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Measurement of the Ultrafine Surface Area of Coals*

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The surface areas of six coals (200 × 325 mesh) have been estimated from the sorption of nitrogen at 77°K, krypton at 195°K, carbon dioxide at 195°K, xenon at 273°K, and carbon dioxide at 298°K. The coals ranged in carbon content (dry, ash free basis) from 72·7 to 95·2%. Surface areas were calculated from sorption isotherms, allowing 30 minutes for each sorption point, using the BET equation. The most promising sorption system to measure most completely the surface area in the microfine structure of coals appears to be carbon dioxide at 298°K. With this system, the surface areas ranged from 224 m²/g to a low of 104 m²/g. This minimum in surface area is substantially greater than that reported previously, even from methanol sorption at room temperature.

INTEREST continues in measuring as closely as possible the total surface area of coal. It is now well accepted that nitrogen at 77°K fails to reach most of the surface area in coals, because of activated diffusion[1]. P. L. WALKER, Jr and I. GELLER[2], K. A. KINI[3], and more recently R. B. ANDERSON, L. J. E. HOFER and J. BAYER[4] have concluded that carbon dioxide at 195°K does reach much of the surface area in coals. Recently, S. P. NANDI and P. L. WALKER, Jr[5], on the basis of unsteady state diffusion measurements of carbon dioxide from coals, concluded that a substantial fraction of the pore volume in coals should be available to carbon dioxide at 195°K, allowing an equilibration time of 30 minutes. However, the results did suggest that some of the surface area in some coals will not be reached under these conditions. K. A. KINI[6], recognizing the importance of working at as high an adsorption temperature as possible, studied the adsorption of krypton at 195°K and xenon at 273°K on coals and cokes. At these temperatures, the vapour pressures of krypton and xenon are 33 and 43 atm, respectively. To use the BET equation[7] to calculate accurately surface areas from adsorption isotherms, it is necessary to measure adsorption up to a relative pressure of *ca.* 0·2. Thus, it was necessary for Kini to use an adsorption apparatus which was capable of operating at pressures considerably above atmospheric so that the required relative pressures could be obtained.

In this paper, adsorption studies have been made on a series of 200 × 325 mesh coals, ranging in rank from anthracite to high volatile bituminous. Adsorption conditions employed were nitrogen (77°K), krypton (195°K), carbon dioxide (195°K), xenon (273°K), and carbon dioxide (298°K). To the authors' knowledge, the latter system has never been used to measure the surface area of coals.

EXPERIMENTAL

Adsorption apparatus and procedure

The adsorption apparatus†, made of stainless steel, was similar in design to that previously described by K. A. KINI[6]. A distinct improvement was

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* Based on a paper contributed to the Sixth International Conference on Coal Science, Münster, 1 to 3 June 1965.

† The apparatus is now manufactured commercially by Tem-Pres, Inc., State College, Pennsylvania.

made to the apparatus, as previously described, by substituting a transducer for a Bourdon-tube gauge to measure pressures. A transducer has an advantage over a Bourdon-tube gauge, because of its small internal volume and the accuracy with which its output can be read potentiometrically. Adsorption measurements could be made conveniently at pressures between *ca.* 10 torr and 40 atm.

Prior to dead space determinations and adsorption measurements, samples were degassed at 150°C for four hours, down to a pressure of *ca.* 10^{-6} torr. The dead space was determined with helium at 473°K. At this temperature, helium adsorption is negligible[8]. For adsorption measurements, 30 minutes was allowed for each adsorption point.

Samples used

Coals—Table 1 presents analyses of the coals used. They varied in rank from anthracite to high volatile bituminous.

Table 1. Analyses of coals

Sample	*Moisture* %	*Proximate analysis (Moisture-free) %*				*Ultimate analysis (Moisture-free) %*			*Carbon, % d.a.f.*
		Ash	*VM*	*FC*	*Sulphur*	C	H	N	
Anthracite									
No. 1	1·1	8·4	4·0	86·4	0·5	87·1	3·0	*Nil*	95·2
Bituminous coals									
No. 912	1·1	4·6	18·8	76·6	0·7	85·9	4·5	1·1	90·0
No. 956	1·6	6·3	33·7	60·0	0·6	80·8	5·0	1·1	86·2
No. 888	1·6	3·8	39·0	57·2	0·6	80·4	5·2	1·4	83·6
No. 885	1·9	5·4	37·6	57·0	0·8	75·0	5·2	1·4	79·2
No. 6	1·9	7·6	45·4	—	2·7	67·2	5·5	—	72·7

Carbons—Adsorption of the gases was studied on selected carbons (Graphon, wear-dust, and Vulcan 3), which are known not to exhibit molecular sieve properties, in order to estimate values for molecular areas of the adsorbates.

Graphon is prepared by heating the carbon black Spheron 6 to about 2750°C. The surface of Graphon is highly homogeneous, it being composed of *ca.* 99 per cent basal plane (or 002) surface[9]. Its internal surface area is negligible; its electron microscope area agrees closely with the surface area calculated from gas adsorption. Its volatile matter and ash content are negligible.

Carbon wear-dust was prepared by grinding artificial graphite in nitrogen. The particles of the wear-dust are highly flake-like[10]. From electron micrographs, the average particle diameter is *ca.* 0·4 μ. For flake-like particles of negligible internal surface area, the particle thickness can be estimated from $t = 2/\rho S$, where ρ is the particle density and S is the specific surface area measured by gas adsorption[11]. The particle thickness is *ca.* 60 Å. Its volatile matter content is *ca.* 4 per cent; its ash content is *ca.* 0·1 per cent.

Vulcan 3 is an oil furnace black, which has an arithmetic mean particle diameter of 235 Å. Its internal surface area is negligible[12]. Its volatile matter content is <1 per cent; its ash content $<0{\cdot}1$ per cent.

RESULTS

Adsorption on carbon surfaces

Table 2 presents the results for the calibration of the different adsorption systems used. The system, nitrogen at 77°K, was taken as the standard, with the area of the nitrogen molecule taken as 16·2 Å². As suggested by P. H. EMMETT[13], this value is calculated from the density of liquid nitrogen assuming two-dimensional close packing on the adsorbent surface. Employing this adsorption system, the surface areas of Graphon, wear-dust, and Vulcan 3 were calculated as 90, 157 and 74 m²/g, respectively, using the BET equation. The cross sectional areas of the other adsorbates were taken so that the specific surface areas calculated from their adsorption isotherms agreed with the nitrogen values.

Table 2. Calibration of adsorption systems

Adsorbate	*Adsorption temperature, °K*	*Molecular areas, Å²*			
		Graphon	*Wear-dust*	*Vulcan 3*	*Average*
N_2	77	16·2	16·2	16·2	16·2
Kr	195	22·2	25·0	18·0	21·7
CO_2	195	21·7	18·9	21·6	20·7
Xe	273	21·6	25·5	18·8	22·0
CO_2	298	25·8	29·0	21·2	25·3

Table 3. Monolayer volumes of gases on coals

Adsorbate	*Adsorption temperature, °K*	*Volume, cm³/g at s.t.p.*					
		1	*912*	*956*	*888*	*885*	*6*
N_2	77	7·8	*Nil*	*Nil*	*Nil*	2·6	5·2
Kr	195	30·1	16·5	5·8	3·7	2·8	14·4
CO_2	195	44·4	26·3	19·3	14·4	16·5	35·8
Xe	273	38·1	23·9	18·4	10·4	14·2	25·2
CO_2	298	33·0	21·5	18·4	15·4	19·5	20·5

It is seen that the molecular areas of the adsorbates are not constant for the different carbons. This is well known; the packing density of the adsorbate can be dependent upon the crystallographic face upon which adsorption occurs[14], the presence of non-carbon atoms in the surface, and the size and shape of pores in the solid. Quite arbitrarily, the average values of the molecular areas, shown in *Table 2*, have been used to calculate the surface areas of coal. As discussed later, a much more serious problem exists in selecting molecular areas of adsorbates which are adsorbed in molecular sieve materials.

Surface area of coals

Table 3 presents monolayer volumes of the gases adsorbed on the coals, calculated from the BET equation. *Table 4* presents the surface area results on the coals for the different adsorption systems used.

Table 4. Surface area of coals

Adsorbate	*Adsorption temperature, °K*	*Surface area of coals, m^2/g*					
		1	*912*	*956*	*888*	*885*	*6*
N_2	77	34	*Nil*	*Nil*	*Nil*	11	22
Kr	195	176	96	34	20	17	84
CO_2	195	246	146	107	80	92	198
Xe	273	226	141	109	62	84	149
CO_2	298	224	146	125	104	132	139

DISCUSSION

In the measurement of the surface area of coal by gas adsorption, there are two major problems of concern: (*1*) the problem of activated diffusion which can restrict the fraction of the total surface area available to the sorbate and (*2*) the problem of what area to take for the sorbate molecule. Certainly, until recently, the first problem has been the more severe. That is, areas measured from nitrogen adsorption at 77°K have often been low by an order of magnitude. This fact is again seen in these results. It now appears that the problem of activated diffusion has been to a great extent overcome, particularly if the particle size of the coal is reasonably small. Carbon dioxide sorption at 195°K and xenon adsorption at 273°K should usually measure, essentially, the total surface area of coal; carbon dioxide sorption at 298°K should always measure essentially the total surface area of coal.

Recently, S. P. NANDI and P. L. WALKER, Jr[5] measured the diffusion parameters for carbon dioxide diffusion from four 200 × 325 mesh coals of varying rank. To a first approximation, these results can be used in conjunction with the general solution of the unsteady-state diffusion equation[15] to calculate the fraction of the pore volume of the coals filled for particular diffusion times. That is, the general solution gives the fraction of pore volume filled as a function of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$, where t is the diffusion time and $D^{\frac{1}{2}}/r_0$ is the measured diffusion parameter. Taking an equilibration time of 30 minutes (per sorption point), it was estimated that 80 per cent of the pore volume of anthracite No. 1 would be filled and 32 per cent of the pore volume of a bituminous coal of 83 per cent carbon (d.a.f.) would be filled at 195°K. At 298°K, very close to 100 per cent of the pore volume of all four coals studied would be filled.

Carbon dioxide appears to be the best selection for the sorbate to be used to measure the surface area of coal. Kinetic diameters can be estimated from viscosity data using the Lennard–Jones (6–12) potential energy expression. T. KIHARA[16] generalized the Lennard–Jones model of spherical molecules to non-spherical molecules, without sacrificing analytical integrability of the second virial coefficient. Assuming carbon dioxide to be a spherocylindrical molecule, he estimated its dimensions to be: length, 5·8 Å and width, 3·7 Å. Thus, carbon dioxide has a small minimum dimension. In addition, carbon dioxide has a relatively high critical temperature, 304°K. Thus, sorption can be carried out at relatively high temperatures, which means that activated diffusion limitations due to temperature are at a minimum. T. G. LAMOND and H. MARSH[17] have shown that the adsorption of carbon dioxide, in the temperature range 195° to 293°K, can be used to measure the total surface area of type 4A zeolite, which has an aperture diameter of *ca.* 3·5 Å.

Previously, S. J. GREGG and M. I. POPE[18] showed that the surface areas of coals go through a minimum area of about 2·5 m^2/g, as measured by *n*-butane adsorption at 273°K. N. BERKOWITZ[19] reported that the surface areas of coals go through a minimum of about 20 m^2/g, as measured by heats of wetting in methanol at room temperature. From *Table 4*, it is seen that the minimum surface area of coals, as measured by carbon dioxide sorption at 298°K, is *ca.* 104 m^2/g. The minimum in specific surface area versus rank is very shallow, appearing to fall somewhere between coals containing 86·2 and 79·2 per cent carbon.

As confident as the authors are that the use of carbon dioxide is desirable to estimate the total capacity of coals, they appreciate that the surface areas which they are reporting are very uncertain on an absolute basis. According to R. L. BOND[20], surface areas of coals should not be reported; he suggests reporting monolayer volumes or total volumes of sorbate uptake. The position of Bond does, of course, not invalidate our conclusion regarding the desirability of the above sorption system. The problem of absolute surface area involves the question of what to take for the molecular area of the sorbate species. In pores of molecular size, the appropriate molecular area could be, in fact, up to four times that found from adsorption on a flat, relatively free, surface like Graphon. Pores in molecular sieve carbons appear to be slit-shaped[21], so a molecular area from two to three times that found on a conventional surface is probably more reasonable.

It is noted that the surface area reported on coal No. 6, as measured by carbon dioxide sorption at 195°K, is significantly greater than that measured by carbon dioxide sorption at 298°K. Certainly, this cannot be explained on the basis of activated diffusion but may be a result of differences in the packing density of sorbed carbon dioxide, which are not allowed for by calibrations shown in *Table 2*. As discussed by P. H. EMMETT[22], the molecular area of the adsorbate is approximately inversely proportional to the density of the adsorbate taken to the $\frac{2}{3}$ power. The liquid densities[23] of carbon dioxide at 195° and 298°K are 1·14 and 0·71 g/cm^3, respectively, or the molecular area at 298°K should be *ca.* 40 per cent greater than the area at 195°K. According to

Table 2, the molecular area at 298°K is *ca.* 22 per cent greater than that at 195°K.

At 195°K, adsorbed carbon dioxide is usually assumed to be in the supercooled liquid state for surface area calculations. Possibly in very fine pores, where the adsorbate has significant attractive interaction with more than one side of the pore wall, carbon dioxide will have properties approximating those of the solid. Since solid carbon dioxide has a density of 1·56 g/cm^3 at 195°K, the molecular area at 298°K could be *ca.* 70 per cent greater than that at 195°K. To check on this possibility further, adsorption of carbon dioxide on the channel black, Carbolac 1, was studied. This black has a surface area of *ca.* 700 m^2/g[17], with essentially half of its area in pores of *ca.* 18 Å in diameter and the other half in geometric surface area[24]. In adsorption of carbon dioxide at 195° and 298°K, monolayer volumes (V_m) of 142·6 and 99·0 cm^3/g (s.t.p.) were calculated. Thus, the ratio of molecular areas would need to be 1·44 to obtain equal surface areas from measurements at these two temperatures.

In a coal where almost all of the area is in molecular size pores, the ratio of molecular areas at 298° and 195°K could be still higher than in Carbolac 1. To obtain equal surface areas for bitumonous coal No. 6 from adsorption of carbon dioxide at 195° and 298°K, the molecular size ratio need be 1·74. Of course, if carbon dioxide adsorbed on coal at 195°K is a solid, the monolayer volume is also wrong, because the vapour pressure of solid carbon dioxide was not used in the BET calculations. A recalculation of V_m for coal No. 6, on the basis of the vapour pressure of solid carbon dioxide at 195°K, gives a value of 25·6 cm^3/g (s.t.p.). Now to obtain equal surface areas for coal No. 6 for adsorption of carbon dioxide, the molecular size ratio at 298° to 195°K need only be 1·25. This is a smaller ratio than that which we estimate from density values (1·70) and suggests that the true state of the carbon dioxide is intermediate between a perfect bulk liquid and a perfect bulk solid, when sorption occurs on coal at 195°K.

CONCLUSIONS

Uptake of carbon dioxide at 298°K on coals should be less affected by diffusion control than any sorbate system yet used. Thus, a truer measure of the total open pore volume in coals can be obtained. From adsorption results, monolayer volumes can be estimated using the BET equation. Uncertainty in the value to use for molecular areas of sorbates held in molecular size pores makes the conversion of V_m values to absolute surface areas unreliable.

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