The Sorption of Water Vapour by Active Carbon.

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A detailed study has been made of sorption isotherms for water vapour on non-porous, heat-treated channel black of known specific area, and on a number of specimens of active carbon.

For channel black or active carbon the main rise of the sorption isotherms up to points where they bend corresponds to unimolecular adsorption. The region of multimolecular adsorption in a direct sorption process extends up to high relative pressures, approaching 0·95. Capillary condensation is insignificant for the specimens of active carbon studied.

Views being developed in this laboratory on the mechanism of adsorption of water vapour by carbon absorbents, and related to a hypothesis of the principal rôle played by hydrogen bonds in such adsorption, are expounded. The experimental results are shown to be in agreement with these views.

The shape of the isotherm for the sorption of water vapour by active carbon differs markedly from that for sorption of organic vapours. Up to relative pressures of 0·4—0·5 (p/p_s, where p is the actual pressure of the vapour and p_s is the saturated vapour pressure), water vapour is adsorbed by active carbon only to a very small extent. At higher relative pressures a sharp rise occurs in the sorption and desorption branches of the isotherm which form a hysteresis loop typical for water vapour sorption (Dubinin and Zaverina, *Zhur. fiz. Khim.*, 1947, **21**, **1373**).

All workers, especially those of the American school, explain the sharp rise in these branches by a process of capillary condensation of the water vapour. On the basis of such views methods for calculating the distribution of the volume of pores in active carbon as a function of their radii have become common (Wiig and Inhola, *J. Amer. Chem. Soc.*, **1949**, **71**, **561**; Inhola and Wiig, *ibid.*, p. 2069). Work conducted jointly by the Sorption Processes Laboratory of the Institute for Physical Chemistry and the Adsorption Laboratory of the Moscow State University in the last two years has necessitated a substantial revision of these accepted views. Experimental investigations included a comparative study of the isotherms of the sorption and the desorption of water vapour by porous and non-porous carbon adsorbents whose surface could not have differed to any extent in chemical properties. The theoretical generalization expresses the views that have been crystallizing in the two laboratories mentioned above.

Experiments were made with non-porous channel blacks with spherical particles and a number of specimens of active carbon among which all types of pores were developed sufficiently. The adsorbents were heat-treated at 950°. Sorption scales employing the vacuum method (Dubinin and Zaverina, *Acta Physicochim. U.R.S.S.*, **1936**, **4**, **647**) were used for obtaining sorption and desorption isotherms for benzene and water vapour at 20°.

Fig. 1 shows the isotherms for the sorption and desorption of benzene vapour by two types of heat-treated channel blacks: C-1, a powder, and C-2, briquetted without the use of binding agents. In the region of adsorption up to $p/p_s = 0{\cdot}78$ the values for adsorption and desorption are well satisfied by one curve. The rise in the curves at higher p/p_s values is mainly due to the capillary condensation of benzene vapours in the spaces formed by the touching particles of channel black.

Fig. 2 gives a linear representation of the experimental results for the adsorption of benzene vapour by powdered and by briquetted channel black at 20°, according to Brunauer, Emmett, and Teller's isotherm equation (*J. Amer. Chem. Soc.*, **1938**, **60**, 309). The volume of gas needed to form an unbroken monolayer on the channel black calculated from the equation constants is $a_m = 0{\cdot}365$ mmole/g. Assuming the most plausible value of the molecular area of benzene in a monolayer to be $\omega = 46{\cdot}5$ Å^2 (after Kiselev, Karnauhov, and Khrapova, *Doklady Akad. Nauk S.S.S.R.*, **1953**, **92**, 361), we find that the specific area of the channel black will be $s = 103$ m.^{2}/g. Direct measurements using an electron microscope, carried out by Radushkevich and Lukjanovich, gave the figure $s = 98$ m.^{2}/g. Hence, the channel black studied may be considered a non-porous carbon adsorbent.

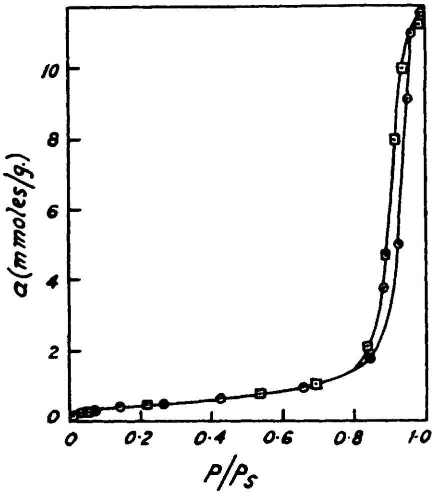


FIG. 1. *Isotherm for the sorption,* ○, *and desorption,* □, *of benzene vapour on channel black at* 20°.

FIG. 2. *Isotherms for the adsorption of benzene vapour at* 20° *in linear form* : ○, *channel black powder*; □, *channel black briquettes*; *black symbols, desorption points.*

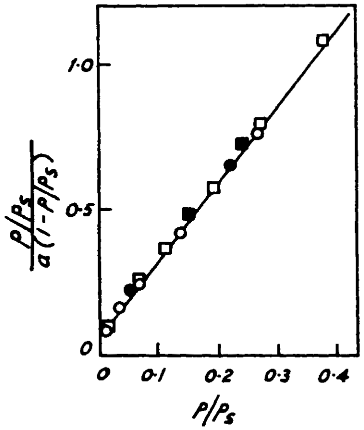


FIG. 3. *Isotherms for the sorption and desorption of water vapour on channel black at* 20° : ○, *adsorption*; □, *desorption.*

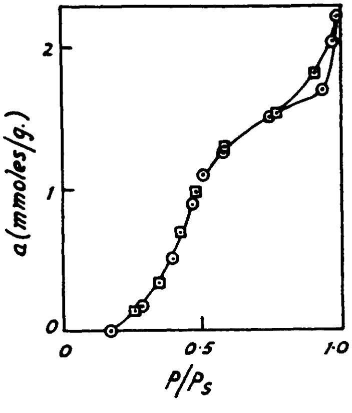


Fig. 3 shows the isotherms for the sorption and desorption of water vapour by channel black at 20°. At low equilibrium pressures there is but little adsorption of water vapour. In the medium range of relative pressures the adsorption is reversible and, as in the case of active carbon, a sharp rise of the isotherm branch is observed. The change in the curve, at a relative pressure of 0·55, corresponds to an adsorption value of a = 1·20 mmoles/g. As the maximum sorption value is approached, there is a rise in the isotherm again, a hysteresis loop being formed by the sorption and desorption branches in this range of relative pressures.

According to Harkins and Jura (*J. Amer. Chem. Soc.*, 1944, **66**, 1366) the molecular area in an unbroken monolayer of water is 14·8 Å^2. The specific area of channel black being 103 m.^{2}/g., the filling of the monolayer corresponds to an adsorption value of a_m = 1·15 mmoles/g. This figure coincides almost exactly with the termination of the main rise of the isotherm and its break at a = 1·20 mmoles/g. Thus, for channel black on the average, only unimolecular adsorption is observed in the range of relative pressures up to 0·55.

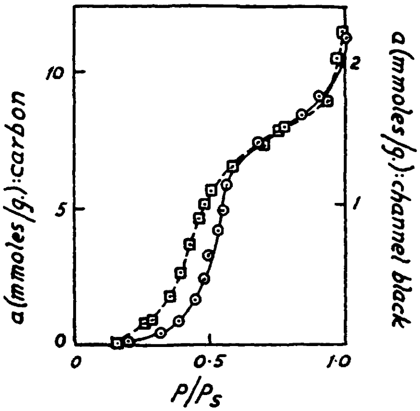


FIG. 4. *Reduced isotherms for water vapour sorption at 20° on channel black* (□) *and active carbon* 1 (○).

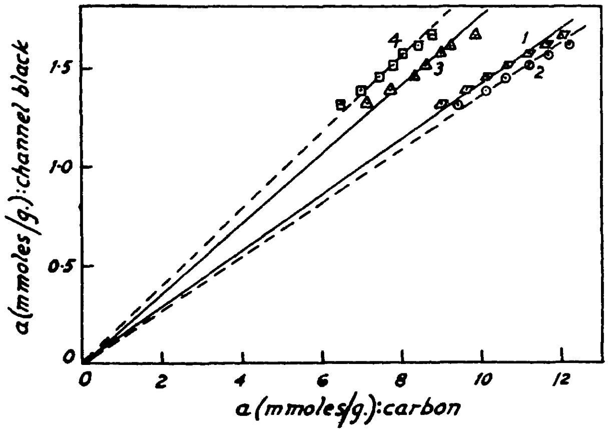
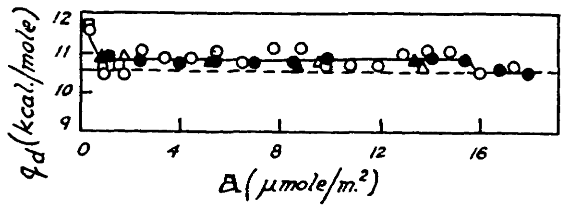


FIG. 5. *The relation of water vapour sorption values at 20° on channel black and active carbons* 1 *and* 4 *at similar equilibrium pressures.*

FIG. 6. *The relation between the differential heat of adsorption and the adsorption value for channel black.*



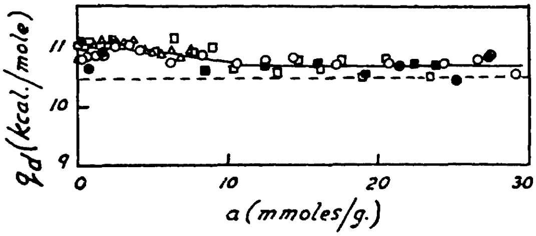


FIG. 7. *The relation between the differential heat of adsorption and the adsorption value for active carbon.*

Multimolecular adsorption at higher pressures is complicated in the vicinity of the saturation point by capillary condensation of water vapour in the spaces between the spherical particles of channel black in contact.

Fig. 4 shows, by way of illustration, the sorption branches of the isotherms for water vapour on channel black and active carbon 1, different scales being used for the y-axis. The regions of sharp rise are moved somewhat, owing to minor differences in the surface properties of active carbon and channel black. The points where the curves bend, both for soot and for active carbon at p/p_s = 0·55, evidently correspond to the completion of the formation of a continuous unimolecular adsorption layer. At this point, the properties of the surfaces of both channel black and carbon for all practical purposes become identical, and the adsorption isotherms shown coincide in the range of relative pressures from 0·55 to 0·95 in which adsorption is multimolecular.

The concurrence of the isotherms shown in the range of relative pressures mentioned points to their identity. The criterion for correspondence of the isotherms is a linear relation between the quantities of water adsorbed on channel black and on carbon at identical equilibrium pressures, it being necessary that the straight lines pass through the origin. This requirement is fulfilled for the carbons studied, as may be seen in Fig. 5.

The coefficients of affinity of the isotherms show how much larger the specific area of the carbons is than that of channel black. In Table 1 the calculated values of the affinity coefficients and the specific areas of the active carbons are listed.

TABLE 1. *Affinity coefficients of the isotherms and specific areas of the active carbons.*

Adsorbent	Affinity coefficient of the isotherms (K)	Specific area, s (m.^{2}/g.)
Channel black	1·00	103
Carbon 1	5·15	530
„ 2	5·75	590
„ 3	7·08	730
„ 4	7·42	765

Another characteristic feature of the adsorption of water vapour by channel black and active carbon is the closeness of the values of the differential heat of adsorption and the heat of condensation of water vapour in the volume phase over practically the entire region of fillings. The charts contain curves of the heat of differential adsorption for channel black (Fig. 6) and active carbon (Fig. 7), based on direct calorimetric measurements by Avgul, Dshigit, Kiselev, and Shtsherbakova (*Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 105). The heat of condensation level is indicated by a broken line.

According to the views held in our Laboratory the sharp rise of the adsorption branch of the isotherms for water vapour on carbon adsorbents is related to the formation of a condensed unimolecular adsorption layer, in which process the main rôle is played by the hydrogen bonds (Avgul, Dshigit, and Kiselev, *ibid.*, 1952, **86**, 95; Baring and Serpinsky, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1953, **6**, 957; Dubinin and Serpinsky, *Doklady Akad. Nauk S.S.S.R.*, 1954, **100**, No. 2). It is important that the nature of the surface of the adsorbent should be taken into account in considering a possible mechanism for sorption of water vapour.

In our experiments, after heat-treatment at 950°, the active carbons and channel black were brought into contact with atmospheric oxygen. Consequently, as a result of activated adsorption or chemisorption, surface oxides were formed which could not be destroyed during the preliminary evacuation of the carbons at 450°. It may be assumed that in the region of low equilibrium pressures the adsorption of water vapour is mainly due to the formation of hydrogen bonds between the adsorbed molecules of water and the surface oxides of the carbon adsorbents (Avgul, Dshigit, Kiselev, and Scherbakova, *loc. cit.*). The relatively low energy of the hydrogen bond results in low adsorption values.

The adsorbed water molecules serve as subsidiary adsorption centres of a special kind which are capable of attaching other molecules by means of hydrogen bonds. As a result of this, with increasing pressure, two-dimensional islands of the condensed phase appear on the carbon surface, formed by the water molecules retained by the hydrogen bonds. The probability that this process will take place will grow with increasing pressure, within certain limits, because of the growth of the number of adsorption centres. The islands merge when the pressure becomes sufficiently large, and a single condensed unimolecular layer is formed. The sharp rise of the isotherm in the range of medium relative pressures is, evidently, a result of this peculiar process of forming islands of two-dimensional liquid which continues until the islands merge.

There are two factors which it is essential to consider when dealing with the problem of the stability of these complexes of associated water molecules formed on the surface of carbon adsorbents. The first is the surface oxides which serve as primary adsorption centres. The relatively weak adsorbent field, in this case resulting mainly from dispersion forces, is the second. Whereas in the gaseous phase the water molecules are not associated since the energy of thermal motion is large enough to disrupt any complexes which may be formed, yet in the surface layer, on the other hand, the field of the adsorbent stabilises any complexes which may be formed and they do not fall apart (Dubinin and Serpinsky, *loc. cit.*).

Further increase of relative pressure after a condensed unimolecular layer has been formed is accompanied by multimolecular adsorption of water vapour, which is complicated by a process of capillary condensation when there is a favourable porous structure of the active carbon. With those active carbon specimens which were studied, capillary condensation is possible only in the region lying beyond the main rise in the sorption isotherms, which corresponds to the formation of a condensed monolayer. That multimolecular adsorption or capillary condensation plays the main part in the sorption of water vapour at relative pressures exceeding 0·55, follows from the maximum values for sorption per square metre of surface of active carbon. In the case of capillary condensation, at a relative pressure of 1, the volume of the filled pores is the main factor determining the maximum sorption capacity. It is difficult to conceive that this volume should be proportional to the surface area of the adsorbent. On the other hand, if the main rôle is played by multimolecular adsorption, the difference between the absolute values for the maximum sorption capacity of various specimens of carbon must be very small. In Table 2, the results of the corresponding calculations made on the basis of the experimental data are given.

TABLE 2. *Maximum sorption capacities per unit of surface area of active carbons.*

Adsorbent	Specific area s (m.^{2}/g.)	Maximum sorption capacity a_s (mmoles/g.)	$\mathfrak{a}_s = a_s/s$ (mmoles/m.^{2})
Channel black	103	2·21	0·021
Carbon 1	530	11·3	0·021
,, 2	590	12·6	0·021
,, 3	730	14·9	0·020
,, 4	765	15·8	0·021

The practical identity of the maximum values for water-vapour sorption for non-porous soot and for the specimens of active carbons studied indicates that in the direct sorption process the region of multimolecular adsorption extends up to high relative pressures that approach unity. Capillary condensation can have played only a very small part in our sorption experiments.

In the light of the results which this study has produced, the region of relative pressures in which capillary condensation of water vapour in the pores of active carbon in the direct sorption process is possible, is shifted into the region of higher relative pressures. The main rise of the sorption branch of the isotherm is not due to capillary condensation, but is a result of the process of formation of a condensed unimolecular adsorption layer, *i.e.*, a stage which precedes capillary condensation. It should be noted that it is possible, as in the case of the carbon specimens studied, that given the proper porous structure of the active carbon, the completion of the formation of a condensed adsorption layer does not involve any noticeable bend in the sorption branch of the isotherm because of a superimposed process of capillary condensation.

The complexity of the sorption process for water vapour over the entire range of equilibrium relative pressures makes a simple approach to a quantitative analysis of the whole sorption branch of the isotherm rather unpromising. Registering the maximum for unimolecular adsorption is of no real interest in the case of active carbons because the volumes of the micropores are filled at maximum sorption. Consequently, we shall restrict ourselves to the region of unimolecular adsorption which, for active carbons, corresponds to adsorption values up to 10 mmole/g. (Dubinin and Serpinsky, *loc. cit.*). This region includes the beginning of the isotherm, the transition to the sharp rise of the sorption branch, and a substantial part of the rapidly rising curve, *i.e.*, all that is most characteristic for the sorption of water vapour.

Let a_0 be the number of primary adsorption centres, expressed in mmoles/g. If a

mmoles/g. is the adsorption at the relative pressure of $h = p/p_s$, then the condition for dynamic equilibrium of adsorption will be

$$k_2(a_0 + a)h = k_1 a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The left-hand expression is the probability of adsorption, which is proportional to the total number of primary and secondary adsorption centres, $a_0 + a$, and to the equilibrium pressure h. The probability of desorption on the right-hand side is proportional to the adsorption value a.

If c indicates the ratio of the rate constants k_2 and k_1, then according to (1) the equation of the adsorption isotherm, true only for the main region of unimolecular filling of the surface, will be

$$a = a_0ch/(1 - ch) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

At relative pressures, for which $ch \ll 1$, the adsorption value is proportional to the pressure. In the vicinity of $h = 1/c$ a sharp rise of the isotherm branch occurs. In keeping with the assumptions made at the outset, equation (2) does not take the maximum of adsorption into account and is valid only for $h < 1/c$. In the linear form, the equation of the adsorption isotherm becomes

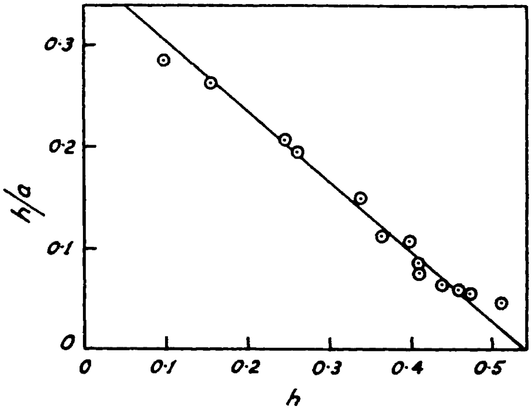


FIG. 8. *Adsorption isotherm for water vapour in linear form for carbon* B2 *over a range of adsorption from* 0·15 *to* 10 *mmoles/g.*

$$h/a = 1/a_0c - h/a_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

An example is shown on Fig. 8, which gives a linear representation of the adsorption branch for water vapour on active carbon B2 with acid surface oxides at $a < 10$ mmoles/g. ($a_s = 26{\cdot}4$ mmoles/g.) according to experiments by E. D. Zaverina. The experimental points are generally well satisfied by a straight line. For the carbon B2, $a_0 = 1{\cdot}43$ mmoles/g. and $c = 1{\cdot}85$. The equation may be used up to $a = 9$ mmoles/g. Thus $a' \gg a$.

For a specimen of active carbon with a surface of the usual type, not containing any acid surface oxides, $a_0 = 0{\cdot}41$ mmole/g. and $c = 1{\cdot}77$. In the case of heat-treated channel black we obtained $a_0 = 0{\cdot}17$ mmole/g. and $c = 1{\cdot}78$. The values of the constants a_0 correspond to the content of chemically combined oxygen in the carbon adsorbents listed. The constants c are confined to a relatively narrow range which indicates that the heat of adsorption entering into the expression for the constant c does not vary substantially for the adsorbents studied. Consequently, in all these cases adsorption depends on forces of one and the same kind, which we believe to be the hydrogen bond. Hence, the values of the constants of the equation of the adsorption isotherm (2) are physically justified.

The value for the heat of condensation of water vapour λ in the volume phase depends mainly on the hydrogen bond. As was mentioned above, according to experiments by Avgul *et al.* (*loc. cit.*, 1953), the differential heat of adsorption q_a of water vapour on channel black and active carbons is close to the heat of condensation for water over the entire range of sorption values ($q_a \approx \lambda$). This is weighty evidence and additional proof that the forces of interaction between the water molecules in the liquid phase and the forces of adsorption are of an identical physical nature. At the same time it indicates that the porous structure of carbon does not, to any considerable degree, influence the extent of adsorptional interaction, in contrast to the case where the dispersion forces are involved. The natural explanation of this fact is the chemical nature of adsorption interaction—the effect of the hydrogen bond.

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