

# SURFACE AREA OF MONTMORILLONITE FROM THE DYNAMIC SORPTION OF NITROGEN AND CARBON DIOXIDE

JOSEPHUS THOMAS, JR. and BRUCE F. BOHOR  
Illinois State Geological Survey, Urbana, Illinois

(Received 29 August 1967)

**Abstract**—Surface area determinations were made on a montmorillonite with various cations emplaced on the exchangeable sites, utilizing nitrogen and carbon dioxide as adsorbates at 77°K and 195°K, respectively, in a dynamic system. From the fraction of a Mississippi montmorillonite less than about 1  $\mu$  in size, samples were prepared by replacing the original exchangeable cations with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Ba<sup>++</sup>, and NH<sub>4</sub><sup>+</sup>, forming a series of homoionic montmorillonite species.

Surface areas from 3-point B.E.T. plots (half-hour adsorption points), with nitrogen as the adsorbate, ranged from 61 m<sup>2</sup>/g for Li-montmorillonite to 138 m<sup>2</sup>/g for Cs-montmorillonite, thus reflecting a certain degree of nitrogen penetration between layers. Complete penetration should theoretically result in a surface area of over 300 m<sup>2</sup>/g for this clay with a nitrogen monolayer between each pair of platelets. The experimental data indicate that the extent of penetration is time-dependent and is also a function of the interlayer forces as governed by the size and charge of the replaceable cation. This finding negates the generally accepted concept that nitrogen at 77°K does not penetrate the layers and provides a measure only of the external surface of expandable clay minerals.

A further measure of the variation of interlayer forces is provided by the adsorption of carbon dioxide at 195°K. Surface area values ranged from 99 m<sup>2</sup>/g for Li-montmorillonite to 315 m<sup>2</sup>/g for Cs-montmorillonite. Although the carbon dioxide molecule is larger than the nitrogen molecule, its greater penetration apparently is a result of its being kinetically more energetic (with a larger diffusion coefficient) at its higher adsorption temperature. Similar differences have been found with both adsorbates in the study of microporous substances, such as coal, where activated diffusion is of considerable significance.

## INTRODUCTION

It is well-recognized that the behavior of clay minerals, soils and soil colloids depends to a great extent upon the specific surface area. Of the various methods in use for determining this parameter, the gas adsorption method of Brunauer, Emmett, and Teller (1938)—B.E.T. method—is generally accepted as the standard procedure.

A number of surface area evaluations from various adsorption isotherms have been reported during the past 30 years on these substances. Among those studies to which reference is frequently made are those by Makower, Shaw, and Alexander (1937), Emmett, Brunauer, and Love (1938), Hendricks, Nelson, and Alexander (1940), Nelson and Hendricks (1943), Mooney, Keenan, and Wood (1952), Quirk (1955), and Zettlemoyer, Young, and Chessick (1955).

It would appear from most of the reported evidence that whereas water vapor and ammonia, both polar adsorbates, are able to penetrate between the layers of montmorillonite thereby yielding a measure of the internal surface, nitrogen as the adsorbate near its boiling point (~77° Kelvin) does

not penetrate the layers and provides a measure only of the external surface. Some preliminary measurements made in this laboratory, however, indicated that this was not true and that some penetration by nitrogen does indeed occur. This paper presents the results of a detailed study on a homoionic series of a montmorillonite in which the B.E.T. method was used with both nitrogen and carbon dioxide as adsorbates at ~77° Kelvin and ~195 Kelvin, respectively in a dynamic system.

## MATERIALS

A commercial southern bentonite\* was selected for this study, instead of a Wyoming-type bentonite, because of the physical difficulties of preparation associated with concentrated suspensions of the latter clay. This particular bentonite is mined in northern Mississippi and is Upper Cretaceous in age. About 85 per cent of the crude clay is a high-iron montmorillonite, which has some substitution

\*Sold by International Minerals and Chemical Corporation under the trade name "Dixie Bond".

of  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$ . The principal exchangeable cation is calcium, and the exchange capacity is 93 m-equiv./100 g (Grim and Cuthbert, 1945).

Additionally, samples of a poorly-ordered kaolinite from the area of Anna, Illinois, and a well-ordered commercial kaolinite from Georgia\* were also studied as examples of clay minerals with no interlayer exchangeable cations to influence gas penetration. In addition to the difference in ordering, the Anna kaolin occurs as much finer-sized particles (85 per cent less than  $0.5 \mu$ ) and has a larger base exchange capacity (about 18 m-equiv./100 g) than does the Georgia kaolin.

The crude clays were fractionated by centrifugation to obtain the less than  $1 \mu$  fraction of each. The method described by Hathaway (1956) was used to obtain this fraction, but the formula he derived contains some factors that are difficult to control or evaluate. Therefore, the upper size limits derived by this technique may not be exactly as calculated. However, whether the resultant upper limit is  $1 \mu$  or  $1.3 \mu$ , it will be the same for all the samples and its actual value is not really significant.

A small amount of a commercial Wyoming-type bentonite from Belle Fourche, South Dakota† (similar in composition to A.P.I. clay no. 27) was size-fractionated also to recover the less than  $1 \mu$  portion. This was treated with certain cations, in a similar manner as described below, for comparison purposes.

After size fractionation and drying, equal portions (about 5 g) of the  $< 1 \mu$  montmorillonite were added to separate 100 ml beakers containing about 50 ml of nearly saturated solutions of Li, Na, K, Rb, Mg, Ca, Ba, and  $\text{NH}_4$  chlorides, and  $\text{Cs}_2\text{SO}_4$ . These concentrated salt solutions were allowed to remain in contact with the montmorillonite for 18 hr, with frequent stirring. Then about 30 ml of distilled water were added to each beaker and the resulting suspensions were stirred and left for another 20 hr. At the end of this time interval, the supernatant liquid was poured off and the samples were washed in distilled water until peptization took place. They were allowed then to stand another 18 hr and washed again with the aid of filter candles. The resulting homoionic series of montmorillonites were dried and lightly ground to break up lumps and aggregates.

#### METHODS

##### *Thermal-conductivity apparatus*

The laboratory-constructed apparatus used in the study, with certain modifications, was similar in design to that described by Nelsen and Eggertsen

(1958). Modifications included (1) precision needle valves which, along with pressure regulators, controlled gas flow rates, (2) a multirange recorder with a mechanical integrator for integrating peak areas, and (3) a stable solid-state D.C. power supply for the bridge circuit. A reversing switch also was included in the bridge circuit to permit either the adsorption or desorption peak to be recorded in the same positive direction.

The principles involved in the use of the apparatus were described in detail in the aforementioned reference. The method was further evaluated and given some additional refinements by Daeschner and Stross (1962). Commercial versions of the apparatus are now available‡.

In brief, the change in composition of a mixed gas (helium as a carrier gas for the adsorbate gas) flowing over a sample either during adsorption or desorption is detected by a thermal conductivity cell, thereby producing a recorded peak. The area under this peak is related through calibration to the volume of gas adsorbed or desorbed.

Some broadening and slight tailing effects are generally associated with the adsorption peak from finely divided substances, owing to slow diffusion of the adsorbate between particles and to the temperature rise during adsorption. The same effects also have been noted with porous solids, such as coals, where diffusion of the adsorbate into very fine pores determines the rate of adsorption (Thomas, Benson, and Hieftje, 1966). The desorption process, however, is rapid and the peak produced is relatively sharp. Therefore, the desorption peak is generally used to represent the total amount adsorbed, because its shape is more closely comparable to those produced during calibration.

##### *Carbon dioxide as an adsorbate*

Carbon dioxide, a linear molecule with zero dipole moment, has gained considerable support from various workers during the past five years as the most favorable adsorbate in studies of the ultra-fine structure of coals. In this regard, the recent studies by Marsh and Siemieniowska (1965), Anderson, Bayer, and Hofer (1965), Walker and Kini (1965), and by Marsh and O'Hair (1966) are perhaps most pertinent for reviewing purposes.

These and other studies indicate that a large proportion of the pores present in coal are less than  $10 \text{ \AA}$  in diameter. Nitrogen and the inert gases at temperatures near their boiling points diffuse into the pore channels at an exceedingly slow rate and adsorption equilibrium is not attained in a reasonable time. Polar adsorbates such as water vapor,

\*Supplied by the Georgia Kaolin Company.

†Sold by the American Colloid Company under the trade name "Volclay".

‡The Sorptometer is sold by the Perkin-Elmer Corp., Norwalk, Connecticut.

ammonia, or methanol are not too desirable, and nonpolar organic adsorbates, besides being too large in some instances to enter the pores, may attack the coal. Carbon dioxide at 195°K penetrates the pores and yields internal surface-area values that are in closer agreement with those from heat-of-wetting data. It is not unusual, for example, to obtain a value of 250 m<sup>2</sup>/g from carbon dioxide adsorption as compared with 5 m<sup>2</sup>/g from nitrogen adsorption.

Unfortunately, there is little unanimity concerning the cross-sectional area ( $\sigma$ ) of the carbon dioxide molecule at temperatures near 195°K. Values based on liquid density data range from 17.0 Å<sup>2</sup> calculated by Emmett and Brunauer (1937), to 24.4 Å<sup>2</sup> reported by Pickering and Eckstrom (1952).

A value of 22.1 Å<sup>2</sup> was used for the studies reported here. This is an average value that was established indirectly from samples of known surface area, as determined in several participating laboratories by nitrogen adsorption, with the assumption that carbon dioxide at 195°K should give the same surface-area value as nitrogen at 77°K. The results are summarized in Table 1.

Slight differences are to be expected for  $\sigma$ , of course, with different types of adsorbents. The large difference noted with the carbon black, however, and in the opposite direction from that noted with the other samples, is likely due to the presence of a micropore system that is not permeated by nitrogen. This was suggested earlier by Lamond and Marsh (1964). The averaging of the data used here for the determination of  $\sigma$  does not include the carbon black data.

In order to check the validity of the  $\sigma$  value for the adsorption of carbon dioxide on clay minerals, surface-area determinations were made on the two kaolinite samples (less than 1  $\mu$  fraction) which should be representative of nonexpandable silicate substances. From nitrogen adsorption data, the values for the Georgia kaolin and Anna kaolin samples were 17.3 m<sup>2</sup>/g and 32.3 m<sup>2</sup>/g, respectively. From carbon dioxide adsorption, the values were 18.3 m<sup>2</sup>/g and 32.6 m<sup>2</sup>/g, respectively.

#### Procedure

Samples of approximately 0.3 g (40–120-mesh aggregates) were degassed in a helium stream for 16 hr. One set of samples was degassed at 110°C,

Table 1. Cross sectional area of carbon dioxide from the surface areas of reference samples

Adsorbent	S.A., m <sup>2</sup> /g* (N <sub>2</sub> -Static)	S.A., m <sup>2</sup> /g (N <sub>2</sub> -Dynamic)	S.A., m <sup>2</sup> /g† (CO <sub>2</sub> -Dynamic)	$\frac{N_2 \text{ S.A.}}{CO_2 \text{ S.A.}}$	$\sigma \text{ CO}_2 \text{ (Å}^2\text{)‡}$
Anatase	10.3	10.6	7.9	1.30	22.1
Silica Spheres	24.3	24.5	18.6	1.31	22.3
Bone Char	69	65	52	1.33	22.6
Carbon Black (Spheron 6)	110	116	117	0.94	16.0
Silica-Alumina Catalyst	550	554	436	1.26	21.4

\* Accepted values from determinations conducted at different laboratories.

† Calculated from experimental data using a value of 17.0 Å<sup>2</sup> for the cross-sectional area of the carbon dioxide molecule.

$$\ddagger \frac{(N_2 \text{ S.A.})}{(CO_2 \text{ S.A.})} (17.0).$$

Values that the authors obtained with nitrogen as the adsorbate in the dynamic system also are shown for comparison purposes. The different substances used are distributed through the Bone Char Research Project, Inc. (Revere Sugar Refinery, 333 Medford Street, Charlestown 29, Mass.).

With the exception of the data shown for the carbon black, it is seen that the values obtained from nitrogen adsorption and carbon dioxide adsorption differ by about the same factor over the rather broad range of surface areas represented.

and another set at 175°C. A third set was degassed in helium for 1 hr at higher temperatures (dependent upon the replaceable cation), where it has been variously reported that expansion of the lattice by glycolation no longer occurs.

Adsorption was conducted at 3 points for the B.E.T. plot within the range of relative pressure of about 0.05–0.25 for nitrogen and about 0.05–0.16 for carbon dioxide. Relative pressure =  $p/p_s$ , where  $p$  is the equilibrium pressure and  $p_s$  is the saturation pressure of the vapor at the temperature of adsorption. A value of 1450 mm was used for  $p_s$ .

of carbon dioxide, which allows for a very slightly higher temperature than the value (1.86 atm at 195°K) calculated from the work by Bridgeman (1927). A value of 800 mm was used for  $p_s$  of nitrogen. A helium flow of 50 ml/min was maintained both for the degassing procedure and in the control of the relative pressure of the adsorbate.

A Dry Ice-absolute ethanol slush (approximately 195°K) was used to establish the adsorption temperature for carbon dioxide. The area under the desorption peak was used as a measure of the total adsorption. Because a significant quantity of carbon dioxide remains adsorbed on a sample at room temperature, it is necessary to conduct the desorption step at an elevated temperature. Consequently, a glycerol bath heated to 120°C was raised into position around the sample tube immediately after the cold bath was removed. The quantity of nitrogen that remains adsorbed on the sample at room temperature is not significant, but the use of a water bath at room temperature or slightly above sharpens the desorption peak.

The B.E.T. plots were linear and, with nitrogen as the adsorbate, passed essentially through the origin. The intercepts were somewhat more positive with carbon dioxide as the adsorbate. The value of  $c$  (in the B.E.T. equation) from the experimental data for the various samples with carbon dioxide as the adsorbate ranged from about 18 to 40.

## RESULTS AND DISCUSSION

The initial indication of diffusion between platelets may be seen from a comparison of the adsorption-desorption curves shown in Fig. 1.

Although the dynamic method used appears more amenable than other methods for rate studies of physical adsorption or desorption, simply because of the high sensitivity of thermal conductivity measurements which are easily monitored, the evaluation of rate data still lacks a theoretical basis. Qualitatively, however, certain differences are apparent. The adsorption peak for Georgia kaolinite is only slightly less intense than the desorption peak. Adsorption equilibrium (return of the adsorption peak to the recorder baseline) is reached in approximately 1 minute. The broadening and tailing effects associated with the adsorption peak for the montmorillonite samples, however, are quite pronounced, and adsorption equilibrium appears to be reached within the longer time period of 2–5 min, depending upon the replaceable cation. In fact, the time required for the apparent adsorption equilibrium with both of the expandable clay mineral samples shown is greater than that required for the silica-alumina catalyst, which is a highly porous adsorbent.

The ratio of peak amplitudes (desorption/adsorption), which provides some index of the broadening phenomenon, is approximately 1.3:1

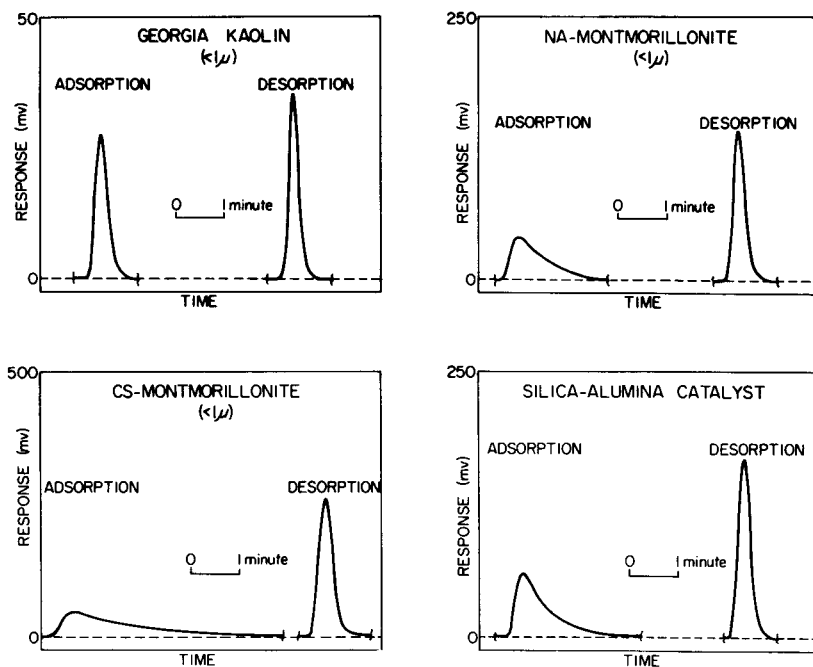


Fig. 1. Comparison of adsorption-desorption curves (integrator record not shown).

for Georgia kaolinite, 2.8:1 for silica-alumina catalyst, 3.3:1 for Na-montmorillonite, and 5.5:1 for Cs-montmorillonite.

The same sample weights (~0.25 g), with the exception of that for the silica-alumina catalyst, were used to provide uniform comparison. It might be argued that, although the upper limit of the size fraction used was the same for the kaolinite as for the montmorillonite samples, the mean particle size of the latter is considerably less with a consequent greater surface area, resulting in slower diffusion of the adsorbate around particles. There is no reason to believe, however, that the further marked tailing of the adsorption peak for Cs-montmorillonite, as compared with that for Na-montmorillonite, is due to a significant difference in the mean particle size or in pore characteristics (greater proportion of micropores) that evolve during sample preparation. That this is a reasonable assumption is more clearly brought out in a later discussion of carbon dioxide adsorption, particularly on Cs-montmorillonite. Consequently, if only external surface (including that within relatively large pores) were involved in the adsorption process, the adsorption rates for all the homoionic montmorillonite samples would be closely comparable.

Although adsorption equilibrium for the montmorillonite samples appeared to be complete within 5 min from the initiation of the adsorption process, it was found that a very small quantity of nitrogen at a constant relative pressure continued to adsorb on (within) a sample over an extended period of time. Because of the small sample size used and the consequent minute increase in the volume of nitrogen being adsorbed, the increase could not be monitored readily as it occurred. Several adsorption-desorption cycles conducted at different time intervals, however, showed the increase. Data for K-montmorillonite and Ca-montmorillonite are shown in Table 2.

It is seen that, after an initial adsorption period of 15 min, about 0.9 cc N<sub>2</sub>/g of each sample is further adsorbed over an approximate 7-hr period.

This amounts to about a 3 per cent increase over the volume adsorbed at the apparent adsorption equilibrium. Thus, the adsorption of nitrogen on montmorillonite proceeds in two stages: The first stage is relatively rapid (but still slower than adsorption on fine particles possessing external surface only), with some rate variation dependent upon the replaceable cation; the second stage is quite slow and does not seem to vary measurably with the replaceable cation.

To account for these phenomena, it is apparent that some diffusion occurs between platelets, rather rapidly at first around the edges, and then more slowly towards the interior. The final extent of penetration, were one to wait long enough, is unknown.

Surface-area values determined after the first stage of adsorption, where adsorption equilibrium appears to have been reached, obviously will be slightly lower than values obtained from longer adsorption periods, and for this reason one hesitates in attaching a specific value to a particular sample without some qualification. It is found, however, that with half-hour adsorption points, the B.E.T. plots are linear, indicating that there is little change in the diffusion rate (after the initial adsorption stage) over the relative pressure range used. From a practical standpoint, the relative surface-area values determined from half-hour adsorption points are revealing, in that they appear to provide a measure of the relative forces between platelets as influenced by the size and charge of the replaceable cation. Values are given in Table 3.

Among the samples degassed at 110°C and 175°C, it is apparent that there is a general increase in the measured surface area as the replaceable monovalent cation increases in size. This effect does not appear to any particular degree (2 or 3 units in surface-area values at the level under discussion are not significant) among the samples containing divalent cations. The latter samples yield somewhat smaller surface-area values than those containing monovalent cations of comparable size.

Table 2. Nitrogen adsorption on < 1 μ fraction of Ca- and K-montmorillonite as a function of time

Adsorption time (min)	Ca-montmorillonite (0.274 g, $p/p_s = 0.200$ )		K-montmorillonite (0.289 g, $p/p_s = 0.200$ )	
	Volume adsorbed (cc)	Volume adsorbed per gram (cc)	Volume adsorbed (cc)	Volume adsorbed per gram (cc)
15	7.62	27.81	10.43	36.08
120	7.65	27.91	10.48	36.26
240	7.70	28.10	10.53	36.44
420	7.87	28.72	10.69	36.99

Table 3. Surface-area values from nitrogen adsorption on  $<1 \mu$  fraction of homoionic montmorillonites using 3-point B.E.T. plots established from half-hour adsorption periods

Replaceable cation	Pauling radius Å	Surface Area, m <sup>2</sup> /g		
		Degassed 110°C	Degassed 175°C	Degassed as indicated
Li <sup>+</sup>	0.60	61	68	81 (300°C)*
Na <sup>+</sup>	0.95	94	100	97 (500°C)*
K <sup>+</sup>	1.33	121	128	114 (500°C)*
Rb <sup>+</sup>	1.48	112	112	105 (500°C)†
Cs <sup>+</sup>	1.69	134	138	118 (380°C)†
NH <sub>4</sub> <sup>+</sup>	1.50	122	118	—
Mg <sup>++</sup>	0.65	84	86	84 (300°C)*
Ca <sup>++</sup>	0.99	86	94	93 (500°C)*
Ba <sup>++</sup>	1.35	78	81	64 (565°C)*

\*Within range of temperatures reported by Greene-Kelly (1953) at which lattice expansion with glycol no longer occurs.

†Temperature used; no reference was found indicating a temperature of irreversibility.

Mooney, Keenan, and Wood (1952) reported similar variations in their nitrogen adsorption studies on Wyoming bentonite, for which they could offer no explanation other than the possibility that the aggregates were smaller in the case of the dry Rb and Cs clays.

The values, in general, are slightly higher for the samples degassed at 175°C as compared with those degassed at 110°C, owing probably to the further removal of water associated with the cations. Additional weight loss was noted at the higher degassing temperature, but the absolute weight-loss figures have little comparative meaning, since the samples were not at the same moisture equilibrium at the beginning of the degassing operation.

Although surface-area values are reported for samples degassed at temperatures sufficiently high that lattice expansion by glycolation no longer occurs, too much significance should not be attached to such values, owing to the large range of temperatures used, which, in some cases, may be sufficient to cause some dehydroxylation. NH<sub>4</sub>-montmorillonite was not included in the study because of possible decomposition effects at the higher temperature.

In general, the surface-area values are a little lower, as would be expected, than values obtained for samples degassed at the lower temperatures. One anomaly, for which there is no adequate explanation, is the increase in surface area of the Li-montmorillonite. It is possible that appreciable water is retained by the small cation, even during an extended period at 175°C, which is later removed more easily at the higher temperature, permitting

faster initial adsorption.

The conclusion that nitrogen penetrates to some extent between platelets is greatly augmented from the adsorption behavior of carbon dioxide on montmorillonite. The adsorption is somewhat analogous to nitrogen adsorption, in that there is a relatively rapid initial adsorption stage followed by a slow diffusion stage. The extent of penetration between layers, however, with carbon dioxide during the initial adsorption stage is considerably greater than with nitrogen, and surface-area values determined from half-hour adsorption points provide an even better measure of the relative forces between platelets than values from nitrogen adsorption. This is apparent from the data shown in Table 4, where the measured surface areas (110°C degassing temperature) range from 99 m<sup>2</sup>/g for Li-montmorillonite to 315 m<sup>2</sup>/g for Cs-montmorillonite.

Values from the 16-hr adsorption period are slightly higher, reflecting the increased adsorption volumes from the slow diffusion stage, with the exception of that for Cs-montmorillonite. The value for this sample remains unchanged, indicating that complete penetration between platelets occurred during the initial adsorption stage. The adsorption of carbon dioxide on Cs-montmorillonite, where adsorption equilibrium is reached within the relatively short time period of 30 min, strongly substantiates the assumption made earlier that significant differences in pore characteristics and in the mean particle size are not expected during sample preparation. If such were the case, the adsorption of carbon dioxide on Cs-montmorillonite would be characterized

Table 4. Surface-area values from carbon dioxide adsorption on  $<1 \mu$  fractions of homoionic montmorillonites

Replaceable cation	Surface Area, m <sup>2</sup> /g			
	Degassed 110°C		Degassed 175°C	Degassed as indicated
	$\frac{1}{2}$ hr. adsorption	16 hr. adsorption*	$\frac{1}{2}$ hr. adsorption	$\frac{1}{2}$ hr. adsorption
Li <sup>+</sup>	99	136	104	93 (300°C)
Na <sup>+</sup>	145	156	146	125 (500°C)
K <sup>+</sup>	200	211	195	147 (500°C)
Rb <sup>+</sup>	203	220	208	136 (500°C)
Cs <sup>+</sup>	315	315	312	237 (380°C)
NH <sub>4</sub> <sup>+</sup>	235	268	213	—
Mg <sup>++</sup>	107	147	110	98 (300°C)
Ca <sup>++</sup>	128	148	126	104 (500°C)
Ba <sup>++</sup>	124	145	123	85 (565°C)

\*Single-point using the same intercept established from 3-point B.E.T. plot and half-hour adsorption.

also by a period of slower diffusion relative to carbon dioxide adsorption on the other samples, in analogy to the different nitrogen adsorption rates.

The actual total surface area should be twice the value obtained for the Cs-montmorillonite (only one molecular layer of carbon dioxide between platelets), or 630 m<sup>2</sup>/g, minus the external surface area. Although the value for the latter parameter remains unknown from this study, a reasonable estimate might be 50 m<sup>2</sup>/g (smaller than Li-montmorillonite but greater than Anna kaolinite). The calculated value then for the total surface area is 580 m<sup>2</sup>/g.

The surface-area values for samples degassed at 175°C are comparable to those from samples degassed at the lower temperature. The value for NH<sub>4</sub>-montmorillonite is significantly lower, indicating that some loss of NH<sub>3</sub> may have occurred.

Again, as would be expected, the values are lower for samples degassed at the higher temperatures. A longer soak time at the designated temperature probably would decrease the values, but possible dehydroxylation effects could cause disproportionate changes.

An apparent paradox is the fact that the nonpolar carbon dioxide molecule, with a larger cross-sectional area than the nitrogen molecule, more easily penetrates between the layers of montmorillonite. This is explained, however, from a consideration of the relative adsorption temperatures used. The carbon dioxide molecule at 195°K is kinetically more energetic, with a greater diffusion coefficient, than the nitrogen molecule at 77°K. From this it is likely that, if nitrogen were able to form a monolayer at 195°K, it also would possess sufficient energy to penetrate completely between the Cs-montmorillonite platelets.

It is only with the Cs-montmorillonite, among

the samples studied, that the combination of forces occurring between platelets is sufficiently weak to permit complete penetration by carbon dioxide. If it is assumed that the attractive forces between platelets are mainly van der Waals forces, then with increasing size of the replaceable cation these forces are greatly weakened as the platelets of the degassed sample are held farther apart. In addition, however, the field strength in the vicinity of the replaceable cation is governed by the cationic charge. This factor presumably influences the forces between platelets and, thus, may account for the lower measured surface-area values with the interlayer divalent cations.

It should be added that the same trend was found with a few selected and similarly prepared homoionic species of  $<1\mu$  fraction of Wyoming bentonite. The surface-area values with similarly substituted samples were a little lower. For example, with the Cs-substituted sample, the surface-area values from nitrogen adsorption and carbon dioxide adsorption were 102 m<sup>2</sup>/g and 262 m<sup>2</sup>/g, respectively.

### CONCLUSIONS

Two distinct stages characterize the adsorption of both nitrogen and carbon dioxide on the  $<1\mu$  fraction of montmorillonite. That is, a relatively rapid initial rate of adsorption is followed by an exceedingly slow rate.

It is apparent from these phenomena and from surface areas determined from the initial rate of adsorption that diffusion occurs between platelets to a varying extent. This is in opposition to the generally held concept that nitrogen is unable to penetrate between the platelets and provides a measure only of the external surface.

The degree of penetration in the initial adsorption stage, as revealed by the measured surface

areas, appears to reflect the relative forces between platelets as influenced by the size and charge of the interlayer cation.

Complete penetration of the Cs-montmorillonite was achieved by carbon dioxide at 195°K, yielding a total surface-area value of approximately 580 m<sup>2</sup>/g.

#### REFERENCES

- Anderson, R. B., Bayer, J., and Hofer, L. J. E. (1956) Determining surface areas from CO<sub>2</sub> isotherms: *J. Fuel* (London) **44**, 443–452.
- Bridgeman, O. C. (1927) A fixed point for the calibration of pressure gauges: the vapor pressure of liquid carbon dioxide at 0°: *J. Am. Chem. Soc.* **49**, 1174–1183.
- Brunauer, S., Emmett, P. H., and Teller, E. (1938) Adsorption of gases in multimolecular layers: *J. Am. Chem. Soc.* **60**, 309–319.
- Daeschner, H. W., and Stross, F. H. (1962) An efficient dynamic method for surface area determinations: *Anal. Chem.* **34**, 1150–1155.
- Emmett, P. H., and Brunauer, S. (1937) The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts: *J. Am. Chem. Soc.* **59**, 1553–1564.
- Emmett, P. H., Brunauer, S., and Love, K. S. (1938) The measurement of surface areas of soils and soil colloids by the use of low temperature van der Waals adsorption: *Soil Sci.* **45**, 57–65.
- Greene-Kelly, R. (1953) Irreversible dehydration in montmorillonite, II: *Clay Minerals Bull.* **2**, 52–56.
- Grim, R. E., and Cuthbert, F. L. (1945) The bonding action of clays, Part I—Clays in green molding sands: *Illinois State Geol. Surv., Rept. Invest.* **102**.
- Hathaway, J. C. (1956) Procedure for clay mineral analyses used in the sedimentary petrology laboratory of the U.S. Geological Survey: *Clay Minerals Bull.* **3**, 8–13.
- Hendricks, S. B., Nelson, R. A., and Alexander, L. T. (1940) Hydration mechanism of the clay mineral montmorillonite saturated with various cations: *J. Am. Chem. Soc.* **62**, 1457–1464.
- Lamond, T. G., and Marsh, H. (1964) The surface properties of carbon: the effect of capillary condensation at low relative pressures upon the determination of surface area: *Carbon* **1**, 281–292.
- Makower, B., Shaw, T. M., and Alexander, L. T. (1937) The specific surface and density of some soils and their colloids: *Soil Sci. Soc. Am. Proc.* **2**, 101–109.
- Marsh, H., and O'Hair, T. E. (1966) The adsorption of nitrous oxide on coals and carbons: considerations of surface area and microporosity: *J. Fuel* (London) **45**, 301–309.
- Marsh, H., and Siemieniewska, T. (1965) The surface areas of coals as evaluated from the adsorption isotherms of carbon dioxide using the Dubinin-Polanyi equation: *J. Fuel* (London) **44**, 355–367.
- Mooney, R. W., Keenan, A. G., and Wood, L. A. (1952) Adsorption of water vapor by montmorillonite: *J. Am. Chem. Soc.* **74**, 1367–1374.
- Nelsen, F. M., and Eggertsen, F. T. (1958) Determination of surface area: adsorption measurements by a continuous flow method: *Anal. Chem.* **30**, 1387–1390.
- Nelson, R. A., and Hendricks, S. B. (1943) Specific surface of some clay minerals, soils, and soil colloids: *Soil Sci.* **56**, 285–296.
- Pickering, H. L., and Eckstrom, H. C. (1952) Physical adsorption of gases on anatase: *J. Am. Chem. Soc.* **74**, 4775–4777.
- Quirk, J. P. (1955) Significance of surface areas calculated from water vapor sorption isotherms by use of the B.E.T. equation: *Soil Sci.* **80**, 423–429.
- Thomas, J., Jr., Benson, G. S., and Hieftje, G. M. (1966) Measurement of the surface areas of coals from the dynamic sorption of carbon dioxide: *Am. Chem. Soc., Div. Fuel Chem., Preprints* **10**, (3) 7–14; *Illinois State Geol. Survey Reprint 1966-N* (Reprinted with permission of the Am. Chem. Soc.).
- Walker, P. L., Jr., and Kini, K. A. (1965) Measurement of the ultrafine surface area of coals: *J. Fuel* (London) **44**, 453–459.
- Zettlemoyer, A. C., Young, G. J., and Chessick, J. J. (1955) Studies of the surface chemistry of silicate minerals, III—Heats of immersion of bentonite in water: *J. Phys. Chem.* **59**, 962–966.

**Résumé**—Des calculs sur la superficie de surface ont été effectuées sur un montmorillonite avec différents cations placés en des lieux d'échange, et en utilisant le nitrogène et le dioxyde de carbone en tant que produits d'adsorption à 77°K et 195°K, respectivement, dans un système dynamique. Pour la fraction d'un montmorillonite du Mississippi inférieure, en taille, à environ 1  $\mu$ , des échantillons ont été préparés en remplaçant les premiers cations échangeables par Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Ba<sup>++</sup> et NH<sub>4</sub><sup>+</sup>, formant une série d'espèces homo-ioniques de montmorillonite.

Les zones de surface à partir des relevés B.E.T. en 3 points (points d'adsorption d'une demi-heure), avec du nitrogène comme produit d'adsorption variaient de 61 m<sup>2</sup>/g pour le Li-montmorillonite à 138 m<sup>2</sup>/g pour le Cs-montmorillonite, reflétant ainsi un certain degré de pénétration de nitrogène entre les feuillets. La pénétration complète devrait théoriquement avoir lieu dans une zone de surface supérieure à 300 m<sup>2</sup>/g pour cette argile, avec une monocouche de nitrogène entre chaque paire de lamelles. Les données expérimentales indiquent que l'étendue de la pénétration dépend du temps et est aussi une fonction des forces intermédiaires commandées par la taille et la charge du cation remplaçable. Cette découverte rend nul le concept généralement accepté, selon lequel le nitrogène à 77°K ne pénètre par les feuillets et fournit seulement une mesure pour la surface externe des minéraux argileux expansibles.

Une autre mesure de la variation des forces intermédiaires est fournie par l'adsorption de dioxyde de carbone à 195°K. Les valeurs de la zone de surface varient de 99 m<sup>2</sup>/g pour le Li-montmorillonite



à 315 m<sup>2</sup>/g pour le Cs-montmorillonite. Bien que la molécule de dioxyde de carbone est plus grande que celle du nitrogène, sa plus grande pénétration résulte apparemment, de ce qu'elle est plus énergétique au point de vue cinétique (avec un coefficient de diffusion plus élevé) à sa plus haute température d'adsorption. Des différences similaires ont été trouvées avec les deux produits d'adsorption dans l'étude de substances microporeuses, telles que le charbon, pour lesquelles la diffusion activée prend une plus grande signification.

**Kurzreferat**—An einem Montmorillonit mit verschiedenen Kationen an den austauschfähigen Stellen wurden Oberflächenmessungen durchgeführt, und zwar unter Verwendung von Stickstoff und Kohlendioxyd als Adsorbate bei 77°K bzw. 195°K in einem dynamischen System. Aus einem Bruch von weniger als ca. 1 μ Dicke eines Mississippi Montmorillonit wurden Proben hergestellt durch Ersatz der ursprünglichen austauschbaren Kationen durch Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Ba<sup>++</sup>, und NH<sub>4</sub><sup>++</sup> und Bildung einer Reihe von homo-ionischen Montmorillonitsorten.

Oberflächen von 3-Punkt B.E.T. Stellen (halbstündige Adsorptionspunkte) mit Stickstoff als Adsorbat betragen von 61 m<sup>2</sup>/g für Li-Montmorillonit bis zu 138 m<sup>2</sup>/g für Cs-Montmorillonit, was einem gewissen Grad von Stickstoffdurchdringung zwischen den Schichten entspricht. Vollständige Durchdringung sollte theoretisch durch eine Oberfläche von über 300 m<sup>2</sup>/g für diesen Ton mit einer einmolekularen Stickstoffschicht zwischen jedem Paar von Plättchen zum Ausdruck kommen. Die Versuchsergebnisse deuten darauf hin, dass das Mass der Durchdringung zeitgebunden ist und daneben auch von den durch die Grösse und Ladung des austauschbaren Kations bestimmten Zwischenschichtkräften abhängt. Dieser Befund widerspricht der allgemein vertretenen Ansicht, wonach Stickstoff bei 77°K die Schichten nicht durchdringt und nur ein Mass der äusseren Oberfläche von aufgeblähten Tonmineralen darstellt.

Ein weiteres Mass für die Änderung der Zwischenschichtkräfte stellt die Adsorption von Kohlendioxyd bei 195°K dar. Die oberflächenwerte legen zwischen 99 m<sup>2</sup>/g für Li-Montmorillonit und 315 m<sup>2</sup>/g für Cs-Montmorillonit. Obwohl das Kohlendioxydmolekül grösser als das Stickstoffmolekül ist, scheint seine stärkere Durchdringung darauf zu beruhen, dass es bei seiner höheren Adsorptionstemperatur mehr kinetische Energie besitzt (mit einem grösseren Diffusionskoeffizienten). Ähnliche Unterschiede wurden bei den zwei Adsorbaten in der Untersuchung von mikroporösen Substanzen wie z. B. Kohle festgestellt, wo die aktivierte Diffusion von beträchtlicher Bedeutung ist.

**Резюме**—Определения поверхностной площади производились на монтмориллоните с различными катионами, размещенными на обмениваемых местах, пользуясь азотом и двуокисью углерода в качестве адсорбатов при 77°K и 195°K соответственно, в динамической системе. Из фракции монтмориллонита Миссиссипи размером менее 1μ приготовили образцы, подставляя Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Ba<sup>++</sup>, NH<sub>4</sub><sup>+</sup> вместо исходных заменяемых катионов и образуя серии гомоионных монтмориллонитовых форм.

Поверхностные площади из трехточечных кривых В.Е.Т. (получасовые адсорбционные точки) с азотом в качестве адсорбата, находятся в пределах от 61 m<sup>2</sup>/g для литий монтмориллонита до 138 m<sup>2</sup>/g для цезиймонтмориллонита, отражая тем самым некоторую степень азотного проникновения между слоями. Полное проникновение в теории должно произойти в поверхностной площади свыше 300 m<sup>2</sup>/g для этой глины, с азотным мономолекулярным слоем между каждой парой пластинок. Экспериментальные данные указывают, что количество проникновения переменено по времени и является также функцией прослоечных усилий, регулируемых размером и зарядом сменяемого катиона. Результат этот отрицает общепринятое понятие, что азот при 77°K не проникает в слои и предоставляет лишь измерение наружной поверхности расширяемых глинистых минералов.

Дальнейшее измерение изменений прослоечных усилий предоставляется адсорбцией двуокиси углерода при 195°K. Значения поверхностной площади колеблются от 99 m<sup>2</sup>/g для лития-монтмориллонита до 315 m<sup>2</sup>/g для цезия-монтмориллонита. Хотя молекула двуокиси углерода больше чем молекула азота, ее большее проникновение является вероятно следствием того, что кинетически она более активная (с более высоким коэффициентом диффузии) при своей более высокой температуре адсорбции. Сходные различия обнаружались с обоими адсорбатами при изучении микропористых веществ, как напр. угля, где активированная диффузия обладает крупным значением.