EXCHANGE OF ALKALI METAL CATIONS ON A NATURAL STILBITE[1]

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ABSTRACT

Cation exchange reactions involving sodium, potassium and cesium with a natural stilbite were investigated. Equilibrium constants of 7.03, 0.131 and 1.03 were derived from the 23 °C isotherms for sodium on the zeolite replaced by cesium, potassium on the zeolite replaced by sodium and potassium on the zeolite replaced by cesium, respectively. The equilibrium constant for sodium on the zeolite replaced by cesium falls to 1.65 at 85 °C.

INTRODUCTION

Stilbite is a relatively common natural zeolite formed as a result of late-stage hydrothermal activity in cooling basalts. The quantity of stilbite found in nature, in comparison to those zeolites such as clinoptilolite, phillipsite and erionite that are derived from the alteration of tuffs under semiarid conditions, is rather small. Knowledge of the cation exchange properties is important, however, in that stilbite readily exchanges cations in several systems.

The purpose of this work was to investigate the alkali metal cation exchange characteristics of a natural stilbite. The results of this investigation, along with some derived data, are given in this report.

METHODS OF INVESTIGATION

The stilbite used in this study was from the Bay of Fundy region in Nova Scotia. The stilbite was associated with basalt, from which it was removed by hand before crushing. The one-half to one-quarter millimeter stilbite fraction was further purified by several passes through a high field strength magnetic separator, resulting in a final stilbite sample that was by *x*-ray and optical examination of greater than 95 per cent purity. The purified stilbite sample was then ground in an alumina ball mill to minus 100 mesh, washed with distilled water and air-dried. All equilibrium data are based on a given weight of the air-dried material with an average water content of 16.6 per cent by weight. A chemical analysis of the purified anhydrous stilbite is given in Table 1.

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TABLE 1. STILBITE, CHEMICAL ANALYSIS AND DERIVED ANHYDROUS OXIDE FORMULA

Constituent	Weight	Formula
SiO_2	71.8	
Al_2O_3	19.6	(0.18 Na, 0.82 Ca) $0.Al_2O_3.6.2\ SiO_2$
Na_2O	2.1	
CaO	8.9	
	102.4	

Equilibrium studies were made by utilizing a small column technique similar to that reported by Howery & Thomas (1965). One-quarter to one-half g powdered stilbite samples were placed in straight sealing tubes containing a fritted glass disc. The sealing tubes had been cut off just below the frit to allow placement of the whole tube into another plastic tube for counting of the adsorbed radioisotope. A solution of known chemical composition plus a radioactive tracer (less than 1×10^{-7} in molarity) was passed through the stilbite until equilibrium was attained. The time necessary to reach equilibrium was determined in a previous study (see Table 2). The small columns then were washed with no more than ten bed volumes of distilled water or ethyl alcohol, placed in plastic counting tubes and counted with an equal volume of influent solution with the same geometry. The milliequivalents of traced cation per gram of stilbite was obtained by dividing the counts per gram of stilbite by the counts per milliequivalent of influent solution. In the case where columns are used, the influent solution is the equilibrium solution. Equal volume gamma counting was shown to be a valid procedure by Eliason (1966). An error can be encountered when sodium-22 is used if energies other than 1.28 Mev peak are counted. The other, and relatively larger, gamma peak at 0.51 Mev is the result of positron annihilation. The distance a positron travels before meeting an electron is a function of the density of the material containing the sodium-22. Counting of solids and liquids on the 0.51 Mev peak thus is often not proportional. It is desirable, too, to keep instrument dead-time below ten per cent by a judicious choice of tracer level in the equilibrating solutions.

From the cation distributions, a mass action quotient, or selectivity quotient, was obtained by the following relationship:

$$\text{Selectivity quotient} = \frac{(A_Z)^{n_A}(B_N)^{n_B}}{(B_Z)^{n_B}(A_N)^{n_A}},$$

where A_N, B_N = concentration of cations A and B in equivalents/liter,
A_Z, B_Z = equivalent fractions of cations 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.

The selectivity quotient was corrected with an appropriate mean activity coefficient ratio for a total solution normality of one, resulting in a corrected selectivity coefficient, K_c (Glueckauf, 1949). The ln K_c values were plotted vs. the equivalent fraction of cation on the zeolite according to the method of Gaines & Thomas (1953). Gibbs free-energy changes and a reaction enthalpy were derived from the above graphs by standard methods.

All solutions used in this study contained reagent grade chlorides of the cations in distilled water. The cesium-134 and sodium-22 were present as high purity radioisotopes.

RESULTS AND DISCUSSION

Cesium and sodium cation exchange capacity determinations on the stilbite are given in table 2. Though the cesium capacity of the stilbite finally equalled the sodium capacity, the time required suggests that a portion of the stilbite structure through which cations must diffuse during exchange reactions approaches the diameter of the cesium cation in size. The slow cesium diffusion may take place through "stacking faults" or distorted eight-membered rings in the stilbite crystal structure.* The structure of stilbite is, unfortunately, unknown (Smith, 1963) so that structural interpretation of the causes of the relatively slow cesium diffusion is not possible at this time. These results also show that up to four days is required to reach equilibrium when cesium is present in the system. The data obtained from the equilibrium experiments are given in Table 3.

TABLE 2. VARIATION IN STILBITE CAPACITY WITH EQUILIBRATION TIME

	Equilibration time, hr.		
Cation	16	32	64
Sodium	1.797 meq/g	1.831 meq/g	1.792 meq/g
Cesium	0.981 meq/g	1.510 meq/g	1.764 meq/g

Isotherms at 23 °C for the systems sodium-cesium, sodium-potassium, potassium-cesium and strontium-cesium with stilbite are given in figures 1, 2, 3 and 4, respectively. The 85 °C isotherm for sodium-cesium with

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*Recent structural work reported by E. Galli and G. Gottardi (*Miner. Petrogr. Acta*, **12**, 1966) indicates that the large channels in stilbite are surrounded by ten tetrahedra rings.

Table 3. Stilbite Equilibrium Data for the Exchange Reactions and Temperatures Indicated. The Subscript "z" refers to the Equivalent Fraction of Cation on the Zeolite and the Subscript "s" to the Equivalent Fraction of Cation in Solution.

$K_z + Na_s \rightleftarrows Na_z + K_s$, 23 °C

Na_z	Na_s	Selectivity Quotient	K_c
0.899	0.990	0.090	0.083
0.737	0.950	0.147	0.136
0.508	0.900	0.115	0.106
0.324	0.700	0.205	0.189
0.186	0.500	0.229	0.210
0.083	0.300	0.211	0.194
0.028	0.100	0.259	0.239

$K_z + Cs_s \rightleftarrows Cs_z + K_s$, 23 °C

Cs_z	Cs_s	Selectivity Quotient	K_c
0.904	0.900	1.043	1.160
0.745	0.700	1.249	1.389
0.646	0.700	0.782	0.870
0.526	0.500	1.112	1.236
0.511	0.500	1.045	1.162
0.343	0.300	1.218	1.354
0.149	0.100	1.576	1.753
0.0174	0.010	1.753	1.949

$Na_z + Cs_s \rightleftarrows Cs_z + Na_s$, 23 °C

Cs_z	Cs_s	Selectivity Quotient	K_c
0.870	0.900	0.744	0.900
0.814	0.800	1.094	1.324
0.756	0.600	2.066	2.500
0.639	0.400	2.655	3.213
0.543	0.200	4.753	5.751
0.460	0.100	7.666	9.275
0.400	0.050	12.565	15.204
0.109	0.005	24.800	30.008

$Na_z + Cs_s \rightleftarrows Cs_z + Na_s$, 85 °C

Cs_z	Cs_s	Selectivity Quotient	K_c
0.862	0.990	0.048	0.058
0.659	0.800	0.483	0.584
0.523	0.600	0.731	0.885
0.430	0.400	1.132	1.370
0.421	0.200	2.908	3.519
0.350	0.100	4.846	5.864
0.0712	0.005	15.530	18.510

$Sr_z + 2Cs_s \rightleftarrows 2Cs_z + Sr_s$, 23 °C

Cs_z	Cs_s	Selectivity Quotient	K_c
0.0331	0.001	566	753
0.118	0.010	78.0	103
0.291	0.100	5.85	7.78
0.378	0.200	2.30	3.05
0.412	0.500	0.289	0.434
0.562	0.700	0.221	0.314
0.694	0.900	0.097	0.128
0.907	0.990	0.0452	0.0588

stilbite also is included in figure 1. The points in each system represent the experimental values given in table 3, while the line is the probable best interpolation between the experimental points. Graphs of ln K_c vs. cation on the zeolite at 23 °C are shown for stilbite in sodium-cesium, sodium-potassium, potassium-cesium and strontium-cesium systems in figures 5, 6, 7 and 8, respectively. The 85 °C plot also is given in figure 5. Note that a straight line results in each case in figures 5, 6 and 7. The rational thermodynamic equilibrium constant, κ, then is equal to the

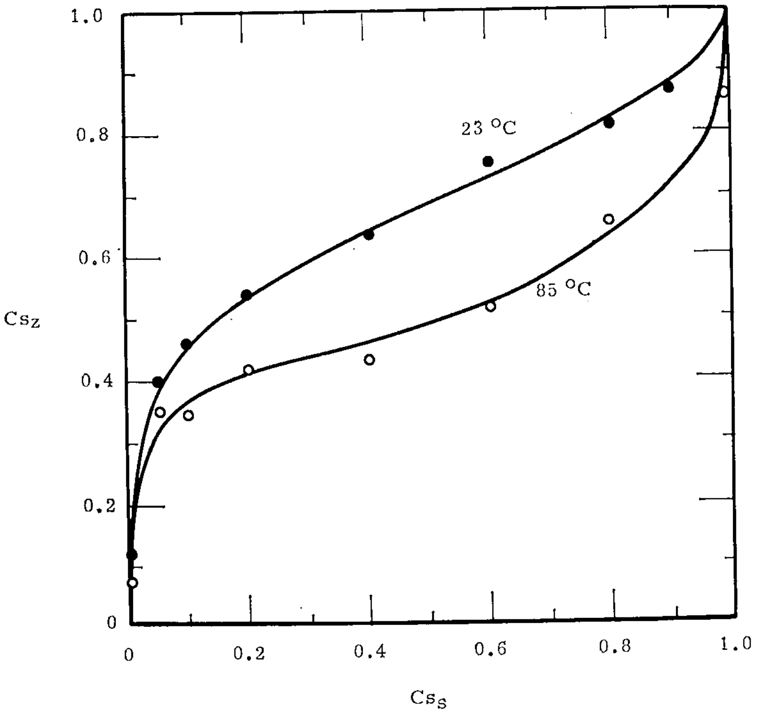

FIG. 1. The 23 °C and 85 °C isotherms for the reaction $Na_z + Cs_s \rightleftarrows Cs_z + Na_s$ with stilbite. Total equilibrium solution normality was constant at 1.0.
Cs_z = equivalent fraction of cesium on the zeolite.
Cs_s = equivalent fraction of cesium in the equilibrium solution.

value of $\ln K_c$ at the fraction of cation on the zeolite of 0.5. A list of the κ values for the various systems is given in table 4, along with related free-energy changes. Stilbite falls between Type X and phillipsite in the cesium selectivity data reported by Ames (1965). The free-energy changes for the various exchange reactions balance quite well. The ΔG° for the reaction ($Na_z + Cs_s \rightleftarrows Cs_z + Na_s$) plus the ΔG° for the reaction ($Cs_z + K_s \rightleftarrows K_z + Cs_s$) should equal the ΔG° for the reaction ($Na_z + K_s \rightleftarrows K_z + Na_s$), or (−1156) + (+15) = (−1204). The above balance is in error by 63 calories, a fortuitously small amount considering that the results are usually 100 to 200 calories from a balance.

According to Barrer & Meier (1959), curves of the type shown in figures 5, 6 and 7 are described by the relationship $\ln \kappa = \ln K_c + C(1\text{–}2B_z)$, based on the Kielland equation, where B_z is the fraction of cation B on the zeolite and C is a constant. The C values for each system were computed, and are listed in table 4.

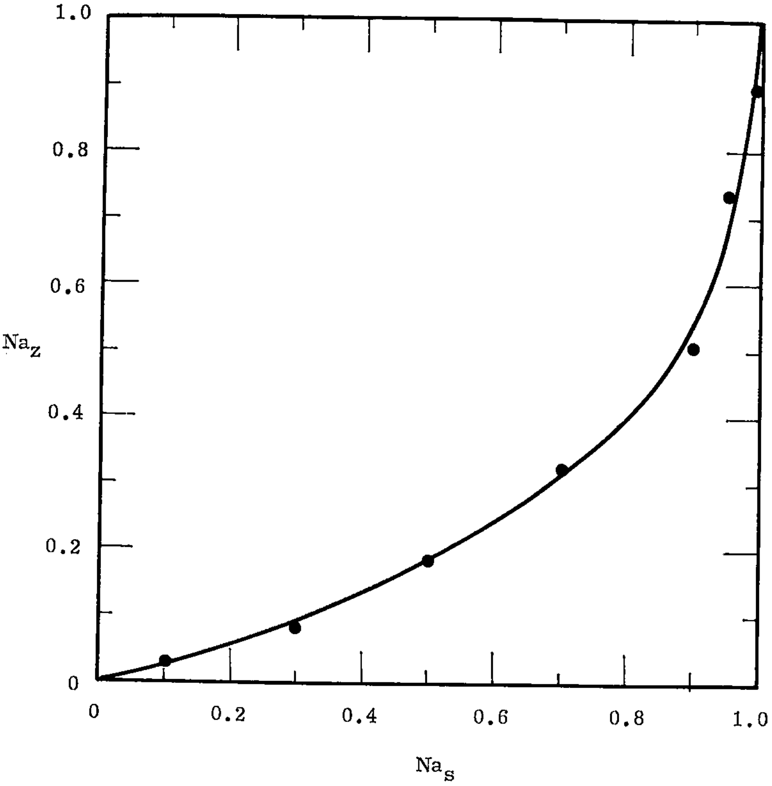

FIG. 2. The 23 °C isotherm for the reaction $K_z + Na_s \rightleftarrows Na_z + K_s$ with stilbite. Total equilibrium solution normality was constant at 1.0.
Na_z = equivalent fraction of sodium on the zeolite.
Na_s = equivalent fraction of sodium in the equilibrium solution.

TABLE 4. STILBITE THERMODYNAMIC DATA. κ IS A RATIONAL THERMODYNAMIC CONSTANT, ΔG° IS THE STANDARD GIBBS FREE-ENERGY CHANGE AND ΔH° IS A REACTION ENTHALPY. THE SUBSCRIPT "*z*" REFERS TO THE CATION ON THE ZEOLITE AND THE SUBSCRIPT "*s*" TO THE CATION IN THE SOLUTION.

Exchange reaction	Temp. °C	κ	ΔG °, cal/mole	ΔH °, cal/mole	*C**
$Na_z + Cs_s \rightleftarrows Cs_z + Na_s$	23	7.03	−1156	−4920	−2.5
$Na_z + Cs_s \rightleftarrows Cs_z + Na_s$	85	1.65	−297		−3.7
$K_z + Na_s \rightleftarrows Na_z + K_s$	23	0.131	+1204		−0.6
$K_z + Cs_s \rightleftarrows Cs_z + K_s$	23	1.03	−15		−0.5
$Sr_z + 2Cs_s \rightleftarrows 2Cs_z + Sr_s$	23	3.46	−735		—

**C* is known as the Kielland constant (p. 586).

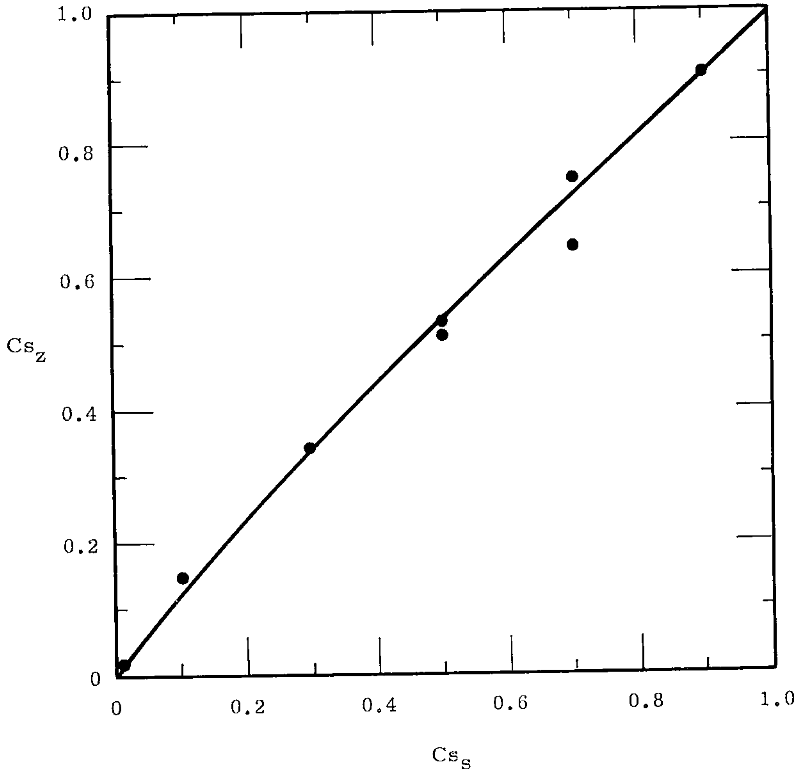

FIG. 3. The 23 °C isotherm for the reaction $K_z + Cs_s \rightleftarrows Cs_z + K_s$ with stilbite. Total equilibrium solution normality was constant at 1.0.
Cs_z = equivalent fraction of cesium on the zeolite.
Cs_s = equivalent fraction of cesium in the equilibrium solution.

A marked selectivity reversal occurs in the strontium-cesium system, similar to the behavior of other zeolites in divalent-univalent cation systems (Ames, 1964). The thermodynamic equilibrium constant was derived with Gaines & Thomas (1953) simplified expression:

$$\ln \kappa = (Y - X) + \int_0^1 \ln K_c \cdot dCs_z,$$

where — κ = a rational equilibrium constant,
Y = the charge of the Sr ion (+2),
X = the charge of the Cs ion (+1),
Cs_z = the equivalent fraction of cesium on the zeolite, and

$$K_c = \frac{(Cs_z)^2(Sr_s)}{(Sr_z)(Cs_s)^2 2(Co)}.$$

The equivalent fractions of cesium and strontium on the zeolite are Cs_z and Sr_z, respectively, and Cs_s and Sr_s are the equivalent fractions of

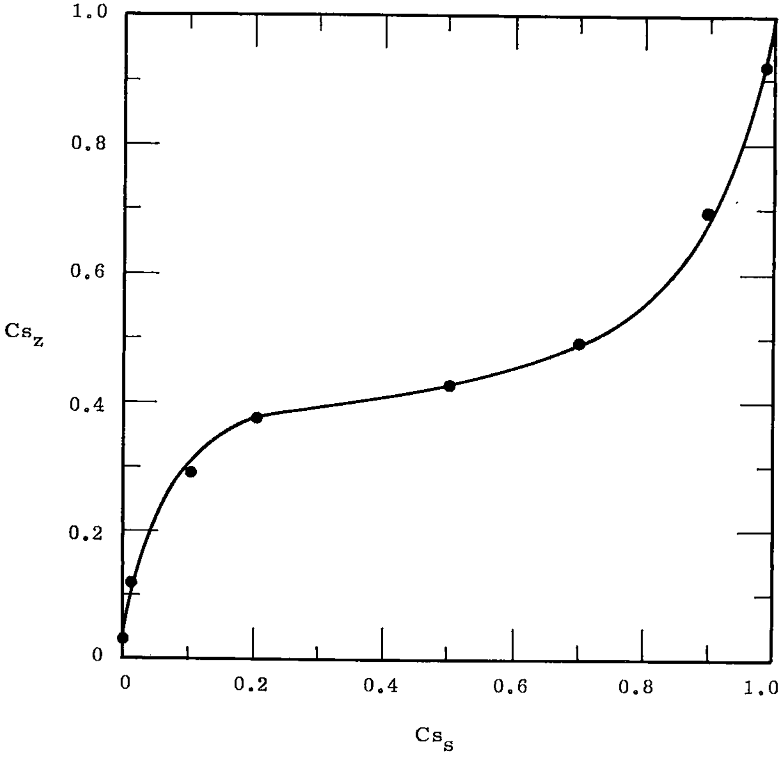

FIG. 4. The 23 °C isotherm for the reaction $Sr_z + 2Cs_s \rightleftarrows 2Cs_z + Sr_s$ with stilbite. Total equilibrium solution normality was constant at 1.0.
Cs_z = equivalent fraction of cesium on the zeolite.
Cs_s = equivalent fraction of cesium in the equilibrium solution.

cesium and strontium in the equilibrium solution. *Co* is the total normality of the equilibrium solution, or 1.0 in the present instance. The κ value for the reaction is given in table 4. No balance of free-energy changes was possible because data from a third related exchange reaction were not available. Equilibria in the strontium-cesium system are therefore tentative.

The single reaction enthalpy shown in table 4 for stilbite in a sodium-cesium system would seem rather high, but in view of the steric difficulties with cesium diffusion, the reaction enthalpy may tend to be high. Loss of cesium selectivity could result from thermal effects on a restricted cesium cavity or adsorption site.

The relatively high cesium and potassium selectivity of the stilbite does not mean that stilbite would normally be potassium- or cesium-based in

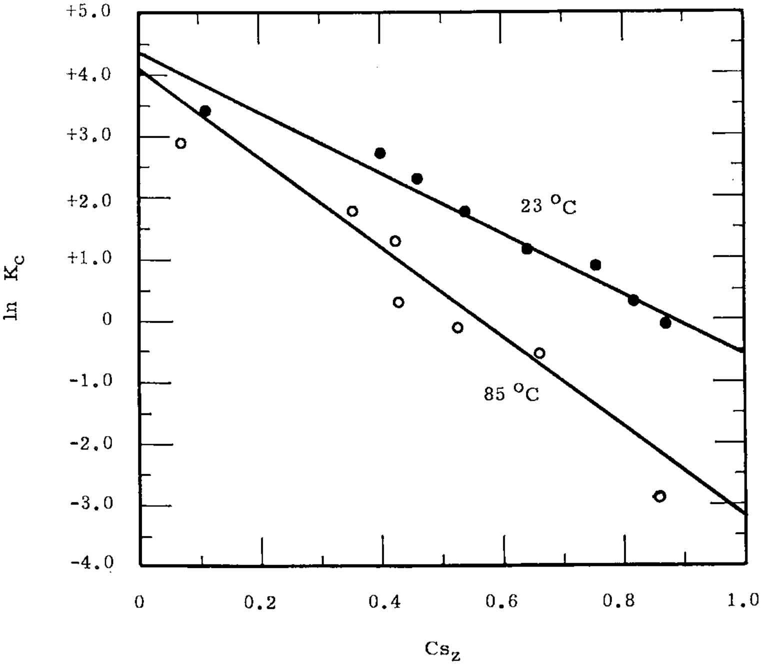

FIG. 5. A graph of the corrected selectivity quotient, K_c, versus the equivalent fraction of cesium on the zeolite, at 23 °C and 85 °C for the reaction $Na_z + Cs_s \rightleftarrows Cs_z + Na_s$ with stilbite.

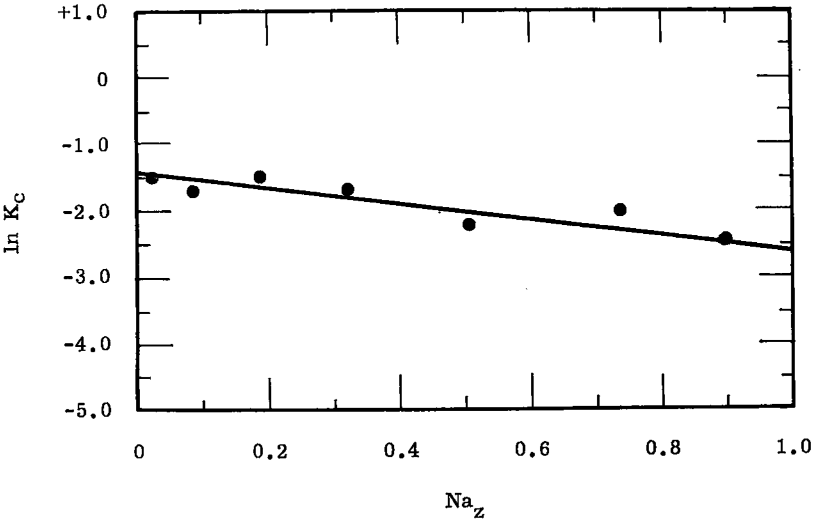

FIG. 6. A graph of the corrected selectivity quotient, K_c, versus the equivalent fraction of sodium on the zeolite, Na_z, for the reaction $K_z + Na_s \rightleftarrows Na_z + K_s$ at 23 °C with stilbite.

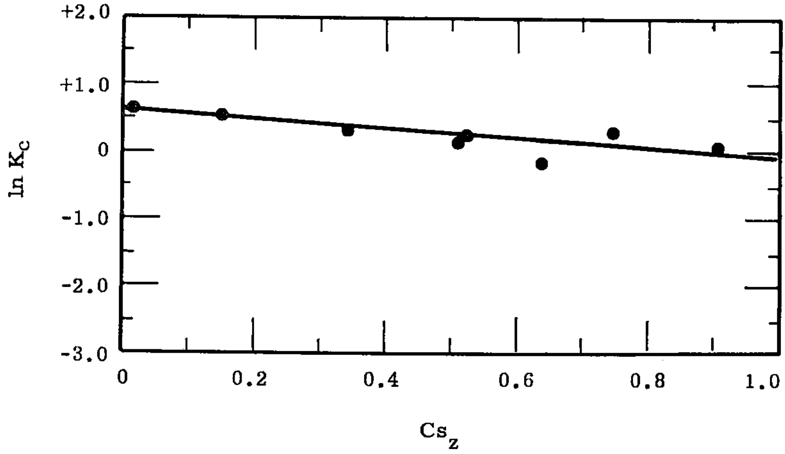

FIG. 7. A graph of the corrected selectivity quotient, K_c, versus the equivalent fraction of cesium on the zeolite, Cs_z, for the reaction $K_z + Cs_s \rightleftarrows Cs_z + K_s$ at 23 °C with stilbite.

nature. Using the data on sea water composition given by Rankama & Sahama (1950, p. 290), the potassium/sodium sea water ratio is 3.6×10^{-2} and the cesium/sodium ratio is about 2×10^{-7}. Under the above conditions, the equivalent fraction of potassium on the zeolite would be 25 per cent or less, of the stilbite capacity, while the equivalent fraction of cesium on the zeolite would be less than 2 per cent of capacity. The effects of any calcium ion in the system that probably would reduce further the fraction of potassium on the zeolite were neglected in the above calculation. It does not follow, therefore, that from the relatively high cesium and potassium selectivity of stilbite that natural stilbites will be encountered with a significant fraction of cesium or potassium on the zeolite. Higher temperatures would tend to reduce further the selectivity of stilbite for cesium and potassium.

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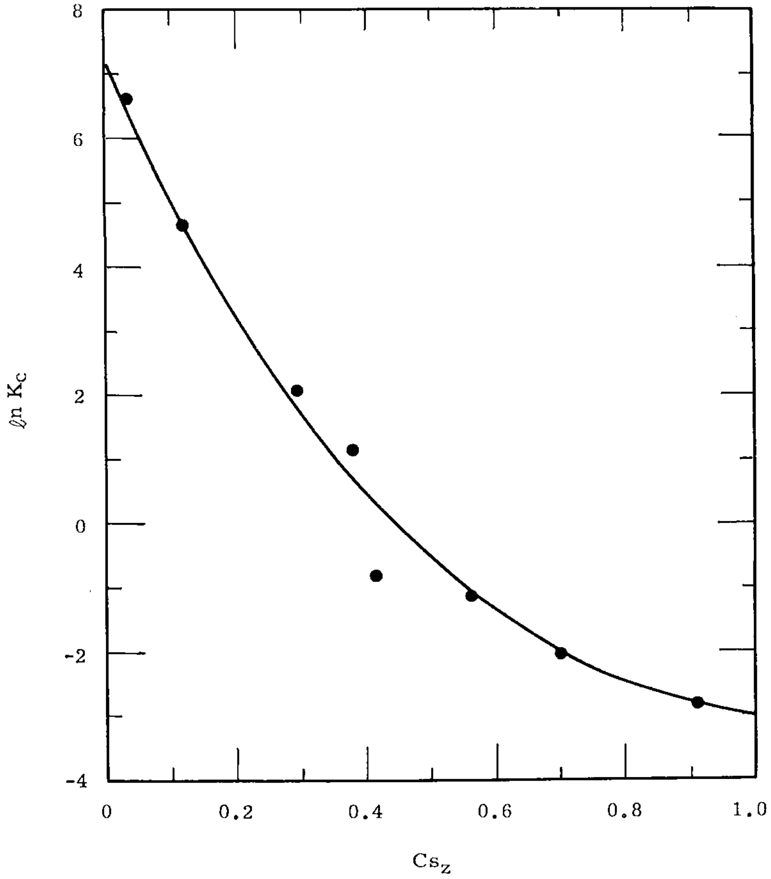

FIG. 8. A graph of the corrected selectivity quotient, K_c, versus the equivalent fraction of cesium on the zeolite, Cs_z, for the reaction $Sr_z + 2Cs_s \rightleftarrows 2Cs_z + Sr_s$ at 23 °C with stilbite.

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