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I. Cornet

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Expansion of the Montmorillonite Lattice on Hydration

I. CORNET*

University of California, Berkeley, California

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When exposed to water vapor, water, or some non-aqueous solvents, montmorillonitic clays display expansion of their lattices. Assuming that the expansion on hydration is a uni-dimensional swelling phenomenon, a thermodynamic analysis has been made which furnishes quantitative evaluation of interplanar forces. This analysis indicates that for lattice expansions of 3 or 4A from the dehydrated contracted state, the force between montmorillonite lattice layers is substantially constant; but for greater expansions the force diminishes in a complex manner. The analysis also indicates the possibility of determining quantitatively the forces exerted by molecules of solvents which expand the lattice, providing ion exchange does not occur. Problems in determining molecular forces and structure are discussed.

INTRODUCTION

THE clay mineral montmorillonite has a layer lattice which in chemical composition and crystal structure is similar to pyrophyllite; the crystal structure Pauling proposed for pyrophyllite¹ has been assigned to montmorillonite with but few modifications by Hofmann,^{2,3} Marshall,⁴ Hendricks⁵ and others. Montmorillonite differs markedly from pyrophyllite in that it possesses high base exchange capacity† and a variable crystal spacing along the *c* axis. A current crystal structure⁶ of montmorillonite which accounts for the differences between montmorillonite and pyrophyllite shows (Fig. 1) regular two-dimensionally crystalline sheets with some isomorphous replacement of magnesium ions for aluminum ions; the crystalline sheets are superposed without any regularity, except for a constant separation, and are held together by relatively weak forces. The crystalline sheets have a diameter of 1000 to 3000A.⁷

When montmorillonite is exposed to water, the lattice swells.² The variable crystal spacing along the *c* axis (the 001 spacing) was first determined for various vapor pressures by Hofmann and Bilke,⁸ and has since been studied by other investigators.^{9,10}

EXPERIMENTAL PROCEDURE AND RESULTS

Samples of montmorillonite saturated with three different cations were exposed to various vapor pressures

* Assistant Professor of Mechanical Engineering; Consultant on Clay Research, Institute of Transportation and Traffic Engineering.

¹ L. Pauling, Proc. Nat. Acad. Sci. **16**, 123-129 (1930).

² Hofmann, Endell, and Wilm, Zeits. f. Krist. **86**, 340-8 (1933).

³ Hofmann, Endell, and Wilm, Zeits. f. angew. Chemie **47**, 539-47 (1934).

⁴ C. E. Marshall, Zeits. f. Krist. **91**, 433-49 (1935).

⁵ S. B. Hendricks, J. Geol. **50**, 276 (1942).

† Base exchange capacity is the quantity of ammonium ions a material will retain on leaching with neutral normal ammonium acetate; it is usually expressed as milli-equivalents per hundred grams of oven dry colloid.

⁶ D. M. C. MacEwan, Trans. Faraday Soc. **44**, 306, 349-367 (1948).

⁷ v. Ardenne, Endell, and Hofmann, Ber. deut. keram. Ges. **21**, 209-27 (1940).

⁸ U. Hofmann and W. Bilke, Kol. Zeits. **77**, 238-51 (1936).

⁹ Bradley, Grim, and Clark, Zeits. f. Krist. **97**, 216-22 (1937).

¹⁰ Hendricks, Nelson, and Alexander, J. Am. Chem. Soc. **62**, 1457-64 (1940).

in desiccators with sulfuric acid-water solutions. When equilibrium was attained, small quantities of the clays were placed in thin walled glass capillary tubes, and returned to the desiccators for one to two weeks to assure equilibrium again. The capillary tubes were then removed and rapidly sealed in a small flame, the seal being at least 2 cm from any clay in the tubes. The tubes were then x-rayed to obtain the *c* spacings, using Cu *K*α-radiation. Lattice spacings were measured from photometric curves after graphical correction for scattered radiation. Data after Hofmann and Bilke⁸ are given in Table I. If 001 spacing be plotted against the vapor pressure on rectangular coordinates, a sigmoid curve is obtained.

THERMODYNAMIC ANALYSIS

The crude mechanical model of the system water liquid-water vapor-montmorillonite (Fig. 2) shows how energy changes in the system must balance. For isothermal pressure changes of infinitesimal magnitude, the change in free energy of the water = $\Delta F = RT \ln(p/p_0)$ where *p* = the pressure of the water vapor and *p*₀ = saturation vapor pressure of water at temperature *T*. This change in free energy must equal the work done on the ideal (frictionless) hydraulic pump system. The pump work is transmitted through the jack to separate the crystalline sheets or layers of the montmorillonite an infinitesimal distance *dx*, the work of separation being done against an interplanar force *f*. Summing the energy terms

$$-\Delta F = -RT \ln(p/p_0) = -RT \ln h = \int f dx,$$

where *h* is the relative humidity. This analysis is consistent with the thermodynamic treatment of swelling presented by Katz,¹¹ but restricted to the case of one-dimensional swelling.

The change in free energy during hydration is shown as a function of the 001 spacing in Fig. 3.

¹¹ J. R. Katz, Trans. Faraday Soc. **29**, 279-300 (1933).

TABLE I. Variation of interplanar spacing of montmorillonite on hydration.

t °C	p_{H_2O} mm	Ca-mont- morillonite 001 spacing, Å	H-mont- morillonite 001 spacing, Å	Na-mont- morillonite 001 spacing, Å
21	0.0	11.25	11.4	10.1
21	0.4	12.1	12.8	11.3
21	2.4	13.4	—	12.7
21	4.9	14.6	14.5	12.9
21	8.7	15.1	15.3	14.
21	12.0	15.6	15.6	14.5
21	14.5	15.7	16.1	16.
21	16.7	17.8	18.9	17.8
21	18.65	—	—	—
20	17.5	20.7*	20.45*	>>30.*

* Measured in distilled water.

DISCUSSION: RESULTS OF THE THERMODYNAMIC ANALYSIS

The slopes of the curves in Fig. 3 represent rates of change of energy with changes in displacement; the slope of a curve at any lattice spacing is therefore the force existing during an infinitesimal lattice displacement at that 001 spacing. For any one of the three curves shown a single higher order equation might possibly be obtained to fit the data. From the physical standpoint, it may be more fruitful to regard the curves as complex.

For vapor pressures of 0.4 mm to about 7.0 mm the expansion of the montmorillonites shown is characterized by a high, and substantially constant, rate of energy change during expansion. For the Na, Ca, and H saturated clays, the slopes are approximately 3.5, 2.7, and 3.3 (respectively), $\times 10^{10}$ ergs per mole per Å of lattice expansion. This constancy of slope, or force, indicates that for the expansion involved, about 3 or 4Å, the lattice may be analyzed substantially as a set of extended planes, and this force should depend primarily on the surface density of the electric charges.¹²

For the next 1 or 2Å of lattice expansion the slopes of the curves, or the forces, diminish rapidly; the forces are inversely proportional to a power of the radius, as might be expected with dipoles. For Ca and H montmorillonite this transition appears to be quite abrupt at 14 to 15 mm pressure. This may indicate shortcomings in the experimental data, but more likely the differences between the three curves in the transition zone are due to differences in degree of hydration of the cations with which the clays are saturated.

For vapor pressures above 15 mm, the rate of change of free energy with lattice expansion of the clays is small, decreasing with increasing expansion, till the curves intersect the abscissa or approach it asymptotically. Unfortunately the data are insufficient to warrant quantitative statements, but it appears that for these broad expansions of the montmorillonite lattice, the

slopes indicate a complex system of dipoles, with forces inversely proportional to higher powers of the displacement. For these high vapor pressures, there may be many layers of water molecules in the interplanar space. The lattice spacing in water is the result of equilibrium among forces (a) between water molecules, (b) between lattice layers, and (c) between water molecules and the lattice layers.

The initial expansion of the montmorillonite lattice from its dry state to a vapor pressure of 0.5 mm has not been discussed yet. Although there are no data presented for this range of vapor pressures, it seems clear that the curves of Fig. 3 must show discontinuity between the dry contracted lattice and the expanded spacings. No spacing should be found which is much too small to accommodate the water molecules. This behavior has been clearly demonstrated experimentally in a study of the sorption of anhydrous ammonia gas

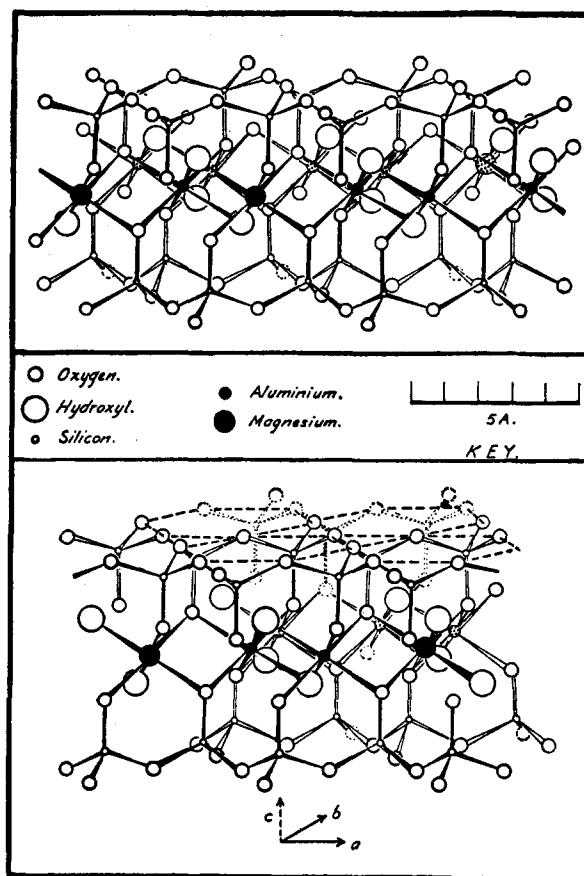


FIG. 1. The structure of montmorillonite. Background Al and Mg ions are spotted. Two structural sheets irregularly superposed are shown. The magnesium content of montmorillonite is from 1 to $\frac{3}{4}$ Mg^{++} per unit cell (containing 4 six-coordinated ions), so the replacement rate shown here (Mg^{++} in 5 octahedral positions out of 18) is rather higher than average. In the lower montmorillonite sheet, some of the rings of six oxygen ions are indicated by means of dotted lines, and one side of each hexagon has been omitted to avoid confusion. Each ring has a hole in the center, beneath which is an OH^- ion (after MacEwan, reference 6).

¹² W. D. MacMillan, *The Theory of Potential* (McGraw-Hill Book Company, Inc., New York, 1930), first edition, cf. pp. 42, 153, 209.

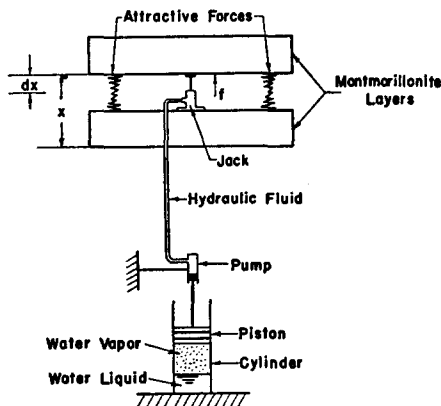


FIG. 2. Thermodynamic model of the process of expansion of montmorillonite on hydration. The work of isothermal expansion of the water vapor in the large cylinder $= \int P dV = -\Delta F = -RT \ln(P_2/P_1)$. This must equal $\int_{x_1}^{x_2} f dx$, where f is the force acting during the infinitesimal displacement, dx , in the lattice spacing x .

by dry hydrogen bentonite.¹³ The x-ray patterns show distinct (001) spacings for a Wyoming-type hydrogen bentonite that has been dried at 100°C. Small quantities of ammonia, if admitted slowly, are sorbed without changing the x-ray pattern; this sorption occurs on exterior planar and on broken bond surfaces.¹³ With larger quantities of ammonia, or more rapid admission of the gas, the lattice expands. The line which characterizes the (001) spacing grows broad and diffuse. In some samples at this stage there is no (001) line and the sample appears to be amorphous. At about 23 millimeters pressure of ammonia, the (001) lines indicate wider spacings, showing that the montmorillonite planes are separating. From this stage on, sharp distinct (001) spacings, showing lattice expansions of more than 2.2 Å, are observed. Thereafter the lattice expands fairly regularly; as the ammonia pressure increases, the (001) spacing widens. A similar loss of x-ray pattern and subsequent re-orientation was observed by P. R. Stout in his study of the fixation of phosphate ion by kaolinite and halloysite.¹⁴

DISCUSSION: IMPORTANCE OF FURTHER UNDERSTANDING OF MONTMORILLONITE

Montmorillonitic clays, commonly called "bentonite," are of considerable importance in industry. They are used in making ceramics, binding foundry molding and core sands, emulsifying asphalt and other bituminous products, carrying insecticides, suspending electrolytes in dry cells.¹⁵ In the oil and petroleum refining industry, montmorillonitic clays have been important as drilling muds,¹⁶ as absorbents for purifying,¹⁵ and as catalysts or catalyst carriers in the Thermoform catalytic cracking

process.^{17,18} Most of these applications of bentonite depend on the colloidal properties, the physical and chemical reactivity of the montmorillonite lattice.

Because of this industrial importance, and because montmorillonite appears related to soil colloids,^{19,20} its structure has been investigated vigorously. However, an important theoretical consideration has arisen which intensifies the need for further and quantitative knowledge of montmorillonite. Investigators have been studying the expansion of montmorillonite by various organic compounds, and have interpreted the structure of the absorbed organic molecules from this expansion.^{6,21-23} This application is not only illuminating, but it may possibly be extended to indicate quantitatively the forces acting between molecules, especially on adsorbing surfaces,²³ thus contributing to studies of permeability, immunology, catalysis and other fields.

To avoid misunderstanding, it should be noted that the force between montmorillonite lattice layers determined by this thermodynamic analysis of the swelling is the resultant force acting during an infinitesimal displacement of the lattice planes. The total free energy change between any two states of the lattice may include free energy changes due to hydration of cations, orientation of solvent molecules between the planes, and polarization of molecules between the lattice planes. The thermodynamic model shown in Fig. 2 is not intended to imply a concept of simple plates held

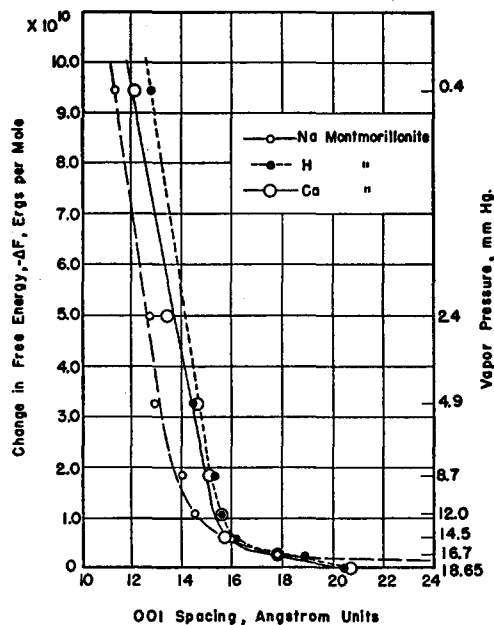


FIG. 3. Change in free energy on expansion of montmorillonite clays during hydration.

¹⁷ Davidson, Ewing, and Shute, *Natl. Petrol. News*, 5 pp. (July 7, 1943).

¹⁸ R. C. Davidson, *Petrol. Refiner*, 12 pp. (Sept. 1947).

¹⁹ S. B. Hendricks and W. H. Fry, *Soil Sci.* **29**, 457-479 (1930).

²⁰ Kelley, Dore, and Brown, *Soil Sci.* **31**, 25-55 (1931).

²¹ S. B. Hendricks, *J. Phys. Chem.* **45**, 65-81 (1941).

²² W. F. Bradley, *J. Am. Chem. Soc.* **67**, 975-981 (1945).

²³ D. M. C. MacEwan, *Nature*, **162**, 935-39 (1948).

¹³ I. Cornet, *J. Chem. Phys.* **11**, 217-226 (1943).

¹⁴ P. R. Stout, *Proc. Soil Sci. Soc. Am.* **4**, 177-182 (1939).

¹⁵ C. W. Davis and H. C. Vacher (revised by J. E. Conley), U. S. Dept. of Interior, *Tech. Paper* 609, 83 pp. (1940).

¹⁶ Loomis, Ford, and Fidiham, *A.I.M.E. Tech. Publ.* 1201, *Petrol. Tech.*, 12 pp. (1940).

together by simple forces; in a montmorillonite saturated with a cation like sodium or lithium, at vapor pressures approaching saturation, the forces of the original aluminosilicate layers will be greatly modified by the absorbed water which may be regarded as part of a new structure.

Studies of the swelling of montmorillonite in various solvents occasionally have been complicated by the possibility of cation exchange. For example, it may be desirable to avoid amines²⁴ in studying the swelling of a hydrogen montmorillonite; solvents displaying more or less prominent hydrogen bond formation²⁵ and small coulombic interaction with hydrogen montmorillonite would be recommended.²⁴

²⁴ I. Cornet, "A Study of the Location and the Properties of Reactive Spots in Montmorillonitic Clay Lattices," Ph.D. Thesis, University of California, 119 pp. (October, 1942).

²⁵ H. L. Huggins, *J. Org. Chem.* **1**, 407-456 (1936).

Structures determined by studies of the lattice expansion of montmorillonite should be regarded in light of the polarizing environment of the interplanar spaces. Bradley has stated that the interaction between hydrogen atoms of aliphatic chains with oxygen ions of the silicate surface involves energy comparable in magnitude with that for O—H···O bonds of a water system, and he has postulated polarization of aromatic rings as a whole.²²

In summary, the thermodynamic analysis of Fig. 3 evaluates force at any lattice displacement, providing ion exchange has not occurred, and providing that effects of variations in hydrogen bonding and in solvation of cations are considered. The same source, preparation and particle size of montmorillonite should be used for thermodynamic calibration analysis as is used for the study of swelling in solvents.

The Determination of Energy Levels from Thermodynamic Data. I. The Effect of Experimental Error

ELLIS BLADE AND GEORGE E. KIMBALL

Department of Chemistry, Columbia University, New York, New York

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The problem of calculating energy levels from thermodynamic data can be reduced to that of inverting the Laplace transform, for which several procedures have been developed. Using the method of Widder, we show that the resultant calculated energy level density function consists of a series of broadened peaks, whereas in the true density the levels are represented by a series of Dirac delta-functions.

Alternatively, if the distribution of the energy levels is specifically assumed to be composed of discrete energies, the calculation reduces to the moment problem.

In either case the calculation is shown to have an inherent "resolving power," in that levels within a certain closeness cannot be distinguished as separate. By a generalization of this idea, it is shown that the computation can lead to a knowledge of the over-all density of energy levels within a given region, but cannot reveal their exact locations.

1. INTRODUCTION

STATISTICAL mechanics provides a relationship between the quantum-mechanical energy levels of a system and the thermodynamic properties. For a system of identical, weakly interacting molecules, the relationship is expressible in terms of the partition function,

$$Q(\beta) = \sum e^{-\beta E_i}, \quad (1)$$

where E_i is the i -th energy level of a molecule, and $\beta = 1/kT$. The free energy of the system is related to the partition function by

$$F = -kT \ln(Q^N/N!) \quad (2)$$

if the system contains N molecules, and the other thermodynamic properties can be found from F by well-known methods.

When the energy levels are known, the calculation of

the thermodynamic functions is a straightforward process, and is known to give accurate results. On the other hand, attempts to reverse this process, to find energy levels, have been less successful. It has been found that energy levels calculated in this way are subject to large errors. It is the purpose of this paper to investigate the origin of these errors and the extent to which information concerning energy levels can be derived from thermodynamic data.

2. THE PARTITION FUNCTION AS A LAPLACE TRANSFORM

It has been pointed out by Bauer¹ that the partition function is mathematically the Laplace transform of the energy level density. That is, if the energy levels can be expressed by a density function $g(E)$ such that

¹ S. H. Bauer, *J. Chem. Phys.* **6**, 403-404 (1938); **7**, 1097-1102 (1939).