29. *Discontinuities in Adsorption Processes.*

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A new technique for measuring the adsorption of gases by solids described in a previous paper (J., 1939, 139) has been applied to the problem of discontinuous adsorption.   Several criticisms of the method are shown to be invalid, and a preliminary investigation of the adsorption of vapours by various solids is described.   New and conclusive evidence for the existence of discontinuous adsorption has been obtained with several different vapours on charcoal, silica gel, chromic oxide, and chabasite. Allmand and Burrage's general conclusion that vapours are adsorbed discontinuously by complex solids is confirmed, and is shown to be true also of the crystalline material, chabasite.

BEFORE 1931 it was believed that the adsorption isotherms of gases and vapours on solids were continuous smooth curves.   In that year, however, Allmand and Burrage published

the first of a series of papers (*Proc. Roy. Soc., A*, **130**, 610) describing measurements by the static method which seemed to show that the isotherms of various vapours on charcoal and silica gel consisted of a series of well-defined loops cutting each other at definite pressures. These loops could only be detected if a very large number of points were determined : generally it was necessary to make at least three measurements for every mm. rise of pressure, and often as many as 10 were required. Since it had never previously been considered necessary to determine as many points as this to fix the exact course of the isotherm, the discontinuities had been missed by earlier workers.

Definite loops were found with carbon tetrachloride, carbon disulphide, benzene, water vapour, *n*-amyl alcohol, and carbon dioxide on several different charcoals, and some evidence for reproducibility of the curves in detail was obtained. Later experiments in which the dynamic retentivity method was employed gave very sharply defined rectangular steps in some cases (*Trans. Faraday Soc.*, 1932, **28**, 218). More recent work by Burrage, with both static and dynamic methods, seemed to indicate that the rectangular stepped type of curve was very common (*ibid.*, 1933, **29**, 458). Some of Burrage's results, however, are open to criticism, because Foster has shown that the retentivity technique often fails to give even a fair approximation to the true isotherm (*ibid.*, 1936, **32**, 1559).

Discontinuous adsorption has been examined in some detail by Benton and White (*J. Amer. Chem. Soc.*, 1931, **53**, 3301) ; with hydrogen on reduced nickel, iron, and copper, very marked discontinuities were observed. A few other cases have been reported : Simon found discontinuities in the adsorption of nitrogen and hydrogen by dehydrated chabasite (*Z. physikal. Chem.*, 1928, *A*, **132**, 456) ; Bull and Garner found complex, discontinuous relationships between the heat of adsorption and the amount of oxygen and nitric oxide adsorbed by charcoal (*Nature*, 1929, **124**, 409) ; Schuster obtained a discontinuous curve for the adsorption of hydrogen by charcoal (*Trans. Faraday Soc.*, 1932, **28**, 423), Storfer (*Z. Elektrochem.*, 1935, **41**, 868) found stepped curves for the adsorption of nitrogen and methane by graphite, and Ubbelohde and Egerton obtained discontinuous dynamic isotherms for the adsorption of hydrogen by charcoal at liquid-air temperatures (*Proc. Roy. Soc.*, 1932, *A*, **134**, 512). The very large steps in the isotherms of carbon tetrachloride and benzene on plane surfaces of mica (Bangham and Mosallam, *ibid.*, 1938, *A*, **165**, 553) are probably of a different type; it seems possible that they may be explained in terms of the completion of molecular layers.

There is then considerable evidence of the discontinuous nature of adsorption processes, but since some of it is unreliable, there has been a tendency for the whole phenomenon to be regarded with suspicion. The present investigation was therefore begun in order to obtain reliable data by an independent method, and in addition to affording new evidence for the existence of discontinuous adsorption, it has shown that the phenomenon is general.
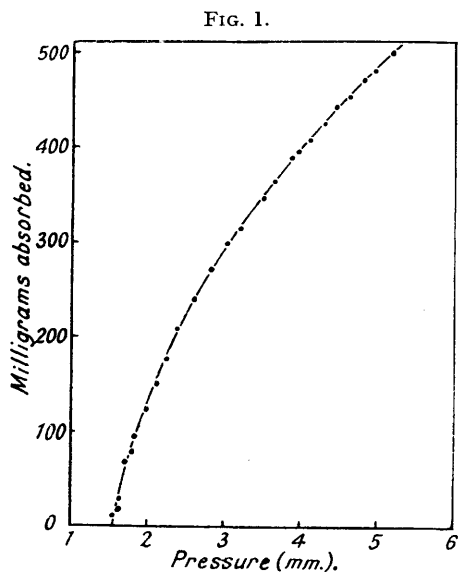
EXPERIMENTAL.

Method.—The principle of the method is that adsorption is measured by observing the rise or fall of a " hydrometer " floating in mercury and carrying the adsorbent in the pan. A detailed account of the technique has already been given (*loc. cit.*), but as the reality of the discontinuities depends upon the exactness of the experimental method, a few possible sources of error must be discussed.

It was found that if the temperature of the thermostat bath was changed by 1°, the level of the float was changed by 0·320 cm. (due to change of density of the mercury); hence a temperature change of 0·01°, which was the maximum variation registered by a Beckmann thermometer, would change the level of the float by 0·03 mm., which is just about the limit of accuracy of estimating the level. The error in the calculated amount of adsorption introduced by temperature changes, could not, therefore, be more than 0·5 mg., and even in the most unfavourable cases it would require an error at least ten times greater than this to explain the deviation of points from smooth curves.

Further possible sources of error might arise from the sticking of the float or inaccuracy of the manometer. When the manometer was calibrated against an oil manometer, however, no appreciable deviation from a straight line was obtained, so the maximum error (0·02 mm.) attributable to the second possibility is far too small to account for the discontinuities. Sticking of the float seemed unlikely, because not only could it be seen to oscillate about its equilibrium

position, which could be reproduced, but also if sticking had occurred the experimental points would have been displaced to the opposite side of the smooth curve from that on which they were observed to lie in many cases. However, an experiment was devised to see whether the technique was capable of giving a smooth curve in a case where discontinuities could not possibly be present. A vapour-pressure curve for mixtures of sulphuric acid and water was determined in exactly the same way as for an adsorption isotherm. A little 80% sulphuric acid was placed in the pan of the float, and after evacuation of the system the acid was allowed to absorb water vapour by opening the apparatus to the storage system for an instant. The curve obtained (Fig. 1) shows conclusively that the technique is sound, and it must therefore be concluded that the discontinuities in the curves given later are not due to experimental error.

Adsorption of Water Vapour by Silica Gel.— The gel was a fine-grade commercial sample. Equilibrium was established fairly rapidly, although there was a slight drift which persisted even after flushing out at a high temperature. The drift was ignored and readings were taken about ½ hr. after admission of the vapour charge. Parts of the isotherm are given in Fig. 2, where some of Allmand and Burrage's results, obtained for a similar system by the retentivity method,

Fig. 1.

Vapour pressure curve of sulphuric acid in water mixtures.

Fig. 2.
Adsorption of water vapour by silica gel.
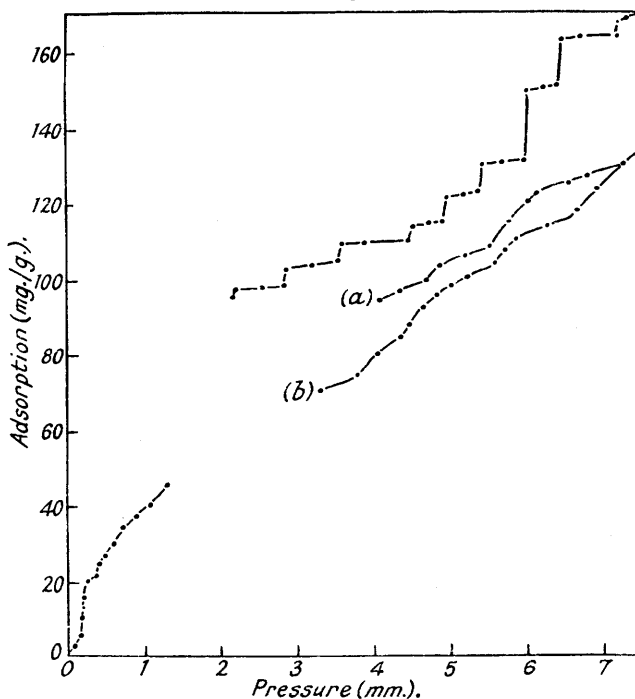

(*a*) Sorption.   (*b*) Desorption.
(*The upper stepped curve is from the results of Allmand and Burrage by the retentivity method.*)

are given on the same scale. The curves are definitely discontinuous but rectangular steps are certainly not present.

Adsorption of Carbon Tetrachloride by Silica Gel (Fig. 3).—Points on the adsorption (V) and the desorption (I, II, III, and IV) curves were determined with the same sample of silica gel. Special attention was paid in this case to the attainment of equilibrium. For curve I the points were determined 1 hr. after the vapour charge had been admitted, for II and III the time intervals were 15 and 10 mins. respectively, for IV and V readings were taken when the pressure had remained constant for 10—15 mins. Drift appeared to be absent with this system : in one case a reading taken 20 mins. after admission of the vapour charge remained unchanged after 15 hours.

FIG. 3.
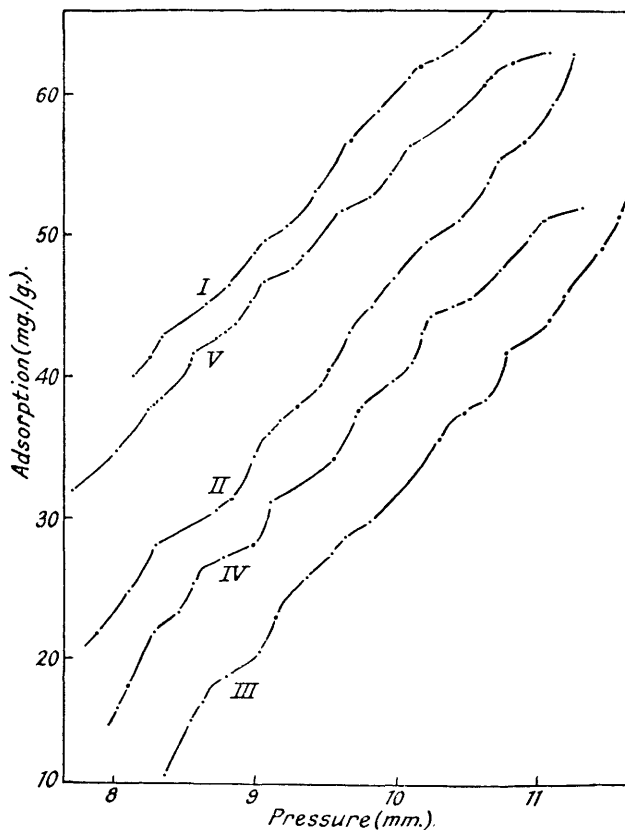
Adsorption of carbon tetrachloride by silica gel.

The magnitude of the breaks in Fig. 3 appears to be approximately constant. The curves are not reproducible in detail, and although there is some indication that the breaks are occurring at the same pressure in every case, too much emphasis should not be placed on this point. There is little doubt that the breaks actually exist, but there is an insufficient number of points to determine the exact course of the curve.

Adsorption of Carbon Tetrachloride by Sugar Charcoal.—A sample of pure sugar charcoal, prepared from " AnalaR " sucrose, was activated in moist oxygen at 800°. It was placed in the apparatus and flushed out with carbon tetrachloride first at room temperature and then at a higher temperature. During the latter flushing out a slight white film was deposited on the cold parts of the apparatus. Microanalysis showed it to consist chiefly of mercurous chloride, formed presumably by reaction between mercury vapour, carbon tetrachloride, and water held on the charcoal surface.
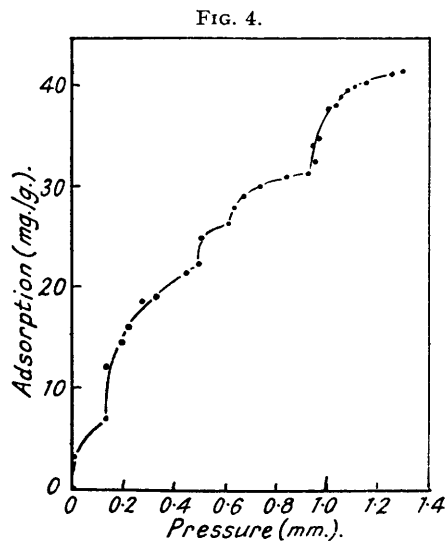
Adsorption and desorption curves for carbon tetrachloride are given in Figs. 4 and 5

respectively. The adsorption curve is particularly convincing because of the large number of points measured. The curves were not reproducible in detail, although it was often possible to go back and put in an extra point, provided the pressure change involved was not too great. Equilibrium was established within 30 mins. and no drift was observed.

FIG. 4.

Adsorption of carbon tetrachloride by sugar charcoal.

Adsorption of Water Vapour by Sugar Charcoal. —The charcoal was the same sample as that used in the previous experiment, and since it had been thoroughly flushed out and not exposed to air at the completion of the run with carbon tetrachloride it is probable that it contained very little chemisorbed oxygen.

The curve given in Fig. 6 is a composite one. The experiment was carried out before the adjustment device had been fitted, and so it was necessary at two stages to open the apparatus and remove a little of the charcoal, so that the float could be brought back to a position with the lower end of the stem in the surface of the mercury. The short vertical lines on the curve show where these adjustments were made. After each adjustment the charcoal was thoroughly flushed out and the run continued, and although the overlapping parts of the curves did not agree in detail, the general direction of the curve remains the same. Even the flat portion of the curve shows well-marked discontinuities when plotted on a larger scale (see the upper curve in Fig. 6).

Adsorption of Water Vapour by Silica Gel.—The adsorption isotherm of water vapour on silica gel was determined with a slightly modified form of the apparatus. By filling the apparatus with vacuum-pump oil instead of mercury, its sensitivity was increased 15-fold. A preliminary

FIG. 5.
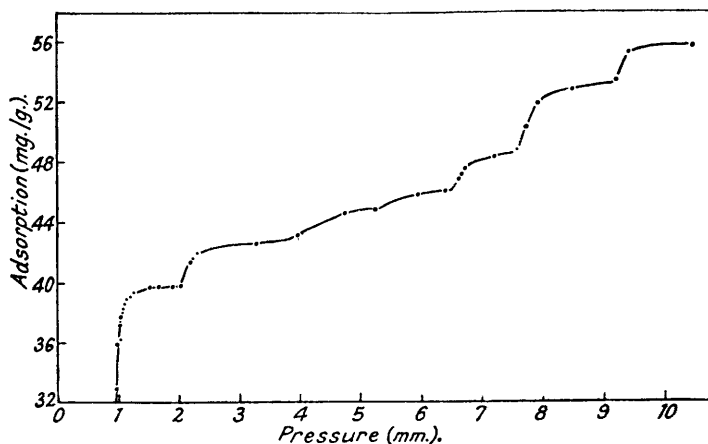
Desorption curve for carbon tetrachloride and charcoal.

determination of the solubility of water vapour in the oil showed it to be so small that no errors could arise from this cause.

A " hydrometer " of the same type as that used with mercury could not be made to float in a stable position in oil, and so the form adopted was that shown in Fig. 7. The vapour had to pass through the hollow stem to reach the adsorbent, but this could not have appreciably

delayed the setting up of equilibrium. The float carried a load of **13** g. and had a sensitivity factor of **13** mg./mm. Sticking was prevented by the film of oil between the float and the outside tube.

FIG. 6.
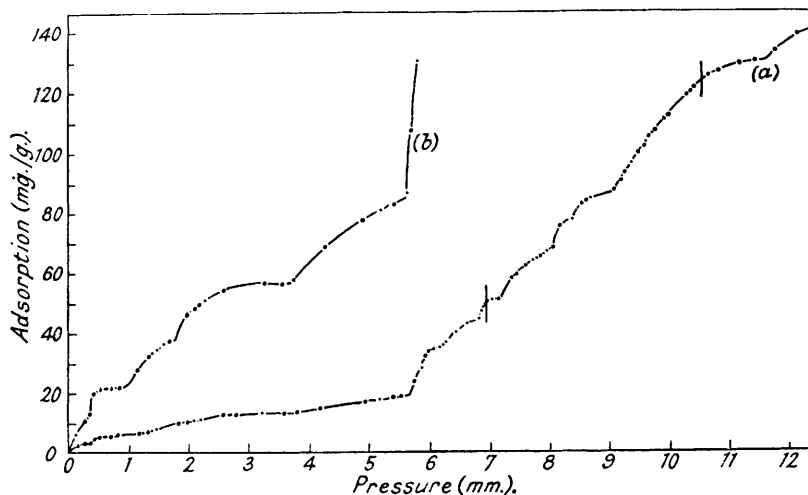
Adsorption of water vapour by charcoal : curve (b) *is the same as curve* (a) *but is drawn to a larger adsorption scale.*

The adsorbent was a sample of the commercial silica gel " Quepric." It was activated by heating in a vacuum at 200° until the pressure had reached a negligible value. As the presence of oil made it impossible to heat the adsorption apparatus, the activation was carried out in a separate tube. At the end of the activation the float and the gel were rapidly transferred to the adsorption apparatus, and the gel was flushed out several times at room temperature.

Several determinations both of adsorption and of desorption isotherms were carried out. The curves were found to be discontinuous but not reproducible in detail. At first, equilibrium was reached slowly, and drift was present, but thorough flushing out reduced it to an insignificant value. In later experiments pressures remained absolutely constant for periods up to $1\frac{1}{2}$ hours after equilibrium had been reached, and in one case the drift overnight was detectable with the oil manometer, but would have been only just outside the probable error of a mercury manometer. Hence it seems that the later curves represent true equilibrium.

One of the later curves is given in Fig. 8, where pressures are expressed in mm. of mercury. The points above 3·8 mm. are desorption points : the others are adsorption points. The precision of the method is such that on the scale of Fig. 8 experimental error is not visible. It will be seen that well-marked loops are present and each loop is quite smooth. They are quite different from the rectangular steps obtained by Allmand and Burrage for a similar system. Arrows have been drawn in Fig. 8 to mark the end of each day's run, and it will be seen that the discontinuities cannot be attributed to drift due to leaving the apparatus overnight.

Adsorption of Chloroform by Chromic Oxide.—Evidence of discontinuous adsorption in the

FIG. 7.
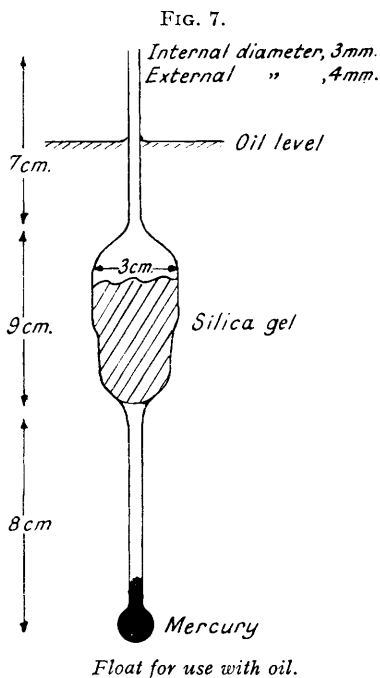
Float for use with oil.

system chromic oxide–chloroform was first obtained in this laboratory by Harbard, using a static method (this vol., p. 19). In order to confirm this fact several experiments were carried out by the present method, with the apparatus filled with mercury again.

A very porous sample of chromic oxide with excellent adsorbent properties was prepared by heating ammonium dichromate. It had a very low bulk density and was easily blown out

FIG. 8.
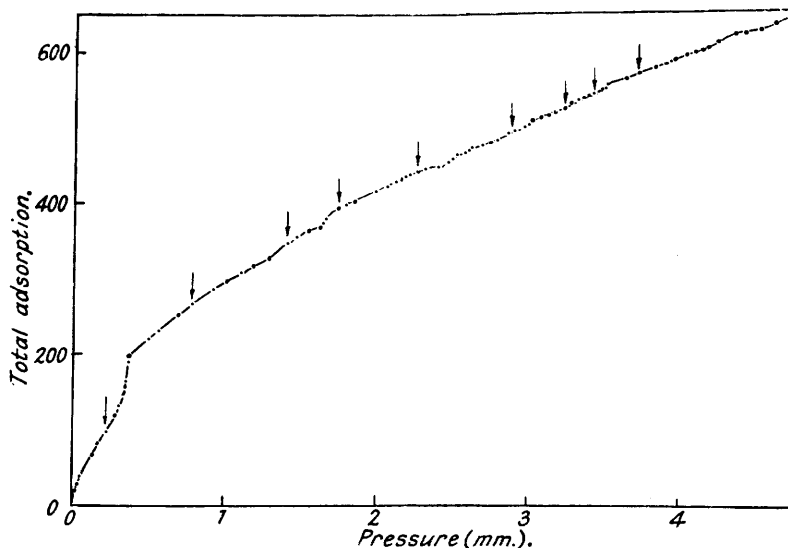
Adsorption of water vapour by silica gel.

of the pan unless great care was taken while the apparatus was being evacuated. The chloroform was dried over calcium chloride, redistilled, and fractionated in a vacuum.

For the first run the oxide was flushed out three times at room temperature with chloroform, and then left overnight in contact with the vapour at 50 mm. pressure. Before the run was

FIG. 9.
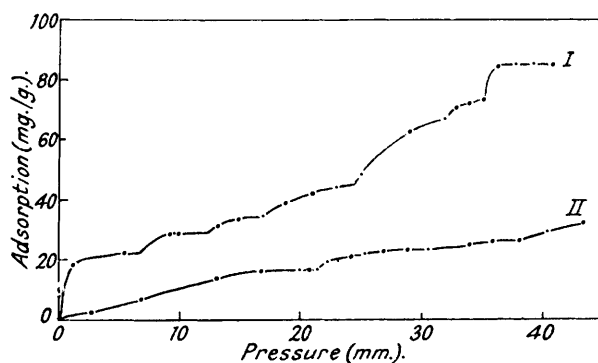
Adsorption of chloroform by chromic oxide.

commenced the oxide was pumped out for $1\frac{1}{2}$ hrs. Equilibrium was established very rapidly : it was quite complete in 5—6 mins. and there was no sign of drift. Readings taken 10 mins. after admission of the adsorbate were constant to 0·2 mm. for 17 hrs.

The result of the first run is given in Fig. 9, I. The breaks extend over comparatively large ranges of pressure. Desorption curves were similar, but were not reproducible in detail.

Curve II in Fig. 9 was obtained after flushing out five times more at room temperature. It confirms the interesting fact, first noticed by Harbard, that flushing out not only

reduces considerably the total adsorption with this system, but also changes the general shape of the isotherm. Some of the smaller breaks seem to have disappeared. In Fig. 10 (in which pressures are expressed in cm.) further effects of flushing out are seen. As far as can be seen the smaller breaks have disappeared. In the flat portion of the curve between 0·5 cm. and 4·5 cm. pressure, only a few points are available, but the vapour was actually added in small successive charges and the float did not move at all. Hence it was not considered worth while to make many measurements in this region. The general shape of the curve has been confirmed by Harbard with the static method.

Adsorption of Ammonia and Water Vapour by Dehydrated Chabasite.—This substance was used in view of Evans's results (*Proc. Roy. Soc.*, 1931, **134**, 97) on its adsorption of ammonia. He found little change in the appearance of the crystals after many hydrations and dehydrations over a period of several months, but as soon as the dehydrated crystals were allowed to adsorb ammonia they were broken down to a microcrystalline powder containing some amorphous material. The heat of adsorption determined with the crystalline solid was abnormally low, since a considerable amount of energy was required to split the crystal lattice, but subsequent determinations on the microcrystalline powder gave normal values.

The reason for the breakdown of the chabasite is clear when its structure is considered (Taylor, *ibid.*, 1934, **145**, 80). The zeolite structure is based on a framework of linked tetra-

FIG. 10.
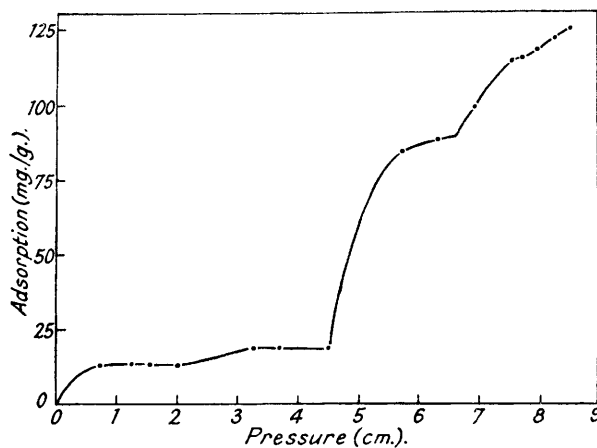
Adsorption of chloroform by chromic oxide.

hedral groups of oxygen atoms arranged about atoms of silicon and aluminium. The framework is rendered electrostatically neutral by the presence of cations (*e.g.*, calcium ions), and the lattice is penetrated by long channels containing water molecules. The stability of the lattice is independent of the presence of water molecules in the case of chabasite. According to the Bernal–Fowler theory, the electron-density distribution in the water molecule is such that the molecule may be considered as a tetrahedron with two positive and two negative corners. The charge distribution in the channels in the lattice of chabasite is similar to this, and consequently water molecules fit into the channels with their negative corners satisfied by cations and their positive corners by oxygen ions. The ammonia molecule, having a different charge distribution and being slightly larger, does not enter the channels so easily, and when water is replaced by ammonia strain is set up and the crystal is shattered.

Hence it is seen that during the process of adsorption of ammonia by dehydrated chabasite, fresh surfaces are constantly being exposed by shattering of the crystals. Piper (*Trans. Faraday Soc.*, 1933, **29**, 538) and Wilkins (*ibid.*, 1932, **28**, 424) have endeavoured to give a general explanation of discontinuous adsorption in terms of the sudden appearance of fresh surfaces due to splitting of the adsorbent, and consequently, if their hypotheses are valid we should expect the adsorption of ammonia by chabasite to exhibit particularly well-marked breaks. Preliminary experiments were carried out to determine if this is so.

A sample of Novia Scotia chabasite was broken into pieces the size of a small pea, and dehydrated by 3 hrs.' evacuation at 100° and a further 12 hrs. at 300°. The colour of the crystals changed slightly, but their external form was unaffected except for a very small amount of

powder which was formed.　The crystals were rapidly transferred to the adsorption apparatus and evacuated to zero pressure at as high a temperature as possible.

The adsorption isotherm of water vapour was first investigated.　Equilibrium was established instantaneously; so rapid was the adsorption, in fact, that even when the apparatus was in direct communication with the reservoir of liquid water the manometer failed to register a
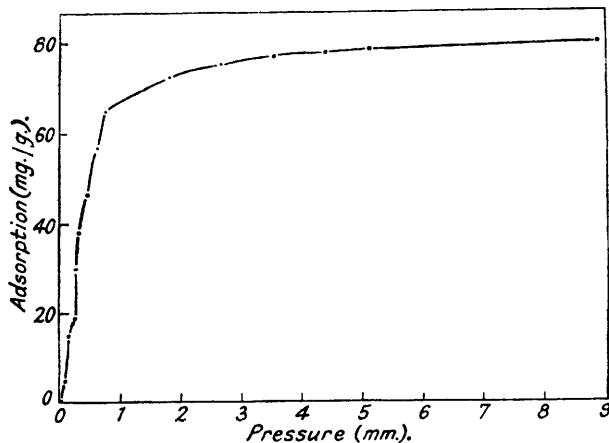
FIG. 11.
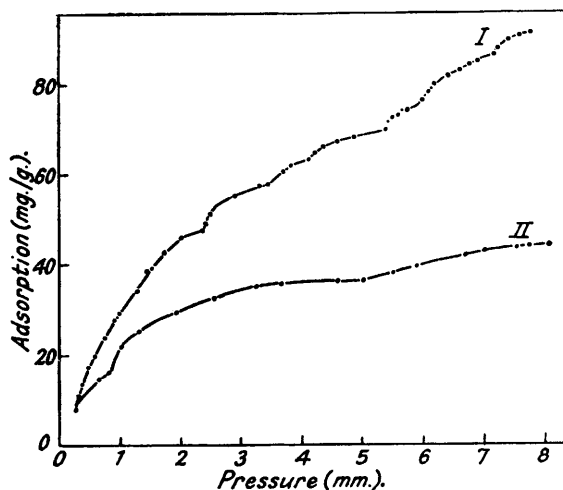
Adsorption of water vapour by dehydrated chabasite.

pressure.　A large amount of water vapour was adsorbed before the pressure began to rise, and since this amount is not known accurately the values for the adsorption in Fig. 11 start from an arbitrary zero.　The isotherm (Fig. 11, curve I) is smooth up to 2 mm. pressure, but

FIG. 12.

Adsorption of ammonia by chabasite.

above this discontinuities begin to appear.　The time required for the establishment of equilibrium was extremely short on the smooth part of the curve, but considerably longer on the discontinuous part.　In no case, however, was it more than 10 mins.　At the end of the run it was found that some of the crystals had crumbled slightly and a very small amount of powder had been formed.　It was not possible to determine a desorption curve because most of the water could not be removed at room temperature, but in view of the slight breakdown of the crystals it seems unlikely that the isotherm is reproducible in detail.

The second determination was of the adsorption isotherm of ammonia on partly dehydrated

chabasite. The ammonia was prepared by dropping concentrated solution on solid potassium hydroxide, and drying the gas with solid potassium hydroxide and metallic sodium. The gas was condensed in a U-bulb containing metallic sodium and immersed in solid carbon dioxide and ether. After fractionation of the liquid ammonia several times, it was allowed to evaporate into a 3 l. glass bulb attached to the storage system. The same sample of chabasite was used and it was evacuated at as high a temperature as possible without being removed from the adsorption apparatus. It was by no means completely dehydrated. The first part of the ammonia isotherm is given in Fig. 12. Equilibrium was reached rapidly at lower pressures (but not as rapidly as with water), but at later stages periods up to 30—40 mins. were required. Breaks occurred on the steep part of the curve, and above 0·75 mm. pressure the curve seems to be continuous. There is no doubt that the crystals were being broken down during adsorption, because at the end of the run they consisted mainly of an extremely fine powder. It seems that drastic breakdown of structure such as this will not give very marked discontinuities.

A final experiment was carried out to measure the adsorption of water vapour on the powder obtained by keeping chabasite in contact with ammonia at 1 atm. pressure for 24 hrs. The results are plotted in curve II, Fig. 11. The small breaks have disappeared, and the total adsorption has decreased, as might be expected, owing to the destruction of the water channels during the disintegration of the crystals.

DISCUSSION.

The preliminary investigation described here has confirmed by a new method the general conclusions of Allmand and Burrage, that adsorption by complex adsorption is a discontinuous process. So far, however, no cases of isotherms exhibiting definite rectangular steps have been found, and no evidence has been obtained that the discontinuous curves can be reproduced in detail. It is hoped to carry out a more exhaustive study of a few typical systems in order to settle these points and to provide data for theoretical considerations.

None of the theories hitherto advanced as explanations of discontinuous adsorption can be regarded as more than tentative. The obvious suggestion that the breaks are due to the existence of areas of different adsorption potential would mean that the surface of the adsorbent is divided into a finite number of regions each possessing a definite surface energy. It is far more likely that there is a continuous variation of adsorption potential from point to point on the surface, and that no particular values predominate. It is true that the surface of, *e.g.*, charcoal is composed of several areas of different catalytic activity, but these areas are associated with chemical rather than with physical sorption, and in any case their number is insufficient to account for the number of breaks observed. The number, magnitude, and irregularity of the breaks also exclude the possibility of their being due to the completion of monolayers of adsorbed gas.

Allmand and Burrage's view (*loc. cit.*), based on ideas of Goldmann and Polanyi, and of Semenoff, is that the breaks are due to the formation of " islands " of sorbate about active centres on the surface of the adsorbent. Concentric rings of molecules are supposed to be built up around active points, and the completion of a ring is marked by a discontinuity. Benton and White's views (*loc. cit.*) are very similar. They consider the formation of concentric rows of molecules on the crystal faces of the adsorbent, starting from the edges and working in towards the centres of the faces. Molecules condensing close together on the surface are assumed to evaporate less readily than isolated molecules. The approximately constant size of the breaks observed by these authors is taken as evidence in support of the theory.

Wilkins suggests that the breaks might be due to adsorbed molecules entering cracks and splitting them open so as to expose fresh surfaces on which further adsorption could take place. It is difficult to see how this theory can be applied if the curves really are reproducible, although Wilkins suggests that the adsorbed molecules may increase the intergranular distances without permanently affecting the structure of the adsorbent. With charcoal the theory can be correlated with the expansion which is known to occur during adsorption. A more serious difficulty is that no reason can be suggested to explain why the sudden increase of intergranular distance should occur at the same pressure for every grain, for unless this happened the breaks would be too small to be observed.

A somewhat similar theory has been put forward by Piper. He suggests that in the neighbourhood of cracks or capillaries, where the lattice of the adsorbent is disarranged, strain may be relieved by the formation of labile linkages between atoms on opposite sides of lattice gaps. These linkages may be broken when gas molecules are adsorbed, and if they happen to be conveniently grouped together the simultaneous breaking of a number of them may result in a drastic rearrangement of the surface to release the strain set up. In this way the pore diameter may be increased or the surface area available for adsorption may undergo a sudden change. The theory is obviously incapable of explaining reproducible discontinuous adsorption.

A theoretical interpretation of the present results cannot yet be given, but the results for dehydrated chabasite are of interest in the light of the theories of Wilkins and Piper. This is the only case where definite proof is available that breakdown of the structure occurs during adsorption. It would be expected, therefore, on the basis of the above theories, that discontinuities would be particularly marked. Actually, the isotherms do not differ greatly from any of the others given here. In fact, the adsorption of ammonia, which gives the greatest amount of disintegration, actually gives a smoother curve than does water, where the disintegration is almost negligible.