hydrocarbon layer increases rapidly with increasing total amount of alcohol until the tie lines change the sign of their slope. These facts are clearly indicated in Fig. 1 in which the % of alcohol in the cyclohexene layer is plotted against the % of alcohol in the water layer.

Increasing the temperature from 15 to 35° causes very little change in the area in which conjugate solutions are found; the area is slightly larger at the lower temperature. The slopes of the tie lines change by a large amount. The plait point at 15° is not far from the highest point of the solubility curve, while at 25° it is farther down on the water-rich side of the curve. It was experimentally difficult to approach very closely to the plait point at 35° but the indications are that at this temperature it is still farther down on the water side of the curve.

Summary

The solubility relationships for the ternary systems containing water and cyclohexene and methyl, ethyl or isopropyl alcohol have been determined at 25°. The system containing isopropyl alcohol has been investigated at 15 and 35°.

LINCOLN, NEBRASKA RECEIVED APRIL 20, 1940

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE]

Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations[1]

BY S. B. HENDRICKS,[2a] R. A. NELSON[2b] AND L. T. ALEXANDER[2b]

Introduction

The hydrous magnesium aluminum silicate mineral montmorillonite, because of its unusual properties and widespread occurrence in clays and soils, has attracted the attention of workers in many fields. It is extremely plastic when moist and can be dispersed in water, readily forming thixotropic gels at moderate concentrations. The dispersed material upon drying reorganizes, forming a crystalline material one lattice constant of which depends upon the humidity. Montmorillonite is a salt of a moderately strong acid, from which other salts and the free acid can be prepared by cation replacement, that is, base exchange. It strongly absorbs organic bases with formation of the corresponding salts and also shows marked adsorption for neutral organic compounds, which is the basis for its use as a clarifying agent. Many reactions are catalyzed by montmorillonite.

Study of montmorillonite as a base exchange complex has come about largely because it is a component of many soils showing high base exchange capacity. Replacement of one cation by another has been investigated to a considerable extent and several series have been set up showing ease of replacement. The one generally accepted shows[3,4]: $H^+ > Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$; thus, for example, a greater fraction of the K^+ ions is displaced at equivalent concentrations by Ca^{++} than by Li^+. These differences usually have been attributed to "ionic hydration."[5] A successful correlation has been found with zeta potentials[6] derived from migration velocities of clay micelles in suspensions. No attempt has been made, however, to determine the environment of the ion in the clay, which is fundamental to understanding the nature of the replacements.

For a number of years the authors have been interested in the identification and structures of minerals present in clays. During the course of this work it became evident that a study of water sorption by the various salts of montmorillonite probably would go far toward determining the environment of the replaceable cation. The material is one of the few in which sorption can be followed by means of lattice changes.

Methods and Materials

Since montmorillonite might be expected to differ in behavior depending upon its origin, samples were obtained from several localities. All of these were bentonites, that is, they were formed by devitrification of volcanic ash. One was a commercial material from Wyoming, sold under the trade name "Volclay," which is known to contain finely divided quartz and appreciable silica that can be dissolved in weak bases. This particular sample has not been ana-

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(1) Not copyrighted.

(2a) Bureau of Agricultural Chemistry and Engineering.

(2b) Bureau of Plant Industry.

(3) G. W. Robinson, "Soils, Their Origin, Constitution, and Classification," D. Van Nostrand Co., New York, N. Y., 1936, Chapter V.

(4) H. Jenny, *J. Phys. Chem.*, **36**, 2217 (1932).

(5) G. Wiegner, *J. Soc. Chem. Ind.*, **50**, 65T, 103T (1931).

(6) H. Jenny and R. F. Reitemeier, *J. Phys. Chem.*, **39**, 593 (1935).

lyzed. Two other samples were furnished by Dr. C. S. Ross and Dr. P. G. Nutting of the U. S. Geological Survey. One was a fine white specimen from Otay, California (Sample G in 7) and the other was a slick yellowish material from the vicinity of Laurel, Mississippi (Sample B in 7). Both are considered to be very pure montmorillonite and analyses for them have been published.[7]

The clays were electrodialyzed to obtain the free acids and these were titrated to *p*H 8.0 with dilute calcium hydroxide or sodium hydroxide solutions to form the corresponding salts. Cesium, potassium, and barium salts of the Mississippi sample were made by titration of the free acid obtained by treatment of the clay for short times with successive lots of dilute (1:10) hydrochloric acid in large excess which was removed by washing with water. Lithium, magnesium, strontium (Miss.), and cerium (Calif.) salts were prepared from the original clays (predominantly the calcium salt) by base exchange from neutral chloride solutions. Base exchange capacities, expressed in milliequivalents per gram, of the three clays as obtained by titration of the hydrogen clays to *p*H 8.0 with sodium hydroxide solution are as follows: Mississippi 0.95, California 0.80, Wyoming 0.85.

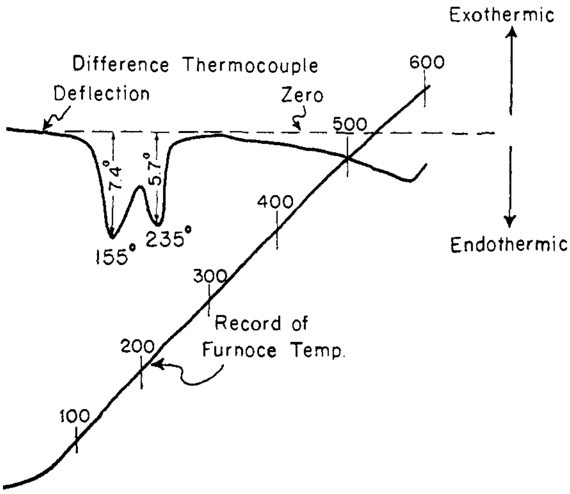

Fig. 1.—Photographic record from differential thermal analysis apparatus.

The clay salts were dried over phosphorus pentoxide in vacuum to constant weight and were then exposed at 30° to water vapor, at various relative humidities, for a week or longer. Amounts of water adsorbed were recorded and samples were removed for differential thermal analysis and for X-ray examination. The samples for X-ray examination were protected from change in water content by sealing them with plastocene in small tubes, 0.5 mm. in diameter, made from Lindemann glass. Unoriented samples were used since the procedure was simple and gave satisfactory results, even though it was realized that oriented samples would have been preferable. Nickel Kα radiation was used throughout.

Differential thermal analyses were made, according to the Le Chatelier[8] method, in an apparatus similar to that described by Norton.[9,10] In this method the temperature of a sample relative to that of an inert material is followed as the two are heated at an equal and approximately constant rate. An endothermic change, such as accompanies loss of water from a clay, results in a temperature lag relative to the inert material. The heating rate used was approximately 12° per minute which is rapid; a photographic record from the apparatus is reproduced as Fig. 1.

Some Structural Features of Montmorillonite.—The approximate crystal structure of montmorillonite, the essential mineral component of bentonites, was suggested by Hofmann, Endell and Wilm.[11] They showed that the lattice consisted of superimposed silicate sheets, similar to those found in the mineral pyrophyllite, having the ideal composition $(OH)_2Al_2Si_4O_{10}$, with replacement of Al^{+++} by Mg^{++}, Fe^{+++} and Fe^{++}, and silicon by aluminum. There is perfect cleavage between the sheets. Water sorption was shown to result in increase of the lattice spacing normal to the cleavage, (001). The water molecules were thus presumably located on the surfaces of the sheets.

Montmorillonite differs from pyrophyllite in having a smaller particle size, a more variable composition, a larger amount of water lost above 300°, and in showing base exchange. The replaceable ions are apparently external to the silicate sheets and usually amount to slightly less than 1 m. e. per gram, which is equivalent to about one-third the amount of potassium in muscovite. Their presence indicates that the sheets have some deficiency of positive ions resulting in an over-all negative charge. Attempts to locate the replaceable ions relative to the lattice have largely been speculative. Hofmann and Bilke[12] assumed that these ions were chiefly around the edges of the layers and to a lesser extent between the layers. Marshall[13] considered them to be between the layers and to be associated with water molecules. The behavior of organic salts of montmorillonite[14] when analyzed in detail shows that the exchangeable ions are predominantly between the silicate sheets. Gieseking, who has carried out the most extensive study of these salts, actually reproduces a drawing due to Hofmann and Bilke, without particular comment, but it is not to be thought that his results support their hypothesis. Results obtained in the present work also show that the most of the ions, probably more than 80%, are between the silicate sheets.

There has been some discussion of the manner in which water molecules are arranged between the silicate layers. A considerable body of opinion contends that they are in some type of close packed arrangement.[15] However, there are several arguments against this hypothesis, the simplest of which is that water usually has tetrahedral coordination. A suggested arrangement of water molecules which is supported by the known structure of vermiculite and which explains the observations that have been made on montmorillonite is shown in Fig. 6. A water layer of this type is of such a structure that if preserved would

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[7] "U. S. Geological Survey Bulletin," No. 878, p. 107, 1937.

[8] H. Le Chatelier, *Z. physik. Chem.*, **1**, 396 (1887).

[9] F. H. Norton, *J. Am. Ceram. Soc.*, **22**, 54 (1939).

[10] S. B. Hendricks and L. T. Alexander, *Soil Sci.*, **48**, 257 (1939).

[11] U. Hofmann, K. Endell and D. Wilm, *Z. Krist.*, **86**, 340 (1933).

[12] U. Hofmann and W. Bilke, *Kolloid. Z.*, **77**, 238 (1936).

[13] C. E. Marshall, *Z. Krist.*, **91**, 446 (1935).

[14] J. E. Gieseking, *Soil Sci.*, **47**, 1 (1939).

[15] See S. B. Hendricks and M. E. Jefferson, *Amer. Mineral.*, **23**, 863 (1938), for a discussion.

propagate the lattice as a whole which is a very strong argument in its favor. If it is assumed that the upper surfaces of all silicate layers in montmorillonite are covered by a single water sheet of this type then 0.10 g. of water will be required for 1.0 g. of mineral.

Addition of a layer of water molecules results in a change of about 3.0 Å. in the separation of the silicate layers. The first layer hydrate would thus have a spacing of about 12.0–13.0 Å., and a hydrate with two water layers about 15.0–16.0 Å.[16] Bradley, Grim and Clark have shown that definite hydrates can at least be formed for a sample of hydrogen Wyoming montmorillonite that they studied. Others have failed to repeat this observation, which, however, does not detract from its possible validity. The more usual situation, and one in accord with all except a single observation made in this work, is that the characteristic cleavage spacing varies continuously but not uniformly with water content.[12] This apparently is a result of an averaging effect from a lattice that contains various numbers of water layers in different parts.[15]

Results and Discussion

Previous studies of water sorption by clays have largely been restricted to measurement of lattice constants and weight increases as functions of humidity or loss on drying to constant weight at fixed temperatures. With one exception, which will be discussed later (note reference 16), the results indicated that water was gained or lost in a monotonous way. Differential thermal analyses, however, carried out in this Laboratory for identification of clay minerals indicated that probably more than one process was involved in water sorption since the low temperature endothermic region had considerable structure (note Fig. 1).

Results obtained by differential thermal analysis for the various clays are reproduced in Figs. 2–5. Curves in these figures show the galvanometer response, in series with the differential couple, as the sample is heated. Ordinates thus are proportional to lag in temperature of the sample, behind the reference body, which depends upon the rate of energy uptake accompanying evolution of water. Energy of desorption is constant to within 10% irrespective of the temperature of water evolution. Thus the area under a curve is a measure of the amount of water associated with each component curve provided it is referred to a uniform dry weight of sample. Values listed in the second line beneath the curves were obtained in this manner and can probably be trusted to within 20%. Amounts of water adsorbed per gram of dry material at room temperature, which of course are accurate, are shown in the first line beneath the curves. Results of X-ray diffraction measurements are given in the third line.

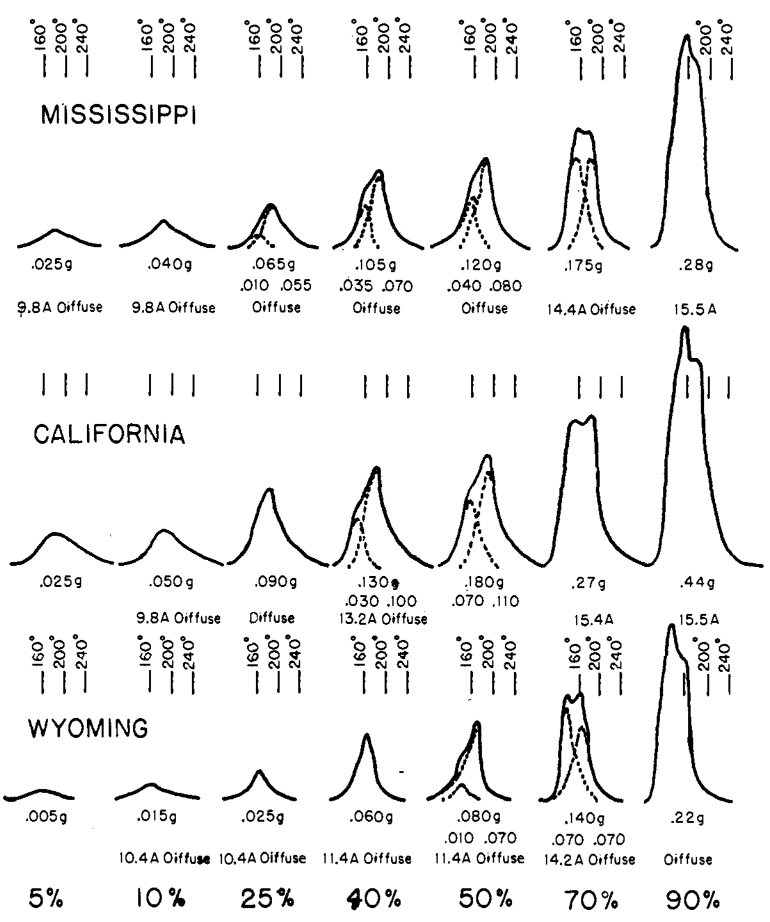

Fig. 2.—Thermal analysis curves of the sodium salts of various montmorillonites. Amounts of adsorbed water and values of the apparent cleavage spacing are given below the curves.

Although differential thermal analysis is a crude method measuring no real physical constant of a system, it enables one to distinguish variations in the binding of water even though such variations might be very small. Temperature of maximum rate of energy absorption is perhaps the best meas-

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(16) W. F. Bradley, R. E. Grim and G. L. Clark, *Z. Krist.*, **97**, 216 (1937).

ure of order of binding energy. Maxima produced by loss of water adsorbed at low humidities occur at the higher temperatures, which is evidence that such water has the higher heat of binding.

Differential thermal analysis curves of the sodium and calcium clays from different localities are reproduced in Figs. 2 and 3. It can perhaps be seen that origin of material is relatively unimportant. For this reason only salts of the Mississippi material were prepared for further examination. Results obtained from them are reproduced in Figs. 4 and 5.

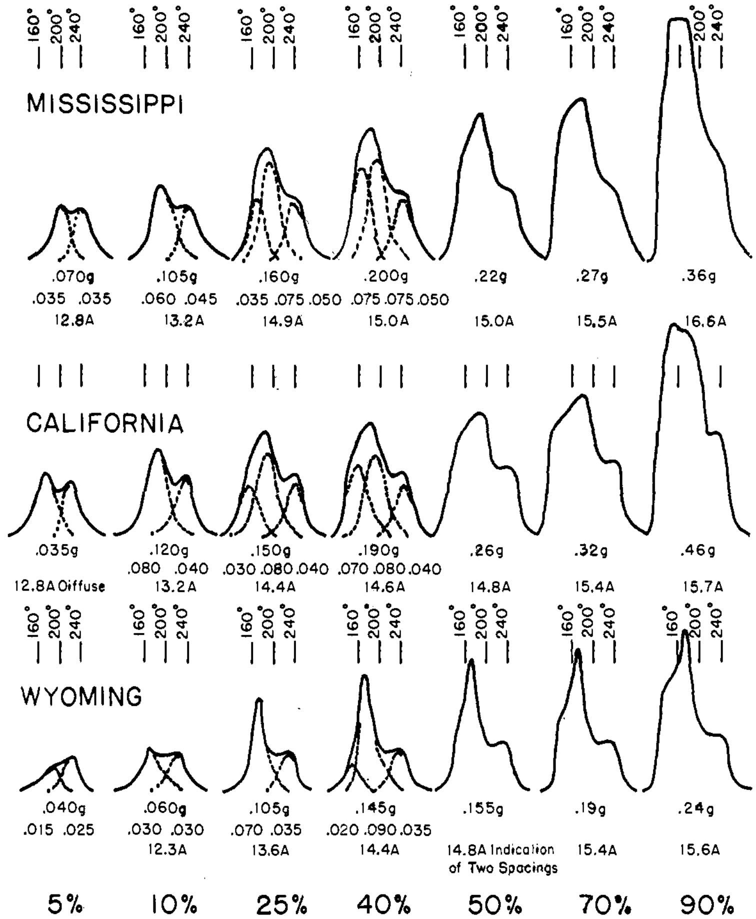

Fig. 3.—Thermal analysis curves, amounts of adsorbed water and values of the apparent cleavage spacing of the calcium salts of various montmorillonites.

An attempt was made, as shown in the figures, to resolve some of the curves into ones with single maxima. This presented some difficulties, but was aided by the fact that the contribution to one maximum was rather well completed before that to another had started. An example will be discussed to illustrate the general procedure. At a 5% R. H. (relative humidity as given at the bottom of the charts) the magnesium salt of Mississippi montmorillonite has a curve that comparison with the alkaline earth salts at the same R. H. indicates is formed from two incompletely resolved components. Moreover, the shape of the curve on the high temperature side shows that the high temperature component is somewhat smaller than the other. At 10% R. H. the second component has increased with little accompanying change of the high temperature component since that part of the curve above 240° has changed but slightly. The slightly convex shape of the low temperature part of the curve, below 180°, suggests that a third component is appearing. This is questionable at 10% R. H. but at 25% R. H. the third component is prominent and apparently accounts for the added water sorption as it also does at 40% R. H. Although the curves of samples with high water content obviously have several components, it was not considered justifiable to attempt the resolution. Attention is called to the cesium salt of Mississippi montmorillonite where the presence of two component curves between 40% and 70% R. H. is indicated by the shifting of the apparent single maximum and the shape of the curve above 180°.

The total area under the two peaks with highest maximum lags in temperature (max. T°C.) of the magnesium and calcium salts of Mississippi montmorillonite represents about 0.12 g. of adsorbed water which is approximately the amount, 0.10 g., required for formation of a single layer of water molecules arranged in the manner shown in Fig. 6. Moreover, the cleavage spacings of the hydrates are between 13.0 and 13.5 Å. which is but slightly more than the expected value, 12.0 to 13.0 Å., for a silicate sheet covered by a single layer of water molecules. Thus it would seem that at least two distinct processes are involved in the formation of the first layer hydrate.

It appears that the peaks having the highest max. T°C. for the magnesium and calcium Mississippi montmorillonites are to be correlated with hydration of the exchangeable cations. The base exchange capacity of this clay is about 0.95 milliequivalent per gram, the actual value varying slightly with the method used for determining it. This is equivalent to 0.00047 mole of Ca^{++} which would require 0.050 g. of water to form a hexahydrate. From the curves it appears that about 0.045 g. of water is associated with the peak having the highest max. T°C. The remaining water contributing to the formation of the first layer hydrate must be that required to hydrate the surface not contiguous to the exchangeable cations. It apparently is held somewhat less strongly since the max. T°C. of the peak associated with it is about 40° lower than the first peak.

Strontium and barium salts of Mississippi montmorillonite show characteristics similar to those discussed above. It is necessary, however, to go to higher humidities in order to have water sorption equivalent to that of the magnesium and calcium salts. As would be expected, accordingly, corresponding max. T°C. peaks are shifted to somewhat lower temperatures, about 20°, for the strontium and barium compounds. This shift makes it difficult to effect the resolution of the experimental curve into three maxima at the higher humidities and thus to determine the point at which the second peak is completed.

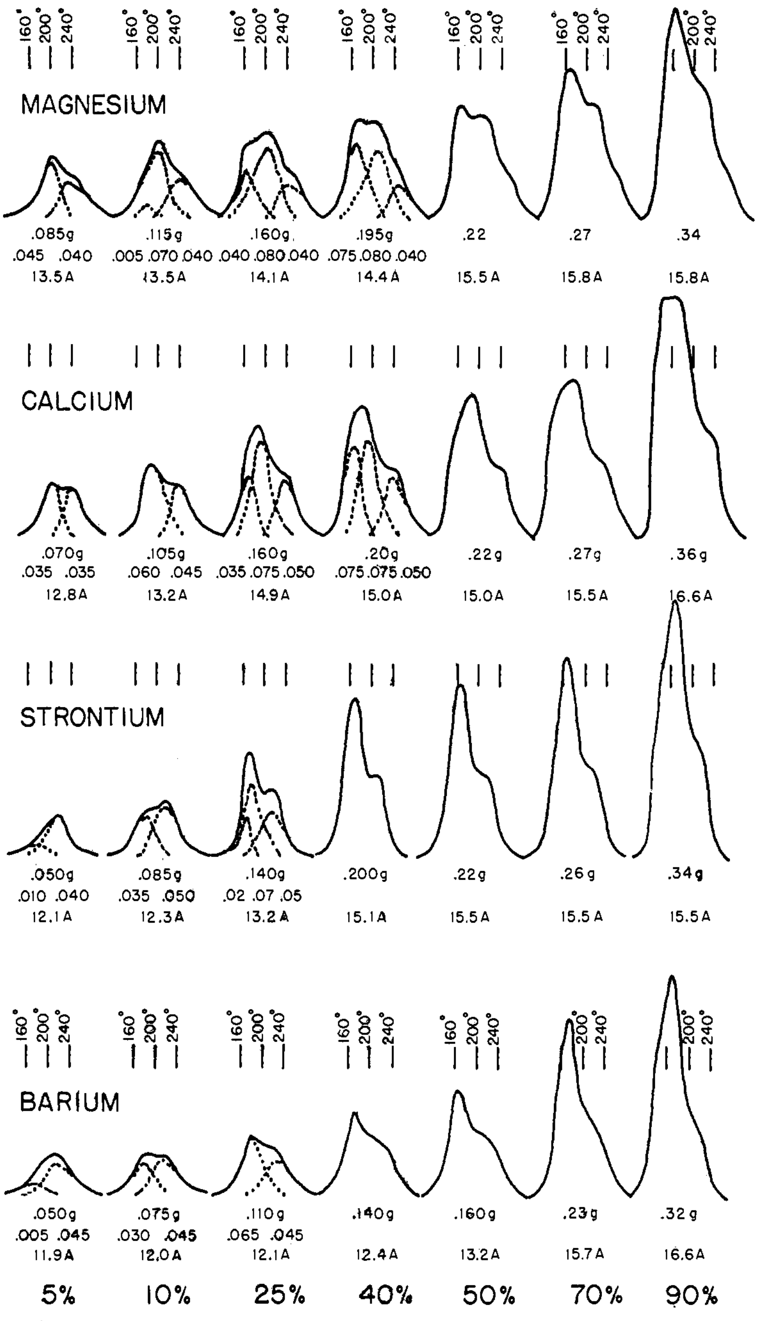

Fig. 4.—Thermal analysis curves, amounts of adsorbed water and values of the apparent cleavage spacing of magnesium, calcium, strontium and barium salts of Mississippi montmorillonite.

Lithium Mississippi montmorillonite is somewhat like the alkaline earth salts in behavior. At low humidities two well-resolved peaks are present. The peak with the highest max. T°C. (235°), which is almost complete at 5% relative humidity, corresponds to about 0.055 g. of water. This is about three (actually 3.3) water molecules for each Li^{+} ion, which is the amount expected for plane coördination about a small ion. The second peak has a considerably lower max. T°C. (170°) than does the second peak of the alkaline earth salts. This, as was the case for the strontium and barium salts, makes it difficult to determine when the third peak begins to appear. The cleavage spacing, however, is constant, as far as can be told, between 5 and 25% relative humidities but increases at 40%.[17] It would appear that the third peak must contribute to the curve at 40% relative humidity and that the second peak is essentially complete at 25%. The total water sorption at 25% relative humidity is about 0.12 g. which again is approximately the same as that required for a single layer of water molecules. While the six-fold coordination of magnesium and the alkaline earth ions would be expected to enhance the stability of a layer of the type shown in Fig. 6, there would possibly be some disrupting effect of lithium. This effect, however, need not completely destroy the structure in the water layer.

The third peak that appears for the lithium, magnesium and alkaline earth salts is probably to be associated with introduction of another layer of water molecules since the cleavage spacing increases, finally reaching a value of 15.0 to 16.0 Å., as the relative humidity is increased. Introduction of a second layer of water molecules is not a particularly simple process since it must influence the energy of binding of water that is already present. As a second layer is started molecules of the first layer are probably redistributed, some of the hydrated ions being in one layer and some in the other. Since the analysis is really made by successive removal of water it does not show what the binding conditions are before any water is removed. Finally at high relative humidities increased water sorption does not further change

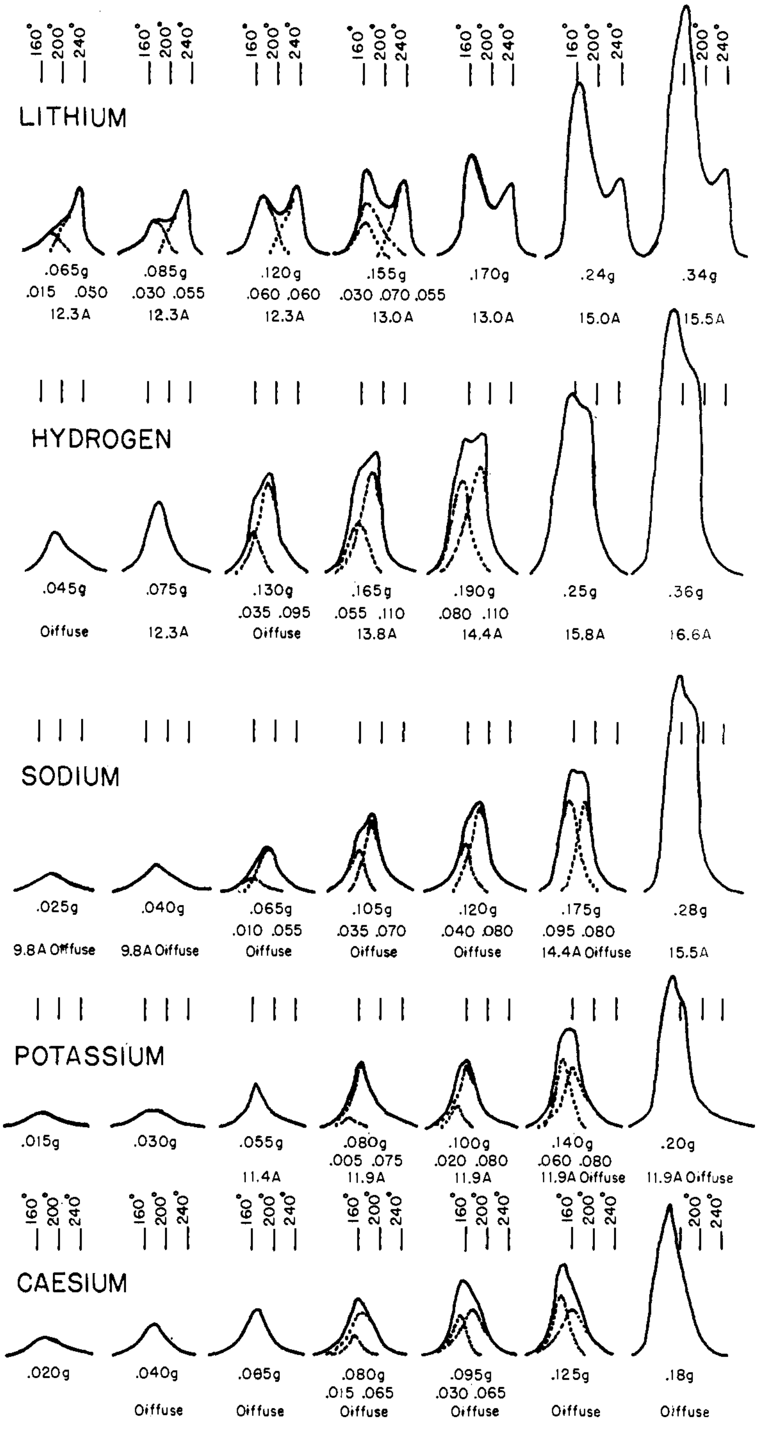

Fig. 5.—Thermal analysis curves, amounts of adsorbed water and values of the apparent cleavage spacing of lithium, hydrogen, sodium, potassium and cesium salts of Mississippi montmorillonite.

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(17) It is outside the scope of this work to discuss the crystal structures of montmorillonite and its hydrates in detail, but attention should be called to several facts. The measured interplanar spacings recorded on the figures are definitely not those of the first observed order (n) for some of the lithium, calcium, and hydrogen samples, but rather appear to be the second order ($2n$) since an apparent third order ($3n$) is present. We suspect, without analysis, that this is a result of the averaging effect previously mentioned.

the apparent cleavage spacing. Either the additional water is not between silicate layers or the diffraction pattern is due to only a minor part of the total sample. Both actually seem to play a part.

The most striking difference in the behavior of the sodium, potassium and cesium salts of Mississippi montmorillonite from that of the salts already considered is that only a single peak is present at low humidities. Furthermore, the value of max. T °C. is about the same for this peak, about 180°, as for the second peak of the strontium and barium salts. The two are completed at about the same value of the relative humidity and correspond to approximately the same amount of water, 0.06 to 0.08 g. These features indicate that the exchangeable cation is probably not hydrated in the sodium, potassium and cesium salts, although this interpretation is open to some question. Such a result might be expected for the cesium ion[18] from its behavior in solutions and to a lesser extent for the potassium ion.

Sodium, potassium and cesium salts are further characterized by a very poor degree of organization, as evidenced by the diffuseness of the X-ray diffraction patterns. Even at 90% relative humidity the potassium salt although containing enough water for two layers still shows the spacing of a single layer hydrate. The general character of these photographs, however, indicates that probably only a small portion of the material is sufficiently organized to give a diffraction pattern. This organized portion then is the single layer hydrate, which is indicative of an even more difficult formation of the multiple layer hydrate. The sodium salt is well enough organized to show the expected increase in X-ray spacing when a considerable amount of the double layer hydrate is present.

The free acid of the Mississippi clay has perhaps the simplest behavior of any of the materials examined. A single peak with a max. T °C. of 180° corresponding to the second peak of the alkaline earth salts is completed at about 25% relative humidity. The cleavage spacing is that of a single layer hydrate and the degree of organization as judged by diffuseness is high. Water sorption associated with this peak is about 0.10 g., which is the amount required for hydration of a layer according to the structure shown in Fig. 6. It would appear therefore that the hydrogen ion has little influence on the hydration. This is reasonable when it is remembered that the hydrogen ion, being very small, is probably embedded in the silicate sheet near the site of the effective negative charge. There is no indication of hydration of the proton with formation of a hydronium $(H_3O)^+$ ion which in turn would hydrate.

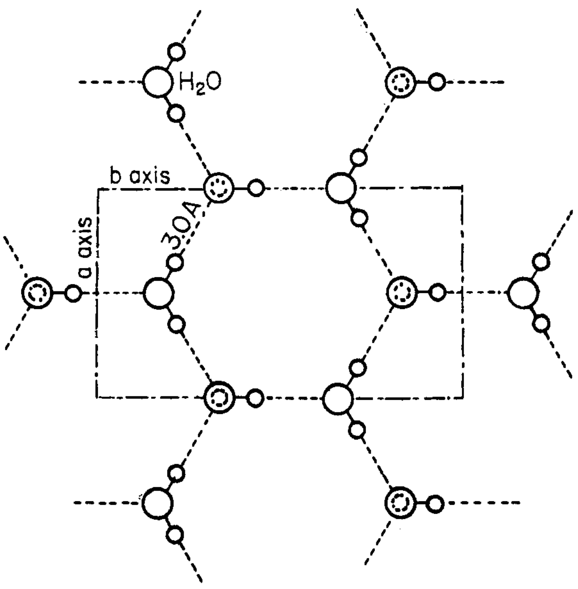

Fig. 6.—Possible arrangement of water molecules in a hydrated layer of vermiculite or montmorillonite.

Consideration of the preceding discussion shows that the evidence for the base exchange ions being between the silicate layers in montmorillonite is rather conclusive.

The total surface of water sorption by montmorillonite is about 8×10^6 sq. cm. per g., which is of the order of fifty times the observed surface for sorption of gases such as nitrogen and oxygen.[19] In other words, the internal surface reached by water in montmorillonite, as might be expected, is not available for van der Waals adsorption of most gases. Adsorption of nitrogen and oxygen rather measure the external surface area of the organized montmorillonite crystal which would not be greatly changed in formation of the internally hydrated material. Comparison of these areas shows that the individual montmorillonite crystals contain fifty to a hundred silicate layers, which is within the range indicated by electron diffraction and interference of visible light.

Summary

The water sorptions at relative humidities between 5 and 90% were measured for the Li$^+$, Na$^+$,

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(18) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(19) B. Makower, T. M. Shaw and L. T. Alexander, *Proc. Soil Sci. Soc. Am.*, **2**, 101 (1937).

K^+, Cs^+, Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++} salts as well as the free acid of the clay mineral montmorillonite. Variations in X-ray diffraction patterns and behaviors upon differential thermal analyses were determined for the materials at the various relative humidities.

Results obtained indicate that the exchangeable cations are located between the silicate layers of which the mineral is formed. In the magnesium and alkaline earth salts, the first step of water sorption is the hydration of the cation with six molecules of water which is followed by completion of a water layer having a hexagonal type structure. A second water layer of similar structure is taken up at high relative humidities. Similar results were obtained for the lithium salt except that only three molecules of water were required for the hydration of the lithium ion. In sodium, potassium, and cesium salts the cation apparently was not hydrated. This was also true for the hydrogen ion in the clay acid.

The methods used in the work although inexact give a clear picture of the sorption process for water, which is entirely different from van der Waals adsorption of gases such as nitrogen.

WASHINGTON, D. C. RECEIVED FEBRUARY 10, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heats of Dilution, Heat Capacities, and Activities of Urea in Aqueous Solutions from the Freezing Points to 40°[1,2]

BY FRANK T. GUCKER, JR., AND HUGH B. PICKARD

Introduction

In the study of solutions of non-electrolytes, a number of thermodynamic properties of aqueous solutions of urea have been determined in this Laboratory. We have found that, up to a concentration of 3 M, the apparent molal volume[3] of urea at 25 and 30° and the apparent molal expansibility[4] at 27.5° are linear functions of the first power of the concentration. Such a relationship is to be expected for many properties of non-electrolytes. Redlich and Klinger[5] found that it was the limiting law for the apparent molal volume of sucrose, and work in this Laboratory showed that it also was the limiting law for the apparent molal heat capacity[6] and heat content[7] of sucrose. An exhaustive study of the specific heats of aqueous solutions of urea[8] failed to determine unequivocally what limiting law was obeyed by the apparent molal heat capacity of urea. Heats of dilution can be measured in very dilute solutions, the specific heats of which differ from unity by an amount too small to measure directly. Hence the limiting value of the apparent molal heat content can be determined more accurately than that of the heat capacity. We therefore undertook a study of the heats of dilution of solutions of urea in order to find the limiting law for this property.

Our results also provide the final thermal data necessary for an accurate calculation of the change of the osmotic and activity coefficients of urea over a temperature range from 2 to 40°. Thus we can compare the results of vapor pressure measurements at different temperatures, and of freezing point depressions, with recent precise measurements of the vapor pressures of aqueous solutions of urea at 25°.

Heats of Dilution at 25°

Materials and Solutions.—The urea used in experiments 1–6 had been purified and used in the density determinations carried out in this Laboratory. It had been reclaimed several times by precipitation from 50% alcohol, as described in this work.[3] The urea used in experiments 7–23 was prepared from Mallinckrodt analytical reagent. It was recrystallized once from water, washed once with 95% alcohol, filtered on a sintered glass filter and dried overnight in a vacuum desiccator connected to a water aspirator. After being ground in an agate mortar, it was dried for seven or eight hours *in vacuo* at 50–60°. This purified material showed a conductance corresponding to only 0.004% electrolyte calculated as sodium chloride.

The distilled water used in making up the solutions had a specific conductance of 3 × 10^{-6} reciprocal ohm or less.

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[1] Most of the material in this paper was presented before the Division of Physical and Inorganic Chemistry at the Boston Meeting of the American Chemical Society, September 14, 1939.

[2] This work was supported by grants from the Penrose Fund of the American Philosophical Society and from the Committee on Research of the Graduate School of Northwestern University.

[3] Gucker, Gage and Moser, THIS JOURNAL, **60**, 2582 (1938).

[4] Gucker and Moser, *ibid.*, **61**, 1558 (1939).

[5] Redlich and Klinger, *Sitzber. Akad. Wiss. Wien.*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).

[6] Gucker and Ayres, THIS JOURNAL, **59**, 447 (1937).

[7] Gucker, Pickard and Planck, *ibid.*, **61**, 459 (1939).

[8] Gucker and Ayres, *ibid.*, **59**, 2152 (1937).