

SORPTION OF AMMONIA BY
HOMOIONIC BENTONITE CLAYS

by

RICHARD HAROLD SIEGEL

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1956

APPROVED:



Associate Professor of Chemistry

In Charge of Major



Chairman of Department of Chemistry



Chairman of School Graduate Committee



Dean of Graduate School

Date thesis is presented April 3, 1956

Typed by Betty Davis

ACKNOWLEDGMENT

The author would like to express his appreciation to Dr. W. H. Slabaugh for his encouragement and invaluable suggestions and to The National Lead Company whose sponsorship made this study possible.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
INTRODUCTION	
History of the Study of Clays	1
The Clay Mineral Concept	4
Types and Classification of Clay Minerals	5
The Structure of Montmorillonite	6
Properties and Applications of Bentonites	11
THE ADSORPTION OF GASES BY SOLIDS	
Types of Adsorption	13
Adsorption Isotherms	15
The Sorption of Gases by Bentonites	18
EXPERIMENTAL PROCEDURE	
Volumetric Apparatus	22
Gravimetric Apparatus	25
Preparation of Homoionic Bentonites	29
Use of the Apparatus in the Determination of Isotherms	33
EXPERIMENTAL RESULTS AND CONCLUSIONS	
Types of Clays Studied	39
Reproducibility of Isotherms	39
Conclusions	46
Suggestions for Further Studies	53

Section

Page

SUMMARY 55

BIBLIOGRAPHY 59

LIST OF TABLES

<u>Table Number</u>	<u>Title</u>	<u>Page</u>
1	Surface Areas of Homoionic Bentonites	48
2	Amounts of H ₂ O Adsorbed by Bentonites at 51 percent Relative Humidity	49

LIST OF FIGURES

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
1	Sketch of Gravimetric Adsorption Apparatus	26
2	Adsorption of Ammonia on Freeze Dried and Oven Dried Hydrogen and Sodium Bentonites at -45°C.	42
3	Adsorption of Ammonia on Freeze Dried and Oven Dried Calcium Bentonites at -45°C.	43
4	B. E. T. Plots of NH ₃ Adsorption at -45°C. on Oven Dried Bentonites	44
5	B. E. T. Plots of NH ₃ Adsorption at -45°C. on Freeze Dried Bentonites	45

SORPTION OF AMMONIA BY HOMOIONIC BENTONITE CLAYS

INTRODUCTION

History of the Study of Clays

Although the clay minerals have been of interest for centuries, only within the last twenty-five years has progress been such as to transform their study into a well integrated part of colloidal chemistry and associated fields. Until the 1930's the body of literature concerning clay minerals, i.e., colloidal silicates, was an almost hopeless mass of empiricism due to the stressing of applications rather than fundamental structural studies and also to a lack of refinement in instrumentation and purification.

Since 1920 however, we find five main lines of investigation: the search for clays of high purity, the development of methods of fractionation and characterization, the search for evidence of crystallinity, the development of structural concepts, and the use of structure to explain the properties of clays and to suggest new applications. This was almost a perfect model of the classical method of scientific investigation but was complicated by the colloidal character of the clays.

(18, p. 3)

Contributing to the early confusion was the fact that the clay materials varied widely in chemical composition.

Clays of the same ultimate chemical composition frequently had widely varying physical attributes, and clays with the same physical qualities might have very different chemical compositions. A considerable number of different concepts were proposed in the older literature to describe the essential components of all clays and account for the variation in properties. Usually these concepts were ideas concerning the manner in which alumina, silica, etc., are combined to form the fundamental units of clay structure. (10, p. 11)

One of the older concepts was the idea that there is a single pure clay substance, kaolinite, and that all differences in chemical composition between natural clays and pure kaolinite could be attributed to impurities of one sort or another. Another widely held viewpoint was that the essential component of all clay materials was a colloid complex. This complex, of course, was thought to be amorphous in line with the thinking of that day concerning all colloidal material.

Von Bemmelen and Streme divided the colloidal material into two parts depending upon the solubilities of the colloidal matter in hydrochloric and sulfuric acids and attempted to classify clays according to their allophaneton and kaolinton content. Allophaneton and kaolinton were the names given to the two different fractions. Mellor and Searle also thought of two essential components in clay

called clayite and pelinite.

Wiegner developed the idea of a kernel upon which anions were adsorbed with exchangeable cations attracted to the anions. This concept has been modified and carried on until recently by Mattson but has been rendered extremely doubtful, if not untenable, by X-ray diffraction studies which show that substantially all the components have definite crystalline structures.

Asch and Byers and his co-workers in the U. S. Department of Agriculture postulated a group of aluminosilicates of definite structures and compositions as the essential components in clays. This viewpoint is nearly the same as the present day clay-mineral concept.

For many years students of clays had suggested that materials having the plastic properties associated with clays were composed of extremely fine particles of a limited number of crystalline minerals. As early as 1887, Le Chatelier had arrived at this conclusion. Unfortunately there were no adequate research tools prior to about 1920 to 1925 to offer positive evidence for the theory. Thus, the clay mineral concept is not new but has only become well established in recent years.

The first concrete evidence of the crystallinity of the finest particles was due to the independent efforts of Hadding and Rinne who conducted the first X-ray diffraction analyses of clay materials. Crystalline materials were

found in the finest fractions of the series of clays studied, and all the samples seemed to be composed of particles of a small group of minerals. There was not a large heterogeneous array of minerals of a wide variety of types in the fine fractions studied.

In 1924 Ross and several colleagues of the U. S. Geological Survey began a study of clays which led to a series of important papers on the mineral composition of clays. Their work was largely done with the petrographic microscope and excellent chemical data, although they later supplemented their work with some X-ray analysis. Their results showed that the components of clay materials were largely crystalline and that there were a limited number of such components to which the name clay minerals was applied.

In 1926, Marshall began a study of optical properties of clay-water suspensions which led to conclusions regarding the crystallinity of the clays and influences due to the exchange cation. Further evidence of crystallinity in even the finest fractions of the clays was supplied by Hendricks and Fry and Kelley, Dore and Brown in 1930 and 1931 respectively, by means of X-ray diffraction.

The Clay Mineral Concept

The so-called clay mineral concept had become firmly established by the early 1930's due to the evidence which

had been accumulated by the people mentioned above. At the present time it is accepted by nearly all students of clays.

According to the clay mineral concept, clays are composed essentially of extremely small crystalline particles of one or more members of a small group of minerals which have come to be known as the clay minerals. These clay minerals are essentially hydrous aluminum silicates with magnesium or iron (or possibly alkalies or alkaline earths) proxying for a part of the aluminum. Some clays contain only one clay mineral while others contain a mixture of them.

While the clay minerals are the essential constituents of clays and largely determine their properties, some non-clay minerals, if present in large enough amounts, may influence the properties of the resulting clay. However, the presence of non-clay materials is limited to a few unique clays. Most clays are composed of entirely crystalline materials.

Types and Classification of Clay Minerals

The clay minerals may be classified conveniently on the basis of structure and composition. Grim proposes a possible classification on this basis and lists ten principal crystalline clay minerals according to this scheme.

(10, pp. 27-28)

Bentonite, the clay under consideration in this study, is a highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming. (10, pp. 361-364) The dominant clay mineral in bentonite is montmorillonite. Other clay minerals are present in many bentonites, but the properties of bentonite are dominantly those due to montmorillonite. Non-clay minerals such as quartzite and crystabollite may be present in various amounts. The composition of the montmorillonite itself may vary greatly in different bentonites. There is variation in the relative abundance of magnesium and iron and in the population of the silica layer as well as a wide variation in the type of exchangeable cation present. Most bentonites carry Ca as the most abundant ion, but those from Wyoming often carry Na as the dominant ion.

Bentonites are formed by the deposition of volcanic ash in lakes and seas. The ash then undergoes alteration in structure to form montmorillonite and, occasionally, other clay minerals. Bentonites are found in other sections of the United States as well as in Europe and Canada and occasionally in Japan.

The Structure of Montmorillonite

The key to the understanding and prediction of the properties of a clay lies in a knowledge of the structure of the predominant clay mineral. It is only natural,

therefore, that great emphasis has been placed upon the structure of clays after it was determined that they were largely crystalline in nature. Only if the minerals were crystalline could definite structures be assigned to them.

The basic ideas making possible the determination of the silicate structures were set forth by modern X-ray crystallographers. Much work has since been done on the structure as well as the properties of most clay minerals, and it is impossible to mention all those who have contributed to the voluminous literature of the clay minerals.

Two structural units are involved in the lattices of most clay minerals. (10, pp. 43-45) The first consists of two sheets of closely packed oxygen atoms or hydroxyl groups in which aluminum, iron or magnesium atoms are embedded in octahedral coordination so that they are equidistant from six oxygens or hydroxyls. The number of positions filled within the octahedrons depends upon the atom present. When aluminum is present, only two-thirds of the positions are filled. When magnesium is present, all of the positions are filled.

The second structural unit consists of silica tetrahedrons. In these units a silicon atom is equidistant from four oxygens, or hydroxyls if needed to balance the structure. These tetrahedral groups are repeated to form a sheet and are usually considered to be arranged so that their tips all point in the same direction with their bases

in a plane. Active oxygens or hydroxyls are those with only one bond to a silicon atom and, thus, are those on the edges of a sheet and at the tips of the tetrahedrons.

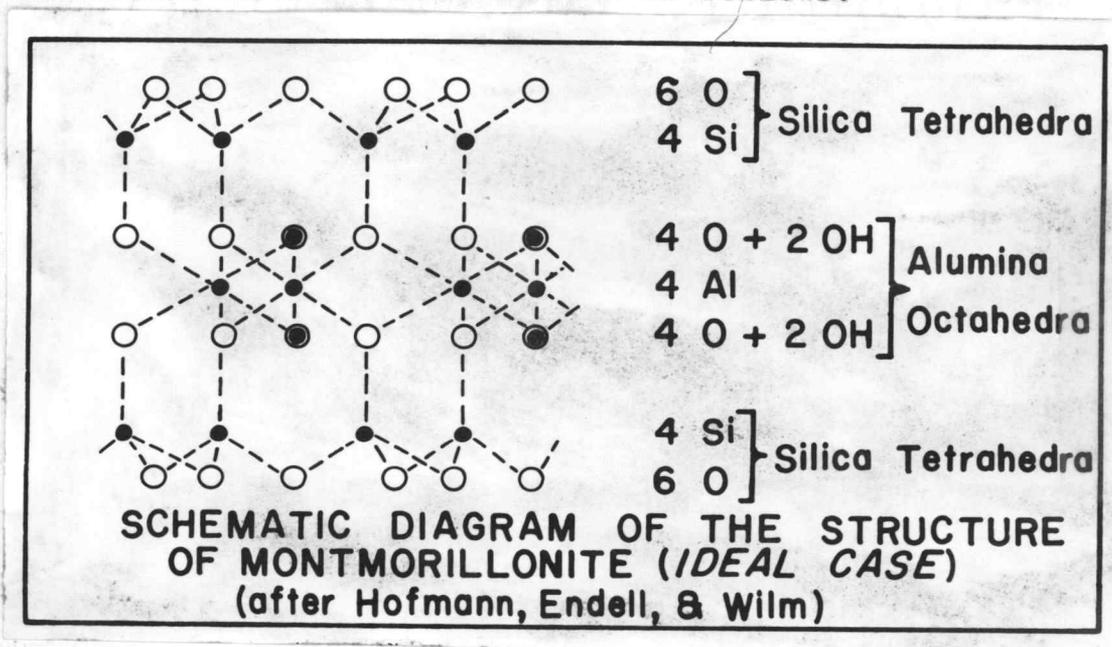
Since the montmorillonite minerals occur as extremely small particles, structural concepts must be deduced from powder data and inferences from better known structures. (10, pp. 55-64) The currently accepted structure was suggested in 1933 by Hofmann, Endell and Wilm (15, pp. 340-349) and modified by later contributions of Maegdefrau and Hofmann, Marshall and Hendricks. Accordingly, montmorillonite is thought to be composed of units made up of two silica tetrahedral sheets with an alumina octahedral sheet interposed between the tetrahedral sheets, much like a sandwich with the alumina sheet in the center. These sheets are continuous in two dimensions. Within the unit the points of the tetrahedrons all point toward the center of the unit.

The particles of the dry clay consist of perhaps several hundred of these unit platelets stacked one upon the other like a deck of cards. The stacking of these units results in the oxygen layers of each unit being adjacent to the oxygen layers of the neighboring units. This results in an extremely weak bond between units and explains the fact that water and other polar molecules may enter between the unit layers in montmorillonite and cause expansion of the lattice. The c axis spacing thus may vary from about 9.6 A,

with no interlayer polar molecules, to almost complete separation of the individual layers.

When the clay particles are placed in water or some other polar liquid or, for that matter, merely exposed to a polar gas, the molecules of gas or liquid are capable of entering between the unit platelets in the particle. This causes marked expansion of the clay particle and accounts for the extremely high swelling and associated colloidal properties exhibited by the montmorillonites.

A convenient diagrammatic sketch of the unit layer in the montmorillonite structure is as follows:



The structure above is a theoretical, ideal structure. The actual structure of montmorillonite always varies from the ideal structure since, as noted by Marshall (18, p. 6), there is substitution within the lattice of aluminum for silicon in the tetrahedral layers and substitution of

magnesium, iron, zinc, nickel, or lithium for aluminum in the octahedral sheets. This substitution results in an unbalancing of the lattice, and usually results in a net charge of about 0.66 - per unit cell.

This charge deficiency is balanced by the presence of exchangeable cations between the layers and gives rise to the high base exchange capacity of the montmorillonites. The base exchange capacity of a clay is defined as the number of milliequivalents of exchangeable cation per one hundred grams of clay. Montmorillonites range in base exchange capacity from 80 to 150 milliequivalents per one hundred grams. The substitutions within the lattice of montmorillonite and the resulting negative charge are responsible for about 80% of the base exchange capacity with the remaining 20% probably due to broken bonds about the edges of the silica-alumina units which give rise to unsatisfied charges.

The structure of montmorillonite as postulated above does not adequately account for all its properties, and Edelman and Favejee (7, pp. 420-423) have suggested an alternative structure which attempts to explain these properties more satisfactorily. In their proposed structure it is suggested that every other one of the silica tetrahedrons is inverted. This structure accounts for the exchange capacity without assuming any substitution within the lattice. However, X-ray, chemical, and dehydration data

are all against the Edelman, Favejee structure, and further investigations are necessary before a definitely correct structure for montmorillonite is achieved. At the present the Hofmann, et. al., structure is the most generally satisfactory.

Properties and Applications of Bentonite

In addition to a large base exchange capacity, the bentonites exhibit marked colloidal properties in many other respects. (14, pp. 207-209) and 13, pp. 302-312) Suspensions of bentonite possess marked thixotropy. Excellent streaming birefringence is shown in bentonite suspensions when viewed in polarized light.

Its most striking property is the extreme swelling which the clay undergoes upon wetting. This phenomena is due to the penetration of polar solvent between the platelets of the particle thus forcing the platelets apart. The amount of swelling varies widely depending upon the exchangeable cation present on the clay and the solvent under consideration. (18, pp. 162-164)

Bentonites have enjoyed the most widespread applications of any of the clays. Their chief use is in suspensions which are critical as drilling fluids for use in oil wells. Other applications are in decolorizing oils, in manufacturing catalysts, and in bonding molding sands.

Further applications are of some importance also.

(10, p. 364) and 13, pp. 314-319)

THE ADSORPTION OF GASES BY SOLIDS

Types of Adsorption

The phenomena of adsorption, the tendency for gases and vapors to condense on the surface of a solid with which they are in contact, was first noted by Scheele in 1773. Since that time much experimental and theoretical work has been done to explain quantitatively and qualitatively how solids adsorb gases.

Adsorption is distinguished from absorption by the fact that the former is strictly a surface process, whereas the latter designates a process whereby the molecules of one phase more or less uniformly penetrate among the molecules of the second phase. Since there is often some difficulty in distinguishing which process occurs, the term sorption has been used when there is an uncertainty as to which is occurring.

The most general type of adsorption is a rapid, low temperature, reversible process. This is generally known as physical adsorption and is attributed to physical forces between the adsorbent and adsorbate in the nature of van der Waals forces. It is characterized by being rather non-specific in that it parallels the physical character of the adsorbent. Physical adsorption increases with decreasing temperature.

A second type of adsorption is known, in general, as chemisorption and is thought to be due to primary valence forces, thus making it chemical in nature. This type of adsorption is largely independent of the physical nature of the adsorbent and therefore depends heavily upon its chemical characteristics. It is characterized by being relatively strong and specific and often increases with increasing temperature.

It is usually possible to differentiate between the two types of adsorption rather easily. Physical adsorption is accompanied by heat effects in the order of magnitude of the heat of liquefaction, while in chemisorption the heat effects are much larger, comparing more favorably with those of a chemical reaction. (27, pp. 36-39) Temperature and pressure effects also may serve to differentiate between the two. Physical adsorption falls off rapidly with increasing temperature, whereas chemisorption increases at first and then decreases with rising temperature. Physical adsorption does not reach a saturation value with increasing pressure until the relative pressure is high, while chemisorption increases rapidly with increasing pressure until a saturation value is reached at a low relative pressure after which an increase in pressure does not alter the amount adsorbed. Very often physical and chemical adsorption occur simultaneously, and a sharp differentiation is impossible.

Adsorption Isotherms

Numerous attempts have been made to explain adsorption by means of mathematical equations. Some, like the Freundlich equation, are largely empirical while others attempt to explain the phenomena theoretically.

Langmuir (17, pp. 1368-1384) proposed the theory of monomolecular and monoatomic adsorption in which he assumed that adsorption was due to forces at the surface of a crystal lattice. These forces caused gas molecules to remain attached to the surface after striking it. He was able to derive an expression for the amount adsorbed as a function of the pressure upon considering an equilibrium to be established between the condensation and evaporation rates of the gas on the surface. The Langmuir theory explains some data on chemical adsorption quite satisfactorily, but it may be criticized since it limits the adsorption to a monomolecular film and postulates a saturation value for the amount of adsorption.

One of the most satisfactory isotherms to date is due to Brunauer, Emmett and Teller (9, p. 1568) and 4, pp. 309-317) and is commonly known as the B. E. T. equation. Their assumptions closely paralleled those of Langmuir in that they assumed an equilibrium between the rates of condensation and evaporation, but they extended the monomolecular layer theory to allow for multilayer adsorption. The equilibrium

expression was applied to each layer of the multilayer. The derivation of the B. E. T. equation results in the following equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0}$$

where V is the volume of gas adsorbed in cubic centimeters at standard temperature and pressure; P is the pressure at which the adsorption takes place; P_0 is the vapor pressure of the gas at the temperature of the adsorbent; C is a constant related to the heat of adsorption; and V_m is the volume of gas in cubic centimeters necessary to form a monomolecular layer over the entire surface of the adsorbent.

It may be seen by inspection of the above form of the B. E. T. equation that, for systems which conform to the B. E. T. theory, a plot of $\frac{P}{V(P_0 - P)}$ versus P/P_0 , the partial pressure of the gas, should result in a straight line. It is also apparent that the intercept on the ordinate $\frac{1}{V_m C}$ and that the slope of the line $\frac{C-1}{V_m C}$; therefore V_m and C may be easily determined. The expression $\frac{P}{V(P_0 - P)}$ is commonly known as the B. E. T. function.

The area occupied by a molecule of adsorbate is usually calculated from the density of the liquified or solidified adsorbate. This area per molecule multiplied by the number of molecules contained in the volume, V_m , gives the surface area of the adsorbent.

The Brunauer, Emmett, and Teller theory thus introduces for the first time a definite concept of the relation between the adsorption of a gas and the extent of surface of the adsorbent. It has become the standard method for measuring surface areas of solids by means of gas adsorption.

Harkins and Jura (11, p. 98) pointed out that any condensed film on liquids or solids obeys the relationship: $\pi = b - a\sigma$ where π is the film pressure, σ is the area per molecule, and a and b are constants. They transformed this relationship into a simple isotherm of the form $\log P/P_0 = B - \frac{A}{v^2}$ where A and B are constants and v and P/P_0 have the same significance as in the B. E. T. equation. This isotherm is the simplest yet derived and seems to be valid over a larger pressure range than any other isotherm.

It is possible to obtain surface areas from the Harkins-Jura isotherm through knowledge of the slope of the curve and a numerical constant for the adsorbate determined from measurements of heats of immersion.

The general applicability of the two methods is discussed by Harkins and Jura (12, p. 1372) and Emmett (8, pp. 1787-1789). In most cases both methods are valid, but this depends upon the type of film formed by the adsorbate upon the surface of the adsorbent.

It was found that the experimental results gave satisfactory B. E. T. plots but did not give satisfactory curves

when treated by the Harkins-Jura method. Therefore, further discussion will be limited largely to the B. E. T. theory.

Although the B. E. T. and the Harkins-Jura methods are very good for representing adsorption on a plane surface, they will not, at times, explain adsorption by porous solids. This deviation is assumed to be due to capillary condensation in the pores or interstices of the adsorbent. A limit is thus placed on the usefulness of the multilayer equations since it cannot be determined what part of the adsorption is due to multilayer formation and what part is due to capillary condensation.

The Sorption of Gases by Bentonites

Relatively little work has been done concerning the adsorption of gases on bentonites. The most significant results are those giving the surface area of the clay. Other adsorption data lead to rather unfruitful conclusions since in few cases are the clays sufficiently characterized to make the data generally useful. Some conclusions of general value have, however, been drawn from consideration of the shape of the isotherm and postulation of various adsorption mechanisms to account for the isotherm.

Two types of adsorption must be considered. First, there is the adsorption of the gas by the external, readily available, surface of the clay. This surface is available to all types of gas molecules. This external surface has

been measured by various investigators using gases varying from nitrogen to normal hydrocarbons. Areas calculated from B. E. T. plots indicate an external surface of about 50 to 55 m²/g for measurement with n-octane, 2-methyl butane and hydrogen. (3, p. 3080) and 24, p. 392) However, all these surfaces are very dependent upon the previous treatment of the clay and other variables. In contrast to the values as given above, Nelson and Hendricks have reported an external surface for montmorillonite of 15.5 m²/g (21, p. 289) measured with nitrogen.

The second type of adsorption is due to the large internal surface of the montmorillonite particle. This surface is generally unavailable to non-polar vapors since they cannot penetrate between the unit layers of the montmorillonite. However, polar vapors can force the platelets apart and enter between them. Thus, the entire internal area of the particle should be available for adsorption, or perhaps more correctly sorption, in the case of a polar molecule. (18, pp. 91-94) Values for the internal or total surface vary widely depending upon the treatment of the clay and the polar adsorbate used. Also a great deal of variation is found between clays containing different exchangeable cations. Most values lie between 300 and 350 m²/g for bentonite. (25, p. 1064) 19, p. 1370) and 22, p. 9101)

Ammonia had been used in only a few cases for

adsorption studies. Cornet (6, pp. 217-226) did some of the first work with it, but his studies were restricted to hydrogen bentonites and to low relative pressures. Further work has been done by others (22, p. 9101) 26, pp. 30-32) and 2, pp. 980-989) but very little of this work has been carried out at low temperatures under conditions where one can obtain a complete isotherm including high relative pressures. Furthermore, few of the studies have characterized the clays sufficiently insofar as the clays were, in most cases, not homoionic. Reproducibility of the isotherms with ammonia has not previously been investigated.

It is felt that there is need for a rather comprehensive series of isotherms for the sorption of ammonia by bentonites. Ammonia being an extremely polar molecule, it should penetrate between the lamellae easily and thoroughly. Furthermore, its relatively small size should make it available to all portions of the clay surface.

Due to the basic properties which ammonia exhibits, it would be interesting also to note any special affinity which hydrogen bentonite might exhibit toward it, since hydrogen bentonite in suspension is a fairly strong acid with an ionization constant of 2×10^{-5} and the clay should, when dry, exhibit highly active acidic sites.

Accordingly, this study has been made on various homoionic bentonites at a low temperature. Ca, H, and Na clays, both oven-dried and freeze-dried, were used, thus

forming a rather comprehensive set of well characterized clays.

The temperature was selected such as to allow a complete isotherm to be run. Furthermore, attempts were made to determine the reproducibility of the isotherms.

EXPERIMENTAL PROCEDURE

Volumetric Apparatus

The first attempts to obtain isotherms of the adsorption of ammonia by bentonite were made using a high vacuum apparatus designed to measure the adsorption by volumetric means.

The principle upon which the operation of the volumetric apparatus is based is relatively simple. An increment of gas is passed into a chamber of calibrated volume and its pressure is measured. The gas is then passed into the adsorption chamber containing the sample of adsorbent. The volume of this adsorption chamber, called the "dead space," is also known and the pressure of the gas in the chamber may be measured. The amount of gas adsorbed may then be readily calculated by use of the gas laws.

The procedure followed in the use of the apparatus was as follows. A sample of clay was weighed, placed in the sample tube and the tube plugged with a weighed amount of cotton (cotton was used to prevent the powdery clay from escaping during outgassing). The sample tube was sealed onto the system, the clay was outgassed and a bath of freezing chlorobenzene was placed around the sample tube, thermostating the sample at -45.2°C . The ammonia which had previously been purified and stored in a storage bulb was admitted into the calibrated chamber and the pressure read

on a manometer. The calibrated bulb was then filled with mercury, forcing the ammonia into the adsorption chamber. The adsorption chamber was isolated from the system, and the pressure in the chamber was read after equilibrium was attained as indicated by no further change in the pressure reading of the manometer. This procedure was repeated, increasing the pressure by addition of suitable increments of ammonia until a pressure close to the saturation pressure was reached.

The calibrated chamber was calibrated by filling it with mercury, removing the mercury from the bulb, and then weighing the mercury. The accuracy of this determination was within 0.04 percent.

The dead space in the adsorption chamber was determined by adding known increments of helium and reading the pressure in exactly the same manner as before except that the helium calibration was made at room temperature. An accuracy of about 0.5 percent was attained in measurement of this dead space. Allowance was made for the volume occupied by the clay and the cotton by calculation of their volumes from their weight and density.

Although the sample tube was immersed in a bath maintained at about -45.2°C ., the entire adsorption chamber was not enclosed within the bath. Thus, much of the gas present in the chamber was not at -45.2°C ., and there was a resulting inhomogeneity in the gas temperature. It is necessary,

however, to know the temperature of the gas in the adsorption chamber if the calculations necessary for the isotherm are to be carried out. We must, therefore, associate with this inhomogeneity in temperature an average or "pseudo-" temperature.

Attempts were made to determine this pseudo-temperature, using ammonia, in an empty sample tube at -45.2°C . Plots of the pseudo-temperature versus P/P_0 were very inconsistent. Most of them showed a relatively high temperature at the low pressures which then dropped rapidly until a plateau was reached in the medium pressure range after which the temperature again dropped rapidly. However, these curves could not be reproduced satisfactorily, there being at least a 10 percent difference between the temperatures in the plateau regions of two different curves. If it had been possible to reproduce these curves, satisfactory isotherms could no doubt have been run since the pseudo-temperature curve would, in effect, be a blank run and would compensate for adsorption of ammonia on the walls, inhomogeneity of temperature, and to some extent for discrepancies of the gas from ideality.

Attempts were next made to measure the pseudo-temperature using helium in the system. These met with difficulties, and it was decided to abandon attempts to obtain isotherms by use of this volumetric system.

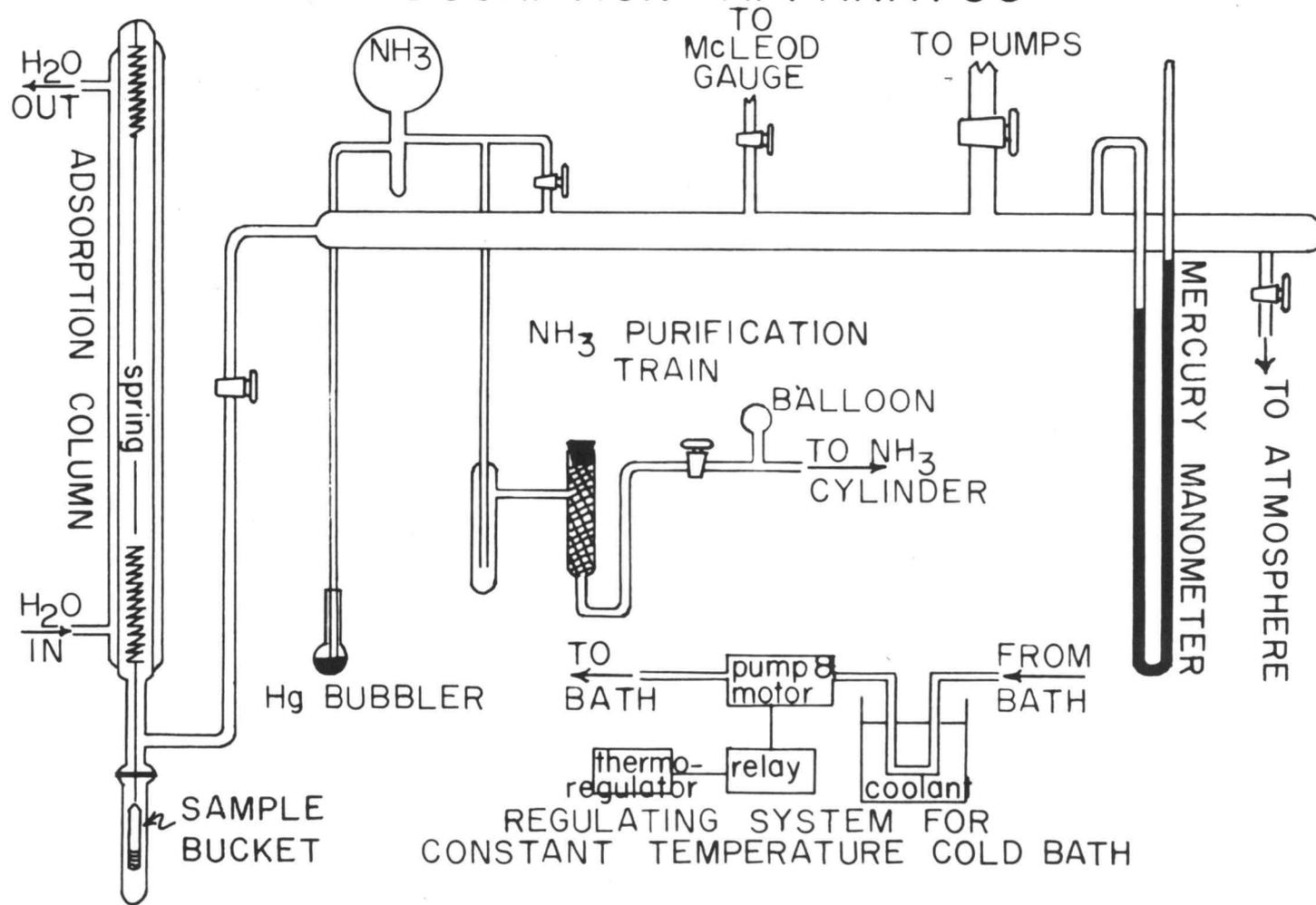
Gravimetric Apparatus

Following the failure of the volumetric apparatus, a gravimetric apparatus was resorted to. The apparatus consisted of a high vacuum system utilizing a Welch Duoseal forepump and a single stage mercury vapor diffusion pump. Under ideal conditions with a -80°C . cold trap in place, a pressure of 10^{-5} mm. of mercury has been measured on a McLeod gauge in the apparatus. This seemed to be the best vacuum possible, but working vacuums of less than 10^{-4} mm. were readily attainable.

The essential parts of the apparatus consisted of a copper-beryllium spring housed in a thermostated column and a mercury manometer for determination of the pressure. A small glass bucket containing the sample was suspended from the spring. A purification and storage system for the ammonia was included as was the aforementioned McLeod gauge. (See Figure 1)

The principles of this gravimetric apparatus are simple. Adsorption of the gas by the sample causes an increase in the weight of the sample thus distending the spring from which it is suspended. Knowledge of the spring constant enables one to determine the amount of gas adsorbed by measurement of the amount the spring is distended. The pressure is simultaneously read by use of the manometer. No knowledge of volumes is involved, and the only critical

FIGURE I GRAVIMETRIC ADSORPTION APPARATUS



factors are accurate measurement of spring movements, the gas pressures, and suitable thermostating facilities for the spring and the sample.

It is desirable to thermostat the sample at a relatively low temperature in order to achieve pressures in the system equal to the vapor pressure of ammonia. At -45°C . ammonia exhibits a vapor pressure of 40.97 cm. of mercury. This pressure is easily achieved and may be measured easily and accurately by use of a common mercury manometer. Therefore a system capable of thermostating the sample at temperatures near -45°C . was designed. (See Figure 1) A Dewar flask of two liter capacity was filled with isopropyl alcohol. The isopropanol was cooled by pumping through a glass coil immersed in a dry ice-isopropanol bath at -80°C . thence back into the Dewar flask. A common gear pump, powered by a small electric motor, was used to circulate the liquid. A Cenco bimetallic thermoregulator was used in conjunction with a Cenco-Gilson electronic relay to regulate the operation of the pump. An electric stirrer was used to insure sufficient agitation of the liquid in the bath, and an alcohol thermometer, graduated in fifths of a degree, was used to determine the temperature.

Some difficulty was encountered from ice crystals, formed on exposed parts of the bath, falling into the bath

and clogging the lines, but this was kept at a minimum by elimination of constrictions in the lines. In addition some water undoubtedly was deposited as ice in the cooling coil, due to the lower temperature of the coil, and this aided in the obstruction of the lines. It was necessary to distill the isopropanol between runs to eliminate this.

Thermostating of the sample was good. No variation in temperature could be noted on the thermometer at any time, and only a slight variation in pressure could be noted on an oil manometer using Apiezon "B" as the manometric fluid (which was included in the system for a time) when the vapor pressure of the ammonia was reached. The oil manometer was about 15.5 times as sensitive as was the mercury manometer. Maximum variation of the vapor pressure was no more than 8 mm. of oil or about 0.52 mm. of mercury. This corresponds to a temperature difference of about 0.025 degree.

Variation of the temperature at which the sample was thermostated between successive runs was not critical since the vapor pressure of ammonia was determined by reading of the manometer at the end of each run. However, the temperature apparently varied no more than 0.2 of a degree between each run, and possibly was as close as 0.1 of a degree.

The copper-beryllium spring which was relatively sensitive to temperature variations was thermostated by means of a water jacket around the column in which it was

enclosed. Water was pumped through the water jacket from a large water bath maintained at 26°C. A determination of the temperature variations in the water bath by use of a Beckmann thermometer indicated that the extreme deviation over a period of fifty minutes was 0.06°C. Even better thermostating could undoubtedly have been achieved if the water bath had been stirred more vigorously.

The variations in length of the spring were measured by use of a traveling microscope with a crosshair. The crosshair was aligned with a glass fiber affixed at right angles to the small glass rod which hung from the spring and from which the bucket containing the sample was hung. The microscope and the micrometer movement associated with it allowed readings to be reproduced to within 0.002 mm. Since the spring had a spring constant of 17.4 mg/mm, this permitted an accuracy of about 0.035 mg. in measuring the amount of ammonia adsorbed.

Preparation of Homoionic Bentonites

The clay used was a Wyoming bentonite with a base exchange capacity of about 90 milliequivalents per gram. It was supplied by the National Lead Company. The clay was prepared for use by passing suspensions of about 1- $\frac{1}{2}$ percent clay in distilled water through ion exchange columns charged with the desired ion and subsequently

drying the clay.

Suspensions of the raw clay were prepared by stirring slowly into a quantity of distilled water enough clay to form a $1\frac{1}{2}$ percent suspension. The suspension was allowed to set for several days, and the supernatant liquid was poured off for use. The residue in the bottom, consisting of silica and other impurities, was discarded. This process is known as clarifying the clay and results in a product containing less than 0.1 percent quartz.

Ion exchange columns consisting of glass tubes of 2.5 cm. diameter and fitted with stopcocks at one end were packed with the ion exchange resin (Amberlite IR-120) to a depth of about 85 cm. The resin was charged by passing about one liter of a 10 percent solution of the appropriate salt through the column. For preparation of sodium bentonite a sodium chloride solution was used. For calcium bentonite a calcium chloride solution was used. In the case of hydrogen bentonite, a 10 percent solution of hydrochloric acid was used. After charging, the columns were thoroughly washed with several liters of distilled water until no further trace of chloride ion could be detected by testing of the eluent with silver nitrate solution.

The clay suspension was slowly passed through the

resin at the rate of about one and one-half liters per hour. This treatment results in a clay which is essentially homoionic, and no additional ions are present to contaminate the suspension due to the use of exchange resins.

Some difficulty in obtaining calcium clay was experienced. Several of the first attempts to produce it resulted in a suspension having a pH almost as low as that of hydrogen clay. Titrations with a radio frequency titrimeter showed that some of the calcium clay had as much as one-third of the exchangeable ion present as hydrogen. This was ascertained to be due to the fact that washing of a resin containing hydrogen with the calcium chloride solution did not replace all of the hydrogen with calcium. The residual hydrogen later exchanged onto the clay. It was found necessary to recharge the column strongly and then wash it thoroughly with distilled water.

Two methods of drying the clay suspension were used. One method, known as oven drying, consisted simply of placing the suspension in an oven at a temperature of 100°C. and evaporating to dryness. The resulting clay film was then ground in a mortar to 200 mesh size.

The other method, known as freeze drying, was somewhat more complicated. The dilute suspension was first concentrated by evaporation in the oven to an 8 to 10 percent

gel. The gel was then placed in a one liter round bottom flask and frozen around the walls of the flask by slowly rotating the flask in a salt-ice mixture. When the gel was completely frozen, the bulb was evacuated by use of a mechanical vacuum pump, and the water which sublimed from the frozen gel was trapped in a cold trap at dry ice temperature. The process required four to five days to completely dry the clay which was kept frozen at all times by means of a salt-ice bath. The resulting clay was extremely light and fluffy.

The dried clays were stored in screw-capped bottles in the laboratory for periods of time varying from a few days to several years. The first runs with each clay were made with the sample at the humidity of the room. It was decided, however, that the variations in amount of water adsorbed on the clay with varying humidities would introduce too much error into the weight of the clay. Therefore, subsequent samples were stored in a constant humidity container maintained at 51 percent relative humidity. All isotherms were corrected for the amount of water adsorbed as will be explained later. Thus, all isotherms represent the volume of ammonia adsorbed per gram of clay equilibrated at 51 percent relative humidity.

Use of the Apparatus in the
Determination of Isotherms

Samples of the desired type of clay were weighed to an accuracy of 0.1 mg. on a damped chainomatic balance. Sample weights were on the order of 280 mg.

The bucket containing the sample was then suspended from the spring and enclosed by means of a tube which was sealed to the system. The sample was then outgassed.

During the period when the sample tube and column were being evacuated, it was noted that the sample would tend to release adsorbed vapors (largely water vapor) suddenly. This caused appreciable amounts of the powdery sample to be carried out of the tube. First attempts to prevent this by means of plugging the tube with cotton were unsuccessful. However, upon testing the cotton for adsorption of ammonia, it was determined that it actually adsorbed more ammonia per gram than the clay. Isotherms were then run on cotton in order to be able to correct for the adsorption due to it. Due to the large amount of adsorption by the cotton and rather unsatisfactory reproducibility of the isotherms, it was impossible to obtain satisfactory isotherms for the clay.

The next attempts at outgassing were made without a

a cotton plug in the sample bucket. The sample was evacuated slowly by isolation of the sample chamber from the system, evacuating the system, and slowly opening the stopcock between the sample chamber and the manifold. This process was repeated several times watching the sample carefully throughout, and re-isolating the sample at the first sign of disturbance in the sample. Invariably when a pressure of about 7 mm. was reached, large amounts of adsorbed vapors would begin to be evolved from the surface tending to carry some powdered clay with it. This was apparently water vapor which had been adsorbed on the surface in large amounts. A small amount of the sample was always carried out of the bucket by this escaping vapor; but since it settled to the bottom of the chamber, it was possible to correct for the loss of sample by weighing the escaped material after the run was completed.

As soon as a serious disturbance was noted in the sample tube (always in the vicinity of 7 mm. pressure), the system was isolated from the pumps and the sample heated to 100°C. for 45 minutes by means of a water bath. This heating sufficed to drive off a large amount of water vapor from the sample, raising the pressure in the system to about 2.5 cm. The sample was evacuated slowly at the end of 45 minutes, and usually only a very slight disturbance was noted. As soon as the sample could be opened to the pumps with no further loss, the water bath was reheated

and the sample was outgassed for two hours at 100°C. with the best possible vacuum in the system. Barrer and MacLeod (2, p. 981) have shown that very nearly as much water vapor is removed from the clay at 50°C. as can be removed by heating to 250°C. Others have also shown that outgassing is essentially complete at 100°C. Above that temperature changes begin to take place within the lattice which are sometimes detrimental to the surface of the clay. It was therefore felt that outgassing at 100°C. for two hours should be sufficient to remove all bothersome adsorbed gases.

The ammonia used in the studies was anhydrous tank ammonia from the Penn Salt Company. It was purified by admitting a convenient amount, measured by the expansion of a small balloon, into the vacuum system. After passing through a soda-lime trap which removed any water and carbon dioxide, it was solidified in a cold trap at liquid nitrogen temperatures. Any air or other gases were then removed by opening the trap to the vacuum. The ammonia was then allowed to distill into another cold trap in the storage system. Here it was again exhaustively pumped off after it had solidified. The ammonia was then allowed to evaporate, after isolating the storage system, until it filled the three liter storage bulb. A mercury bubbler was supplied to insure that the pressure in the storage system did not exceed one atmosphere -- thus eliminating the danger

of blowing out stopcocks due to there being a high pressure in the system.

After the sample had been sufficiently outgassed and a supply of ammonia was at hand, the sample was isolated from the pumps and a reading taken with the traveling microscope, the sample being in vacuum at room temperature. Air was then admitted into the system having been dried by its passage through a calcium chloride tube. The pressure of the air was noted and another reading taken on the microscope. These data served for the calculation of the effect of gas buoyancy on the sample due to the weight of gas displaced by the sample, bucket, spring, etc. The sample was again pumped down to vacuum, isolated from the pumps, and cooled to -45° by means of the thermostated cold bath. No residual gas was left on the sample as noted by a return of the microscope reading to the original value in vacuum.

When the sample had reached thermal equilibrium at -45° , a zero point reading was taken with the microscope. Then a suitable increment of ammonia was allowed to enter the system from the storage system. The new microscope and pressure readings were taken when the sample had attained equilibrium.

The time necessary for attainment of equilibrium varied with the portion of the isotherm under consideration. On the first portion of the curve it required nearly ten hours to reach equilibrium, but above a relative pressure of about

0.1 equilibrium was established easily in six hours. The establishment of equilibrium was determined by noting any changes in manometer or microscope readings. As mentioned previously, an oil manometer was included in the system during part of the experimental work, and it proved very convenient for determining when equilibrium was obtained since it was much more sensitive than the mercury manometer. Other investigators have noted similar lengths of time necessary for equilibrium. Barrer and MacLeod attribute it to the time necessary to conduct away the heat of sorption by the thermostating agent as well as a slowing down due to the diffusion of gas between the particles of sorbent and redistribution of sorbed gas by evaporation-condensation processes until a uniform distribution of sorbed material throughout the bed is achieved. (2, p. 982)

At the end of each run enough ammonia was admitted to the system to exceed the vapor pressure of the ammonia at -45°C . and the vapor pressure was then read on the manometer. This served as a good, accurate measurement of P_0 , much superior to extrapolating from a curve of vapor pressure versus temperature, since it was possible to measure the vapor pressure much more accurately than the temperature could be measured.

At the end of each run an aspirator was used to flush the ammonia from the system. This is a much more satisfactory method than pumping the ammonia through the

mechanical pump, since not only are the fumes annoying but they also tend to contaminate the oil in the pump.

EXPERIMENTAL RESULTS AND CONCLUSIONS

Types of Clays Studied

In order to provide comparative data on a complete set of clays, isotherms were determined for six clays representing the two drying methods and three exchangeable cations. Thus, runs were made on Na, H, and Ca bentonites, both oven dried and freeze dried. The effect of univalent or divalent exchangeable cations was studied through the Na and Ca bentonites. The effect of hydrogen as the exchangeable cation, producing an acid clay, was also studied.

Any changes of the clay surface caused by the various drying methods could be noticed by comparison of the results from clays of like cation but different drying method.

Reproducibility of Isotherms

The study of the reproducibility of the isotherms is marred by the fact that correction factors were applied to approximately half of the data. This was necessary since, as mentioned previously, some isotherms were run with clays which were not at known humidity when weighed. This fact caused apparent discrepancies in the amount of ammonia adsorbed. For instance, if one sample of the clay was drier when weighed than another sample, it would apparently weigh less than a sample of the same amount of clay which had adsorbed more water. This would cause the drier sample

to apparently adsorb more ammonia per gram.

To overcome this variation, samples were placed in a constant humidity container at 51 percent relative humidity. Check runs were then made on all isotherms using the humidified clay. Isotherms which were run on clays not at constant humidity were corrected for this fact. This correction was made after the two comparative isotherms had been plotted and was done as follows. At a relative pressure of 0.5 the volumes of ammonia adsorbed per gram of clay were noted from each of the isotherms. The amount adsorbed per gram for the humidified clay divided by the amount adsorbed per gram for the unhumidified clay formed a correction factor which was applied to the data for the unhumidified clay to cause it to fall in line with the data for the humidified clay. Therefore, in noting the reproducibility of the isotherms, the important factor is not the relative displacement along the ordinate but rather whether the shapes of the two sets of data coincide reasonably well with one another at all relative pressure values.

Using this criterion for determining reproducibility, it will be noted that all the data are fairly reproducible. On any isotherm the data points from each data set, corrected and standard, coincide fairly well and are distributed about the resulting isotherm in a manner which indicates reproducibility. That is, data points from each set occur

on both sides of the isotherm at all relative pressures. The spread of points thus indicates that deviation from the isotherm is due to experimental error rather than irreproducibility of the isotherm.

Further and more convincing proof that the data are reproducible is presented by the data on freeze dried sodium bentonite. Two separate runs were made with humidified clay. No correction factor was applied to the data. As may be seen from the isotherm, the two data sets fall closely along the isotherm.

Deviations in the data do not exceed a few percent. In a few cases the deviation of a few points is as much as five percent, but most points are within two or three percent of the values determined by the resulting isotherm.

Some of the data on oven dried hydrogen bentonite were taken before the experimental techniques were thoroughly perfected, and thus do not show as close agreement as the other data.

Sources of error stem from several different factors. Any movement of the microscope during a run would cause appreciable error. Leaks in the system also could cause errors, but these were usually noted on the manometer and the data discarded. Experimental error due to inaccuracies or lack of precision in the microscope or manometer readings were probably so small as to be unnoticeable.

Another source of error is due to the fact that the

FIGURE 2
ADSORPTION OF NH_3 ON FREEZE DRIED
AND OVEN DRIED HYDROGEN AND
SODIUM BENTONITES AT -45°C .

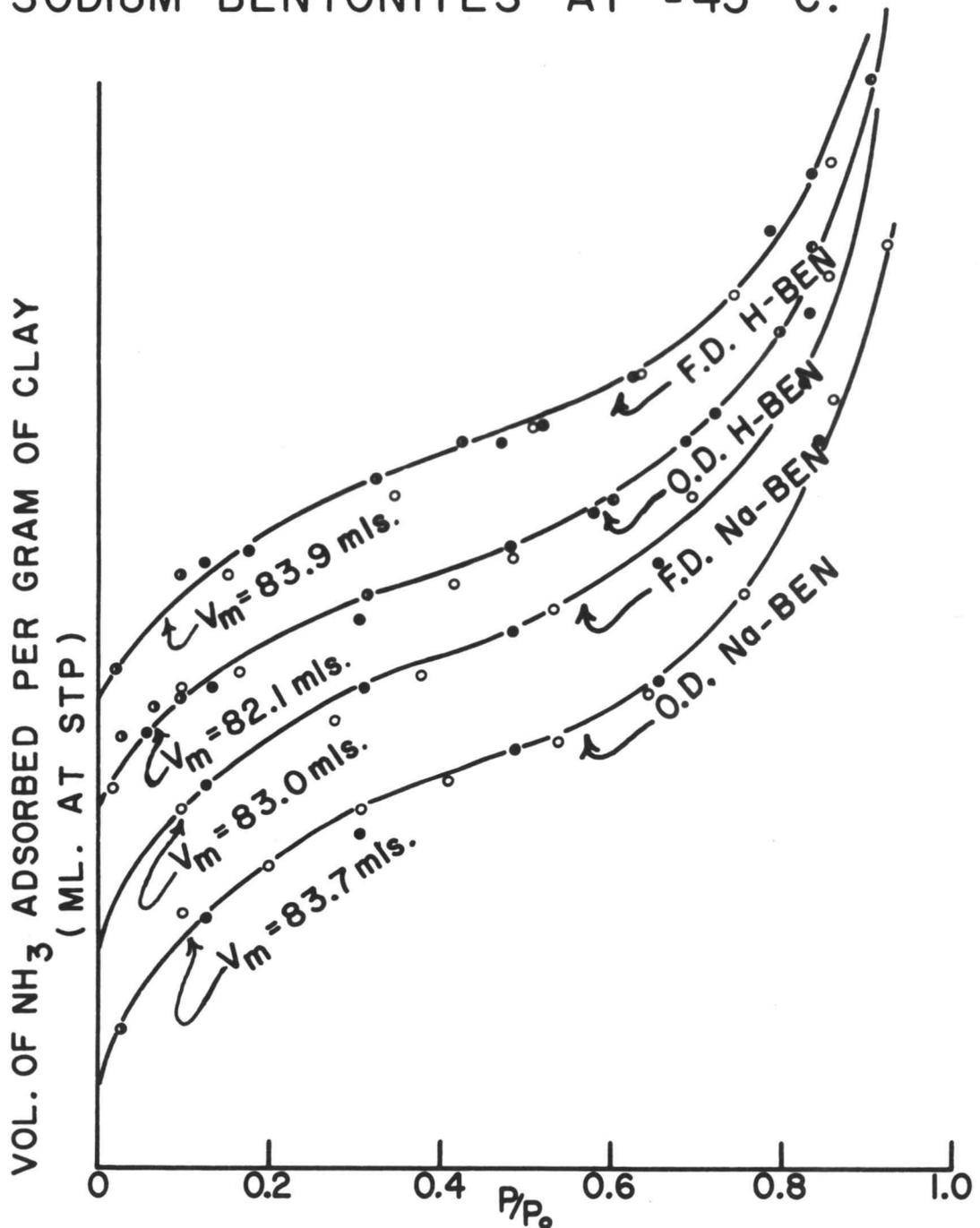
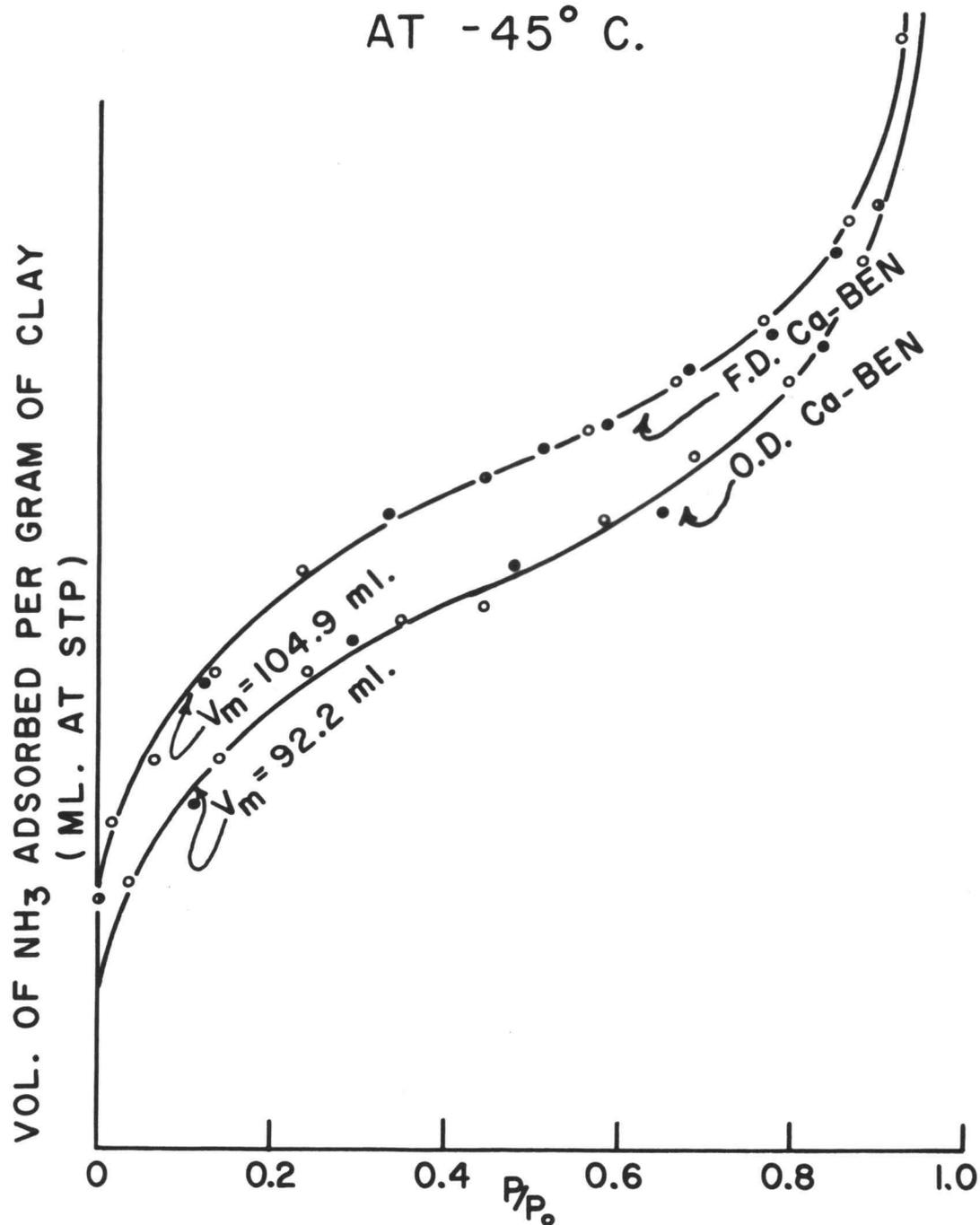
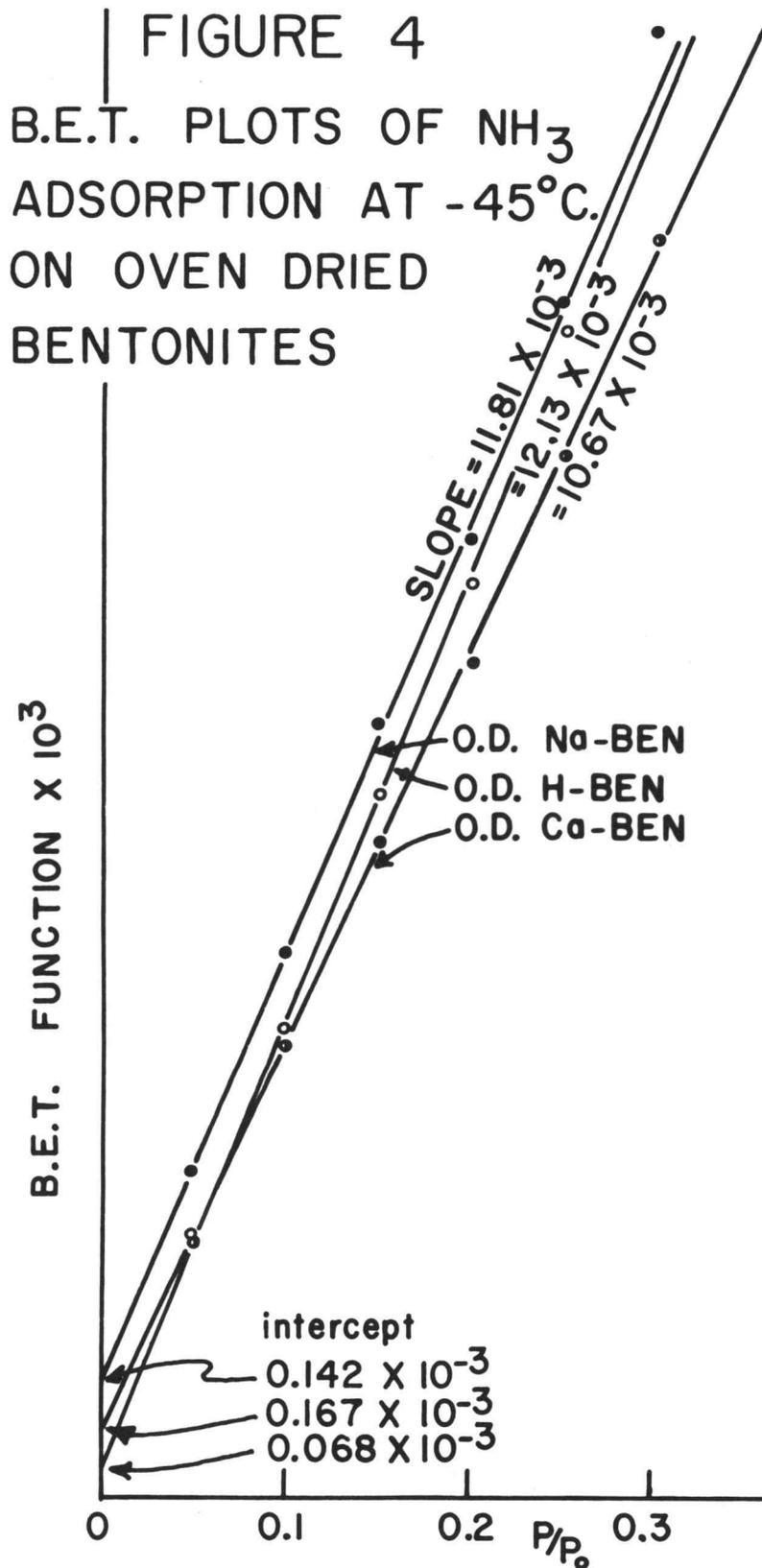
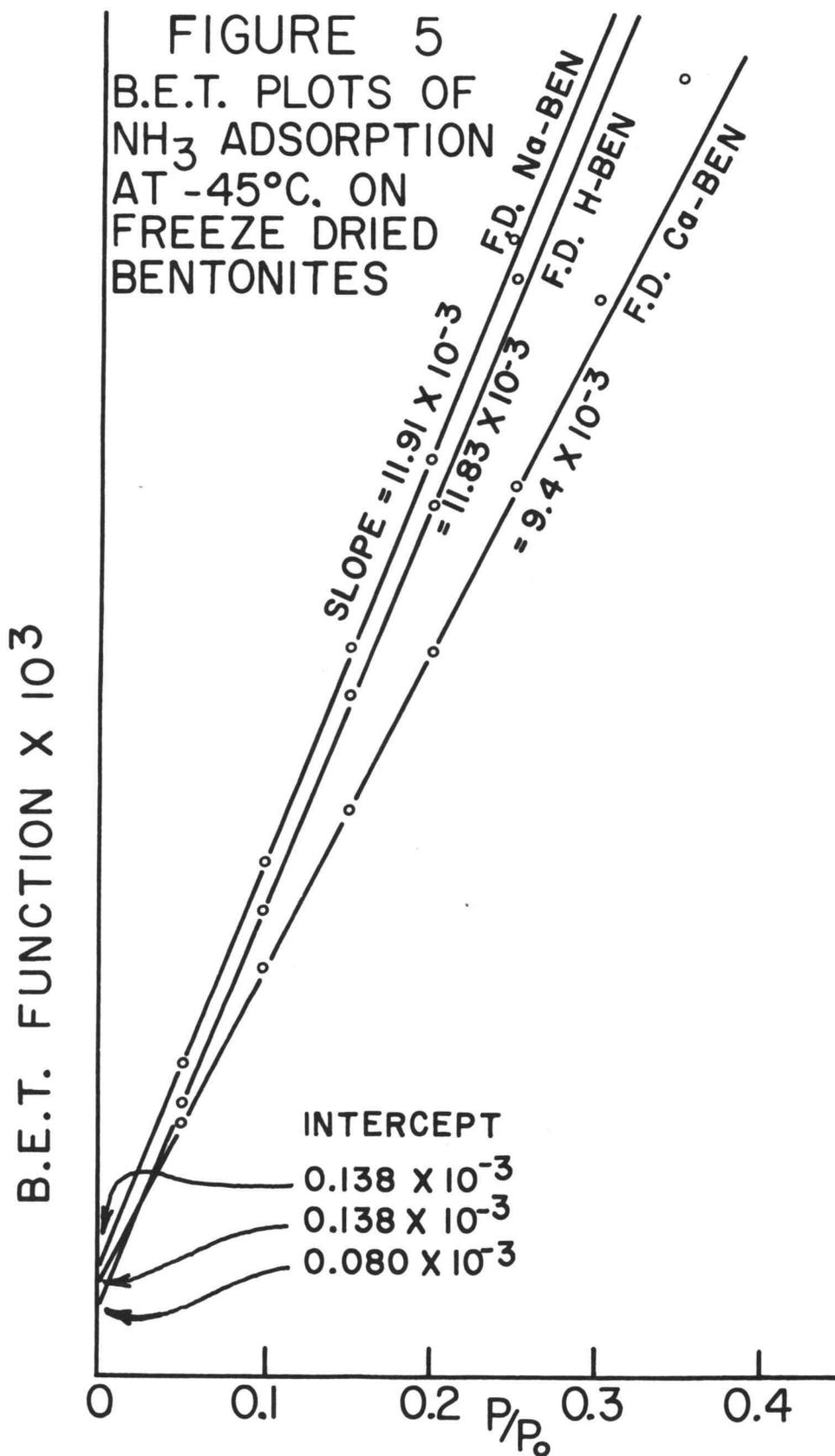


FIGURE 3
ADSORPTION OF NH_3 ON FREEZE DRIED
AND OVEN DRIED CALCIUM BENTONITE
AT -45°C .







desorption isotherms of ammonia on montmorillonites show appreciable hysteresis. (2, pp. 983-984) This can cause some error in the measurement of amounts adsorbed in relation to the pressure at which they are adsorbed if the pressure of ammonia in the system falls during the attainment of equilibrium. Any error from this source was probably quite small.

Conclusions

All isotherms obtained in this study were good examples of Type II S-shaped isotherms. There was no tendency toward stepwise isotherms. Cornet (6, p. 221) has reported stepwise isotherms with ammonia on hydrogen montmorillonite at very low relative pressures at room temperature. Our work does not disclose any steps, probably because of the widely different temperatures used and the resultant effect on the adsorption as well as the fact that very low relative pressures are not easily nor accurately measured at such low temperatures.

Comparison of the isotherms on sodium and hydrogen bentonite reveal slightly more ammonia sorbed at the lower pressures by the hydrogen clay. The difference is very small, however, and becomes smaller as the pressure increases. It is felt that this does not show that the hydrogen clay exhibits a greater capacity for the sorption of ammonia, but rather that the hydrogen clay sorbs the

ammonia more strongly than does the sodium. This is borne out by comparison of surface areas of the two clays.

Stronger attraction for ammonia by hydrogen bentonite would be expected since it is acidic and should attract the basic ammonia. This attraction would logically be expected to take the form of stronger active sites rather than a greater number of active sites, since both clays have the same base exchange capacity and therefore the same number of exchange cations. Each base exchange cation can be taken as an active site on the clay. However, other types of active sites are also present on both clays.

One would expect the forces between the sodium ions on the clay and ammonia to be strictly those for the formation of coordination products of some sort, whereas those between hydrogen and ammonia should also include a stronger component due to the acid-base characteristics of the reactants. There is ample evidence that ammonia does react anhydrously with hydrogen clay to form an ammonium clay according to the reaction: $\text{H-bentonite} + \text{NH}_3 \longrightarrow \text{NH}_4\text{-bentonite}$. (6, p. 222)

B. E. T. plots of the adsorption data yield very good straight lines up to relative pressure values of about 0.3. Above this point the data begins to deviate from a linear plot. Surface areas for the clays were calculated on the basis of humidified clay. (See Table 1) On this basis sodium and hydrogen clays, whether freeze dried or oven

dried, exhibit practically the same surface area. The surface areas of these clays are within 2.1 percent of each other, and this is undoubtedly within the experimental error for the data. Surface area calculations were made using 12.9 \AA^2 as the area occupied per ammonia molecule.

TABLE 1
SURFACE AREAS OF HOMIOIONIC BENTONITES

Type of Bentonite	Uncorr. V_m (ml.)	Uncorr. surf.area ($\text{m}^2/\text{g}.$)	Corr. V_m (ml.)	Corr. surf.area ($\text{m}^2/\text{g}.$)	N_2 area ($\text{m}^2/\text{g}.$)	Total surf.area ($\text{m}^2/\text{g}.$)
O. D. Na	83.7	290	90.7	314	33	595
O. D. H.	82.1	284	92.3	319	40	598
O. D. Ca	92.2	319	105	363.5	50	677
F. D. Na	83	287	91.3	316	49	583
F. D. H.	83.9	290.1	97.5	338	58	616
F. D. Ca	105	362.5	121.3	420	70	770

The surface area values are such as to make it plain that the ammonia does penetrate between platelets of the clay and thus becomes available to the entire surface of the bentonite. This has been substantiated by other investigators (6, pp. 222-224), 1, pp. 564-568) and 2, p. 986), and it would seem extremely remarkable if the ammonia did not penetrate between lamellae.

It is not fruitful to further investigate the relationship between the surface areas of the various clays without

making allowance for the water vapor adsorbed on the clay when it was weighed and its effect on the apparent weight and, hence, the surface area of the clay. The amounts of water vapor adsorbed are presented as percentages in Table 2. These values were used to arrive at the corrected surface areas listed in Table 1. It is seen that appreciable amounts of water are adsorbed by the clay and that the amount of this adsorption depends markedly upon the exchangeable ion present on the clay and the method used to prepare the clay.

TABLE 2
AMOUNTS OF H₂O ADSORBED BY BENTONITES
AT 51 PERCENT RELATIVE HUMIDITY

(Expressed as percent by weight of wet clay)

<u>Type of Bentonite</u>	<u>Percent H₂O Adsorbed</u>
O. D. Na	7.7
O. D. H.	11.0
O. D. Ca	12.2
F. D. Na	9.1
F. D. H.	14.0
F. D. Ca	13.7

It should be noted that, in general, the freeze dried clays exhibit a larger surface area than do oven dried clays with the same cation. This would be expected since

freeze drying seems to result in a more disperse clay. Call (5, p. 126) has reported values for nitrogen areas on freeze dried clays which are slightly larger than other external areas reported by other workers on oven dried clays. (19, p. 1370) and 20, p. 1373) Freeze drying apparently breaks up the clay particles to a larger extent than does oven drying resulting in a particle with more of the platelet surface exposed in such a manner that nitrogen can adsorb on it.

Recent X-ray studies (19, p. 1370) have shown that only one layer of water is present between two adjacent platelets in bentonite at the point given by V_m . This suggests that the B. E. T. theory does not, in this case, give a value for the volume necessary to form a monolayer on each and every surface, but rather that two adjacent bentonite platelets share the same monolayer. Therefore, calculations of the surface area using this value of V_m do not give a measure of the total surface. These calculations instead give a value for the surface which actually is about one-half that of the true surface area.

It would seem reasonable that ammonia should exhibit the same phenomena as water in this respect. Experimental evidence through X-ray work would be necessary to prove this, however. Comparison of surface areas obtained in this study with those by water vapor on montmorillonite by Mooney, et al., (20, p. 1370) seems to indicate that a

similar process is occurring. Calculations based on this assumption are listed in Table 1 under "Total surface area."

The nitrogen area presumably gives only the external area, whereas the large surface area values for ammonia include the external area plus one-half the internal area. Therefore, the total surface area (external and internal) should be obtained by subtracting the nitrogen area from twice the ammonia area. The nitrogen areas listed in Table 2 for freeze dried clays are after Call; the areas for oven dried sodium and hydrogen are after Mooney, et al. The value for oven dried calcium is an estimate.

Calculations based on the dimensions of the clay lattice give values of about $800 \text{ m}^2/\text{g}$. for the total surface of a completely disperse bentonite. The values obtained for total surface in this study are somewhat below this value, but this may be due to the possibility that the ammonia cannot penetrate to all parts of the clay lattice. Both types of sodium and hydrogen clays have total surfaces in the vicinity of $600 \text{ m}^2/\text{g}$. but the calcium clays exhibit considerably larger total surfaces. Furthermore, the freeze dried calcium has a very appreciably larger surface than does the oven dried.

Two interdependent factors may account for this. It has been shown that the calcium ion in an exchange site exerts forces tending to hold two adjacent platelets together. (23, p. 1135) It is possible that these forces

are not completely overcome by ammonia molecules tending to enter between the platelets. However, in freeze drying some of these bonds may be broken resulting in more of the surface becoming accessible to the ammonia. Furthermore, it is probable that some ammonia molecules coordinate about the calcium ions. Possibly the disrupting of the forces between the platelets which occurs in freeze drying allows the calcium ions on the freeze dried clay to coordinate with more ammonia molecules than the calcium on oven dried clay is capable of doing.

Insufficient data are present to allow one to explain thoroughly why the calcium bentonites exhibit such a markedly larger surface area than do the sodium and hydrogen clays. It is possible that this is due more to increased coordination of ammonia with the calcium than it is to an increase in the actual surface area of the clay. Mooney, et al, (20, p. 1373) and 16, p. 1467) have pointed out that calcium does show greater coordination with water than do sodium and hydrogen. No significant calculations can be made in this case, however. Attempts to explain the increased adsorption of calcium clay over sodium clay on the basis of increased coordination only results in values for the number of extra ammonia molecules coordinated about calcium in the order of 1.4 for oven dried and 2.9 for freeze dried calcium. These values, at least in the first case, differ from integral numbers by such a margin as to

cause one to conclude that increased coordination is not the only reason for the increased adsorption of the calcium clays. In other words, the increased adsorption of calcium clays is probably due not to one single factor but to a combination of increased surface as well as increased coordination formation.

The data do not give linear Harkins-Jura plots. This indicates that the adsorbed phase is of the upper intermediate or lower condensed type. The B. E. T. equation is applicable to this type of film, whereas the Harkins-Jura equation is only applicable where a condensed film is formed. (12, p. 1372)

Suggestions for Further Studies

These investigations suggest possible further studies which would help differentiate between the many factors involved in a complete explanation of the complex problem of the sorption of ammonia by bentonites. Several suggested lines of study are listed here:

1. Study of various types of bentonites to determine the extent of coordination formation about the exchange cation and selection of one type as a basis for comparison. It is suggested that studies of ammonia adsorption on ammonium bentonite might be interesting insofar as ammonia would not be expected to coordinate with the ammonium ion.

2. Studies using sorbates of a less polar character and comparison of the extent of adsorption as a function of the dipole moment. The amount of surface available should vary with the polar character of the molecule, and further information on the forces between platelets should be obtained. Suggested sorbates are CO_2 , CS_2 , CO , and alcohols.

3. Studies with bentonites containing trivalent ions such as Al to study more fully the function of valency on the adsorptive properties of the clays.

4. X-ray diffraction studies to determine the effect of ammonia sorption on the interlamellar spacing. Such data would prove or disprove the assumption that only a single layer is present between layers at the value of V_m .

SUMMARY

The clay mineral concept has made possible the determination, by X-ray diffraction studies, of the crystalline structure of clays. The structure of the montmorillonite family of clays is that of a series of platelets stacked one upon the other to form a clay particle. The platelets are made up of three layers -- two silica tetrahedral layers with an alumina octahedral layer between. Unsatisfied charges and broken bonds about the edges and between the platelets give rise to a large base exchange capacity for montmorillonite.

Some studies have been made of the sorptive properties of montmorillonite clays using bentonites, which are composed largely of the montmorillonite clay mineral, with polar and nonpolar sorbates, and surface areas have been reported in some cases. The purpose of this study was to obtain a more thorough set of data on the sorptive properties of homoionic bentonites (both oven dried and freeze dried) using the polar sorbate, ammonia. The exchangeable cations of interest were sodium, hydrogen, and calcium. All isotherms were run at -45°C .

The homoionic bentonites were prepared by passage through an ion exchange column charged with the appropriate cation. The clays were dried by two different methods -- oven drying and freeze drying.

The isotherms were obtained by the use of a high vacuum apparatus designed to measure the amount of adsorption gravimetrically. Samples of the clay were suspended from a spring, and the distension of the spring served as a measure of the amount of adsorption.

The samples were outgassed in high vacuum for two hours at 100°C. Then the sample tube was cooled to -45°C. and the sample thermostated at this temperature throughout the runs. Increments of purified ammonia were added and the distention of the spring was measured as was the pressure of the ammonia in the system after equilibrium was achieved. Equilibrium was attained within six hours at the intermediate and higher pressures but required about ten hours at low pressures.

Curves were plotted of the volume of ammonia adsorbed as a function of the partial pressure of the ammonia. Isotherms run on clays which were humidified at 51 percent relative humidity were used as standards, and all curves which had been run on clays at unknown and variable humidities were corrected to agree with the standards.

Experimental error was within a few percent. Reproducibility of the isotherms was good.

B. E. T. plots of the data resulted in good straight lines. Surface areas were calculated from the B. E. T. plots. The data did not give linear Harkins-Jura plots.

Studies were made concerning the loss of weight of the

humidified clay upon drying in a desiccator. The amount of water loss gave a correction factor which was applied to calculate the surface areas of the various dry clays.

It is apparent from the isotherms that the adsorption of ammonia by hydrogen bentonite is only slightly different from the adsorption by sodium bentonite.

Apparently hydrogen bentonite possesses essentially the same number of active sites as does sodium bentonite, but some of these sites appear to sorb the ammonia more strongly than do the sites on sodium bentonite. This is evidenced by the slightly increased sorption of the hydrogen bentonite at low pressures with the initial portion of the curve rising more rapidly.

Little or no significant difference between the freeze dried and oven dried clays was noted in the case of sodium and hydrogen. Freeze dried clays did appear to show a slightly greater surface area and increased water adsorption.

Calcium clays, whether freeze dried or oven dried, showed greatly increased adsorption. Furthermore, there was in this case a much greater adsorption by the freeze dried clay.

Attempts to explain the increased adsorption of calcium clay should take into account two factors: the forces exerted by calcium ions which tend to hold the platelets together, and any possible coordination of

ammonia about the calcium ions. The possibility of greater coordination about calcium ions in the freeze dried clay should not be overlooked.

No satisfactory estimate of the extent of coordination about a calcium ion can be given with the present data.

Calculations of the total surface area of the clay on the assumption that only one layer of ammonia is present between platelets at the point V_m result in surface areas in the order of 600 $m^2/g.$ for Na and H clays and 677 to 770 $m^2/g.$ for the Ca clays. These values compare favorably with the theoretical values of about 800 $m^2/g.$

Suggestions for further studies included the use of other, less polar, sorbates; possible X-ray diffraction data; and the use of different exchangeable cations including aluminum and ammonium. Such studies should result in better understanding of the fundamental role played by the exchangeable ion in sorption phenomena and a more precise differentiation between the variation of surface area with different ions besides further information regarding the extent of coordination formation.

BIBLIOGRAPHY

1. Barrer, R. M. and N. Mackenzie. Sorption by attapulgite. I. Availability of intracrystalline channels. *Journal of physical chemistry* 58:560-568. 1954.
2. Barrer, R. M. and D. M. MacLeod. Intercalation and sorption by montmorillonite. *Transactions of the Faraday society* 50:980-989. 1954.
3. Bering, B. P. et al. Adsorption properties of montmorillonite clays. *Kolloidnyi zhurnal* 14:399-407. 1952. (Abstracted in *chemical abstracts* 47:3080c. 1953)
4. Brunauer, Stephen, Paul H. Emmett and Edward Teller. Adsorption of gases in multimolecular layers. *Journal of the American chemical society* 60:309-319. 1938.
5. Call, F. Preparation of dry clay-gels by freeze-drying. *Nature* 172:126. 1953.
6. Cornet, I. Sorption of NH_3 on montmorillonitic clay. *Journal of chemical physics* 11:217-226. 1943.
7. Edelman, C. H. and J. C. L. Favejee. On the crystal structure of montmorillonite and halloysite. *Zeitschrift fur Kristallographie* 102:417-431. 1940.
8. Emmett, Paul H. Multilayer adsorption equations. *Journal of the American chemical society* 68:1784-1789. 1946.
9. Emmett, Paul H. and Stephen Brunauer. The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts. *Journal of the American chemical society* 59:1553-1564. 1937.
10. Grim, Ralph E. *Clay mineralogy*. New York, McGraw-Hill, 1953. 384 p.
11. Harkins, William D. The surfaces of solids and liquids and the films that form upon them. In Jerome Alexander's *Colloid chemistry*. vol. 5. New York, Reinhold, 1944. pp. 12-102.

12. Harkins, William D. and George Jura. Surfaces of solids. XIII. A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surface of a solid. *Journal of the American chemical society* 66:1366-1373. 1944.
13. Hauser, Ernest A. Colloid chemistry of clays. *Chemical reviews* 37:287-321. 1945.
14. Hauser, Ernest A. and D. S. le Beau. Colloid chemistry of clay minerals and clay films. In Jerome Alexander's *Colloid chemistry*. vol. 6. New York, Reinhold, 1946. pp. 191-213.
15. Hofmann, Ulrich, Kurd Endell and Diederich Wilm. Kristallstruktur and Quellung von Montmorillonit. *Zeitschrift fur Kristallographie* 86:340-348. 1933.
16. Keenan, A. G., R. W. Mooney and L. A. Wood. The relation between exchangeable ions and water adsorption on kaolinite. *Journal of physical and colloid chemistry* 55:1462-1474. 1951.
17. Langmuir, Irving. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American chemical society* 40:1361-1403. 1918.
18. Marshall, C. Edmund. The colloid chemistry of the silicate minerals. New York, Academic Press, 1949. 195p. (American society of agronomy monograph, vol. 1)
19. Mooney, R. W., A. G. Keenan and L. A. Wood. Adsorption of water vapor by montmorillonite. I. Heat of desorption and application of the B. E. T. theory. *Journal of the American chemical society* 74:1367-1371. 1952.
20. Mooney, R. W., A. G. Keenan and L. A. Wood. Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction. *Journal of the American chemical society* 74:1371-1374. 1952.

21. Nelson, R. A. and S. B. Hendricks. Specific surfaces of some clay minerals, soils and soil colloids. *Soil Science* 56:285-299. 1943.
22. Sato, Choei. Chemical studies of the surfaces of clay minerals. I. Sorption of ammonia and methanol by bentonite. *Journal of the chemical society of Japan, pure chemistry section* 74: 167-170. 1953. (Abstracted in *Chemical abstracts* 47:9101h. 1953)
23. Slabaugh, Wendell H., and J. L. Culbertson. The effect of certain reagents upon the properties of bentonite colloids. *Journal of physical and colloid chemistry* 55:1131-1139. 1951.
24. Teichner, Stanislas. Influence de traitements thermiques sur la texture et la structure d'une montmorillonite. *Comptes rendus* 227:392-393. 1948.
25. Teichner, Stanislas. Sur la mesure des surfaces spécifiques de certaines argiles. *Comptes rendus* 231:1063-1064. 1950.
26. Wieden, von P. and H. Balduin. Gasadsorption an Bentoniten. *Kolloid Zeitschrift* 227:30-32. 1952.
27. Weiser, Harry Boyer. A textbook of colloid chemistry. 2d ed. New York, John Wiley and Sons. 1950, 444p.