

SELF-DIFFUSION OF CALCIUM IONS
IN CALCIUM BENTONITE GELS

by

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INTRODUCTION

Definition

In general the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water, and a particle size of less than two microns to the soil chemist. Clays may be the product of weathering, hydrothermal action, or sedimentation (8, p. 1). Most natural clays contain some non-clay material but sufficient amounts of one or more clay minerals to meet the above plasticity and particle size requirements to be called a clay.

History of Clay Study (8, p. 11-26)

Although two of the oldest constructive human activities, agriculture and pottery making, have been deeply concerned with the study of clay minerals, the literature concerning their study remained an almost hopeless mass of empirical confusion prior to about 1930. This was the understandable result of stressing applications since no adequate analytical tools were available to determine the fundamental structure of the clay materials, and there was little interest in

determining the structure since it was widely thought that colloidal clays were amorphous. The fact that many clays with similar physical properties were different chemically and that clays with the same chemical composition differed in their physical properties contributed to the confusion.

Prior to 1920 many different concepts portraying the fundamental components of clay materials and explaining their properties existed contemporaneously in the minds of various investigators. One very old idea was that there was but a single pure clay substance, kaolin or the mineral kaolinite, that was responsible for the clay-like properties of all clay materials. The chemical and physical differences in different clays were attributed to the presence of varying amounts of non-clay impurities. This concept was quite popular and, unfortunately, still persists with some geologists.

Another widely held concept was that a colloid complex was the essential component of all clay materials. The colloid complex was thought to be amorphous, as were all colloidal materials in the early days of colloid chemistry. There were several ideas concerning the character of the complex. One was that of Van Bemmelen and Stremme who regarded the complex not as a definite compound but as a loose mixture of the

oxides of silicon, aluminum, and iron. Another idea regarded the complex as a mixture of compounds generally thought of as salts of weak ferroalumino-siliceous acids.

Mellor and Searle developed the idea that there were two essential components of clay: clayite and pelinite. Clayite was thought to be the true clay substance in kaolins and pelinite the true clay substance in materials other than kaolins. Both were thought to be amorphous.

Oden suggested that clays could be composed of almost any mineral if the particles were small enough, and that particle size was the major factor determining the special attributes of clays.

The work of many researchers was responsible for dispelling the above and other erroneous notions and establishing the current clay mineral concept. In 1921 P. Koettgen separated a series of clays by centrifugation in aqueous thallous formate solutions of various densities and showed that the fractions differed both in composition and in properties. This led to the recognition of the individuality of clay species and to a search for naturally occurring pure clays. Further study by Ross and Shannon of the refractive index and birefringence of bentonites showed that even these highly colloidal clays were essentially crystalline.

Hadding, in 1923, and Rinne, in 1924, working independently, published the first x-ray-diffraction analyses of clay materials. Both found crystalline material in the finest fractions of a series of clays and also found that all of the samples studied seemed to be composed of particles of the same small group of minerals.

A great deal of further x-ray work combined with structural principles, particularly those of Linus Pauling (16, p. 1010-1026), led to the development of structural formulas for the clays and a clay-mineral concept accepted today by nearly all students of clays. In brief, 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. The following sections on classification and structure may be considered as part of this clay-mineral concept.

Classification of Clays

Grim (8, p. 27) suggests a tentative classification of clay minerals on the basis of currently available data on structure and composition of the various clay minerals. This classification is found in Table I

TABLE I. Classification of the Clay Minerals

- I Amorphous
 - Allophane group
- II Crystalline
 - A. Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
 - 1. Equidimensional
 - Kaolinite group
 - Kaolinite, nacrite, etc.
 - 2. Elongate
 - Halloysite group
 - B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)
 - 1. Expanding lattice
 - a. Equidimensional
 - Montmorillonite group
 - Montmorillonite, sauconite, etc.
 - Vermiculite
 - b. Elongate
 - Montmorillonite group
 - Nontronite, saponite, hectorite
 - 2. Nonexpanding lattice
 - Illite group
 - C. Regular mixed-layer types (ordered stacking of alternate layers of different types)
 - Chlorite group
 - D. Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
 - Attapulgite
 - Sepiolite
 - Palygorskite

and it is seen that the name montmorillonite is used both as a group name for all clay minerals with an expanding lattice except vermiculite and also as a specific mineral name. The term montmorillonoid will be used hereafter in this thesis for the group name to avoid confusion with montmorillonite as a specific mineral name; this was suggested in 1951 by MacEwan (8, p. 34).

The Structure of Montmorillonoids

Structural concepts must be deduced from powder x-ray-diffraction data and inferences from better known structures since the montmorillonoid minerals occur only as particles too small to permit single-crystal diffraction study. Hoffman, Endell, and Wilm (11, p. 340-348), in 1933, were the first to assign a successful structure to the montmorillonoids. Other structures, such as that of Edelman and Favejee, have been proposed, but the slightly modified Hoffman-Endell-Wilm structure is the most widely accepted today.

The two basic structural units involved in the lattice of the montmorillonoids are the same as those of most clay minerals. Ideally, the first unit consists of two sheets of closely packed oxygen atoms or hydroxyl groups between which aluminum atoms are embedded in

octahedral coordination so that they are equidistant from six oxygens or hydroxyls. The second unit is a sheet of silica tetrahedrons in which a silicon atom is equidistant from four oxygen atoms.

The montmorillonoid unit consists of an alumina octahedral sheet between two silica tetrahedral sheets. These units are continuous in two dimensions. Within each unit the points of the tetrahedrons all point toward the middle sheet and the oxygen atoms at these points form a common layer with one of the oxygen-hydroxyl layers of the octahedral sheet. This ideal montmorillonoid structure is represented diagrammatically in Figure 1.

In particles of dry clay the silica-alumina-silica units are stacked one above the other much like a deck of playing cards. The units are held together only by the very weak bonds between the adjacent oxygen layers which explains the fact that polar molecules may enter between the unit layers and expand the lattice in most clays of this group. The c axis spacing may vary from about 9.6 Å, when no polar molecules are between the unit layers, to complete separation of the layers.

The montmorillonoids always differ from the above ideal structure because of substitution within the lattice of aluminum for silicon in the tetrahedral

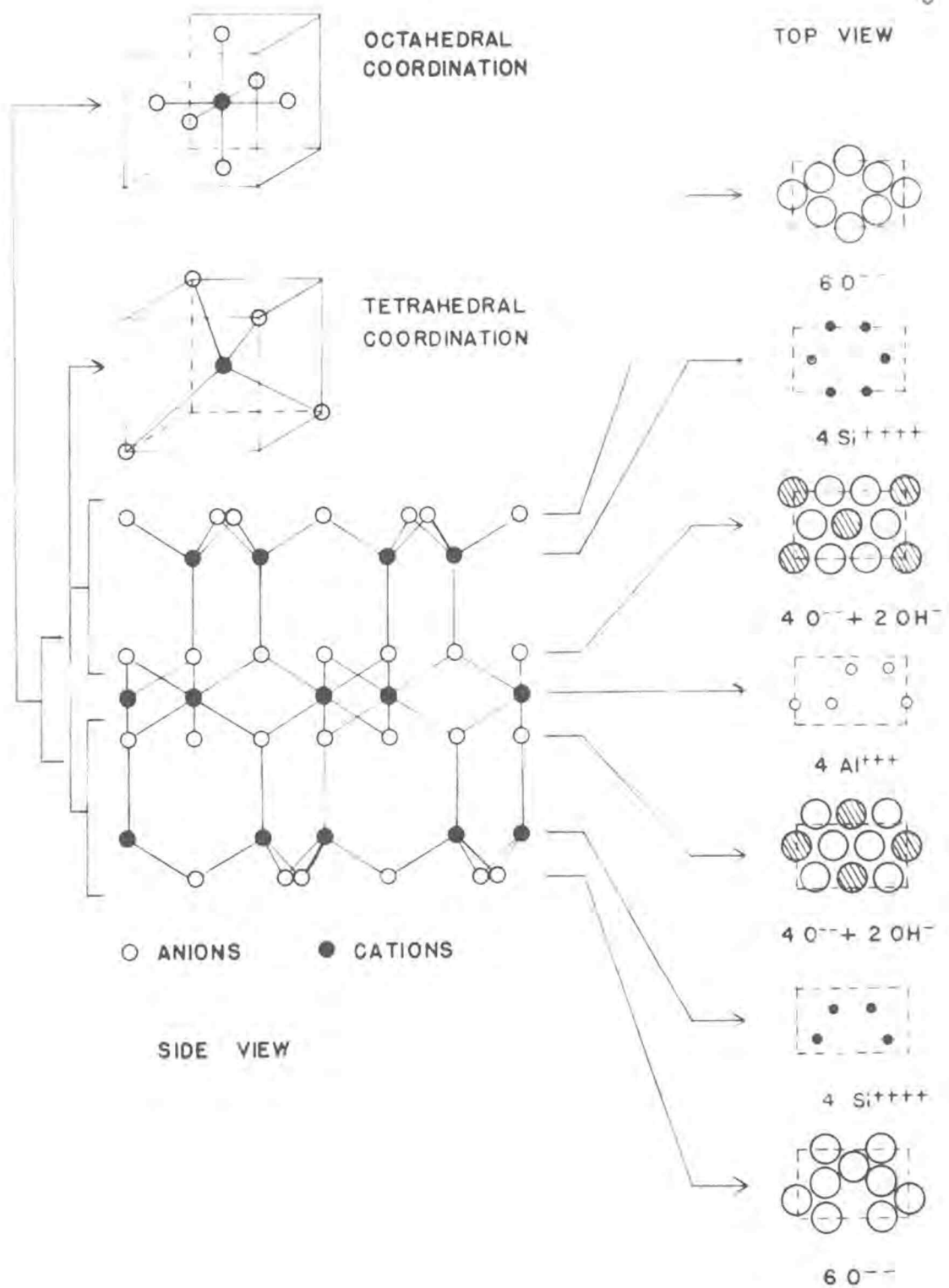


FIGURE 1. STRUCTURE OF MONTMORILLONITE
(AFTER ILER (12, P. 192))

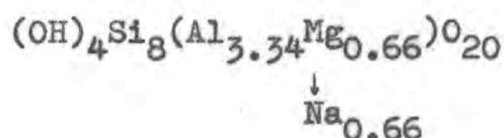
sheet and/or magnesium, iron, zinc, nickel, lithium, etc., for aluminum in the octahedral sheet. In the tetrahedral sheet the substitution of Al^{+++} for Si^{++++} appears to be limited to less than about 15 percent. Since in the ideal case only two thirds of the possible positions in the octahedral sheets are filled with Al, the substitution of Mg^{++} for Al^{+++} can be one for one, or three Mg^{++} for two Al^{+++} in which case all the positions are filled.

When these substitutions give rise to an unbalance of charge on the lattice, it is balanced by exchangeable cations adsorbed between the unit layers. The number of milliequivalents of this exchangeable cation per one hundred grams of clay is defined as the cation exchange capacity of the clay, and it may vary from 80 to 150 meq per 100 g of clay. However, the substitutions within the lattice are responsible for only about 80 percent of the total cation exchange capacity; the remaining 20 percent probably is due to broken bonds at the edges of the units and the resulting unsatisfied charges.

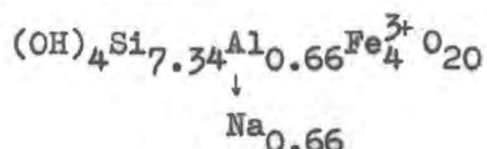
The ideal montmorillonoid structure may be represented as $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}$.

Montmorillonite, in which Mg^{++} substitutes for some Al^{+++} in the octahedral sheet, may have the

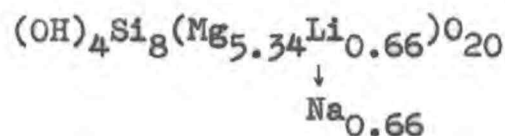
following typical composition, the exchangeable cation being indicated by the arrow:



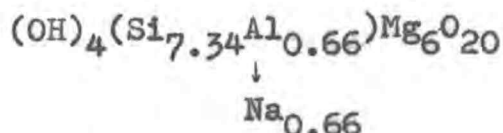
Nontronite, in which iron is present in the octahedral sheet and which tends to occur in lathlike forms, has the typical composition:



Hectorite is an extremely fine-particled, ribbonlike clay in which the octahedral layer is filled by Mg^{++} instead of Al^{+++} and the charge on the lattice is due to some replacement of Mg^{++} by Li^+ :



Saponite is a magnesium type clay similar to hectorite except that the charge on the sheets is due to some replacement of Si^{++++} by Al^{+++} in the tetrahedral sheets (12, p. 193):



Properties and Applications of Montmorillonoids

Besides the high cation-exchange capacity perhaps the most striking property of the montmorillonoids is the extreme swelling the clay undergoes on wetting. The amount of swelling depends on the type of solvent and the exchangeable cation present; normally the sodium ion produces a highly swelling clay while the calcium ion in the exchange position limits the swelling. The swelling characteristics and adhesive forces between the layers permit dispersions of montmorillonite to form thixotropic, gelatinous suspensions at concentrations as low as three percent.

Suspensions of the montmorillonoids show excellent streaming birefringence and exhibit marked colloidal properties in many other respects.

Ross and Shannon (17, p. 77-96) have defined the term bentonite as clay produced by the alteration of volcanic ash in situ and have pointed out that it is composed largely of montmorillonite. The term is widely used rather loosely to refer to natural clay deposits high in montmorillonite content. Bentonite deposits

are found throughout the world and principally in South Dakota and Wyoming in the United States where about one million tons were mined in 1957 (20, p. 370). About two thirds of this was of the sodium type which swells in water and is used in drilling muds, portland cements, concrete, ceramics, emulsions, insecticides, soaps, pharmaceuticals and paints. It is also used to seal dams, to bond foundry sands, asbestos and mineral wool, for clarifying water, juices and liquors, and as a water softener. The other one third of the bentonite is mostly of the non-swelling calcium variety that is widely used as an absorbent clay in oil refining (1, p. 119).

DIFFUSION

Diffusion Equations

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular, atomic, or ionic motions. It is classically illustrated by partially filling a tall cylindrical vessel with an iodine-water solution and then carefully filling with water; the sharp, well defined boundary soon disappears and the upper part gradually darkens and the lower part becomes less intensely colored due to the diffusion of the iodine molecules from regions of high concentration to regions of low concentration. After sufficient time the whole solution appears uniformly colored.

That the motion of the iodine molecules is random has been demonstrated by replacing them with particles small enough to share the molecular motions of the solvent but large enough to be visible under the microscope.

Consider a horizontal section normal to the concentration gradient in the above cylinder and two thin elements of volume one just below and one just above the section. Although it is impossible to predict the direction of any particular molecule, it can be said

that on the average a definite fraction of the molecules in the lower element will cross the section from below and the same fraction of molecules in the upper element will cross the section from above in a given time. Thus there is a net transfer of iodine molecules from the lower to the upper element as a result of random molecular motions simply because there were more iodine molecules in the lower than in the upper element.

About 1885 Fick (6, p. 30-39) recognized the analogy between diffusion and the transfer of heat by conduction (which is also due to random molecular motions), and was the first to put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived some years earlier by Fourier (7, p. 581-621). Thus the theory of diffusion in isotropic substances is based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section:

$$F = -D \frac{\partial C}{\partial x} \quad (1)$$

where F is the rate of transfer per unit area of section, C is the concentration of the diffusing substance, x is the space coordinate measured normal to the section, and D is called the diffusion coefficient.

In dilute solutions D can reasonably be taken as constant. The dimensions of D are $\text{length}^2\text{time}^{-1}$. Usually D is expressed in $\text{cm}^2\text{sec}^{-1}$, and values of D range from greater than $10^5 \text{ cm}^2\text{sec}^{-1}$ (thermal neutrons) to less than $10^{-11} \text{ cm}^2\text{sec}^{-1}$ (atoms in metals).

The fundamental differential equation of diffusion in an isotropic medium is derived from equation (1) (5, p. 3-4), and for one-dimensional diffusion (a concentration gradient only along the x axis) it takes the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

where t is time. Equations (1) and (2) are usually referred to as Fick's first and second laws of diffusion.

General solutions of the diffusion equation have been obtained for a variety of initial and boundary conditions when the diffusion coefficient is constant. The solutions are usually either comprised of a series of error functions or take the form of a converging trigonometrical series.

In this thesis a long cylinder is filled with a clay paste; Ca-45-clay is at one end, Ca-clay is at the other, and $\text{Ca}^{++}\text{-45}$ is the diffusing substance. The initial conditions may be defined as $C = C_0$ for $x < 0$

and $C = 0$ for $x > 0$ when $t = 0$. C is the concentration of Ca^{++-45} , x is the distance measured along the axis of the cylinder, and $x = 0$ at the interface of the two clays.

Crank shows (5, p. 9-12) that

$$C = \frac{1}{2} C_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (3)$$

is a solution to the diffusion equation for the above initial and boundary conditions by differentiating equation (2) and by summing the effect of a series of line sources. Values of erfc , referred to as the error-function compliment, are found in tables such as those in the National Bureau of Standards Applied Mathematics Series (21, p. 1-302).

If A equals the total amount of diffusate, Ca^{++-45} , and S equals the cross sectional area of the cylinder, then equation (3) takes the form

$$\frac{2A}{C_0 S} = \int (\operatorname{erfc} \frac{x}{2\sqrt{Dt}}) dx \quad (4)$$

and $2A/C_0 S$ may be experimentally determined as is done in these experiments.

The dependence of D on the absolute temperature, T , can be expressed as

$$D = A' e^{-E/RT} \quad (5)$$

where E is the activation energy, A' the activation constant, and R the gas constant.

Diffusion of Cations in Clay Pastes

In infinitely dilute solutions the relationship between the self-diffusion coefficient D_i^0 , the mobility ω_i^0 and the limiting equivalent conductance λ_i^0 of the ion i is (9, p. 245)

$$D_i^0 = kT\omega_i^0 = \frac{\lambda_i^0 RT}{|Z_i| F^2} \quad (6)$$

where ω_i is defined as the velocity of i under an external force of one dyne, k is Boltzmann's constant, R is the gas constant, T is the absolute temperature, F is the Faraday, and Z_i is the valency of i .

At finite concentrations the ionic self-diffusion coefficient theoretically varies with concentration as follows (9, p. 256):

$$D_i = D_i^0 - \mathfrak{D}_{(D_i)} \sqrt{c} \quad (7)$$

where $\mathfrak{D}_{(D_i)}$ is a limiting theoretical constant.

However, it has been found by Wang (25, p. 1769) that experimentally determined values of the self-diffusion coefficient for calcium ions do not decrease according to equation (7) as concentration is increased; instead,

the value of $D_{Ca^{++}}$ remains almost constant until the concentration reaches about 0.2N and then decreases gradually as the concentration increases.

Since the calcium ion concentrations in these experiments are about 0.1N or less, $D_{Ca^{++}}$ or $kT\omega_{Ca^{++}}$ may be calculated using equation (6) and the well known and accurate value for $\lambda_{Ca^{++}}^0$.

In porous materials such as clay pastes, diffusion is affected by electrical charges on the clay particles and by the geometry of the diffusion path. Allowance may be made for the geometry by adding a labyrinth factor h to the second term of equation (6):

$$D_1 = kT\omega_1 h \quad (8)$$

In this case D_1 is the self-diffusion coefficient for the ion diffusing through the clay-water paste and ω_1 is the ion mobility through water.

The fraction h is not proportional alone to the pore fraction, S^1 , but is considered by Machie (13, p. 506) as the mean value of the square of the cosine of the angle between the channels through which diffusion occurs and the direction of over-all diffusion. DeVries (21, p. 41-43) has calculated h for assemblies of oblate

¹The pore fraction is the ratio of the volume of the pores to the total volume.

spheroids and has shown how it is dependent on the eccentricity of the particles and the pore fraction S .

Equation (8) is supposed to be valid only for ions and molecules that are not attracted by the charge on the clay particle; in the montmorillonite clay pastes under consideration here it would be valid only for molecules and anions, since cations are attracted by the negative charge on the clay particles and occupy the exchange positions.

The pastes in these experiments contained calcium ions as the exchangeable ion at a concentration s per ml and calcium ions in solution at a concentration n per ml. The mobility for cations remains ω_1 in solution but is unknown for the exchangeable cations. The labyrinth factor for cations is expected to be different from h , so a factor g is assigned to the exchangeable ions that describes the joint effects of the diffusion path geometry and of forces exerted on the cations by the electric charges of the colloid particles. Since ion exchange is a fast process (2, p. 253) compared with diffusion, all calcium ions during a fraction of time $s/(n + s)$ are considered to have properties of ions in the exchange position and an apparent labyrinth factor g ; during the remainder of the time they are considered to have a labyrinth factor h equal to that of the anions.

The self-diffusion coefficient of calcium ions is then

$$D_{Ca^{++}} = kT \omega_{Ca^{++}} \frac{(nh + sg)}{n + s} \quad (9)$$

The object of this thesis is to determine experimentally the self-diffusion coefficient for calcium ions in Ca-montmorillonite pastes and from these values to calculate h and g and estimate the eccentricity of the clay particles by using the above relationships.

Methods of Determining Self-Diffusion Coefficients

The term self-diffusion, strictly speaking, implies diffusion of something into its exact counterpart. Since it is impossible to follow the motion of particles possessing no feature distinguishing them from other particles of the system, the interdiffusion of radio-isotopes, a measurable process, is usually spoken of as self-diffusion. The difference between the isotopic self-diffusion coefficient and the true self-diffusion coefficient is usually much smaller than the experimental error for the method used to determine them.

As in equations (3) and (4) and other one dimensional integrated forms of Fick's law, the concentration of the diffusing species is always expressed in terms of two independent variables; the time t and the

coordinate x along which diffusion takes place. Consequently, the self-diffusion coefficient can be determined by measurement of either the change in isotope concentration along x at a constant time or the change in isotope concentration with respect to time at a constant coordinate. This discussion will be limited to only a few of the methods that have been used to determine diffusion coefficients in pastes and methods in liquids that can apply to pastes.

A common method in which the change in radioisotope concentration is measured at a constant value of x is illustrated by Jehle (23, p. 75). He measured the self-diffusion coefficients for Na-24 and Cl-38 in various sodium chloride solutions by filling halves of a pyrex tube 11 cm in diameter with sodium chloride solution; one half of the tube contained the tracer form of the element studied. A shielded gamma counter situated over the initially active half of the tube and at a definite distance from the original sharp boundary was used to determine the radioactivity from time to time, and the decrease in activity was described by equation (3). Walker (24, p. 757-758) used a similar method but moved the diffusion tube past the counter so as to scan along the x axis at a particular time. Methods of this sort are limited to diffusing isotopes

whose radiation can be detected through the cylinder walls.

Salvinien (18, p. 465-473) determined the diffusion coefficient for phosphate ion in a gel using radio-phosphorous. He placed the gel in a plastic tube and sliced both the tube and the gel into thin sections normal to the x axis after diffusion had taken place. By counting each slice separately, knowing the distance of each slice along x, and by using equation (3) he calculated the self-diffusion coefficient.

Wang and Kennedy (26, p. 2080-2083) and Bloksma (2, p. 40-52) both used the method of layer analysis in which whole sections of a tube are analyzed for the amount of diffusing substance in the section after a definite diffusion time. Wang determined the self-diffusion coefficient for sodium and iodide ions in sodium iodide solutions and Bloksma determined the self-diffusion coefficients for sodium and iodide ions and for urea in clay pastes. Wang's apparatus was of the plastic Castolite with 1/16 inch diameter diffusion holes and that of Bloksma was made of Bakelite. Their apparatus and procedure were similar to that used in this thesis and will be discussed more fully later.

EXPERIMENTAL METHODS

Preparation of Clay Pastes

Three pairs of calcium-montmorillonite pastes were prepared that had values of 0, 0.1 and 1.0 for the ratio n/s. The two pastes of each pair were nearly identical except that part of the exchangeable calcium on one was radioactive calcium (Ca-45).

The clay used was a finely ground Wyoming bentonite supplied by the Baroid Division of the National Lead Company who also supplied the following analysis of the bentonite:

<u>X-ray Diffraction</u>	<u>Percent</u>
Montmorillonite	Major Phase
Quartz	8
Cristobalite	3
Feldspar	3
<u>Chemical Analysis</u>	<u>Percent</u>
SiO ₂	63.20
Al ₂ O ₃	20.54
Fe ₂ O ₃	3.51
TiO ₂	0.15
R ₂ O ₃	24.20
CaO	1.30
MgO	2.49
Na ₂ O	2.16
K ₂ O	0.50
SO ₃	0.53

<u>Chem. Analysis (cont'd.)</u>	<u>Percent</u>
CO ₂	0.30
H ₂ O (110°C)	7.19
H ₂ O (900°C)	5.06

An approximately two percent¹ bentonite suspension was prepared by slowly adding the necessary amount of clay to a vigorously stirred aqueous phase. The stirring was continued for several hours to thoroughly wet the powder. The suspension was then diluted to about one percent solids and allowed to stand for three days so that the non-clay particles and large clay particles would settle out. The suspended material was removed by syphoning and the residue on the bottom discarded. This process is known as clarifying the clay and supposedly results in a product containing less than 0.1 percent quartz. The predominant cation in the exchange position was sodium and to replace it with calcium the suspension was diluted once more to about 0.5 percent, divided into two equal portions, and each portion passed through an ion exchange column.

The exchange columns were glass tubes of 2.14 cm diameter with a stopcock at one end and were packed to

¹The concentrations of clay-water systems referred to in this way, or simply as concentrations, throughout this thesis will mean percent solids by weight obtained by drying at 110°C unless otherwise qualified.

a depth of 95 cm with Amberlite IR-120, a high capacity sulfonic acid cation resin. The resin was converted first to the hydrogen form by passing three liters of 3N hydrochloric acid through the column, and then converted to the calcium form by passing one liter of 1M calcium chloride through the column at a rate of about one liter per hour. The excess calcium chloride was removed by washing with distilled water. Two columns were prepared in this way: one with ordinary CaCl_2 and the other with Ca-45-Cl_2 .

The radio-calcium was obtained from the Oak Ridge National Laboratory and was in the form of a CaCl_2 solution which contained 4.43 millicuries of Ca-45 per ml and 111 mg total Ca per ml. Three-tenths of a ml of this solution was added to one liter of a 1M CaCl_2 solution giving a ratio of 6.64×10^{-4} mc Ca-45 to one meq total Ca. This Ca-45-Cl_2 solution was then used to charge one of the exchange columns.

After the clay was passed through the columns the percent solids in the suspension was determined and each half of the clay was divided into three portions. Then CaCl_2 was added to obtain the ratios $n/s = 0$, $n/s = 0.1$, and $n/s = 1.0$ for each half of the suspension. The amount of CaCl_2 added was based on the percent solids in the suspension and a base exchange

capacity of 90 meq per 100 grams of clay. Each portion was dried at 80°C until a paste of about the right consistency was obtained. The pastes were then placed in small jars and final concentration adjustments were made by further drying at room temperature or by adding water until the clays of each pair had nearly the same concentration.

A fairly thick paste was required to minimize the complications of sedimentation, convection currents, and mechanical vibrations. The paste could not have been too rigid or it would have been difficult to remove air bubbles from the clay. The concentrations of the pastes used varied from six to ten percent.

Description of the Apparatus

After a review of the methods of determining diffusion coefficients it was decided to use the layer analysis technique used by Wang and Kennedy (26, p. 2080-2083) and by Bloksma (2, p. 40-52). The apparatus used here was based on their apparatus and a suggestion of Bloksma to use two additional plates. The apparatus (Figure 2), then, is composed of a pile of six horizontal, circular Plexiglass disks each 0.5 inch thick and 3.75 inches in diameter. The disks turn separately around a 5/8 inch vertical steel rod on which they are

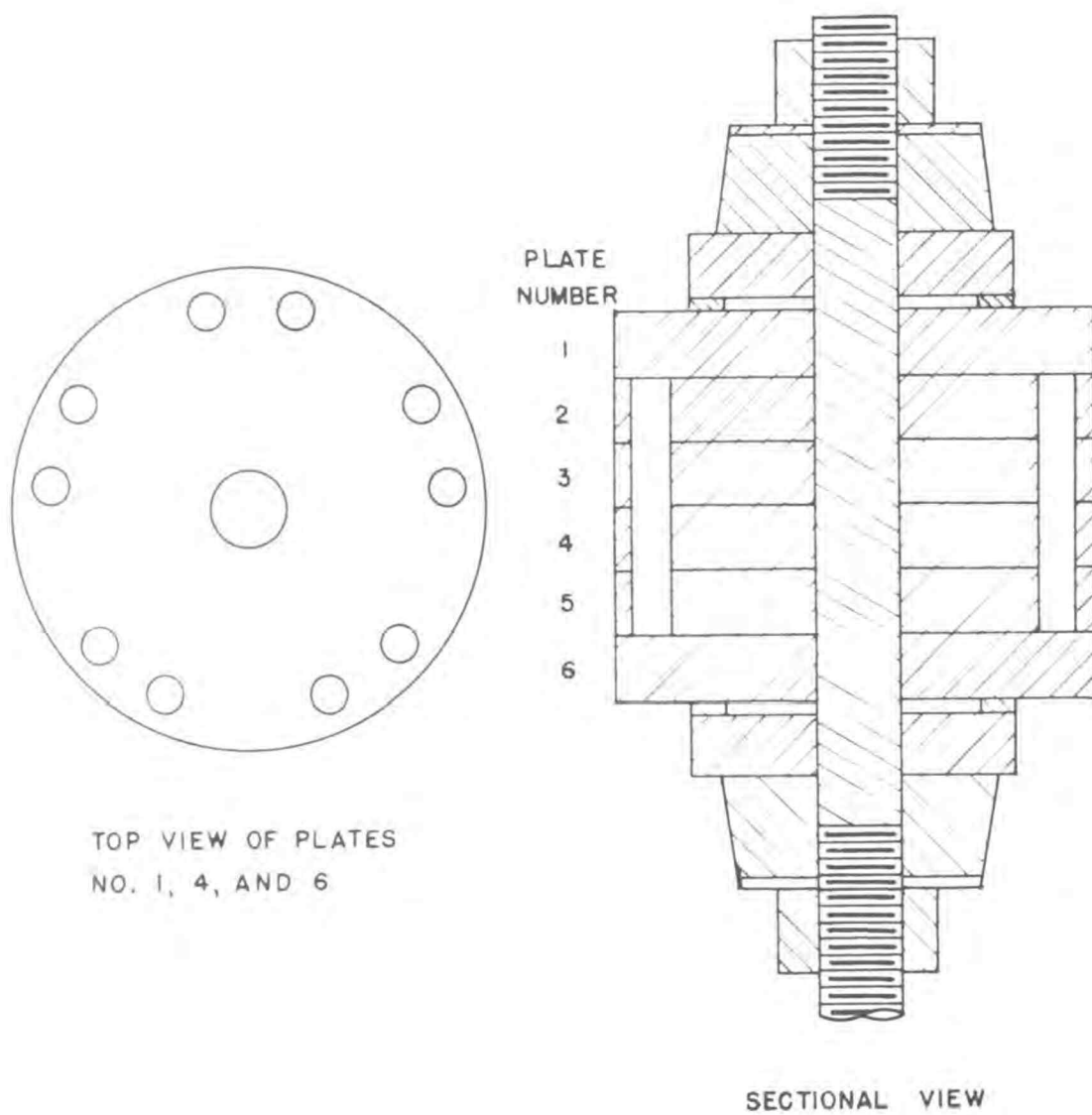


FIGURE 2. DIFFUSION APPARATUS

mounted and are held firmly together by two rubber stoppers compressed by tightening nuts on both ends of the axial rod. The holes that hold the clay pastes are 0.314 inch in diameter and were drilled vertically 3.2 inches from the disk centers and spaced about 24° apart, or, for the top, bottom and one of the middle disks, alternately 24° and 48° apart.

Procedure

After the clay pastes were adjusted to the proper concentrations they were placed in glass cylinders about one inch in diameter and about three inches long. Care was taken to remove air bubbles from the pastes and they were well mixed. One end of the cylinder was constricted so that it would fit just inside the holes of the diffusion apparatus. A plunger was used to push the clays into the apparatus. The apparatus was filled with one pair of clays at a time as in Figure 3A, and diffusion was started by lining up the holes as indicated in Figure 3B. All diffusion runs were made at $24 \pm 1^\circ\text{C}$.

There are a total of fifteen vertical holes in the apparatus and, as seen in Figure 2, diffusion took place in every third hole. However, iron rods were placed in one set of holes to line up the other holes during diffusion, and another set of holes was used

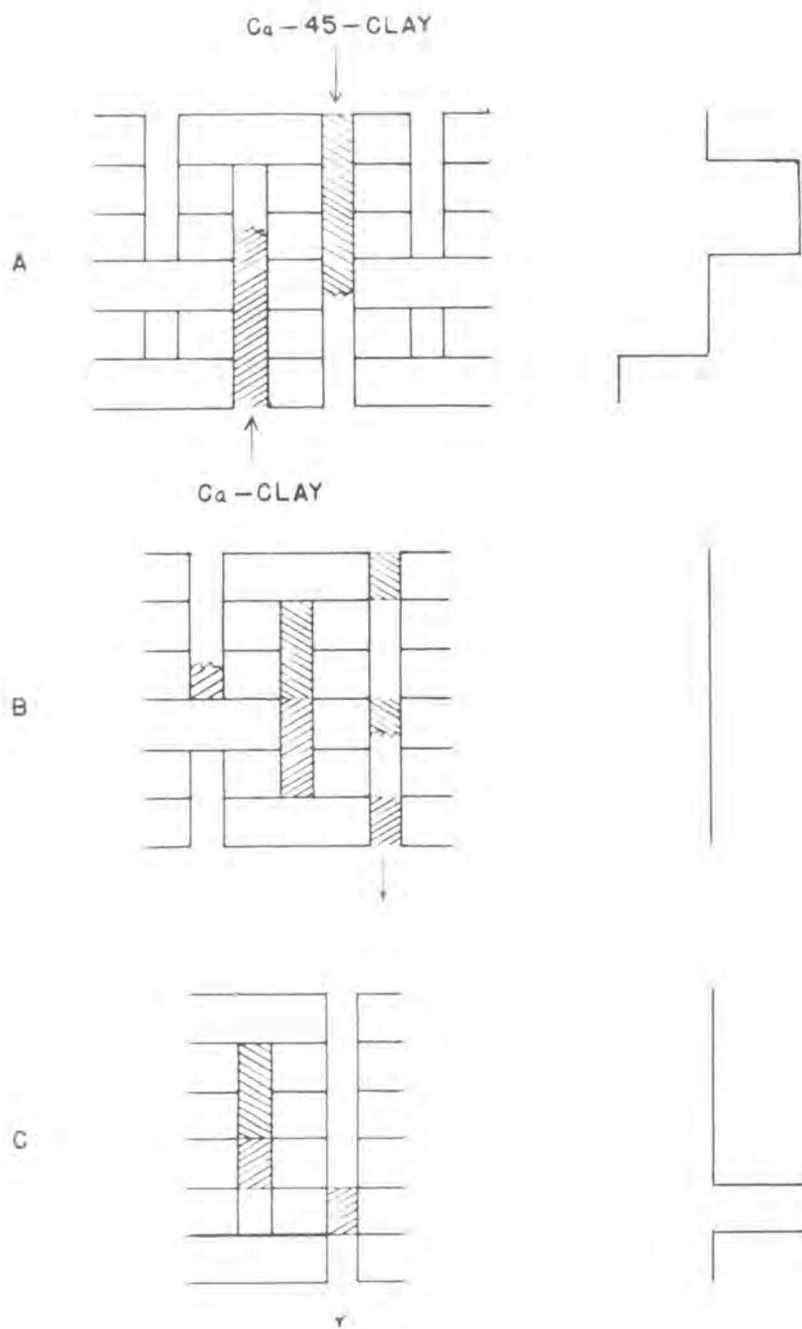


FIGURE 3.

SCHEMATIC SECTION OF THE DIFFUSION APPARATUS

THE LINES AT THE RIGHT REPRESENT A VERTICAL LINE
DRAWN ON THE CYLINDER SURFACE DURING STAGE B.

for Ca-45-clay only so that C_0 , the original concentration of Ca-45, could be determined. Since only the clay in compartments of plates number three and number four was pushed out and analyzed for Ca-45 after diffusion, six diffusion constants were calculated for each pair of clays for each run and four values of C_0 determined.

Another plunger was used to push the pastes from the apparatus after diffusion as in Figure 2C. The pastes from each compartment were shaken with 5 ml of 2M ammonium acetate to remove the calcium from the clay; the resulting suspension was centrifuged and the supernatant liquid containing the calcium was removed by decantation. Then 3 ml of 0.05M CaCl_2 was added to insure more complete precipitation of the Ca-45 when oxalic acid was added and to provide enough calcium oxalate for a uniform layer on the planchet. The solution was then acidified with HCl as indicated by methyl orange and placed in a hot water bath. Then 5 ml of 0.2N oxalic acid was added. The solution was digested for five minutes, cooled to room temperature, and made basic by adding 3N NH_3 dropwise. The precipitated calcium oxalate was then removed by centrifugation and shaken with a 70% ethanol in water solution. This suspension was centrifuged so that the calcium oxalate would plate

out evenly on a weighed planchet at the bottom of the centrifuge cup. The calcium oxalate was then dried on the planchet at 110°C and weighed as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

The samples were counted with a G-M thin mica window counter and a Tracerlab utility scaler. A sufficient number of counts were totalled to obtain a statistical standard deviation in the sample counting rate minus the background counting rate of one percent or less.

The counting rates of the samples were corrected for coincidence loss and for self absorption. The coincidence correction factor was taken from a slide-chart supplied by the Nuclear-Chicago Corporation using a dead time of 180 usec for the counting apparatus.

A self absorption curve for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was obtained as follows: different amounts of $\text{Ca-45-C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, all having the same actual specific activity, a_0 , were counted on planchets, and the measured specific activities, a , in cpm per mg, were calculated. The values of a were plotted on a log scale against the thickness of the $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in mg cm^{-2} , and the value of a_0 was determined by extrapolating to zero thickness. The self absorption curve in Figure 4 was obtained by plotting the total weight of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ on the planchet vs a/a_0 .

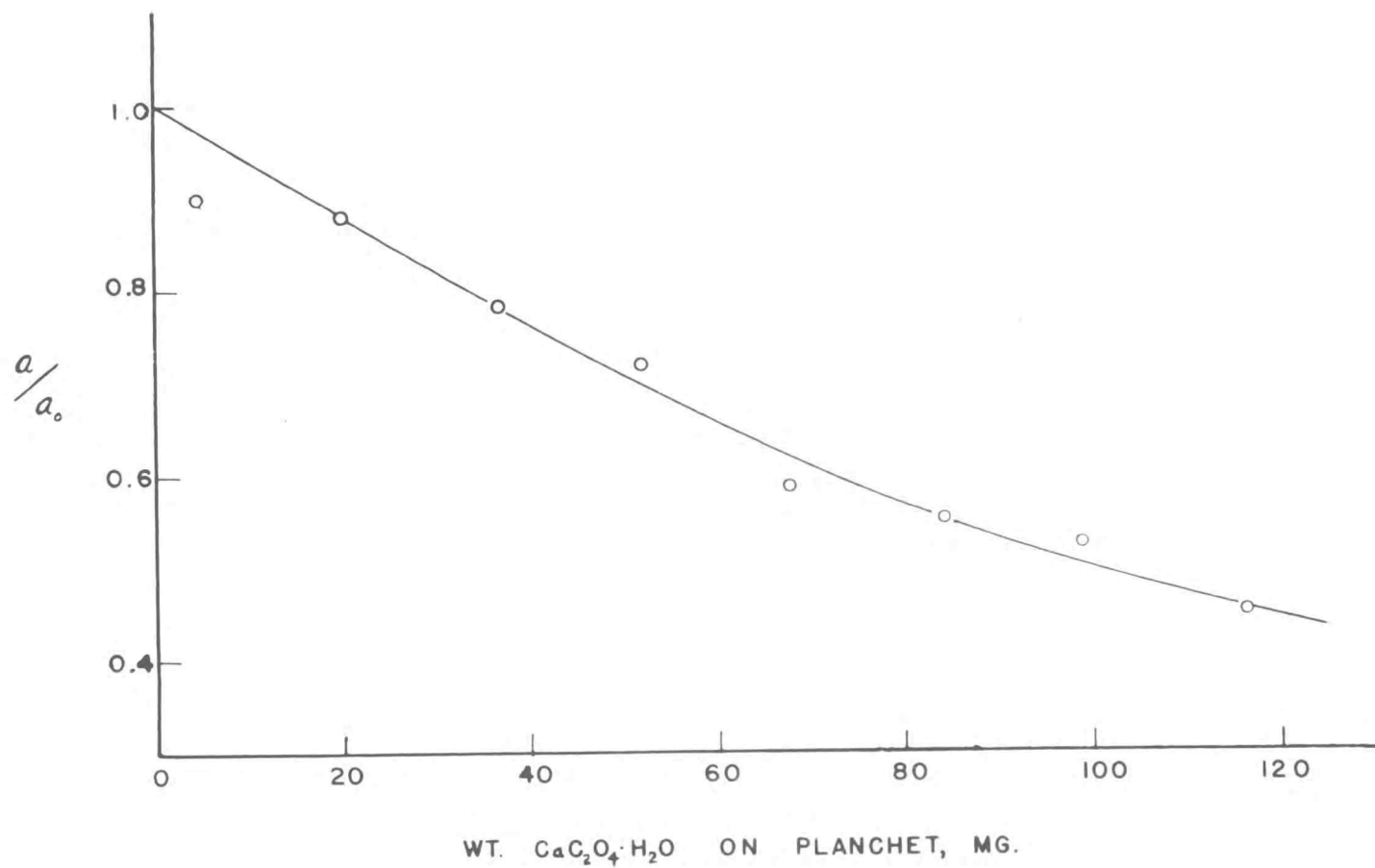


FIGURE 4. SELF ADSORPTION CURVE FOR CALCIUM OXALATE

The amount of ammonium acetate necessary to remove the calcium from the clay plugs was determined as follows: the diffusion apparatus was filled with a Ca-45-clay of known concentration, and plugs of the clay were pushed from the apparatus and shaken with different amounts of 0.2N ammonium acetate. The Ca-45 removed from the plugs was precipitated and counted as described above, and meq ammonium acetate/meq Ca on the clay was plotted against m , the corrected counting rate for the sample (Figure 5). The amount of calcium removed from the clay was proportional to m .

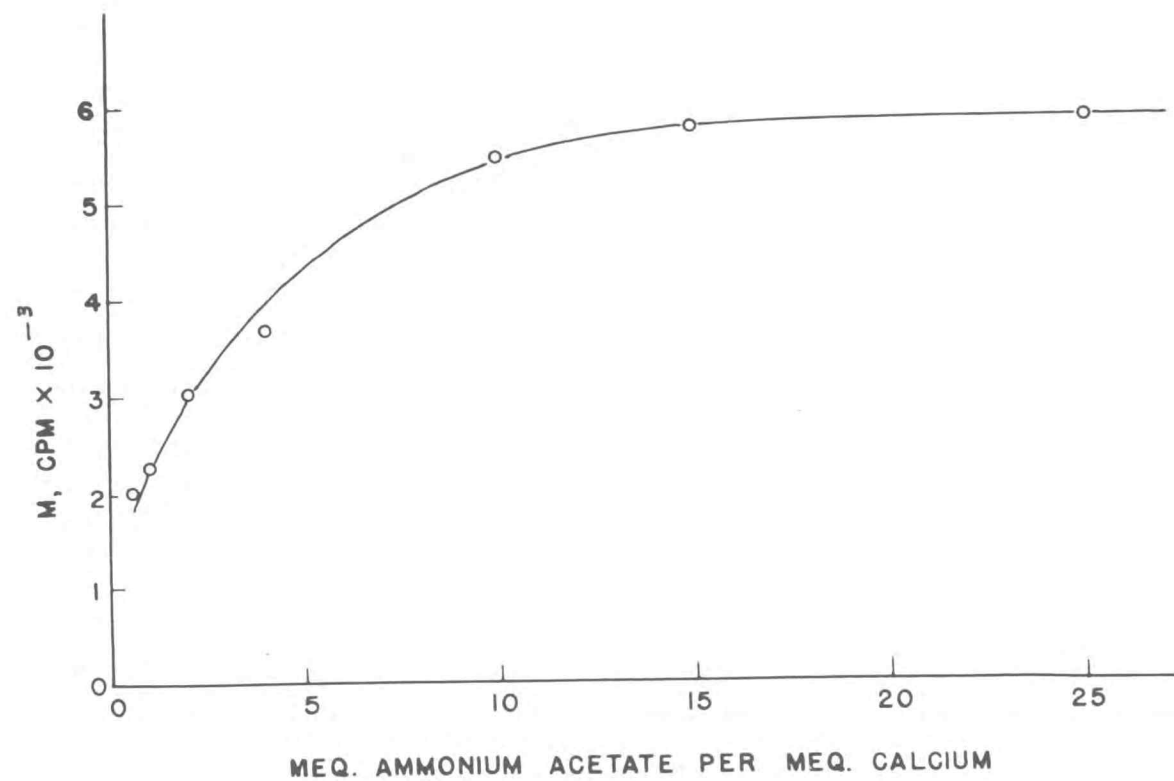


FIGURE 5. CURVE FOR THE REMOVAL OF Ca
FROM Ca -MONTMORILLONITE

RESULTS AND CONCLUSIONS

Method of Calculation

The expression $2A/C_0S$ from equation (4) may be more conveniently written as $2Cl/C_0$ where l is the length of the particular section of the cylinder that is analyzed; the limits of the integral side of equation (4) would then be from one end of l to the other. Values of l were obtained by measuring the thickness of the plates near the holes with a micrometer and were found to vary from 1.249 cm to 1.298 cm.

Since m is proportional to C if the lengths of the holes were all the same, $m/m_0 = C/C_0$ (m_0 here is the corrected measured activity for samples from which C_0 was to be determined). To correct for differences in l each experimentally determined value of m and m_0 was multiplied by a factor $1.27/l$. The average of the four values of m_0 was used for each run.

Using the error-function tables a series of curves for various values of Dt were plotted for $2C/C_0$ vs x using equation (3) as shown in Figure 6. Equation (4) was then integrated graphically by measuring the areas under these curves by using a compensating polar planimeter. Thus a series of values of $2Cl/C_0$ corresponding to different values of Dt were obtained and plotted as

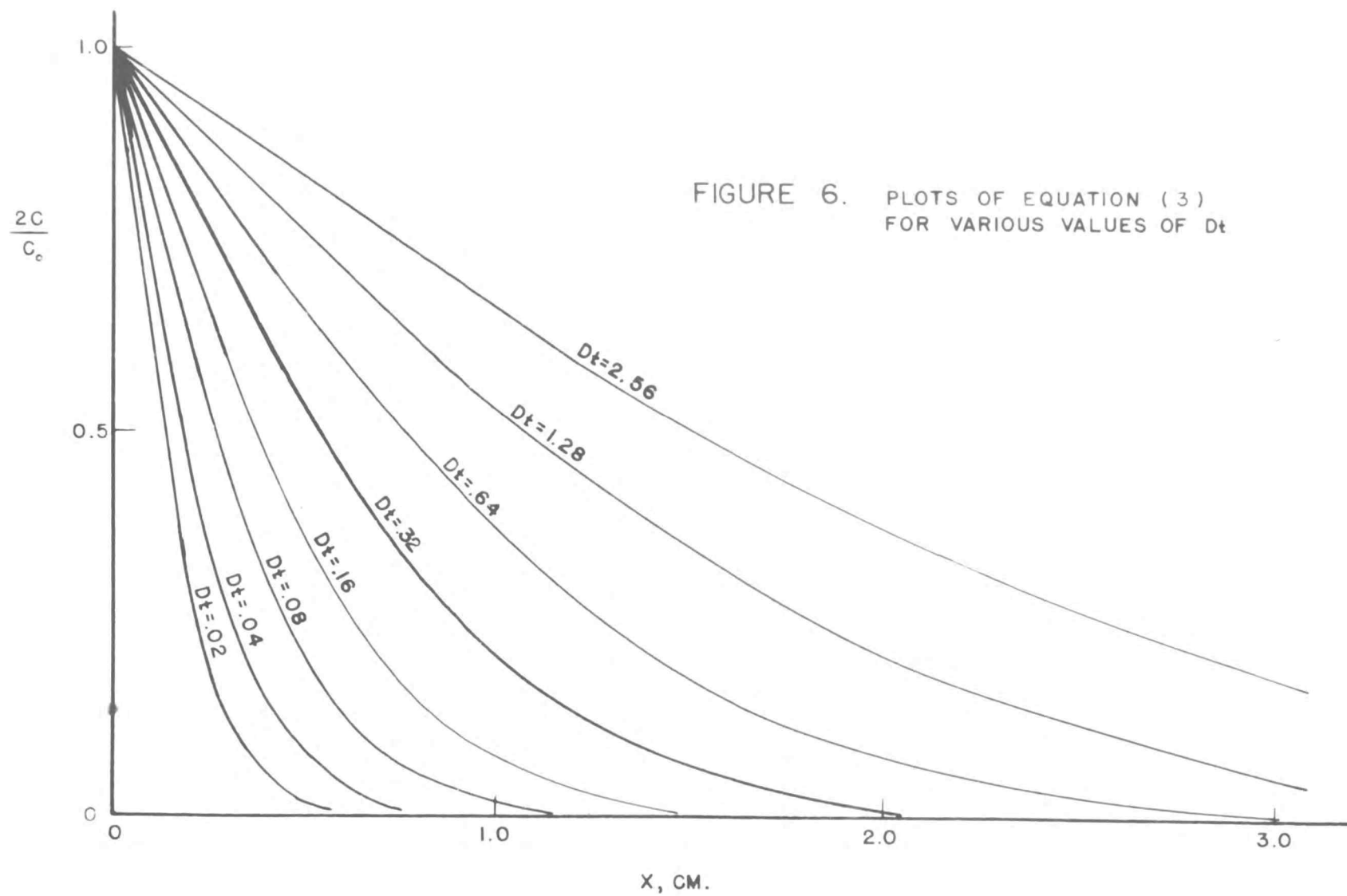


FIGURE 6. PLOTS OF EQUATION (3)
FOR VARIOUS VALUES OF Dt

in Figures 7 and 8. Several graphs such as these were plotted for different values of l , and the appropriate graph was used to calculate D when $2Cl/C_0$ and t were measured.

Values of D calculated in this way for six diffusion runs appear in Table II. The values of the concentrations are the averages of the concentrations of the two clays used in each case; the two values usually varied less than a few tenths of a percent from each other.

The labyrinth factor g was calculated using equation (9), $D = 0.0664 \times 10^{-5} \text{ cm sec}^{-1}$, $kT \omega_{Ca^{++}} = 0.7915 \times 10^{-5} \text{ cm sec}^{-1}$, and $n/s = 0$. The value of D was the average of the six values from runs number one and number two obtained using plate number four. The value of $kT \omega_{Ca^{++}}$ was calculated using equation (6) and $\lambda_{Ca^{++}}^0 = 59.50 \text{ mhos}$ (9, p. 231). The value of zero for n/s is not quite correct but the work of Marshall (14, p. 671-681) and of Chao (4, p. 47) on fractions active and ion ratios indicates that the amount of free calcium in solution is probably less than three percent of the total exchangeable calcium on the clay; this is within the experimental error here and is neglected.

The factor h was calculated twice: once using $n/s = 0.1$ and the average value of D from plate number

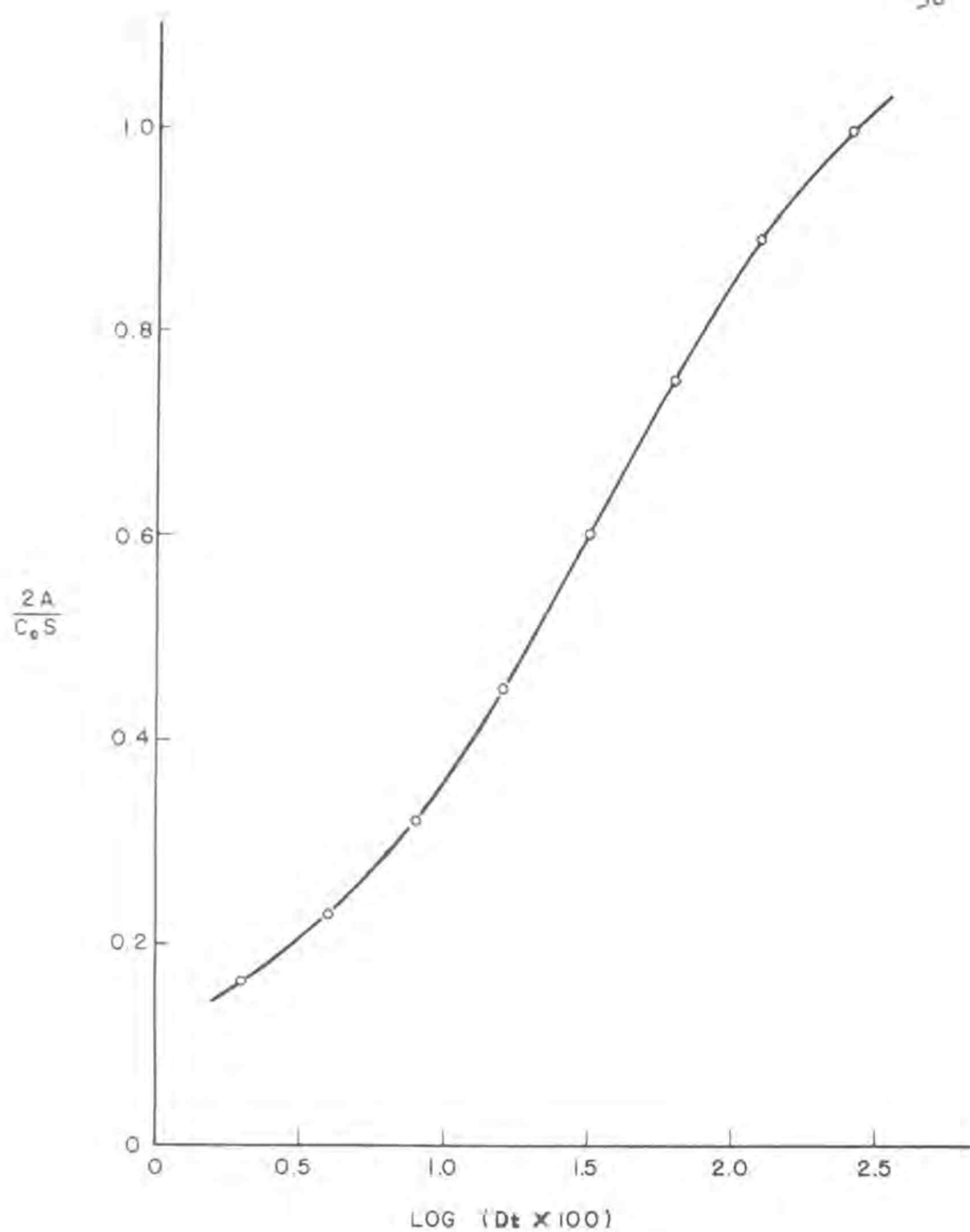


FIGURE 7.

$\text{LOG } (Dt \times 100)$ VS. $2A / C_e S$ FROM GRAPHICAL
INTEGRATION OF FIGURE 6 FROM $X=0$ TO $X=1.27$

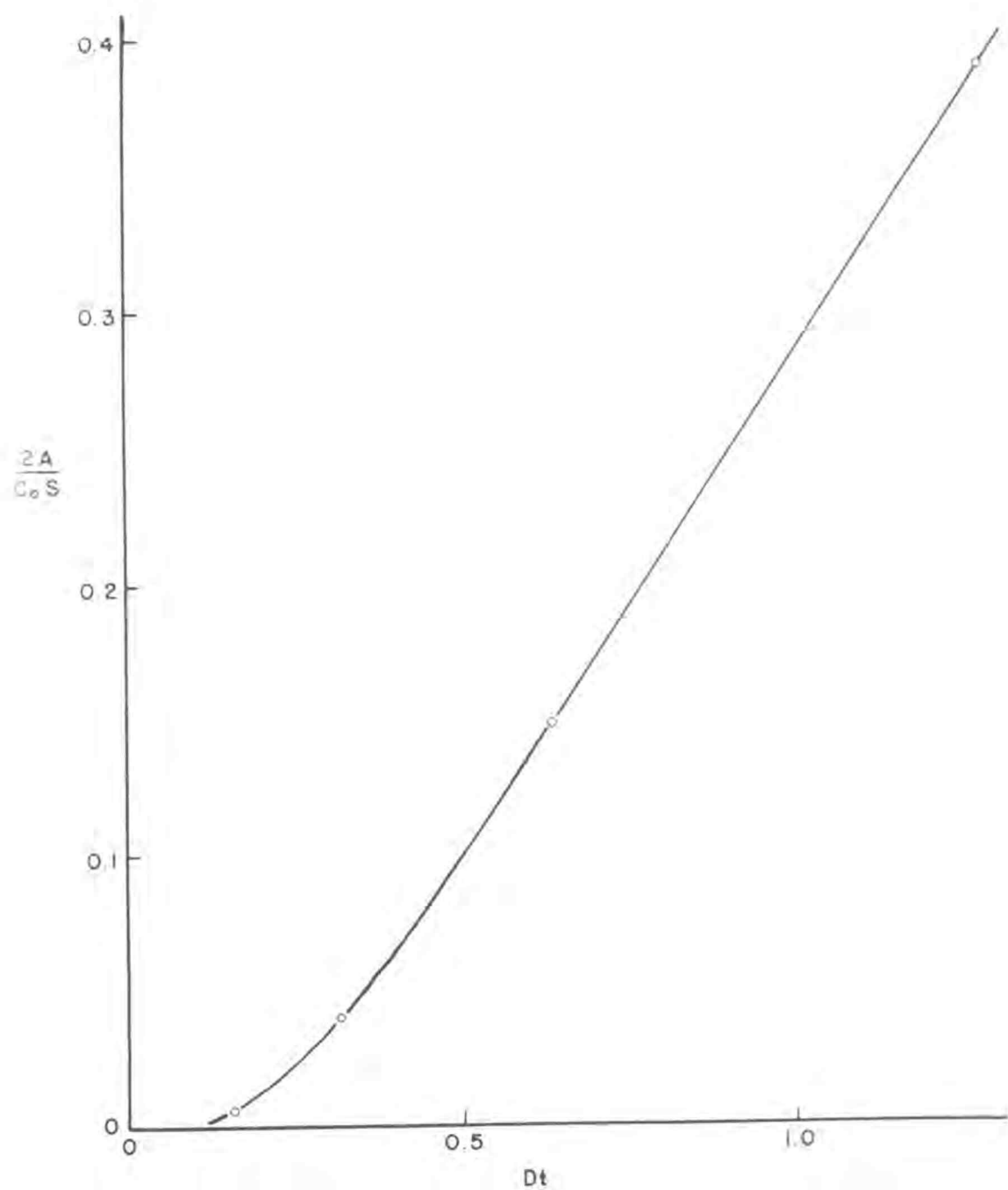


FIGURE 8.

Dt VS. $2A/C_0 S$ FROM GRAPHICAL INTEGRATION
OF FIGURE 6 FROM $X=1.27$ TO $X=\infty$

TABLE II. Experimental Results

Run No.	Plate No.	Number of Deter-minations	Clay Conc. wt. %	n/s	S	$t \times 10^{-5}$ sec.	$D \times 10^5$ cm ² sec ⁻¹	Error std. dev. %
1	3	3	4.91	0	.982	2.608	.0519	3.25
	4	3					.0706	0.58
2	3	3	7.90	0	.970	3.117	.0469	4.3
	4	3					.0622	5.0
3	3	3	10.6	0.1	.960	4.418	.0641	1.6
	4	3					.0880	5.1
4	3	3	9.02	0.1	.966	3.547	.0774	9.1
	4	3					.1234	8.9
5	3	3	5.72	1.0	.979	2.895	.171	21.7
	4	2					.243	0.62
6	3	3	8.20	1.0	.969	2.612	.283	17.7
	4	3					.264	0.53

four in runs number three and four, and once using $n/s = 1.0$ and the average value of D from plate number four in runs number five and six. Equation (9) and the calculated value of g were also used.

The eccentricity of the oblate spheroids, that may serve as a model for the particles in the paste, was obtained from a graph of DeVries (22, p. 42) by using the average of the two values calculated for h and an average value of the pore fraction, S , calculated using a density of 2.65 gm cm^{-3} (8, p. 313) for the clay. Values for these constants appear in Table III.

Discussion of Errors

The errors in Table II represent the standard deviation of the values of D calculated for each plate from the average value for that plate. The average of all of these deviations for plate number four is 3.5 percent and for plate number three is 9.6 percent. This error may be compared to an average error of about 8 percent for twenty runs obtained by Bloksma (1, p. 49) who measured D for K^+ diffusing into only one plate by a similar method.

For each run the four values of m_0 varied about 5 percent among themselves. An error of 5 percent in m_0 would lead to an error of about 16 percent in

TABLE III. Constants Calculated from Experimental Results

g	h	Eccentricity of Particles
0.084	0.630 ^a <u>0.557</u> ^b 0.590 (Av.)	~ 100 ^c

a from runs three and four

b from runs five and six

c from the average value of S for all clays

calculating the value of D using plate number three and an error of from 3 percent to 4 percent in D using plate four, the error in plate number four depending on the value of Dt. Therefore, the values of D calculated using plate number four are probably more reliable.

These errors may have arisen from undetected air bubbles in the clays, the clay pastes being inhomogeneous, uneven plating of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ on the planchet, and from other indeterminate errors in the technique.

Conclusions

By measuring the self-diffusion coefficients of calcium ions in calcium montmorillonite pastes, values for g and h have been calculated. The labyrinth factor, g, is much lower in a calcium system than in a sodium-clay system as evidenced by comparing the value obtained here ($g = 0.084$) to that reported by Bloksma (2, p. 47) where $g = 0.37$ for sodium-montmorillonite. This comparison is substantiated by Spiegler and Coryell (19, p. 687-690) and by Heymann and O'Donnell (10, p. 405-416) who studied the diffusion of various cations in cation-exchange membranes and resins.

According to Overbeek (15, p. 603), a knowledge of g for the exchangeable ion under consideration is required for the interpretation of the Donnan-emf in a suspension system; he states that the mobilities of all particles in the suspension system must be known. The mobilities of non-exchangeable ions in solutions can be calculated from conductance data and the mobilities of the colloidal particles determined by electrophoresis. Since the motion of the exchangeable ion in a colloidal electrolyte is probably restricted to the surface of the colloidal particle, the factor g offers a means of describing these ionic mobilities in such a system.

The labyrinth factor h , which is dependent on the geometry of the diffusion path for non-exchangeable ions, supplies a further quantitative description of the calcium-clay system. The value obtained in this study (0.59) is somewhat higher than that (0.49) given by Bloksma (2, p. 49) for self-diffusion of iodide ions in sodium-montmorillonite pastes. This difference may be attributed to the differences in structure among various clays and particularly to the different type of cation present on the clay.

The axial ratios obtained here of about 100 for the clay particles agree with similar results of

Bloksma (2, p. 49-50) and ratios of 10 to 100 obtained by electron micrographs with shadow casting (8, p. 116); these ratios confirm the platelike shape of the montmorillonite particles.

The knowledge of the diffusion of the calcium ion obtained here should also find applications with soil scientists in their studies of plant nutrition and root environment.

SUMMARY

The structures of clay have been determined only in the last few decades. A particle of the clay montmorillonite consists of a series of flat platelets stacked one upon the other. Each platelet is made up of three layers: two silica tetrahedral layers with an alumina octahedral layer between. Unsatisfied charges from cationic substitutions within the platelet and from broken bonds at the edges of the platelet give rise to a high base exchange capacity for montmorillonite.

The fairly recent use of radioisotopes has made possible the determination of self-diffusion coefficients. Self-diffusion has been described by one dimensional integrated forms of Fick's law. These equations express the concentration of the diffusing isotope in terms of the independent variables of time and of distance.

Homoionic calcium-montmorillonite pastes were prepared by passing dilute suspensions of bentonite through an exchange column containing the calcium form of a cation exchange resin, and then concentrating in an oven at 80°C. Three pairs of pastes were prepared and different amounts of calcium chloride added to each. The two pastes of each pair were similar except one

contained some Ca-45.

The diffusion apparatus consisted of a pile of six horizontal circular Plexiglass discs free to rotate individually around a central vertical axis. A series of vertical holes was drilled near the edges of the discs.

To start diffusion one half of each hole was filled with Ca-45-paste and the other half with ordinary Ca-paste. At the end of the diffusion run the paste was removed in sections from each hole, and the amount of radio-calcium in each section was measured with a G-M counter.

The self-diffusion coefficient for Ca^{++} ions was calculated for each of the three clay pastes by solving the appropriate diffusion equation. Using these three values of the self-diffusion coefficient two labyrinth factors h and g were calculated; the mobility of non-exchangeable ions or molecules in the pastes is a fraction ($h = 0.59$) of the mobility in aqueous solutions, and the mobility of ions in the exchange position is a fraction ($g = 0.084$) of the mobility in aqueous solutions.

The eccentricity of the clay particles was estimated from h and the pore fraction S .

The experimental error for the self-diffusion coefficients was about 4 percent and the values obtained

were of the expected magnitude.

The value of g should find use in the study of the Donnan-emf since it describes the mobility of Ca^{++} adsorbed on montmorillonite particles even in dilute suspensions.

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