THE THERMODYNAMICS OF ION EXCHANGE ON CLAY MINERALS. A PRELIMINARY REPORT ON THE SYSTEM MONTMORILLONITE-Cs-Sr[1]

By

HENRY C. THOMAS and GEORGE L. GAINES, Jr.
Yale University, New Haven, Connecticut

ABSTRACT

A discussion is given of the advantages of the thermodynamic approach in the study of clay-ion-water systems. Generally valid equations for the description of the systems are given, and the relative significance of the osmotic terms is roughly assessed. The principal theoretical and experimental problem is the determination of the initial slopes of the exchange isotherms, and a formal method for handling this difficulty is described. Preliminary results on the system montmorillonite-cesium-strontium are used for illustrative purposes.

It is always desirable to define a physico-chemical problem involving only equilibrium states in precise thermodynamic terms. The point of view may be sterile from the standpoint of suggesting fundamental, that is, atomistic, interpretations of the experiments, but has the great advantage of so organizing the experimental results that it immediately becomes clear at what points theoretical help is needed for further progress.

The study of ion exchange on the clay minerals affords an excellent illustration of the advantages of the thermodynamic approach. Certainly the detailed effects observed in the experiments are of great complexity, and no simple interpretations can adequately account for them. We are here interested in highly specific behavior of ions associated with the clay skeleton, in a structure which can be looked upon as a concentrated solution of a polyelectrolyte. A theory of sufficient detail to account for specific effects in such a system might well be of such complexity as to be practically useless. It is then even more desirable to summarize properly in thermodynamic terms the experimental results so as to make clear the region of applicability of specific experiments.

We must consider for this purpose the description of the equilibria of a solid substance capable of exchanging cations with, and of adsorbing solvent from, a solution. For simplicity we will suppose that this solid, the clay, is incapable of taking up anions from the solution. In certain cases this latter restriction will have to be relaxed and the broader problem considered. This has been done by Gaines and Thomas (1953, p. 717).

---

[1] Contribution No. 1195 from the Sterling Chemistry Laboratory of Yale University.

398

The problem here indicated is a case of membrane equilibrium if we suppose that the silicate structure is incapable of becoming molecularly dispersed in the solution phase and hence is in effect subject to a membrane permeable only to ions and to water molecules.

The equilibrium constant for this system, for the exchange of two cations A and B, is

$$K = \frac{N_A^{Z_B} m_B^{Z_A}}{N_B^{Z_A} m_A^{Z_B}} \cdot \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} \cdot \frac{f_A^{Z_B}}{f_B^{Z_A}} = K_c^{'} \cdot \frac{\gamma_{BX}^{Z_A/Z_X}}{\gamma_{AX}^{Z_B/Z_A}} \cdot \frac{f_A^{Z_B}}{f_B^{Z_A}}$$

$$\equiv K_c \frac{f_A^{Z_B}}{f_B^{Z_A}}$$

Here we have written K for the true thermodynamic constant; $K_c^{'}$ for the equilibrium constant expression in terms of fractions of sites occupied and molalities in solution; γ_{AX}, γ_{BX} for activity coefficients of the salts in solution; and f_A and f_B for the activity coefficients of the two forms of the clay substance. The determination of the f's is the heart of the problem of summarizing the behavior of the clay. In solutions of constant total molality the ratio of the activity coefficients in the solution will frequently be nearly constant and is, in any case, determinable by well-known methods; it is convenient to absorb this ratio in $K_c^{'}$, thus defining K_c.

To make possible the determination of a useful and consistent set of values of f_A and f_B, we must define standard states for the wet clay phase. (We take the γ's as usual, so that $\gamma_A \to 1$ for $m_A \to 0$.) The f's are made unambiguous by taking as the standard state for the solid the pure mono-ion clay in equilibrium with an infinitely dilute solution of a salt of that ion. The application of the Gibbs-Duhem equation enables the calculation of the f's and of K from appropriate ion-exchange data, subject, however, to a difficulty of experimental origin which we will shortly describe.

We suppose that we have an experimentally determined map of the isothermal surface for the system of interest; i.e., we know $N_B = 1-N_A$ as a function of m_A and m_B. Integration of the Gibbs-Duhem equation along a path across this surface through point $Q(m_A, m_B)$ gives the following results:

$$lnK = Z_B - Z_A + ln \frac{f_A^{Z_B}(a)}{f_B^{Z_A}(b)} + \int_0^1 lnK_c \cdot dN_B - Z_A Z_B \int_a^b n_{H_2O} d\,ln\,a_{H_2O}$$

and

$$\ln f_A^{Z_B}(Q) = \ln f_A^{Z_B}(a) + (Z_B - Z_A)N_B - N_B \ln K_c(Q)$$

$$+ \int_0^{N_B} \ln K_c \cdot dN_B - Z_A Z_B \int_a^Q n_{H_2O} \, d\ln a_{H_2O}$$

with a similar equation for f_B.

The activity coefficients f at a and b, that is, for the mono-ion clays in contact with solutions of finite concentration, are determined by relations of the form

$$\ln f_A^{Z_B}(a) = Z_A Z_B \int_{a_{H_2O}=1}^{a_{H_2O}(a)} \left(\frac{V}{\mathcal{T}} - n_{H_2O}\right) \, d\ln a_{H_2O}$$

in which V is the volume of an exchange equivalent of the clay phase, and $\mathcal{T}$ is the molar volume of water vapor at the pressure under consideration. Throughout, η_{H_2O} is the number of moles of water associated with one exchange equivalent of clay, a mass of clay carrying one equivalent of ions. The activity of the water in the system is denoted by a_{H_2O}. It is apparent that for equilibria in dilute solution $f_A(a), f_B(b) \simeq 1$.

Relatively few measurements of the ion-exchange equilibria of clays have been made under conditions sufficiently well defined to make possible accurate calculations of K_c. Measurements of water content under applicable conditions are very scarce. However, the contributions to K and the f's of the water activity terms are of minor importance for equilibria in dilute solutions, although the absorption of water by a clay does introduce complications into the experimental measurements of the various concentrations. We have started in this laboratory experiments designed to obtain these data (Gelewitz and Thomas, in press). We are not, however, sufficiently advanced in this work to be able to assess the importance of the effects in ion-exchange work.

As is apparent from the expressions for $\ln K$ and for $\ln f$, we must have determinations of K_c at sufficiently small values of N_B to make possible the extrapolation of $\ln K_c$ to $N_B = O$. This extrapolation on the basis of experimental evidence only may be a highly uncertain procedure. Thermodynamics alone can tell us nothing about the shape of the isotherm, and we must appeal to more detailed theoretical considerations to develop a means of extrapolating $\ln K_c$ to $N_B = O$. It appears not unreasonable to suppose that within the clay crystal the long-range coulomb forces between the ions present in small proportion are either lacking or are of small

importance. In a potassium montmorillonite in which four mole percent of the potassium is replaced by cesium, the cesium ions will be separated on the average by five lattice spacings, say 50 A, and the coulomb repulsions will be only some one percent of their maximum value. We are thus led to suppose that the excess free energy of the cesium clay can be represented in a manner similar to that useful for mixtures of non-electrolytes, *viz.*:

$$RTlnf_A = \mu_A - (\mu_A^O + RTlnN_A) = A_1 N_B + A_2 N_B^2 + \cdots$$

$$RTlnf_B = \mu_B - (\mu_B^O + RTlnN_B) = B_1 N_A + B_2 N_A^2 + \cdots$$

so that we have, since $N_A + N_B = 1$

$$RTlnf_B = A + BN_B + \cdots$$

On the basis of these considerations the limiting value of K_c (at low total concentration of the aqueous solution) is $K \exp (Z_A A / RT)$ and for N_B small we have

$$N_B = m_B \Big/ m^{Z_B/Z_A} K^{\frac{1}{Z_A}} e^{\frac{A}{RT}}$$

The isotherm should come into the origin with *finite* slope

$$S = m^{-Z_B/Z_A} K^{-\frac{1}{Z_A}} e^{-\frac{A}{RT}}$$

We are thus afforded with an extrapolation procedure for lnK_c namely

$$lim \ lnK_c = - \ lnS^{Z_A} m^{Z_B}.$$

It should be noted that this conclusion insofar as the finite limiting slope is concerned is independent of the "non-electrolyte" approximation mentioned above (which may indeed be subject to much revision). The isotherm will have a finite limiting slope provided only that the excess free energy $RTlnf_B$ be finite for vanishing N_B.

These points are illustrated by the data in Table 1 for the system montmorillonite-cesium-strontium. It must be emphasized that these results are of a preliminary character. The initial slope of the isotherm has been estimated from a plot of the experimental data obtained thus far only down to $N_{Cs} = 0.685$, at a cesium concentration of 0.0035 molar (in solutions of constant total *normality* 0.05). The estimate of the initial slope may well be in error by a factor of two, which would mean an error in log K of approximately 0.2. We cannot claim that we know the thermodynamic constant, based on these data alone, much better than to a factor of two. Our present value is $- \log K = 3.533$.

The techniques used in obtaining the data of Table 1 have been described elsewhere (Faucher, Southworth, and Thomas, 1952, p. 157). The clay used in the present work is again the montmorillonite from Chambers, Arizona. The data of the table have been taken from a smooth curve drawn through the points obtained from several chromatographic elutions.

TABLE 1. — THE EXCHANGE OF CESIUM AND STRONTIUM ON
CHAMBERS MONTMORILLONITE, API 23.

Chloride solutions of constant total normality $C_0 = 0.05$. Room temperature.

C_{Cs}/C_0	$N_B = N_{Cs}$	K_0^*
0.070	0.6849	0.0003539
.080	.7026	.0004191
.100	.7285	.0005685
.111	.7401	.0006566
.150	.7734	.001003
.200	.8055	.001499
.250	.8313	.002034
.300	.8532	.002593
.350	.8717	.003182
.400	.8882	.003779
.500	.9169	.004942
.600	.9407	.006031
.800	.9787	.007115

In Figure 1 is given the plot of log K_c^* based on the estimated initial slope of the isotherm, and the computed values of the activity coefficients are given in Figure 2. The marked difference in the behavior of the univalent and divalent ions is at once apparent. Any detailed discussion of these differences must await the time when more precise determinations of the f's are available.

Data on the water content of these clays are completely lacking. We can make at this time only an estimate of the contributions due to changes in water activity as the composition of the solution changes from cesium
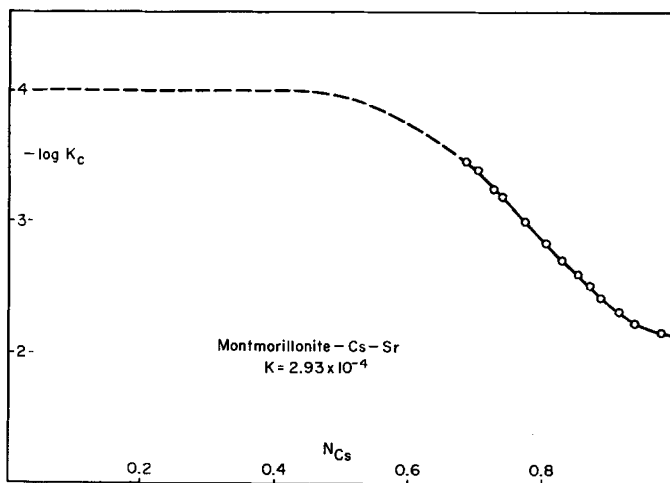

FIGURE 1. — Equilibrium constant in the system montmorillonite-cesium-strontium.
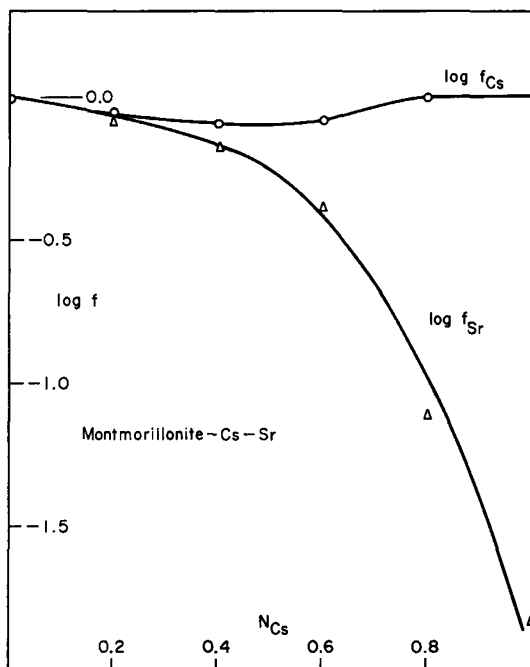
FIGURE 2. — Activity coefficients in the mixed system montmorillonite-cesium-strontium.

chloride to strontium chloride. This contribution is certainly small and probably amounts to less than a unit in the third decimal of $\log K$.

We wish to express our thanks to Brookhaven National Laboratory, Upton, N. Y., for its support of this work.

BIBLIOGRAPHY

Faucher, J. A., Southworth, R. W., and Thomas, H. C. (1952) *Adsorption studies on clay minerals. I. Chromatography on clays:* Journal of Chemical Physics, v. 20, p. 157-160.

Gaines, G. L., and Thomas, H. C. (1953) *Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption:* Journal of Chemical Physics, v. 21, p. 714-718.

Gelewitz, E. W., and Thomas, H. C. *Adsorption studies on clay minerals. III. A torsion pendulum adsorption balance:* Review of Scientific Instruments, in press.