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SOME ZEOLITE EQUILIBRIA WITH ALKALI METAL CATIONS

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ABSTRACT

Cation exchange equilibria for natural zeolites (erionite, clinoptilolite and phillipsite) and the synthetic zeolites (Linde AW-300, AW-400, AW-500, 13X, 4A and Norton Zeolon) in the systems sodium-cesium, potassium-sodium and potassium-cesium are presented along with derived thermodynamic data. Gibbs free-energies and enthalpies for the various exchange reactions were relatively small. Reaction enthalpies diminished as the sizes of the two exchanging cations approached one another. Thermodynamic data proved to be useful in several cases for interpretation of zeolite equilibria but proved to be most valuable when used in correlation with other properties of the zeolite exchange systems.

INTRODUCTION

Several process applications of zeolites for specialized cation exchange reactions have recently been proposed including cesium removal from high-level radioactive wastes with clinoptilolite (Nelson *et al.*, 1960; Tomlinson, 1962; Nelson, 1963) and the use of several synthetic zeolites as media for packaging and storage of radioactive isotopes (Tomlinson, 1962). It is necessary to know more about specific cation exchange equilibria than is presently known in order to select the best zeolite for a given application.

Barrer (1950) qualitatively determined the ion exchange properties of mordenite, analcime and chabazite. The ion-exchange properties of analcime and leucite were investigated further by Barrer and Hinds (1953) who reported several binary isotherms. Barrer and Sammon (1955) gave several binary isotherms for chabazite and derived related thermodynamic data. Barrer *et al.* (1956) determined the alkali metal and alkaline earth metal cation replacement series on a synthetic faujasite. Barrer and Meier (1958 and 1959) related the structure of Type A zeolite to its ion-exchange properties. Meier (1961) determined the crystal structure of a natural mordenite and accounted for the difficulty with which cations above 4.0 Å in diameter are adsorbed by mordenite (Barrer, 1954), postulating "stacking faults" within the mordenite crystal. Ames (1963) determined the mass action relationships of several zeolites in the region of high competing cation concentrations.

With the exception of the work of Barrer and Sammon (1955) on chabazite and Barrer and Meier (1959) on 4A, little detailed thermodynamic work has been done on the cation exchange equilibria of zeolites. A consideration of the thermodynamics of cation exchange equilibria would appear to be helpful in understanding the cation exchange properties of zeolites. Consequently, the thermodynamics of several alkali metal cation exchange equilibria were derived and the results reported herein.

METHODS OF INVESTIGATION

The clinoptilolite used in this study was obtained from two different locations, Hector, California and John Day, Oregon. The clinoptilolite from Hector, California, was described previously (Ames, 1963). Impurities included quartz, feldspar, unaltered glass, secondary halite and small amounts of montmorillonite and calcite (zero to three per cent by weight calcite in selected material). Consequently, the Hector clinoptilolite was contacted for one hour with ten per cent nitric acid to remove calcite and other acid-soluble contaminants prior to normal cation-basing procedure.

TABLE 1. ZEOLITE PROPERTIES

Zeolite	SiO_2/Al_2O_3	Wt. % binder	Wt. % H_2O 25C	Structural type	Capacity, meq/g
Hector clinoptilolite	8–10	5–15	12	clinoptilolite	1.7
Oregon clinoptilolite	8–10	5	11	clinoptilolite	2.0
Nevada erionite	6	5–10	13	erionite	2.2
Nevada phillipsite	4	5–15	14	phillipsite (monoclinic)	2.3
4AXW	2	10	30	A	3.9
13X	2.4	20	25	faujasite	3.6
AW-300	9–10	25	9	mordenite	1.6
AW-400	6–7	25	12	erionite	2.0
AW-500	4–5	25	15	chabazite	2.2
Zeolon	10	—	12	mordenite	1.9

The other clinoptilolite was obtained from the Deep Creek Tuff of the John Day Formation (Fisher, 1952; Hay, 1962), Oregon. The Oregon clinoptilolite was relatively free of impurities except for minor amounts of plagioclase and unaltered glass. The average Oregon clinoptilolite purity was 95 per cent or greater, as shown by the 2.0 meq/g capacity in Table 1. Part of the Oregon clinoptilolite was contacted with ten per cent nitric acid to determine the effect of acid treatment on cation exchange properties.

The erionite and phillipsite used in this study were from Pine Valley, Nevada, and averaged 90 per cent or greater in purity.

Several synthetic zeolites were obtained as one-sixteenth-inch diameter, sodium-based pellets from the Linde Company of Tonawanda, New York. Included were 13X, 4AXW, AW-300, AW-400 and AW-500. The Norton Company of Worcester, Massachusetts, supplied one-eighth-inch, sodium-based Zeolon pellets. Table 1 gives some of the pertinent properties of the zeolites used in this study.

Zeolites used in the equilibrium experiments were based with saturated, reagent-grade chloride solutions of the desired cations. Zeolites already based with sodium were rebased with sodium chloride solution in several contacting steps (Ames, 1963). The zeolites were thoroughly washed with distilled water which was tested for chloride ion with silver nitrate solution. A final test for chloride ion was conducted on the distilled water after two days of contact with the zeolite. A negative chloride test was indicative of minimum NaCl inclusion.

Cation exchange capacities were determined by a double tracing technique. Weighed, sodium-based zeolite samples in polyethylene bottles were contacted with a solution containing 0.1 N CsCl plus 0.1 N NaCl plus Cs^{134} tracer to determine cesium removal. Cesium-based zeolites, corrected for the sodium-cesium weight differential, were then contacted with a solution containing 0.1 N CsCl plus 0.1 N NaCl plus Na^{22} to determine sodium removal onto the same zeolites. Total zeolite capacity pertinent to the study of cesium, sodium or potassium equilibrium systems was assumed to be the sum of cesium plus sodium loading. A higher capacity could have been obtained in some instances if capacities were determined with smaller size or different valence cations (Barrer, 1959; Barrer and Sammon, 1955).

At least two days of contact time in a controlled-temperature shaking bath were allowed to assure equilibrium between zeolite and solution. High specific activity Na^{22} and Cs^{134} were used to trace the equilibrium solution. Solution-to-zeolite ratios were adjusted to yield statistically reliable Cs^{134} and Na^{22} counting rates in the equilibrium solution. Zeolites were originally based with the untraced cation in the system. For example, in the system potassium-sodium-Na^{22}, the zeolites were originally potassium-based. The total capacity of the zeolite minus the amount of traced cation removed from the equilibrium solution was assumed to represent the amount of traced cation on the zeolite. Eight to twelve points were determined on each isotherm by varying the ratios of contacting cations. The equilibrium solution was held constant at a total normality of one. Errors introduced by zeolitic salt inclusion probably were less than one per cent (Barrer and Meier, 1958). A determination of equilibrium relationships in the sodium-cesium system at a total solution normality of 0.1 resulted in essentially the same equilibria after solution activity corrections, confirming that salt inclusion was not a major problem.

Because the equilibrium solution was one normal, it was necessary to determine mean activities of the two salts. Only the ratios of cations were varied so that Glueckauf's equation (1949) was employed to determine mean activities. Figure 1 is a graph of the mean activity coefficients of NaCl, KCl and CsCl from Conway (1952) used in this study. Note that concentration is expressed in molality rather than normality. An error of between two and three per cent was introduced in the worst possible case at a molality of one for one of the salts (CsCl) by direct application of molal activity coefficients. Consequently, the molal activity coefficients were directly applied to equilibrium solution concentrations. The use of mean activity coefficients to correct equilibrium solution cation concentrations is a first step in the determination of a rational thermodynamic equilibrium constant for the reaction. It is also necessary to determine activity coefficients for the cations on the zeolite (Helfferich, 1962). For example, given the reaction for the zeolite phillipsite for which the equilibrium data are shown in Fig. 2, $K_{zeolite}+Na_{solution}\rightarrow Na_{zeolite}+K_{solution}$, the mass action quotient uncorrected for solution activities is $(Na_z)(K_s)/(K_z)(Na_s)$. Table 2 gives several of the mass action quotients from the data of Figure 2, the associated mean activity coefficients from Fig. 1, and the corrected mass action quotient, or $\mathcal{K}c$. The fraction of potassium on the zeolite (K_z) is equal to one minus the fraction of sodium on the zeolite (Na_z). The normality of potassium in the equilibrium solution (K_s) equals one minus the normality of sodium in the equilibrium (Na_s) because the total normality of the equilibrium solution is constant at one.

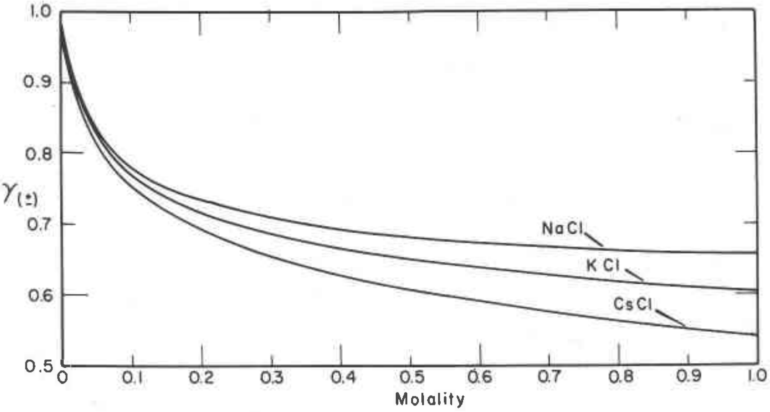


FIG. 1. The mean activity coefficients for NaCl, KCl and CsCl up to one molal in concentration (Conway, 1952).

Figure 3 shows a plot of log $\mathcal{K}c$ *vs.* Na_z that was used to derive activity coefficients for potassium and sodium on the phillipsite according to the method of Ekedahl *et al.* (1950). In the example given in Fig. 3, $-\log f_{K_z}$ at 0.4 Na_z (or 0.6 K_z) is the non-cross-hatched area under the curve from 0.0 Na_z to 0.4 Na_z. Likewise, $-\log f_{Na_z}$ at 0.6 K_z is the non-cross-hatched

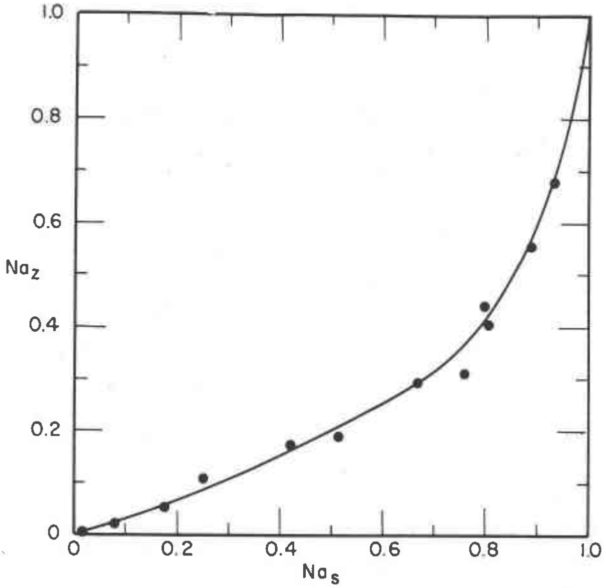


FIG. 2. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with monoclinic phillipsite. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

area under the curve from 0.0 K_z to 0.6 K_z. The activity coefficients are graphical solutions to an equation of the type $\ln f_{Na_z} = -K_z \ln \mathcal{K}c + \int_{Na_z}^{1} \ln \mathcal{K}c \, d\, Na_z$ (Helfferich, 1962, p. 196) in decadic logarithm form, where

f_{Na_z} = the activity coefficient of sodium on the zeolite.

TABLE 2. DETERMINATION OF A CORRECTED MASS ACTION QUOTIENT, $\mathcal{K}c$, FROM MASS ACTION QUOTIENT THROUGH USE OF SODIUM AND POTASSIUM MEAN ACTIVITY COEFFICIENTS, f_{NaCl} AND f_{KCl}

Na_z	Na_s	$\frac{(Na_z)(K_s)}{(K_z)(Na_s)}$	f_{KCl}	f_{NaCl}	f_{KCl}/f_{NaCl}	$\mathcal{K}c$	Log $\mathcal{K}c$
0.02	0.06	0.388	0.607	0.835	0.727	0.282	−0.5498
0.10	0.28	0.286	0.625	0.725	0.862	0.247	−0.6073
0.20	0.52	0.231	0.652	0.678	0.962	0.222	−0.6536
0.30	0.68	0.202	0.683	0.670	1.019	0.206	−0.6861
0.40	0.79	0.177	0.733	0.665	1.102	0.195	−0.7100
0.50	0.86	0.163	0.740	0.663	1.116	0.182	−0.7399
0.60	0.91	0.148	0.780	0.661	1.180	0.175	−0.7570
0.80	0.97	0.124	0.885	0.658	1.299	0.161	−0.7932

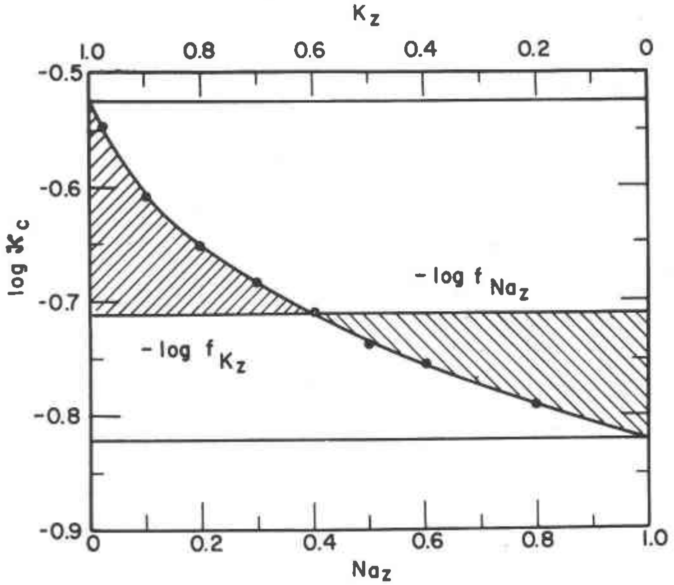


FIG. 3. A graph of the log of the corrected mass action quotients $\mathcal{K}c$) from Table 3 *vs*. potassium fraction on the zeolite (K_z) and sodium fraction on the zeolite (Na_z). In the example given, the non-cross-hatched area to the right of the curve from 0.0 to 0.6 K_z is the negative log of the activity of sodium on the zeolite ($-\log f_{Na_z}$) at $K_z=0.6$. The non-cross-hatched area to the left of the curve is the negative log of the activity of potassium on the zeolite ($-\log f_{K_z}$) at $Na_z=0.4$.

K_z = the equivalent fraction of potassium on the zeolite.
Na_z = the equivalent fraction of sodium on the zeolite, and
$\mathcal{K}c$ = a mass action quotient corrected for solution activities.

Figure 4 is a graph of sodium and potassium activity coefficients on the

TABLE 3. DETERMINATION OF AN AVERAGE RATIONAL THERMOCYNAMIC EQUILIBRIUM CONSTANT, $\mathcal{K}$, FROM SEVERAL MASS ACTION QUOTIENTS CORRECTED WITH SOLUTION ACTIVITY COEFFICIENTS, $\mathcal{K}c$

Na_z	$\mathcal{K}c$	f_{Na_z}/f_{K_z}	$\mathcal{K}$	Average $\mathcal{K}$
0.1	0.247	0.767	0.189	
0.2	0.222	0.855	0.190	
0.3	0.206	0.926	0.191	
0.4	0.195	0.983	0.192	0.190
0.5	0.182	1.038	0.189	
0.6	0.175	1.091	0.191	
0.8	0.161	1.187	0.191	

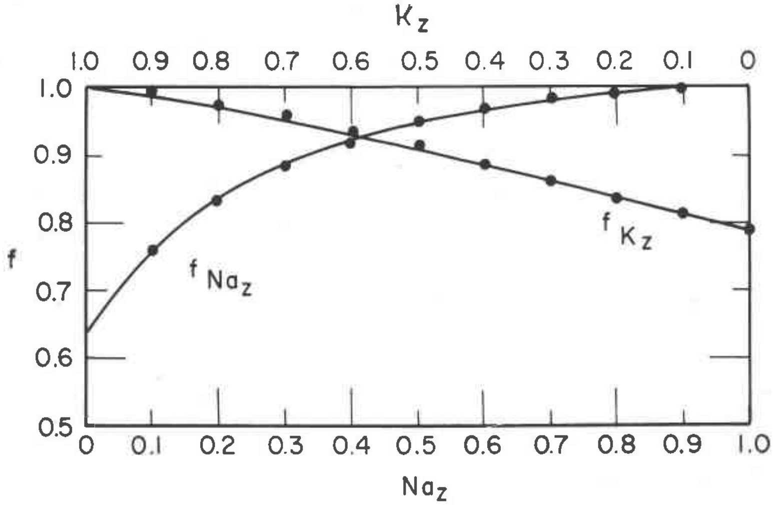


FIG. 4. A graph of the activities of sodium on the zeolite (f_{Na_z}) and potassium on the zeolite (f_{K_z}) *vs.* sodium on the zeolite (Na_z) and potassium on the zeolite (K_z) for phillipsite. These data are derived from Fig. 3.

zeolite computed from Fig. 3. As shown in Table 3, the activity coefficients may be used to compute an average rational thermodynamic equilibrium constant, $\mathcal{K}$. The reader will note that in the derivation of the rational equilibrium constant, several assumptions were made. Cation activity coefficients, as usual, were considered to be unity in infinitely-dilute solutions. The zeolite, however, was treated as a solid solution of sodium-zeolite and potassium-zeolite, and the monoionic end-members, pure sodium-zeolite and potassium-zeolite, were assumed to have activity coefficients equal to unity. There are other standard and reference states that one may choose to describe exchange reactions. The reader is referred to Helfferich (1962) for a detailed account of other data treatment methods.

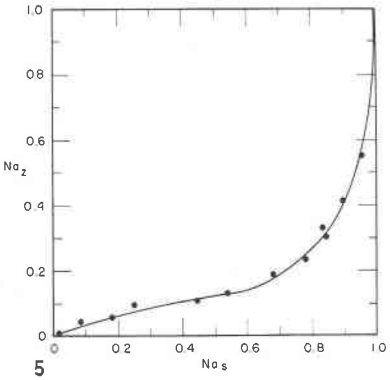
A standard reaction enthalpy, ΔH^0, may be derived from the effect of heat on the equilibrium constant, $\mathcal{K}$, by use of a standard equation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^0 (T_2 - T_1)}{(2.303)(R)(T_1)(T_2)} \quad \text{(Daniels and Alberty 1961).}$$

If the reaction enthalpy is negative, $\mathcal{K}_2$ is smaller than $\mathcal{K}_1$; *i.e.*, a temperature rise lowers the equilibrium constant, all other things being equal.

A Gibbs standard free-energy, ΔG^0, may also be calculated for the reaction with the use of the relationship, $\Delta G^0 = RT \ln \mathcal{K}$ (Daniels and Alberty, 1961).

If ΔG^0 is negative, the exchange reaction is favorable; *i.e.*, $\mathcal{K}$ is greater



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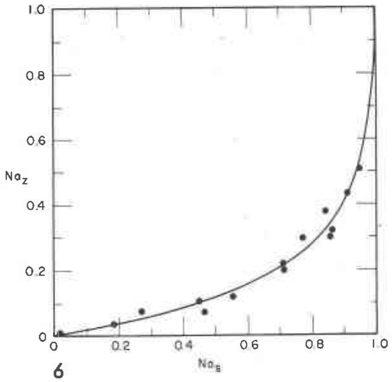

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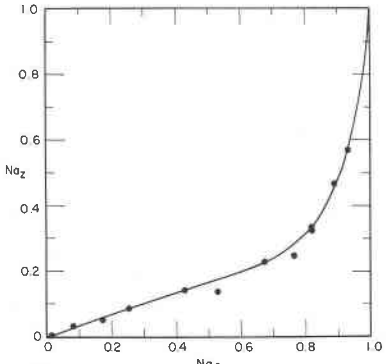

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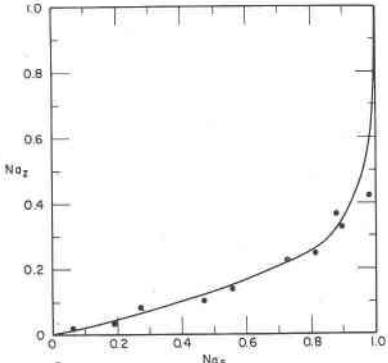

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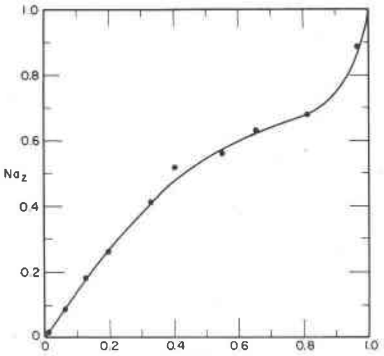

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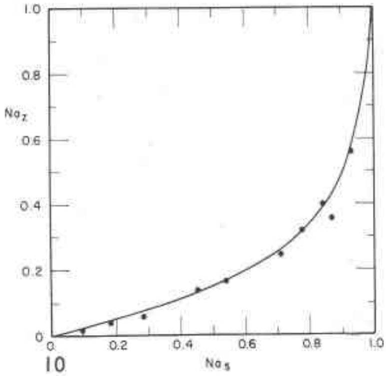

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than 1.0. The reaction entropy, ΔS^0, may also be determined using the relationship, $\Delta G^0 = \Delta H^0 - T\Delta S^0$ (Daniels and Alberty, 1961). However, reaction entropies for exchange reactions are difficult to interpret and, for that reason, have been omitted.

The accuracy of ΔG^0 determination (and hence $\mathcal{K}$) for a given reaction can be checked by the determinations of the Gibbs free-energy of two other related exchange reactions. For example, with phillipsite, the Gibbs free-energy for the reaction $K_z \rightarrow Cs_z$, minus the Gibbs free-energy for the reaction $K_z \rightarrow Na_z$ should equal the Gibbs free-energy for the reaction $Na_z \rightarrow Cs_z$, or from Table 5, (−1000 cal/mole)−(+1000 cal/mole) ≡(−1900 cal/mole). Several redeterminations of cation exchange isotherms have indicated an average error of 100 cal/mole in the rounded values of ΔG^0 given in Table 5.

RESULTS

The isotherms for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ are presumed to be of primary interest to mineralogists and geologists because most natural

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FIG. 5. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with AW-400. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

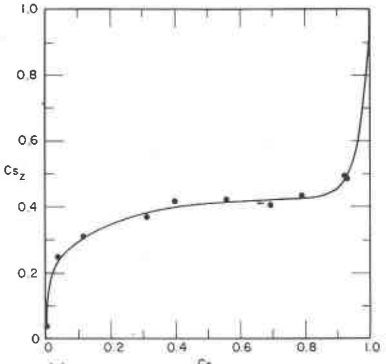
FIG. 6. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with Nevada erionite. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

FIG. 7. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with AW-500. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

FIG. 8. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with Hector clinoptilolite. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

FIG. 9. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with 4AXW. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

FIG. 10. The 25° C. isotherm for the reaction $K_z + Na_s \rightarrow Na_z + K_s$ with Zeolon. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.



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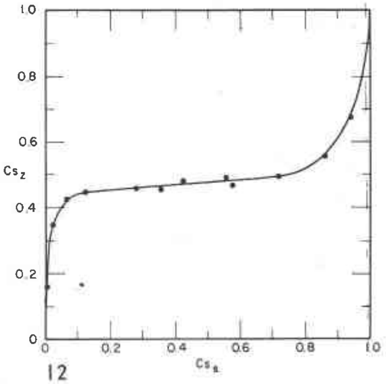

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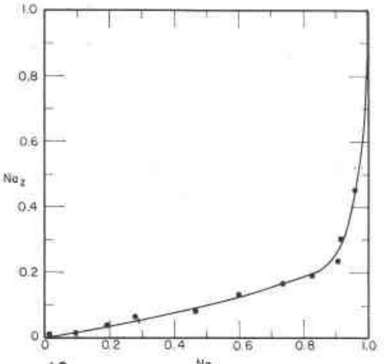

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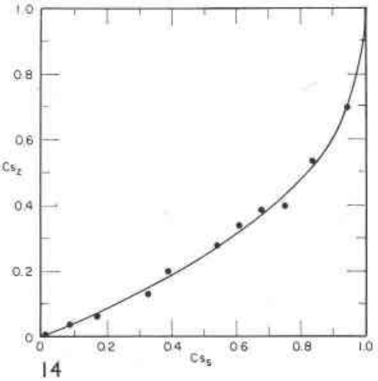

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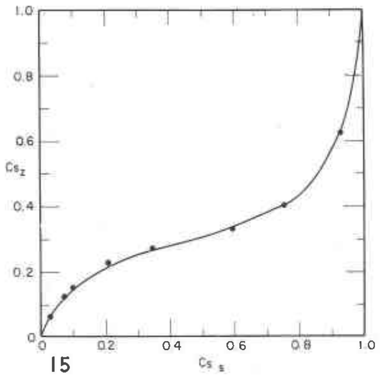

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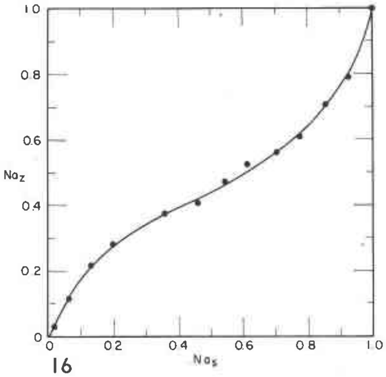

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zeolites are predominantly based with sodium and potassium. The sodium-potassium isotherms at 25° C. are given for AW-400, erionite, AW-500, Hector clinoptilolite, 4AXW and Zeolon in Figures 5 through 10, respectively. AW-300 and 13X isotherms at 25° C. are given for three reactions Figures 11, 12 and 13 show equilibrium results obtained with AW-300 in the systems potassium-cesium, sodium-cesium and potassium-sodium, respectively. For the same systems in the same order, Figs. 14, 15 and 16 show 13X equilibrium results.

The equilibrium constant data are summarized in Table 4. The exchange reaction is identified along with the temperature. Table 5 gives the derived thermodynamic data.

DISCUSSION

An accurate determination of zeolite capacity is a prerequisite to the study of zeolite cation equilibria. The accuracy of the capacity data given in Table 1 can be confirmed in part by some simple calculations. The chemical composition of Type A is fairly constant, and approximate

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FIG. 11. The 25° C. isotherm for the reaction $K_z+Cs_z \rightarrow Cs_z+K_s$ with AW-300. Total equilibrium solution normality was constant at one.
Cs_z = fraction of cesium on the zeolite.
Cs_s = fraction of cesium in the equilibrium solution.

FIG. 12. The 25° C. isotherm for the reaction $Na_z+Cs_s \rightarrow Cs_z+Na_s$ with AW-300. Total equilibrium solution normality was constant at one.
Cs_z = fraction of cesium on the zeolite.
Cs_s = fraction of cesium in the equilibrium solution.

FIG. 13. The 25° C. isotherm for the reaction $K_z+Na_s \rightarrow Na_z+K_s$ with AW-300. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

FIG. 14. The 25° C. isotherm for the reaction $K_z+Cs_s \rightarrow Cs_z+K_s$ with 13X. Total equilibrium solution normality was constant at one.
Cs_z = fraction of cesium on the zeolite.
Cs_s = fraction of cesium in the equilibrium solution.

FIG. 15. The 25° C. isotherm for the reaction $Na_z+Cs_s \rightarrow Cs_z+Na_s$ with 13X. Total equilibrium solution normality was constant at one.
Cs_z = fraction of cesium on the zeolite.
Cs_s = fraction of cesium in the equilibrium solution.

FIG. 16. The 25° C. isotherm for the reaction $K_z+Na_s \rightarrow Na_z+K_s$ with 13X. Total equilibrium solution normality was constant at one.
Na_z = fraction of sodium on the zeolite.
Na_s = fraction of sodium in the equilibrium solution.

TABLE 4. EQUILIBRIUM DATA. THE NOTATION $K_z \rightarrow Cs_z$ MEANS THE EXCHANGE OF POTASSIUM ON THE ZEOLITE TO CESIUM ON THE ZEOLITE, $K_z \rightarrow Na_z$ MEANS THE EXCHANGE OF POTASSIUM ON THE ZEOLITE TO SODIUM ON THE ZEOLITE, AND $Na_z \rightarrow Cs_z$ MEANS THE EXCHANGE OF SODIUM ON THE ZEOLITE TO CESIUM ON THE ZEOLITE

Zeolite	Thermodynamic equilibrium constant, $\mathcal{K}$					
	Computed $K_z \rightarrow Cs_z$ 25° C.	Experimental $K_z \rightarrow Cs_z$ 25° C.	$K_z \rightarrow Na_z$ 25° C.	$Na_z \rightarrow Cs_z$ 25° C.	$K_z \rightarrow Cs_z$ 70° C.	$Na_z \rightarrow Cs_z$ 70° C.
13X	0.239	0.235	0.674	0.355	—	0.374
4AXW	0.241	0.236	0.747	0.323	—	0.346
AW-300	0.091	0.566	0.050	1.814	—	2.78
AW-400	3.24	3.20	0.083	39.0	—	20.8
AW-500	4.10	4.45	0.138	29.7	4.45	13.3
Zeolon	4.18	4.57	0.143	29.2	4.09	18.3
erionite	2.99	—	0.091	32.9	—	17.5
phillipsite	5.04	5.29	0.191	26.4	5.02	13.3
Hector clinoptilolite	4.10	3.68	0.079	51.9	—	18.9
Oregon clinoptilolite	—	—	000	47.6	—	24.8

TABLE 5. THERMODYNAMIC DATA. ΔG^0 IS THE STANDARD GIBBS FREE-ENERGY IN CAL/MOLE. ΔH^0 IS THE STANDARD REACTION ENTHALPY IN CAL/MOLE. THE REACTIONS ARE IDENTIFIED AS IN TABLE 4

Zeolite	$Na_z \rightarrow Cs_z$ ΔH^0, 25° C., 70° C.	$Na_z \rightarrow Cs_z$ ΔG^0, 25° C.	$K_z \rightarrow Cs_z$ ΔH^0, 25° C., 70° C.	$K_z \rightarrow Cs_z$ ΔG^0, 25° C.,	$K_z \rightarrow Na_z$ ΔG^0, 25° C.
13X	+ 200	+ 600	—	+ 900	+ 200
4AXW	+ 300	+ 700	—	+ 800	+ 200
AW-300	—	—	—	—	+1800
AW-400	−2800	−2200	—	− 700	+1500
AW-500	−3600	−2000	0	− 900	+1200
Zeolon	−2100	−2000	−500	− 900	+1100
erionite	−2800	−2100	—	—	+1400
phillipsite	−3100	−1900	−200	−1000	+1000
Hector clinoptilolite	−4600	−2300	—	− 800	+1500
Oregon clinoptilolite	−2900	−2300	—	—	—

$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (Breck, *et al.*, 1956), unhydrated and without binder. The above oxide formula contains 16.2 weight per cent sodium, about the same value found by Barrer and Meier (1958) for Type A. The 0.162 g of sodium per g of 4A gives the 4A a capacity of 7.0 meq/g, assuming that all the sodium is exchangeable. However, the binder and adsorbed water lower the 4AXW capacity per unit weight by 40 per cent to 4.2 meq/g. Furthermore, cesium cannot enter the smaller sodalite-type cages found in Type A (Barrer and Meier, 1958), so that one-thirteenth of the remaining theoretical capacity is lost as a result of the previously-described double-tracing technique for capacity determinations. The resulting capacity should be reduced from 4.2 meq/g to about 3.9 meq/g, which is the capacity for 4AXW given in Table 1.

Likewise, from the chemical analysis of Oregon clinoptilolite given by Hay (1962), the total capacity should be 2.3 meq/g if all the potassium sodium and calcium is exchangeable. The actual capacity obtained was 2.0 meq/g. There is also good agreement between the computed and actual capacities of the other zeolites. It should be emphasized, however, that zeolite capacities can vary for many reasons including differences in chemical composition, binding agents, water content and the occurrence of non-stoichiometric adsorption. The capacities given in Table 1 apply only to the particular zeolite samples used in this study.

It is evident from an inspection of the sodium-potassium results shown in Figs. 2, 5 through 10, 13 and 16 that the majority of zeolites studied prefer potassium to sodium cations. Yet potassium is usually present to a lesser extent than sodium on the exchange sites of natural zeolites. Perhaps the example of sea water in contact with a phillipsite would illustrate why phillipsite normally would be loaded predominantly with sodium.

According to Rankama and Sahama (1950), the average sea water composition contains 0.495 N Na^+ and 0.00972 N K^+. Neglecting the effects of all the other constituents of sea water on K^+ removal onto phillipsite and solution activity coefficients, the ratio of Na^+ in the equilibrium solution to Na^+ plus K^+, or

$$\frac{Na_s}{Na_s + K_s}, \text{ is } \frac{0.495}{0.495 + 0.00972}$$

or 0.981. We may read directly from Fig. 2, since the equilibrium solution was constant at one normal, that about 86 per cent of the phillipsite cation load would be Na^+ and 14 per cent K^+ from an equilibrium solution containing 98.1 per cent Na^+ and 1.9 per cent K^+. Less than 14 per cent K^+ may be loaded on the zeolite if the other cations in sea water are considered. It should be emphasized, however, that the phillipsite of Fig.

2 represents the monoclinic modification (Barrer, *et al.*, 1959). Other phillipsite modifications would yield other cation exchange equilibria. Changes in the sodium to potassium ratio of the equilibrium solution would cause corresponding changes in the fraction of potassium and sodium on the zeolite. The reader should also keep in mind that this study was with the chloride salts of the various cations. If the less-dissociated carbonate salts were used, for example, the equilibria curves would be different than those for the same chloride salts. Since the approach to equilibrium of the zeolites derived from altered tuffs is relatively rapid, the supposition that the present exchangeable cations represent the original exchangeable cations is a shaky one.

The phillipsite equilibrium data illustrate another general point concerning zeolite equilibria. As the loading of a given cation onto a zeolite proceeds, the selectivity of the zeolite for that cation decreases. Table 2 shows that the mass action quotient of phillipsite for sodium decreases with the amount loaded on the zeolite. All of the other zeolite equilibria seen in Figs. 5 through 16 show the same decreased selectivity with increased cation loaded on the zeolite. Irregular exchange isotherms are the rule for the majority of zeolites studied to date.

The synthetic mordenite, AW-300, yielded unusual exchange isotherms in the potassium-cesium, sodium-cesium and potassium-sodium systems as seen in Figs. 11, 12 and 13, respectively. Highly irregular isotherms for the potassium-cesium and sodium-cesium are apparent, whereas the potassium-sodium isotherm is less irregular. Upon examination of the "equilibrium constants" derived from the above potassium-cesium and sodium-cesium isotherms and shown in Table 5, it is seen that equilibrium probably was not attained.

According to Meier (1961), "stacking faults" in the mordenite crystal may reduce the size of the diffusion channels to about 4.0 Å. Using Ahren's cation radii data (1952), the sum of Cs^+ and K^+ diameters is 6.00 Å, Cs^+ plus Na^+ is 5.22 Å and K^+ plus Na^+ is 4.54 Å. If the smallest diffusion channels are 3.0 to 4.0 Å, kinetic difficulties could be forecast for exchange in the sodium-cesium and potassium-cesium systems, especially with the equilibrium solution compositions of Figs. 11 and 12 where it would be most likely that equal quantities of both cations would be in the diffusion channels at the same time.

Another, and less likely, explanation of the isotherms of Figs. 11 and 12 is that the smallest diffusion channels in AW-300 are less than 3.0 Å in diameter, and exclude 3.34 Å diameter Cs^+. If the AW-300 did have less than 3.0 Å diffusion channels, the cesium capacity would be extremely low. We must assume that the first explanation postulating kinetic difficulties is correct because the cesium capacity of AW-300 is 1.6 meq/g.

The increase of the "equilibrium constant," $\mathcal{K}$, at 70° C. for the sodium-cesium system is further indication that equilibrium was not reached at 25° C, and that the problem is a diffusional one.

Zeolon, a mordenite without the "stacking faults" of AW-300 (Anonymous, 1962), yielded normal sodium-cesium and potassium-cesium isotherms as shown by the derived thermodynamic data of Table 5. The Gibbs free-energies for the three related equilibria on Zeolon balance within the experimental error as required, while those for AW-300 fail to balance by a wide margin. The Gibbs free-energies for the three exchange reactions are related by $(K_z \rightarrow Cs_z) - (K_z \rightarrow Na_z) = (Na_z \rightarrow Cs_z)$, or for Zeolon $(-900) - (+1100) = (-2000)$, and AW-300, assuming that equilibrium was reached, $(+300) - (+1800) \neq (-400)$. The thermodynamic data derived from the AW-300 sodium-cesium and potassium-cesium isotherms are, of course, valueless because equilibrium was not achieved.

Several sigmoidal, or S-shaped isotherms were obtained during the present investigation, notably with 4AXW and 13X (Figs. 15, 16). The sigmoidal isotherm contains a selectivity reversal, *i.e.*, the mass action quotient changes from greater than one to less than one as zeolite loading proceeds. Synthetic faujasite, or 13X, is a zeolite with very accessible anionic or exchange sites (Barrer, *et al.*, 1957; Broussard and Shoemaker, 1960). The smallest dimension through which cations must diffuse to accomplish exchange is about 9 Å. The dimension inside the main cavity containing the available anionic sites varies from 13 to 20 Å. There is, therefore, ample room for all alkali metal cations, including cesium, to reach the exchange sites in 13X. It is interesting to note, however, that the sodium-cesium and potassium-sodium isotherms of Figs. 15 and 16 are irregular or sigmoidal in form, whereas the potassium-cesium isotherm of Fig. 14 is the least irregular.

Apparently cesium and sodium and potassium and sodium do not occupy energetically equivalent sites on 13X (Barrer and Sammon, 1955; an hypothesis supported by studies on polyfunctional resins (Helfferich, 1962, p. 183). The form of the isotherm is a function of the difference in site energies between cesium and sodium and potassium and sodium, which in turn is related to cation size differences. For example, the difference in the diameters of Cs^+ and Na^+ is 1.46 Å according to Ahrens (1952), and the resulting isotherm is markedly sigmoidal. The difference in the diameters of K^+ and Na^+ is 0.78 Å, and the isotherm is less sigmoidal in form. The diameter difference between Cs^+ and K^+ is 0.68 Å, and the isotherm is nearly regular. Apparently the 0.68 Å diameter difference is not large enough to cause the Cs^+ and K^+ bonding sites in 13X to be greatly energetically dissimilar. The selectivity reversal occurs as it becomes increasingly difficult for the incoming cations to find energetically favorable positions. One may begin with either the larger or smaller cation initially on the zeolite. The exchange isotherm is sigmoidal in either case.

Barrer and Meier (1959) and Helfferich (1962) have derived expressions from similar assumptions describing the energetic relationships of two cations on a zeolite such as 13X. Barrer's expression is $\ln \mathcal{K}c = \ln \mathcal{K} + C(1-2B_z)$, where $\mathcal{K}c$ = the mass action quotient corrected with solution activity coefficients,

$\mathcal{K}$ = a rational thermodynamic equilibrium constant.
C = a constant, and
B_z = the fraction of cation B on the zeolite from the expression. $A_z + B_s \rightarrow B_z + A_s$.

Table 6 shows four computations of "C" using Barrer's expression to describe the isotherm for potassium-sodium on 13X. The results are fair.

TABLE 6. DETERMINATION OF SOME VALUES FOR "C" IN THE EXPRESSION $\ln \mathcal{K}c = \ln \mathcal{K} + C(1-2Na_z)$ FOR THE 13X POTASSIUM-SODIUM ISOTHERM SHOWN IN FIGURE 16

Na_z	$\mathcal{K}c$	Average $\mathcal{K}$	C
0.2	1.464		+1.3
0.4	0.854	0.674	+1.2
0.6	0.502		+1.4
0.8	0.367		+1.1

An attempt to describe the isotherm for sodium-cesium was totally unsuccessful. The constant "C" was no longer even fairly constant, yielding "C" values with opposite signs. Within the experimental error of 100 cal/mole, ΔG^0 values balance as required for the three related exchange reactions, and it is assumed that the three isotherms are essentially correct. Apparently Barrer and Meier's third case (p. 140, 1959), where $d \log \mathcal{K}c/d\,B_z \neq$ a constant, is not uncommon.

Several generalizations concerning zeolite cation exchange equilibria may be drawn from the thermodynamic data of Table 5. A comparison of the reaction enthalpies and Gibbs free-energies of Table 5 with those of most chemical reactions show that considerably less energy is involved in zeolitic ion exchange reactions. Reaction enthalpies of greater than 15 Kcal/mole are usual for chemical reactions.

As the cations approach each other in size, the thermodynamic equilibrium constant, $\mathcal{K}$, decreases. The K for the reaction $K_z \rightarrow Cs_z$ was generally less than the $\mathcal{K}$ for $Na_z \rightarrow Cs_z$. Raising the temperature of an equilibrium system can cause $\mathcal{K}$ to increase, decrease or change very little. The effect of heat was a function of whether or not the $\mathcal{K}$ was favorable, or greater than one. For example, the $\mathcal{K}$ of the reaction $Na_z \rightarrow Cs_z$ for 13X and 4AXW were unfavorable and slightly increased by raising the temperature while the $\mathcal{K}$ of the same reaction for nearly all the other zeolites was highly favorable and appreciably reduced by raising the temperature. As the size of the two competing cations approached one another, the effect of a temperature rise on equilibrium constants was reduced. The $\mathcal{K}$ for the reaction $K_z \rightarrow Cs_z$ was much less effected to 70° C. than the $\mathcal{K}$ of the reaction $Na_z \rightarrow Cs_z$.

Zeolon and AW-300 are both mordenite-type structures (Keough and Sand, 1961). Zeolon, however, lacks the "stacking faults" of natural mordenite and AW-300 (Anonymous, 1962). Comparable equilibrium data are available only for the reaction $K_z \rightarrow Na_z$. A comparison of the Gibbs free-energies for the $K_z \rightarrow Na_z$ reaction with Zeolon and AW-300 shows that there is a considerable difference. The relatively large free-energy difference for the same exchange reaction is caused by the presence of the AW-300 "stacking faults." As far as cation exchange is concerned, Zeolon and AW-300 behave like two different zeolite structures. For contrast with the above situation, note the close agreement of the free-energies of AW-400 (synthetic erionite) and natural erionite for the reactions $K_z \rightarrow Na_z$, and $Na_z \rightarrow Cs_z$. The $Na_z \rightarrow Cs_z$ reaction enthalpies of AW-400 and erionite also are the same, indicating that the two zeolites are structurally and compositionally very similar. The two clinoptilolite samples also are of interest as the $Na_z \rightarrow Cs_z$ reaction enthalpy of the Hector clinoptilolite is considerably larger than for the same reaction of Oregon clinoptilolite. Experimental work to date on, the synthesis of clinoptilolite indicates that considerable compositional variation is possible while maintaining the clinoptilolite structure (Ames, 1963). An Oregon clinoptilolite analysis reported by Hay (1962) indicates that the Oregon material is at the low-silica end of the clinoptilolite series. The higher capacity of the Oregon clinoptilolite supports the low-silica premise. The similarity in Gibbs free-energy for the $Na_z \rightarrow Cs_z$ reaction with Hector and Oregon clinoptilolite suggests that there are no essential structural differences between the two clinoptilolites, and none was found.

There are clearly many similarities as well as differences in the thermodynamic data. It may be concluded that while the thermodynamic data are certainly helpful in interpretation and understanding of zeolitic cation exchange equilibria, one should not rely solely on such data. All related compositional, structural and kinetic data must be included as well if complete understanding of zeolite equilibria is to be achieved. The thermodynamic data are of limited value unless correlated with other physical and chemical properties of the zeolite-cation system.

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