

CHEMISORPTION OF GASES ON METALS

A thesis

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by

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ABSTRACT

The general characteristics of the adsorption of CO, H₂ and NO on evaporated metal films of palladium, platinum, titanium, chromium, manganese, copper, silver and gold, have been investigated. The surface areas of all films have been determined by the B.E.T. method. Isotherms for CO on these metals in the temperature range 273°K to 78°K are given and the heat of adsorption calculated as the function of coverage. The surface structure of the adsorbed layer of krypton and CO are discussed in some detail and it is shown that the carbon monoxide is linearly bonded to all metals and that krypton is best described by a close-packing arrangement where its effective cross-sectional area is the normal value of 19.5Å. Some discussion of the relative abundance of the normal crystal planes in these metal films is given and it seems probable that three planes, i.e. (110), (100) and (111) are equally present in palladium, titanium and manganese; (110) is in abundance for platinum, chromium and cobalt films.

Rate of adsorption could be measured on palladium, titanium, chromium and copper and shown to obey the Elovich equation. Following the theory of Gundry and Tompkins, it is confirmed that the rate is largely determined by the heterogeneous structure of the surface of the metal.

In those systems where adsorption was measurable NO was found to be less strongly adsorbed than CO, and with chromium unusual results obtained indicated chemical attack of the metal by the gas.

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INTRODUCTION

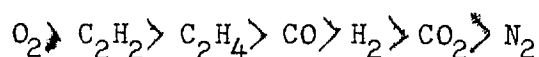
An atom at the surface of a solid is in a different energetic state from that in the bulk material, because whatever the nature of the forces holding the atoms together, those inside the bulk are subjected to equal forces in all directions, whereas those on the surface are subjected to unbalanced forces. It is this unsaturation of forces which causes adsorption. The adsorbed particles are either localised at the surface or can move about in two dimensions; in either case there is an entropy decrease since prior to adsorption process the gas molecules moved freely in three dimensions. The change in heat content of the system is given by

$$\Delta H = \Delta G + T \Delta S,$$

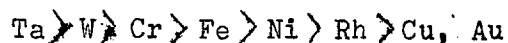
and since both ΔG and ΔS are negative, ΔH must be negative, i.e. the adsorption process is exothermic, the heat evolved being the heat of adsorption. The magnitude of this heat determines which of the two types of adsorption is taking place. In van der Waal's adsorption the heat has a value close to the heat of liquéfaction of the gas. Usually this type of adsorption is only significant at low temperature and fairly high pressure (1 mm Hg and upwards). Adsorption is reversible and requires no activation energy. It is therefore, exceedingly rapid, and takes place as fast as the adsorbate

reaches the surface. The term chemisorption is given to adsorption when the heat evolved is high (10 k.cal. or higher). Chemisorption, being similar to a chemical reaction, often requires an energy of activation.

The heat of adsorption in any system depends both on the metal and on the gas, and it is possible to place a number of gases in sequence such that any one is more strongly adsorbed by any metal than one succeeding it⁽¹⁾, viz.



Trapnell⁽¹⁾ has also shown that initial heats of adsorption on different metals for many gases are in the following sequences



Beck has pointed out the order of decreasing initial heats of adsorption is the same as the increasing d character of the metal. Increasing d character signifies that more and more d-electrons are used for the mutual cohesion of the metal atoms in the lattice of the crystal and are therefore not available for chemical bonding⁽²⁾. This suggests that the metal-adatom bond is essentially covalent in character^(3,4,5) and is in agreement with the experimental findings where an apparent low-ionic moment of the surface-adatom complex is assigned to non-ionic bonding. Only for some alkaline metals ~~on~~ tungsten film^(6,7,8) are the high values comparable with those calculated for ionic bondings found.

The influence of the d character of the metal on catalytic properties has been studied in detail, e.g. in the ortho-para hydrogen conversion carried out on a series of palladium-gold alloy wire. This work showed that there was a sharp rise in the activation energy as the d-band of the palladium was filled by s electron from gold. Similarly Eley⁽⁹⁾ has studied the decomposition of formic acid on a range of palladium-gold alloys and finds an increase in the activation energy as the holes in d-band were filled. Magnetic susceptibility data on nickel by Selwood⁽¹⁰⁾ and Eley⁽¹¹⁾ also emphasise the importance of the d-band in chemisorption.

It is difficult to find any simple correlation between the heat of chemisorption and d-electron structure⁽¹²⁾, but a semi-empirical formula for calculating the heat of adsorption for a system in which bonding is predominantly covalent has been suggested by Eley⁽¹¹⁾. By using the Pauling's equation⁽¹³⁾ which gives the energy of the bond A - A and B - B, plus a term for the ionic character of the bond, he obtained the equation

$$E(A-B) = \frac{1}{2} \{E(A-A) + E(B-B)\} + 23.06 (X_A - X_B)^2$$

where X_A and X_B are the electronegativities of A and B.

Equating the dipole moment μ of the chemisorbed bond with the difference of electronegativities, Eley obtained reasonable agreement between calculated and observed values of the heat of chemisorption of hydrogen on several metals. In order to

apply this treatment to the chemisorption of carbon monoxide, it is necessary to assign a structure to the surface complex. If therefore the chemisorption of carbon monoxide can be represented by the equation



then the heat of chemisorption is given by

$$q = E(M=C) + E(C=O) - E(CO) \dots \quad (i)$$

where $E(M=C)$, $E(C=O)$ and $E(CO)$ are the respective bond energies. $E(C=O)$ and $E(CO)$ are given by Cotterell⁽¹⁴⁾ as 177.5 k.cals. and 255.8 k.cals. respectively. Application of Pauling's equation gives

$$E(M=C) = \frac{1}{2} \{ E(M=M) + E(C=C) \} + 23.06 (X_M - X_C)^2 \quad (ii)$$

$E(C=C)$ is given by Cotterell⁽¹⁴⁾ as 145.8 k.cals. The bond energy $E(M=M)$ is obtained from energy of sublimation S , using the equation $E(M=M) = \frac{S}{2}$, and $(X_M - X_C) = \mu$ is the dipole moment of $M - C$ bond. Now since $=C=O$ has a large dipole moment of its own it would not be valid simply to use the dipole moment of a chemisorbed carbon monoxide molecule in evaluating the electronegativity difference. This is also indicated by the fact that the dipole moment for chemisorbed carbon monoxide decreases with increasing heat of chemisorption. Thus, if it is assumed that $=C=O$ part of the complex retains more or less the same charge distribution as it has in the free molecule, then the term involving the difference in the electronegativities of the $M=C$ bond can be

obtained by subtracting the observed dipole moment for the surface species from that of the C=O bond. Le Fevre⁽¹⁵⁾ lists the value of dipole moment for a series of aldehyde and ketones which are given in table 1.1 from which it is clear that dipole moment of the >C=O group is 2.73D.

Table 1.1

<u>Compound</u>	<u>Dipole moment, debye</u>
CH ₃ CHO	2.72
(CH ₃) ₂ CO	2.74
(C ₂ H ₅) ₂ CO	2.72
C ₆ H ₅ CHO	2.98
C ₆ H ₅ COCH ₃	2.96
(C ₆ H ₅) ₂ CO	3.0

Surface potential measurements have been made for a number of metals by Culver and Tompkins⁽¹⁶⁾ and the values of μ can be calculated by using the expression

$$\mu = \frac{V}{2\pi \times 300 \times C \times \theta_{\max}}$$

where μ = dipole moment in debye

V = surface potential in volts

C = number of sites per sq.cm

$\theta_{\max}$ = maximum fractional coverage

Combining the equations (i) and (ii) the heat of adsorption is given by

$$q = \frac{1}{2} \{E(M=M) + E(C=C)\} + E(C=O) - E(CO) + 23.06 (2.73 - \mu) \quad (iii)$$

Eley's method gives fairly good agreement for hydrogen⁽⁴⁾ nitrogen⁽¹⁷⁾ and carbon monoxide⁽¹⁸⁾, but not for oxygen⁽¹⁹⁾.

The heat of adsorption frequently falls with coverage; this fall is one of the difficult problems in chemisorption theory, and has been variously interpreted. One explanation is that the fall in heat is due to surface heterogeneity - on a heterogeneous surface, there will be a tendency for the most active sites to be covered first, if the adsorbate is mobile even if initially there has been a random coverage, as the coverage increases, the sites of lesser activity will be covered, and the heat of adsorption will fall.

Alternative explanations of the fall in heat have been given in terms of interaction energies between the adsorbate atoms⁽²⁰⁾. Miller⁽²¹⁾ has deduced relationship between heat and coverage resulting from statistical consideration of interaction between both mobile and immobile dipoles on a uniform surface using terms involving interaction between nearest and next nearest neighbours. Some difficulty exists with the interaction mechanisms as to the magnitude of the fall in heat. On the basis of the known W - H dipole, Rideal and Trapnell⁽²²⁾ have calculated that only one-tenth

of the actual fall in heat may be ascribed to interaction. Similarly, Halsey⁽²³⁾ pointed out that if the slope of curve of heat against coverage is greater than 0.25, then only surface heterogeneity can explain the fall in heat.

Finally, initial fast chemisorption is often followed by a slow uptake, the activation energy of which increases with the amount adsorbed. Gundry and Tompkins⁽²⁴⁾ find evidence that this is due to heterogeneity, by studying the kinetics of the slow uptake of hydrogen and carbon monoxide on nickel.

1.1. CARBON MONOXIDE ON METALS

A large amount of data on the nature of adsorption of carbon monoxide on metals are available; this can be divided into five groups, based mainly on the technique employed, viz. (i) evaporated metal film adsorbents first used by Beeck and his co-workers⁽²⁵⁾, (ii) the infra-red spectrum technique employed to study the adsorption of gases on supported and unsupported metals, (iii) the field emission microscope, (iv) flash filament technique, (v) other techniques such as electron diffraction, magnetic susceptibilities and radio tracer studies. In the present study evaporated metal films have been used and therefore previous work on these is discussed in some detail.

1.1.1. Evaporated metal films

Owing to the great difficulty in preparing the clean metal surface by reduction of oxide, evaporated films have proved

invaluable in the investigation of adsorption and catalysis phenomena. The films are prepared by evaporation from pure metal filaments^(22,25) or by heating the metal on some other high melting point metal like tungsten or molybdenum^(26,27,28), refractory crucibles are also employed in cases where eutectics are formed between these two metals and the metal to be evaporated. A film usually has about $10^2 - 10^4$ times greater surface area than that provided by a filament⁽²⁹⁾. The large area may be maintained uncontaminated for longer periods, and makes volumetric determination of the amount adsorbed much easier. The high surface/weight ratio, together with good thermal contact with the walls of the containing vessel helps in the establishment of thermal equilibrium when the adsorption isotherms are determined at different temperatures, and hence they have found application in calorimetric determination of heat of adsorption^(30,35,36) surface potential measurements, kinetic studies and in the observation of change in a resistance of the films due to adsorption of the gases.

Adsorption Isotherms

Isotherms have been obtained for carbon monoxide on tungsten by Rideal and Trapnell⁽³¹⁾, a Freundlich plot was obtained, and the heats decreased exponentially with the coverage. At liquid air temperature, the adsorption of carbon monoxide was more than twice the fast adsorption of oxygen, so they concluded that this

marked the beginning of second-layer of adsorption. They assumed that the heat of physical adsorption of carbon monoxide on tungsten to be about $5.5 \text{ k.cal.mole}^{-1}$ and it was considered to correspond with a monolayer of carbon monoxide at this heat. 1.85 molecules of carbon monoxide were adsorbed relative to one molecule of oxygen (after the oxygen adsorption has been divided by 1.08), indicating as reported by Beeck and co-worker earlier, that one molecule of carbon monoxide occupied one site. (The results (Beeck et al.) also precluded dissociative adsorption of carbon monoxide). There is, however, no discontinuity in the adsorption isotherm or the heat plot to justify the separation of second layer adsorption at a heat $5.5 \text{ k.cal.mole}^{-1}$. They found that heat of adsorption of carbon monoxide on tungsten fell from $14.8 \text{ k.cal.mole}^{-1}$ to $3.6 \text{ k.cal.mole}^{-1}$.

Isotherms have also been carried out with carbon monoxide on iron⁽³²⁾ and nickel⁽³³⁾, between pressure $10^{-5} - 10^{-1}$ mm Hg and temperatures between 300°K to 78°K . These isotherms resemble those of hydrogen on sintered film of these metals in that they curve upwards at higher pressures, after an initially linear plot of coverage against log pressure. With iron the heats fall from $20 \text{ k.cal.mole}^{-1}$ to $4 \text{ k.cal.mole}^{-1}$ and with nickel from $17 \text{ k.cal.mole}^{-1}$ to about $1.5 \text{ k.cal.mole}^{-1}$. At the same coverage there is considerable variation of heat with temperature. This probably results from the non attainment of equilibrium.

Porter and Tompkins⁽³²⁾ found a ratio 1.68 for fast adsorption of carbon monoxide to hydrogen at 90°K, and 1.47 for the equilibrium adsorption at 273°K and 10^{-1} mm, whereas Bagg⁽³⁵⁾ obtained a ratio of 1.52 between the adsorption of these two gases at 10^{-1} mm and room temperature for iron film. Gundry and Tompkins⁽³⁷⁾ find the ratio of 1.67 for fast and 1.39 for total sorption at 78° K (calculated from the mean slow and fast sorption) of carbon monoxide and hydrogen on nickel films. All these values are considerably lower than the value of 2 reported by Beeck. Trapnell⁽³⁴⁾ has reported 9 k.cal.mole⁻¹ of initial heat of adsorption for carbon monoxide on copper and gold, determined isothermally. Except from these no isothermally determined heats are available for any other metal.

Rate of Adsorption

Kinetic studies of the adsorption of gases on metals can be divided into two parts, the fast rate of adsorption, which takes place in the initial stage of adsorption and is often followed by a slow adsorption process.

Slow Rate of Adsorption

The rate of adsorption of hydrogen and carbon monoxide on iron film following the fast adsorption ($\sim 70\%$ coverage) was found by Porter and Tompkins⁽³²⁾ to obey the equation

$$dq/dt = a \exp(-bq)$$

where q is the amount adsorbed at constant pressure p , and

and a , b are constants at particular temperature. They observed that (i) a twenty-fold decrease in surface area on sintering the film at 638°K compared with that sintered at 78°K , resulted only in a 40% increase in the ratio of the fast to the slow sorption. (ii) The value of b for films sintered at different temperatures varied inversely as the surface area. (iii) When a hydrogen covered film at 78°K was exposed to mercury vapour, 95% of gas was desorbed instantaneously. From these observations they concluded that the rate process was a surface phenomena, thereby differing from Beeck et al.⁽³⁰⁾ who concluded that the slow process of hydrogen uptake by nickel film was absorption into the bulk metal. Gundry and Tompkins^(38,39) studied extensively the rate of slow sorption of hydrogen and carbon monoxide on nickel and found that the rate of hydrogen uptake V_s was proportional to p^{λ} where the value for $\lambda = 0.51 \pm 2$ for hydrogen. With carbon monoxide mean λ -value was 0.65 for nickel and 0.85 for iron. Originally, these results were explained in terms of the rate determining process, being one involving activated migration of the adsorbed molecule over a non-uniform surface from sites of low to high adsorption potential. It was also postulated that the high potential sites were not filled by adsorption direct from the gas phase, by reason of a higher activation energy for the transition from the van der Waal layer to the chemisorbed layer.

Later, however, Gundry and Tompkins assume that the final chemisorbed state was attained only by passing through an initial chemisorbed state of higher potential energy following Dowden⁽⁴⁰⁾. This transfer from the initially chemisorbed state to the final chemisorbed state required an activation energy, which increased with increase in coverage. The concept of non-uniform surface was therefore not necessary.

Fast Adsorption

The initial fast adsorption on evaporated metal films cannot be followed in detail by a static method, but can be followed by using a constant flow method^(41,42,43). A capillary tubing of known conductance was used to leak the gas into the vessel on which the film was deposited, and an ionisation gauge to measure the change in pressure. The amount adsorbed was calculated from the rate of supply of gas, and the rate of change in pressure, and the results were generally plotted as sticking probability against coverage.

Oda⁽⁴¹⁾ has studied the adsorption of carbon monoxide on nickel, while Wagener^(42,43) has investigated the adsorption of different gases on a number of metals, including carbon monoxide on nickel, silver, titanium and chromium. Generally it was found that the sticking probability value remained constant initially but decreased rapidly, which suggested that the fast

adsorption before the completion of the monolayer is not a single process. It is therefore suggested⁽²⁴⁾ that chemisorption on a partly covered surface does not occur predominantly through direct collision of a gas molecule with the empty site, but involved a prior physical adsorption in a second layer on the top of the first chemisorbed layer, and that empty sites in the first layer are filled by migration of second layer molecules over the filled first layer sites.

Heat Determination by Calorimeter

A calorimetric method for the determination of the heats of adsorption of hydrogen and carbon monoxide on nickel films was used by Beeck et al.⁽³⁰⁾. His value 9.35 k.cal.mole⁻¹ for carbon monoxide was confirmed by Klemperer and Stone⁽³⁶⁾. Bagg and Tompkins⁽³⁵⁾ have determined the heat of adsorption of carbon monoxide on iron films; it remained constant at 32 k.cal.mole⁻¹ up to 50% coverage and then fell linearly with coverage. Recently F.H. Hoyes⁽⁴⁴⁾ has determined the heat of adsorption of carbon monoxide on a number of metal films and his values will be referred to in some detail in the discussion.

Surface Potential Measurements

Surface potential changes on chemisorption may be obtained by (i) direct determination of the work function as in the thermionic or photoelectric cell method, or (ii) indirectly by

by the contact potential difference as in the Kelvin, Magnetron and diode method. A comprehensive review of the surface potential work has been presented by Culver and Tompkins⁽¹⁶⁾.

In general there is good agreement in the results reported by different workers for adsorption of carbon monoxide on metals. The diode measurements of Culver, Pritchard and Tompkins⁽⁴⁵⁾ for the adsorption of carbon monoxide on various evaporated films at -183°C were:

Copper	+ 0.30 V
Silver	+ 0.31 V
Gold	+ 0.92 V
Iron	- 1.64 V
Cobalt	- 1.48 V
Nickel	- 1.35 V

The data on copper, iron and nickel are in reasonable agreement with those of Bloyaert et al.⁽⁴⁶⁾. To explain the positive surface potential of carbon monoxide on copper, silver and gold a co-ordinate binding via the oxygen of the carbon monoxide molecule has been suggested. Spectrographic evidence for some types of mechanism has been found⁽⁴⁷⁾. On the other hand, with transition metals, the surface potential is negative and the binding is via the carbon atom, with oxygen outwards from the surface.

Conductivity Measurements

When a gas molecule is chemisorbed on a metal surface, if the electron of the adsorbed molecule becomes part of the electron shell of the gas molecule, a change in the electrical resistance of the metal will be observed in addition to a change in work function^(48,49). The change in resistance will become measurable when the adsorbing layer is not thicker than a hundred or a thousand times the thickness of the layer undergoing electronic interaction; consequently most of the investigations have been restricted to very thin film.

With carbon monoxide as adsorbate, increase in resistance with nickel^(50,51,52), iron^(50,51) and titanium⁽⁵⁰⁾ is obtained. The change in resistance depends markedly on the temperature. At liquid air temperature the increase in resistance is small; at higher temperatures the increase is greater. It is possible that the change of energy between the molecules and the cold surface occurs so slowly that the thermal energy of the molecules serves as the activation energy for the place exchange on the nickel surface.

Sahrmann and his co-workers^(52,53) interpret this increase in resistance as a displacement of metal electrons towards the adsorbed molecule, because the electron affinity of the carbon monoxide molecule is greater than that of surface. Zwetetering,

Koks and van Heeder⁽⁵⁰⁾ have calculated the number of bonds formed in the adsorption of a carbon monoxide molecule, by comparing the fractional increase in the resistance for hydrogen and carbon monoxide, assuming that the adsorption of one hydrogen molecule results in the formation of two bonds with the surface. They obtained a magnitude slightly greater than two, and proposed different structures to account for this number. Ehrlich⁽⁵⁴⁾ has recently questioned this interpretation, and suggested that the contribution to the observed resistance increases arises from any of the following; (a) a localised resistance change at the neck between crystallites of the films, (b) change in the surface stress on adsorption, (c) a decrease in the rate of electron tunnelling across-gaps in the film accompanying an increase in the work function. The last mechanism appears most likely.

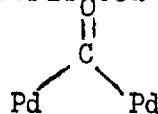
1.1.2. Infra-red Spectra

Infra-red spectrometry has proved valuable in providing information of the interaction of molecules with surfaces. The major requirement for obtaining well-defined spectra are (i) that there be a sufficiently high concentration of adsorbate in the path of the incident-radiation by using an adsorbent of sufficiently high specific surface; (ii) scattering by the particles of the adsorbent should be decreased as much as possible

by using particles of such a dimension smaller than the wavelength of the incident radiation; (iii) the adsorbent should be transparent to the infra-red radiation. The infra-red spectroscopy work on the adsorption of carbon monoxide on metals can be divided into two parts, the adsorption on supported metals, and on evaporated metal films.

Infra-red Spectra on Supported Metals.

Spectra of chemisorbed carbon monoxide on silica supported palladium, nickel and platinum were obtained by Eischen, Francis and Pliskin⁽⁵⁵⁾. The spectrum on palladium and nickel show two distinct bonds, and by comparing the spectrum of the surface compound with that of corresponding carbonyls of known structure, these bonds were identified. For example, the spectrum of carbon monoxide on palladium⁽⁵⁶⁾ has a strong bond at 1820 and at 1925 cm^{-1} and a weak one at 2070 cm^{-1} . The latter was attributed to the linearly chemisorbed carbon monoxide since this value is close to the frequency of the carbon-oxygen stretching vibration of metal carbonyls in which the CO group is bonded to single metal atoms through the carbon atom, i.e. $\text{M} - \text{C} \equiv \text{O}$. The bonds in the 1820 - 1925 cm^{-1} region are similar to those found in the spectra of carbonyls such as $\text{Fe}_2(\text{CO})_9$ which contain CO groups bridged between two metal atoms, and these are attributed to a bridged-type chemisorbed carbon monoxide, i.e.



The intensities of these two types of bonds vary with coverage⁽⁵⁵⁾ and for different metals the ratio between linear and bridged form of bonding varies. With nickel^(55,47,60,61,62) and palladium^(56,47,57), the bridged structure predominates, but with platinum^(55,56), copper⁽⁵⁶⁾ and iron^(58,59) there is a predominance of linear bonding.

The spectra of carbon monoxide on platinum⁽⁵⁸⁾ show differences when the support was changed from silica to alumina, more of the bridged species being present when the alumina was used. Recently O'Neill and Yates⁽⁶⁰⁾, in an extensive investigation on CO + Ni system finds (a) with a silica supported at 1.3 mm pressure of carbon monoxide the linear species was at 2075 cm^{-1} and bridged one at 1925 cm^{-1} (b) with an alumina support linear carbon monoxide adsorb at 2040 cm^{-1} at low pressure and at 2070 cm^{-1} at high pressure; over the same pressure range the bridged species moved from 1945 to 1958 cm^{-1} . Similarly, Garland⁽⁶¹⁾ finds at low coverage bonds at 2045 and 1910 cm^{-1} for linear and bridged species respectively, (c) titania showed linear and bridged species at 2080 and 1975 cm^{-1} . It was found that ratio of linear and bridged species also varies with pressure.

A marked variation in the strength of adsorption of two types of species was also observed as the support was changed. Thus, after saturating a nickel surface with carbon monoxide and then evacuating, 90% of linear species was removed in 30 minutes and

64% of the bridged form in the same time using nickel supported on titania, 48% and 19% from nickel supported on alumina, and 34% and 18% from nickel supported on silica.

There is some evidence that the chemisorption of hydrogen is enhanced by a pre-adsorbed layer of carbon monoxide⁽⁶³⁾ and Eischen and co-worker⁽⁶⁴⁾ have found that presence of hydrogen on nickel effect the nature of bonding of carbon monoxide molecules with surface atoms.

Evaporated Metal Films

From the spectra of carbon monoxide on evaporated platinum film, Eischen⁽⁵⁸⁾ finds a linear structure. Recently Pickering and Eckstron⁽⁶⁵⁾ and Gardinear and Peterucci⁽⁶⁶⁾ for carbon monoxide on nickel films find bonds at 2174, 2115 and 2060 cm^{-1} , the intensity of these being proportional to the pressure of gaseous carbon monoxide. At low pressure only 2060 cm^{-1} bond was observed, and on evacuation all the bonds disappeared. On rhodium⁽⁶⁵⁾ a shift in the bond wavelength was found.

1.1.3. Field-emission Microscopy

This technique had been widely used to study the adsorption and surface diffusion of gases on metal, particularly of carbon monoxide on tungsten. In field-emission microscopy⁽⁶⁷⁾ a high potential of several thousand volts is applied between a fine metal tip (diameter 10^{-5} - 10^{-4} cm) and a fluorescent screen, so as to

initiate electron emission from the tip at room temperature. The electrons impinge on the fluorescent screen, where an electron emission map of the tip magnified $10^5 - 10^6$ times is produced. Different intensities are found for different faces, and from the symmetry of the pattern and the angular separation of the various faces, crystallographic indices can be assigned. As both physical and chemical adsorption change the work function of the metal, the change in the patterns provides information about the location and movement of the adsorbed species over different crystal planes.

It has been shown that the adsorption of carbon monoxide on tungsten is non-dissociative (18,69,70) because the characteristic pattern of carbon was not observed even on heating the tungsten tip to 2300°K in a carbon monoxide pressure of $2 \times 10^{-8}\text{ mm}$. It has been shown (71,72) that, like hydrogen and oxygen, carbon monoxide shows three distinct types of surface diffusion, each taking place in different temperature ranges.

Type I. This type of diffusion occurs at very low temperature ($2 > T > 70^\circ\text{K}$ depending on the gas) and high coverage. The simplest interpretation is that, on the clean tip, the first layer is chemisorbed, and then the gas is physically adsorbed on top of it (73). The molecules wander over chemisorbed layer, fall over the edge and then become chemisorbed, thus extending

the chemisorbed layer, over which other molecules can be physically adsorbed. Diffusion therefore takes place though the chemisorbed layer itself is immobile. This explanation accounts for the experimental facts (i) diffusion occurs with sharp boundary at low temperature, (ii) if the initial deposit is insufficient for complete spreading, the sharp boundary at first advances and then stops. If more gas is deposited the movement is resumed. (iii) Why after a certain upper temperature limit no migration of molecules is observed. At this temperature limit the physically held molecules are desorbed before they have time to move to the edge and be chemisorbed on the bare surface.

Type II. This type of diffusion (which becomes observable at 750°K) takes place with sharp boundary. The activation energy for this process is $36 \text{ k.cal.mole}^{-1}$ (so this phenomenon must involve chemisorption) and the activation energy for desorption is $52 \text{ k.cal.mole}^{-1}$.

Type III. This occurs at even higher temperatures, when type II diffusion has ceased. It occurs with a boundary and with a higher activation energy for diffusion ($60 \text{ k.cal.mole}^{-1}$) and for desorption it is $90 \text{ k.cal.mole}^{-1}$.

The nature of the activation energy has been compared with the desorption energy for various gases on tungsten⁽⁷¹⁾. For carbon monoxide the ratio for type II and type III diffusion are 0.66

and 0.7 which are greater than the corresponding values for oxygen 0.2 and hydrogen which varies from 0.1 to 0.2. The difference between these rates has been attributed to size of adsorbed species, hydrogen being able to squeeze between, rather than be compelled to move over the surface metal atoms. The difference ratios found for carbon monoxide on different faces of tungsten have been explained qualitatively by the fact that place change of a carbon monoxide molecule in a cube site requires the number of contacts with tungsten atoms to be reduced from five to two, and the activation energy approaches >50% of the heat of binding, (the large size of carbon monoxide molecule precludes any squeezing between tungsten atoms), whereas on the close-packed (110) face, only a 33% reduction in bonding is necessary.

1.1.4. Flash filament technique

Measurement of the adsorption of carbon monoxide on tungsten using flash filament techniques has been reported by Hickmott⁽⁷⁴⁾, Eisinger⁽⁷⁵⁾ and Schlier⁽⁷⁶⁾, and more recently by Redhead⁽⁷⁷⁾ and Ehrlich⁽⁷⁸⁾ on adsorption and desorption of carbon monoxide on tungsten. The time taken to raise the temperature of the filament from 300°K to 2300°K in Ehrlich experiments was less than one second, but extended to one minute between the same range in Redhead experiments. The variation in pressure in the system during the desorption cycle was recorded. The slow desorption allowed observation of the various desorbed phases

in some detail. The activation energy of the different phases was estimated from the temperature at which the peaks in desorption spectra occurred⁽⁷⁷⁾, assuming in the work of Ehrlich a first order desorption process for β_2 state. For α , β_1 and β_3 state the values were estimated and confirmed by field emission microscope. The heat of binding obtained by these investigators for different states of binding agree well with others obtained using the field emission technique. Heats for different states in kcal.mole⁻¹ are given in table 1.2.

Table 1.2.

α	β_1	β_2	β_3	Ref.
20	53	75	100	(78)
29	59	70	76	(77)
-	52	-	96	(71)
12	53	-	-	(72)

Ehrlich⁽⁷⁹⁾ has proposed that the surface heterogeneity is responsible for the different forms of binding states of carbon monoxide, and both Ehrlich and Redhead have shown that adsorption on different crystal faces can account for the presence of chemisorbed species with different adsorption energies.

1.1.5. Electron diffraction and other techniques

The electron diffraction method has lately been greatly improved by Germer and co-worker^(80,81) and used to study the chemisorption of carbon monoxide on nickel. On the ⁽¹¹¹⁾ nickel face, the diffraction pattern suggests that the spacing between adjacent carbon monoxide molecule is double that between adjacent nickel atoms. A sticking probability of about one was found, suggesting that the carbon monoxide molecules were free to move over the surface at room temperature.

Magnetic measurements have been carried out by Selwood⁽⁸²⁾ for carbon monoxide and carbon dioxide on silica-supported nickel. The results suggest two forms of adsorbed species, the linear and bridged form for chemisorption of carbon monoxide on nickel, the ratio of these depending on coverage.

The technique used by Crowell⁽⁸³⁾, to follow the desorption of labelled gases from metal surfaces by means of a counting device, although as yet only reported briefly, seems potentially to be of considerable value. So far only carbon monoxide adsorbed on nickel has been studied. For the desorption process, an activation energy of 25 k.cal.mole⁻¹ was obtained, in fair agreement with values obtained by other workers.

1.2. NITRIC OXIDE ON METALS AND ON CARBON

Nitric oxide reacts with a carbon surface at 0° and -78°C forming gaseous nitrogen and carbon-oxygen surface complexes^(84,85) but at -154° normal adsorption occurs; the adsorbed state was thought to be N_2O_2 . At $450 - 600^{\circ}\text{C}$, it is postulated that nitric oxide first reacts with the surface carbon giving nitrogen and carbon-oxygen surface complexes, and that these carbon-oxygen complexes react with another nitric oxide molecule to form nitrogen and carbon dioxide, and an oxygen complex on an adjacent carbon atom. The new oxygen complex serving as a site for further adsorption of nitric oxide.

Terenin and Roev⁽⁸⁶⁾ have studied the spectra of nitric oxide adsorbed on transition metals and their oxides. The intensity and position of different bands observed were found to be dependent on experimental conditions. Adsorption bands (strong 2008 cm^{-1} , weak $1805 - 1625\text{ cm}^{-1}$) of nitric oxide adsorbed at 20°C on these metals, disappeared on heating to 350°C . The bonds obtained for nitric oxide chemisorbed on the metals dispersed on alumina are summarised below.

<u>Metal</u>	<u>Frequency (in cm^{-1})</u>	<u>Desorption behaviour</u>
Iron	2008 strong	disappear on desorption at 20°
	1805 weak)	disappeared after 1 hr. at 150°
	1735 weak)	

<u>Metal</u>	<u>Frequency (in cm^{-1})</u>	<u>Desorption behaviour</u>
Iron	1698 weak)	disappear on desorption at 350°C
	1660 weak)	
	1625 weak)	
Nickel	1850 strong	
	1735 weak	
	1698 weak	
	1660 weak	
	1625 weak	
Chromium	2010) Approx. the	disappear after long desorption at room temperature
	1905) same intensity)	
	1830)	
		disappear after heating
	1735 weak	
	1698 weak	
	1660 weak	
	1625 weak	

The characteristic frequency of $\text{N} = \text{O}$ is known⁽⁸⁷⁾ to be located in the range $1700 - 1870 \text{ cm}^{-1}$, so presence of a bond in this range indicates covalent bonding with the bonding between nitrogen and surface atoms. A strong bond at 2008 cm^{-1} in the case of iron indicates an ionised chemisorbed molecule, because the characteristic frequency of NO^+ ion is⁽⁸⁸⁾ in the range of

2000 - 2400 cm^{-1} . The spectra obtained with chromium, like that of iron indicate the occurrence of more than one type of bonding. In no case is there any spectroscopic evidence for the formation of NO^- bond (Cp. carbon monoxide, which is always chemisorbed with electron transfer from gas to the solid).

More recently D.D. Eley and P.R. Wilkinson⁽⁸⁹⁾ have studied the adsorption of nitric oxide on evaporated aluminium film. Nitric oxide was found to react with the metal to give a surface oxide. Thus on admitting a series of small increments of nitric oxide, it was found that the first increments were taken up with 10% liberation of nitrogen but when the nitric oxide adsorption reached monolayer, evolution of nitrogen approached 90% of the theoretical figure, and that N_2O evolution began. They also found that if nitric oxide is admitted at -183°C , the evolution of nitrogen and N_2O only takes place when the film is warmed to 20°C and the coverage is high. They postulated that reaction between a gas molecule and an $\text{Al} = \text{O}$ monolayer must occur on aluminium sites set free by the migration of surface oxygen to underlying aluminium atoms. Except for these, it appears that no work has been done on the adsorption of nitric oxide on other metals.

1.3. METAL CARBONYLS

Metal carbonyls are compounds in which CO groups are attached to a metallic atom through the carbon atom. The M-C-O structures are found by X-ray analysis or electron diffraction to be linear, so that the group may be written as either $M^-C \equiv O^+$ or $M \leftarrow C \equiv O$. The M - C distance is, however, usually abnormally short, for example, in nickel carbonyl it is 1.82 Å compared with a theoretical value of 2.16 Å and the C - O distance 1.13 Å lies between the theoretical value for a double bond 1.21 Å, and that of triple C $\equiv$ O bond 1.1 Å; thus favouring the structure $M = C = O$ ⁽⁹⁰⁾. The carbonyls are formed by group VIA, VIIA, and VIII metals, and the spectroscopic studies of carbon monoxide adsorbed on such metals show bands of different intensities in the range usually found in the spectra of metal carbonyls. It is of interest to compare the heats of formation of metal carbonyls with the heats of chemisorption of carbon monoxide. Trapnell et al.⁽⁹¹⁾ has shown that the heat of chemisorption of oxygen is equal to the heat of formation of oxide, and this property is not limited to oxygen adsorption⁽⁹²⁾. The thermodynamic data concerning metal carbonyl compounds is still meagre. Cotton, Fisher and Wilkinson^(93,94,95) have determined the heats of combustion of the carbonyls of chromium, molybdenum, tungsten on nickel and iron. From these they have computed

their respective heats of formation. These are given in table (1.3) as the enthalpy change for the reaction

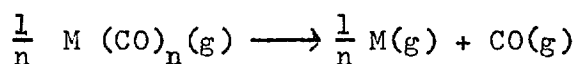


Table 1.3

Carbonyl	ΔH formation k.cal.	ΔH heat of chemisorption
Cr(CO) ₆	27.1	
Mo(CO) ₆	35.9	60
W(CO) ₆	42.1	80
Fe(CO) ₅	27,7	35
Ni(CO) ₄	35.2	40

1.4. Surface Area of Metal Films

The surface area of metal films has usually been determined using krypton as the adsorbate at liquid nitrogen temperature. Simultaneous measurements of the surface area of various types of adsorbents have been made with krypton and with nitrogen^(96,97) and by comparison with nitrogen cross-sectional area, that of the krypton molecule was evaluated (19.5Å). The surface area is then estimated by multiplying this area by the number of krypton atoms required to form a monolayer as determined by the B.E.T. plot. However, several papers have appeared recently dealing

with the nature of the interaction between rare gas atoms and clean metal surfaces, and it has been shown that drastic changes in the nature of the interaction energy and compatability factor occurs as the coverage approaches a monolayer⁽⁹⁸⁾. Such changes, which are considered to reflect differences in the mechanism of krypton adsorption at low and high coverage, effect the nature of surface area.

Recently Graham⁽⁹⁹⁾ has determined the -196°C isotherm for both krypton, xenone on some metal films. It is seen from his results (fig.1.1.1) that the points for both rare gases fall on a single isotherm when this is plotted as relative pressures against amounts adsorbed. The value of V_m (the amount adsorbed in a monolayer) obtained from point B (which is well defined) and the B.E.T. equation agree well in this region, but at higher pressures no sharp point B is available. Similarly in some cases, the B.E.T. derived plot is not linear, as it should be, thereby indicating a much more complex situation than that assumed in the B.E.T. theory. As the krypton isotherms show no well defined point B in most of the cases, it is thought that adsorption takes place initially on those parts of the surface where the geometry is most favourable and then proceeds on other regions where the molecules are more weakly held, i.e. multilayer formation occurs before the completion of the monolayer, as is

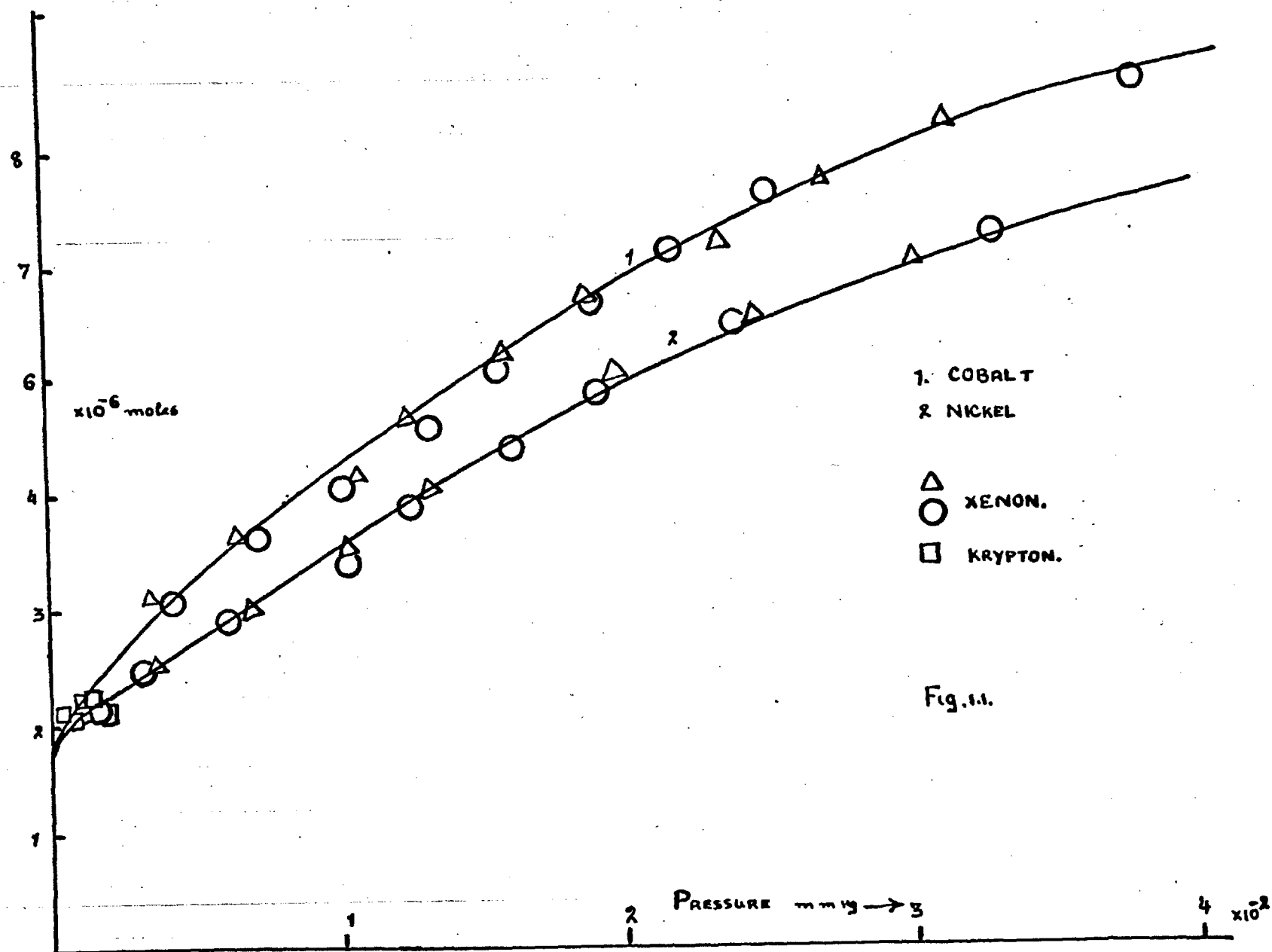


Fig. 11.1.

confirmed by field emission studies⁽¹⁰⁰⁾. Two different states of binding have also been found for xenon on tungsten⁽¹⁰⁰⁾.

Roberts⁽⁹⁸⁾ has shown that krypton forms a monolayer on iron films at 78°K at pressures around 10^{-2} mm Hg, and the isotherm obeys the B.E.T. equation, in this range of pressure, which is well outside the generally accepted valid range of relative pressure. The area of the film was found to decrease with time because of sintering (sintering temperature, 23°C). Pre-adsorbed oxygen decreased the value of V_m for krypton, but pre-adsorbed hydrogen increases it. Hayes⁽¹⁸⁾ also found a similar effect for carbon monoxide on a number of metals, e.g. chemisorbed carbon monoxide and carbon dioxide reduces the value of V_m by 48 and 33%. But in contrast to Roberts⁽⁹⁹⁾ observation on iron, he finds that adsorption of hydrogen has no effect on the V_m value.

J. Pritchard⁽¹⁰¹⁾ has measured the surface area of copper, gold and platinum films by following the change of the surface potential of adsorbed xenon⁽¹⁰²⁾ using the diode method. The surface potential showed a linear dependence on coverage up to a critical value beyond which it changed very little. He associated this point with the completion of the monolayer. For calculation of the surface area, 24Å was used as the effective area of xenon atom.

Configuration of the first layer adatoms

Not only is there enough evidence to doubt that V_m is in fact the monolayer volume, but, even accepting this statement, the question of the configuration in the first layer remains since this may be either hexagonal close-packing or be determined by the surface structure of the adsorbent.

There are many experimental facts which point to localised adsorption at specific sites, e.g. (i) the number of molecules in the monolayer of krypton and xenon are approximately the same⁽⁹⁹⁾ although the atomic diameter of krypton is $4.93\text{\AA}$ and that of xenon $3.96\text{\AA}$ (as derived from the crystal lattice⁽⁸⁾, i.e. the cross-sectional area of krypton is 20% greater than that of xenon, (ii) rare gases on different metals give high heats of adsorption for the first layer, consistent with a site adsorption. These heats have been determined by calorimetry, by field emission and by isosteric method.

One point in favour of a close packed configuration is that although the diameter of the krypton, xenon and carbon monoxide are very nearly the same (krypton $3.96\text{\AA}$, xenon $4.36\text{\AA}$ and carbon monoxide $4.08\text{\AA}$) the ratio of carbon monoxide molecules at 0°C to the number of molecules of krypton in the monolayer is always more than unity. If we assume one krypton molecule to be attached to one surface site then it means that more than one carbon monoxide molecule is attached to one site, but this difficulty is removed if a close packed configuration is accepted for the krypton monolayer.

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APPARATUS AND EXPERIMENTAL

2.1. APPARATUS

The apparatus used for adsorption measurements was constructed of Pyrex glass, and is shown in Fig.(2.1.). The main pumping leads were of 25 mm diameter to facilitate rapid evacuation, in the remainder of the apparatus, 6 and 10 mm internal diameter tubing was used. Edwards high vacuum grease and silicone high vacuum grease were employed as tap lubricant. For the purpose of discussion the apparatus is divided in different sections.

1. Pumping section

The pumping section consists of two two stage mercury diffusion pumps in series, backed by a rotary oil pump. To prevent mercury vapour from passing either to the adsorption section or into the pump, liquid air cooled traps were used on either side of the mercury diffusion pumps. This pumping arrangement was capable of obtaining vacuo of about 10^{-7} mm of Hg in about two minutes from 10^{-1} mm of Hg.

2.1.2. Gas storage and purification section

This section could be separated from the rest of the apparatus by mercury cut off C_3 and tap T_1 . The gases were stored in bulbs as shown in figure.

Hydrogen

The hydrogen storage and purification section is shown in Fig.(2.2a). The bulb A was evacuated through the two way tap I

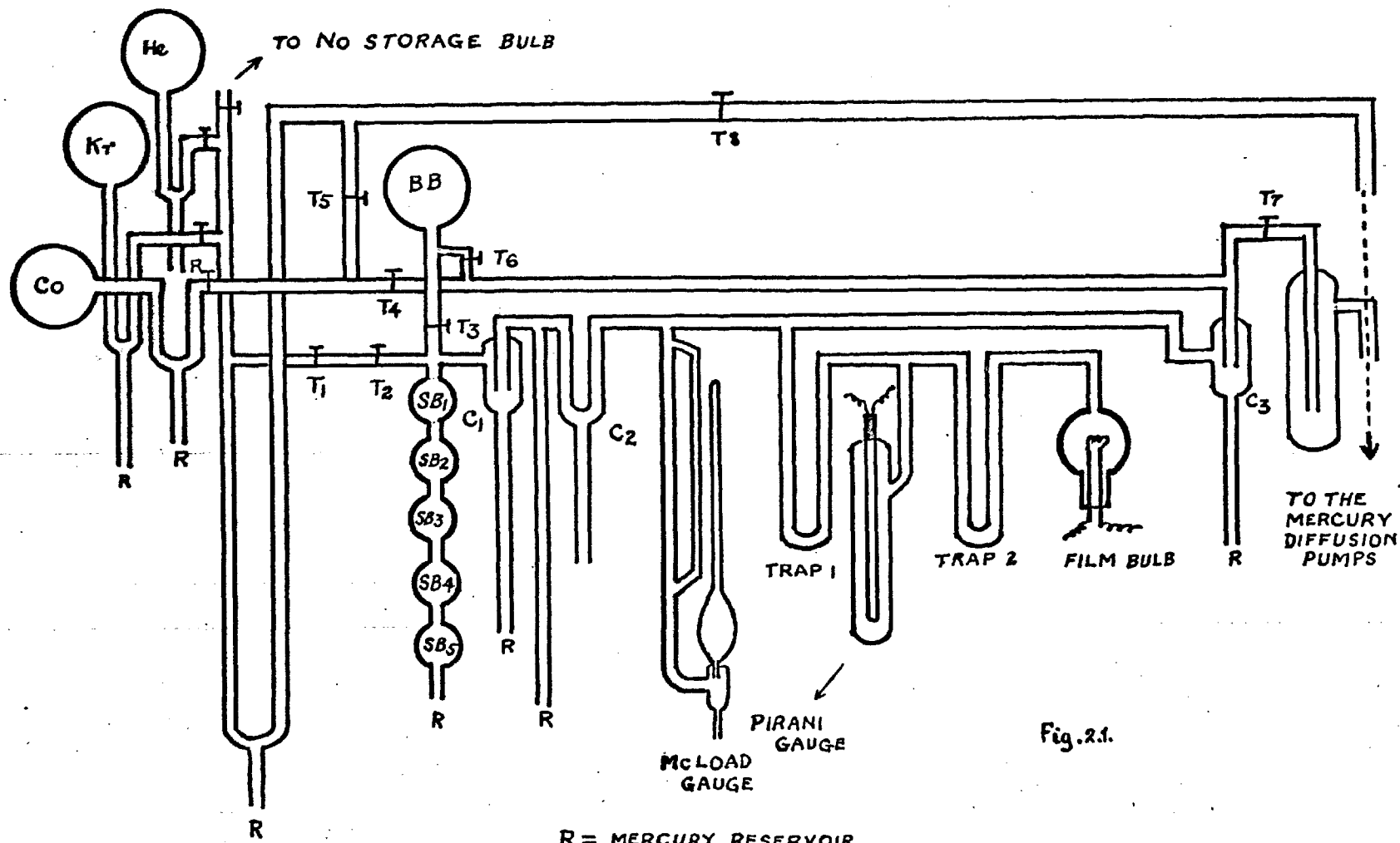


Fig. 2.1.

and then filled with hydrogen from the cylinder, this hydrogen was pumped out and then refilled. This procedure was repeated twice to ensure the complete removal of air from this section and the connecting tubings. The hydrogen was purified by diffusion through a palladium thimble which was heated externally to about 300°C .

Nitric Oxide

The nitric oxide gas used was supplied by the Matheson Co. Inc. U.S.A. in a cylinder. The nitric oxide storage section Fig.(2.2.b) was evacuated and flamed for a considerable time to remove water vapour. The trap I was cooled in carbon dioxide + alcohol mixture in order to trap any NO_2 (NO_2 condenses at 21.1°C) and solidifies at -11.2°C). The gas was passed first through the bulb containing anhydrous calcium chloride, and the two-litre bulb A was filled with gas with taps 2 and 3 closed. This gas was pumped out, and the procedure was repeated twice in order to remove air in the bulb, and the connecting tubings. The tap I was closed, and tap 2 opened, nitric oxide was condensed in trap 2 which was cooled in liquid oxygen. Even with such precautions it was observed that some air (oxygen) condensed with the nitric oxide, giving a greenish blue colour to it. To remove this dissolved oxygen, first, all the gas present in the apparatus was pumped out, and trap 2 was slightly warmed by taking away the liquid oxygen bath. The dissolved oxygen evaporated first because the boiling

TO THE PUMP

HYDROGEN
CYLINDER

PALLADIUM
THIMBLE

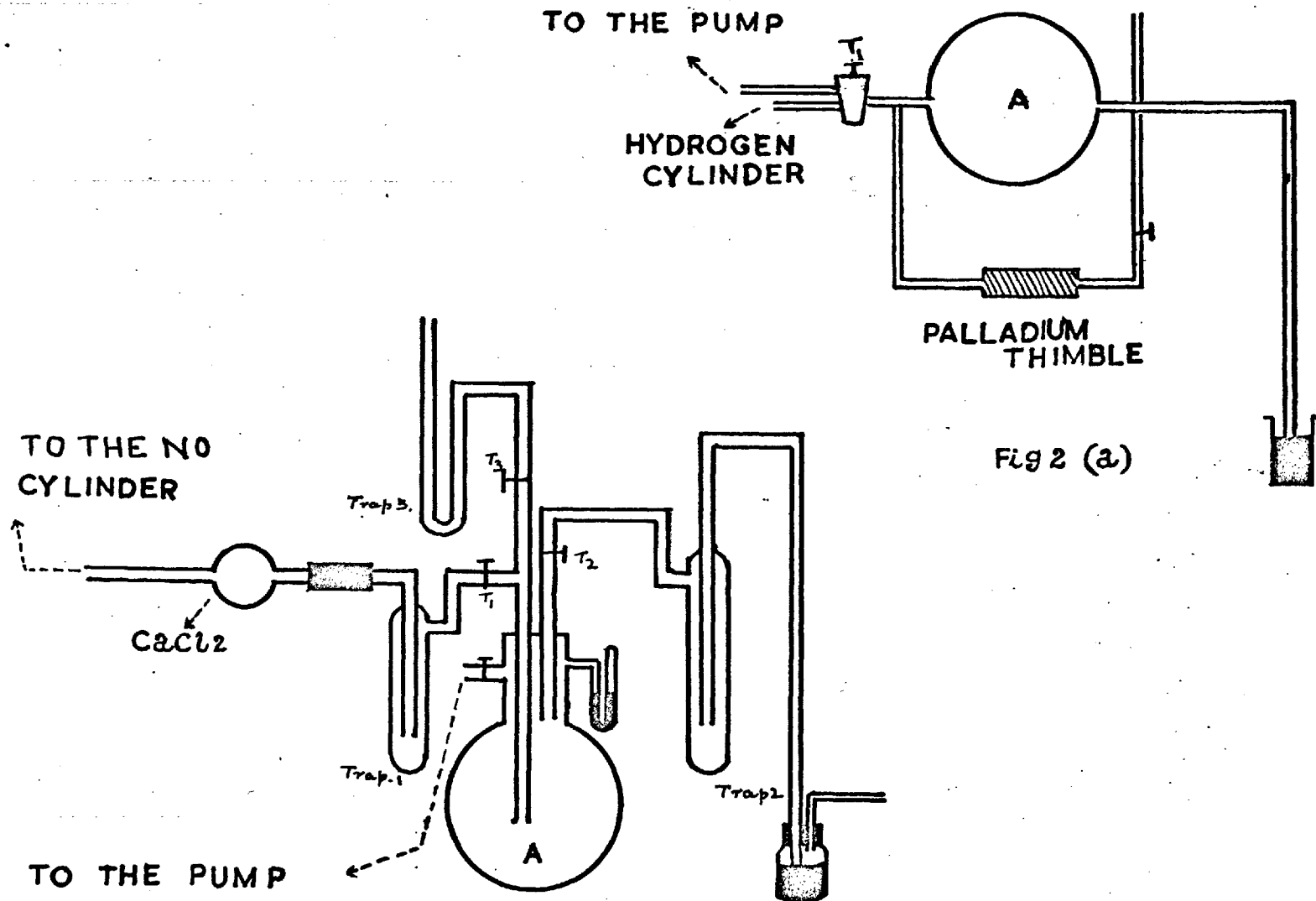
Fig 2 (a)

TO THE NO
CYLINDER

CaCl_2

TO THE PUMP

Fig 2 (b)



point of nitric oxide gas is -152°C ⁽¹⁾ tap 2 was closed and the gas in the bulb was pumped out. This procedure was repeated again and again until a colourless solid was left in trap 2. (Pure nitric oxide solidifies as colourless substance). The vapour pressure of nitric oxide at 90°K is 3.1 mm. Hg ⁽²⁾ compared with a measured value of 3.02 mm Hg . This purified gas was stored in the two litre bulb B. Every time the gas was taken from the bulb for adsorption studies, it was condensed in trap 3, cooled in liquid oxygen. The vapour pressure of the gas was measured. If the vapour pressure or the colour was found to be different, a fresh preparation was made. Nitric oxide was found to react with grease.

Carbon monoxide, krypton and helium purchased as spectroscopically pure gas (British Oxygen Co.) were used.

2.1.3. Dosing section

Gas, in any desired amount could be obtained by opening the bulb tap to the manometer (which was of wide bore to eliminate surface tension errors) with taps T_2 , T_4 and T_5 closed, the pressure was read on the manometer with a cathetometer, and tap T_1 closed. The volume $T_1 - T_2$ has been previously calibrated both by weighing mercury enclosed between them, and also by the gas expansion method. Helium gas was used for volume calibrations. The gas volume in between T_1 and T_2 could directly be introduced into the adsorption section, by lowering the cut-offs C_1 and C_2 . When

smaller doses were required, the full dose was admitted to C_3 only. The volume between T_1 and C_2 could be adjusted, depending on the size of the dose required, by raising the mercury in the small bulbs (numbered as SB_1 , SB_2 , SB_3 , SB_4 and SB_5). The big bulb (BB) could be included or excluded from the system by opening or closing the tap T_3 . A small dose could then be admitted to the adsorption section by raising the cut-off C_1 and lowering the cut-off C_2 .

2.1.4. Adsorption section

This section could be isolated from the main pumps by cut-off C_3 and from the gas dosing section by cut-off C_2 . The uptake of the gas on the film was followed by the change in the pressure, measured either by a Pirani or McLeod gauge. The McLeod gauge with a pressure range from 10^{-6} mm Hg to about 10^{-1} mm Hg was also used to calibrate the Pirani gauge. The two U-tube traps 1 and 2 fitted into narrow-neck thermos flasks, and so could be left overnight without any danger of liquid refrigerant evaporating completely. In fact after 16 hours the traps were found to be half filled. To permit a rapid change in temperature between 78°K and 273°K , a number of temperature baths were employed :

	<u>Refrigerant</u>	<u>Temperature</u>
1.	Boiling nitrogen	$78^\circ \pm 0.05^\circ\text{K}$
2.	Boiling oxygen	$90^\circ \pm 0.05^\circ\text{K}$
3.	Melting methyl cyclohexane	$147.0 \pm 1.5^\circ\text{K}$
4.	Melting toluene	$177.8 \pm 0.7^\circ\text{K}$

5. Carbon dioxide + alcohol mixtures $195 \pm 0.1^{\circ}\text{K}$
6. Melting chlorobenzene 227°K
7. Melting ice $273.2 \pm 0.1^{\circ}\text{K}$

2.2 Pirani Gauge

The Pirani head contained a ⁽³⁾ tungsten filament (0.01 mm diameter and about 150 ohms resistance) stretched between and spot welded to nickel clips approximately 15 cm apart which in turn were spot welded to the tungsten rods 1.5 mm in diameter. Care was taken to ensure that the tungsten wire was stretched uniformly and not twisted. Since the sensitivity of the Pirani gauge is proportional to the temperature difference between the wall and the wire its head was immersed in liquid nitrogen. The level of the refrigerant was always kept to a constant mark, which was well above the top of the filament. The Pirani head was protected from mercury vapours by the liquid nitrogen trap I. In the nitric oxide experiments the Pirani head was cooled in ice, and cool traps 1 and 2 were kept at 195°K .

The measuring circuit was a simple Wheatstone bridge, Fig.(2.4). A high stabilised voltage (about 280 volts) was supplied across the bridge, which was stepped down by high resistors in two of the ratio arms, consequently there was a constant voltage and virtually a constant current supply since the current drawn through the Pirani was almost negligible. The circuit of the constant voltage stabiliser is shown in Fig.(2.4). The ratio of the fixed arms of the bridge

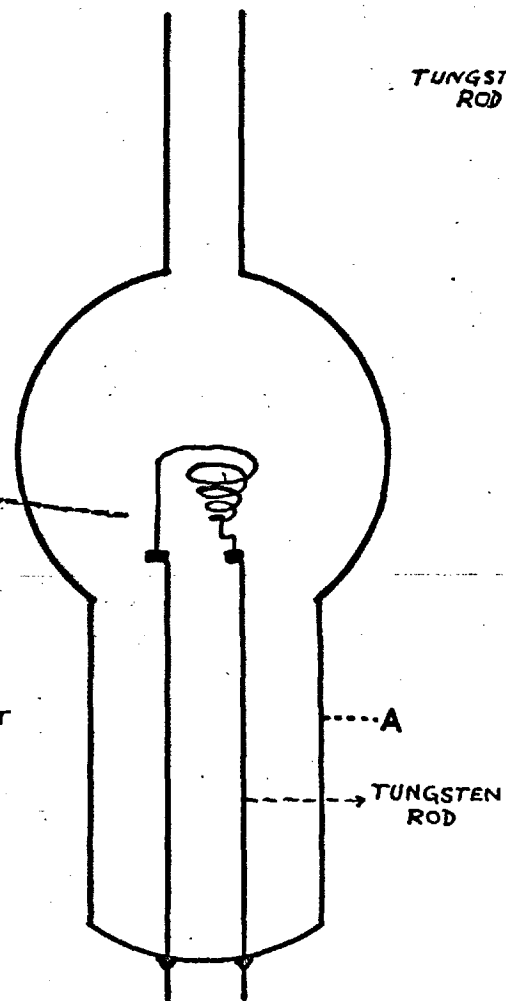
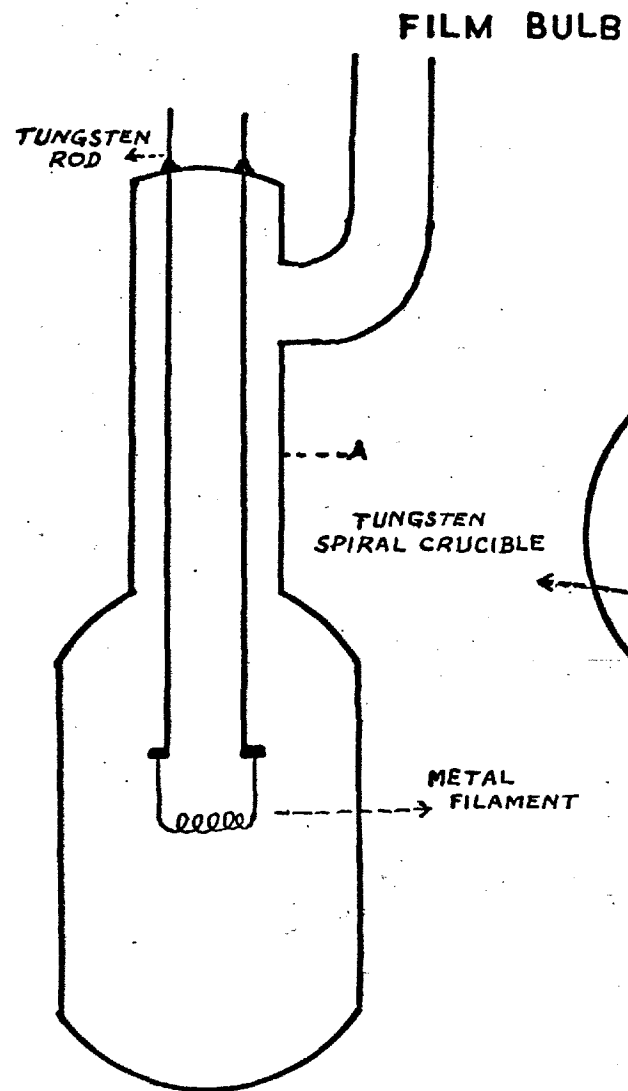


FIG 2.3.

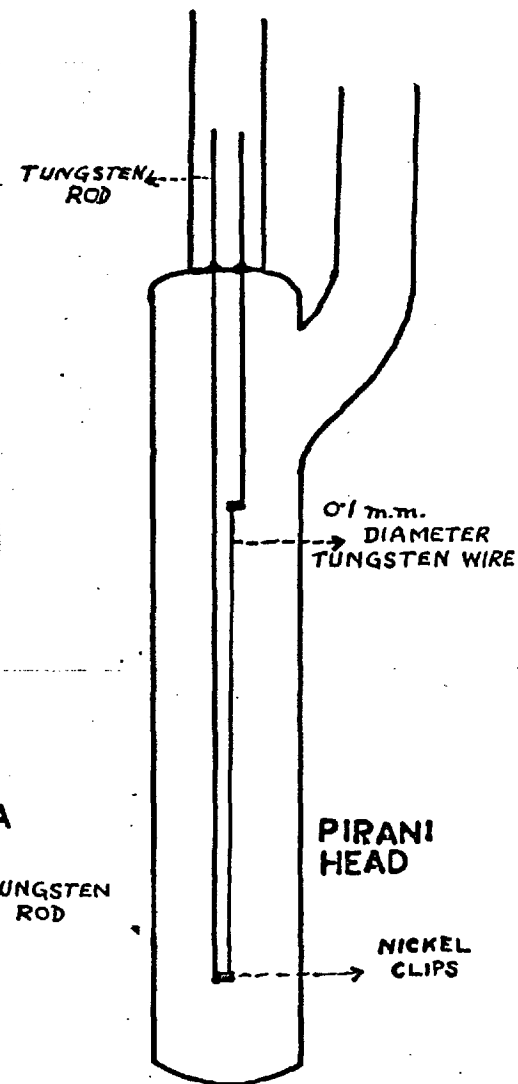
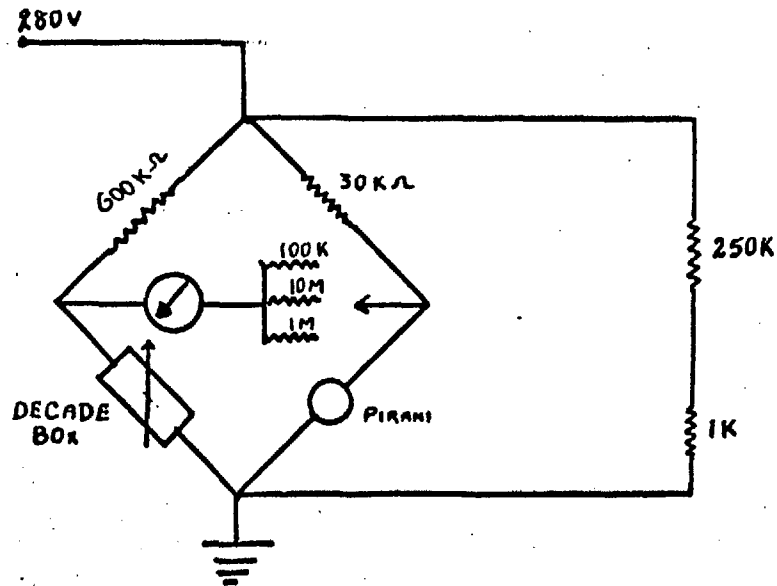


FIG 2.3.a.

PIRANI CIRCUIT.



VOLTAGE STABILIZER CIRCUIT

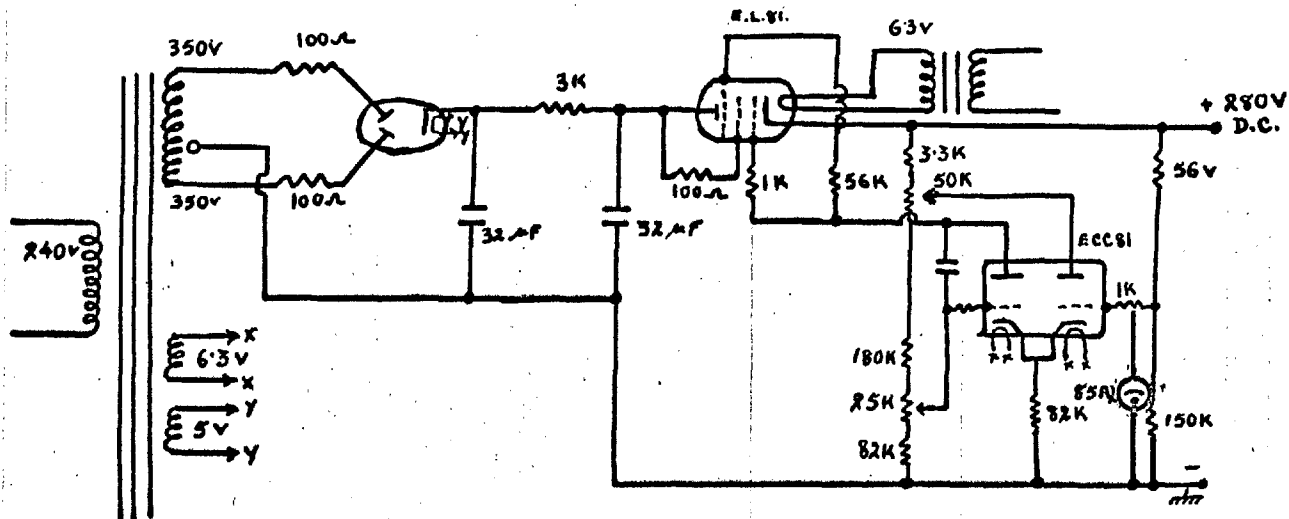


Fig. 2.4

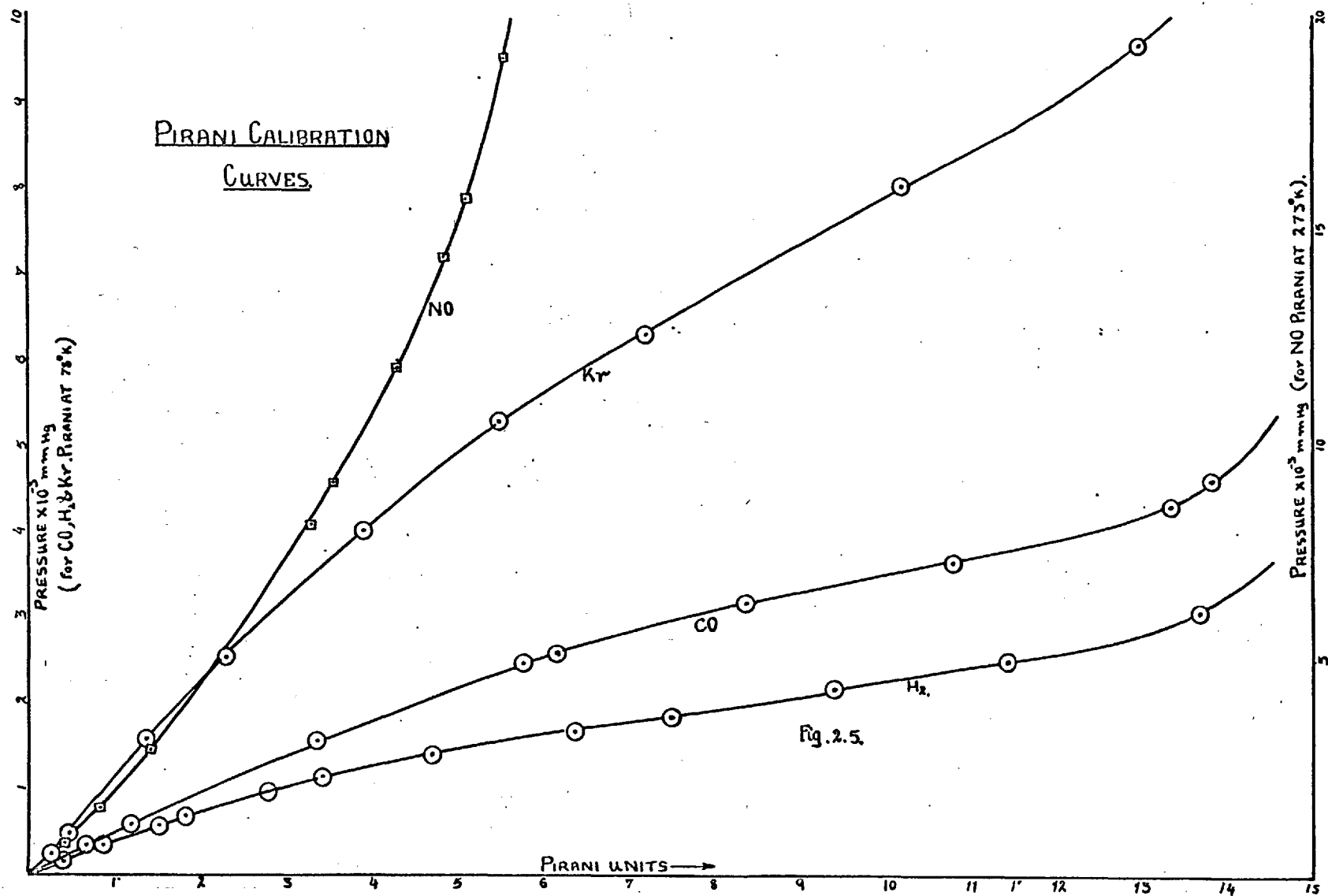
was 20 to 1; a Pye galvanometer type 7893/S sensitivity 210 mm/ μ A was found to be sufficiently sensitive for use in the measuring circuit.

The Pirani zero, R_0 , was the resistance of the filament at 10^{-7} mm Hg pressure and 78°K. Equilibrium was established in about 15 minutes after switching on the current supply. No fluctuations in the zero value were noticed during the experiments. A change in the zero value of about ± 10 ohms was found after 10 to 12 weeks, but that did not affect the calibrations, because change in resistance $\Delta R [= (R_0 - R)$ where R is the resistance at pressure P] is plotted against pressure. During every run sufficient McLeod gauge readings were taken to check the calibration. The sensitivity of the gauge decreased rapidly above 8×10^{-3} mm Hg; above this pressure all measurements were taken with the McLeod gauge. For low pressure the Pirani was extremely sensitive (1 ohm was equivalent to 10^{-6} mm Hg). The Pirani was calibrated for carbon monoxide, hydrogen and krypton at 78°K, and for nitric oxide gas at ice temperature (Fig.2.5).

For rate measurements the change in Pirani filament resistance with decrease in pressure was taken after every 30 seconds and the uptake of gas calculated. At higher pressures in the adsorption section there was a time lag of up to 3 minutes, before equilibrium was attained.

Film Bulb

Figure (2.3) shows the details of the film bulb used for most of the metal except chromium and manganese, it consists of



a cylindrical bulb 4 cm in diameter and about 6 cm long, with a narrow neck of 8 cm long and 2 cm in diameter. The 1 mm ground tungsten rod through the spiral seal carried 10 A current safely. To replace the filament, the bulb was cut at A, and the films were removed by dissolving them in dilute nitric acid (except chromium, which was dissolved in hot dilute hydrochloric acid). Then it was rinsed thoroughly with distilled water, and dried by hot dry air stream. A fresh weighed filament was then fitted into the nickel clips and the bulb was sealed.

Manganese and chromium were not available in the form of wire, so they were evaporated from a tungsten spiral as shown in Fig.(2.3). The tungsten wire 0.3 mm in diameter and bulb was 6 cm diameter, with the lower cylindrical part 5 cm long and 4 cm in diameter.

2.3 Calibration of McLeod Gauge and Volume Calibration of the Apparatus

$$\begin{aligned} \text{McLeod gauge : cross-section of the capillary} &= 0.7771 \text{ mm}^2 \\ \text{volume of bulb} &= 218.1 \text{ ml} \end{aligned}$$

The pressure is related to the position of mercury in the closed and open end of the capillaries, by the formula

$$P_{\text{mm}} = h_1 \times h_2 \times 0.3563 \times 10^{-4}$$

where h_1 (cm) is the difference in height between the mercury level and the top of the closed limb, and h_2 (cm) the difference in height between the level of the mercury in the closed and the open capillary. At 10^{-4} mm and below the pressure reproducibility was within 10%, and at higher pressure, within 2%. The following

volumes were calibrated with water in the usual way :

Trap 1 and 2 up to the mark L, 42 ml; film bulb 105 ml;
Pirani head 57 ml; bulb (BB) 554 ml;

volume between mark SB_0 and SB_1 = 53 ml;

volume between mark SB_0 and SB_2 = 118 ml;

volume between mark SB_0 and SB_3 = 180 ml;

volume between mark SB_0 and SB_4 = 242 ml;

volume between mark SB_0 and SB_5 = 310 ml;

volume between mark C_1 and C_3 = 654 ml;

volume between mark T_1 and C_3 = 1576 ml.

The water calibrated volumes were confirmed by gas expansion method.

Volume between T_1 and T_2 (mercury calibrated) = 2.136 ml.

When a volume of the gas between T_1 and T_2 at a pressure P_{mm} was expanded between T_1 and C_2 , the pressure P_2 in the dosing section could be varied between $P_1 \times 0.00232$ and $P_1 \times 0.038$ mm Hg depending on the position of mercury in the expansion column.

The different fractions with the position of mercury in expansion column were :

mercury at SB_5 and bulb (BB) included, $P_2 = P_1 \times .00232$

mercury at SB_4 and bulb (BB) included, $P_2 = P_1 \times .00251$

mercury at SB_3 and bulb (BB) included, $P_2 = P_1 \times .0027$

mercury at SB_2 and bulb (BB) included, $P_2 = P_1 \times .0029$

mercury at SB_1 and bulb (BB) included, $P_2 = P_1 \times .0032$

When the bulb (BB) was excluded by closing the tap T_3 , the following fractions could be obtained depending on the position of mercury in the expansion column.

$$\text{mercury at SB}_5 = P_1 \times 0.0058$$

$$\text{mercury at SB}_4 = P_1 \times 0.00717$$

$$\text{mercury at SB}_3 = P_1 \times 0.00905$$

$$\text{mercury at SB}_2 = P_1 \times 0.0123$$

$$\text{mercury at SB}_1 = P_1 \times 0.0196$$

$$\text{mercury at SB}_0 = P_1 \times 0.038$$

2.4. Outgassing of the Apparatus and Preparation of the Film

After fitting the fresh filament, and evacuating the apparatus to 10^{-6} mm Hg, the film bulb was outgassed at 410°C and the traps, connecting tubings and the Pirani head at 200°C . Outgassing lasted 12 hours, during which period all the glass tubing and McLeod gauge was flamed extensively. The filament was then outgassed by passing a current sufficient to maintain a temperature slightly below that at which evaporation commenced. To remove surface oxide from the filament and the nickel clips, the filament was heated for 15 minutes in hydrogen at 2 mm Hg. The hydrogen was then pumped out and the filament was further outgassed. The outgassing period (24 hours to 48 hours) varied from metal to metal. The glass apparatus was again outgassed for another 4 to 6 hours, with the filament faintly glowing. Finally heaters of the traps and the Pirani head were replaced

by liquid nitrogen baths; the temperature of the filament was increased to the outgassing temperature and maintained there for another 8 hours. When the outgassing rate became less than 10^{-6} mm per hour, a liquid nitrogen bath was put around the film bulb. The film was thrown by increasing the current very slowly, generally by 0.2 A every 15 minutes. All the films were thrown in about one and a half hours, except chromium which took 3 hours, thereby avoiding evaporation of tungsten. Halfway through the evaporation, the cut-off C_3 was closed. Generally no change in the Pirani reading was noticed, showing that filament had been completely outgassed.

The area of the film of a given weight, measured by the difference in weight of the filament before and after the experiment, depends mainly on the maximum temperature at which it was sintered. To avoid any change in area of the film during the adsorption measurements, the film was heated and cooled four times between the extreme temperatures of measurements, which were usually 273°K and 78°K .

2.5 Thermal Transpiration Corrections

It was necessary to apply thermal transpiration corrections to obtain the pressure in different parts of the apparatus which were at different temperatures. The necessity of such corrections has been demonstrated by Tompkins and Wheeler⁽⁴⁾, Porter⁽⁵⁾ and other workers^(6,7). Various theoretical approaches have been

made, of these that due to Liang^(8,9,10,11) is the most simple and easy to compute as compared with the derivation of Webers and Keelson⁽¹²⁾, which was later developed⁽¹³⁾.

More recently Bennett and Tompkins⁽¹⁴⁾ suggested some modifications to Liang's empirical equation.

$$\frac{P_1}{P_2} = \frac{\alpha_{H_2} (f \phi_g x)^2 + \beta_{H_2} (f \phi_g x) + R_m}{\alpha_{H_2} (f \phi_g x)^2 + \beta_{H_2} (f \phi_g x) + 1}$$

in which

$f = 1$ for tubing of int. diam. less than 1 cm

and $f = 1.22$ for diam. greater than 1 cm.

$x = P_2 d$ (P_2 mm Hg is pressure at room temperature,

d , diameter of tubing in mm).

$$R_m = \left(\frac{T_1}{T_2} \right)^{1/2} (T_1 \text{ and } T_2 \text{ in } ^\circ K)$$

$$\alpha_{H_2} = 3.70 (1.70 - 2.6 \times 10^{-3} \Delta T)$$

$$\beta_{H_2} = 7.88 (1 - R_m) \text{ for } R_m \leq 1$$

The calculated values for P_1/P_2 are plotted in Fig.(2.6) against $\log P_2$. The same correction curve was used for krypton without any loss of accuracy. For hydrogen however a further set of curves was drawn, Fig.(2.7).

2.6. CALCULATION OF RESULTS

Equilibrium measurements

To obtain an isotherm, the pressure of the gas in equilibrium with the film was obtained as the product of the measured

THERMOMOLECULAR FLOW CORRECTION FOR OBSERVED
 PRESSURES AT VARIOUS TEMPERATURES, FOR CO.

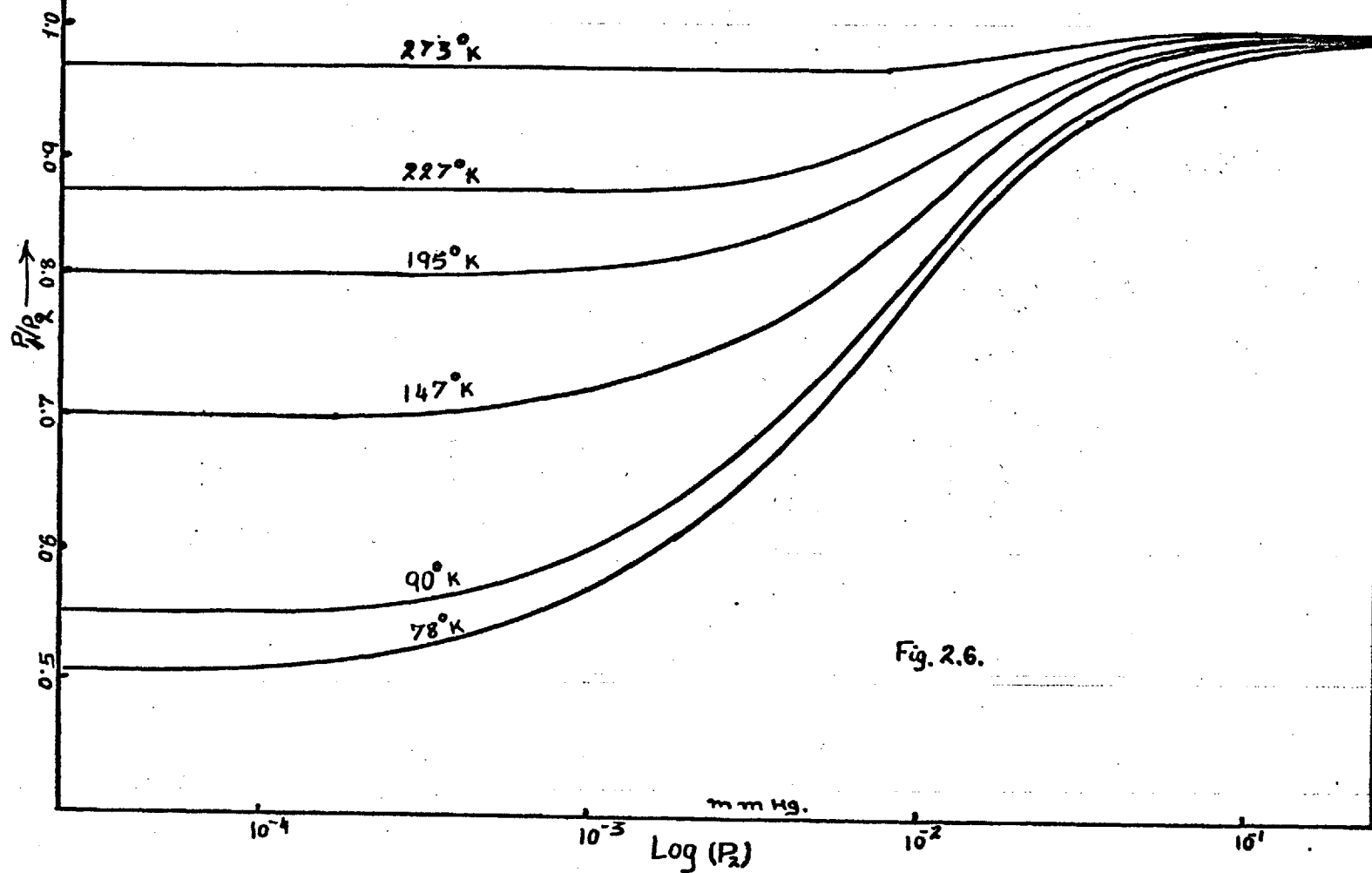


Fig. 2.6.

THERMOMOLECULAR FLOW CORRECTION FOR OBSERVED
 PRESSURES AT VARIOUS TEMPERATURES FOR H_2 .

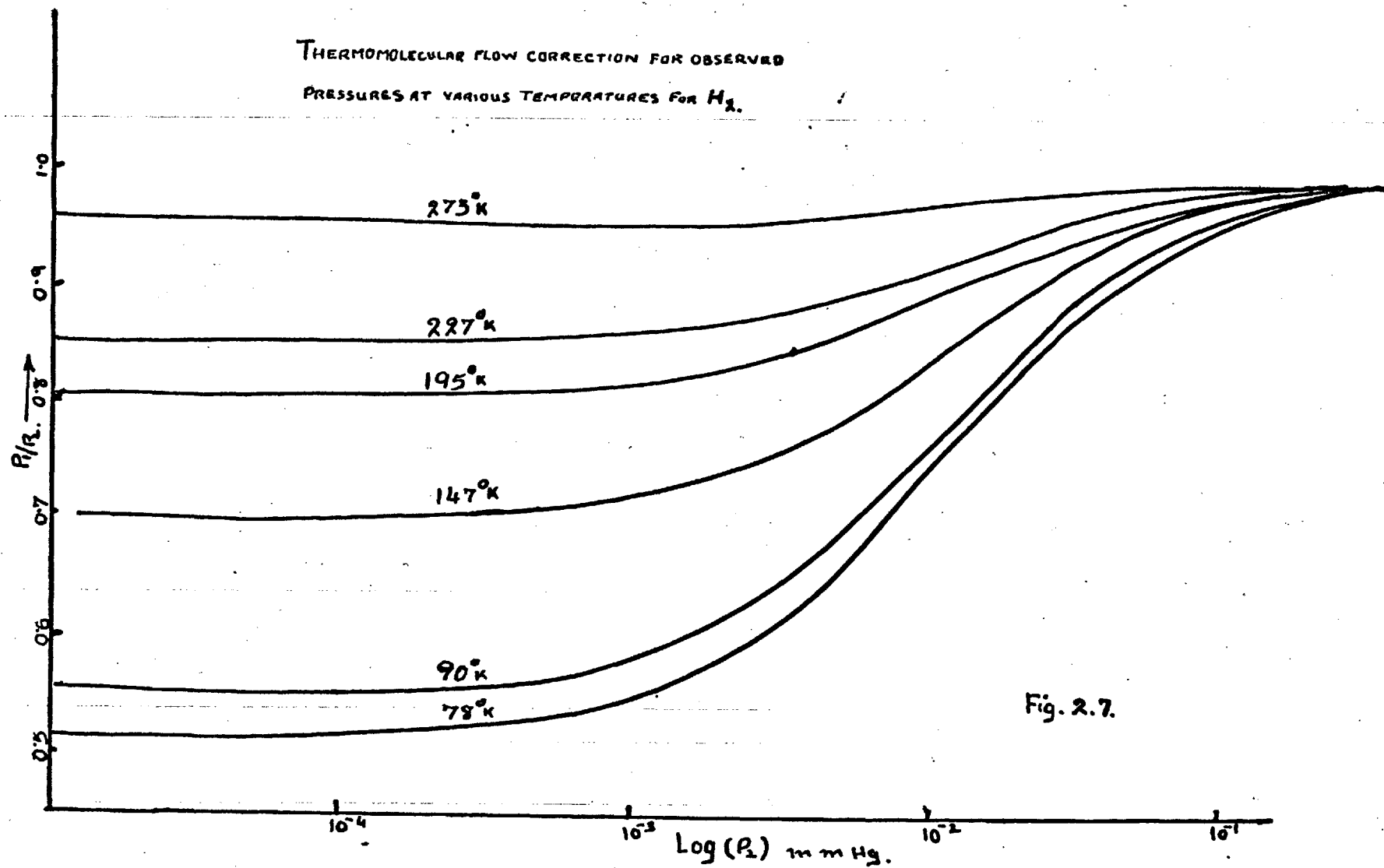


Fig. 2.7.

pressure P_2 (measured by the Pirani or McLeod gauge) times the factor $\frac{P_4}{P_2}$, which depends on the temperatures of the film bulb T_4 and the measured pressure P_2 . This factor is read directly from the figure (2.6) for carbon monoxide and krypton and from Fig.(2.7) for hydrogen.

The amount of the gas adsorbed by the film is given by the difference between the number of the moles of the gas added (n_a) and the number of the moles left in the gas phase (n_g) at the equilibrium pressure in the adsorption section. n_a , the number of moles added, was calculated, from the contents of the dosing section, temperature and the gas pressure, n_g was calculated as follows.

Since the level of the liquid nitrogen surrounding the cool traps 1 and 2 was kept approximately 3 cm below the top of the Dewar flasks, the temperature in this part of the tubing was always below room temperature. To calculate the number of moles of gas in the adsorption section it was found sufficiently accurate to consider the volume in the cold trap 1 and 2, 47.5 ml (instead of 42 ml) at 78°K. The total number of moles in gas phase n_g is calculated from

$$n_g = \frac{P_1 V_1}{R T_1} + \frac{P_2 V_2}{R T_2} + \frac{P_3 V_3}{R T_3} + \frac{P_4 V_4}{R T_4} \quad (2.1.)$$

where 1, 2, 3 and 4 refer to the cold traps, the part of the adsorption section at room temperature, the Pirani head and the

film bulb respectively. P_2 is the measured pressure. The values of P_1 , P_3 and P_4 can be calculated from Fig.(2.6). The equation (2.1) can be simplified to

$$\frac{R n_g}{P_2} = \frac{P_1}{P_2} \frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{P_3}{P_2} \left(\frac{V_3}{T_3} \right) + \frac{P_4}{P_2} \left(\frac{V_4}{T_4} \right) \quad (2.2.)$$

The number of the moles adsorbed were multiplied by 6.023×10^{23} to give the number of molecules adsorbed, then divided by the number of molecules of the gas required to form a monolayer (V_m), assuming that one molecule of the adsorbed gas was adsorbed on each available site (i.e. V/V_m or % coverage was plotted against P). The number of sites on each metal film was obtained by dividing the B.E.T. area of the film by the average area of the site. The number of sites depends on the crystal structure of the metal⁽¹⁵⁾ and was calculated with the help of the equation given below :

$$\text{No. of sites per sq.cm for f.c.c. metal} = \frac{1.91}{a^2} \times 10^{16} \quad (2.3.)$$

$$\text{No. of sites per sq.cm for b.c.c. metal} = \frac{1.35}{a^2} \times 10^{16} \quad (2.4.)$$

$$\text{No. of sites per sq.cm for l.c.p.} = \frac{2}{3} \left(\frac{1}{a^2 \sqrt{3}} + \frac{1}{ac} + \frac{1}{a \sqrt{3a^2 + 4c^2}} \right) \quad (2.4.)$$

The calculated values are given in Table 2.1..

Table 2.1

Metal	Crystal type	a	c	Sites/sq.cm x 10 ¹⁵
Copper	f.c.c.	3.61		1.47
Silver	f.c.c.	4.079		1.15
Gold	f.c.c.	4.070		1.15
Palladium	f.c.c.	3.873		1.27
Platinum	f.c.c.	3.91		1.25
Nickel	f.c.c.	3.52		1.54
Cobalt	f.c.c.	3.554		1.51
Titanium	h.c.p.	2.95	4.68	1.35
Chromium	b.c.c.			1.63
Manganese	b.c.c.	2.7		1.24

(Lattice parameters are taken from F. Seitz -

"Modern theory of solids", McGraw Hill, N.Y. (1940))

Heat of Adsorption

The Clausius Clapeyron equation

$$-\Delta H = 2.303 R \frac{\log_{10} P_2 - \log_{10} P_1}{\frac{1}{T_1} - \frac{1}{T_2}}$$

where R = gas constant

was used to calculate the isotheric heat of sorption between temperature T_1 and T_2 . This equation can only be used for

thermodynamically reversible process. Consequently it was necessary to prove that the required condition was fulfilled, i.e. as on warming the film from T_1 to T_2 the pressure changed from P_1 to P_2 ; for reversibility the pressure should return to P_1 on lowering the temperature to T_1 . In general this was found to be so.

Surface Area Measurements

The well known method of Brunauer, Emmett and Teller⁽¹⁶⁾ in its simplified form was used.

$$\frac{P}{V_o (P_o - P)} = \frac{1}{V_m C} + \frac{(C - 1) P}{V_m P_o} \quad (2.6.)$$

where P_o = saturated vapour pressure of krypton or nitrogen at the temperature at which adsorption was carried out

V_o = volume of krypton adsorbed at pressure P

V_m = volume of the gas required to form monolayer

C = constant, which depends on the nature of the adsorbent and adsorbate.

The underlying assumption of equation (2.6) has been questioned Hill⁽¹⁷⁾ but consistent results have been reported by Harkin and Jura⁽¹⁸⁾, when they compared the surface area of their anatase sample, determined by their absolute method and the B.E.T. knowing the area occupied by one molecule of the adsorbed gas, the area of the surface could be calculated, assuming close-packing.

The krypton adsorption at liquid nitrogen temperature was used for determination of the small area^(19,20,23). The cross-sectional area of a krypton molecule for use here has been determined by various workers^(19,24,25) on the bases of accepted cross-sectional area of nitrogen molecules as $16.2\text{\AA}^2$. The values of $\frac{\sigma_{\text{Kr}}}{\sigma_{\text{N}_2}}$ obtained varies from 1.09 to 1.33. Beebe, Beckwith and Honig have determined the area of an anotose sample obtained from Harkin and Jura⁽¹⁸⁾. The cross-sectional area of a krypton molecule determined by them was $19.5 \pm .4\text{\AA}^2$. In the present work this value was used.

Beebe⁽²⁴⁾ found that the temperature of liquid nitrogen varies from -195.5°C to 193.9°C and in this temperature range the vapour pressure of solid krypton varies from 1.8 mm to 2.62 mm. His extrapolated values for the liquid krypton ranged from 2.63 mm to 3.72 mm. A value of 1.73 mm has been determined by Kingston and Holmes⁽²⁶⁾. However due to the low pressure range in which surface has been determined in this work the value of P_0 has little effect⁽²⁷⁾ on the value of the area of the film. The value of V_m obtained by B.E.T. was always found to be higher than the value of V_m corresponding to the "Point B". In the present work B.E.T. area has been used.

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RESULTS

3.1. CARBON MONOXIDE ON METAL

3.1.1. Palladium

0.1 mm diameter spectroscopically pure palladium wire was used as evaporating source. The wire was wound on 0.3 mm diameter pure tungsten wire. The film was formed with the substrate at 78°K and sintered at 273°K. The first dose of carbon monoxide was admitted at 273°, and 90% of the gas was adsorbed within less than one minute, and the next few doses were completely adsorbed. The first measurable pressure was at 0.4 μ . At this stage the film was cooled to 227°K, more gas was taken up, but the equilibrium pressure was reached at this pressure much more quickly than at 273°K.

Isotherms were obtained at different temperatures and are shown in ~~table~~ *Fig* (3.1), the data being given in table (1). The isotherms are plotted as log p against θ , where θ is V/V_m ; V is volume of the carbon monoxide adsorbed at pressure p and V_m is the total number of the adsorption sites available on the surface. This number depends on the area of the film, which was determined by B.E.T. method, *fig*.(3.4).

The heats of adsorption were calculated using the Clausius Clapeyron equation. Errors in these heats can arise from three sources, (a) the non-attainment of the equilibrium pressure, (b) fluctuation in the temperature of the baths, (c) the measurements of the equilibrium pressure. As all the pressure readings were

taken when the Pirani reading had been constant for 10 minutes, it was safe to assume that (a) will have negligible effect. As the pressure was plotted as $\log p$, errors in equilibrium pressure readings will be more significant at low pressure, than at high pressure, and do have an effect on the calculated heats. An error of $\pm 2 \times 10^{-4}$ mmHg in pressure reading will result in an error of approximately $\pm 3 \times 10^{15}$ molecules adsorbed. Taking this together with possible errors in calibration of the dead space etc. the error in heats will be, at most, ± 1 k.cal./mole.

The heats of adsorption for carbon monoxide on palladium are plotted against θ , fig.(3.2). The heats fall smoothly with coverage from 7 k.cal./mole⁻¹ to 2.3 k.cal./mole⁻¹ as the coverage increases from 0.70 to 0.

The rate measurements at 90°K of carbon monoxide on palladium were also taken and are shown in fig.(3.3). It will be noted that there is a fast adsorption followed by a slow uptake.

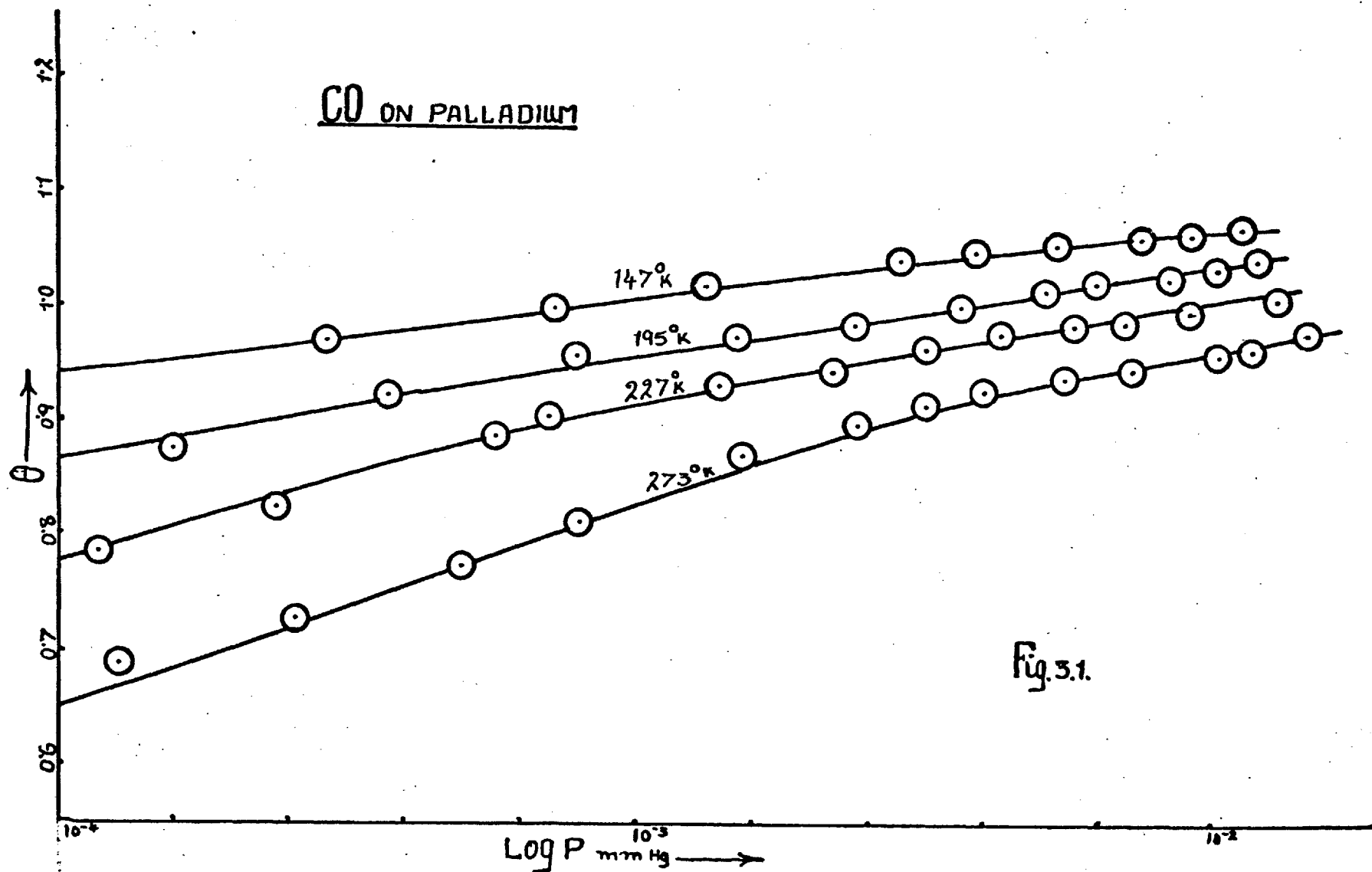


Fig. 3.1.

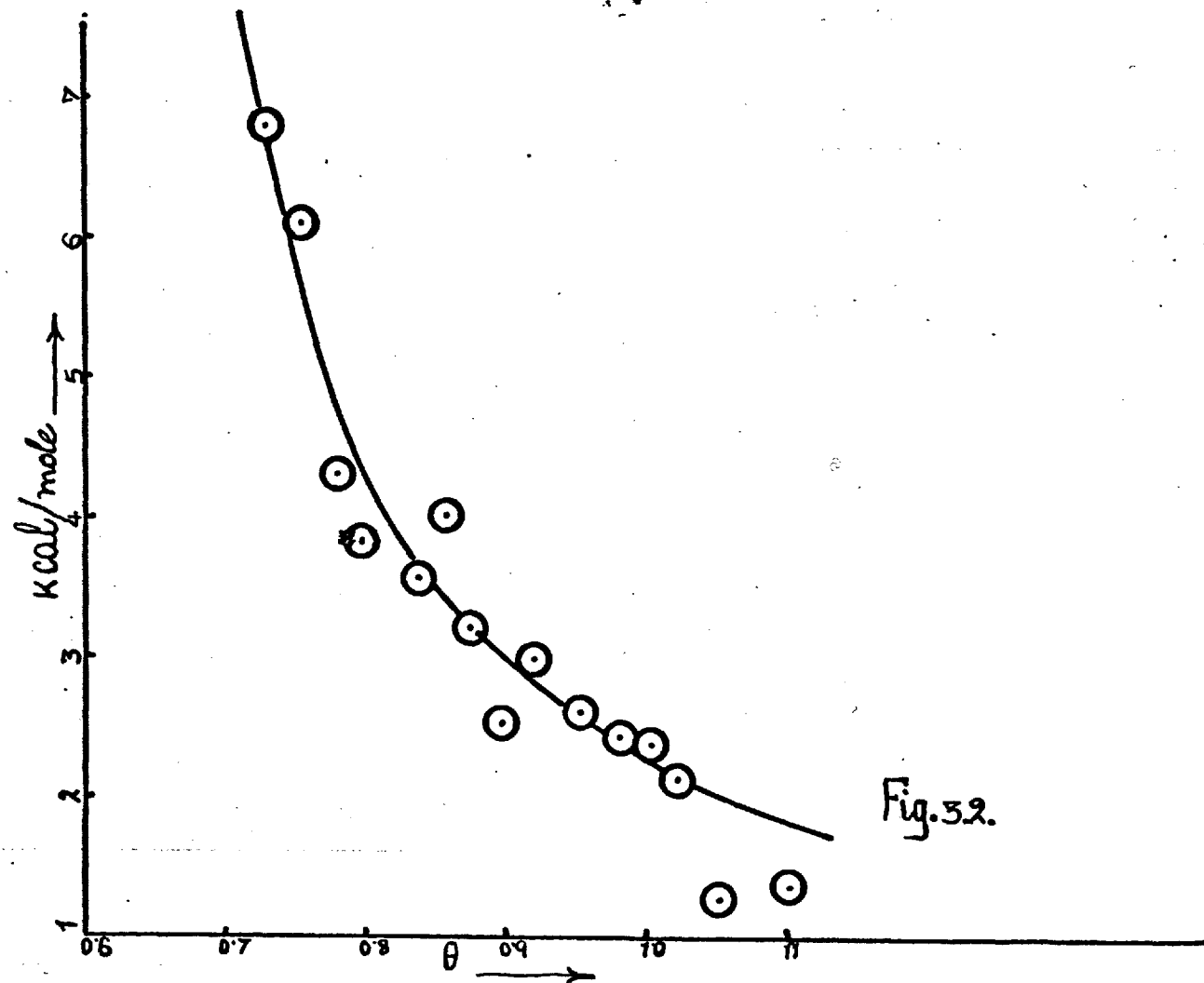


Fig. 32.

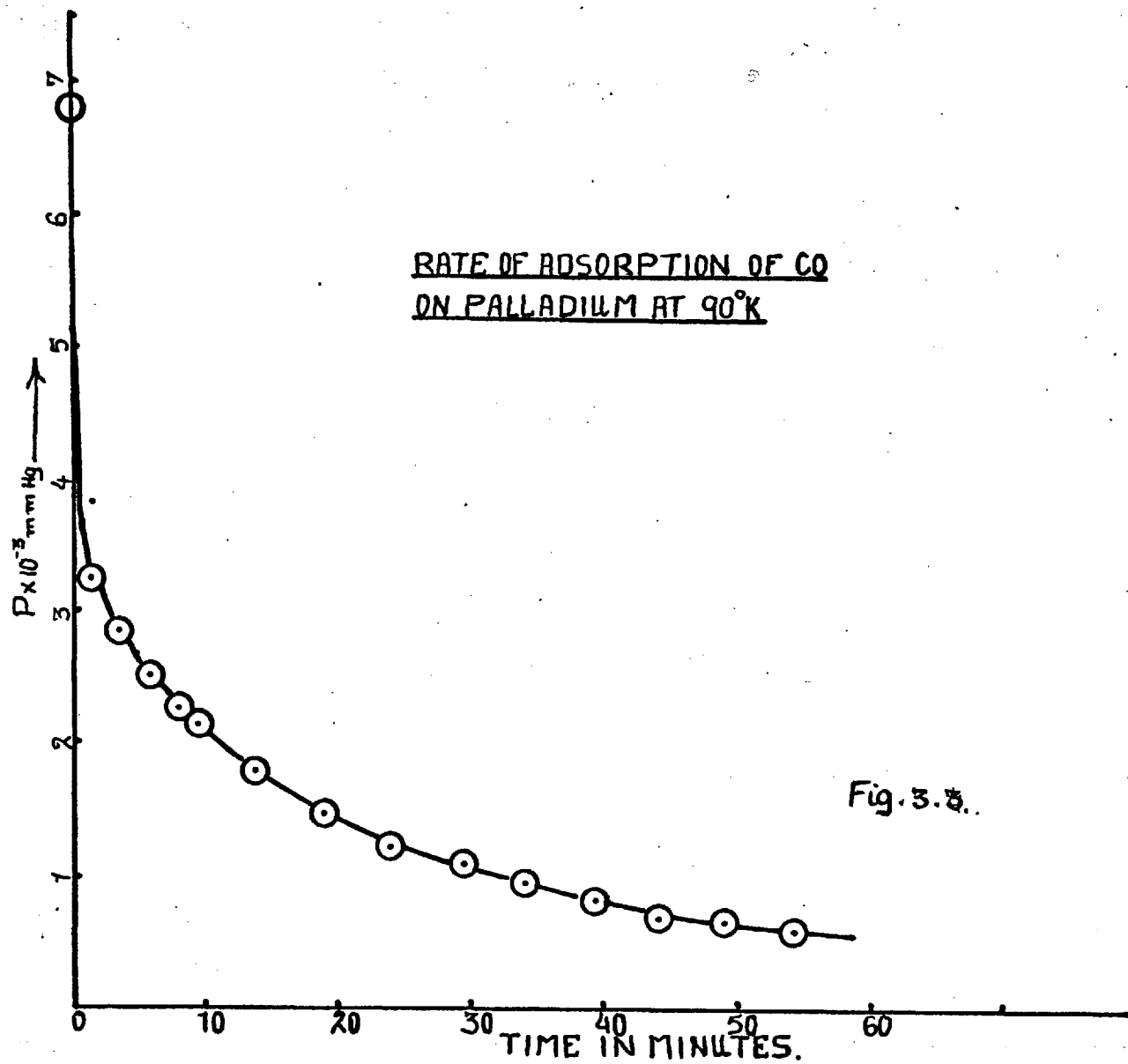


Fig. 3.8..

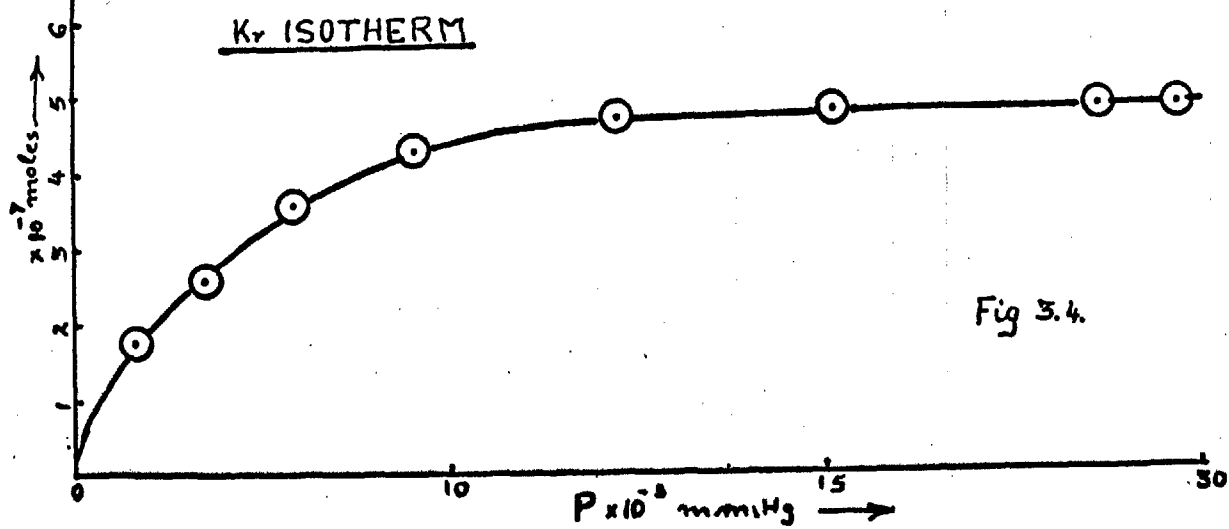
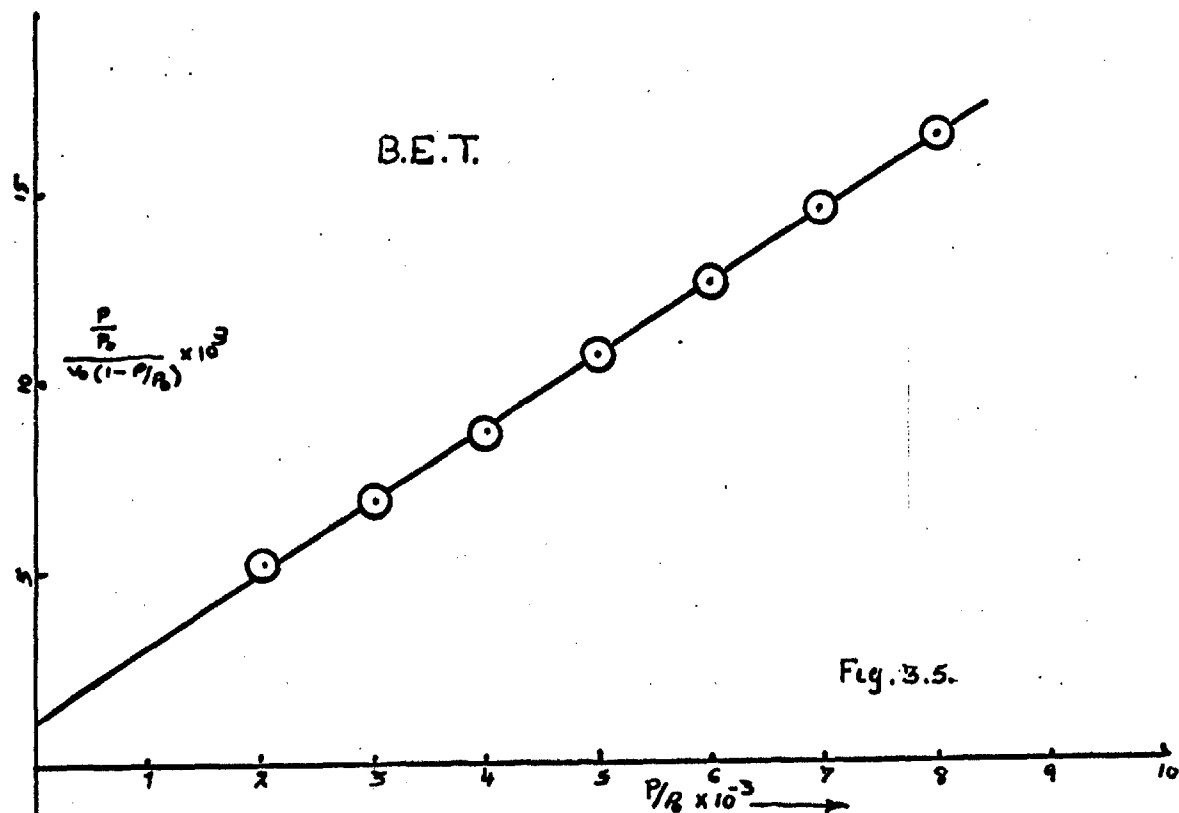


Table 3.1.Equilibrium adsorption of CO on Palladium

Weight of film = 35.3 mg

Area of film = 582.13 sq.cm

Total no. of sites = 7.392×10^{17}

273°K		227°K		195°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
1.103×10^{-4}	5.093	1.21×10^{-4}	5.81	1.601×10^{-4}	6.446
2.613×10^{-4}	5.389	2.412×10^{-4}	6.113	3.812×10^{-4}	6.808
5.001×10^{-4}	5.721	5.802×10^{-4}	6.564	7.981×10^{-4}	7.045
8.024×10^{-4}	6.024	7.202×10^{-4}	6.690	1.481×10^{-3}	7.20
1.521×10^{-3}	6.475	1.402×10^{-3}	6.867	2.413×10^{-3}	7.289
2.404×10^{-3}	6.653	3.115×10^{-3}	7.111	3.685×10^{-3}	7.407
3.151×10^{-3}	6.778	4.312×10^{-3}	7.229	5.213×10^{-3}	7.503
4.015×10^{-3}	6.867	5.814×10^{-3}	7.259	6.301×10^{-3}	7.532
5.512×10^{-3}	6.926	7.089×10^{-3}	7.289	8.611×10^{-3}	7.592
7.423×10^{-3}	6.985	9.203×10^{-3}	7.348	1.042×10^{-2}	7.651
8.400×10^{-3}	7.015	1.148×10^{-2}	7.407	1.212×10^{-2}	7.740
1.06×10^{-2}	7.082	1.321×10^{-2}	7.562		
1.232×10^{-2}	7.141				
1.452×10^{-2}	7.259				

Table 3.1 (continued)

147°K	
Pressure mm Hg	Molecules x 10 ¹⁸
6 x 10 ⁻⁵	6.565
3 x 10 ⁻⁴	7.167
7.4x10 ⁻⁴	7.378
1.34x10 ⁻³	7.529
2.9x10 ⁻³	7.679
3.9x10 ⁻³	7.770
5.4x10 ⁻³	7.800
7.7x10 ⁻³	7.830
9.3x10 ⁻³	7.86
1.12x10 ⁻²	7.89

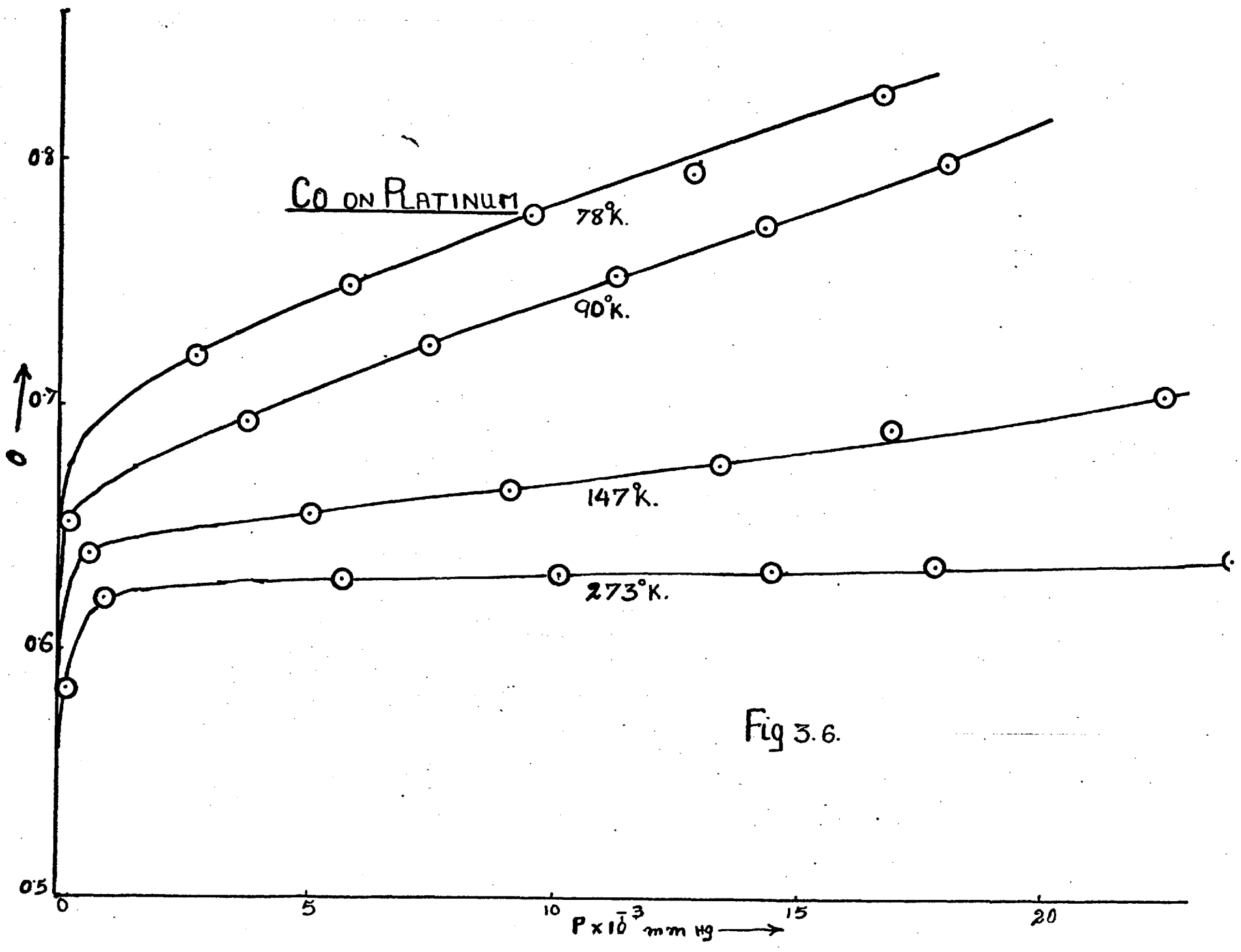
3.1.2. Platinum

The film was prepared in the same way as that of palladium and was sintered at 273°K . The first dose of carbon monoxide was completely adsorbed at a fast rate (within less than 30 seconds). Adsorption equilibrium on platinum films at 273°K was always attained within three or four minutes, so it was not possible to carry out any rate measurement at this stage. However, rate measurements were taken at different temperatures (after pumping out the gas at 273°K) at the end of the run. The isotherms at 273°K turn very sharply at 0.62 θ , and become practically flat, which show that no more gas is taken up by the film at this temperature. A very small amount of gas was adsorbed on lowering the temperature. Thus the difference between the amount of gas adsorbed at 273° , 227° and 195°K was so small that it was difficult to separate the isotherms on these temperatures, fig.(3.6). The isotherm at 147° , 90° and 78°K show an upward trend with increasing coverage.

Heats of adsorption have been calculated for different values of θ , and are plotted in fig.(3.7). The B.E.T. plot is shown in fig.(3.9).

After determining the area of the film, the krypton was pumped out at 273° for two hours, and then a big dose of carbon monoxide was introduced in the adsorption section, and the rate measurements were taken at 273°K . About 80% of the adsorbable

gas was taken up by the film in one minute; this was followed by a slow adsorption and equilibrium was established after 60 minutes, fig.(3.8). When the film was cooled to 78°K , 95% of the CO was adsorbed in one minute and the equilibrium was attained in five minutes.



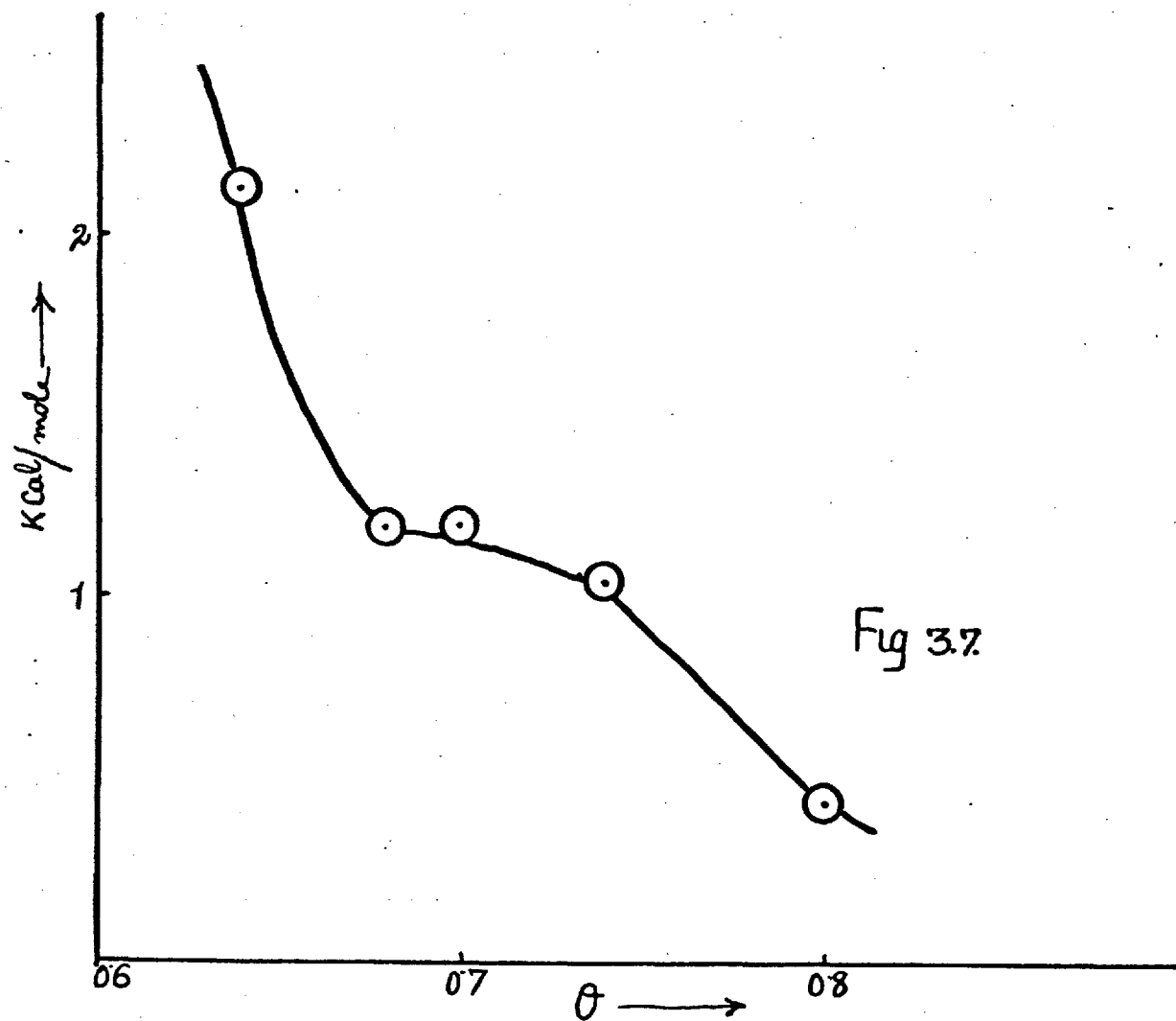
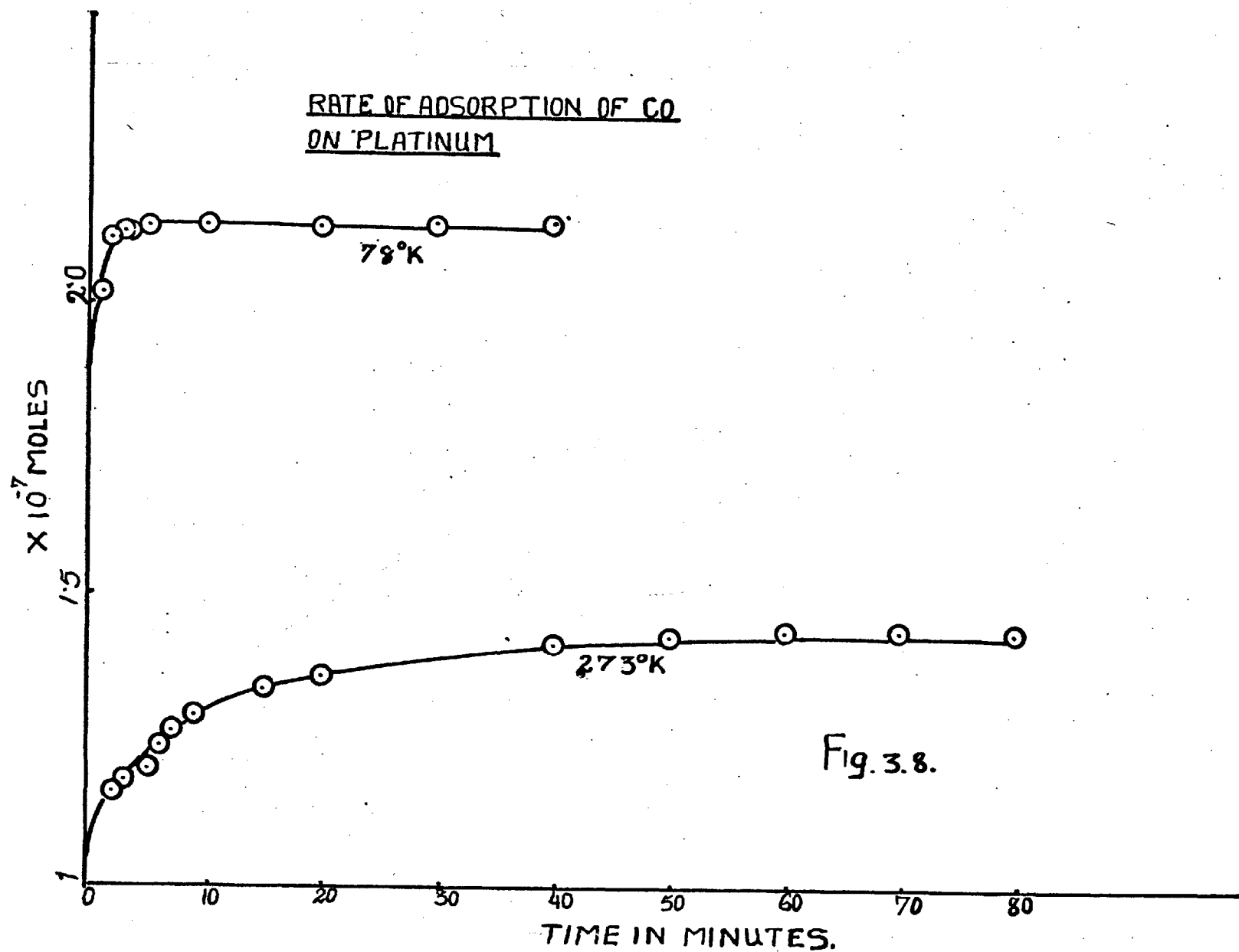


Fig 3.7



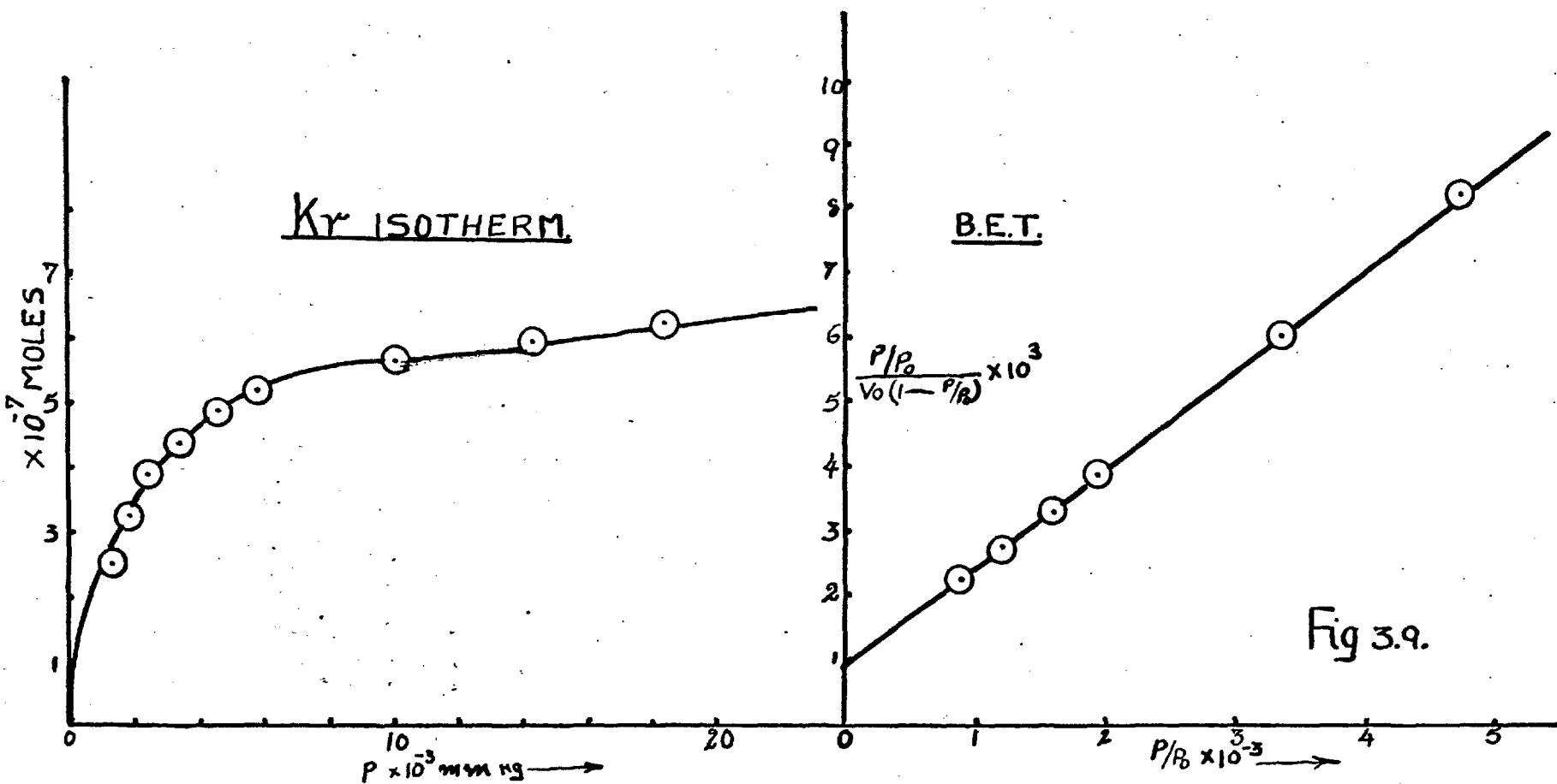


Table 3.2

Equilibrium adsorption of CO on Platinum

Weight of the film = 29.8 mg

Area of film = 793.1 sq. cm

No. of sites = 9.121×10^{17}

273°K		147°K	
Pressure mm Hg	Molecules $\times 10^{17}$	Pressure mm Hg	Molecules $\times 10^{17}$
1.82×10^{-4}	5.327	5.66×10^{-4}	5.847
8.66×10^{-4}	5.682	5.08×10^{-3}	5.965
5.71×10^{-3}	5.755	9.2×10^{-3}	6.093
1.02×10^{-2}	5.764	1.34×10^{-2}	6.175
1.45×10^{-2}	5.764	1.69×10^{-2}	6.522
1.78×10^{-2}	5.965	2.25×10^{-2}	6.540
2.42×10^{-2}	5.701		
90°K		78°K	
1.79×10^{-4}	5.892	2.86×10^{-3}	6.567
3.78×10^{-3}	6.323	5.96×10^{-3}	6.841
7.5×10^{-3}	6.622	9.65×10^{-3}	7.114
1.12×10^{-2}	6.905	1.29×10^{-2}	7.260
1.44×10^{-2}	7.06	1.67×10^{-2}	7.570
1.81×10^{-2}	7.324		

3.1.3. Titanium

The film was produced by passing current through the spectroscopically pure titanium wire. Before introducing the first dose of carbon monoxide, the film was sintered at 273°K as described previously. A large amount of gas was adsorbed, the first four doses were taken up within one minute. With increasing adsorption, the rate decreases with increases of coverage. The first measurable pressure at 273°K was at 0.78 θ . The isotherms at different temperatures were obtained in the usual way, fig.(3.10). Isotherms of all temperatures show an upward trend at higher pressure. All the point on the isotherms can be retraced both on increasing and decreasing the temperature, the adsorption was reversible.

Heats of adsorption were calculated at equal intervals of the amount adsorbed and the results are plotted against θ , fig.(3.11). The heat of adsorption at 0.83 θ is 7.5 K.cal., mole⁻¹ and decreases to about 2.2 k.cal.mole⁻¹ at θ equals one, after which there is a rapid decrease, and at θ value 1.15, the heat of adsorption is ~ 100 cal.mole⁻¹.

The rate of adsorption of carbon monoxide on titanium was determined at 273°K and 227°K , fig.(3.12), the arrow shows the position at approximately 0.8 θ where the dose was added. The uptake of the gas was rather slow, only 33% being adsorbed in one minute. At lower temperatures, however, the equilibrium was reached in five minutes. The area of the film at the end of the run was determined by B.E.T. fig.(3.13).

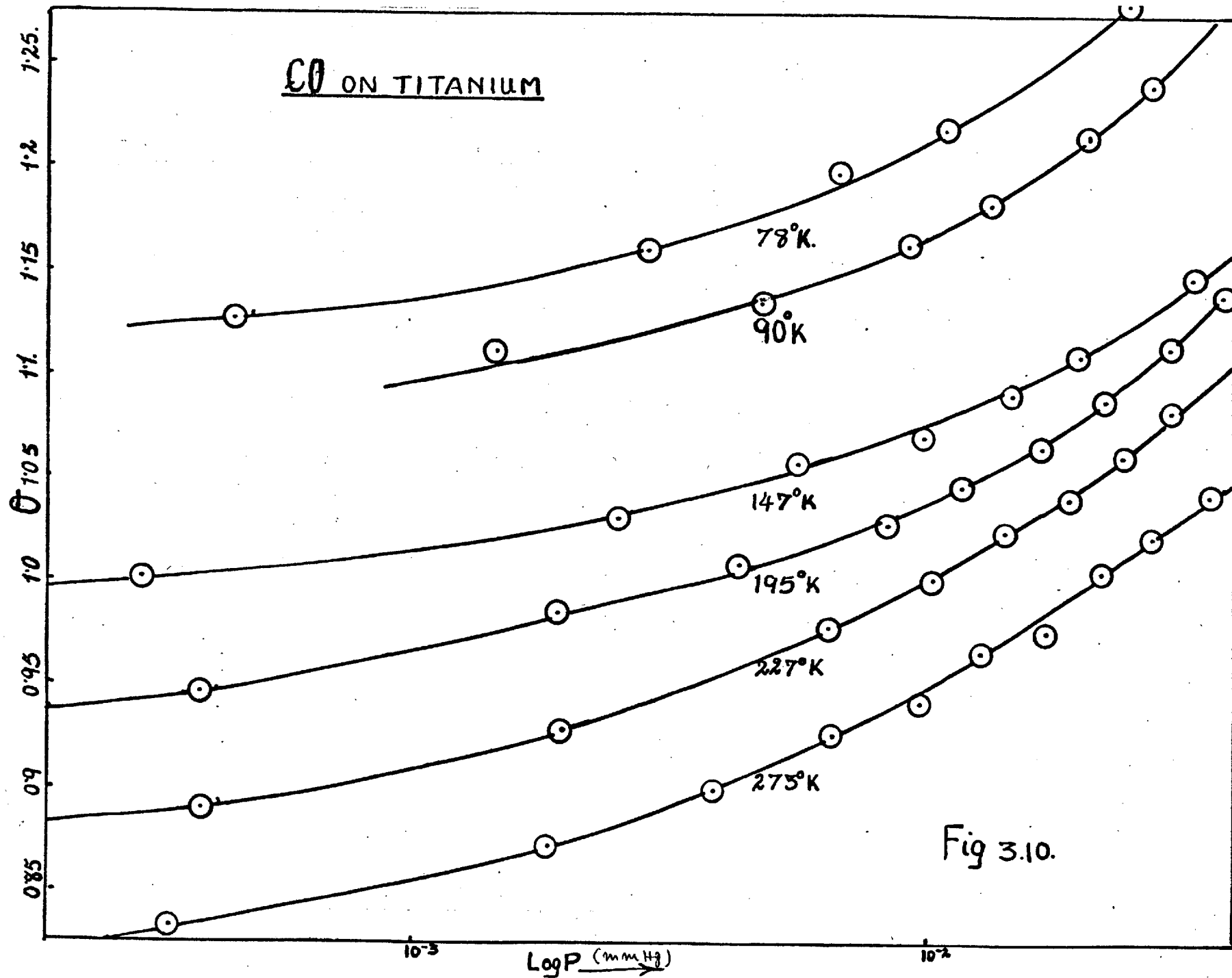


Fig 3.10.

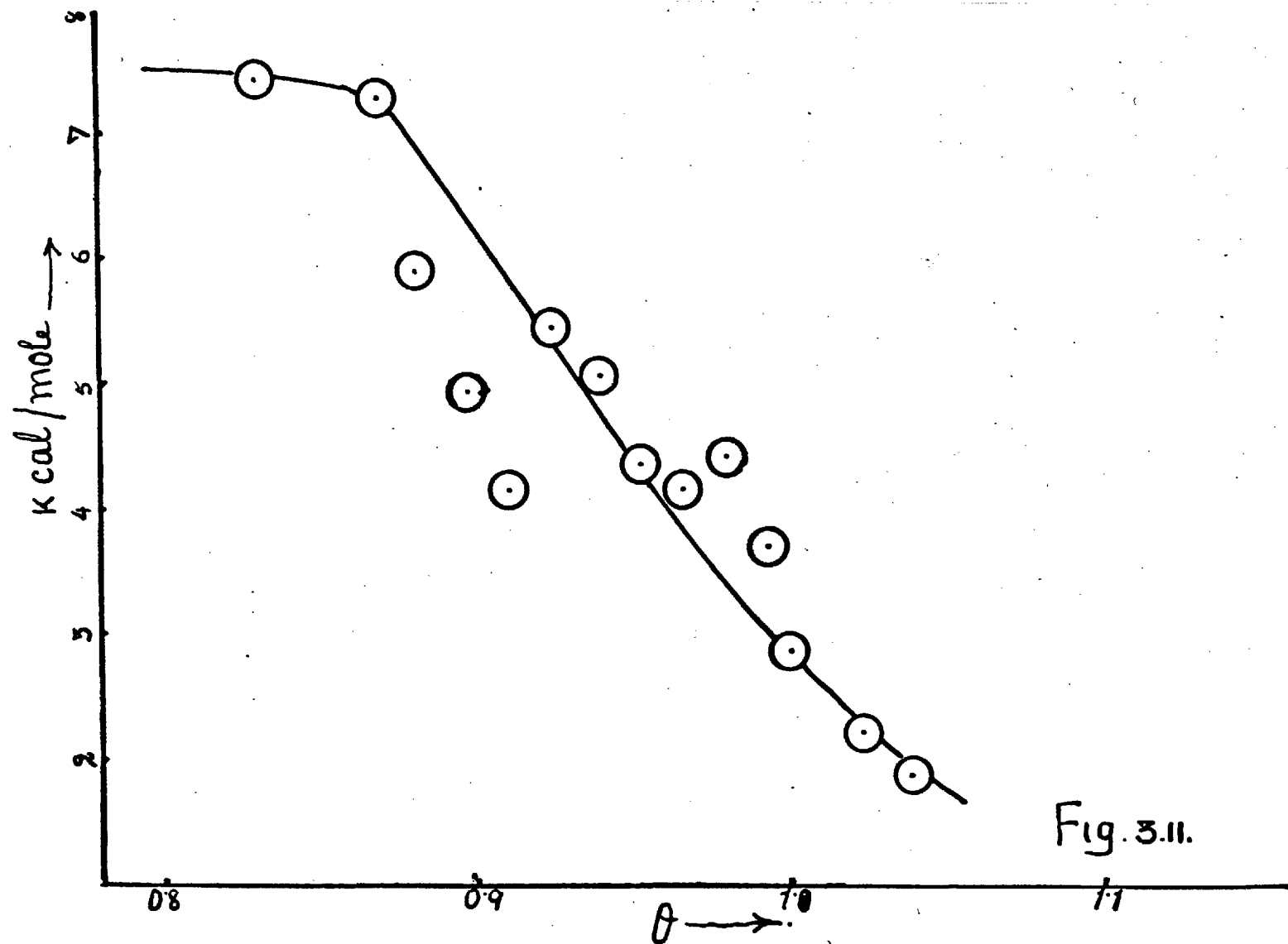


Fig. 3.11.

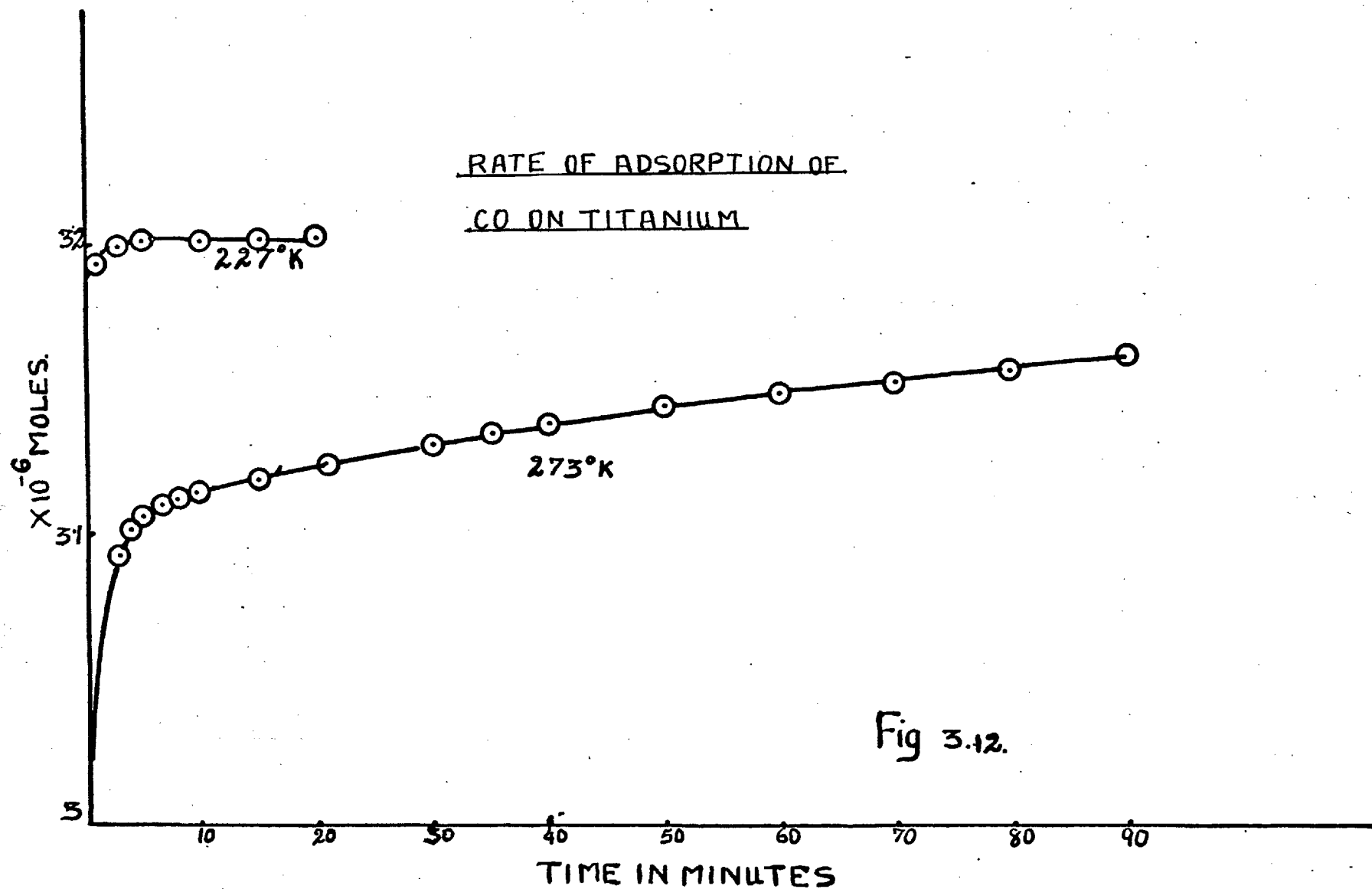


Fig 3.12.

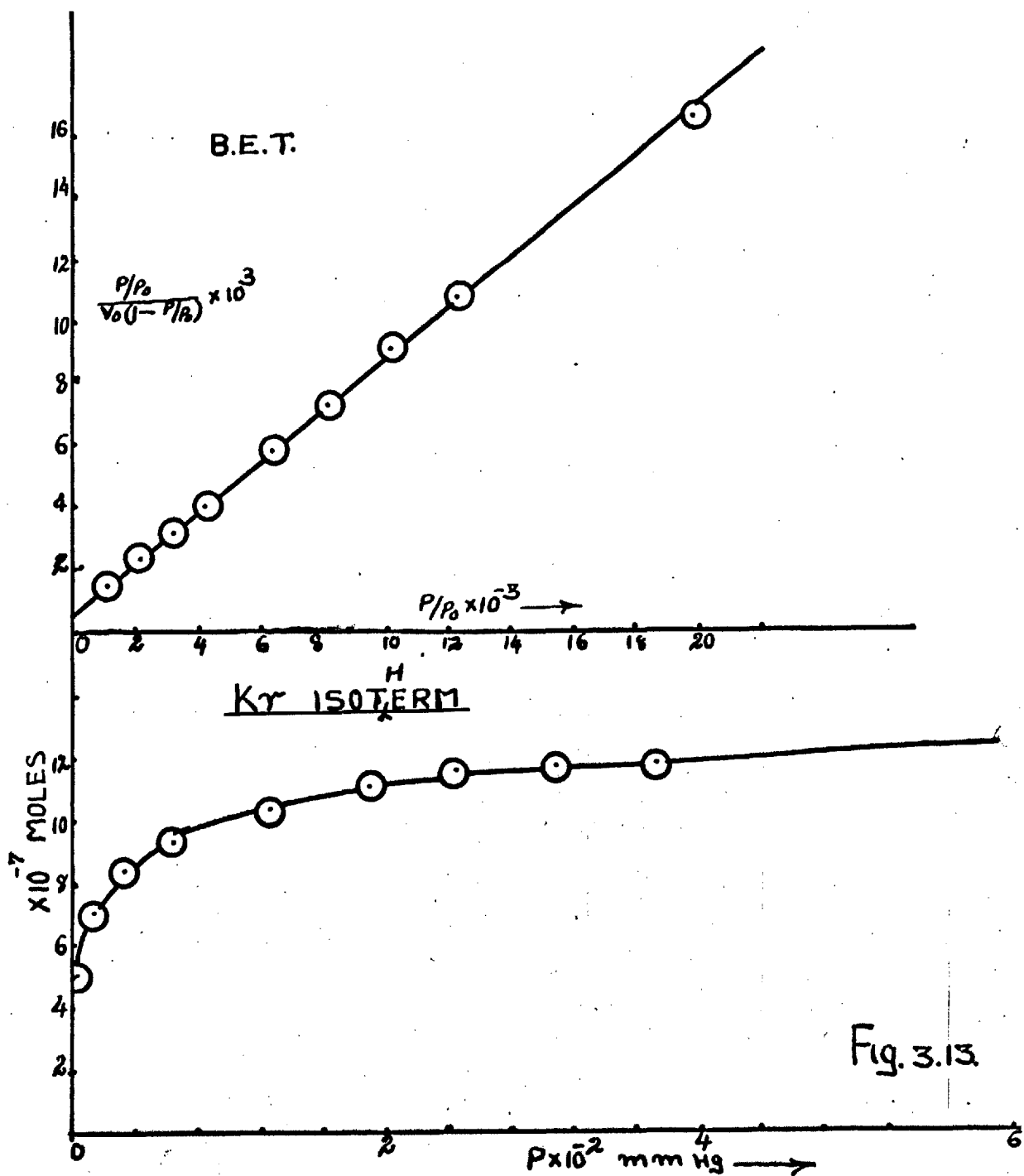


Fig. 3.13.

Table 3.3Equilibrium adsorption of CO on Titanium

Weight of the film = 15.2 mg

Area of the film = 1616.29 sq.cm

No. of sites = 2.182×10^{18}

273°K		227°K		195°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
3.44×10^{-4}	1.816	3.93×10^{-4}	1.941	4.115×10^{-4}	2.054
1.81×10^{-3}	1.905	1.97×10^{-3}	2.025	1.91×10^{-3}	2.148
3.96×10^{-3}	1.971	5.1×10^{-3}	2.063	4.29×10^{-3}	2.201
6.54×10^{-3}	2.022	6.58×10^{-3}	2.141	8.36×10^{-3}	2.234
9.48×10^{-3}	2.054	1.04×10^{-2}	2.160	1.18×10^{-2}	2.280
1.31×10^{-2}	2.106	1.44×10^{-2}	2.206	1.68×10^{-2}	2.333
1.72×10^{-2}	2.128	1.92×10^{-2}	2.266	2.21×10^{-2}	2.373
2.2×10^{-2}	2.193	2.42×10^{-2}	2.319	3.05×10^{-2}	2.428
2.75×10^{-2}	2.232			3.86×10^{-2}	2.483
3.66×10^{-2}	2.277				
4.53×10^{-2}	2.323				

Table 3.3 continued

147°K		90°K		78°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
3.05×10^{-4}	2.189	1.47×10^{-3}	2.430	4.61×10^{-4}	2.458
2.55×10^{-3}	2.248	4.79×10^{-3}	2.477	2.91×10^{-3}	2.53
5.73×10^{-3}	2.308	9.14×10^{-3}	2.539	6.8×10^{-3}	2.616
9.77×10^{-3}	2.333	1.37×10^{-2}	2.584	1.12×10^{-2}	2.661
1.48×10^{-2}	2.384	2.06×10^{-2}	2.650	2.46×10^{-2}	2.795
1.95×10^{-2}	2.422	2.77×10^{-2}	2.709		
3.31×10^{-2}	2.504				

3.1.4. Chromium

The chromium metal was supplied by Johnson Matthey & Company in the form of pellets. The film was thrown by heating the pellet in a tungsten spiral made from 0.3 mm diameter wire. After outgassing the spiral and pellet over night, these were heated to approximately 1000°C in hydrogen at 1 mm Hg pressure for one hour, to reduce the surface oxide on the pellet. The current never exceeded 7A because tungsten starts to evaporate between 8.5 - 9A. The chromium film was deposited at 78°K , very slowly in three hours, and sintered at 273°K in the usual way.

Isotherms were carried out at different temperatures, fig.(3.14). The isotherms bend slightly upward at higher pressure. Comparatively large amounts of carbon monoxide were adsorbed by chromium. Thus the twelve doses at 273°K were completely adsorbed, the rate of adsorption at this stage being very fast, so that no rate measurements could be made. The rate curve at different low temperatures of different doses are given in fig.(3.16); a fast sorption is followed by a short slow process, the equilibrium being reached within 30 minutes, but at 273°K a fast process is followed by a long slow adsorption process, and at low coverage the attainment of equilibrium required 90 minutes.

The heat of adsorption decreases with coverage, at .5020 the heat of adsorption was 13.2 k.cal.mole and are plotted in fig.(3.15). The area of film was determined by B.E.T. method, fig.(3.17).

CO ON CHROMIUM

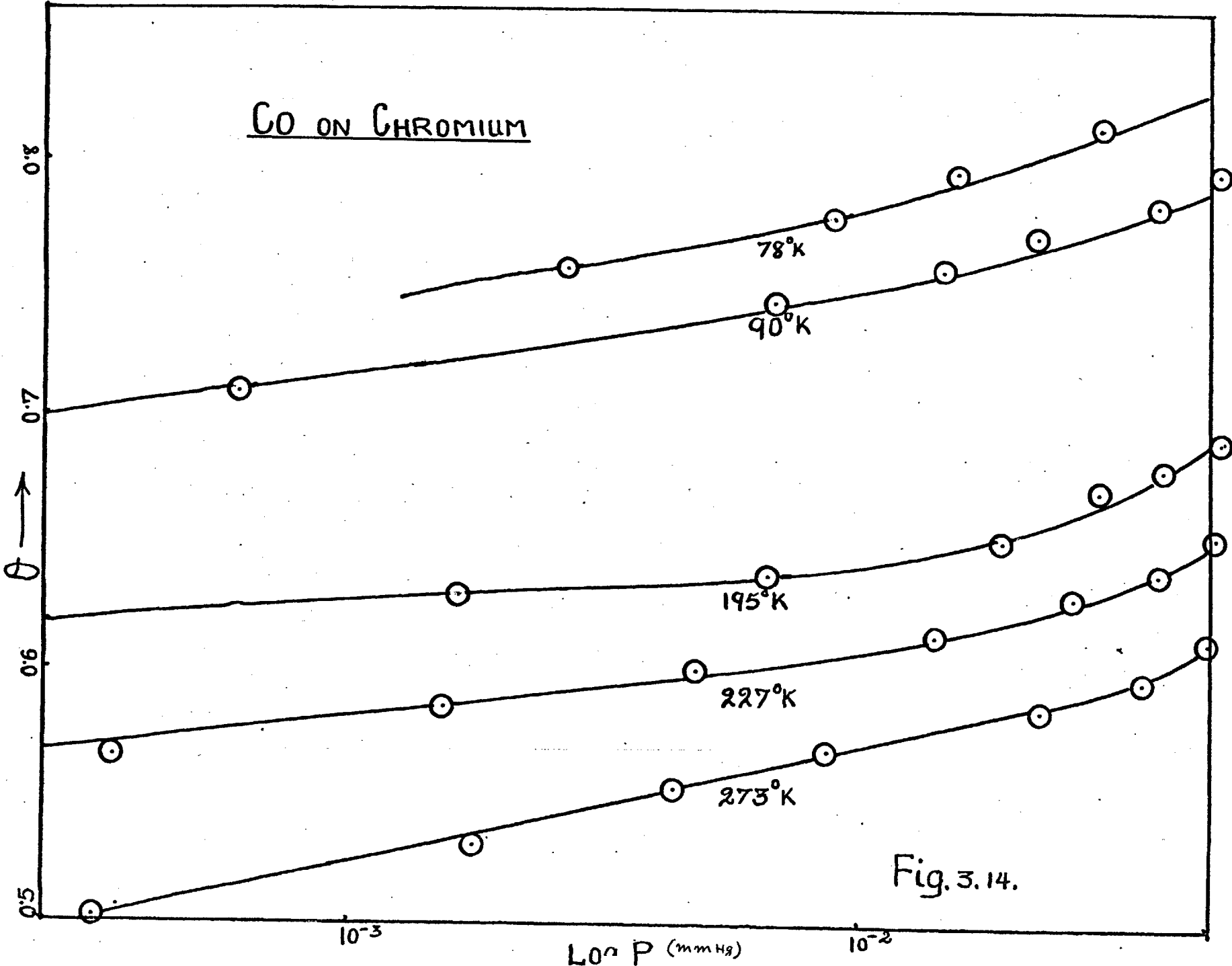


Fig. 3.14.

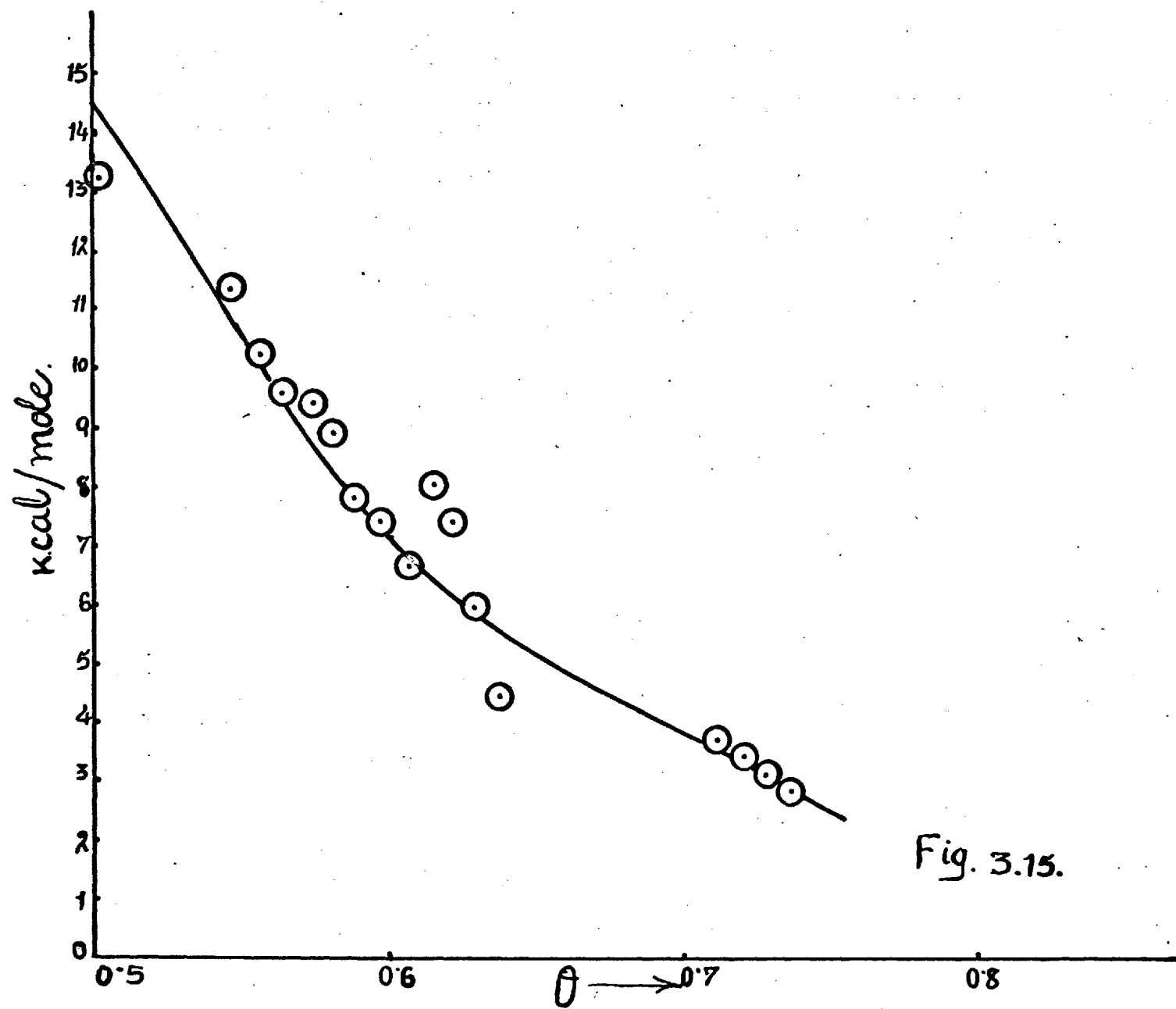


Fig. 3.15.

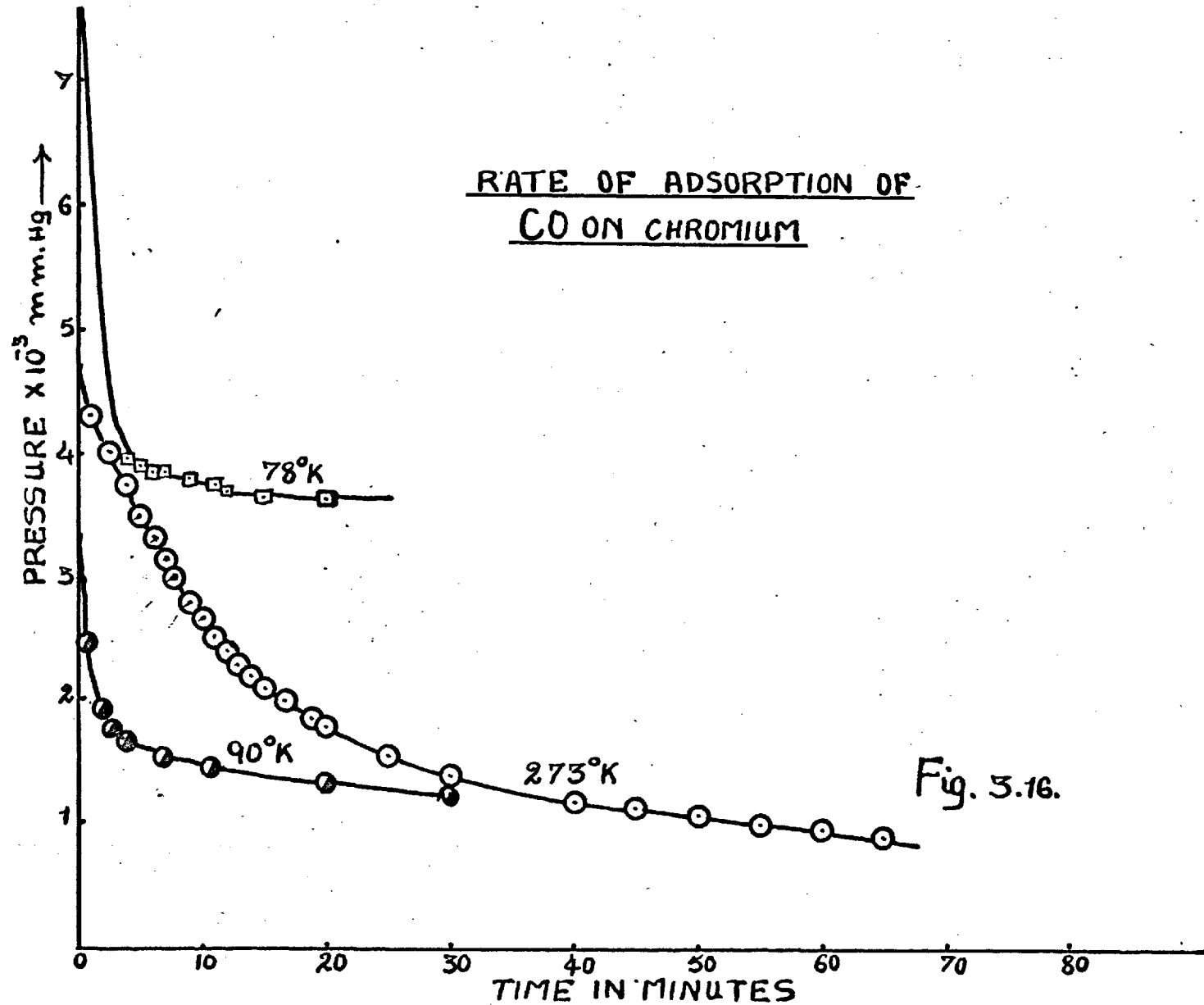


Fig. 3.16.

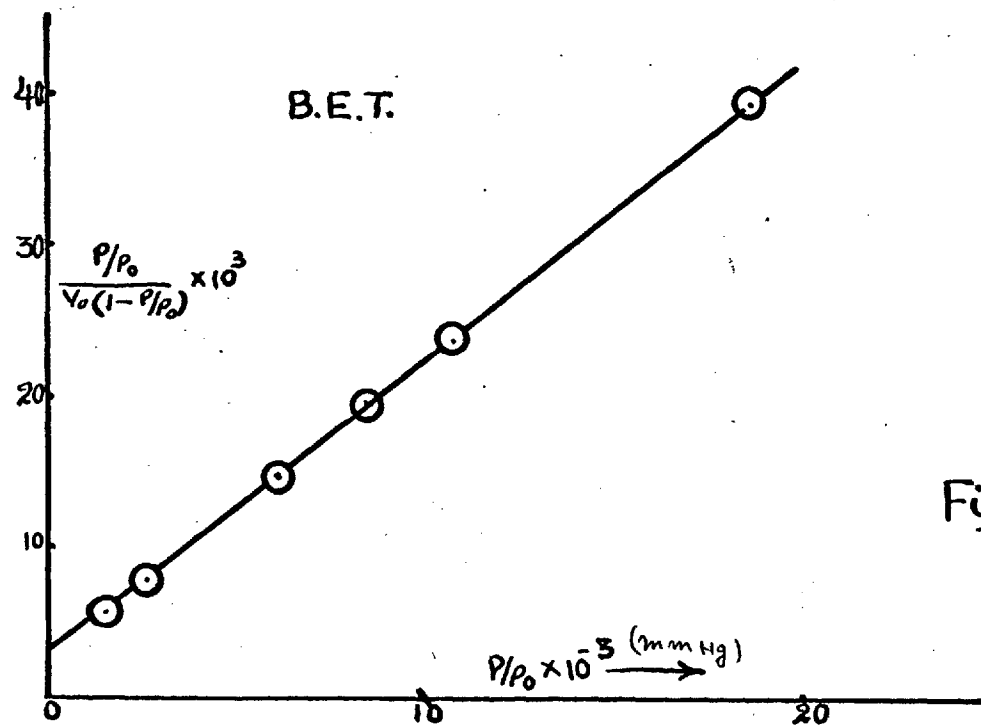
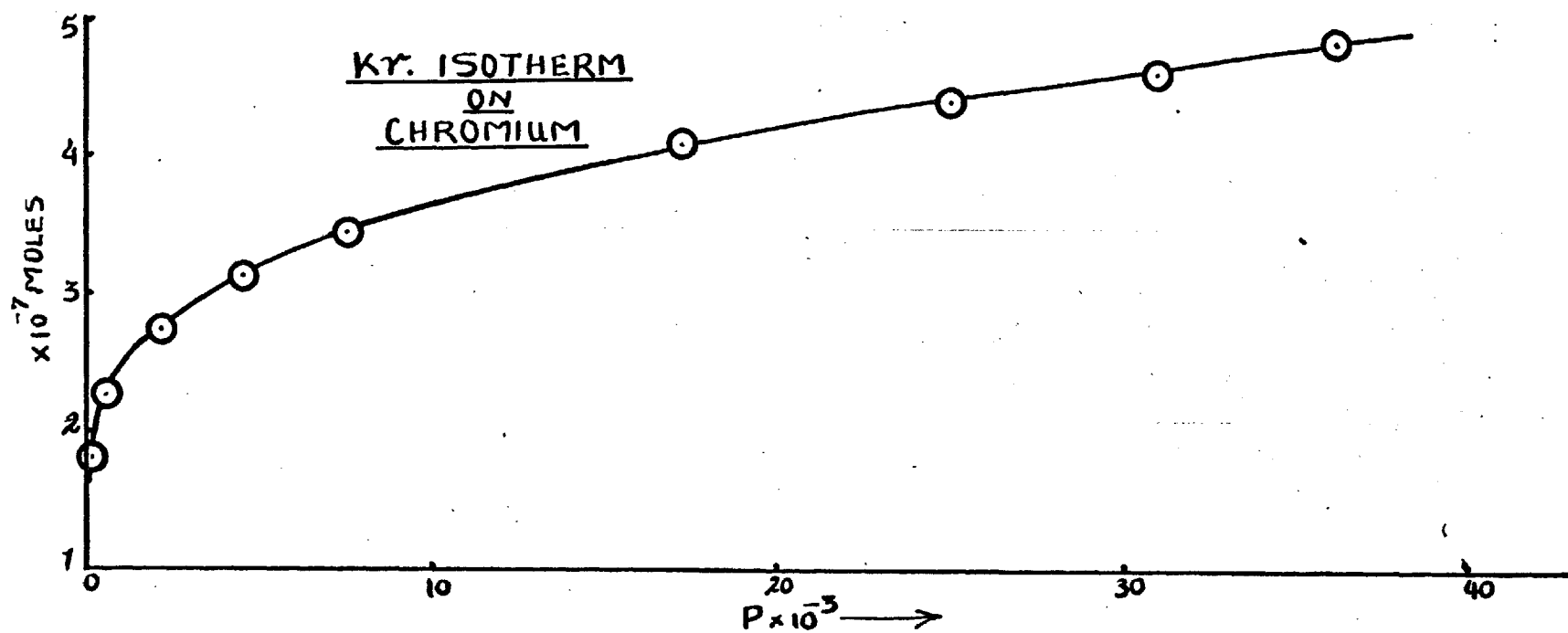


Fig. 5.17

Table 3.4Equilibrium adsorption of CO on Chromium

Weight of the film = 13.0 mg

B.E.T. area of film = 5946.33 sq.cm

No. of sites = 9.693×10^{18}

273°K		227°K		195°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
3.2×10^{-4}	4.88	3.5×10^{-4}	5.473	1.62×10^{-3}	6.087
1.81×10^{-3}	5.145	1.55×10^{-3}	5.706	6.77×10^{-3}	6.174
4.39×10^{-3}	5.359	4.91×10^{-3}	5.943	1.96×10^{-2}	6.3
8.73×10^{-3}	5.504	1.45×10^{-2}	5.943	3.06×10^{-2}	6.501
2.39×10^{-2}	5.663	2.71×10^{-2}	6.083	4.21×10^{-2}	6.576
3.80×10^{-2}	5.762	4.05×10^{-2}	6.177	5.35×10^{-2}	6.679
5.097×10^{-2}	5.922	5.11×10^{-2}	6.317	7.62×10^{-2}	6.645
90°K		78°K			
6.4×10^{-4}	6.868	2.78×10^{-3}	7.352		
6.94×10^{-3}	7.218	9.31×10^{-3}	7.562		
1.54×10^{-2}	7.353	1.62×10^{-2}	7.712		
2.31×10^{-2}	7.497	3.13×10^{-2}	7.893		
4.04×10^{-2}	7.596	4.52×10^{-2}	8.604		
5.46×10^{-2}	7.718				

3.1.5. Manganese

The manganese used was supplied by Johnson Matthey & Company in the form of small broken chips which contain 5 parts per million of magnesium and silicon, and less than one part per million of copper. The film was deposited at 78°K by heating the manganese in tungsten spiral, and sintered at 273°K . The first dose of carbon monoxide was introduced at 78°K (in another run it was observed that exceptionally large amounts of carbon monoxide were adsorbed at 273°K). The first eight doses were completely adsorbed. When the film was warmed to 90°K , gas was first desorbed, but was followed by a slight adsorption. In a similar way equilibrium at 195°K could be established. But on further warming the film to 227° or 273°K , no gas was desorbed. The film was again cooled to 195°K , and then to 90°K and 78°K , slightly more gas was adsorbed. The isotherms at these three temperatures are given in fig.(3.18) as the plot of θ against $\log p$. The number of sites per sq.cm has been calculated by taking the interatomic distance as $2.7\text{\AA}$, according to Bradley and Thewlis⁽¹⁾ who have tested the values for α -manganese. If it is assumed that manganese is b.c.c.⁽²⁾, the sites per sq.cm work out to be roughly 1.4×10^{15} .

The heats have been calculated and are given in table (3.5). The heats were very small, e.g. at 0.75θ the heat was $2.77 \text{ k.cal.mole}^{-1}$. The area of the film was determined by B.E.T. method, fig.(3.19).

CO ON MANGANESE.

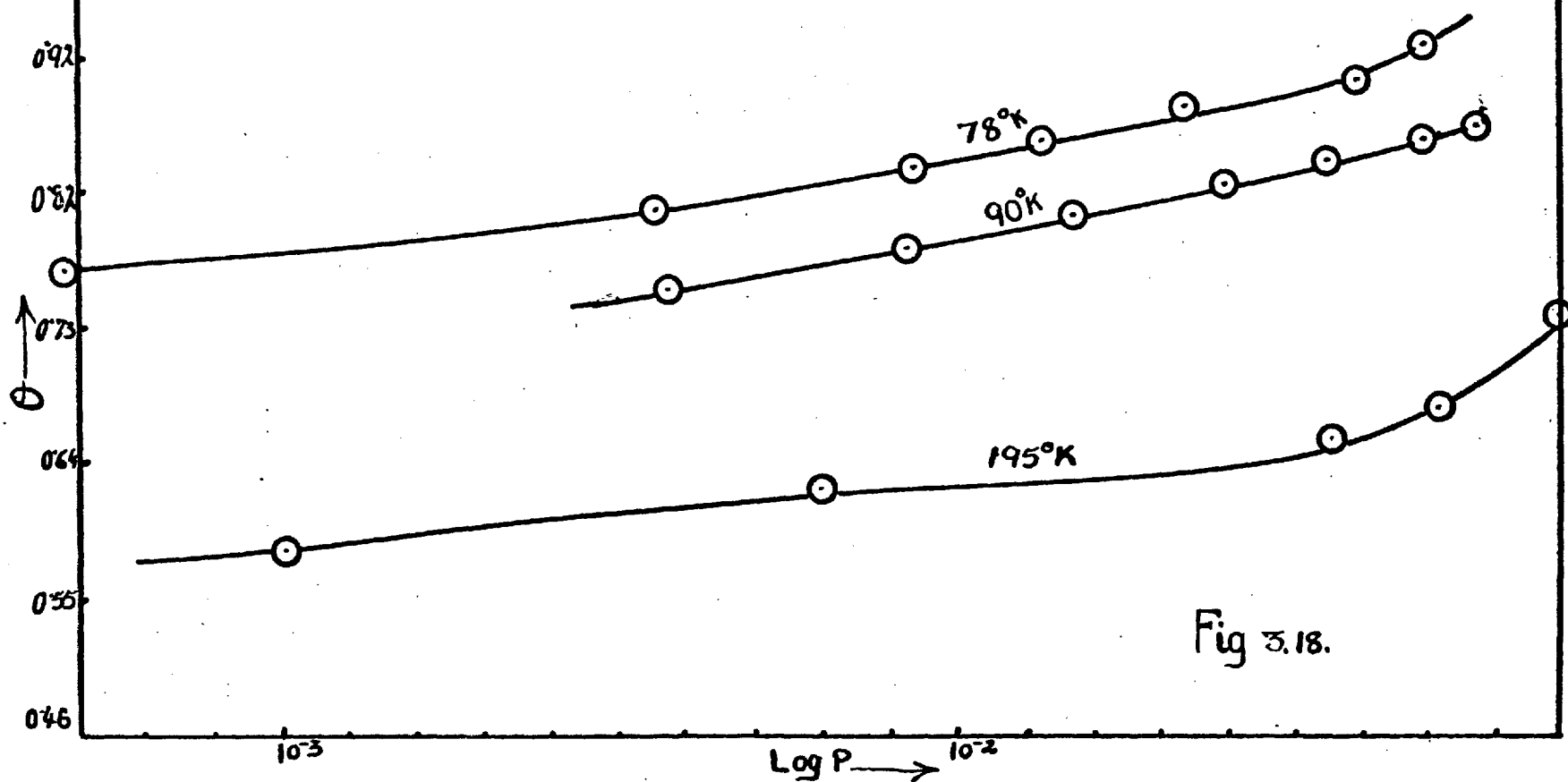


Fig 3.18.

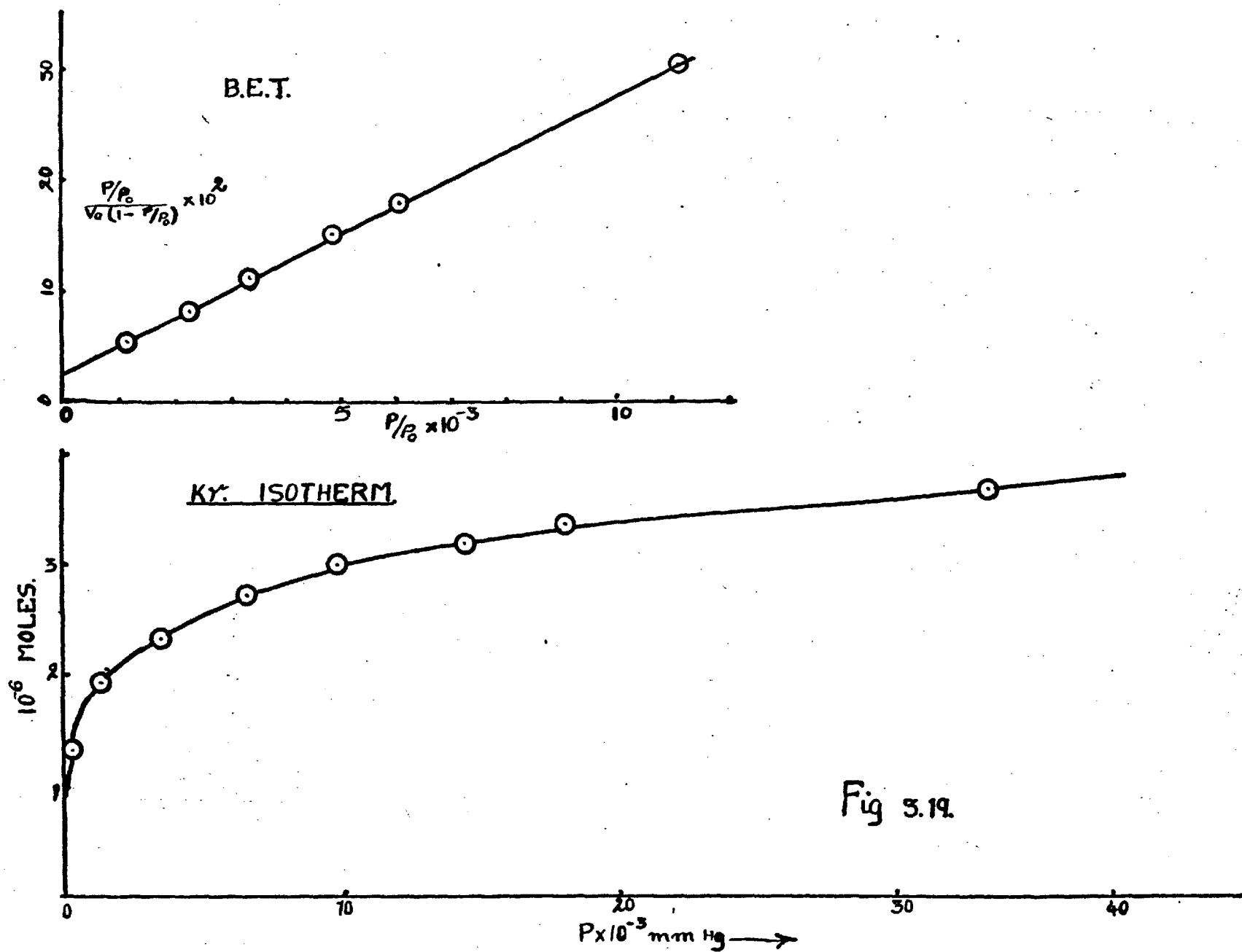


Fig 3.19.

Table 3.5

<u>θ</u>	<u>k.cal.mole⁻¹</u>
0.733	1.28
0.7455	2.77
0.824	1.83
0.8695	1.47

Table 3.6Equilibrium adsorption of CO on Manganese

Weight of film = 12.8

Area of film = 4697.94 sq.cm

No. of sites = 6.577×10^{18}

195°K		90°K		78°K	
Pressure mm Hg	Molecules adsorbed $\times 10^{18}$	Pressure mm Hg	Molecules adsorbed $\times 10^{18}$	Pressure mm Hg	Molecules adsorbed $\times 10^{18}$
1.05×10^{-3}	3.79	3.8×10^{-3}	4.993	5.0×10^{-4}	5.089
6.36×10^{-3}	4.12	8.67×10^{-3}	5.189	8.91×10^{-3}	5.351
3.6×10^{-2}	4.338	1.46×10^{-2}	5.326	1.39×10^{-2}	5.674
5.28×10^{-2}	4.506	2.11×10^{-2}	5.444	2.73×10^{-2}	5.833
8.129×10^{-2}	4.862	3.58×10^{-2}	5.557	3.99×10^{-2}	5.937
		4.92×10^{-2}	5.645	5.06×10^{-2}	6.025
		6.14×10^{-2}	5.697		

3.1.6. Copper

The copper film was deposited at 78°K by heating the 99.99% pure copper wire wound on a 0.3 mm diameter pure tungsten wire. The film was sintered at 273°K . The first dose of carbon monoxide was completely adsorbed. Adsorption took place slowly, but at all temperatures equilibrium was reached within 15 minutes. The rate curves at different temperatures are shown in fig.(3.22). The isotherms obtained at different temperatures are shown in fig.(3.20).

Heats of adsorption were calculated; at .030 the heat was 5.8 k.cal.mole. Trapnell⁽³⁾ finds 9 k.cal.mole as the initial heat of adsorption of carbon monoxide on copper. If the heat curve, fig.(3.21), is extrapolated to zero coverage a value of 8.5 k.cal.mole is obtained.

The area of film was determined by B.E.T. method, fig.(3.23).

CO ON COPPER.

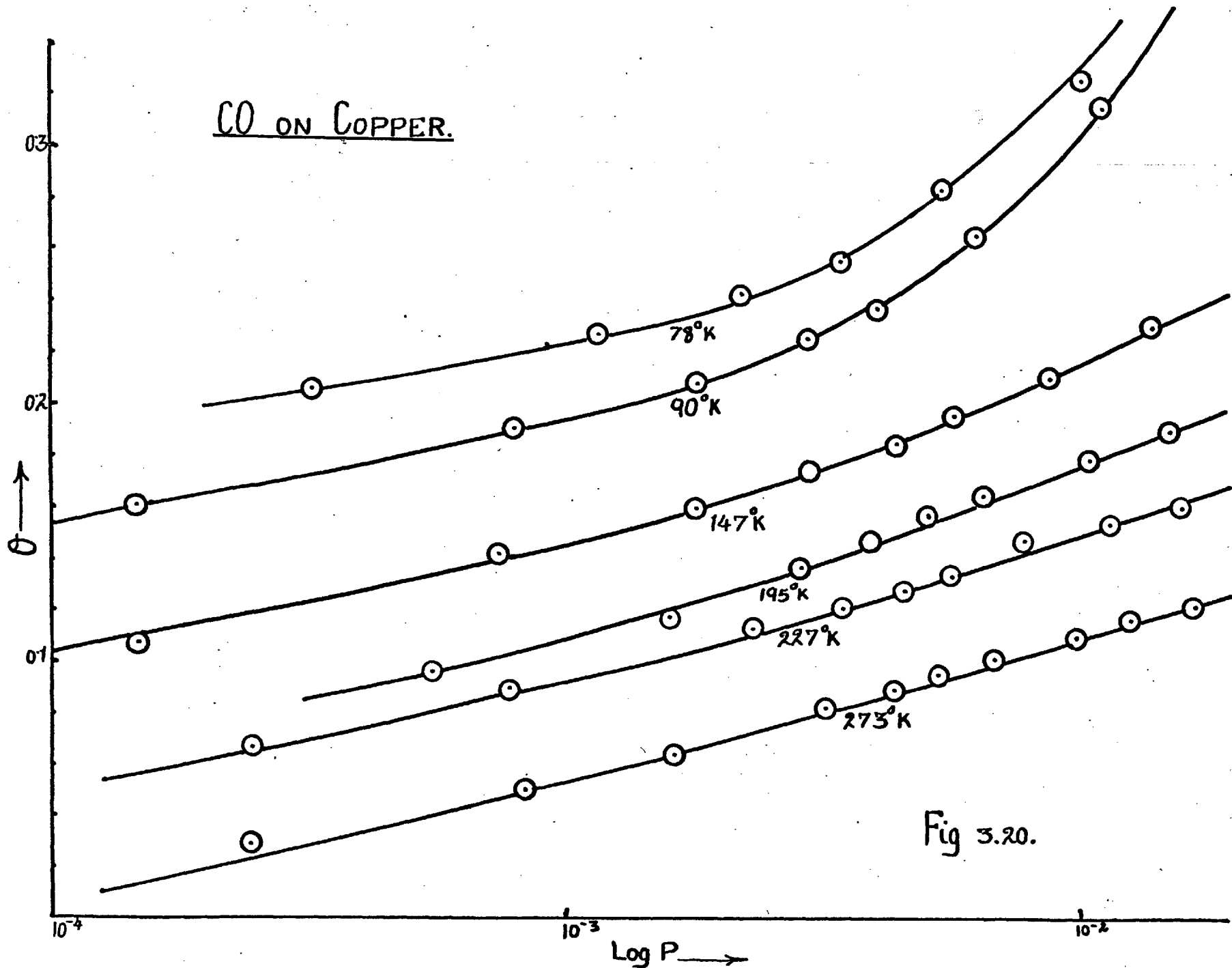


Fig 3.20.

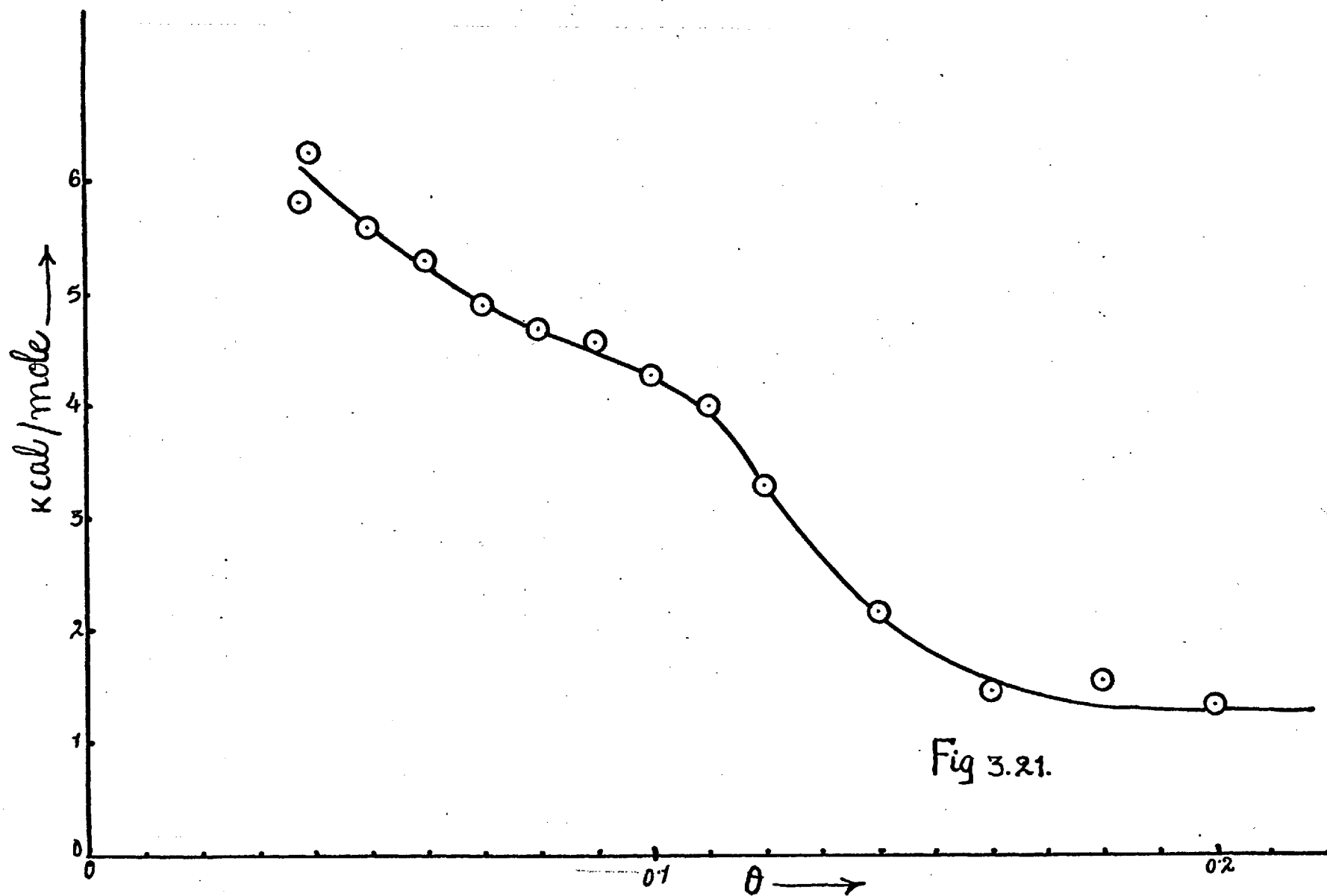


Fig 3.21.

RATE OF ADSORPTION OF
CO ON COPPER

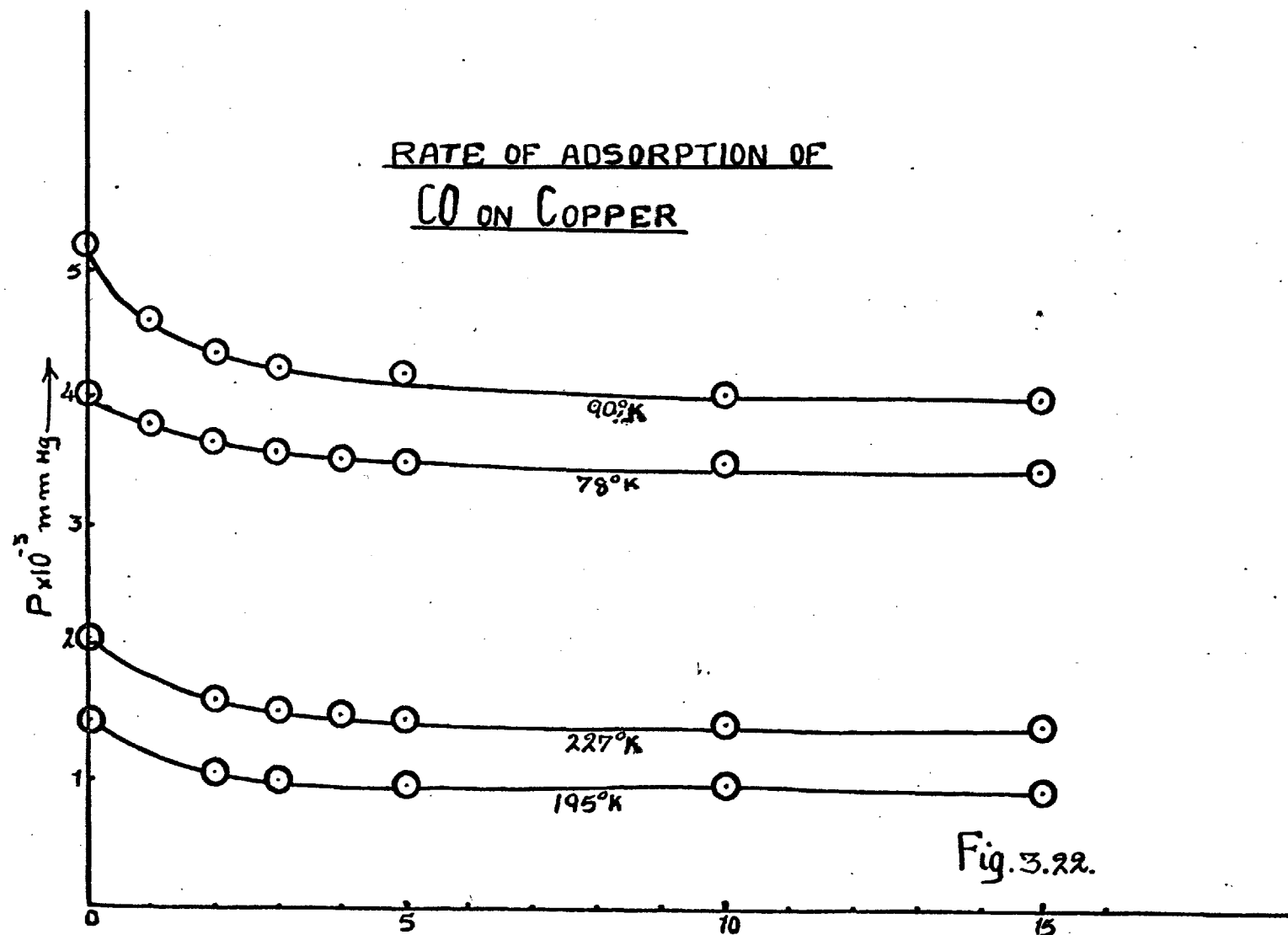


Fig. 3.22.

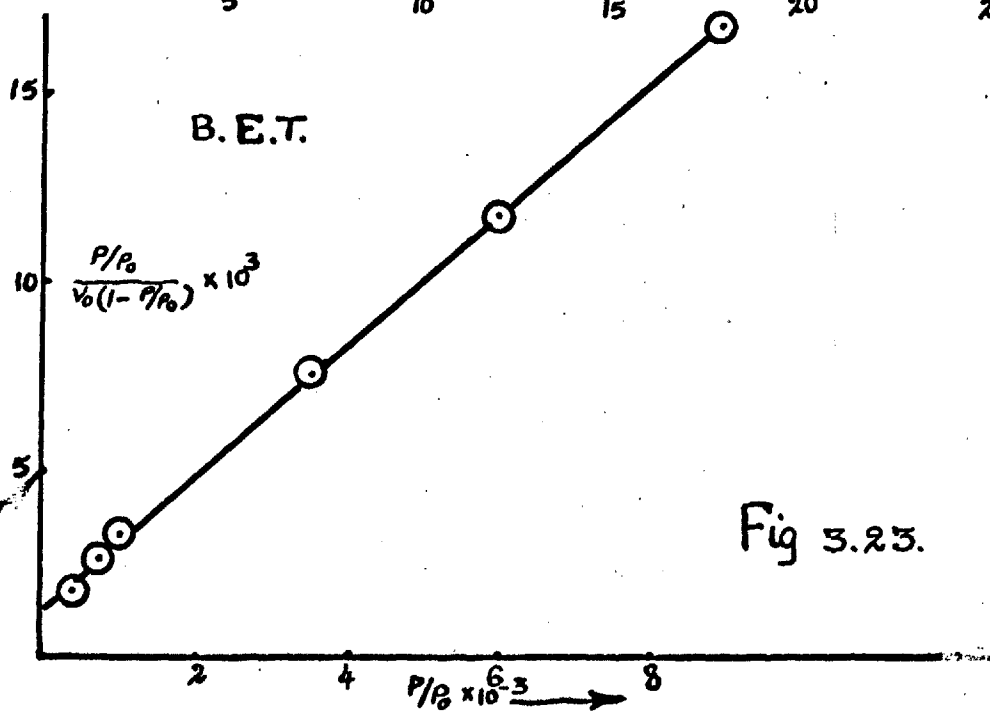
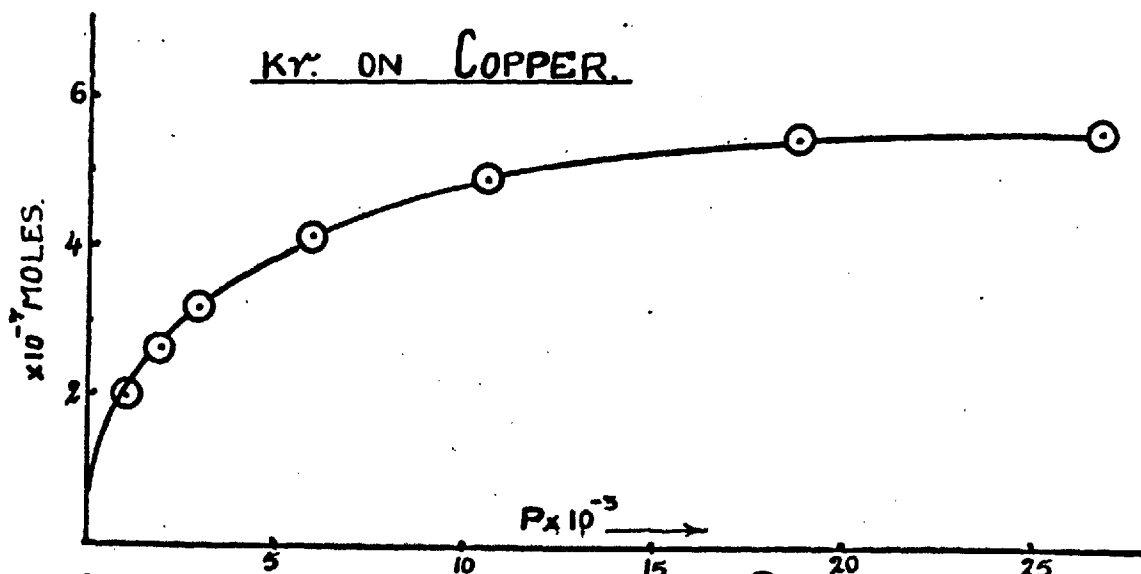


Fig 3.23.

Table 3.7Equilibrium adsorption of CO on Copper

Weight of film = 13.2 mg

Area of film = 647.01 sq.cm

No. of sites = 9.511×10^{17}

273°K		227°K	
Pressure mm Hg	Molecules $\times 10^{16}$	Pressure mm Hg	Molecules $\times 10^{16}$
2.5×10^{-4}	2.91	8×10^{-5}	3.55
8.5×10^{-4}	4.84	2.5×10^{-4}	6.44
1.65×10^{-3}	6.08	7.8×10^{-4}	8.49
3.2×10^{-3}	7.83	2.3×10^{-3}	10.84
4.3×10^{-3}	8.43	3.5×10^{-3}	11.44
5.7×10^{-3}	9.03	4.54×10^{-3}	12.05
6.8×10^{-3}	9.64	7.18×10^{-3}	14.034
8.45×10^{-3}	10.24	1.61×10^{-2}	15.17
1.76×10^{-2}	11.20		

Table 3.7 continued

195°K			147°K		
Pressure mm Hg		Molecules $\times 10^{16}$	Pressure mm Hg		Molecules $\times 10^{16}$
6	$\times 10^{-5}$	7.1	1.5	$\times 10^{-4}$	10.20
5.6	$\times 10^{-4}$	9.08	7.5	$\times 10^{-4}$	13.55
1.6	$\times 10^{-3}$	11.11	1.85	$\times 10^{-3}$	15.18
2.85	$\times 10^{-3}$	12.95	3.0	$\times 10^{-3}$	16.56
3.9	$\times 10^{-3}$	13.85	4.25	$\times 10^{-3}$	17.47
5.1	$\times 10^{-3}$	15.06	5.65	$\times 10^{-3}$	18.67
6.6	$\times 10^{-3}$	15.96	1.4	$\times 10^{-2}$	21.98
1.53	$\times 10^{-2}$	18.06			
90°K			78°K		
1.5	$\times 10^{-4}$	15.18	6	$\times 10^{-5}$	15.6
8.0	$\times 10^{-4}$	18.13	3.3	$\times 10^{-4}$	19.57
1.801	$\times 10^{-3}$	19.88	1.2	$\times 10^{-3}$	21.68
3.03	$\times 10^{-3}$	21.38	2.21	$\times 10^{-3}$	23.13
3.99	$\times 10^{-3}$	22.59	3.45	$\times 10^{-3}$	24.15
1.1	$\times 10^{-2}$	30.12	1.04	$\times 10^{-2}$	31.02

3.1.7. Silver

The silver film was deposited from a 0.1 mm diameter 'specpure' wire in the same way as copper. Due to low melting point of silver it was difficult to outgas thoroughly and some metal was deposited during the outgassing process. On the sintered film a small dose of carbon monoxide was admitted; at 273°K the gas was taken up very slowly, and the equilibrium was attained in 45 minutes. When the temperature of the film was lowered to 227°K , there was a very small change in pressure, which was due to temperature effect, and no more gas was adsorbed. No isotherm was carried out at this temperature. Isotherms on the temperature are shown in fig.(3.24). All the isotherms after certain coverage become flat, indicating that at all temperatures after certain coverage, no more gas was taken up. The maximum coverage at 78°K and 7.5×10^{-3} mm Hg was 0.350. Carbon monoxide on silver gives very low heats even at very low coverage, heats are given in table (3.8) and the surface area of the film in fig.(3.26).

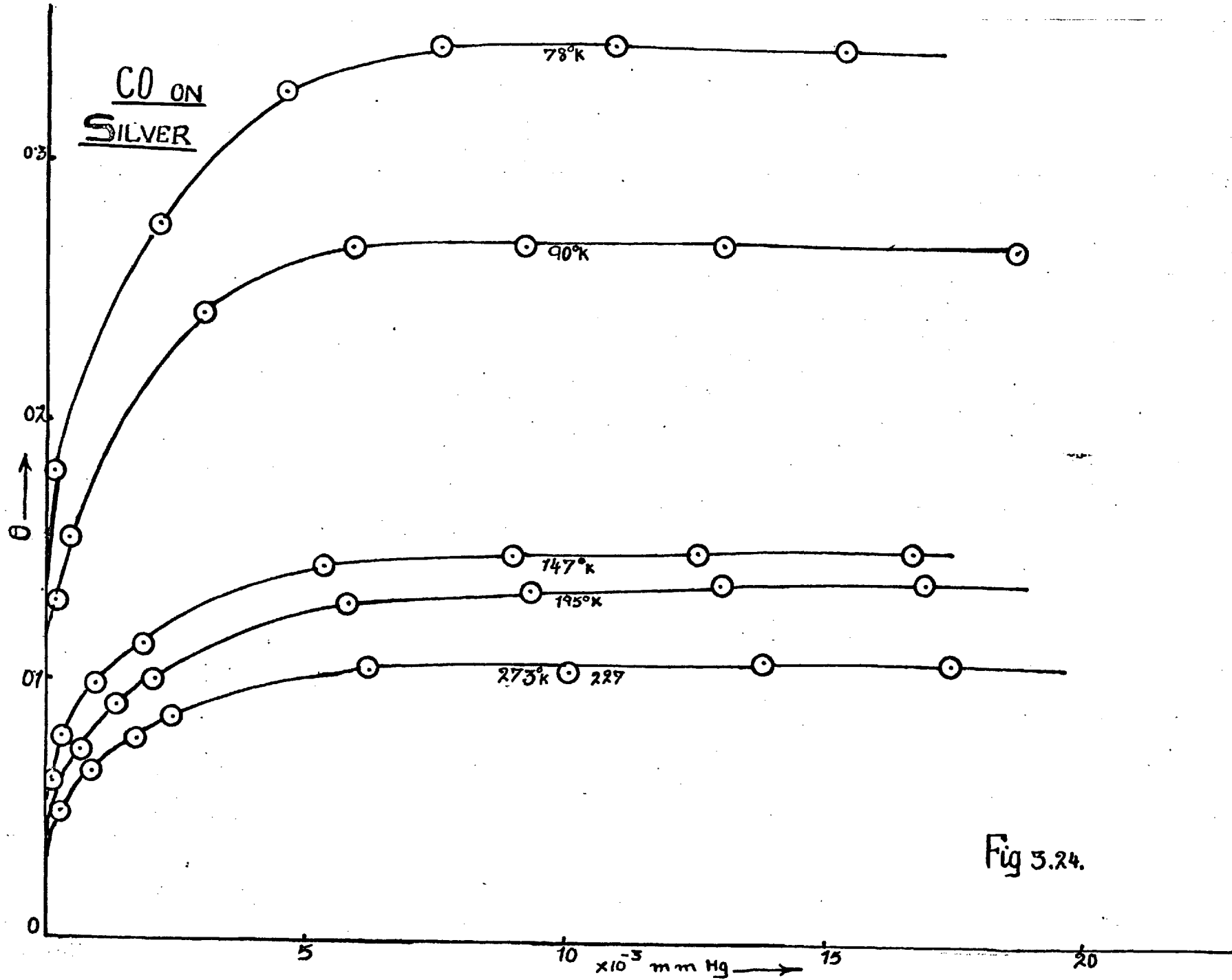
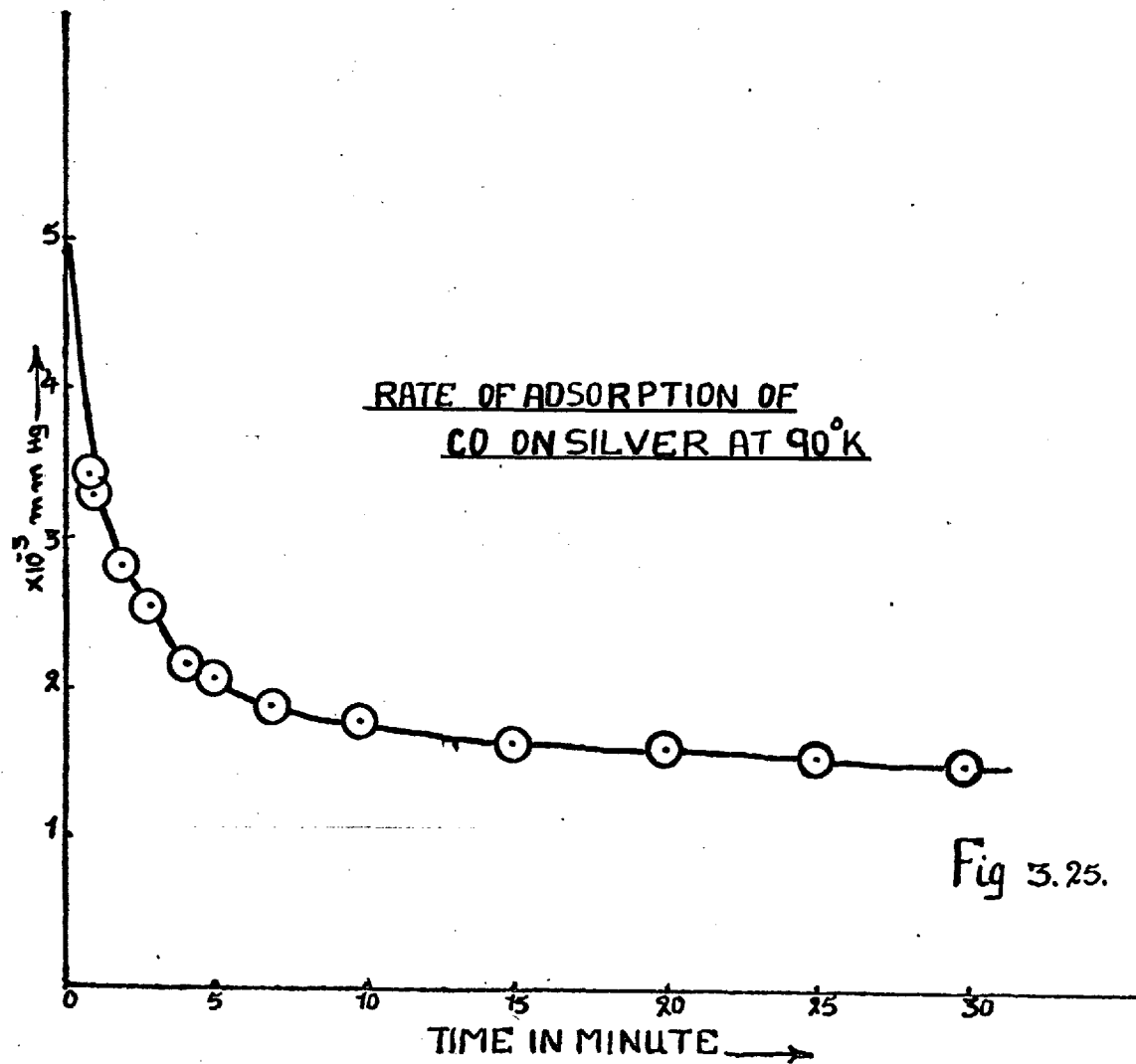


Fig 3.24.



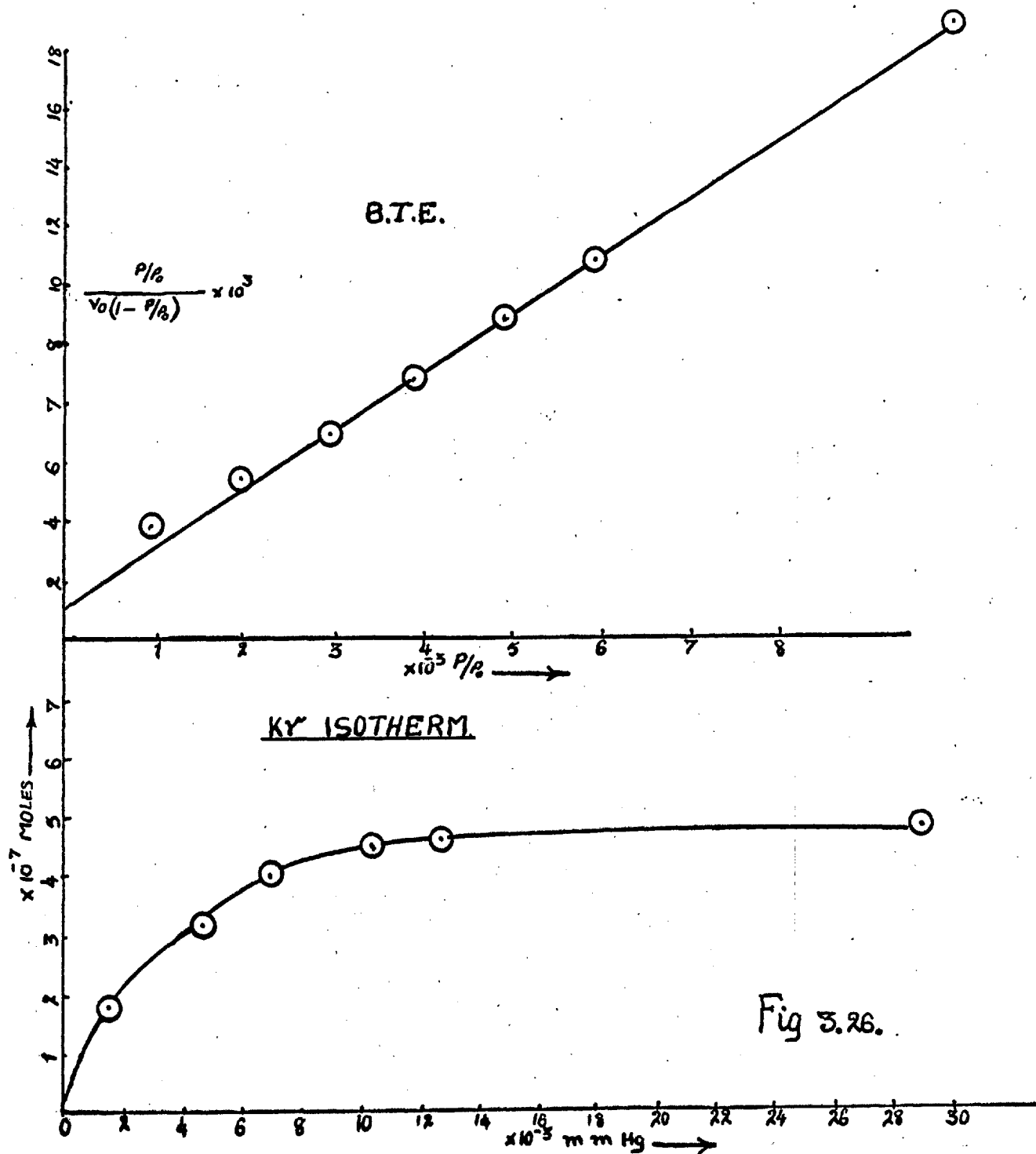


Fig 3.26.

Table 3.8

<u>θ</u>	<u>ΔH k.cal.mole</u>
0.1	1.095
0.101	2.11
0.102	0.743
0.103	1.578

Table 3.9Equilibrium adsorption of CO on Silver

Weight of film = 13.0 mg

Area of film = 607.23 sq.cm

No. of sites = 6.983×10^{17}

273°K		195°K	
Pressure mm Hg	Molecules $\times 10^{16}$	Pressure mm Hg	Molecules $\times 10^{16}$
3 $\times 10^{-4}$	3.35	7 $\times 10^{-4}$	5.028
8.99 $\times 10^{-4}$	4.471	1.4 $\times 10^{-3}$	6.285
1.61 $\times 10^{-4}$	5.379	2.101 $\times 10^{-3}$	6.983
2.39 $\times 10^{-3}$	6.01	5.714 $\times 10^{-3}$	9.078
6.15 $\times 10^{-3}$	7.262	9.303 $\times 10^{-3}$	9.357
1.01 $\times 10^{-1}$	7.262	1.292 $\times 10^{-2}$	9.637
1.37 $\times 10^{-2}$	7.54	1.69 $\times 10^{-2}$	9.776
1.74 $\times 10^{-2}$	7.54		

Table 3.9 - continued

147°K			90°K		
Pressure mm Hg		Molecules x 10 ¹⁷	Pressure mm Hg		Molecules x 10 ¹⁷
4	x10 ⁻⁴	5.447	2.5	x10 ⁻⁴	9.075
1.0	x10 ⁻³	6.843	5.14	x10 ⁻⁴	10.893
1.8	x10 ⁻³	7.821	3.012	x10 ⁻³	16.759
5.3	x10 ⁻³	10.195	5.91	x10 ⁻³	18.575
8.99	x10 ⁻³	10.335	9.19	x10 ⁻³	18.714
1.25	x10 ⁻²	10.475	1.30	x10 ⁻²	18.854
1.67	x10 ⁻²	10.475	1.86	x10 ⁻²	18.854
78°K					
1.5	x10 ⁻⁴	12.569			
2.21	x10 ⁻³	19.273			
4.60	x10 ⁻³	22.904			
7.60	x10 ⁻³	24.161			
1.09	x10 ⁻²	24.161			
1.53	x10 ⁻²	24.161			

3.1.8. Gold

0.1 mm diameter 'specpure' gold wire was used. Small doses of carbon monoxide were introduced into the pre-sintered film at 273°K, and isotherms at different temperatures obtained; these are shown in fig.(3.27). The isotherms bend upward, as the equilibrium pressure reaches 10^{-3} mm Hg, and in the range of 10^{-2} mm Hg they show a tendency to coverage. Carbon monoxide isotherms at 90° and 78° on copper show the same type of behaviour, but not at the higher temperatures.

Heats of adsorption, calculated at equal intervals of θ were initially constant but with increasing θ decreases sharply to 4.1 k.cal.mole⁻¹ from 7.5 k.cal.mole⁻¹, fig.(3.28), and then smoothly to 1.2 k.cal.mole⁻¹ at 0.2 θ . Area of the film was determined by the B.E.T. method, fig.(3.29).

CO ON GOLD

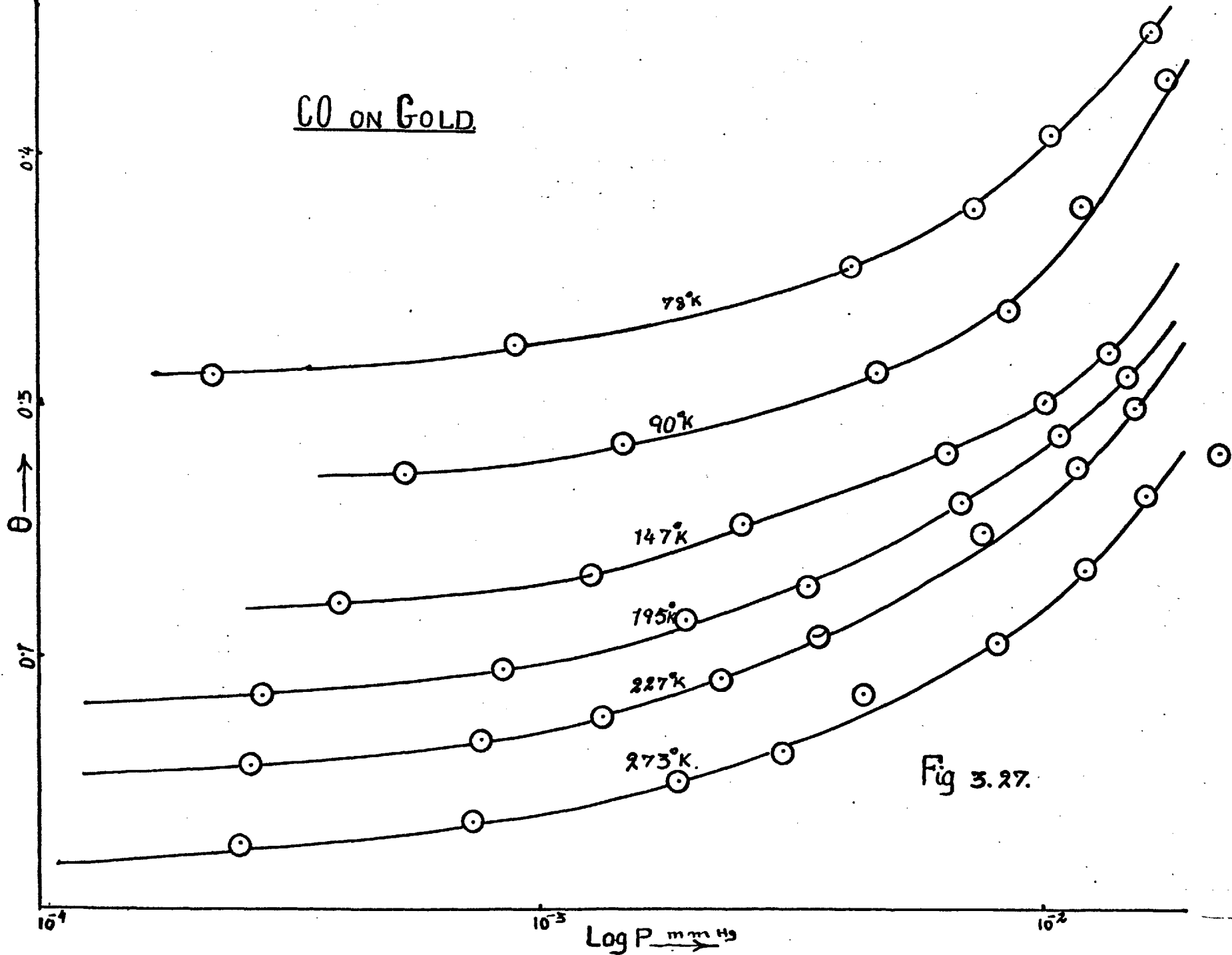


Fig 3.27.

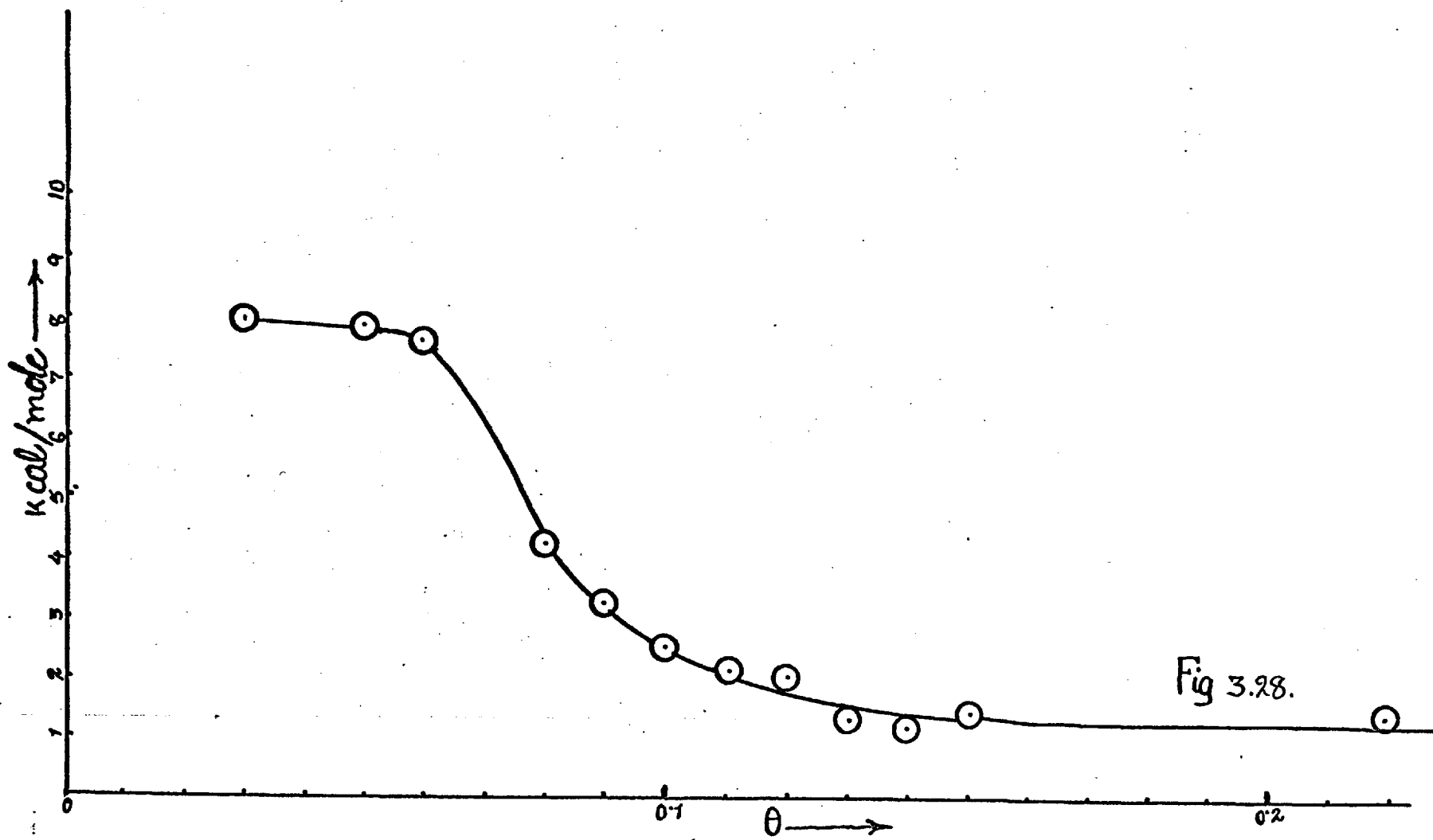


Fig 3.28.

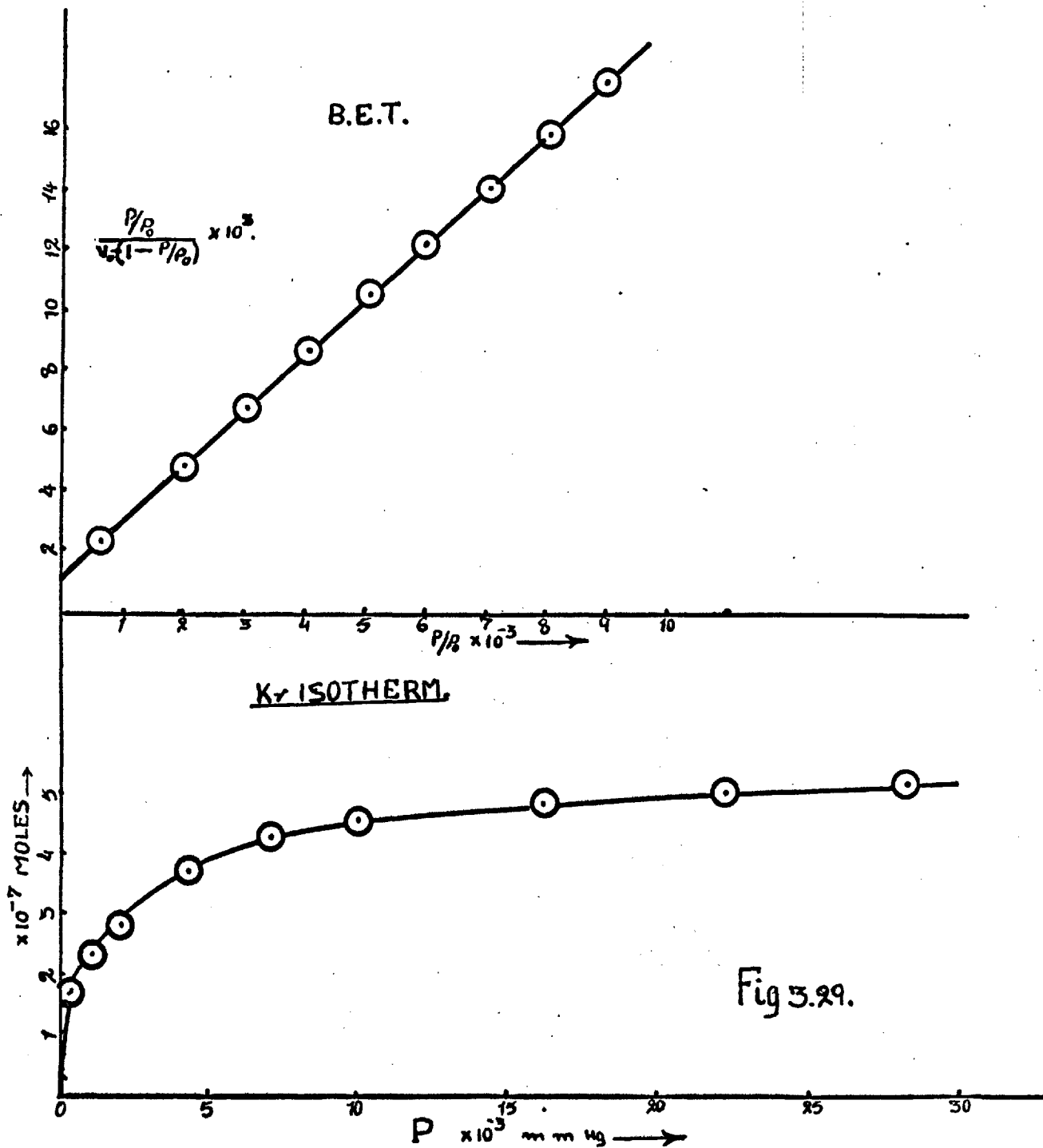


Fig 3.29.

Table 3.10Equilibrium adsorption of CO by Gold

Weight of film = 17.57 mg

Area of film = 643.11 sq.cm

No. of sites = 7.396×10^{17}

273°K		227°K	
Pressure mm Hg	molecules $\times 10^{16}$	Pressure mm Hg	molecules $\times 10^{16}$
2.54×10^{-4}	1.775	2.81×10^{-4}	3.402
7.22×10^{-4}	2.515	7.58×10^{-4}	4.881
1.87×10^{-3}	3.698	1.25×10^{-3}	5.621
3.05×10^{-3}	4.586	2.29×10^{-3}	6.804
4.41×10^{-3}	6.361	3.44×10^{-3}	7.988
8.41×10^{-3}	7.84	7.60×10^{-3}	11.094
1.22×10^{-2}	10.06	1.15×10^{-2}	13.017
1.64×10^{-2}	12.425	1.52×10^{-2}	14.792

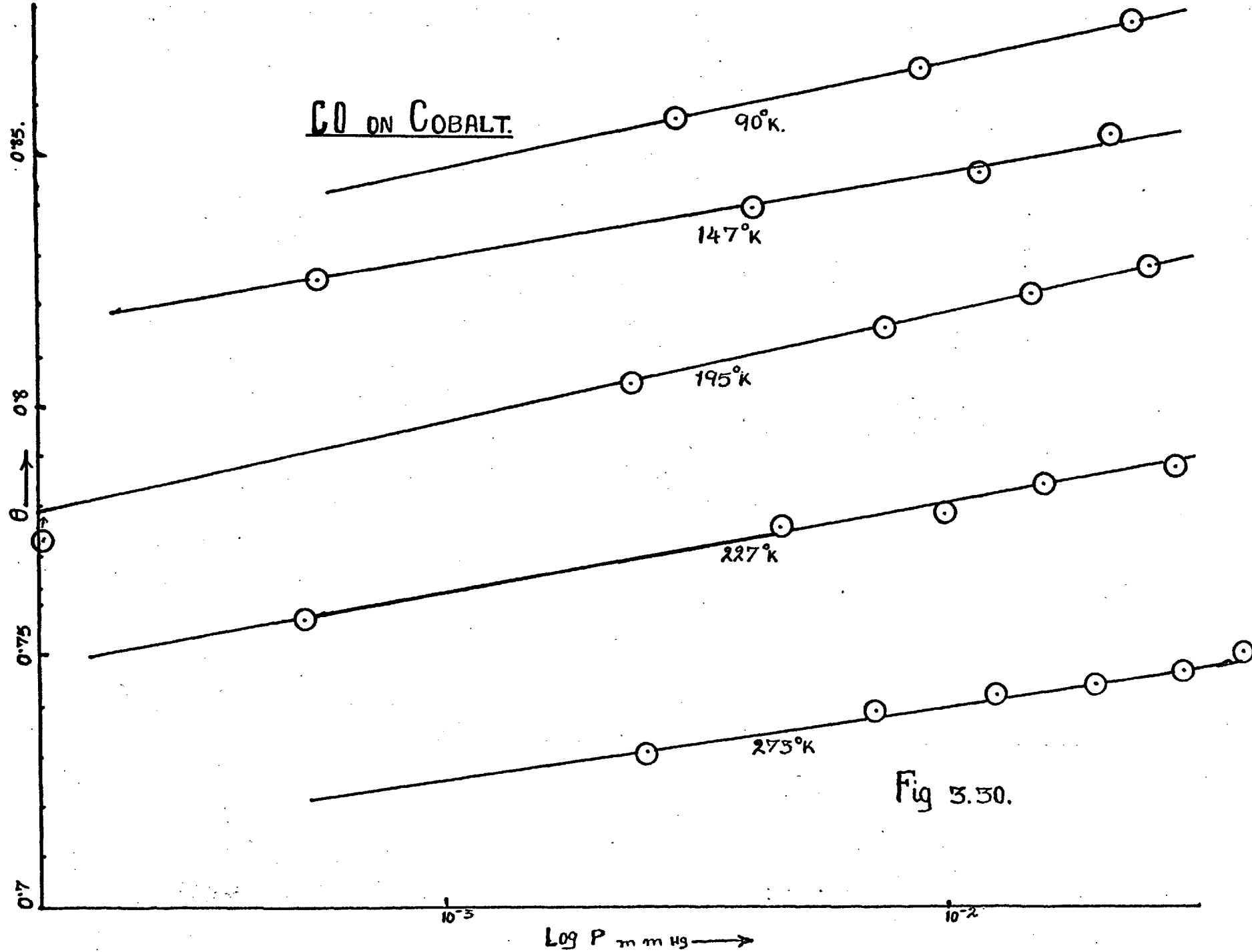
Table 3.10 continued

195°K		147°K	
Pressure mm Hg	Molecules x 10 ¹⁶	Pressure mm Hg	Molecules x 10 ¹⁶
2.75 x10 ⁻⁴	6.213	4.44 x10 ⁻⁴	8.875
8.87 x10 ⁻⁴	6.952	1.34 x10 ⁻³	9.763
1.95 x10 ⁻³	8.579	2.57 x10 ⁻³	11.242
3.09 x10 ⁻³	9.467	6.69 x10 ⁻³	13.461
6.97 x10 ⁻³	11.834	1.03 x10 ⁻²	14.792
1.1 x10 ⁻²	14.052	1.39 x10 ⁻²	16.419
1.48 x10 ⁻²	15.68		
90°K		78°K	
5.49 x10 ⁻⁴	12.869	2.24 x10 ⁻⁴	15.68
1.49 x10 ⁻³	13.757	8.78 x10 ⁻⁴	16.567
4.68 x10 ⁻³	15.827	4.23 x10 ⁻³	19.082
8.57 x10 ⁻³	17.602	7.51 x10 ⁻³	20.709
1.18 x10 ⁻²	20.709	1.05 x10 ⁻²	22.78
1.77 x10 ⁻²	24.407	1.68 x10 ⁻²	25.886

3.1.9. Cobalt

Isotherm of carbon monoxide was carried out on cobalt film sintered at 273°K . The gas was taken up by the film at a very fast rate, and the first ten doses were completely adsorbed. The equilibrium at all temperatures was reached within 5 minutes. The isotherms are plotted as $\log p$ against coverage, fig.(3.30), and the data are given in table (3.11).

Heats of adsorption fall with coverage. It was not possible to calculate the heats of adsorption at equal intervals of θ value, because of the shape of the isotherms. The calculated values are plotted in fig.(3.31). The area of the film was determined by B.E.T. method, fig.(3.32).



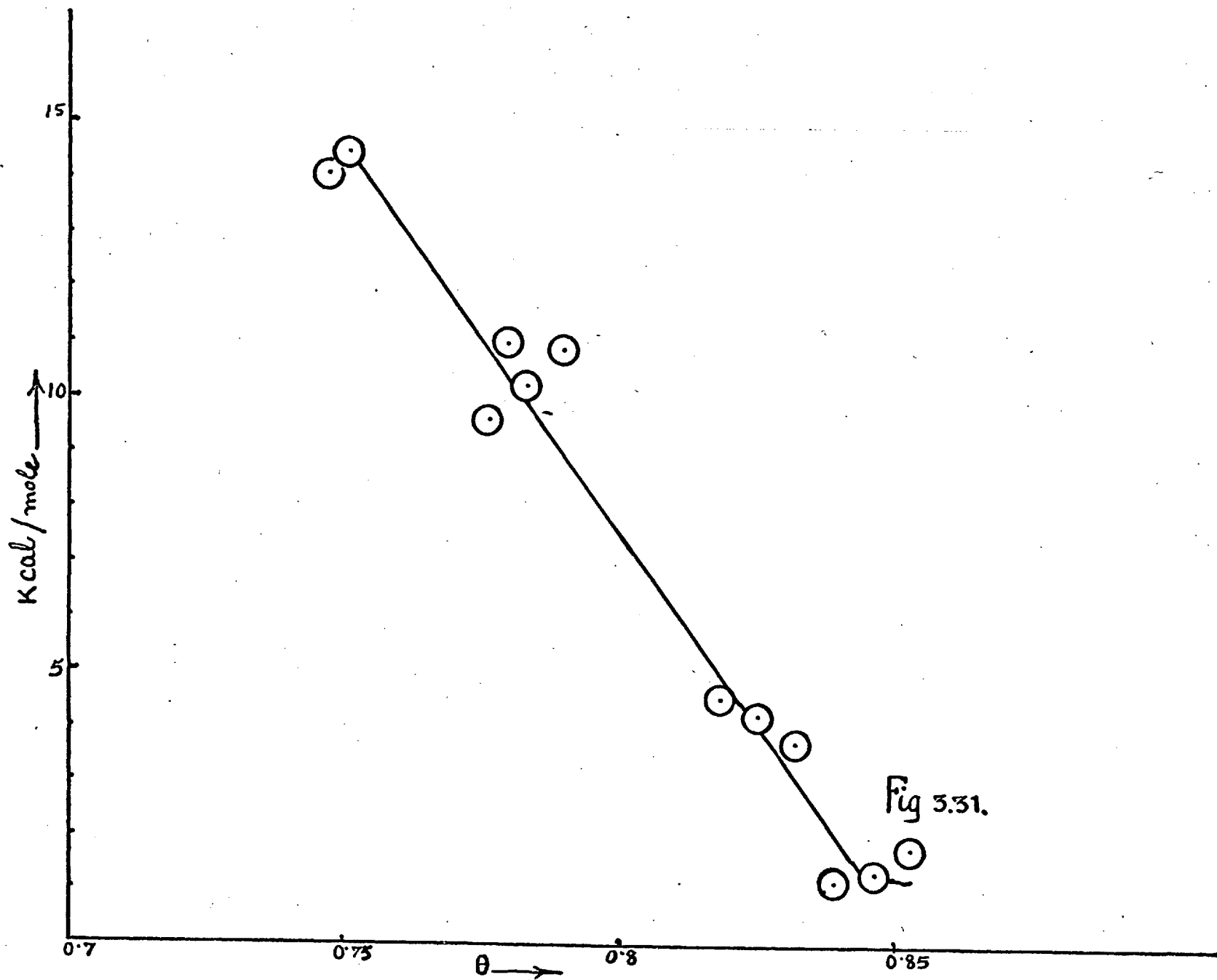


Fig 3.31.

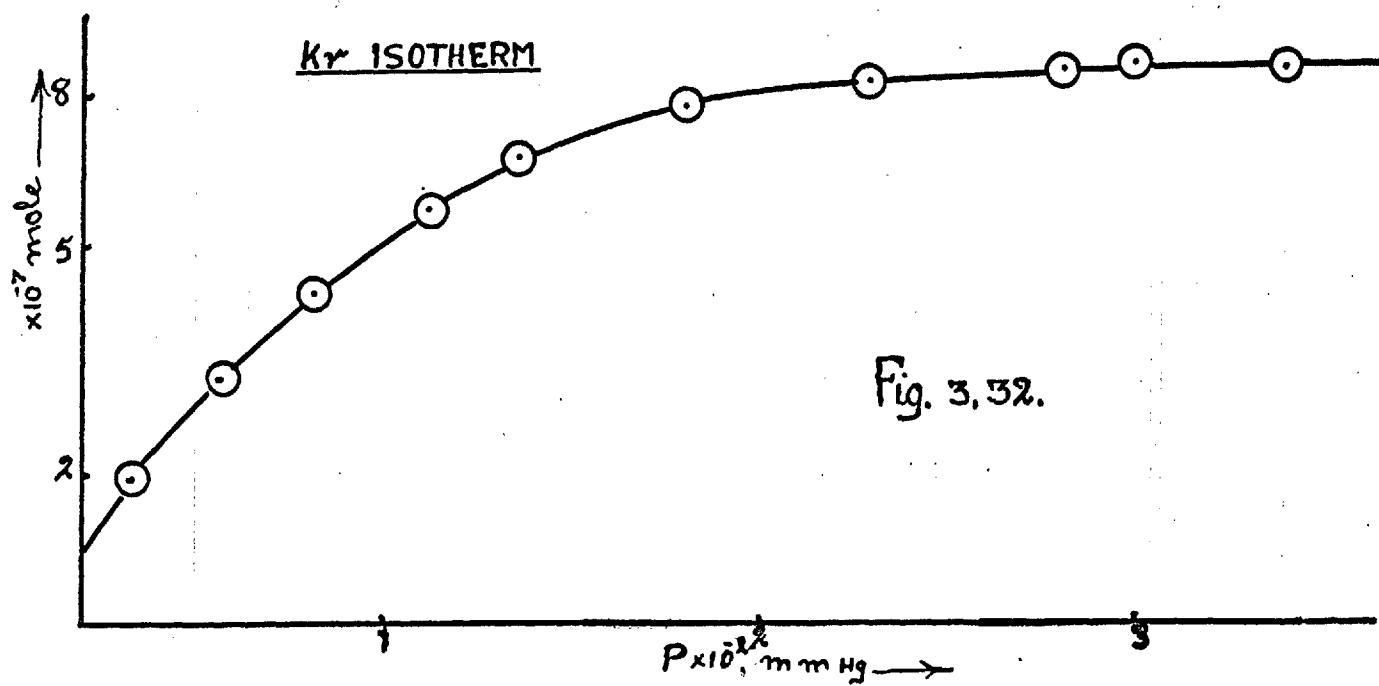
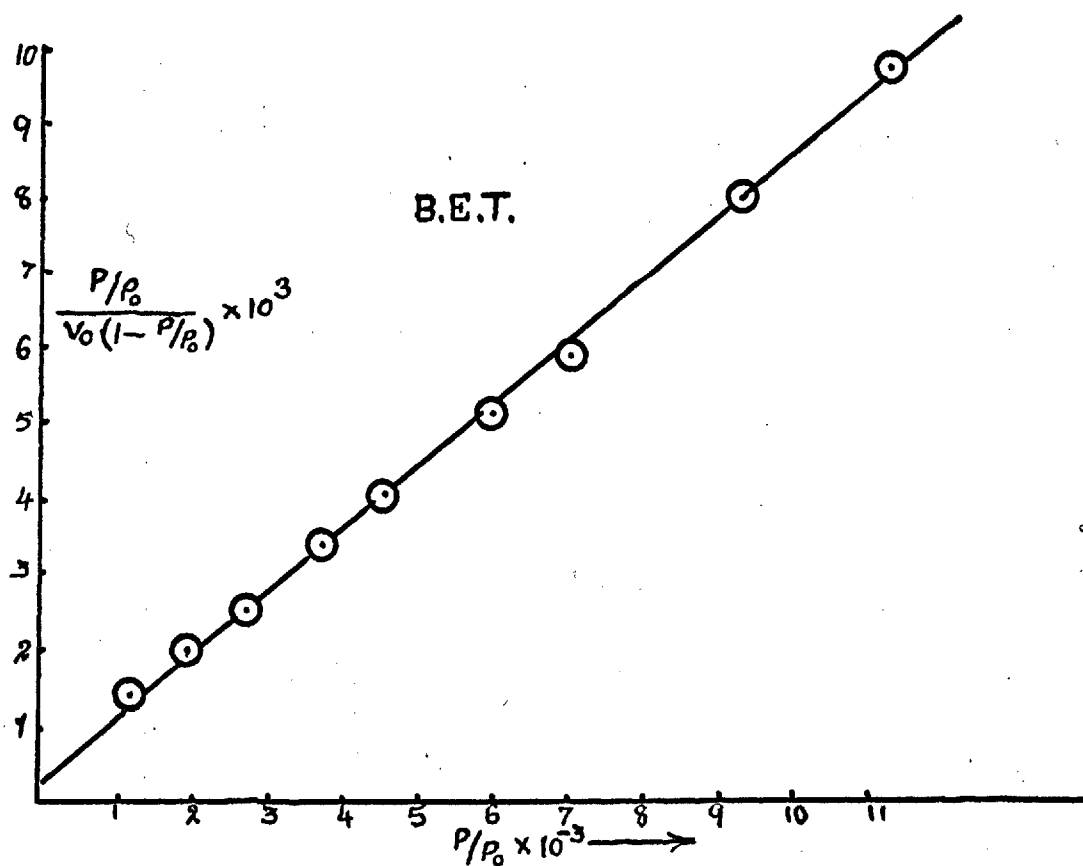


Fig. 3.32.

Table 3.11Equilibrium adsorption of CO by Cobalt

Weight of film = 18.1 mg

Area of film = 1415.3 sq.cm

No. of sites = 2.137×10^{18}

273°K		227°K	
Pressure mm Hg	molecules $\times 10^{18}$	Pressure mm Hg	molecules $\times 10^{18}$
2×10^{-3}	1.56	5.27×10^{-4}	1.618
7.24×10^{-3}	1.578	4.67×10^{-3}	1.656
1.25×10^{-2}	1.584	1.0×10^{-2}	1.662
2.0×10^{-2}	1.590	1.58×10^{-2}	1.674
2.95×10^{-2}	1.593	2.88×10^{-2}	1.680
3.89×10^{-2}	1.602		
195°K		147°K	
1.58×10^{-4}	1.65	5.75×10^{-4}	1.762
2.4×10^{-3}	1.717	4.17×10^{-3}	1.792
7.59×10^{-3}	1.741	1.20×10^{-2}	1.807
1.51×10^{-2}	1.756	2.18×10^{-2}	1.825
2.52×10^{-2}	1.768		
90°K			
2.95×10^{-2}	1.831		
9.12×10^{-2}	1.852		
2.4×10^{-2}	1.872		

3.2. Hydrogen on Metals

3.2.1. Palladium

The palladium film for hydrogen adsorption was prepared in the usual way. The isotherms are shown in fig.(3.33). The adsorption takes place in two stages at all temperatures, a fast adsorption being always followed by a long period of slow adsorption, and the equilibrium was not attained for more than one hour. In run 2, fig.(3.34), the equilibrium pressure was taken after 15 minutes of adsorption, but in run I all points in the isotherms represent true equilibrium. Thus the temperature of the film was increased and decreased several times until all the points were reproducible. The isotherms at 195°K and 178°K turn very sharply, at approximately 10^{-3} mm Hg, but at higher temperatures, the isotherms bend upwards around 10^{-1} mm Hg.

Heats of adsorption are shown in fig.(3.35). Heats fall sharply from 20 k.cal.mole to 8 k.cal.mole⁻¹ and then decrease slowly with coverage.

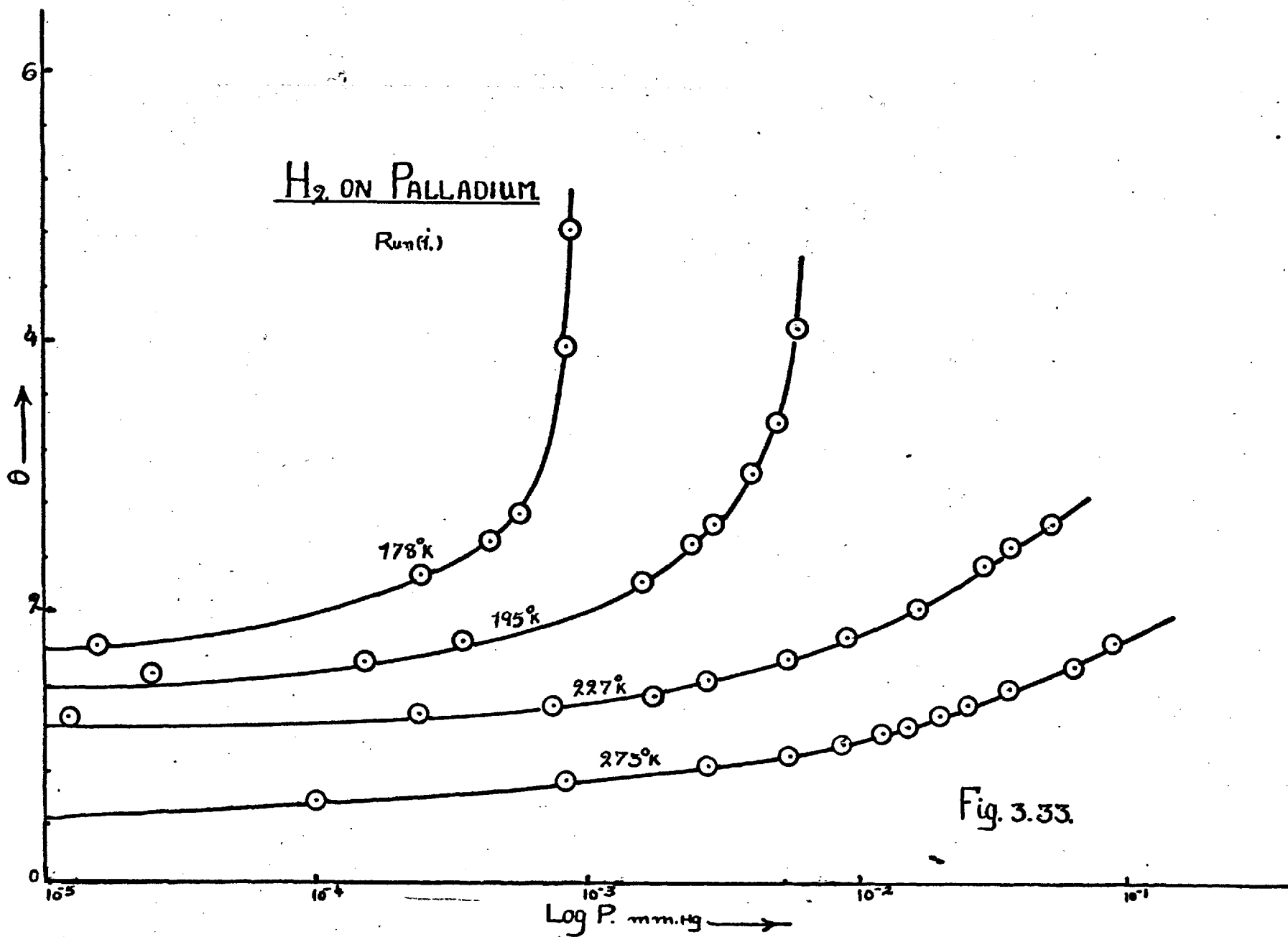
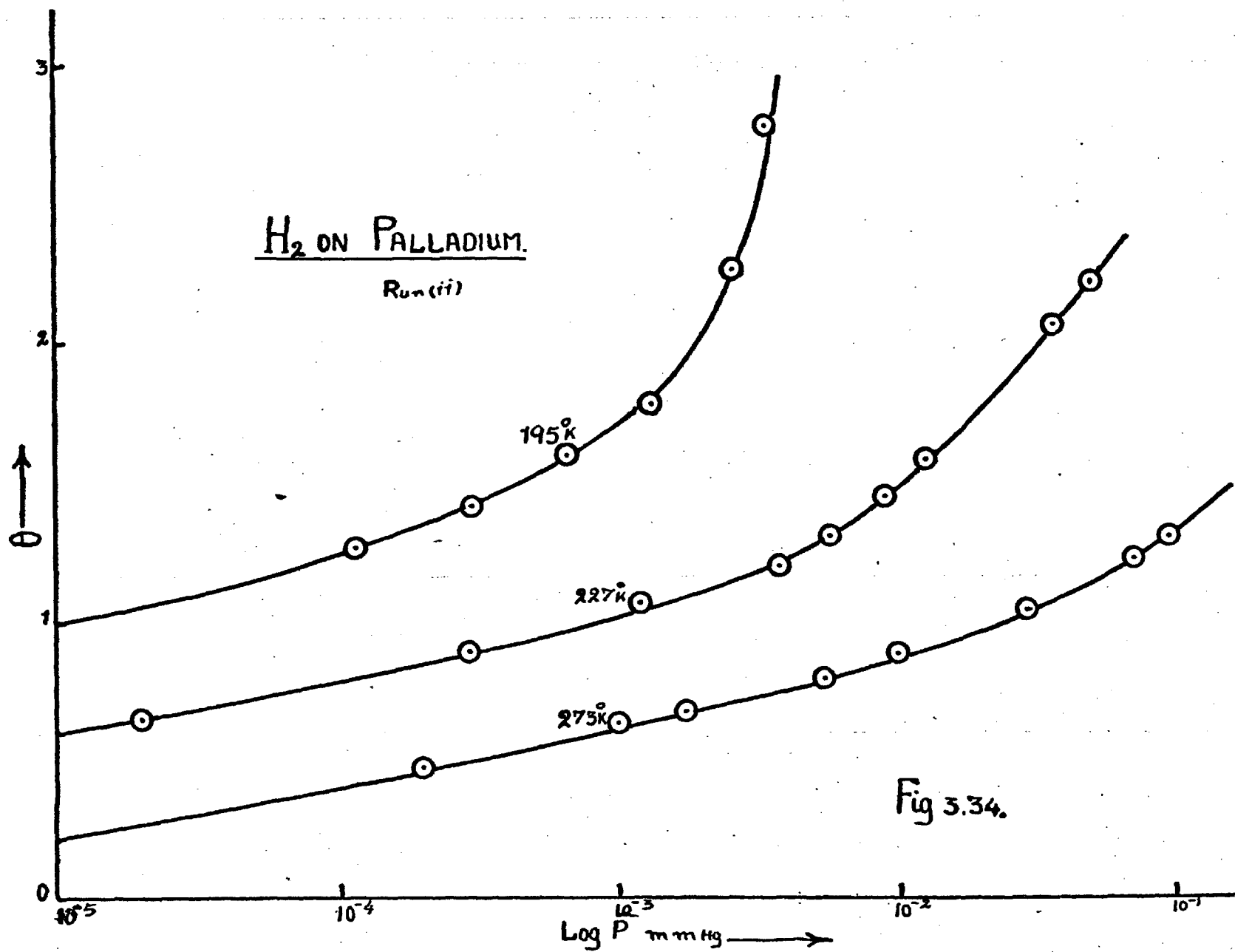


Fig. 3.33.



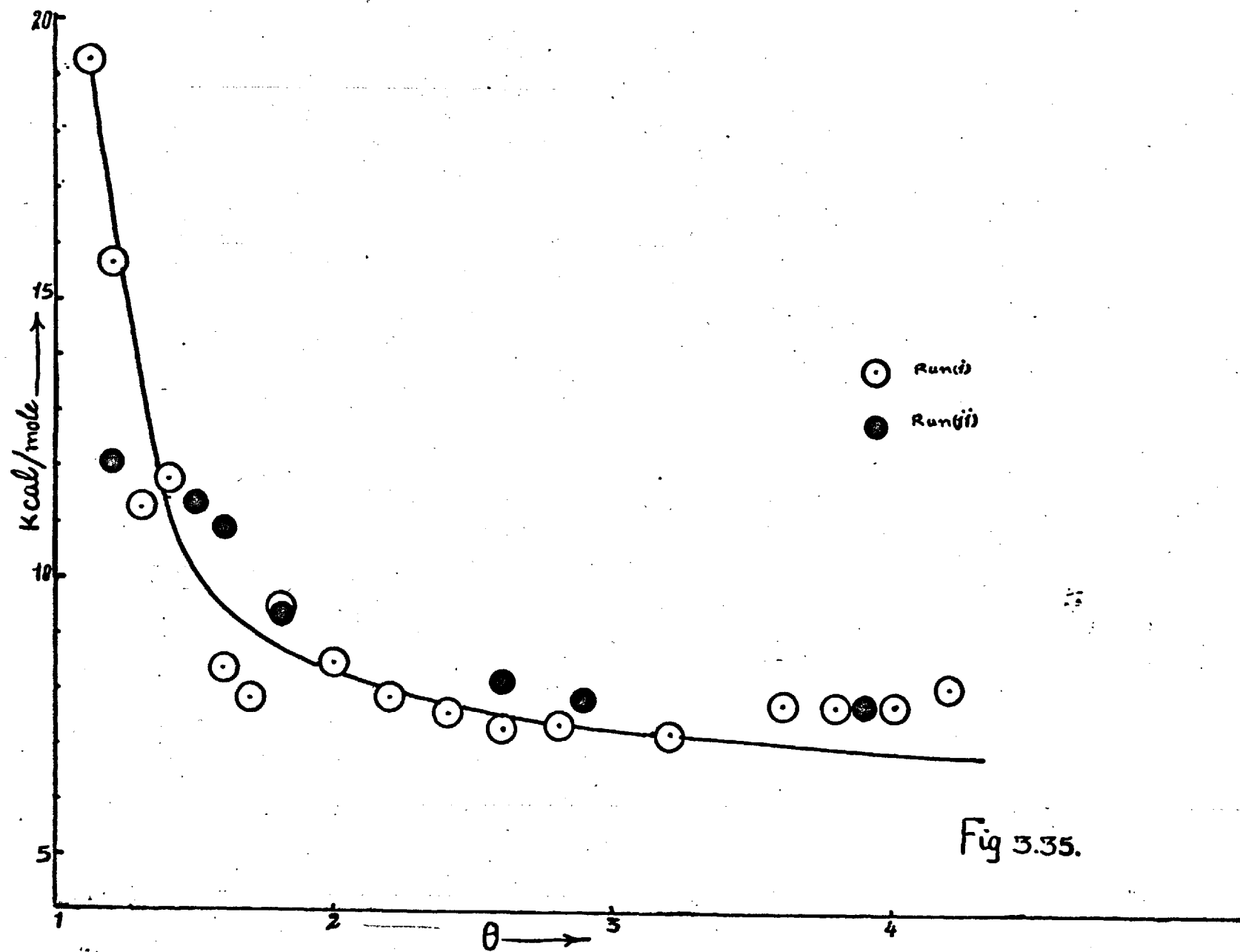


Fig 3.35.

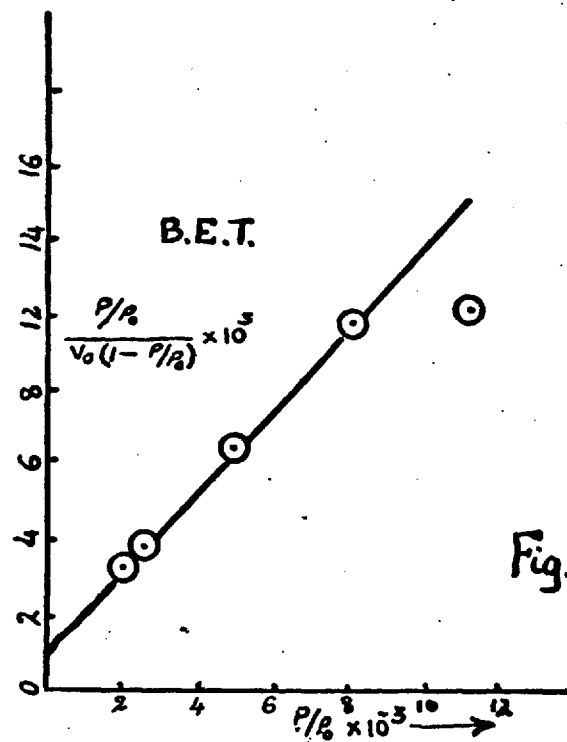
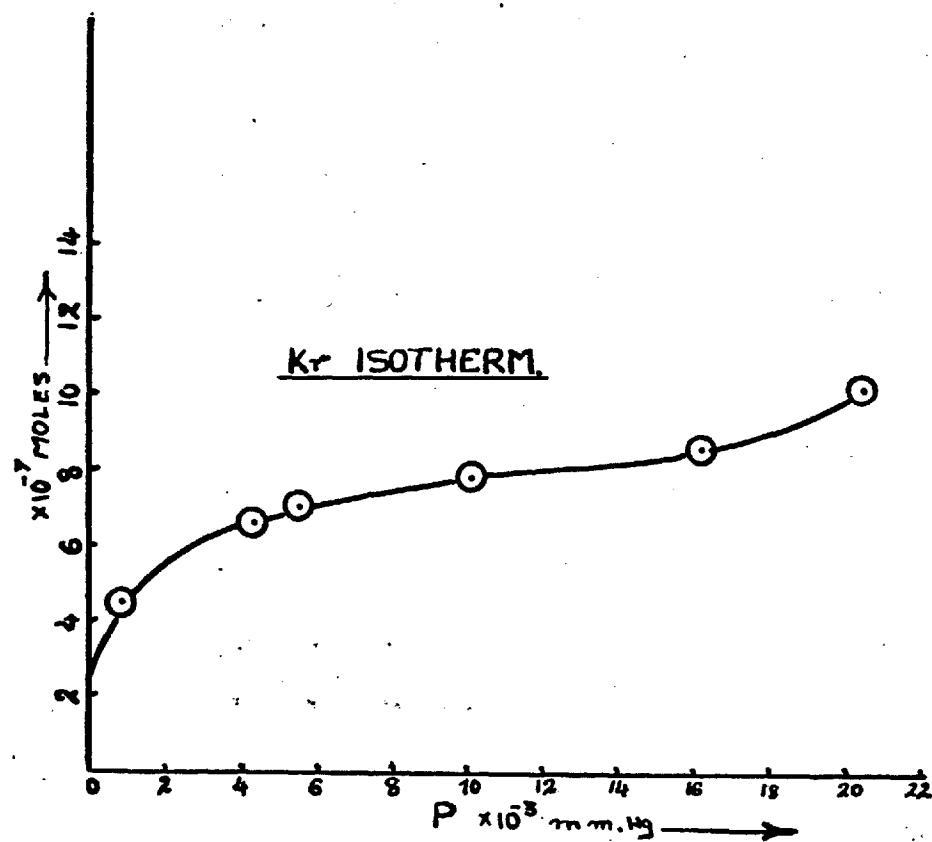


Fig. 3.36.

Table 3.12Sorption of Hydrogen by Palladium

Weight of film = 35.6 mg
 Area of film = 1553.7 sq. cm
 (Run I)
 No. of sites = 1.973×10^{18}

Run I.

273°K		227°K	
Pressure mm Hg	Molecules $\times 10^{17}$	Pressure mm Hg	Molecules $\times 10^{17}$
1 $\times 10^{-4}$	5.66	2.4 $\times 10^{-4}$	10.79
8.32 $\times 10^{-4}$	7.08	7.41 $\times 10^{-4}$	12.39
2.75 $\times 10^{-3}$	8.50	1.74 $\times 10^{-3}$	13.46
5.49 $\times 10^{-3}$	9.21	2.75 $\times 10^{-3}$	14.88
8.71 $\times 10^{-3}$	9.92	5.50 $\times 10^{-3}$	16.12
1.20 $\times 10^{-2}$	10.63	9.12 $\times 10^{-3}$	17.72
1.51 $\times 10^{-2}$	11.33	1.66 $\times 10^{-2}$	19.83
1.99 $\times 10^{-2}$	12.04	2.88 $\times 10^{-2}$	23.02
2.51 $\times 10^{-2}$	12.75	3.63 $\times 10^{-2}$	24.45
3.63 $\times 10^{-2}$	13.81	5.24 $\times 10^{-2}$	26.20
6.31 $\times 10^{-2}$	15.95		
8.71 $\times 10^{-2}$	17.36		

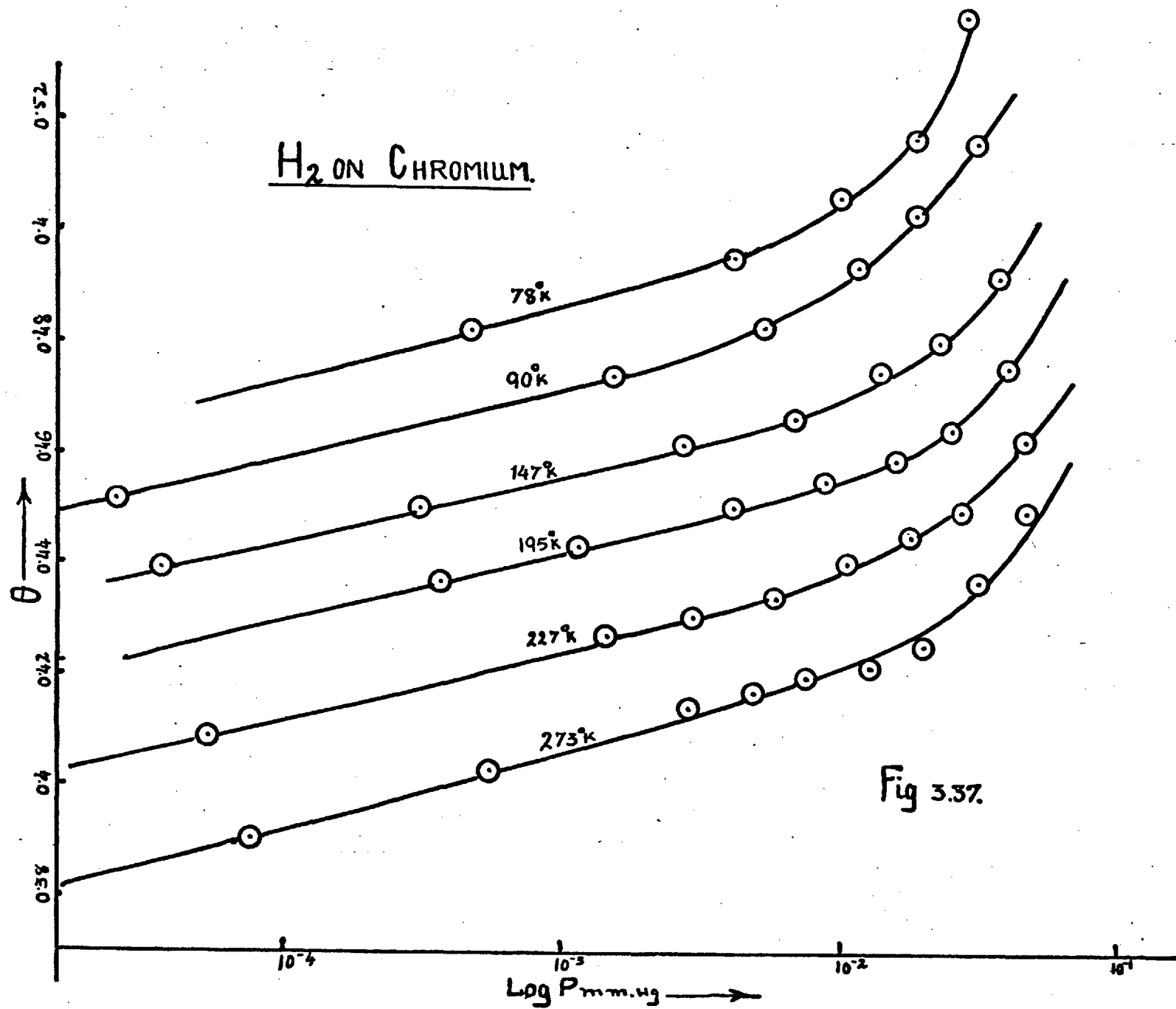
Table 3.12 continued

195°K		178°K	
Pressure mm Hg	Molecules $\times 10^{17}$	Pressure mm Hg	Molecules $\times 10^{17}$
1.51×10^{-4}	15.59	2.399×10^{-4}	22.31
3.46×10^{-4}	17.32	4.36×10^{-4}	24.80
7.24×10^{-4}	19.83	6.03×10^{-4}	26.91
1.58×10^{-3}	21.96	8.31×10^{-4}	47.81
2.40×10^{-3}	24.45		
2.88×10^{-3}	26.20		
3.98×10^{-3}	29.75		
5.01×10^{-3}	33.64		
5.75×10^{-3}	40.37		

3.2.2. Chromium

Hydrogen adsorption isotherms at different temperatures on chromium film sintered at 273°K are shown in fig.(3.37). These isotherms bend upwards at higher equilibrium pressure, a tendency not shown by the carbon monoxide isotherms. At 273°K hydrogen was adsorbed at a very slow rate, and the equilibrium was reached in about one hour at low equilibrium pressure. But at low temperatures the equilibrium was attained more quickly in less than 15 minutes. Two typical rate curves at 273° and 227°K are shown in fig.(3.40).

The heats were calculated at equal intervals of amount of gas adsorbed, and are plotted against θ in fig.(3.38). The area of film was determined by B.E.T. method, fig.(3.39).



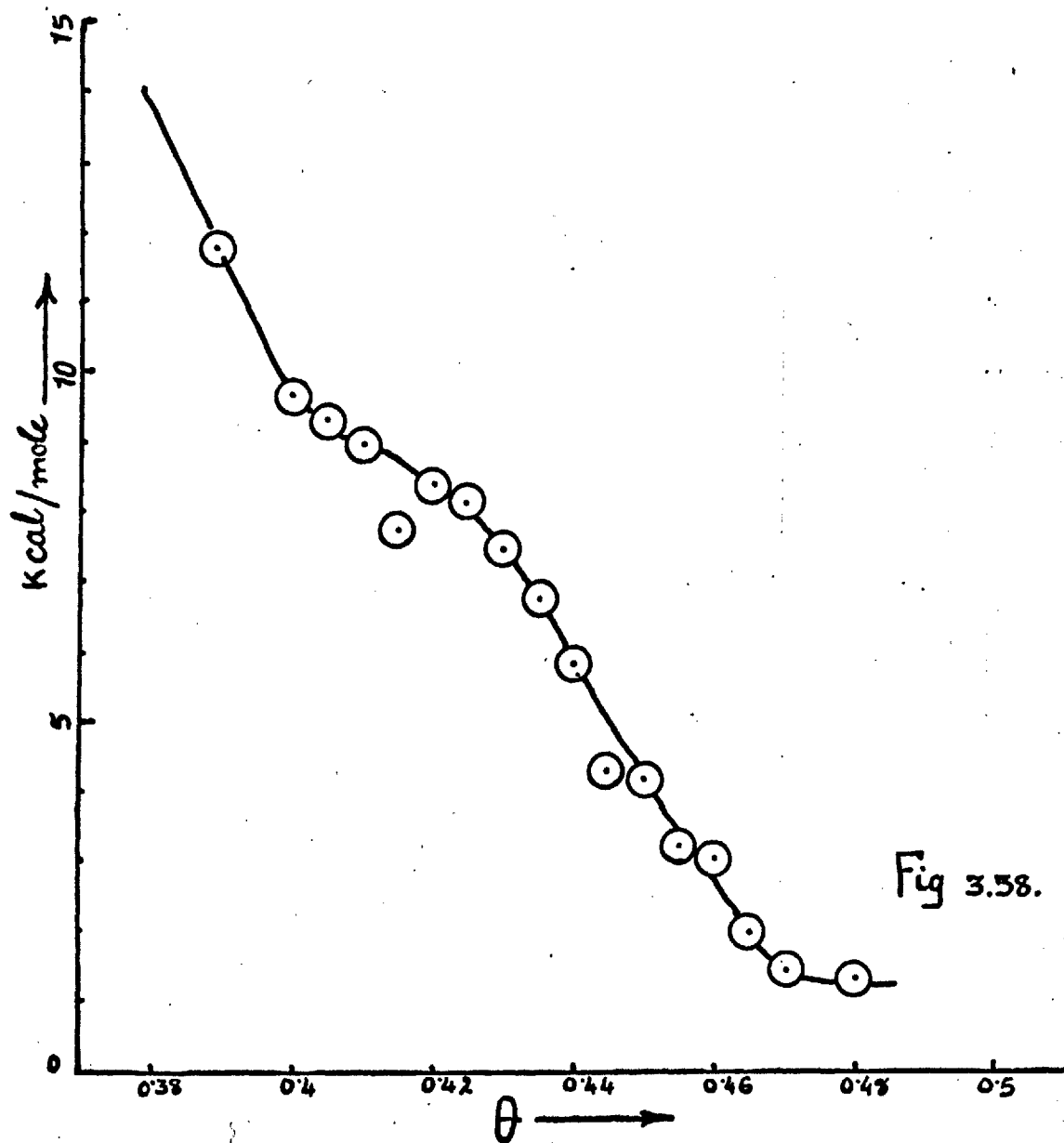


Fig 3.58.

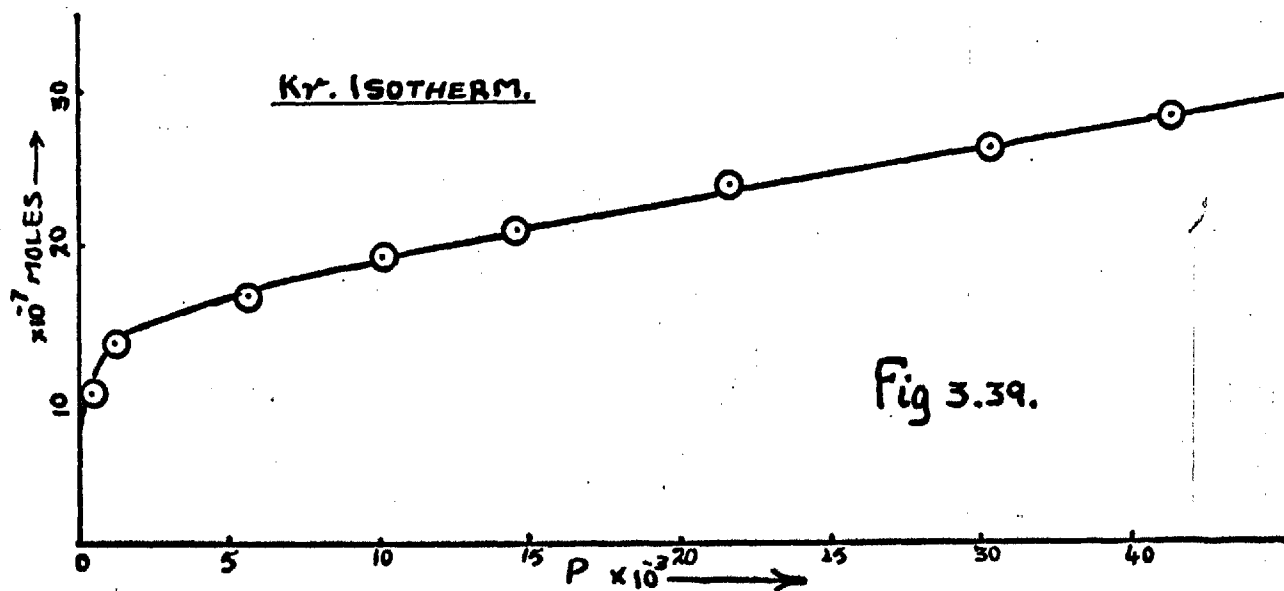
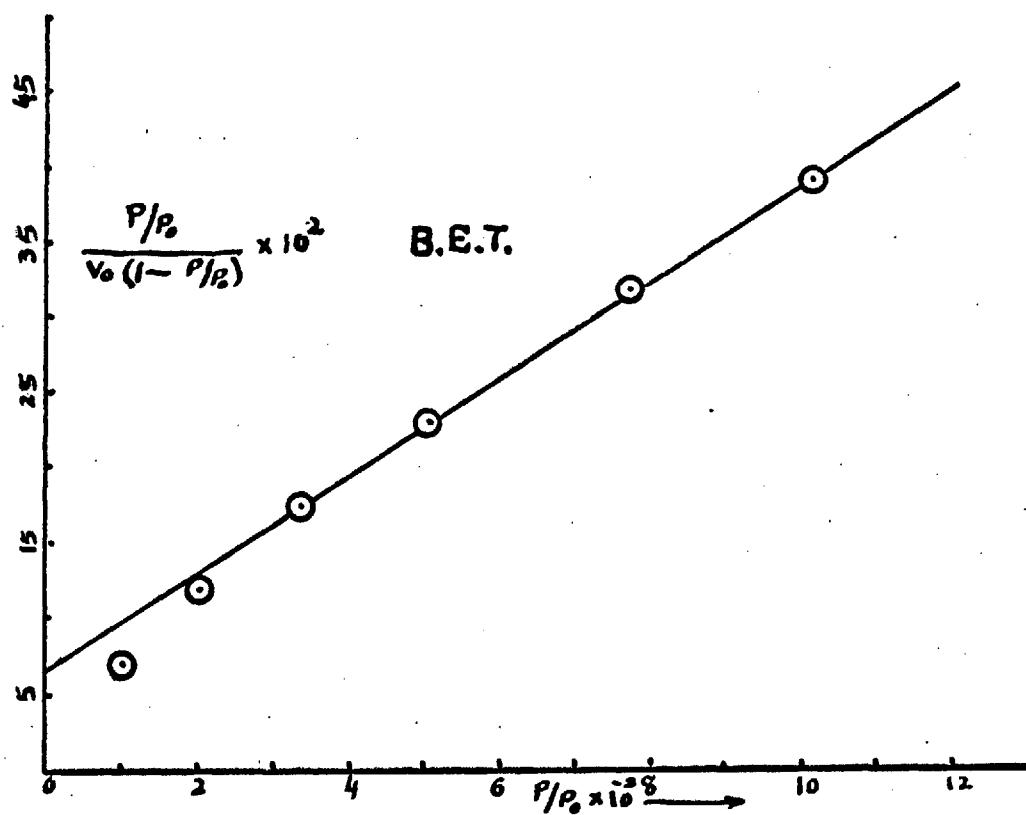


Fig 3.39.

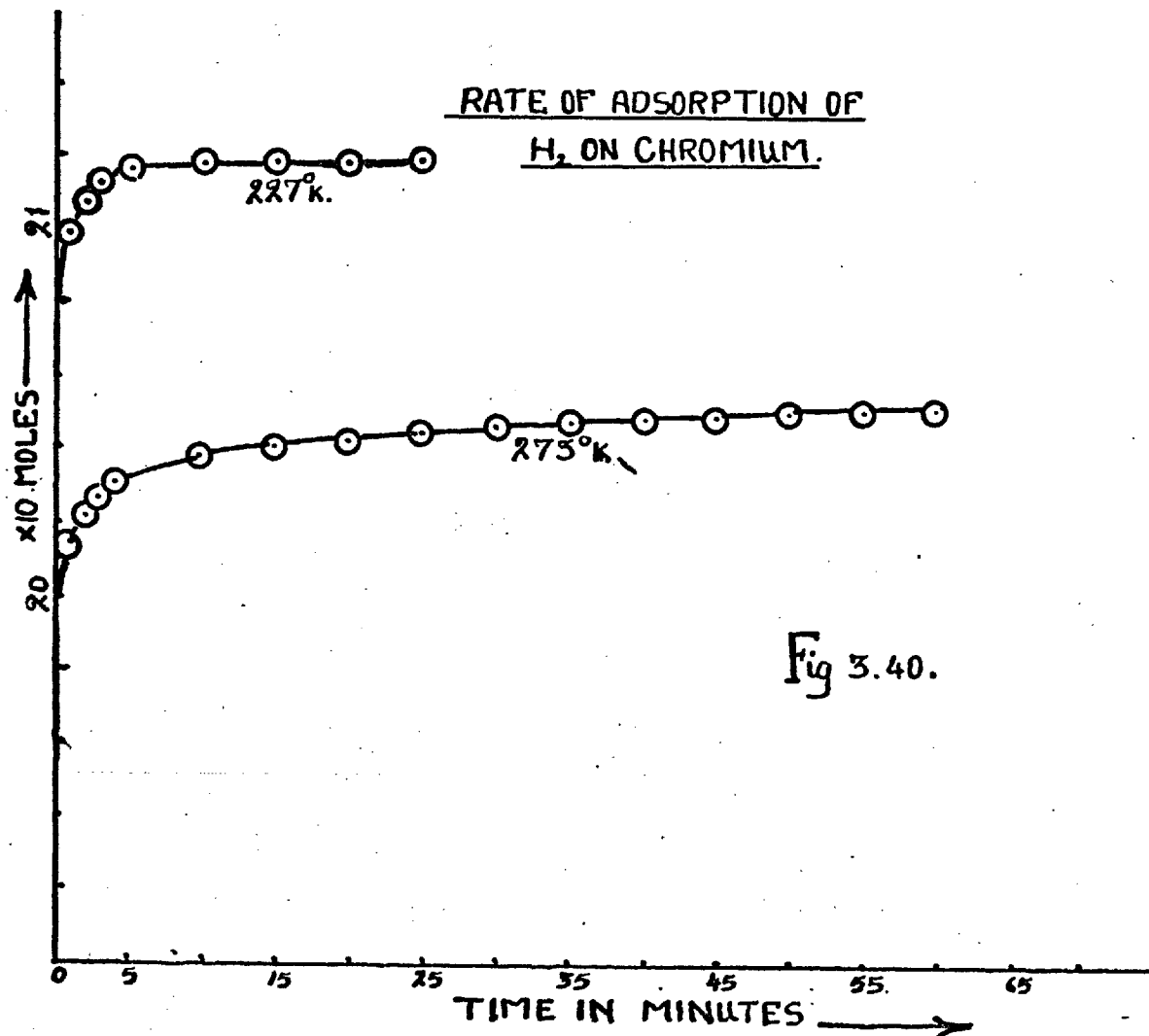


Fig 3.40.

Table 3.13Equilibrium sorption of Hydrogen by Chromium

Weight of film = 1.9 mg
 Area of film = 4180.98 sq.cm
 No. of sites = 6.815×10^{18}

273°K		227°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
7.58×10^{-5}	1.174	5.37×10^{-5}	1.232
5.50×10^{-4}	1.211	1.44×10^{-3}	1.286
2.88×10^{-3}	1.247	2.88×10^{-3}	1.295
4.78×10^{-3}	1.256	5.75×10^{-3}	1.307
7.58×10^{-3}	1.262	1.04×10^{-2}	1.325
1.26×10^{-2}	1.271	1.78×10^{-2}	1.34
2.0×10^{-2}	1.283	2.75×10^{-2}	1.352
3.16×10^{-2}	1.31	4.57×10^{-2}	1.391
4.78×10^{-2}	1.382		

Table 3.13 continued

195°K		147°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
3.631×10^{-4}	1.313	3.63×10^{-5}	1.322
1.14×10^{-3}	1.334	3.02×10^{-4}	1.355
4.17×10^{-3}	1.355	2.75×10^{-3}	1.391
8.71×10^{-3}	1.370	6.91×10^{-3}	1.403
1.58×10^{-2}	1.382	1.38×10^{-2}	1.43
2.51×10^{-2}	1.397	2.40×10^{-2}	1.446
3.98×10^{-2}	1.430	3.80×10^{-2}	1.479
90°K		78°K	
2.51×10^{-5}	1.361	4.78×10^{-4}	1.452
9.55×10^{-4}	1.427	4.17×10^{-3}	1.491
5.50×10^{-3}	1.455	1.0×10^{-2}	1.524
1.15×10^{-2}	1.488	1.90×10^{-2}	1.557
1.90×10^{-2}	1.515	2.89×10^{-2}	1.623
3.16×10^{-2}	1.554		

3.3. Nitric Oxide on Metals

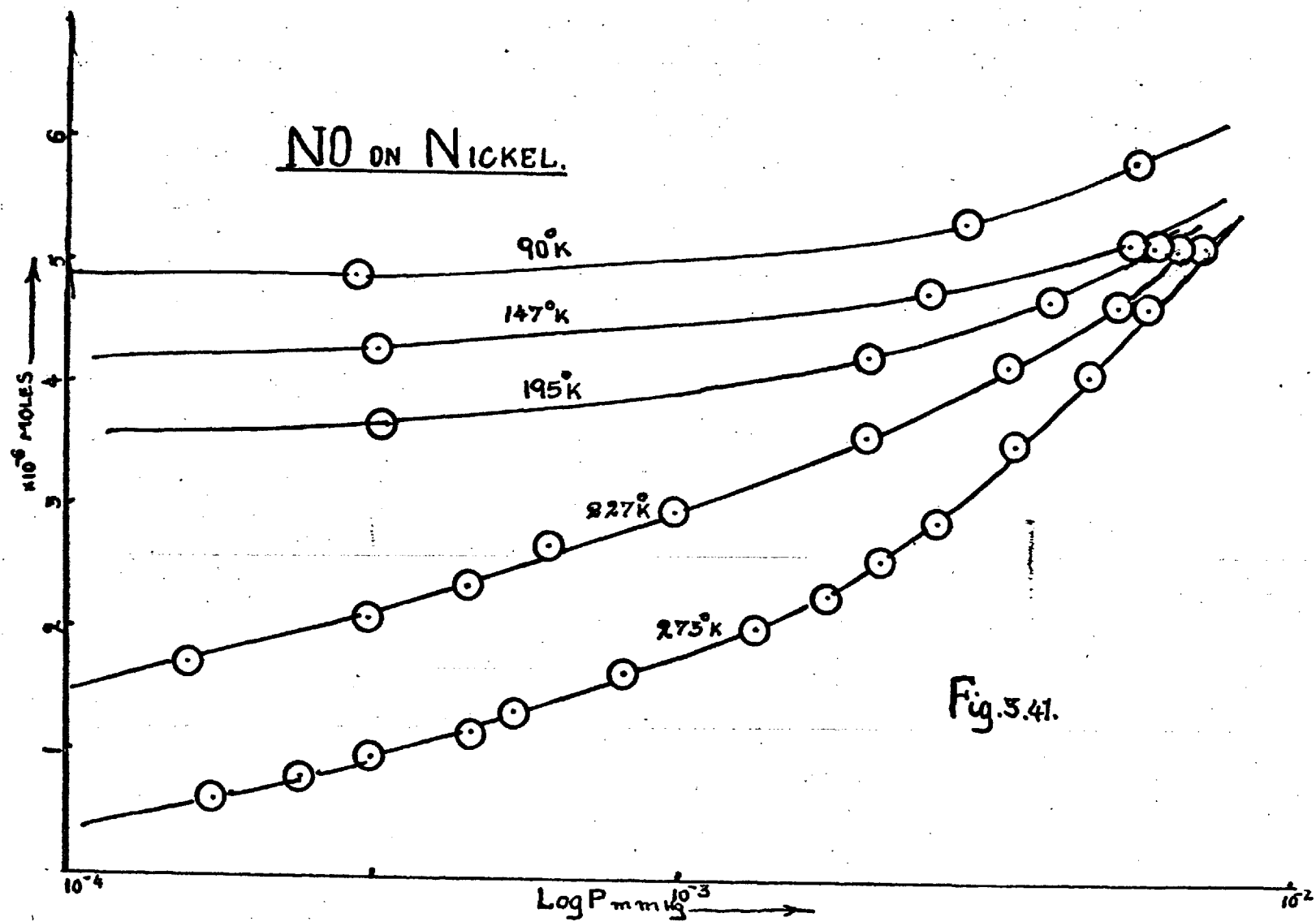
Adsorption of nitric oxide was studied on a number of metals. Very little adsorption of this gas was observed on copper, silver, gold and titanium film. With manganese the same kind of behaviour as with carbon monoxide was found, that is, no desorption took place, when the film was warmed from 195°K to 273°K , similarly if the gas was introduced at 273°K to the film, and the equilibrium obtained then no more gas was adsorbed on lowering the temperature to 195°K . Large amounts of gas were apparently adsorbed at 90° and 78°K .

3.3.1. Nickel

Adsorption isotherms of nitric oxide on nickel film sintered at 273°K are shown in fig.(3.41). The first measurable pressure was obtained after 3×10^{17} molecules had been adsorbed at 273°K ; the isotherms bend upwards and show a tendency to converge at higher coverage. Isotherms are plotted as amounts adsorbed : (number of moles) against $\log p$, as unfortunately no surface area was determined. for this film.

In Run II the film was sintered at 300°K , less amount of gas is taken up by the film and isotherms start bending up and come closer at a much lower equilibrium pressure than the isotherms in Run I. The isotherms are shown in fig.(3.42).

Comparatively less heat of adsorption is obtained for the same amount adsorbed and are plotted in fig.(3.43). The area of the film was determined by B.E.T. method, fig.(3.44).



NO ON NICKEL.
SINTERED AT 300°K.

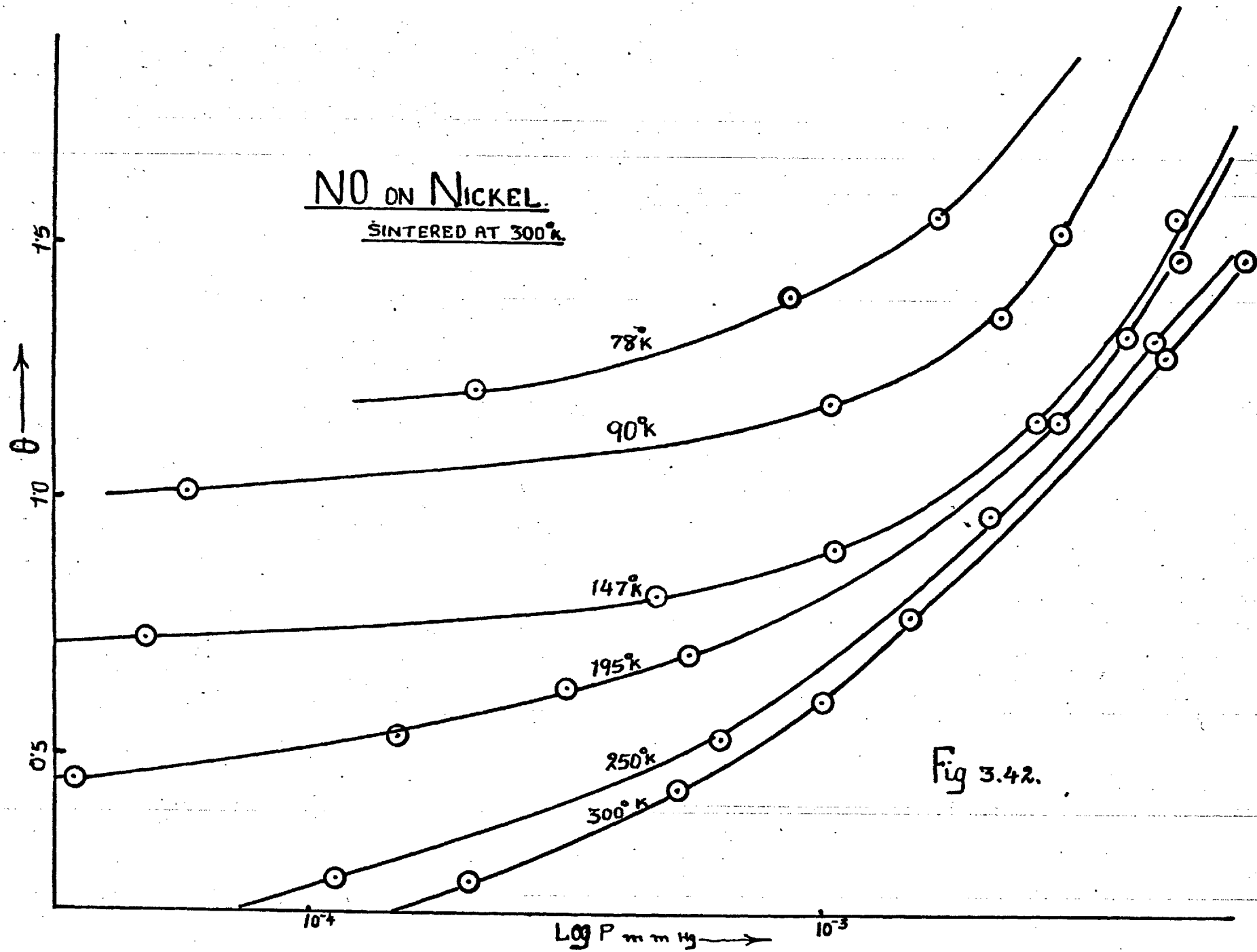
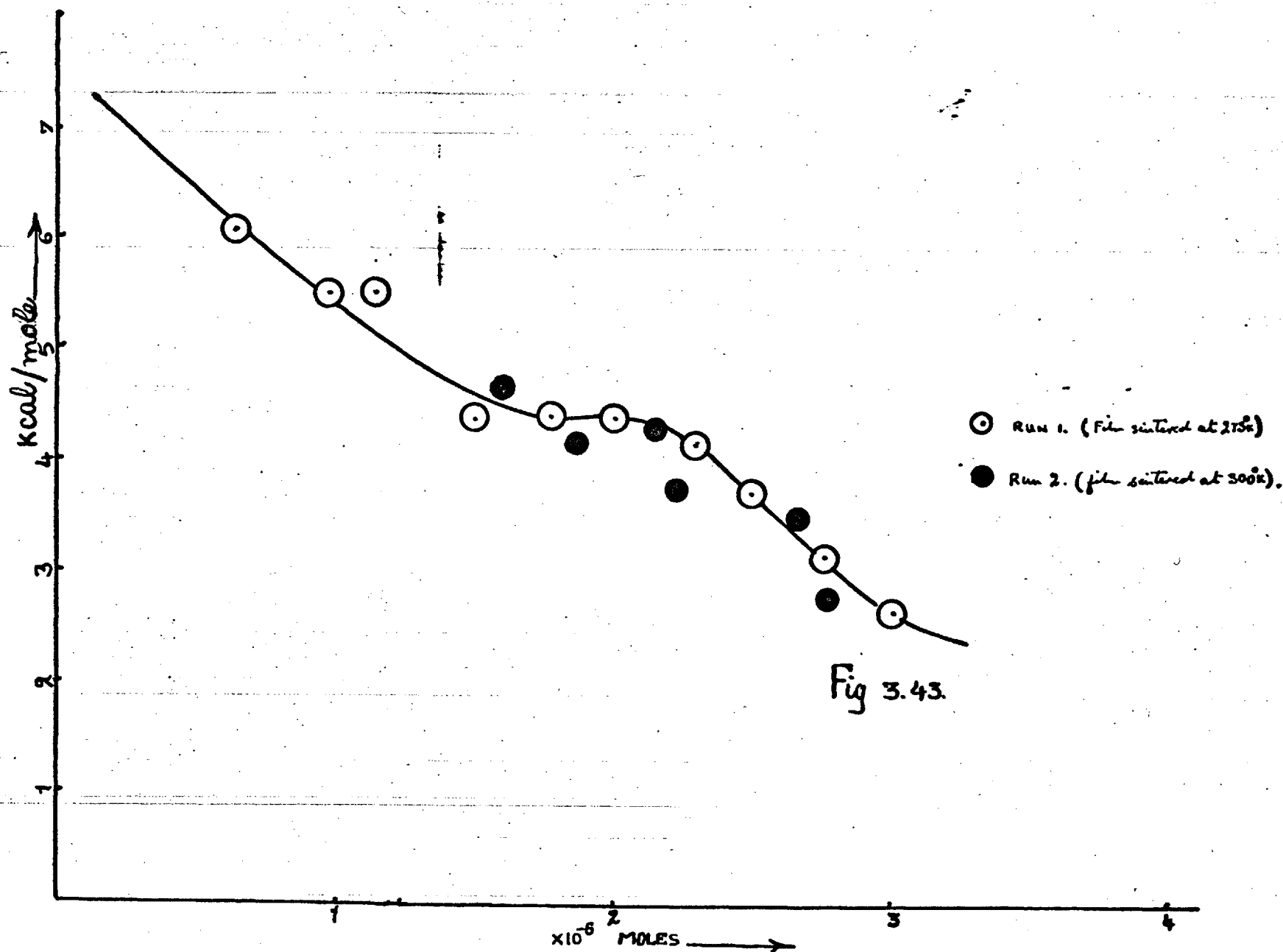


Fig 3.42.



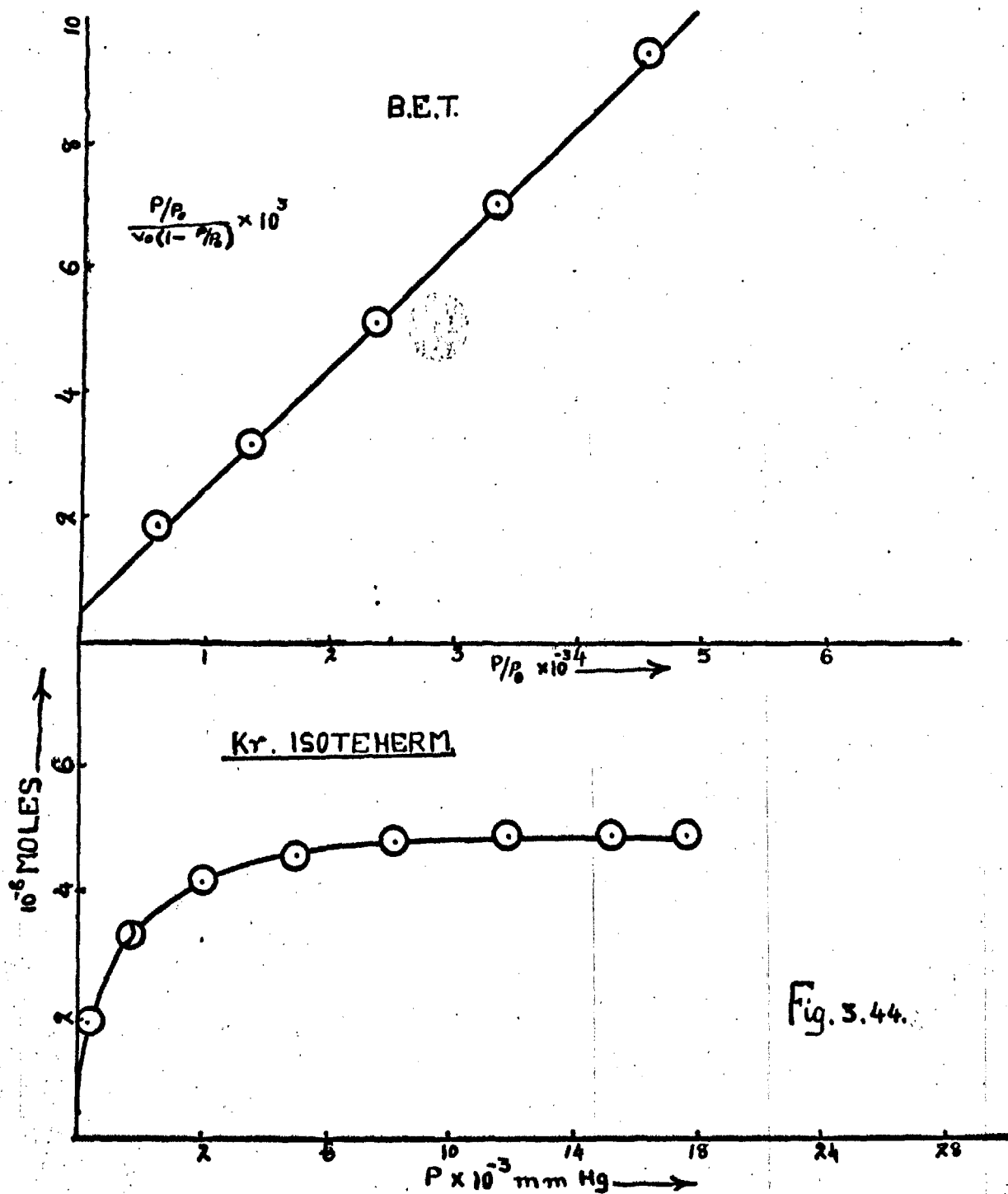


Fig. 3.44.

Table 3.14

Equilibrium adsorption of nitric oxide on Nickel
sintered at 300°K

Weight of the film = 22.2 mg

Area of film = 759.92 sq.cm

No. of sites = 1.1703×10^{18}

273°K		250°K	
Pressure mm Hg	Molecules $\times 10^{17}$	Pressure mm Hg	Molecules $\times 10^{17}$
1.45×10^{-4}	2.349	1.12×10^{-4}	2.409
2.04×10^{-4}	3.072	1.74×10^{-4}	3.01
5.25×10^{-4}	5.18	6.31×10^{-4}	6.26
1.0×10^{-3}	7.23	2.14×10^{-3}	11.44
1.45×10^{-3}	9.28	6.17×10^{-3}	17.47
4.37×10^{-3}	15.66		
6.61×10^{-3}	17.47		

Table 3.14 continued

195°K		147°K	
Pressure mm Hg	Molecules $\times 10^{17}$	Pressure mm Hg	Molecules $\times 10^{17}$
3.46×10^{-5}	5.30	4.78×10^{-5}	8.55
1.48×10^{-4}	6.38	4.68×10^{-4}	9.52
3.16×10^{-4}	7.47	1.05×10^{-3}	10.48
5.49×10^{-4}	8.31	1.51×10^{-3}	11.56
2.88×10^{-3}	13.61	2.63×10^{-3}	13.73
3.89×10^{-3}	15.66	4.9×10^{-3}	18.43
5.75×10^{-3}	17.47		
90°K		78°K	
5.75×10^{-5}	11.93	2.09×10^{-4}	14.21
1.02×10^{-3}	14.09	8.51×10^{-4}	16.5
2.19×10^{-3}	16.02	1.66×10^{-3}	18.43
2.88×10^{-3}	18.07		

Table 3.15Equilibrium adsorption of Nitric oxideon Nickel

Film sintered at 273°K

Film weight = 26,2 mg

273°K		227°K	
Pressure mm Hg	Molecules x 10 ¹⁷	Pressure mm Hg	Molecules x 10 ¹⁷
1.74 x10 ⁻⁴	3.8551	1.6 x10 ⁻³	10.18
2.43 x10 ⁻⁴	4.935	3.11 x10 ⁻⁴	12.266
3.098x10 ⁻⁴	5.92	4.44 x10 ⁻⁴	14.281
4.53 x10 ⁻⁴	6.91	6.05 x10 ⁻⁴	16.214
5.3 x10 ⁻⁴	7.896	9.82 x10 ⁻⁴	18.023
8.03 x10 ⁻⁴	9.911	1.992x10 ⁻³	21.771
1.34 x10 ⁻³	12.03	3.41 x10 ⁻³	25.189
1.74 x10 ⁻³	13.98	5.08 x10 ⁻³	28.327
2.13 x10 ⁻³	15.87	6.48 x10 ⁻³	31.320
2.603x10 ⁻³	17.625		
3.49 x10 ⁻³	21.43		
4.675x10 ⁻³	24.906		
5.772x10 ⁻³	28.185		
7.164x10 ⁻³	31.188		

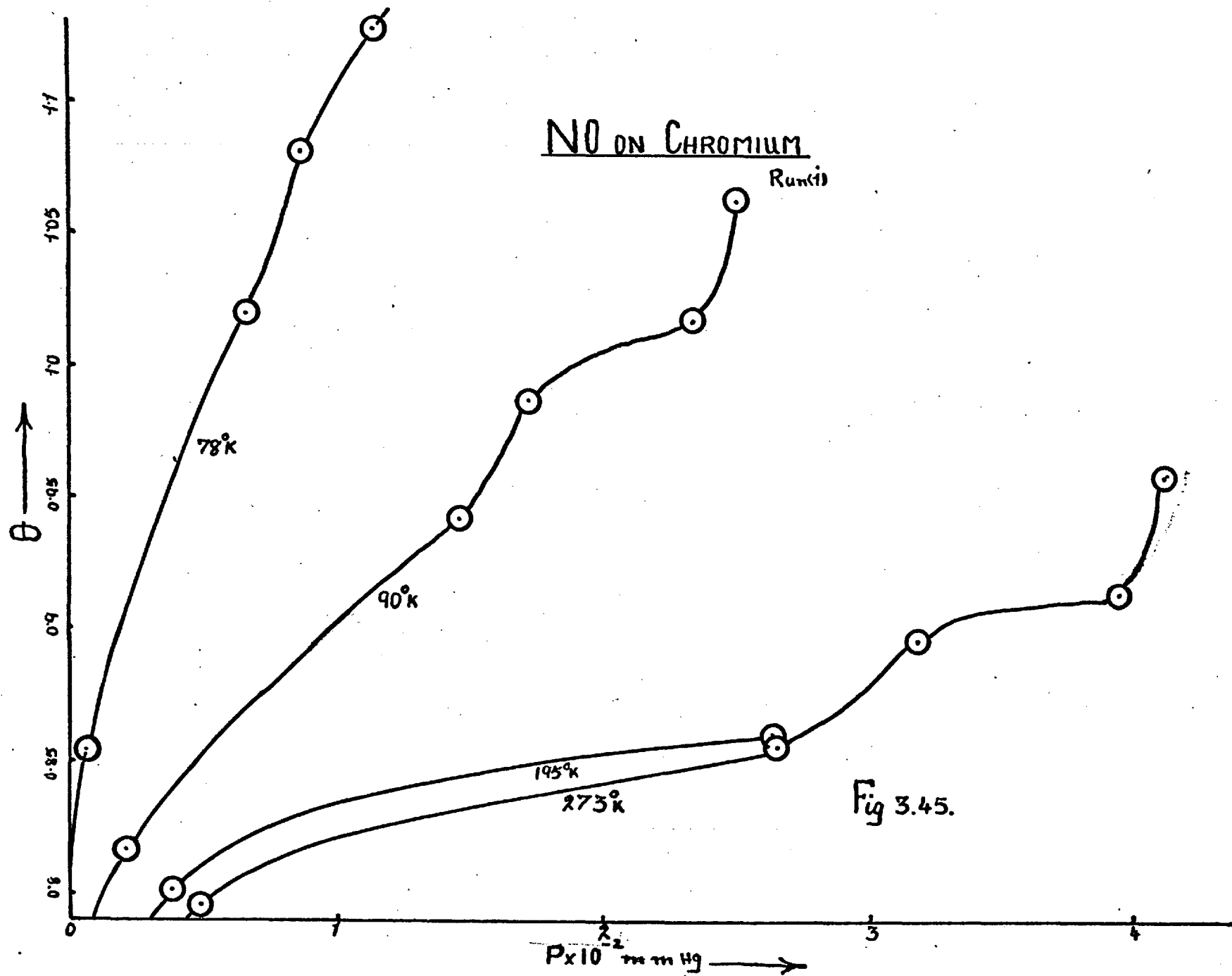
Table 3.15 continued

195°K	
Pressure mm Hg	Molecules $\times 10^{17}$
3.3×10^{-4}	22.16
1.975×10^{-3}	25.52
4.00×10^{-3}	28.571
6.1×10^{-3}	31.38
147°K	
3.21×10^{-4}	25.915
2.493×10^{-3}	28.104
5.68×10^{-3}	31.425
90°K	
2.943×10^{-4}	29.453
2.89×10^{-3}	32.073
5.61×10^{-3}	35.511

3.3.2. Chromium

Large amounts of nitric oxide was adsorbed on chromium film sintered at 273°K . At low coverage a further small amount of gas was taken up by the metal on lowering the temperature of the film to 195°K . Above a certain coverage the isotherms at 273° , 90° and 78°K show stepwise adsorption, fig.(3.45).

In Run II the film was sintered at 273°K and the isotherms were obtained at 195°K , 90°K and 78°K , fig.(3.46). There was little difference in the amount adsorbed at 195°K and 147°K . The isotherms as in Run I show a stepwise adsorption. At the end of the run the film was warmed to 273°K ; there was a slight desorption, which was followed by more gas being taken up at this temperature than at 195°K . After the equilibrium was reached, the film was cooled to 195°K , but no adsorption took place. However, more gas was taken up at 90°K and 78°K , fig.(3.49).



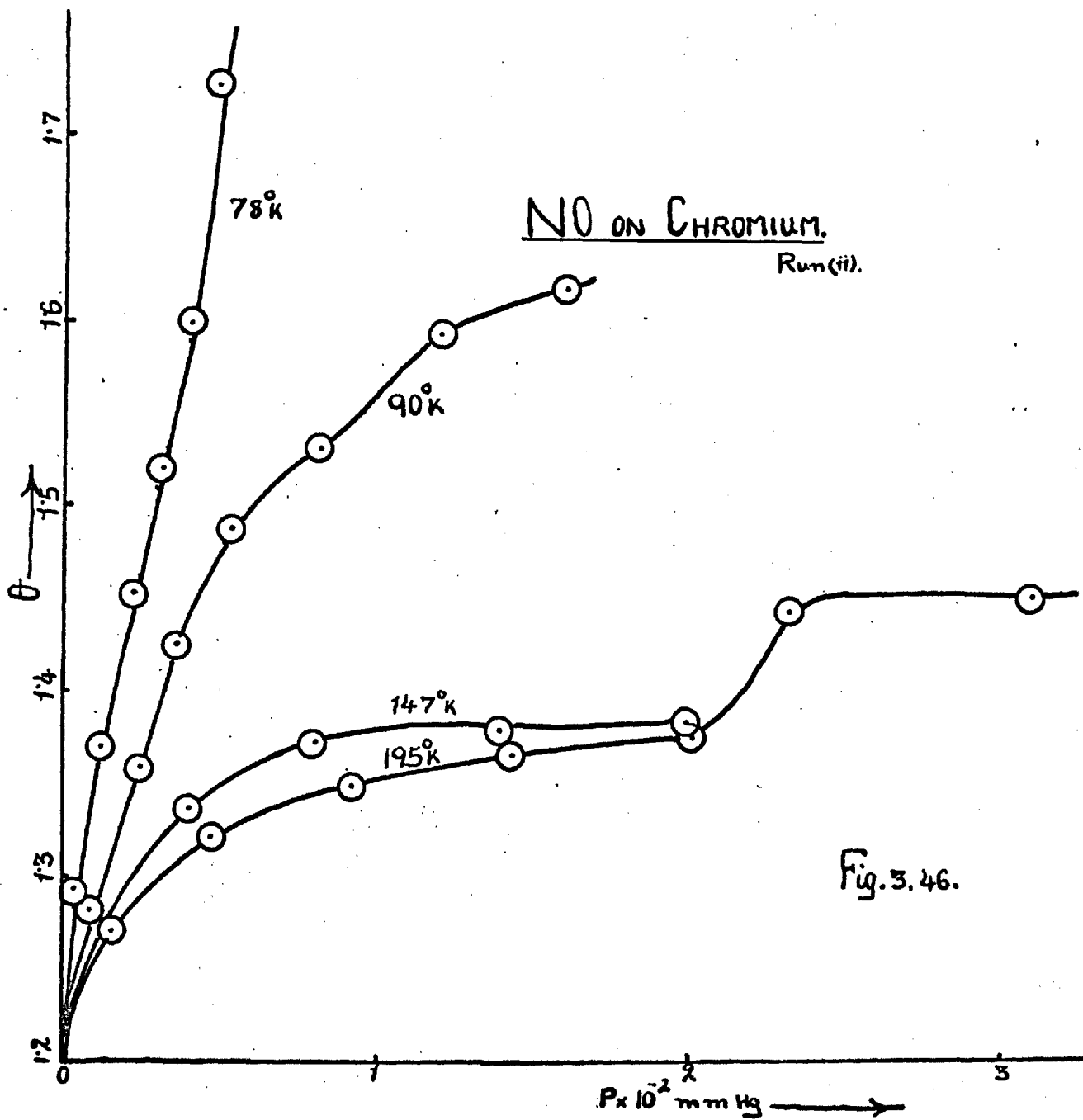
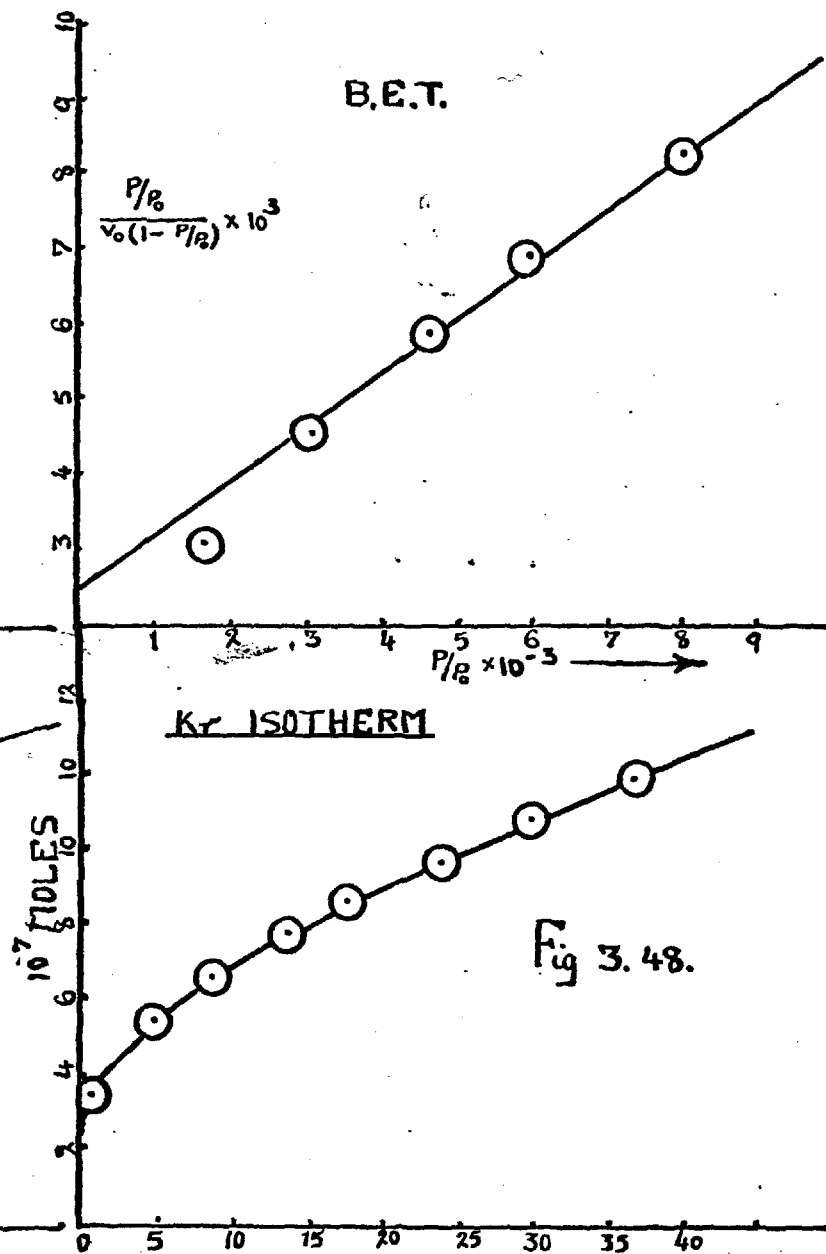
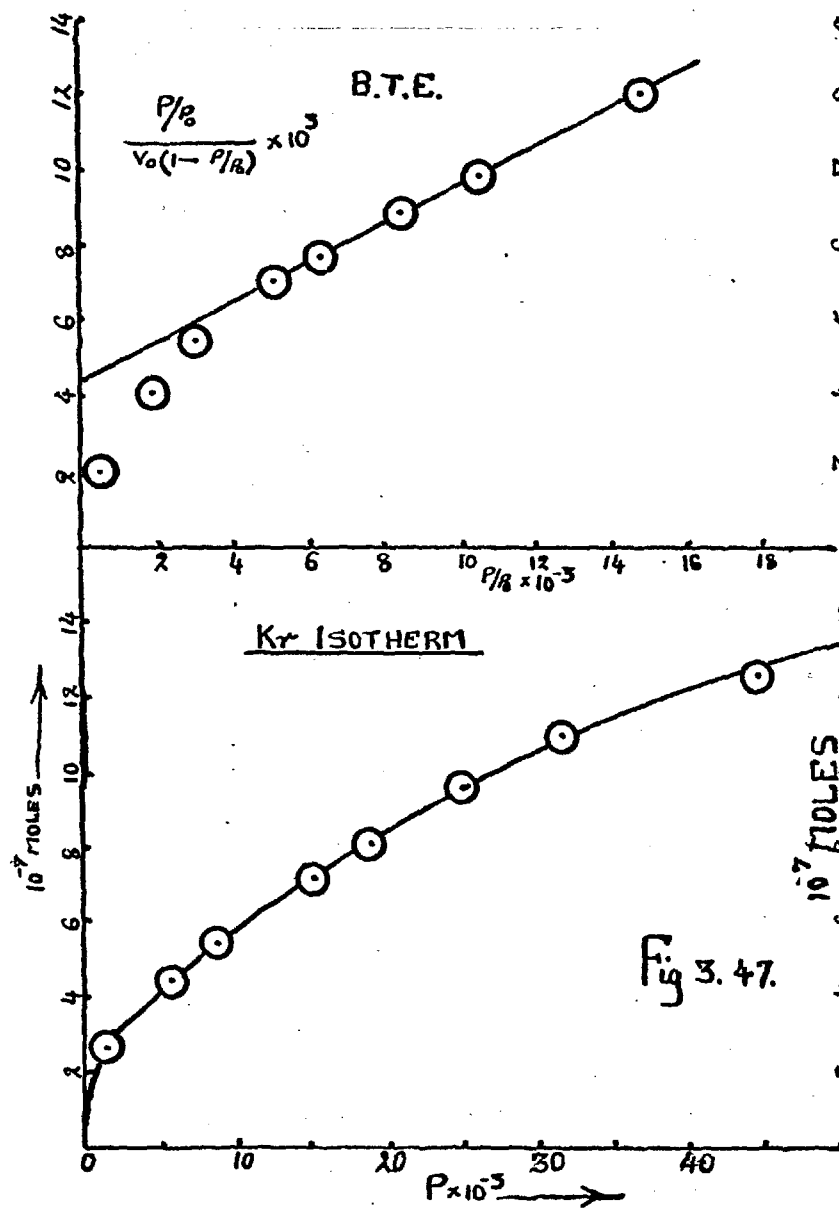


Fig. 3.46.



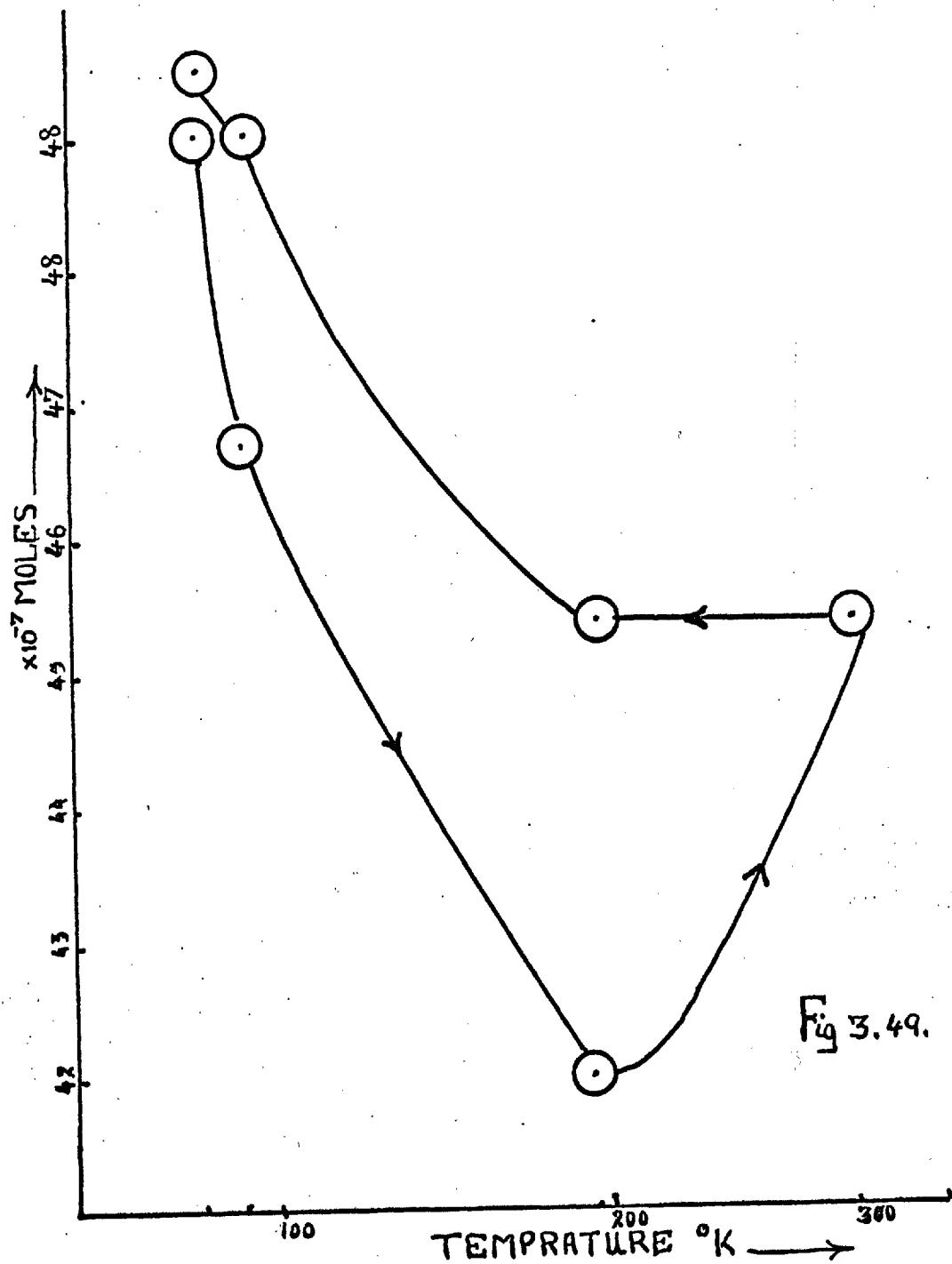


Table 3.16
Equilibrium adsorption of nitric oxide
on Chromium

Run I

Weight of film = 6.3 mg
 Area of film = 2265.9 sq.cm
 No. of sites = 2.801×10^{18}

273°K		195°K	
Pressure mm Hg	Molecules $\times 10^{18}$	Pressure mm Hg	Molecules $\times 10^{18}$
3.18×10^{-3}	2.168	2.64×10^{-3}	2.18
4.85×10^{-3}	2.228	3.58×10^{-3}	2.259
2.65×10^{-3}	2.397	2.64×10^{-3}	2.403
3.16×10^{-2}	2.512		
3.865×10^{-2}	2.560		
4.16×10^{-2}	2.686		
90°K		78°K	
2.19×10^{-3}	2.289	4.77×10^{-4}	2.391
1.47×10^{-2}	2.638	6.64×10^{-3}	2.855
1.78×10^{-2}	2.765	8.53×10^{-3}	3.03
2.259×10^{-2}	2.849	1.14×10^{-2}	3.156
2.51×10^{-2}	2.975		

Table 3.17

Equilibrium adsorption of Nitric Oxide on ChromiumRun II

Weight of film = 3.6 mg

Area of film (II)=1405.17 sq.cm

No. of sites = 1.742×10^{18}

195°K		147°K	
Pressure	Molecules $\times 10^{18}$	Pressure	Molecules $\times 10^{18}$
1.8×10^{-3}	2.210	4.02×10^{-3}	2.325
4.4×10^{-3}	2.306	8.12×10^{-3}	2.385
9.21×10^{-3}	2.349	1.435×10^{-2}	2.397
1.45×10^{-2}	2.379	2.0×10^{-2}	2.403
2.03×10^{-2}	2.397		
2.42×10^{-2}	2.518		
3.1×10^{-2}	2.524		
90°K		78°K	
9.8×10^{-4}	2.229	4.25×10^{-4}	2.247
2.36×10^{-3}	2.361	1.24×10^{-3}	2.246
3.65×10^{-3}	2.481	2.3×10^{-3}	2.391
5.41×10^{-3}	2.590	3.27×10^{-3}	2.524
8.198×10^{-3}	2.662	3.78×10^{-3}	2.644
1.2×10^{-2}	2.771	5.026×10^{-3}	2.783
1.59×10^{-2}	2.813		

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2. Wyckoff, Crystal Structure, 1948.
3. Trapnell, Proc. Roy. Soc. A.218, 566, 1953.

4.1. Carbon Monoxide Adsorption

It was found that carbon monoxide adsorption on palladium, platinum, titanium, chromium, manganese and cobalt, obeyed the Langmuir equation in that when P/V is plotted against p , all the points fall on a straight line, whereas the Freundlich equation is followed by carbon monoxide adsorption on copper and gold. Silver is the only exception in that neither of the two isotherms was obeyed.

Langmuir Isotherm

The isotherm may be written in the form

$$\frac{p}{\theta} = \frac{1}{a} + p$$
$$\text{or } \frac{p}{V} = \frac{1}{aV_m} + \frac{p}{V_m}$$

where V_m is volume adsorbed in the monolayer. The Langmuir isotherm is derived making the three main assumptions :-

1. Adsorption is localised.
2. Only one molecule of the gas is adsorbed on one site.
3. The energy of the adsorbed particle is the same at all points on the surface, and is independent of coverage, i.e. there is no lateral interaction between adsorbed molecules, and the heat of adsorption is constant with coverage.

The first two conditions are met by the carbon monoxide adsorption on palladium, titanium, chromium, manganese and cobalt, i.e. one molecule of carbon monoxide is adsorbed on one site. Thus if

the number of carbon monoxide molecules in the monolayer is n_{CO} , and the area A_S of one site on the film is known, then the area A_F of the film can be calculated from

$$A_F = A_S \times n_{CO} \quad (i)$$

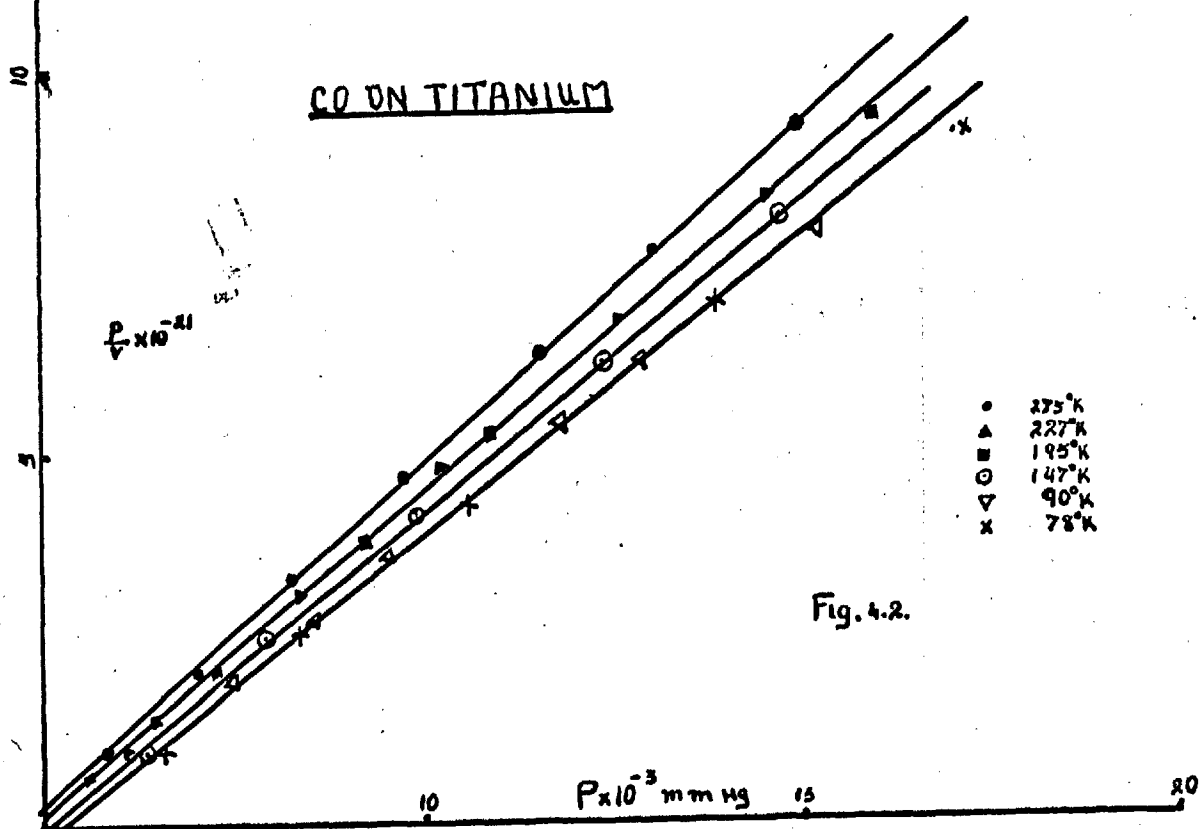
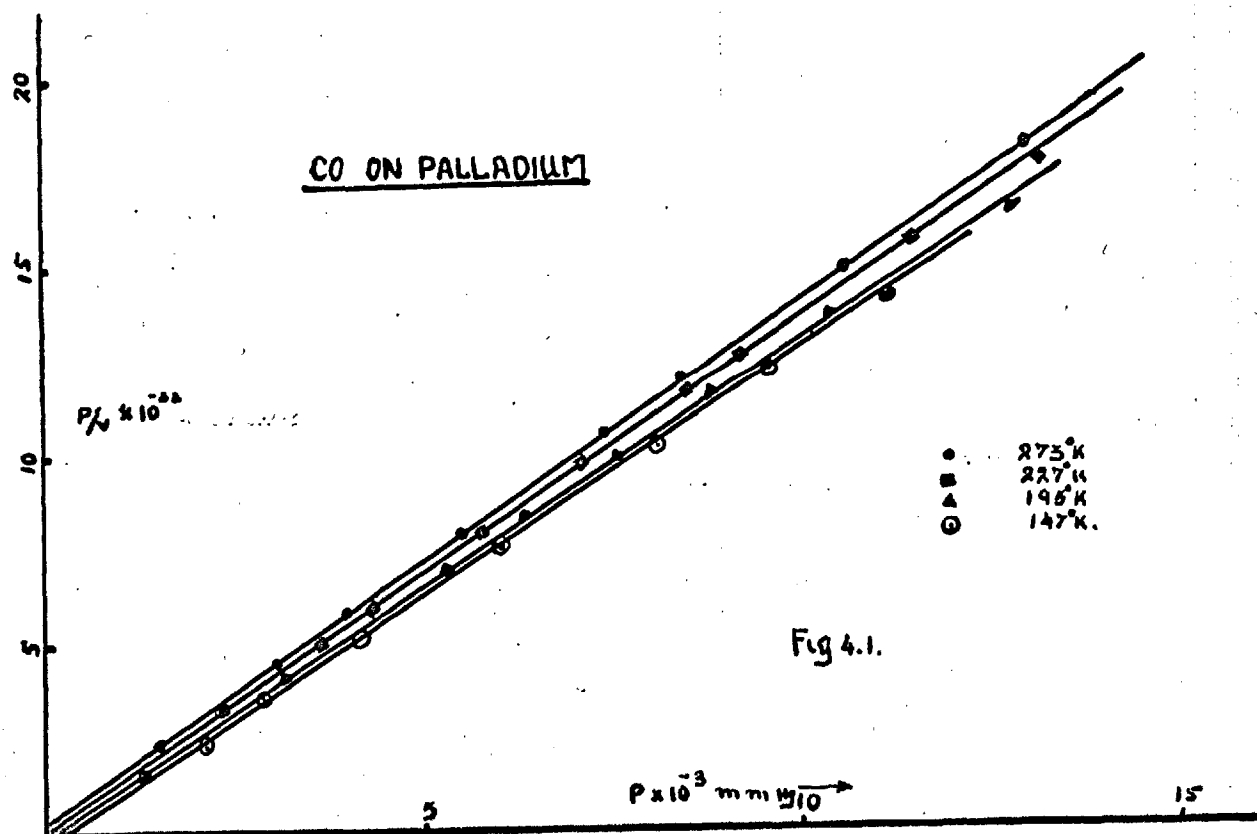
The area of each film was also determined by the B.E.T. method using krypton, after the carbon monoxide adsorption isotherm had been determined. Thus, using the number of krypton molecules in the monolayer n_{Kr} , and the cross-sectional area of the krypton molecule (which is generally taken as 19.5×10^{-16} sq.cm) corresponding to some type of close-packing on the surface,

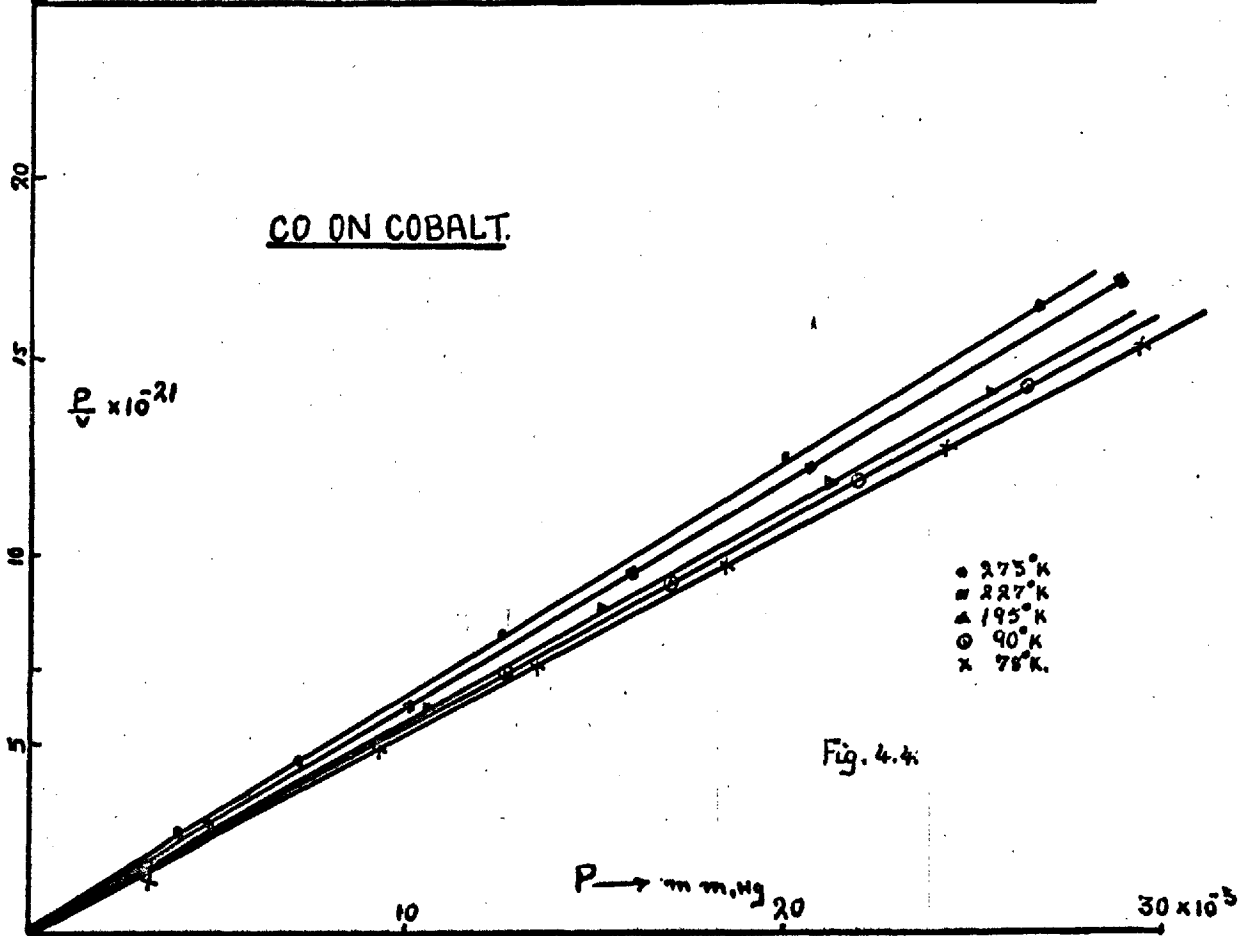
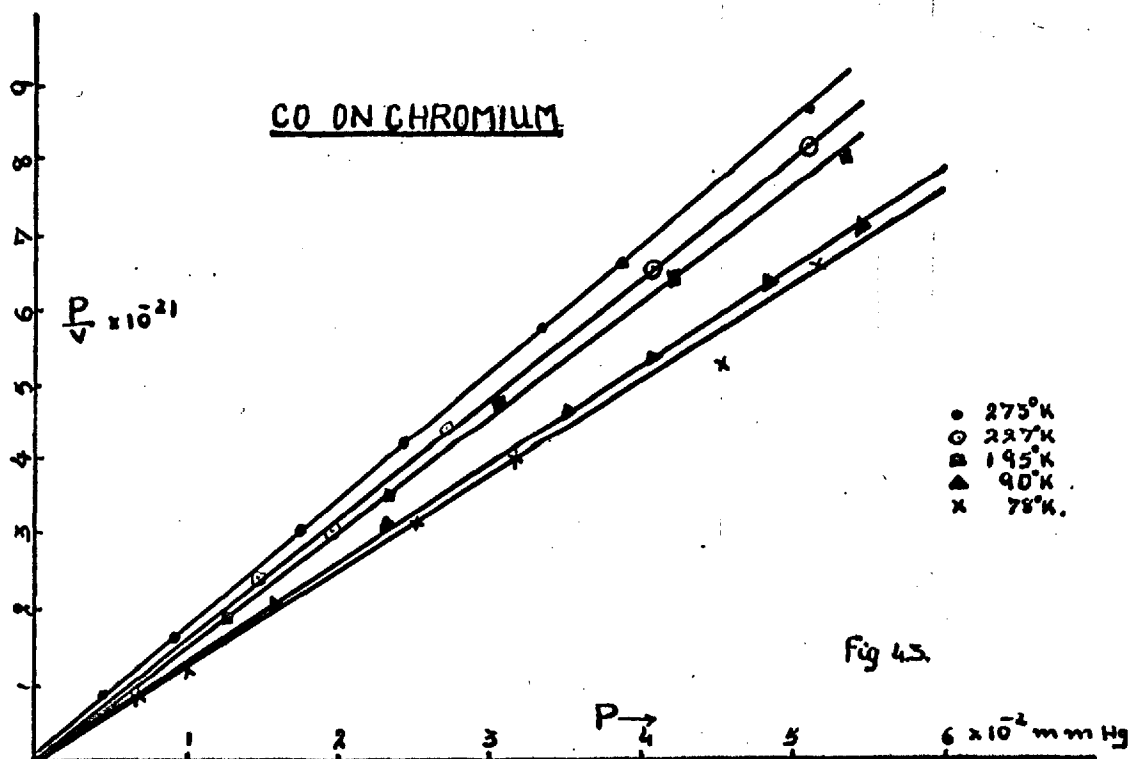
$$A_F = n_{Kr} \times 19.5 \times 10^{-16} \text{ sq.cm} \quad (ii)$$

From (i) and (ii)

$$\frac{n_{CO}}{n_{Kr}} = \frac{19.5 \times 10^{-16}}{A_S}$$

n_{CO} value at different temperatures for palladium, platinum, chromium, manganese and cobalt are given in table 4.1. These values were calculated from their respective p/V against V plots, shown in fig.4.1 to 4.6.





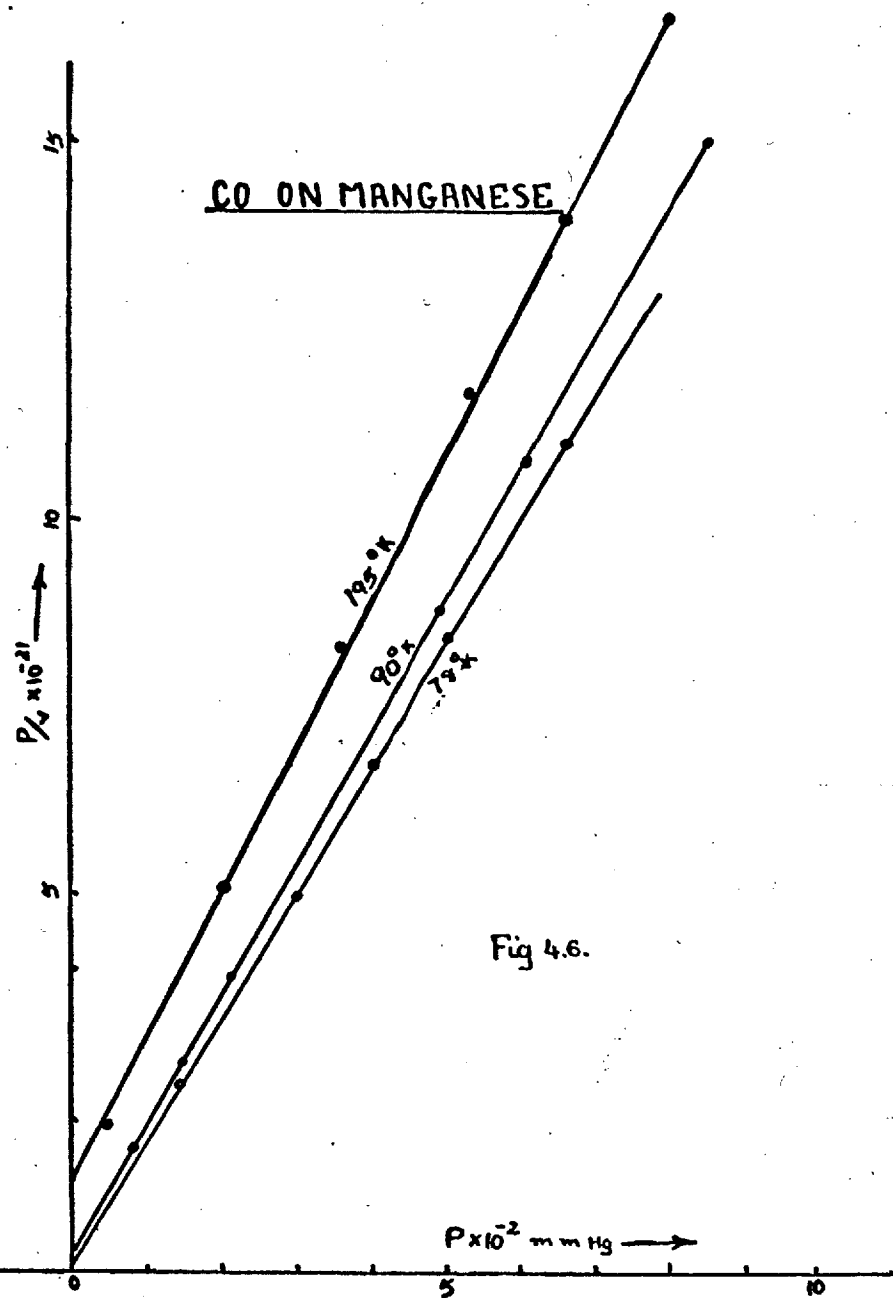
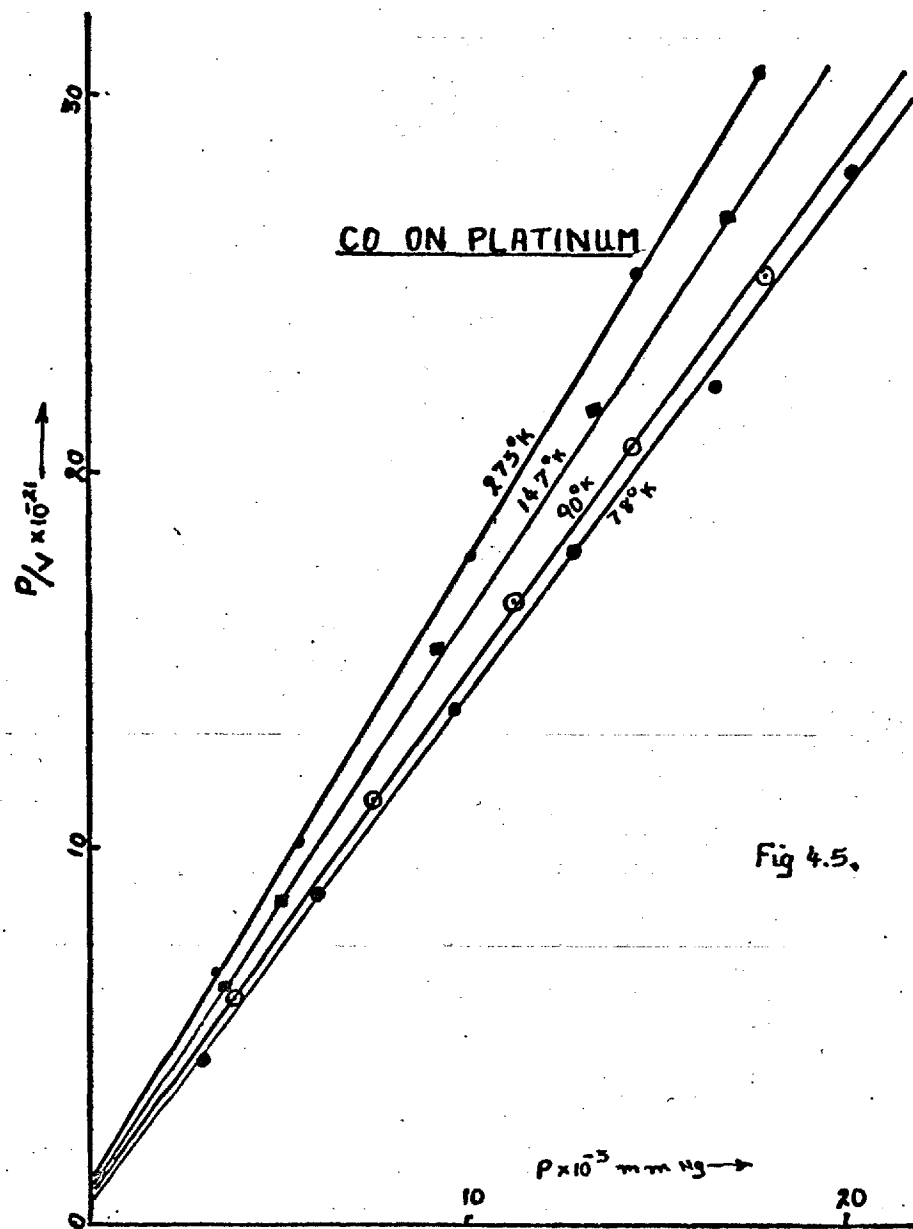


Table 4.1

Metal	Temperature	No. of CO molecules in the monolayer n_{CO}	No. of Kr molecules in the monolayer n_{Kr} (B.E.T)	n_{CO}/n_{Kr} experimental	Mean n_{CO}/n_{Kr}	n_{CO}/n_{Kr} (semi-theoretical)
Palladium	273°K	7.25×10^{17}	2.99×10^{17}	2.42	2.53	2.48
	227°K	7.52×10^{17}		2.51		
	195°K	7.52×10^{17}		2.51		
	147°K	8.0×10^{17}		2.68		
Platinum	273°K	5.75×10^{17}	4.07×10^{17}	1.41	1.695	2.43
	147°K	6.71×10^{17}		1.65		
	90°K	7.46×10^{17}		1.83		
	78°K	7.69×10^{17}		1.89		
Titanium	273°K	2.3×10^{18}	8.29×10^{17}	2.77	2.91	2.63
	227°K	2.25×10^{18}		2.71		
	195°K	2.31×10^{18}		2.78		
	147°K	2.4×10^{18}		2.89		
	90°K	2.62×10^{18}		3.16		
	78°K	2.62×10^{18}		3.16		
Chromium	273°K	5.47×10^{18}	3.05×10^{18}	(1.71)	2.35	3.18
	227°K	6.25×10^{18}		2.05		
	195°K	6.45×10^{18}		2.11		
	90°K	7.75×10^{18}		2.55		
	78°K	8.06×10^{18}		2.64		

Table 4.1 (continued)

Metal	Temperature	No. of CO molecules in the monolayer n_{CO}	No. of Kr molecules in the monolayer n_{Kr} (B.E.T)	n_{CO}/n_{Kr} experimental	Mean n_{CO}/n_{Kr}	n_{CO}/n_{Kr} (semi-theoretical)
Manganese	195°K	4.386×10^{18}	2.41×10^{18}	1.82	(2.26) 2.48 (best value)	2.42
	90°K	5.983×10^{18}		2.48		
	78°K	5.988×10^{18}		2.48		
Cobalt	273°K	1.58×10^{18}	7.25×10^{17}	2.19	2.36	2.94
	227°K	1.667×10^{18}		2.3		
	195°K	1.786×10^{18}		2.46		
	147°K	1.852×10^{18}		2.56		
	90°K	1.887×10^{18}		2.6		

For palladium, titanium, chromium and manganese, the experimental ratio $\frac{n_{CO}}{n_{Kr}}$ is in good agreement with the theoretical value (which is obtained by dividing the cross-sectional area of the krypton molecule by the average area of one site, obtained from table 2.1, in which the number of sites per sq.cm is given for each metal) showing that one carbon monoxide molecule is adsorbed on one site.

The fact that the krypton molecules are "close-packed" on the surface rather than adsorbed at specific lattice sites

receives some confirmation from its adsorption heat. The heat of adsorption of krypton on different metals was therefore calculated, from the B.E.T. equation, in which $c = e^{(q-q_L)/RT}$; q is the heat of adsorption, and q_L is the heat of liquifaction of krypton at 78°K . The calculated values of q with the corresponding values of c for each metal are given in table 4.2. A value of $q_L = 2.24$ kcal./mole was used in these calculations.

Table 4.2

Metal	c	Melting point $^\circ\text{C}$	Area/100 mg in sq.cm	q in kcal.mole ⁻¹
Palladium	2779	1549.4	1649.1	3.47
Platinum	1681	1773.5	2661	3.39
Titanium	2701	1800.0	10633	3.47
Chromium	781	1890.0	45741	3.28
Manganese	1301	1260.0	36703	3.36
Cobalt	639	1495.0	7819	3.24
Copper	1231	1083.0	4902	3.35
Silver	1951	960.8	4671	3.42
Gold	1551	1063.0	3660	3.38

The heats are practically the same for all metals, which shows that the average heat of adsorption of krypton is almost

independent of the nature of the surface. One would expect from this that adsorbed krypton has the same type of configuration on each metal, the most likely being the close-packed arrangement.

The agreement of $n_{\text{CO}}/n_{\text{Kr}}$ with the theoretical value is based on two assumptions.

(i) The krypton cross-sectional area is usually taken as the normal "B.E.T." value of 19.5×10^{-16} sq.cm. This value was derived originally by comparison of nitrogen and krypton isotherms on non-metallic adsorbents, but it is, in fact, larger than the area derived from close-packing, viz. 13.53×10^{-16} sq.cm.

(ii) The carbon monoxide is linearly bonded, i.e. one carbon monoxide molecule is adsorbed per lattice square or per surface metal atom. Now there is considerable infra-red spectra data showing that the bridged form of bonding (i.e., one carbon monoxide molecule attached to two metal sites) is often present. However, one would expect that at the monolayer the linear form would be preferred, because the higher adsorption corresponds to a smaller free energy of the system.

However, there are two possible configurations for the krypton molecules present in the monolayer.

(i) A close-packed configuration,

(ii) a configuration decided by the surface structure of the adsorbent.

Hayes⁽¹⁾ has found, using films of nickel, cobalt and platinum,

that the number of atoms of krypton and xenon in the monolayer are the same, which suggests a site mechanism, because the area of xenon atom is some 20% greater than that of the krypton atom (the diameters are respectively $4.39\text{\AA}$ and $3.96\text{\AA}$ as derived from the dimension of their crystal lattices). In most cases, he found that the value of V_m as determined by the isotherm was the same to within 2%. Field emission studies also very clearly demonstrated the dependence of the adsorption of argon, krypton and xenon on the different crystal faces of tungsten^(3,4,5) and of xenon on molybdenum⁽⁶⁾. This in itself is not a proof of site adsorption since the observation can be accounted for in terms of the varying polarisability of one face compared with the other. However, the theoretical treatment of Margenau and Pollard⁽⁷⁾ has shown that a metal functions as a dielectric in van der Waal adsorption, and on this basis the dependence of adsorption on crystal face would be a function of the surface structure of the individual atoms comprising a given face rather than of the overall polarisability of the crystal plane, and this supports a site mechanism.

It may be noted that the diameters of the krypton, xenon and carbon monoxide molecules are very nearly the same, but the ratio of the carbon monoxide molecules adsorbed at 0°C to the number of molecules of krypton in the monolayer is always greater than one. Consequently if a close-packed arrangement for krypton is accepted, then a site adsorption for the carbon monoxide molecules must be

assumed; or, accepting the latter from infra-red studies, the krypton layer is close-packed.

On the other hand, if site adsorption for krypton molecules is accepted, then the ratios between $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ given in table 4.1 are always greater than 2 for all metals at all temperatures except for platinum, indicating an improbable arrangement of two carbon monoxide molecules per surface metal atom, although this has been suggested for rhodium from infra-red spectra. Hence, to obtain the theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ there must be a close-packed configuration of krypton molecules, and the good agreement with palladium, titanium and manganese between the experimental and theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ show that there is a predominance of linear bonding of carbon monoxide molecules.

It should be noted that the area of the lattice site has been taken on the average of the (100), (110) and (111) planes present in equal amounts. However, the n_{CO} value for chromium increases with decreasing temperature, and the average experimental value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ is less than the theoretical value. The area of its three lattice planes, (110), (100) and (111) is $7.21\text{\AA}^2$, $8.32\text{\AA}^2$ and $2.9\text{\AA}^2$ respectively (lattice areas are calculated from the X-ray lattice constants $2.498\text{\AA}$ and $2.885\text{\AA}$ ⁽⁸⁾). If the surface is orientated with the (110) face uppermost, the theoretical value for $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ is 2.7, and for the (100) face, the theoretical ratio becomes 2.34 compared with the experimental average value is 2.35.

This agreement could indicate that the (100) face predominates, although within the accuracy expected the (110) face cannot be ruled out. Similarly with cobalt, the theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ is higher than the experimental value. Now the area of the lattice planes (110), (100) and (111) are $8.97\text{\AA}^2$, $6.35\text{\AA}^2$ and $4.54\text{\AA}^2$ respectively (X-ray lattice constants are $2.52\text{\AA}$ and $3.56\text{\AA}$). The theoretical values of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ for each site if one plane of the crystal is present in the surface of the film are :-

Lattice plane	(110)	(100)	(111)
$\frac{n_{\text{CO}}}{n_{\text{Kr}}}$	2.17	3.07	4.3

Exact agreement is possible only if (110) and (100) faces are present and would require about 80% of the area to correspond with the (110) face. This is a highly arbitrary procedure, but it may be recalled that it has been shown by Beeck and co-workers⁽⁹⁾ for nickel that high vacuum deposited films sintered at 23°C are oriented with their (110) plane exposed to the gas phase. As the cobalt film was deposited at 78°K and sintered at 273°K , it might be argued that it is the (110) face which does in fact predominate in our surface films.

Platinum

The value of the number of carbon monoxide molecules in the monolayer increases with decreasing temperature, and the average experimental value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ is much smaller than the corresponding theoretical value of 2.43. Possible reasons to account for this difference from the theoretical value are listed and discussed below.

(i) In calculating the theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ 19.5×10^{-16} sq.cm was used as the cross-sectional area of the krypton molecule, but if 12.31×10^{-16} sq.cm, i.e. the value calculated from the diameter of the krypton molecule $3.96\text{\AA}$ is taken, then the theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ becomes 1.54, which is close to the experimental value of 1.69. However, as can be seen from table 4.3, the theoretical value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ for other metal would then become much smaller than their experimental value, and this explanation is unlikely to be correct.

Table 4.3

Metal	Mean value of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ (Experimental)	$\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ using $n_{\text{Kr}} =$ 12.31×10^{-16} sq.cm (theoretical)
Palladium	2.53	1.56
Platinum	1.69	1.54
Titanium	2.91	1.66
Chromium	2.35	2.01
Manganese	2.48	1.86
Cobalt	2.36	1.52

(ii) The second possibility is that the carbon monoxide is close-packed, and the CO molecule is lying flat on the surface; the diameter of the carbon monoxide molecule is $4.08\text{\AA}$ and the cross-sectional area of the molecule is $13.06\text{\AA}^2$.

In this case,

$$A_F = n_{\text{CO}} \times 13.06 \times 10^{-16} = n_{\text{Kr}} \times 19.5 \times 10^{-16}$$

or

$$\frac{n_{\text{CO}}}{n_{\text{Kr}}} = \frac{19.5 \times 10^{-16}}{13.06 \times 10^{-16}} = 1.49$$

However, this value should be the same for all metals, which is not in accord with our experimental data. It might, however, be valid for platinum since very low heats of adsorption were obtained and this means that close-packing will be a more favoured arrangement.

(iii) The other possible reason for a high theoretical value, discussed previously, is the use of our average site area. Thus the area of the (110), (100) and (111) faces are $10.75\text{\AA}^2$, $7.62\text{\AA}^2$ and $5.73\text{\AA}^2$ respectively. The corresponding theoretical values of $\frac{n_{\text{CO}}}{n_{\text{Kr}}}$ for these faces are given below :

Lattice plane	(110)	(100)	(111)
$\frac{n_{\text{CO}}}{n_{\text{Kr}}}$	1.81	2.56	3.4

The figure of 1.81, corresponding to the sole presence of the (110) face, is in reasonable agreement with the experimental value of 1.7.

Of the three possible reasons for the "abnormal" value, it seems most likely that (110) plane predominate for platinum as seems probable for cobalt and possibly chromium.

Decreasing Heats

From the above discussion it is clear that the first two conditions required in the Langmuir equation are obeyed in the adsorption of carbon monoxide on those metals, but that the third condition, that heat of adsorption is independent of coverage, is not followed. Thus, the heat of adsorption was found to decrease steadily with coverage. It may be noted that Hayes⁽¹⁾ has determined the heat of adsorption of carbon monoxide on palladium, platinum and titanium, by calorimetric methods, and found constant values up to about 60% coverage; then the heat falls very sharply. This decrease in heat can be due to repulsive interaction between the adsorbed carbon monoxide molecule as was suggested by Roberts⁽¹⁰⁾ or can arise from the heterogeneity of the surface^(11,12). For example, a number of properties of crystal surface, notably the magnitude of work function⁽¹³⁾ differs among different faces and if different crystal planes are exposed, the surface would be energetically heterogeneous.

The decrease in ΔH with Θ makes the obedience to the Langmuir equation unexpected. It would therefore appear that the linearity of the P/V against p plots arises from the presence of a factor which compensates for the effect of varying heat. The decrease of ΔH would mean that our derived V_m values are too low. When (100), (110) and (111) faces are present, the fall of ΔH is accounted for by adsorption predominating first on the plane of highest potential having a lattice site area of, say, a_1 ; then adsorption becomes increasingly important on the plane of next highest potential having a different site area of a_2 ; and similarly for the third plane. Since for chemisorption, the most open face would be of highest potential and have the smallest number of sites per sq.cm surface, the effect is, as Θ increases, to give the appearance of a greater number of sites per unit area and hence this will tend to decrease the effect of a decreasing heat of adsorption.

Copper, Silver and Gold

The adsorption characteristics of carbon monoxide on these three metals were quite different from those on the other metals. Straight lines were obtained when P/V was plotted against p in the case of copper and silver, fig.4.7-8, but the number of carbon molecules in the monolayer varies largely with temperature. The values are given in table 4.4. In the case of gold, straight lines were not obtained.

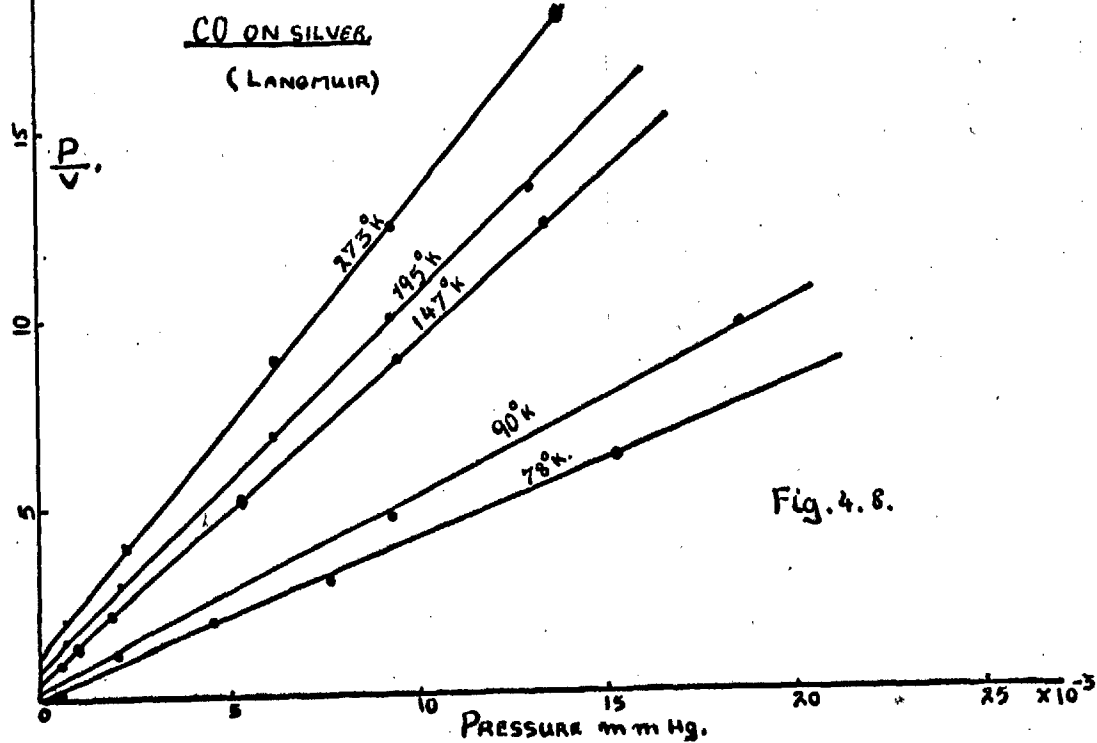
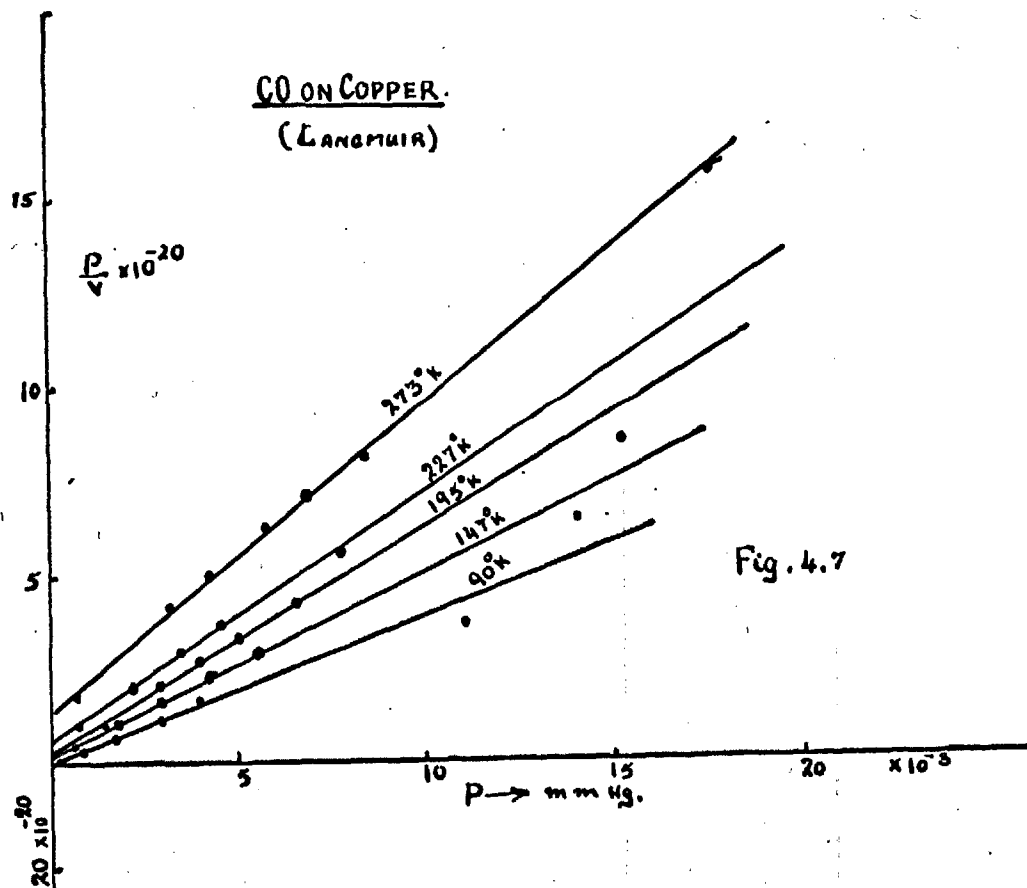


Table 4.4

Metal	Temperature	No. of CO molecules in the monolayer n_{CO}	No. of Kr molecules in the monolayer n_{Kr} (B.E.T)	Experimental		
				$\frac{n_{CO}}{n_{Kr}}$	Mean value of $\frac{n_{CO}}{n_{Kr}}$	Theoretical value $\frac{n_{CO}}{n_{Kr}}$
Cu	273	1.253×10^{17}	3.32×10^{17}	0.387	0.57	2.87
	227	1.511×10^{17}		0.46		
	195	1.94×10^{17}		0.58		
	147	2.38×10^{17}		0.72		
	90	2.33×10^{17}		0.70		
Ag	273	8.13×10^{16}	3.114×10^{17}	0.26	0.47	2.24
	195	1.04×10^{17}		0.34		
	147	1.14×10^{17}		0.37		
	90	1.923×10^{17}		0.62		
	78	2.38×10^{17}		0.76		

However, even taking the highest value of n_{CO} , the magnitude differed by a factor of 4 when the experimental and theoretical value of $\frac{n_{CO}}{n_{Kr}}$ were compared. In view of the large variation of n_{CO} with temperature, it seems that the experimental n_{CO} value has little significance. This variation undoubtedly arises from the rapid decrease of heat of adsorption with coverage at comparatively low θ values (with other metals, the decrease is only measurable at

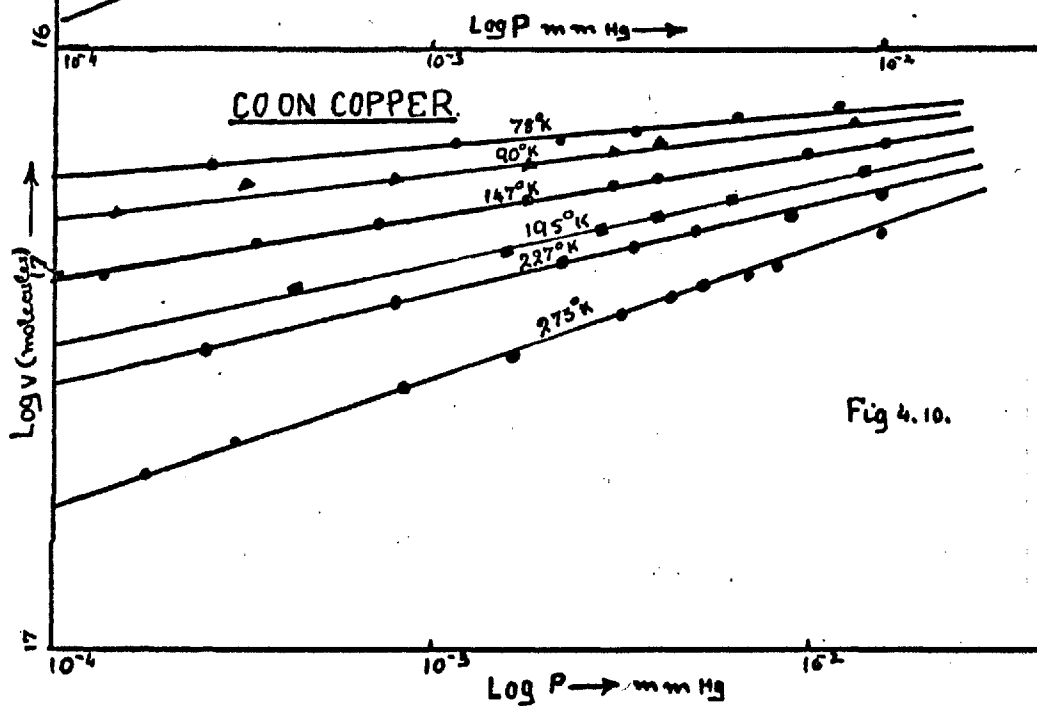
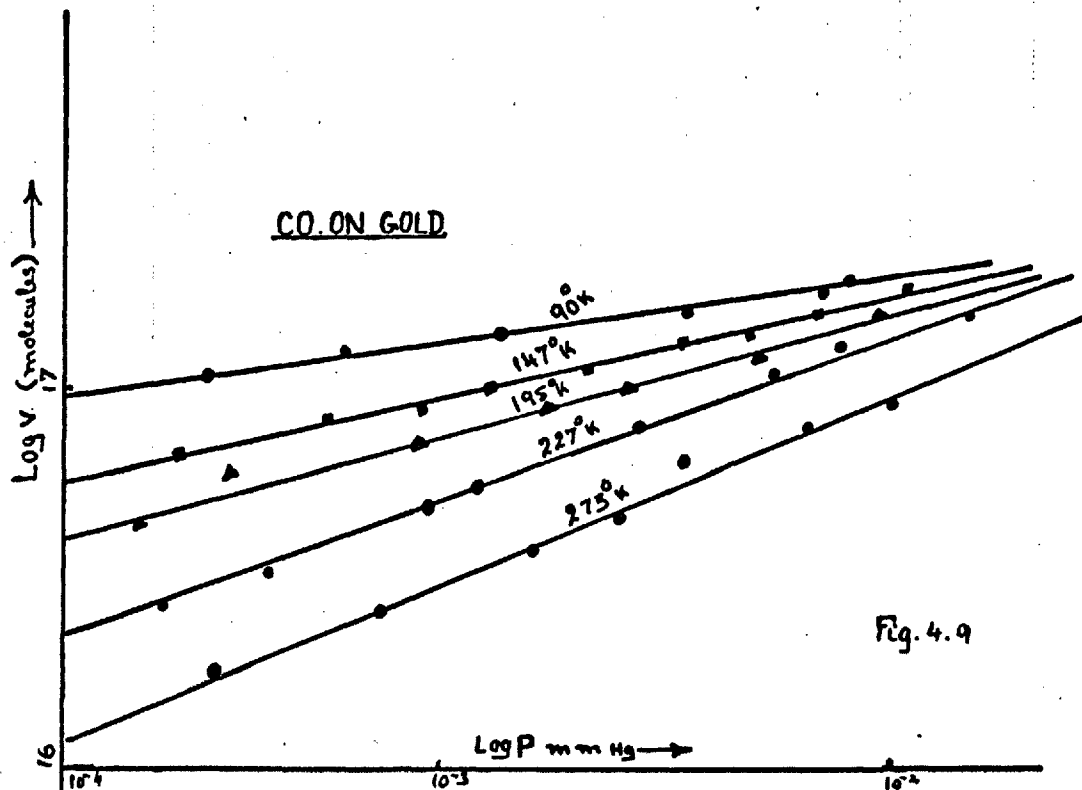
high θ values since there is a very large chemisorption at very low pressures) and this suggests that the Freundlich equation would be valid. This isotherm

$$\log V = \log V_m + \frac{RT}{q_m} \log a + \frac{RT}{q_m} \log p$$

was in fact obeyed by copper and gold (fig.4.9-10). The straight lines show a tendency to converge at a point in the higher pressure region. Obedience to this isotherm implies that heats fall logarithmically as θ increases. The number of carbon monoxide molecules in the monolayer can be obtained by extending the straight lines to the point where they meet, giving value for copper and gold of 3.5×10^{17} and 1.95×10^{17} respectively, compared with the number of available sites, 9.51×10^{17} and 7.39×10^{17} . This ratio of about one to three indicates that the monolayer is far from complete.

Now heat of adsorption of carbon monoxide on both copper and gold falls very sharply to the heat of liquifaction of carbon monoxide much before the completion of the monolayer. This arises from the presence of high repulsive forces between the adsorbed molecules, which do not allow the monolayer to be completed before the second layer starts to fill up, and this accounts for the low values for the number of carbon monoxide molecules in the monolayer.

It may be noted that the heats extrapolated back to zero coverage, using the experimental ΔH against θ curve are 8.5 and



8.1 kcal.mole⁻¹ for copper and gold, in good agreement with Trapnell's value of 9 kcal.mole⁻¹ (14). Comparative values on charcoal (3.4 kcal.mole⁻¹ (15), chromia (3.54 kcal.mole⁻¹ (16)) and iron catalysts (3.7 - 5.0 kcal.mole⁻¹ (17)), where the adsorption is of the van der Waal type, suggests that the adsorption on gold and copper is also physical. Pritchard and Tompkins⁽¹⁸⁾ also postulated that this gas is physically adsorbed by these two metals and that the heat is enhanced by polarisation on charge-transfer forces⁽¹⁹⁾.

It is therefore clear why the behaviour on palladium, platinum, titanium, manganese, chromium and cobalt (where chemisorption takes place) is quite different from that on copper, silver and gold. This difference is undoubtedly associated with the d-structure of the first group of metals, this presence seems essential for chemisorption of carbon monoxide.

Manganese

Dowden⁽²²⁾ has predicted that manganese would behave rather like copper. At low temperature (90°K and 78°K) the adsorption of carbon monoxide was reversible and probably physical in nature, as is shown by the low heats of adsorption. However, at high temperatures large amounts of carbon monoxide were adsorbed. At 273°K the rate of uptake of gas was very fast, but there was no subsequent slow uptake. Again at 195°K equilibrium was reached very rapidly, and on warming the film to 273°K no desorption takes place, indicating that carbon monoxide is strongly chemisorbed, as might be expected because manganese forms stable carbonyls.

This is the only metal where physical adsorption takes place at the low temperature, but forms a strongly chemisorbed layer at 195°K and above. It would therefore seem that there is an activation energy required for this second type of adsorption to occur.

4.2. Rate of Adsorption of Carbon Monoxide

Rate measurements were only possible on a few metals, and it was found that the Elovich equation⁽²⁰⁾ $\frac{dq}{dt} = a \exp. (-bq)$, (where q is the amount sorbed at time t , and a , b are constant at a particular temperature) was valid for carbon monoxide adsorption, a linear plot being obtained on plotting the amount q adsorbed against log time, t , for palladium and copper as adsorbent, (fig.4.11) and (fig.4.14). For titanium and chromium,

however, it was necessary to add a small constant t_0 to obtain a straight line, (fig.4.12) and (fig.4.13), i.e. to plot q against $\log (t + t_0)$. The procedure can be seen from the rate plot on titanium, where on the extreme left, $t_0 = 0$; in the next curve $t_0 = 2$ minutes, when 4 minutes are added, the straight line is obtained.

The linear amount against log time plots have been used to calculate the value of the constant b of the rate equation.

On integrating the equation

$$\frac{dq}{dt} = a e^{-bq}, \quad (i)$$

$$at + \text{constant} = \frac{1}{b} e^{bq} \quad (ii)$$

Taking logarithms,

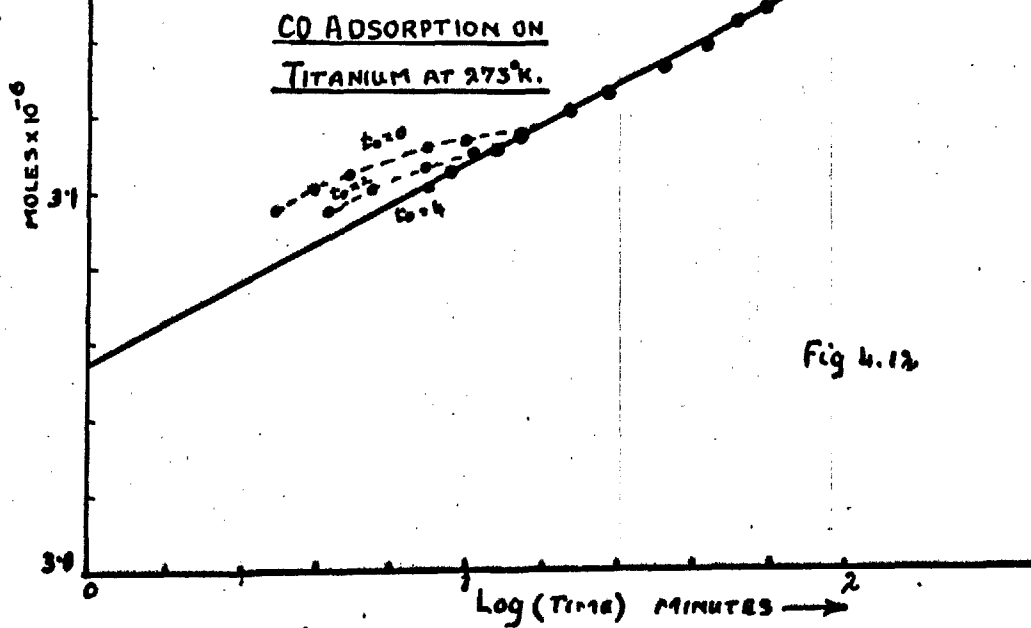
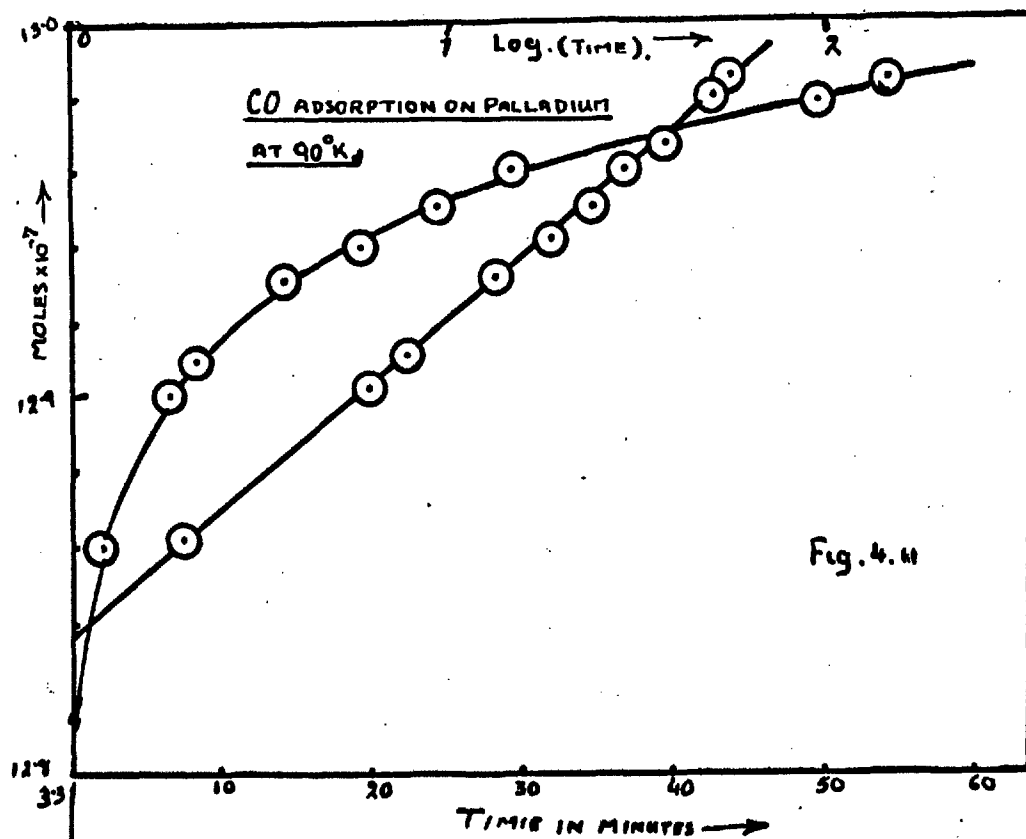
$$bq = \log (t + t_0) + \log ab \quad (iii)$$

where $t_0 = \frac{1}{ab} e^{bq_0}$ and q_0 is the instantaneous adsorption.

If q_0 is small and a and b large, t_0 is very small, and the above expression can be written

$$bq = \log t + \log (ab) \quad (iv)$$

The slope of q against $\log t$ gives $\frac{1}{b}$. The units of b are therefore $(\text{mole})^{-1}$, but to compare the value of b for different metals given in table 4.5, it is expressed in $(\text{millimole/gram})^{-1}$.



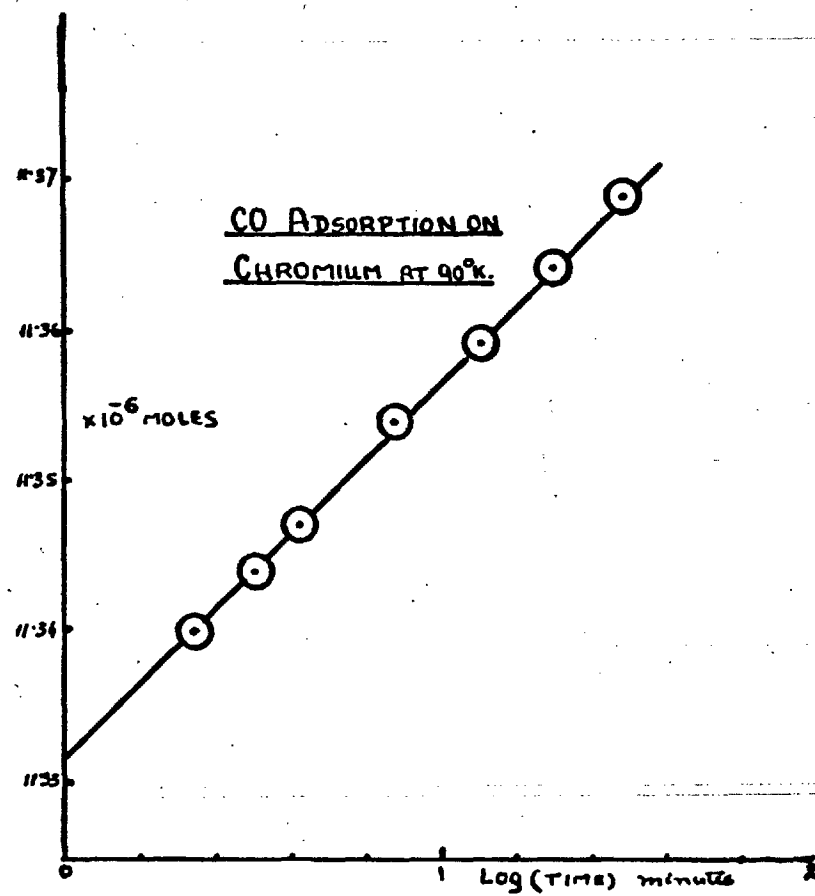
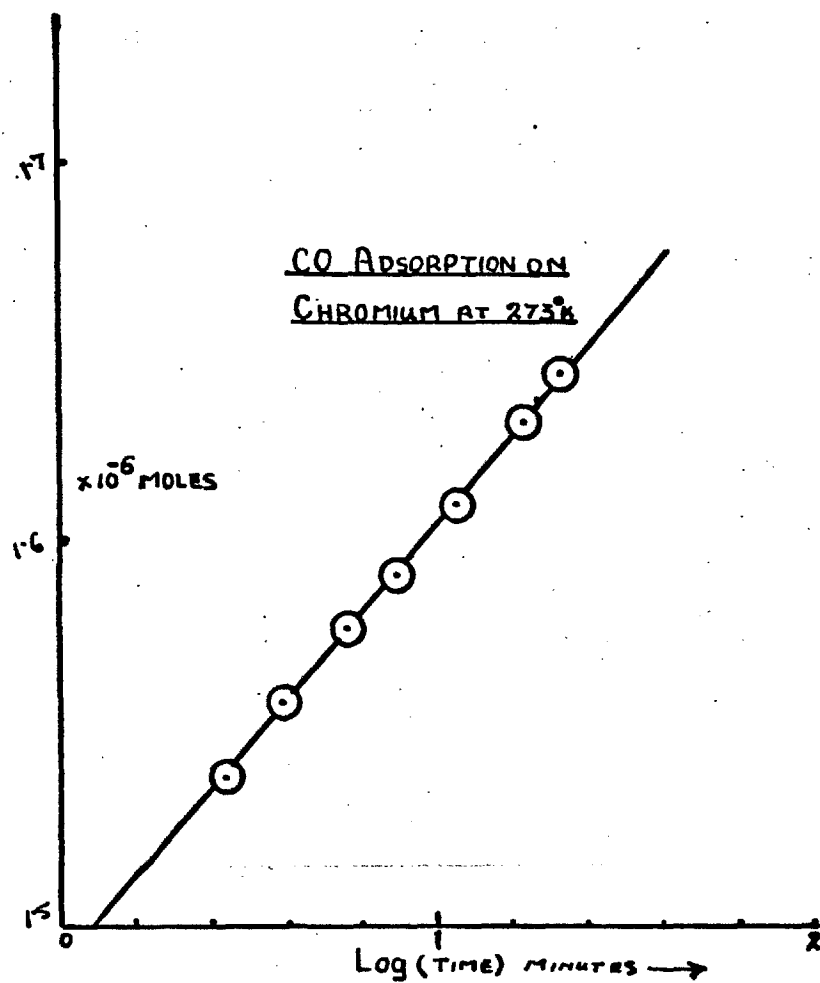


Fig. 4.13.

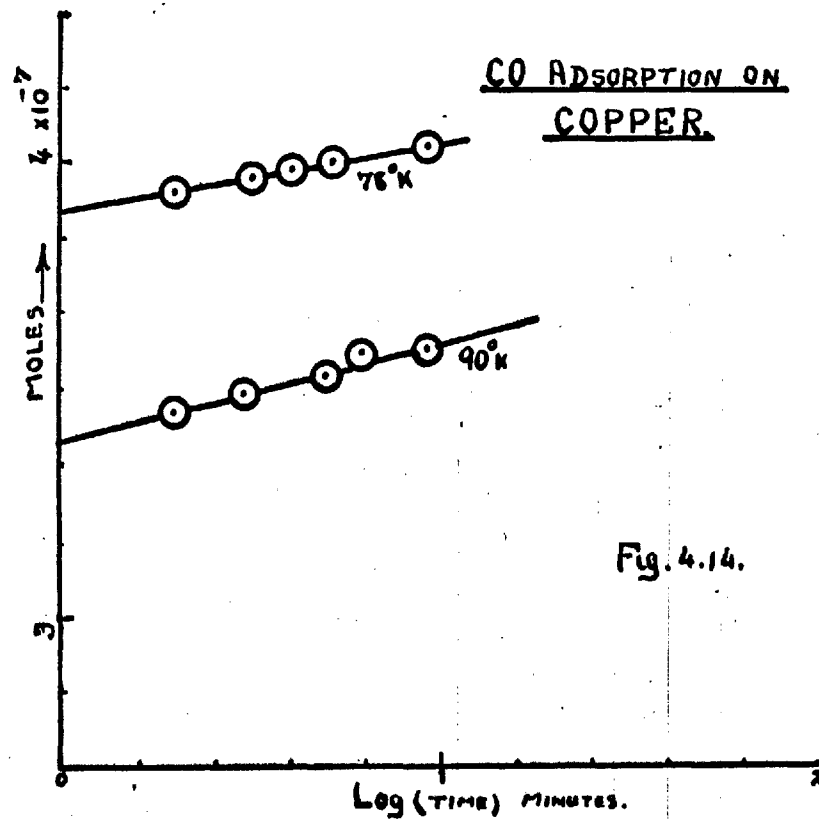


Fig. 4.14.

Table 4.5

Metal	Temperature at which rate is measured	b (millimole/ gram) ⁻¹	t ₀	bT
Palladium	90°K	9540	0.0	86x10 ⁴
Titanium	273°K	680	4.0	18x10 ⁴
Chromium	273°K	259	0.8	
	90°K	1200	0.2	11x10 ⁴
Copper	90°K	1170	0.0	10x10 ⁴
	78°K	1740	0.0	14x10 ⁴
				mean 13.0x10 ⁴

The magnitude of the b value is similar to those obtained by Gundry and Tompkins⁽²¹⁾ for carbon monoxide adsorption on iron and nickel. For the adsorption of carbon monoxide and hydrogen on nickel, Gundry and Tompkins postulated that final chemisorbed state C_f is attained only by passing through an initial chemisorbed state C_i of high potential energy. This possibility was also pointed out by Dowden. It is clear that $E(C_f) > EC_i > E_{v.d.w.}$ where E is enthalpy of adsorption. The transformation from C_i to C_f requires an enthalpy of activation $E(q)$, which increases with increase in q. But as the free energy of activation $E(q)$ reaches 500 cal.mole⁻¹ or more, the transference

from C_i to C_f becomes slow compared with the rate of adsorption from, and desorption to, the van der Waals layer. For high coverage between 85 and 95 per cent, the heat of adsorption decreases linearly with q , and hence it is reasonable to assume $E'(q)$ to vary similarly provided that the potential energy curves are linear in the region thus

$$E'(q) = C(q - q_0)$$

where q_0 is value of q at which the activation energy is just apparent. For carbon monoxide adsorption on iron

$$r_s = \text{constant } p^{0.85} \exp.(-\Delta F/RT) \exp.(-E'(q)/RT)$$

where ΔF is free energy difference per mole for carbon monoxide adsorption in C_i state and in the van der Waals layer.

This equation may be written in the form

$$r_s = \text{constant } \exp.(-eq/RT)$$

which is the Elovich equation, where $a = \text{constant}$ and $b = C/RT$. Hence should the theory be correct then C should be independent of temperature for a particular film, i.e. $bT = \text{constant}$.

Their mean bT value for carbon monoxide on nickel is 14.6×10^4 , in the temperature range of 78°K to 195°K . Except palladium (the reason being obscure) the value for other metals is about the same magnitude, the mean value being 13.0×10^4 . For hydrogen in the same range of temperature they found that bT value was 10.3×10^4 ; the higher magnitude bT value for carbon

monoxide they interpreted as reflecting the more rapid fall of heat of adsorption with coverage than for hydrogen.

The agreement of the bT value on these metals with that of Gundry and Tompkins for carbon monoxide, and the fact that with hydrogen the magnitude is similar seems to confirm their suggestion that b is the measure of the heterogeneity of the surface and that the distribution of sites of different adsorption potentials is about the same for all evaporated metal films.

Similarly Gundry and Tompkins found, with films of the same metals but of different area/mass ratio obtained by sintering at different temperatures, that the product q_1 , where q_1 is the number of millimoles per gram in the monolayer (here using Beeck's criterion of amount adsorbed at $P = 10^{-1}$ mm Hg at 273°K), was constant having a mean value of 210 ± 70 .

In table 4.6 we have calculated q_1 , for the four metals, palladium, titanium, chromium and copper, where q_1 , hence is the monolayer capacity deduced from a B.E.T. determination using krypton.

Table 4.6

Metal	q_1 (molecules)	q_1 millimoles/ gm	b	bq_1
Palladium	7.392×10^{17}	0.035	9548	334
Titanium	2.182×10^{18}	0.238	680	162
Chromium	9.693×10^{18}	1.24	259	321
Copper	9.511×10^{18}	0.12	1740	208

$$\text{Mean } bq_1 = 256$$

It will be seen that bq_1 is reasonably constant and that the mean value is not very different from that on nickel. This consideration should follow if b is merely defining the distribution of adsorption potentials on the surface and that this distribution does not vary greatly from one metal film to another different metal film prepared under the same conditions.

4.3. Nitric Oxide Adsorption on Metals

The nitric oxide molecule contains one more electron than carbon monoxide. If this electron is removed by ionization a univalent cation $[\text{NO}]^+$, with the same structure as that of neutral carbon monoxide molecules ($[\text{N} = \text{O}]^+$, $\text{C} = \text{O}$) is obtained. With many metals, nitric oxide reacts to give nitroxyl compounds, which resemble carbonyls in many ways. Similarly, the spectra

of nitric oxide on nickel, iron and cobalt show that it is attached to the metal atom through the nitrogen⁽²³⁾, just as the CO molecule is linked with metal atoms through carbon.

Thus the adsorption characteristics were expected to be similar to those of carbon monoxide. However, with the Sp metals, copper, silver, gold, and also with titanium, the adsorption was extremely small, even at the lowest temperature, and no isotherm could be obtained using the present apparatus.

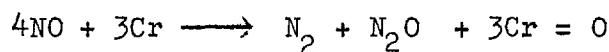
Nickel

On this metal there was however appreciable adsorption; the isotherm did not follow the Langmuir equation, but the Freundlich equation could be fitted well in the low pressure region. The heat of adsorption is small, the highest value obtained being about 6 kcal.mole⁻¹ as compared with 16 kcal.mole⁻¹ for carbon monoxide adsorption on nickel⁽²⁴⁾. This result is in keeping with the general behaviour that nitric oxide is much less strongly adsorbed than carbon monoxide on metals.

Chromium

Nitric oxide on chromium gives rather unusual results. The isotherm above certain coverages displayed a stepwise character. For small amounts of adsorption the equilibrium was reached quite quickly, but at higher coverage the rate of adsorption becomes slow. In Run I it was observed that at 273°K, after the establishment

of the equilibrium, the McLeod gauge recording the total pressure of the gas in the gas-phase, and the Pirani gauge which was calibrated for nitric oxide apparently gave different pressure readings. This indicated that the composition in the gas-phase was not solely nitric oxide, and that some chemical reaction with the chromium surface has taken place. Now Eley and Wilkinson⁽²⁵⁾ have found that nitric oxide on aluminium films, reacted to give N_2 and N_2O , with the formation of surface oxide film. The same type of reaction might have taken place with chromium film, and be represented as



In another run the nitric oxide isotherms were carried out at 195° , 90° and $78^\circ K$ (the isotherm at $195^\circ K$ show steps as at $273^\circ K$ (fig.3.46)). At the point where 4.2×10^{-7} moles of nitric oxide had been adsorbed on the film at $195^\circ K$, it was warmed to $273^\circ K$, a slight desorption was followed by a long slow adsorption and at equilibrium more gas was apparently adsorbed than at $195^\circ K$ (fig.3.49), which means that by raising the temperature of the film, more surface sites were made available for adsorption. The chromium sites are probably set free by O and Cr changing places, i.e. surface oxygen atoms diffuse in the film.

It is clear therefore that a study of the adsorption of nitric oxide on the metal is complicated by chemical processes occurring at the metal surface, and therefore further work on this system was terminated.

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