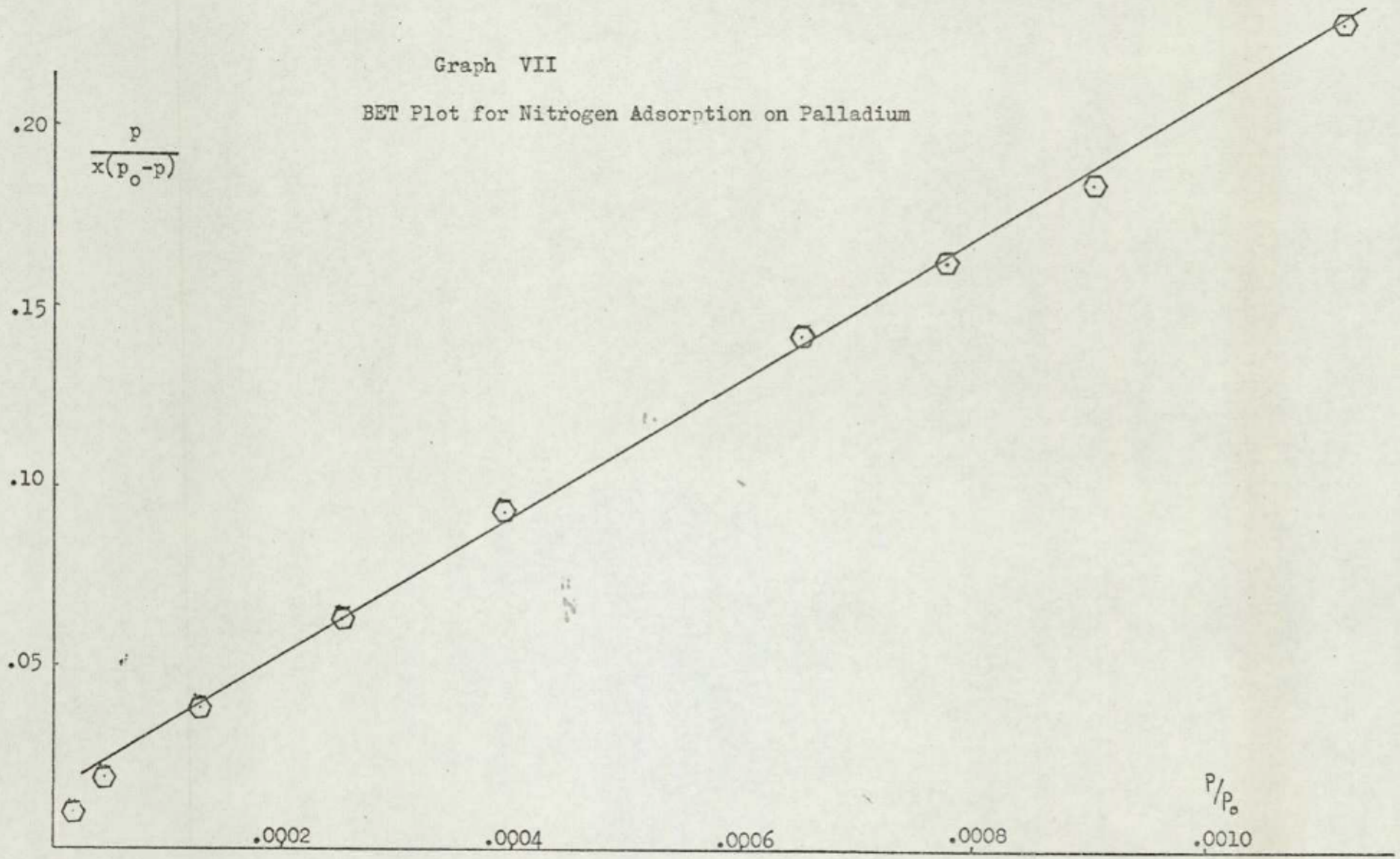
Adsorption isotherm of nitrogen on Palladium at 77°K.



Graph 8

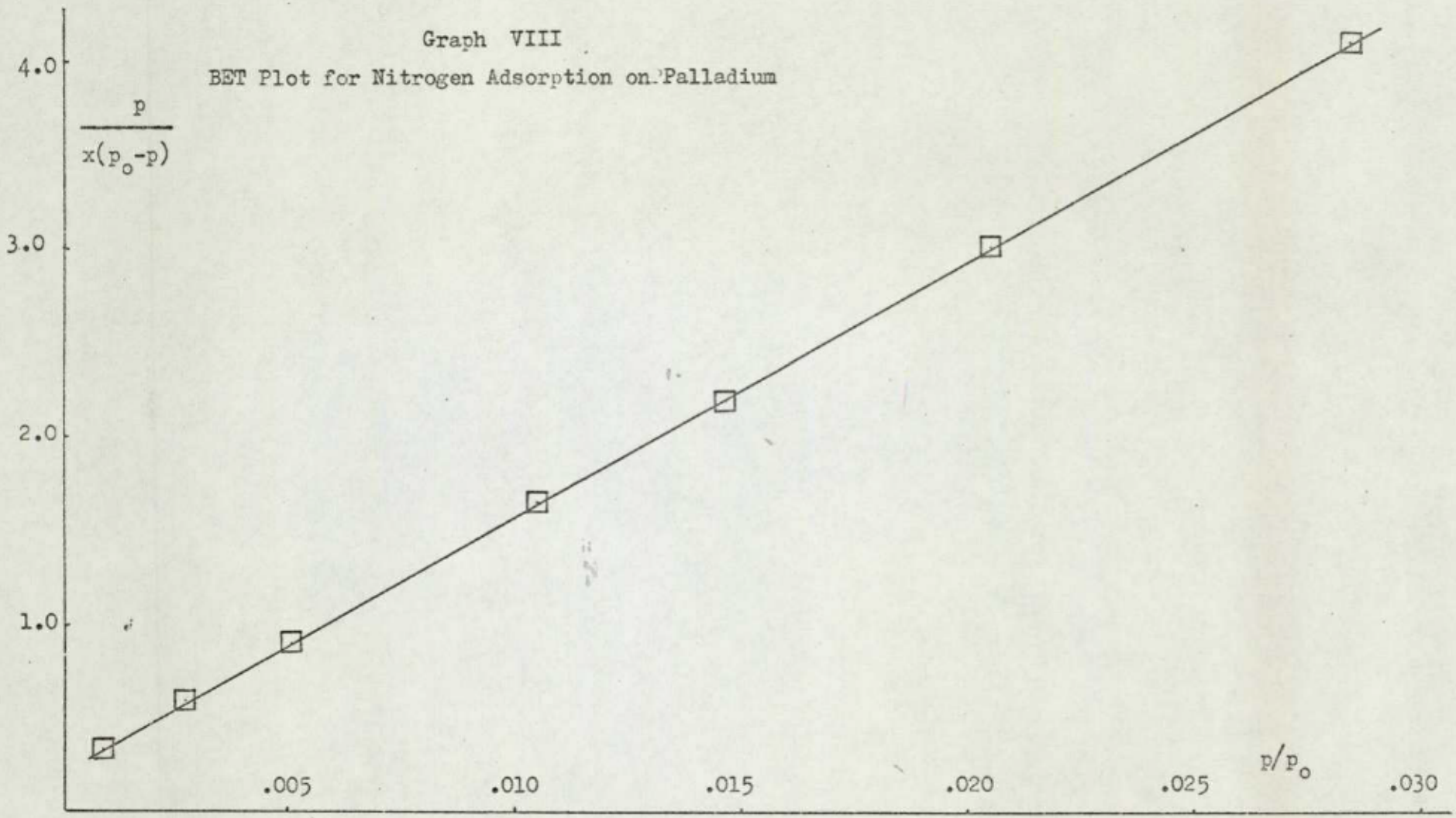
Graph VII

BET Plot for Nitrogen Adsorption on Palladium



Graph VIII

BET Plot for Nitrogen Adsorption on Palladium



indicating that the interaction of the nitrogen molecules with one another is weak compared with the interaction between the nitrogen molecules and the surface. The area occupied by one nitrogen molecule at monolayer coverage is $16.2A^2$ (Brunauer, Emmett, and Teller, 1938) and at the first point of deviation of linearity in the graph is about $50A^2$.

4.52 The Position of the Nitrogen Molecule If the area occupied by one nitrogen molecule with its long axis perpendicular to the surface is calculated from the Van der Waals radius the value obtained is $1.5^2 \times \pi$, i.e. $7.06A^2$. The area actually occupied is $16.2A^2$, a value 2.3 times that calculated. This discrepancy is probably due to the fact that the nitrogen is present on the surface as a two dimensional gas. For molecules lying horizontally on the surface and rotating at high speed the calculated area is $13.9A^2$ and hence the area for a two dimensional gas of molecules lying in this position might be taken as $13.9 \times 2.3A^2$, i.e. $32A^2$. It thus appears that when the surface is rather more than half covered with molecules (lying mainly in the horizontal position), the interactions become strong enough to cause appreciable deviations from ideality.

4.53 The Isotherm at Different Pressure Ranges - The BET Plot The isotherms have been plotted over three pressure ranges (Graphs IV, V, and VI) and it can be seen that the general shape of the curves is the same for each and that the BET plots (Graphs VII &VIII) for the two higher ranges are linear. The surface obtained from the high pressure part of the isotherm (0 - 20mm) is $23.6m^2g^{-1}$, and from the middle pressure range is $8.60m^2g^{-1}$. The general similarity in

shape arises from the fact that the gradient decreases very rapidly over the pressure range 0 - 1 mm. Thus the 0 - 20mm isotherm appears to have a knee at about 1mm pressure. However, the gradient has already decreased a great deal at 0.01mm pressure so that the gradient between 0.01 and 0.1mm pressure is much less than below 0.01mm and the isotherm over the range 0 - 1mm again appears to contain a knee. This is reflected in a non-linear BET plot over the range 0 - 20mm but the non-linearity occurs only in the lowest 20% of the plot and is thus not apparent on visual inspection and does not affect the calculated area. The BET theory was derived for the pressure range of relative vapour pressure 0.05 - 0.35 (35 - 270mm for nitrogen) and is thus entirely outside the range used in any of the present measurements.

It is usually stated that the criterion for the applicability of the BET equation is that the BET plot should be linear, the values given above being those over which the plot is most often found to be linear. When the present work was first evaluated it was assumed that as the BET plot over the range RVP = 0.005 - 0.035 was apparently linear, the area obtained was a true surface area. However, as stated above, the BET plot at even lower pressures is also apparently linear, though of a different gradient from that at higher pressures. The reason for this seems to be that the measurements have been taken over a pressure range of five orders of magnitude and it is not possible to plot enough of this range on one graph to detect the non-linearity. The same observation is apparent from the isotherms themselves. The BET theory assumes that the isotherms consist of a steeply rising portion followed by a much flatter

linear portion rising sharply again at higher pressures. The statistical monolayer is then taken as being just formed at 'point B', the beginning of the linear part of the graph. The BET plot is simply a method of locating analytically the point B, (Halsey 1950). When, as in the present case, the isotherms do not have a well-defined linear portion the BET equation picks out a point just above the knee as representing the completion of a monolayer. It is evident from the isotherms that this is possible for each of the pressure ranges and that the area will be different for each case.

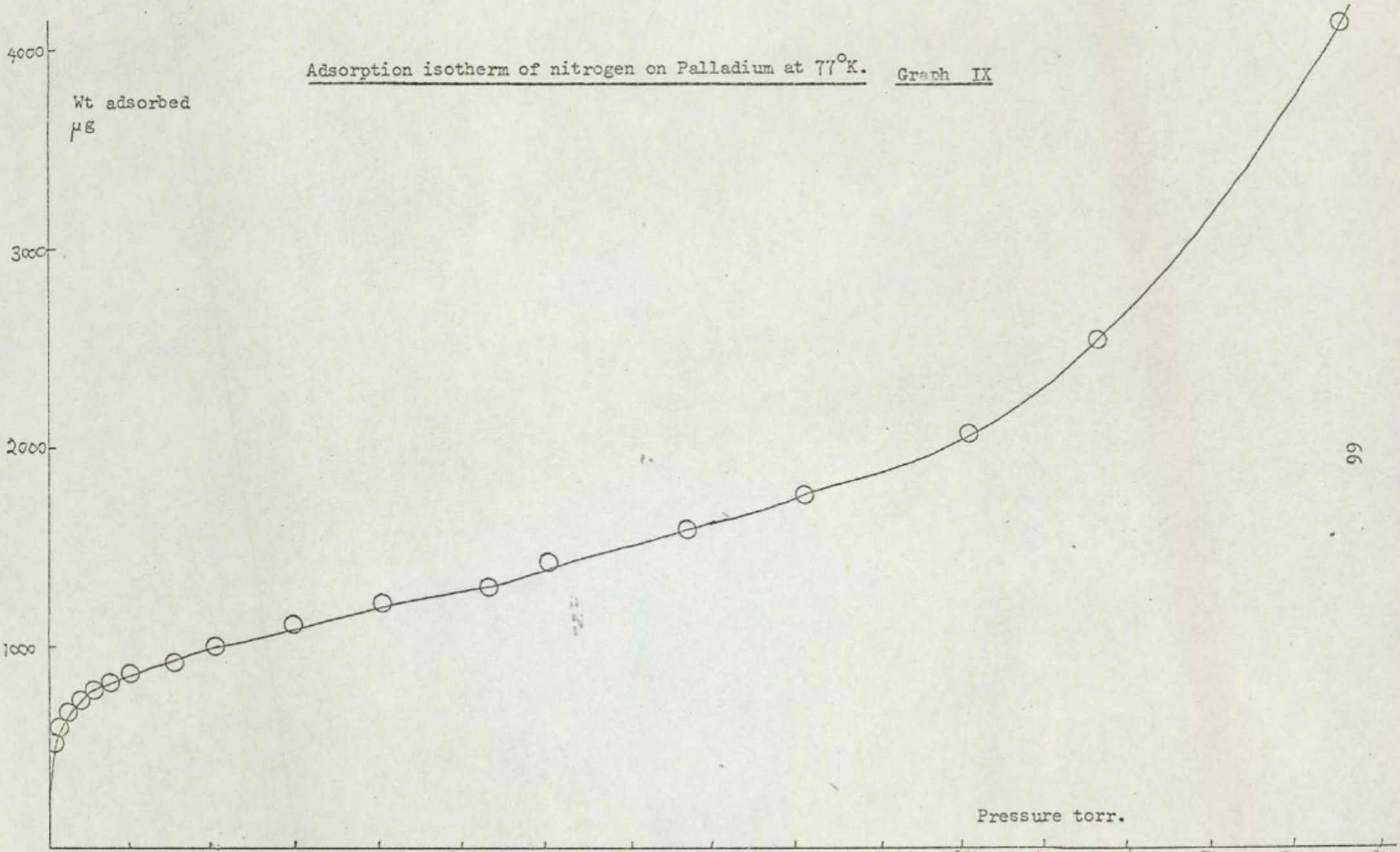
4.54 The Isotherms at High Pressures To resolve these difficulties a mercury manometer was inserted into the vacuum line close to the cold trap to extend the measurements up to the SVP. The isotherm at high pressures is plotted in graph IX . The BET areas were calculated for four pressures and the results are tabulated below.

RVP	S ($m^2 g^{-1}$)
$1.3 - 93 \times 10^{-6}$	13.8
$1.3 - 55 \times 10^{-4}$	18.7
$8.0 - 27.6 \times 10^{-3}$	23.4
$3.2 - 40 \times 10^{-2}$	24.0

4.541 The Computer Program For these measurements a computer program was developed to take the experimental results, calculate the values for the BET plot, and, after selecting those in the appropriate pressure range, calculate the specific surface area, the statistical monolayer capacity and the BET c constant using a least squares procedure.

4.55 Results Since all the BET plots (except those at the

Adsorption isotherm of nitrogen on Palladium at 77°K. Graph IX



Graph 9

lowest pressures) were linear, and since the highest pressure range corresponds to the 'BET range' it appears that whilst the BET equation is strictly only applicable to the highest range, the error in using the second range is not very great but the error in using the first two is considerable. Experiments in this second range did not involve the use of a mercury manometer.

CHAPTER V

THE ADSORPTION OF WATER ON PALLADIUM

5.1 The Apparatus

For the experiments involving the adsorption of water the apparatus was as in Chapter IV with the addition of a water circulating system for control of the adsorbate temperature. This consisted of copper coils which surrounded the hangdown tubes of the balance and through which water was circulated from a cyclotherm. The coils were themselves immersed in dewars containing water to eliminate any effects due to draughts and the sample was maintained at a temperature constant to $\pm 0.02^{\circ}C$.

5.2 Experimental

The experiments were done following two different outgassing procedures. These will be designated Series A and Series B.

5.21 The Adsorption Experiments - Series A Pumping at room temperature and 10^{-5}mmHg removed a few monolayers of gas (of molecular weight 25 and occupying $13 \times 10^{-20} m^2$.molecules^{-1}). Raising the temperature to $100^{\circ}C$ removed another monolayer but on subsequent heating to $150^{\circ}C$ virtually no more gas was desorbed. The standard surface was, therefore, prepared by heating at $100^{\circ}C$ and 10^{-5}mmHg for 48hrs. Cooling to the temperature of the experiment produced very little weight increase.

On admitting water vapour the weight of the sample increased to a maximum within 2 - 60 minutes, after which there was a decrease in weight and pressure due to redistribution of adsorbed water between the sample and the glass walls

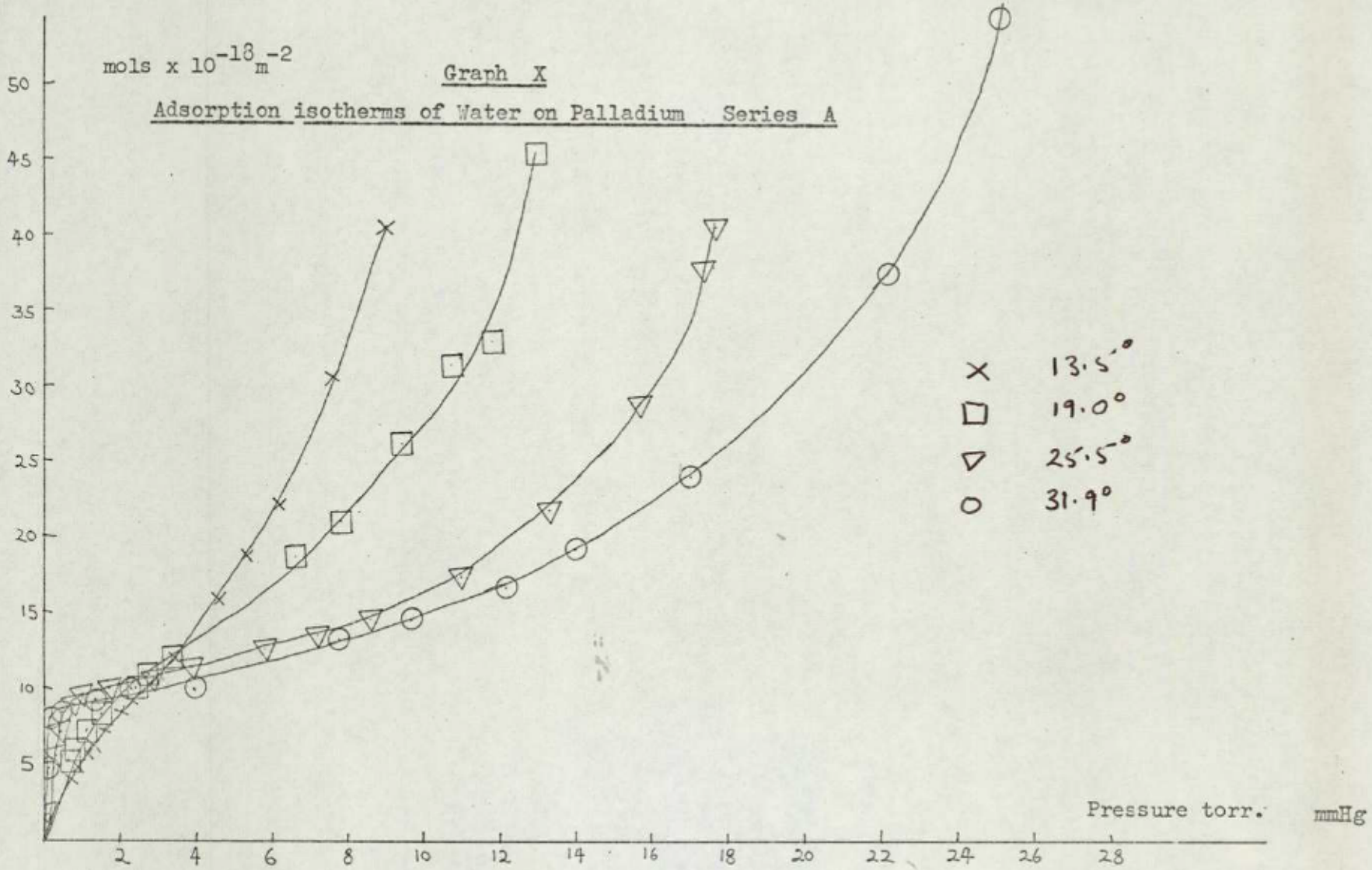
of the apparatus. Final equilibrium was reached in 6 - 8 hours. Nevertheless, any reading taken after the point of maximum uptake was sufficiently close to equilibrium at the pressure observed for practical purposes, indicating the absence of hysteresis. However, at the lowest pressures (< 1mmHg) and higher temperatures ($> 19^{\circ}$) the gas was irreversibly adsorbed and here it was necessary to obtain final equilibrium values which, at these pressures, always appeared to be attained in less than 30 minutes. The standard practice of measuring the weight and pressure at maximum uptake was adopted.

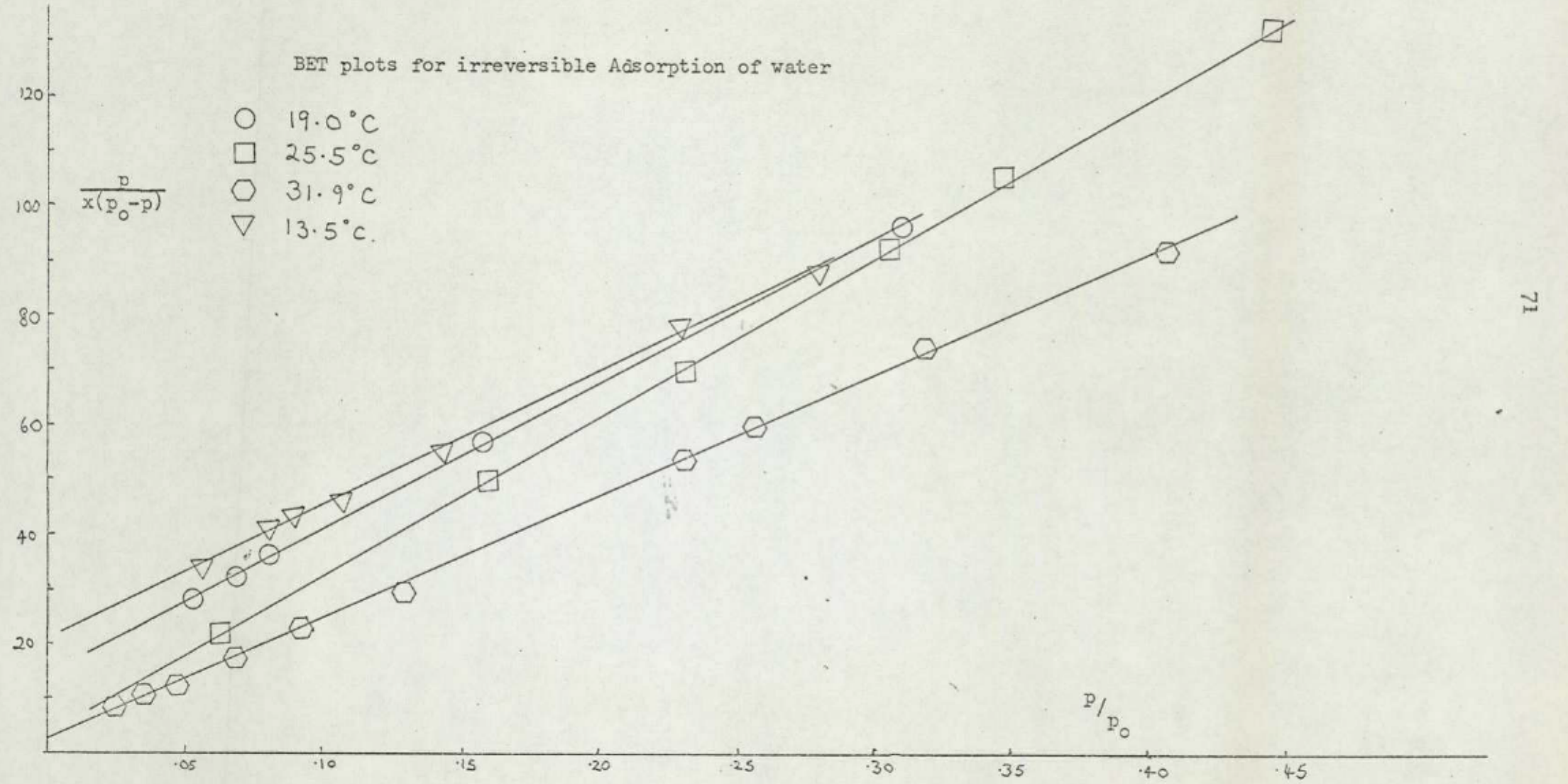
When these experiments were repeated, changes in the specific surface area of the palladium on heating caused the amount of gas taken up to change. Similar changes have been reported in detail for platinum black by McKee (1963), and have been studied in the present system by nitrogen adsorption. To overcome this the isotherms (Graph X) are plotted in terms of coverage after taking a new BET area from each run. The BET plots are shown in Graph XI and when plotted in this way the reproducibility was much improved.

5.22 The Molecular Area A coverage of 9.8×10^{18} molecules.m^{-2} represents one monolayer based on the assumption that one adsorbed water molecule occupies $10.2A^2$. This is the value given by de Boer (1968 p30) but other workers (Harkins 1952 and Hackermann and Hall 1958) give values ranging up to $14.8A^2$. The simple equation:

$$\sigma_m = 1.091(M/\rho N)^{\frac{2}{3}}$$

gives $\sigma_m = 10.5A^2$ so that $10.2A^2$ is a lower limit. However, this value does not affect the interpretation of the results at this stage since they are plotted in terms of


mols x 10^{-18} m^{-2}
Graph X
Adsorption isotherms of Water on Palladium Series A
50
45
40
35
30
25
20
15
10
5
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Pressure torr. mmHg
13.5°
19.0°
25.5°
31.9°

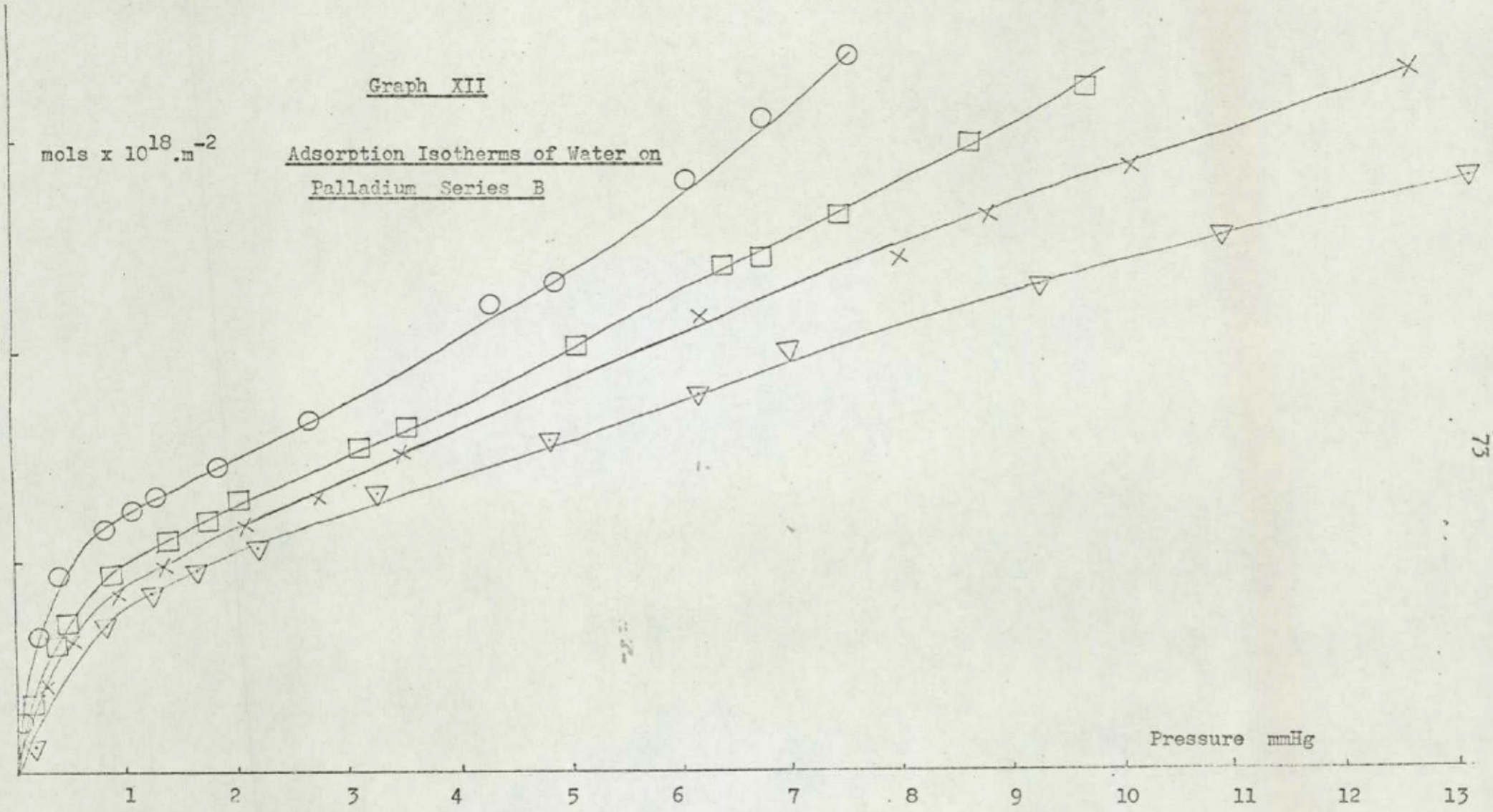

BET plots for irreversible Adsorption of water
19.0°C
25.5°C
31.9°C
13.5°C.
$\frac{p}{x(p_o-p)}$
120
100
80
60
40
20
·05
·10
·15
·20
·25
·30
·35
·40
·45
p/p_o

coverage. Simple comparison of the results obtained here with those using nitrogen as the adsorbate suggests that a molecular area of 19.0 A^2 for water would be more appropriate. However, this probably represents a composite hydrophobic/hydrophilic surface (see section 5.41).

5.23 Adsorption Experiments - Series B Because some of the gas was irreversibly adsorbed a study was then made of a surface free of reversibly bound material but covered by more strongly bound molecules. A sample of palladium was outgassed as described previously and then exposed to a water vapour pressure of about 5 mmHg for one hour. The residual gas was pumped away and a number of adsorption runs carried out without preheating. After the sixth exposure to gas the adsorption was reversible i.e. it was possible to move up or down an isotherm by adding or pumping away water vapour and without observing hysteresis. When a surface had been established in this way, a further series of experiments at different temperatures was carried out. The isotherms, each representing three or four separate experiments, are plotted in Graph XII and the BET plots in Graph XIII.

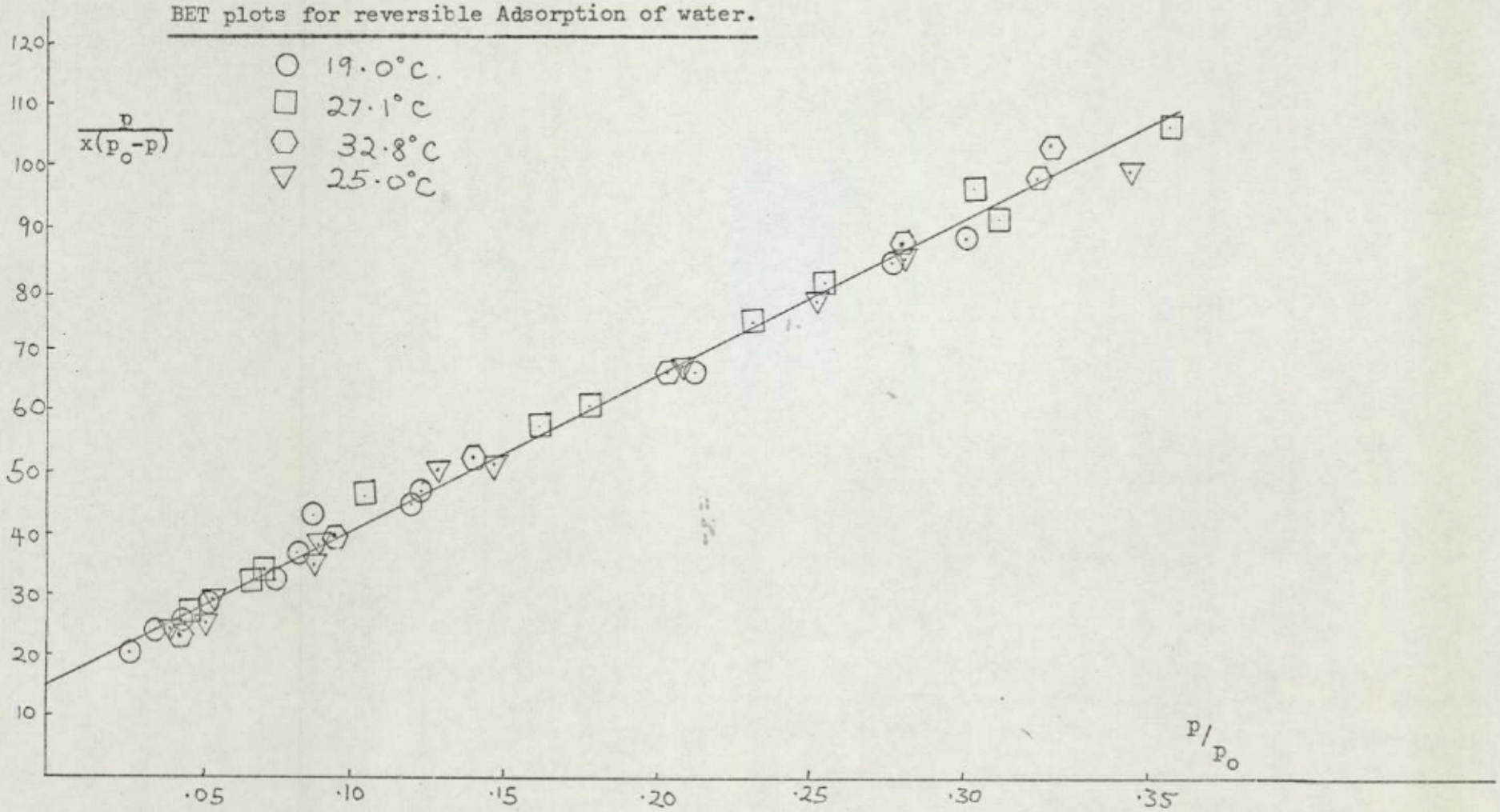
5.3 Results and Discussion

5.31 Isotherms and BET Plots The isotherms are of the form described by Brunauer, Emmett, and Teller (1945) as type II and whereas for the experiments of series B the amount of gas adsorbed decreases with increasing temperature over the whole range as expected, for series A the amount of gas increases with increasing temperature below monolayer coverage: at this point the isotherms cross and then behave


Graph XII
Adsorption Isotherms of Water on
Palladium Series B
mols x 10^{18}.m^{-2}
15
10
5
Pressure mmHg
1
2
3
4
5
6
7
8
9
10
11
12
13

Graph XIII

BET plots for reversible Adsorption of water.



normally. The BET plots are linear over the BET range (p/p_o = 0.05 - 0.35) for both series of experiments. The values of the 'c constant', the weight, x_m, of gas adsorbed at monolayer coverage, and the specific surface area, S, are tabulated below.

Irreversible - Series A

Temperature °C	13.5	19.0	25.5	31.9
c constant	13.1	50.7	96.0	597.0
x_m g.g^{-1}	.00377	.00321	.00345	.00442
S m^{2}g^{-1}	12.9	10.9	11.8	15.1

Reversible - Series B

Temperature °C	19.8	25.0	27.1	32.8
c constant	16.6	18.5	18.9	17.5
x_m g.g^{-1}	.00375	.00383	.00387	.00376
S m^{2}g^{-1}	12.8	13.1	12.9	12.8

5.32 Discussion The specific surface areas obtained from the experiments of series A were much less reproducible than those obtained from series B. This may represent a change in the adsorption process from physisorption to chemisorption. To investigate this the effect of temperature changes was considered for each type of isotherm separately. Firstly, for physisorption, the amount of gas adsorbed is proportional to the number of collisions of water molecules with the surface and inversely proportional to the rate of desorption which itself depends on an exponential function of temperature arising from the activation energy for the process. Thus increasing the temperature will increase the rate of desorption much more than the rate of adsorption and the equilibrium amount of adsorbed gas will decrease as

the temperature increases at a given pressure; or equivalently, any given coverage will be attained at progressively higher pressures as the temperature is raised. For chemisorption however, both the adsorption and desorption processes are activated, with the activation energy for desorption greater than that for adsorption. This means that at any given pressure the adsorption will be greater the higher the temperature and any given coverage will be attained at lower pressures as the temperature is increased. But water is rather unusual in having a heat of liquefaction which is not much lower than the activation energy of many room temperature chemical reactions and it is thus quite conceivable that both chemical and physical adsorption processes might take place simultaneously over a narrow temperature range around room temperature. If chemi- and physisorption were taking place simultaneously it might be expected that at lower temperatures the physical process might predominate at low pressures, with the adsorbed molecules transferring to the chemisorbed state rather slowly and with a rather ill defined knee as monolayer coverage is reached, due to the fall in the heat of adsorption in the second layer. At higher temperatures the adsorption should increase much more rapidly with pressure, giving rise to a much sharper knee at monolayer coverage due to the predominance of chemisorption. Since there is no possibility of chemisorption into the second layer of molecules there will then be a rather flat portion of the curve with further adsorption taking place only at much higher pressures where physical adsorption is taking place.

Comparison of the experimental isotherms shown in Graph X indicates that this is just the type of behaviour

to be found in the present case, indicating that after outgassing at elevated temperature the adsorption of water vapour on palladium is a process involving a considerable activation energy.

5.4 The BET Treatment

5.41 The Surface Area The surface areas obtained from the adsorption of water vapour were consistently just over half those obtained from the adsorption of nitrogen, ($24 m^2 g^{-1}$), indicating that each water molecule occupies $19.0 A^2$, almost twice the $10.2 A^2$ generally accepted for the water molecular area.

This implies either a composite hydrophobic/hydrophilic surface so that not all the surface sites are occupied, or that the water occupies definite sites so that the molecular area depends on the substrate rather than on the properties of water. In either case, the fact that the surface areas obtained from the series B experiments are almost identical to those obtained from series A (i.e. on conditioned and 'bare' surfaces) indicates that any site spacing due to the metal must persist through several layers giving a very open structure to the adsorbed layer as a whole.

5.42 The Heat of Adsorption The BET equation states that:

$$\frac{p}{x(p_o - p)} = \frac{1}{x_m c} + \frac{(c - 1)}{x_m c} \cdot \frac{p}{p_o}$$

and in the original derivation (Brunauer, Emmett, and Teller 1937,1938) the constant c was given by the relation:

$$c = \exp((E_1 - \lambda)/RT) \qquad \lambda = \text{latent heat}$$

It might then be thought possible to obtain a value for the heat of adsorption, E_1, in the first layer from the value of c. However, whilst it is thermodynamically sound to define c in this way (Gregg and Jacobs 1948), c could equally be defined by:

$$c = K\exp((E_1 - \lambda)/RT)$$

where K is a constant of integration which first appears in the rate equations from which the BET equation is derived. In the usual notation, it is equal to a_1b_2/a_2b_1 and it was originally put equal to unity on the implicit assumption that the entropy changes on adsorption into the first and subsequent layers were always the same. In the present case it is possible to derive a value for K from the isotherms taken at different temperatures. If the Clapeyron-Clausius equation is applied to the isotherms it is possible to construct a graph of the isosteric heat of adsorption against coverage, (see section 5.5). Then, by calculating the average heat of adsorption over the range of coverage of the BET equation a value for K may be obtained. This method still makes the assumption that the difference between the entropies of adsorption into the first and second layers is the same at all temperatures examined but later work (section 5.6) has shown this to be so and it should give more reasonable values than are obtained by putting K = 1. Using the value of 6.73 for K obtained in this way, the heats of adsorption is the BET region for the four different temperatures for the adsorption following a pre-heat are tabulated

below.

Temperature ^{o}C	19.0	25.0	27.1	32.8
ΔH $(=E_1)$kcals.mol^{-1}	10.1	10.9	11.3	12.4

It may be noted that whilst the value of c changes very markedly with temperature, the values for the heat of adsorption do not change very much and that the trend of the results would not be altered if K were put equal to unity.

A discussion of the significance of K has been given by Hill (1948) who, by deriving an expression for the partition function of the adsorbed molecule, arives at an expression for K in terms of the separate interactions between the atoms of the adsorbate and the surface and simple molecular constants. Hill also derived an expression for the energy barrier to rotation of a diatomic molecule about an axis parallel to the surface in terms of the same parameters. In a numerical example it was shown that a value for K of 6.71 is consistant with non-rotating molecules. This is the situation we might expect for water in which the molecular dipole is likely to present a strong orienting influence with respect to the surface. However, it should be pointed out that Hill's treatment is for a symmetric diatomic molecule and that the results for water might well be different.

5.5 The Heat of Adsorption from the Clapeyron-Clausius Equation

The values for the isosteric heats of adsorption for both series of experiments at different coverages were calculated using the Clapeyron-Clausius equation and are plotted in

Graphs XIV and XV.

The Clapeyron Clausius equqtion states that:

$$\ln(p_2/p_1) = (-\Delta H/RT^2)(T_2 - T_1)$$

and the values for the heat of adsorption were obtained by plotting log p vs T at constant coverage. The graphs obtained were straight lines and the scatter of the points indicates an uncertainty of less than $0.2 kcal.mol^{-1}$. It may be noted that at high coverage both plots approach a value slightly less than the latent heat of evaporation. Comparison of these two graphs shows that the heat of adsorption into the first and subsequent layers of series B corresponds to that in the fourth and subsequent layers of series A.

5.6 Entropy Calculations

Entropy calculations were done to find whether the molecules were adsorbed onto fixed sites, using the method of Kemball and Rideal (1946), extended by de Boer and Kruyer (1952), and summarised by Wake (1960). The method involves calculating the entropy change on adsorption from the experimental isotherms using the equations:

$$\Delta G_i = -RT_i \ln(p_o/p_i) \qquad \text{and} \qquad \Delta G_i = \Delta H - T_i \Delta S$$

where the subscripts refer to different temperatures and the other symbols have their usual significance. The values are then converted to a standard state corresponding either to mobile or localised adsorption using

$$-\Delta S_i = -\Delta S - R.\ln(\theta/(1-\theta))$$

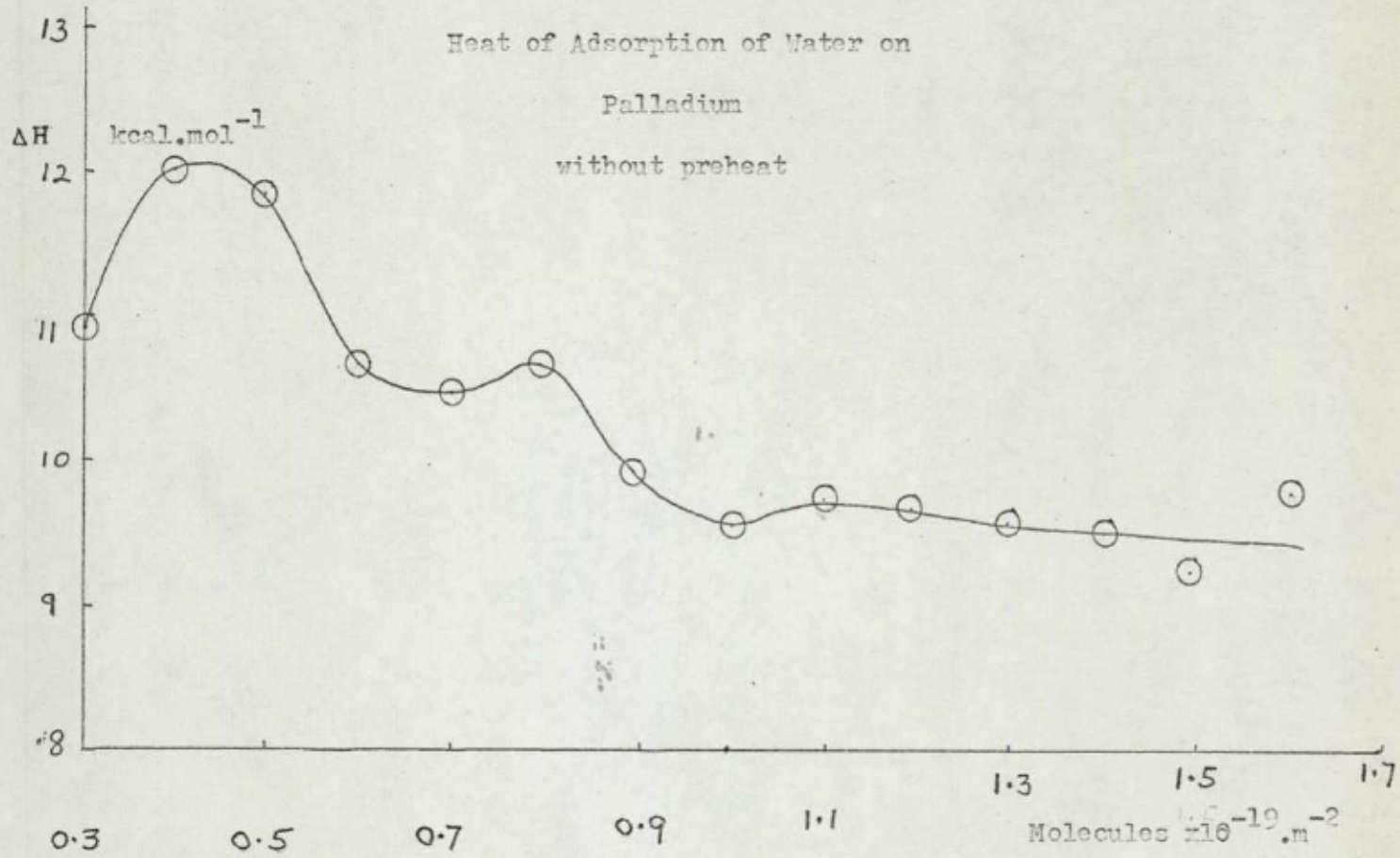
for localised adsorption and:

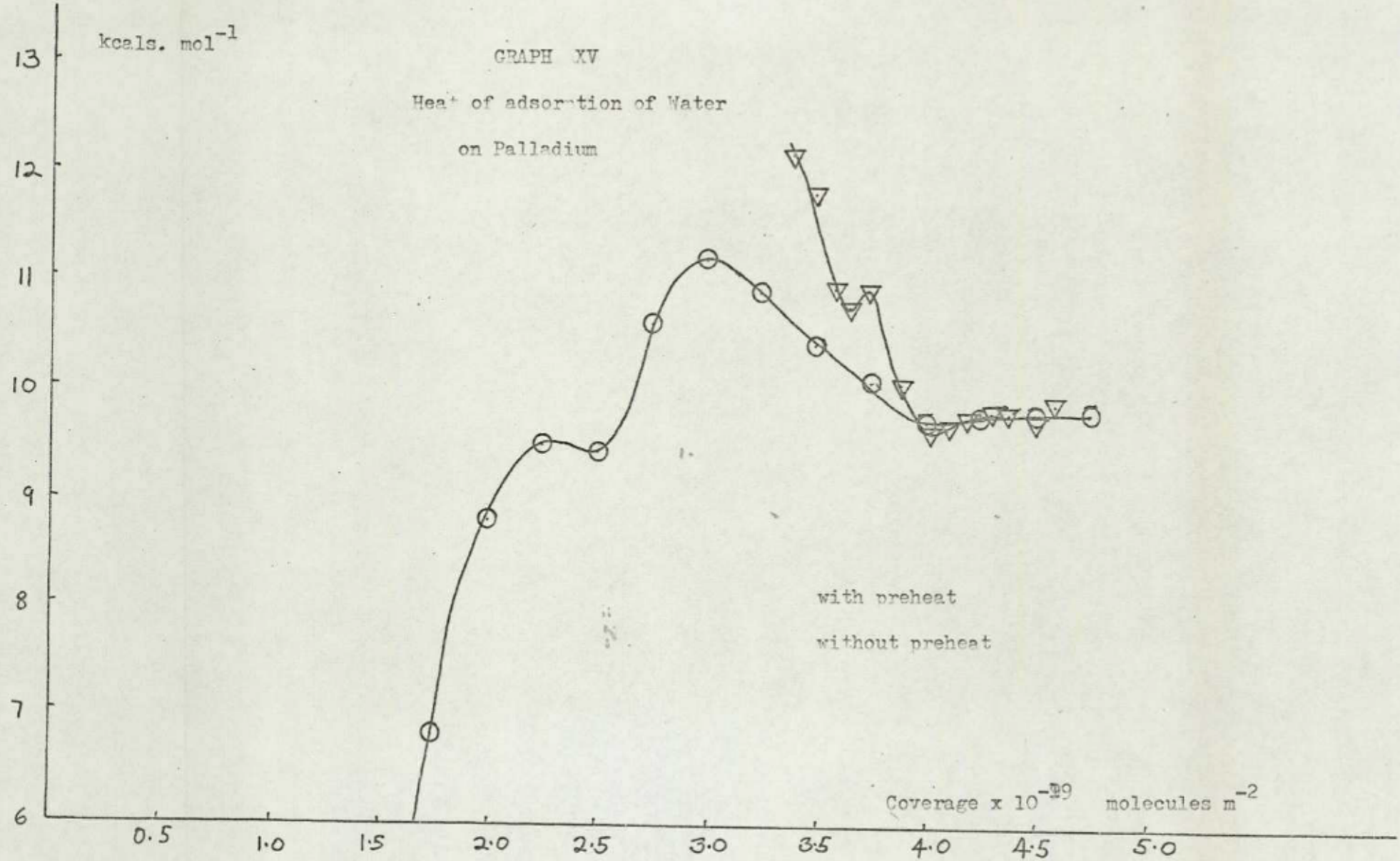
GRAPH XIV

Heat of Adsorption of Water on

Palladium

without preheat





GRAPH XV

Heat of adsorption of Water on Palladium

$$-\Delta S^{o}_{m} = -\Delta S - R \ln(A^{o}/A)$$

(in which A^{o} and A are the areas occupied by one molecule in the standard state and the state being considered respectively) for mobile adsorption.

The standard entropies obtained were compared with theoretical values calculated by a method similar to that of Wake but with extra terms to include rotational and vibrational entropies of the adsorbed molecule.

5.61 Theoretical Entropy Values For entropically ideal site adsorption:

$$-\Delta S_{i} = {}_{g}S_{tr} + {}_{g}S_{rot} - {}_{a}S_{loc}$$

and for entropically ideal mobile adsorption:

$$-\Delta S_{m} = {}_{g}S_{tr} + {}_{g}S_{rot} - ({}_{a}S_{tr} + {}_{a}S_{rot} + {}_{a}S_{vib})$$

The following standard states were assumed:

1)For the gas a pressure of 1 atmosphere (p^{o}).

2)For the mobile adsorbed layer a pressure of 0.338dyne.cm^{-1} (F^{o}).

3)For the immobile surface layer a standard molecular area of $4.08T \times 10^{-20} m^{2}$, ($A^{o}$).

Then for p^{o}

$${}_{g}S^{o}_{tr} = R \ln(M^{3/2}T^{5/2}) - 2.30$$

and

$${}_{g}S_{rot} = R(3/2 \ln T + 1/2 \ln ABC - \ln \sigma - 2.709)$$

where A, B, and C are the three moments of inertia and σ the symmetry factor.

The total entropy of molecules in the gas phase is thus:

$$_{g}S^{\circ}_{total} = {}_{s}S^{\circ}_{tr} + {}_{g}S^{\circ}_{rot} = 48.8 \text{ cal.K}^{-1}\text{mol}^{-1}$$

The calculations for the adsorbed state were made on the following assumptions:

1)That when a molecule is localised on the surface it loses all its translational and rotational freedom.

2)That when an adsorbed molecule is mobile it loses one degree of translational freedom and two degrees of rotational freedom.

3)That when the molecule is adsorbed its internal vibrations do not change but that an extra vibration perpendicular to the surface is introduced.

4)That the two dimensional gas is ideal.

It is obviously possible to make other assumptions concerning the state of rotation of the adsorbed molecule, but those given above correspond to a reasonable physical situation and give the best fit with experiment. The one remaining degree of rotational freedom assumed was that corresponding to the smallest moment of inertia.

For immobile adsorption:

$$_{a}S_{loc} = -R \ln \theta/(1-\theta)$$

and when the coverage, θ, is known the entropy change can be calculated immediately.

It was assumed that adsorption in the second layer does not begin until the first layer is almost completely formed.

For mobile adsorption:

$$_{a}S^{\circ}_{tr} = \tfrac{2}{3}\,{}_{g}S^{\circ}_{tr} + \tfrac{1}{3}R \ln \frac{T}{273.15} + 1$$

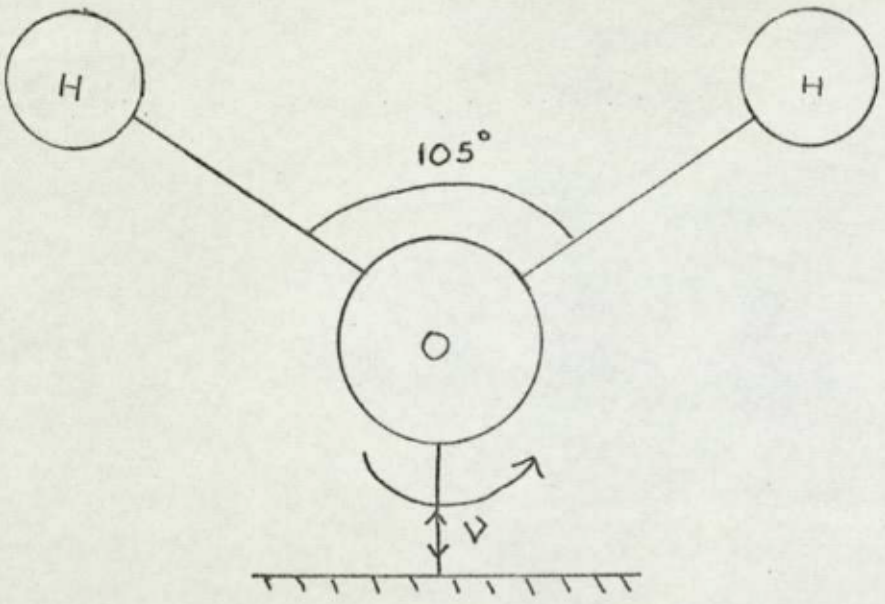


Diagram Showing Rotation and Vibration of Water Molecule on the Surface.

$$ {}_aS^{\circ}_{rot} = R\left(\tfrac{1}{2} \ln T + \tfrac{1}{2} \ln I - \ln \sigma - 0.552\right) $$

and if the frequency of the vibration perpendicular to the surface is ν then:

$$ {}_aS^{\circ}_{vib} = Nh\nu/(e^{h\nu/kT} - 1) - R \ln(1 - e^{-h\nu/kT}) $$

Fripiat, André, Jelli and Poncelot (1965) give a value for ν of 6×10^{-12} based on a morse function for water adsorbed on ferric oxide and this gives a value for ${}_aS^{\circ}_{vib}$ of 2.1 cal.K^{-1}.mol^{-1}. This decreases the numerical value of ΔS since the vibration represents an additional degree of freedom over the gaseous state.

5.62 Results and Conclusions The experimental and theoretical entropies for mobile and site adsorption are shown in table 1. Comparing the first column of the table with the third and the second with the fourth it is clear that much better agreement is found in the second case, corresponding to mobile adsorption.

5.7 t-curve Analysis

The isotherms were also examined by the t method of Lippens, Linsen and de Boer (1964) using the t-curves for water vapour published by Hagymassey Jr., Brunauer, and Mikhail (1969). The curves, shown in graph, XVI, are for the 13.5° and 31.9° isotherms of series A and the 19.5° isotherm from series B. The ordinates represent the coverage at a number of different pressures and the abscissae are the values of coverage found by Hagymassey et al. at the same same pressures on their standard solids. Both axes are plotted in terms of monolayers coverage.

The following observations may be made:

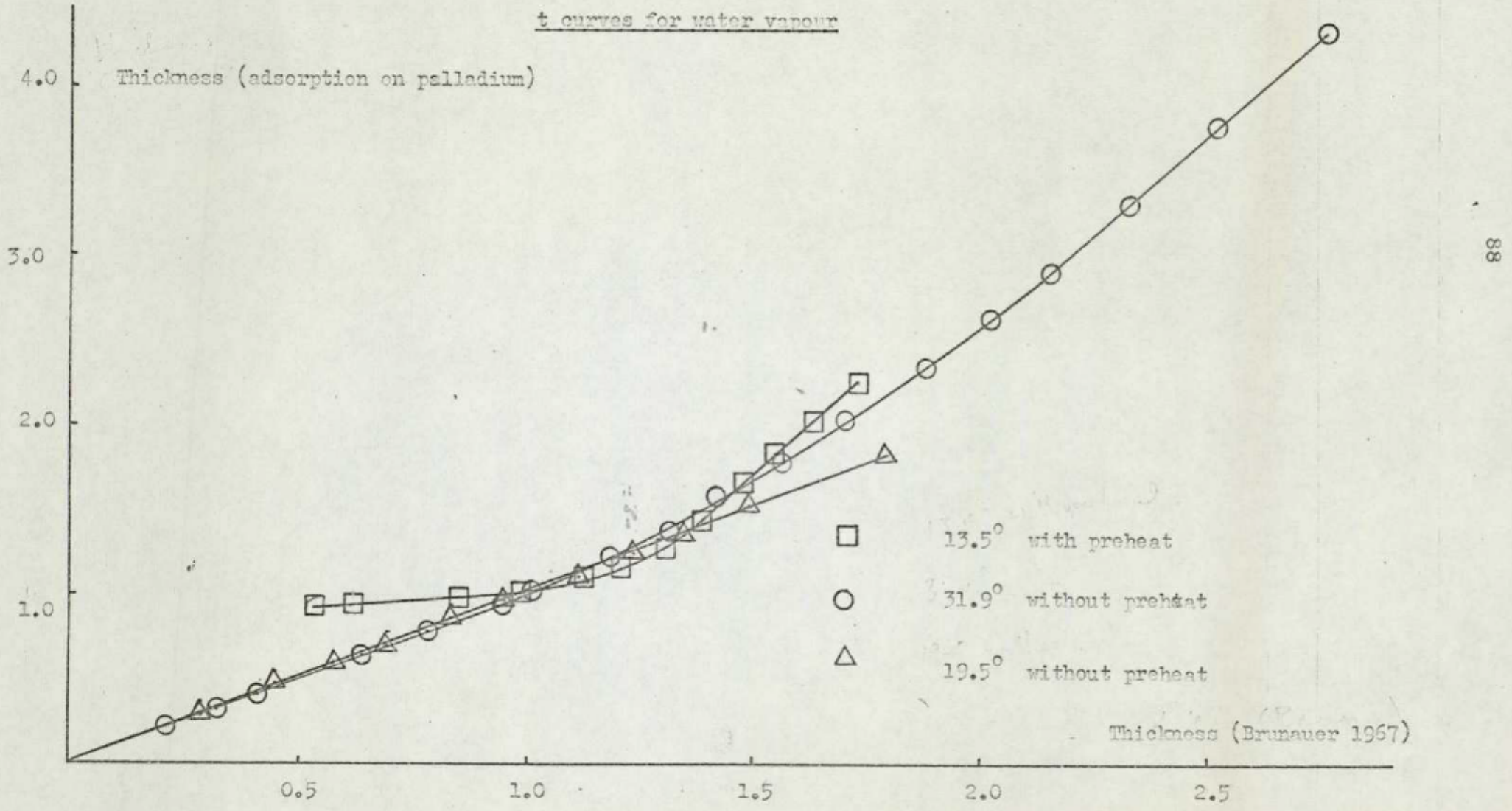
1)In the region of low surface coverage the series B isotherm

TABLE I

Experimental and Calculated Entropies of Adsorption

θ	S_i calculated	S_m calculated	S_i experimental	S_m experimental
0.4	46.7	17.7	23.0	19.1
0.5	46.7	17.7	20.5	16.2
0.6	46.7	17.7	22.6	17.5
0.7	46.7	17.7	25.3	15.5
0.8	46.7	17.7	22.7	14.2
0.9	46.7	17.7	28.5	16.1
1.1	46.7	17.7	23.4	14.1
1.2	46.7	17.7	24.3	15.1
1.3	46.7	17.7	24.6	15.7
1.4	46.7	17.7	26.5	18.0
1.5	46.7	17.7	28.4	20.1
1.6	46.7	17.7	28.2	20.4

Graph XVI


t curves for water vapour
Thickness (adsorption on palladium)
4.0
3.0
2.0
1.0
0.5
1.0
1.5
2.0
2.5
13.5° with preheat
31.9° without preheat
19.5° without preheat
Thickness (Brunauer 1967)

lies fairly close to the theoretical one (the straight line through the origin and having a gradient of 1). At higher pressures the plot lies above the theoretical one and this suggests either that the surface area available is increasing or that the water is condensing in capillaries. The high value of coverage at which this occurs and the absence of hysteresis suggests that the first of these possibilities is more likely, i.e. a composite hydrophobic/hydrophilic surface.

2)The curve for the 13.5° isotherm for the irreversible series follows exactly the same line indicating that the the adsorption is identical in kind to that on a conditioned surface. Furthermore the gradient of these plots is unity indicating that the adsorption is identical to that found by Hagymassey et al. for their standard anatase. That used by these workers was undoubtedly hydroxylated so that these results suggest that the palladium surface is also hydroxylated at least on that part of its area on which adsorption is taking place.

3)As stated previously, part of the palladium appears to be hydroxylated and part hydrophobic. This is bourne out by the t-curve for the 31.9° isotherm. Here, although the surface for adsorption is identical to (2) above, the initial adsorption is much greater. This bears out the conclusion reached in 5.32 that the adsorption on the outgassed surface is activated.

5.8 General Conclusions

After outgassing at elevated temperature a considerable amount of water is removed from the palladium surface.

When water is adsorbed on this surface the initial process has a considerable activation energy, and is thus chemical, although involving a smaller heat change than is

although involving a smaller heat than is normally associated with chemisorption.

When the experiment is carried out after outgassing at room temperature and 10^{-5} mmHg no activation energy of adsorption is observed and process is physisorption. Comparison of the heats of adsorption for the two cases suggests that physisorption commences with adsorption into the fourth layer.

Results of the entropy calculations indicate that the model proposed gives entropy values in agreement with those obtained from experiment, although this does not mean that the entropy is necessarily distributed in the way described. However, it is difficult to see how the molecule could have more freedom than that assigned in the model and hence the one degree of rotational freedom assigned represents a lower limit, i.e. the water may have more freedom than that assumed in the model.

Everett (1957) claims that it is difficult to distinguish between mobile and localized adsorption on the basis of entropy calculations and illustrates his assertion with results for the adsorption of argon on rutile which can be made to fit either state by a suitable choice of ν. In the present case, however, such an objection is difficult to support since the difference between the two cases is so great that the results could be made to fit localized adsorption only by the assignment of an unrealistically low value for ν. We may thus say that the molecule is adsorbed in an essentially mobile state and that it retains some, but not all, of its rotational freedom.

CHAPTER VI

The Adsorption of Ethanol on Palladium

To obtain more information about the palladium surface and, in particular, to find out how easily water vapour is displaced from the metal the adsorption of ethanol was investigated in a similar way to that described for water in the last chapter.

6.1 Experimental

6.11 Purification of the Ethanol The alcohol used was "absolute" alcohol redistilled three times under reduced pressure onto a cold surface from freshly calcined calcium oxide. The alcohol was stored over calcium oxide in the vacuum line until required.

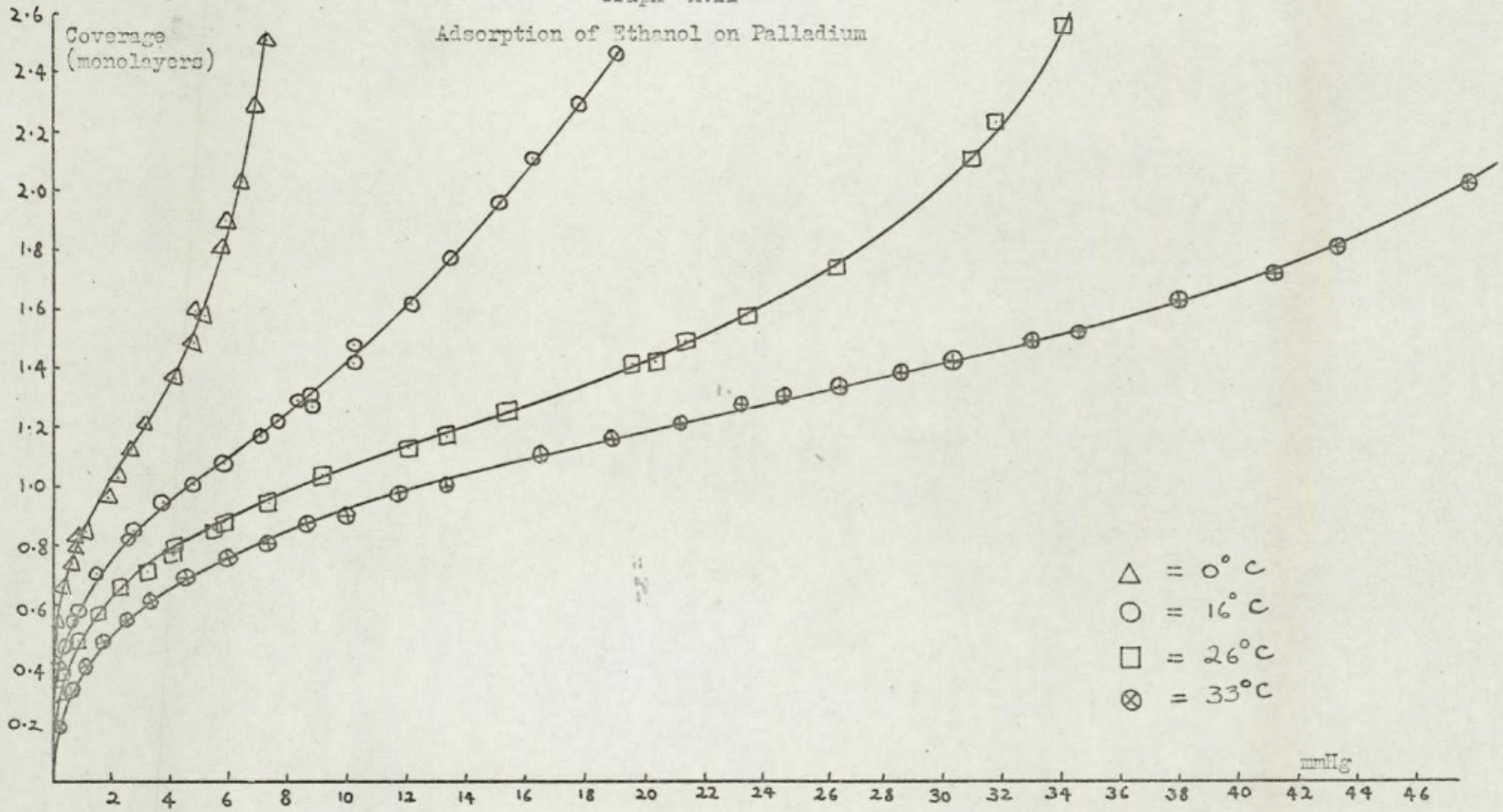
6.12 The Adsorption Experiments The sample was outgassed initially in the same way as for the water adsorption experiments of series A. That is, the pressure was reduced as far as possible and the furnace temperature was set at 100°C until the pressure had been at 10^{-5}mmHg for 48 hours. The isotherms obtained at four different temperatures are shown in graph XVII. The points showed no measurable hysteresis and equilibrium was attained in a relatively short time, (less than 30 minutes). The reproducibility was good and each isotherm shown is the amalgamation of three or four runs.

Next the surface was conditioned with water by pumping off all the alcohol at 100°C (a rapid process) and then exposing to water vapour at just below its saturation vapour pressure and at the temperature of the experiment for 24 hours. The water was then pumped off as far as possible at the same temperature and an alcohol adsorption experiment carried out.

The lowest part of the isotherm was identical to that

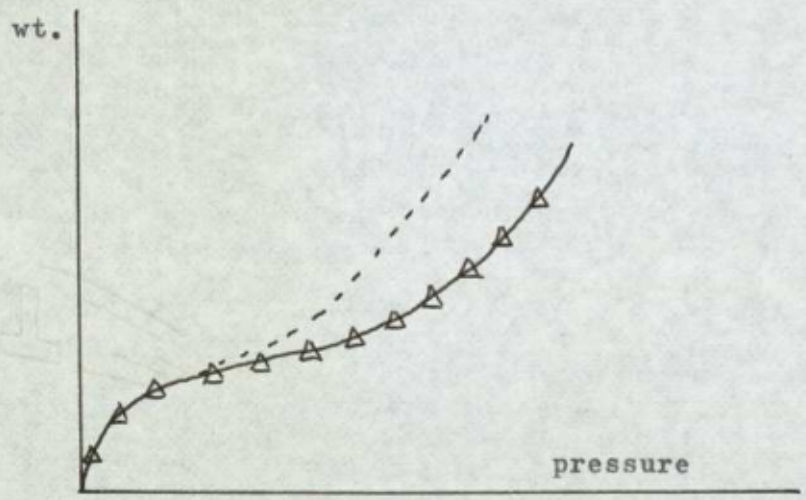
Graph XVII

Adsorption of Ethanol on Palladium



obtained on an outgassed surface up to a certain pressure: then the weight fell off sharply relative to that on the first curve. On measuring the desorption loop the weight was found to decrease far below its initial value. Above the point of divergence the weight increased sharply when the alcohol vapour was admitted and then decreased to its equilibrium value over a relatively long period (4 - 6 hours). The decrease was quite different from that found in the water vapour runs (section 5.11) in that it was accompanied by an increase in pressure and that the final weight was often only slightly above that of the previous point.

The sketch below indicates the type of curve obtained. Here, the solid line and triangles represent the results of these experiments and the dashed line represents the curve obtained under identical conditions on an outgassed surface.



Next, all the alcohol was pumped away (without either heating or admitting water vapour) and a second adsorption experiment carried out. The isotherm accurately reproduced that obtained after a thorough outgassing up to the maximum pressure used in the previous experiment at which point a break occurred as before. The process could be repeated at

successively higher pressures up to the saturation vapour pressure.

Unfortunately, the long time taken to reach equilibrium and the poor long term stability of the balance prevented a detailed study at different temperatures and after different conditioning procedures. However, two typical isotherms were studied in detail and are shown in graph XVIII. In these graphs, as in the sketch above, the points represent those obtained in these experiments and the dashed line the curve obtained under identical conditions on an outgassed surface.

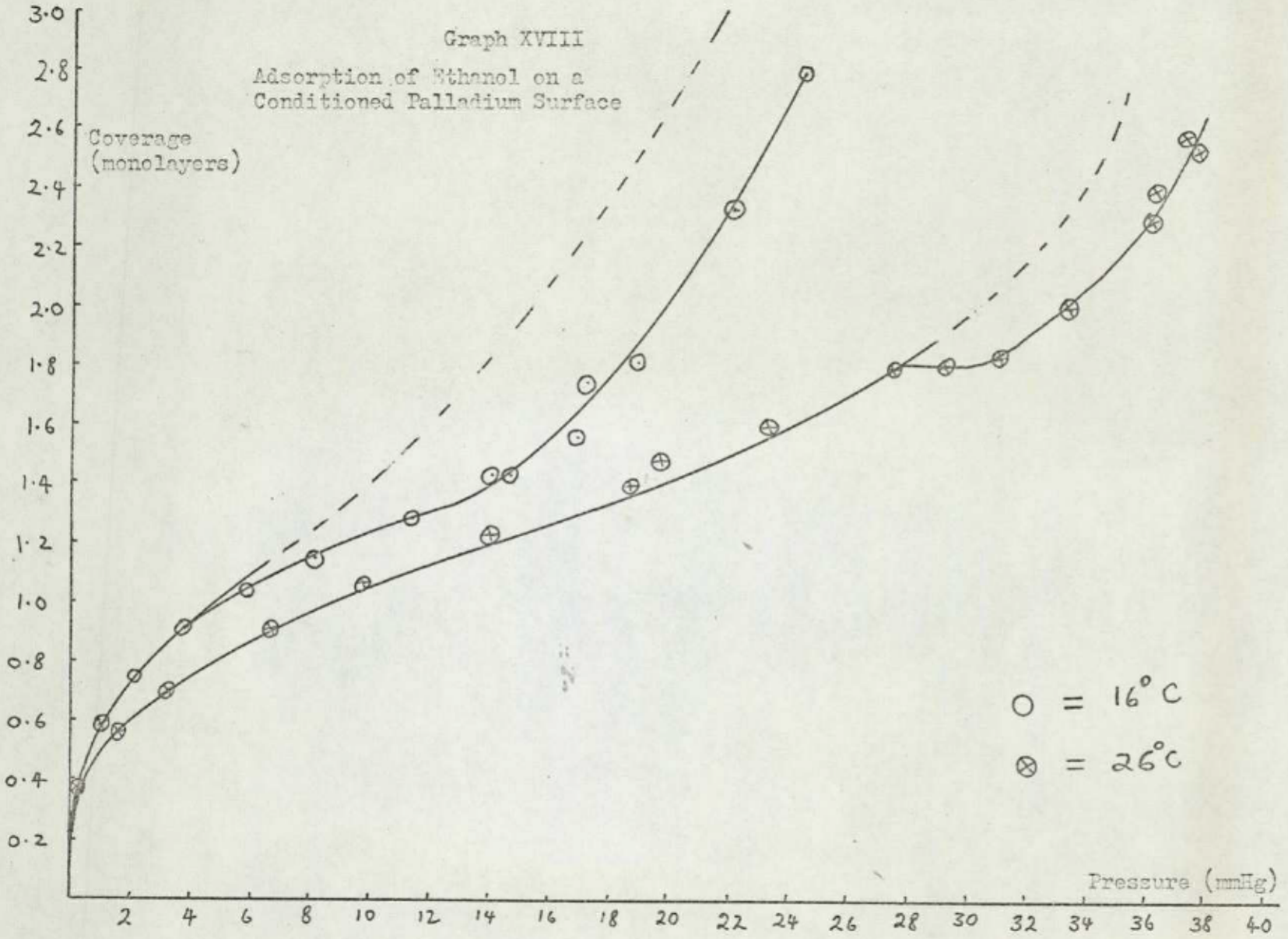
6.2 Results

6.21 The BET Treatment The BET equation was applied to each of the isotherms (on an outgassed surface) using the computer programs given in Appendix II. This gave values for the monolayer coverage, the specific surface of the palladium, and the BET 'c' constant, provided that the molecular area of the alcohol is known. The simple formula:

$$\sigma_m = 1.091(M/\rho N)^{\frac{2}{3}}$$

corresponding to twelve coordination gives a molecular area of 23.0 A^2. Use of this value with the BET equation gives specific surface areas almost identical to those obtained with water and considerably lower than those found using nitrogen as the adsorbate.

The results obtained from the BET equation are tabulated overleaf. The quantity x_m is the monolayer


Graph XVIII
Adsorption of Ethanol on a
Conditioned Palladium Surface
Coverage
(monolayers)
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
Pressure (mmHg)
○ = 16° C
⊗ = 26° C

coverage in grams per gram, and S is the specific surface area obtained using $\sigma_m = 23.0A^2$. The BET plots are shown in graph XIX.

Temperature (°C)	0°	16°	26°	35°
c constant	109.0	90.2	75.4	53.5
x_m $(g.g^{-1})$	0.00408	0.00433	0.00384	0.00376
S (m^2g^{-1})	12.4	13.1	11.6	11.4

As explained above it is possible to adsorb some alcohol onto the palladium surface, even when the latter has been conditioned with water, up to a certain pressure without displacing any water. This suggests that at low alcohol concentrations the vapour adsorbs on the hydrophobic part of the surface. Further evidence for this comes from the fact that the isotherm for these low pressures is identical to that obtained on an outgassed surface. It also appears that at higher pressures the ethanol can displace water from the metal. Since the isotherms on an outgassed metal surface are completely reversible the specific interactions noted for water are absent.

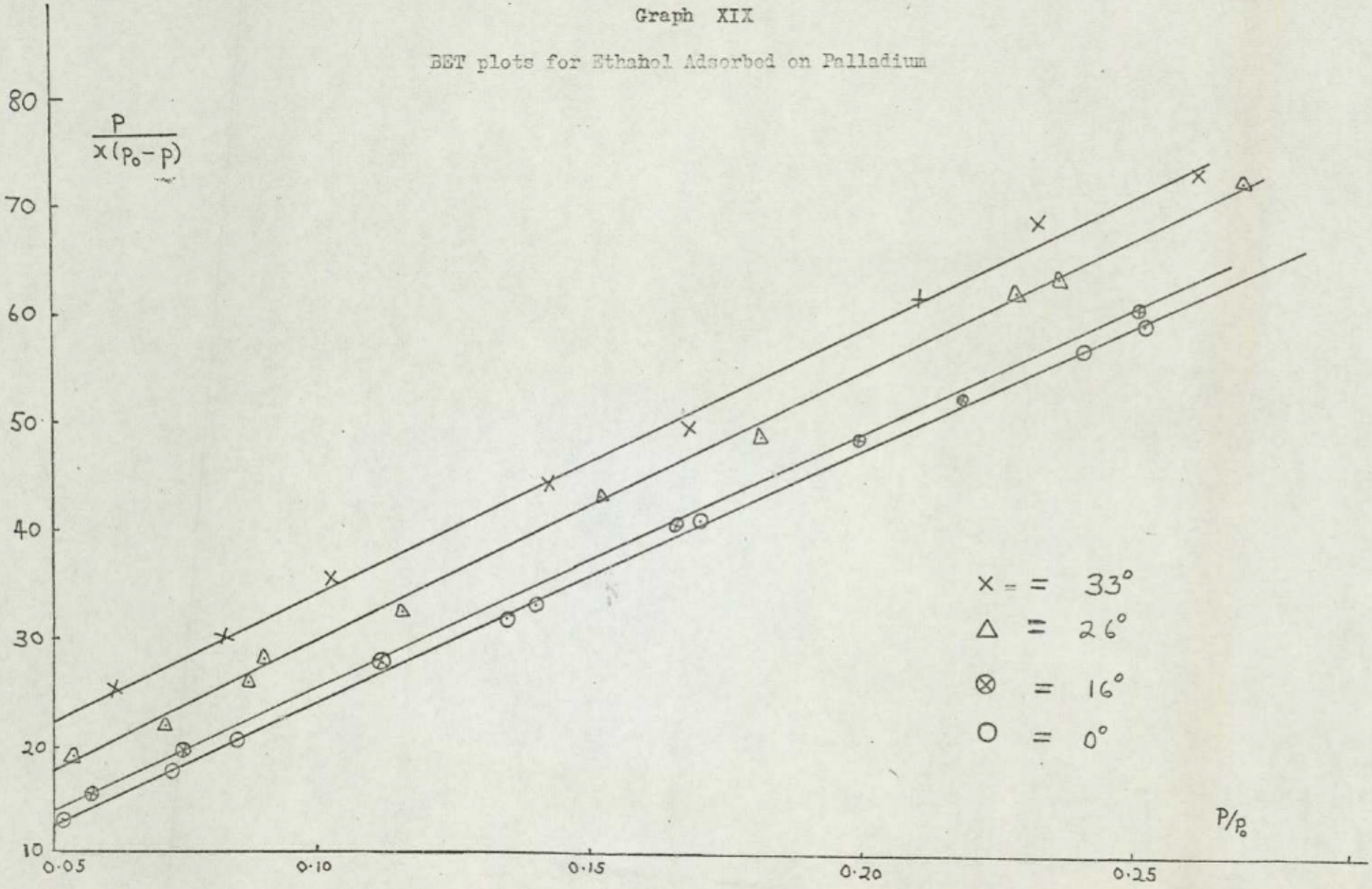
6.22 The Heat and Entropy of Adsorption The heat of adsorption and entropy of adsorption were calculated using the computer programs developed for the water vapour experiments and given in Appendix III. These took readings of the coverage and the corresponding pressure for each of the four different temperatures and calculated the heat of adsorption and entropy of adsorption from straight line plots, based on the Clapeyron-Clausius equation for the Heat of adsorption and on the relation:

$$\Delta G = \Delta H - T\Delta S$$

for the entropy.

Graph XIX

BET plots for Ethanol Adsorbed on Palladium



The values of the heat of adsorption and the entropy of adsorption at different coverages are tabulated overleaf. The entropy values given are for the same standard states as were used for the water isotherms and were calculated using the following equations.

For mobile adsorption:

$$-\Delta S^{\circ}_{m} = -\Delta S - R \ln(A^{\circ}/A)$$

where A° is the standard molecular area and is given by:

$$A^{\circ} = 4.08T \times 10^{-20} m^2$$

and for immobile adsorption:

$$-\Delta S_{i} = -\Delta S - R \ln(\theta/(1-\theta)).$$

6.3 Discussion

6.31 The Heat of Adsorption The variation of the heat of adsorption with coverage is plotted in graph XX. The curve is unusual in that the heat of adsorption is less than the heat of liquefaction (indicated by a dotted line) at coverages below one monolayer and rises to a value just above the heat of liquefaction at higher coverages.

6.32 The Entropy of Adsorption The experimentally determined isotherms were converted to standard states as described and may be compared with theoretical entropies of adsorption for the same standard states calculated using the following equations.

For the gaseous state:

$$_{g}S^{\circ}_{tr} = R \ln (M^{3/2}T^{5/2}) - 2.30$$

and $$_{g}S^{\circ}_{rot} = R(3/2 \ln T - 1/2 \ln ABC - \ln \sigma - 2.709)$$

and for the adsorbed state:

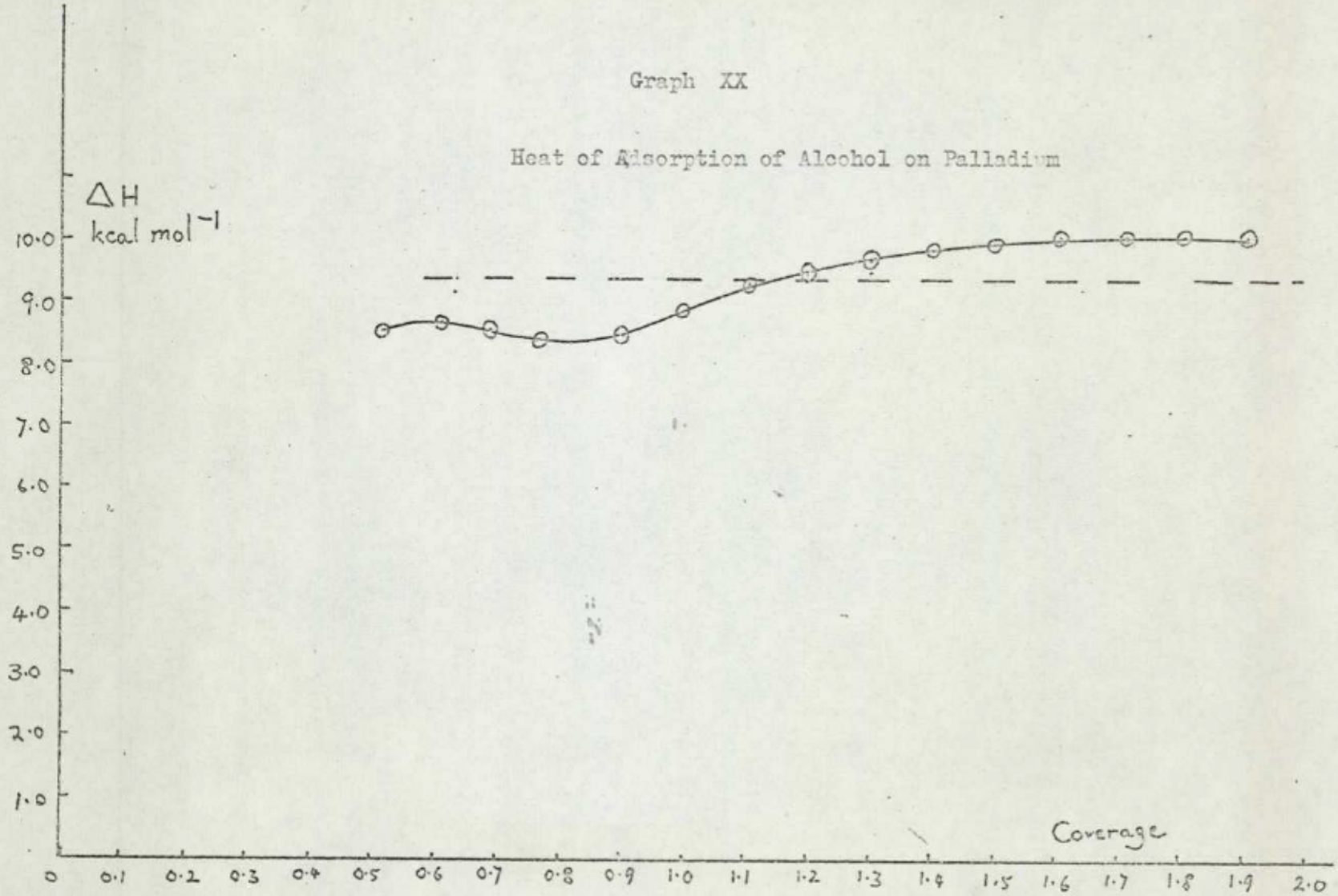
TABLE II.

HEAT OF ADSORPTION AND ENTROPY VARIATION WITH COVERAGE

Coverage	Delta S Mobile (ΔS_m)	Delta S Immobile (ΔS_i)	Heat of Adsorption
0.5	9.50	15,93	8.53
0.6	10.69	16.69	8.67
0.7	10.85	16.27	8.55
0.8	10.63	15.25	8.32
0.9	11.79	15.03	8.48
1.0			8.89
1.1	19.82	27.42	9.38
1.2	19.01	26.38	9.40
1.3	18.72	25.82	9.46
1.4	19.62	26.42	9.78
1.5	19.97	26.41	9.94
1.6	20.16	26.16	10.05
1.7	19.93	25.36	10.03
1.8	20.00	24.62	10.09
1.9	19.75	22.99	10.07

Graph XX

Heat of Adsorption of Alcohol on Palladium



and for the adsorbed state:

$$ {}_aS^{\circ}_{tr} = 2/3\,{}_gS^{\circ}_{tr} + 1/3\,R\ln(T/273.15) + 1 $$

$$ {}_aS^{\circ}_{rot} = R(\tfrac{1}{2}\ln T + \tfrac{1}{2}\ln I - \ln\sigma - 0.552) $$

$$ {}_aS^{\circ}_{vib} = Nh\nu/(e^{h\nu/kT} - 1) - R\ln(1 - e^{-h\nu/kT}) $$

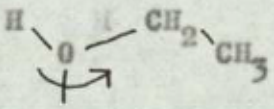
These expressions refer to an adsorbed gas which has two degrees of translational freedom, and one degree of rotational freedom.

The values for the entropy changes on adsorption were then calculated by subtracting the appropriate values for the entropy of the adsorbed state obtained from the above equations from the total gaseous entropy.

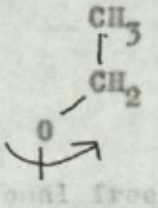
It was assumed that in the gaseous state the alcohol molecules have complete rotational freedom in three dimensions and that in the adsorbed state one of the conditions described below obtains.

1)The molecules have complete freedom of translation in two dimensions and of rotation in three dimensions.

2)That the molecule can rotate about an axis through the oxygen atom as shown below.



3)That the molecule can rotate about an axis as shown.



4)The molecule has no translational freedom or rotational freedom.

These states of the adsorbed molecule will be designated states 1, 2, ...

It was also necessary to consider the rotational state of the Methyl group, both in the gaseous and in the adsorbed state. Three possibilities were considered as follows.

A)The methyl group is free to rotate in both the gaseous and the adsorbed states.

B)The methyl group is free to rotate in the gaseous state only.

C)The methyl group is not free to rotate at any time. These are designated A, B, C, in the table.below.

These conditions gave rise to twelve possible values for entropy change on adsorption from the gaseous state and these are tabulated below.

		Methyl Group Rotational State		
Molecular		A	B	C
Rotational	1	8.37	3.30	9.37
State	2	29.09	25.11	31.18
(Adsorbed)	3	29.97	26.06	32.13
	4	41.59	35.52	41.59

All these results assume complete freedom of translational movement. Assumption of localised adsorption gives rise to values 26.76 cal.K^{-1}.mol^{-1} higher than those quoted

corresponding to the loss of two extra degrees of freedom. It can be seen that the experimental values of ΔS are a little larger than those given in the first row of the table on the previous page. This means that the molecules almost certainly have most of their translational freedom and that their rotational freedom is restricted only slightly, i.e. not enough to suggest specific interactions with one atom in the ethanol molecule.

CHAPTER VII

ADHESION STUDIES

7.1 Preliminary experiments It was desired to choose an adhesive which was not greatly affected by water in order to separate the effects due to the action of water on the polymer from the effects due to the action of water on the bond itself. Styrene was initially chosen to fulfil these requirements. The butt joint was chosen as this bond geometry has been used with good reproducibility by many workers. The specimens consisted of 2" lengths of brass rod of 5/8" diameter each of which had one end faced by a disc of palladium of thickness 0.002". The palladium was held in place by solder paste. The specimens also had a $\frac{1}{4}$" hole perpendicular to the main axis by which they could be held in the Instron tensile tester. A jig was constructed for making up the specimens for testing. This consisted of six brass tubes of diameter equal to the outside diameter of the test pieces. The specimens were placed in these tubes, two drops of the adhesive placed on the face of each one and a second specimen placed face downward on top of it. Pressure was applied by means of a spring also placed in the tube and the whole assembly held together by a screwed rod. The styrene was polymerised using 0.2% benzoyl peroxide initiator by heating to about 100^{0}C for one hour. It was found, however, even after many experiments in which the cure conditions and mode of sample preparation were varied that the reproducibility of the results was very poor indeed (standard deviation $\sim$200%). Inspection showed that the adhesive was brittle and although the samples stuck together

on heating, as soon as the samples cooled to room temperature the adhesive cracked in an unpredictable manner. The bond strength was a function, therefore, not of the adhesion between the palladium and the adhesive, but of the number and size of the cracks at the interface. Accordingly, an attempt was made to find a way of polymerising styrene at room temperature by adding an accelerator and N,N-Dimethyl toluidine was chosen for this purpose. However, even this was not entirely successful and efforts were made to find a new adhesive and/or bond geometry to eliminate these drawbacks.

7.2 The Final Choice of Materials

7.21 The Test Method Various types of test geometry were considered in an effort to find one which was easily made, reproducible, and used the minimum quantity of palladium. To eliminate the effects of any small cracks it was desired that the stresses in the bond should be as close to pure shear as possible (see section 2.5). This last condition limited the specimens to the napkin ring or pull through variety and the latter was finally chosen as the test pieces could be made from brass plated with palladium at relatively low cost.

7.22 The Adhesive It was necessary to choose an adhesive which fulfilled certain conditions as follows:

1) The adhesive must be one which bonds easily to palladium.
2) It must not be prone to swelling when subjected to high concentrations of water vapour, since this will introduce stresses which were not present in the dry joint.
3) The adhesive must either be plastic or curable at

room temperature to avoid the introduction of thermal stresses on cooling.

To fulfil these conditions the adhesive chosen was Cellobond A2784 obtained from BP Ltd., and this was attacked to the plated brass pins as described in section 7.3.

Cellobond A2784 adhesive is described by the manufacturers as a medium to high viscosity chemical resistant resin with a high heat distortion temperature, suitable for contact moulding applications and for hot moulding applications.

The resin comprises about 60 parts by weight of an unsaturated polyester (isophthalic acid and maleic anhydride reacted with propylene glycol) and 40 parts by weight of styrene monomer.

The initial formulation was as follows. 5g of the resin was mixed well with 5g of styrene monomer and 0.2g of benzoyl peroxide (as 65%paste)added and stirred well in. One drop of N,N-Dimethyl toluidine was then added and the mixture stirred vigorously. The resulting liquid was then used as soon as possible.

7.23 The Substrate The palladium coated pins were made by plating 1/16" x 1" brass pins with palladium of thickness 0.0002". This work was undertaken by Johnson Matthey Ltd.

The pins were degreased in a Soxhlet type apparatus using dichloromethane. This also removed the adhesive prior to re-use of the pins. Some simple adsorption experiments showed that any dichloromethane adsorbed on the pins during washing was removed in less than 1 minute by exposure to the air.

7.3 Experimental

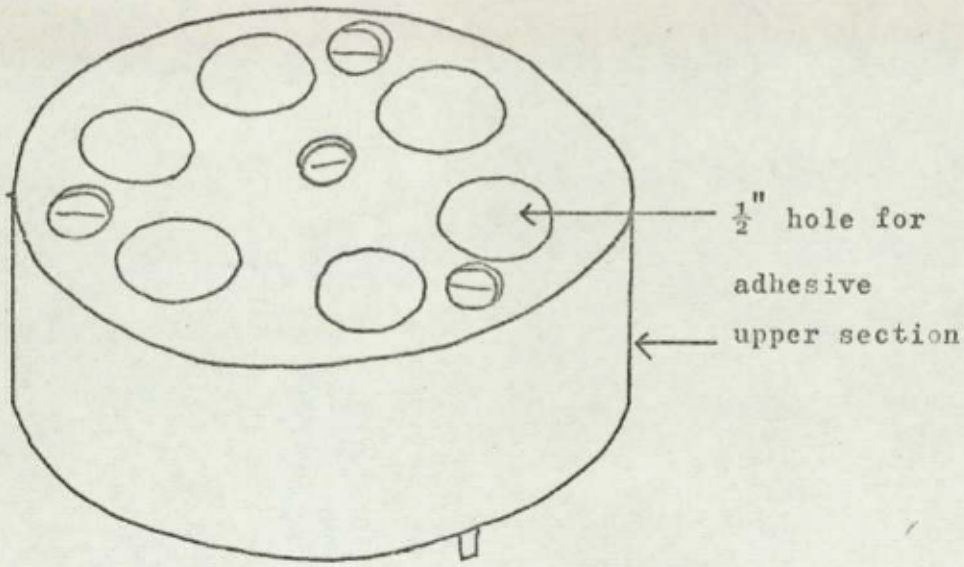
7.31 Making the Bonds The apparatus for making the bonds

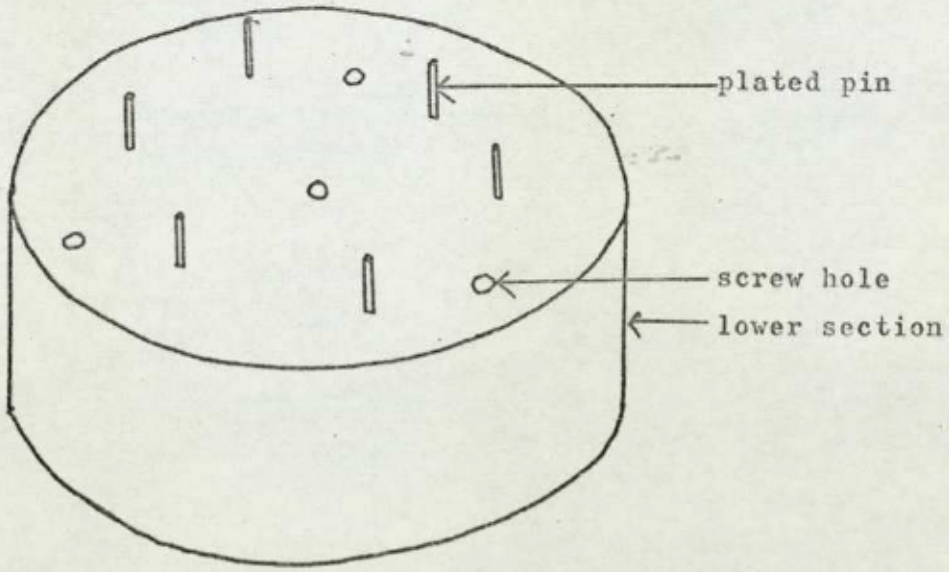
is shown overleaf. The main part of the apparatus was made of 2.5" diameter polytetrafluoroethylene rod and was in two sections. The lower section consisted of a cylinder of PTFE drilled with six holes of nominally 0.0635" diameter. This represented a loose, but not too loose, fit for a piece of 1/16" diameter brass rod coated with 0.0002" of palladium (giving an overall diameter of 0.0629"). The holes were drilled to a depth of ¾" so that when the 1" long pins were inserted they protruded ¼". The upper piece of PTFE, of the same overall diameter as the lower one, contained six holes of ½" diameter with their centres so arranged as to coincide with those in the lower piece. The two parts of the apparatus were bolted together by means of four 0 BA brass screws, one of which was placed centrally and the other three peripherally.

In order to control the environmental conditions as far as possible during the making of the bonds most of the experimental work was done in a constant humidity chamber as maintained at constant humidity by means of saturated salt solutions.

The metal substrate was placed in the chamber at least 24 hours before the bonds were to be made to allow the surface to equilibrate with water vapour. The adhesive was then mixed in a small beaker and placed inside the box. The box was opened for only about 10 seconds, during which time the relative humidity rose, at worst, by about 3%. Since the adhesive had a gel time of only about 20 minutes, no attempt was made to allow the the substrate or adhesive to equilibrate again and the liquid was poured into the mould immediately using a dropping pipette. After about 20 minutes a rapid exothermic reaction occurred and in some early experiments this led to

APPARATUS FOR MAKING UP ADHESIVE SPECIMANS - ACTUAL SIZE





the loss of some monomeric styrene with subsequent cracking of the solid adhesive on cooling. To obviate this, rubber bungs were used to seal the top of the mould after the adhesive had been poured in.

The joints were left to cure for about 48 hours before the mould was dismantled and the bonds removed for storage.

Unfortunately, it was not possible to vary the amounts of styrene monomer used in the formulation of the adhesive (section 7.22) very greatly because the adhesive tended to cure incompletely or tended to lose monomer, and shrink, giving rise to strained or even cracked bonds. However, formulations were made with the proportion of resin to styrene: 4:6, 5:5, and 6:4. These adhesives will be referred to as 4:6 adhesive, etc.

7.32 Storing the Bonds After removing from the mould the specimens were stored in jars until they were tested. These jars were maintained at the relative humidity at which the bonds were made by saturated salt solutions. The storage time was 2 - 3 weeks to allow the adhesive to cure completely as well as to allow the bonds to equilibrate with the water vapour.

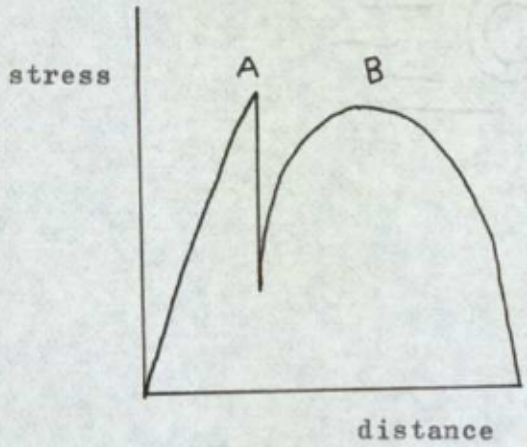
7.33 Testing the Bonds The bonds were tested using an Instron 1024 tensile tester at a crosshead speed of 50mm.min^{-1}. The adhesive plug was placed in a cylinder drilled to take a rod which was passed through the upper mounting of the Instron. The lower end of the cylinder was closed and contained a 1/16" hole through which the palladium coated rod could pass. The rod was gripped by a small collar which was itself retained by a saddle connected to the lower mounting of the Instron. Since the bottom of the upper mounting was made of thick brass any deformation of the specimen in the direction of

stress was very small, thus simplifying the stress analysis. A diagram of the mounting is given overleaf.

The maximum applied stress before failure was recorded as the bond strength.

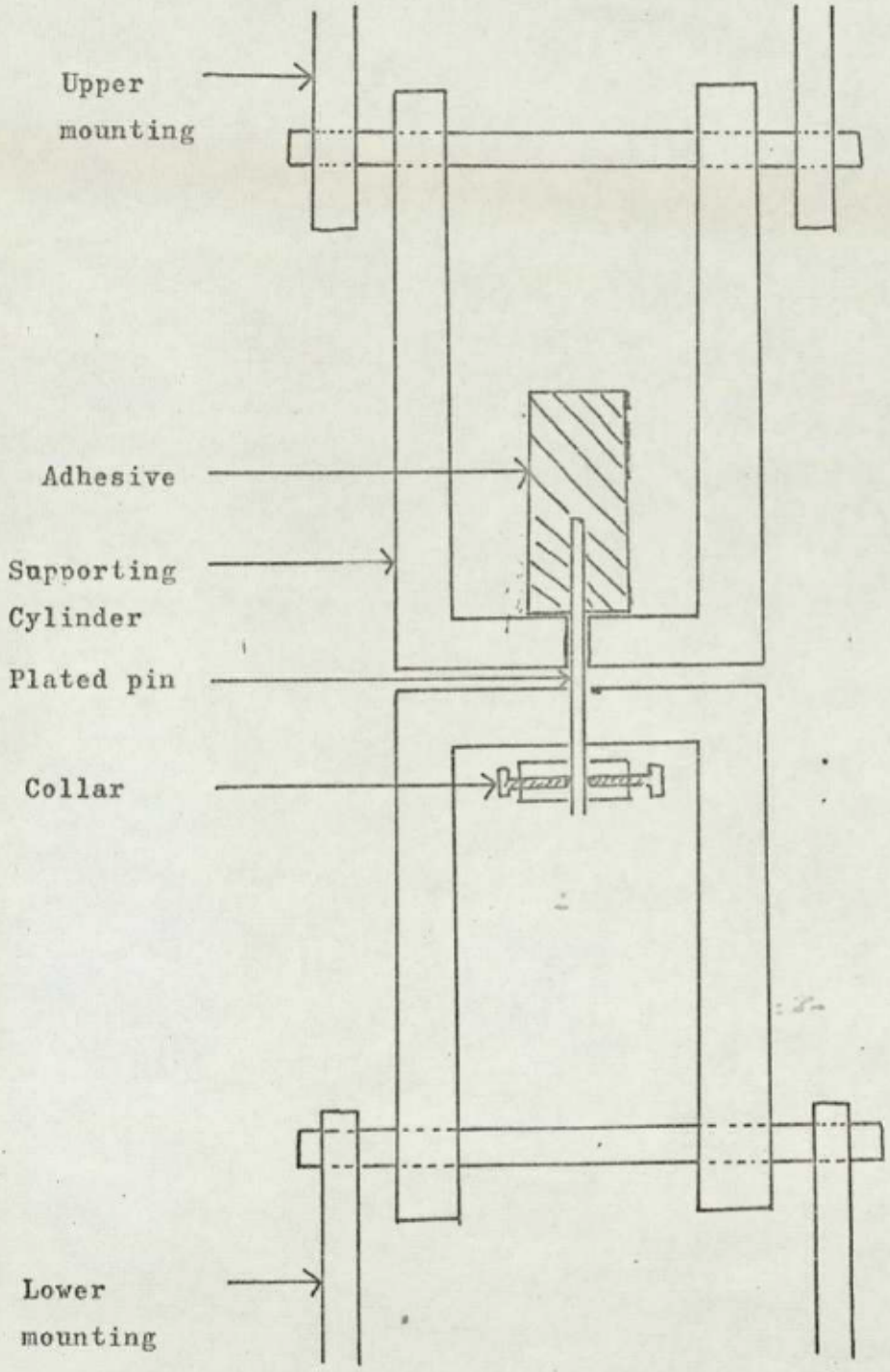
In general, two sets of replicates were tested for each experimental reading and in no case was there any significant difference between the two sets of results. The standard deviation within each group of six was about 10% and overall about 12%.

The form of the stress vs distance curve is of considerable interest and a typical example is illustrated below.



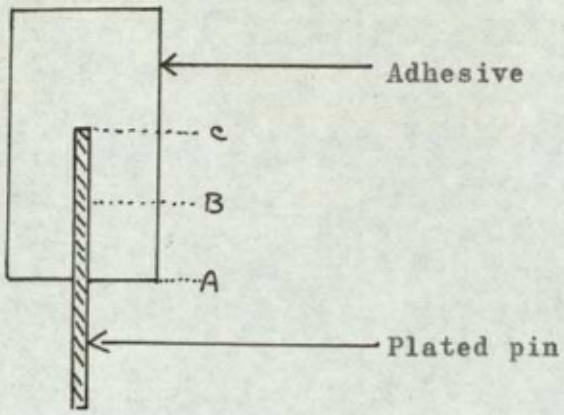
It can be seen that the stress increased to a maximum at A, at which point the bond failed catastrophically in shear. However, as the palladium pin was withdrawn from the adhesive frictional forces caused a second maximum to be observed at B.

This effect is known as the "pinch effect" and is explained as follows: As the bond is subjected to increasing stress, the palladium tends to stretch slightly within the adhesive which is prevented from extending in the direction of stress by the mounting. Eventually the bond fails at the point of entry of the palladium into the adhesive. As soon as a



SPECIMEN MOUNTED IN INSTRON TENSILE TESTING MACHINE

crack is formed at this point it will propogate rapidly for a certain distance. However, as soon as the strain in shear is removed a further effect is observed. The diagram below represents a sample which has partly failed.



Suppose the crack has moved as far as B and has ceased to move. Then as the force F is increased the sample between A and B will be subjected to a compressional force. The adhesive will then tend to expand in a direction perpendicular to the applied load. This will cause a pinching effect on the palladium which will tend to inhibit further movement. This effect will increase as the crack moves towards C giving rise to a second maximum in the stress vs distance curve. When the crack reaches C the effect will decrease as the palladium is pulled out of the adhesive.

7.4 Results and Conclusions

The results of the adhesion tests are shown in the table overleaf. The measured bond strength is the quantity actually measured on the Instron tester. It represents the maximum stress applied to a sample of the geometry described and with an overlap area of 0.0492 sq in. This has been

converted to $kg.cm^{-2}$ in the last column.

Table of Experimental Results

Adhesive	Relative Humidity percent	Measured Bond Strength $lb./0.0492in^2$	Bond Strength $kg.cm^{-2}$
4:6	20	10.5	16.6
	40	1.5	2.5
	66	3.1	4.9
	100	1.5	2.5
5:5	20	17.0	26.9
	40	8.5	13.5
	66	11.8	18.7
	100	7.8	12.3
6:4	20	9.5	15.1
	66	10.1	16.0
	66	7.2	11.4
	100	7.3	11.5

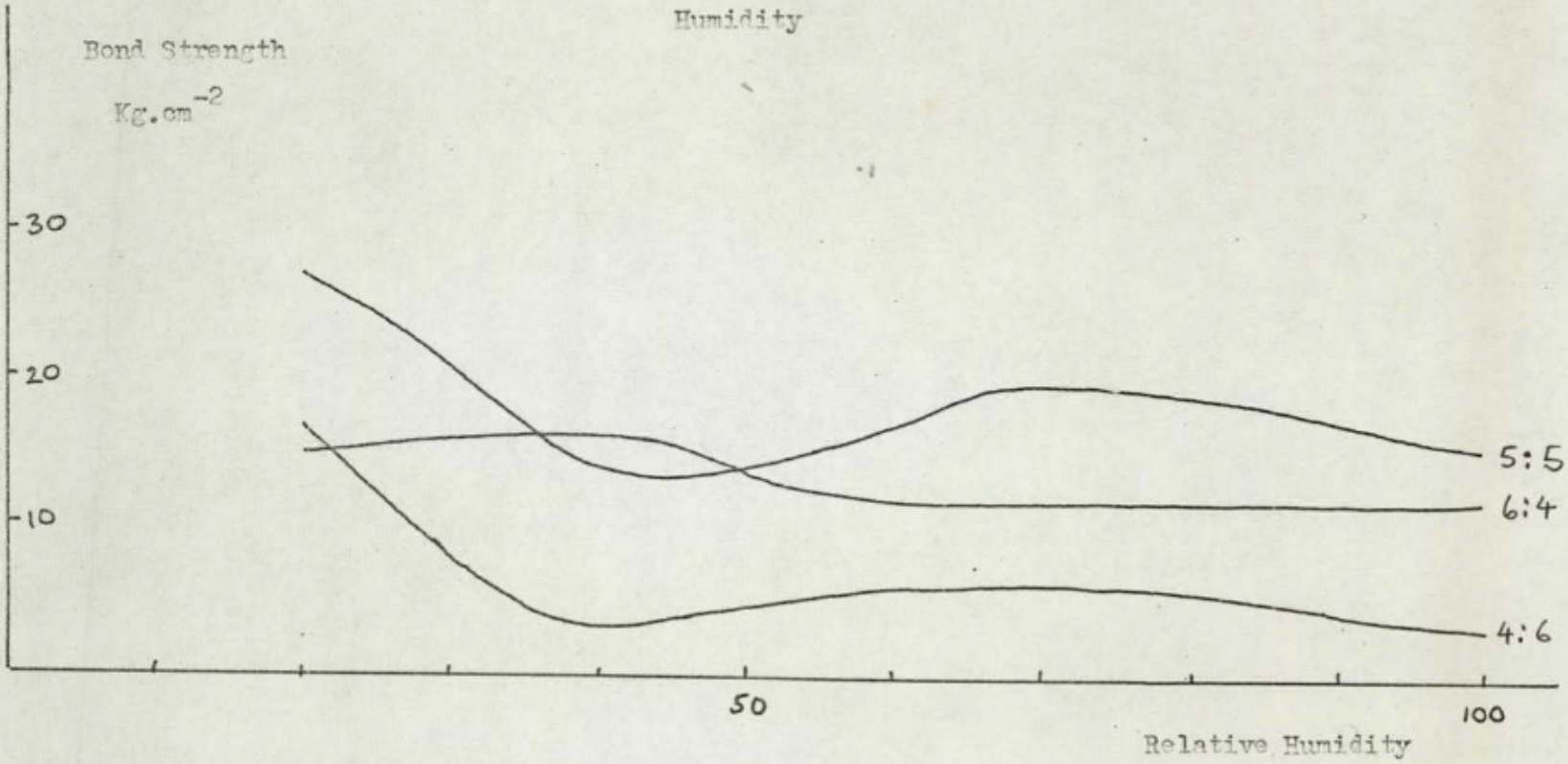
The results are plotted in graph XXI.

Irregular variations in the bond strength within a particular series are thought to be due to temperature variations during curing.

It appears that the two more polar adhesives are not significantly affected by changes in the relative humidity from 40% to 100%, but that the 4:6 and the 5:5 adhesives are much stronger when made at 20% relative humidity. A more detailed discussion is given in Chapter IX.

GRAPH XXI

Variation of Bond Strength with Relative Humidity



CHAPTER VIII

CONTACT ANGLE MEASUREMENTS

To obtain information about the surface properties and interaction energies of the adhesive a number of contact angle and surface free energy measurements were made.

8.1 Experimental and Results

8.11 Contact Angle Measurements A number of mixtures of ethanol and water were made up and the contact angles of each of them on each of the three formulations of the adhesive and and on a medium grade paraffin wax measured. The measurements were made by the sessile drop technique using a microscope fitted with a goniometer eyepiece. The solid samples were made under identical conditions to those of the adhesion tests and the drops were placed on them using an Agla micrometer pipette. Both sides of each drop were measured and the angles were measured for different samples of each formulation not only to find the reproducibility of the contact angles but also as a check on the consistancy of the polymerisation process. It was found that the results of ten measurements on four samples varied by about 3^{o}. Contact angles were also measured for tricresylphosphate and for water.

8.12 Surface Tension Measurements The surface tensions of the liquids were measured using a du Nouy balance made by Gallenkamp, Ltd. The measurements were reproducible to ± 0.1 dyne.cm^{-1} and were, in practice, normally replicated only once.

8.13 Results The experimental results obtained are shown in table I. A few other measurements, particularly on paraffin wax, were required for the calculation of the results and these have been taken from the paper

TABLE I

Contact angle and Surface Free Energy Measurements

Liquid		θ(wax)	Cosθ(wax)	θ(4+6)	Cosθ(4+6)	θ(5+5)	Cosθ(5+5)	θ(6+4)	Cosθ(6+4)	γ
EtOH/	0%	128°	-0.385	92.2	-.0384	86.0	.0698	80.1	.172	72.0
H_2O	16%	92°	-0.035	60.5	0.491	56.2	.556	52.8	.605	45.6
	21%	88°	0.0349	56.1	0.556	52.1	.628	47.1	.681	41.1
	26%	84°	0.105	54.5	0.580	46.9	.683	41.9	.744	38.1
	31%	79°	0.191	50.1	0.646	42.6	.736	35.9	.810	36.0
	34%	76°	0.212	44.9	0.703	39.4	.772	32.5	.845	34.8
	41%	70°	0.342	32.9	0.838	28.0	.873	27.6	.886	32.6
	51%	60°	0.500	19.1	0.944	22.4	.925	22.3	.926	30.0
	54%	58°	0.530	16.2	0.962	18.3	.950	20.0	.940	29.4
Tricresyl phosphate				29.0	0.866	24.5	.911	19.1	.945	44.8

have been taken from the paper by Dann (1970a). Where Dann's measurements overlap those of the present study the agreement is excellent, being always better than the experimental uncertainty.

8.2 Calculations

8.21 Measurements on Paraffin Wax The contact angles on paraffin wax for each of the liquids were then used to characterise them using the Good-Girifalco-Fowkes-Young equation:

$$\cos\theta = \frac{-\gamma_L + 2\sqrt{\gamma_S^D \gamma_L^D}}{\gamma_L}$$

the spreading pressures being neglected in this case. The critical surface tension of paraffin wax (identified with γ_S^D in this case) was taken as 25.5 dyne.cm^{-1} (Dann 1970a) as the present measurements were not wide enough in scope to enable this quantity to be determined. Then, since $\cos\theta$ and γ_L were known, it was possible to derive a value for γ_L^D for each liquid in the series. It was also possible to find the polar contribution to γ_L by subtracting γ_L^D from γ_L for each liquid. The results are shown in Table II.

8.22 The Surface Properties of the Adhesive Zisman's γ_c, determined by plotting $\cos\theta$ vs γ_L for a series of liquids and noting the value of γ_L when $\cos\theta = 1$, has often been identified with the surface free energy of the solid and such plots for the series of alcohol/water mixtures are given in graph XXII. The graphs give values for the critical surface

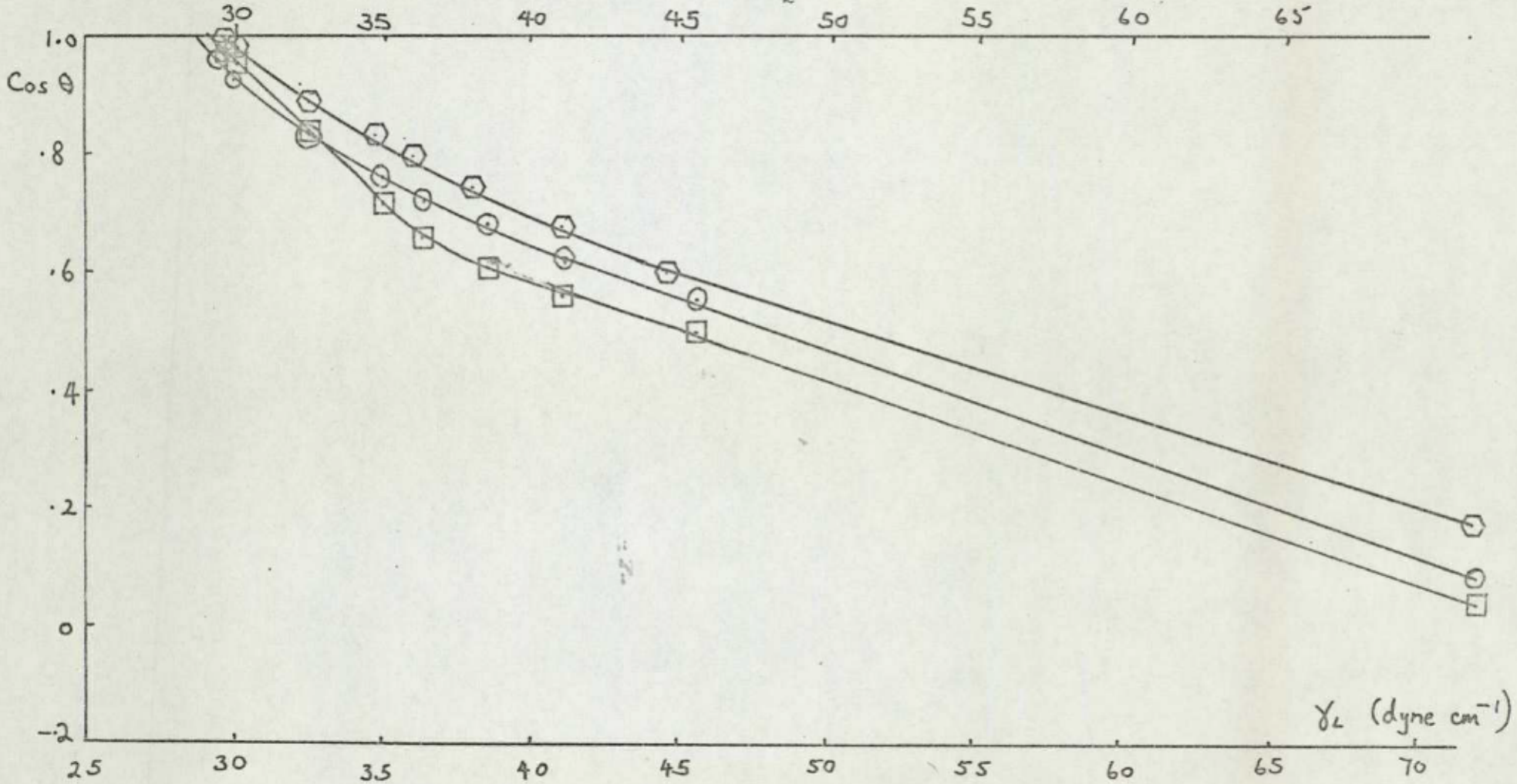
TABLE II

Properties of Alcohol/water Mixtures from Measurements on Paraffin Wax

Liquid %EtOH	γ	γ_L^D	γ_L^P	$2\sqrt{\gamma_L^D}$
0%	72.0	22.1	49.9	9.42
16%	45.6	18.5	27.1	8.61
21%	41.1	17.8	23.3	8.44
26%	38.1	17.7	20.4	8.43
31%	36.0	18.1	17.9	8.51
34%	34.8	18.2	16.6	8.54
41%	32.6	18.9	13.7	8.70
51%	30.0	19.9	11.1	8.93
54%	29.4	19.8	9.6	8.90

Graph XXII

Zisman Plots for EtOH/H_2O on three Adhesives



tension as shown below:

Adhesive	4:6	5:5	6:4
γ_c	29.0	28.8	29.4

It is also possible to calculate the surface free energy of the various adhesive formulations with respect to dispersion forces only using the equation:

$$\cos\theta = \frac{-\gamma_L + 2\sqrt{\gamma_L^D \gamma_S^D}}{\gamma_L}$$

in conjunction with the contact angles of tricresyl phosphate on each adhesive. This liquid is known to interact by dispersion forces only and hence $\gamma_L = \gamma_L^D = 44.8$ dyne.cm^{-1}.
The following results are obtained:

Adhesive	θ	$\cos\theta$	γ_S^D
4:6	29.0°	0.8746	43.1
5:5	24.5	0.9100	44.6
6:4	19.1	0.9449	46.2

It can be seen that the values for the critical surface tension determined by the Zisman method are much less than the surface free energies for dispersion forces only determined using the equation above.

Dann (1970a) gives a method by which the critical surface tension of a solid determined using one series of liquids may be used to find the critical surface tension using some other series. Dann's method was applied, using graphs redrawn from his results and gave the following values for γ_c with respect to dispersion forces only:

Adhesive	4:6	5:5	6:4
γ_c (Dann's Method)	47.6	47.0	48.8
γ_c (Contact Angle)	43.1	44.6	46.2

The quantity "γ_c (contact angle)' is the value of the surface free energy calculated using the Good-Girifalco-Fowkes-Young equation in conjunction with the contact angle of tricresyl phosphate. The discrepancy is thought to be due to the forces acting within the alcohol mixtures (and giving rise to the surface tension) being, in general, different from those acting across the interface when a drop of the liquid is placed on the solid.

8.23 Polar Interactions Fowkes (1972) arrives at values for the interaction of various liquids with certain polymeric solids with respect to polar interactions only by subtracting the dispersion interaction (calculated using the relation $I^D = 2\sqrt{\gamma_L^D \gamma_S^D}$) from the total work of adhesion W_a which is given by:

$$W_a = (\cos\theta + 1)\gamma_L$$

The relevant quantities are shown in table III where

$$I_{SL}^P = W_a - 2\sqrt{\gamma_L^D \gamma_S^D}$$

and plots of I_{SL}^P vs γ_L^P are given in graph XXIII. Fowkes (who gives similar plots derived from Dann's work) points out that the work of adhesion is given by:

$$W_a = W_a^D + W_a^H + W_a^P + W_a^I + W_a^{AB} .$$

Here D refers to dispersion forces,

H refers to hydrogen bonding,

P refers to dipole-dipole interactions,

I refers to dipole-induced dipole interactions,

and AB refers to acid-base interactions.

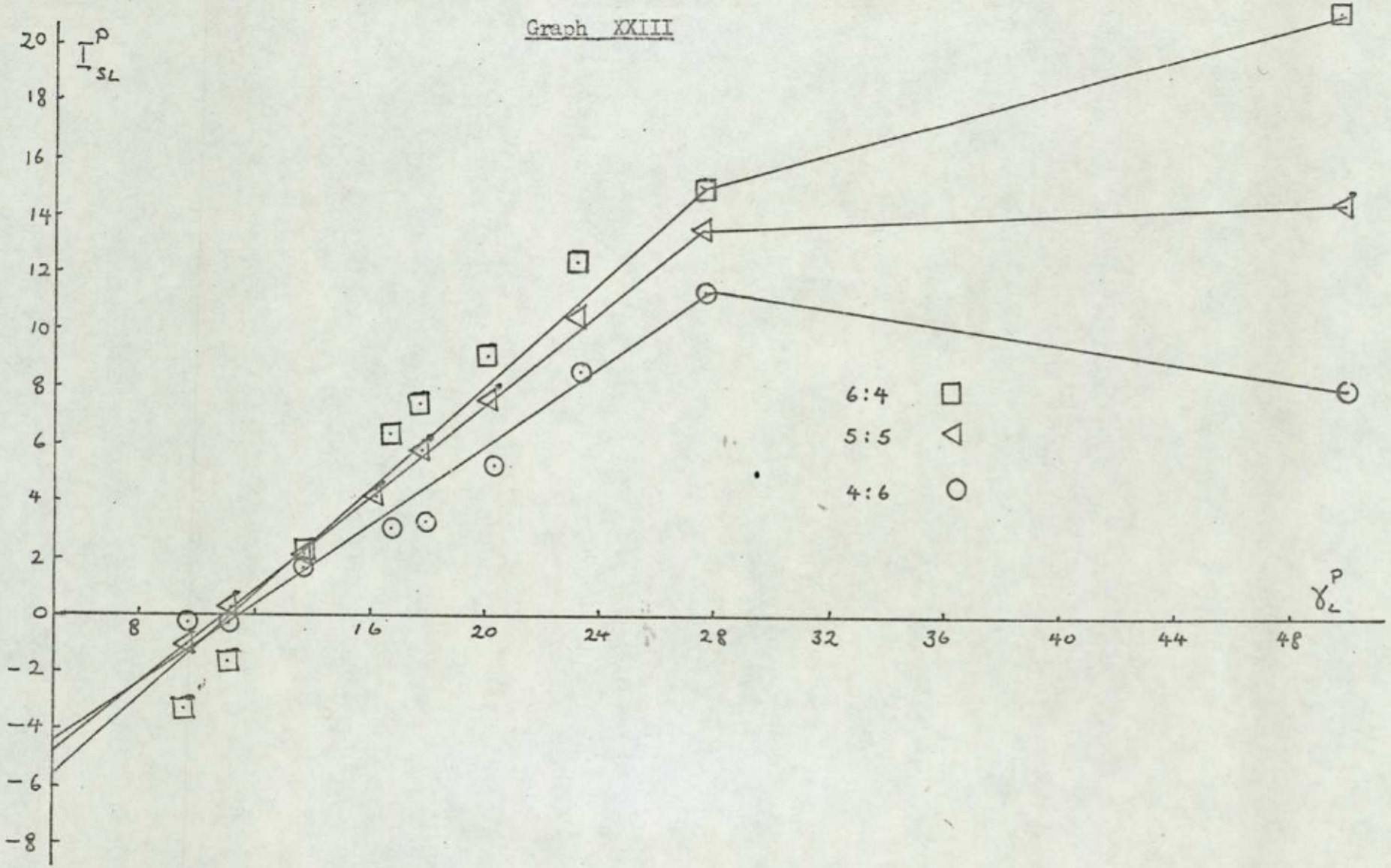
W_a^P and W_a^I may be considered small compared with the others and so:

$$W_a - W_a^D = W_a^H + W_a^{AB} .$$

TABLE III

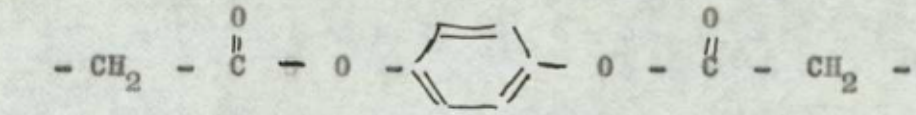
	4:6				5:5			6:4		
γ	$\gamma_L - \gamma_L^D$	$\gamma_L(\cos\theta+1)$	$2\sqrt{\gamma_L^D \gamma_S^D}$	I_{SL}^P	$\gamma_L(\cos\theta+1)$	$2\sqrt{\gamma_L^D \gamma_S^D}$	I_{SL}^P	$\gamma_L(\cos\theta+1)$	$2\sqrt{\gamma_L^D \gamma_S^D}$	I_{SL}^P
72.0	49.9	69.9	61.9	8.0	77.1	62.9	14.2	85.1	64.1	21.0
45.6	27.7	68.0	56.6	11.4	70.9	57.5	13.4	73.3	58.5	14.8
41.1	23.3	64.0	55.4	8.6	67.1	56.4	10.7	69.7	57.4	12.3
38.1	20.3	60.6	55.4	5.2	64.2	56.3	7.4	66.4	57.3	9.0
36.0	17.9	59.2	55.9	3.3	62.5	56.8	5.7	65.2	57.8	7.4
34.8	16.6	59.2	56.1	3.1	61.8	57.1	3.7	64.3	58.0	6.3
32.6	13.7	59.9	58.2	1.7	61.1	58.2	2.9	61.6	59.1	2.5
30.0	11.1	58.4	58.7	-0.3	59.8	59.6	0.2	58.9	60.7	-1.8
29.4	9.6	58.3	58.5	-0.2	58.1	59.4	-1.3	57.1	60.5	-3.4

Graph XXIII


I_{SL}^{P}
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
8
16
20
24
28
32
36
40
44
48
γ_L^P
6:4
5:5
4:6

The plots shown in graph XXIII suggest a linear relation between γ_L^P and I_{SL}^P with the proviso that water lies below the line of the ethanol/water series.

Now the adhesive contains numerous ester groupings of the form:



and these will form strong hydrogen bonds with water or ethanol via the C=O groups. They will also have slight basic character due to the styrene segments and these will tend to interact more strongly with ethanol than with water. Hence it is to be expected that the least polar polymer (i.e. that containing most styrene) will give the biggest deviation for water and this is indeed the case.

CHAPTER IX

GENERAL CONCLUSIONS

There are potentially several types of interaction across the interface and this chapter attempts to relate the measurements of the previous chapters to the overall bond strength. It should be emphasised at this stage that although fairly detailed measurements have been made of the surface properties of the adhesive and the substrate, it is still impossible to predict the strength of the bond, and still less the effect of a third component, water, on the strength of the bond.

9.1 The Components of the Joint

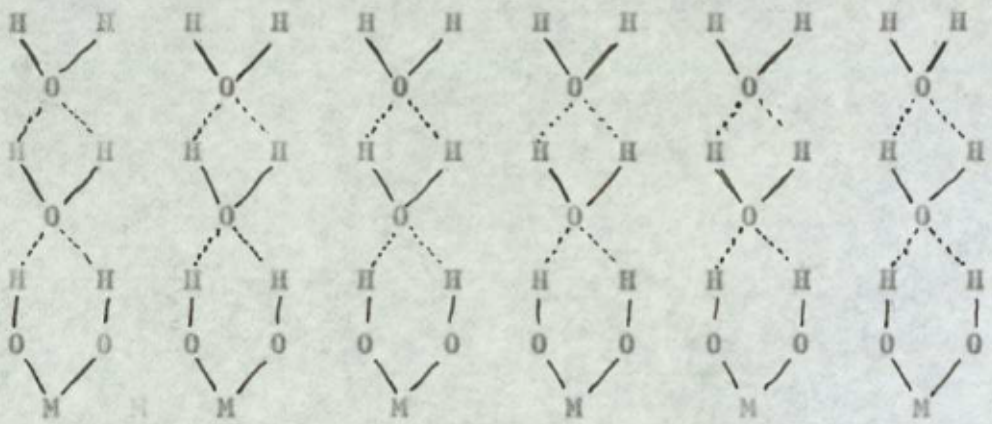
It is first useful to review in some detail the components of the joint separately, during formation, storage and rupture of the bond.

9.11 The Metal The substrate consists of a metal/metal oxide surface comprising partly hydrophilic and partly hydrophobic sites. The surface area per gram as measured by nitrogen adsorption was $24.0 m^2.g^{-1}$ and as measured by water adsorption was $12.8 \pm 2.0\ m^2.g^{-1}$. Unfortunately, the true area occupied by one water molecule is not known with certainty, but if $10.2A^2$ is taken as correct the proportion of the surface which is hydrophilic is:

$$\frac{12.8}{24.0} \times 100\% = 53\%$$

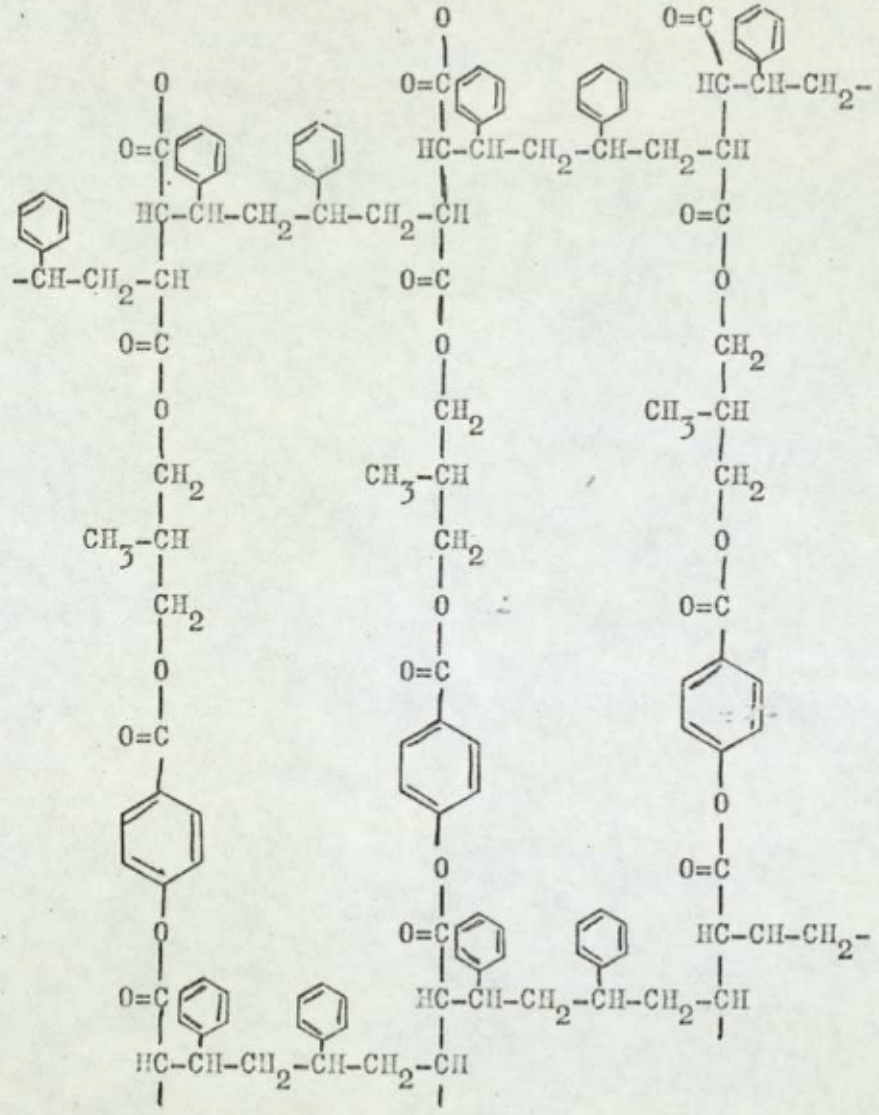
Erb (1965) has shown that rigorously purified palladium

is hydrophobic, and it is assumed here that Erb's pure palladium corresponds to the hydrophobic part of the surface used here. The hydrophilic part of the surface is assumed to be some form of palladium oxide which is, under any practical conditions, hydroxylated. It may be represented ideally as shown below (Bolger and Michaels, 1967).



Approximately three layers of water vapour are bound firmly to the surface and above this, further, weaker adsorption will take place.

9.12 The Adhesive An idealised segment of the adhesive is represented overleaf. It can be seen from the diagram that the polyester part of the adhesive contains, initially, a small proportion of unsaturation. This unsaturation enables styrene to polymerise into the polyester chain giving rise to cross linking. It is also easy to see that there are two types of site in the adhesive by which the polymer might attach itself to the substrate. These are the -C=O groupings which can hydrogen bond to the hydroxylated part



A Section of the Adhesive (idealised), showing the Polyester Chains (Vertical) and the Polystyrene Cross-links.

of the metal surface and the styrene units which can undergo acid - base interactions with the protons of the hydroxyl groups of the metal surface.

9.13 Adsorbed Gases It is possible to estimate the thickness of the layer of adsorbed water from the graphs from which the t-curves were constructed, (paragraph 5.7). As shown in paragraph 5.5, the curves obtained after conditioning with water (and which correspond to the conditions of the present adhesion experiments) represent adsorption onto three layers of water molecules which are fairly strongly bound. Thus, at the relative humidities used in the present experiments, the following are the approximate coverages with respect to water vapour.

Relative Humidity	20%	40%	66%	~100%
Coverage (monolayers)	4.05	4.72	5.90	$\gg 7$

For each of these, the first three layers are fairly firmly bound.

However, the temperature rises to about 50 - 60°C during the curing of the adhesive and this means that conditions inside the bond may be rather different from those described. When the temperature rises, the bonds between the metal and the most loosely bound water will break, the number of broken bonds being very dependant on the temperature. It is not possible to say, on the basis of the present experiments, exactly what temperatures were reached in each case, but However, it is clear that although most of the bonds in the outermost layer of water will be broken, the water will not have time to migrate away from the interface and into the

adhesive because the polymers used here exhibit low waterr solubility and diffusion. Hence, when the adhesive cools to room temperature after curing ample water will be present at the interface to saturate the metal surface at the original relative humidity. After curing, the bonds were stored at the same relative humidity until they were tested and so it is fairly certain that equilibrium, with respect to ingress of water, was achieved in these experiments.

9.2 Displacement by Water

Suppose the adhesive has just set and is cooling to room temperature. Since the adhesive wets the substrate (contact angle equals zero) displacement of the polymer will only take place if the following free energy change is negative.

ΔG = Work of adhesion between polymer and adhesive
- Work of adhesion between polymer and water
- Work of adhesion between palladium and water.

that is:

$$\Delta G = W_{a(Pd/Ad)} - (W_{a(Ad/H_2O)} + W_{a(Pd/H_2O)})$$

Unfortunately, the work of adhesion of the polymer to palladium is not known but the quantity ΔG with respect to dispersion forces only (i.e. on the hydrophobic part of the surface) may be calculated as follows.

9.21 Dispersion Interactions

The work of adhesion between two surfaces is given by:

$$W_a = (\cos\theta + 1)\gamma_L$$

or for dispersion interactions only:

$$W_a^D = 2\sqrt{\gamma_L^D \gamma_S^D}$$

so within one liquid (e.g. water)

$$W_a^D = 2\gamma_L^D$$

Also, if true thermodynamic equilibrium obtains at the interface between the adhesive and the metal:

$$W_a^D = 2\sqrt{\gamma_{Pd}^D \gamma_{Ad}^D}$$

and hence:

$$\Delta G = 2\gamma_{H_2O} + 2\sqrt{\gamma_{Pd}^D \gamma_{Ad}^D} - 2\sqrt{\gamma_{Pd}^D \gamma_{H_2O}^D} - (\cos\theta + 1)\gamma_{H_2O}$$

where the superscript D's refer to dispersion interactions only, subscripts Ad to the adhesiven, subscripts Pd to the palladium and $\cos\theta$ is the contact angle of water on the adhesive.

For palladium, γ_{Pd}^D may be calculated using the relation

$$\cos\theta = \frac{-\gamma_{H_2O} + 2\sqrt{\gamma_{H_2O}^D \gamma_{Pd}^D}}{\gamma_{H_2O}}$$

in conjunction with the contact angles of water on very pure palladium determined by Erb (1965). His surface was hydrophobic and it is here assumed that it corresponded to the hydrophobic part of the palladium surface used in the present experiments.

Substitution of Erb's value of 74° for the contact angle of water on palladium gives a value of 96.1 $erg.cm^{-2}$ for γ^{D}_{Pd}.

Hence, for the 4:6 adhesive:

$$\Delta G = 2x72 + 2\sqrt{96.1x39.4} - 2\sqrt{96.1x21.8} - 72(-0.0384 + 1)$$
$$= 106.9 \text{ erg.cm}^{-2}.$$

Similarly, for the 5:5 formulation:

$\Delta G = 102.1 \text{ erg.cm}^{-2}$,

and for the 6:4 adhesive

$\Delta G = 98.5 \text{ erg.cm}^{-2}$.

Although this free energy change is positive, it should be noted that it does not mean that there is no tendency for water to destroy the bond since it is very unlikely that equilibrium exists on the surface. However, the equation will be affected significantly by non equilibrium conditions only in the second term and as the total value of this term is only $\sim 125 \text{ erg.cm}^{-2}$ it is difficult to envisage its being so reduced by cracks of flaws as to render ΔG negative.

9.22 Polar Interactions Now consider the hydrophilic part of the palladium surface. The free energy change for the displacement may be written exactly as before except that it must include terms corresponding to forces other than dispersion forces. Unfortunately, the total interaction of the metal with the polymer is not known and resort must be made to qualitative arguements.

9.221 The Polyester Initially, the polyester will attach itself to the substrate by hydrogen bonding to the most firmly water molecules of surface hydroxyl groups. It will therefore be to fixed sites. Furthermore, even when the adhesive cools to

room temperature and the relative vapour pressure of the water in the adhesive increases again, it is unlikely that the water will displace the polyester since the atoms or groups adjacent to the -C=O groups are fairly strong electron donors.

9.222 Polystyrene The polystyrene will bond to the metal substrate by acid-base interaction since polystyrene has weak proton acceptor tendencies. However, because polystyrene is such a weak base the interaction will be weak and although it probably contributes to the adhesion under dry conditions it is likely that the water will displace the polystyrene as the relative humidity increases.

9.23 General Conclusions As described in the previous two paragraphs, it is likely that the polyester is adsorbed to localised sites whereas the polystyrene is more mobile. The non-polar (polystyrene) part of the adhesive will thus require a relatively low interfacial pressure of water for displacement. It is therefore to be expected that although part of the adhesive will be displaced from the substrate very easily, some residual adhesion should remain due to strong interactions with the ester groupings. The experimental observations that thepolar adhesives are less easily affected by water is thus explained together with the residual adhesion which remains even in bonds made at $\sim$100% relative humidity.

CHAPTER X

SUGGESTIONS FOR FURTHER WORK

The treatment given in the last chapter has involved a discussion of the free energy change which would accompany possible displacement of the adhesive by water. The limited success of the results in accounting for the observed trends and the qualitative nature of some of the arguments used indicate that further work is required before satisfactory explanation may be found.

Firstly, the observed bond strengths are, as usual, much less than the free energies of interaction would indicate. Thus Fowkes (1965) gives 105×10^8 ergs.cm^{-2} for the theoretical adhesion of polyethylene to iron by dispersion forces only and the considerations of this study cannot account for discrepancies of this order. Williams and de Vriess (1971) give a continuum mechanics account of the rupture of an adhesive bond but point out that most of the parameters needed for their equation are unknown. In particular, it is necessary to know the effect of varying the chemical composition of the adhesive on the mechanical properties and even the effect of such fundamental quantities as cross link densities, chain stiffness and molecular weight is unknown. Until these quantities are determined, it is difficult to draw any definite conclusions in a particular case since whilst a theory may fit the experimental results the apparent agreement may well be coincidental. Thus, in the present case, although the free energy change for displacement may be an important factor it may be overshadowed by more important mechanical considerations.

Although this study has involved a detailed investigation of the metal surface, the adhesives are not nearly so well

characterised, and a further study should involve the measurement of more free energies of interaction with a greater variety of liquids. It would then be interesting to compare the results for the present adhesive with those for other polymers of varying polarity, and particularly those with similar total surface free energies, (e.g. polymethyl methacrylate). A more detailed study of the adhesion could then be made giving values at every 5% relative humidity and facilitating graphical treatment of the results. It might then be possible to separate the artifacts from the real effects and formulate a new theory of more general applicability.

Erb (1965) has measured the contact angles of water on a number of rigorously purified metal surfaces and in many cases has found that the clean surface is hydrophobic. It would now be informative to carry out adsorption studies on some of these to see whether the adsorption pattern for water is similar to that on palladium. Adhesion studies could then be made on these metals and, since the adsorption of water is onto sites suitable for adsorption of adhesive, differences in adsorption behaviour should be reflected by differences in adhesion behaviour.

Finally, it would be possible to put all the adhesion measurements onto a quantitative basis by measuring the total interaction of polymer and substrate. Since the polymers are of low vapour pressure this might best be accomplished be measurements of the heats of immersion. If these measurements were made calorimetrically after conditioning the metal with

varying amounts of water vapour, it should be possible to estimate the ease or otherwise of displacement of water by the adhesive.

APPENDIX I

Preparation and Properties of Sugar Grease

To make up the sugar grease, 25g of glycerin, 7g white dextrin, and 3.5g of pure d-mannitol were thoroughly mixed together to give a white paste. The mixture was then heated very gently until it just began to boil. The mix was then kept just below its boiling point and stirred continously until all the solid material had dissolved. The heat was then removed and the mix allowed to cool to room temperature with stirring. The liquid became highly viscous as it cooled and took on the appearance of mother of pearl. The grease was stored in a dessicator until it was used.

The grease prepared as above appears to have excellent lubricating properties at pressures down to 10^{-4} mmHg. Below this pressure a certain amount of water vapour is released into the vacuum line causing an appreciable rise in pressure. It was found to be unaffected by benzene but was quickly dissolved by water. When the system was in continous use it was necessary to renew the grease about once every two weeks.

APPENDIX II

Computer Program for Applying the BET Equation to Experimental Isotherms

```
  COMPILER FORTRAN
  LIST (LP)
  PROGRAM (PTHO 52113)
  INPUT 1 = CRO
  OUTPUT 2 = LPO
  DIMENSION X(100),Y(100),G(200),Z(100),THETA(100),A(100),B(100)
  REAL INTER
  READ (1,1) NOS
  DO 100 NNOS = 1,NOS
  READ (1,1) N
1 FORMAT(I0)
  READ (1,2) (X(I),Y(I),I=1,N),P
2 FORMAT (2F0.0)
  DO 11 I = 1,N
  G(I) =Y(I)
11Z(I) =X(I)
  READ (1,9)AN,AM,BM
9 FORMAT (3E0.0)
  DO 8 I = 1,N
  Y(I) = X(I)/((P-X(I))*Y(I))
8 X(I) = X(I)/P
  K = 0
  DO 77 I = 1,N
  IF(X(I).LE.0.05.OR.X(I).GT.0.35)GO TO 77
  K=K+1
  A(K) = X(I)
  B(K) = Y(I)
77 CONTINUE
```

```
      SUMX = 0
      SUMY =0
      SUMXX = 0
      SUMXY = 0
      WRITE (2,3)
    3 FORMAT (1H1,1HX,15X,1HY)
      DO 4 (J = 1,K)
      SUMX = SUMX + A(J)
      SUMY = SUMY + B(J)
      SUMXX = SUMXX + A(J)*A(J)
      SUMXY = SUMXY + A(J)*B(J)
      WRITE (2,5)(A(J),B(J))
    5 FORMAT (1X,E12.4,3X,E12.4/)
    4 CONTINUE
      WRITE (2,6)SUMX,SUMY,SUMXX,SUMYY
    6 FORMAT(7HO SUMX = E14.6/6H SUMY = E14.6/7H SUMXX=E17.9/7H
               SUMXY = E17.9)
      S1 = SUMXY*K-SUMX*SUMY
      S2 = SUMXX*K - SUMX**2
      S3 = SUMXX*SUMY - SUMX*SUMXY
      GRAD = S1/S2
      INTER = S3/S2
      WRITE (2,7) GRAD,INTER
    7 FORMAT(22 HO GRADIENT OF LINE M =E13.5/24H INTERCEPT AT
           Y AXIS C = E20.12)
      XM = 1/(GRAD + INTER)
      S = XM*AN*AM/BM
      C= (GRAD + INTER)/INTER
      WRITE(2,10) XM,S,C
   10 FORMAT (6HOXM = E13.5/3H S=E13.5/4H C= F13.5)
      DO 13 I = 1,N
```

```
 13 THETA(I)= G(I)/XM
    WRITE(2,12)
 12 FORMAT (1H0, 1HE, 20X, 5HTHETA)
    WRITE (2,14) (Z(I),THETA(I),I=1,N)
 14 FORMAT (1H0,E12.4,18X,E12.4)
100 CONTINUE
    STOP
    END
```

APPENDIX III

Computer Program for Calculating Entropies and Heats of Adsopption

```
COMPILER FORTRAN
LIST (LP)
PROGRAM (PDHO 52113)
INPUT 1 = CRO
OUTPUT 2 = LPO
TRACE 2
END
DIMENSION A(100),T(10),X(100),DSI(100),DSM(100),DS(100),
      THETA(30),HEAT(20),TA(100),B(100)
REAL INTER
READ (1,1)N
READ (1,21)(T(I),I = 1,N)
21  FORMAT(8F 10.0)
   READ (1,1)NOS
 1 FORMAT(I0)
   READ(1,20)(THETA(J),J = 1,NOS)
20  FORMAT (1F0.0)
   DO 100 J = 1,NOS
   READ(1,2)(A(I),I = 1,N)
 2 FORMAT (8F6.0)
   SUMX = 0
   SUMY = 0
   SUMXX = 0
   SUMXY = 0
   DO 60 I=1,N
   SUMX = SUMX + 1/T(I)
   SUMY = SUMY+ALOG(A(I))
```

```
      SUMXX =SUMXX+(1/T(I))*(1/T(I))
      SUMXY =SUMXY+(1/T(I)*ALOG(A(I))
   60 CONTINUE
      S1 = SUMXY*N - SUMX*SUMY
      S2 = SUMXX * N - SUMX*SUMX
      HEAT(J) = (S1/S2)*1.987
      DO 70 I=1,N
      TA(I)=1/T(I)
      B(I)=ALOG(A(I))
   70 CONTINUE
      WRITE(2,61)(TA(I),B(I),I=1,N)
   61 FORMAT(1HO,E12.4,4X,E12.4)
      DO 3 I=1,N
    3 A(I)=-1.987*T(I)*ALOG(760/A(I))
      SUMX =0
      SUMY =0
      SUMXY =0
      SUMXX =0
      WRITE (2,4)
    4 FORMAT(1HO,1HT,15X,2HDG)
      DO5 I = 1,N
      SUMX = SUMX +T(I)
      SUMY = SUMY+A(I)
      SUMXX = SUMXX + T(I)*T(I)
      SUMXY = SUMXY + T(I)*A(I)
      WRITE (2,6)(T(I),A(I))
    6 FORMAT(1HO,E12.4,3X,E12.4)
    5 CONTINUE
      WRITE(2,7) SUMX,SUMY,SUMXX,SUMXY
```

```
  7 FORMAT(7HO SUMX=E14.6/6H SUMY=E14.6/7H SUMXX=E17.9
           /7H SUMXY=E17.9)
     S1 = SUMXY*N-SUMX*SUMY
     S2 = SUMXX*N-SUMX*SUMX
     DS(J) =(S1/S2)
100  CONTINUE
     WRITE (2,8)
  8  FORMAT(1H1, 5HTHETA, 20X, 7HDELTA S)
     WRITE(2,9)(THETA(J), DS(J), J = 1,NOS)
  9  FORMAT(1HO,E12.4,18X,E12.4)
     DO 30 J = 1,NOS
 30  DSI(J)=DS(J)-1.987*ALOG(THETA(J)/(1-THETA(J)))
     READ(1,32)TEM,BA
 32  FORMAT(2E0.0)
     DO 31 J=1,NOS
 31  DSM(J)=DS(J)-1.987*ALOG(4.08*TEM*THETA(J)/BA)
     WRITE(2,33)
 33  (FORMAT(1HO,5HTHETA,7X,7HDELTA S,7X,6HMOBILE,7X,
                    8HIMMOBILE,7X,2HDH))
     WRITE(2,34)(THETA(J),DS(J),DSM(J),DSI(J),HEAT(J),J=1,NOS)
 34  FORMAT(1HO,E12.4,2X,E12.4,4X,E12.4,3X,E12.4,3X,E12.4)
     STOP
     END
```

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