4. *Chromic Oxide as an Adsorbent.*

By E. H. Harbard and A. King.

The adsorption of carbon tetrachloride on chromic oxide prepared by different methods has been measured. It is possible to correlate the adsorption capacity with the mode of formation. The isotherms are of a common type showing unimolecular adsorption, completed in the middle pressure range, and capillary condensation, which sets in at higher pressures. The greater the amount of unimolecular adsorption the lower is the pressure at which capillary condensation commences. There is a greater size distribution of the capillaries than with most other adsorbents. On the assumption that a capillary condensation mechanism is operative, a relationship has been worked out between the surface area and the mass of vapour adsorbed at a given pressure.

The adsorption isotherms of a series of organic vapours and of water on chromic oxide have been compared, and the effect of dipole moment discussed. On successive adsorptions and desorptions of chloroform on chromic oxide, the shape of the isotherm changes and the amount of adsorption becomes progressively smaller until it is only a fraction of its initial value. This is accompanied by capillary condensation setting in at increasingly higher pressures, and appears to be due to a destruction of the smaller capillaries by the adsorption of the vapour.

The fine structure of the adsorption isotherm of chloroform on chromic oxide has been measured by a new type of static apparatus. The isotherm is discontinuous both in the unimolecular and in the Langmuir portion of the curve.

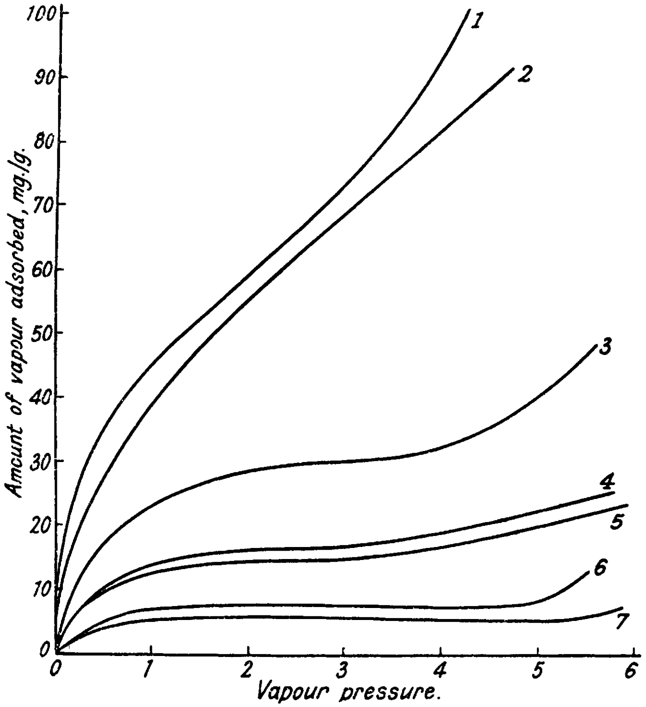
One of us (King, *Trans. Faraday Soc.*, 1935, **31**, 935) suggested that the great porosity and hence adsorption capacity of charcoal is due to its formation by chemical reaction in the solid state accompanied by copious gas evolution, rearrangement and orientation of molecules being relatively slow under these conditions. It was shown that the adsorption capacity of different samples of charcoal is conditioned by the amount of gas evolution and physical state during charring.

In order to test this theory, an attempt was made to investigate the properties of adsorbents formed by other solid reactions in which large amounts of gas are evolved. Chromic oxide seemed suitable for this purpose, since it is chemically simpler than charcoal and might therefore be expected to have reproducible surface properties. The chromic oxide initially chosen was that produced by thermal decomposition of ammonium dichromate since it is very bulky. It was hoped that, by decomposing the dichromate under reduced pressure, a still more porous material might be obtained, and that by controlling the pressure, a series of preparations of graded porosity would result. It was found, however, that at low pressures the reaction afforded a different product (see J., 1938, 955; 1939, 55).

Chromic oxide was prepared by a variety of methods calculated to produce samples of widely different porosity. In each case the adsorption isotherm of carbon tetrachloride on the oxide was measured, the adsorption capacity of the oxide for an inert, volatile liquid being presumably proportional to its specific surface area. The following modes of preparation were employed, the numbers corresponding to the adsorption isotherms plotted in Fig. 1: Ignition of (1) ammonium dichromate, (2) chromic hydroxide in a vacuum at 400°, (3) chromic hydroxide at atmospheric pressure, (4) a mixture of ammonium chloride and potassium dichromate, (5) chromic acid, (6) mercurous chromate in a vacuum, (7) mercurous chromate at atmospheric pressure.

The carbon tetrachloride isotherms for the pressure range 0—60 mm. which are plotted in Fig. 1 show the great differences in adsorption capacity of the different preparations; the oxide (1) has the greatest capacity, as is to be expected from its mode of preparation, large volumes of gases being evolved during the reaction at a temperature below that at which the molecules could easily rearrange themselves into the regular lattice. This is indicated also by the bulky nature of the sample. Specimen (2) is only slightly less active, being prepared in a physically analogous manner to that of (1), yet it was relatively compact, indicating, as with charcoal, that a low bulk density shows the existence of a coarse porosity but not necessarily the presence of the ultra-pores which form the main contribution to the surface area and adsorption capacity of the sample. Comparison of oxides (2) and (3) shows that the porosity increases with the rate of evolution of the gases during their formation : this is again borne out by the relative adsorptions of (6) and (7). In spite of the copious gas evolution during the preparation of sample (4) this oxide did not show such a high capacity for adsorption as samples (1) and (2), probably owing to the less intimate mechanical mixture in (4). The adsorption capacity of samples (6) and (7) is a mere fraction of that of the first members of the series, in spite of the fact that mercury vapour was given off during the formation of the oxide. This is no doubt partly due to the smaller volume of evolved gases, but probably more to the higher temperature required for the removal of the mercury. It was found, however, that once the oxide had been prepared, prolonged ignition had only a minor effect on its adsorption isotherm; the initial structure produced by gas evolution thus seems difficult to break up, a fact which it is difficult to reconcile with the great mobility of the surface in the presence of adsorbed layers (see p. 25).

FIG. 1.



Capillary Condensation.—The form of isotherm shown in Fig. 1 is of a very common type; *e.g.*, curve (3) may be separated into two distinct parts, the first, ranging from 0 to 30 mm., corresponding in shape to the typical Langmuir isotherm, and the second, in which the adsorption increases continuously to saturation pressure, being very similar to the curves attributed by other workers to capillary condensation.

The capillary condensation theory regards the adsorbent as consisting of a large number of capillary tubes of different diameter. Since the vapour-pressure lowering in these tubes should be considerable, condensation will take place at a pressure much below the normal vapour pressure of the adsorbate. The various samples of chromic oxide should therefore differ in their adsorptive properties, not only because of differences in the total surface areas of the different preparations, but also because of the difference in the number, size, and distribution of the capillaries. There should thus be two variables: (1) The surface area, which can be estimated relatively from the weight of vapour corresponding to the flat portion of the Langmuir part of the isotherm where there is presumed to be a unimolecular layer on the whole effective surface. (2) The porosity of the powder, depending on the rate and extent of gas evolution during formation, and measured by the slope of the second part of the curve and by the pressure at which it commences.

Examination of the curves suggests that these two variables are directly connected, as might be expected, since the surface area of the capillary tubes will be a large fraction of the total surface area. Those curves showing the largest surface area per unit weight are also those in which the capillary condensation portions have maximum slope and commence at the lowest pressures. Thus samples (1) and (2) which show maximum Langmuir adsorption have adsorption isotherms in which the sloping portion attributed to capillary condensation commences at a point where Langmuir adsorption is not yet complete. In the other isotherms there is a flat portion extending over a wide pressure range where unimolecular adsorption is complete but capillary condensation has not yet set in. It can be seen that the pressure at which capillary condensation commences increases as the adsorptive capacity decreases until, in sample (7), which is a very poor adsorbent, there is very little condensation, indicating a coarse structure with lack of small capillaries.

The slope of the capillary condensation curves shown in Fig. 1 is somewhat different from that of those curves attributed to capillary condensation in other systems. In most of the cases where this phenomenon has previously been noticed, the curve rises very steeply from the unimolecular equilibrium position, being a nearly vertical straight line, and indicating the presence of capillaries of almost uniform size. In the case of chromic oxide, however, especially in specimen (1), the capillaries appear to extend over a wide range, unlike those in, *e.g.*, charcoal and the hydrous oxide gels.

It is clear that the chromic oxide system is ideal for the study of capillary condensation. An attempt has therefore been made to relate the capillary condensation portion of the curve with that due to unimolecular adsorption, on the assumption that this solid is composed of a collection of small pores of different diameter.

Much theoretical work on capillary condensation depends on the validity of the Kelvin equation, *viz.*,

$$\log p/p' = 2SM/d\mathbf{R}Tr$$

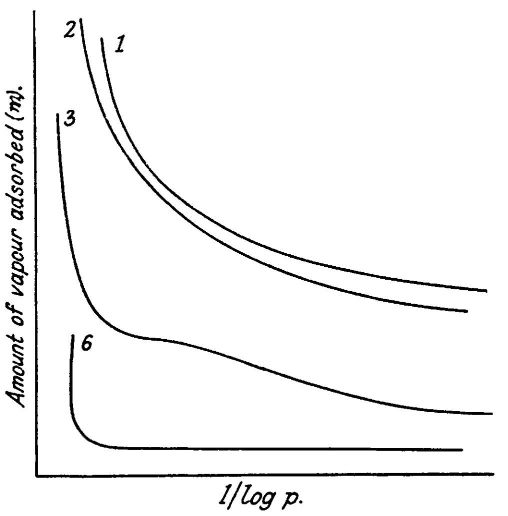
where p is the saturation vapour pressure, p' that in the capillary, S is the surface tension of the liquid of density d, M the molecular weight of the vapour, $\mathbf{R}$ the gas constant, T the absolute temperature, and r the radius of the capillary; but this equation is only valid for a liquid whose surface tension and angle of contact with the solid remain constant with varying radius of curvature.

If this equation is used to calculate from the adsorption isotherms the radius of the smallest capillary existing in chromic oxide, this is found to be about $1{\cdot}7 \times 10^{-8}$ cm., *i.e.*, it is smaller than the radius of the carbon tetrachloride molecule. This apparent contradiction has been noticed by other workers (Patrick, *J. Physical Chem.*, 1925, **29**, 220) and may be due to the invalidity of the Kelvin equation for very small capillaries because of variation in surface tension or angle of contact of the liquid as the diameter of the capillary approaches molecular dimensions. Shereshefsky (*J. Amer. Chem. Soc.*, 1928, **50**, 2966) found that the vapour pressure in small glass capillaries is lower than the theoretical value calculated from the Kelvin equation, and attributed this to changing surface tension.

If it is assumed that a relationship similar to the Kelvin equation is valid except for those capillaries approaching molecular dimensions, the distribution of capillary sizes may be estimated, and the capillary condensation phenomena related to the unimolecular adsorption as follows. In Fig. 2, the amount of vapour (m) adsorbed by different samples of chromic oxide is plotted against $1/\log p$, where p is the pressure of the adsorbate. Now, if it is assumed that $r = k/\log p$, where k is a constant, the curve in Fig. 2 may be assumed to be that of the mass adsorbed plotted against the radius of the capillary. If the slope of the previous curve, dm/dr, is plotted against $1/\log p$ or r, it will be noticed that, for the section of the isotherm which has been attributed to capillary condensation, the curve is almost a straight line; *i.e.*, $dm/dr = Kr$ where K is a constant, or

$$m = \tfrac{1}{2}Kr^2 \quad . \quad . \quad . \quad (1)$$

FIG. 2.



Let f(r) represent the total length of all the capillaries of radius r; then M, the mass of vapour adsorbed by capillary condensation by all capillaries of radius r_1 and less, is given by

$$M = \sum_{r=0}^{r=r_1} \pi r^2 . \mathrm{f}(r) d = \pi d \int_0^{r_1} r^2 . \mathrm{f}(r) . \mathrm{d}r$$

Introduction of equation (1), obtained from the practical results, then gives

$$\tfrac{1}{2}Kr_1^2 = k\int_0^{r_1} r^2 . \mathrm{f}(r) . \mathrm{d}r$$

or

$$\mathrm{f}(r_1) = c/r_1 \quad . \quad . \quad . \quad (2)$$

Now the total surface area of a porous material can be considered to be that of the capillaries, as this will be very great compared with the rest of the surface. Let A represent the surface area of unit mass of the powder and r_2 the radius of the largest capillary. Then

$$A = \int_0^{r_2} 2\pi r . \mathrm{f}(r) . \mathrm{d}r = 2\pi\int_0^{r_2} r . (c/r) . \mathrm{d}r \text{ [from equation (2)]}$$

$$= 2\pi c r_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By substituting the value c/r instead of f(r) in the equation for M, we obtain

$$M = \pi c\int_0^{r_1} r . \mathrm{d}r = \tfrac{1}{2}\pi c r_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Considering the different samples of oxide whose isotherms have been determined, and to which the above reasoning should apply, there are only three variables, namely, c, r_1, and r_2. The value of the radius of the largest capillary, r_2, should be roughly the same for all the samples, and the value of r_1 can be fixed by comparing the capillary condensation curves at the same pressure. Suppose that two curves a and b are compared, and let the values of the variables be correspondingly A_a, A_b, M_a, M_b, c_a, c_b. From equations (3) and (4) it follows that $A_a/c_a = 2\pi r_2 = A_b/c_b$ and that $M_a/c_a = \frac{1}{2}\pi r_1^2 = M_b/c_b$, hence $A_a/A_b = c_a/c_b = M_a/M_b$.

In the table are collected values of surface area and of mass of vapour adsorbed per g. of adsorbent as obtained experimentally for preparations 2—6 (Fig. 1). The ratio M/A is practically constant, and the greatest discrepancy occurs in curve 6, where the assumption that the total surface area is represented by the surface area of the capillaries is no longer valid owing to the low porosity of the sample. It would appear that the relationship which has been assumed between the radius of a capillary tube and the vapour pressure of the liquid contained in it is tenable at least for chromic oxide. It follows then that the second part of the adsorption isotherm is to be attributed to capillary condensation. This is further discussed on p. 27.

		Mass of adsorbed gas measured at		Ratio M/A.	
Curve.	Area.	50 mm. (1).	60 mm. (2).	(1).	(2).
2	5·5	8·90	9·78	1·62	1·78
3	2·65	4·05	4·49	1·53	1·76
4	1·45	2·10	2·43	1·45	1·68
5	1·22	1·70	1·88	1·40	1·54
6	0·52	0·85	1·10	1·63	2·10

The Adsorption of Different Vapours on Chromic Oxide.—A series of adsorption isotherms of carbon tetrachloride, chloroform, methylene chloride, and water vapours were determined on similar samples of chromic oxide. The series of halogen compounds was chosen because of the negligible change in the size of the molecule, thus ruling out complexities due to steric effects, and because their difference in dipole moment should make noticeable any effect of this on the isotherms. The results are plotted in Fig. 3. Sample (1) of oxide was used, as for Fig. 1. The pressure is expressed as a fraction of the saturated vapour pressure at the temperature of the experiment (relative humidity) and the mass adsorbed as mg.-mols. of vapour per g. of oxide, so as to facilitate comparison of the isotherms.

Of the adsorption isotherms shown in Fig. 3 those representing the carbon compounds are all of the same type as that for carbon tetrachloride. Whereas unimolecular saturation is reached for chloroform and methylene chloride before the onset of capillary condensation, yet for carbon tetrachloride the two processes are combined over the middle range of the isotherm. The isotherms for chloroform and methylene chloride, whose dipoles do not differ greatly, are almost identical over a large pressure range, the total adsorption and the pressure at which capillary condensation sets in being the same. In the initial part of the curve, however, the methylene chloride completes its Langmuir adsorption at a lower relative pressure than the chloroform.

FIG. 3.

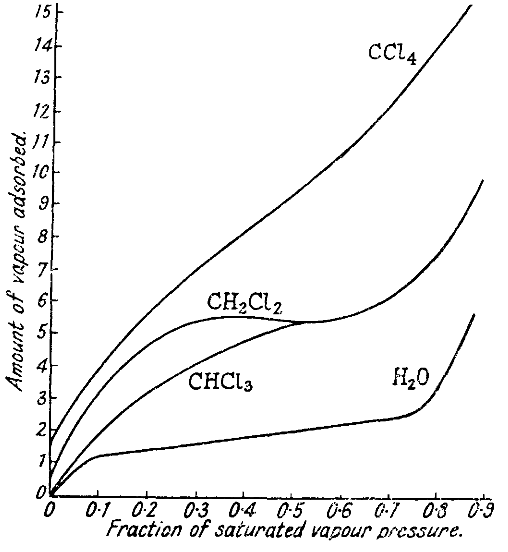
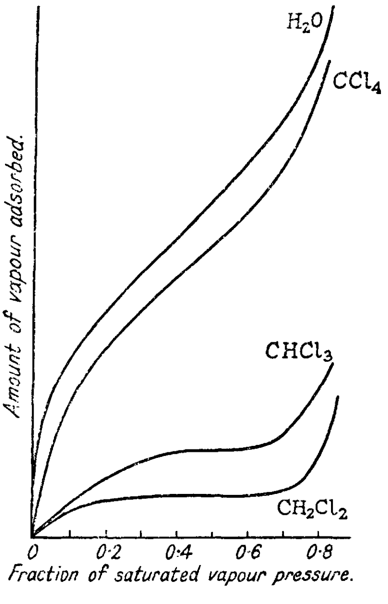


FIG. 4.



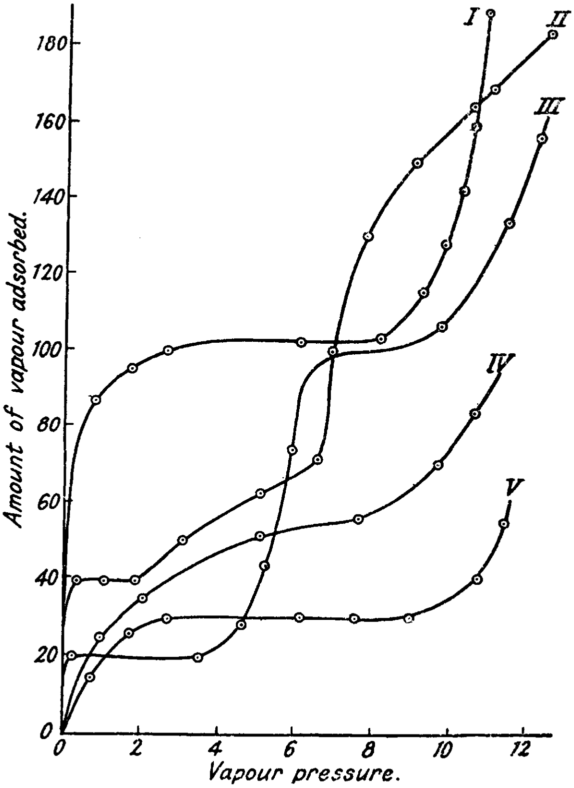
The adsorption isotherm for water is somewhat different from that of the organic vapours, initial adsorption being complete at about 0·1 relative humidity. From this point the curve shows a constant increase in the amount of vapour adsorbed with increasing pressure over a considerable range, until the inception of capillary condensation is reached. It would appear that in this case a third type of adsorption mechanism is operating. This form of isotherm was noticed also for the adsorption of water vapour on some of the less active samples of chromic oxide.

For a more direct comparison of the total adsorption of the various adsorbates it is necessary to allow for the widely differing saturation vapour pressures. For instance, at any relative vapour pressure the ratio of the number of water vapour molecules per litre to those of methylene chloride at the same relative vapour pressure is 1 : 16; *i.e.*, there are 16 times as many methylene chloride molecules arriving in unit time on unit surface of the adsorbent as water molecules. Hence, in Fig. 4 the amount of vapour adsorbed has been expressed as mg.-mols. per g. of adsorbent, divided by the saturated vapour pressure of the vapour, *i.e.*, as the proportion of vapour molecules in the vapour phase which are adsorbed by the solid.

Plotting the curve in this fashion shows that the carbon tetrachloride isotherm now falls between those of water and chloroform. There is a definite decrease in the amount of adsorption of the organic vapours with dipole moment, a result contrary to that usually assumed. The water curve is comparable with that of carbon tetrachloride; this is probably due to the smaller size of the water molecules, which are able to penetrate the smaller ultrapores inaccessible to the larger organic molecules.

Successive Adsorptions on the Chromic Oxide Surface.—The adsorption isotherms shown in Figs. 1 and 3 were determined on samples of the oxide which had been thoroughly flushed out with the adsorbate several times before measurement. This was considered necessary to remove surface impurities which might considerably modify the isotherms and render them unsuitable for theoretical discussion. It was assumed that these impurities are eliminated after about six flushings. Even after this treatment it was noticed, especially in the very porous samples, that there was a gradual drift in the position of the isotherm if the same sample was used for repeated determinations. The amount of the various vapours adsorbed by the powder became less and less as repeated adsorptions and desorptions were carried out, the effect continuing for such a large number of treatments that it was impossible to attribute it to cleaning of the surface. This phenomenon, which has not been noticed in other systems, is so marked that it was studied in some detail by carrying out the determination of the complete isotherm on a given sample of adsorbent a large number of times. A series of typical isotherms obtained with chloroform on chromic oxide prepared by method (1) are shown in Fig. 5. The curves were obtained

FIG. 5.



as follows: (1) not flushed, (2) flushed twice, (3) flushed 5 times, (4) flushed 10 times, (5) flushed 20 times.

It will be seen that the unflushed oxide has a typical Langmuir adsorption isotherm, with considerable evidence of capillary condensation; this is very similar in shape to that obtained previously on a sample which had been repeatedly flushed and was presumably free from surface impurities. The rapid establishment of unimolecular saturation at low vapour pressures and the large surface area are features of this isotherm. The isotherm redetermined, however, shows a distinct change of shape, a sudden break appearing in the curve at about 2 cm. In isotherm (3) this break is even more marked, there being two pressure ranges where no increase in the amount of adsorption takes place, the effect being much the same as two Langmuir curves, one after the other, followed by capillary condensation at higher pressures. The amount of adsorption is now much less than on the fresh sample. Isotherm (4) no longer shows the break in the middle of the curve, the shape being that of the normal type, but again the total amount of adsorption is much smaller. Repeated flushings have apparently no further pronounced effect except to lower still more the total adsorption, the isotherm remaining of the same shape. The total amount of unimolecular adsorption as indicated by isotherm (5) is less than a third of that given by curve (1) although the same sample of chromic oxide was used throughout this series. As the amount of adsorption decreases from isotherm (1) to isotherm (5) the onset of capillary condensation is at an increasingly higher pressure, as shown by curves (4) and (5).

Although removal of impurities no doubt occurs during the first few flushings of the sample, the subsequent decrease in adsorptive capacity cannot, for several reasons, be attributed to this cause. First, the effect persists even when the sample has been flushed out 20 or 30 times, although removal of surface impurities, if not complete, must then be too small to bring about any finite change in the adsorption. Secondly, mere cleaning of the surface would be expected to increase rather than to decrease the available surface and hence the adsorptive capacity of the sample.

In order to test the suggestion that the decrease in adsorption might be due to the removal of a small proportion of small particles of high surface activity during the evacuation, a weighed sample of the oxide was placed in the adsorption apparatus and flushed out several times with chloroform, but its weight was found to be unaltered. Another possibility was that some of the chloroform might have been retained in the smaller capillaries on desorption, but this was excluded by the fact that in several experiments the amounts of chloroform adsorbed on to the sample and recovered from it by desorption were measured and found to be equal.

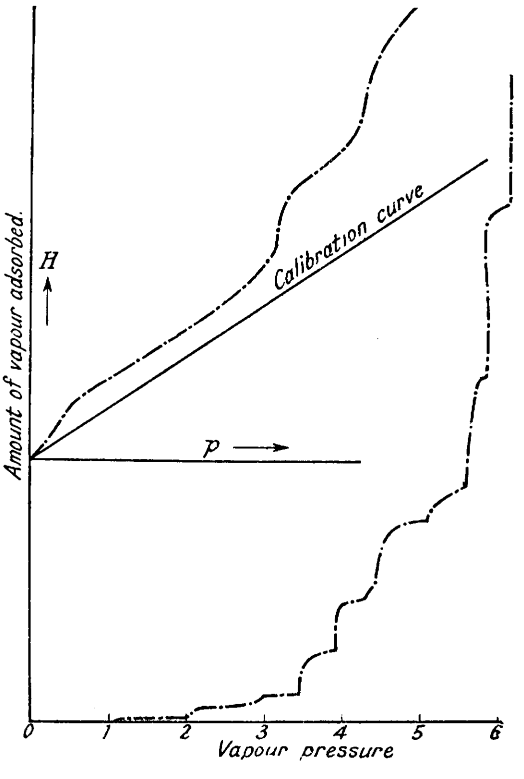
The reduction of the total amount of adsorption and the higher pressure of capillary condensation is probably due to a destruction of the smaller capillaries, either by the surface atoms becoming mobile when in contact with the adsorbate and therefore tending to crystallise, or more probably by the pressure of the condensed liquid in them. The fact that the condensation of a liquid in the capillaries of a solid may distort the structure and cause the powder to crumble has been noticed with charcoal, and the destruction of chabesite crystals by the adsorption of ammonia is very marked.

As we have seen from the earlier part of this paper, effects (1) and (2) are closely connected and it may thus be assumed that they are due to the same cause, namely, decrease in the area of the sample by destruction of small capillaries. This may be caused by the surface atoms of the material becoming mobile when in contact with the adsorbate and hence tending to crystallise into a more regular surface structure with the elimination of capillaries. A more likely reason for the decrease in surface area is the destruction of the smaller capillaries by crumbling of the powder by the pressure of the condensed liquid in these capillaries.

The Fine Structure of the Adsorption Isotherm.—Although discontinuities in the adsorption isotherm are often attributed to experimental error, those found by Allmand (*Proc. Roy. Soc.*, 1931, **130**, 610) by the static method seem well substantiated and their reality is further indicated by work in progress in this laboratory by a direct-measuring flotation method (J., **1939**, p. 139), but it was thought advisable to carry out a determination of the fine structure of the adsorption isotherm of chloroform on chromic oxide by another method, special attention being given to that part of the curve due to capillary condensation. It was hoped also to confirm the peculiar shape of the isotherm obtained during the flushing out process (p. 24).

The method adopted was a modification of the static type (see p. 28). The apparatus was small and compact, capable of efficient temperature control and having little dead space. Several blank runs were carried out without any oxide in the apparatus, chloroform being used in some cases and air in others. Errors due to the adsorption of chloroform on the walls of the apparatus were well within the experimental error of measurement of the vapour pressure. The calibration curve was plotted in the form of a straight line and, although a large number of points were determined per cm. rise in pressure, no deviation from the linear, due to irregularities in the walls, etc., could be detected. Redetermination of the calibration curve using air with the oxide in the apparatus gave a result very similar to that using the empty vessel, so the error due to the volume of adsorbent in the apparatus is very small. The facts that the various calibration curves were smooth and that over a considerable pressure range the actual adsorption isotherms obtained indicated no adsorption (*i.e.*, the curves were parallel to the axis) seem to verify that discontinuities obtained in other sections are due to some cause other than experimental error.

FIG. 6.



The results obtained upon a sample of chromic oxide prepared by method (1) are shown in Fig. 6. The discontinuities are obvious. By the present method, determination of a complete isotherm is difficult, that in Fig. 6 representing the Langmuir saturation and the capillary condensation parts of the curve. In other experiments discontinuities were also obtained for the initial unimolecular adsorption, which was also found to consist of a number of small, intersecting curves. It would appear then that, although there are two different types of adsorption mechanism in operation, both give rise to discontinuities.

The general shape and size of the discontinuities has been checked by Chambers, using the flotation method on the same system.

Examination of the curves does not reveal any regular trend in the shape of the discontinuities, except that there seems to be some relationship between the pressure range over which the discontinuity extends and the amount of vapour adsorbed during the discontinuity. For instance, the discontinuities at the beginning of the isotherm extend over a range of nearly 1 cm. pressure, but only a small amount of vapour is adsorbed in this range, whereas in the capillary condensation part of the curve, the discontinuities are very steep and only extend over a small pressure range. It is remarkable that over considerable pressure ranges the isotherm is a straight line parallel to the axis, *i.e.*, an increase of pressure did not result in any increase in the amount of vapour adsorbed. This is shown clearly in the inset to Fig. 6 and in some other cases was still more marked. These flat portions of the curve occurred in the middle part of the isotherm and support the hypothesis advanced to explain the adsorption mechanism of systems such as this, since, if the pressure at which unimolecular adsorption is completed is below that at which capillary condensation commences, there should be a region of zero adsorption between the two.

In isotherms measured for some of the intermediate samples of Fig. 5 discontinuities larger than those of Fig. 6 were obtained. The operation of some exceptional factor during the cleaning of the surface is thus verified.

It has been suggested that discontinuities in the adsorption isotherm may be due to the condensation of the vapour in concentric circles round some active centre, each circle being added only when a certain definite pressure is attained. This would require that the discontinuities should increase regularly with pressure from the beginning of the isotherm. The fact that such an increase is noticeable in the second part of the isotherms does not support the theory, however, since this is the region of capillary condensation where the active centre mechanism cannot possibly apply.

Radulescu and Tilenschi (*Z. physikal. Chem.*, 1937, **179**, 210) have shown that the radius of curvature of a liquid in a capillary tube must be an integral multiple of the radius of the liquid molecule. Hence an integer n should be included in the Kelvin equation, and the capillary condensation can be assumed to be discontinuous. These steps in the curve would, however, be exceedingly small, and it is doubtful whether any available method for the measurement of adsorption would be sufficiently sensitive to detect them.

Another hypothesis which might be advanced to explain these discontinuities is that of the regular formation of capillaries. It is supposed that there are a limited number of stable capillary formations, with definite diameters, and that, owing in some way to the crystal structure of the material, only capillaries of these diameters are stable. Hence the porous adsorbent consists, not of capillaries of continuously varying diameters, but of groups of capillaries of definite, fixed diameter. If this is the case, the isotherm would consist of a large number of " steps " rather than the smooth curve previously expected.

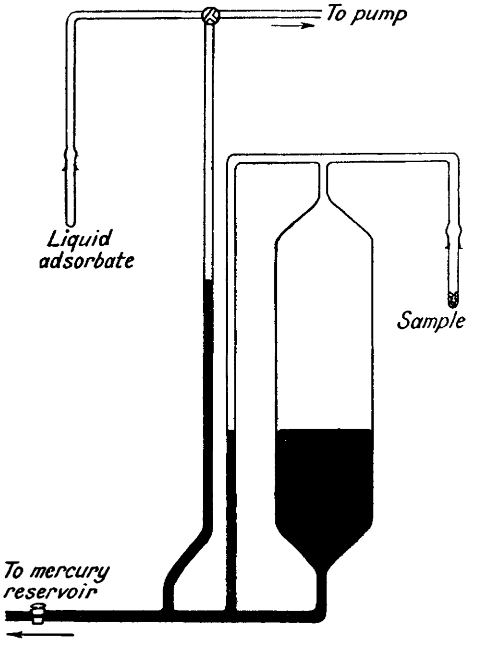
Summing up, we can be sure that the isotherm on chromic oxide is discontinuous in both the unimolecular adsorption and the capillary condensation region. There may be two distinct factors causing this result, but it seems more probable that the same factor is operating in different ways in the two sections of the curve. There are not sufficient data upon which to base an explanation of these phenomena, but it is probable that the steric arrangement of the atoms will provide a solution.

EXPERIMENTAL.

Preparation of Chromic Oxide.—The samples of chromic oxide used in the determinations of the isotherms shown in Fig. 1 were prepared as follows: (1) Powdered ammonium dichromate was ignited in an open crucible, and the residue thoroughly ignited for an hour over a Meker burner and allowed to cool in a desiccator; the resulting dull green powder was very light and flaky. (2) Chromic hydroxide was precipitated from a dilute solution of chromic sulphate by ammonia, filtered off, washed thoroughly with distilled water, partly dried by filter papers, and placed in a small bulb attached to the adsorption apparatus which was then evacuated; the product was finally ignited over a Meker burner. (3) Chromic hydroxide was prepared as in (2) but thoroughly ignited immediately after being washed. (4) Chromium trioxide was gently heated in a crucible; it swelled to give a hard compound of metallic appearance (presumably one of the intermediate oxides) which on further ignition gave the usual grey-green chromic oxide. (5) A finely ground, intimate mixture of ammonium chloride and potassium dichromate was heated over a Bunsen burner. The resulting powder was then washed free from any excess of the initial materials and thoroughly ignited; it was very similar to (1) but slightly more compact. (6) Mercurous chromate, prepared from solutions of mercurous nitrate and potassium dichromate, was washed with a dilute solution of mercurous nitrate, and ignited in a vacuum at 400° and finally over a Meker burner. (7) Mercurous chromate, prepared as above, was directly heated over a Meker burner.

Determination of the Adsorption Isotherm.—The apparatus used for the determination of all the isotherms except in the fine structure experiments was of the simple static type. The oxide samples were used immediately after preparation or stored in a desiccator over phosphoric oxide. If they were allowed to adsorb the slightest trace of water vapour they began to " froth " on evacuation, scattering a shower of fine particles throughout the apparatus, but as soon as the water vapour had been removed, either by ignition or by flushing (adsorption of organic vapour followed by desorption), this no longer occurred. This phenomenon is not due to the presence of adsorbed gases in general, but to water vapour, for a flushed sample could be made to froth on evacuation by keeping it in contact with a very low pressure of water vapour.

FIG. 7.



All the substances used in the preparation of the samples of oxide were of " AnalaR " standard, and all adsorbates were redistilled before use.

Apparatus for the Study of Discontinuities in the Adsorption Isotherm.—The apparatus used for this purpose is shown in Fig. 7. It consists of a wide tube forming the main vessel, to which is attached a side arm ending in a small bulb containing the sample of solid the adsorption isotherm of which is to be determined. Two tubes of smaller diameter in parallel with the main vessel, one leading to the vessel, the other to the vacuum line, serve to measure the vapour pressure. The flushed sample is placed in the bulb, and the apparatus thoroughly evacuated. A small amount of chloroform vapour is let in from the reservoir, after the level of the mercury has been lowered. The mercury level is then raised, and the side tube evacuated; the apparatus is now ready for measurements to be taken. Small quantities of mercury are allowed to enter the vessel, decreasing the volume and hence increasing the pressure. The change in volume is measured by the change in the height of mercury in the main vessel, the diameter of the tube being assumed uniform. The pressure is measured directly by the difference between the levels of mercury in the side tubes. Hence, by plotting the reciprocal of the pressure against the volume as measured by the height (H) of the mercury, a straight line should be obtained if there is no adsorption. Any deviation from the straight line is a measure of the amount of vapour adsorbed by the sample.

Let there be a certain mass of vapour M_1 in the vessel under a pressure p_1, the volume, v, of the vessel being fixed by the height of the mercury. Then $p_1v = M_1\boldsymbol{R}T$. If we now plot the calibration curve $1/p$ against v, we obtain a straight line of slope $M_1\boldsymbol{R}T$. Now let the mass of vapour in the vessel be changed to M_2, the pressure at the same volume, v, being p_2. The slope of the new calibration curve will be $M_2\boldsymbol{R}T$. But

$$p_1/M_1 = \boldsymbol{RT}/v = p_2/M_2$$

hence

$$p_1/p_2 = M_1/M_2 = M_1\boldsymbol{RT}/M_2\boldsymbol{RT}$$

i.e., the slopes of the two calibration curves are in the ratio $p_1 : p_2$. Hence, by one calibration of the apparatus, the actual isotherm can easily be determined.

Under the experimental conditions employed, the error due to the volume occupied by the solid powder was never more than 0·25%, and this did not in any case produce deviations from the smooth isotherm.

The inset of Fig. 6 shows the experimental results as plotted with respect to the calibration curve. This indicates the magnitude of the discontinuities and shows also a flat portion of the isotherm where the experimental curve is parallel with the calibration curve.

All the pressure measurements were taken by means of a cathetometer, the readings being accurate to ± 0·02 mm.

IMPERIAL COLLEGE OF SCIENCE, LONDON, S.W. 7.

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