MULTIFUNCTIONAL IONIZATION AS ILLUSTRATED BY THE CLAY MINERALS[1]

By

C. E. MARSHALL

ABSTRACT

The electrochemical properties of clays are discussed under four rules which arise from considerations of the bonding energy of ions associated with charged surfaces. The mean free bonding energy of a cation associated with a negatively charged surface is determined by calculation from conventional potentiometric measurements with membrane electrodes.

The first three rules are concerned with the effects of valency upon ionization. They arise directly from the method of calculating cationic mean free bonding energies, applicable to monofunctional surfaces as regards Rule 3, and to polyfunctional surfaces also as regards Rules 1 and 2.

The fourth rule (Jarusov's rule) deals with mixtures of cations on polyfunctional surfaces. It may be expressed verbally by stating that the cation with the higher mean free bonding energy preempts those positions on the surface which manifest greater mean free bonding energy.

The incidence of each rule is examined, using data from studies of cationic activities in clay systems. The factors which cause deviations from these idealized rules are discussed. Graphical data are presented for Wyoming bentonite, Arizona bentonite (montmorillonite), and Putnam clay (montmorillonite group); illite, kaolinite and attapulgite.

INTRODUCTION

During the past twelve years our development of membrane electrodes has led to precise measurements of such quantities as pK, pNa, pCa, pMg (analogous to pH) in colloidal systems (Chatterjee and Marshall, 1950; Marshall and Ayers, 1946; Marshall and Bergman, 1942; Marshall and Krinbill, 1942). From these, using conventional assumptions, we have calculated the respective cationic activities at successive points on the titration curves of a number of colloidal clays. The ratio of the measured activity to the total amount of the given cation has been termed the fraction active (f). It corresponds to the ionic activity coefficient in a true solution. It was shown that the clay minerals gave, in general, small and very variable values of f, in contrast to colloidal electrolytes like agar for which the fractions active are of the order 0.8-1.0. In conventional terms, agar is a "strong" colloidal electrolyte, while the clays in their ionization are "weak." This type of terminology, however, can be highly misleading, since the clays, in many of their properties, behave quite

differently from weak electrolytes in true solution. The clays are mainly multifunctional in their ionization, as shown by the fact that during the course of a titration with base, the values of f for the added cation vary over a two- to five-fold range, up to the assumed equivalence point.

TYPES OF MULTIFUNCTIONAL BEHAVIOR

There are in colloidal systems two main causes of multifunctional behavior, which belong in separate categories although they frequently occur together. The first concerns the mechanism of ionization and the geometry of the ionic atmosphere. It shows itself through variations in the mean free bonding energy of the cation to the surface. The second concerns the site of ionization; crudely expressed, whether the surfaces under consideration are internal or external, freely or less freely accessible. This becomes manifest through Donnan effects and their consequences. The present paper concerns the former.

CALCULATION AND REPRESENTATION OF CATIONIC MEAN FREE BONDING ENERGIES

If the hypothetical condition of complete dissociation of the surface is taken as a standard state, then the mean free bonding energy of the cation to the surface can readily be calculated as follows (Marshall, 1949; 1950): Let a represent the measured cationic activity, c the total concentration of the given cation, f the fraction active $\left(= \dfrac{a}{c}\right)$ and $(\triangle F)$ the mean free bonding energy of the cation.

Then $(\triangle F) = R T \ln \dfrac{1}{f} = RT \ln \dfrac{c}{a}$ ————(1) Expressed in calories per mole at 25° C. $(\triangle F) = 1363 \log \dfrac{1}{f}$. Inspection of equation 1 shows that a tenfold change in the value of the fraction active f will increase or diminish $(\triangle F)$ by 1363 calories per mole; a twofold change by 410 calories per mole. A potential change of 1 millivolt corresponds to a change in $(\triangle F)$ of 23 calories. Under the experimental condition adopted here the measured potentials are believed reliable to 0.5 millivolts within a given series.

Bonding Energy Curves

From the activity measurements made at different points of a titration curve, the mean cationic free bonding energies can readily be calculated. Each represents the mean value for all the cation added up to that point. From these values it is possible to calculate, increment by increment, the bonding energy distribution for the whole titration curve. If the mean free bonding energy $(\triangle F)_a$ corresponds to a total addition of base a, and $(\triangle F)_b$ corresponds to a total addition b then we have $(\triangle F)_{b \cdot a} = \dfrac{b(\triangle F)_b - a (\triangle F)_a}{b - a}$, where $(\triangle F)_{b \cdot a}$ is the incremental bonding energy

for the interval $(b\text{-}a)$. By definition, the total mean free bonding energy is always positive in sign, but this is not necessarily true of the incremental free bonding energy. The reason is that two other variables are present in the system: H Clay + NaOH = Na Clay + H_2O; namely, the incremental energy change for the whole reaction and the incremental mean free bonding energy for the hydrogen ion as it disappears. The reaction will proceed in such a way that the total diminution in free energy is a maximum.

The full meaning of the bonding energy distribution curves probably cannot be extracted until calorimetric data of high precision can be combined with potentiometric determinations. However, the realization that the individual cationic activities must adjust themselves to the condition of minimum free energy for the system as a whole, helps to explain certain peculiarities which have shown themselves repeatedly in clay titration curves. It has frequently been found that small additions of base give not only higher fractions active but even higher cationic activities than somewhat larger quantities. This seems anomalous when the neutralization is thought of in terms of additions in true solution, but becomes comprehensible when the mean free bonding energy of the cation is considered as a function of that of the hydrogen ion as well as of the total free energy change.

In the following discussion we shall therefore use only the total mean free bonding energy curves for various cations to illustrate characteristic features of clay behavior.

As an example of the complex nature of bonding energy curves, titrations of electrodialysed Wyoming bentonite (montmorillonite, fraction $<0.2\mu$) may be considered (Fig. 1). The lowest curve is derived from sodium activity measurements on 1 percent clay. The middle curves give data for magnesium, calcium, and barium, and the upper one for hydrogen (this last curve from the calcium hydroxide titration of 1.0 percent clay). The bonding energy curves for the metallic cations resemble one another in many ways but that for the hydrogen is entirely different. Small amounts of hydrogen are held with very great bonding energies, although the values are not accurately determinable owing to uncertainty as to the total hydrogen. The curves for sodium and calcium both show a rather flat plateau from about 40 to 80 percent neutralization with base. Here intermediate degrees of saturation afford the highest mean free bonding energies. The contrast in mean free bonding energy for different parts or functions of the silicate surface is considerably enhanced by the use of the divalent cation calcium as compared with the monovalent cation sodium. The specific features of these cations show themselves in the fact that the bonding energies for magnesium, calcium, and barium differ considerably from one another.
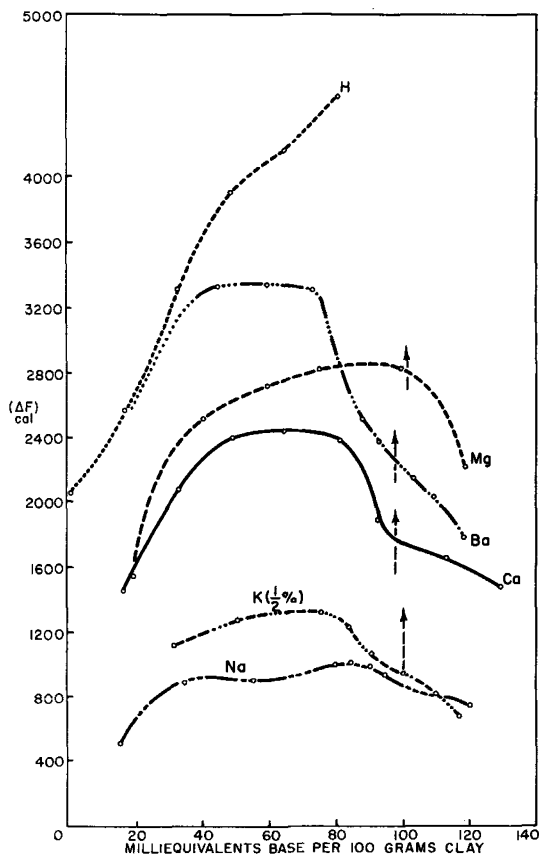
FIGURE 1. — Mean free bonding energies of various cations on Wyoming bentonite at increasing degrees of base saturation of the clay with the cations.

The secondary maximum in the sodium curve at about 85 percent neutralization is also noteworthy. It is much less evident in the cases of ammonium and potassium.

The hydrogen ion curve with its strong upward trend does not display any characteristic features which would enable one to separate different mechanisms of ionization. The early points may well be affected by a reaction such as Al clay $+ 3H^+ = Al^{3+} + H_3$ clay. Paver and Marshall (1930) pointed out that this reaction could proceed in steps by the progressive breaking of Si-O-Al linkages at exposed surfaces. However, although there is good evidence that electrodialysed clays are mixed hydrogen-aluminum clays, the dissociation of the aluminum from the clay surface must be small, since the aluminum has thus far not been determinable by membrane electrode methods. This might be expected

since, under Rule 1 below, a trivalent ion would give a very low fraction active.

GENERAL RULES FOR IONIZATION FOR SURFACES

Rule 1 (Marshall, 1950)

If the bonding energy per exchange site remains the same while the valency of the cation changes, then the fraction active for a polyvalent cation of valency n is obtained by taking that of the monovalent to the power n.

Proof for a monofunctional surface is readily obtained by dividing the one equation by the other.

$$(\Delta F) \text{ monovalent} = R\ T\ \ln \frac{1}{f \text{ monovalent}}$$

$$(\Delta F) \text{ polyvalent} = n(\Delta F) \text{ monovalent} = R\ T\ \ln \frac{1}{f \text{ polyvalent}}$$

Thus $n = \ln f$ polyvalent$/\ln f$ monovalent

or f polyvalent, $= (f \text{ monovalent})^n$

This general rule is extremely powerful in its consequences, since it sets the scale for valency in its effect on ionization. It is, of course, subject to modification by many factors. The study of departures from this rule may serve to throw light on the modifying factors themselves.

This valency rule applies also to multi-functional surfaces in the absence of disturbing factors.

The clay minerals in relation to rule 1. — From Figures 1-5 which give the bonding energy curves for montmorillonite, beidellite, illite, kaolinite, attapulgite, and Arizona bentonite (intermediate between montmorillonite and saponite), it can be seen that considerable differences are found amongst ions of the same valency. With monovalent cations the normal hydration series is usually followed, that is, sodium has a lower bonding energy than potassium owing to the greater hydration of the sodium ion. Divalent cations, however, show distinctly different orders for different clay minerals, kaolinite being distinguished for the consistent series $Mg > Ca > Ba$; and illite for the opposite sequence $Ba > Ca > Mg$. Montmorillonite and beidellite give curves which cross for these cations. Here the spread in bonding energies varies greatly according to the degree of saturation. The Putnam clay (beidellite) gives curves for the divalent cations which are close together and approximate twice the bonding energy of potassium, but the other clays are considerably farther from a close approximation to the 2:1 ratio in bonding energies.

The specific factors which belong recognizably to properties of ionizing Si_2O_3 surfaces are best seen before the sharp drop in bonding energy which usually starts at about 80 percent of equivalence. One would anticipate a considerable tendency for K and Ba to become fixed, thus raising their respective bonding energies. Barium shows this clearly for
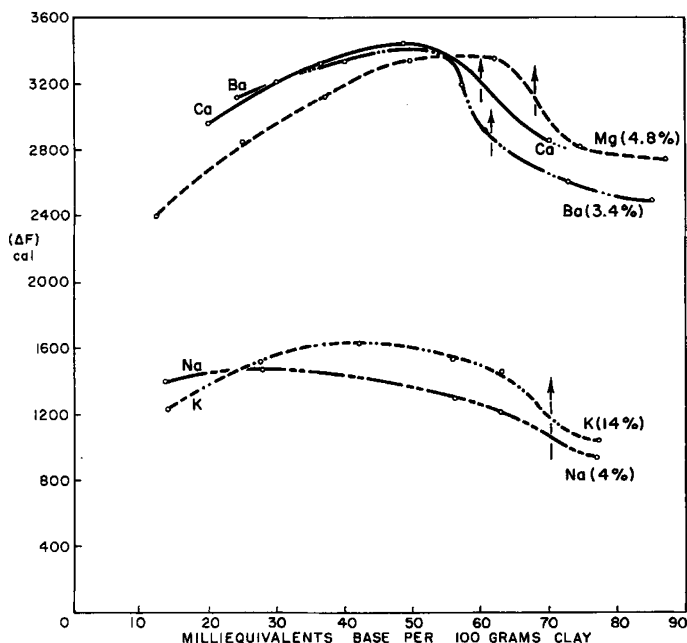
FIGURE 2. — Mean free bonding energies of various cations on beidellite (Putnam clay) at increasing degrees of base saturation of the clay with the cations.

illite and montmorillonite but not so evidently in Putnam clay. A charged lattice caused by atomic proxying thus seems to favor the order Ba>Ca> Mg for the bonding energies. On the other hand kaolinite, in which the exchange property is supposedly due to OH groups at the terminal edges of the sheets, shows a consistent order Mg>Ca>Ba. The other clays also tend to approach this same order beyond the equivalence point. This may be considered a manifestation of their own tendency to ionize at the edges of the sheets, where the mechanism would be essentially the same as in kaolinite. The occurrence of the order Mg>Ca>Ba was first commented upon by Mitra (1942) and by Mukherjee and others (1937) in their discussions of the pH titration curves of clays on the alkaline side. They suggest that the ion which forms the least soluble hydroxide is the most tightly held.

There is also a distinct difference in shape between the kaolinite curves for divalent cations and those of all the other clays. The montmorillonite group clays, the illites and the attapulgite all give flat maxima extending over a considerable range of cation amount, whereas kaolinite gives a very distinct peak which is displaced more to the right following the series Mg, Ca, Ba. A somewhat similar curve has been noted with an impure halloysite, using calcium as the cation. Thus although kaolinite
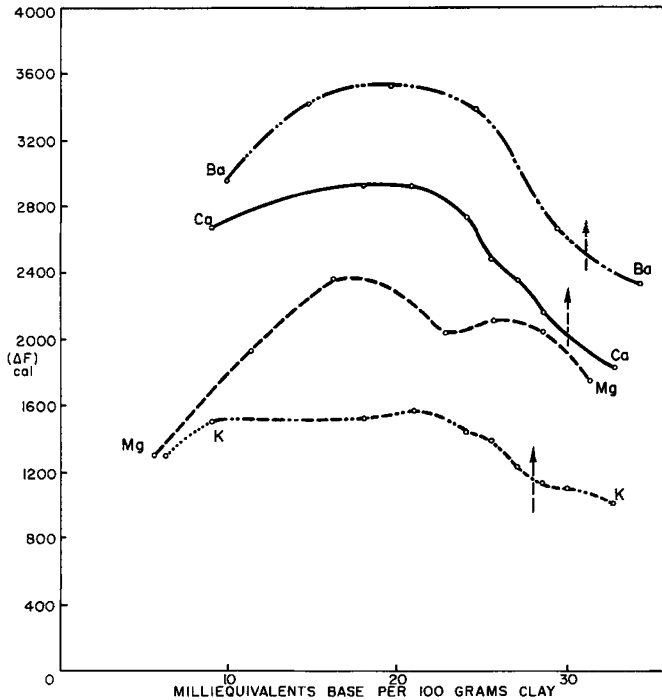
FIGURE 3. — Mean free bonding energies of various cations on illite at increasing degrees of base saturation with the cations.

shows a region of fairly high bonding energy for calcium it is of limited extent and is bounded on both sides by regions of much lower bonding energy. The very steep fall as equivalence is approached lies in the pH range 6-7 and corresponds to a smaller addition of base than is found for the monovalent cations.

Thus three features distinguish the kaolinite clays — the order of ionization for divalent cations, the shapes of the bonding energy curves with divalent cations, and the large shift in the inflection on the pH titration curves in going from monovalent to divalent cations.

Rule 2

Dissimilar ionizing surfaces show greater and greater disparity as the valency of the cation increases.

Consider two monofunctional surfaces with bonding energies $(\Delta F)_1$ and $(\Delta F)_2$ corresponding to fractions active f_1 and f_2 for monovalent cations. With a cation of valency n the bonding energies will be $n(\Delta F)_1$ and $n(\Delta F)_2$, and the respective fractions active $(f_1)^n$ and $(f_2)^n$. The ionization ratio which was f_1/f_2 for monovalent cations thus becomes
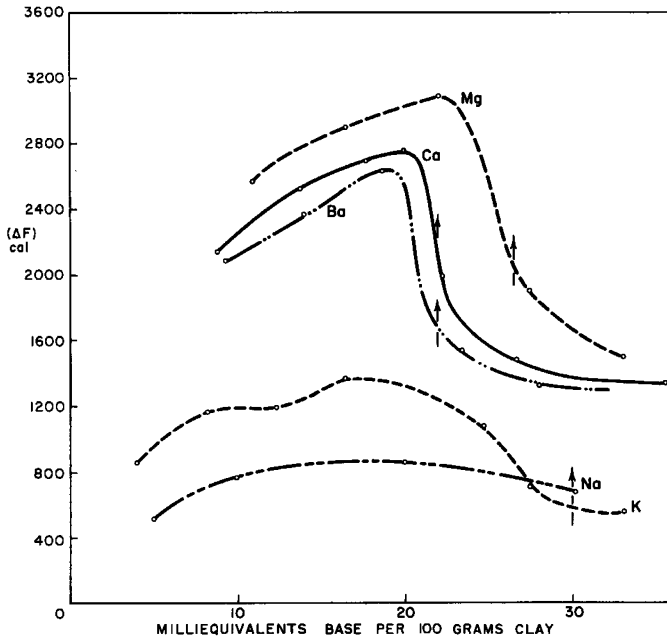
FIGURE 4. — Mean free bonding energies of various cations on kaolinite at increasing degrees of base saturation with the cations.

$(f_1/f_2)^n$ for the polyvalent. This rule, as a corollary of Rule 1, is subject to the same kind of modifying influences. It can be extended to multifunctional surfaces, provided the different sites for ionization operate independently of one another.

The clay minerals in relation to Rule 2. — The curves in Figures 1 to 5 afford some evidence of the operation of Rule 2 when attention is focussed on cations showing the minimum specific effects; for instance, sodium or potassium and calcium: but it is somewhat obscured by the fact that the clay concentrations used do not correspond to the same total cation concentrations. Figure 5, showing attapulgite and Arizona bentonite, illustrates this rule for two clays of highly contrasted character. The difference between the two calcium clays is considerably greater than twice the difference between the two potassium clays in the middle range, but at the equivalence point the expected relationship holds.

The most striking examples of the operation of this general rule are found using cations of valency higher than two. Precise activity measurements have not proved possible, but determinations of cataphoretic velocity have been made by Beavers and Marshall (1950). These reflect the general chemistry of reactive surfaces, although less directly than do activity measurements. It was shown that characteristic curves were
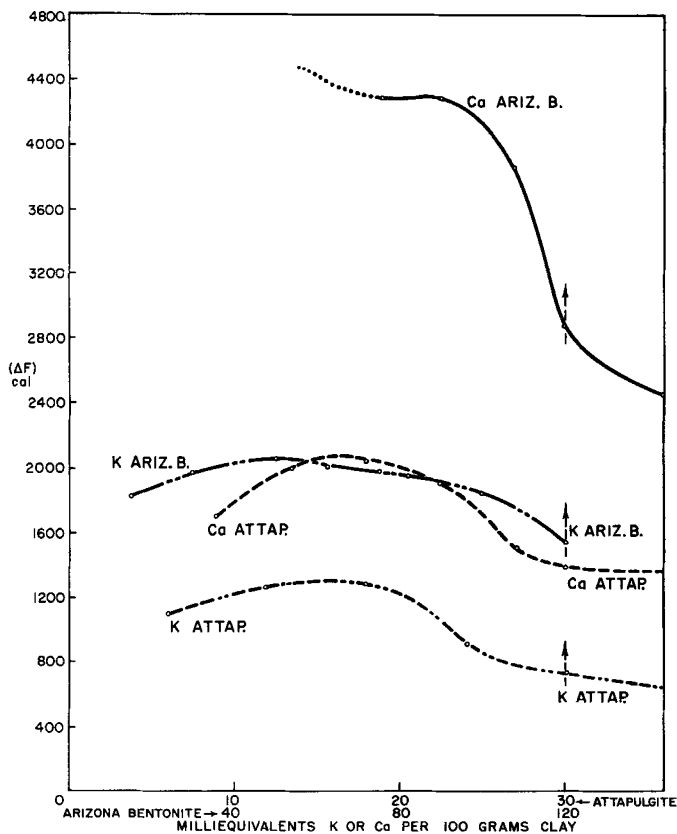
FIGURE 5. — Mean free bonding energies of various cations on attapulgite and Arizona bentonite at increasing degrees of base saturation with the cations.

obtained for the various clay minerals when cataphoretic velocity was plotted against the amount of the polyvalent cation added to the system. With cations of valency three and upwards the bonding energy must be great. Thus the exchange reaction of clay with salt proceeds almost to completion and as soon as the added salt begins to exceed the exchange capacity, one may, for practical purposes, assume that a clay saturated with the polyvalent cation is present. Owing to the insolubility of the hydroxides of metals such as thorium it was found advisable to arrange conditions so that the final mixtures of clay and salt were not alkaline.

Very significant differences were found when the amounts of lanthanum chloride, thorium chloride, and hexol chloride needed to reverse the sign of charge from negative to positive were determined. (Hexol chloride is a cobaltammine of formula $Co \left\{ {OH \atop OH} Co,(NH_3)_4 \right\}_3 Cl_6.$) These exceeded

somewhat the exchange capacities of the clays where reversal was prac-
ticable, but in numerous cases no reversal could be effected. With the
hexavalent hexol chloride all clays could be made positive except Wyoming
bentonite and Arizona bentonite; with thorium chloride, illite, halloysite,
kaolinite, and quartz could be rendered positive but not the two bentonites
or Putnam clay (beidellite); with lanthanum chloride reversal of charge
was found only with kaolinite and quartz. Procedures for the separation of
mixtures can be based on such differences.

It would seem that the detailed process by which silicate surfaces ionize
largely determines their behavior with highly polyvalent cations. Where a
charge exists on the inner alumina layer its dominance is so great that no
reversal of charge is found. A charge on the silica sheets which is due to
substitution of Al for Si falls into an intermediate category. It withstands
reversal by lanthanum but not by hexol. Finally an uncharged lattice like
that of kaolinite resembles quartz; the charge being reversed by lanthanum,
thorium, and hexol.

Rule 3

The monovalent cation/divalent cation activity ratios for dissimilar
surfaces should fall in the inverse order of the fractions active for mono-
valent cations (when comparisons are made at the same relative cation
concentrations).

For the two monofunctional surfaces I and II we have, ideally —

$$(f'_I)^2 = f''_I \quad \text{and} \quad (f'_{II})^2 = f''_{II}$$
$$\text{or } f'_I/f''_I = 1/f'_I \quad \text{and} \quad f'_{II}/f''_{II} = 1/f'_{II}$$

$$\text{or } \left(\frac{a'/c'}{a''/c''}\right)_I = 1/f'_I \quad \text{and} \quad \left(\frac{a'/c'}{a''/c''}\right)_{II} = 1/f'_{II}$$

Dividing the one equation by the other and arranging that
$$(c'/c'')_I = (c'/c'')_{II}$$
we find
$$(a'/a'')_I / (a'/a'')_{II} = f'_{II}/f'_I$$

Alternatively we may take each cation singly and set $c'_I = 2c''_I$ and
$c'_{II} = 2c''_{II}$, and arrive at the same result, since for each clay we then
have $a'/a'' = 2/f'$.

If we deal with monofunctional surfaces, the exchange sites of which
are so far separated as to have no mutual influence, then the above relation-
ship should hold true for mixed cationic systems. We shall see later, how-
ever, that a multifunctional character immediately implies a mutual in-
fluence in mixed systems.

This rule will therefore be shown to best advantage when the activity
ratios are calculated for homionic systems, for instance, with clays fully
saturated either with potassium or calcium.

The clay minerals in relation to Rule 3. — Taking homionic potassium and calcium clays at equivalence, the activity data obtained by Barber (1949) and Barber and Marshall (1952) illustrate Rule 3 very well. Table 1 gives the comparisons.

TABLE 1. — RELATIVE IONIZATION OF POTASSIUM AND CALCIUM CLAYS

Clay	Equivalence meq/100 g	Cation Conc. meq/liter	f_K	a_{Ca}/a_K
Kaolinite	2.75	2.75	0.309	0.220
Attapulgite	30	4.5	0.289	0.169
Bentonite (Wyo.)	100	5.0	0.202	0.140
Illite (Maq.)	22.5	11.25	0.155	0.150
Illite (Grund.)	28.5	13.75	0.145	0.087
Putnam (Beid.)	70	17.50	0.118	0.057
Bentonite (Ariz.)	120	18.0	0.079	0.049

It can readily be seen that the order of the fractions active for potassium (f_K) agrees with that of the activity ratio a_{Ca}/a_K except in one instance, that of Maquoketa illite which gives a higher activity ratio than corresponds to the f_K value. This may well be a manifestation of the tendency to fix potassium, which in smaller degree may also affect the values for other clays. In general also a_{Ca}/a_K is greater than $f_K/2$ whereas according to Rule 3 they should be equal.

When mixed calcium-potassium clays are employed and the activity ratios calculated, the agreement in the above order deteriorates. This shows the disturbing effect of Rule 4 (below) in addition to simple fixation effects. It can well be appreciated from Figure 6, in which the activity ratio a_K/a_{Ca} is plotted against the percentage saturation with potassium using potassium-calcium clays at 100 percent saturation with bases. The order is now kaolinite, attapulgite, illite, Putnam clay (beidellite), Wyoming bentonite, and Arizona bentonite. The extremes are still the same, but some intermediate members have shifted their positions as compared with the order shown in Table 1.

Rule 4. Jarusov's Rule.

For multifunctional systems containing more than one cation some new effects can be predicted, as was first pointed out by Jarusov (1937) on the basis of cation exchange data. Although Jarusov arrived at his formulation by a consideration of the nature of the ionic atmosphere for mixed systems, his general conclusions are identical with deductions made by more strictly thermodynamic methods. There is good justification, therefore, for attaching his name to this rule.

Consider for simplicity a bifunctional surface with two different cations simultaneously present. The system will naturally tend to assume the condition of minimum free energy. As far as the two cations are concerned, this is equivalent to stating that the sum of their mean free
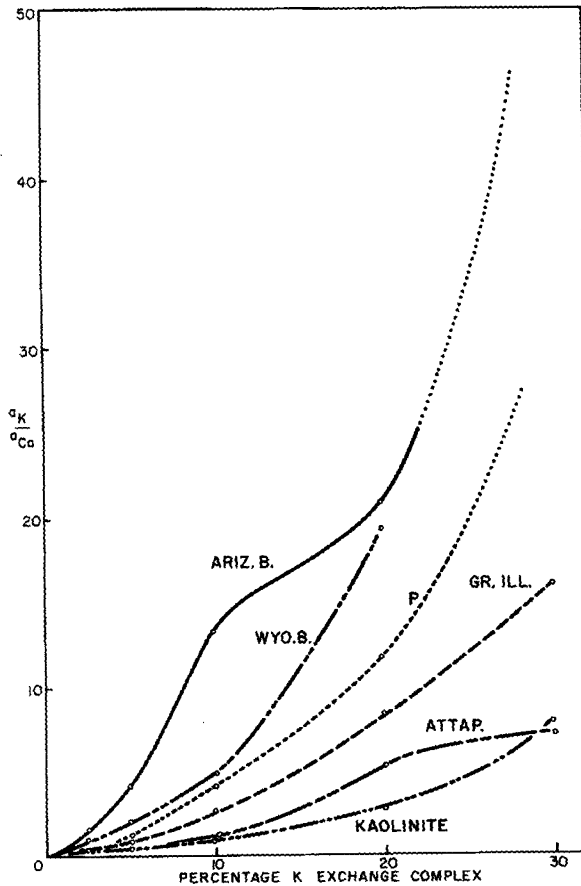
FIGURE 6. — Ratios of active potassium to active calcium for various clays saturated with different levels of potassium and calcium.

bonding energies should be a maximum. (Entropy differences between the different distributions of the cations amongst the possible sites are assumed to be small.) In a mixed system, for a given composition, this will be the case when the cation with the higher mean free bonding energy preempts those positions on the surface having the higher bonding energy. Thus the cation with the lower free bonding energy is forced to take those positions which normally liberate less energy. It is easy to take arithmetical examples of simple cases to illustrate this. Thus one cation affects the bonding energy and activity of another, not directly, but through the energy relationships of the ionizing sites on the surface and those in the ionic atmosphere. Where single cations are held with a wide range of bonding energies, the situation involving two or more cations whose

bonding energy curves overlap may become quite complex. The clay minerals afford many illustrations of these complexities, as was first shown by McLean and Marshall (1947). This kind of situation greatly affects the magnitudes of such ratios as a_K/a_{Ca} in mixed potassium-calcium systems, causing large departures from what might be anticipated from Rule 3 alone.

The effects predictable under Jarusov's rule can be clearly observed by using ions of the same valency; even those having relatively slight differences in bonding energy. The recent work of McLean (1950) with sodium and potassium on Putnam clay illustrates this. The effect of this rule is to magnify greatly the disparity in ionization of any pair of cations. *Thus it can be seen that in any problem involving the use of exchange surfaces to separate closely similar ions, multifunctional materials should have a great advantage over monofunctional.* In any actual exchange of ions, the Jenny and Ayers complementary ion effect (1939), which was deduced for monofunctional surfaces, would be superimposed upon the Jarusov effect.

In respect to Jarusov's rule the hydrogen ion, as in so many of its other properties, seems exceptional. As calculated from pH measurements its bonding energy is high, and it increases steadily as the inflection point on the pH curve is approached. Yet when it is compared with calcium in its effect on the bonding energy of potassium, in every case calcium behaves as though more firmly held than hydrogen. In consequence the bonding energy of potassium is less in potassium-calcium systems than in the corresponding potassium-hydrogen systems.

The clay minerals in relation to Jarusov's Rule. — The following systems have now been studied using membrane electrodes so as to obtain the activities of pairs of cations.

Wyoming bentonite	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Marshall and McLean, 1947).
	Potassium-hydrogen, magnesium-hydrogen and potassium-magnesium systems (McLean, 1949).
Arizona bentonite (montmorillonite-saponite)	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).
Putnam clay (beidellite)	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).
	Potassium-hydrogen, magnesium-hydrogen and potassium-magnesium systems (McLean, 1949).
	Potassium-hydrogen, sodium-hydrogen, potassium-calcium, sodium-calcium, and sodium-potassium systems (McLean, 1950).
Grundite illite	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).
	Potassium-hydrogen, magnesium-hydrogen and potassium-magnesium systems (McLean, 1949).

Maquoketa illite	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952). Potassium-hydrogen, magnesium-hydrogen and potassium-magnesium systems (McLean, 1949).
Kaolinite	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).
Halloysite (impure)	Potassium-hydrogen, magnesium-hydrogen and potassium-magnesium systems (McLean, 1949). Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).
Attapulgite	Potassium-hydrogen, calcium-hydrogen and potassium-calcium systems (Barber, 1949; Marshall and Barber, 1949; Barber and Marshall, 1952).

In a limited way certain tri-cationic systems have been investigated. For Wyoming bentonite these were potassium-calcium-hydrogen systems (Marshall and McLean, 1947). For Putnam clay they were potassium-calcium-hydrogen systems, sodium-potassium-hydrogen, and sodium-potassium-calcium systems (McLean, 1950).

Sodium-potassium relationships in Putnam clay. — The application of Jarusov's rule is least complex in cases where both cations have the same valency. Sodium and potassium differ relatively little in their bonding energies on Putnam clay, potassium being held up to 25 percent more strongly than sodium, although at equivalence the difference is only about 10 percent. When both are present together, however, the disparity becomes very great, as may readily be seen from Table 2. Here the sodium and potassium are compared when present singly and when together in equal amounts. In the mixed systems the bonding energy of potassium is about 30 percent higher than in the corresponding homionic systems. The reduction in bonding energy of the sodium is even greater. Thus in the mixed systems the bonding energy of sodium is, on the average, less than one-half that of the potassium. Evidently it is not possible to predict cationic activities in polyionic clays from data obtained only on homionic systems. The Jarusov effect is very powerful in its incidence. The data of Table 2 certainly indicate that multifunctional surfaces should be much better

TABLE 2. — BONDING ENERGIES (IN CALORIES PER MOLE) OF SODIUM AND POTASSIUM IN 4 PERCENT PUTNAM CLAY (BEIDELLITE) SUSPENSIONS
(Data by McLean, 1950)

Total saturation with bases, percent	$(\Delta F)_K$ in K system	$(\Delta F)_K$ in K-Na system	$(\Delta F)_{Na}$ in Na system	$(\Delta F)_{Na}$ in K-Na system
40	1508	2045	1480	847
60	1630	2190	1210	937
80	1530	1726	1350	902
100	1169	1695	1054	764

Note. In K-Na systems $C_{Na} = C_K$

adapted than monofunctional surfaces for the separation of mixtures of closely similar cations.

In terms of ionic activities, the difference between sodium and potassium in the mixed systems is large. At saturation, with 50 percent of each cation present, the activity of sodium is five times that of potassium; and the disparity is even greater at 40 and 60 percent total saturation. Thus the ionic atmosphere is dominated by sodium to a remarkable extent. However, when the proportion of potassium exceeds that of sodium this dominance becomes sharply reduced, since the mean bonding energy of sodium then rises.
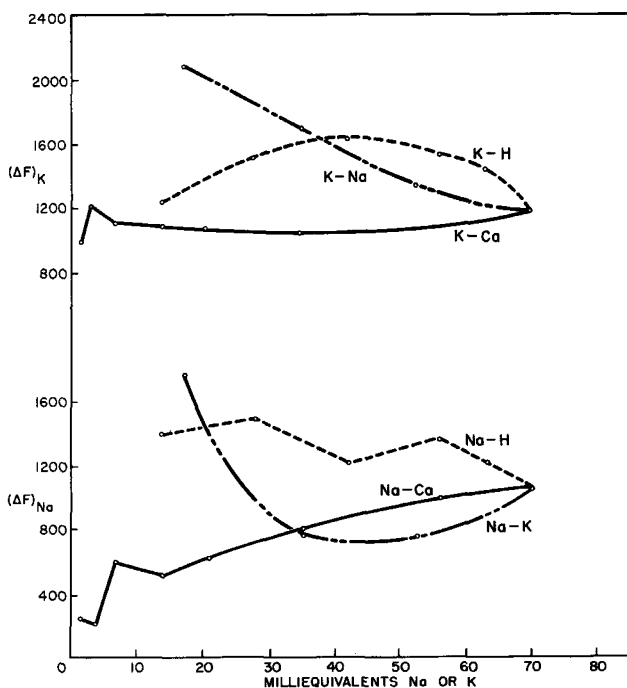

FIGURE 7. — Mean free bonding energies of potassium and of sodium at different degrees of saturation of 4 percent Putnam clay with potassium and sodium in the presence of various complementary cations.

The great influence which amount and kind of the accompanying or complementary ion has upon the bonding energy of a given ion can be appreciated from Figure 7, drawn from the data of McLean (1950). Here the bonding energies for different degrees of saturation of 4 percent Putnam clay with potassium and with sodium are compared for three complementary cations. The potassium-sodium and potassium-calcium curves show the expected relationship, namely that potassium is less firmly

held when calcium is the accompanying ion than when sodium is the accompanying ion. Calcium is always more firmly held than sodium or hydrogen. Very peculiar relationships seem to exist in the potassium-hydrogen system. From the fact that potassium is held less firmly in K-Ca systems than in K-H systems, it would be concluded that calcium is more firmly bound to the clay than hydrogen. On comparing the K-H and K-Na systems whose curves cross, application of Jarusov's rule would suggest that above 50 percent saturation with potassium, sodium is held more firmly than hydrogen, but that up to this point the reverse is true. However, when the bonding energies of sodium and hydrogen in these systems are taken from activity measurements, no region can be found in which the bonding energy of sodium even approaches that of hydrogen.

Monovalent-Divalent Cation Relationships

In the work of Marshall and McLean (1947), Barber and Marshall (1952), and Marshall and Barber (1949) data on potassium-calcium relationships in a number of clay minerals have been presented. The simplest case encountered was that of Wyoming bentonite which, in the fraction employed, is a pure montmorillonite having a predominant charge on the inner alumina layer. Its ionization is relatively high. The effect of calcium on the bonding energy of potassium is a well-marked reduction (Fig. 8). This feature is displayed by all the clay minerals we have examined. The effect of potassium on the bonding energy of calcium is to cause a very great increase (Fig. 8). In fact, the activity of calcium became so low below 60 percent saturation with calcium that it could not be measured. A similar result was obtained by McLean, using magnesium-potassium bentonite. Here the magnesium activity became too small for measurement below 90 percent saturation. This relative situation as between calcium and magnesium is in line with their bonding energies when present alone. Magnesium is held on montmorillonite with considerably greater bonding energy than is calcium, as was shown by Chatterjee and Marshall (1950).

Other minerals of the montmorillonite group show distinctly different behavior. Potassium-calcium studies have been made both on Putnam clay (beidellite) and on an Arizona bentonite, which, from its chemical composition, lies between a typical montmorillonite and a typical saponite. Its exchange capacity is very high (120 meq per 100 g), but its ionization is very low. The bonding energies both for monovalent and for divalent cations are the highest we have so far encountered. The charge on the lattice is found both on the inner Al layer and on the outer Si layers (Barber and Marshall, 1952).

This Arizona bentonite resembles Wyoming bentonite in the general course of the bonding energy curves for potassium (Fig. 9) but the relative change with varying amounts of potassium is different. At full saturation the bonding energies for potassium are about 900 calories for Wyoming bentonite and about 1500 for Arizona bentonite. With 2-2½
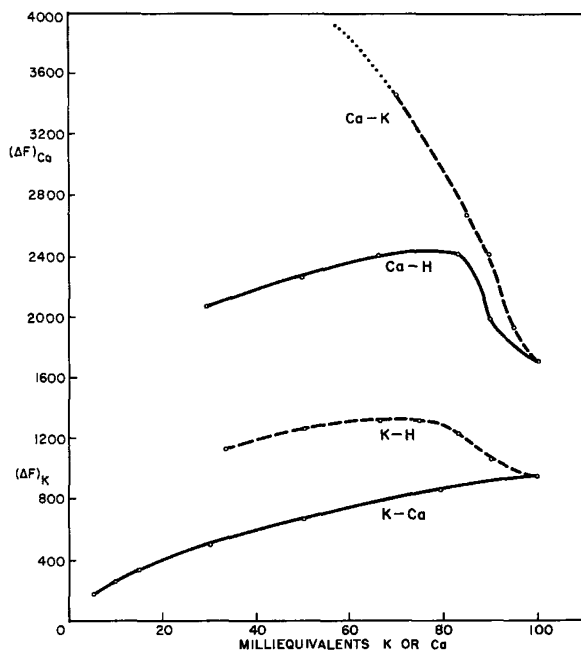
FIGURE 8. — Mean free bonding energies of calcium and of potassium at increasing levels of the respective cations on Wyoming bentonite with potassium, calcium, and hydrogen as the accompanying cations.

percent potassium present (the rest being calcium) the respective bonding energies are 200 and 1000 calories. Both relatively and absolutely the Wyoming bentonite shows the greater decrease.

In its calcium relationships, however, the Arizona bentonite bears little resemblance to Wyoming bentonite (Fig. 9). The calcium-hydrogen curve now lies above the calcium-potassium curve between 65 percent and full saturation, but below 65 percent the curves cross. A similar behavior has been found in the case of Putnam clay, illite, attapulgite and kaolinite. Thus only at the lower degrees of saturation is the bonding energy of calcium in the calcium-potassium system greater than that in the·calcium-hydrogen system. Consequently, in these clays application of the Jarusov rule implies that over part of the range, potassium is held more firmly than hydrogen.

Specific Factors Incident Upon Rules 1-4

This is not the place to take up all the peculiarities found in mixed cationic systems. Sufficient data have been given to show that Jarusov's rule is of very great importance. The more accentuated is the multifunctional character, the more this rule, through the energy relationships of the surface, dominates the conditions of ionization.
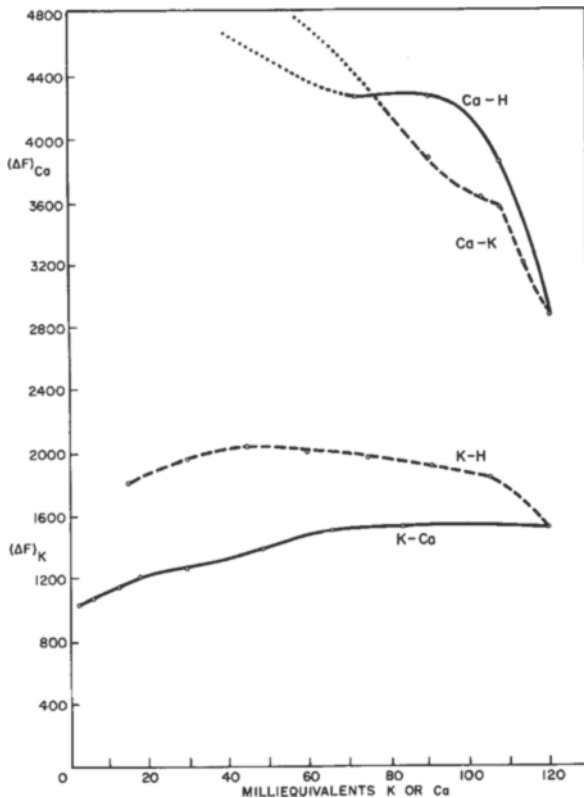
FIGURE 9. — Mean free bonding energies of calcium and of potassium at increasing levels of the respective cations on Arizona bentonite with potassium, calcium and hydrogen as the accompanying cations.

At the same time the factors which cause deviations from the ideal behavior according to Rules 1, 2, and 3, and which affect also the quantitative aspects of Rule 4, can now be seen. They are:

(1) *The specific properties of polyvalent cations with respect to surfaces containing hydroxyl groups.* — In the case of divalent cations, kaolinite gives the consistent bonding energy sequence $Mg > Ca > Ba$. Other clays tend to this order near the equivalence point and beyond it. A crossing of the bonding energy curves at about 80 percent of equivalence is found in these clays.

(2) *The ease with which cations of suitable size take up positions in the exposed Si_2O_3 layers, corresponding to the potassium sites in micas.* — These are fixation effects. It has been shown that barium and ammonium in addition to potassium are prone to take up such positions. The very high bonding energy of barium on illite may well be a manifestation of this.

Another interesting effect which may perhaps fall into a similar category is found with potassium in calcium-potassium and sometimes in hydrogen-potassium systems, in which the potassium is present only in small amounts. Figure 10 illustrates this for Putnam clay. Up to about 10 percent saturation with K, the following clays all show higher bonding energy than for larger amounts: two illites, Putnam clay, attapulgite and impure halloysite (Barber and Marshall, 1952). The illites, Putnam clay and attapulgite all show a predominant charge in the Si_2O_3 layers. Further work is needed on halloysite in order to determine whether the effect found is inherent or due to impurities.

(3) *The peculiar properties of hydrogen ions associated with clay surfaces.* — The actual bonding energy of hydrogen cannot be satisfac-
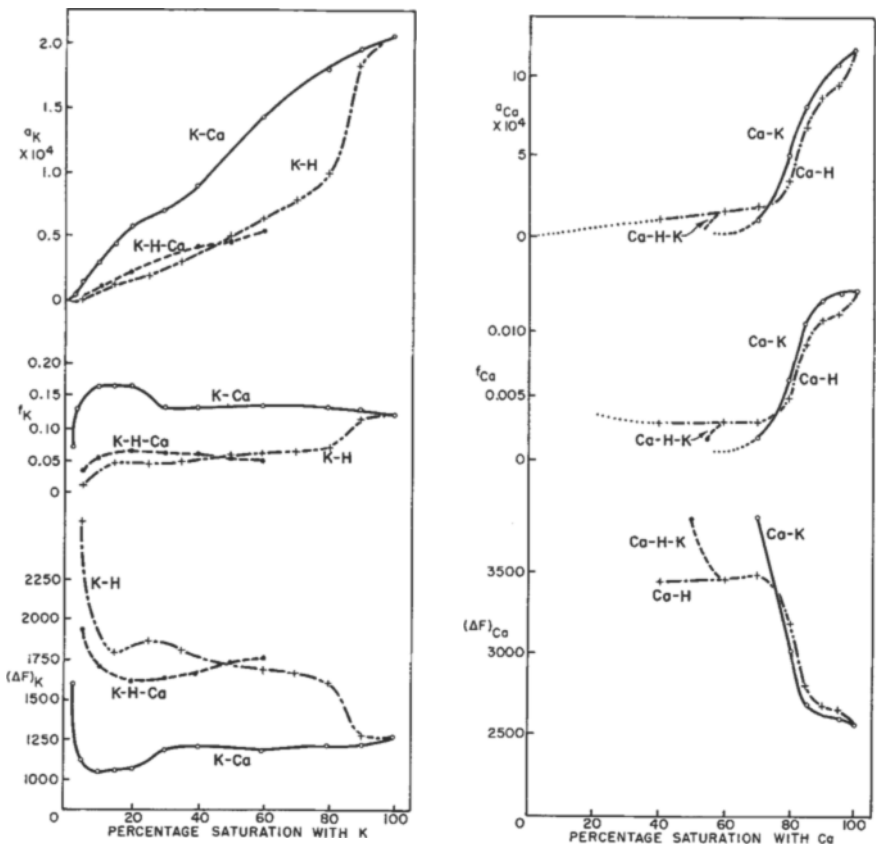

FIGURE 10. — Activities, fraction active, and mean free bonding energies of potassium and of calcium on Putnam clay at increasing degrees of saturation of the clay in the presence of calcium, potassium, and hydrogen as accompanying cations.

torily determined. The decomposition of acid clays in releasing aluminum tends naturally to reduce the apparent strength of the clays as acids; that is, bonding energies calculated from pH values tend to be too high in the most acid range. Secondly, the point of equivalence as determined by the inflection point on the pH curve does not represent the conclusion of the neutralization process. Hence the calculated bonding energy is less than the real value, the discrepancy being smallest at early points on the titration curve but very large near the point of equivalence. These two effects thus act in opposition; and whether there exists a middle region, say from pH 5 to pH 6 in which neither is highly important, is a matter which future research should clarify. Thus, the application of Jarusov's rule is rendered uncertain.

(4) *Consequences of interpenetration of ionic atmospheres.* — The theories of interparticle forces in colloidal sols reviewed and discussed by Verwey and Overbeek (1948) take into account the osmotic properties of the counter ions. The work done in moving a given ion from its mean environment in a colloidal system to any standard solution is readily calculated from the activity measurements. It will naturally vary according to the environment of the ion. Thus activity measurements and calculations of bonding energies may serve to throw some light on interparticle relationships, especially those which change with changing concentration of the colloidal particles. Variation of the fraction active and of the mean free bonding energy with concentration is commonly well marked in clay systems (Marshall and Bergman, 1942; Marshall and Krinbill, 1942). Discussion of these variations will probably center around this general topic of the interpenetration of ionic atmospheres, although very little has yet been attempted.

SUMMARY

The electrochemical properties of clays are discussed under four rules which arise from considerations of the bonding energy of ions associated with charged surfaces. The mean free bonding energy of a cation associated with a negatively charged surface is determined by calculation from conventional potentiometric measurements with membrane electrodes.

The first three rules are concerned with the effects of valency upon ionization. They arise directly from the method of calculating cationic mean free bonding energies, applicable to monofunctional surfaces as regards Rule 3, and to polyfunctional surfaces also as regards Rules 1 and 2.

The fourth rule (Jarusov's rule) deals with mixtures of cations on polyfunctional surfaces. It may be expressed verbally by stating that the cation with the higher mean free bonding energy preempts those surface positions which manifest greater mean free bonding energy.

The incidence of each rule is examined, using data from studies of cationic activities in clay systems. The factors which cause deviations from

these idealized rules are discussed. Graphical data are presented for Wyoming bentonite, Arizona bentonite (montmorillonite), and Putnam clay (montmorillonite group) ; illite, kaolinite, and attapulgite.

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DISCUSSION

George T. Kerr. — In titrating acid clays with bases does not a drifting end point cause some difficulties? That is, is not time an important factor in reaching the endpoint?

C. E. Marshall. — The titrations are run discontinuously over a 24-hour period. It is true that pH measurement is affected by time, but sodium and calcium ionic free energies are not as dependent upon time.

D. R. Lewis. — What is the significance of the variation of the equivalence point with neutralizing ion?

C. E. Marshall. — The variation in equivalence point with neutralizing ion shows the effect of what the Indian soil scientists term the "irregular ion effect." This goes in the order Mg-Ca-Ba whereas the normal effect is Ba-Ca-Mg. They ascribe this to the primary adsorption of hydroxyl and formation of surface hydroxide.

W. J. Weiss. — In the Ca-K system studies is it correct that the studies were at 100 percent saturation, i.e., no residual H^+ was present on the clay surfaces?

W. L. Hall. — Have you carried your measurements past the equivalence point which I presume represents the base exchange capacity at a pH of 7.0?

I had specifically in mind the measurements of Ca^{2+} and K^+ activities in the Ca-K system. Do they become equivalent when the titrations are carried to a point that represents the additional contribution of the clays' hydroxyl groups?

C. E. Marshall (reply to W.J.W. and W.L.H.). — The point chosen for equivalence corresponded for each clay to the inflection on the pH titration curve with KOH. Thus the pH was somewhat above 8 and varied a little according to the clay used. We have not examined the relationships for more alkaline systems.