

## SOME ZEOLITE EQUILIBRIA WITH ALKALINE EARTH METAL CATIONS<sup>1</sup>

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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  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and divalent cation selectivities. The above data plotted as  $\log \kappa_c$  vs. cation B on the zeolite were adequately described by Barrer and Meier's case where  $d \log \kappa_c / dB_c$  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 ( $2\text{Na}_{\text{solution}}^{22} + \text{Sr}_{\text{zeolite}} \rightleftharpoons \text{Na}_{\text{zeolite}}^{22} + \text{Sr}_{\text{solution}}$ , and  $\text{Sr}_{\text{solution}}^{85} + 2\text{Na}_{\text{zeolite}} \rightleftharpoons \text{Sr}_{\text{zeolite}}^{85} + 2\text{Na}_{\text{solution}}$ ), 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  $X_1 = \text{Na}^+$ ,  $X_2 = \text{Sr}^{2+}$ , and  $Y = \text{Cl}^-$ , 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

$$f^{X_1 Y} = (fX_1 \cdot fY)^{1/2} = f^{X_1 Y} \text{ and } f^{X_2 Y} = (fX_2 \cdot fY^2)^{1/3} = f^{X_2 Y}.$$

Consolidating,

$$\frac{f^{X_1 Y}}{f^{X_2 Y}} = \frac{(fX_1 \cdot fY)^{1/2}}{(fX_2 \cdot fY^2)^{1/3}}, \text{ or } \frac{fX_1^2}{fX_2} = \frac{\left[ \frac{X_1 Y}{X_2 Y} \right]^4}{\left[ \frac{X_1 Y}{X_2 Y} \right]^3} \quad (\text{a})$$

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

$$\log_{10} f^{X_2 Y} = \log_{10} f^{X_1 Y} - \frac{X_2}{4I} \left( K_1 \log_{10} f^{X_1 Y} - K_2 \log_{10} f^{X_2 Y} - \frac{K_3}{(1 + I^{-1/2})} \right), \quad (\text{b})$$

where

$f_{(X_2Y)}^{X_1Y}$  = a mean activity coefficient of NaCl in the presence of SrCl<sub>2</sub>,

$f_{(X_1^2Y)}^{X_2Y}$  = a mean activity coefficient of SrCl<sub>2</sub> in the presence of NaCl,

$f^{X_1Y}$  = a mean activity coefficient of NaCl,

$f^{X_2Y}$  = a mean activity coefficient of SrCl<sub>2</sub>,

I = the total ionic strength,

X<sub>1</sub> = moles per liter of Na,

X<sub>2</sub> = moles per liter of Sr,

K<sub>1</sub> = x<sub>2</sub>(2x<sub>2</sub> - x<sub>1</sub> + y),

K<sub>2</sub> = x<sub>1</sub>(x<sub>2</sub> + y)<sup>2</sup>(x<sub>1</sub> + y)<sup>-1</sup>, and

K<sub>3</sub> = 1/2x<sub>1</sub>x<sub>2</sub>y(x<sub>1</sub> - x<sub>2</sub>)<sup>2</sup>(x<sub>1</sub> + y)<sup>-1</sup> with x<sub>1</sub> = the ionic charge of Na or 1, x<sub>2</sub> = the ionic charge of Sr or 2, and y = the ionic charge of Cl or 1.

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

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

with K<sub>1</sub> = 8, K<sub>2</sub> = 9/2, K<sub>3</sub> = 1/2, K<sub>1</sub>' = 1, K<sub>2</sub>' = 8/3, K<sub>3</sub>' = 1/3 and I = X<sub>1</sub> + 3X<sub>2</sub>.

Consolidating:

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

Letting r = X<sub>1</sub>/X<sub>2</sub>, we obtain

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

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<sub>1</sub> = Ca, X<sub>2</sub> = Sr, and Y = a common anion, Cl, then by definition:

$$f^{X_1Y} = f_{(X_2Y)}^{X_1Y} = (f^{X_1} \cdot f^{Y^2})^{1/3}$$

and

$$f_{X_2}^{X_2Y} = f_{(X_2Y)}^{X_2Y} = (f_{X_2} \cdot f_{Y^2})^{1/3},$$

or

$$\frac{(f_{X_1} \cdot f_{Y^2})^{1/3}}{(f_{X_2} \cdot f_{Y^2})^{1/3}} = \left( \frac{f_{X_1}^{X_1Y}}{f_{X_2}^{X_2Y}} \right)^{3/2} = \frac{f_{X_1}}{f_{X_2}}.$$

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 reac-

TABLE 1. COMPUTATION OF SOME  $\kappa_c$  VALUES FROM FIG. 1

$Sr_s$	$Sr_z$	$\frac{(Sr_z)(Na_s)^2}{(Na_z)^2(Sr_s)}$	$f_{Na_s}^2/f_{Sr_s}$	$\kappa_c$	$\text{Log}_{10}\kappa_c$
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

tion for which the equilibrium data are shown in Fig. 1,  $2Na_{zeolite} + Sr_{solution} \rightleftharpoons Sr_{zeolite} + 2Na_{solution}$ , the uncorrected mass action quotient is:

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

and

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

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  $\kappa_c$  values are then plotted vs. the fraction of strontium on the zeolite. A graphical integration to determine the cumulative area under the  $\kappa_c$  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,  $\Delta G^\circ$ , may be calculated for cation exchange reactions by use of the relationship,  $\Delta G^\circ = -RT \ln \kappa$ . If  $\Delta G^\circ$  is negative, the exchange reaction is favorable; *i.e.*,  $\kappa$  is greater than 1.0. The accuracy of a  $\Delta G^\circ$  determination for a given reaction can be checked by the determination of the  $\Delta G^\circ$  of two other related exchange reactions. For example, the Gibbs free-energy of phillipsite for the exchange reaction ( $2\text{Na}_z + \text{Sr}_s^{2+} \rightleftharpoons \text{Sr}_z + 2\text{Na}_s^+$ ) minus the Gibbs free-energy for the reaction ( $\text{Ca}_z + \text{Sr}_s^{2+} \rightleftharpoons \text{Sr}_z + \text{Ca}_s^{2+}$ ) should equal the Gibbs free-energy for the reaction ( $2\text{Na}_z + \text{Ca}_s^{2+} \rightleftharpoons \text{Ca}_z + 2\text{Na}_s^+$ ), or from Table 2, (+1300 cal/mole) - (+300 cal/mole) = (+1100 cal/mole). An average error of  $\pm 100$  cal/

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

Zeolite	$\kappa$				$\Delta G^\circ$		
	$2\text{Na}_z \rightarrow \text{Ca}_z$	$\text{Ca}_s \rightarrow \text{Sr}_s$	$2\text{Na}_z \rightarrow \text{Sr}_z$	Com- puted $2\text{Na}_z \rightarrow \text{Sr}_z$	$2\text{Na}_z \rightarrow \text{Ca}_z$	$\text{Ca}_z \rightarrow \text{Sr}_z$	$2\text{Na}_z \rightarrow \text{Sr}_z$
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

mole for the above free-energy relationship may be noted for the zeolites listed in Table 2.

## 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.

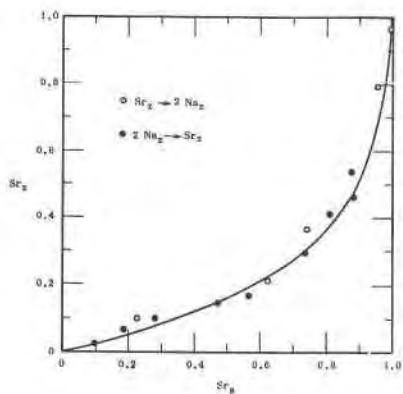


FIG. 1. The 25° C. isotherm for the reaction  $2\text{Na}_z + \text{Sr}_s \rightleftharpoons \text{Sr}_z + 2\text{Na}_s$  with philipsite. Total equilibrium solution normality was constant at 1.0.

$\text{Sr}_z$  = equivalent fraction of strontium on the zeolite.

$\text{Sr}_s$  = equivalent fraction of strontium in the equilibrium solution.

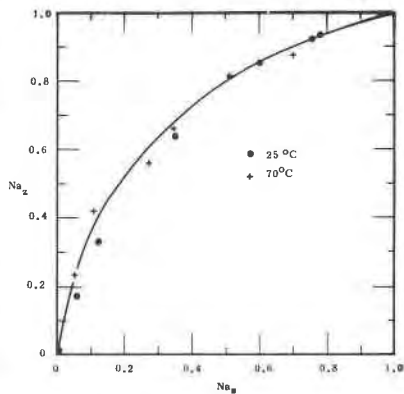


FIG. 2. The 25° C. isotherm for the reaction  $\text{Ca}_z + 2\text{Na}_s \rightleftharpoons 2\text{Na}_z + \text{Ca}_s$  with philipsite. Total equilibrium solution normality was constant at 1.0.

$\text{Na}_z$  = equivalent fraction of sodium on the zeolite.

$\text{Na}_s$  = equivalent fraction of sodium in the equilibrium solution.

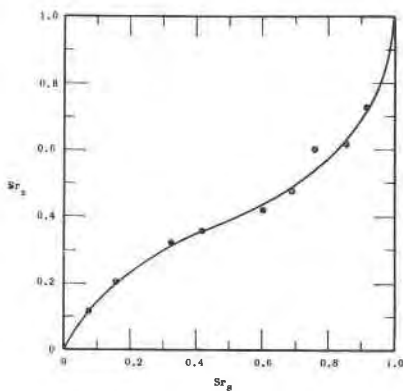


FIG. 3. The 25° C. isotherm for the reaction  $\text{Ca}_z + \text{Sr}_s \rightleftharpoons \text{Sr}_z + \text{Ca}_s$  with philipsite. Total equilibrium solution normality was constant at 1.0.

$\text{Sr}_z$  = equivalent fraction of strontium on the zeolite.

$\text{Sr}_s$  = equivalent fraction of strontium in the equilibrium solution.

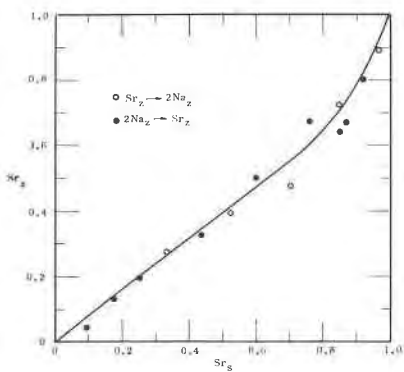


FIG. 4. The 25° C. isotherm for the reaction  $2\text{Na}_z + \text{Sr}_s \rightleftharpoons \text{Sr}_z + 2\text{Na}_s$  with erionite. Total equilibrium solution normality was constant at 1.0.

$\text{Sr}_z$  = equivalent fraction of strontium on the zeolite.

$\text{Sr}_s$  = 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  $2\text{Na}_z \rightarrow \text{Ca}_z\kappa$  by the  $\text{Ca}_z \rightarrow \text{Sr}_z\kappa$ . All other  $\kappa$  values were derived from experimental data. Agreement between experimental and computed  $\kappa$  values is good. The sums of Gibbs free-energies for exchanges in Na-Ca and Ca-Sr systems are  $\pm 100$  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,  $A_z + B_s \rightleftharpoons B_z + A_s$ . The condition of  $d \log \kappa_c / dB_z = 0$ , 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  $\kappa_{c_1}$  is the value of  $\kappa_c$  when  $B_z = 1.0$ ,  $\kappa_{c_0}$  is equal to the value of  $\kappa_c$  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

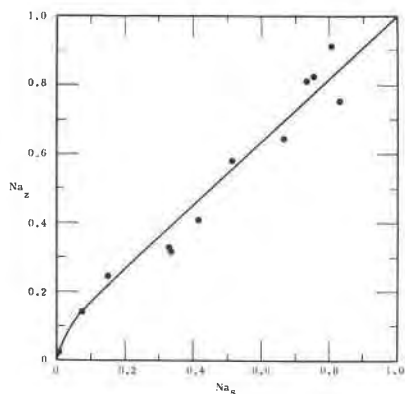


FIG. 5. The 25° C. isotherm for the reaction  $\text{Ca}_z + 2\text{Na}_s \rightleftharpoons 2\text{Na}_z + \text{Ca}_s$  with erionite. Total equilibrium solution normality was constant at 1.0.

$\text{Na}_z$  = equivalent fraction of sodium on the zeolite.

$\text{Na}_s$  = equivalent fraction of sodium in the equilibrium solution.

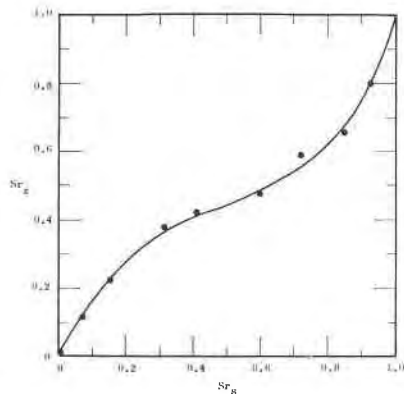


FIG. 6. The 25° C. isotherm for the reaction  $\text{Ca}_z + \text{Sr}_s \rightleftharpoons \text{Sr}_z + \text{Ca}_s$  with erionite. Total equilibrium solution normality was constant at 1.0.

$\text{Sr}_z$  = equivalent fraction of strontium on the zeolite.

$\text{Sr}_s$  = equivalent fraction of strontium in the equilibrium solution.

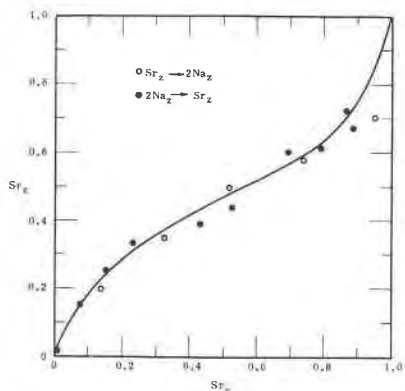


FIG. 7. The 25° C. isotherm for the reaction  $2\text{Na}_z + \text{Sr}_s \rightleftharpoons \text{Sr}_z + 2\text{Na}_s$  with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

$\text{Sr}_z$  = equivalent fraction of strontium on the zeolite.

$\text{Sr}_s$  = equivalent fraction of strontium in the equilibrium solution.

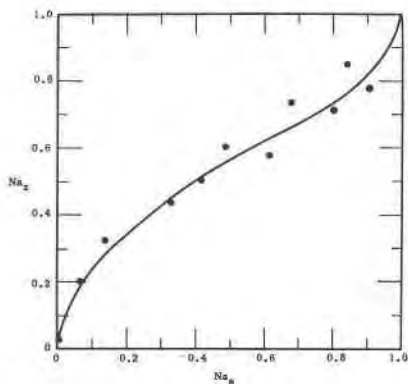


FIG. 8. The 25° C. isotherm for the reaction  $\text{Ca}_z + 2\text{Na}_s \rightleftharpoons 2\text{Na}_z + \text{Ca}_s$  with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

$\text{Na}_z$  = equivalent fraction of sodium on the zeolite.

$\text{Na}_s$  = 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  $\text{dlog } \kappa_c/\text{dB}_z$ . The three related Type A curves of  $\log \kappa_c$  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  $\text{Ca}_z$  as a molar fraction (Barrer, personal communication), whereas the  $\text{Ca}_z$  of this paper is expressed in equivalent fractions.

It may be assumed that  $\text{Na}^+$  and  $\text{Sr}^{2+}$  cannot occupy thermodynamically (or spatially) equivalent positions in relation to Type A anionic sites. Beginning with 12 exchangeable  $\text{Na}^+$  cations on the Type A unit cell, and progressing toward replacement with 6  $\text{Sr}^{2+}$  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  $\text{Sr}_4\text{Na}_4$  or  $\text{Sr}_5\text{Na}_2$ , two adjacent anionic sites are not occupied by  $\text{Na}^+$ . It thus becomes increasingly difficult with the Type A in a Na–Sr system to exchange  $\text{Sr}^{2+}$  on the last 30 per cent of the originally sodium-based anionic sites in the required local order. In a Ca–Sr system, the  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  positions must be nearly equivalent. This hypothesis is substantiated by the fact that  $\text{dlog } \kappa_c/\text{dB}_z$  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  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  cations relative to univalent cations are required to neutralize the same number of anionic sites.

None of the plots of  $\log \kappa_c$  vs.  $B_z$  obtained during the present study were found to yield constant or zero values for  $\text{dlog } \kappa_c/\text{dB}_z$  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  $\kappa$  resulted in  $\kappa$  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 ( $\kappa$ ) in Table 2, Type A and 13X are

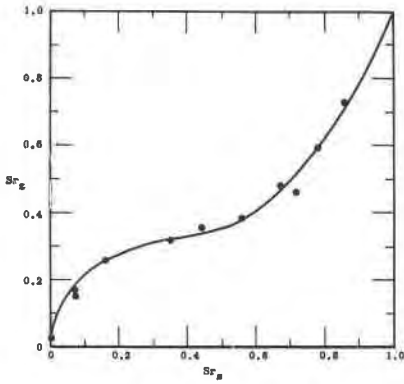


FIG. 9. The 25° C. isotherm for the reaction  $Ca_z + Sr_s \rightleftharpoons Sr_z + Ca_s$  with Hector clinoptilolite. Total equilibrium solution normality was constant at 1.0.

$Sr_z$  = equivalent fraction of strontium on the zeolite.

$Sr_s$  = equivalent fraction of strontium in the equilibrium solution.

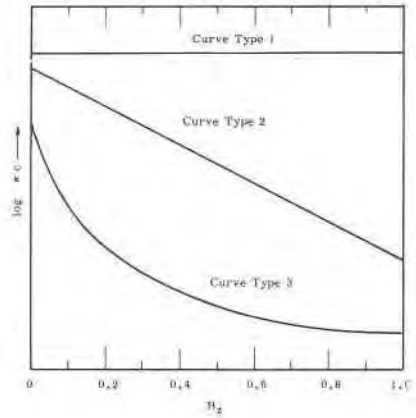


FIG. 10. Typical curves that may result when  $\log \kappa_c$  is plotted vs. fraction of cation B on the zeolite ( $B_z$ ).

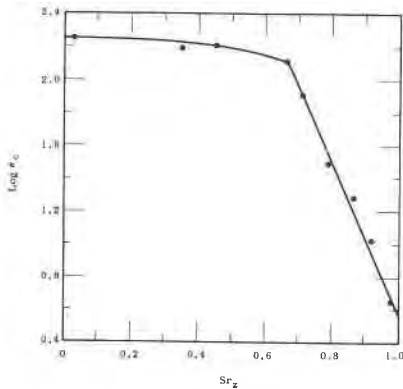


FIG. 11. A plot of  $\log \kappa_c$  vs. fraction of strontium on the zeolite ( $Sr_z$ ) for the reaction  $2Na_z + Sr_s \rightleftharpoons Sr_z + 2Na_s$  with Type A at 25° C.

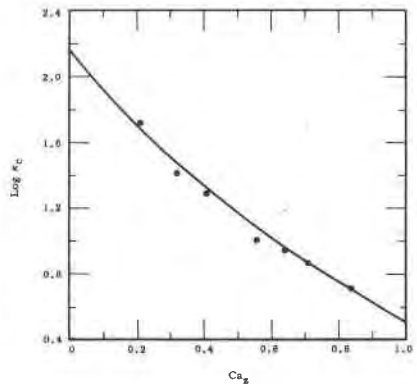
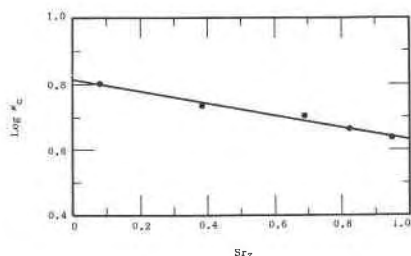


FIG. 12. A plot of  $\log \kappa_c$  vs. fraction of calcium on the zeolite ( $Ca_z$ ) for the reaction  $2Na_z + Ca_s \rightleftharpoons Ca_z + 2Na_s$  with Type A at 25° C.

FIG. 13. A plot of  $\log \kappa_c$  vs. fraction of strontium on the zeolite ( $Sr_z$ ) for the reaction  $Ca_z + Sr_{z'} \rightleftharpoons Sr_z + Ca_{z'}$  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  $7 \text{ \AA}$ , and in the main cavity of 13X, about  $8.3 \text{ \AA}$ , (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  $4 \text{ \AA}$  rather than  $7 \text{ \AA}$ . Only 48 of the sodium

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

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

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

Zeolite	$\int_{\kappa_{c_0}}^{\kappa_{c_1}} B_z \text{dlog } \kappa_c$	$\text{Log } \kappa_{c_1}$	Barrer's $\text{log } \kappa$	Average $\text{log } \kappa$
		<i>Na-Sr</i>		
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
		<i>Ca-Sr</i>		
Clinoptilolite	-0.429	-0.390	0.039	0.049
Phillipsite	$C = -0.690$			
Erionite	$C = -0.567$			
		<i>Ca-Na</i>		
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<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio.

The important point is that zeolite selectivity, as indicated by  $\kappa$ , 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 5 Å 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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