

Reprinted from Vol 50 1971

FUEL

**the science of
fuel and energy**

IPC Science and Technology Press Ltd

Water adsorption on coals

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Adsorption of water on six coals of rank varying from anthracite to HVC bituminous has been studied at 0°C and 20°C. From BET plots, the calculated surface areas vary from 17.5m²/g for the low volatile bituminous coal to 82.5m²/g for the HVC coal of 45.4% volatile matter. The fraction of the total surface area (measured by carbon dioxide at 25°C) covered by water in a monolayer varies from 12% for the low volatile bituminous coal to 60% for the HVC coal. In the monolayer, water adsorbs on hydrophilic sites provided by oxygen functional groups on the coal surface and by mineral matter. The heat of adsorption of water on the coals is closely equal to the heat of liquefaction (10.6 kcal/mol)* at all adsorption pressures studied, that is above about 0.03 relative pressure. Hysteresis is observed on all the isotherms down to essentially zero relative pressure of water. Reasons for the hysteresis are discussed.

A CONSIDERABLE amount of work has been reported in the literature on moisture sorption on coals¹⁻⁴, charcoals⁵⁻⁷, raw carbon blacks⁸⁻¹⁰ and graphitized carbon blacks¹⁰⁻¹². However, the results and interpretation of the data, even for the same type of adsorbents, have often been at variance with one another. The present study describes moisture sorption on coals varying in rank from anthracite to high volatile bituminous coals. An attempt has been made to offer plausible explanations for the various aspects of moisture sorption on coals.

EXPERIMENTAL

Materials

Six coal samples of 200 × 325 mesh size, varying in rank from anthracite to high volatile bituminous, were used. The samples were the same as used by Walker and Kini¹³ for the determination of the ultrafine surface area of coals. Analyses of the coal samples are given in Table 1.

Table 1 Analyses of coals

Sample number	moisture (%)	Proximate analysis moisture-free (%)				Ultimate analysis moisture-free (%)			Carbon (% d.a.f.)
		Ash	VM	FC	Sulphur	C	H	N	
<i>Anthracite</i>									
1	1.1	8.4	4.0	86.4	0.5	87.1	3.0	Nil	95.2
<i>Bituminous coals</i>									
912	1.1	4.6	18.8	76.6	0.7	85.9	4.5	1.1	90.0
956	1.6	6.3	33.7	60.0	0.6	80.8	5.0	1.1	86.2
888	1.6	3.8	39.0	57.2	0.6	80.4	5.2	1.4	83.6
885	1.9	5.4	37.6	57.0	0.8	75.0	5.2	1.4	79.2
6	1.9	7.6	45.4	—	2.7	67.2	5.5	—	72.7

* 1 kcal = 4.186 kJ

Sorption studies

Moisture sorption was followed gravimetrically using a helical quartz spring having a sensitivity of 2×10^{-5} g. The details of the experimental technique have been described elsewhere¹². About 0.250 g of the sample was held in a quartz bucket. The bucket was suspended from a 15 cm long Pyrex hook, which in turn was suspended from a quartz spring hook. Before making an adsorption run, the sample was outgassed to 10^{-6} torr* at 110°C for 8 h. The desired vapour pressure of water was generated by immersing a bulb of water in a Forma temperature bath containing a water-antifreeze mixture. The bath temperature could be controlled to $\pm 0.1^{\circ}\text{C}$. Since the Forma unit did not cool below -20°C , lower temperatures, down to -40°C , were obtained by using suitable mixtures of ethanol and water, cooled by liquid nitrogen. An arbitrary adsorption time of 90 min was allowed for each point on the isotherm.

RESULTS AND DISCUSSIONS

The moisture sorption isotherms, measured at 20°C , on various coal samples are given in *Figures 1* and *2*. It is seen that both the isotherm shape and the

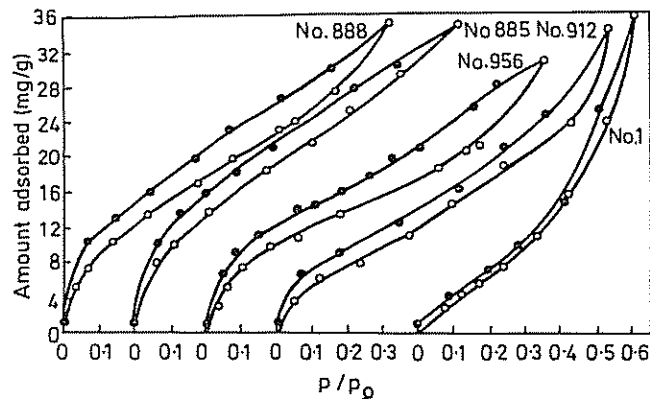


Figure 1 Moisture sorption isotherm (20°C) on coals. Solid points denote desorption data

extent of adsorption depend on the coal rank. Bituminous coals are seen to adsorb more water at low relative vapour pressures than does anthracite. Furthermore, sorption on bituminous coals is characterized by Type II isotherms, while anthracite gives a Type III isotherm.

It is well known that moisture sorption on carbons is influenced by the volatile matter content. Our results show (*Figures 1* and *2* and *Table 1*) that for a given coal rank, moisture sorption does not vary necessarily in the same order or in the same proportion as the volatile matter content. This could be

* torr = 133.322 Nm^{-2}

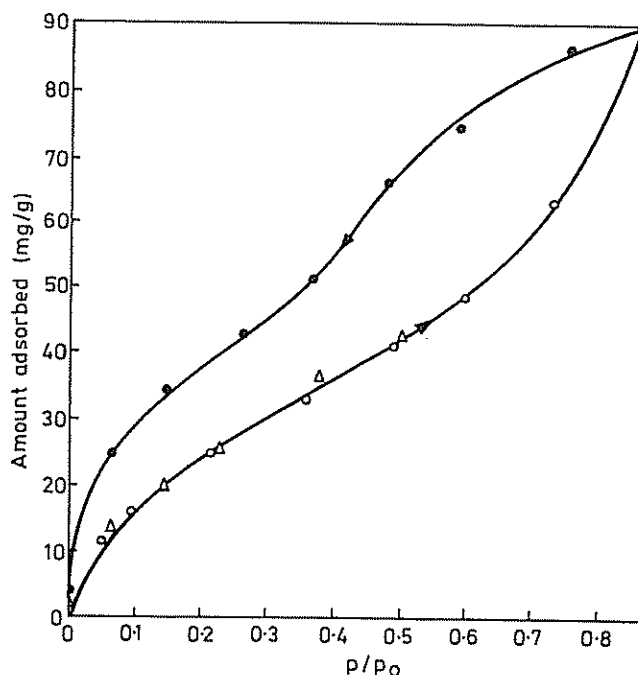


Figure 2 Moisture sorption isotherm (20°C) on bituminous coal No 6.
 Solid points denote desorption data.
 ○ 90 min for each absorption point △ Equilibrium conditions

due either to the influence of the amount or type of impurities or to the role of specific oxygen functional groups present on the carbon sample, on moisture sorption.

When the sorption-desorption results are considered for the various coal samples, it is seen that hysteresis exists in each case. Anderson *et al*¹ have reported that in the case of coals, the hysteresis loops usually do not close until the relative pressure is reduced to zero. However, in the present work sorption-desorption isotherms do not meet even at zero relative vapour pressure. A certain amount of water cannot be desorbed even on outgassing the system to constant weight at 20°C. The irreversibly adsorbed water is presumably held tightly within the micropores, or, as suggested by Puri *et al*⁶, held at the surface by a mechanism involving hydrogen bonding to certain oxygenated functional groups. Dacey and coworkers¹⁴ have shown that after desorption to zero relative vapour pressure, the small amounts of water still retained on Saran charcoals could not be removed even by pumping at 300°C; the charcoals were restored to their original weight in a reasonable time only at 450°C. In the present work, regeneration was completed at 110°C.

The BET plots give sensible straight lines even for the anthracite, which gives a Type III isotherm. A Type III isotherm is certainly not characteristic of a system of pores of molecular dimensions. Instead, it is typical of pores of appreciable size.

The BET surface areas calculated from moisture sorption isotherms

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Table 2 Surface areas of coals

Sample number	Surface area (m ² /g)		S _{BET}	Surface area from water isotherms (20°C) (m ² /g)		
	CO ₂ (25°C)	N ₂ (-195°C)		S*	S _r	C†
1	224	Nil	33	73	-	4
912	146	Nil	17	32	17	12
956	125	Nil	24	41	22	23
888	104	Nil	38	71	37	26
885	132	11	42	77	44	27
6	139	22	82	148	74	17

* assuming monolayer coverage at $p/p_s = 0.5$

† Constant in BET equation

(20°C), using 10.6\AA^2 ($1\text{\AA}=0.1\text{nm}$) for the molecular area of water, are given in Table 2. It is seen that the water surface areas are much less than those obtained from carbon dioxide adsorption isotherms (25°C). Areas calculated from carbon dioxide adsorption have been shown¹³ to represent, most completely, the surface area in the microfine structure of coals. Furthermore, when moisture sorption isotherms for the different coal samples are considered, it is seen that there is no correlation between moisture sorption capacity and the BET carbon dioxide surface areas. In this respect, our results differ from those of Anderson *et al*¹⁵ who have reported that the surface areas of coals calculated from carbon dioxide isotherms are of the same magnitude as those from water isotherms. The disparity in our surface area results is explicable in terms of the difference in the nature of the adsorptive forces involved in the sorption of polar molecules and those envisaged for the BET model using non-polar adsorbates. Since a carbon surface is essentially hydro-phobic, the role of dispersive forces involved in moisture sorption is negligible. Therefore, the magnitude of the surface plays a minor role in moisture sorption. It appears more probable that besides adsorption on impurities, the sorption of water on coals essentially involves adsorption at the 'primary' specific oxygen sites. Because of the strong intermolecular forces in water, the adsorbed water could act as 'secondary sites' for the adsorption of additional water, thus leading to 'cluster' formation, the growth of clusters increasing with increasing surface coverage. At some stage, the clusters could merge to cover the surface with a statistical monolayer of adsorbed water, leading ultimately to the filling of the entire micropore volume.

In the case of microporous adsorbents such as coals, the concept of monomolecular coverage, and hence surface area, estimated from moisture sorption isotherms must be used with some caution. Dannenberg and Opie⁸ have suggested that in the case of porous carbon blacks, condensation of water in the capillaries probably starts before monomolecular coverage is achieved; so that in such a case it is not possible to estimate accurately the point at which monomolecular coverage is completed. In view of both this suggestion and the mechanism postulated for moisture sorption, we concur with the view of Iyengar and Lahiri² that the application of the BET equation to moisture sorption isotherms on coals gives a measure of the specific adsorption sites

on the coal surface, as determined by oxygen functional groups, rather than the amount of the adsorbate needed for monolayer formation. In fact, the recent work of Walker and Janov¹² on oxidized Graphon samples quantitatively confirms this view.

An attempt will now be made to explain the hysteresis phenomenon observed in the present work. The conventional capillary condensation concept, as implied by the Kelvin equation, cannot explain hysteresis, at least at low pressures, in the case of adsorbents associated with pores of molecular dimensions. The equation envisages meniscus formation and assumes *a priori* that the diameter of the adsorbate molecule is negligible in comparison to the capillary radius. However, the very concepts of a hemispherical meniscus and of ordinary surface tension lose their macroscopic sense in pores of molecular dimensions¹⁶. Guggenheim¹⁷ has reported that surface tension becomes independent of capillary radius only when the latter exceeds 500Å. Moreover, Kipling and Wilson¹⁸ have shown that the pore dimensions estimated from a molecular probe study of a series of carbon specimens were up to four times smaller than those calculated by the application of the Kelvin equation to the moisture sorption isotherms.

The cluster model of adsorption described elsewhere in this paper has been used to explain hysteresis in the case of charcoals^{6,19}. Desorption in such a model would involve evaporation from the surface after the merger of the clusters, the process continuing until the continuous adsorbed water film breaks up into separate clumps. Thereafter, adsorption would be reversible. However, it is highly unlikely that this approach can explain hysteresis at very low pressures.

The 'independent domain model' proposed by Everett²⁰ attributes hysteresis to a large number of independent domains, each one capable of existing in two physical states or microphases. In the case of coals, the capillaries could define the boundaries of such domains. According to this model, hysteresis results from the conversion of one state to another. The work of Enderby²¹ and Quinn and McIntosh²² supports the Everett model. However, it has been reported²³ that the domains are not independent of one another.

It is well known^{1,16} that coals swell on adsorption of polar molecules. It is quite probable that the observed hysteresis at lower pressures can be accounted for by swelling and shrinkage effects during adsorption and desorption of water. This view receives support when the results of Pope²³ on the swelling isotherm for water vapour adsorbed on a compact of coal are considered. A reasonable explanation has been offered for these results by Hirst²⁴ and Gregg¹⁶. The probable cause for the failure of adsorption and desorption isotherms to meet, even at zero relative vapour pressure, has been discussed elsewhere.

The heats of adsorption on the various coal samples were calculated from isotherms measured at 20°C and 0°C. For each sample, the extent of adsorption was greater at 0°C than at 20°C, as expected. However, when the data for a given sample are plotted on a relative pressure basis, one smooth curve represents the data at the two temperatures (*Figure 3*). This would imply that the isosteric heat of adsorption over the temperature and pressure range considered closely approaches the value for the heat of liquefaction of water, that is, 10.6 kcal/mol. Others have also reported that moisture

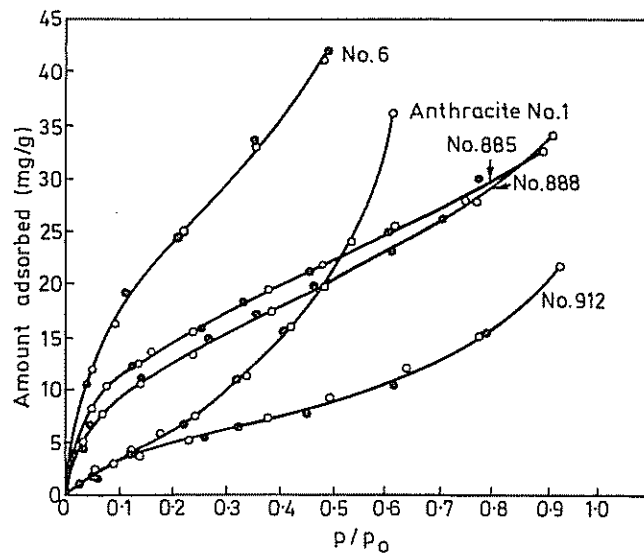


Figure 3 Water adsorption on coals at zero and 20°C as a function of relative pressure. Solid points denote data at 0°C

sorption isotherms at several temperatures on charcoal⁵, Graphon²⁵ and coals²⁶ closely coincide when plotted on a relative pressure basis.

The equivalence of heat of adsorption of water and its heat of liquefaction is possible only if the adsorbed water molecules are bound to the coal surface in such a manner that the length and the strength of the bonds of water in the adsorbed state are of about the same magnitude as those found in bulk water. Walker and Janov¹² have offered a plausible explanation for such a possibility for water adsorbed on structural well-defined oxidized Graphon samples. However, it is doubtful if such an explanation is valid in the case of poorly defined, highly turbostratic, microporous coals.

It has been reported that at low surface coverages, the heat of adsorption of water on Saran charcoals¹⁴ and Spheron²⁷ is significantly greater than the heat of liquefaction. At higher coverages, the two heats are about equal. The initial higher heats of adsorption were of the same order as those for hydrogen bonding. Such a bonding is likely to be formed between the hydrogen atoms in water and the oxygen atoms in functional groups present on the carbon surface. The heat of immersion results also show² that hydrogen bonds play an important role in the sorption of water on low rank coals. It was expected that because of the possibility of the formation of hydrogen bonds, heats of adsorption for the initial amounts of water adsorbed on coals would be higher than the heat of liquefaction. It may be recalled that in the present work an arbitrary time of 90 min was allowed for each adsorption point on the isotherm. However, even if 6–8 h are allowed for each point, the adsorption values do not change significantly, at least up to a relative pressure of 0.5 (Figure 2). For all the samples studied, monolayer coverage is attained well below this relative pressure. Therefore, the absence of higher

heats of adsorption for the initial amounts of water adsorbed cannot be attributed to failure to establish equilibrium conditions.

It has been reported⁵ that the impurities greatly enhance the extent of moisture sorption at low relative vapour pressures. In order to see if the absence of higher heats of adsorption for the initial amounts of water adsorbed could be due to some endothermic process involving solution of impurities in water, it was essential to estimate isosteric heats of adsorption on a sample free from impurities. A de-ashed sample of medium activated coconut shell charcoal was selected. It was oxidized with nitric acid (5ml/g) in the manner described elsewhere²⁰. The treatment would have resulted in the chemisorption of large amounts of oxygen²⁰. As a result, there should be a greater possibility of hydrogen bonding of hydrogen in water with the chemisorbed oxygen which should result in a higher heat of adsorption, at least at the lower pressures. However, it is seen (*Figure 4*) that moisture

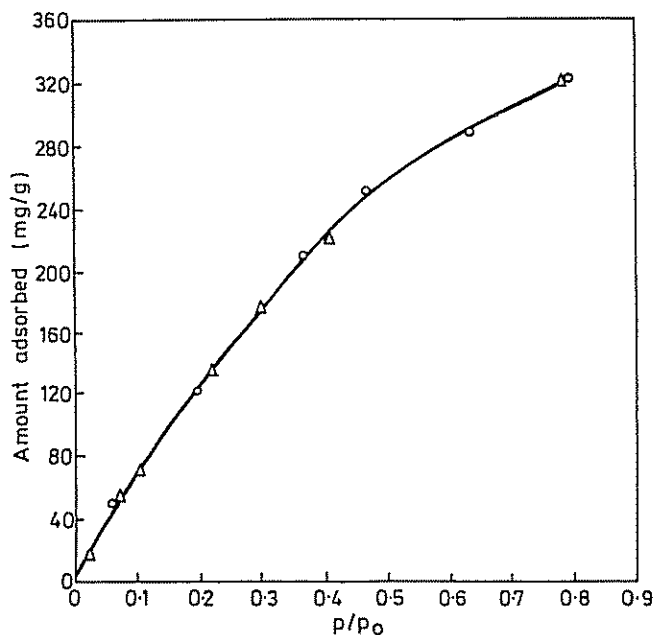


Figure 4 Moisture sorption isotherm on oxidized activated charcoal
○ 20°C △ 10°C

sorption isotherms at 0° and 20°C closely coincide when plotted on a relative pressure basis, indicating that the net heat of adsorption over the pressure range studied is zero. In the present case, each data point on the isotherm represent an equilibrium condition.

The initial higher heats of adsorption reported in the literature refer to extremely small surface coverages. For instance, Dacy *et al*¹⁴ have reported the heat of adsorption of water on Saran charcoals at a surface coverage of about 1% to be 15kcal/mol; at about 5% surface coverage, the value approaches the heat of liquefaction. A cursory examination of our moisture sorption isotherms on various coal samples and oxidized activated charcoal

shows that the first adsorption point on the isotherm corresponds to much higher surface coverages, in some cases as high as 40–50%. If the sorption data could be obtained at much lower surface coverages, of the order of 1% or so, it is possible that higher heats of adsorption might have been observed. In view of the very profound influence of oxygen complexes on moisture sorption capacity at lower pressures²⁰, such low surface coverages would be attained only at extremely low relative pressures and, hence, temperatures. Using our experimental technique, attaining such low temperatures was extremely difficult.

The fact that the net isosteric heat of adsorption of water on coals is zero would imply that the value of the constant C in the BET equation is unity. This is in direct conflict with the values of C obtained from the BET plots, where the values vary from 5 for anthracite to 25 for the bituminous coals (Table 2). If C is assumed ≈ 1 , the BET equation predicts that the amount adsorbed at a relative vapour pressure of 0.5 should correspond to monolayer capacity. This approach has recently been used successfully by Walker and Janov¹² to estimate the 'active' surface area of Graphon samples. The values agree remarkably well with those obtained from oxygen chemisorption. Surface areas of various coal samples, assuming monolayer coverage at a relative pressure of 0.5, are given in Table 2. These values are seen to be much higher than those obtained from the normal BET plots. The higher values in the former case are possibly due to intraparticle condensation of water. Besides, condensation may also occur at $p/p_0 = 0.5$ in the small interparticle spaces.

Thermodynamic considerations show that when the net heat of adsorption is zero, a decrease in free energy and spontaneous adsorption can occur only if the process of adsorption is accompanied by an increase in entropy. When the results for a few representative samples are considered (Figure 5), it is

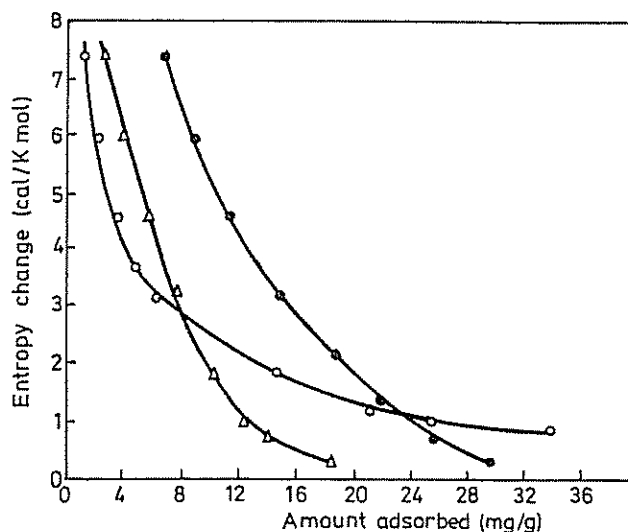


Figure 5 Entropy change for adsorption of water on selected coals
 ○ Anthracite No 1 △ Bituminous coal No 956 ● Bituminous coals
 No 885

seen that the entropy of adsorption has a positive value over the entire pressure range, the value decreasing in magnitude with progressive increase in the extent of adsorption.

Brunauer *et al*³⁰ have used the t -method, obtained from nitrogen isotherms, to determine the pore volume and pore surface distribution of micropores. Realizing that many adsorbents have pores that are inaccessible to nitrogen but may be accessible to water, Brunauer and co-workers³¹ have recently suggested the use of t -curves, obtained from water vapour adsorption, for the pore structure analysis of microporous adsorbents. This approach should be strictly applicable only for completely hydrophilic surfaces, such as those of ionic solids. However, these workers argue that the method can be valid even in the case of composite hydrophilic-hydrophobic surfaces up to a relative pressure of about 0.4. They have offered several t -curves, for different values of C , for the pore structure analysis of micropores. In order to see if the method can be used for the pore structure analysis of coals, our isotherms were converted to V_t - t plots (Figure 6). It is seen that above $t = 2.5$,

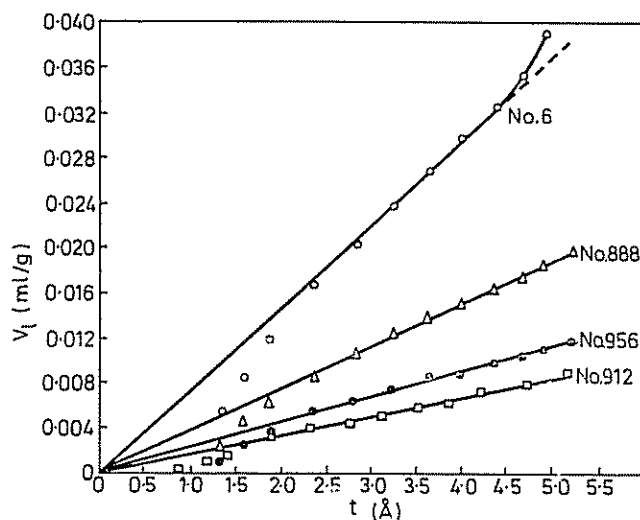


Figure 6 t plots for adsorption on selected coals at 20°C

which corresponds to a relative pressure ranging between 0.10 and 0.15 for our range of C -values, the data for each sample are represented by a smooth straight line passing through the origin. The departure from linearity at the lower t values may be due to the fact that the V_t values corresponding to relative pressures less than 0.05 were extrapolated and as such may be in error. The fact that the straight lines pass through the origin would imply that the samples under examination do not contain pores of width less than twice the thickness of an adsorbed layer of water i.e. 6Å. If this were so, the nitrogen surface areas (77K) should have been greater than those obtained experimentally (Table 2). Moreover, a straight line relation for the V_t - t plots rules out the possibility of using the plots for pore structure analysis. This is so because the t -curves can be used for such analysis only after the filling up of the micropores as a result of multilayer adsorption,

the points on the V_t-t plots begin to deviate downward from a straight line³⁰. Such behaviour, obviously, is possible only for Type I isotherms. Recently the concept of multilayer adsorption in micropores has been criticized sharply by Dubinin⁷.

The values of surface areas, S_t , obtained from the slopes of the V_t-t plots are seen to be in close agreement with those obtained from the BET plots (Table 2). It cannot be otherwise, as suggested by Brunauer *et al*³⁰.

ACKNOWLEDGEMENTS

This research was supported by the Commonwealth of Pennsylvania through its continuing Coal State programme.

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(Received 4 August 1970)

(Revised 3 December 1970)

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