A New Technique for the Measurement of Adsorption of Gases and Vapours on Solids.

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A new technique, capable of detecting very small changes of adsorption by a direct-reading, floating balance method, is described. The advantages of this method over others in common use are discussed, and applications suggested.

THREE types of method are available for the measurement of the adsorption of gases and vapours on solids, *viz.*, the static, the dynamic, and the silica-spring technique. Although these are all of great general utility, and the first especially is capable of some accuracy, there is need for a new and more accurate method for specific purposes, and especially for the verification of the discontinuities in the adsorption isotherm such as have been reported by Allmand and his co-workers (*Proc. Roy. Soc.*, 1931, *A*, **130**, 610) but remain largely unconfirmed.

The standard, static method involves passing a known amount of vapour into a vessel containing the adsorbent, and comparing the observed pressure with that which would have been exerted if no adsorption had taken place. The amount of vapour adsorbed is calculated from the simple gas laws. There are several objections to this method, the most serious being (i) that the " dead space " not occupied by the adsorbent cannot be accurately estimated, and (ii) that errors may arise from the fact that different parts of the apparatus may be at different temperatures. The fact that this method is reliable, however, is shown by a whole series of excellent isotherms obtained in Allmand's laboratory.

The McBain–Bakr sorption balance is free from these two objections, but its application to the problem of discontinuity is somewhat limited by its lack of sensitivity. This balance consists essentially of a small bucket containing the adsorbent and attached to a helical silica spring, the whole being enclosed in a sealed system. Adsorption is measured by extension of the spring. A sensitive spring will carry a load of not more than 0·5 g. of adsorbent, and the permissible load can only be increased by making the spring more robust and hence less sensitive. It is true that the sensitivity of the robust spring might be increased by increasing the number of turns, but very long springs are inconvenient in use, quite apart from the mechanical difficulties of their manufacture.

Dynamic methods have been employed for practical purposes such as testing the efficiency of technical adsorbents. A dynamic retentivity method for this purpose, devised by Allmand, Manning, and Burrage (*J. Soc. Chem. Ind.*, 1928, **47**, 372), was modified by Burrage (*J. Physical Chem.*, 1930, **34**, 2202) to give true adsorption isotherms. Foster (*Trans. Faraday Soc.*, 1936, **32**, 1559) has shown, however, that this method is unreliable in some cases. Using a static method, he was unable to obtain definite evidence of breaks in the isotherm, but concluded that there was a possibility of discontinuities of only slightly greater magnitude than the experimental error being present.

Much of Allmand and Burrage's evidence for discontinuous adsorption has been obtained by the retentivity method. In certain cases isotherms were carefully redetermined by a static method in order to verify the existence of discontinuities.

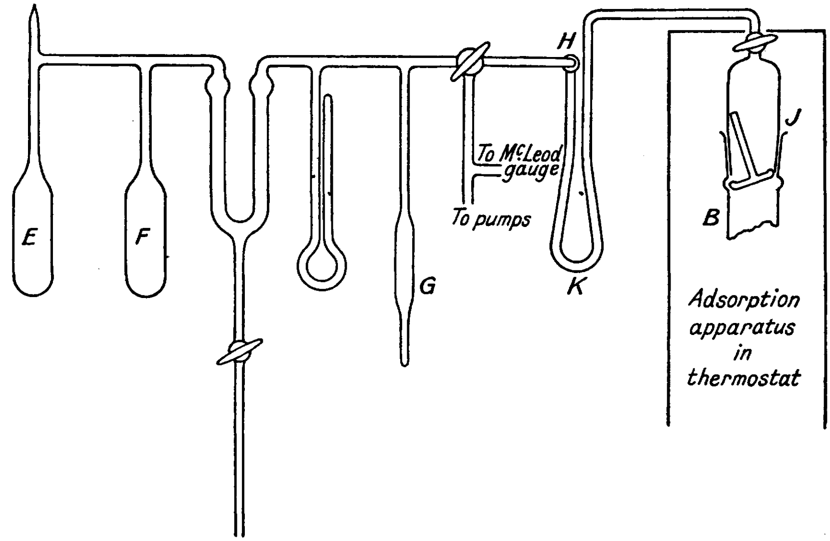
The technique now described was devised in order to establish beyond all possible doubt the existence or non-existence of discontinuities in the sorption process, and to provide a method of sufficient sensitivity to examine the detailed structure of the adsorption isotherm should it be discontinuous.

It was considered advisable to make all observations in a closed system by the use of a self-contained apparatus which could be completely immersed in a thermostat and would be free, therefore, from all errors due to temperature effects. In addition, it was desirable that all errors due to estimation of " dead space " should be avoided; this suggested the suitability of an apparatus of similar type to the McBain balance but of increased sensitivity.

The complete apparatus, which is constructed entirely of Pyrex glass, is shown in Fig. 1. The part to the left of the three-way tap is merely a storage system and will be described later. Adsorption is measured in the apparatus in the thermostat, shown on a larger scale in Fig. 2, where a slight modification, to be described later, is also incorporated. The apparatus consists essentially of a Nicholson hydrometer floating in mercury and carrying the adsorbent in the pan. The hydrometer rises or sinks during adsorption or desorption and the level of a reference mark is read with a cathetometer.

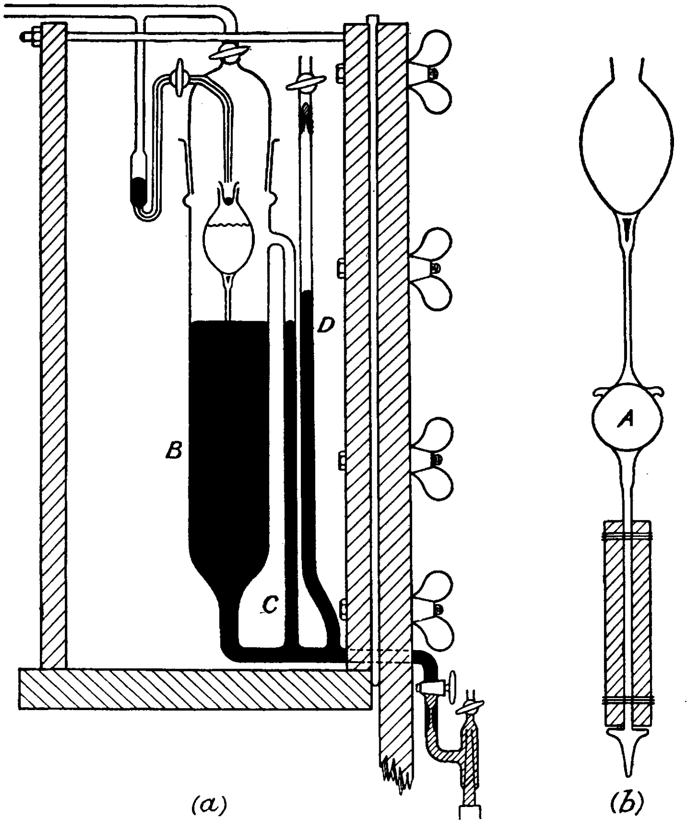
The hydrometer, shown in Fig. 2*b*, is constructed of Pyrex glass. It is weighted with four solid tungsten rods, each 7·5 cm. long and 0·8 cm. in diameter, bound together with iron wire. The small hooks fused on to the hollow glass bulb *A* enable the hydrometer to be easily lifted out of the tube. The diameter of the glass stem is about 1·2 mm., and calibration showed it to be perfectly uniform except at the extreme ends where it is fused to the pan and the bulb. It was found that an increase of weight of 15 mg. caused the hydrometer to sink 1 mm. The reference mark is a pointed platinum wire fused in a capillary just below the pan.

FIG. 1.



General arrangement of apparatus.

FIG. 2.



(a) (b)

The adsorption apparatus.

The hydrometer floats in mercury inside the tube *B* (Fig. 2) of diameter 3·5 cm., the lower end of which is connected to a mercury reservoir through a bubble trap. Owing to the difficulty of estimating the exact level of the mercury in this wide tube, a side tube *C* is provided. The pressure is obtained by difference of levels in *C* and *D*. The top of *D* just below the tap is constricted to a very fine capillary. When the level in the tube falls, a small amount of mercury is left above the constriction, effectively sealing the tube and preventing air or tap grease from entering.

The **T**-shaped glass rod at the top of the tube *B* (Fig. 1) was inserted to overcome a difficulty arising from the existence of two stable positions of flotation of the hydrometer. It was found that if the hydrometer is floating in a stable position with the stem in the mercury surface, it is possible to find a second stable position by pulling the hydrometer out of the liquid until the conical part of the bulb is in the surface. In this position the decreased upthrust due to buoyancy is compensated by the increased surface tension effect due to the increased line of contact between the glass and the mercury. The hydrometer can only be returned to its original position by raising the mercury level until the top of the hydrometer touches the glass rod. The hydrometer will always return to its first stable position as long as the stem remains in the mercury surface, but as soon as the conical part of the bulb comes into the surface, it will take up its second stable position and tapping or shaking will not move it.

The modification referred to above, and shown in Fig. 2, is a device for adjusting the level of the float without opening the apparatus. Mercury is passed into or removed from a small cup at the top of the pan by suitably adjusting the pressures on each side of the tap. This device was installed later in order to overcome the disadvantage of the somewhat limited range over which measurements could be made. By the use of this device complete isotherms can be measured. In the modified apparatus the end of the capillary tube which delivers the mercury serves the same purpose as the glass rod mentioned in the previous paragraph.

The thermostat bath is constructed of wood with ¼″ plate-glass sides. The right-hand wall, to which the apparatus is rigidly attached, is screwed to the bench, and the body of the bath slides away from this wall when adjustments have to be made in the apparatus. A water-tight joint is obtained by means of pressure tubing attached to the body of the bath and fitting into a groove in the fixed wall, the two parts being held together by the bolts and wing nuts shown in the diagram. The thermostat is controlled by means of a hot-wire vacuum switch, the variation being only 0·01°. The isotherms were measured at 20°.

The storage system for the adsorbate (Fig. 1) consists of reservoirs *E* and *F* for holding the liquid adsorbate, a tube *G* for measuring roughly the amount of liquid passing over into the adsorbent, and a mercury manometer. The mercury cut-off is used to prevent the adsorbate from remaining for long periods in contact with the tap grease (Apiezon L).

The storage system and adsorption system are connected by a glass tube with ground joints at *H* and *J*. The loop at *K* makes the apparatus sufficiently flexible to take up any strains which may arise during connexion.

The third tube of the three-way tap leads through a liquid-air trap to a mercury-vapour pump backed by a " Hyvac " pump : a side connexion goes to a McLeod gauge for indicating the extent of evacuation.

Discussion of Method.—The float used in the preliminary work carries a load of 6 g. of adsorbent and has a sensitivity factor of 15 mg. per mm. The level of the reference mark is read to 0·01 mm. with a " Cambridge " travelling microscope. The float has but little tendency to stick, but if it does, slight tapping will cause it to oscillate about its equilibrium position and finally come to rest within 0·01 mm. of its mean position. The maximum uncertainty in estimating the equilibrium position is 0·02 mm., corresponding to 0·3 mg. Thus the method is capable of detecting a change of weight of the adsorbent of 1 part in 20,000. The sensitive silica springs described by King, Lawson, Tapp, and Watson (*J. Sci. Instr.*, 1935, **12**, 249) will detect a change of about 1 part in 7000 under comparable conditions, so the increased sensitivity of the present apparatus, together with its much greater robustness, makes it specially suitable for the present work. By making the bulb *A* of the float larger, and therefore making it possible for the float to carry a larger load, the sensitivity could be increased even further. The float used in the present work could be made to carry 25 g. and so be capable of detecting a change of weight of about 1 part in 100,000.

A further advantage of the present method over the McBain balance is that it allows observations to be made on a truly representative sample of the adsorbent. One can never be certain that quantities as small as 0·5 g. or less are really representative of the bulk of the substance, since any small amount of foreign material accidentally introduced forms a considerable proportion of the total weight.

For most purposes the presence of mercury vapour in the system is immaterial Coolidge has shown that at the ordinary temperature the maximum amount of mercury vapour adsorbed by charcoal is 0·3 mg. per g. of adsorbent. In any case, mercury manometers have been used by most other workers, so their apparatus has always contained mercury vapour.

Contamination of the mercury surface is a possible source of error, but preliminary experiments showed that this was not serious. The mercury was distilled before use, but even so, a visible film formed on the surface after standing for some time in the air. In the presence of vapours at low pressures, however, the film was not formed, and the condition of the surface appeared to be constant over long periods. Any change which might have taken place had little effect on the position of the float, although this may account for the fact that the first point determined after the apparatus had been allowed to stand for some time was sometimes unreliable.

The least sensitive part of the new technique is the measurment of pressure. For purposes requiring greater sensitivity we have used an oil manometer, and comparison between this and the mercury manometer shows that the latter is accurate to within 0·02 mm. if care is taken in reading the cathetometer.

Generally, the adsorbent is baked out before introduction into the apparatus. Even with charcoal, this is found to be sufficient if followed by " flushing out " with carbon tetrachloride, but where the adsorbent has to be baked out at a high temperature within the apparatus, it may be contained within a platinum cup and heated by means of an induction furnace. The boiled out liquid adsorbate was introduced into the reservoir *E* and frozen by means of solid carbon dioxide and ether. The air was then pumped off, and the system baked out. The liquid was then distilled into *F* and any air liberated pumped off. This process was repeated several times until all dissolved air had been removed.

Meanwhile the pan of the float was filled with adsorbent and the weight was adjusted with glass beads. The connecting tube to the storage apparatus was placed in position. The mercury level in *B* was lowered until the whole of the float was exposed, and the apparatus was then evacuated and baked out. It is very important to carry out this operation thoroughly with the whole surface of the float exposed, otherwise air carried down into the mercury on the surface causes trouble. If the float touches the side of the tube beneath the mercury surface, the film of air causes it to stick, but if this film is removed there is no trouble from sticking.

When the out-gassing had been completed, the mercury level was raised, and the adsorbent flushed out with adsorbate. After the thermostat had been placed in position and the system allowed to come to thermal equilibrium, the first reading was taken. A small amount of vapour was then admitted, and when equilibrium was reached, a second reading was taken. Further quantities of adsorbate were added, and the process repeated. For determining the desorption isotherm, the adsorbent was charged up to the highest pressure, and small amounts of adsorbate were removed by opening the system to the pump for an instant.

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