ADSORPTION ISOTHERMS AND ISOSTERIC HEATS OF ADSORPTION OF CARBON DIOXIDE, CARBON MONOXIDE AND HYDROGEN ON ZINC OXIDES WITH AND WITHOUT VALENCY INDUCTION.

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by

PETER MILES GOYEN HART

(B.Sc. App. and Ind. Chem.)

Department of Chemistry,
University of Cape Town.

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PART A.

INTRODUCTION.

Crystalline solids containing structural defects which cannot be detected by normal X-ray diffraction methods are generally known as defect solids or semi-conductors. These defect solids have been classified roughly into three main types[36] :-

(i) Imperfect crystals have stoichiometric compositions but atoms or ions are misplaced throughout the structure. They may be missing completely or they may be displaced from their proper lattice sites into interstitial positions (i.e. Schottky and Frenkel defects).

(ii) Non stoichiometric crystals show an excess or deficiency of one component, and quite marked departures from the ideal composition may occur without change of phase.

(iii) Impurity systems have structural defects created by solid solution of foreign atoms or compounds in non stoichiometric proportions.

Zinc oxide is a defect solid of type (ii), having a deficiency of oxygen. Its departure from stoichiometry is a function of temperature and tends to zero as $T \rightarrow 0^{\circ}K$[37]. The excess zinc in the solid is probably located in interstitial positions as atoms or ions[38,39], and conduction arises from the presence of the quasi free electrons associated with the excess zinc. As the charge carriers are electrons, the conductivity is described as n-type (n = negative). The defective zinc oxide lattice can be represented thus

$$Zn^{++} (e^-)_{2x} O^{=}_{1-x} \quad \text{where } (e^-) = \text{quasi free electron}^{40}.$$

According to the energy band theory the defects in n-type semiconductors are associated with discrete donor energy levels between the topmost filled band and the conduction band and just below the latter[41,42]. Hence electrons may be excited easily into the normal conduction band. These n-type semiconductors are electron donors. They have a low work function due to the effective raising of the Fermi level, so that it is relatively easy for electrons to leave the lattice.

Defects due to impurities (type (iii)) may be added to the defects already present in zinc oxide by the additions of small amounts of metal ions of different valency to zinc. The system then becomes what has been called a controlled valency semiconductor[43]. These small additions can alter the conductivity of the zinc oxide very considerably[1,2].

An important condition to be realised is that the added ions should be approximately the same size as the parent cation[44], e.g.

Ion	Zn^{++}	Ga^{+++}	Li^{+}
Ionic radius (A^{o})[45]	0.74	0.62	0.60

The addition of gallium increases the concentration of quasi free electrons in the lattice, and lithium decreases it. The results of these small additions of impurities may be represented thus

$Zn^{++}_{1-y}\ Ga^{+++}_{y}\ (e^{-})_{2x+y}\ O^{=}_{1-x}$ Increased conductivity.

$Zn^{++}_{1-y}\ Li^{+}_{y}\ (e^{-})_{2x-y}\ O^{=}_{1-x}$ Decreased conductivity.

The influence of this modification of the concentration of charges may be regarded as a raising or a lowering of the Fermi level[46]. Thus the activity of the zinc oxide as an electron donor should be affected.

If heterogeneous processes at the surface of a solid involve transfer or sharing of electrons then it may be expected that changes

in the electron concentration, such as those described above, will effect the heterogeneous processes. This has been tested experimentally for a number of catalytic reactions and found to be true,

e.g.

The oxidation of carbon monoxide over NiO and ZnO[5].

The decomposition of nitrous oxide (N_2O) on ZnO[5].

The hydrogen-deuterium exchange reaction on ZnO[4].

The reduction of CO_2 with H_2 over ZnO[7].

Some confusion has existed where electronic processes at the semiconductor surface have been working in conjunction with ionic processes[47,48], but if reactions are studied below the Tamann point so that equilibrium between the bulk of the solid and the surface is frozen, then this difficulty is avoided.

Catalysis by a solid surface involves the chemisorption of a reactant or reactants on to the surface and the subsequent desorption of reaction products[49]. In other words chemisorption is believed to be an essential factor in the study of heterogeneous catalysis.

Stone states, "Measurements of electrical conductivity have established that the chemisorption of gases and vapours on semiconductors is accompanied by electron transfer from the semiconductor to the chemisorbed gas, or vice versa, or by localisation of the charge carriers of the semiconductor between the gas and the semiconductor surface"[50]. Bearing this in mind it should be interesting to determine the effect of change of electron concentration in the adsorbent on its adsorptive properties. Considerable work has been done on the adsorption characteristics of mixed oxides[51] but, apart from the work of Cimino, Cipollini and Molinari, little work has been done on adsorption on controlled valency semiconductors[6].

Wiggill[7] studied the reaction

$$CO_2 + H_2 \xrightarrow{ZnO} CO + H_2O$$

He found that the activation energy for this reaction was decreased slightly by adding a small percentage of gallium oxide to the zinc oxide and increased slightly by adding lithium oxide. Pretreatment of the catalyst with oxygen was found to have a poisoning effect.

It was decided to carry this work further by measuring the adsorption of carbon dioxide, carbon monoxide and hydrogen on zinc oxide with and without valency induction caused by addition of gallium oxide and lithium oxide.

In a reaction of this sort, it would be of interest to know which of the species are chemisorbed and some idea of the relative free energy loss on adsorption. If there was some marked variability in the heats of chemisorption on zinc oxide with and without valency induction and if there was any correlation between that and the energies of activation, it was hoped that this might offer a clue to the mechanism operating. For obvious reasons, it was desirable to get these values at approximately the same temperature as the catalysis experiments.

In the present work it was decided to omit measurements for water, because in the first place private communications from Sebba and Wiggill had indicated that water produced a poisoning of the zinc oxide surface, and secondly the measurement of water vapour pressure would have been impossible with McLeod gauges, which are suitable for CO_2, CO and H_2.

A fairly comprehensive study of the adsorption of a gas on a solid can be made by measuring its adsorption isotherms at a number of temperatures within the range in which the worker is interested. It is then a simple matter to convert the family of isotherms to isobars or isosteres. Heats of adsorption are probably best determined directly using a calorimeter[52] but the technique is very refined even at room temperatures. At higher temperatures the cooling correction

becomes extremely difficult to apply[53]. For this reason it was decided to determine isosteric heats of adsorption, although their validity is open to criticism if there is any doubt about the absolute reversibility of the adsorption.

If q_i is the integral heat of adsorption for "a" moles of gas adsorbed, then the differential coefficient $\left(\frac{\partial q_i}{\partial a}\right)_T$ is called the differential heat of adsorption, q_d. When da moles are adsorbed at constant temperature and without a change in the total number of moles, then from the gas law

$$pdv = da\ RT$$

so that the work done per mole of gas adsorbed is RT[54].

On the adsorption isostere every point represents a temperature and pressure at which the adsorbent-adsorbate complex is in equilibrium with the gas for a constant amount of gas adsorbed. It can be shown thermodynamically that[55]

$$RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_a = q_d + RT$$

Since the energy term $(q_d + RT)$ always refers to a definite amount of gas adsorbed at different temperatures and pressures it is called the isosteric heat of adsorption

$$q_{isosteric} = RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_a$$

$$= R \left(\frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)}\right)_a$$

The heat of adsorption is effectively constant over a small range of pressure and temperature so that a plot of ln P against $\frac{1}{T}$ for a constant amount of gas adsorbed should be a straight line. The isosteric heat of adsorption can then be calculated from the slope of the line.

The adsorption measurements were made in a constant volume apparatus, the pressure being the variable which was measured[56,57]. The isotherms were measured by the method of cumulative additions. The log pressure vs. $\frac{1}{T}$ graphs plotted from this data showed excellent linearity, confirming the validity of this method of obtaining the heats.

The work was a comparative study of the adsorption on three slightly different adsorbents, so that absolute accuracy was sometimes sacrificed to simplification of the experimental method. If identical methods were used for a particular gas on each adsorbent, then the differences between adsorbents should show up clearly in spite of small systematic errors.

PART B.

EXPERIMENTAL WORK.

I. Scope of the experimental work.

The objective of the experimental work was the measurement of the adsorption isotherms of carbon dioxide, carbon monoxide and hydrogen on zinc oxide adsorbents, with and without small percentages of impurity oxides, namely gallium oxide and lithium oxide, at temperatures between 250°C and 320°C and at pressures below 1 mm. Hg.

The amount of impurity oxide mixed with the zinc oxide was 0.5 mole %. Previous workers [1,2,3,4,5,6,7] had used amounts varying from 0.1 to 1.0 mole %. Schwab and Block[5] found little change in catalytic activity for values over 1%.

The temperature range for reasons of comparison was the same as that chosen by J.B. Wiggill[7]. 250°C is the temperature above which normal chemisorption of hydrogen on zinc oxide is found[6,8,9]. 320°C was the highest permissible temperature for the thermostat which was available. Heats of adsorption vary slowly with temperature and 50 to 60 centigrade degrees is about the maximum range for a reasonably constant value. This restriction in range was necessary as the heats were determined using the Clausius Clapeyron equation on data obtained from the isotherms.

The low pressure range was chosen firstly because Wiggill had done his activation energy measurements at low pressures; secondly, because initial adsorption on active centres is most rapid, and so adsorption in the low pressure region where the complete surface was not covered would proceed more quickly than adsorption at higher pressures. This time factor was important for the fairly slow chemi-

sorptions encountered. Low pressures also eliminated the need for large quantities of gas and so simplified gas generation and purification.

At low pressures, too, the heat of adsorption would be affected mainly by the activity of surface sites as the coverage would be small, whereas at higher coverages the interaction between adsorbed molecules would probably be important.

II. Requirements in the design of the apparatus.

In the design of the apparatus used for the experiments certain general requirements had to be fulfilled.

(1) For the low operating pressures a high vacuum apparatus was needed so that impurity gases could be eliminated from adsorbents and adsorbing gases.

(2) The high vacuum apparatus needed to be as simple as possible to facilitate the attainment of low pressures. A large number of greased taps were especially undesirable as they would be potential leak sources.

(3) Construction of the apparatus could not be beyond the scope of the facilities available in the department and materials used in its operation had to be readily available.

(4) For a knowledge of the number of moles of gas adsorbed at any pressure, the temperature, pressure and volume of the gas had to be measurable.

(5) Gases used in the experiments had to be pure, but simple gas trains were desirable. Solid adsorbents were necessary so as to permit evacuation of the gas trains.

(6) Pure zinc oxide, gallium oxide and lithium oxide were required. In the apparatus the adsorbents had to be activated under high vacuum and at a high temperature.

(7) To measure isotherms the adsorbents had to be maintained at constant temperatures over periods of a number of days.

III. Design of apparatus and preparation of gases and adsorbents.

The diagram (Fig. 1) shows the general layout of the pyrex glass high vacuum apparatus. The design will be discussed in the light of the general requirements of the experiments laid down in the previous section. In general it largely follows designs used by previous workers[10,11,12,13].

(1) Rotary oil pump. (Speedivac, Type 1A, Series No. 1A/667, Edwards and Co., London). This mechanical fore pump was capable of giving a backing pressure of 1×10^{-3} mm. Hg. An Edwards motor was used to drive it (No. VI - 8773; 1425 R.P.M., ¼ H.P.). Vibration was eliminated by mounting the pump and motor assembly on a sponge rubber sheet.

(2) Oil trap. A glass bulb of one litre capacity was used as a trap to prevent the pump oil sucking back into the vacuum apparatus.

(3) Three way tap. This tap enabled the rotary pump to be connected to the vacuum apparatus while pumping, or to the atmosphere before turning off the pump.

(4) Cold trap. This trap, cooled by surrounding it with liquid oxygen in a Dewar flask, was used to protect the rotary oil pump from condensable vapours.

(5) Mercury diffusion pump. This pump, backed by the rotary pump produced a pressure of 1×10^{-5} mm. Hg fairly quickly in a well out-

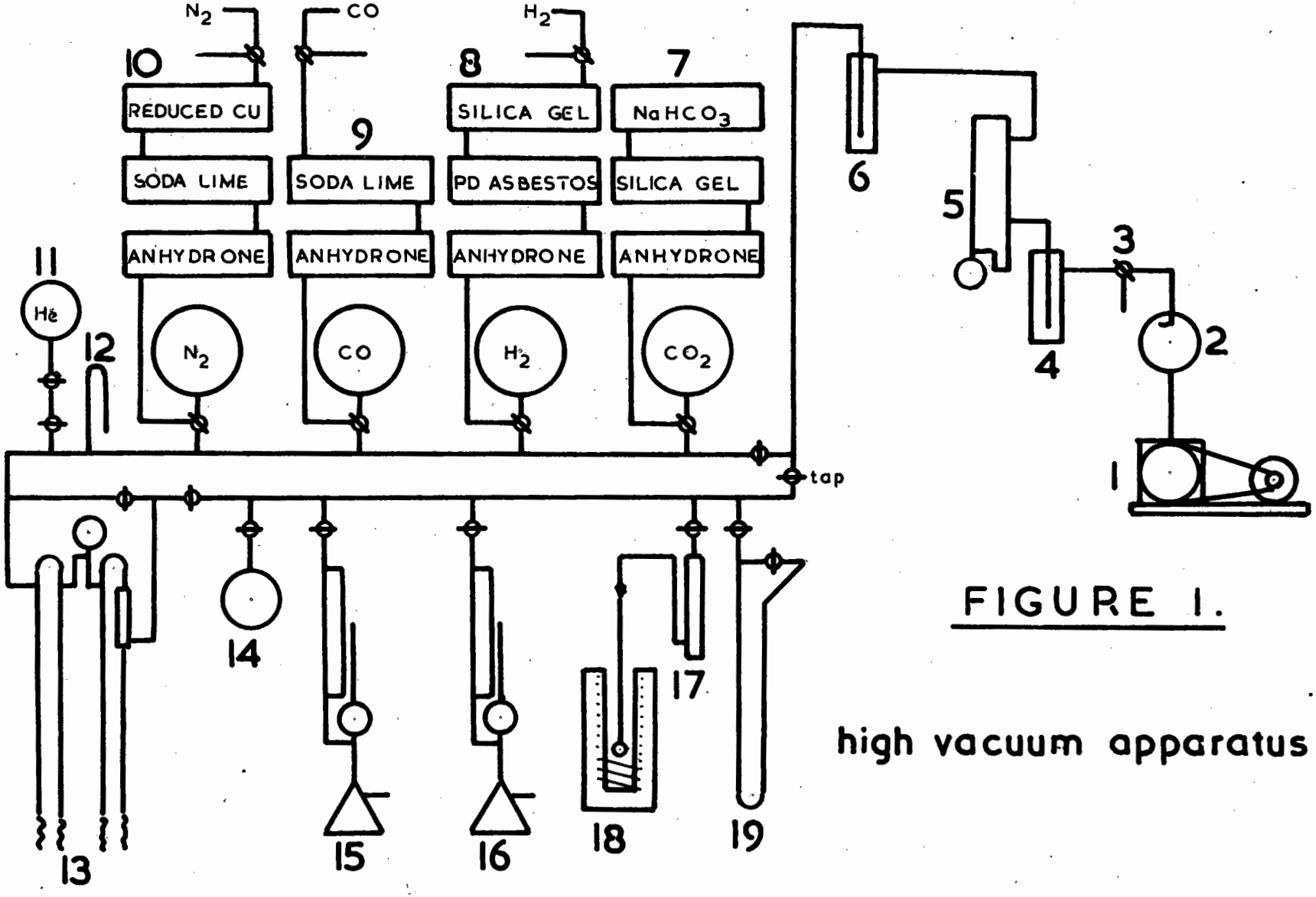


FIGURE 1.

high vacuum apparatus.

gassed apparatus. Pressures as low as 1 x 10^{-6} mm. Hg were obtained. The mercury was heated with a small bunsen flame.

(6) Cold trap. This trap, also at liquid oxygen temperature, was used to prevent mercury vapour from the pump diffusing back into the high vacuum apparatus.

(7) Gas train for preparation of carbon dioxide[14]. High quality sodium bicarbonate on heating gives off only carbon dioxide and water vapour. For the production of carbon dioxide in these experiments the bicarbonate was heated in a tube with a bunsen flame and the evolved gases then had to pass through tubes containing self indicating silica gel and anhydrone, $Mg(ClO_4)_2$, before reaching the three-litre storage bulb. Anhydrone gives a residual moisture pressure of 5 x 10^{-4} mm. Hg[15] and as the carbon dioxide pressure in the storage bulb was about 100 mm. Hg, the percentage of water vapour in the carbon dioxide would be very small, viz. 5 x 10^{-4}%. The tubes had ground glass stoppers at one end for the introduction of the reagents. The drying agents could be regenerated between 200 and 300°C.

Materials used:- Sodium bicarbonate, "Judex", A.R.
Silica gel. Self indicating. "B.D.H.".
Magnesium perchlorate. Anhydrous. "B.D.H.".

(8) Gas train for preparation of hydrogen[16,17]. Electrolysis of 30% NaOH solution at nickel electrodes yields hydrogen of high purity containing only a very little oxygen, though saturated with water vapour. In these experiments the sodium hydroxide solution was electrolysed in a vessel as shown (Fig. 2). The hydrogen evolved was passed through three tubes containing silica gel, palladised asbestos at 300°C and anhydrone respectively. The silica gel removed most of the water, the palladised asbestos converted O_2 to H_2O, and the residual moisture was absorbed by the anhydrone. The hydrogen was stored in a three-litre bulb at

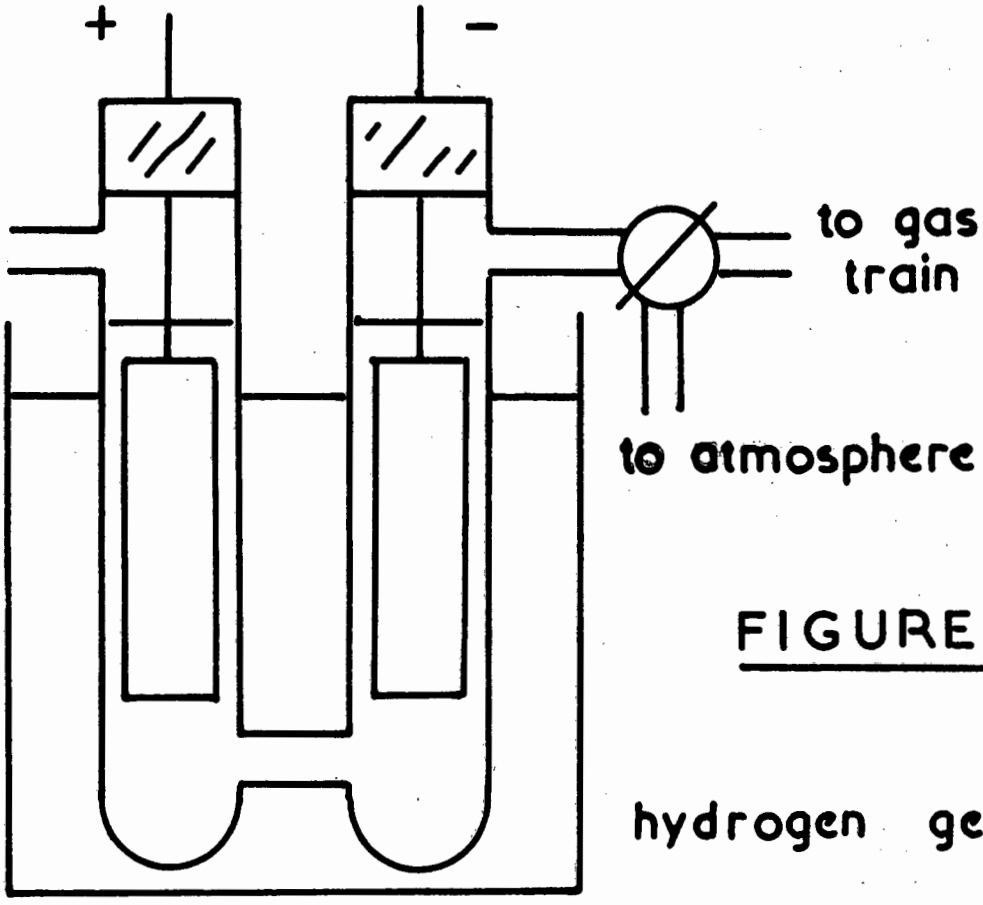


FIGURE 2.

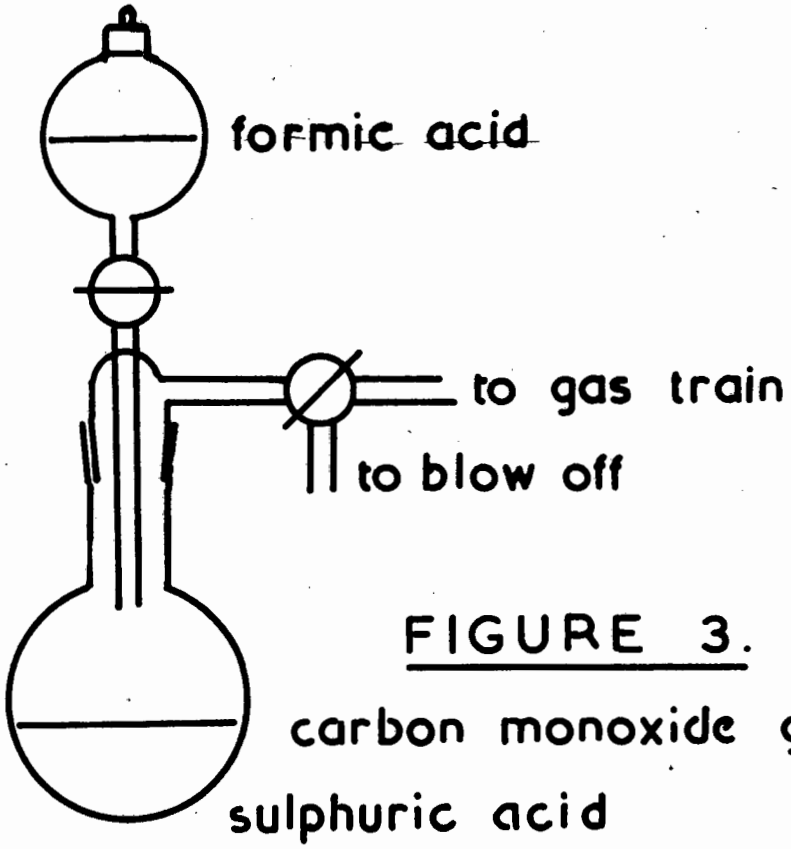


FIGURE 3.

about atmospheric pressure.

The furnace for the reduction of oxygen was constructed from a pyrex glass tube containing palladised asbestos fibres, using nichrome wire (2.1 ohms/ft.) for the heating element and asbestos rope and a mixture of magnesia and asbestos fibre for the lagging. A tube to hold a thermocouple was placed lengthwise down the furnace with its end at the centre of the furnace.

Palladised asbestos. 5% Pd. "B.D.H.".

(9) Gas train for preparation of carbon monoxide[14,18]. High quality carbon monoxide can be obtained by dehydrating boiled out concentrated formic acid with hot concentrated boiled out sulphuric acid. The impurities which require removal are acid fumes and traces of moisture. Care is required to prevent contamination of the air in the laboratory with the poisonous carbon monoxide.

For the adsorption experiments a gas generator was used as shown in Fig. 3. At one centimetre above atmospheric pressure the carbon monoxide bubbled off through a mercury blow off and was led out of the laboratory window. Granulated soda lime and anhydrone in two tubes were used to purify the gas which was stored in a three-litre bulb at nearly atmospheric pressure.

Soda lime. Non deliquescent. "B.D.H.".

Formic acid 98 - 100%. Sulphuric acid A.R.

(10) Gas train for preparation of nitrogen[19,20]. Commercial nitrogen from a cylinder was used. The impurities in tank nitrogen are oxygen, carbon dioxide, water vapour and the rare gases. The first three were removed in tubes containing reduced copper at 500°C, soda lime granules and anhydrone. Rare gases were ignored.

The reduced copper furnace was constructed from a pyrex glass tube containing a roll of copper gauze. The copper was activated

at 500°C by passing oxygen through the furnace for 20 minutes followed by nitrogen to flush, then hydrogen for 20 minutes and finally nitrogen again to flush. The furnace was then ready to be sealed on to the apparatus.

(11) Bulb of helium. Helium was required for the determination of the dead space volume of the adsorption bulb when it was charged with adsorbent. It was supplied by the "Airco" Co., U.S.A., in 1.1 litre sealed glass flasks. The soft glass flask was joined to the pyrex glass apparatus with a graded seal. The use of two taps with only a small volume of tube between them enabled small quantities of helium to be removed from the flask at high pressure to the apparatus at low pressure. After the connecting tubes had been thoroughly evacuated the seal on the flash was broken with a steel ball bearing, using a magnet.

(12) U tube manometer. A small mercury manometer was attached to the gas train manifold to give an indication of the pressure up to 5 cms. Hg. Larger pressures could be measured in the limbs of the doser.

(13) Doser. The doser was designed to transfer small quantities of gas from the gas train section of the apparatus at a few mm. Hg pressure to the adsorption section of the apparatus at below 1 mm. Hg pressure. It was used mainly on nitrogen for the volume calibration measurements and also for the comparison of the two McLeod gauges.

The two main advantages of this doser over other designs were (a) it used no complicated arrangement of taps and bulbs, (b) it was capable of giving any pressure (which could be calculated approximately) down to 10^{-6} or 10^{-7} times the starting pressure. Its maximum starting pressure was 2 cms. Hg.

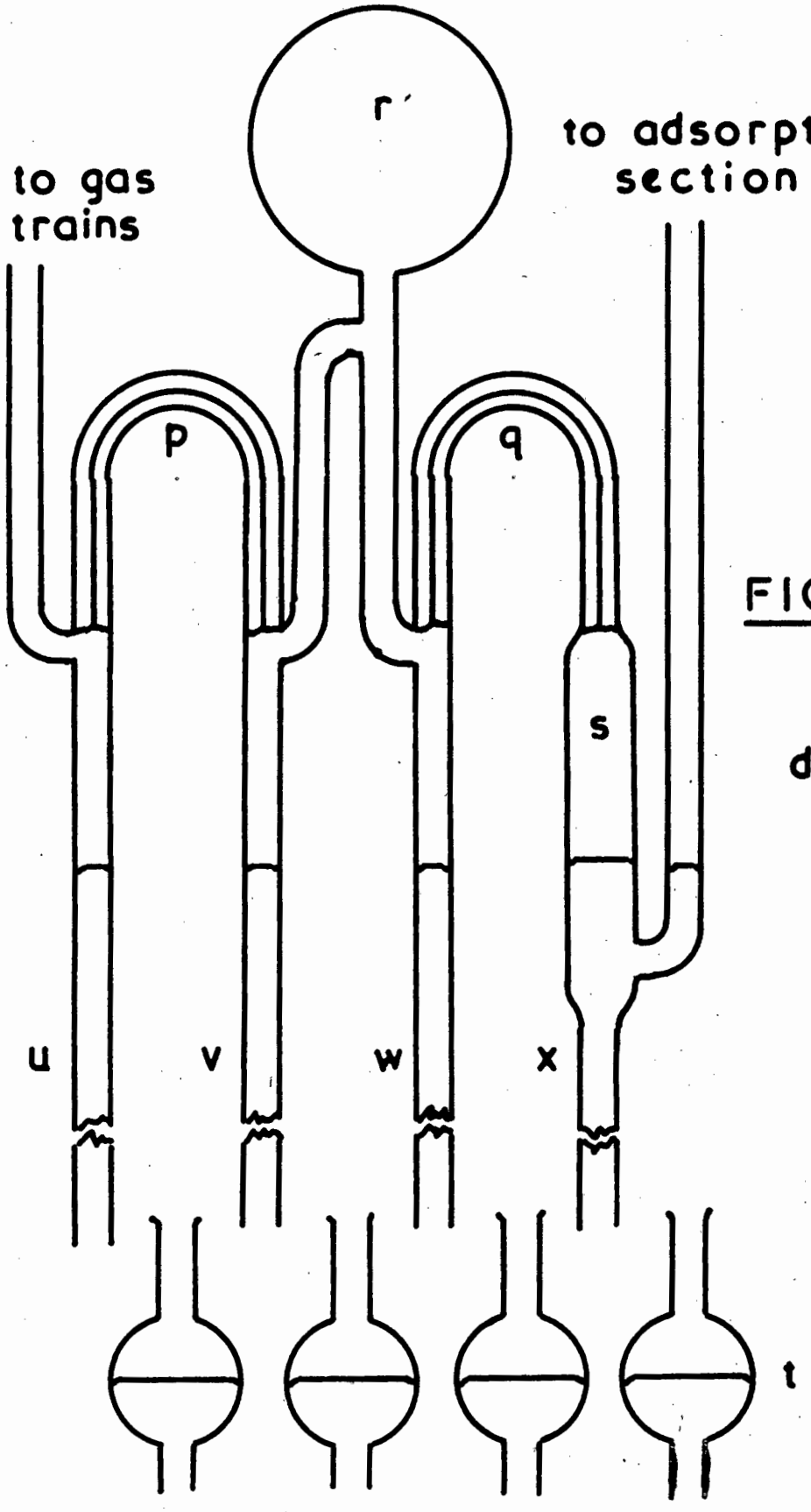


FIGURE 4.

doser.

The two curved sections p and q (see Fig. 4) were capillary tubes of about 0.1 c.c. capacity each. The capacity of bulb r was 100 c.c. and of the tube s, 10 c.c. The remainder of the tubing used had I.D. 5 mm. The bulbs t were attached to the rest of the unit with plastic tubing so that they could be raised and lowered.

The doser was used in the following way. Mercury in v was raised just above the side inlet tube and gas was let into p from the gas train. With the levels in u, w and x below the side tubes, r, q and s were evacuated from the right hand side. The levels in u and x were then raised above the side inlets, the level in v was dropped, and so about 0.1 c.c. gas in p expanded to about 100 c.c. in q and r. The level in x was then adjusted to give the desired volume in s, and the level in w was raised above the side inlet to trap this volume. The level in x was then dropped and a second expansion was obtained into the adsorption section of the apparatus. By varying the mercury level in s and/or omitting one expansion a whole series of final pressures could be obtained.

(14) Standard volume bulb. In order to determine the volumes of the various parts of the adsorption section of the apparatus it was necessary to have a standard volume attached to the apparatus from which to expand gas. Boyles Law could then be used to calculate volumes if initial and final pressures were measured.

The volume of the bulb, up to and including the bore of the tap was determined by weighing it, full of water, before it was sealed on to the apparatus. The volume was found to be 1040 c.c. (see Appendix I).

(15 and 16) McLeod Gauges A and B. McLeod gauges were chosen for pressure measurement. They are absolute gauges and could be constructed and calibrated in the department. In the pressure range

1 mm. - 1 x 10^{-3} mm. Hg the maximum error is not greater than ± 1%[21,22].

The table shows the dimensions of the two gauges, designated A and B.

a = cross section area of capillary tube.

l = length of closed capillary tube.

v = volume of compression bulb.

V = initial volume, i.e. volume of bulb + capillary tube.

Gauge	A	B
a ($mm.^2$)	0.5076	1.797
l (mm.)	147	187.5
v ($mm.^3$)	335700	55303
V ($mm.^3$)	335800	55640
Accurately readable pressure range (mm. Hg)	1 x 10^{-3} - 3 x 10^{-2}	1 x 10^{-2} - 1.0

An accurate millimeter scale was placed behind the capillary tubeswith the zero mark at the top of the closed tube. Pressures were read by compressing the gas in the closed capillary until the mercury level in the open capillary was at the zero mark.
If s = scale reading for mercury level in closed tube
and p = pressure to be measured in apparatus,

$$\text{by Boyles Law } pV = s(sa)$$

$$\therefore \quad p = s^2\left(\frac{a}{V}\right)$$

(see Appendix II for calibration data).

The following table compares readings given by the two gauges in the pressure range where they overlap. Columns two and four show the readings given by the two gauges for the same pressures.

The gas used was nitrogen.

Gauge A		Gauge B	
s (mm.)	p (mm. Hg)	s (mm.)	p (mm. Hg)
69.1	7.21×10^{-3}	15.0	7.27×10^{-3}
82.8	1.04×10^{-2}	17.9	1.04×10^{-2}
85.7	1.10 "	18.5	1.10 "
92.9	1.30 "	20.0	1.29 "
93.8	1.33 "	20.3	1.33 "
106.0	1.70 "	23.0	1.71 "
111.4	1.87 "	24.0	1.86 "
117.0	2.07 "	25.3	2.07 "
117.2	2.08 "	25.5	2.10 "
123.5	2.31 "	27.0	2.35 "
127.3	2.45 "	27.6	2.46 "
133.1	2.68 "	29.0	2.71 "
138.5	2.89 "	30.2	2.94 "
138.6	2.90 "	30.2	2.94 "

The fact that the two gauges agreed closely for pressures in the region where their ranges overlapped was taken as an indication that their accuracy over the whole range 10^{-3} mm. Hg to 1.0 mm. Hg could be relied on. From the above table it can be seen that no reading was observed which differed by more than 1% from the average of the readings given by the two guages for a particular pressure.

(17) Cold trap. This trap, cooled by a freezing mixture of ice and salt was kept at -20°C so as to prevent the adsorbent from becoming contaminated with mercury vapour from the pressure gauges. The vapour pressure of mercury at this temperature is very small

viz. 1.8×10^{-5} mm. Hg. Liquid oxygen or dry ice were not used as refrigerants because of:-

(a) the danger of condensing CO_2 at liquid air temperatures;
(b) the greater errors due to thermomolecular flow introduced by using lower temperatures;
(c) the greatly increased expense of maintaining these constantly in the trap.

(18) Adsorption bulb. Figure 5 shows the design of the adsorption bulb. It was joined to the rest of the apparatus through a ground glass joint which enabled it to be removed easily for recharging with adsorbent. The joint was sealed with very low vapour pressure picein wax. The bulb held about 22 gm. of pelletised adsorbent and the purpose of the side tube was to facilitate thermal flow of the adsorbing gas at low pressures. The bulb was immersed in the adsorption furnace to the level h.

(19) Differential mercury manometer. This manometer was used for measuring pressure of gas before adsorption, and vapour pressures in surface area determinations. The limbs of the manometer were of I.D. 5 mm. and a millimeter scale was glued to the hard board backing. The mercury could be vibrated by tapping with the finger, to prevent sticking. The levels were read using a lens and sighting along a right angled bracket which could be slid up and down the backing board. The estimated absolute accuracy was better than ± 0.2 mm. Hg. (Less than ± 1% for all pressures over 20 mm. Hg).

(20) Adsorption furnace. It was first thought that the vapours of boiling organic liquids would give the best constant temperature baths for the isotherms, but in the temperature range 250°C - 320°C, diphenyl (b.p. 255°C) and diphenylamine (b.p. 302°C) were the only compounds found which did not decompose on prolonged heating.

Finally an electric furnace was used. A relay (Sunvic Control,

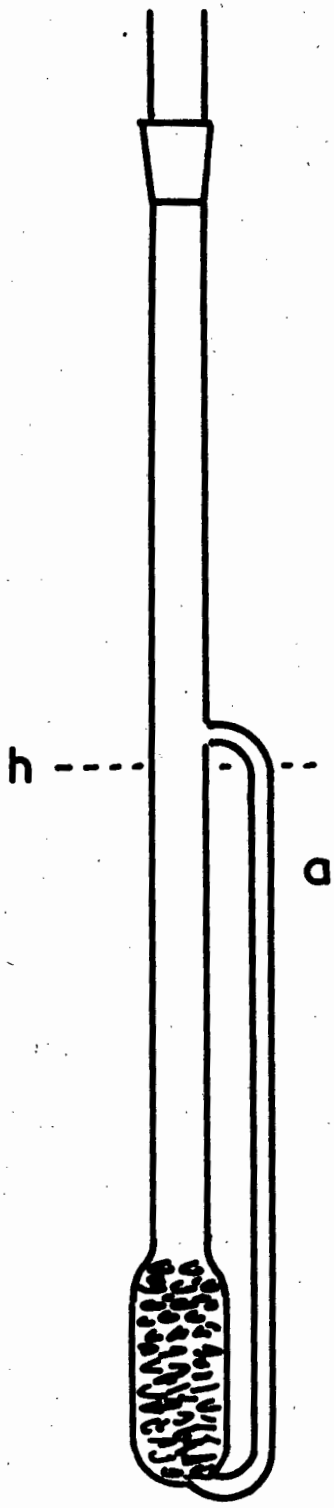


FIGURE 5.

adsorption bulb.

Type F102/4) in series with one resistance and in parallel with another was used to regulate the heating current to values 0.1 amp greater or less than the steady current required to maintain the isotherm temperature. The make and break used with the relay was a stainless steel cartridge thermostat unit (Electromethods Series 311. Normally open type. Temperature range up to 320°C) which was suspended inside the furnace alongside the adsorption bulb. This system of control gave a steady temperature. There was a maximum variation of ± 1°C about the mean temperature over a period of many days.

(21) Activation furnace. Another electric furnace was used to heat the adsorbent in the bulb during activation. Its temperature was controlled by the expansion of gas enclosed between its double glass walls. The activation temperature of 450°C was measured with an iron/constantan thermocouple which had been calibrated in boiling sulphur at 444°C. The temperature for every activation was 450°C (± 10°C).

(22) A.C. wiring diagram. Power was required for four furnaces and the oil pump motor. The electrical circuits were connected up as shown in the diagram (Fig. 6).

(23) Room temperature control. To avoid variations of pressure in the apparatus due to changes in ambient temperature, the temperature of the laboratory was thermostatically controlled at 25°C (± 0.5°C). The sensitive element was a brass cartridge thermostat unit (Electromethods. Series 310. Normally closed type) which operated 3000 Watts of heaters through relays. A small fan was used to circulate the air in the 17' x 10' laboratory.

(24) Vacuum tap lubricant. Apiezon L grease was used on most of the vacuum taps and was found to give good service (6 months and more). Tap performance was improved by slow one way rotation of taps and

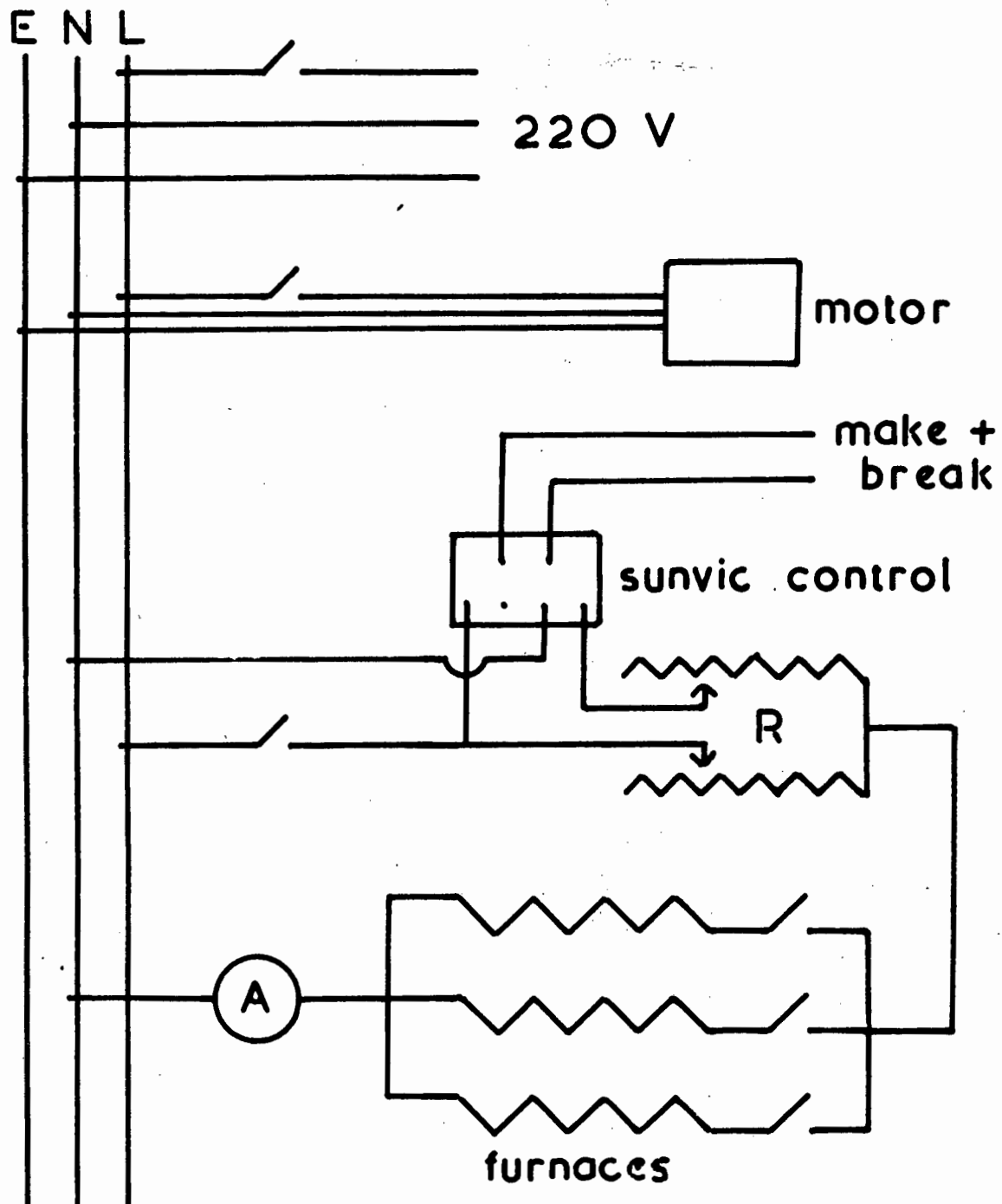


FIGURE 6.

wiring diagram.

by the constant room temperature.

(25) Mercury. All mercury used in the apparatus was cleaned by spraying it through 10% HNO_3 through which air was bubbled[23,24]. It was washed with water and passed three times through a pin hole before use.

(26) Preparation of the zinc oxide adsorbents.

(i) Pure zinc oxide[6,7,8,25,26]. Just less than the stoichiometric quantity of zinc chloride was added slowly to a hot concentrated solution of ammonium oxalate. The precipitate of zinc oxalate was filtered off and washed with distilled water, dried overnight at 110°C and then heated in a stream of air in a tube furnace at 450°C for 10 hours. All the batches of zinc oxide thus produced were well mixed together to form one homogeneous stock of the oxide.

Zinc chloride. "B.D.H.".

Ammonium oxalate. Analar "B.D.H.".

(ii) Zinc oxide plus 0.5 mole % gallium oxide[4,6,7,27]. Spectroscopically pure gallium was dissolved in concentrated nitric acid as described by Sebba and Pugh[28]. The solution was evaporated almost to dryness several times to remove most of the excess acid, and then the gallium nitrate was dissolved in distilled water and made into a paste with zinc oxide powder from the stock prepared previously. The paste was then dried and heated as before to decompose the gallium nitrate to gallium oxide.

(iii) Zinc oxide plus 0.5 mole % lithium oxide. It was doubtful whether lithium oxide could be prepared from the nitrate[4,6,25,29] or the carbonate[5] at 450°C. In order to keep the conditions of preparation the same for all three

catalysts lithium oxalate was used which was found to decompose well below 450°C. A certain amount of carbonisation occurs when the oxalate is heated alone[30], but when it was heated with a large quantity of zinc oxide no black carbon particles could be observed in the resulting mixture, even when it was examined under a microscope.

Lithium oxalate was dissolved in distilled water and made into a paste with zinc oxide powder. The paste was dried, and heated as before to decompose the oxalate to the oxide.

Lithium oxalate. "B.D.H.".

The adsorbent powders were compressed into tablets of diameter 5.5 mm. and thickness 1 - 2 mm., so as to allow free flow of gas in the adsorption bulb.

IV. Experimental Methods.

(1) Calibration of volumes.

Figure 7 is a diagram of the adsorption section of the apparatus with its various parts lettered for simple reference.

V is the standard volume. Volume = 1040 c.c.

A is McLeod gauge A.

B is McLeod gauge B.

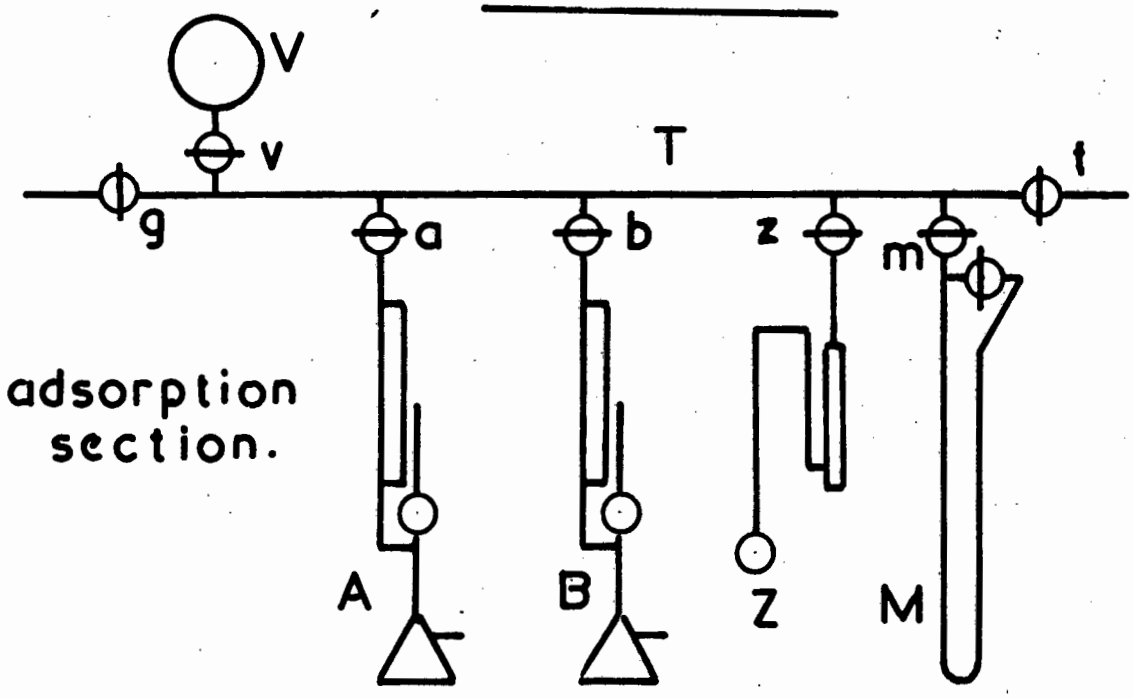
Z is the adsorption bulb and its cold trap.

M is the differential mercury manometer.

T is the manifold tubing.

In the following discussion these letters will also represent the volumes of the respective sections in c.c.

FIGURE 7.



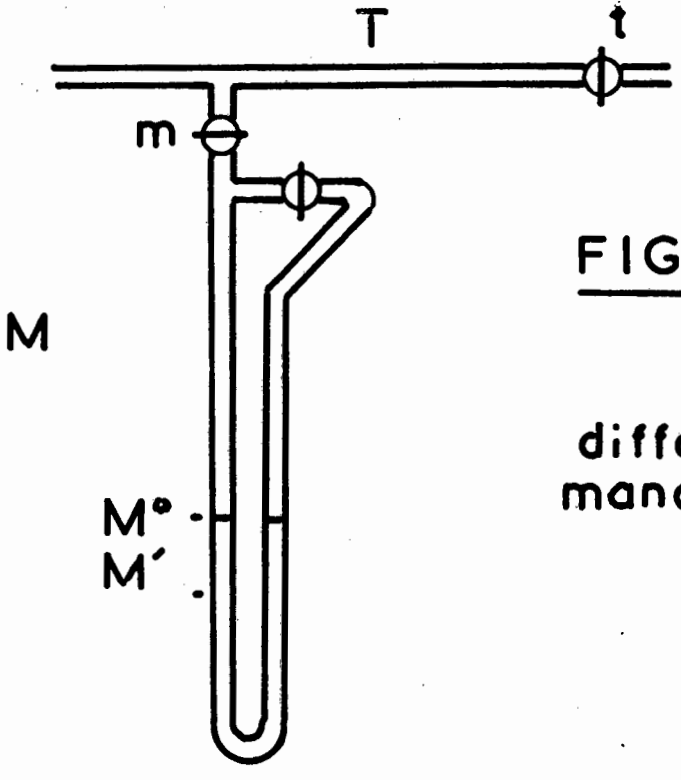


FIGURE 8.

differential
manometer.

(i) Determination of volumes of A, B and T using the McLeod gauges.

For these calibrations the gas used was nitrogen, obtained from a cylinder and passed over soda lime and anhydrone. Before starting the calibrations the apparatus was thoroughly outgassed.

Volume of (T + A):- T, A and V were evacuated to 1 x 10^{-6} mm. Hg. The doser was then used to introduce nitrogen and the pressure, P_1, was measured using gauge A. Tap v was then closed and T and A were evacuated to a low pressure, p, which was measured. With tap t closed tap v was opened and nitrogen was expanded from V into T and A. The new pressure, P_2, was measured.

With the low pressures used the nitrogen could be assumed to obey Boyles Law,

$$\text{so } P_1V_1 = P_2V_2 \quad \text{where } V_1 = V, \quad V_2 = (V + T + A)$$

$$\therefore P_1V = P_2(V + T + A)$$

$$\therefore T + A = \frac{(P_1 - P_2)\,V}{P_2}$$

A small correction had to be applied for the residual pressure, p. Taking this into consideration the effective initial and final pressures were $P_1 - p$ and $P_2 - p$. However, the correction cancels out in the term $(P_1 - P_2)$ and so needed only to be applied in the denominator.

Fifteen values for (T + A) were obtained and the mean value found.

Mean value of (T + A) = 604 c.c.

Probable error of mean[31] $= \pm \frac{0.8453}{n\sqrt{n-1}} (\Sigma d)$

$= \pm (0.0151 \times 164)$

$= \pm 2.5$ c.c.

where n = 15

d = arithmetical deviation of each value from the mean value.

Probable percentage error of mean = $\pm$ 0.4%.

The results of the other determinations are shown in the table below. They were obtained using the same method.

Section	Mean value of volume	Probable error of mean	Probable percentage error	n
T + A	604 c.c.	$\pm$ 2.5 c.c.	$\pm$ 0.4	15
T + B	369 c.c.	$\pm$ 1.7 c.c.	$\pm$ 0.5	14
T + A + B	849 c.c.	$\pm$ 4.1 c.c.	$\pm$ 0.5	7

From these results,

volume of (2T + A + B) = 973 c.c.

volume of T + A + B = 849 c.c.

$\therefore$ volume of T = 124 c.c.

volume of A = 480 c.c.

volume of B = 245 c.c. using McLeod gauges.

(ii) Determination of the volume of the differential manometer.

Figure 8 is a diagram of the manometer. The right hand side was thoroughly evacuated before use and then the tap on the horizontal tube was closed. The manometer was made with tubing of uniform bore so the volume of gas space in the left hand side could be calculated from the dimensions of the manometer.

Volume of M up to M^0 = 14.5 c.c. ($\pm$ 0.1 c.c.). Call it M^0.

Cross section area of bore = 0.196 $cm.^2$.

$\therefore$ there was a 1 c.c. increase in volume of M for every 10 cm. rise in pressure.

Therefore volume of M, when mercury level stands at M' and

pressure is $P_{M'}$

$$= M^o + \frac{P_{M'}}{10} \quad . \quad \text{Call it } M' \qquad \ldots\ldots \text{ Equation I}$$

(iii) Determination of volume of $(T + M^o)$ using differential manometer.

Using the same method as used earlier, nitrogen was expanded from V into T and M and from the twenty values of $(T + M')$ so obtained values of $(T + M^o)$ were calculated.

Mean value of $(T + M^o)$ = 137.8 c.c.

Probable error of mean = $\pm$ 0.2 c.c. Where n = 20.

(iv) Comparison of values obtained for volume of T.

By McLeod gauges. T = 124 c.c.

Using differential manometer. $(T + M^o)$ = 137.8 c.c.

and M^o = 14.5 c.c.

$\therefore$ T = 123.3 c.c.

The two values for the volume of T agree to within 1%, which provides confirmation that the volume calibrations were reliable.

(2) Methods used in adsorption isotherm measurements.

In order to develop a technique for the adsorption measurements, trial runs were done adsorbing carbon dioxide on zinc oxide. This was a non representative sample used before the whole batch of zinc oxide had been made up. In the following description of the methods used in the adsorption measurements the results of some of these trial experiments will be used as illustrations.

(i) Introduction of adsorbent into apparatus.

For introduction of a new sample of adsorbent into the apparatus the adsorption bulb was removed, emptied of used

adsorbent, washed with conc. HCl to dissolve out remaining oxide, and then rinsed with water, acetone and ether. The dry bulb was recharged with 22.10 gm. (± 0.05 gm.) of new adsorbent and sealed on to the apparatus. Once the new adsorbent was in place the cold tap was kept constantly at -20°C to prevent Hg contamination of the oxide surface.

(ii) Activation of a new sample of adsorbent.

Each new sample of adsorbent was heated at 450°C for 24 hours with the pumps running to clean the oxide surface. For about the last five hours of this time the pressure was always in the range 1.5×10^{-4} - 3.5×10^{-4} mm. Hg. On cooling to about 300°C the pressure dropped below 1×10^{-5} mm. Hg. There is no sintering of zinc oxide at 450°C in a vacuum[8].

(iii) Determination of dead space in the adsorption bulb.

With the cold trap at -20°C and the adsorption bulb at room temperature values of the volume of the dead space in Z were obtained by expanding helium at low pressure from B into T and Z. As helium is not adsorbed on the oxide[35], Boyles Law could be applied.

Mean value of (T + Z)	=	288 c.c.
Probable error of mean value	=	± 0.7 c.c.
Probable percentage error	=	± 0.25%
∴ Volume of dead space in Z	=	164 c.c.

This determination of the volume was valid for all the adsorption experiments as the same weight of adsorbent was used each time and the three adsorbents were identical except for the very small additions of gallium and lithium oxides. Any variations would be well within the experimental error of the determination of the whole dead space, $(T + A + B + Z + M^{o})$.

(iv) Constant temperature conditions for the isotherms.

The furnace to provide the constant temperatures for the isotherms has already been described. For the calculation of isosteric heats of adsorption, temperature difference between the isotherms is the important factor, not the absolute value of the temperature itself. So while a standardised thermometer was not essential it was necessary to apply stem corrections to the thermometer readings for the isotherm temperatures.

Thermometer used: E-Mil Goldline. No. G.S. 10010.
0 - 360°C in 1°C. Tolerance ± 1.5°C. Total imm.

The thermometer was suspended inside the adsorption furnace with its bulb alongside the adsorption bulb. For each isotherm it was hung in exactly the same position. The temperature just inside the top of the furnace was measured with a second thermometer, and the top of the furnace was closed off with a wad of asbestos paper.

Somewhat idealised, the temperature conditions along the stem of the first thermometer are shown in Figure 9.

Dodd and Robinson[32] give the following equation for estimating stem corrections:-

$$\Delta t = l\left(\frac{\rho_a - \rho_o}{\rho_o}\right)$$

where Δt = correction to be applied to measured temperature t_o of absorption bulb.

l = length of mercury thread in degrees exposed to ambient temperature t_a above the adsorption bulb.

ρ_a = density of mercury at temperature t_a.

ρ_o = density of mercury at temperature t_o.

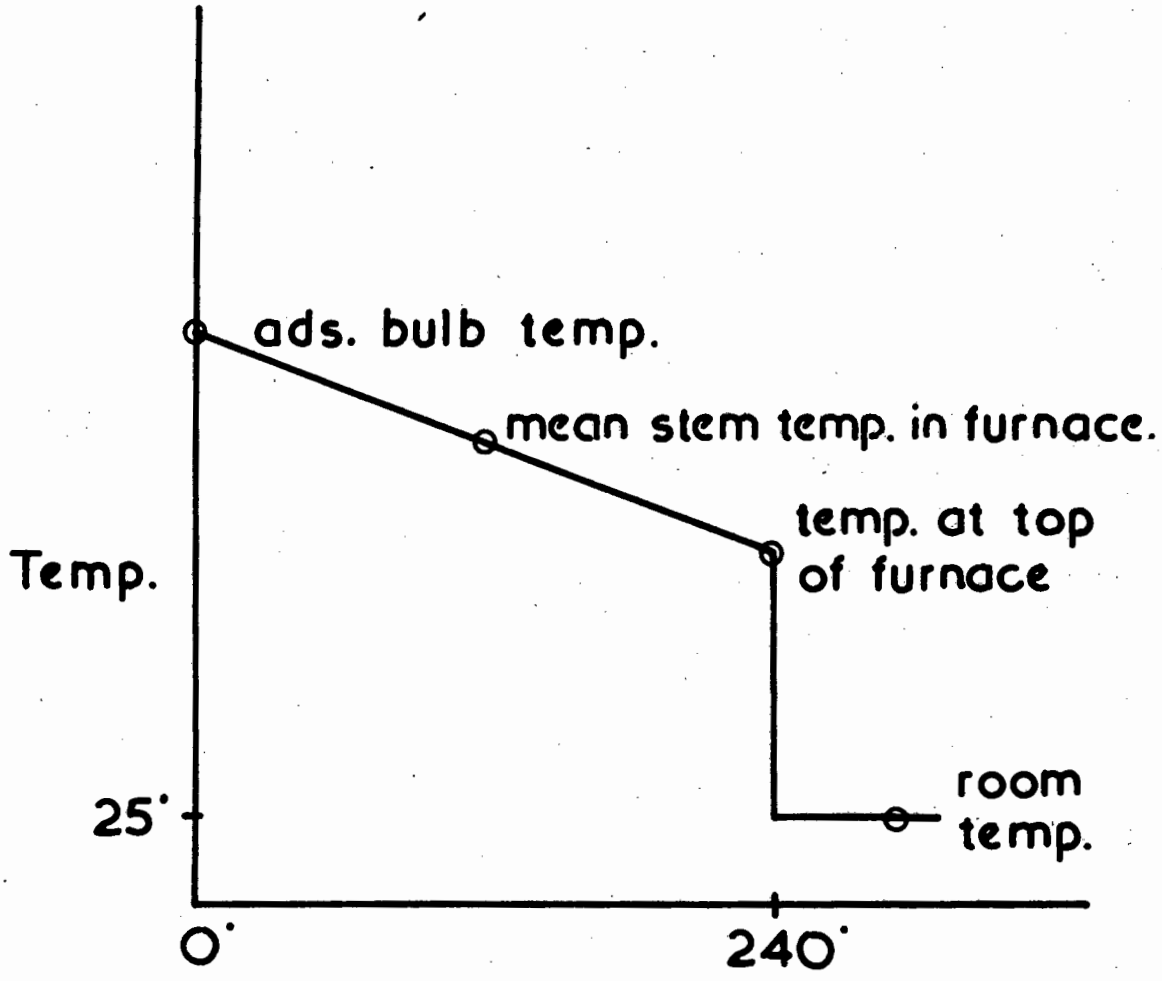


FIGURE 9.

temp. conditions along therm. stem.

The correction was applied in two parts, for the section of the stem inside the furnace, and for that above the furnace.

For the first section:- $l = 240^{\circ}C$

t_a = mean temp. up to 240° mark.

For the second section:- $l = t_o - 240^{\circ}C$

$t_a = 25^{\circ}C$.

(Mercury densities obtained from International Critical Tables).

(v) Preparation of gases for adsorption.

Carbon dioxide: The gas train was evacuated to about 4×10^{-4} mm. Hg for a few hours. The sodium bicarbonate was then warmed gently until the carbon dioxide pressure rose to a few cms. Hg, and the train was evacuated again after a few hours to remove any gases or vapours which may have desorbed due to preferential adsorption of carbon dioxide on the reagents. When carbon dioxide was required for adsorption the bicarbonate was warmed until the correct pressure was obtained.

Carbon monoxide: The air in the gas generator (see Fig 3) was swept out by generating carbon monoxide (by dripping formic acid from the funnel into the sulphuric acid and warming) and at the same time connecting the blow-off tube to a vacuum pump. When the generator was clear of air the pump was disconnected, and the carbon monoxide pressure then built up to atmospheric pressure. The previously evacuated gas train (5×10^{-4} mm. Hg) was flushed with carbon monoxide, re-evacuated, and filled with gas to almost atmospheric pressure. The carbon monoxide could then be drawn off as required. The one bulb-full was sufficient for all the carbon monoxide experiments.

Hydrogen: The gas space in the electrode vessel (see Fig. 2) was cleared of air by generating hydrogen and blowing it off to atmosphere. The gas train was evacuated, while the palladised asbestos furnace was kept at $300^{\circ}C$; it was flushed with hydrogen,

re-evacuated and filled with gas to about atmospheric pressure. Hydrogen was then drawn off as required.

(vi) Adsorption isotherms.

(a) Determination of experimental data.

Before the start of any isotherm the adsorbent was evacuated for 4½ hours at 450°C. The activation furnace was replaced by the adsorption furnace and the temperature was regulated to that required for the isotherm by adjusting the make and break of the cartridge thermostat unit. An hour or two was allowed to pass to obtain temperature equilibrium within the furnace and the adsorption bulb.

Gas at the requisite pressure (determined previously in a rough trial run) was then let into T and M through tap g (see Fig. 7). Tap m was closed and T was evacuated to about 10^{-3} - 10^{-4} mm. Hg. The pressure in M was measured accurately. Taps a, b, m and z were then opened in that order and the adsorption was begun to obtain the first point on the isotherm, i.e. at the lowest pressure.

When sufficient time had elapsed for the equilibrium pressure to be obtained by direct measurement or graphical means, the taps a, b and z were closed and more gas was allowed into T and M. Tap m was closed, T was evacuated and the pressure in M measured. Taps a, b, m and z were again opened and adsorption begun to give the second point on the isotherm at a higher equilibrium pressure.

In the same way all the points on the isotherm were obtained up to the limiting pressure of 1 mm. Hg.

While chemisorption was taking place equilibrium was not attained rapidly, so that graphs of pressure in the apparatus vs.

time were drawn to show the progress of the adsorption process. The time taken for equilibrium to be reached increased with the amount of gas adsorbed. In the 10^{-3} mm. Hg pressure range it was about 4 - 10 hours. In the 10^{-1} mm. Hg. range it was anything from 20 - 100 hours. For example see Figure 10 which shows the drop of pressure with time for a point on one of the trial isotherms. Obviously from the point of view of saving time it was desirable to make an accurate estimate of the equilibrium pressure without waiting to actually measure it, especially for the higher pressures.

The reciprocal of time $^{1}/_{t}$ was plotted against various functions of the pressure P, where P was the pressure at time t after admission of a sample of gas. However, none of these graphs gave good values of P as $t \to \infty$.

When Figure 10 was replotted showing log $(P - P_0)$ vs. t where P_0 was the equilibrium value for the gas pressure over the adsorbent (i.e. $P \to P_0$ as $t \to \infty$), a straight line was obtained (see Figure 11).

Hence $\ln (P - P_0) = -kt + c$ ..... Equation 2

where k and c are constants

$\therefore P - P_0 = e^{c - kt}$

$\therefore P = P_0 + e^{c - kt}$ for this curve.

This relationship was tested and found to be true for the variation of pressure with time for the points on the other trial isotherms too (see Figure 11).

So without waiting for P_0 to be obtained three values of the pressure P_1, P_2 and P_3 could be measured at times t_1, t_2 and t_3

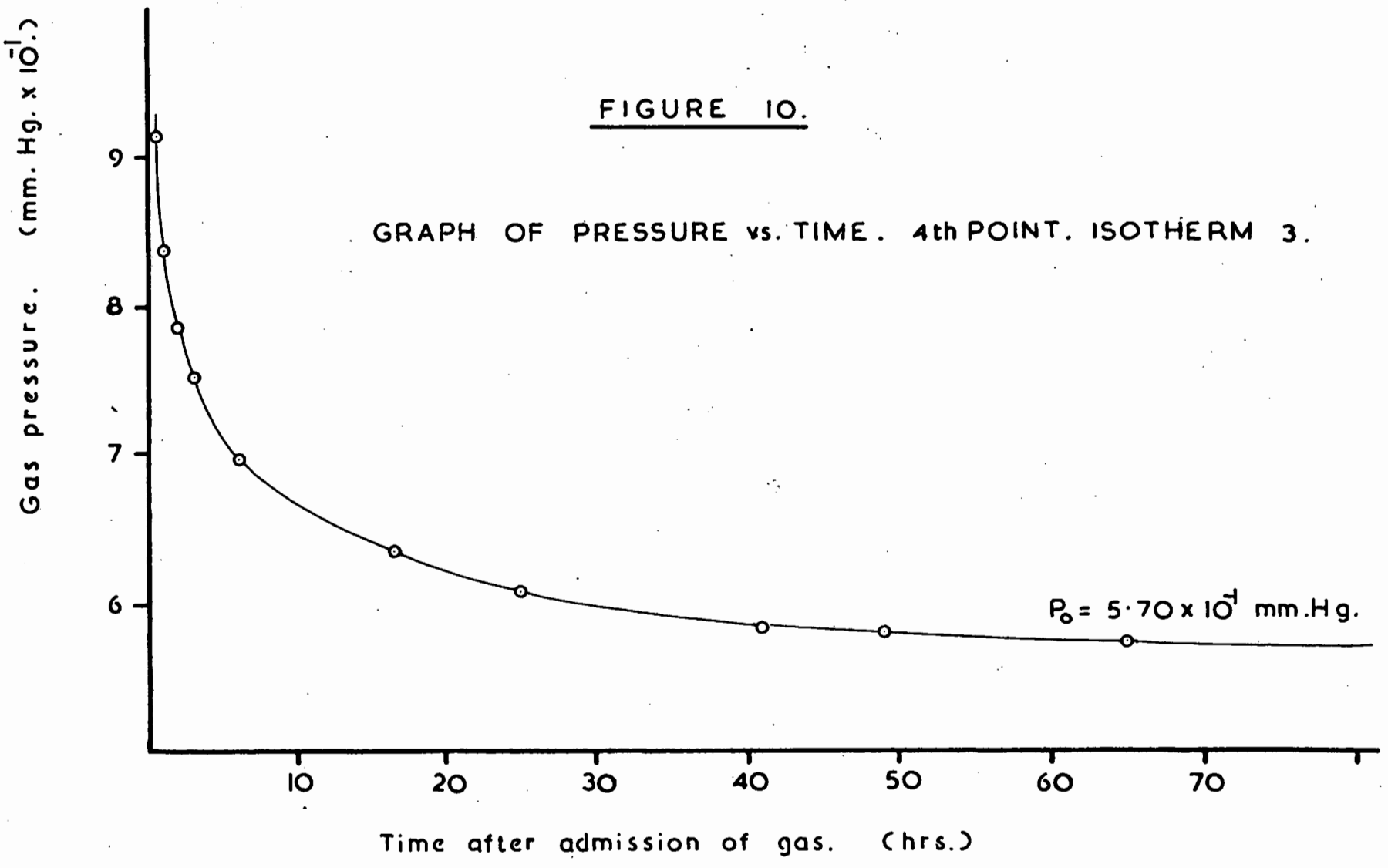


FIGURE 10.
GRAPH OF PRESSURE vs. TIME. 4th POINT. ISOTHERM 3.
Gas pressure. (mm. Hg. x 10⁻¹.)
9
8
7
6
10
20
30
40
50
60
70
Time after admission of gas. (hrs.)
P₀ = 5·70 x 10⁻¹ mm.Hg.

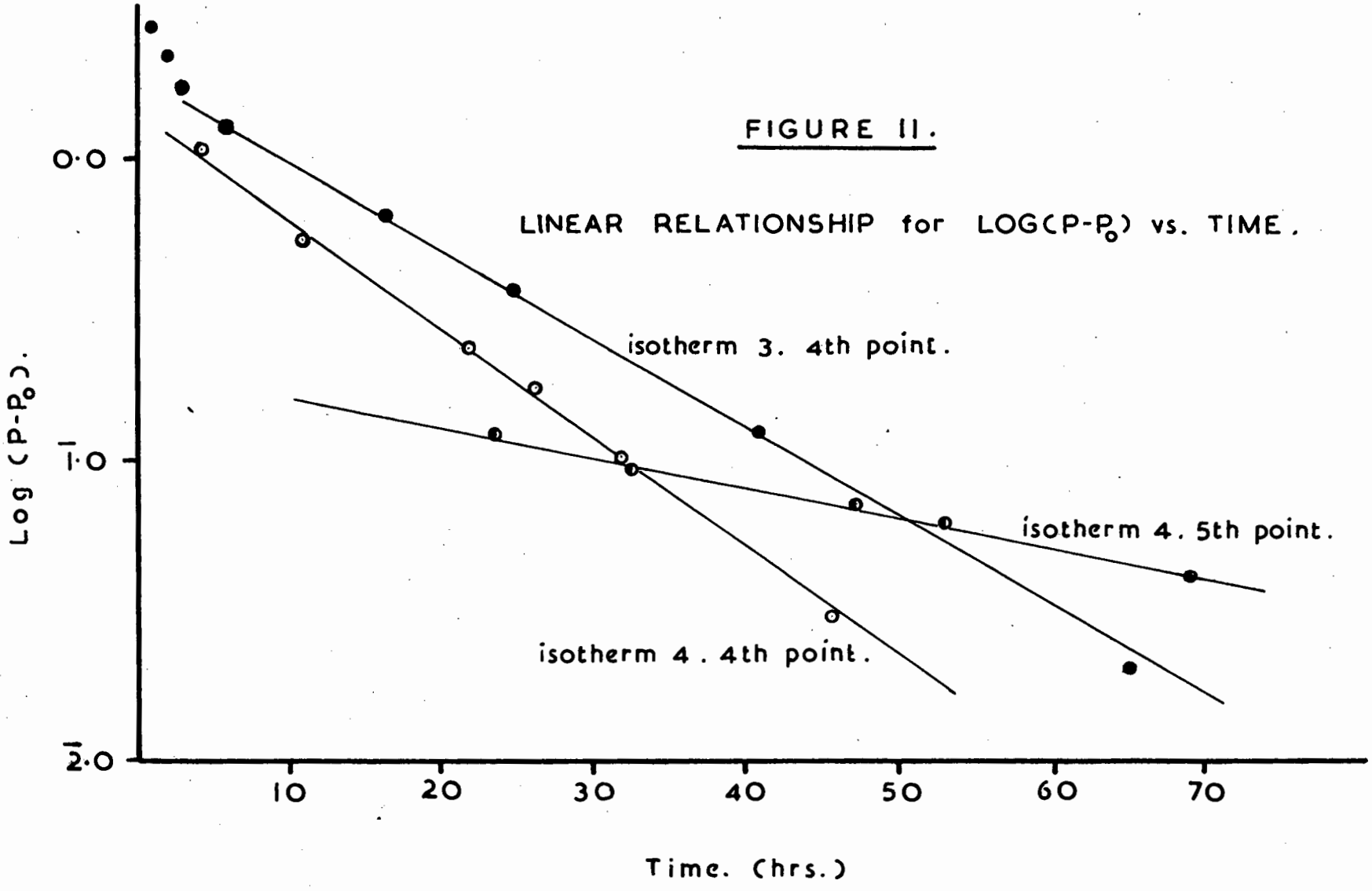


FIGURE II.
LINEAR RELATIONSHIP for LOG(P-P$_o$) vs. TIME.
isotherm 3. 4th point.
isotherm 4. 5th point.
isotherm 4. 4th point.
0·0
$\bar{1}$·0
$\bar{2}$·0
Log (P-P$_o$).
10
20
30
40
50
60
70
Time. (hrs.)

respectively, preferably with $t_2 - t_1 = t_3 - t_2$. P_0 was then found by substituting these values in equation 2. From the lines in Figure 11 it can be seen that only values of t greater than about 6 hours could be used for solving for P_0.

It was then found that as much of the curve had to be determined experimentally to calculate P_0 as was required to extrapolate it to P_0, so the simpler extrapolation method was most often used. The calculation method using equation 2 was used as an occasional check.

Figure 12 shows the curves obtained of Pressure vs. Time for points on Isotherm 4. Very similar ones were obtained for all the isotherms, though the time required in each pressure range to get sufficient of the curve to extrapolate it accurately, varied for the various gases and adsorbents. The variation was not very appreciable except in a couple of cases which will be pointed out.

(b) Calculation of isotherms from the experimental data.

The method of calculation of the isotherms from the data obtained was the same for all the isotherms. One of the trial runs will be used as an example.

E.g. Isotherm 4.

Adsorption of carbon dioxide on zinc oxide.
Weight of adsorbent used = 22.10 gm.
Corrected isotherm temperature = 258.5°C
Starting conditions:- T, A, B, Z and M all at a pressure of less than 1×10^{-5} mm. Hg.

1st admission of gas:-

Pressure of gas sample let in measured in differential manometer = $P_{M'}$.

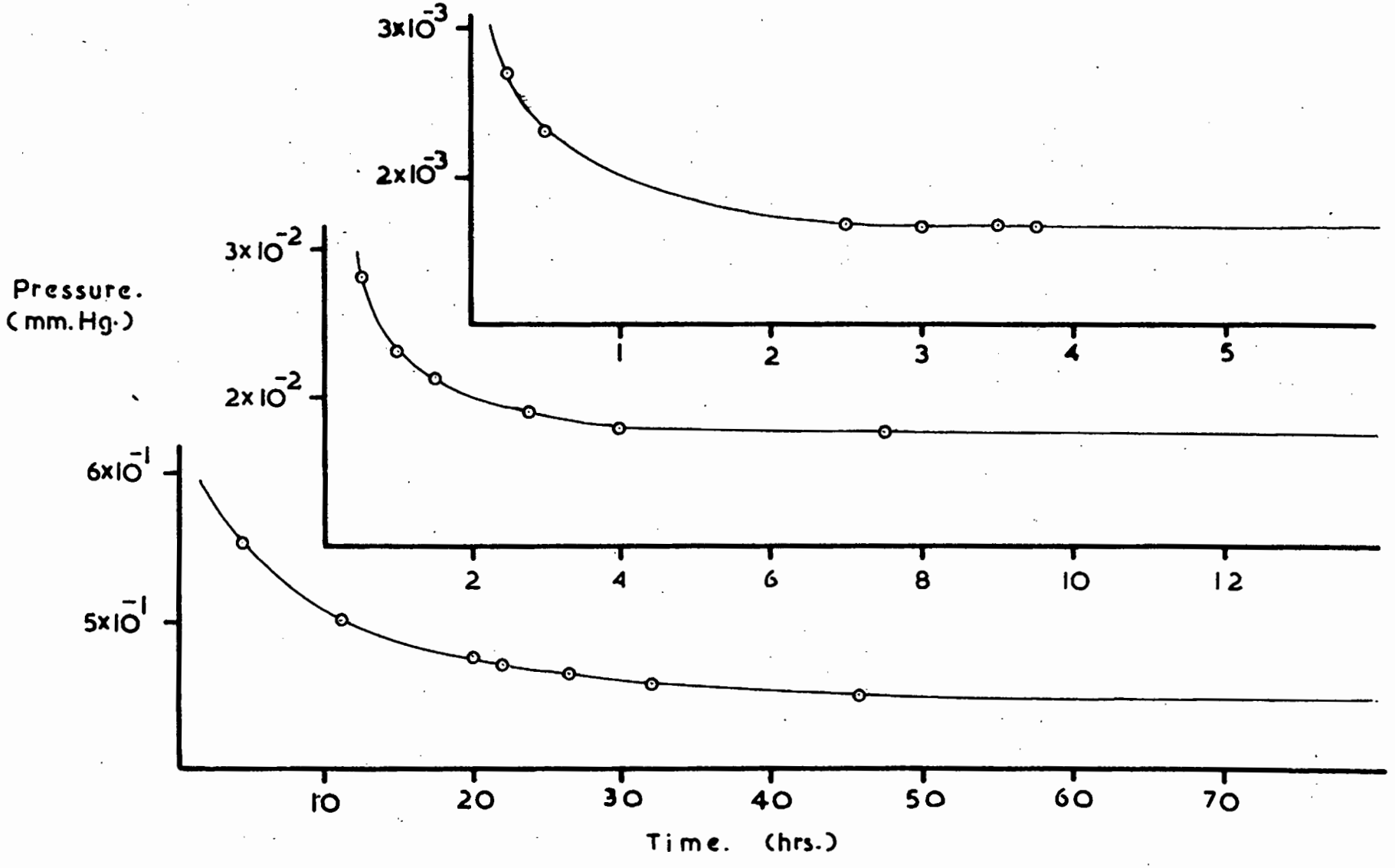


FIGURE 12. PRESS. vs. TIME CURVES. POINTS ON ISOTHERM 4.

Mercury level, R.H. limb of manometer = 55.22 cm

" " , L.H. " " " = 42.35 cm.

$\therefore$ Gas pressure $P_{M'}$ = 12.87 cm.

= 128.7 mm.

Volume of gas sample = $M' = M^o + \frac{P_{M'}}{10}$ c.c.

= (14.5 + 1.3) c.c.

= 15.8 c.c.

Now $PV = nRT$ or $n = PV/RT$

where P = gas pressure in mm. Hg

V = volume of gas in c.c.

T = absolute temperature, °K

n = number of moles of gas present

and $R = \frac{760 \times 22414}{273}$ = 62400 c.c. mm. Hg/deg. K, mole.

$\therefore$ Number of moles of gas admitted = $\frac{128.7 \times 15.8}{RT}$

= $\frac{2030}{RT}$

(Where T = room temperature = 298°K).

Equilibrium pressure after adsorption of first sample of gas

= 1.67×10^{-3} mm. Hg

Volume of gas space = (T + A + B) + Z + M^o

= 849 + 164 + 14.5

= 1028 c.c.

$\therefore$ Number of moles of gas left in gas space = $\frac{1.67 \times 10^{-3} \times 1028}{RT} = {}^{2}/_{RT}$.

$\therefore$ Number of moles of gas adsorbed = $\frac{2030 - 2}{RT} = \frac{2028}{RT}$.

$\therefore$ Number of moles of gas adsorbed per gram of adsorbent = $\frac{2028}{62400 \times 298 \times 22.10}$

= $2028 \times 2.43 \times 10^{-9}$

= 4.9×10^{-6}.

2nd admission of gas:-

Pressure of gas sample = 136.2 mm. Hg

Volume of gas sample = 15.9 c.c.

$\therefore$ Additional number of moles of gas admitted $= \frac{136.2 \times 15.9}{RT} = \frac{2165}{RT}$.

$\therefore$ Total number of moles of gas admitted $= \frac{2030 + 2165}{RT} = \frac{4195}{RT}$.

Equilibrium pressure after second adsorption = 1.74×10^{-2} mm. Hg

Volume of gas space = 1028 c.c.

$\therefore$ Number of moles of gas left in gas space $= \frac{1.74 \times 10^{-2} \times 1028}{RT} = \frac{18}{RT}$.

$\therefore$ Total number of moles of gas adsorbed $= \frac{4195 - 18}{RT} = \frac{4177}{RT}$

In the same way the number of moles of gas adsorbed for each new equilibrium pressure was calculated. The data may be summarised in tabular form.

Before adsorption					After ads.		Total moles in x RT	Moles left x RT	Moles ads. x RT	Moles ads. per gram x 10^6
Manometer readings			Vol. M'	Moles in x RT	Equi. press.	log press.				
Right	Left	Press.								
cm.	cm.	mm. Hg	c.c.		mm. Hg					
55.22	42.35	128.7	15.8	2030	1.67×10^{-3}	$\bar{3}.22$	2030	2	2028	4.9
55.61	41.99	136.2	15.9	2165	1.74×10^{-2}	$\bar{2}.24$	4195	18	4177	10.2
55.33	42.20	131.3	15.8	2075	1.15×10^{-1}	$\bar{1}.06$	6270	120	6150	14.9
56.21	41.29	149.2	16.0	2390	4.45×10^{-1}	$\bar{1}.65$	8660	460	8200	19.9
56.48	41.03	154.5	16.0	2470	1.00×10^{0}	0.00	11130	1028	10100	24.5

(c) Reproducibility of isotherms.

After isotherm 4 had been obtained, the adsorbent was activated at 450°C for 4½ hours under vacuum and then isotherm 5 was determined, also for carbon dioxide and at the same temperature. Figures 13 and 14 show the good agreement. Isotherms 8

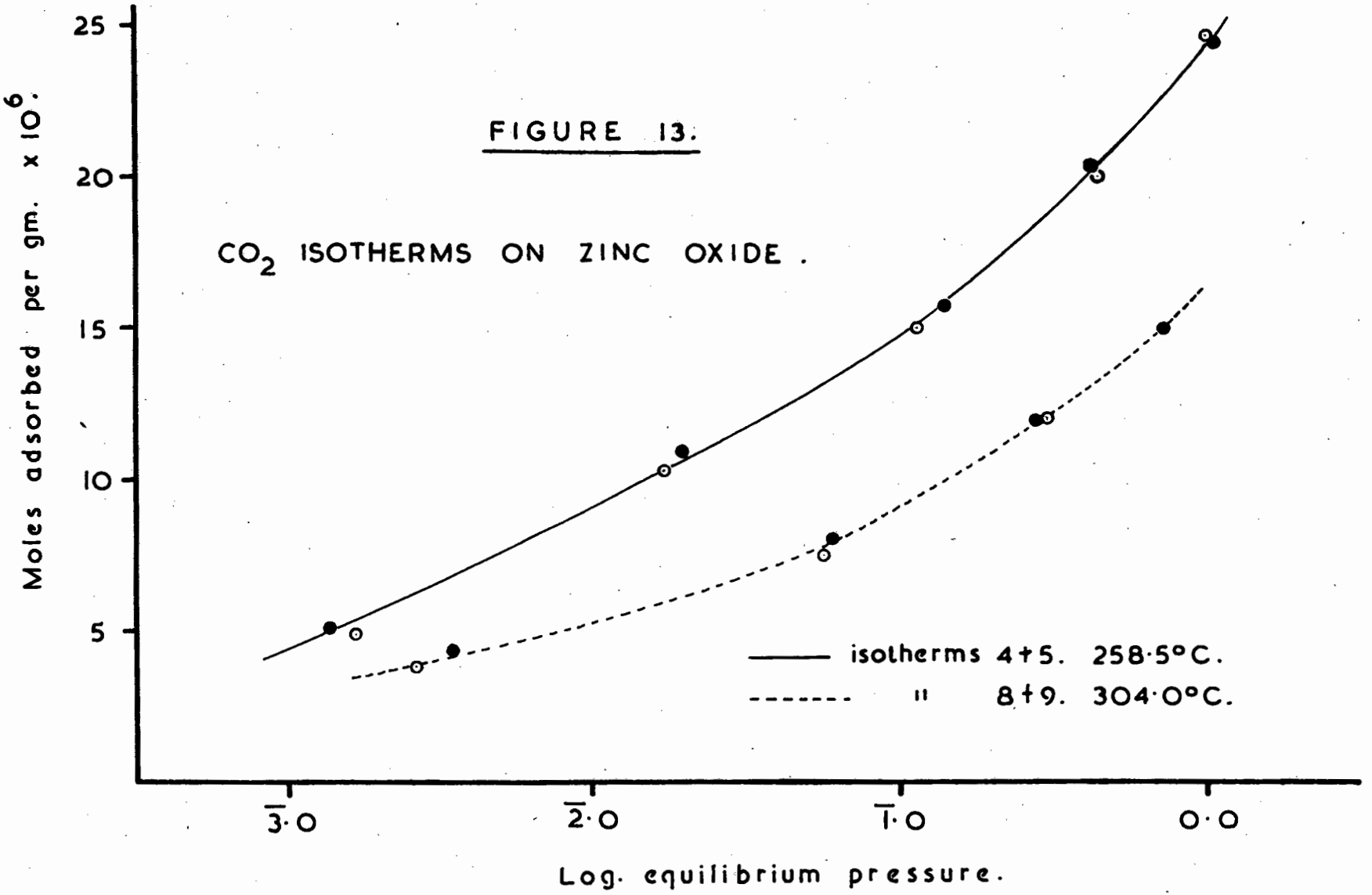


FIGURE 13.
CO_2 ISOTHERMS ON ZINC OXIDE.
Moles adsorbed per gm. x 10^6.
25
20
15
10
5
isotherms 4+5. 258·5°C.
" 8+9. 304·0°C.
$\overline{3}\cdot0$
$\overline{2}\cdot0$
$\overline{1}\cdot0$
0·0
Log. equilibrium pressure.

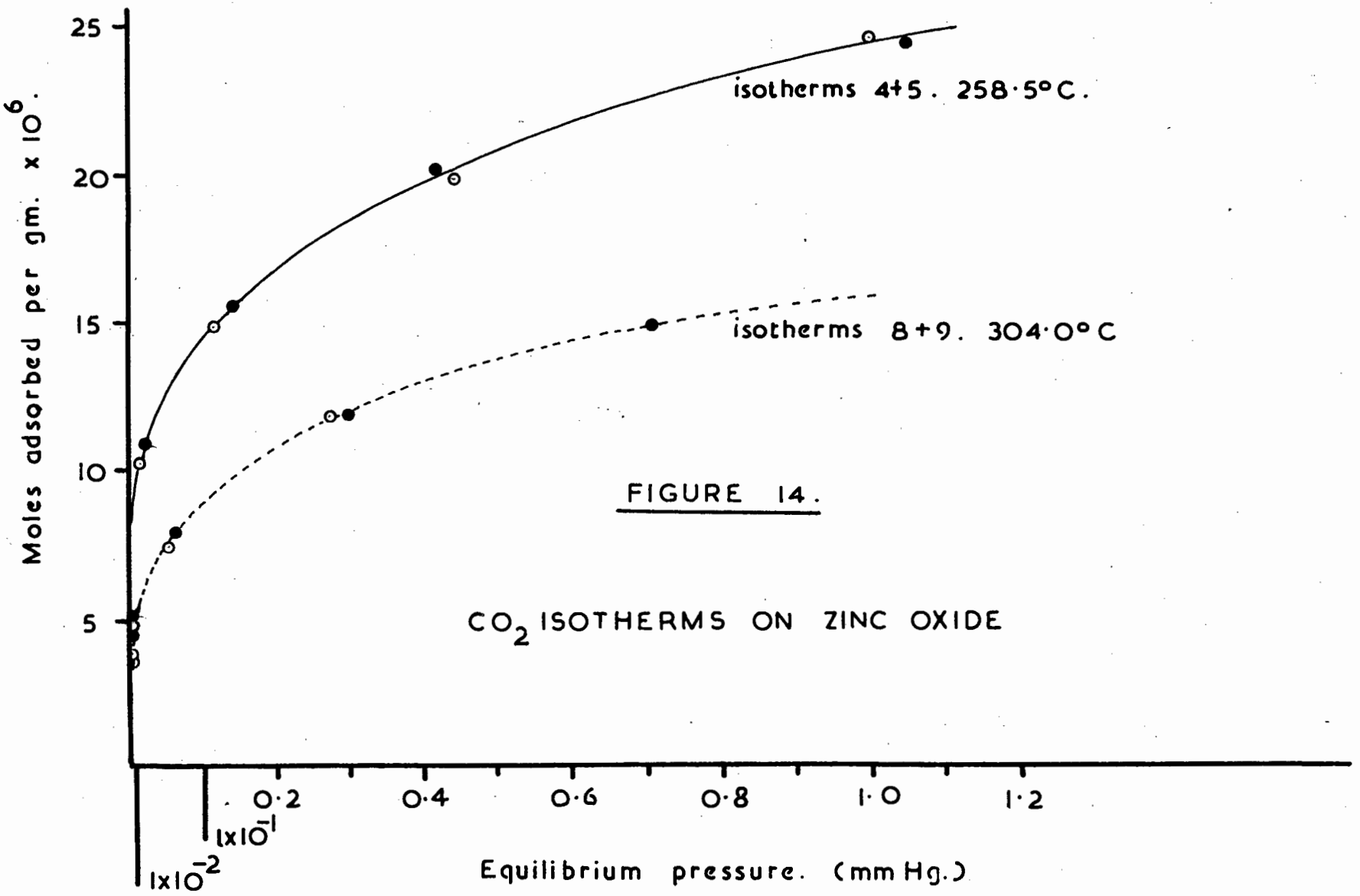


FIGURE 14.

CO_2 ISOTHERMS ON ZINC OXIDE

and 9 were obtained for carbon dioxide at 304°C (Fig. 13 and 14). It can be seen that the adsorbent surface was reproducible for carbon dioxide.

In general the isotherms were drawn with the equilibrium pressure on a log scale because of the wide range of pressure.

(vii) Family of isotherms for one gas on one adsorbent.

Each adsorbent sample was used to determine a series of isotherms for one gas in the temperature range 250° - 320°C. The sample was activated for 24 hours after insertion, a trial isotherm was done somewhere in the temperature range to find the order of size of the adsorption, and then the isotherms were measured in turn, starting at the highest temperature, and activating for 4½ hours between isotherms.

(viii) Heats of adsorption.

From a family of isotherms for a particular gas on a particular adsorbent graphs were drawn showing "Log Equilibrium Pressure" vs. "Reciprocal of Absolute Temperature" for various amounts of gas adsorbed. The heats of adsorption at the various coverages were calculated from the slopes of these lines using the equation[33,34].

$$\text{Isosteric heat of adsorption} = (\text{slope})\ (2.303\ R)$$

$$= \left[\frac{(\text{slope}) \times 2.303 \times 1.987}{1000}\right] \frac{\text{Kcal}}{\text{mole}}.$$

PART C.

EXPERIMENTAL RESULTS.

I (1) Adsorption of carbon dioxide on pure zinc oxide.

The isotherms obtained are shown in Fig. 15, and a full table of results appears in Appendix III. The experiments gave a very consistent family of isotherms, which on conversion to log P vs. $\frac{1}{T}$ data gave the straight lines shown in Fig. 18. Heats of adsorption calculated from the slopes of these lines decreased from about 20 to 16 Kcals/mole with increasing coverage. They are shown in Fig. 21. (Garner and Veal[58] using a calorimeter at room temperature obtained values varying from about 13 to 9 Kcals/mole. Kwan, Kinuyama and Fujita[59] obtained a value of 44 Kcal/mole in the temperature range 300° - 500°C). The results indicate quite normal chemisorption. The only unusual phenomenon noticed was a distinct blackening of the top layer of pellets in the adsorption bulb. The remainder of the pellets showed no signs of darkening.

(2) Adsorption of carbon dioxide on zinc oxide with gallium oxide impurity.

The isotherms are shown in Fig. 16 and the table of results is in Appendix IV. The determination of Isotherm 13 was obviously in error, but since the other three isotherms gave consistent results it was not necessary to repeat it. The dotted curve shows its probable true position. This curve was deduced from the log P vs. $\frac{1}{T}$ data which are shown in Fig. 19. The heats of adsorption which are shown in Fig. 21 decreased from about 28 to 20 Kcals/mole with increasing coverage. The top layer of pellets was again blackened.

(3) Adsorption of carbon dioxide on zinc oxide with lithium oxide impurity.

Fig. 17 shows the isotherms obtained in this case.

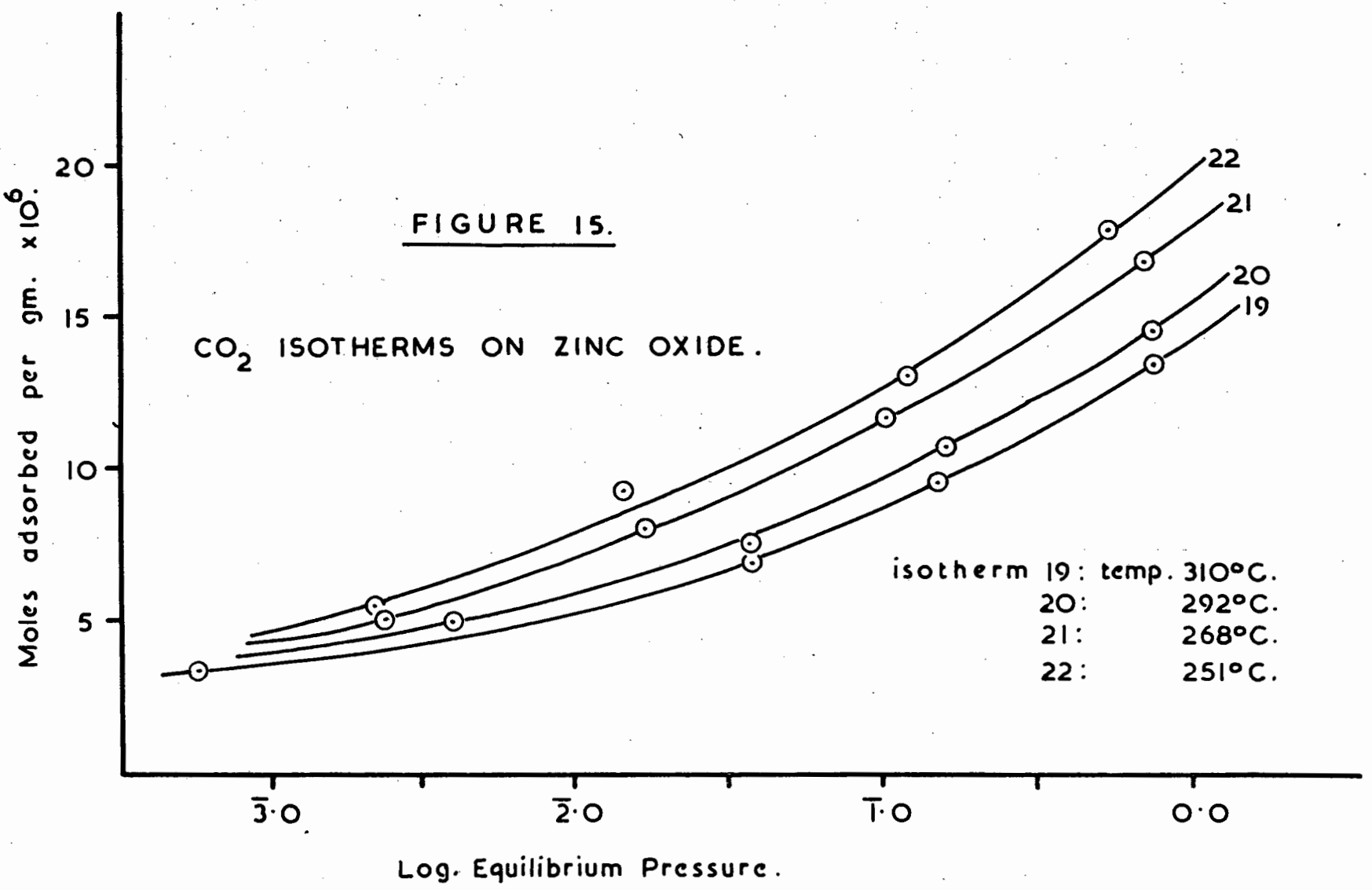


FIGURE 15.
CO_2 ISOTHERMS ON ZINC OXIDE.
Moles adsorbed per gm. x 10^6.
20
15
10
5
22
21
20
19
isotherm 19 : temp. 310°C.
20: 292°C.
21: 268°C.
22: 251°C.
$\bar{3}\cdot0$
$\bar{2}\cdot0$
$\bar{1}\cdot0$
0·0
Log. Equilibrium Pressure.

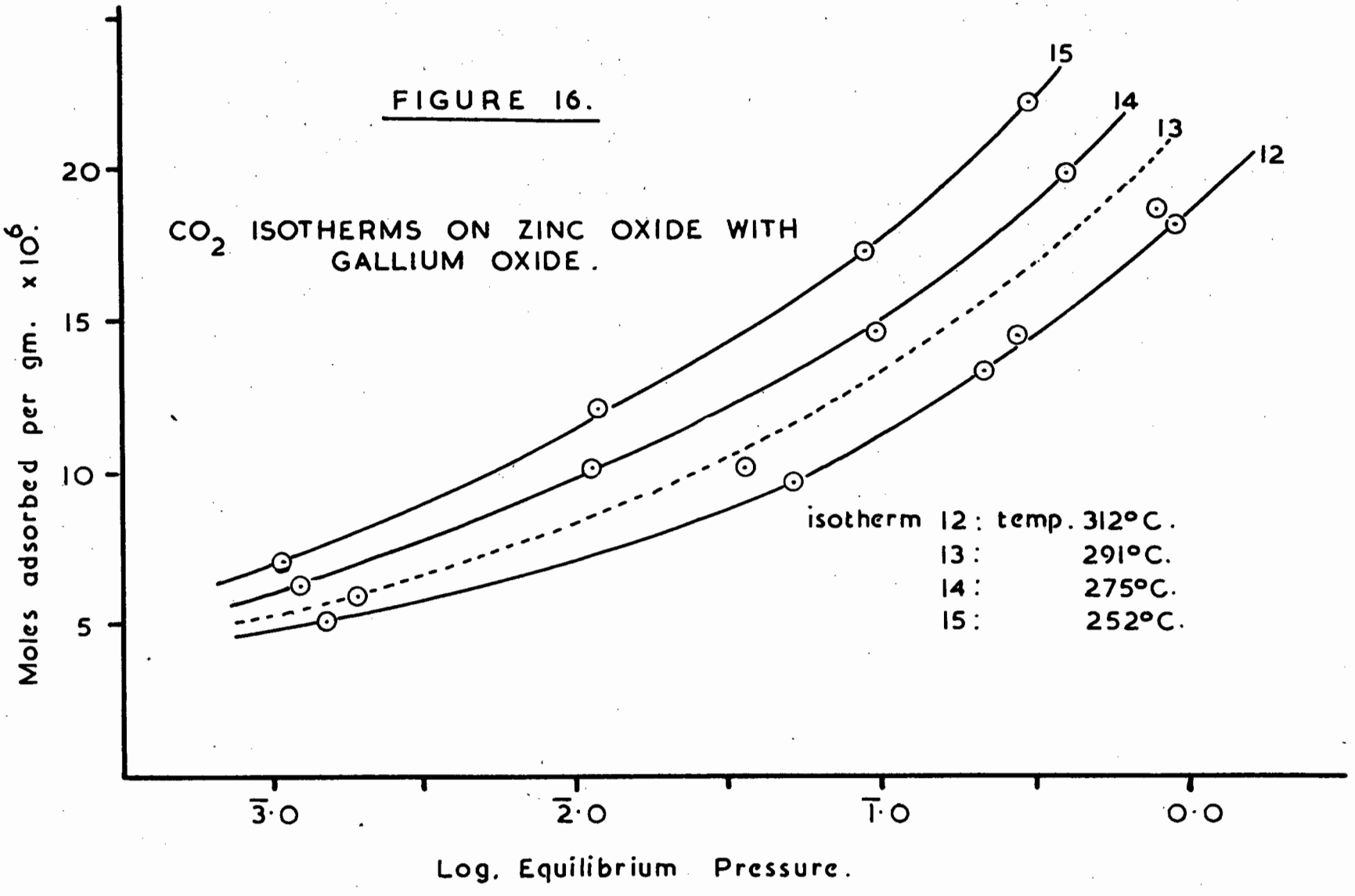


FIGURE 16.
CO_2 ISOTHERMS ON ZINC OXIDE WITH GALLIUM OXIDE.
Moles adsorbed per gm. x 10^6.
20
15
10
5
15
14
13
12
isotherm 12 : temp. 312°C.
13 : 291°C.
14 : 275°C.
15 : 252°C.
$\bar{3}\cdot0$
$\bar{2}\cdot0$
$\bar{1}\cdot0$
0·0
Log. Equilibrium Pressure.

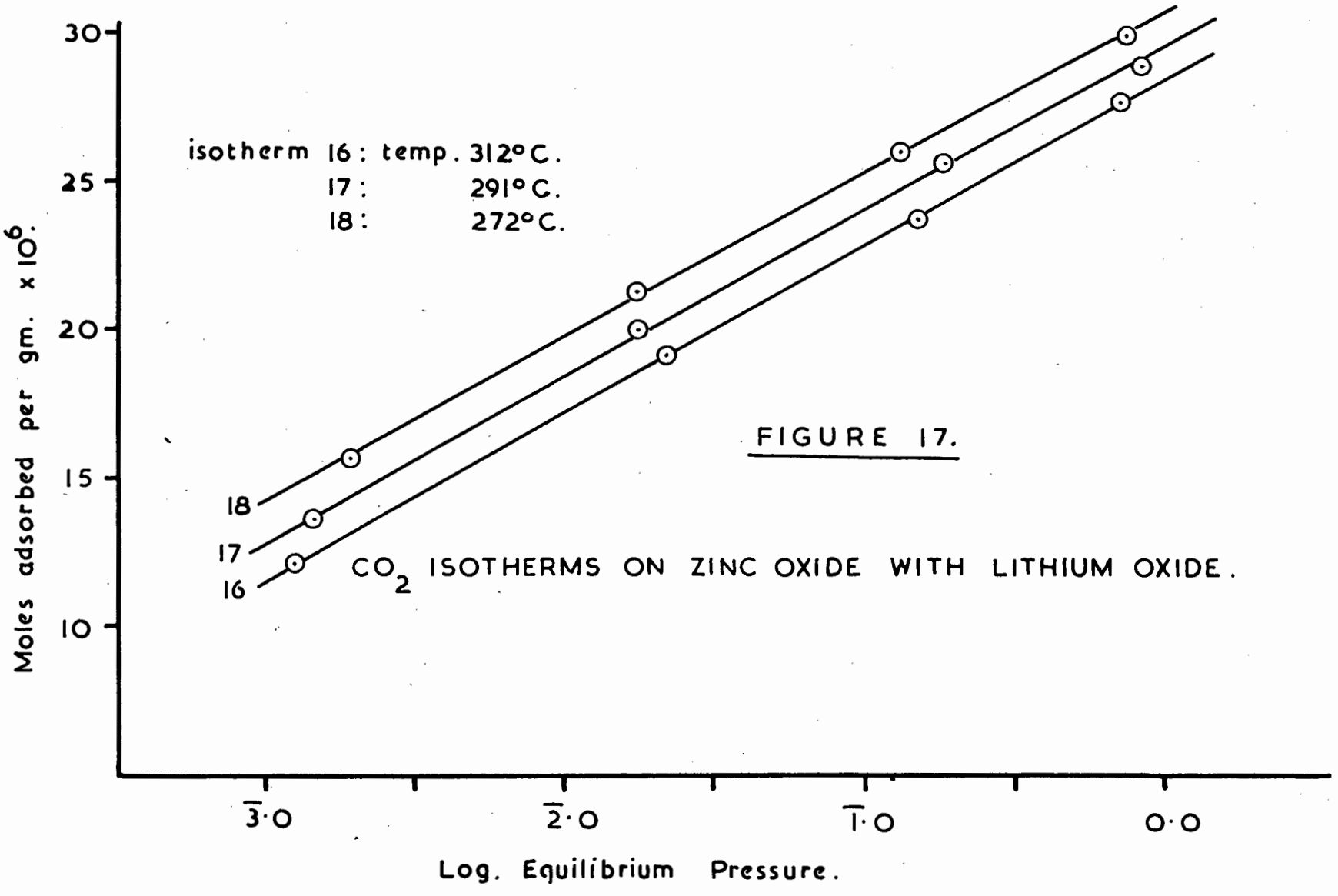


FIGURE 17.

CO_2 ISOTHERMS ON ZINC OXIDE WITH LITHIUM OXIDE.

FIGURE 18.

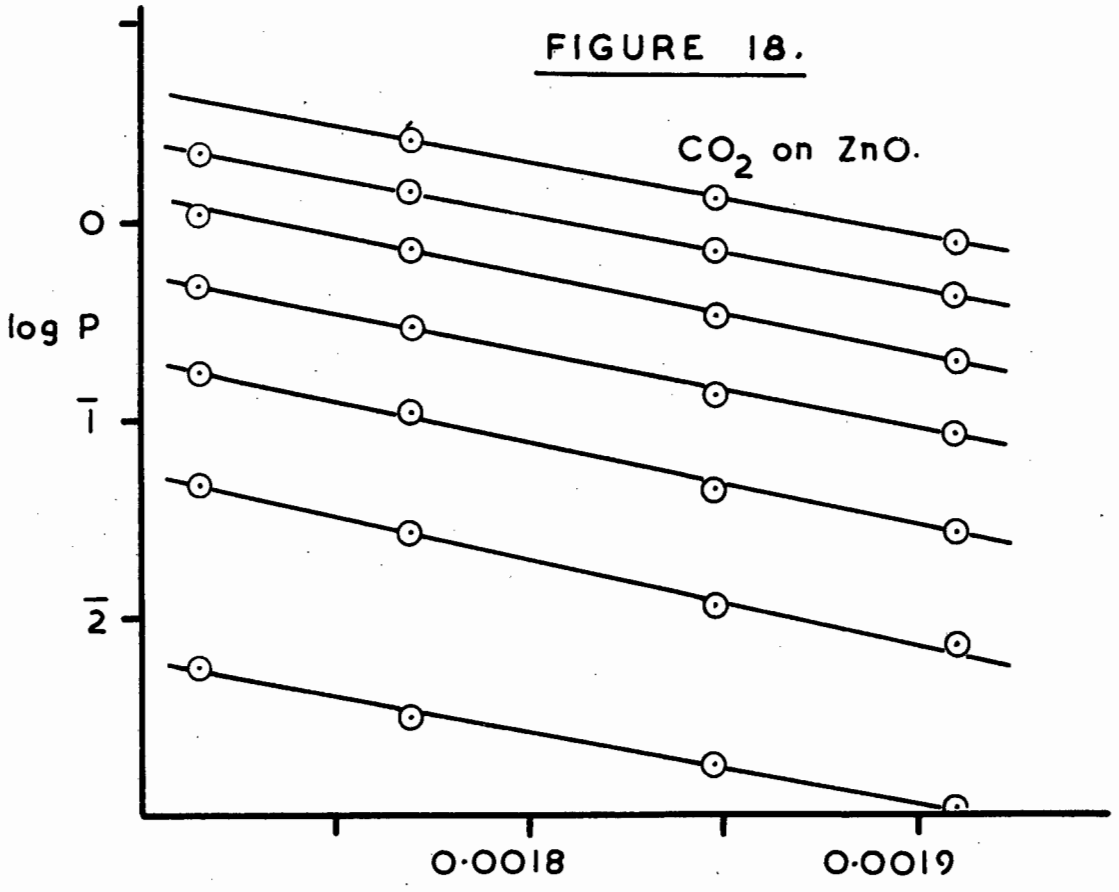


FIGURE 19.

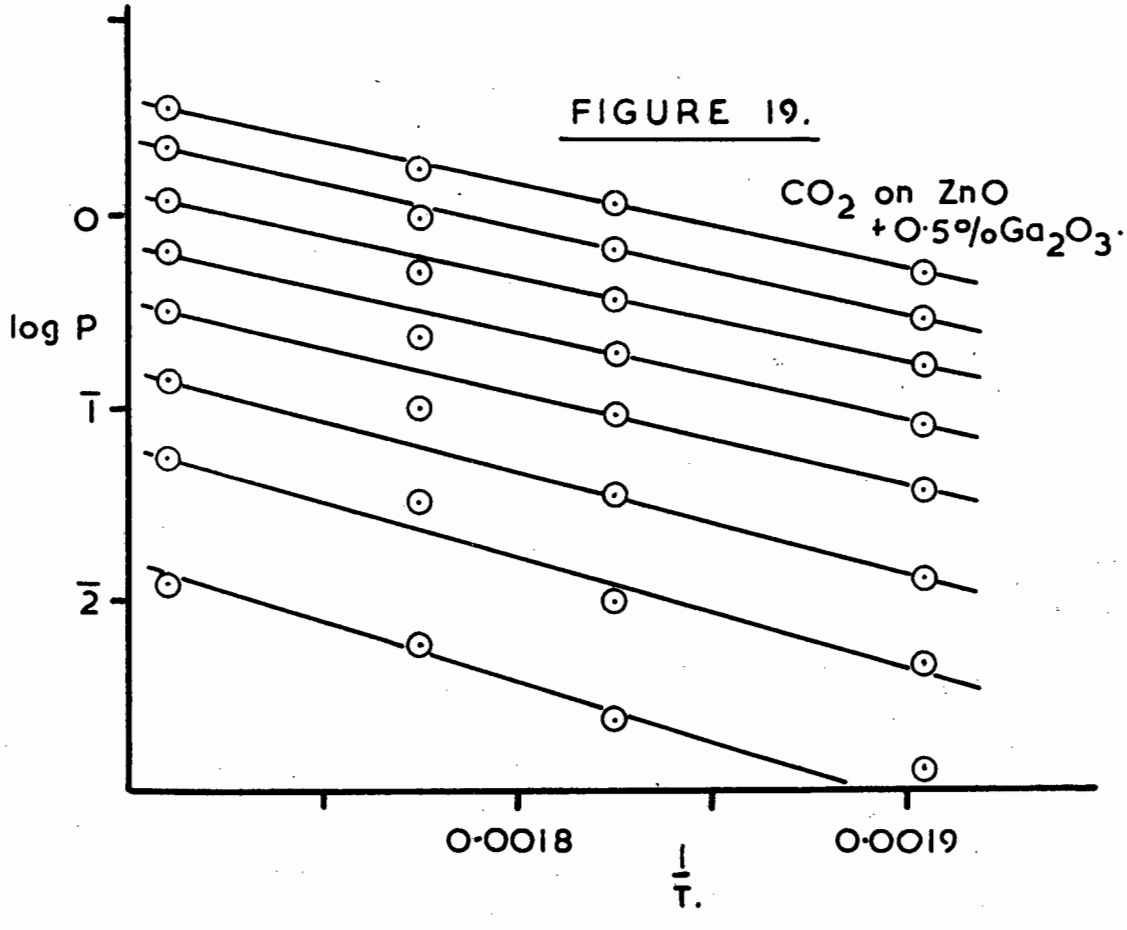


FIGURE 20.

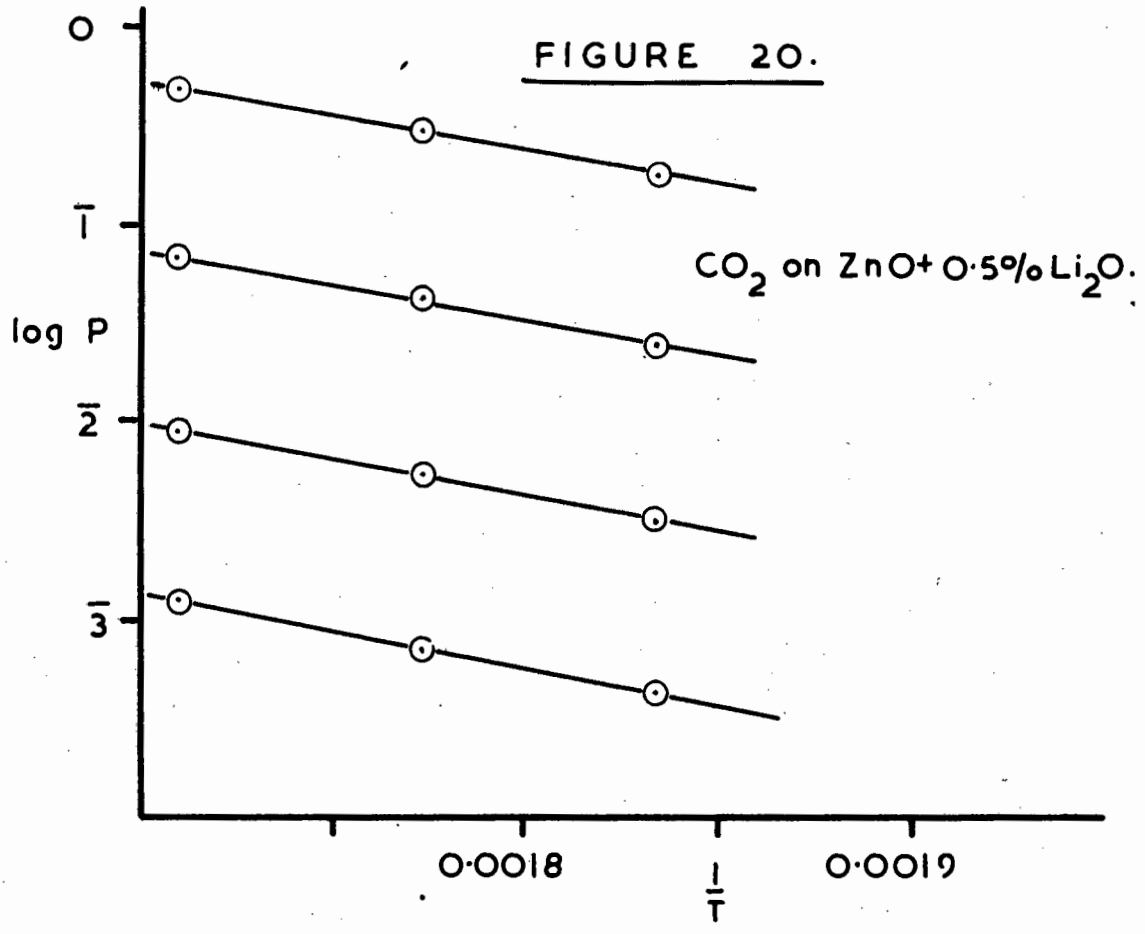
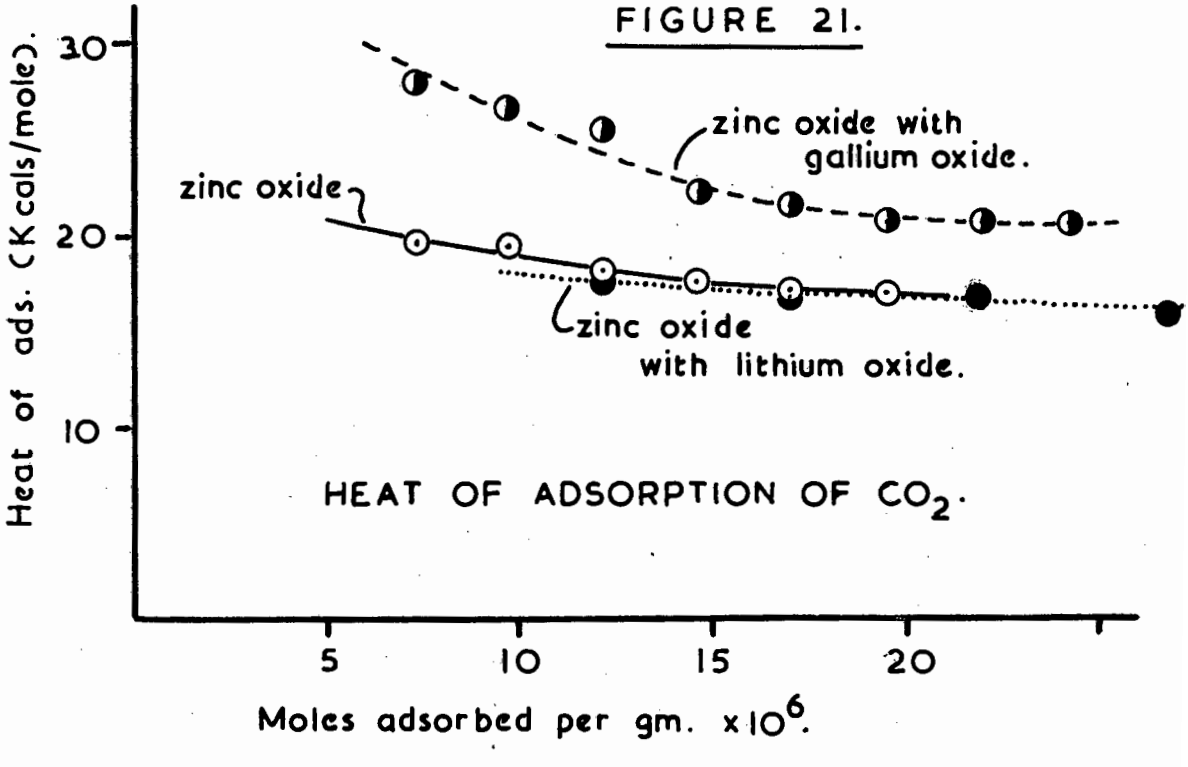


FIGURE 21.



Appendix V contains the tables of results. Markedly more adsorption occurred than on the other two adsorbents, and the shapes of the isotherms were slightly changed. Their linear nature only means that on the normal "moles adsorbed" vs. "equilibrium pressure" isotherm, a more sudden flattening out of the curve would occur. The log P vs. $\frac{1}{T}$ data shown in Fig. 20 are very regular, and give heats of adsorption in the range 17 to 15 Kcals/mole (Fig. 21). Values for the heat of adsorption at lower coverages could not be obtained because of the increased adsorption.

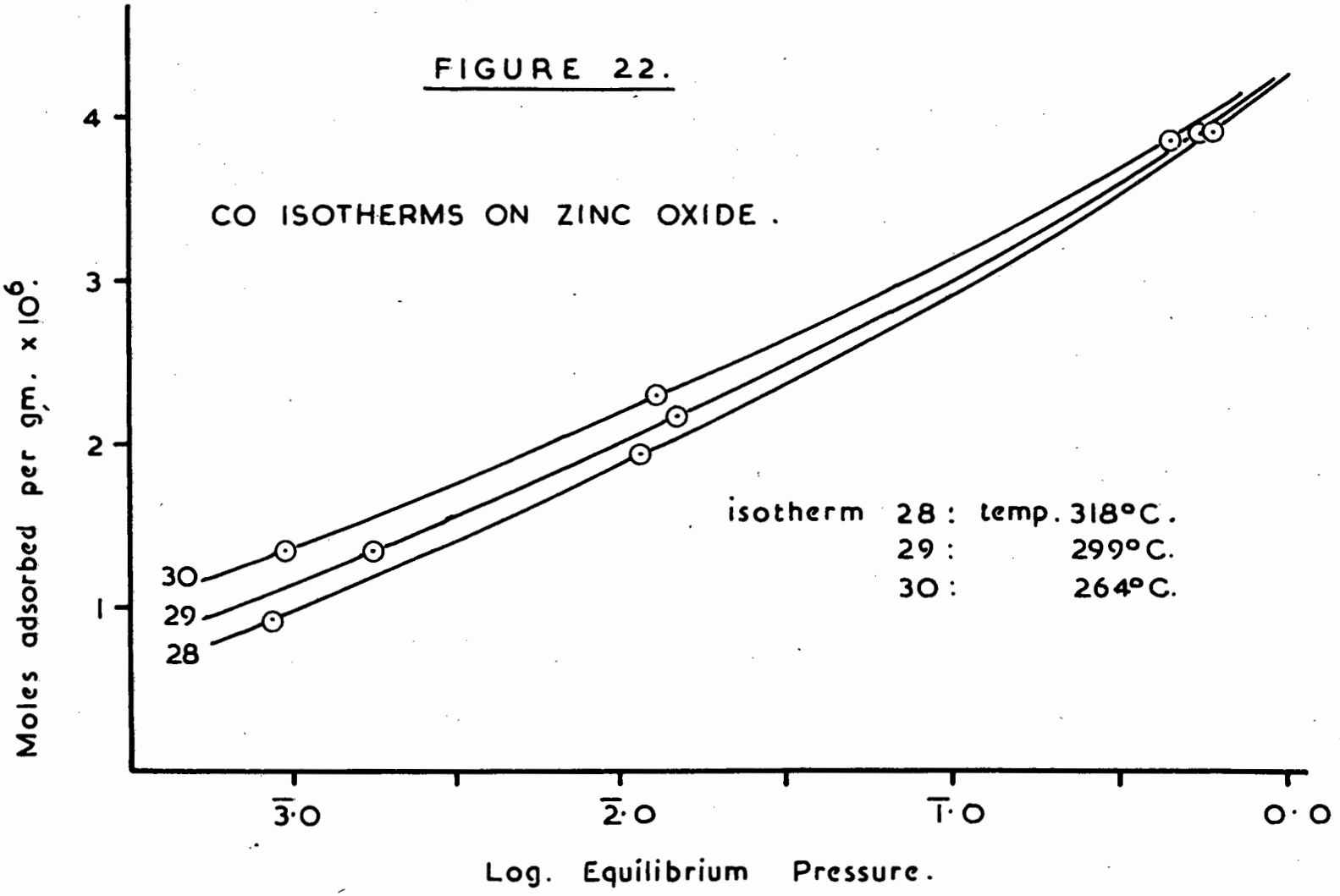
In contrast to the adsorption of CO_2 on the other two adsorbents there was no blackening of the top layer of pellets in the adsorption bulb. Some of the pellets appeared to be marked with little dark smudges, but they were quite generally distributed throughout the bulb.

II. 1. Adsorption of carbon monoxide on pure zinc oxide.

The isotherms obtained are shown in Fig. 22 while the full table of results appears in Appendix VI. The adsorption was only about one fifth of that of carbon dioxide. Because of the much smaller adsorption a small correction had to be applied in the calculation of the number of moles let in. The manifold T (see Fig. 7) was completely evacuated each time after gas had been let through into M, so that the residual gas in T after the previous adsorption, was lost. At the higher pressures the amount of gas lost in this way was appreciable, so the small correction shown in the third column of the table was applied.

The log P vs. $\frac{1}{T}$ data are shown in Fig. 24 and the heats of adsorption in Fig. 26. The heat values dropped steeply with increasing coverage from about 13 to 2 Kcals/mole. (Garner and Veal[58] obtained values varying from 20 to 12 Kcals/mole at room temperature using a calorimeter. Garner and Maggs[80] at around room temperature calculated the heat of adsorption from the isotherms and found it to be about 14 Kcals/mole).

FIGURE 22.


CO ISOTHERMS ON ZINC OXIDE.
Moles adsorbed per gm. x 10^6.
4
3
2
1
30
29
28
isotherm 28 : temp. 318°C.
29 : 299°C.
30 : 264°C.
$\bar{3}\cdot0$
$\bar{2}\cdot0$
$\bar{1}\cdot0$
0·0
Log. Equilibrium Pressure.

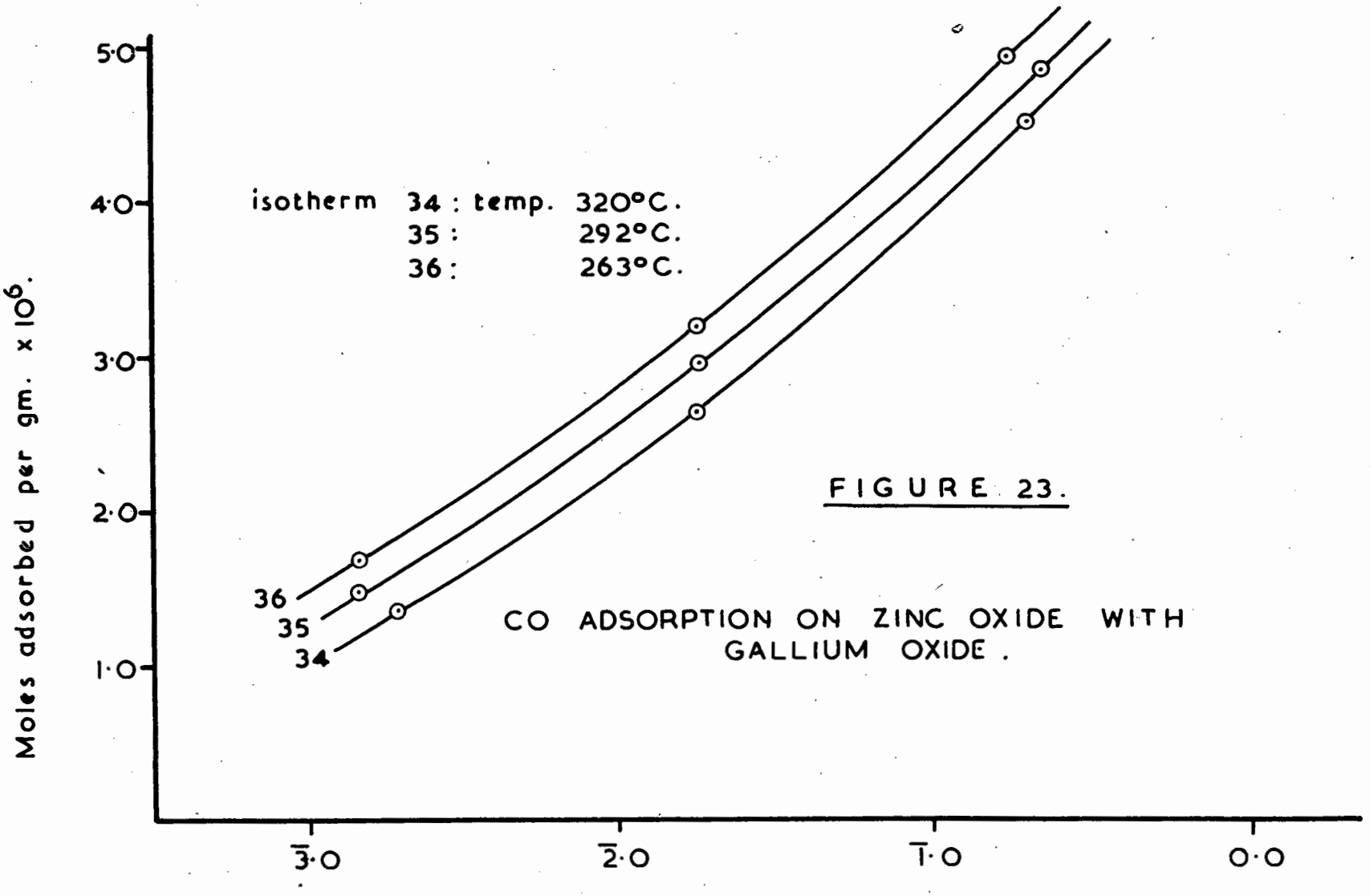

5·0
4·0
3·0
2·0
1·0
Moles adsorbed per gm. x 10⁶.
isotherm 34 : temp. 320°C.
35 : 292°C.
36 : 263°C.
36
35
34
CO ADSORPTION ON ZINC OXIDE WITH GALLIUM OXIDE.
$\bar{3}\cdot0$
$\bar{2}\cdot0$
$\bar{1}\cdot0$
0·0
Log. equilibrium pressure.

FIGURE 23.

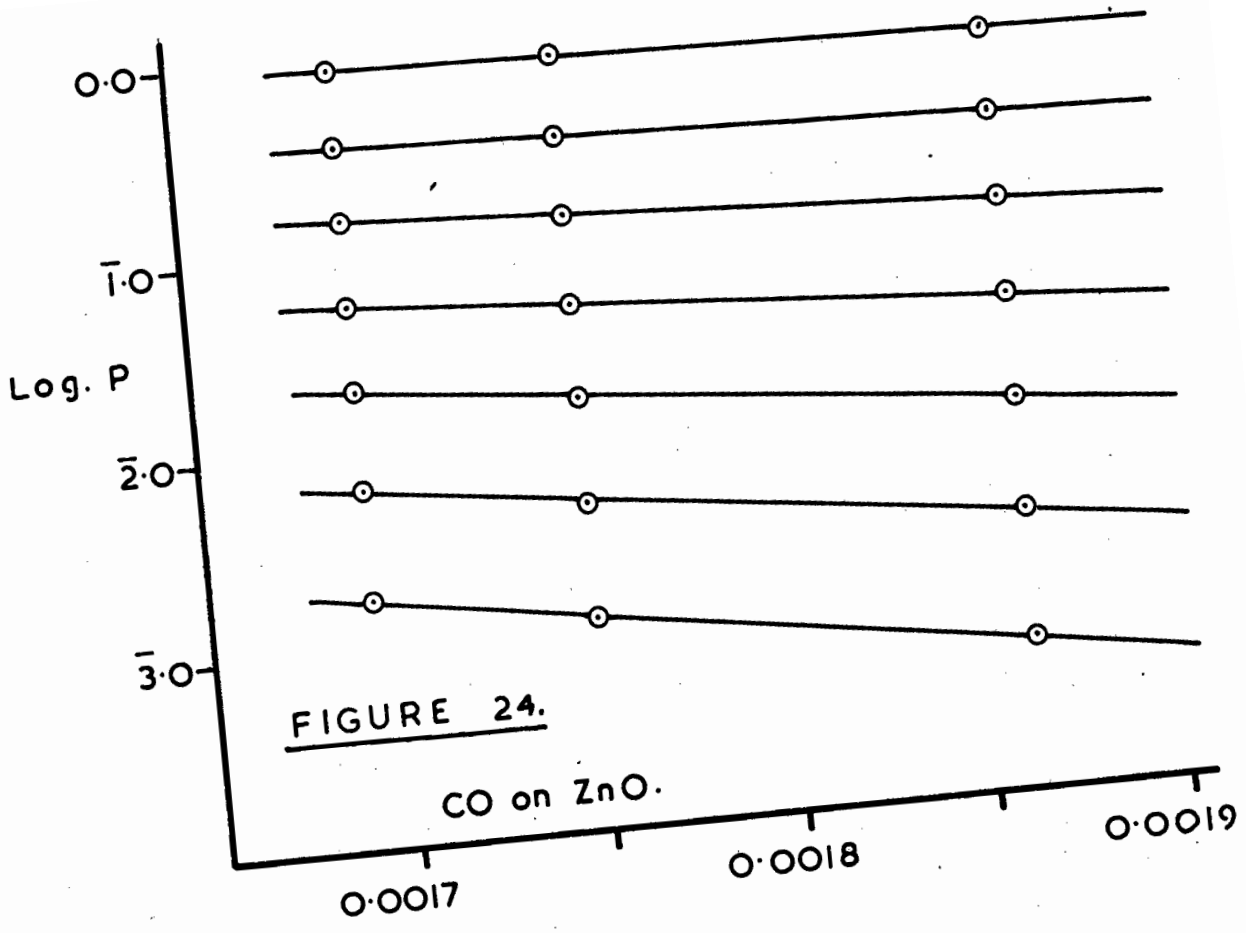


FIGURE 24.

CO on ZnO.

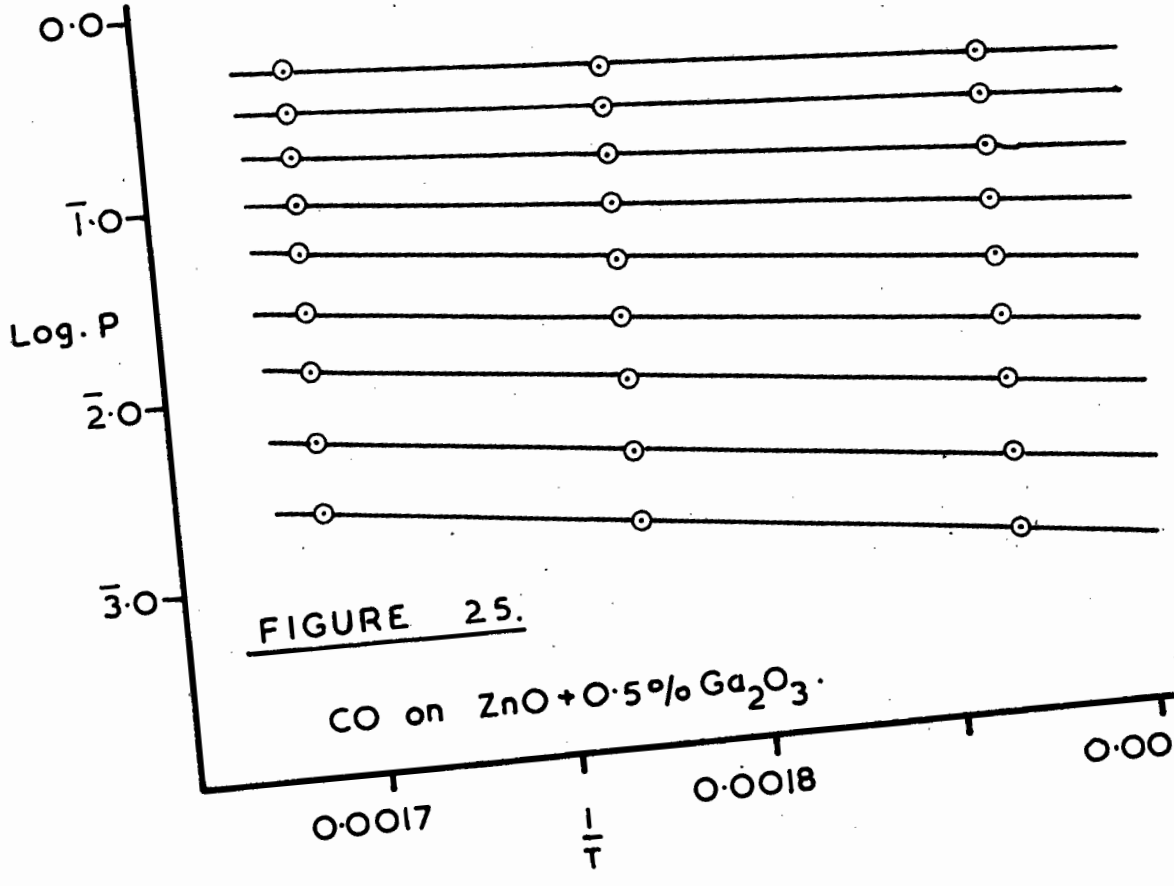
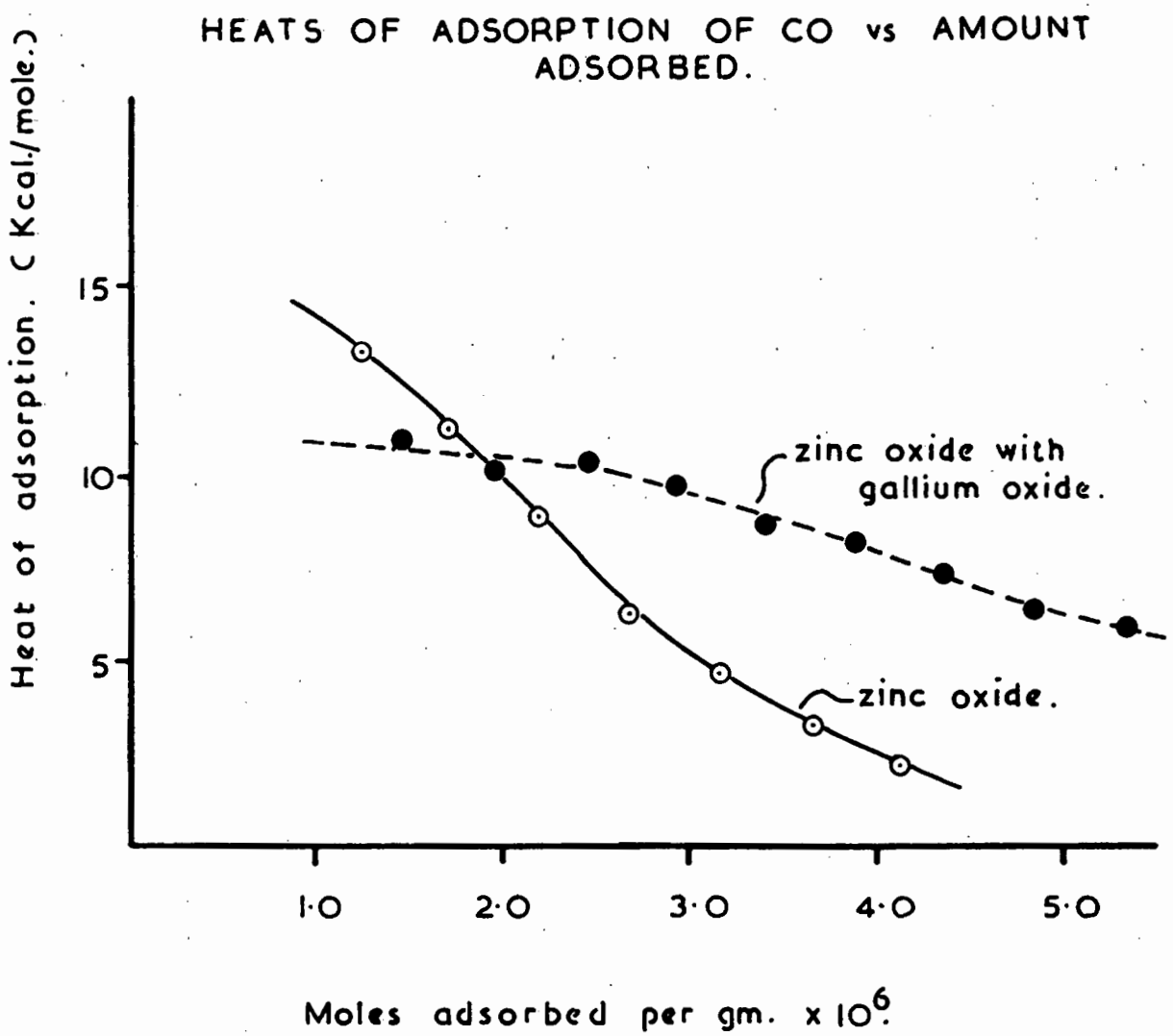


FIGURE 25.

CO on ZnO + 0·5% Ga_2O_3.

FIGURE 26.


HEATS OF ADSORPTION OF CO vs AMOUNT ADSORBED.
Heat of adsorption. (Kcal./mole.)
15
10
5
zinc oxide with gallium oxide.
zinc oxide.
1·0
2·0
3·0
4·0
5·0
Moles adsorbed per gm. x 10^6.

The top layers of pellets were again found to be blackened when the adsorption runs were finished. A dark metallic looking deposit was also found inside the tube leading to the adsorption bulb at the point where it entered the adsorption furnace. The deposit was soluble in conc. HCl and spectrochemical analysis showed that it contained zinc.

At higher pressures especially, the "pressure" vs. "time after admission of gas" curves did not flatten out so well as did the ones for carbon dioxide. This made it more difficult to extrapolate accurately to constant pressure.

2. Adsorption of carbon monoxide on zinc oxide with gallium oxide impurity.

The isotherms are shown in Fig. 23 and the table of results appears in Appendix VII. The correction for the gas lost from the manifold T was again applied as the amount of gas adsorbed was of the same order as that for the pure zinc oxide.

Fig. 25 shows the log P vs. $\frac{1}{T}$ data, and Fig. 26 shows the heats of adsorption which drop from about 11 to 6 Kcals/mole.

The top layers of pellets were again blackened and the dark deposit was again found in the tube to the adsorption bulb. Spectrochemical analysis showed that it contained zinc and gallium.

As with the pure zinc oxide adsorbent the "pressure" vs. "time" curves for the higher pressures (i.e. in the range 10^{-1} to 1 mm. Hg) did not flatten out well and extrapolation to an equilibrium value was uncertain.

3. Adsorption of carbon monoxide on zinc oxide with lithium oxide impurity.

Isotherms on this adsorbent could not be determined because the "pressure" vs. "time after admission of gas" curves did not flatten out towards a constant equilibrium pressure value even for the lowest

pressures used. For example, in the 10^{-3} mm. Hg range the pressure was still dropping steadily after more than fifty hours, and in the 10^{-1} mm. Hg range it was still dropping steadily after more than a hundred hours.

When the adsorbent was removed from the bulb it was found to be considerably blackened all over. The deposit inside the tube to the adsorption bulb was heavy, and on analysis was found to contain zinc and lithium.

III. Adsorption of hydrogen.

Trial runs showed that even in the 10^{-3} mm. Hg pressure range about 80 hours were required to obtain equilibrium after admission of gas to the adsorbent. To get results in as short a time as possible, it was decided to use Frankenburg's[12] method for the determination of isotherms. In this method gas is let in to the clean adsorbent at the lowest pressure and highest isotherm temperature. Equilibrium is attained and the pressure measured. The temperature is then lowered to that for the next isotherm, and the new equilibrium pressure is measured. This process is continued until the lowest isotherm temperature is reached, and then the temperature is progressively raised again to check the points on the various isotherms. When the equilibrium pressure for the highest temperature isotherm has been checked, a second admission of gas is made and the whole process is repeated to get the second point on each isotherm.

For the experiments with hydrogen it was found that on lowering the temperature the new equilibrium pressures were obtained within about one hour which is probably the time required to get temperature equilibrium in the adsorption bulb. On raising the temperature no appreciable differences in the equilibrium pressures were found compared with those found on dropping the temperature.

1. Adsorption on pure zinc oxide.

The isotherms are shown in Fig. 27 and the tables of results appear in Appendix VIII. For the first point on isotherm 38 about 90 hours were required for equilibrium to be reached. For the other two points the pressure value used was that read at 110 hours. Though equilibrium had not been reached the curves were definitely flattening out. This means that the isotherms do not represent equilibrium conditions except at the lowest pressures.

Fig. 29 shows the log P vs. $\frac{1}{T}$ data and Fig. 30 the heats of adsorption. The magnitudes of the heats are slightly lower than values obtained by Taylor and Sickman[8] (16 - 20 Kcals/mole) and Garner and Kingman[81] (10 - 25 Kcals/mole). The temperature ranges are, however, not identical.

After the experiments the adsorbent was found to be blackened all over. There was also a black deposit in the tube to the adsorption bulb. It was shown to contain zinc.

2. Adsorption on zinc oxide with gallium oxide impurity.

The isotherms for this adsorbent are shown in Fig. 28, and the tables of results are in Appendix IX. Equilibrium was attained in about 60 hours for the first point on isotherm 41. The second and third points were obtained in the same way as for the pure zinc oxide adsorbent. Again only the lower portions of the isotherms are reliable.

The log P vs. $\frac{1}{T}$ data and the heats of adsorption are shown in Figs. 29 and 30.

The adsorbent was blackened all over and the usual black deposit in the tube was found to contain zinc and gallium.

3. Adsorption on zinc oxide with lithium oxide impurity.

For this adsorbent only the first points on the isotherms

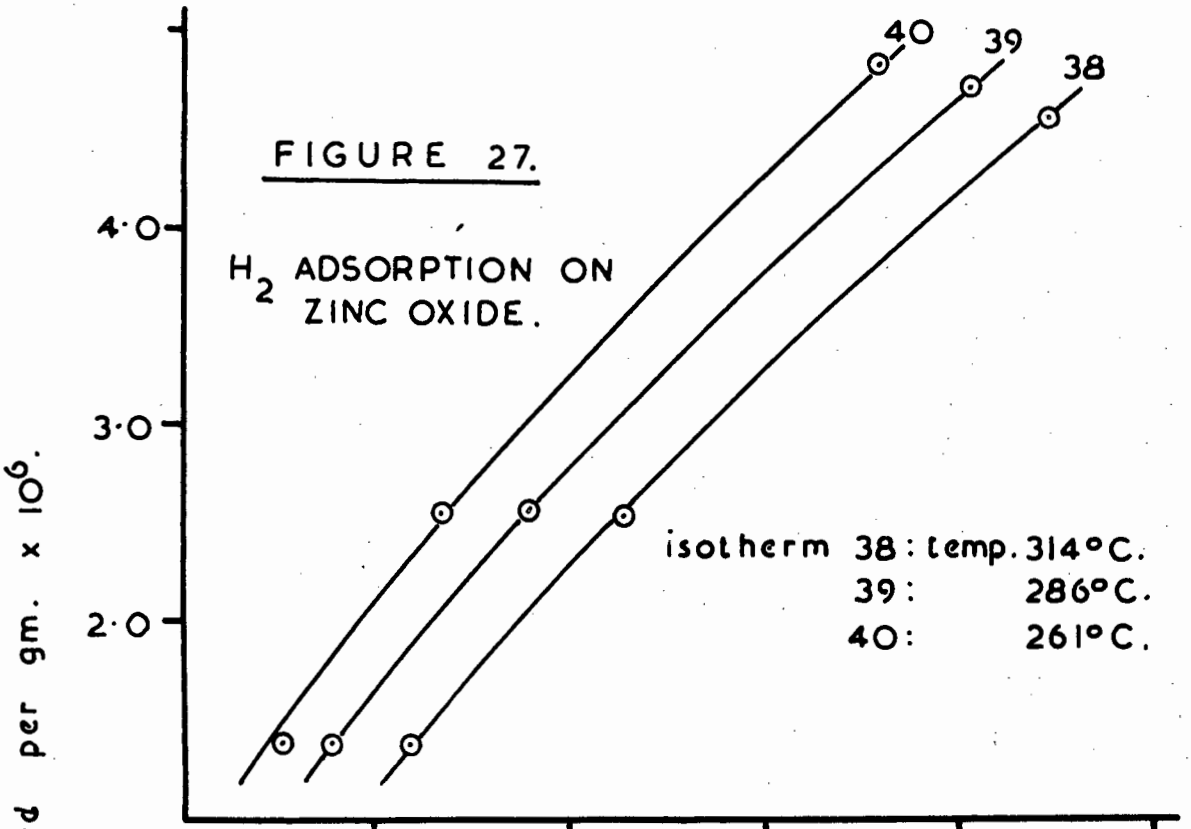


FIGURE 27.

H_2 ADSORPTION ON ZINC OXIDE.

isotherm 38 : temp. 314°C.
39 : 286°C.
40 : 261°C.

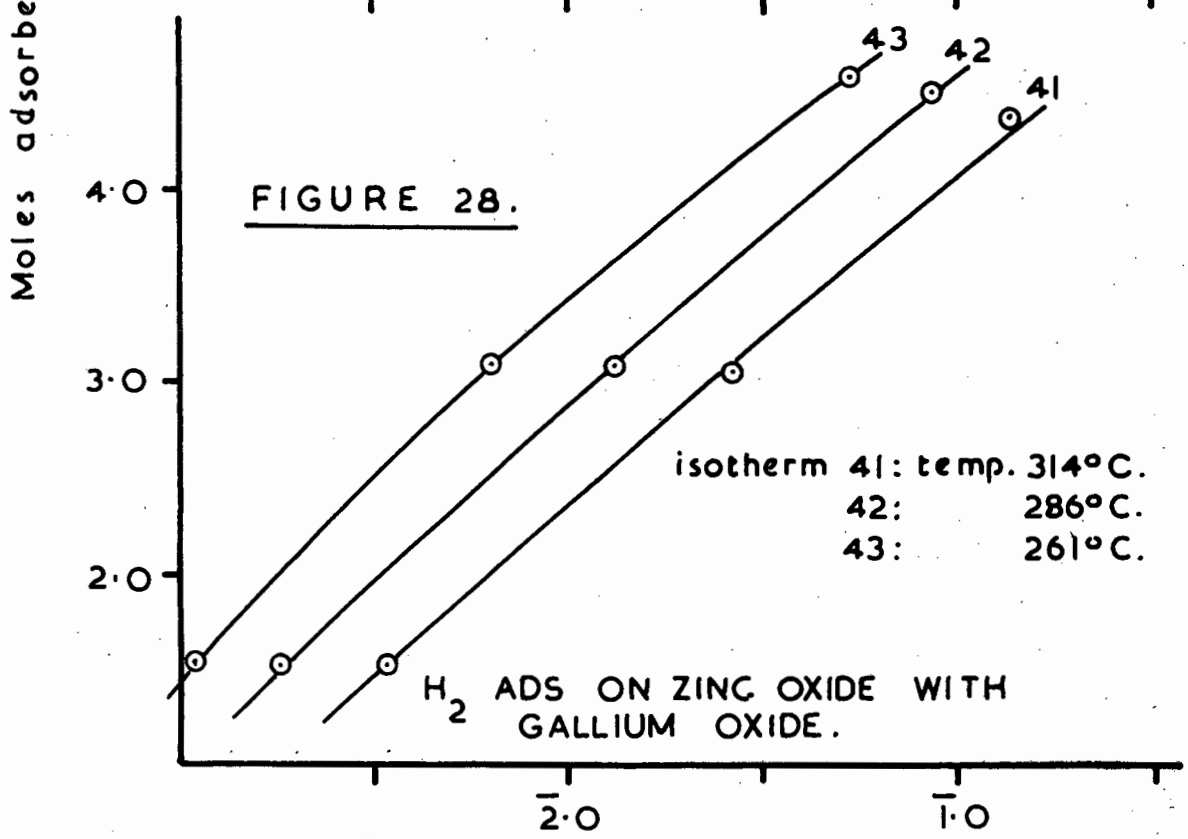
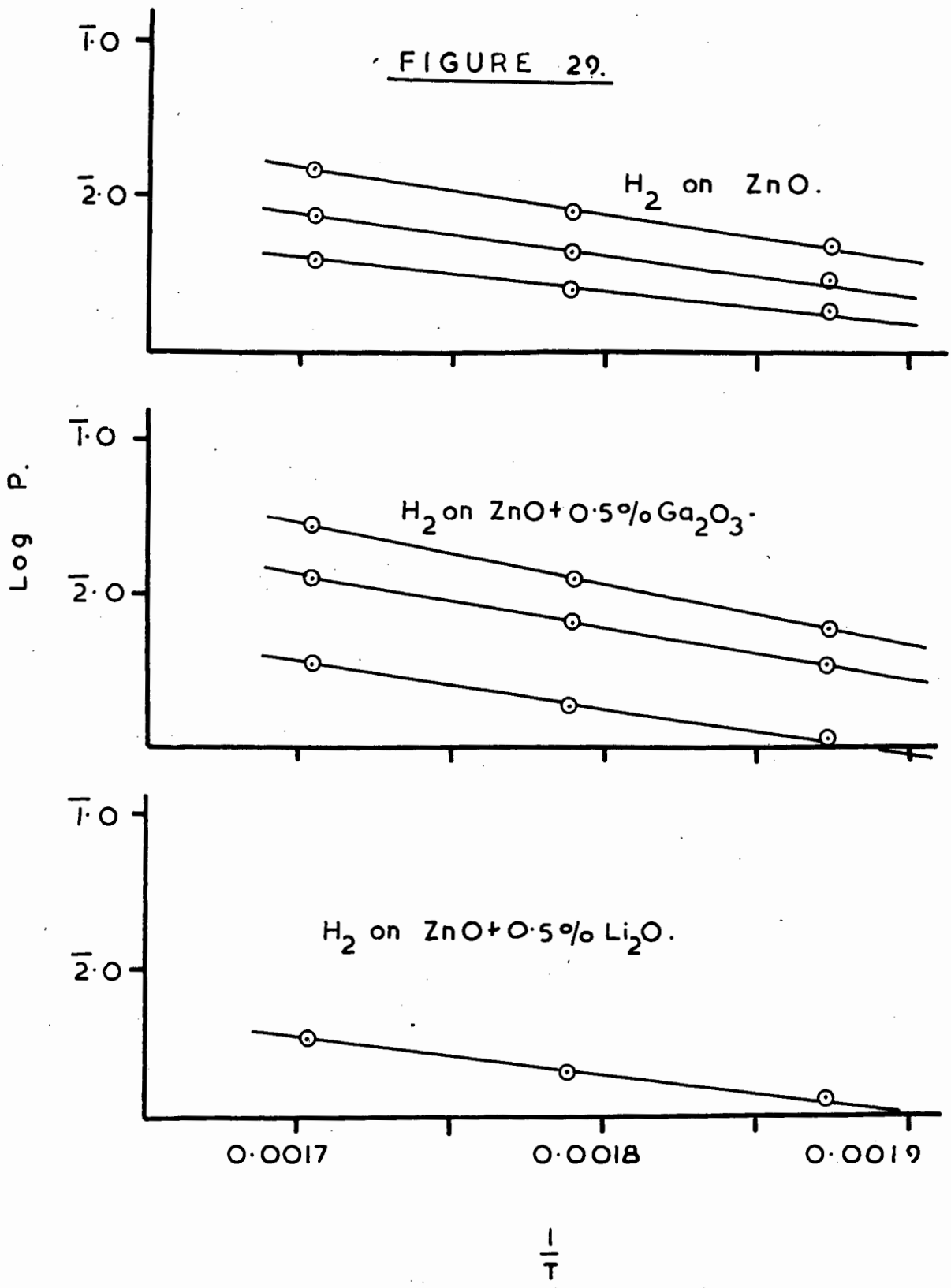


FIGURE 28.

isotherm 41 : temp. 314°C.
42 : 286°C.
43 : 261°C.

H_2 ADS ON ZINC OXIDE WITH GALLIUM OXIDE.

FIGURE 29.


$\bar{1}\cdot0$
$\bar{2}\cdot0$
H_2 on ZnO.
$\bar{1}\cdot0$
$\bar{2}\cdot0$
H_2 on ZnO + 0·5% Ga_2O_3.
Log P.
$\bar{1}\cdot0$
$\bar{2}\cdot0$
H_2 on ZnO + 0·5% Li_2O.
0·0017
0·0018
0·0019
$\frac{1}{T}$

HEATS OF ADSORPTION OF HYDROGEN.

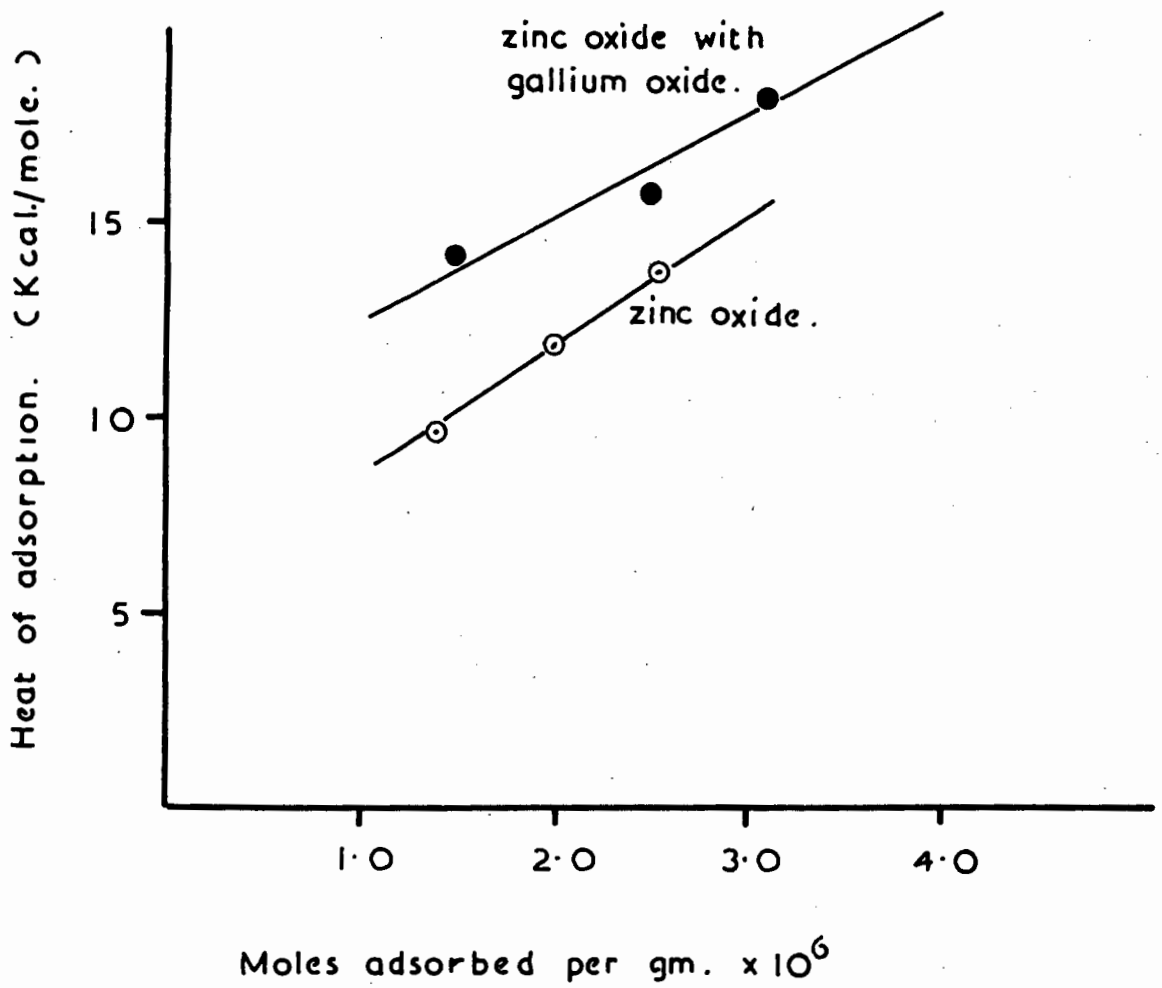


FIGURE 30.

could be determined. The data are shown in Appendix X. Equilibrium was attained in about 120 hours for the first points. For the second points the pressure was still dropping sharply even after 120 hours, so the isotherms were abandoned.

The heat of adsorption determined from the first points was about 12 Kcal/mole, for 1 x 10^{-6} moles adsorbed.

Again there was general blackening of the adsorbent and the black deposit was found to contain zinc and lithium.

IV. Determination of surface areas of adsorbents.

The physical adsorption data of sulphur dioxide on the three adsorbents were used to determine their surface areas by the B.E.T. method [60 - 64].

Three conditions determined the choice of sulphur dioxide as the adsorbing vapour for the surface area measurements. Firstly, the range of temperature covered by available thermometers was from -40°C upwards. Secondly, the lower limit of pressure which would be measured with accuracy on the available manometer M was 20 mm. Hg. Thirdly, the molecule chosen had to be a simple one.

An ice-salt bath provided the constant temperature conditions (-20.5°C corrected). The temperature was measured with an N.P.L. tested standard thermometer (No. 533408. A. Gallenkamp and Co., Ltd. -40 to +10°C. Divided to 0.1°C). The pressures were measured on the differential manometer M. They varied from about 20 to 180 mm. Hg, covering the P/P_0 range from 0.05 to 0.4 where P_0 was the vapour pressure of SO_2 at the adsorbent temperature.

The dead space in Z, the adsorption bulb section, was redetermined with the adsorption bulb in the freezing mixture and the cold trap at room temperature. Eight closely agreeing values for the volume were

obtained, using helium.

Mean dead space volume of Z = 154 c.c.

Volume of T + M' = $137.8 + \frac{P_{M'}}{10}$

T + Z + M' = $291.8 + \frac{P_{M'}}{10}$

where as before $P_{M'}$ was the pressure measured in M.

The sulphur dioxide used was obtained from a syphon of the liquid. It was condensed in a cold trap, non condensable gases were boiled off under vacuum, and then the gas was passed over silica gel and anhydrone to dry it. The sulphur dioxide was expanded from T + M' into T + Z + M', the pressure being measured before and after to determine the amount adsorbed. The adsorbent samples used were those on which the CO_2 isotherms had been measured earlier.

Adsorption on pure zinc oxide:- The adsorbent was evacuated for about two hours at 25°C. The total adsorption of SO_2 was then measured at -20.5°C (curve I, Fig. 31). After re-evacuation at 25°C the physical adsorption isotherm was measured at -20.5°C (curve II). On subtracting the physical adsorption from the total adsorption, the correct shaped curve was obtained for the chemisorption (curve III).

Adsorption on zinc oxide with gallium oxide impurity:- The adsorbent was evacuated at 25°C, saturated with SO_2 at -20.5°C and 18 cms. Hg pressure, re-evacuated at 25°C for two hours and then the physical adsorption isotherm was determined at -20.5°C. The isotherm was checked in a second run (curve IV).

Adsorption on zinc oxide with lithium oxide impurity:- The same procedure was used as for the gallium oxide sample, and curve V was obtained.

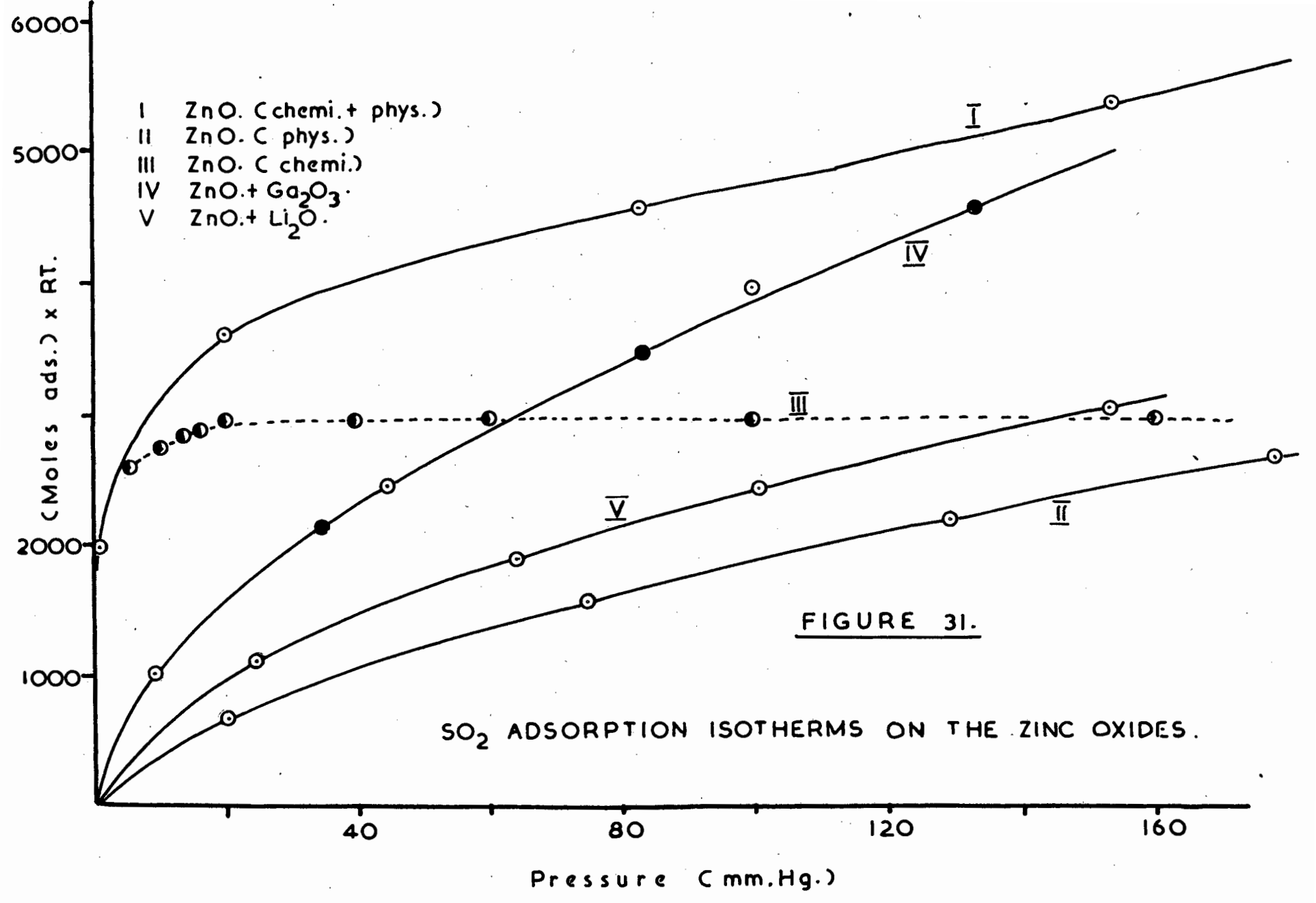


FIGURE 31.

SO_2 ADSORPTION ISOTHERMS ON THE ZINC OXIDES.

Linear plot of the B.E.T. equation:- The simple B.E.T. equation is:-

$$\frac{P}{V(P_o - P)} = \frac{1}{Vm\ C} + \frac{C - 1}{Vm\ C} \cdot \frac{P}{P_o}$$

where P = pressure of adsorbing vapour

P_o = vapour pressure of gas at temperature of adsorbent = 464 mm. Hg[65]

V = volume of gas adsorbed

Vm = volume of gas to form monolayer on surface

C = a constant.

Plotting $\frac{P}{V(P_o - P)}$ against P/P_o for sulphur dioxide for P/P_o values from 0.05 to 0.3 gave straight lines for all three adsorbents (see Fig. 32) where the

$$\text{slope } S = \frac{C - 1}{Vm\ C} \text{ and intercept } I = \frac{1}{Vm\ C},$$

$$\text{whence } Vm = \frac{1}{S + I}.$$

To reduce the amount of arithmetic required the volumes adsorbed were left as (PV) values in (c.c., cm. Hg) so that Vm was evaluated in these units too.

Tables of results for the SO_2 adsorption isotherms and data for the B.E.T. plots are gathered in Appendix XI.

Adsorbent	ZnO	ZnO + Ga_2O_3	ZnO + Li_2O
Vm (c.c., cm. Hg)	1960	3860	2350
Surface area (m^2/gm.)	4.6	9.1	5.5

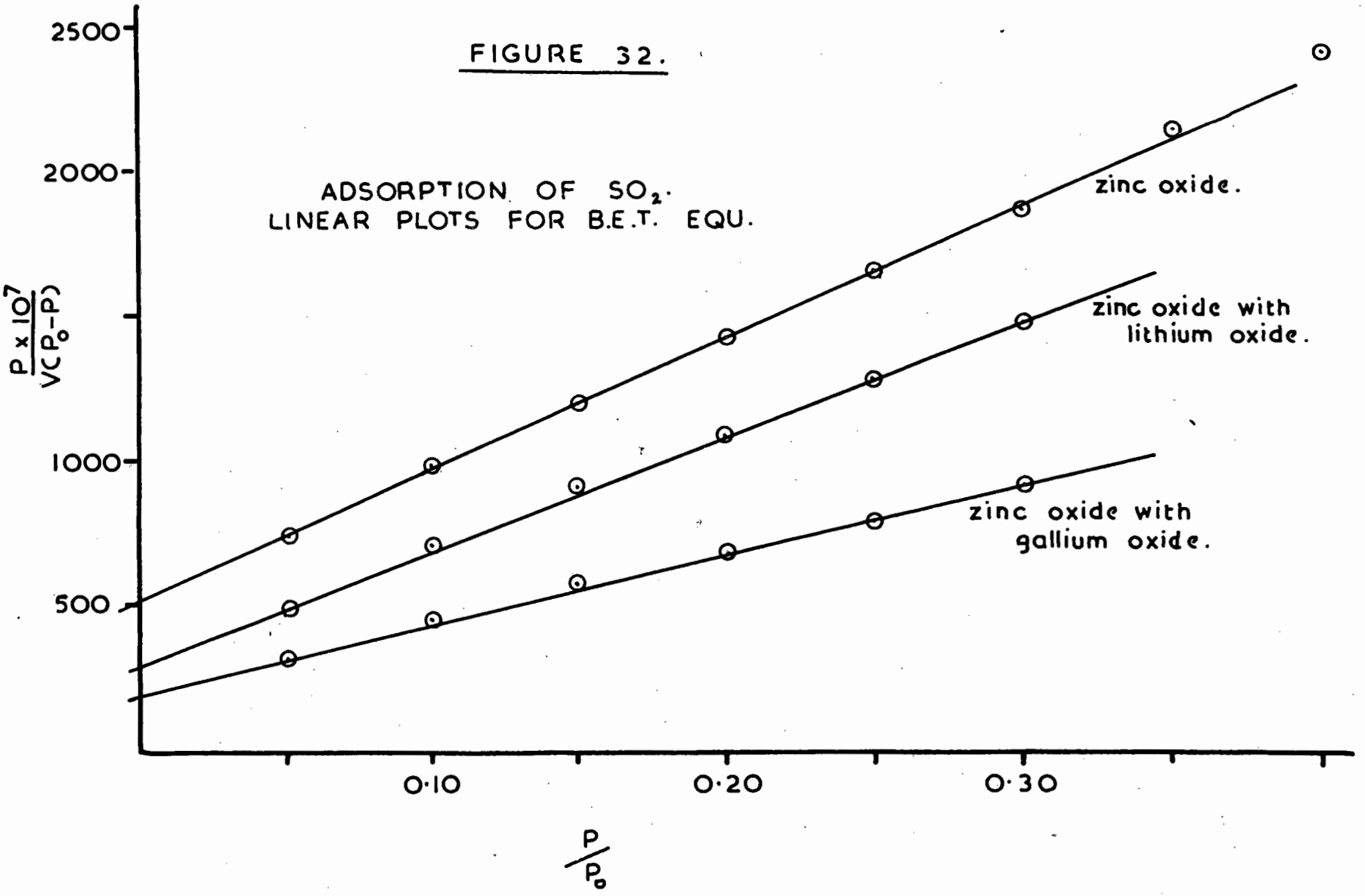
Conversion of Vm to moles/gm. adsorbent is made by multiplying by $\frac{1}{RTG}$ where R = 6240 c.c., cm. Hg/°K, mole

T = 298°K

G = weight of adsorbent sample = 22.10 gms.

$\frac{1}{RTG}$ = 2.43×10^{-8} moles/c.c., cm. Hg., gm.

FIGURE 32.


ADSORPTION OF SO_2.
LINEAR PLOTS FOR B.E.T. EQU.
zinc oxide.
zinc oxide with lithium oxide.
zinc oxide with gallium oxide.
2500
2000
1000
500
$\frac{P \times 10^7}{V(P_o - P)}$
0·10
0·20
0·30
$\frac{P}{P_o}$

Therefore for pure zinc oxide:-

Moles in monolayer/gm. = $1960 \times 2.43 \times 10^{-8}$

Molecules in monolayer/gm. = $1.96 \times 2.43 \times 10^{-5} \times 6.023 \times 10^{23}$

Area of surface/gm. = $1.96 \times 2.43 \times 6.023 \times 10^{18} \times 16.2 \times 10^{-16} \times 10^{-4}$ m.^{2}

= 4.6 m.^{2}.

where 16.2 A^2 is the estimated area occupied by a sulphur dioxide molecule on the surface, obtained as follows:-

Area occupied by sulphur dioxide molecule on surface. Emmett and Brunauer[60] give the formula

$$\text{Area occupied by molecule} = 1.091 \left(\frac{M}{Nd}\right)^{2/3}$$

For sulphur dioxide

M = molecular weight = 64

N = Avogadro's number = 6.023×10^{23}

d = density of liquid at temperature of adsorbent[66]

= 92.9 lbs./ft.^{3} = 1.49 gm./c.c.

Hence area = 1.62×10^{-15} cm.^{2}

= 16.2 A^2.

This value for the area occupied by the molecule is equivalent to a molecular radius of 2.16 A, where, calculated on two dimensional hexagonal close packing of circular molecules,

$$\text{Area per molecule} = 1.102\ \pi\ r^2$$

where r = molecular radius.

Gmelin[67] lists a number of values for the molecular radius of sulphur dioxide, most of them rather lower than this value of 2.16 A.

Hill[68] proposes the use of the two dimensional v. d. Waals constant b for the cross section area of molecules. He evaluates it as

$$b = 6.354 \times 10^{-16} \left(\frac{Tc}{Pc}\right)^{2/3} = 19.9 \text{ A}^2 \text{ for sulphur dioxide.}$$

Livingston's[69] review of the best data for cross sectional areas of molecules used in surface area determinations does not mention sulphur dioxide.

PART D.

DISCUSSION.

I. RELIABILITY OF ADSORPTION MEASUREMENTS.

1. Thermomolecular flow effects.

It is a well known fact that thermomolecular flow occurs in a system at low gas pressures when different parts of it are not at the same temperature[70-74,35]. Unless the mean free path, λ, of the molecules is negligible compared with the diameter, d, of the connecting tube, the pressure will not be equal in the two sections of the system.

When $\frac{d}{\lambda} \ll 1$, the relation $\frac{P_1}{P_2} = \left(\frac{T_1}{T_2}\right)^{1/2}$ applies, where P_1 is the pressure in the section at absolute temperature T_1, and P_2 is the pressure where the temperature is T_2.

When $\frac{d}{\lambda} < 1$ or $\frac{d}{\lambda} > 10$ other more complicated equations can be applied. The following table shows that the adsorption experiments were carried out in a pressure range where neither the simple relationship $\frac{P_1}{P_2} = \left(\frac{T_1}{T_2}\right)^{1/2}$ could be applied nor where thermomolecular flow could be neglected.

Tube diameter d = 1.3 cm.

Temperature = 20°C (values of λ quoted at this temperature).

Gas	at 1 mm. Hg		at 1 x 10^{-3} mm. Hg	
	λ (cm.)	$\frac{d}{\lambda}$	λ (cm.)	$\frac{d}{\lambda}$
H_2	13.9 x 10^{-3}	100	13.9	0.10
CO_2	4.8 "	270	4.8	0.27
CO	7.0 "	190	7.0	0.19
N_2	7.2 "	180	7.2	0.18
He	21.3 "	60	21.3	0.06

For a particular gas on any of the three adsorbents the errors would be identical, so that the relative values of the amounts of gas adsorbed, or the heats of adsorption on the three adsorbents would be correct.

As the pressure in the high temperature section of the system i.e. the adsorption bulb, was greater than that actually measured in the McLeod gauges, the isotherms are slightly to the left of their true positions; and more so at the lowest pressures than at the higher ones.

As the equilibrium pressures for a particular amount of gas adsorbed are all slightly low, but rather more so for the higher temperature isotherms than the lower ones, the values of the heats of adsorption obtained from the slopes of the lines in the log P vs. $\frac{1}{T}$ graphs will be a little below their true values. However, recalculation of the heat of adsorption of hydrogen on zinc oxide with gallium oxide impurity for an adsorption of 1.5×10^{-6} moles/gm. showed that the value of 14.2 Kcal per mole previously obtained was only 4% too low. This figure was calculated using the expression $P_1/P_2 = (T_1/T_2)^{1/2}$ which gives the maximum deviation of P_1 from P_2 for any particular temperature difference. In these results therefore a 4% error in the heats of adsorption is the largest one possible due to thermomolecular flow.

2. Dead space determinations.

Helium tends to diffuse into glass at high temperatures[35] so the dead space determinations were made with the adsorption bulb at 25°C and not in the adsorption range of 250° - 320°C. That of course introduced another error, because the amount of gas calculated to be left in the dead space after adsorption would be larger than the amount really there. However, the volume of the dead space at adsorption temperatures was only about 15 c.c. The total dead space was 1028 c.c., so the error was very small.

3. Measurement of the temperature of the adsorbent.

The fact that the adsorption furnace was as narrow as possible and extended five inches above and below the adsorption bulb made the presence of temperature gradients in the adsorbent improbable, especially once some gas had been admitted to the bulb.

As already noted (Part B, IV, 2, iv) the absolute values of the isotherm temperatures were not so important as the differences in temperature between them.

Thermometer stem corrections were applied and identical positions for furnace and thermometer were used throughout the adsorptions, so it is unlikely that the temperature differences were significantly in error. This is supported by the fact that the log P vs. $\frac{1}{T}$ plots in general show very little deviation from linearity.

4. Measurement of pressure.

It has already been shown (Part B, III, 15 + 16) that the maximum error of the McLeod gauges was about ± 1%.

The error in reading the manometer M was less than ± 1% above 20 mm. Hg (Part B, III, 19) and the pressure correction factor for the thermal expansion of mercury is 0.45% at 25°C[75].

Good evidence that the gauges were accurate was the agreement between the volume of the manifold T obtained by measurements with the McLeod gauges and by using the manometer M (Part B, IV, 1, iv).

5. Purity of gases.

Three possible sources of impurities in the gases existed: firstly, the starting materials; secondly, the purification reagents; and thirdly, leaks in the vacuum system. The methods of preparation and purification were taken from reliable sources. The reagents were of high quality. The gas trains were evacuated beforehand to remove

adsorbed impurities. The hydrogen and carbon monoxide were stored at approximately atmospheric pressure and no leaks were observed in any of the gas trains. For these reasons it seems improbable that the gases were contaminated.

6. Purity of adsorbents.

High quality starting materials were used in the preparation of adsorbents; operations were carried out in clean glassware and only distilled water was used. If there was any appreciable impurity in the zinc oxide it was present in all three adsorbents, and so only effects due to the gallium oxide and lithium oxide would show up in comparisons.

7. Estimation of equilibrium pressures.

It has already been shown (Part B, IV, 2, vi, a) that for carbon dioxide, at any rate, extrapolation of the pressure vs. time curves was an accurate method of determining the equilibrium pressure after adsorption. For carbon monoxide and hydrogen, however, where considerable reduction of the adsorbent surface was indicated at higher pressures, the method was less valid, but this will be discussed more fully when the individual sets of isotherms are examined.

II. Examination of isotherms.

1. Isotherms of carbon dioxide. (Figs. 15, 16, 17).

All these isotherms are typically chemisorption isotherms in shape, which is what would be expected because of the high temperature range used. The amount adsorbed rises very rapidly with pressure below about 10^{-2} mm. Hg and drops off more or less rapidly above that pressure. The curves are concave to the pressure axis throughout their measured lengths. That chemisorption was responsible for the measured adsorption was confirmed by the fact that the isosteric heats of adsorption were

calculated to vary from 16 - 28 Kcal per mole.

The classical Langmuir equation is

$$\theta = \frac{kP}{1 + kP}$$

where θ = surface coverage

P = pressure of adsorbing gas

k = a constant.

To obtain a linear equation put $\theta = \frac{V}{Vm}$ where V is the volume of gas adsorbed and Vm is the volume of gas required to complete a monolayer on the surface of the adsorbent.

Then $\frac{V}{Vm} = \frac{kP}{1 + kP}$

$\therefore \quad \frac{P}{V} = \frac{1}{k\ Vm} + \frac{P}{Vm}$

So if the isotherms obey the Langmuir equation a plot of $\frac{P}{V}$ vs. P should be linear.

The carbon dioxide isotherms were tested in this way and only found to obey the Langmuir equation reasonably well above a pressure of about 0.3 mm. Hg.

The Langmuir equation indicates that at very low pressures the amount of gas adsorbed should be directly proportional to the pressure. This was only true of the carbon dioxide isotherms well below 10^{-3} mm. Hg.

For the isotherms of carbon dioxide on pure zinc oxide and on zinc oxide with gallium oxide impurity the Freundlich equation was found to be valid over a wider pressure range than the Langmuir equation. The classical Freundlich equation is

$V = k P^{1/n}$ where n = a constant greater than unity.

Hence $\log V = k' + \frac{1}{n} \log P$, so that a plot of log V vs. log P should

give a straight line. This was found to be true for the two above-mentioned adsorbents in the pressure range 10^{-2} to 1 mm. Hg. Below 10^{-2} mm. Hg the plot tended to deviate slightly from linearity. As the plot of V vs. log P for carbon dioxide on zinc oxide with lithium oxide impurity was linear, the Freundlich equation was definitely not valid in that case.

Halsey and Taylor[76] have shown that the Freundlich equation can be derived when the relative energies of a series of sites follow an exponential relationship. If may be noted that the curves for the heats of adsorption of carbon dioxide in Fig. 21 are of the exponential type in general shape, if not mathematically.

2. Isotherms of carbon monoxide. (Figs. 22, 23).

These are also typically chemisorption isotherms, though their tendency to run into one another is perplexing as it reduced the isosteric heats of adsorption to very low values at higher coverages.

It has been noted (Part C, II, 1 and 2) that the pressure vs. time curves for carbon monoxide did not show a marked tendency to flatten out to a constant equilibrium pressure value, most noticeably in the pressure range 0.1 - 1.0 mm. Hg. The dark metallic looking deposit and the blackening of the pellets of adsorbent have also been noted. The most reasonable explanation of these phenomena seems to be that reduction of the zinc oxide was taking place. It is most likely that above a certain carbon monoxide pressure the rate of reaction becomes measurable, and that the carbon dioxide produced is immediately adsorbed, (much larger quantities of the dioxide than the monoxide are adsorbed on zinc oxide) thus causing the continued drop of pressure with time. The zinc formed in this way would darken the adsorbent, and having a small, but appreciable vapour pressure at 300°C (about 10^{-3} mm. Hg from I.C.T.) would also tend to sublime and condense on the cooler parts of the apparatus. This would explain the deposit observed where the tube to the adsorption bulb emerged from the furnace.

Garner[77], while finding that carbon monoxide is reversibly chemisorbed on zinc oxide at room temperature also states that reduction takes place at 400°C. He also reports volatilisation of the zinc formed. Burwell and Taylor[78] reported more carbon dioxide produced than could be explained by reduction of the zinc oxide only. They postulated some decomposition of the monoxide to carbon and carbon dioxide. There is no evidence here to deny that this reaction may not have been taking place simultaneously to the reduction reaction.

In view of the fact that reduction involves an acceptance of electrons by the substance being reduced it is not surprising that for the adsorbent with the lowest Fermi level, viz. the ZnO + 0.5 mole% Li_2O, the reduction effect was most marked. So much so in fact that equilibrium pressures could not even be measured for the smaller adsorptions.

Owing to the reduction effect the higher pressure sections of the isotherms are of doubtful value, and so the isosteric heats of adsorption may be considerably in error at the higher coverages.

Similarly to the adsorption of carbon dioxide the isotherms obey the Langmuir equation fairly well above a pressure of about 0.3 mm. Hg. Again the pressure was only directly proportional to the volume adsorbed well below 10^{-3} mm. Hg.

The Freundlich equation was not obeyed by carbon monoxide over any section of the pressure range, and the curves for heats of adsorption shown in Fig. 26 certainly show no sign of exponential character.

3. Hydrogen isotherms. (Figs. 27, 28).

The isotherms for hydrogen were most unsatisfactory because of reduction effects. Only for the lowest adsorptions could an equilibrium pressure be obtained. The same argument could be applied in the case of hydrogen as was applied for carbon monoxide. In this case water

would be formed, and most probably rapidly adsorbed. (Taylor and Sickman[8] found a large adsorption of water with a heat of adsorption of about 30 Kcal/mole. Burwell and Taylor[79] found that water was rapidly adsorbed at low temperatures, and rather more slowly at the temperatures used here). Taylor and Sickman[8] also found reduction of the zinc oxide when they tried to measure the isotherm of hydrogen at 306°C. Keier and Roginskii[82] on the contrary report that there is no reduction of zinc oxide by hydrogen below 500°C. However, the deposit of zinc in the adsorption tube and the darkening of the adsorbent pellets are again strong evidence for reduction. They also help refute the argument that the continued drop of hydrogen pressure with time was due to intra lattic adsorption. Ling Yang[83] in an electron diffraction study found no support for the idea of sorption of hydrogen into the zinc oxide lattice.

Again any adsorption measured was on a reduced surface because trial runs were always done first. This was deemed a reasonable procedure as catalytic reactions are of necessity not studied on virgin surfaces.

At this point some comment should be made on the method used here to obtain the hydrogen isotherms. The same method was used by Frankenburg[12] in his work on the adsorption of hydrogen on tungsten powder and he obtained the same type of surprising result.

Gas was let in to the adsorbent at the highest temperature in the working range, so as to get as rapid adsorption as possible. When equilibrium was eventually attained the temperature was lowered to that for the next isotherm to be measured. The peculiar phenomenon noted was this. Considering that a small period of time is necessary for all of the adsorbent to come to the new temperature, the new equilibrium pressure was, to all intents and purposes, attained immediately (see Part C, III).

Now the adsorption was a slow process having taken a large number of hours or even days to reach equilibrium at the highest temperature. Yet on lowering the temperature the extra adsorption that took place was a very rapid process, and on raising the temperature back to its original value the desorption was a very rapid process.

The only explanation seems to be this. For the sake of simplicity consider that there are just two types of adsorption sites; one having a negligible activation energy of adsorption, and the other having a considerable activation energy. At any particular temperature the adsorbed molecules will be distributed statistically between the two types of site. The higher the temperature the higher will be the proportion of the adsorbed molecules on the sites with high activation energy. Now consider the adsorption taking place at the highest temperature in the working range. At equilibrium the adsorbed molecules will be distributed in a certain ratio between the two types of sites. On cooling to a lower isotherm temperature more adsorption must take place. From the observed results this adsorption took place on the low activation energy sites only, because it was instantaneous.

The situation could then be either of two. Firstly it could represent true equilibrium at the new temperature. This would mean that conditions had so rearranged themselves that for the particular temperature and pressure the total number of molecules adsorbed were again distributed in the correct ratio between the two types of site, although the total number of molecules adsorbed on the sites with high activation energy had not changed.

Secondly it could represent a freezing in of the equilibrium on the high activation energy sites. True equilibrium would require less adsorption on the high activation energy sites at the lower temperature, but because the temperature had been lowered desorption from these sites could not occur. Hence the total adsorption measured at the lower temperature would be too high by a small amount, and so only the

isotherm at the highest temperature in the range would represent true equilibrium conditions. All the other isotherms would show a larger adsorption than that which would have been obtained if they had each been measured alone starting from a clean surface.

For this reason the isotherms obtained by Frankenburg appear to be open to some doubt. In the present work it was not considered worth while to check any results of the hydrogen adsorption as so much reduction was taking place that the results would be unreliable by whatever method they were obtained.

4. Isotherms of sulphur dioxide and derived surface areas.

Curves I, II and III in Fig. 31 show very clearly that chemisorption of sulphur dioxide took place at -20.5°C on the zinc oxide. Though the shape of the chemisorption curve (III) is correct; this does not necessarily prove that curve II represents pure physical adsorption. Some chemisorbed gas may have been removed by the process of evacuating at 25°C, but the amount was probably small. Besides this possible source of error in the determination of the absolute surface areas of the adsorbents, the correct value of the effective cross section area of the sulphur dioxide molecule is not known with any certainty. However, either of the two values 16.2 A^2 or 19.9 A^2 give quite reasonable values for the surface areas of the adsorbents. Values obtained by other workers for zinc oxides have been inter alia:-

4.4, 5.5 $m^2/gm.$ (Gans, Brooks, Boyd)[62]
4.2 $m^2/gm.$ (Schreiner and Kemball)[63]
14, 24 $m^2/gm.$ (Shekhter and Zhabrova)[84].

The relative surface areas of the three adsorbents are very interesting. The adsorbents were prepared by as closely similar methods as possible, and yet the addition of 0.5 mole % Ga_2O_3 almost doubled the surface area of the zinc oxide, and the addition of 0.5 mole % Li_2O increased it by 20%. It is difficult to see how this effect could have

been lessened or eliminated in order that the comparisons of adsorption could have been between more closely similar surfaces. The reason for the larger surface areas of the impurity adsorbents is at present obscure.

III. Comparison of the heats of adsorption calculated for the three adsorbents.

1. Heat of adsorption of carbon dioxide.

Fig. 21 showed the heats of adsorption of carbon dioxide on the three adsorbents plotted against the number of moles adsorbed per gm. of adsorbent. The result was somewhat perplexing for while the gallium oxide impurity increased the heat of adsorption considerably, the lithium oxide seemed to make no difference. However, on replotting the heats of adsorption against surface coverage in moles adsorbed/m^2 the differences stood out clearly (see Fig. 33).

Firstly the three curves tend to diverge as the coverage becomes less. At low coverages the differences in heat of adsorption for the three adsorbents is very marked. At high coverage there is barely any difference at all. Working on the assumption that both the carbon dioxide[69] and sulphur dioxide molecules have an effective cross section area of about 16 A^2, complete coverage of the surface would involve about 10×10^{-6} moles/m^2. So the maximum adsorption of carbon dioxide measured (about 5×10^{-6} moles/m^2, see Fig. 33) was equivalent to a surface coverage of about one half (i.e. $\theta = 0.5$).

So it would appear that the Fermi level in the adsorbent was only of primary importance in determining the heat of adsorption at low coverage, and that as the coverage increased other factors such as repulsive interactions between molecules became more important.

Secondly the curves show clearly that the carbon dioxide acts as an electron acceptor in the adsorption, because the addition of gallium

FIGURE 33.

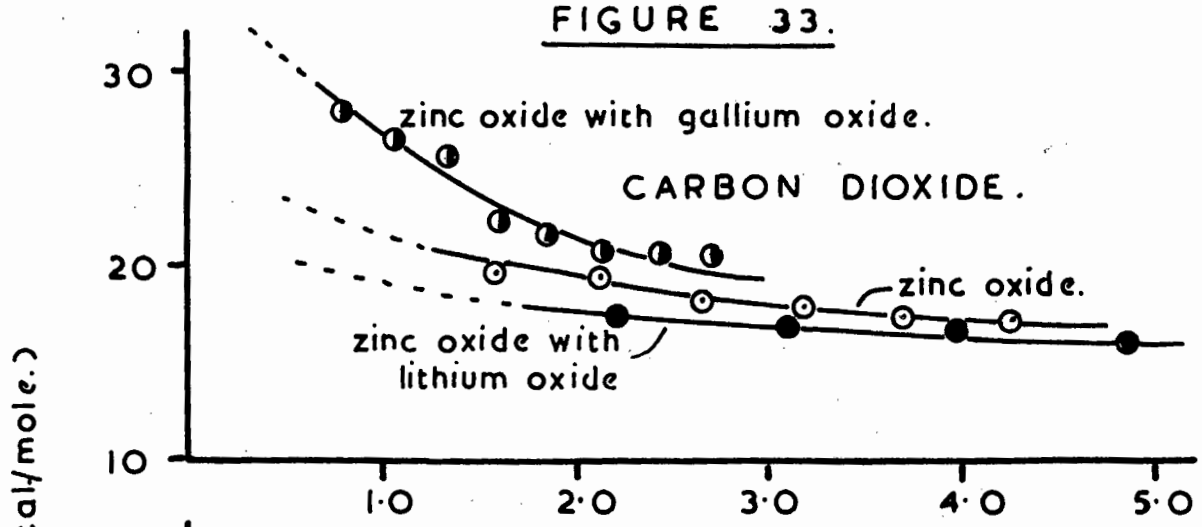
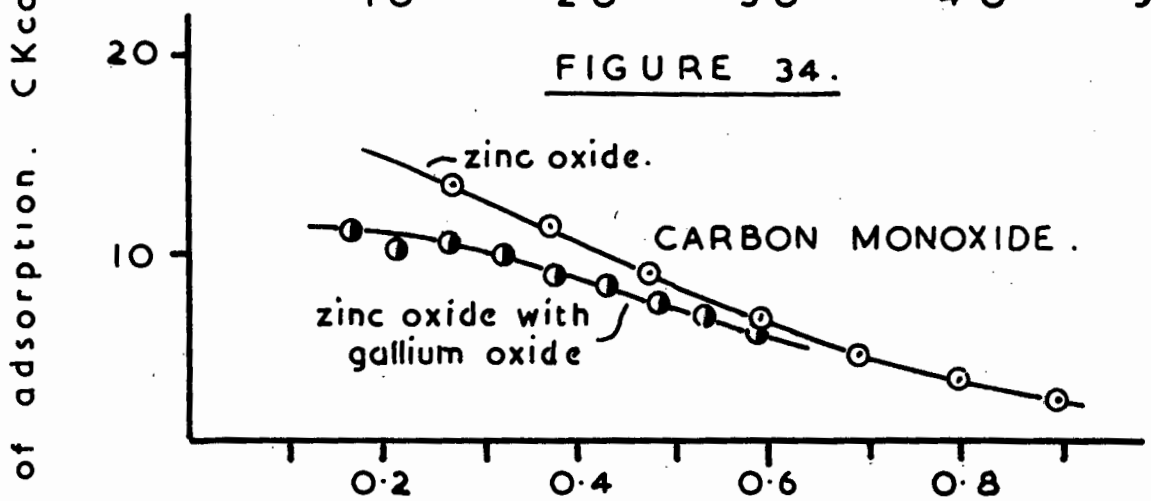


FIGURE 34.



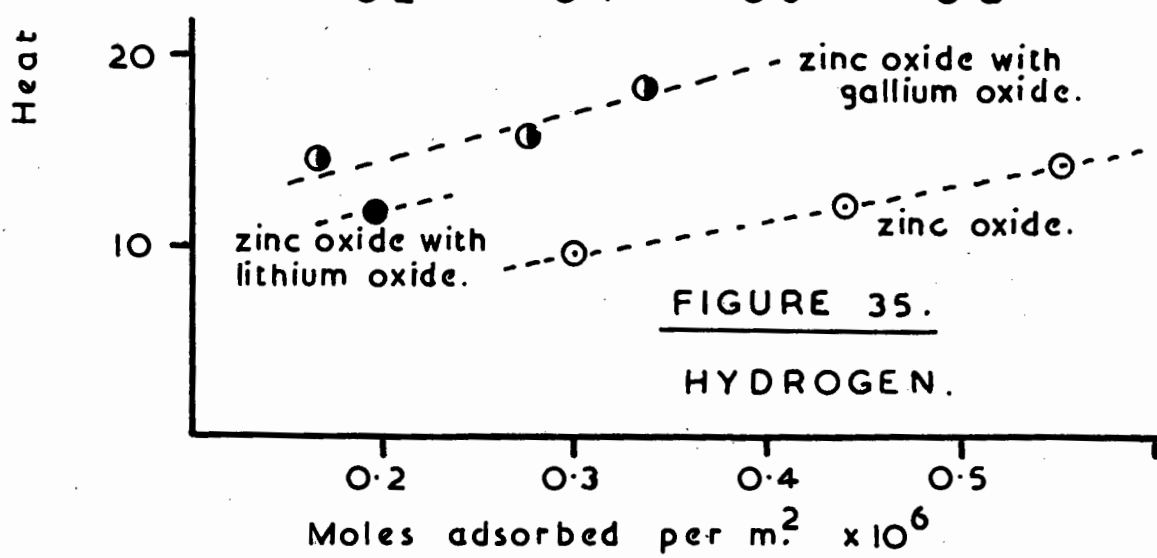


FIGURE 35.

HYDROGEN.

HEATS OF ADSORPTION vs SURFACE COVERAGE.

oxide which increases the availability of electrons in the zinc oxide increases the heat of adsorption, and the addition of lithium oxide which depresses the Fermi level in the zinc oxide decreases the heat of adsorption. In other words a high electron concentration in the adsorbent increases the strength of the adsorption bond. The effect is what would be expected since carbon dioxide is normally a Lewis acid, i.e. an electron acceptor.

Thirdly, the large adsorption of carbon dioxide correlates with the fact that both the adsorbent and adsorbate are behaving as would be expected. Zinc oxide, an n type semiconductor is acting as an electron donor, and carbon dioxide as an electron acceptor.

2. Heat of adsorption of carbon monoxide.

Plotting heat of adsorption vs. coverage for carbon monoxide makes the effect of the impurities much more clear. Fig. 34 gives a better picture of the situation than Fig. 26.

Again the effect of the impurity on the heat of adsorption is most noticeable at very low coverage. The relative values of the heats of adsorption for the adsorbents at higher coverage are not as reliable as for carbon dioxide owing to the possible falsification of the isotherms by reduction effects.

Secondly the carbon monoxide is shown to act as an electron donor in the adsorption, because the raising of the Fermi level when the gallium oxide impurity was used, caused a decrease in the heat of adsorption. Lowering of the Fermi level in the zinc oxide due to addition of lithium oxide so facilitated the donation of electrons by the carbon monoxide that reduction became too rapid to measure the adsorption. This confirms Garner's[77] suggestion that the irreversible adsorption of carbon monoxide takes place on an acceptor site.

Finally the total adsorption was small (if the carbon monoxide

molecule has approximately the same cross section area as the dioxide molecule[69] then maximum coverage measured was less than $\theta = 0.1$) because though the reducing agent carbon monoxide behaved as would be expected in that it donated electrons, zinc oxide had to accept electrons.

3. Heats of adsorption of hydrogen.

Because hydrogen is a reducing agent it might have been expected to give a similar type of result as carbon monoxide for the heats of adsorption. However, what results could be obtained (see Fig. 35) are quite different. Not only are the magnitudes of the heats for the three adsorbents in an unexpected order, but the heats appear to increase with increasing coverage. Whether these results are significant or whether they are merely due to erroneous readings caused by reduction effects cannot be said with any certainty at all.

IV. Comments on possible mechanisms for the reaction.

The results obtained for the adsorption of carbon dioxide and carbon monoxide on the zinc oxides agree with the activation energy results obtained by Wiggill for the reaction,

$$CO_2 + H_2 \xrightarrow{ZnO} CO + H_2O.$$

He found that addition of gallium oxide to the catalyst reduced the activation energy of the reaction and that addition of lithium oxide increased it.

If the mechanism of the reaction is dependent on the adsorption of carbon dioxide then naturally the higher heat of adsorption on the gallium impurity catalyst will cause a lowering of the activation energy[86]. With lithium oxide the converse would be true.

If the above paragraph is correct then carbon monoxide must be desorbed, and consequently the lower heat of adsorption on the gallium

oxide impurity catalyst will facilitate this by reducing the activation energy of desorption.

Another interesting fact is that the adsorption of carbon dioxide is about five times as great as the adsorption of carbon monoxide. For this reason, at any particular reaction pressure only about one fifth of the sites which could be covered with carbon dioxide could be covered with carbon monoxide, so that on reduction of the dioxide it is most probable that a large proportion of the monoxide formed must desorb.

There is the possibility that the reaction could be analogous to the oxidation of carbon monoxide by oxygen over zinc oxide. Schwab and Block[5] suggest that oxygen is first adsorbed on an electron donating defect giving adsorbed O^-. Carbon monoxide then reacts with the adsorbed oxygen to give carbon dioxide and restore the defect site on the surface. With carbon dioxide and hydrogen the reaction might be

$$CO_2 + \ominus \rightarrow CO_2^- \text{(ads)}$$
$$CO_2^- \text{(ads)} + H_2 \rightarrow H_2O + CO^- \text{(ads)}$$
$$CO^- \text{(ads)} \rightarrow CO + \ominus$$

where $\ominus$ = electron donating active centre on catalyst surface. However, in the absence of kinetic data on the reaction which would be necessary to find the rate determining steps, this is speculation.

SUMMARY.

The adsorption properties of carbon dioxide, monoxide and hydrogen on zinc oxide and zinc oxide with impurities were determined in order to see whether there was any correlation between them and the reported differences in catalytic activity of the adsorbents in the catalysed reaction

$$CO_2 + H_2 \xrightarrow{ZnO} CO + H_2O.$$

A constant volume high vacuum apparatus built to measure the adsorption of the abovementioned three gases is described.

Adsorption isotherms of the gases on pure ZnO, ZnO + 0.5 mole % Ga_2O_3 and ZnO + 0.5 mole % Li_2O were measured where possible in the temperature range 250° to 320°C and at pressures from 1×10^{-3} to 1 mm. Hg.

Isosteric heats of adsorption were calculated and found to be as follows:-

Carbon dioxide	16 - 28 Kcals/mole
Carbon monoxide	2 - 14 Kcals/mole
Hydrogen	10 - 18 Kcals/mole.

The surface areas of the three adsorbents were measured by the B.E.T. method using sulphur dioxide as the adsorbing vapour.

Heats of adsorption of the three gases on the three adsorbents were plotted against surface coverage of the adsorbents and deductions made as to the mechanisms of the adsorptions.

A C K N O W L E D G E M E N T S.

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APPENDIX I.

Calibration of Standard Volume Bulb.

A water thermostat was set at 25°C (± 0.2°C) and the bulb was submerged in it up to the tap. It was then filled with distilled water which had been kept in the thermostat for some hours. The filled bulb was weighed. This process was repeated four times. The clean dry bulb was weighed before, during and after these measurements.

	I	II	III	IV	Mean
Wt. full	1247.01	1247.09	1246.93	1247.13	1247.04
Wt. empty	210.35	210.35		210.35	210.35
Wt. of water					1036.69

Density of air at N.T.P. = 0.00129 gm./c.c.

" " " " 25°C = $0.00129 \times \frac{273}{298} = 0.00118$ gm./c.c.

Wt. of air displaced by water = approx. (1037 x 0.00118) gm.

= 1.23 gm.

∴ Error in weight of water = $\frac{1.23}{1037} \times 100 = 0.1\%$

Error in reading pressure gauges is up to 1%.

∴ neglect buoyancy correction.

Density of water at 25°C = 0.9971 gm./c.c.

∴ Volume of bulb = $\frac{1036.7}{0.9971} = 1040 \pm 1.5$ c.c.

APPENDIX II.

Calibration of McLeod Gauges.

Uniform bore "Veridia" (Chance product) tubing was used for the McLeod gauge capillaries. It was cleaned with conc. HCl, conc. HNO_3 and chromic acid, washed with distilled water and dried.

Capillary cross section areas were determined by the method of measuring the length of a thread of mercury at different positions in the tube with a travelling microscope, and then weighing the mercury. For the larger diameter capillary a correction to the volume of the mercury thread was made for the volume of the two menisci. Calibrated weights were used for weighing the mercury.

Graphs of "Length of mercury thread" vs. "Position of thread in tube" were drawn, and as far as possible the variation of bore with position in the tube was matched for the open and closed capillaries.

The volumes of the bulbs were determined by weighing them full of distilled water, and the lengths of the closed capillaries attached to the bulbs were measured. The following table shows the relevant data. [Gauge A was calibrated by another member of the Chemistry Department staff, Mr. L.A. du Plessis, B.Sc.].

	A	B
Length of mercury thread	102.10 ± 0.2 mm.	19.20 ± 0.05 mm.
Weight of mercury thread	0.7020 ± 0.0002 gm.	0.4748 ± 0.0002 gm.
Density of mercury	13.55 g./c.c. (17°C)	13.54 g./c.c. (22°C)
∴ Vol. of thread	51.81 mm.^{3}	35.06 mm.^{3}
Corrected vol.	51.81 mm.^{3}	34.49 mm.^{3}
∴ Vol./mm. of tube	0.507 mm.^{3}	1.797 mm.^{3}
Weight of water in bulb	336.2 ± 0.2 gm.	55.18(9) ± 0.02 gm.
Density of water	0.9986 g./c.c. (18°C)	0.9979 g./c.c. (21.4°C)
∴ Vol. of bulb	335700 mm.^{3}	55303 mm.^{3}
Length of capillary	147.0 mm.	187.5 mm.
∴ Vol. of capillary	75 mm.^{3}	337 mm.^{3}
Total volume	335800 mm.^{3}	55640 mm.^{3}

APPENDIX III.

Adsorbent: ZnO

Gas: Carbon Dioxide

Isotherms 19 - 22

Before adsorption			After Adsorption		Total moles in (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. ($\times 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	log Press.				
		Isotherm 19		Corrected Temperature = 310°C				
90.2	15.4	1390	5.60×10^{-4}	$\underline{4}.748$	1390	1	1390	3.4
95.3	15.5	1475	3.70×10^{-2}	$\underline{2}.568$	2865	40	2825	6.9
77.0	15.3	1180	1.50×10^{-1}	$\underline{1}.176$	4045	155	3890	9.5
139.5	15.9	2220	7.45×10^{-1}	1.872	6265	765	5500	13.4
		Isotherm 20		Corrected Temperature = 292°C				
129.7	15.8	2050	3.93×10^{-3}	$\underline{3}.594$	2050	4	2045	5.0
70.7	15.2	1075	3.70×10^{-2}	$\underline{2}.568$	3125	40	3085	7.5
93.8	15.4	1445	1.60×10^{-1}	$\underline{1}.204$	4570	165	4405	10.7
135.6	15.9	2150	7.40×10^{-1}	1.868	6720	760	5960	14.5
		Isotherm 21		Corrected Temperature = 268°C				
131.5	15.8	2080	2.40×10^{-3}	$\underline{3}.380$	2080	2	2080	5.1
81.3	15.3	1245	1.70×10^{-2}	$\underline{2}.230$	3325	15	3310	8.0
99.8	15.5	1545	1.03×10^{-1}	$\underline{1}.013$	4870	105	4765	11.6
170.0	16.2	2750	6.85×10^{-1}	1.836	7620	700	6920	16.8
		Isotherm 22		Corrected Temperature = 251°C				
141.5	15.9	2250	2.19×10^{-3}	$\underline{3}.340$	2250	2	2250	5.5
103.8	15.5	1610	1.45×10^{-2}	$\underline{2}.161$	3860	15	3845	9.3
104.5	15.5	1620	1.21×10^{-1}	1.082	5480	120	5360	13.0
150.6	16.0	2410	5.25×10^{-1}	$\overline{1}.720$	7890	540	7350	17.9

Moles ads./gm. ($\times 10^6$)	Log pressure from isotherms				Slope	Heat of abs. (Kcals/mole)
	310°C	292°C	268°C	251°C	log P vs $^1/_T$	
4.9	$\bar{3}.75$	$\bar{3}.50$	$\bar{3}.27$	$\bar{3}.03$	(3600)	
7.3	$\bar{2}.68$	$\bar{2}.43$	$\bar{2}.07$	$\bar{3}.86$	4300	19.6
9.7	$\bar{1}.24$	$\bar{1}.04$	$\bar{2}.66$	$\bar{2}.43$	4250	19.4
12.2	$\bar{1}.68$	$\bar{1}.48$	$\bar{1}.13$	$\bar{2}.93$	3950	18.0
14.6	0.05	$\bar{1}.87$	$\bar{1}.53$	$\bar{1}.30$	3850	17.6
17.0	0.35	0.17	$\bar{1}.87$	$\bar{1}.62$	3750	17.1
19.5	-	0.41	0.12	$\bar{1}.90$	3700	16.9

A P P E N D I X I V.

Absorbent: ZnO + 0.5 mole % Ga_2O_3.

Gas: Carbon Dioxide.

Isotherms 12 - 15.

Before Adsorption			After Adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles Ads. per gm. ($\times 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	log Press.				
		Isotherm 12		Corrected Temperature	= 312°C			
133.1	15.8	2105	1.50×10^{-3}	$\underline{3}.176$	2105	2	2105	5.1
123.7	15.7	1940	5.20×10^{-2}	$\underline{2}.716$	4045	55	3990	9.7
105.9	15.6	1650	2.20×10^{-1}	$\underline{1}.342$	5695	230	5465	13.3
166.5	16.2	2700	8.90×10^{-1}	1.949	8395	915	7480	18.2
		Isotherm 13		Corrected Temperature	= 291°C			
151.0	16.0	2415	1.90×10^{-3}	$\underline{3}.280$	2415	2	2415	5.9
113.5	15.6	1770	3.60×10^{-2}	$\underline{2}.556$	4185	40	4145	10.1
129.3	15.8	2040	2.75×10^{-1}	$\underline{1}.440$	6225	280	5945	14.5
141.5	15.9	2250	7.80×10^{-1}	1.891	8475	800	7675	18.7
		Isotherm 14		Corrected Temperature	= 275°C			
161.9	16.1	2605	1.25×10^{-3}	$\underline{3}.097$	2605	1	2605	6.3
99.2	15.5	1540	1.15×10^{-2}	$\underline{2}.060$	4145	10	4135	10.1
127.2	15.8	2010	9.70×10^{-2}	$\underline{2}.987$	6155	100	6055	14.7
153.0	16.0	2440	4.00×10^{-1}	1.602	8595	410	8185	19.9
		Isotherm 15		Corrected Temperature	= 252°C			
179.7	16.3	2930	1.07×10^{-3}	$\underline{3}.030$	2930	1	2930	7.1
129.9	15.8	2050	1.20×10^{-2}	$\underline{2}.080$	4980	10	4970	12.1
141.3	15.9	2245	8.90×10^{-2}	$\underline{2}.950$	7225	90	7135	17.3
139.8	15.9	2220	3.00×10^{-1}	1.478	9445	310	9135	22.2

Moles ads./gm. ($\times 10^6$)	Log pressure from isotherms				Slope	Heat of ads. (kcals/ mole)
	312°C	291°C	275°C	252°C	log P vs $^1/_T$	
7.3	$\bar{2}.09$	$\bar{3}.77$	$\bar{3}.37$	$\bar{3}.10$	6100	27.9
9.7	$\bar{2}.74$	$\bar{2}.50$	$\bar{3}.99$	$\bar{3}.65$	5800	26.5
12.2	$\bar{1}.16$	$\bar{2}.99$	$\bar{2}.54$	$\bar{2}.10$	5500	25.4
14.6	$\bar{1}.50$	$\bar{1}.36$	$\bar{2}.96$	$\bar{2}.55$	4850	22.2
17.0	$\bar{1}.81$	$\bar{1}.70$	$\bar{1}.28$	$\bar{2}.90$	4700	21.5
19.5	0.08	$\bar{1}.98$	$\bar{1}.56$	$\bar{1}.20$	4500	20.6
21.9	0.34	0.22	$\bar{1}.81$	$\bar{1}.45$	4500	20.6
24.3	0.56	0.45	0.05	$\bar{1}.68$	4500	20.6

A P P E N D I X V.

Adsorbent: ZnO + 0.5 mole % Li_2O

Gas: Carbon Dioxide

Isotherms 16 - 18.

Before Adsorption			After Adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles Ads. per gm. ($\times 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	Log Press.				
		Isotherm 16		Corrected Temperature = 312°C				
181.8	16.3	2960	-	-	-	-	-	-
129.2	15.8	2040	1.25×10^{-3}	$\bar{3}.097$	5000	2	5000	12.2
180.3	16.3	2940	2.25×10^{-2}	$\bar{2}.352$	7940	25	7915	19.2
126.1	15.8	1990	1.56×10^{-1}	$\bar{1}.192$	9930	160	9770	23.7
135.6	15.9	2155	7.10×10^{-1}	1.851	12085	730	11355	27.6
		Isotherm 17		Corrected Temperature = 291°C				
197.4	16.5	3260	-	-	-	-	-	-
147.1	16.0	2355	1.45×10^{-3}	$\bar{3}.162$	5615	2	5615	13.6
163.1	16.1	2625	1.80×10^{-2}	$\bar{2}.256$	8240	20	8220	20.0
154.0	16.0	2465	1.90×10^{-1}	$\bar{1}.278$	10705	195	10510	25.6
131.6	15.8	2080	8.60×10^{-1}	1.934	12785	885	11900	28.9
		Isotherm 18		Corrected Temperature = 272°C				
196.0	16.5	3230	-	-	-	-	-	-
195.0	16.5	3220	1.95×10^{-3}	$\bar{3}.290$	6450	2	6450	15.7
146.0	16.0	2340	1.80×10^{-2}	$\bar{2}.255$	8790	20	8770	21.3
129.0	15.8	2040	1.35×10^{-1}	$\bar{1}.130$	10830	140	10690	26.0
141.4	15.9	2250	7.50×10^{-1}	1.874	13080	770	12310	29.9

Moles ads./gm. ($\times 10^6$)	Log Pressure from Isotherms			Slope	Heat of ads. (kcals/ mole)
	312°C	291°C	272°C	log P vs $^1/_T$	
12.2	$\bar{3}.10$	$\bar{4}.85$	$\bar{4}.62$	3800	17.4
17.0	$\bar{3}.95$	$\bar{3}.73$	$\bar{3}.50$	3670	16.8
21.9	$\bar{2}.83$	$\bar{2}.62$	$\bar{2}.39$	3660	16.7
26.8	$\bar{1}.68$	$\bar{1}.48$	$\bar{1}.25$	3470	15.8

APPENDIX VI.

Adsorbent: ZnO

Gas: Carbon Monoxide

Isotherms 28 - 30.

Before adsorption			After adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. ($\times 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Pressure (mm Hg)	Log Press.				
		Isotherm 28.		Corrected Temperature = 318°C				
25.8	14.76	380	8.50×10^{-4}	$\bar{4}.930$	380	1	379	0.92
28.9	14.79	427	1.15×10^{-2}	2.060	807	12	795	1.93
37.3	14.87	555-2	–	–	1360	–	–	–
58.0	15.08	875-19	5.95×10^{-1}	1.774	2216	611	1605	3.90
		Isotherm 29.		Corrected Temperature = 299°C				
37.3	14.87	555	1.76×10^{-3}	$\bar{3}.245$	555	2	553	1.34
23.8	14.74	351	1.50×10^{-2}	2.175	906	15	891	2.17
32.5	14.83	482-2	–	–	1386	–	–	–
53.3	15.03	801-19	5.50×10^{-1}	1.740	2168	565	1603	3.89
		Isotherm 30.		Corrected Temperature = 264°C				
37.5	14.88	558	9.45×10^{-4}	$\bar{4}.976$	558	1	557	1.35
26.9	14.77	397	1.30×10^{-2}	$\bar{2}.114$	955	13	942	2.29
71.7	15.22	1090-2	4.50×10^{-1}	1.650	2043	460	1583	3.84

Moles ads./gm. ($\times 10^6$)	Log Pressure from Isotherms			Slope	Heat of ads. (Kcals / mole)
	318° C	299° C	264° C	log P vs $1/T$	
1.22	$\bar{3}.27$	$\bar{3}.08$	$\bar{4}.78$	2900	13.2
1.70	$\bar{3}.82$	$\bar{3}.67$	$\bar{3}.43$	2450	11.2
2.19	$\bar{2}.32$	$\bar{2}.20$	$\bar{2}.00$	1950	8.9
2.67	$\bar{2}.77$	$\bar{2}.67$	$\bar{2}.52$	1350	6.2
3.16	$\bar{1}.19$	$\bar{1}.12$	$\bar{1}.01$	1000	4.6
3.64	$\bar{1}.57$	$\bar{1}.52$	$\bar{1}.47$	700	3.2
4.13	$\bar{1}.96$	$\bar{1}.93$	$\bar{1}.89$	450	2.1

A P P E N D I X V I I .

Adsorbent: ZnO + 0.5mole% Ga_2O_3

Gas: Carbon Monoxide

Isotherms 34 - 36.

Before Adsorption			After Adsorption		Total moles (xRT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. ($x 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	Log Press.				
		Isotherm 34		Corrected Temperature = 320°C				
37.6	14.88	559	1.95×10^{-3}	$\bar{3}.290$	559	2	557	1.35
36.1	14.86	536	1.80×10^{-2}	$\bar{2}.255$	1095	18	1077	2.62
63.8	15.14	966 - 3	2.00×10^{-1}	1.300	2058	206	1852	4.50
		Isotherm 35		Corrected Temperature = 292°C				
41.0	14.91	611	1.45×10^{-3}	$\bar{3}.162$	611	2	609	1.48
41.6	14.92	621	1.85×10^{-2}	$\bar{2}.266$	1232	19	1213	2.94
65.7	15.16	996 - 3	2.25×10^{-1}	1.350	2225	230	1995	4.85
		Isotherm 36		Corrected Temperature = 263°C				
46.5	14.97	696	1.47×10^{-3}	$\bar{3}.167$	696	2	694	1.69
42.8	14.93	639	1.80×10^{-2}	$\bar{2}.255$	1335	18	1317	3.20
58.1	15.08	875 - 3	1.75×10^{-1}	1.243	2207	180	2027	4.92

Moles ads./ gm. ($\times 10^6$)	Log Pressure from Isotherms			Slope	Heat of ads.
	320°C	292°C	263°C	log P vs $\frac{1}{T}$	(Kcals/mole)
1.46	$\bar{3}.39$	$\bar{3}.19$	$\bar{4}.97$	2400	11.0
1.94	$\bar{3}.77$	$\bar{3}.57$	$\bar{3}.37$	2200	10.1
2.43	$\bar{2}.12$	$\bar{3}.93$	$\bar{3}.74$	2250	10.3
2.92	$\bar{2}.44$	$\bar{2}.26$	$\bar{2}.08$	2150	9.8
3.40	$\bar{2}.74$	$\bar{2}.57$	$\bar{2}.40$	1900	8.7
3.89	$\bar{1}.00$	$\bar{2}.85$	$\bar{2}.69$	1800	8.2
4.37	$\bar{1}.24$	$\bar{1}.10$	$\bar{2}.96$	1600	7.3
4.85	$\bar{1}.48$	$\bar{1}.35$	$\bar{1}.22$	1400	6.4
5.34	1.69	1.57	1.45	1300	5.9

A P P E N D I X V I I I.

Adsorbent: ZnO

Gas: Hydrogen

Isotherms 38 - 40

Before Adsorption			After Adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. (x 10^6)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	Log Press.				
		Isotherm 38		Corrected Temperature = 314°C				
38.5	14.89	573	3.92×10^{-3}	$\bar{3}.593$	573	4	569	1.38
32.5	14.83	482	1.40×10^{-2}	$\bar{2}.146$	1055	15	1040	2.53
65.7	15.16	995 - 2	1.72×10^{-1}	1.236	2048	177	1871	4.55
		Isotherm 39		Corrected Temperature = 286°C				
			2.41×10^{-3}	$\bar{3}.382$		2	571	1.39
			7.83×10^{-3}	$\bar{3}.894$		8	1047	2.54
			1.08×10^{-1}	1.033		111	1937	4.70
		Isotherm 40		Corrected Temperature = 261°C				
			1.83×10^{-3}	$\bar{3}.262$		2	571	1.39
			4.73×10^{-3}	$\bar{3}.674$		5	1050	2.55
			6.22×10^{-2}	$\bar{2}.794$		64	1984	4.82

Moles ads./gm. ($x\ 10^6$)	Log Pressure from Isotherms			Slope	Heat of ads.
	314°C	286°C	261°C	log P vs $^1/T$	(Kcals/mole)
1.38	$\bar{3}.59$	$\bar{3}.38$	$\bar{3}.26$	2100	9.6
2.00	$\bar{3}.88$	$\bar{3}.63$	$\bar{3}.44$	2600	11.9
2.53	$\bar{2}.14$	$\bar{3}.89$	$\bar{3}.67$	3000	13.7

A P P E N D I X I X.

Adsorbent: ZnO + 0.5mole% Ga_2O_3

Gas: Hydrogen

Isotherms 41 - 43.

Before Adsorption			After Adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. ($\times 10^6$)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	Log Press.				
		Isotherm 41		Corrected Temperature = 314°C				
41.9	14.92	625	3.33×10^{-3}	$\bar{3}.522$	625	3	622	1.51
43.7	14.94	653	2.59×10^{-2}	$\bar{2}.413$	1278	27	1251	3.04
43.9	14.94	656 - 3	1.36×10^{-1}	1.133	1931	140	1791	4.35
		Isotherm 42		Corrected Temperature = 286°C				
			1.80×10^{-3}	$\bar{3}.255$		2	623	1.51
			1.28×10^{-2}	$\bar{2}.107$		13	1265	3.08
			8.62×10^{-2}	2.936		89	1842	4.48
		Isotherm 43		Corrected Temperature = 261°C				
			1.10×10^{-3}	$\bar{3}.041$		1	624	1.52
			6.18×10^{-3}	$\bar{3}.791$		6	1272	3.09
			5.25×10^{-2}	2.720		54	1877	4.56

Moles ads./gm. ($\times 10^6$)	Log Pressure from Isotherms			Slope	Heat of ads.
	314°C	286°C	261°C	log P vs $^1/T$	(Kcals/mole)
1.51	$\bar{3}.52$	$\bar{3}.26$	$\bar{3}.04$	3100	14.2
2.50	$\bar{2}.10$	$\bar{3}.80$	$\bar{3}.52$	3400	15.6
3.04	$\bar{2}.41$	$\bar{2}.10$	$\bar{3}.78$	3950	18.1

A P P E N D I X X.

Adsorbent: ZnO + 0.5mole% Li_2O

Gas: Hydrogen

Isotherms 44 - 46.

Before Adsorption			After Adsorption		Total moles (x RT)	Moles left (x RT)	Moles ads. (x RT)	Moles ads. per gm. (x 10^6)
Press. (mm Hg)	Vol. M' (c.c.)	Moles in (x RT)	Press. (mm Hg)	Log Press.				
		Isotherm 44		Corrected Temperature = 314°C				
30.3	14.80	449	3.43×10^{-3}	$\bar{3}.524$	449	3	446	1.08
55.0	15.05	828	(4.79×10^{-2})	pressure dropping steadily after 100 hours.				
		Isotherm 45		Corrected Temperature = 286°C				
			1.96×10^{-3}	$\bar{3}.292$		2	447	1.09
		Isotherm 46		Corrected Temperature = 261°C				
			1.35×10^{-3}	$\bar{3}.130$		1	448	1.09

A P P E N D I X X I.

Adsorption data of sulphur dioxide on the three adsorbents.

Surface area determinations.

Adsorption of sulphur dioxide at -20.5°C.

Adsorbent	Curve	Run	Adsorption (c.c., cmHg)	Pressure (mm Hg)
ZnO	I	a	1995	0.5
			3606	20.0
			4564	83.0
			5384	153.6
			5804	186.0
ZnO	II	b	676	20.0
			1555	75.3
			2185	129.4
			2678	177.8
ZnO + Ga_2O_3	IV	c	1010	9.5
			2446	44.8
			3961	100.0
ZnO + Ga_2O_3	IV	d	2110	34.4
			3445	83.5
			4535	133.5
ZnO + Li_2O	V	e	1109	24.6
			1887	64.6
			2404	100.9
			3030	152.8

$\frac{P}{P_o}$	P (mm Hg)	(P_o-P) (mm Hg)	ZnO		$ZnO + Ga_2O_3$		$ZnO + Li_2O$	
			V (cc, cm Hg)	$\frac{P \times 10^7}{V(P_o-P)}$ (cc^{-1}, $cmHg^{-1}$)	V (cc, cm Hg)	$\frac{P \times 10^7}{V(P_o-P)}$ (cc^{-1}, $cmHg^{-1}$)	V (cc, cm Hg)	$\frac{P \times 10^7}{V(P_o-P)}$ (cc^{-1}, $cmHg^{-1}$)
0.05	23.2	440.8	720	731	1690	311	1070	491
0.10	46.4	417.6	1140	976	2480	449	1590	700
0.15	69.6	394.4	1480	1193	3090	571	1950	905
0.20	92.7	371.2	1770	1413	3660	683	2300	1087
0.25	116.0	348.0	2020	1650	4180	797	2600	1281
0.30	139.0	324.8	2300	1860	4690	912	2880	1484
0.35	162.3	301.6	2510	2145				
0.40	185.7	278.4	2760	2415				

Sulphur dioxide adsorption data for B.E.T. plots.

	ZnO	ZnO + Ga_2O_3	ZnO + Li_2O
Intercept x 10^7	510	190	290
Slope x 10^7	4600	2400	3970
V_m (cc, cmHg)	1960	3860	2350
Area of surface ($m^2/gm.$)	4.6	9.1	5.5

Data from B.E.T. plots.

BIBLIOGRAPHY.

* 1. Hauffe and Vierk, Z. physik. Chem., 196, 160 (1950), (see C.A. 45, 8860).

2. Wagner, J. Chem. Phys., 18, 65, (1950).

3. Wagner, J. Chem. Phys., 18, 71, (1950).

4. Molinari and Parravano, J.A.C.S., 75, 5233, (1953).

5. Schwab and Block, J. chim. phys., 51, 644, (1954).

6. Cimino, Cipollini, Molinari, Naturwiss., 43, 58, (1956).

7. Wiggill. Unpublished work done at the University of Cape Town.

8. Taylor and Sickman, J.A.C.S., 54, 612, (1932).

9. Taylor and Strother, J.A.C.S., 56, 588, (1934).

10. Pease, J.A.C.S., 45, 1197, (1923).

11. Blench and Garner, J. Chem. Soc., 125, 1288, (1924).

12. Frankenburg, J.A.C.S., 66, 1827, (1944).

13. Garner, Gray, Stone, Proc. Roy. Soc., A197, 294, (1949).

14. Farkas and Melville. Experimental methods in gas reactions, (1939), p. 161.

15. Dodd and Robinson. Experimental Inorganic Chemistry, (1954), p. 137.

16. Dodd and Robinson, p. 158.

17. Farkas and Melville, p. 151.

18. Dodd and Robinson, p. 228.

19. Dodd and Robinson, p. 164.

20. Farkas and Melville, p. 162.

21. Dodd and Robinson, p. 125.

22. Jnanananda, High Vacua, (1947), p. 159.

23. Wickers, Rev. Sci. Instrum., 13, 502, (1942).

24. Fushillo, Rev. Sci. Instrum., 27, 410 (1956).

25. Kubokawa and Toyama, J. Phys. Chem., 60, 833, (1956).

26. Gmelin, Handbuch der Anorganischen Chemie, 8 Auflage, No. 32, p. 775.

27. Gmelin, No. 36, pp. 71 - 72.

28. Sebba and Pugh, J. Chem. Soc., 1376, (1937).

29. Gmelin, No. 20, p. 97.

30. Gmelin, No. 20, p. 232.

31. Handbook of Chemistry and Physics, 19th Ed., p. 277. (Chemical Rubber Publishing Co.).

32. Dodd and Robinson, p. 63.

33. Trapnell, Chemisorption, (1955), p. 144.

34. Brunauer, Physical adsorption of gases and vapours, (1943), p. 25.

35. Brunauer, p. 33.

36. Rees, Chemistry of the defect solid state,(1954), p. 4.

37. Rees, p. 21.

38. Rees, p. 7.

39. Garner (Ed) Chemistry of the solid state, (1955), p. 133.

* 40. Marshall, Enright, Weyl. Proc. Intern. Symposium on reactivity of solids. Gothenburg (1952), p. 273. (See C.A. 48, 7979, (1954)).

41. Garner, p. 124.

42. Dowden, J. Chem. Soc., 242, (1950).

43. Garner, p. 134.

44. Rees, p. 14.

45. Conway. Electrochemical data (1952), p. 29, (from Pauling, Nature of the chemical bond (1948)).

46. Boudart, J.A.C.S., 74, 1531, (1952).

* 47. Wagner and Hauffe, Z. Elektrochem. 44, 172, (1938),(see C.A. 32, 4061).

48. Garner, p. 395.

49. Emmett, (Ed.) Catalysis, Vol. I, (1954), p. 75.

50. Garner, p. 377.

51. For references see Emmett, Vol. I, pp. 78 - 83.

* 52. Beebe, Handb. Katalyse, Vol. IV, (1943), p. 473.

53. Garner, p. 370.

54. Brunauer, Physical adsorption of gases and vapours, (1943), p. 219.

55. Brunauer, pp. 220 - 222.

56. Brunauer, p. 32.

57. Trapnell, Chemisorption, (1955), p. 22.

58. Garner and Veal, J. Chem. Soc., 1487, (1935).

* 59. Kwan, Kimuyama and Fujita, J.R.I. Cat. Hokkaido Univ., 3, 28 (1953), (See C.A. 48, 8007).

60. Emmett and Brunauer, J.A.C.S., 59, 1553, (1937).

61. Brunauer, Emmett and Teller, J.A.C.S., 60, 309, (1938).

62. Gans, Brooks, Boyd. Ind. Eng. Chem. Anal. Ed. 14, 396, (1942).

63. Schreiner and Kemball, Trans. Far. Soc., 49, 190, (1953).

64. Barr and Anhorn, Scientific Glassblowing and Laboratory Techniques, p. 257.

65. Farkas and Melville, p. 106.

66. Handbook of Chemistry and Physics, 19th Ed., p. 1295.

67. Gmelin, 9.B.1, p. 206.

68. Hill, J. Chem. Phys., 16, 181, (1948).

69. Livingston, J. Colloid Science, 4, 447, (1949).

70. Partington, Advanced Treatise in Phys. Chem., Vol. I, p. 267.

71. Dunoyer, Vacuum Practice, pp. 133 - 141.

72. Jnanananda, High Vacua, pp. 68 - 73.

73. Trapnell, pp. 23 - 24.

74. Porter, Disc. Far. Soc., 8, 358, (1950).

75. Sanderson, Vacuum manipulation of volatile compounds, (1948), p. 47.

76. Halsey and Taylor, J. Chem. Phys., 15, 624, (1947).

77. Garner, J. Chem. Soc., 1239, (1947).

78. Burwell and Taylor, J.A.C.S., 59, 697, (1937).

79. Burwell and Taylor, J.A.C.S., 58, 1753, (1936).

80. Garner and Maggs, Trans. Far. Soc., 32, 1744, (1936).

81. Garner and Kingman, Trans. Far. Soc., 27, 322, (1931).

* 82. Keier and Roginskii, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk 27 - 38 (1950) (taken from C.A. 44, 5690).

83. Ling Yang, J. Electrochem. Soc., 97, No. 4, 91c, (1950).

* 84. Shekhter and Zhabrova, Izvest. Akad. Nauk, Otdel. Khim. Nauk, 500, (1951), (taken from C.A. 46, 3839).

85. Glasstone, Textbook of Physical Chemistry, Second ed. (1951), p.1147.

* It was not possible to consult these references directly. The information cited was usually taken from Chemical Abstracts.