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SOME ZEOLITE EQUILIBRIA WITH ALKALINE EARTH METAL CATIONS[1]

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ABSTRACT

Isotherms for the zeolites Linde Type A, natural erionite, phillipsite, and clinoptilolite in the systems sodium-strontium, sodium-calcium, and strontium-calcium are presented. Thermodynamic data derived from the above isotherms indicated that reaction enthalpies are very small from 25° C. to 70° C. An inverse relationship was noted between SiO_2/Al_2O_3 ratios and divalent cation selectivities. The above data plotted as log κ_c vs. cation B on the zeolite were adequately described by Barrer and Meier's case where dlog κ_c/dB_z does not equal a constant.

INTRODUCTION

Studies continued on the cation exchange equilibria of several zeolites in support of the use of synthetic zeolites as media for packaging and storage of radioactive isotopes (Tomlinson, 1962). The solution containing the radioactive isotopes is expected to be of considerably greater purity in respect to competing calcium and sodium cations than the original process stream, but may still contain more calcium and sodium than radioactive cesium and strontium. It was necessary, therefore, to obtain equilibrium data in systems containing alkaline earth metal cations, with the fraction of alkaline earth metal cations on the zeolite varying from zero to one.

Barrer and Sammon (1955) previously determined and reported isotherms in a sodium-calcium system for chabazite, and for Type A (Barrer and Meier, 1959). Ames (1963) determined and reported sodium-strontium and calcium-strontium isotherms, but only in the region of relatively low fraction of strontium on the zeolite. Otherwise there is little quantitative information available in the literature on zeolite cation exchange reactions involving alkaline earth metal cations.

This report is concerned with work on zeolite cation exchange equilibria of strontium and calcium-containing systems. Only the equilibrium data of the natural zeolites clinoptilolite, erionite and phillipsite are reported in detail.

METHODS OF INVESTIGATION

The zeolites used in this study were the same samples described in a previous paper (Ames, 1964). The same procedures also were used to base the zeolites and determine exchange isotherms. By tracing the sodium-

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strontium exchange reaction from both directions ($2\mathrm{Na}_{\mathrm{solution}}{}^{22}+\mathrm{Sr}_{\mathrm{zeolite}} \leftrightarrows \mathrm{Na}_{\mathrm{zeolite}}{}^{22}+\mathrm{Sr}_{\mathrm{solution}}$, and $\mathrm{Sr}_{\mathrm{solution}}{}^{85}+2\mathrm{Na}_{\mathrm{zeolite}} \leftrightarrows \mathrm{Sr}_{\mathrm{zeolite}}{}^{85}+2\mathrm{Na}_{\mathrm{solution}}$), it was shown that the capacity determination, using cesium and sodium, also were valid for the sodium-strontium reactions, and that equilibrium was attained. The thirteenth anionic site of Type A (Barrer and Meier, 1958) was ignored because no exchange could be expected on the above site by divalent cations.

The general equation for the initial calculation from a given isotherm was:

$$\text{Mass action quotient} = \frac{(A_z)^{n_A}(B_N)^{n_B}}{(B_z)^{n_B}(A_N)^{n_A}}$$

where,

A_N, B_N = concentration of cations A and B in equivalents per liter,
A_z, B_z = equivalent fractions of cation A and B on the zeolite, and
n_A, n_B = the number of cations of A and B represented in the chemical equation for the exchange reaction of A and B.

Because the cation concentrations in the equilibrium solution were relatively high, it was necessary to determine mean activities of the two cations. Salts with a common anion were used so that a simplified Glueckauf's equation (1949) could be employed to determine activity ratios in the mixed cation solutions. To show how Glueckauf's equation was used to compute activities in mixed solutions, the example of sodium-strontium will suffice.

Let us assume that $X_1 = \mathrm{Na}^+$, $X_2 = \mathrm{Sr}^{2+}$, and $Y = \mathrm{Cl}^-$, a common anion. By definition, the mean activity coefficient is described by

$$f_{(\pm)} = (f^{+v^+} \cdot f^{-v^-})^{1/(v^+)+(v^-)},$$

where v^+ is the number of cations and v^- is the number of anions. So

$$f^{X_1Y} = (fX_1 \cdot fY)^{1/2} = f\overset{X_1Y}{(X_2Y)} \text{ and } f^{X_2Y} = (fX_2 \cdot fY^2)^{1/3} = f\overset{X_2Y}{(X_1Y)}.$$

Consolidating,

$$\frac{f\overset{X_1Y}{(X_2Y)}}{f\overset{X_2Y}{(X_1Y)}} = \frac{(fX_1 \cdot fY)^{1/2}}{(fX_2 \cdot fY^2)^{1/3}}, \text{ or } \frac{fX_1{}^2}{fX_2} = \frac{\left[\overset{X_1Y}{(X_2Y)}\right]^4}{\left[f\overset{X_1Y}{(X_1Y)}\right]^3}. \tag{a}$$

Glueckauf's equation for two salts with a common anion is:

$$\log_{10} f\overset{X_1Y}{(X_2Y)} = \log_{10} f^{X_1Y} - \frac{X_2}{4I}\left(K_1 \log_{10} f^{X_1Y} - K_2 \log_{10} f^{X_2Y} - \frac{K_3}{(1+I^{-1/2})}\right), \tag{b}$$

where

$f^{X_1Y}_{(X_2Y)}$ = a mean activity coefficient of NaCl in the presence of $SrCl_2$,
$f^{X_2Y}_{(X_1Y)}$ = a mean activity coefficient of $SrCl_2$ in the presence of NaCl,
f^{X_1Y} = a mean activity coefficient of NaCl,
f^{X_2Y} = a mean activity coefficient of $SrCl_2$,
I = the total ionic strength,
X_1 = moles per liter of Na,
X_2 = moles per liter of Sr,
$K_1 = x_2(2x_2 - x_1 + y)$,
$K_2 = x_1(x_2+y)^2(x_1+y)^{-1}$, and
$K_3 = 1/2x_1x_2y(x_1-x_2)^2(x_1+y)^{-1}$ with x_1 = the ionic charge of Na or 1, x_2 = the ionic charge of Sr or 2, and y = the ionic charge of Cl or 1.

Substituting equation (a) into (b), we obtain:

$$4 \log_{10} f^{X_1Y}_{(X_2Y)} - 3 \log_{10} f^{X_2Y}_{(X_1Y)} = 4 \log_{10} f^{X_1Y}$$
$$- \frac{4X_2}{4I}\left(K_1 \log_{10} f^{X_1Y} - K_2 \log_{10} f^{X_2Y} - \frac{K_3}{1 + I^{-1/2}}\right) - 3 \log_{10} f^{X_2Y}$$
$$- \frac{3X_1}{4I}\left(K_1' \log_{10} f^{X_2Y} - K_2' \log_{10} f^{X_1Y} - \frac{K_3'}{1 + I^{-1/2}}\right),$$

with $K_1 = 8$, $K_2 = 9/2$, $K_3 = 1/2$, $K_1' = 1$, $K_2' = 8/3$, $K_3' = 1/3$ and $I = X_1 + 3X_2$.

Consolidating:

$$\frac{fX_1^2}{fX_2} = \left(4 - \frac{8X_2}{I} - \frac{2X_1}{I}\right) \log_{10} f^{X_1Y}$$
$$- \left(3 - \frac{9/2X_2}{I} - \frac{3/4X_1}{I}\right) \log_{10} f^{X_2Y} - \frac{1/4X_1 - 1/2X_2}{I(1 + I^{-1/2})}.$$

Letting $r = X_1/X_2$, we obtain

$$\frac{fX_1^2}{fX_2} = \frac{r+2}{r+3}\left(2 \log_{10} f^{X_1Y} - 9/4 \log_{10} f^{X_2Y}\right) - \frac{1/4(r-2)}{I(1 + I^{-1/2})}(X_2). \quad \text{(c)}$$

Equation (c) was used to obtain activity coefficients in the sodium-strontium and sodium-calcium systems. Computation of activity coefficients in a calcium-strontium system was less complicated. If $X_1 = Ca$, $X_2 = Sr$, and Y = a common anion, Cl, then by definition:

$$f^{X_1Y} = f^{X_1Y}_{(X_2Y)} = (fX_1 \cdot fY^2)^{1/3}$$

and

$$f^{X_2Y} = f^{X_2Y}_{(X_1Y)} = (fX_2 \cdot fY^2)^{1/3},$$

or

$$\frac{(fX_1 \cdot fY^2)^{1/3}}{(fX_2 \cdot fY^2)^{1/3}} = \left(\frac{f^{X_1Y}}{f^{X_2Y}}\right)^{3/2} = \frac{fX_1}{fX_2}.$$

The use of mean activity coefficients to correct equilibrium solution cation concentrations is a second step in the determination of a rational thermodynamic equilibrium constant for the reaction. It also may be necessary to determine activity coefficients for the cations on the zeolite (Hogfeldt *et al.*, 1950). For example, given the phillipsite exchange reaction for which the equilibrium data are shown in Fig. 1, $2Na_{zeolite}$ $Sr_{solution} \leftrightarrows Sr_{zeolite} + 2Na_{solution}$, the uncorrected mass action quotient is:

TABLE 1. COMPUTATION OF SOME κ_c VALUES FROM FIG. 1

Sr_s	Sr_z	$\frac{(Sr_z)(Na_s)^2}{(Na_z)^2(Sr_s)}$	$fNa_s{}^2/fSr_s$	κ_c	$Log_{10}\kappa_c$
0.080	0.020	0.2200	2.13	0.469	−0.3288
0.160	0.042	0.2020	2.18	0.440	−0.3575
0.430	0.135	0.1360	2.30	0.313	−0.5045
0.660	0.250	0.0778	2.42	0.188	−0.7258
0.850	0.430	0.0350	2.50	0.088	−1.0580
0.970	0.820	0.0235	2.55	0.060	−1.2218

$$\frac{(Sr_{zeolite})(Na_{solution})^2}{(Na_{zeolite})^2(Sr_{solution})}, \quad \text{or} \quad \frac{(Sr_z)(Na_s)^2}{(Na_z)^2(Sr_s)},$$

and

$$\kappa_c = \frac{(Sr_z)(Na_s)^2(fNa_s)^2}{(Na_z)^2(Sr_s)(fSr_s)}.$$

Since total solution equilibrium normality was constant at 1.0 in Fig. 1, and by definition $Sr_z + Na_z = 1$, the fraction of sodium in solution (and normality in this case) is $1.0 - Sr_{solution}$, and $Na_{zeolite} = 1 - Sr_{zeolite}$.

Table 1 shows the correction of several mass action quotients with solution activity coefficients. The resulting κ_c values are then plotted vs. the fraction of strontium on the zeolite. A graphical integration to determine the cumulative area under the κ_c curve, summing from Sr_z or $Na_z = 1.0$ to Sr_z or $Na_z = 0$, was required to obtain an equilibrium constant. The mathematics for the determination of cation activities on the zeolite are given in Hogfeldt *et al.* (1950)

A Gibbs standard free-energy, $\Delta G°$, may be calculated for cation exchange reactions by use of the relationship, $\Delta G° = -RT \ln\kappa$. If $\Delta G°$ is negative, the exchange reaction is favorable; *i.e.*, κ is greater than 1.0. The accuracy of a $\Delta G°$ determination for a given reaction can be checked by the determination of the $\Delta G°$ of two other related exchange reactions. For example, the Gibbs free-energy of phillipsite for the exchange reaction $(2Na_z + Sr_s^{2+} \rightleftarrows Sr_z + 2Na_s^+)$ minus the Gibbs free-energy for the reaction $(Ca_z + Sr_s^{2+} \rightleftarrows Sr_z + Ca_s^{2+})$ should equal the Gibbs free-energy for the reaction $(2Na_z + Ca_s^{2+} \rightleftarrows Ca_z + 2Na_s^+)$, or from Table 2, (+1300 cal/mole) − (+300 cal/mole) = (+1100 cal/mole). An average error of ±100 cal/mole for the above free-energy relationship may be noted for the zeolites listed in Table 2.

TABLE 2. THERMODYNAMIC DATA. κ IS A RATIONAL THERMODYNAMIC EQUILIBRIUM CONSTANT AND $\Delta G°$ IS A STANDARD GIBBS FREE-ENERGY EXPRESSED TO THE NEAREST 100 CAL/MOLE

Zeolite	κ				$\Delta G°$		
	$2Na_z \rightarrow Ca_z$	$Ca_z \rightarrow Sr_z$	$2Na_z \rightarrow Sr_z$	Computed $2Na_z \rightarrow Sr_z$	$2Na_z \rightarrow Ca_z$	$Ca_z \rightarrow Sr_z$	$2Na_z \rightarrow Sr_z$
4AXW	17.0	5.31	83.2	90.3	−1700	−1000	−2600
13X	5.13	3.16	19.9	16.2	−1000	− 700	−1800
AW 400	0.708	0.603	0.363	0.427	+ 200	+ 300	+ 600
AW 500	0.724	0.371	0.288	0.269	+ 200	+ 600	+ 700
Zeolon	0.691	0.316	0.235	0.218	+ 200	+ 700	+ 900
Clinoptilolite	0.851	1.12	1.29	0.953	+ 100	− 100	− 100
Phillipsite	0.163	0.588	0.107	0.096	+1100	+ 300	+1300
Erionite	1.05	0.758	0.794	0.796	0	+ 200	+ 100

RESULTS

The phillipsite isotherms for the systems Na − Sr, Na − Ca, and Sr − Ca are shown in Fig. 1, 2 and 3, respectively. An example of the effect of temperature on equilibria in the Na-Ca system is shown in Fig. 2. Reaction enthalpies for the other zeolites and for the Na–Sr and Sr–Ca systems also were close to zero for the temperature interval 25° C. to 70° C. All other isotherms in this paper are at 25° C.

The exchange isotherms for erionite in the systems Na–Sr, Na–Ca, and Sr–Ca are presented in Figs. 4, 5 and 6, respectively. Isotherms with Hector clinoptilolite are given in Figs. 7, 8 and 9 for the systems Na–Sr, Na–Ca, and Sr–Ca, respectively.

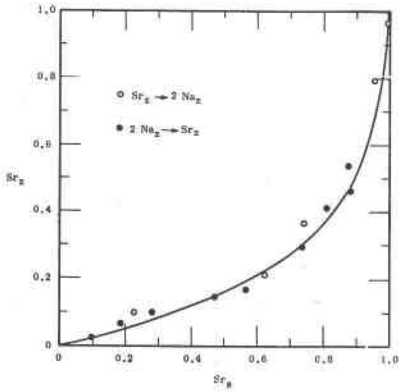

FIG. 1. The 25° C. isotherm for the reaction $2Na_z + Sr_s \rightleftharpoons Sr_z + 2Na_s$ with phillipsite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

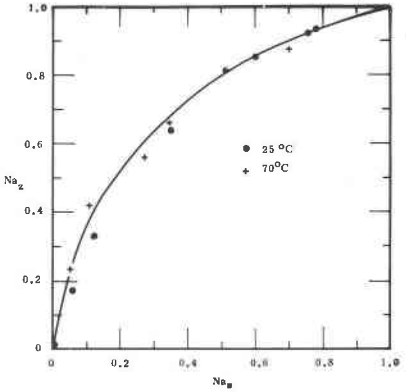

FIG. 2. The 25° C. isotherm for the reaction $Ca_z + 2Na_s \rightleftharpoons 2Na_s + Ca_s$ with phillipsite. Total equilibrium solution normality was constant at 1.0.

Na_z = equivalent fraction of sodium on the zeolite.

Na_s = equivalent fraction of sodium in the equilibrium solution.

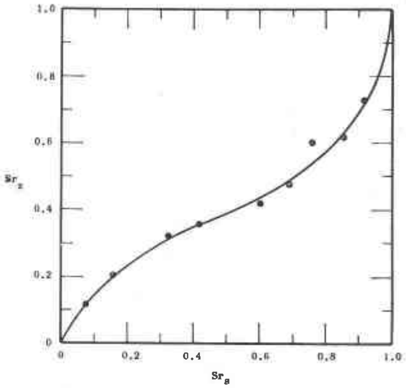

FIG. 3. The 25° C. isotherm for the reaction $Ca_z + Sr_s \rightleftharpoons Sr_z + Ca_s$ with phillipsite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

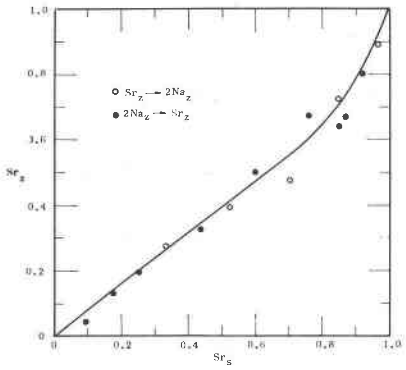

FIG. 4. The 25° C. isotherm for the reaction $2Na_z + Sr_s \rightleftharpoons Sr_z + 2Na_s$ with erionite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

DISCUSSION

The thermodynamic data derived from the experimental isotherms are given in Table 2. Computed Na–Sr results were obtained by multiplying the $2Na_z \rightarrow Ca_z \kappa$ by the $Ca_z \rightarrow Sr_z \kappa$. All other κ values were derived from experimental data. Agreement between experimental and computed κ values is good. The sums of Gibbs free-energies for exchanges in Na–Ca and Ca–Sr systems are ± 100 cal/mole for exchanges in the Na–Sr system. The effect of a temperature increase on the equilibrium constants of Table 2 is practically nil between 25° C. and 70° C. Exchange isotherms at the two temperatures were nearly identical.

It may be noted that erionite and AW 400 showed nearly the same cation exchange properties with alkali metal cations (Ames, 1964), and the same relationship can be deduced from Table 2. The sodium selectivity of AW 400 is greater than that of erionite, while calcium and strontium selectivities are nearly identical. The original conclusion that the two zeolites are probably compositionally and structurally very similar remains valid.

Barrer and Meier (1959, p. 140) have proposed three cases of $d\log \kappa_c/dB_z$, where B_z is the fraction of cation B on the zeolite in the exchange reaction, $A_z + B_s \rightleftarrows B_z + A_s$. The condition of $d\log \kappa_c/dB_z$ may be assessed from a plot of B_z *vs.* $\log \kappa_c$. If $d\log \kappa_c/dB_z = 0$, curve type 1 of Fig. 10 is typical, and $\kappa = \kappa_c$. If $d\log \kappa_c/dB_z$ is constant but not zero, curve 2 is representative, and $\log \kappa = \frac{1}{2}(\log \kappa_{c_1} + \log \kappa_{c_0}) \log \kappa_c = C(1 - 2B_z)$, where κ_{c_1} is the value of κ_c when $B_z = 1.0$, κ_{c_0} is equal to the value of κ_c when $B_z = 0$, and $C =$ a constant. If $d\log \kappa_c/dB_z$ is not a constant, curve type 3 of Fig. 10 may result, and

$$\log \kappa = \log \kappa_c - \int_{\kappa_{c_0}}^{\kappa_{c_1}} B_z \, d\log \kappa_c.$$

Curve type 3 is only one of many possible forms.

From an inspection of the isotherms, several instances of selectivity reversals are apparent (Figs. 3, 6, 7, 8, 9). A selectivity reversal occurs when the mass action quotient for cation B on the zeolite (B_z) proceeds from greater than 1.0 to less than 1.0 as a function of the fraction of B in solution (B_s). Three of the five equilibria exhibiting a selectivity reversal are in the system Ca–Sr. There are no examples of regular isotherms ($\kappa = \kappa_c$ = mass action quotient) shown in Figs. 1 through 9, or evidence of limited mutual solid solution between binary endmembers such as reported by Barrer and Falconer (1956).

Discounting the AW 300 equilibria, there were only three isotherms showing a selectivity reversal out of a total of 24 isotherms in univalent-univalent cation systems (Ames, 1964). A paper in preparation will show

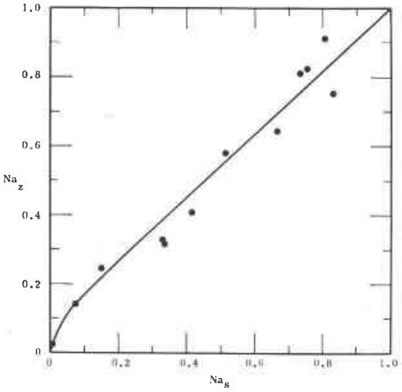

FIG. 5. The 25° C. isotherm for the reaction $Ca_z+2Na_s \rightleftharpoons 2Na_z+Ca_s$ with erionite. Total equilibrium solution normality was constant at 1.0.

Na_z = equivalent fraction of sodium on the zeolite.

Na_s = equivalent fraction of sodium in the equilibrium solution.

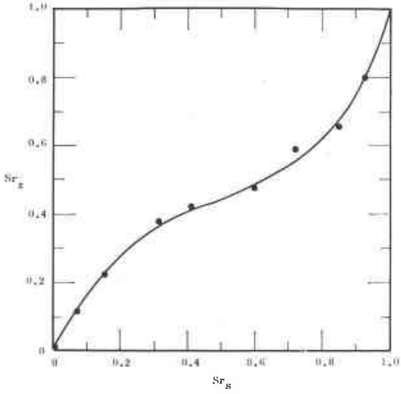

FIG. 6. The 25° C. isotherm for the reaction $Ca_z+Sr_s \rightleftharpoons Sr_z+Ca_s$ with erionite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

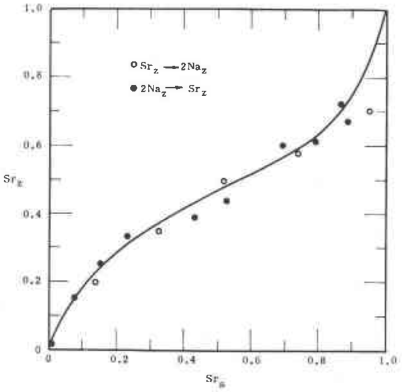

FIG. 7. The 25° C. isotherm for the reaction $2Na_z+Sr_s \rightleftharpoons Sr_z+2Na_s$ with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

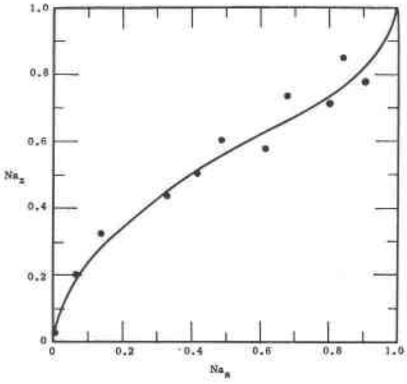

FIG. 8. The 25° C. isotherm for the reaction $Ca_z+2Na_s \rightleftharpoons 2Na_z+Ca_s$ with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

Na_z = equivalent fraction of sodium on the zeolite.

Na_s = equivalent fraction of sodium in the equilibrium solution.

that all exchange isotherms in systems containing trivalent cerium have some degree of selectivity reversal.

Type A exhibited a Sr–Ca isotherm with constant dlog κ_c/dB_z. The three related Type A curves of log κ_c *vs.* B_z for the systems Na–Sr, Na–Ca, and Ca–Sr are given in Figs. 11, 12 and 13, respectively. The progression toward more highly irregular curves from the Sr–Ca to Na–Ca to Na–Sr systems can be observed. Figure 12 cannot be directly compared with Barrer and Meier's Fig. 5a (Barrer and Meier, 1959, p. 134). Barrer and Meier plotted Ca_z as a molar fraction (Barrer, personal communication), whereas the Ca_z of this paper is expressed in equivalent fractions.

It may be assumed that Na^+ and Sr^{2+} cannot occupy thermodynamically (or spatially) equivalent positions in relation to Type A anionic sites. Beginning with 12 exchangeable Na^+ cations on the Type A unit cell, and progressing toward replacement with 6 Sr^{2+} cations, it is not too difficult to see why a pronounced selectivity reversal is encountered in the Na–Sr system (Fig. 11). There are many cation configurations on Type A so that with a composition such as Sr_4Na_4 or Sr_5Na_2, two adjacent anionic sites are not occupied by Na^+. It thus becomes increasingly difficult with the Type A in a Na–Sr system to exchange Sr^{2+} on the last 30 per cent of the originally sodium-based anionic sites in the required local order. In a Ca–Sr system, the Sr^{2+} and Ca^{2+} positions must be nearly equivalent. This hypothesis is substantiated by the fact that dlog κ_c/dB_z a constant in a Ca–Sr system (Fig. 13) and the isotherm is almost regular. The above qualitative summary may be somewhat over-simplified. There also is evidence for a steric effect on Type A cation exchange as well (Ames, 1964). Of the above three systems, Ca–Sr would be the least likely to show steric effects because only half as many Sr^{2+} and Ca^{2+} cations relative to univalent cations are required to neutralize the same number of anionic sites.

None of the plots of log κ_c *vs.* B_z obtained during the present study were found to yield constant or zero values for dlog κ_c/dB_z with the exceptions of Type A, AW 400, AW 500, 13X, phillipsite and erionite, all in a Ca–Sr system. The thermodynamic equilibrium constants obtained from the isotherms given in this paper are listed in Table 3.

Values determined by computing several activity coefficients for the cations on the zeolite and determining an average κ resulted in κ values nearly identical with those obtained with Barrer and Meier's equation. There are slight differences, but the differences are small and undoubtedly represent experimental error.

Having completed both univalent and divalent cation exchange systems for several zeolites, we may examine the relationship between zeolite composition, crystal structure, and cation selectivity, if any. From an examination of zeolite selectivities (κ) in Table 2, Type A and 13X are

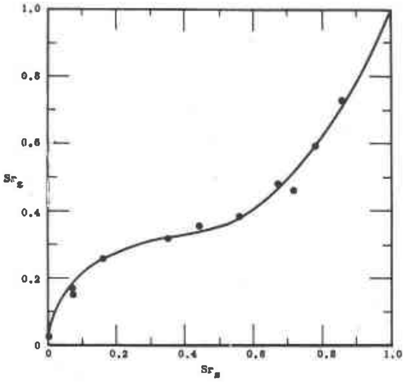

FIG. 9. The 25° C. isotherm for the reaction $Ca_z+Sr_s \rightleftharpoons Sr_z+Ca_s$ with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

Sr_z = equivalent fraction of strontium on the zeolite.

Sr_s = equivalent fraction of strontium in the equilibrium solution.

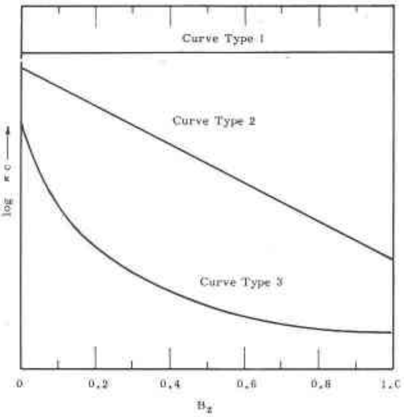

FIG. 10. Typical curves that may result when log κ_c is plotted *vs.* fraction of cation B on the zeolite (B_z).

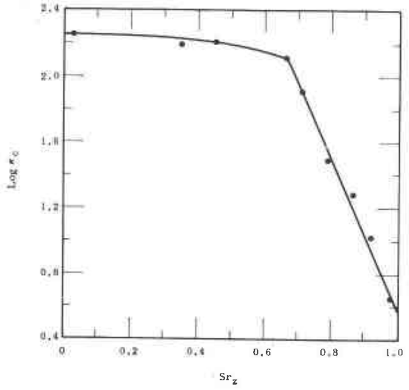

FIG. 11. A plot of log κ_c *vs.* fraction of strontium on the zeolite (Sr_z) for the reaction $2Na_z+Sr_s \rightleftharpoons Sr_z+2Na_s$ with Type A at 25° C.

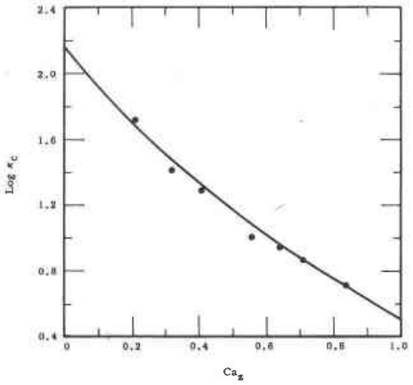

FIG. 12. A plot of log κ_c *vs.* fraction of calcium on the zeolite (Ca_z) for the reaction $2Na_z+Ca_s \rightleftharpoons Ca_z+2Na_s$ with Type A at 25° C.

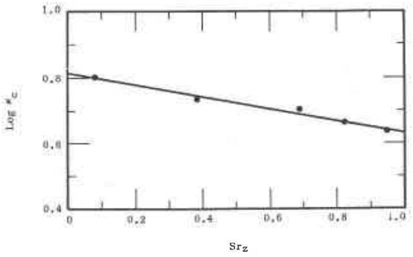

FIG. 13. A plot of log κ_c *vs*. fraction of strontium on the zeolite (Sr_z) for the reaction $Ca_z + Sr_s \rightleftharpoons Sr_z + Ca_s$ with Type A at 25° C. $C = -0.094$.

the only two zeolites that prefer divalent cations to any great extent. It is highly probable that the Type A exchange sites are regularly distributed (Reed and Breck, 1956, p. 5975; Barrer and Meier, 1958); *i.e*., the (AlO_2) groups are bonded only to (SiO_2) groups because the (SiO_2) to (AlO_2) ratio is 1:1 in Type A. Based on the assumption that the anionic sites are regularly distributed, the average distance between cations in the main exchange cavity of Type A is about 7 Å, and in the main cavity of 13X, about 8.3 Å, (Broussard and Shoemaker, 1960, p. 1048–1051). The above distances are for the known positions of sodium cations. Because only 8 of 12 sodium cations were located in Type A, the actual distances between sites may be on the order of 4 Å rather than 7 Å. Only 48 of the sodium

TABLE 3. A COMPARISON OF THE κ OBTAINED FROM BARRER AND MEIER'S EQUATION,

$$\text{LOG } \kappa = \text{LOG } \kappa_{c_1} - \int_{\kappa_{c_0}}^{\kappa_{c_1}} B_z \, d\log \kappa_c,$$

AND AN AVERAGE LOG κ OBTAINED BY DETERMINING f_{B_z} AND f_{A_z} VALUES AT SEVERAL POINTS ON THE LOG κ_c VS. B_z CURVE. LOG VALUES ARE ROUNDED TO THREE PLACES. THE $d\log \kappa_c/dB_z$ FOR PHILLIPSITE AND ERIONITE EQUALS A CONSTANT

Zeolite	$\int_{\kappa_{c_0}}^{\kappa_{c_1}} B_z \, d\log \kappa_c$	Log κ_{c_1}	Barrer's log κ	Average log κ
		Na–Sr		
Clinoptilolite	−0.809	−0.720	0.089	0.110
Phillipsite	−0.291	−1.250	−0.959	−0.960
Erionite	−0.777	−0.880	−0.103	−0.100
		Ca–Sr		
Clinoptilolite	−0.429	−0.390	0.039	0.049
Phillipsite	C = −0.690			
Erionite	C = −0.567			
		Ca–Na		
Clinoptilolite	−0.892	−0.995	−0.103	−0.089
Phillipsite	−0.405	−1.186	−0.781	−0.788
Erionite	−0.821	−0.810	0.011	0.021

cations were located out of a total of 80 for 13X, so that the 13X anionic sites also may be closer together than 8.3 Å. The above distances do indicate that the relative distances between anionic sites tends to increase with increasing $SiO_2:Al_2O_3$ ratio.

The important point is that zeolite selectivity, as indicated by κ, is related to distances between anionic sites. The distance between anionic sites is, in turn, a function of zeolite structure and composition. The work of Truesdell (1963) is pertinent to zeolite cation selectivity. He has reported that separation of anionic sites can be no more than 5Å if the exchanger is to be divalent cation selective. It is probable that Truesdell's model also is applicable to a basic explanation for the cation selectivities of zeolites.

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