

# ION EXCHANGE REACTIONS OF CLAYS \*

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## ABSTRACT

It has been recognized for many years that many aspects of clay technology including soil treatment and drilling mud treatment must remain in an essentially empirical state until a basis for the understanding of ion exchange reactions is established.

Much of the work on ion exchange reactions of clays in the past has been directed toward establishing total exchange capacities or determining the ionic distribution empirically. This information in general is not suitable for the evaluation of hypotheses designed to provide a basis for understanding the exchange reaction. When the techniques for characterizing the various clay minerals offered the possibility of quantitative study, the solution and exchanger phase contributions to the ionic distribution could be experimentally evaluated in principle. The particular experimental techniques which have been used to measure ionic distribution, however, frequently neglected observations which are essential if the data are to be used for testing and developing theories of ion exchange. It is now well recognized that molecular adsorption, complex ion formation in solution, and ion-pair formation between a mobile solution ion and a fixed exchanger group may occur in addition to the ion exchange reaction. Therefore, if the data are to be useful to develop theories of ion exchange, the whole system must be selected to minimize such extraneous contributions. On the basis of recent theoretical work, various experimental techniques are evaluated from the point of view of their suitability for equilibrium ion distribution studies.

The mass action, adsorption isotherm, and Gibbs-Donnan equilibrium formulations of the ion exchange theory are discussed as they may apply to clay systems. Recent progress is summarized in (1) solution thermodynamics of mixed electrolytes as it is relevant to ion exchange processes of clays, (2) the contributions of non-ideality of the clay exchanger phase, and (3) the work of swelling of clays which affects the ionic distributions in ion exchange reactions.

It is concluded that the parameters which relate to the solid phase of the exchanger and those which relate to the solution are now sufficiently well recognized that future experiments can be planned which may more realistically provide an experimental basis for understanding the process of equilibrium ion exchange distributions in aqueous clay-electrolyte systems.

## INTRODUCTION

In principle, all of the answers to questions involving the interaction of matter are calculable from relatively few basic concepts. In this sense, it has been pointed out that all of Chemistry is now reducible to applied mathematics. It appears unlikely, however, that the entirely theoretical computations will soon displace the experimental aspects of chemistry.

At the other extreme, experimental work which is without the guidance offered by a coherent body of theory frequently lacks the integration and direction necessary to achieve useful results. The experimental work concerned with the distribution of ions that will be reached when a clay mineral is placed in a solution of electrolytes originally was without such a guide, and only quite recently has there been any adequate theoretical body on which experimental studies might be planned. There have been some excellent systematic experimental studies which are outstanding examples of intelligently planned work (Schachtschabel, no date; Wiklander, 1950), but the colloidal nature of the clays and the great number of variations provided by the different members of each of the major clay mineral groups add many complexities which must be separated and

measured if the results of the experiments are to be useful for any system other than the specific one which has been investigated.

Accordingly, this discussion of the basis of ion exchange behavior will exclude non-exchange phenomena. We will define an ion exchange reaction as a thermodynamically reversible interaction between the ions originally occupying a fixed number of reacting sites of the insoluble exchanger with the several ionic species in the solution. This definition eliminates from this discussion such interesting and important topics as the irreversible fixation of ions such as potassium (Wicklander, 1950), ammonium (Barshad, 1951; Joffe and Levine, 1947), zinc (Elgabaly, 1950; Elgabaly and Jenny, 1943), and lithium (Hoffmann and Klemen, 1950). Neither will this discussion concern itself with reactions resulting in covalent bonds between certain clays and hydrogen, or with molecular adsorption from solution. By restricting our discussion to the clays, moreover, we have eliminated discussion of the reactions of the organic ion exchangers and of the inorganic zeolites.

The early history of ion exchange studies starting with the systematic studies by Thompson and Way a century ago has recently been summarized by Deuel and Hostettler (1950), Duncan and Lister (1948), Kelley (1948), and Kunin and Myers (1950).

When a clay mineral is placed in a solution containing several dissolved salts, the whole assembly will in time reach a steady-state condition of ionic distribution between the clay and the solution which will persist for a very long period of time. It is important to know how this equilibrium distribution depends upon the nature of the exchanger and its physical condition and how it depends on the nature of the solution. In general, however, it is to be expected that a variety of processes, including the ion exchange reaction itself, may determine this distribution. Such processes as molecular adsorption, formation of complex solution ions, formation of difficultly soluble salts, or formation of complexes with the exchanger phase may be superimposed on the ion exchange reaction itself in a given system. (Bonner, Argersinger, and Davidson, 1952). In the present discussion of the ion exchange reaction, attention will be directed toward those systems in which the distribution of ions arises primarily from the ion exchange reaction itself.

## ION EXCHANGE PROPERTIES OF THE CLAY MINERAL GROUPS

It is convenient to consider clays as multivalent poly-electrolytes in ion exchange reactions. For each of the major crystal structure groups, however, it is important to take into consideration the effect of the distribution of charges in the lattice. The relationship between crystalline structure of the silicate minerals and their ion-exchanging properties have been discussed in considerable detail by Bagechi (1949).

*Kaolin Group.* Many members of the kaolin group of clay minerals exhibit an almost complete freedom from

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isomorphous substitution yet have a small but definite ion exchange capacity. The sites of the exchange reactivity of kaolinite are generally agreed to be associated with the structural OH groups on the exposed clay surfaces. Because of the differences in the balance of electrical charges of those hydroxyl ions along the lateral surfaces and those formed by the hydration of silica at the broken edges of the crystals, there may well be more than one class of exchange sites on kaolinite. This picture of the exchange activity arising from the dissociation of the surface hydroxyl protons is consistent with the low magnitude of the total exchange capacities of minerals of this group.

*Attapulgite Group.* The fibrous clay group typified by attapulgite exhibits a very different geometry from the platy minerals and, accordingly, a different distribution of the charges on the surface ions. In attapulgite itself a small amount of the silicon is frequently replaced by aluminum ions which give rise to the charge deficiency causing the ion exchange activity of attapulgite (Marshall, 1949). Because of its fibrous structure and the presence of channels parallel to the long axis of the crystals in which many of the mobile exchange ions are found, the rate of the ion exchange reaction in attapulgite minerals may be much slower than in platy minerals. This would be expected if the ions along the channel must diffuse into the solution phase to reach an equilibrium.

*Illite Group.* The illite group of clay minerals are small particle size, plate-shaped clay minerals distinguished by their ability to fix potassium irreversibly. The ion exchange activity for the illites is attributed to isomorphous substitution occurring largely in the surface tetrahedral silica layers. This gives rise both to more favorable geometric configuration for microscopic counter-balancing of the unbalance in electrical charge and also to the possibility of formation of co-valent linkages. Either condition is likely to produce an irreversible reaction.

*Montmorillonite Group.* The most active clay group in terms of amount of ion exchange reactivity per unit weight of clay is the montmorillonite family. The high degree of their base exchange capacity and the rapidity of their reactions have long been recognized as outstanding attributes of this class of clay minerals. Minerals of this group are plate shaped, three-layer lattice minerals with a very high degree of isomorphous substitution, distributed both in the octahedral positions in which chiefly magnesium substitutes for aluminum, and in the tetrahedral coordination in which predominantly aluminum substitutes for silicon (Harry, 1950; Hendricks, 1945; Ross and Hendricks, 1945). Because of both the large base-exchange capacity and the widespread occurrence and economic importance of this group of minerals, a great deal of the experimental work has been done (Hauser, 1951).

As there are these marked differences in the structure both geometrically and in electrical charge density of the principal groups of clay minerals, there will be large variations in the relative contributions of reversible ion exchange reactions, the degree of amphoteric nature of the clay minerals and physical adsorption to the equi-

librium distribution of ions in an aqueous clay-electrolyte system.

#### EXPERIMENTAL TECHNIQUES

*Methods of Preparing Hydrogen-Clay.* Although this discussion is more directly concerned with the interpretation of the data having to do with ion exchange properties of clays than with the determination of the exchange properties themselves, the usefulness of the data is frequently affected considerably by the exact details of the method of determination of the exchange properties, and, accordingly, some attention must be given to the limitations of various techniques. One group of techniques which are commonly employed involves the preparation of the hydrogen form of the clay either by dialysis or electrodialysis or by direct action of a solution of a mineral acid. The acid form of the clay is then treated with the base of the desired salt form and the equilibrium distribution determined from the degree of conversion (often measured by the change in pH of the suspension system), or the inflection in the titration curve is used to determine the total exchange capacity. The difficulties of interpretation of the titration curves of acid clays by either inorganic or organic bases are widely recognized (Marshall, 1949; Mitra and Rajagopalan, 1948; 1948a; Mukherjee and Mitra, 1946). In the first place, there is no general agreement about the nature of the exchange titration curve. The results of various researchers have varied from the production of definitely diprotic (Slabaugh and Culbertson, 1951) character in the titration curves to curves which have a very broad inflection or none at all and in which the establishment of an end-point corresponding to the completion of a reaction is very difficult even to estimate. Some investigators have titrated to an arbitrary pH which they considered to be an end-point for the reaction, assuming that the distribution of proton activity of all the clays in the samples being titrated is the same, and that legitimate and reproducible conditions for measuring cell potentials in suspension are established in each suspension. The colloidal nature of the system complicates both the measurement of potentials and the interpretation of the potentials in terms of hydrogen ion activities (Mysels, 1951). Moreover, the anomalous behavior of the hydrogen ion in its reactions with clays has long been known, and recently the behavior of hydrogen ions in ion exchange reactions of clays has been found to exhibit a pattern that suggests that these ions are held to many clays partly by covalent bonds (Krishnamoorthy and Overstreet, 1950, 1950b). It is likely that studies of the equilibrium distribution ions on clays should not involve the preparation of the hydrogen form as a necessary step (Glaeser, 1946a; Vendl and Hlung, 1943). A great deal of useful information concerning the polyelectrolyte nature of the clays can probably be derived ultimately from the studies on the titration behavior of the hydrogen form of the clays, but such information is not a necessary and integral part of the study of the exchange behavior of the clays.

*Method for Preparing Ammonium-Clay.* The most satisfactory experimental technique to employ in a given set of experiments will depend to some extent on the intention of the application of the data. For example,

for the determination of the total exchange capacity of the clay minerals, a variety of satisfactory procedures employing either ammonium acetate or ammonium chloride solutions neutralized with ammonium hydroxide have been described which differ only in the details of the preparation and manipulation of the sample. (Bray, 1942; Glaeser, 1946; Graham and Sullivan, 1938; Lewis, 1951). The ammonium ions retained by the clay may either be determined directly on the clay or eluted and determined separately. For the determination of the total exchange capacity of a number of clays the use of an ammonium-form ion exchange resin of suitable character has proved very satisfactory (Lewis, 1952; Wiklander, 1949, 1951).

*Experimental Techniques.* Experimental techniques may be adapted to micro quantities of clay, or methods may be used that permit the colorimetric determination of the exchange cations rapidly and easily, if less accurately. If the equilibrium distribution of ions between a clay phase and a solution phase is to be determined, the most direct method involves placing a clay with a known ion population in an electrolyte solution of known composition. After a suitable length of time both phases of this system are analyzed to determine the distribution of ions at equilibrium. This method, so direct in principle, is replete with pitfalls. It may be convenient to analyze chemically only the solution phase before and after the reaction, to determine the distribution of ions accomplished by the exchanger phase, thus requiring that the analytical procedure be very accurate in determining a small difference between two large numbers. Moreover, because the equilibrium water content of the clay depends strongly on its ion form, the concentration of the external solution changes as the ionic composition of the clay changes, and the degree of exclusion of molecular salts by the Donnan mechanism from the hydrated clay changes as the ionic form of the clay changes. The effect of the change in equilibrium water content with change in the ionic form of the exchanger may be so great that failure to consider it may so distort the results that ion exchange in its ordinary sense does not appear to take place (Lowen, Stoener, and Argersinger, 1951). For the most accurate equilibrium determination, the solution phase and the exchanger phase should be physically separated in a manner which does not disturb the ionic equilibrium already established. For accurate work it is desirable to bring the clay to equilibrium with a given composition of electrolyte solution, separate the clay phase and repeatedly bring the clay to equilibrium with successive portions of the same solution. In this way the composition of the electrolyte solution is not altered by the contribution of the displaced cations from the exchanger phase, so that the composition of the equilibrium solution phase may be determined accurately either from an accurately prepared composition of the equilibrium solution or an accurate analysis of the initial solution. The clay phase should finally be separated and analyzed directly for the distribution of the ions participating in the exchange reaction or the exchanging pair displaced by a third cation and analyzed in the elution product. The direct experimental determination of equilibrium ionic distribution can be successful for studies of ion exchange if

careful attention is paid to the details of the experiment, with suitable attention to analytical accuracy and proper manipulation of the sample, so that the final data provide an accurate picture of the equilibrium partition of electrolyte ions between the solution phase and the exchanger phase at equilibrium.

*Clay Chromatographic Methods.* A modification of the column chromatographic technique has been used recently in determining the exchange isotherms for clays. This technique involves the preparation of a column consisting of the clay in an inert matrix (asbestos) that provides suitable flow properties for the column. The exchange isotherm is obtained by measuring the composition of the solution passing through the column as one exchange cation on the clay is displaced by another. This technique in principle possesses the virtues of greatly reducing the amount of analytical work required and of having inherent in the process the separation of the clay and electrolyte phases. If radioactive isotopes are used as tracers for following changes in composition of the eluted solution, the whole process can be put on an essentially automatic basis. The recently reported determination of the cesium-sodium isotherm at room temperature on a montmorillonite from Chambers, Arizona, (API 23) indicated considerable promise for this technique with the clay minerals (Faucher, Southworth, and Thomas, 1952). The colloidal character of the clay minerals, however, may cause mechanical difficulties in the preparation of suitable chromatographic columns, unless the columns are always operated with solutions having relatively high ionic strengths.

*Clay-Resin Reaction Methods.* For the determination of the ionic distribution on clay particles at low solution concentrations, monofunctional sulfonic acid resins may be used by bringing an electrolyte solution and resin to equilibrium with the clay. After equilibrium is reached, it is possible from only a material balance and an analysis of the washed resin phase to determine the equilibrium distribution of ions on the clay equilibrium with the electrolyte solution. It has been demonstrated that the distribution of ions between a clay and a solution is independent of the presence of the exchanging resin.

#### EXPERIMENTAL CONSIDERATIONS

There are two major classes of objectives in the examination of the data which are obtained in the study of ion exchange reactions. The first of these requires only that sufficient data be accumulated so that a working equation or graph can describe the data and permit interpolation and extrapolation of the behavior of this system to conditions not precisely covered by the experiments. This method permits considerable latitude in the type of parameters and the manner of the mathematical combination to provide a description of the actual behavior of the particular process. With such a description the behavior of the distribution of calcium ions and sodium ions, for example, on a specified clay, could be summarized at the temperature and solution strength of the experiments over a relatively wide range of compositions of the exchanger and solution phases. Such descriptions of behavior serve a useful practical purpose. On the other hand, such descriptions in themselves pro-

vide no clues which suggest either the magnitude or direction of changes in selectivity of sodium with respect to calcium as the temperature, the total strength of the solution, or the mineral species should change. The other objective is that of establishing a sound theoretical basis for understanding the different selectivities of the various ions when reacting with different exchanger phases. The mathematical expression of these theoretical views would provide not only a description of the process, but also a basis for prediction of changes in the nature of the distribution with changes in a wide variety of parameters which enter either explicitly or implicitly into the equations. Good experimental data obtained from well-characterized solutions of electrolytes interacting with well-defined clay mineral species are necessary for either of these considerations. At present there is a great need for more experimental information on the ion exchange behavior of clays under circumstances which permit the examination of the data with a view to testing various hypotheses and theories which have been offered as a basis for the ionic selectivity in ion exchangers. Although the nature of the experimental work which is needed from both practical and theoretical standpoints in the study of ion exchange of clays was clearly pointed out by Bray in 1942, the present need for these data in clay systems is as great as it was at that time. Both the theoretical and the experimental studies designed to establish the contribution of the several conceivable parameters to the actual selectivity of an exchanger for ions in solution has proceeded at a greatly accelerated rate in systems involving synthetic organic resin exchangers. The intensity of activity in the investigation of clay systems is increasing at present. Those aspects which Bray pointed out as much-needed extensions of the experimental effort involve leaving the convenient range of ion distributions from the standpoint of analytical techniques in general and extending these studies to very wide ranges of composition of the exchanger phase and over wide ranges of total concentrations of the solution as well. While both of these directions are now being actively pursued by investigators of resin-electrolyte systems, similar progress has not been made in clay investigations. Another aspect on which Bray felt that considerably more work should be done is that of greatly increasing the number of different ions present in a system. From a practical standpoint, particularly in connection with soils, the need for such investigations is undoubtedly great. From the standpoint of theory, however, our knowledge of the specific interactions between ions in solution and in the exchanger phase is much too inadequate to enable us to apply this information theoretically at present.

In his recent review of the theoretical progress being made in the elucidation of the mechanism of ion exchange reactions, Boyd summarized the current status of ion exchange equilibrium theory as being somewhat confused and the disagreements in the literature far more numerous than agreements (1951). This sentiment echoed the conclusions expressed by Marshall in his discussion of the ion exchange reactions of clays when he reported that the only certain conclusion one can draw at present is that better experiments are needed (1949). The various approaches which are presently being made

to establish the principal mechanisms by which the solid exchanger phase controls the distribution of exchangeable cations among its available ion exchange sites when in equilibrium with a solution of a given composition may be classified into several broad groups. The ion exchange equilibrium has been considered (1) as a class of reversible double-decomposition reaction which may be described by the principles of the law of mass action, (2) as an ionic adsorption reaction the behavior of which may be described by a suitable isotherm equation for a mixture of electrolytes, (3) as a Gibbs-Donnan distribution between two phases, and (4) as reflecting the behavior of solution ions under the influence of a heteropolar ionic solid surface. Most investigators have preferred either the mass action or the adsorption description of the exchange process.

In general, there are a number of changes which accompany the redistribution of ions in the ion exchange reaction. These variables must be considered when designing experiments to test the various hypotheses of the equilibrium distribution of ions in ion exchange reactions. They include the following processes which compete with the exchange reaction or accompany it:

- A. Ion-pair formation between solution ions and exchangers.
- B. Molecular adsorption of partially dissociated electrolytes.
- C. Complex ion formation in solution.
- D. Change in distribution of ion species with changes in concentration of electrolytes.

In addition to these processes, the solution concentration and composition may change during the ion exchange reaction because of the following factors which must be evaluated to permit calculation of the equilibrium distribution:

- A. Variation of equilibrium water content of exchanger with change in ion composition.
- B. Change in solution volume resulting from exchange of electrolytes having different partial molar volumes.

#### MASS-ACTION DESCRIPTION OF ION EXCHANGE REACTION

If we consider a reversible reaction of the following form between monovalent cations  $A^+$  and  $B^+$  in solution and an exchange phase  $Z$ ,



the law of mass-action describes the equilibrium distribution in terms of a product

$$K = \frac{(B^+) (AZ)}{(A^+) (BZ)} \quad (2)$$

In this expression the quantities in parentheses represent the activities of the various species. The activity of each species is a quantity  $a_i$ , such that

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (3)$$

where  $\mu_i$  is the chemical potential of the species  $i$ ,  $\mu_i^\circ$  its chemical potential in some arbitrary standard state,  $R$  the universal gas constant and  $T$  the absolute temperature.

If the ion exchange reaction is truly reversible and if the activities  $a_i = (A_i)$  can be evaluated, at constant temperature and pressure, the constant  $K$  can be calculated and the Gibbs free energy of the reaction computed from its value.

As a first approximation, the concentration of the ions in solution and in the exchanger phase have been substituted for the activities. In this form, the value of  $K$  is a mass law concentration product which is not expected to remain constant. For practical purposes, a closely related quantity, the selectivity coefficient  $D$  is frequently calculated as

$$D = \frac{(AZ/BZ)}{(A^+/B^+)} \quad (4)$$

The type of variation of equilibrium mass law product is illustrated in figure 1. Both the mass law concentration product and the selectivity coefficient are without direct theoretical utility themselves, although they are useful working quantities which differ from the thermodynamic quantities by suitable functions to convert the concentrations of ions to activities. The evaluation of the activities in both the solution and exchanger phases, however, involves several uncertainties at the present stage of our knowledge of these reactions.

A number of approaches have been employed to evaluate the activities of the ions which are reacting both in the solution phase and the clay phase. For the solution phase the basic data required are the activity coefficients of the electrolytes in mixed ion solutions over the concentration and composition ranges employed in the reactions. In general, this information is not available, although Harned and Owen (1950) have summarized the available data and some rules for computing estimates of activities of electrolytes. The approximation is frequently made that the ion activity is that of the single electrolyte at a total ionic strength of the reacting mixed solution. There is the possible objection to all these methods that the activity of the dilute mixed electrolyte solution may not be the correct activity to use on the

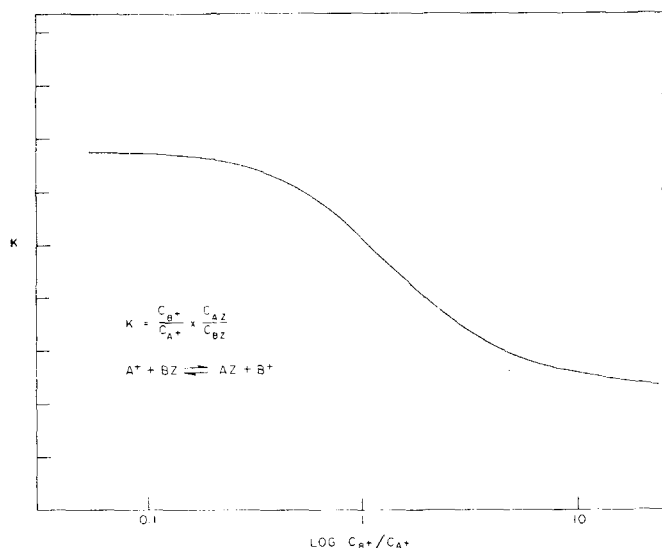


FIGURE 1. Variation in mass-law product.

grounds that the exchange reaction occurs only in the immediate vicinity of the highly ionic crystalline clay exchanger, where its activity would be expected to be significantly different from that in the dilute solution both because of the change of dielectric constant of the

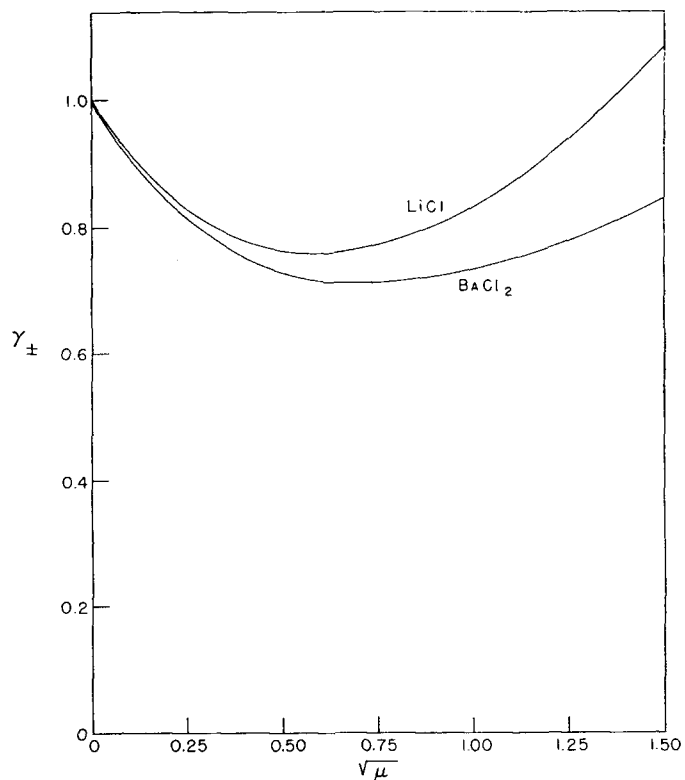


FIGURE 2. Activity coefficients for 0.01 m HCl in electrolyte solutions.

solvent and the potential energy of the ion in this environment (Davis and Rideal, 1948; Greyhume, 1951; Grimley, 1950; Weyl, 1950). Since the over-all process is the transfer of ions from the dilute solution to the exchanger, however, and since at equilibrium the chemical potential of ions of any species is the same throughout the system, the solution thermodynamic activities should be suitable when they are known.

The equilibrium constant for the reaction (1) can be written for the mono-monovalent exchange as

$$K = \frac{m_{\pm}(B) \gamma_{\pm}(B) (AZ)}{m_{\pm}(A) \gamma_{\pm}(A) (BZ)} \quad (5)$$

where  $m_{\pm}(B)$  is the main ionic molality of the cation  $B^+$  with the solution anion, and  $\gamma_{\pm}(B)$  is the mean ionic activity coefficient for this electrolyte. These quantities are defined in terms of the molalities of the cation  $m_+$  and anion  $m_-$  as

$$m_{\pm}^{v_+} = m_+^{v_+} + m_-^{v_-} \quad (6)$$

In this expression  $v_+$  is the valence of the cation,  $v_-$  the valence of the anion and

$$v = v_+ + v_- \quad (7)$$

Analogously, the mean ionic activity coefficients are

$$\gamma_{\pm}^{v_+} = \gamma_+^{v_+} + \gamma_-^{v_-} \quad (8)$$

The mean ionic activities of ions are influenced by the presence of dissimilar ions. The values of the mean ionic activity coefficients for electrolytes have been determined by emf measurements in suitable cells. The effect of

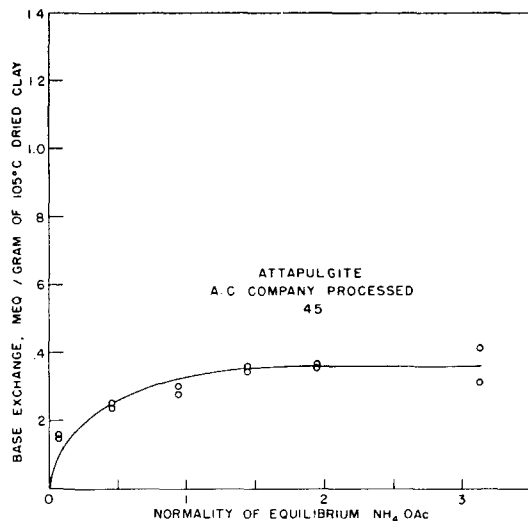


FIGURE 3. Exchange isotherms for clay samples.

added electrolyte is shown in figure 2, in which the mean ionic activity coefficients and hydrochloric acid in the presence of LiCl and BaCl<sub>2</sub> are plotted as a function of the total solution concentration. As this figure illustrates, the magnitude of the activity correction is significant at relatively low concentration levels and is materially affected by the nature of the accompanying ions.

Another more direct manner of evaluating the activity of the various ions in solution is to determine them by emf measurements involving reversible electrodes (Kressman and Kitchener, 1949a) or membrane electrodes (Barber and Marshall, 1951; Clarke, Marinsky, Juda, Rosenberg, and Alexander, 1952; Marshall, 1949; Marshall and Barber, 1949) in the exchange solutions. The application of the electrode or membrane measurements to systems containing suspended colloids, however, raises other problems (Mysels, 1951).

In attempting to evaluate the activity of the exchanger, earlier approaches considered the exchanger as an ideal binary solid solution in which the activities of the ions in the exchanger were proportional to their molal fractions (Boyd, Schubert, and Adams, 1947). This might be satisfactory if the exchange ions are monovalent and similar in size. Kielland (1935) has pointed out that the assumption of an ideal solid solution is probably not justified and has suggested a method for estimating activity coefficients for the solid exchanger phase based on the Margules equation, from which the activity coefficients are calculated as

$$\log \gamma_{AZ} = CX_{AZ} \quad (9)$$

and

$$\log \gamma_{BZ} = CX_{BZ}$$

where  $X_{AZ}$  is the molal fraction of the ion  $A$  in the exchanger, and  $C$  is a constant value for each particular system and may be positive or negative most commonly varying from zero to one.

On the basis of these considerations, estimates may be made of the apparent activity in the exchanger phase, after suitable exchange data are available to permit evaluation of the parameters  $C$  in equations. Recently, however, it has been pointed out that the constancy of  $K$

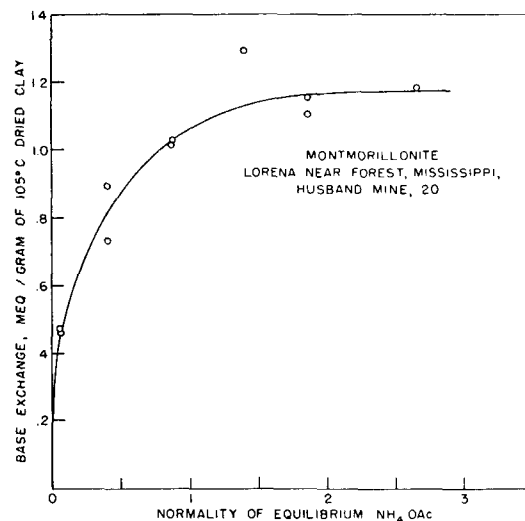


FIGURE 4. Exchange isotherms for clay samples.

in equation (2) is a thermodynamic necessity (Argeringer, et al., 1950; Bonner, et al., 1952; Ekedahl, et al., 1950; Högfeldt, et al., 1950, 1950a) arising from the definition of activities and independent of the mechanism of the reaction. Accordingly, the expression for the equilibrium constant is combined with the Gibbs-Duhem equation to determine from the experimental data, when the activities of the ions in the mixed electrolyte solutions are known, both the true equilibrium constant and the activity coefficients for the ions in the solid phase. The Gibbs-Duhem equation at constant temperature and pressure for a binary system is

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (10)$$

In this expression  $n_i$  is the mole fraction and  $\mu_i$  the chemical potential of the ion species  $i$ . Combining this with the definition of activity, equation (3) gives

$$n_{AZ} d \ln a_{AZ} + n_{BZ} d \ln a_{BZ} = 0 \quad (11)$$

which may be shown to be equal to

$$n_{AZ} d \ln f_{AZ} + n_{BZ} d \ln f_{BZ} = 0 \quad (12)$$

Combining this expression with the mass-action equation (2), and integrating, with the boundary conditions  $f_{AZ} \rightarrow 1$  as  $n_{AZ} \rightarrow 1$  and  $f_{BZ} \rightarrow 1$  as  $n_{BZ} \rightarrow 1$  gives

$$\ln f_{AZ} = -n_{BZ} \ln K^1 + \int_{N_{AZ}}^1 \ln K^1 dn_{AZ}, \quad (13a)$$

and

$$\ln f_{BZ} = n_{AZ} \ln K^1 - \int_0^{N_{AZ}} \ln K^1 dn_{AZ} \quad (13b)$$

The substitution of these results into the logarithmic form of the equilibrium equation yields

$$\ln K = \int_0^1 \ln K^1 dn_{AZ} \quad (14)$$

The apparent equilibrium constant  $K^1$  is the quantity which is obtained from the experiment coupled with suitable values for the solution activity coefficients. By graphical integration of a plot of  $\ln K^1$  versus  $n_{AZ}$  the  $\ln K$  and the true equilibrium constant for the reaction may be calculated. This procedure has not previously

been applied to clay exchange systems, but has been applied with internal consistency to the sodium hydrogen exchange on Dowex-50 (Lowen et al., 1951), although the values of the equilibrium constants were somewhat different from those reported by other workers. (Bauman and Eichhorn, 1947; Duncan and Lister, 1949; Marinsky, no date).

A separate explanation has been suggested to account for the variation of the apparent equilibrium constant in addition to the assumption of non-ideality of the solid solution model of the exchanger (Marinsky, no date). This view proposes that the reaction does not progress from the initial to final product in the straightforward manner postulated in equation 1. Rather the reaction is assumed to proceed through a number of mixed intermediate compounds each of which is in equilibrium with its products. By a suitable choice of steps in the reaction and selection of the proper values for the assumed equilibria, the deviation from constancy of the experimental equilibrium constants can be fitted. The existence of the hypothetical intermediate compounds, however, would be very difficult to establish, and any curve can be fitted by the combination of enough variables.

#### LANGMUIR'S ADSORPTION ISOTHERM DESCRIPTION OF ION EXCHANGE REACTIONS

The first attempts to describe the ion exchange behavior on a rational basis were in terms of the Freundlich isotherm. This was a very reasonable approach to the problem of describing the exchange behavior and many workers employed a form of the equation,

$$\frac{x}{m} = kc^{1/p} \quad (15)$$

in which  $x$  amount of the exchanging cation is taken up by  $m$  grams of exchange when immersed in an equilibrium concentration  $c$  of electrolyte. Both  $k$  and  $p$  are constants. The calculation of the exchange behavior in a form resembling adsorption isotherms has been common practice (see figs. 3 and 4).

The earliest mathematical descriptions of the process did not approach a finite limit corresponding to the total capacity of the exchanger, so that a revised form was offered by Wiegner and Jenny (1951):

$$\frac{x}{m} = k \left[ \frac{c}{c-a} \right]^{1/p} \quad (16)$$

where the additional quantity  $a$  is the amount of electrolyte added.

Another essentially empirical equation which resembles the Freundlich isotherm is that of Vageler

$$y = \frac{sa}{a+c} \quad (17)$$

in which  $y$  is the amount taken up per gram of exchanger,  $s$  the saturation capacity of the exchanger,  $a$  the number of equivalents of salt per unit weight of exchanger initially added, and  $c$  is the "half-value," that is, the value of  $a$  at which half of  $s$  is exchanged.

The hyperbolic form of the Langmuir adsorption isotherm provided an analytical form which represented the observed degree of exchange rather closely. This analogy has been most successfully exploited by Boyd, Schubert, and Adamson (1947), who expressed the Langmuir adsorption isotherm for ion exchange reactions between two monovalent cations  $A^+$  and  $B^+$  as

$$\left[ \frac{x}{m} \right]_{A^+} = \frac{kb_1C_{A^+}}{1 + b_1C_{A^+} + b_2C_{B^+}} \quad (18)$$

in which  $(x/m)_{A^+}$  is the amount of  $A^+$  taken up per unit weight of exchanger,  $C_{A^+}$  and  $C_{B^+}$  the equilibrium concentrations of the two ion species and  $k$ ,  $b_1$  and  $b_2$  are constants.

If the assumption is made that the number of unoccupied exchange sites is small at any moment, the quantity unity in the denominator of equation (18) may be neglected in comparison with  $b_1C_{A^+} + b_2C_{B^+}$ . This approximation permits the equation to be written in the linear form

$$\frac{C_{A^+}/C_{B^+}}{(x/m)_{A^+}} = \frac{b_2}{b_1k} + \frac{1}{k} \frac{C_{A^+}}{C_{B^+}} \quad (19)$$

This form permits a convenient means for plotting the exchange data, and has an added virtue since  $b_1$  and  $b_2$  are related to the energies of adsorption of the ions,  $E_{A^+}$  and  $E_{B^+}$ . A plot of the quantity on the left  $(C_{A^+}/C_{B^+})/(x/m)_{A^+}$  versus  $C_{A^+}/C_{B^+}$  has been found to give a linear plot in some systems, permitting the calculation of  $k$  and  $b_2/b_1$ .

Another description of the exchange reactions which is closely related to the adsorption isotherm equations was initially proposed by Jenny (1936) who derived on the basis of probability the distribution of ions near the interface of the exchanger phase and in the bulk solution on the assumption that different species of ions occupied different oscillation volumes. For ions having the same oscillation volumes this expression reduces to the same form as Vageler's equation. This equation of Jenny was the first direct approach to the description of ionic distributions on a statistical basis. The statistical method, however, has been extended by Davis (1950, 1950a, and Rible, 1950) who applied the method of Guggenheim (1944) to the ion distribution between the solution and exchanger. The statistical approach was originally developed to describe the mixed adsorption of two species of neutral molecules from solution under conditions of zero energy of mixing. To apply this approach to ion exchange, several assumptions had to be made in addition to those in the original derivation for molecular adsorption. The most important of these are the assumptions that ions of the same sign do not display specific interactions, that all interactions between ions may be neglected except for nearest neighbors, and that the internal degrees of freedom of each ion are independent of its neighbors.

The mathematical statement of the ionic distribution which is derived on the basis of the statistics and assumptions outlined above is of the form

$$k = \frac{(A)^{r_B} [B]^{r_A} (\sum_i q_i [i])^{(r_A-r_B)}}{(B)^{r_A} [A]^{r_B}} \quad (20)$$

Here the quantities in brackets [ ] refer to number of moles in the exchanger phase while the quantities in parentheses ( ) refer to the activities in the solution phase,  $r_i$  is the valence of species  $i$ , and  $q_i$  is a coefficient such that

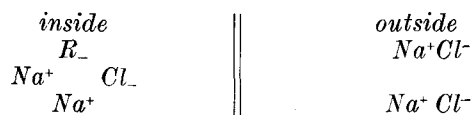
$$(Z/2) (r_i - q_i) = r_i - 1, \quad (21)$$

where  $Z$  is an integer related to the geometry of the exchanger. In practice, the integer  $Z$  is obtained by finding which value gives the best agreement with experiment. Also, for a value of  $Z = 2$ , the expression reduces to a form identical with an empirical equation suggested by Vanselow (1932, 1932a).

As the mathematical forms of the expressions arising from a description of the process in terms of adsorption are similar to those based on mass-action considerations, no conclusions can be reached concerning the mechanism of the process from the similarity of the appearance of exchange isotherms and adsorption isotherms.

#### GIBBS-DONNAN EQUILIBRIUM DESCRIPTION OF ION EXCHANGE REACTIONS

The use of the Donnan equilibrium to describe the distribution of ions between a solution and an exchanger phase was suggested by Mattson (Mattson and Wicklander, 1950), and has since been applied by a number of investigators. The Donnan equilibrium is a description of the behavior of a system which is physically accessible to part, but not all of the ions. Such a system would be one in which a semi-permeable membrane separated two solutions, one of which contained megamolecular species to which the membrane was impermeable. On the assumption that the megamolecules were anionic, the model which is commonly employed to visualize the system is



Here the vertical lines represent the semi-permeable membrane. The basic conditions which must be fulfilled for this system at equilibrium are electroneutrality and the equality of activity products for the electrolyte on both sides of this system, namely

$$[Na^+] [Cl^-] \text{ inside} = [Na^+] [Cl^-] \text{ outside} \quad (22)$$

If, now, the process of ion exchange is considered as



by analogy with the equation (1), at equilibrium the application of the Donnan condition, equation (23), results in

$$\frac{[A_i^+] [B_o^+]}{[A_o^+] [B_i^+]} = K, \quad (24)$$

which is identical with the mass-action equation. This simple form, however, neglects other contributions which have been discussed by Donnan and Guggenheim and by Donnan, particularly the free energy contribution which arises from the change of swelling for the swelling clays and from the activity of the ions in the exchanger. The simplified Donnan equilibrium is derived on the as-

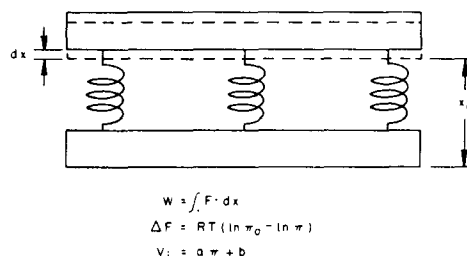


FIGURE 5. Idealized osmotic work of swelling.

sumption that the osmotic pressures be equilibrated in all parts of the system. If this condition is not fulfilled, then the free energy change associated with the swelling of the exchanger must be included.

By neglecting the activity coefficients, Gregor has developed the relations which describe the contributions of the swelling free energy to the free energy change of the reaction. The model of a clay which is described by this swelling equation is indicated schematically in figure 5. The whole volume of this assemblage consists of both the incompressible volume of the crystal lattice and the inner volume,  $V_i$ , of the spaces occupied by the hydrated exchange ions and any other water which may be present in excess of that coordinated by the exchange ions. The osmotic force which opposes the spring tension is the thermodynamic osmotic pressure  $\pi$  within the exchanger phase. Gregor postulates that a linear relation exists between the volume and the osmotic pressure (1951).

$$V_i = m\pi + b. \quad (25)$$

In terms of the model proposed by Cornet (1950), this same assumption would be

$$A dx = m\pi + b, \quad (26)$$

where  $A$  is the cross-sectional area,  $dx$  the separation of the clay, and  $m$  and  $b$  are constants. The form of the Donnan equation which applies to the system of taking the free energy of swelling into consideration in terms of the number of moles of univalent cations exchanging as in equation (23) is the following:

$$RT \ln \left[ \left( \frac{MA}{MB} \right)_i \left( \frac{MA}{MB} \right)_o \right] = \pi (v_B - v_A) \quad (27)$$

Furthermore, if the exchange of cations is accompanied by the transfer of  $f$  moles of solvent from  $o \rightarrow i$  and  $g$  moles of solvent from  $i \rightarrow o$ , then

$$\Delta F^\circ = RT \ln K_x = -\pi [v_B - v_A - (f - g)v_o] \quad (28)$$

where  $v_i$  is the molar volume of species  $i$  and  $v_o$  is the molar volume of the solvent. Since the quantity  $[v_B - v_A - (f - g)v_o]$  is the change in volume of the exchanging system this can be measured directly. It is significant to note that all of the parameters in this expression can be evaluated independently of the exchange process itself. In this sense it is unique since all of the other methods of describing the reaction involve unknown values which can only be defined in terms of the exchange process.



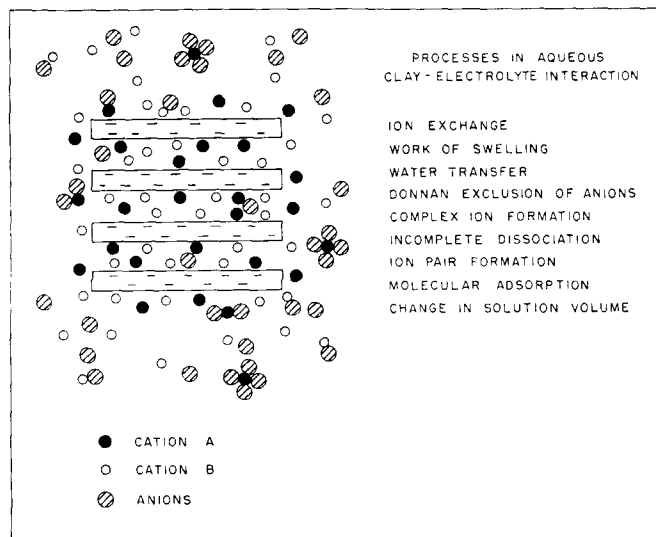


FIGURE 6. Schematic summary of processes in aqueous clay-electrolyte interaction.

It has been reported by Glueckauf (1949) that the linear relation equation (25) is not valid for resin exchangers, but no studies of this aspect have been made using swelling clays. The neglect of activity coefficients of the ions in the exchanger phase is also an oversimplification which will need to be refined as our understanding of ion exchange processes grows.

For the highly colloidal clay systems, moreover, it is difficult to erect an arbitrary surface in the neighborhood of the particle such that all ions beyond this surface are said to be "outside" the exchanger and those within are said to be "inside." Marshall (1949) has indicated some of these complexities and concludes from them that the application of the Donnan principle to clay systems may involve experimentally inaccessible quantities.

#### SUMMARY AND CONCLUSIONS

The ion-exchange process is only one of a group of reactions that may occur between a clay and an electrolyte solution. Figure 6 presents a schematic summary of the processes that take place. For practical purposes it is necessary to know what will be the final result of all of these several processes in any given situation. The resolution of the contributions of these several processes requires that the study of each aspect be initially carried out separated from the competing reactions as much as possible. Accordingly, the investigation of the *ion exchange* reactions of clay minerals should be made under circumstances in which competing processes make either a negligible contribution or one which can be independently evaluated.

The nature of the clay mineral should be known in as complete detail as the techniques for establishing structure permit. As any specific clay material is a member of a structural series, it is important to establish the origin and nature of the exchange sites as fully as possible. For example, the distribution of the isomorphous substitution between the tetrahedral and octahedral coordinations is important because the difference in the

energies of these two classes of exchange sites would be expected to influence the ionic selectivity, associated with each type. As far as is possible, the distribution of metal ions either as exchange cations or as lattice units should be established. This is especially important for such metals as magnesium and aluminum which play a central role in the exchange properties of the lattice (Foster, 1951).

As Kelley (1948) has pointed out, the ion-exchange properties of members of the major classes of clay minerals will vary considerably so that it is not to be expected that all montmorillonites or illites or kaolinities can be fitted by a type exchange isotherm but it is rather to be hoped that the developing knowledge of mineral structure will ultimately permit us to use the number and distribution of exchange sites in a lattice to predict with useful accuracy the exchange reaction properties of a clay mineral.

The electrolyte solution introduces another group of variables. Much more must be known about the specific ion interactions which give rise to the changes in ionic activities with solution composition in mixed electrolytes. This is one aspect of the solution thermodynamics which must be faced squarely, since all ion exchange reactions with the exception of isotopic exchanges take place in mixed ion systems. More needs to be learned about the change in ionic species distribution with concentration and composition for incompletely dissociating salts and for ions which may dissociate stepwise. For the same direct reason—that equilibria cannot be described thermodynamically unless the distribution of reacting species is known at equilibrium—the use of ions which may form covalent bonds with the exchanger, ions which react chemically with the clay or the exchange ions displaced from the clay, or ions which form complexes with the solution anions all introduce uncertainties which have contributed to the compounded confusion which currently exists in the literature of ion exchange.

The transfer of solvent in the exchange reactions of the swelling clays, and the change of volume of the solution phase which may result from differences in partial molal volumes of the displacing and displaced ions demand that experiments be designed so that these contributions may be evaluated directly. Neglect of these contributions has led some investigators to the extreme view of concluding that ion exchange was not an ion-equivalent process.

Future experimental work can now be planned in such a manner that the clay exchanger phase and the solution composition can be determined completely enough to give permanent significance to the data. It is to be expected that when the actual behavior of well-characterized ion-exchanging clay systems is known quantitatively, the mechanism of ionic selectivity can be established and the exchange behavior of clays will be capable of prediction to a useful degree on the basis of general thermodynamic considerations.

#### DISCUSSION

##### W. J. Weiss:

What forces hold the non-exchangeable cations on clays and cause differentiation between exchangeable and non-exchangeable forms, and how do these non-exchangeable cations affect the physical properties of the clays?

**E. C. Henry:**

Perhaps someone else will answer this question directly, but it seems worthwhile at this point to call attention to the work of Fajans and of Weyl and associates on the polarizability of ions on surfaces. Weyl (1950a) has interpreted results obtained with crushed pottery flint as follows: The silicon ions at the surface of this material are not surrounded by four oxygen ions, as is the case in the interior of quartz. Consequently, the charges of the surface silicon ions are not completely neutralized. The result is a force field surrounding the silicon ions. When quartz is crushed many silicon ions become exposed, and upon adding water the unsatisfied charges on these silicons cause dissociation of  $H_2O$  into  $H^+$  and  $OH^-$  ions. The  $OH^-$  ions are adsorbed, leaving  $H^+$  ions in the solution and thus a pH below that of pure water. When the particles of flint are allowed to settle, the pH rises. A hypothesis by Weyl explains this on the assumption that the adsorbed  $OH^-$  ions are given up to the liquid because of adequate "screening effect" caused when the particles themselves came close together. This might account for the preferential adsorption of  $OH^-$  ions by colloids as has been previously suggested.

**I. Barshad:**

Fajans' experiments suggest results that have been obtained by grinding kaolinite which show an increase in base-exchange capacity. This may be because the broken bonds that result from grinding adsorb cations that are exchangeable; or some of the finely-ground material may recombine to form a permutite-like substance which has base exchange properties similar to ordinary permutite. Other minerals seem to give the same results. Similarly, the base-exchange capacity of halloysite was increased from 20 me. to 300 me. by heating to boiling in the presence of a solution of NaOH. After this treatment the material was no longer halloysite but amorphous and had the properties of permutite.

**Duncan McConnell:**

I also believe that upon grinding, and also after electro dialysis of unground samples, the material may no longer be a pure mineral but a substance disorganized structurally. Thus, true "base exchange" should be of the zeolytic type while "base exchange" of kaolinite seems to be adsorption.

**I. Goldberg:**

Dr. Lewis referred to several methods of preparation of hydrogen clays in his paper, among which were electro dialysis and leaching with acid.

Another method is that of passing a suspension of clay through a column of cation-exchange resin, whereby the exchangeable ions of the clay are exchanged for hydrogen of the H-resin. The work done in our basic research laboratory has indicated that this method is considerably faster and perhaps more efficient in effecting the exchange. In addition, it has been found that the mineralogical composition of the clays treated in this manner is much less changed than by employing the other methods.

Has Dr. Lewis had any experience in this method of treatment of clays?

**D. R. Lewis:**

We have prepared hydrogen clays by electro-dialysis, ordinary dialysis, acid treatment, and by passing the clays through columns of resin. Electro-dialysis is extremely drastic in its action, because structural elements are removed and caused to pass through the separating membranes by prolonged electro-dialysis. The method of passing the clay through H-resin causes the least damage to the clay and is extremely efficient. Some data have already been given on the comparative results obtained with a clay previously saturated with different cations, using the sulphonated styrene type of resin. With the Na-clay complete conversion to H-clay was obtained at the highest rate of flow through the resin, indicating extremely favorable equilibrium distribution and a very mobile reacting ion.

**Duncan McConnell:**

On the basis of the hypothesis (McConnell, 1950) that tetrahedral  $(OH)_4$  is present, it is suggested that the cation exchange of montmorillonite could be explained on the basis of highly mobile protons in the tetrahedral  $(OH)_4$  groups. This would avoid the necessity of considering octahedral charge by placing the charge differences in the tetrahedral layer.

**J. W. Jordon:**

Why should the seat of cation exchange be in the tetrahedral layer rather than in the octahedral layer?

**Duncan McConnell:**

If the bonding forces of the exchangeable cations are of a low order, it would be well to have them as close to the other ions involved as possible. That is the only reason. The only possible alternative to this explanation would be the shifting of the layers one above the other.

**G. W. Brindley:**

The tetrahedral  $(OH)_4$  hypothesis of McConnell arose in the first place as a means of accounting for the  $H_2O$  found upon dehydration at high temperature. The same is well established for kaolinite; that after expulsion of water about 550-600° C there is another small inflexion in the curve around 800°. Recently (Knorring et al. 1952) we have found that nacrite showed a very similar distinct loss in weight between 800-850°. This raises the question as to whether the same hypothesis is applicable to the kaolinite-type minerals.

**Duncan McConnell:**

The answer will depend on whether or not the water content of the sample exceeds the theoretical amount.

**G. W. Brindley:**

Chemical analyses gave 14.48 percent, 14.21 percent, and 14.40 percent of  $H_2O^+$  in three specimens of nacrite as compared with 13.96 percent calculated from the ideal formula.

**J. W. Jordon:**

Has anyone determined the energy of the ion-exchange reaction (reaction entropies)?

**D. R. Lewis:**

I consider this to be an area of major confusion. The difficulty seems to be in the determination of the thermodynamically correct exchange equilibrium constant which is commonly the basis for calculating the entropy. In exchange experiments the apparent equilibrium constant seems to be greatly influenced by the ratio of ions in the solution. With cation-exchange materials and the use of a solution containing two kinds of cations, the selectivity seems to be enhanced toward the cation that is present in the solution in least amount, a characteristic of all cation exchangers. The opposite has been reported for anion exchange where the preference is for the ion present in greatest relative amount. Temperature also influences the results. If one calculates the entropy from published data on Na-Li or Na-K exchange, the values of  $T\Delta S$  vary from approximately 1500 calories per mole to as little as 100 calories per mole. Accurate equilibrium constants are needed. When entropy is calculated we assume that the activities of ions in true solution are known, but the activities of adsorbed ions are less certain. The latter must be taken into account and several approaches have been proposed none of which seems to be entirely satisfactory.

**Roy Overstreet:**

Soil chemists find that by substituting molal fractions, or something quite similar to molal fractions obtained by statistical approach, a very good constant is obtained over a wide range of concentration down to as low as one percent suspensions when ions of the same valence, excepting the  $H^+$  ion, are involved.

**D. R. Lewis:**

Accurate analytical methods can be devised and, if the statistical scheme referred to by Davis is used, the variations in calculated entropies will not be nearly so great. However, I have a strong preference for classical thermodynamic treatment which should achieve universality, but we may never be able to obtain independently measurable quantities.

**A. L. Johnson:**

Exchange principles may differ with different clay minerals. As mentioned, grinding of kaolinite may increase the base-exchange capacity and change the structure. Such mild treatment as raising the pH above 7 increases base-exchange capacity of kaolinite and halloysite by a few milli-equivalents. Possibly this is caused by the adsorption of  $OH^-$  ions on the kaolinite particles and these  $OH^-$  ions may then give rise to base-exchange.

**I. Barshad:**

A recent paper by Mooney and Wood (1952) raises some interesting questions concerning the distribution of exchangeable cations on kaolinite surfaces. I have found that by calculating cation-exchange capacity on a surface-area basis rather than on a weight basis, the number of exchangeable cations per unit surface appears to be considerably greater with kaolinite than with montmorillonite, even when both external and interlayer surfaces of the latter are considered. With kaolinite I have found 1.9 me. per 1000 sq. m., while with montmorillonite the calculated concentration of exchangeable cations was only about 1.1 me. per 1000 sq. m. These results raise a question as to the origin of the charge on kaolinite. According to Hendricks (1945), cation exchange with kaolinite results from cations held on the terminal edges of the particles. My calculations indicate that if all the cations are located on the edges, they must lie literally adjacent to one another, which seems very questionable. These calculations suggest that some of the exchangeable cations may be between lattice layers of kaolinite as well as on edges. By mild crushing only some interlayer surfaces become exposed and by prolonged grinding many more undoubtedly are exposed. Accordingly, some, at least, of the increase in cation exchange by grinding might be explained.

**R. L. Stone:**

Dr. Lewis, on what basis do you judge a clay to be highly acid?

**D. R. Lewis:**

The strong acid character of a clay is evidenced by gas-phase reactions. By comparing decomposition-pressure curves obtained by heating ammonium salts of weak and strong acids, and plotting the pressure of ammonia against temperature, we find striking differences. The curve obtained with the  $\text{NH}_4$  form of Wyoming montmorillonite is much more like that obtained with  $\text{NH}_4\text{Cl}$  than with  $(\text{NH}_4)_2\text{S}$ , suggesting that montmorillonite is a strong acid rather than a weak one.

**A. L. Johnson:**

Noting that little has thus far been said about the order of replacement of cations, I would like to hear some discussion on this point especially in its relation to different minerals.

**D. R. Lewis:**

In my paper I deliberately avoided this question because it is a large and complicated subject. Apparently many factors influence the selection of the substances that undergo cation exchange. The order of selection found under some conditions may even be reversed under different conditions. For example, the order of cation selectivity exhibited by sulfonated polystyrene resins, while closely resembling that of montmorillonites, except as regards the H ion, is reversed with the same kind of phosphorylated aromatic compounds. It is interesting to note that the order of selectivity parallels that of the solubility of the phosphates. It is suggested that these experiments may help in deciding whether exchange involves direct isomorphous replacement or whether the exchange is due to localized negative charges on the surfaces operating through oxygen-hydrogen bonds.

**L. E. Davis:**

Two Japanese workers, Salai and Seiyania (1952) recently employed statistical mechanics in the development of an ion exchange series, but in a different way than in my work. There are two general points of view with less plausible variants about the "lyotropic exchange series." One may assume either (1) that the forces between the ions and the surfaces are different for different ions; or (2) that the forces between the ions and water dipoles are different for different ions. The theory of these workers is radically different from either of these alternatives for they seem to assume that the peculiarities found by experiment are caused by interactions between exchangeable ions. Neglecting the surface forces and water entirely they assume that the only interacting entities are ions which by interaction tend to lock each other out. This seems to violate the principle of non-specific interaction of ions. The idea appears to be new.

**A. L. Johnson:**

In our work on exchange in kaolinite, we have found that not only the  $\text{H}^+$  ion gives results that are out of line, but also the  $\text{NH}_4^+$  ion as well. When ammonium acetate was used the results were rather peculiar, but  $\text{BaCl}_2$  or  $\text{AlCl}_3$  gave more consistent data.

**Roy Overstreet:**

One further point should be mentioned in connection with the determination of equilibrium constants. With a given clay-mineral type, such as the montmorillonite- or the kaolinite-type, reasonably good exchange constants are obtained, but mixtures of types give poor constants. The same is true of mixtures of exchange resins.

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