ALKALI METAL CATION EQUILIBRIA WITH CHABAZITE

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Abstract

Chabazite equilibria were studied in the systems sodium-potassium, sodium-cesium and cesium-potassium at 23 °C. The Gibbs free-energy change derived from the isotherm for the reaction $Na_{zeolite} + K_{solution} \rightleftarrows K_{zeolite} + Na_{solution}$ showed good agreement with Barrer's chabazite results for the same system. Only 85 per cent of the 3.53 sodium atoms per unit cell, or 3.00 cesium atoms, were contained in the chabazite cell at equilibrium. These equilibria can be explained in terms of the chabazite crystal structure given by Smith.

Introduction

Many investigators have studied one aspect or another of chabazite, but the studies concerned with quantitative cation exchange equilibria and crystal structure are relatively scarce. Barrer & Sammon (1955) first made a quantitative study of the exchange reactions of chabazite in systems containing sodium-silver, potassium-silver, sodium-rubidium and sodium-thallium. Thermodynamic equilibrium constants were computed for the above systems and, using the "triangle rule," a sodium-potassium equilibrium constant was computed as well. A value of 13.3 was given for the equilibrium constant of sodium on the zeolite exchanging to potassium on the zeolite. The unit cell content of the chabazite used by Barrer & Sammon in their study was $Ca_{1.59}Na_{0.37}Al_{3.49}Si_{8.50}O_{24}$, or approximately 3.55 exchangeable sodium atoms per 24 oxygen atoms. Using the above zeolite, only one-third to three-quarters of the sodium on the zeolite could be exchanged to cesium on the zeolite. Barrer & Langley (1958) later reported cesium exchange of 89.7 per cent on a natural chabazite at 110 °C.

Of direct concern to any explanation of the cation exchange characteristics is the crystal structure of chabazite. The work of Dent & Smith (1958) and Smith (1962, 1964) on chabazite crystal structure is pertinent to any interpretation of cation exchange properties. The chabazite structure is thus well-enough characterized to allow a structural interpretation of exchange properties. The present study was concerned with alkali metal cation equilibria on chabazite and their structural interpretation.

METHODS OF INVESTIGATION

The chabazite used in this study was from the Bay of Fundy region of Nova Scotia. The as-received chabazite contained basalt rock as the major impurity. Consequently, the chabazite was hand-picked free of basalt, as far as possible, and the clean fraction crushed. The one-quarter to one-half millimeter size of the clean, crushed fraction was passed through an electromagnetic separator several times to insure a basalt-free chabazite fraction for study. The resulting clean fraction was crushed to minus 100 mesh, washed with distilled water and air-dried at room temperature. Water loss on ignition to 700 °C of the clean, powdered, air-dried zeolite was 19.1 weight per cent. All subsequent zeolite capacity determinations include the above weight per cent water as a part of the zeolite weight. A chemical analysis of the anhydrous chabazite is given in Table 1.

TABLE 1. CHEMICAL ANALYSIS OF THE ANHYDROUS CHABAZITE SAMPLE

Constituent	Weight %	Unit cell contents
SiO_2	66.6	
Al_2O_3	22.8	$Na_{0.09}Ca_{1.72}Al_{3.47}Si_{8.51}O_{24}$
CaO	12.3	
Na_2O	0.7	
	102.4	

A small column technique was used to determine chabazite exchange capacities and equilibria (Howery & Thomas, 1965; Eliason, 1966). The double-tracing technique used in some previous studies (Ames, 1964a; Ames, 1964b) was adequate to establish cesium and strontium selectivity trends in relation to zeolite composition (Ames, 1965a), and to provide useful and applicable zeolite ion exchange engineering data (Mercer & Ames, 1963; Popovich, 1964). The small column technique, being a more precise method for zeolite capacity measurement than double-tracing, sometimes reveals small but measurable differences in zeolite capacities as measured with different cations. When significantly large, the capacity differences become obvious even with use of the double-tracing technique (Ames, 1965b). The present study was concerned with a small difference between chabazite cesium and sodium capacities shown to exist by the small column technique.

Briefly, the small column technique consists of passing a solution of known chemical composition containing a radioactive tracer through a one-quarter to one-half gram zeolite powder column until equilibrium between solution and zeolite is attained. Equal volume counting of an influent sample with the same geometry yields the counts per milliequivalent of influent solution (Eliason, 1966). The counts per gram of chabazite divided by the counts per milliequivalent of influent solution (the equilibrium solution) gives the chabazite capacity for the traced cation. Solutions with a total normality of 1.0 were used, so 1.0 minus the normality of the traced cation on the zeolite, or in the solution, equals the amount of untraced cation in the zeolite or solution of a binary system. Knowing the equivalent fractions of each of the cations of the binary system, a mass action or selectivity quotient can be derived by using the classical relationship:

$$\text{Selectivity quotient} = \frac{(A_Z)^{nA}(B_N)^{nB}}{(B_Z)^{nB}(A_N)^{nA}}, \text{ where}$$

A_N, B_N = concentration of cations A and B in the solution in equivalents per 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.

In one case, the selectivity quotient was corrected using a mean activity coefficient ratio of KCl and NaCl at a normality of 1.0, resulting in a corrected selectivity quotient, K_c (Glueckauf, 1949). The values for the natural log of K_c then were plotted vs. the equivalent fraction of cation on the zeolite, and a rational thermodynamic equilibrium constant derived by the method of Gaines & Thomas (1953).

Reagent grade chlorides in distilled water were used for solution constituents. High purity cesium-134 and sodium-22 were used as radiotracers.

Results and Discussion

The chabazite isotherm for sodium-potassium equilibrium at 23 °C is given in figure 1. Note that the chabazite is highly unselective for sodium in the presence of potassium. The selectivity coefficients of the experimental points given in figure 1 were determined, corrected with the appropriate mean activity coefficient ratio, and plotted as the natural log of the corrected selectivity quotient ($\ln K_c$) vs. the equivalent fraction of sodium on the zeolite (Na_z) as shown in figure 2. The experimental values are all listed in table 2. The thermodynamic equilibrium constant (κ) derived from the data of figure 2 was 0.0708, and the free-energy change was + 1570 cal/mole. The above values may be directly compared to values given by Barrer & Sammon (1955) for a chabazite very similar in chemical composition to the chabazite utilized in this study.

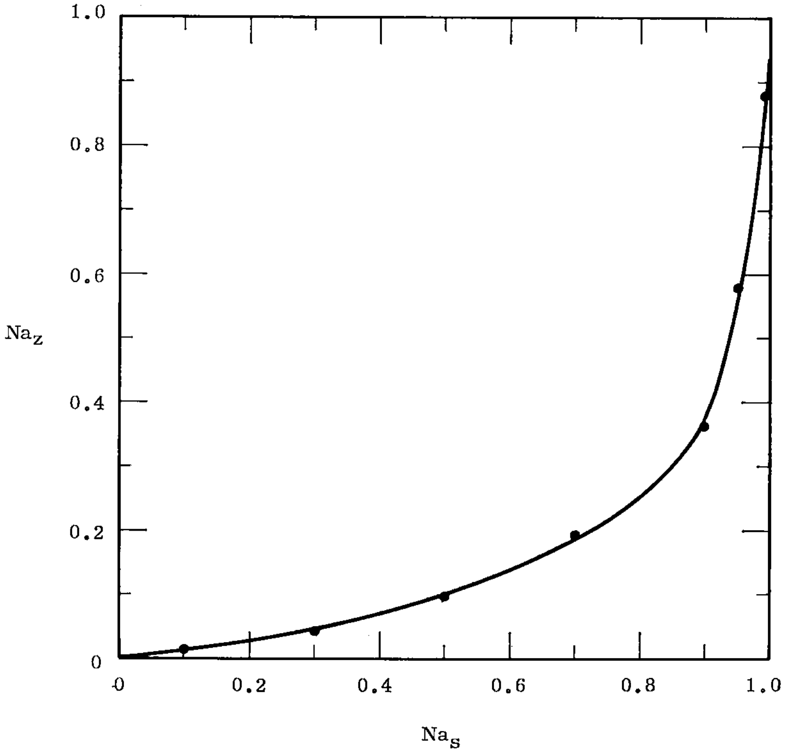

FIG. 1. The 23 °C isotherm for the reaction $K_z + Na_s \rightleftarrows Na_z + K_s$ with chabazite. Total equilibrium solution normality was constant at 1.0. K_z, Na_z = equivalent fraction of potassium or sodium on the zeolite. K_s, Na_s = equivalent fraction of potassium or sodium in the equilibrium solution.

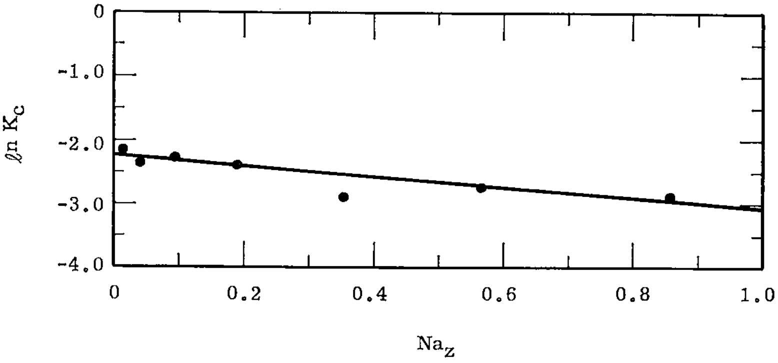

FIG. 2. A graph of the natural log of the corrected selectivity quotients (ln K_c) vs. the equivalent fraction of sodium on the zeolite (Na_z) for the reaction $K_z + Na_s \rightleftarrows Na_z + K_s$ at 23 °C with chabazite.

The comparable equilibrium constant given by Barrer & Sammon was 0.0752 (1/13.3), and a free energy change of +1530 cal/mole. Within the experimental error, they are the same values. The relationship $\ln \kappa = \ln K_c + C(1\text{–}2\text{Na}_z)$, based on the Kielland equation, describes the curve shown in figure 2. Na_z is sodium on the zeolite and C is a constant, minus 0.42 in the above case.

Chabazite binary systems containing cesium were of special interest because the cesium capacity was not the same as the sodium or potassium capacity. Chabazite sodium and potassium capacities averaged 2.59 meq/g, while the cesium capacity was 2.20 meq/g. Extended equilibrations (up to ten days) yielded cesium capacity results very similar to the two-day equilibrations. Equilibrium was attained in a normal two-day equilibration time, so that poor cesium kinetics were not a contributing factor to the low cesium capacity.

The plotting of cation exchange data in the standard form of an isotherm required modifications because of the different exchange capacities of the two cations.

TABLE 2. CHABAZITE EQUILIBRIUM DATA BASED ON THE SODIUM AND POTASSIUM CAPACITY OF 2.59 MEQ/G. A CAPACITY OF 2.20 MEQ/G WAS USED FOR THE Sr-Cs SYSTEM.

$\text{K}_z + \text{Na}_s \rightleftarrows \text{Na}_z + \text{K}_s$, 23 °C			
Na_z	Na_s	Selectivity quotient	K_c
0.880	0.990	0.0741	0.0557
0.581	0.950	0.0730	0.0672
0.362	0.900	0.0606	0.0558
0.190	0.700	0.1005	0.0925
0.0982	0.500	0.1089	0.1002
0.0421	0.300	0.1026	0.0944
0.0143	0.100	0.1306	0.1202

$\text{Na}_z + \text{Cs}_s \rightleftarrows \text{Cs}_z + \text{Na}_s$, 23 °C	
Cs_z	Cs_s
0.229	0.010
0.675	0.100
0.734	0.200
0.764	0.400
0.822	0.600
0.831	0.800
0.822	0.900
0.823	0.990

$\text{K}_z + \text{Cs}_s \rightleftarrows \text{Cs}_z + \text{K}_s$, 23 °C	
Cs_z	Cs_s
0.135	0.010
0.466	0.100
0.566	0.300
0.648	0.500
0.710	0.700
0.820	0.950

$2\text{Cs}_s + \text{Sr}_z \rightleftarrows \text{Sr}_s + 2\text{Cs}_z$, 23 °C			
Cs_z	Cs_s	Cs_z	Cs_s
0.177	0.001	0.964	0.684
0.670	0.010	0.971	0.700
0.780	0.035	0.984	0.711
0.879	0.100	0.978	0.816
0.896	0.100	0.977	0.900
0.893	0.179	0.974	0.913
0.929	0.252	1.000	0.990
0.936	0.447		
0.940	0.500		

Two scales were used for the equivalent fraction of cation on the zeolite as seen in the data of figure 3. Cesium on the zeolite at 1.0 is 2.20 meq/g, and sodium on the zeolite at 1.0 is 2.59 meq/g. The two zeolite scales are

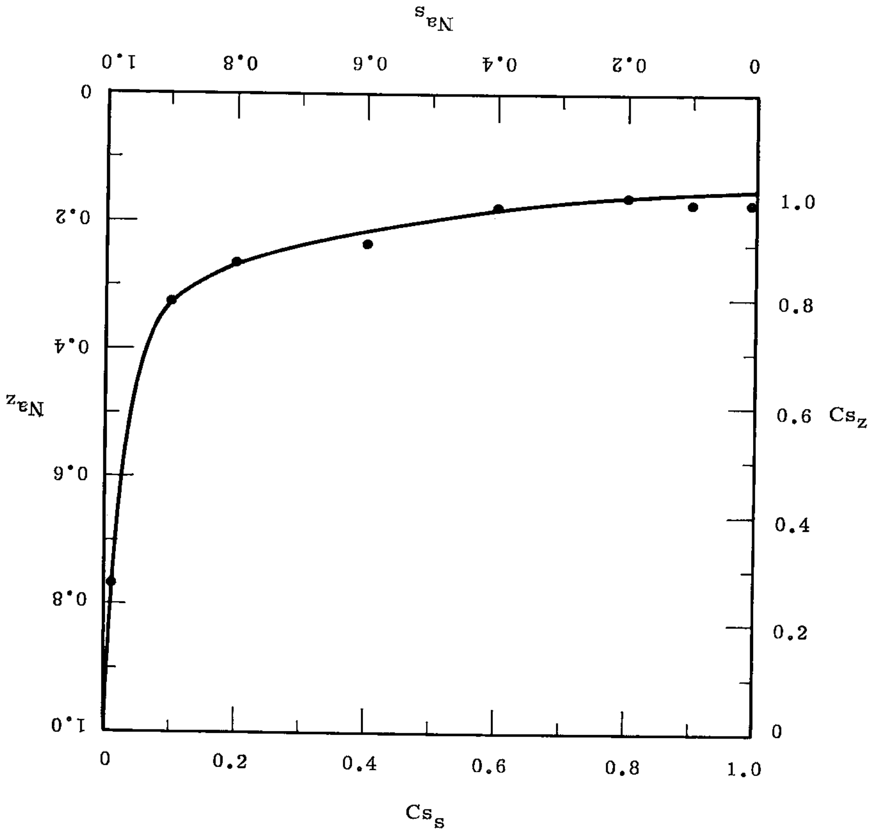

FIG. 3. The 23 °C isotherm for the reaction $Na_z + Cs_s \rightleftarrows Cs_z + Na_s$ with chabazite. Total equilibrium solution normality was constant at 1.0. Cs_z, Na_z = equivalent fraction of cesium or sodium on the zeolite; the equivalent fraction of sodium on the zeolite is plotted as a fraction of the chabazite sodium capacity of 2.59 meq/g; the equivalent fraction of cesium on the zeolite is plotted as a fraction of the chabazite cesium capacity of 2.20 meq/g. Cs_s, Na_s = equivalent fraction of cesium or sodium in the equilibrium solution.

plotted so that rotation of the figure 180 degrees shows the isotherm in terms of the other cation of the binary system. Note that cesium zeolite loading begins at 15 per cent sodium loading, or the equivalent fraction on the zeolite at 1.0 cesium in the solution is 85 per cent cesium on the zeolite plus 15 per cent sodium on the zeolite. The potassium-cesium isotherm is presented in the same manner in figure 4.

The failure of chabazite to completely exchange sodium for cesium can be explained on the basis of the structure of chabazite as elucidated by Smith (1964). The basic feature of the chabazite structure is a distorted

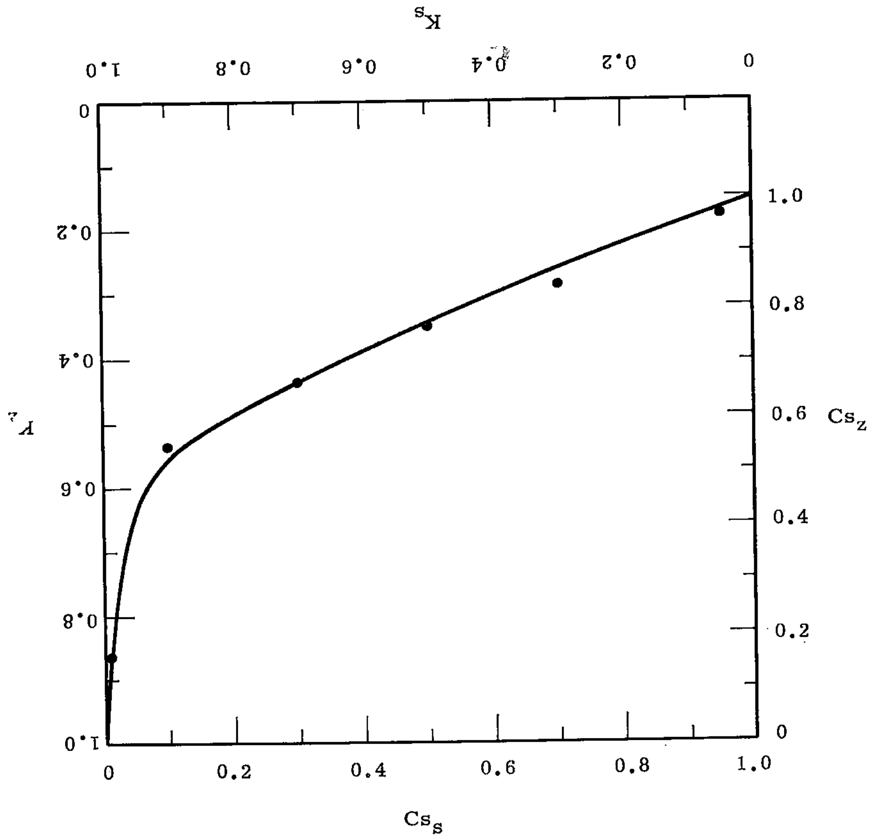

Fig. 4. The 23 °C isotherm for the reaction $K_z + Cs_s \rightleftarrows Cs_z + K_s$ with chabazite. Total equilibrium solution normality was constant at 1.0. Cs_z, K_z = equivalent fraction of cesium or potassium on the zeolite; the equivalent fraction of potassium on the zeolite is plotted as a fraction of the chabazite potassium capacity of 2.59 meq/g; the equivalent fraction of cesium on the zeolite is plotted as a fraction of the chabazite cesium capacity of 2.20 meq/g. Cs_s, K_s = equivalent fraction of cesium or potassium in the equilibrium solution.

ditrigonal prism of two six-membered rings. The main chabazite adsorption cavity is six to seven angstroms in diameter, 10 Å in length and contains four- six- and eight-membered rings. As Smith reported (1964, p. 3762), some of the larger cations such as cesium should be able to occupy the 3 to 4 Å, eight-membered rings, bonding across the aperture. There are six eight-membered rings per unit cell so that the theoretical four exchangeable sodium cations per unit cell would be displaced by only three cesium ions per unit cell (each eight-membered ring is shared) plus a remaining sodium ion within the main adsorption cavity that could not be displaced because of the cesium spatial requirements. The unit cell contents of exchangeable sodium for the chabazite of this study is 3.53 atoms per unit cell, as shown in table 1. If the final cesium content of the chabazite unit cell is 85 per cent of the original sodium content, the cesium content is 85 per cent of 3.53 sodium atoms or 3.00 cesium atoms plus 0.53 sodium atoms per unit cell. It would seem, therefore, that the cesium atom does occupy the eight-membered ring aperture, while sodium and potassium, being smaller in diameter, probably occupy positions within the main adsorption cavity of chabazite. The high cesium selectivity of chabazite would indicate that the cesium "thermodynamic fit" into the eight-membered rings is a good one. Little, if any, polar molecule sorption could be expected when the eight-membered rings of chabazite are blocked by cesium cations.

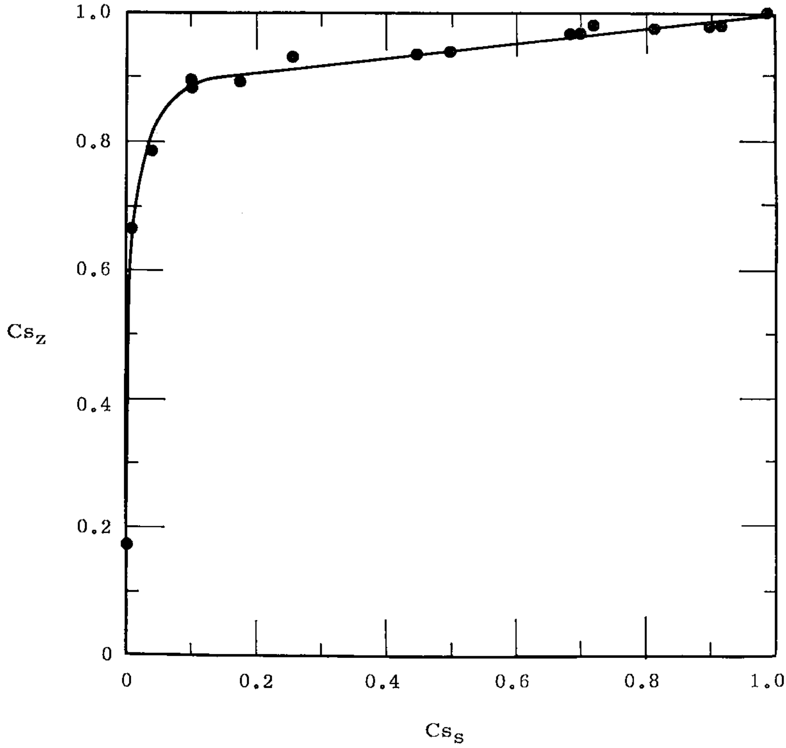

FIG. 5. The 25 °C isotherm for the reaction $2Cs_s + Sr_z \rightleftarrows Sr_s + 2Cs_z$ with chabazite. Total equilibrium solution normality was constant at 1.0. $Cs_z = 1.0 = 2.20$ meq Cs/g. Sr_z, Cs_z = equivalent fraction of strontium or cesium on the zeolite. Sr_s, Cs_s = equivalent fraction of strontium or cesium in the equilibrium solution.

The data of figures 3 and 4 did not result in a constant when selectivity quotients were corrected with mean activity coefficient ratios; i.e., the chabazite did not behave ideally. To further correct the above K_c values with computed mean activity coefficients for cations on the zeolite requires definition of a standard or reference state. Where rational activities are concerned, such as the example of chabazite in a sodium-potassium system, the standard and reference states for potassium and sodium on the chabazite are the monoionic sodium and monoionic potassium chabazites. Since a monoionic cesium chabazite was not attained, or the standard state could not be readily defined, no attempt was made to derive rational thermodynamic constants in the systems containing cesium. Thermodynamics do not, in any case, give much insight into the physical causes of zeolite cation exchange behaviour.

The 23 °C isotherm for the system strontium-cesium is given in figure 5. These data are plotted in terms of the cesium capacity of chabazite, or $Cs_z = 1.0 = 2.20$ meq Cs/g. The strontium capacity of chabazite was not determined. The strontium-cesium isotherm is given here only to show that univalent cesium that fits well into the eight-membered ring is strongly preferred to divalent strontium that does not fit into the ring or satisfy the anionic site charge distribution of chabazite.

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REFERENCES

AMES, JR., L. L. (1964a): Some zeolite equilibria with alkaline earth metal cations: *Am. Min.*, **49**, 1099–1110.

——— (1964b): Some zeolite equilibria with alkali metal cations: *Am. Min.*, **49**, 127–145.

——— (1965a): Zeolite cation selectivity: *Can. Mineral.*, **8**, 325–333.

——— (1965b): Zeolite type X equilibria with trivalent cerium and yttrium cations: *J. Inorg. and Nuclear Chem.*, **27**, 885–894.

BARRER, R. M. & LANGLEY, D. A. (1958): Reactions and stability of chabazite-like phases. Part I. Ion-exchanged forms of natural chabazite: *J. Chem. Soc. London*, 3804–3811.

BARRER, R. M. & SAMMON, D. C. (1955): Exchange equilibria in crystals of chabazite: *J. Chem. Soc. London*, 2838–2849.

DENT, L. S. & SMITH, J. V. (1958): Crystal structure of chabazite, a molecular sieve: *Nature*, **181**, 1794–1796.

ELIASON, J. R. (1966): Montmorillonite exchange equilibria with strontium-sodium-cesium: *Am. Min.* **51**, 324–335.

GAINES, G. L. & THOMAS, H. C. (1953): Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption: *J. Phys. Chem.*, **21**, 714–718.

GLUECKAUF, E. (1949): Activity coefficients in concentrated solutions containing several electrolytes: *Nature*, **163**, 414–415.

HOWERY, D. G. & THOMAS, H. C. (1965): Ion exchange on the mineral clinoptilolite: *J. Phys. Chem.*, **69**, 531–537.

MERCER, JR., B. W. & AMES, JR., L. L. (1963): The adsorption of cesium, strontium and cerium on zeolites from multication systems: *U.S. Atomic Energy Commission Document* HW-78461 (unclassified), 65 p.

POPOVICH, R. P. (1964): Ion exchange recovery of cesium from alkaline supernatant; waste scale-up studies: *U.S. Atomic Energy Commission Document* HW-83461 (unclassified), 41 p.

SMITH, J. V. (1962): Crystal structures with a chabazite framework. I. Dehydrated Ca-chabazite: *Acta Cryst.*, **15**, 835–845.

SMITH, J. V. (1964): Crystal structures with a chabazite framework. Part V. Interpretation of physiochemical properties in terms of crystal structure: *J. Chem. Soc. London*, 3759–3770.

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