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LETTERS TO THE EDITOR

SURFACE AREA MEASUREMENTS ON CLAYS

Comments to Aylmore, J. G., Sills, I. D. and Quirk, J. P. (1970) The surface area of homoionic illite and montmorillonite clay minerals as measured by the sorption of nitrogen and carbon dioxide. *Clays and Clay Minerals* **18**, 91 (1970).

IN A PAPER recently published in this journal, Aylmore, Sills and Quirk (1970) presented experimental sorption data, obtained in a standard pressure–volume system that were not in agreement with the data in a similar study reported by Thomas and Bohor (1968). We concluded from our data, obtained with a dynamic system, that nitrogen and, to a greater extent, carbon dioxide penetrated between the layers of homoionic montmorillonites to a degree governed by the size and charge of the replaceable interlayer cation. The conclusions of Aylmore *et al.*, are that, with the possible exception of Cs-montmorillonite, there is little penetration of either gas between the layers if the samples have been satisfactorily outgassed. As the dynamic method is in use in many laboratories and has been found to give reproducible results that are in close agreement with those obtained with standard pressure–volume apparatus, it is necessary to look beyond differences in apparatus to explain the disagreement.

The major factors influencing the calculated surface areas from carbon dioxide adsorption are in the values assigned to P_0 (saturation vapor pressure) and to the cross-sectional area (σ) of the carbon dioxide molecule. We assigned values of $\sigma = 22{\cdot}1$ Å^2 and $P_0 = 1450$ mm Hg. Aylmore *et al.* also used a value of $22{\cdot}1$ Å^2 for σ and stated that this made their results "directly comparable" with ours; however, they failed to state what value they had assigned to P_0. We have learned recently from Quirk (personal communication) that they used 760 mm in their calculations, but this is not given in their paper. When this lower value of P_0 for carbon dioxide is used in combination with $\sigma = 22{\cdot}1$ Å^2, their calculated surface area values from carbon dioxide adsorption are bound to be lower than ours by an estimated 20–25 per cent.

What are the correct parameters to be used for carbon dixoide? As we pointed out in our paper, there is little unanimity concerning the value of σ at temperatures near 195°K. This lack of agreement will be found for most common adsorbates, with the exception of nitrogen, although possibly not to the same extent. The exact nature of the molecular packing in the adsorbed mono-layer is not known. Published values for σ range from the $17{\cdot}0$ Å^2 calculated by Emmett and Brunauer (1937) on the basis of liquid density, to the $24{\cdot}4$ Å^2 reported by Pickering and Eckstrom (1952).

Carbon dioxide sublimes at about 195°K, and it is a liquid at 215°K only under approximately 5 atm pressure. Lamond and Marsh (1964) showed that at 195°K carbon dioxide, in the adsorbed layer, behaves like a super-cooled liquid, and that at this temperature $P_0 = 1{\cdot}86$ atm, calculated by extrapolating the data of Bridgeman (1927).

The uncertainties need not be a deterrent to the use of carbon dioxide as an adsorbate. The effective cross-sectional area can be established indirectly, under the experimental conditions in use, from a comparison with surface area values determined by the adsorption of nitrogen, the classic standard adsorbate. It is necessary, of course, to use samples having "external surface" only. The assumption is made that carbon dioxide "reaches" essentially the same surface as nitrogen. That this is a fair assumption is shown by the fact that we get equivalent (within 3–5 per cent) surface area results with nitrogen and carbon dioxide on several substances in the range from 10 m^2/g to 550 m^2/g. If it were not a fair assumption, then the error would increase markedly with increasing surface area. If we were to use $22{\cdot}1$ Å^2 and 760 mm in our calculations (as Aylmore *et al.* did) our surface area results from carbon dioxide adsorption also would be 20–25 per cent lower than nitrogen values on "external surface" substances. We have no serious objection to the use of $P_0 = 760$ by Aylmore *et al.*, but if they do, it is necessary for them to use a value greater than $22{\cdot}1$ Å^2 for σ to obtain results comparable to those from nitrogen adsorption. The actual value would need to be established with "external surface" substances in their own adsorption apparatus. We saw no mention in their paper of their having done this.

The complete removal of water from the surfaces of certain substances such as cellulose, coal, and montmorillonite is, of course, extremely difficult owing to the strong physical attraction of the solid surface for discrete water molecules, particularly within micropores or between layers. However, our experience with coals (which have interconnecting pore systems), as well as with clay minerals, indicates that we are not at a disadvantage when outgassing samples in a flow of dry helium, compared with vacuum outgassing at the same temperature. Our unpublished studies of water weight-loss vs. time, in which a Cahn Electrobalance was used, even indicate some superiority for helium outgassing of such porous substances. This may be a result of the small atomic size and high thermal conductivity of helium, which permit it to enter micropores readily, transfer heat more rapidly, and remove the adsorbed water by a nonadsorbing displacement mechanism.

As we reported in our paper, surface area values of the homoionic montmorillonites tended to be only slightly higher with both nitrogen and carbon dioxide as adsorbates when outgassing was carried out at 175°C rather than at 110°C. When outgassing was carried out above temperatures where dehydroxylation is known to occur, the surface area values

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were lower. At all outgassing temperatures, however, surface area values from carbon dioxide adsorption were appreciably higher than those from nitrogen adsorption. Aylmore *et al.* did not find this to be true except with Cs-montmorillonite. In addition, they obtained higher surface area values for the homoionic illites when nitrogen was used as the adsorbate than when carbon dioxide was used. We have found the reverse to be true with illites (unpublished work).

Their interpretation of their data is that the surfaces of clays, including those within intercrystalline micropores, are more accessible to the smaller nitrogen molecule. However, with pores approaching molecular dimensions, the rate of diffusion of adsorbate molecules is governed not only by their size but also by the adsorption temperature. As we shall show, it is not to be expected that micropores (and clay mineral interlayer spacings are micropores of a very special shape) are more accessible to the smaller nitrogen molecule than to the carbon dioxide molecule at their respective adsorption temperatures.

We discussed rather briefly in our paper the apparent paradox of the superior penetration of the larger carbon dioxide molecule into pores of molecular dimensions. This phenomenon has been recognized for some time by those working with coals and molecular sieves. Maggs (1952) first reported the increased adsorption of nitrogen in coals at 195°K compared to that occurring at 90°K. We have duplicated these results, as have others, finding that for certain coals three times as much nitrogen is adsorbed at 195°K as at 77°K. Lamond (1962) studied the adsorption of nitrogen (77°K) and carbon dioxide (195°K) on 4A and 5A Linde molecular sieves. When the 5A was used, the nitrogen and carbon dioxide surface areas were 770 m^2/g and 695 m^2/g, respectively, whereas when the 4A sieve (apertures are about 4·0 Å or less) was used the nitrogen and carbon dioxide areas were 1 m^2/g and 610 m^2/g, respectively. Walker and Kini (1965) reported the use of carbon dioxide as an adsorbate for measuring surface areas of coals and obtained values considerably higher than those obtained from nitrogen adsorption. Anderson and co-workers (1962, 1965) reported similar results. In certain coals we have found surface areas from nitrogen adsorption to be 2–5 m^2/g, whereas carbon dioxide values on the same coals are 250–300 m^2/g. It would appear that a large number of pores in coal are less than 4–5 Å in diameter.

Nandi and Walker (1964) discussed, in terms of activated diffusion, the superior penetration of carbon dioxide at 195°K compared to that of nitrogen at 77°K. They show that the activation energy for the diffusion of carbon dioxide is less than that for nitrogen and, at their respective adsorption temperatures, the diffusion coefficient of carbon dioxide greatly exceeds that of nitrogen.

An excellent treatment of the diffusion of gas in capillaries was given in the text by de Boer (1968). Figure 1 shows, from calculations based on differential heats of adsorption (Q_{diff}), the time of passage (t) of a gas molecule through a cylindrical pore, with the dimensions shown, as a function of Q_{diff}. The chosen values for Q_{diff} are reasonably close to the known values. The same situation would prevail with slit-shaped pores, with some slight shift in values. The time of passage for nitrogen at 77°K is clearly about 10^5 times that for carbon dioxide at 195°K. This would not be true with nitrogen at 195°K, in which case nitrogen diffusion would be greater.

Clearly, carbon dioxide (195°K) penetrates to any internal surface that is accessible to nitrogen (77°K) and, furthermore, even penetrates to surfaces (<4 Å) that are not "reached" by nitrogen. There is little difference in the diffusion rates of the two gases into pores down to about 5 Å in diameter. Therefore, if the proper carbon dioxide parameters established with "external surface" substances are used, significantly higher surface area values would not be obtained from nitrogen adsorption (77°K).

The adsorption curves we presented in our study were ample evidence of a time dependency for diffusion. Although we did not find a large quantity adsorbed during a period of several hours, we did find a measurable amount. This was determined from the volume of adsorbate desorbed from the sample. The dynamic method has a distinct advantage

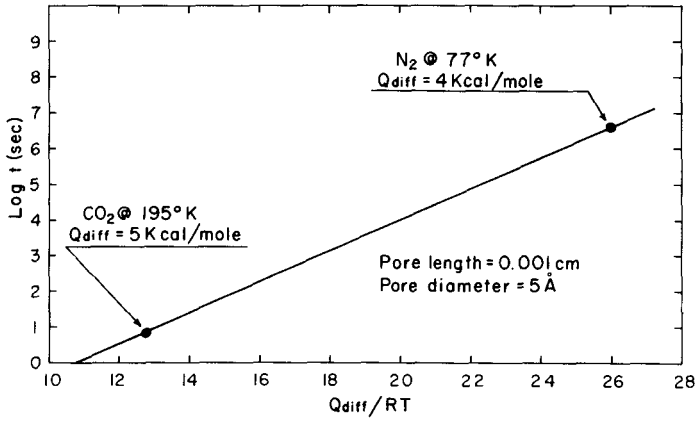


Fig. 1. Plot showing the time of passage (t) of a gas molecule as a function of the reduced differential heat of adsorption (Q_{diff}).

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over techniques employing standard apparatus in determining the total amount of gas adsorbed via the elution (desorption) of the adsorbate. The dynamic method is based on gas chromatography principles, and is very sensitive to volume changes and quite accurate with proper calibration. We are not surprised that Aylmore *et al.*, with standard pressure–volume apparatus, were unable to detect the very slight additional adsorption, with time, on Na-montmorillonite as they were able to do more easily with Cs-montmorillonite.

To reiterate our position, from our data and that of others, we believe that penetration occurs between layers and we feel that, had Aylmore *et al.* used the proper combination of parameters for carbon dioxide, they would have found greater penetration by carbon dioxide than by nitrogen, as we did.

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*The comments presented in this paper are those of Thomas and Bohor in defense of their published work. Frost contributed the valuable supplementary data and calculations in the plot of Fig. 1.

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Reply to comments of Thomas, Bohor and Frost on Aylmore, L. A. G., Sills, I. D. and Quirk, J. P. (1970) The surface area of homoionic illite and montmorillonite clay minerals as measured by the sorption of nitrogen and carbon dioxide, *Clays and Clay Minerals* **18**, 91.

IN THEIR comments on our paper (Aylmore, Sills and Quirk, 1970), Thomas, Bohor and Frost (1970) have discussed the way in which the relative magnitude of the B.E.T. specific surface area obtained for clay mineral systems using carbon dioxide at 195°K and nitrogen at 78°K depends upon the values of saturation vapour pressure and molecular area accepted for carbon dioxide when nitrogen is taken as the standard. This variation is not disputed. However, the question of the correct values to use for the saturation vapour pressure and molecular area of carbon dioxide at 195°K will await further elucidation and should not be allowed to obscure the real point of contention debated in our paper which is whether or not these gases penetrate into the quasi-crystalline (Aylmore and Quirk, 1960; Quirk, 1967) regions of the montmorillonite matrix and their use for measurement of the external surface area of these regions. As indicated in the following notes, acceptance of the values assigned by Thomas and Bohor (1968) would not reverse our conclusions with respect to these points.

As pointed out in both their papers and by various other authors, the "absolute" values for surface area obtained by gas sorption depend entirely on the values assigned to the molecular area and saturation vapour pressure for a particular gas. These considerations recently led Pierce and Ewing (1964) to reiterate the conclusions of Brunauer (1943) that it is perhaps unrealistic to expect even nitrogen adsorption to give the absolute surface areas within better than 20 per cent. We have in fact, attempted to "calibrate" the molecular area for carbon dioxide on various clay

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