ACTIVITY MEASUREMENTS IN WATER AND CLAY-WATER SYSTEMS

By

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AN ABSTRACT

Submitted to the School of Graduate Studies of
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ABSTRACT

Electrometric methods were utilized to measure plant nutrient activities in water and clay-water systems on the premise that activity is better than concentration as a measure of nutrient availability. A tertiary amalgam electrode, silver-silver chloride electrode and a glass electrode were used with each other or in conjunction with a reference calomel electrode to measure ion and ion pair activities.

The relationship between the activity and the chemical potential, as well as the significance of the electrochemical potential and the total activity in heterogeneous systems, were discussed.

An experiment was devised to measure the relative replacing power of several alkali and alkaline earth metals for calcium in calcium saturated clay suspensions. The order of replacing power was found to be $Rb > Mg > K > Na > Li$.

Measurements of calcium ion, hydrogen ion, calcium chloride and hydrochloric acid activities were carried out in clay suspensions containing various ratios of bentonite and kaolinite. Similar measurements were made in suspensions containing bentonite-vermiculite mixtures. The data showed that: (1) bentonite formed a stronger acid than kaolinite, (2) calcium and calcium chloride activities were higher in kaolinite and vermiculite suspensions than

in the corresponding bentonite suspensions, (3) when bentonite was mixed with kaolinite or vermiculite the ion activity values were not a purely additive function of the two clays, but were greater than the sum of the activities of the individual clays. Interaction between exchange sites of the different clays was cited as the cause for the last observation.

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CHAPTER I

INTRODUCTION

Generalizations Pertaining to Nutrient Uptake

The agronomist is constantly faced with two fundamental problems: (a) increasing crop yields per unit area of cultivated land and (b) predicting magnitudes of yields for a given set of field conditions. Before he can begin to solve these problems he must understand the variables which control crop yield. First of all the agronomist must consider all the factors that affect yield; he can do this symbolically as a functional relationship thus:

$$y = f(a, b, c, \ldots, a', b', c', \ldots)(a'', b'', c'', \ldots) \quad (1)$$

where y represents yield; a, b, c, . . . are such nutrients as nitrogen, phosphorous, potassium, etc.; a', b', c', . . . the soil physical factors such as temperature, moisture, soil structure, etc.,; and a'', b'', c'', . . . represent such factors as the genetic make-up of the plant, plant population, method of cultivation and planting, etc.

Having listed the factors which control yield, the agronomist then attempts to show the exact functional relationship between yield and a given variable. Any change in yield as a result of a change in this variable is expressed as:

$$dy = (dy/da)da_{b,c\ldots,a',b',c'\ldots,a'',b'',c''\ldots} \qquad (2)$$

where a is the variable under investigation. The evaluation of similar equations is in fact the whole essence of agronomic science. There is, however, one very important difference in the above equation as compared to other expressions of this type. It is not enough in equation 2 to maintain constancy of the other variables; it is equally important that these variables be kept at an optimum level. This point cannot be overemphasized in agronomic work.

Let us take a case in point to clarify this statement. Consider the case of an agronomist trying to show the essentiality of a minor element. He takes great pains to keep all other yield factors constant and demonstrates to his satisfaction that application of increasing increments of the element in question has no effect on yield. Evaluation of this kind of data might lead one to believe that the element was not essential for plant growth, or was at least present in sufficient concentration in the growing medium. The conclusions drawn from this seemingly simple experiment may prove to be wrong.

Liebig, long ago realized that crop yields were controlled by the nutrient that was most deficient. He believed that increasing application of one nutrient could not increase yield if another essential element was deficient to a greater degree. More recently Baule (31) and Bray (6) have made modifications to Liebig's concept, but the fundamental generalization proposed by Liebig is essentially correct. The importance of maintaining the constant variables at an optimum level now becomes apparent.

If the function $y = f(a)$ is to attain a maximum, none of the constant variables should be deficient, and finally, the true functional relationship between 'y' and 'a' can be obtained only when this condition is maintained. We can further extend Liebig's argument to include physical properties of the growing medium as well.

In brief, we should not be expected to demonstrate true functional relationships between yield and the independent variables if a single nutrient or physical growth factor deviates even slightly from their optimum levels. As far as the plant is concerned, the expression $(dy/da) = 0$, for all values of 'a', has no significance unless 'a' is the only limiting growth factor.

Having at last established the functional relationship between yield and growth factors, the agronomist is now in a position to predict crop yields - if he can quantitatively measure the magnitudes of the growth factors; this is a difficult task indeed. The degree with which he measures and controls these growth factors represents in part his success as an agronomist.

A soil physicist may spend a life time developing methods for measuring the moisture content in the soil.

He learns early in his training that the total moisture content is not a very useful measurement. He turns his attention to measuring the "available" water in the soil. Similarly, the soil chemist attempts to measure the nutrient content in the soil; he too learns that total elemental analysis is not the best measure of nutrient availability.

The agronomist who spends his time correlating yield data to soil chemical tests often finds his results disheartening. Examination of equation 2 reveals, in part, reasons for this kind of results. Too many variables must be kept under rigid control. Costly green houses and complex experimental field designs can be used to overcome some of these difficulties. Another source of error in the data is inherent in chemical tests themselves. A chemical test showing acceptable correlation for a given nutrient, a particular soil and requiring edisonian trial and error method for its development may ultimately fail when applied to another soil. The weakness of soil tests may lie in their use of concentration as a measure of nutrient availability.

If we consider the plant root and the mechanism of nutrient uptake, we might obtain an insight to why use of concentration might fail as a measure of nutrient availability. Take for example a plant root penetrating the soil medium; each root has many microscopic root hairs which actively absorb plant nutrients from the soil solution. There is reason to believe that nutrient uptake involves two steps, first a reversible, physical movement of nutrient from the soil solution into the "apparent free space" (18) located somewhere in the plant body, and second, an active irreversible absorption, involving biological carriers (7) from the "free space" into the plant tissue.

We might look upon the surface of the root hair as a membrane separating the soil solution from the "free space". If we assume the movement of nutrients across the membrane to be a purely physical process, then when the system is in equilibrium, i.e. when the phases on either side of the membrane are in equilibrium with each other, the chemical potential u, for a particular nutrient must be the same on both sides of the membrane. Symbolically this same idea can be expressed as

$$u_o = u_1$$

where the subscripts o and i represent the soil solution and the "free space" respectively.

Of course this system never attains equilibrium; the plant continuously depletes the solution in the "free space" of its nutrients and the chemical potentials of the components will be higher in the soil solution than in the "free space". There will then be a tendency for the nutrients to pass spontaneously from the soil solution into the "free space".

The chemical potential is related to the activity a, of the nutrient by the expression

$$u = u^o + RT\ln(a)$$

where the constant u^o is a function of the temperature T alone and is the chemical potential of the nutrient in its standard state of unit activity. R is the universal gas constant. If we look upon the chemical potential, defined in terms of activities as a tendency of the nutrients to pass into the plant, then activities should be a somewhat better measure of nutrient availability than concentration.

Up to this point nothing has been said about the nature of the plant nutrient. Most plant nutrients are absorbed into the plant tissue as ions so that the significance of the chemical potential as described earlier is true only if the electrical potential ψ is the same in both the soil solution and the plant tissue. Since the inequality of the electrical potential between these phases is probably the rule rather than the exception, a special chapter has been devoted to this subject.

Purpose of Study

It is not the purpose of this work to correlate nutrient uptake with nutrient activity in soil systems. Soil systems are too complex and interpretation of activity data would be at best difficult. Instead activity measurements were conducted in systems of known composition in the hopes that generalizations from such measurements could be extended to more complex soil systems.

Activity measurements were made electrometrically, utilizing reversible electrodes. Measurement of approximate single ion activities was also attempted.

CHAPTER II

THE ACTIVITY CONCEPT

In measuring the colligative property of an ionic solution it is evident that the measured property, for example the depression of freezing point, does not increase linearly with the number of dissolved particles contained in the system. According to early proponents of the classical theory, this behavior was considered to be associated with the degree of dissociation of the solute.

It is well accepted today that partial dissociation of strong electrolytes is not the cause for this anomalous behavior of electrolytic solutions. If we apply the laws of chemical equilibrium to the dissociation of a uni-univalent salt MA, which ionized into a cation M^+, and an anion A^-, it necessarily follows that the quantity

$$\frac{(M^+)\ (A^-)}{(MA)}$$

calculated by means of the Arrhenius theory, must be a constant. We know, as a matter of fact, that when concentration is used in equilibrium studies the quantity is found to vary markedly with concentration.

X-ray diffraction studies on the crystal structure of salts indicate that many salts exist in the ionized form even in the solid state. Consequently, when such a salt is dissolved in water, the particles going into solution do so as ions and not as molecules. With this newer concept in mind the physical chemist was forced to look for a new approach to the problem of accounting for the departure of electrolytic solutions from ideal behavior.

The early workers logically assumed that if electrolytes in solutions existed as charged ions then at least part of the anomalous behavior could be attributed to interionic attraction and repulsion between charged particles. This idea has helped to clarify many of the inconsistencies observed in experimental work resulting from the use of the Arrhenius theory. Although the newer concept has wider theoretical significance and predicts various properties of electrolytic solutions, it has by no means solved all problems pertaining to solutions and particularly to heterogeneous colloidal systems.

In the following paragraphs the theoretical aspects of the interionic attraction theory will be discussed. The material covered in this section are for the most part summarized from several textbooks of physical chemistry (8), (12), (21), (29). The activity concept is described here in the hopes that it will aid in the understanding of this study.

The basis for the theory of interionic attraction depends on the assumption that strong electrolytes are completely ionized, and that the anomalous effects observed are due to the unequal distribution of ions resulting from interionic attraction. Consider the case of a strong uni-univalent electrolyte in solution. There will be electrostatic forces of repulsion and of attraction between ions of opposite charge. We can therefore expect the probability of locating ions of opposite charge around a central ion to decrease as the distance from the central ion is increased. Pictorially we might think of an ion swarm around a central ion of opposite charge. If we can measure or assume some functional relation describing the distribution of the ions with respect to one another and similarly, assume a relationship of the forces acting on the ions due to the ions themselves in the absence of external forces, we have a starting point for the development of this theory.

Debye and Huckel who popularized this concept selected the Piosson equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi\rho}{D} \qquad (3)$$

to describe the electrostatic potential ψ, due to an ion and its atmosphere, where ρ is the net charge per cm^3 at any point (x,y,z) and D is the dielectric constant of the solvent. In the absence of external fields the ionic swarm or atmosphere is radially symmetrical with respect to the central ion. Equation 3 expressed in polar coordinate is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi\rho}{D} \qquad (4)$$

where r is the radial distance from the central ion.

The second fundamental assumption considered in the development of this concept is the selection of some distribution furmula which will describe the average charge density ρ at the point where the potential is ψ. Assuming the Boltzmann distribution formula which states that if n_i is the average number of i-ions in the differential volume dV, the number of n_i' whose potential energy is $z_i e \psi_j$ above the average is

$$n_i' = n_i e^{-\frac{z_i e \psi_j}{kT}} \tag{5}$$

where $z_i e$ and kT are the charge and kinetic energy of the i-ion and ψ is the potential ~~energy~~ of the i-ion in the vicinity of the central j-ion. The charge density ρ in this volume is then the sum of the product $n' z_i e$ and may be expressed as

$$\rho = \sum_{i=1}^{n} n_i' z_i e = \sum_{i=1}^{n} n_i z_i e \, e^{-\frac{z_i e \psi_j}{kT}} \tag{6}$$

The exponential $e^{-\frac{z_i e \psi_j}{kT}}$ converges rapidly when expanded for values of $\frac{z_i e \psi_j}{kT}$ much less than one. This condition is true for very dilute solutions where the interionic potential energy is much less than the kinetic energy. For dilute solutions then

$$e^{-\frac{z_i e \psi_j}{kT}} = 1 - \frac{z_i e \psi_j}{kT} \tag{7}$$

for a good approximation and

$$\rho = \sum_{i=1}^{n} n_i z_i e - \frac{\psi_j}{kT} \sum_{i=1}^{n} n_i z_i^2 e^2 \tag{8}$$

Electrical neutrality for the system as a whole requires that

$$\sum_{i=1}^{n} n_i z_i e = 0 \qquad (9)$$

so that equation (8) reduces to

$$\rho = - \sum_{i=1}^{n} \frac{n_i z_i^2 e^2 \psi_j}{kT} \qquad (10)$$

Combining equations (4) and (10) we finally arrive at

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi_j}{dr}\right) = \frac{4\pi}{DkT}\sum_{i=1}^{n} n_i z_i^2 e^2 \psi_j = K^2 \psi_j \qquad (11)$$

where for convenience we define K as

$$K^2 \equiv \frac{4\pi}{DkT}\sum_{i=1}^{n} n_i z_i^2 e^2 \qquad (12)$$

The quantity K called the Debye has the dimensions of reciprocal length and varies with the number of ions, ionic charge, temperature and dielectric constant of the solvent. It can be shown that the general solution of equation (11) is

$$\psi_j = \frac{A}{r} e^{-Kr} + \frac{B}{r} e^{Kr} \qquad (13)$$

From this equation it is obvious that ψ_j becomes very large as r approaches infinity; this difficulty is solved by setting B=0 and the solution reduces to

$$\psi_j = \frac{A}{r} e^{-Kr}$$

or

$$= \frac{A}{r}(1 - Kr) \qquad (14)$$

for small values of kr.

If we make the assumption that ions can be treated as point charges, the constant can be determined by choosing an infinity dilute solution so that K approaches zero and ψ_j simply becomes A/r. On the other hand if we consider a point charge z_1e in a medium of dielectric constant D, the potential ψ at a distance r due to this charge alone is z_1e/Dr. Since in the limit as K becomes zero

$$\psi_j = \frac{A}{r} = \frac{z_i e}{D r} \tag{15}$$

we arrive at a point where A is evaluated to be

$$A = \frac{z_i e}{D} \tag{16}$$

and equation (14) becomes

$$\psi_j = - \frac{z_i e K}{D} + \frac{z_i e}{D r} \tag{17}$$

Equation (14) informs us that the potential ψ_j is the algebraic sum of two potentials, the last term on the right being the potential of the central ion in the absence of an ionic atmosphere. The first term must then be the potential due to the ionic atmosphere; it is this part that is of interest in this discussion and shall be denoted by the expersion

$$\varphi_j = - \frac{z_i e K}{D} \tag{18}$$

However, it is not quite correct to treat ions as point charges. If we consider Gauss' theorem of electrostatics we can write

$$\int_a^\infty 4\pi r^2 \rho \, dr = - z_j e \tag{19}$$

where the lower limit a, represents the effective diameter of the central j-ion. The theorem in words is that the total electric flux over any closed surface equals 4 pi times the total charge inside the surface. The integral can be evaluated if ρ is expressed as some function of r. The charge density ρ was shown to be

$$\rho = -\sum_{i=1}^{n} \frac{n_i z_i^2 e^2 \psi_j}{kT} \tag{20}$$

and ψ_j to be

$$\psi_j = \frac{A}{r} e^{-Kr} \tag{21}$$

Combining (20) and (21) we have

$$\rho = -\frac{A}{r} e^{-Kr} \sum_{i=1}^{n} \frac{n_i z_i^2 e^2}{kT} = -\frac{AK^2 D}{4\pi r} e^{-Kr} \tag{22}$$

where K has the same meaning as before. Substituting this expression for ρ in equation (19) we have

$$AK^2 D \int_a^{\infty} r e^{-Kr} dr = z_j e \tag{23}$$

which when integrated between the expressed limits becomes

$$\frac{AD(1+Ka)}{e^{Ka}} = + z_j e \tag{24}$$

If equation (24) is solved for A and this value substituted in equation (21) we have an expression for ψ_j.

$$\psi_j = + \frac{z_i e}{D} \frac{e^{Ka}}{(1+Ka)} \frac{e^{-Ka}}{r} \tag{25}$$

which does not make the assumption of treating ions as point charges. This potential ψ_j however, includes the potential that is due to the charge on the central ion along with that part due to the ionic atmosphere. If we subtract that part due to the central ion, namely z_1e/Dr from equation (25) we have

$$\varphi_j = -\frac{z_i e K}{D(1+Ka)} \qquad (26)$$

which is again that part of the potential of the ion of charge z_1e which is due to the surrounding ions. For a single ion the extra free energy F_{el} , is equal to the work that must be expended to charge the ion reversibly to the required potential ψ which is $-z_1eK/D(1+Ka)$.

$$\Delta F_{el} = \int_0^{\psi} z_i e \, d\psi = \int_0^{\psi} \frac{D(1+Ka)}{K} \psi \, d\psi$$
$$= -\frac{z_i^2 e^2 K}{2D(1+Ka)} \qquad (27)$$

If the supposition is made that the deviation of ionic solution from ideal behavior is entirely due to the existence of electric charges on the solute particles, it follows that the expression for the total free energy of this system will differ from that of an ideal one by an additional term due to the electrical energy of the solution. Thus the free energy F of an ionic solution may be expressed by the equation

$$F = F_{id} + F_{el} \qquad (28)$$

where F_{id} and F_{el} are the free energies due to the ideal solution and electrical energy respectively. Furthermore, for an ideal solution of concentration c, the chemical potential u_{id} per molecule is defined as

$$u_{id} = \text{constant} + kT\ln C \qquad (29)$$

If the solution is not ideal the chemical potential u per molecule is

$$\begin{aligned} u &= \text{constant} + kT\ln a_i \\ &= \text{constant} + kT\ln C_i + kT\ln f_i \\ &= u_{id} + kT\ln f_i \qquad (30) \end{aligned}$$

where a_i is the activity and f_i the activity coefficient of the solute Equation 30 expresses the actual chemical potential u, in terms of the ideal chemical potential u_{id} and the activity coefficient f_i. The importance of this expression is that $kT\ln f_i$ is the extra electric free energy per ion and is equal to the work expended to charge the ion reversibly to the potential ψ which is $-z_i e\, K/D(1 + Ka)$ so that

$$kT\ln f_i = -\frac{z_i^2 e^2 K}{2D(Ka+1)} \qquad (31)$$

It follows from the above expression that the activity coefficient of the ion of valence z_i is given by the equation

$$-\ln f_i = \frac{z_i^2 e^2 K}{2DkT(1+Ka)} \qquad (32)$$

It is frequently convenient to speak of the mean activity coefficient of the electrolyte because the individual ion activity coefficient is experimentally not measurable. The mean activity coefficient $f_\pm$ of the electrolyte is defined by the equation

$$\nu \ln f_\pm = \nu_+ \ln f_+ + \nu_- \ln f_- \qquad (33a)$$

$$f_\pm = \left(f_+^{\nu_+} f_-^{\nu_-}\right)^{\frac{1}{\nu}} \qquad (33b)$$

for an electrolyte molecule which ionizes in solution to yield v number of ions of which v+ are positive and v- are negative. The individual ionic activity coefficients are represented by f+ and f- for the positive and negative ions respectively.

Before equation 32 is substituted into equation 33a to obtain an expression which is experimentally measurable, it is convenient to introduce practical units such as concentration C_i

$$C_i = \frac{n_i}{N} 1000 \qquad (34)$$

and the ionic strength I

$$I = \frac{1}{2} \sum_{i=1}^{n} C_i z_i^2 \qquad (35)$$

as well as to combine constants such as

$$A = \frac{e^3}{2.303(DkT)^{3/2}} \left(\frac{2\pi N}{1000}\right)^{1/2}$$

$$B = \left(\frac{8\pi N e^2}{1000\, DkT}\right)^{\frac{1}{2}}$$

so that equation 32 becomes

$$-\log_{10} f_i = \frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}}$$

Finally substituting the expression for the activity coefficient of the positive and negative ions into equation 33a we have

$$-\log_{10} f_\pm = \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\right) \frac{A\sqrt{I}}{1 + B a_i \sqrt{I}} \qquad (36)$$

for the mean activity coefficient. Since $\nu_+ z_+ = \nu_- z_-$ the quantity

$$\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} = z_+ z_-$$

and equation 36 reduces to

$$-\log_{10} f_{\pm} = \frac{A z_+ z_- \sqrt{I}}{1 + B a_i \sqrt{I}} \qquad (37)$$

which is the expression for the mean activity coefficient of strong electrolytes as developed by Debye and Huckel. The constants A and B vary with the temperature and the dielectric constant of the solvent so that for a given solvent and temperature the mean activity coefficient depends upon the ionic strength I of the solution and the average effective ionic diameter a_i. The mean activity $a_{\pm}$ of an electrolyte is related to the mean molarity $C_{\pm}$ and the mean activity coefficient $f_{\pm}$ by the identity

$$a_{\pm} = f_{\pm} C_{\pm}$$

The mean ionic quantities are in turn related to the individual ionic quantities, indicated by the subscripts plus and minus, in the following manner.

$$a_{\pm} = (a_+^{\nu_+} a_-^{\nu_-})^{\frac{1}{\nu}}$$

$$C_{\pm} = (C_+^{\nu_+} C_-^{\nu_-})^{\frac{1}{\nu}}$$

$$f_{\pm} = (f_+^{\nu_+} f_-^{\nu_-})^{\frac{1}{\nu}}$$

Equation 37 fails for concentrated solutions because in the expansion of the exponential in the Boltzmann equation only the first two terms were considered. Other factors such as the effect of the solute on the solvent molecules were not considered. Extension of the Debye-Huckel theory to more concentrated solutions can be found in advanced textbooks of physical chemistry and will not be discussed here.

CHAPTER III

THE ACTIVITY AND THE ELECTROMOTIVE FORCE OF CELLS

The emf of a cell depends upon the activities of the constituents of the solution. For any reaction such as

$$\alpha A + \beta B + \cdots = \gamma C + \delta D + \tag{38}$$

if the activities of A and B at the start are a_A and a_B, while the activities of C and D at the end of the reaction are a_C and a_D respectively, then the free energies of each of these substances per mole at a temperature T are given by the expressions

$$F_A = F_A^{\circ} + RT \ln a_A \tag{39a}$$

$$F_B = F_B^{\circ} + RT \ln a_B \tag{39b}$$

$$F_C = F_C^{\circ} + RT \ln a_C \tag{39c}$$

$$F_D = F_D^{\circ} + RT \ln a_D \tag{39d}$$

where the F°'s represent the free energies at unit activity of the respective species and R is the universal gas constant. By definition the free energy change of the reaction is

$$\Delta F = (\gamma F_C + \delta F_D) - (\alpha F_A - \beta F_B) \tag{40}$$

Substituting equation 39a, 39b, 39c and 39d into equation 40 we have

$$\Delta F = \left[(\gamma F_C^\circ + \delta F_D^\circ) - (\alpha F_A^\circ + \beta F_B^\circ) \right] + RT \ln \frac{a_C^\gamma a_D^\delta \cdots}{a_A^\alpha a_B^\beta \cdots} \quad (41)$$

where $\left[(\gamma F_C^\circ + \delta F_D^\circ) - (\alpha F_A^\circ + \beta F_B^\circ) \right]$ represents the free energy change of the reaction in the standard state. This expression is usually written as ΔF°, and equation 41 becomes

$$\Delta F = \Delta F^\circ + RT \ln \frac{a_C^\gamma a_D^\delta \cdots}{a_A^\alpha a_B^\beta \cdots} \quad (42)$$

Any work performed by a cell can be accomplished only at the expense of a decrease in free energy taking place in the cell. When the cell operates reversibly, the electrical work is a maximum and the decrease in free energy must equal the electrical work done. The above statement describes the fundamental relation between emf and ΔF which is

$$\Delta F = - z \mathcal{F} E \quad (43)$$

where z represents the number of electrons involved, $\mathcal{F}$ the faraday unit and E the emf of the cell.

Dividing equation 42 by $-z\mathcal{F}$ we have

$$E = -\frac{\Delta F^\circ}{z\mathcal{F}} - \frac{RT}{z\mathcal{F}} \ln \frac{a_C^\gamma a_D^\delta \cdots}{a_A^\alpha a_B^\beta \cdots} \quad (44)$$

When the activities of all the products and reactants are unity, the value of the emf is $E^\circ = -\frac{\Delta F^\circ}{z\mathcal{F}}$. The E° is called the standard emf of the cell. If we now substitute E° for $-\frac{\Delta F^\circ}{z\mathcal{F}}$ in equation 44, we have the important relation describing the dependence of cell emf to temperature and activities of the reactants and products, which is

$$E = E^{\circ} - \frac{RT}{zF} \ln \frac{a_C^{\gamma} a_D^{\delta} \cdots}{a_A^{\alpha} a_B^{\beta} \cdots} \qquad (45)$$

CHAPTER IV

ELECTRODE THEORY

In electrochemical work it is often possible to use a pure metal in equilibrium with a solution of its ions as one of the electrodes in the cell. The general reaction of these metal-metal ion electrode is

$$M = M^{+n} + ne^{-} \qquad (46)$$

and for which the electrode potential is expressed by

$$E_M = E^{\circ}_M - \frac{RT}{n\mathcal{F}} \ln a_{M^{+n}} \qquad (47)$$

The pure metal in contact with a solution is reversible to its own ions and the measured potential E_M is determined by the activity of its own ion $a_{M^{+n}}$ and the standard electrode potential E°_M of the pure metal.

In many instances, however, the metal reacts violently with aqueous solutions and provisions must be employed to reduce the activity of the metal. This can often be accomplished by substituting an amalgam of the metal for the pure metal.

Amalgams of metals more active than mercury behave essentially as do the pure metals, the only difference being that the activity of the metal is lowered somewhat by dilution in the mercury. Electrodes of these amalgams are preferred frequently because equilibrium can be established much more rapidly than with the pure metal, and because they are more readily reversible.

The successful use of amalgam electrodes in homogeneous systems is evident from the large number of published data obtained from use of such electrodes, but measurements of ion activity in heterogeneous systems present certain difficulties. Extraneous ions may react with the amalgam and render the electrode ineffective unless some protective measure is undertaken. Joseph (15) using a cell involving a calcium amalgam and a silver-silver chloride electrode obtained activity coefficients of various calcium chloride solutions which compared favorably with data obtained by other workers. He was less successful when similar measurements were made in heterogeneous biological systems containing diffusible amines and ammonium ions. In a later paper (16), Joseph prepared an amalgam electrode suitable for use in heterogeneous systems. It is on the strength of Joseph's work that a similar electrode is prepared for activity measurements in colloidal silicate systems. The theory of this particular electrode is described in the following paragraphs.

In a saturated solution containing lead and calcium oxalate the activity of each cation depends on that of the other. The solubility product of each electrolyte is expressed as

$$[Ca^{++}][C_2O_4^{--}] = K_1$$
$$[Pb^{++}][C_2O_4^{--}] = K_2$$

where the bracketed quantities represent activities of the ions. Since the oxalate ion is common to both cations it follows that

$$\frac{[Ca^{++}]}{[Pb^{++}]} = \frac{K_1}{K_2} = K_3 \qquad (48)$$

and from the above equation we see that the activity of each cation is proportional to the other; the proportionality constant being determined by the solubility products of both oxalates.

An electrode described by the chain

$$Pb(Hg);\ PbC_2O_4;\ CaC_2O_4,\ Ca^{++} \qquad (49)$$

in which calcium ions made contact with lead amalgam through lead oxalate reacts according to the equation

$$Pb + CaC_2O_4 = PbC_2O_4 + Ca^{++} + 2e^- \qquad (50)$$

If a silver-silver chloride electrode is immersed in a calcium chloride solution along with the amalgam electrode to form a cell, the amalgam electrode is negative and undergoes an oxidation. For the oxidation the electrode reaction is given by the preceeding equation with an electrode potential given by

$$E_{Ca} = E^{o}_{Ca} - \frac{RT}{2\mathcal{F}} \ln a_{Ca^{++}} \qquad (51)$$

The significance of this equation lies in its similarity to equation 47. Although the standard electrode potential E^{o}_{Ca} in equation 51 is characteristic of the amalgam electrode and not that of the calcium metal, the important feature of the amalgam electrode is the dependence of the single electrode potential E_{Ca} on the activity of the calcium ion $a_{Ca^{++}}$.

The silver-silver chloride electrode will undergo reduction for which the reaction is

$$2AgCl + 2e^{-} = 2Ag + 2Cl^{-} \qquad (52)$$

and the single electrode potential is

$$E_{Cl} = E_{Cl}^{o} - \frac{RT}{2F} \ln a^{2}_{Cl^{-}} \qquad (53)$$

On adding equation 50 and 52 we find the cell reaction to be

$$Pb + CaC_2O_4 + 2AgCl = 2Ag + PbC_2O_4 + 2Cl^{-} + Ca^{++} \qquad (54)$$

and similarly on adding equations 51 and 53 the cell emf becomes

$$E = E^{o} - \frac{3RT}{2\mathcal{F}} \ln a_{\pm CaCl_2} \qquad (55)$$

where $a_{\pm}C_aCl_2$ is the mean activity of the electrolyte and is defined in terms of the individual ionic activities a+ and a- as

$$a_{\pm} = \left(a_{+}^{\nu_{+}} a_{-}^{\nu_{-}}\right)^{\frac{1}{\nu}}$$

for an electrolyte whose molecule ionizes into v number of ions of which v+ are positive and v- are negative.

This amalgam electrode behaves as a reversible calcium electrode only if other cations capable of forming insoluble oxalates and anions which form insoluble lead salts are absent or are present in sufficiently low concentration.

CHAPTER V

PREPARATION OF ELECTRODES

The cell employed in the experiment is illustrated in figure 1. A silver-silver chloride and an amalgam electrode reversible to calcium ions are suspended in the arms of an H-shaped tube.

In order to prevent oxidation of the amalgam by atmospheric oxygen the amalgam was sealed in a calcium chloride drying tube as shown in figure 1. A platinum wire was sealed in a capillary tube and welded to one end of the calcium chloride drying tube. Contact with the amalgam was made by placing an exposed section of the platinum wire approximately 0.5 cm from the mouth of the tube.

Lead amalgam was prepared by using triple distilled mercury as a cathode in a 0.5N solution of recrystallized lead nitrate. The anode was a perforated platinum foil in a solution of 1N nitric acid; the two solutions being connected by means of an inverted glass U-tube filled with 1N nitric acid. Nitrogen gas was bubbled through the cathode compartment throughout the electrolytic process. Figure 2 illustrates the arrangement employed for preparation of the amalgam. This arrangement was necessary

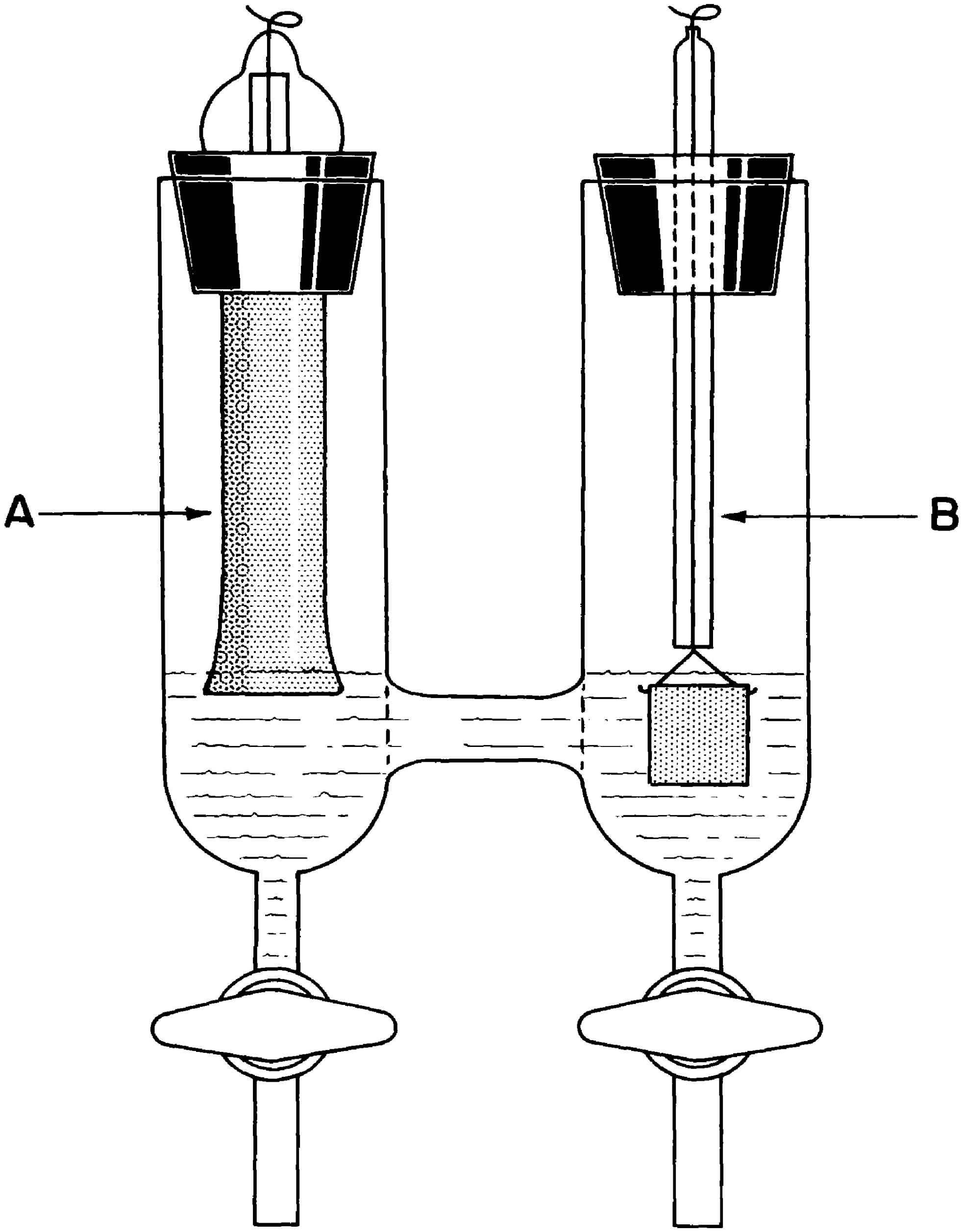

Figure 1. Cell for measuring $CaCl_2$ activity; A - tertiary amalgam electrode, B - silver-silver chloride electrode.

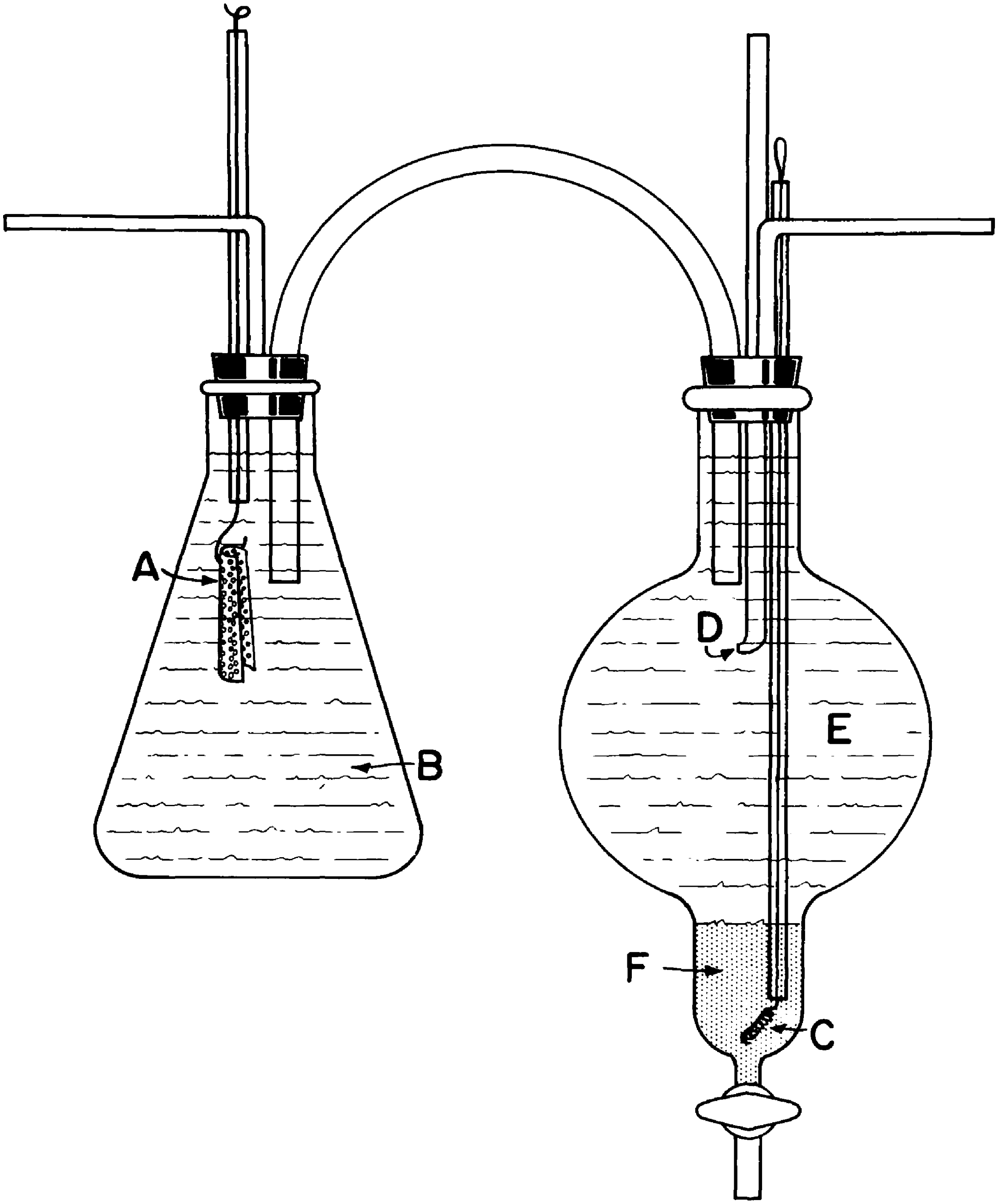

Figure 2. Cell arrangement for amalgam preparation; A - platinum anode, B - 1N nitric acid, C - platinum contact, D - inlet for nitrogen gas, E - 0.5N lead nitrate, F - Mercury.

because amorphous lead peroxide formed on the anode during electrolysis.

A rectifier provided with a powerstat was used as a direct current power source. A milliameter connected in series with the cell was employed to measure the current. Approximately 0.2 amperes of current was passed until the lead concentration in the mercury reached a value in the neighborhood of five percent. Fay and North (9) report that all amalgams between the limits two and fifty five percent of lead form a two phase system at 25°C, consisting of a granular phase of constant composition represented by Pb_2Hg, and a liquid phase which also has a definite composition when equilibrium is reached. Henderson and Stegman (14) studying lead standard cells, found that amalgams having a percentage of lead between 2.5% and 6.0% possessed a constant and reproducible electromotive force.

When the electrolysis was complete, the cathode compartment was detached from the cell and used as the container for washing the amalgam. Conductance water freed of oxygen by heating and saturated with nitrogen was used for washing the amalgam. The amalgam was subjected to at least ten washings, with the water being removed by siphoning. In the final washing the last traces of water were removed by blotting with the tip of a clean filter paper. During the whole washing process, a stream of nitrogen gas was constantly passed into the mouth of the flask containing the amalgam.

The cathode compartment still holding the amalgam and filled with nitrogen gas was suspended into a tall half liter beaker half filled with distilled water and heated. A five percent lead amalgam has two phases at 25°C as described earlier, but becomes completely liquid when heated to 100°C. This hot melt was poured into the calcium chloride tube which had just been flushed with a stream of nitrogen. A moist cellophane membrane was blotted between filter papers and immediately stretched over the mouth of the tube and held in place with a rubber band. Lead oxalate freshly precipitated from lead acetate and excess oxalic acid was evenly spread over the cellophane membrane and covered with a second membrane. The membranes were cemented in place with collodion. When the collodion hardened, the tube was inverted and inserted into the H-cell. In each case enough amalgam was prepared to construct two electrodes. These two electrodes were placed in a 0.05M $CaCl_2$ solution, short circuited and allowed to reach equilibrium. When no potential difference between the two electrodes could be measured, the electrodes were considered ready for use.

There are three general types of the silver-silver chloride electrodes in common use today. Smith and Taylor (32), (33) have made a thorough study on the reproducibility of these three types. They classified these electrodes into the electrolytic, thermal electrotytic and thermal type. The electrolytic type (2), (23) is prepared by electroplating a platinum gauze, foil or wire with silver and then converting part of this silver to silver chloride by using it as an anode in a chloride solution. Alternatively, the thermal-electrolytic type is made by coating a spiral of platinum wire with freshly percipitated silver oxide and heating this in an electric furnace to 400°C. This heating reduces the oxide of silver to porous, finely divided silver which in turn is coated with silver chloride by electrolysis in a chloride solution. Preparation of the thermal type electrode involves the thermal decomposition of a paste mixture of silver chlorate, silver oxide and water. This last method avoids the step of electrolytically coating silver chloride on the electrode surface by automatically forming a silver and silver chloride mixture in the process of heating the paste.

Initial activity measurements were made with the thermal type electrode as described by Noyes and Ellis (26) and modified by Harned (11). Harned omits the step of electrolytically depositing a film of silver on the platinum spiral before placing the silver oxide paste on the wire. Electrodes prepared in this manner gave favorable results in aqueous systems but failed in clay-water systems. This failure was attributed to infiltration of fine clay particles into the pores of the electrode. Preparation and use of the thermal type electrode was not attempted since similar difficulties were anticipated.

There remained the last choice of using the electrolytic type silver-silver chloride electrode. The method of preparation suggested by Brown (2) was used. Electrodes were prepared by electroplating silver on a platinum wire and then partly converting the silver to silver chloride by electrolysis in a hydrochloric acid solution. A serious weakness was observed in the use of this electrode. When the potential of the cell was measured, the balance point was reached very slowly. This characteristic of the electrode was probably due to a polarization effect resulting from a small electrode surface. Construction of an electrode with a larger surface to reduce both the polarization effect and the electrical resistance of the solid-liquid interface was considered necessary.

The most consistent results were obtained by using an electrode prepared by a method described in a text, Experimental Physical Chemistry, by W. G. Palmer (28). Figure (3) shows the general features of this electrode. A strip of pure, untarnished silver, one cm by five cm, was washed in acetone. This rectangular piece was rolled into a spiral and suspended by means of two platinum wires from a silver wire sealed in a glass tube. The clean silver metal was coated with silver chloride by electrolysis in normal hydrochloric acid solution with a current of six milli-amperes for about an hour. Two or more electrodes were prepared at any given time and they were short circuited and allowed to stand overnight in tenth normal

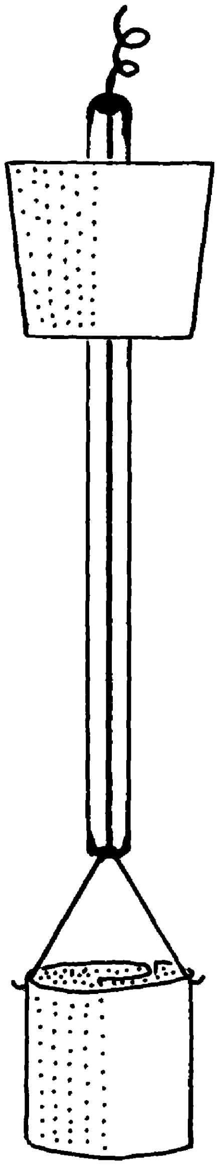

Figure 3. Silver-silver chloride electrode.

calcium chloride solution. Electrodes prepared in this manner gave potentials which agreed within 0.1 millivolts.

CHAPTER VI

CLAYS AND CLAY PREPARATION

Clays selected for this study were bentonite from Upton, Wyoming and kaolinite from Bath, North Carolina. These two clays were selected as representative members of the two major clays types occuring in soils. The montmorillonite group minerals, of which bentonite is a member, are characterized by their high cation exchange capacity and their plastic and swelling properties associated with their high capacity for adsorbing water. Kaolinite, which is a member of the kaolin group minerals, is contrasted from montmorillonite by its low exchange capacity and non-swelling property. Chemical analysis, cation exchange capacity, X-ray and differential thermal data of both clays are given below.

Chemical Analysis

Montmorillonite Upton, Wyoming		Kaolinite Bath, South Carolina	
SiO_2	57.49%	SiO_2	45.58%
Al_2O_3	20.27	Al_2O_3	37.62
Fe_2O_3	2.92	Fe_2O_3	1.00
FeO	0.19	FeO	0.13
MgO	3.18	MgO	0.03
CaO	0.23	CaO	0.32
Na_2O	1.32	Na_2O	0.42
K_2O	0.28	K_2O	0.49
H_2O+	6.85	H_2O+	13.42
H_2O-	7.63	H_2O-	0.63
TiO_2	0.12	TiO_2	1.42
Total	100.48%	Total	100.06%

The total chemical analysis data were extracted from Reference Clay Minerals, American Petroleum Institute Project 49. The symbols H_2O^- and H_2O^+ represents water loss below 105 degree centigrade and above 105 degrees respectively. The formula proposed for this bentonite is $(Al_{1.55}Fe_{.15}Mg_{.33})\ (Al_{.08}Si_{3.92})O_{1}P\,(OH)_2(Na_{.17}\frac{Ca}{2}{}_{.03})$. This formula was calculated after allocating appropriate amounts of the oxides to impurities in the sample. It is evident from the proposed formula that the exchange sites, satisfied by sodium and calcium ions, arise from substitution of magnesium for aluminum in the octahedral positions.

In the case of kaolinite most mineralogists agree to the formula $Al_4Si_4O_{10}(OH)_8$. All oxides other than silica, alumina and water were attributed to impurities in the sample. Cation exchange capacities in kaolinite is believed to arise from broken bonds around the edges of the silica-alumina units.

It must be realized that chemical analyses of clays will vary even among samples taken from the same deposit. Different leaching rates and composition of percolating water, minor variations in the mineralogy of the parent rock, degree of weathering and additions of impurities all contribute to variations in chemical data. Optical studies on the Upton deposit show impurities in the form of quartz, feldspars and traces of limonite. Impurities expressed on a weight basis ranged from six to twelve percent in the Upton deposit. Similar studies on the Bath, South Carolina kaolinite deposit show impurities of sericite, quartz, feldspar and limonite. The percent impurity was determined to be in the neighborhood of six percent.

Cation exchange capacities of the clays were determined conductometrically as outlined by Mortland (25). The cation exchange capacity of the clays were 72.5 and 3.00 milliequivalents per 100 grams of oven dried (100°C) clay respectively for bentonite and kaolinite. Briefly, the method involves saturating a clay with barium ions and titrating the clay in an alcohol-water system with standard magnesium sulfate.

X-ray data were obtained by depositing a thin layer of the calcium saturated, glycerol-solvated clay on a porous ceramic plate and rotating the sample with respect to a beam of monochromatic X-ray with a scanning goniometer. The instrument used was a Norelco X-Ray Diffractometer (Philips Electronic, Inc), equipped with a Geiger-Müller counter and a scaler-rate meter with an automatic strip-chart recorder, utilizing a copper tube and nickel filters. Identification of bentonite and kaolinite by X-ray diffraction methods is relatively simple for pure clays. When the clays are deposited on the ceramic plate, each particle preferentially orients with its ab plane parallel to the surface of the ceramic plate. This condition is favored because the clay particles themselves are platy in structure. Mineralogists have been quick to put this property to good use; clays oriented thus give d-spacings of the unit cell thickness in the c- crystallographic direction. Fortunately, the common clay minerals have d-spacings along this axis which are characteristic for each group. For example, the 17.7 angstrom spacing of the glycerol solvated bentonite (see figure 4) represents an alumina layer sandwiched between two silica layers plus two layers of glycerol molecules; this arrangement being repeated many times along the c axis. In the case of kaolinite the 7.2 angstrom peak corresponds to the unit cell thickness in the direction of the c-crystallographic axis (see figure 5). The 17.7 and 7.2 angstrom lines of bentonite and kaolinite are used as identifying features for these two minerals.

Thermal analyses were run on a hand-made differential thermal apparatus constructed by Dr. R. L. Stone of the University of Texas. The analyses were obtained by using platinum-rhodium thermocouples with anhydrous aluminum oxide as a reference material. A temperature range from room temperature to 1000°C at a rate of 15° per minute was utilized. The high water adsorptive capacity of bentonite is reflected in the first endothermic peak at 150°C (see figure 7). This endothermic reaction corresponds to the release of adsorbed water from the interlayer spacings of the bentonite clay. The magnitude of this peak varies considerably with the amount of adsorbed water on the clay. The second endothermic peak beginning at about 600° is analytically more useful and corresponds to the destruction of the crystal lattice with release of hydroxyl water. The

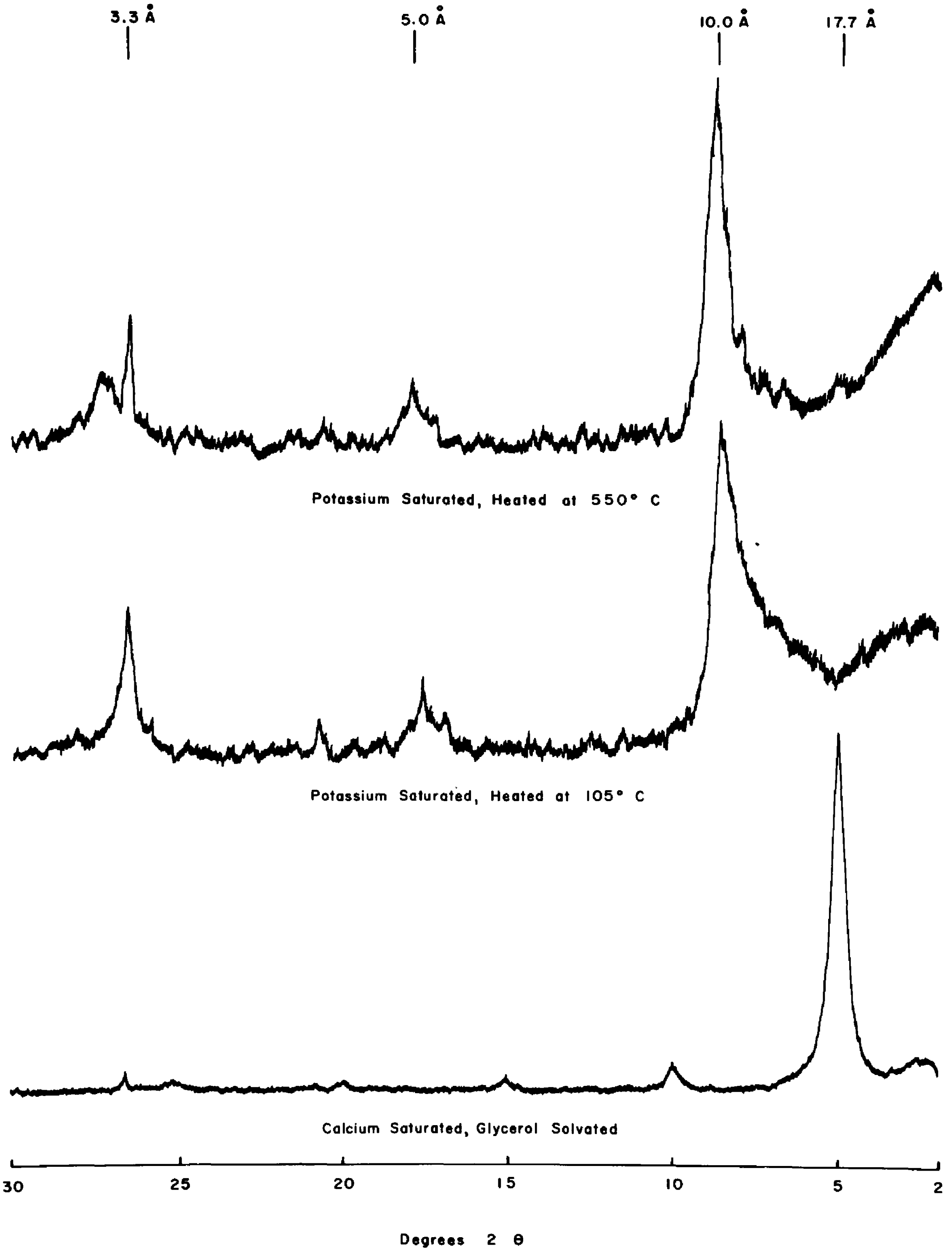

Figure 4. X-ray diffraction patterns for the less than two micron fraction of bentonite from Upton, Wyoming.

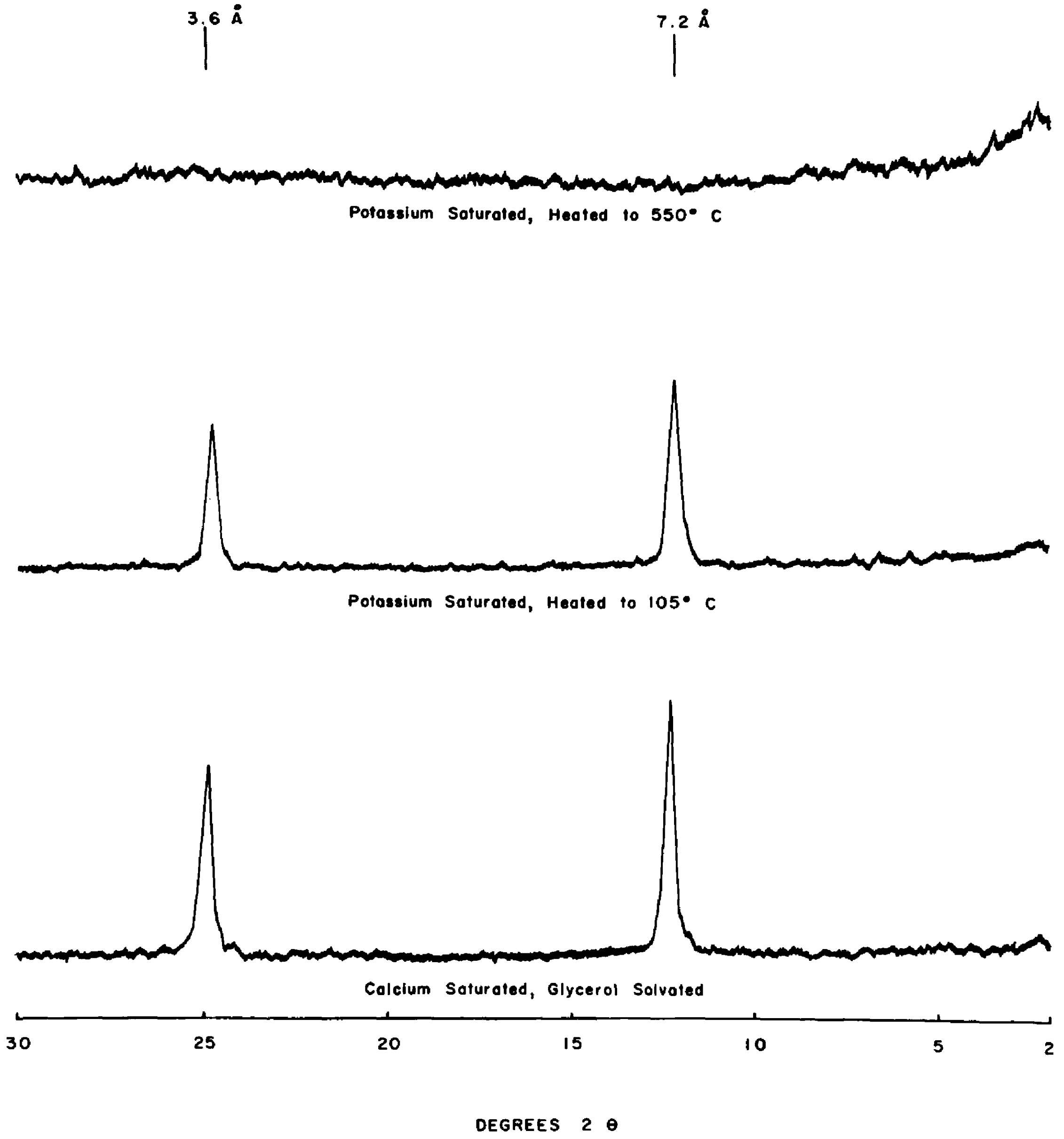

Figure 5. X-ray diffraction patterns for the less than five micron fraction of kaolinite from Bath, North Carolina.

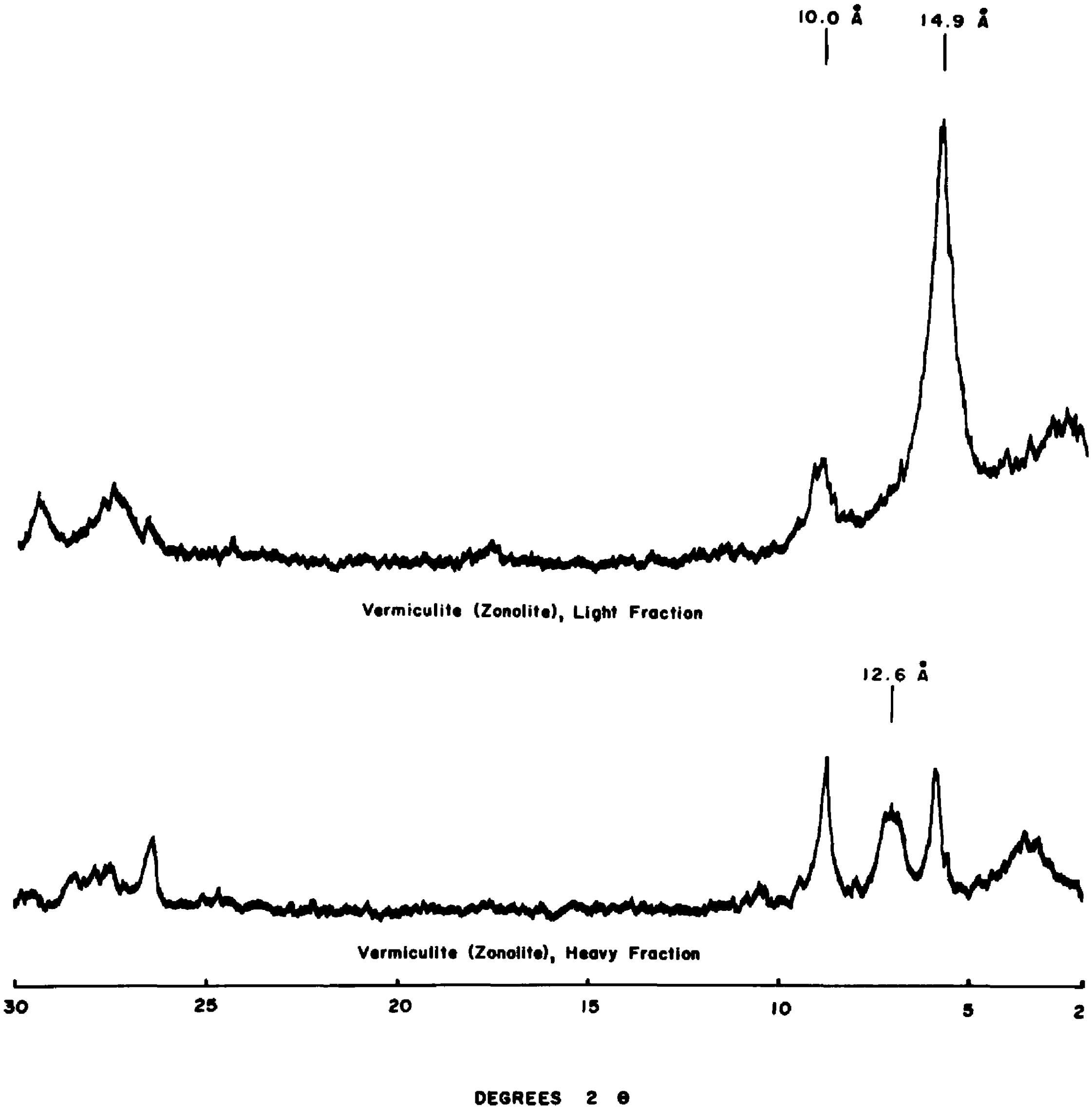

Figure 6. X-ray diffraction patterns of vermiculite (Zonolite).

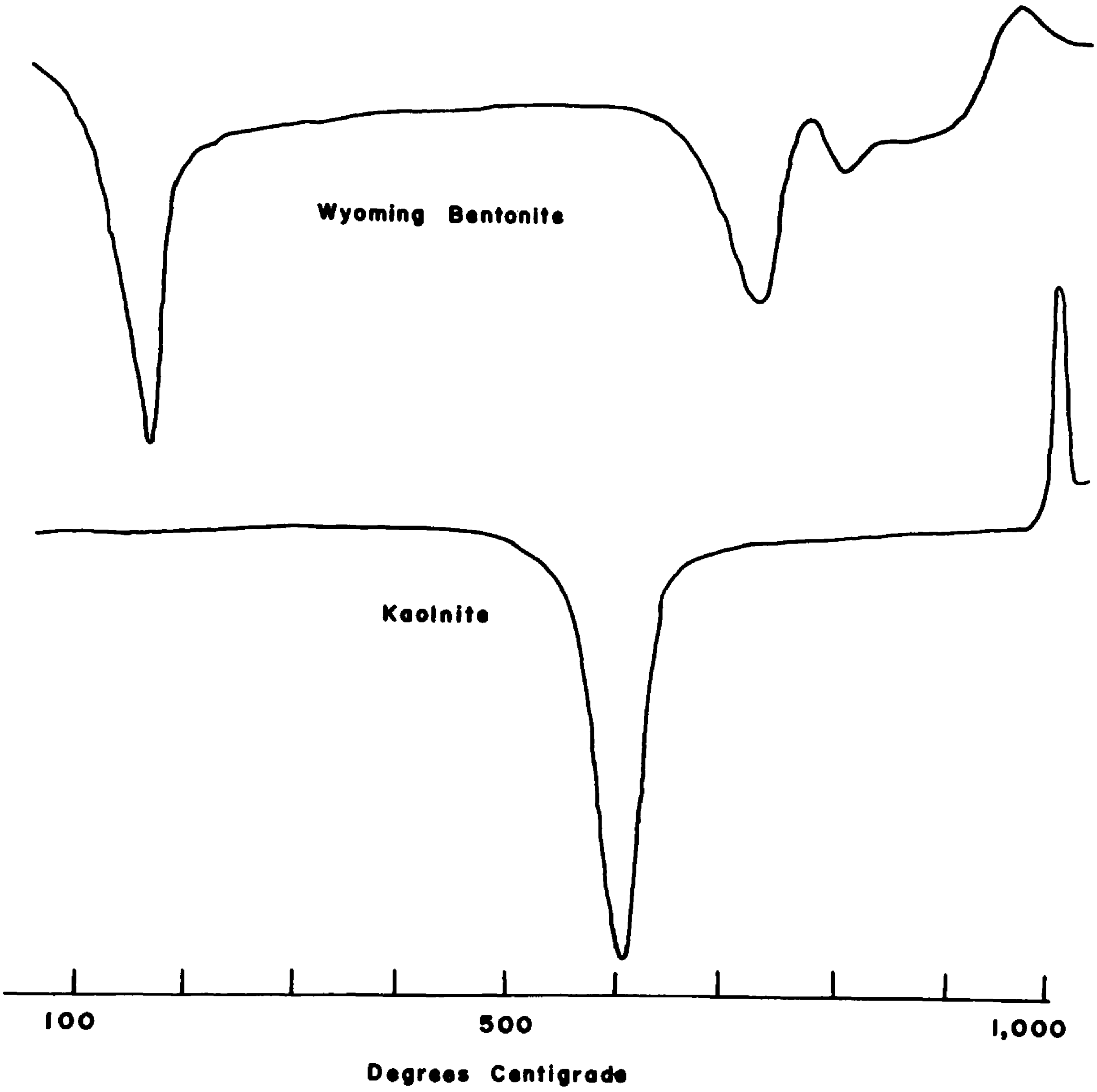

Figure 7. Differential thermal analysis curves of bentonite and kaolinite.

third endothermic peak is caused by further thermal destruction of the lattice and is followed by an exothermic reaction probably resulting from recrystallization of the thermal decomposition products.

Kaolinite gives a characteristic endothermic reaction which starts at about 500° and reaches a maximum at 610°C. This reaction is associated with the thermal decomposition of the lattice and the resultant release of water. Recrystallization of amorphous alumina is believed to be the cause of the charp exothermic peak occuring at 980-1000°C.

Both X-ray and thermal data indicate high purity of the samples. No thermally identifiable impurity is discernable in the differential thermal curves (see figure 1) and only a small trace of quartz is evident in the X-ray curves.

Vermiculite, another common soil mineral was prepared for use in this study. The chemical composition and structure of vermiculite is probably related to the mineral biotite, $K(Mg,Fe)_3Si_3AlO_{10}(OH)_2$. In vermiculite much of the potassium has been weathered out so that the interlayer spaces are accessible to water and exchangeable ions. Zonolite, a vermiculite commerically used as an insulator was selected. The mineral was stirred in water and allowed to settle. The lighter fraction which remained afloat was removed and saved for this study. Figure 6 shows the X-ray patterns of the light and heavy fractions. The heavy fraction is mainly interstratified mica and vermiculite with some discrete mica and vermiculite. Mica is indicated in the X-ray patterns by the ten angstrom line, interstratified mica-vermiculite by the broad peak at 12.6 angstrom and vermiculite by the 14.9 angstrom line. The light fraction was mainly vermiculite with some mica. Cation exchange capacity was determined to be 63.1 milliequivalents per 100 grams of the clay.

Before ion activity measurements can be made in clay-water systems it is necessary to saturate the clay with the ion whose activity is to be measured. Soil scientists have in the past saturated clays with the desired ions by neutralizing the hydrogen saturated clay with the appropriate hydroxides. This method should best be discouraged. It is well accepted today that hydrogen saturated clays remain so only for a short time; acid clays are unstable and become aluminum saturated as a result of lattice decomposition and release of aluminum ions into the clay solution.

Bentonite is for the most part sodium saturated in its natural state and kaolinite is probably saturated with aluminum and hydrogen ions. Both clays were electrodialyzed to a pH of about 5.0 and dispersed immediately with addition of 0.1N sodium hydroxide to a pH of about 8.0. This dispersed clay suspension was stirred and allowed to settle. Using Stokes law for the determination of the sedimentation rate, the less than two and five micron fractions of bentonite and kaolinite respectively were siphoned off for use in this study. The larger size fraction which included undispersed clay aggregates, quartz and feldspar was discarded. Selection of the five micron size for kaolinite was based on the observation that kaolinite generally occurs in the larger size clay fraction in soils. The sodium saturated clay was flocculated with a large excess of calcium chloride and filtered. Several washings of the clay with increments of calcium chloride solution assured complete saturation with calcium ions. The clay was washed with conductance water until test with silver nitrate solution showed no trace of chloride ions in the filtrate. Lastly, the clays were air dried and stored in bottles for use at a later time.

CHAPTER VII

ACTIVITY MEASUREMENTS IN WATER

Measurement of Mean Activities

Before activity measurements were initiated in clay-water systems it was thought advisable to test the electrodes in water systems. Calcium chloride solutions ranging in concentrations from 0.001 to 0.1 molar were prepared by dilution of a standard molar solution of the electrolyte. Standardization of the molar calcium chloride solution was carried out gravimetrically by precipitation of the chloride ion as the silver salt.

About 75 ml. of the dilute calcium chloride solution were poured into the H-shaped container and the amalgam and silver-silver chloride electrodes suspended into the solution as illustrated in figure 1. A slow stream of nitrogen gas was bubbled through the solution via the stopcock located at the bottom of each arm of the container. This step was necessary to create uniform conditions throughout the clay water system. Bubbling nitrogen gas had the added advantage of reducing the oxygen content of the solution thereby increasing the longevity of the amalgam electrode, and also eliminated the question of the effect of oxygen on the properties of the silver-silver chloride electrode. Dissolution of carbon dioxide gas was also kept at a minimum and thus the effect of the carbonate ion on the activity of calcium chloride was reduced.

All activity measurements were carried out at 25°± 0.5°C by employing a constant temperature bath. The electrodes were allowed to equilibrate for an hour at which time the amalgam electrode was removed and inverted to allow a fresh amalgam surface to make contact with the lead oxalate. The amalgam electrode was then placed in its former position. Approximately ten to fifteen minutes were required after the last step for the cell to reach a constant emf reading.

Cell emf's were measured on a Sargent Recorder, an automatic self-balancing, variable range, potentiometer having an accuracy of 0.1% or 20 micro volts whichever is greater. There are certain difficulties encountered when the emf of a single cell is measured. For example, the accuracy of the cell emf reading of a 0.002 molar calcium chloride solution is 517± 1.0 mv. An accuracy of at least a tenth of a millivolt is required for good results. This cannot be attained in the higher ranges of this instrument. This problem can be readily remedied by using cells of the type

$$\mathrm{Ag;AgCl/CaCl_2(m_1)/CaOx/PbOx/Pb(Hg)-(Hg)Pb/}$$
$$\mathrm{PbOx/CaOx/CaCl_2(m_2)/AgCl;Hg}$$

For such an arrangement the emf of the cell is

$$(E-E^{*}) = (E_1^{o} - E_2^{o}) - \frac{3RT}{2F} \ln \frac{A_1}{A_2}$$

Since the quantity ($E_1^0 - E_2^0$) is equal to zero, the potential measured from such a combination of cells is proportional only to the ratios of the activities of each cell. It now becomes possible to read the potential of the cell on a lower range of the potentiometer, thus making possible readings of greater accuracy. E^* is the emf of the cell containing the reference solution; the activity coefficient for this solution is extracted from the literature (30), thereby giving a basis of reference for the activity coefficient of all the other calcium chloride solutions. In Column 6 and 7 of Table I are listed the measured activity coefficients obtained experimentally as compared to values calculated from an equation derived by Shedlovsky and MacInnes (30). The equation

$$-\log f = \frac{1.7515\sqrt{C}}{1+2.814\sqrt{C}} - 0.147C$$

where f and C are the mean activity coefficient and the molar concentration respectively, has been shown to give accurate values of activity coefficients from C = 0.002 to 0.10.

The experimentally determined activity coefficient $f_{(obs)}$ was calculated from the relation $-\log f/f^* = 11.27 (E - E^*) + \log c/c^*$, where f^*, E^* and C^* represent the mean activity coefficient, the measured emf and the concentration respectively of the reference 0.002 molar solution. The constant 11.27 is equal to the reciprocal of the ratio $3 \times 2.303RT/2F$ at 25°C.

TABLE I

ACTIVITY COEFFICIENTS f, AT 25° ON THE MOLARITY SCALE OF SOME CALCIUM CHLORIDE SOLUTIONS

Concentration in moles per liter	Millivolts - (E - E*)	11.27(E - E*)	$\log \frac{c}{c^*}$	$-\log \frac{f}{f^*}$	f(obs)	f(cal)
0.001	-0.0247					
.002	0.0000	0.000	0.000	0.000	0.8525	.8525
.004	0.0240	0.2705	0.3010	0.03055	.795	.8064
.006	0.0380	0.4283	0.4771	0.04886	.762	.7753
.01	0.0558	0.6289	0.6990	0.07010	.725	.7325
.02	0.0801	0.90273	1.0000	0.09727	.681	.6695
.04	0.1021	1.1507	1.3010	0.14036	.617	.6050
.06	0.115	1.3017	1.4771	0.17544	.569	.5688
.10	0.1325	1.4933	1.6990	0.2057	.531	.5267

Approximation of Individual Ion Activity

There is presently no known method for measuring in a strictly thermodynamic sense the activity of a single ion species. It is possible to predict the activity coefficient of an ion species from the Debye-Huckel formula, but this formula holds only for very dilute solutions. Kielland (17) has tabulated individual activity coefficients for various inorganic and organic ions. His calculations were based on the utilization of the diameter of the hydrated ion as the effective ion diameter.

Although a strictly thermodynamic method for determining the activity of a given ion species is still non-existent, it is sometimes convenient to speak of the activity of ions. A classical example is the use of the pH concept. Even though pH is often defined as "the logarithm of the reciprocal of the hydrogen ion activity", there is no way of knowing whether such a quantity is actually being measured. The ambiguity arises in part from an uncertain liquid junction potential developing from the use of the reference calomel electrode. This has not discouraged the use of the pH concept among research workers; in fact pH has been widely used in the biological and agricultural sciences with great benefit to both.

When an electrode reversible to calcium ions and another reversible to chloride ions are inserted into a solution containing both ions, the emf of this cell measures the mean ionic activity of the two ions. Unfortunately, the mean activity tells nothing about the activity of the individual ions.

If one wishes to estimate the activity of each ion he can do so by making certain assumptions. MacInness (22) was one of the earliest investigators to propose generalizations concerning the possible determination of individual ion activities. He is credited with suggesting the equality of the activity coefficient of both ions in a potassium chloride solution. Harned (13) employing the assumptions suggested by MacInnes proceeded to determine individual ion activity coefficients potentiometrically using cells having liquid junctions. He assumed the liquid junction potential to be negligible. Lewis and Randall (19) described a method for calculating individual ion activities based on non-thermodynamic methods. Two assumptions are inherent in their method, first that the mean activity coefficient of the potassium chloride salt is the same as the individual ion activity coefficients of the potassium and chloride ions, and secondly that for solutions of equal ionic strengths the activity coefficient of the chloride ion is the same whether the solution be a calcium chloride or potassium chloride solution, or for that matter any solution containing chloride ions. This method implies that if some value of activity coefficient is assigned to an ion in a solution of ionic strength I, one can then proceed to determine the activity coefficient of any other ion.

For example, a 0.01 molar calcium chloride solution has the same ionic strength as a 0.03 molar potassium chloride solution. If the activity coefficient of the chloride ion is assumed in the manner just described and the mean activity coefficient of the 0.01 molar calcium chloride is known, the activity coefficient of the calcium ion can be calculated from the relationship

$$f_{Ca} = \frac{(f_{CaCl_2})^3}{(f_{Cl})^2} \qquad (56)$$

where f_{Ca} and f_{Cl} represent the individual activity coefficients of the calcium and chloride ions and f_{CaCl_2}, the mean activity coefficient of calcium chloride.

The calcium ion activity coefficient for several concentrations of calcium chloride solutions as calculated by the method suggested by Lewis and Randall is listed in Column 8 of Table II.

The method just described is quite satisfactory for solutions of known ionic strength. In clay water-systems containing mixtures of electrolytes the ionic strength is not always known or can be measured only with great difficulty. Some other method must be developed for approximating individual ion activities in solution of unknown ionic strength. In the following paragraphs such a method will be described.

If the emf of the cell

$$Ag; AgCl/KCl(m)/KCl(sat)/HgCl; Hg$$

is measured, the cell emf will be

$$E = E_o' - \frac{RT}{F} \ln a_{Cl} \tag{57}$$

where E_o' represents the algebraic sum of the standard electrode potential of the silver-silver chloride electrode, the potential of the reference calomel electrode and the liquid junction potential. The assumption is made here that E_o' is a true constant and does not vary with the composition of the solution. This same electrode combination can be employed to measure the chloride ion activity in a calcium chloride solution. If a solution of calcium chloride of concentration A gives an identical emf reading with a potassium chloride solution of concentration B, then the previously made assumption leads to a useful conclusion, namely, that both solutions have the same chloride ion activity. If now the mean activity of the potassium chloride solution is known, we can obtain the chloride ion activity from the assumption made earlier that

$$(a_{KCl})^2 = (a_{Cl})^2 = (a_K)^2 \tag{58}$$

and finally the calcium ion activity can be calculated from the relationship

$$(a_{CaCl_2})^3 = (a_{Ca}) \times (a_{Cl})^2 \tag{59}$$

The activity coefficient of the calcium ion f_{Ca} can be determined if the concentration of the calcium ion C_{Ca} is known from the relation

$$f_{Ca} = \frac{a_{Ca}}{c_{Ca}} \qquad (60)$$

Briefly this method involves measuring the emf of the cell for various standard calcium and potassium chloride solutions. Concentrations of both chloride solutions are plotted against cell emf on semi-log paper so that for a given emf a calcium chloride solution of say concentration A, one can easily pick off the potassium chloride concentration having the same chloride activity. As an example, a 0.00500 molar calcium chloride solution gives the same emf reading as a 0.00955 molar potassium chloride solution. The activity coefficient of potassium chloride solution of this concentration is 0.9046 and the activity of the chloride ion is 0.08639 = 0.0955x0.9046. The activity coefficient of the chloride ion in the calcium chloride solution is 0.8639 = 0.08639/2x0.00500. Since the mean activity of calcium chloride is 0.7905, the activity coefficient of the calcium ion f_{Ca} is calculated to be

$$f_{Ca} = 0.7905^3/0.8639^2 = 0.6620$$

The activity coefficient of calcium ion as calculated by this method is given in Column 7 of Table II. It is evident from the data in Table II that the activity coefficient of the calcium ion as determined potentiometrically is slightly larger than the values obtained by the method described by Lewis and Randall. The values deviate considerably at the higher concentrations. This deviation may be the result of the fallacy of assuming constancy of the liquid junction potential. There are two possible sources of error in the method of Lewis and Randall: first, the assumption of equal activity coefficients for potassium and chloride ions may not hold for high concentrations of potassium chloride solutions and second, the equality of single ion activity coefficients in solution of constant ionic strength fails at higher concentration unless the effective diameters of the various ions are considered.

If the error lies in the potentiometric method, it might be said in defense of the data that the error is by a constant factor in the lower concentrations, a fortuitous situation because this is the range utilized in most of the experimental work with clay-water systems. Furthermore, although the true calcium ion activity is of real interest to us, the ability to demonstrate relative difference between systems is of greater significance.

TABLE II

INDIVIDUAL ION ACTIVITY COEFFICIENTS

Conc. in moles/l of $CaCl_2$ and KCl having equivalent activities of chloride ions		Activity Coefficients for KCl solution	Activities of chloride ions in $CaCl_2$ and KCl soln.
$CaCl_2$	KCl		
0.100	0.171	0.7346	0.1256
0.0800	0.138	0.7490	0.1034
0.0600	0.105	0.7680	0.08064
0.0400	0.0710	0.7950	0.05645
0.0200	0.0366	0.8375	0.03065
0.0100	0.0188	0.8740	0.01643
0.00900	0.0171	0.8788	0.01503
0.00800	0.0153	0.8840	0.01353
0.00700	0.0134	0.8900	0.01193
0.00600	0.0115	0.8964	0.01031
0.00500	0.00955	0.9046	0.008639
0.00400	0.00771	0.9132	0.007041
0.00300	0.00580	0.9228	0.005352
0.00200	0.00390	0.9343	0.003644
0.00100	0.00195	0.9523	0.001856

Activity Coeff. of chloride ions in $CaCl_2$ solutions	Mean Activity Coefficients of $CaCl_2$ solutions	Ca ion activity coefficients	
		Experimental	Lewis & Randall
0.6280	0.5269	0.377	0.307
0.6463	0.5444	.386	.323
0.6720	0.5688	.407	.346
0.7056	0.6050	.445	.385
0.7663	0.6695	.511	.461
0.8175	0.7326	.589	.545
0.8350	0.7413	.584	.557
0.8456	0.7519	.595	.574
0.8521	0.7628	.611	.589
0.8592	0.7752	.631	.607
0.8639	0.7905	.662	.631
0.8801	0.8052	.674	.653
0.8920	0.8265	.710	.686
0.9110	0.8525	.746	.729
0.9280	0.888	.813	.790

CHAPTER VIII

THE ELECTROCHEMICAL POTENTIAL AND THE TOTAL ACTIVITY

In speaking of equilibrium conditions in a system containing two or more phases the equality of the chemical potential u, of the soluble constituents in all phases was cited. However, when electrically charged particles are considered, the chemical potential must be replaced by the electrochemical potential $\bar{u}$, a term first suggested by Guggenheim (10), which contains the additional energy term $ze\psi$, where z is the valency of the ion, e is the electronic charge, and ψ the electrical potential. The quantity $ze\psi$ is the potential energy of a body with an electric charge ze at a point where the electric potential is ψ. If the particle under investigation is an ion, the potential energy per mole becomes $zF\psi$, where F is a farady of electricity. For charged particles in equilibrium between two phases of different electric potential

$$\bar{u}_1 = \bar{u}_2$$
$$u_1 + zF\psi_1 = u_2 + zF\psi_2 \qquad (61)$$

If a suspension of a hydrogen-clay is allowed to equilibrate in a beaker for several days, two distinct phases will develop. The clay particles will settle to the bottom leaving a clear supernatant portion near the surface; the boundary between phases may be sharp. Measurement of pH will disclose a difference of 2 - 3 pH units between phases, the pH being higher in the supernatant portion. In making these measurements two assumptions are made, first that the system is in equilibrium and second, that the liquid junction potential arising from the use of the calomel reference electrode is negligible. If the assumptions are correct, then it can be said that the hydrogen ion activity and therefore the chemical potential of the ion is greater in the sediment than in the supernatant liquid. If the position of the calomel electrode is held constant and that of the reversible glass electrode is varied, no change in pH value is discernable. This is equivalent to observing a zero emf between two reversible electrodes placed in each of the two phases. The zero emf between the two reversible electrodes signifies that the electrochemical potential $\bar{u}$, is the same in both phases and that the system is in a state of equilibrium. In other words a system in equilibrium can do no work and a zero potential is to be expected. If instead of two reversible electrodes, calomel reference electrodes are used, a potential difference will be observed. If we examine equation 61, we see the reason for this phenomenon. Equation 61 can be re-written in the form

$$u_1 - u_2 = zF(\psi_2 - \psi_1)$$

$$\psi_1 - \psi_2 = \frac{u_1^\circ + RT\ln a_1 - u_2^\circ - RT\ln a_2}{zF} = \frac{RT}{zF}\ln\frac{a_1}{a_2} \qquad (62)$$

Presumably the calomel electrodes measures the quantity $(\psi_2 - \psi_1)$, but the problem of the liquid junction potential again lends ambiguity to the measured quantity.

Adair and Adair (1), however, used this quantity to calculate the charge on protein particles, and also the relationship between $(\psi_2 - \psi_1)$ and the pH of protein solutions. Low (20) using a method similar to Adairs' showed relationship between $(\psi_2 - \psi_1)$ and the ionic strength, clay concentration and zeta potential in heterogenous clay-water systems. He strongly suggests the greater significance of the electrochemical potential $\bar{u}$, and the total activity over the chemical potential and the corresponding individual ion activity. His argument is based on the premise that the total activity $\bar{a}$, defined in terms of the electrochemical potential $\bar{u}$ by the relationship

$$\bar{u} = \bar{u}^{o} + RT\ln\bar{a} \qquad (63)$$

is the true measure of the escaping tendency of an ion.

The significance of the total activity in soils has yet to be determined. Overstreet (21) postulated that owing to the higher chemical potential of cations in soil sediments than in the equilibrium soil solution, it would be expected that cations would be more readily absorbed from the sediment than from the corresponding supernatant liquid. No experimental data were given to support this theory. Overstreet probably is in error in this respect. Thermodynamics predict that a plant sending roots into a soil sediment as well as the equilibrium soil solution will absorb ions equally well at both points. This is assuming, of course, that the electrical potential of the root is the same at both points. Since the soil and soil solution are in equilibrium the escaping tendency of the cation into the root must be the same at all points in the system.

The agronomist making activity measurements in soils must be aware of the difference between the chemical potential and the electrochemical potential if he is to interpret his data correctly.

CHAPTER IX

CALCIUM CHLORIDE ACTIVITY MEASUREMENTS IN CLAY-WATER SYSTEMS

Cell emf measurements were carried out in clay-water systems in very much the same manner as was described earlier for the water systems. In the double cell arrangement one cell contained a standard 0.002000 molar calcium chloride solution while the other held the variable clay-water system of unknown calcium chloride activity. A zero emf reading for such an arrangement indicated equal calcium chloride activity in both cells. A concentration of 0.002000 molar was selected for the reference solution because this was the lowest concentration giving a steady emf reading over a long period of time.

After each measurement involving a clay-water system, the cells were washed and tested in aqueous calcium chloride solution. The cells were considered operative when equal concentration of calcium chloride in both cells gave a zero emf reading.

Two sets of activity measurements were carried out; the first involving measurement of calcium ion and calcium chloride activities in clay-water systems to which free chloride salts had been added. This particular experiment was made to measure the relative replacing power by various cations for calcium adsorbed on clays.

The second series of activity measurements were made to show the variation of ion and salt activity as a function of the clay type and the clay composition of the systems.

In the following paragraphs the results of these measurements will be discussed in detail.

Ion Competition in Clays

Different cations have different affinities for ion exchange sites in clay minerals. For example, if an equivalent concentration of cation A and the same concentration of cation B is added to a clay, both ions will not be equally adsorbed. This is analougous to the differential adsorption of ions observed in synthetic ion exchangers.

This experiment was set up to study the relative affinities of various cations for clays. Since an electrode reversible to calcium ion was the only one available, it was necessary to devise some method for utilizing the change in calcium or calcium chloride activity as a measure of relative cation affinities. This problem was solved in the following manner: four grams of calcium saturated bentonite were placed in each of five 250 cc Erlenmyer flasks. One hundred ml of solution containing thirty eight m.e. of lithium chloride equivalent to a symmetry concentration of the four grams of clay, were poured into one of the flasks. In the same manner equivalent concentrations of sodium, potassium, rubidium and magnesium chloride were added to the remaining flasks. The flasks were stoppered and allowed to sit for two weeks with intermittent shaking.

The principle underlying this experiment is that the added cation will replace a portion of calcium from the clay into the solution phase, thereby making possible measurement of calcium chloride activity. The cation having the greatest affinity for the clay necessarily replaces the largest fraction of the calcium and thus gives the highest activity value.

This experiment was repeated with kaolinite clay. Fourty five grams of clay having an exchange capacity of 3.30 m.e. per 100 grams of clay was used. The larger sample size was necessary to maintain a sufficient concentration of calcium ions in the solution phase in order for the amalgam electrode to function as an electrode reversible to calcium ions. One hundred ml of solution containing 14.85 milliequivalents of the cation were added to each of five flasks holding the clay.

In each of the above systems only one symmetry concentration of salt was added. These systems were also studied for calcium chloride and calcium ion activities in which two and three symmetries of the salts were added. This particular phase of this experiment was carried out to determine the effect of increasing salt concentration on the activity values.

Figures 8 and 9 show the dependence of calcium ion and calcium chloride activities on the kind and amount of chloride salt added to the clay suspensions. The data show that the relative affinities of the cation for the exchange site follow the sequence $\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Mg} \ll \mathrm{Rb}$.

Calcium Chloride Activity Measurements in Clay Suspensions Containing Mixtures of Clay

The variability in physico-chemical properties among the various soil clays has immense practical significance in the field. As an example, 100 grams of calcium saturated bentonite have approximately 100 milliequivalents of adsorbed calcium; on the other hand an equal weight of calcium saturated kaolinite has only three to ten milliequivalents of this ion. It is not surprising then that for equal weights of the clays a bentonite suspension would have a higher calcium activity.

Will a mass of calcium saturated bentonite having ten milliequivalents of calcium release calcium ions more readily than a larger weight of kaolinite also having ten milliequivalents of adsorbed calcium? Furthermore, if five milliequivalents of calcium bentonite were mixed with five milliequivalents of calcium kaolinite, would the calcium released into the solution phase simply be an additive property of the two clays? The following experiment was designed to answer these two questions.

One gram of calcium bentonite having 0.950

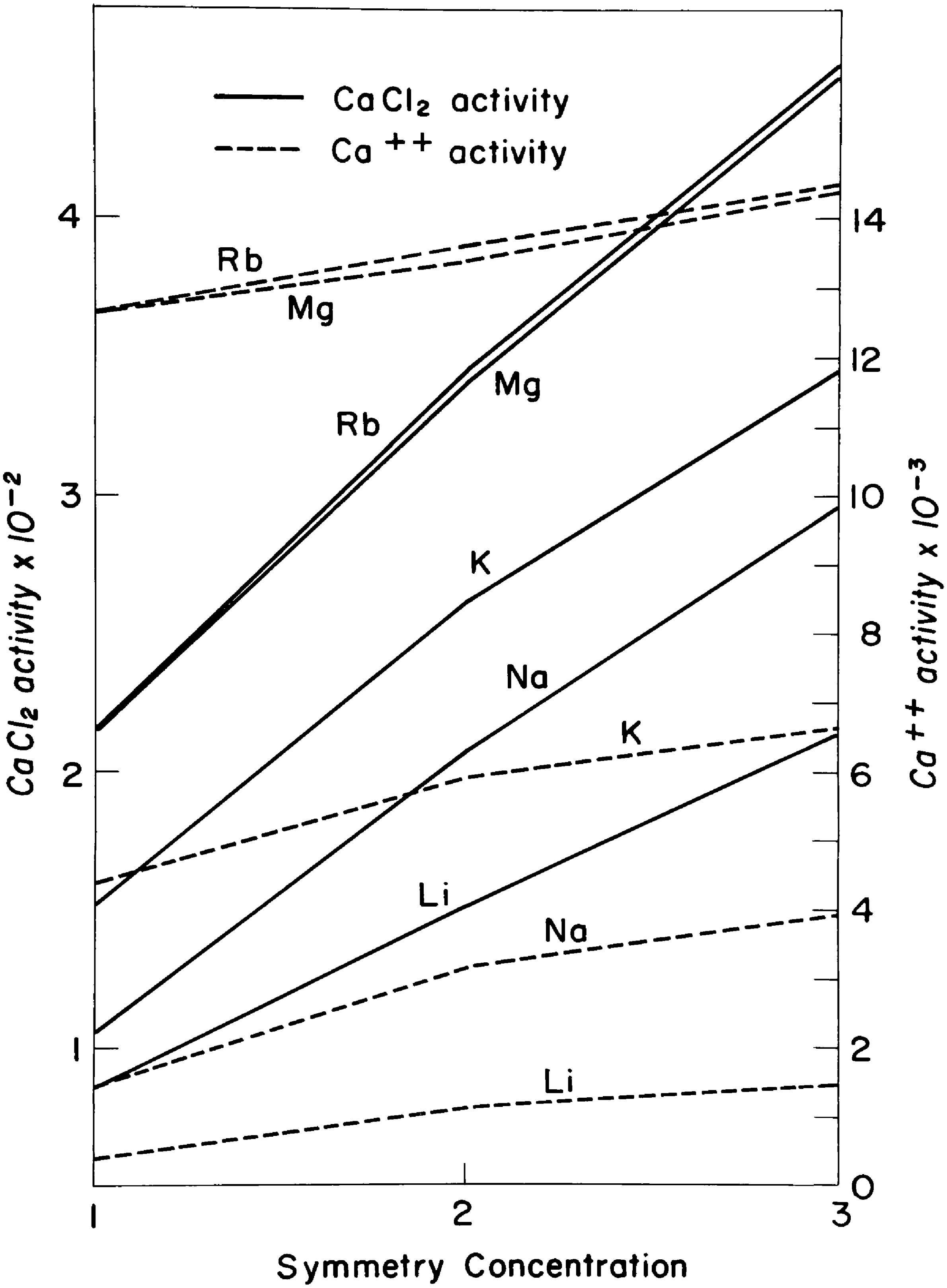

Figure 8. Dependence of calcium and calcium chloride activities in bentonite suspensions on the addition of symmetry concentrations of chloride salts.

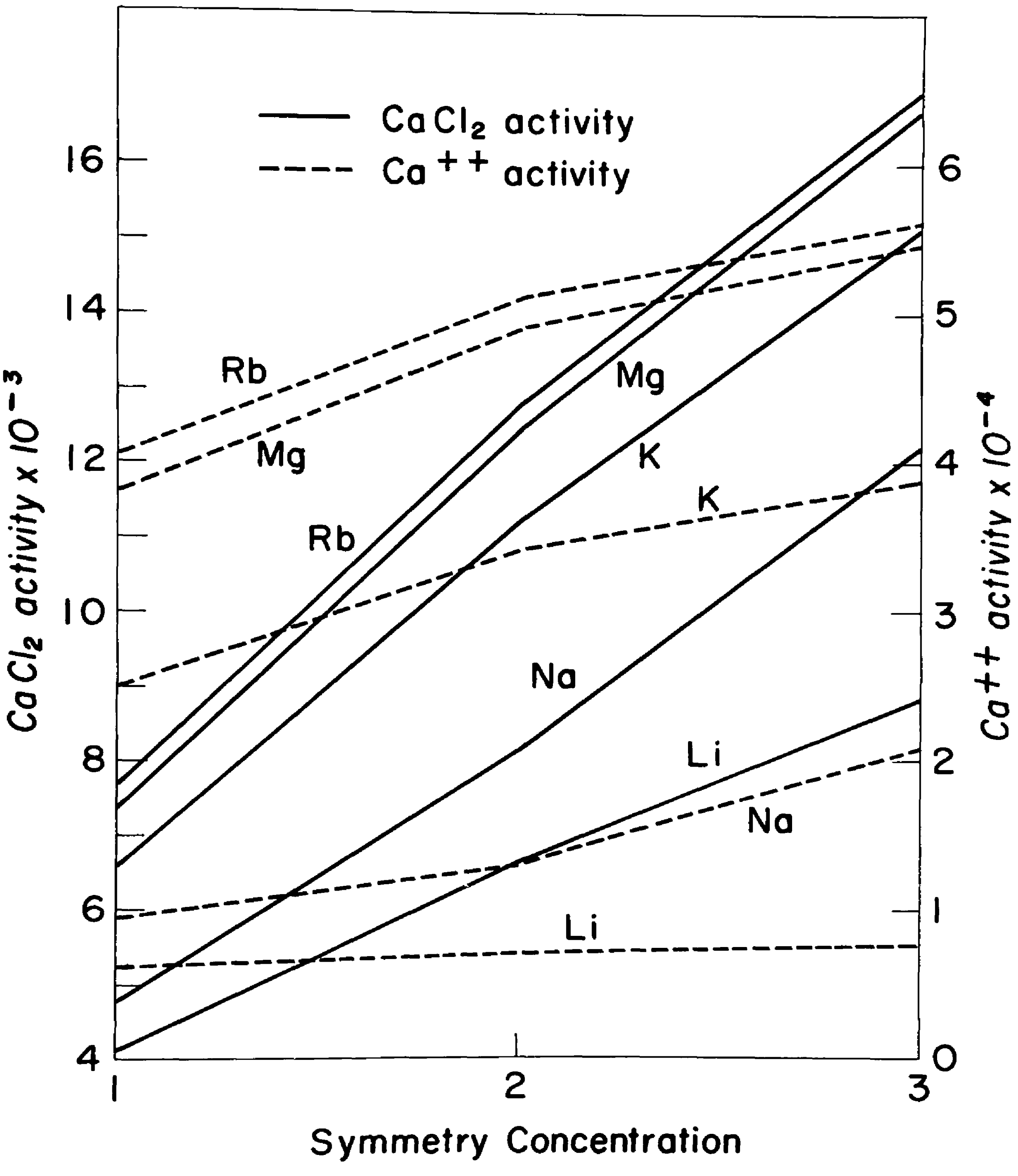

Figure 9. Dependence of calcium and calcium chloride activities in kaolinite suspensions on the addition of symmetry concentrations of chloride salts.

milliequivalent of adsorbed calcium was placed in a 250 ml Erlenmyer flask and similarly 28.787 grams of calcium kaolinite having an equal amount of adsorbed calcium ions were placed in another flask. Systems containing bentonite-kaolinite mixtures were also prepared. In each case the sum of the concentration of the adsorbed calcium ions from both clays was 0.950 milliequivalents. Calcium saturated clays were used in all cases. To each of these flasks 100 ml of solution containing 0.950 milliequivalents of hydrochloric acid was added. Hydrochloric acid was added for two reasons; (1) to add chloride ions into the system and (2) to release part of the calcium ions into the solution phase by exchange with hydrogen ions so that the activity of calcium chloride in the suspension could be measured.

The flasks were allowed to equilibrate for two weeks with intermittent shaking. The data in figure 10 illustrate the variation of calcium chloride, hydrochloric acid, hydrogen and calcium ion activities with change in the composition of the system. There was some doubt as to the validity of the data, owing to the low pH values of the suspensions. There is reason to believe that at low pH aluminum from the crystal lattice is released into the solution rendering the activity values more a function of the aluminum content than that of the clay composition. In order to avoid this problem activity measurements were made in systems to which neutral potassium chloride was added instead of hydrochloric acid (see figure 11). Similarly, calcium chloride activity was measured in a series of systems containing bentonite-vermiculite mixtures. Figure 13 summarizes the data obtained for measurements in the bentonite-vermiculite mixtures.

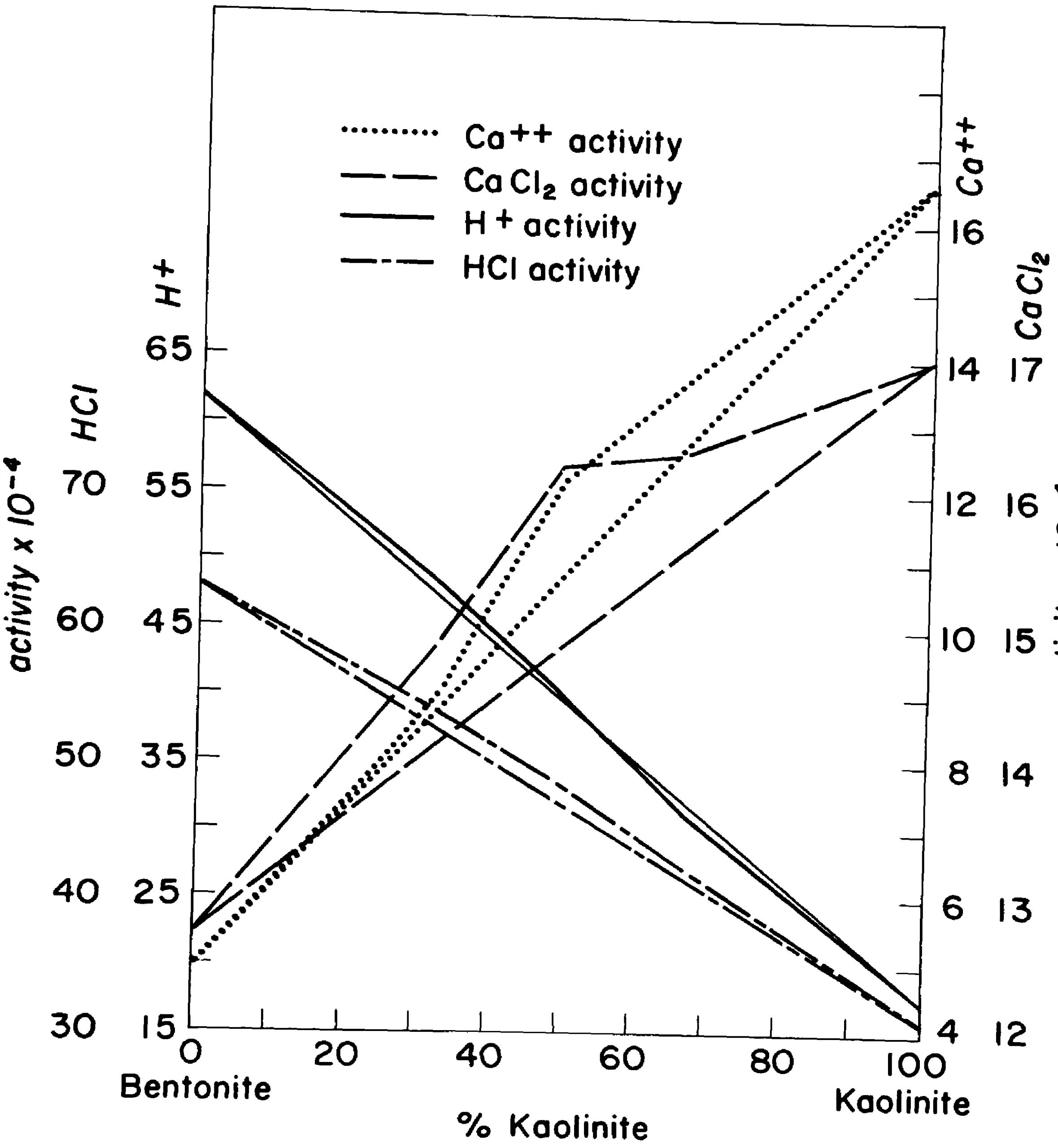

Figure 10. Dependence of calcium, calcium chloride, hydrogen and hydrochloric acid activities on the clay composition of calcium saturated bentonite-kaolinite suspensions containing one symmetry concentration of hydrochloric acid.

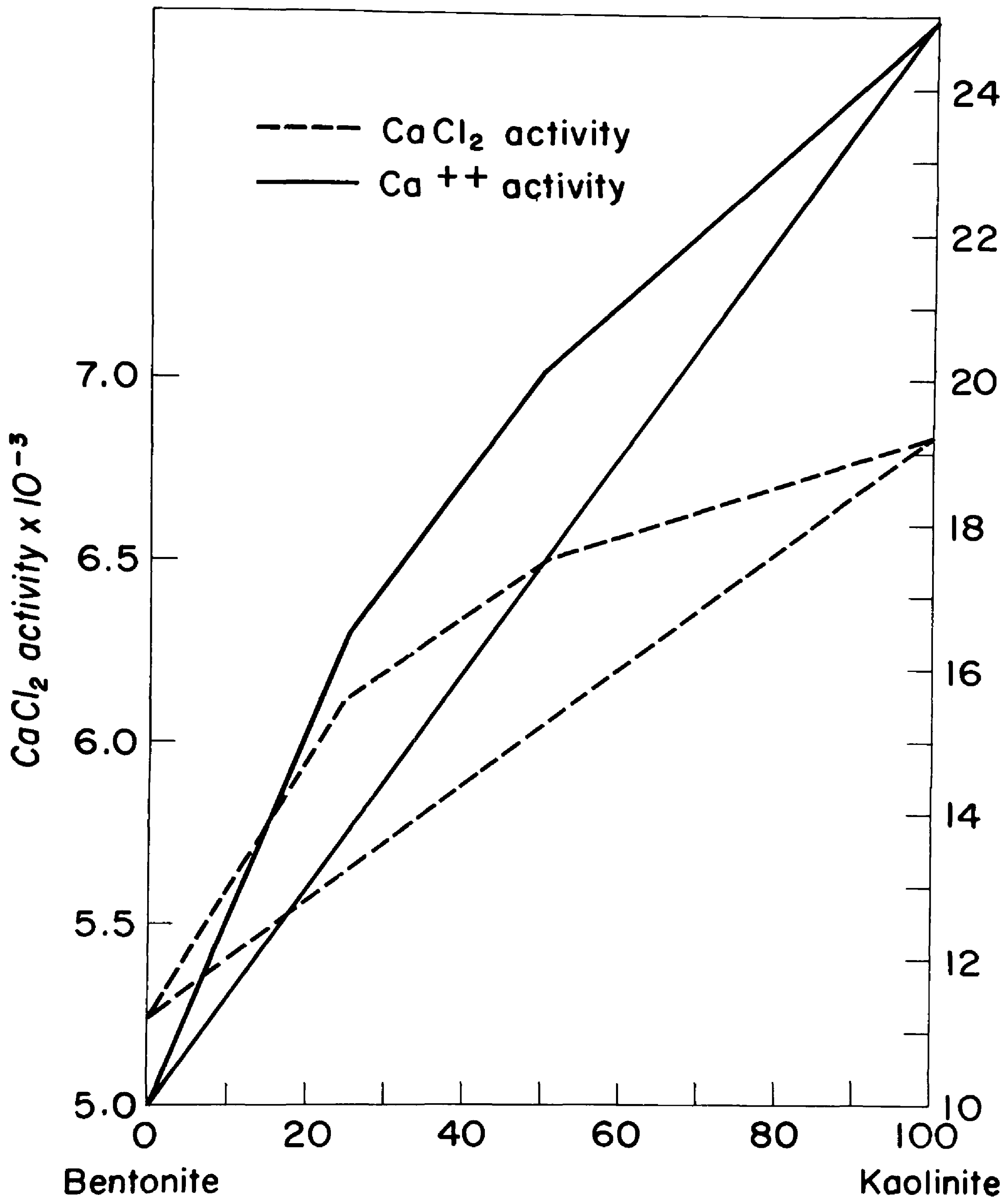

Figure 11. Dependence of calcium and calcium chloride activities on the clay composition of calcium saturated bentonite-kaolinite suspensions containing one symmetry concentration of potassium chloride.

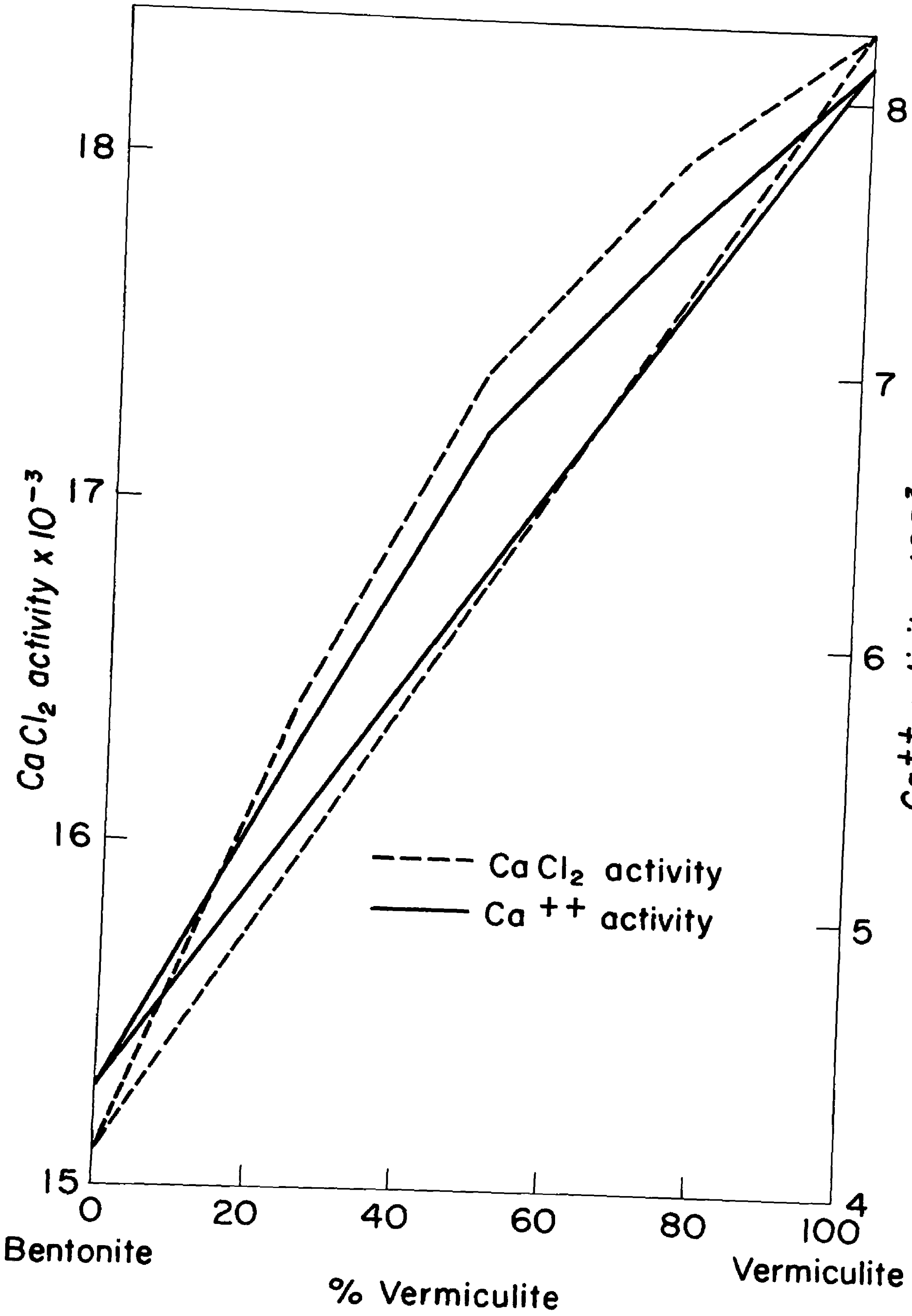

Figure 12. Dependence of calcium and calcium chloride activities on the clay composition of calcium saturated bentonite-vermiculite suspensions containing one symmetry concentration of potassium chloride.

CHAPTER X

DISCUSSION

Validity of the data obtained in this work depends on several factors. All data depend on the truly reversible character of the amalgam and silver-silver chloride electrodes. For the single ion activity measurements, not only is the reversibility of the amalgam and the silver-silver chloride electrode essential, but the liquid junction potential arising from the use of the reference calomel electrode must be negligible. Finally, the data must be of systems in equilibrium if they are to have any significance.

It is evident from the comparison of mean activity coefficients in Table I that the amalgam and the silver-silver chloride electrodes are reversible to calcium and chloride ions. The tertiary amalgam electrode has certain limitations. The amalgam electrode cannot be used to measure calcium activity for calcium ion concentrations much less than 0.001 moles per liter, and any cation other than calcium forming insoluble oxalates interferes with the proper functioning of the electrode.

There are certain barriers to demonstrating the significance of the single ion activity data. In the first place liquid junction potentials cannot be measured and secondly, the assumption of the equality of the potassium and chloride activities in potassium chloride solutions may not hold for concentrated solutions. An excellent discussion on the problem of the liquid junction potential arising from use of the calomel reference electrode in soil suspensions can be found in a paper by Coleman, et.al. (4), with a lengthy comment by Marshall at the end of the article. Coleman and his coworkers hold the view that the liquid junction potential may be as large as 300 millivolts in clay suspensions while Marshall favors the idea that for calomel electrodes, making contact with the suspension through a saturated potassium chloride salt bridge, the potential is negligible. The argument continues for obvious reasons; there is no proven method for measuring liquid junction potentials, and much of the argument is based on conjecture rather than experimental data. Unless a sound experimental method is devised for measuring the liquid junction potential this question will have to be left unanswered.

To assure activity measurements in equilibrated systems the clay suspensions were allowed to sit on the shelf for two weeks or more with intermittent shaking. Direct evidence for equilibrium in these systems was obtained by inserting a silver-silver chloride electrode in the sediment and another in the supernatant portion of a clay suspension that had been allowed to settle, and observing a zero emf between the two electrodes.

The experiment for measuring the relative affinities of the various cations for exchange sites needs little explanation. The wide differences in the replacing power of the various cations for calcium ions are obvious from the data. There is some uncertainty in all measurements carried out in systems containing magnesium ions. If the concentration of magnesium ions is too high, precipitation of magnesium oxalate is possible so that the activity values reflect not only calcium but also magnesium ions. Joseph (16) has shown that addition of as high as 0.024 moles of magnesium chloride per liter of solvent has no effect on the activity values of calcium chloride with the exception of course of the effect due to the ionic strength.

Davis (5), in a study very similar to the one presented here, added to a monoionic bentonite suspension increments of the corresponding chlorides and measured ion pair activities. By plotting the mean activity against the molality of the added chloride, he was able to show the relative affinities of several metals for the exchange sites on bentonite clays.

In one variety of bentonite the order was $Rb > Cs > K > Na > Li$, while for another bentonite, no definite trend could be observed. In the present study the relative affinities of cations for exchange site, measured by their ability to replace calcium, was found to be $Rb > Mg > K > Na > Li$. This was true for both clays. This order is in accord with general observations on the relative adsorbability of the various ions.

The activity values measured in the suspensions containing lithium ions may be in error. It was stated earlier that the amalgam electrode was incapable of measuring calcium ion activity in solutions of concentrations much less than 0.001 moles per liter. The activity values for the lithium systems indicate that the calcium ion concentration may have been below the critical level. If the values are in error then they are values which are probably too high, for values much higher than those observed would indicate that calcium ion concentrations were sufficiently high to allow proper functioning of the electrode..

Another point which may warrant examination is the relative difference of the replacing powers for calcium of the various cations between the two clays. The general trend is similar in both clays but potassium appears to have a replacing power for calcium more like rubidium and magnesium in bentonite than in the corresponding kaolinite suspensions.

Two features of the activity measurements in mixed clay systems are significant. First, the activity of calcium ions and calcium chloride are higher in pure kaolinite than in bentonite, while an opposite effect is noted for hydrogen and hydrochloric acid. Secondly, calcium and calcium chloride activities are not additive functions of the two clays in systems containing mixtures of clays.

The first phenomenon has been observed in the green house. Chu and Turk (3) showed that plants absorbed more calcium from kaolinite than bentonite when equivalent concentrations of the calcium clays were added to sand cultures. Here is an example of the failure of concentrations to give a true picture of nutrient availability. The acidic properties of hydrogen bentonite and kaolinite have been known for some time. Marshall (24) explains this difference on the basis of the nature of exchange sites on each of the two clay types. Exchange sites on kaolinite arise from broken bonds having weak acidic properties, whereas, montmorillonite (bentonite) particles possess negative charges arising from substitution in the lattice which when balanced by hydrogen ions dissociate to a greater degree. The salts of bentonite are less dissociated than kaolinite because the cations penetrate far into the lattice. This explanation fails when applied to the bentonite-vermiculite mixtures. Both bentonite and vermiculite are structurally alike and both derive their charges from lattice substitutions. The origin of the charges are different in these clays. For bentonite the charge originates from substitution in the octahedral layer while vermiculite has most of its charge from substitution in the tetrahedral layers. The origin of charge site may be an explanation for the wide difference in the measured activities between these two clays.

Comparison of figures 9 and 11 indicates that the exaltation of the calcium and calcium chloride activities is not due to aluminum. It is unlikely that free aluminum ions can be in the KCl system since the pH was near seven. The fact that the exaltation effect remains even in neutral suspensions suggests an interaction of the clay minerals. The difference in the hydrogen and calcium ion activities as shown in figure 13 has practical significance to the agronomist. It is the general recommendation to farmers in the Michigan area to maintain inorganic soils at approximately 70% calcium, 15% hydrogen, 10-15% magnesium and 1-2% potassium saturation, accompanied by trace amounts of the minor elements. On the basis of figure 11 it is evident that the ratio of the activities of the hydrogen to the square root of calcium ions varies with the kind of clay present in the soil. This is apparently one reason why nutrient recommendations vary from soil to soil.

Several possible explanations for the exaltation of the activities were considered. Error in the calculation of the cation exchange capacity, failure to use completely saturated clays, and negative adsorption of anions were considered as possible causes of this phenomenon. These factors may change the slope or the intercept of the ideal curve, but will not account for the deviation from it. It appear inescapable that there is an interaction between the two kinds of clays. The most plausible explanation seems to be the supposition that the total cation exchange capacity of the mixture is reduced when bentonite is mixed with kaolinite. Clays not only have cation exchange properties, but also possess some anion exchange capacities as well,

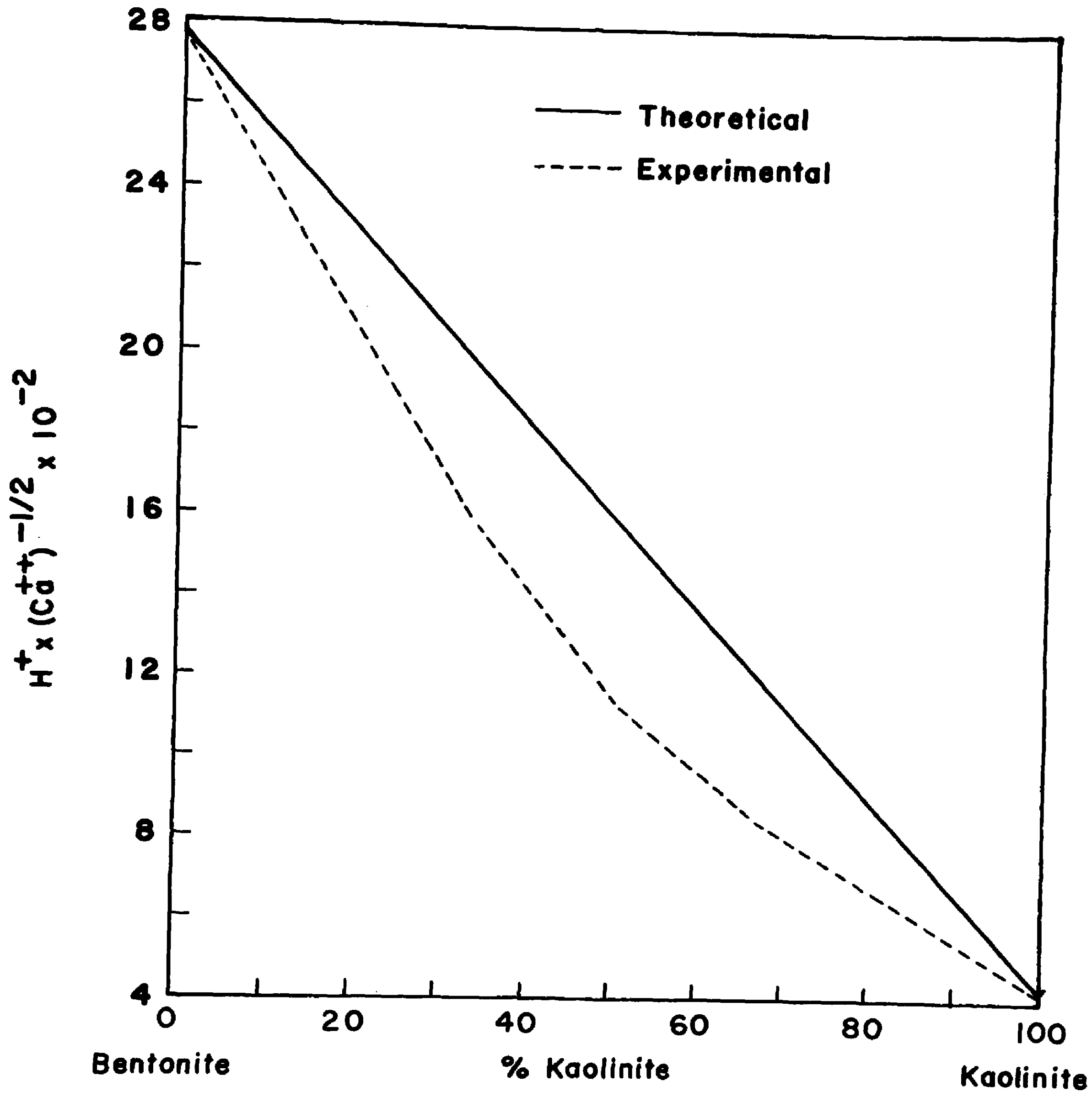

Figure 13. Dependence of the ratio of the hydrogen to the square root of the calcium ion activity on the clay composition of calcium saturated bentonite-kaolinite suspensions containing one symmetry concentration of hydrochloric acid.

with the latter property being greater in kaolinite than bentonite. When these two clays are mixed, the cation exchange sites of bentonite may be partially satisfied by the positive exchange sites of kaolinite resulting in a net decrease in the cation exchange capacity of the mixture. This same argument may be applied to the bentonite-vermiculite systems.

Activity studies in heterogeneous soil systems are hindered by the lack of suitable activity measuring devices. It is hoped that in the future durable instruments similar to the glass electrode will be developed so that activity measurements can be made on a routine basis. It is felt that the successful measure of available nutrients lies with the application of the activity concept to soil systems. The understanding of the chemical potential, and for heterogeneous systems, the electrochemical potential and the corresponding total activity is essential for intelligent interpretation of chemical data pertaining to nutrient uptake.

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APPENDIX

TABLE III

DEPENDENCE OF MEAN ACTIVITY OF CALCIUM CHLORIDE ON emf

emf in millivolts	conc.	mean ionic conc.	mean activity coefficient	mean activity
---	0.00100	0.00159	0.888*	0.00141
0.00	0.00200	0.00318	0.8523	0.00271
24.00	0.00400	0.00635	0.795	0.00505
38.00	0.00600	0.00952	0.762	0.00726
55.8	0.0100	0.0159	0.725	0.0115
80.1	0.0200	0.0318	0.618	0.0216
102.1	0.0400	0.0635	0.617	0.0392
115.55	0.0600	0.0952	0.569	0.0542
132.5	0.1000	0.159	0.531	0.0845

*Mean activity coefficient on the molality scale extracted from Prutton and Maron, "Fundamental Principles of Physical Chemistry," The MacMillan Company, New York, Revised edition, 1951, p. 478.

TABLE IV

DEPENDENCE OF CALCIUM AND CALCIUM CHLORIDE ACTIVITIES IN BENTONITE SUSPENSIONS ON THE ADDITION OF SYMMETRY CONCENTRATIONS OF CHLORIDE SALTS

	E - E	$A_{\pm}$ $CaCl_2$	$A_{\pm}^3 CaCl_2$	$\underline{F}ACe^-$	ACl^-	A^2Cl^-	$A+$
L_1	45.8	.00889	7026	68.5	.0283	.008004	.000877
Na	52.2	.0105	1158	68.5	.0283	.0008009	.00145
K	66.5	.0152	3512	68.5	.0283	.0008909	.00439
Rb	79.8	.0215	9938	68.7	.0281	.0007896	.0126
Mg	79.6	.0214	9800	68.9	.0279	.0007784	.0126
L_1	65.9	.0149	3308	51.8	.0550	.003025	.00109
Na	79.2	.0211	9394	51.8	.0550	.003025	.00311
K	87.2	.0261	1778	51.8	.0550	.003025	.00588
Rb	98.2	.0345	4106	51.8	.0550	.003025	.0136
Mg	97.9	.0342	4000	52.0	.0547	.002992	.0134
L_1	79.3	.0212	9528	42.2	.0810	.006561	.00145
Na	92.0	.0295	2567	42.2	.0810	.006561	.00391
K	98.7	.0350	4288	42.3	.0806	.006496	.00660
Rb	108.9	.0454	9358	42.4	.0803	.006448	.0145
Mg	108.7	.0452	9235	42.5	.0800	.006400	.0144

TABLE V

DEPENDENCE OF CALCIUM AND CALCIUM CHLORIDE ACTIVITIES IN KAOLINITE SUSPENSIONS ON THE ADDITION OF SYMMETRY CONCENTRATIONS OF CHLORIDE SALTS

	E - E	$A\pm\ CaCl_2$	$A\pm^3 CaCl_2$	$E\ a_{Cl^-}$	a_{Cl^-}	$a_{Cl^{-2}}$	$a_{Ca^{++}}$
L_1	15.9	.00410	6892	93.0	.0107	.0001145	.000602
Na	21.5	.00475	1072	93.0	.0107	1145	.000936
K	34.2	.00659	2862	93.0	.0107	1145	.00250
Rb	40.2	.00770	4565	93.2	.0106	1124	.00406
Mg	38.7	.00739	4036	93.8	.0103	1061	.00380
L_1	34.2	.00660	2875	76.8	.0204	.0004162	.000691
Na	42.2	.00810	5314	76.9	.0203	4121	.00129
K	54.8	.0112	1405	76.9	.0203	4121	.00341
Rb	60.0	.0128	2097	76.9	.0203	4121	.00509
Mg	59.0	.0125	1953	77.1	.0200	4000	.00488
L_1	45.4	.00880	6815	67.3	.0297	.0008821	.000773
Na	58.0	.0122	1816	67.3	.0297	8821	.00206
K	66.1	.0151	3443	67.2	.0298	8880	.00388
Rb	70.9	.0170	4913	67.4	.0296	8762	.00561
Mg	70.1	.0167	4657	67.8	.0292	8526	.00546

TABLE VI

DEPENDENCE OF CALCIUM, CALCIUM CHLORIDE, HYDROGEN AND HYDROCHLORIC ACID ACTIVITIES ON THE CLAY COMPOSITION OF CALCIUM SATURATED BENTONITE-KAOLINITE SUSPENSIONS CONTAINING ONE SYMMETRY CONCENTRATION OF HYDROCHLORIC ACID

Systems	$(E - E^*)$	$O_{\pm}CaCl_2$	$A_{\pm}^{3}CaCl_2$	$E\,^{a}Cl^{-}$	a_{Cl^-}	$a_{Cl^-}{}^2$	$a_{Ca^{++}}$	pH	a_{H^+}	$a_{H^+}/$	$a_{Ca^{++}}$
26.852 grams Kaol 0.000 gram Bent	-22.3	.00170	4913	109.6	.00543	.00002948	.00167	2.76	.00174	.00307	.0426
17.902 grams Kaol .333 gram Bent	-20.7	.00163	4331	108.6	.00565	3192	.00136	2.50	.00316	.00422	.0856
13.426 gram Kaol .500 gram Bent	-20.5	.00162	4252	107.5	.00590	3481	.00122	2.40	.00398	.00485	.114
8.951 gram Kaol .6667 gram Bent	-18.7	.00149	3308	106.9	.00604	3648	.000907	2.32	.00478	.00537	.159
0.0000 gram Kaol 1.0000 gram Bent	-11.5	.00127	2048	105.4	.00641	4109	.000498	2.2.	.00817	.00629	.277

TABLE VII

DEPENDENCE OF CALCIUM AND CALCIUM CHLORIDE ACTIVITIES ON THE CLAY COMPOSITION OF CALCIUM SATURATED BENTONITE-KAOLINITE SUSPENSIONS CONTAINING ONE SYMMETRY CONCENTRATION OF POTASSIUM CHLORIDE

Systems	(E - E*)	$A_\pm$ $CaCl_2$	$A_\pm^3 CaCl_2$	E a_{Cl}	a_{Cl}	a_{Cl}^2	$a_{Ca^{++}}$
1.6667 grams Bent 0.0000 grams Kaol	24.6	.00524	10^{-9}x143.9	90.2	.0119	.0001416	.00102
1.2500 grams Bent 11.9945 grams Kaol	31.2	.00612	2292	90.4	.0118	.0001392	.00165
0.8333 gram Bent 23.9900 grams Kaol	33.7	.00650	2746	90.6	.0117	.0001369	.00201
0.000 gram Bent 47.9784 gram Kaol	35.6	.00683	3186	91.4	.0113	.0001277	.00249

TABLE VIII

DEPENDENCE OF CALCIUM AND CALCIUM CHLORIDE ACTIVITIES ON THE CLAY COMPOSITION OF CALCIUM SATURATED BENTONITE-VERMICULITE SUSPENSIONS CONTAINING ONE SYMMETRY CONCENTRATION OF POTASSIUM CHLORIDE

Systems	$(E - E_o)$	$A_{\pm}$ $CaCl_2$	$A_{\pm}^3$ $CaCl_2$	Ea^-	a-	a_-^2	a+
4.000 grams Bent 0.000 grams Verm	66.4	0.0151	$3.442x10^{-6}$	68.7	.0281	.0007896	.00436
3.000 grams Bent 1.5055 grams Verm	69.0	0.0164	4.411	68.7	.0281	.0007896	.00559
2.000 grams Bent 3.0111 grams Verm	71.6	0.0174	5.268	68.9	.0279	.0007784	.00677
1.0000 grams Bent 4.5166 grams Verm	73.0	0.0180	5.832	68.9	.0279	.0007784	.00749
0.000 gram Bent 6.0222 grams Verm	73.8	0.0184	6.229	69.0	.077	.0007673	.00812