Exchange Equilibria in Crystals of Chabazite.

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Exchange equilibria between aqueous solutions and crystals of chabazite have been studied quantitatively for the ion pairs Na–Cu, Na–Ag, Na–Tl, Na–Rb, Na–Ca, Na–Ba, and K–Ag. In all cases the pure chabazite salts formed continuous series of solid solutions. Equilibria were reached reversibly and were nearly independent of temperature within the ranges studied. The Na–Ag exchange was nearly ideal in as far as the simple law of mass action was valid. The other uni-univalent exchange equilibria were satisfactorily represented by the relation

$$\log K = \log \frac{B_z(1 - B_s)}{B_s(1 - B_z)} + C(1 - 2B_z)$$

where K and C are constants and B_z, B_s are the equivalent cation fractions of ionic species B in zeolite and in solution respectively. A number of these isotherms were sigmoid. Some of them have been subjected to thermodynamic analysis.

Chabazite samples rich in H, Li, Mg, Sr, NH_4, Co^{2+}, Ni^{2+}, and Pb^{2+} were also prepared. Attempts to prepare La^{3+}-, NMe_4-, and NEt_4-rich forms were unsuccessful in the case of the organic ions on account of an ion-sieve effect. Properties of various pure chabazite salts have been determined, such as refractive indices, water content, X-ray diffraction patterns, and unit cells. The unit cell of chabazite is changed very little by ion exchange.

In crystalline media ion exchange may be considered a type of solid-state reaction. There are many crystalline aluminosilicates in which ion exchange occurs freely, notably some members of the clay-minerals group, the zeolite group, and the felspathoids. The clays, although widely studied from this viewpoint, do not lend themselves well to investigations of ion exchange as a solid-state reaction. The crystals are small and often imperfect, and the exchange may be accompanied by extensive swelling and shrinking along the *c*-axis. By contrast with these layer-lattice minerals, the felspathoids and many of the zeolites are excellently crystalline with robust three-dimensional network structures, permeated by intersecting or interconnected channels of molecular dimensions. In such media one may seek for an exchanger which is " ideal " from the theoretical viewpoint : this means a crystal in which the anionic framework forms a wholly inert, unchanging, and charged structure, into which cations A may be inserted with the displacement of an electrochemical equivalent of cations B. Barrer (Colloq. Internat., " Reactions dans l'État Solide," C.N.R.S., Paris, 1948) assumed each ion to go on to definite sites, and from statistical considerations evaluated the equilibrium constants for the reactions

$$AX_{(s)} + BZ_{(s)} \longrightarrow BX_{(s)} + AZ_{(s)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where X is an anion (Cl^-, NO_3^-, etc.) and Z denotes the zeolitic framework. It was considered that BZ and AZ were in solid solution with each other (these solid solutions being ideal in accordance with the above definition of the ideal exchanger). Cases were considered where each salt AX and BX was in equilibrium with its saturated aqueous solution and the zeolite crystals, where the ion-exchanging medium was and was not hydrated, and where the water content did and did not change during the process of exchange. Systems were also considered where AX and BX formed a mixed ionic melt or were in unsaturated aqueous solution together. The zeolites represent typical hydrated crystals while the felspathoids are anhydrous.

Investigations have now been made of ion-exchange processes in analcite, mordenite, and chabazite (Barrer, *J.*, 1948, 2158; *J.*, 1950, 2342). Quantitative studies of ion-exchange diffusion kinetics and equilibria have been made in the zeolites analcite (Barrer and Hinds, *J.*, 1953, 1879; Barrer and Falconer, unpublished work), chabazite (this paper), and faujasite (Barrer, Buser, and Grutter, unpublished work); and in the felspathoids ultramarine (Barrer and Raitt, *J.*, 1954, **4641**) and cancrinite (Barrer and Falconer, unpublished work). It has been clearly established that analcite is not an ideal exchanger in the sense given by Barrer (*loc. cit.*). The framework does participate in the exchange process, and where the exchanging cation pairs differ appreciably in ion size the exchange isotherms may exhibit discontinuities due to limited mutual solid solubility of the end members, pure AZ and pure BZ. Associated with this behaviour there arises hysteresis due to the difficulty of nucleating one solid phase in or on another (Barrer and Hinds, *loc. cit.*; Thomas and Staveley, *J.*, 1951, 2572; Barrer, Drake, and Whittam, *Proc. Roy. Soc.*, 1953, *A*, **219**, 32). Ultramarine also may sometimes exhibit continuous and sometimes discontinuous solid solubility (Barrer and Raitt, *loc. cit.*).

For more open structures (mordenite, chabazite, faujasite) one may enquire whether the behaviour will be more ideal, and in particular whether the end members will exhibit continuous solid solubility. The anionic frameworks here include cages fully large enough to contain without strain either of two ions of widely differing sizes. However, difficulties may still arise over valency differences between ions (*e.g.*, $2Na^+ \rightleftharpoons Ca^{2+}$) and local balance of anionic charge; and also the ion size and polarisability may influence the equilibrium constants substantially. We present in this paper an investigation of ion-exchange equilibria in chabazite and their interpretation.

EXPERIMENTAL

Naturally occurring chabazite crystals from the Bay of Fundy, Nova Scotia, were detached, as interpenetrating clusters, from their rock matrices, and separated from intergrown stilbite and calcite. The crystals were ground and in nearly all the quantitative work the portion between 120 and 200 mesh was used. The methods of exchange employed involved heating the crystals with salt solutions [LiCl, NaCl, KCl, RbCl, CsCl, $MgCl_2$, $SrCl_2$, $BaCl_2$, $AgNO_3$, $TlNO_3$, NH_4Cl, $CuSO_4$, $CuCl_2$, $NiCl_2$, $Pb(NO_3)_2$, $La(NO_3)_3$, NMe_4Br, NEt_4I], heating with fused salts ($NaClO_4$, $AgNO_3$), or heating in presence of vaporised salt (NH_4Cl).

Exchanging salts were, except where otherwise stated, of " AnalaR " grade; rubidium and cæsium chlorides of 99·9% purity were supplied by Johnson, Matthey Ltd.; thallium nitrate from B.D.H. was recrystallised once from water, filtered off, washed with water, and vacuum-dried before use. Distilled water was produced in a tin-plated copper still and gave a residue on evaporation of about 0·5 mg. per 100 ml. This residue contained copper. For some experiments de-ionised water was used.

Most of the quantitative exchange reactions were carried out in sealed Pyrex-glass tubes. The lengths of tubing before use were extracted in boiling distilled water for about 5 hr. to remove any soluble material from the glass. To permit exchanger and solution to react at constant temperature and to keep mixing them, the sealed tubes were secured to rotating carriers in water or air thermostats. Water thermostats were used up to 45°, and air thermostats at higher temperatures up to 120°.

Chabazite was analysed by methods which are essentially those given by Groves (" Silicate Analysis," Allen and Unwin, London). The means of three analyses of the original natural chabazite, and of two analyses of Ca-chabazite formed by exchange of Na by Ca in the natural crystals are given in Table 1. The crystals are thus rich in Ca in the natural state and also higher in silica than the " ideal " formula with $SiO_2 : Al_2O_3 = 4 : 1$. It is known, however, that

TABLE 1. *Analyses of chabazite.*

	Natural chabazite Composition :		Ca-Chabazite Composition :	
	%	Molar	%	Molar
SiO_2	50·08	4·87	50·03	4·82
Al_2O_3	17·44	1·00	17·70	1·00
CaO	8·76	0·913	9·96	1·023
Na_2O	1·14	0·107	—	—
H_2O	21·90	7·10	22·16	7·08
Total	99·32	—	99·85	—

this ratio may vary rather widely in chabazite (*e.g.*, Wyart, *Bull. Soc. franç. Minér.*, 1933, **56**, 103). The ratio Al_2O_3/(Total Bases) is 0·981 and 0·978 in natural and in Ca-chabazite, respectively.

In quantitative analyses for other cations, standard methods were used where possible. Silver was estimated as silver chloride; lead and barium as chromate, and also as sulphate; calcium as CaC_2O_4,H_2O; copper as thiocyanate; thallium as iodide (precipitated at 0°) and also as chromate. Mixtures of rubidium and sodium chlorides were determined as follows. The solution was evaporated to dryness in a platinum dish and weighed. A blank correction was made for solids extracted from the wall of the reaction tube and present in the distilled water (*loc. cit.*). The chloride content of the solution was known since pipetted volumes of rubidium and sodium chlorides of known concentrations (N/4) were mixed. Accordingly, from the weight of mixed chlorides and the weight of Cl the Na and Rb may be found. The same procedure was used with cæsium and sodium chloride mixtures.

X-Ray examination of exchange products was made by using a Hilger HRX *X*-ray unit, with 9-cm. powder cameras. Filtered Cu-K_α radiation was used. Optical examination was carried out with a Leitz research microscope. Refractive indices were measured approximately by the Becke line method, using immersion liquids for which refractive indices had been determined by using an Abbé refractometer. When liquids with refractive indices just above and just below that of the crystals had been found, these liquids were mixed in different proportions until the crystals were no longer visible when immersed in the liquid. The refractive index of this liquid was then found with the Abbé refractometer, and taken as equal to that of the crystals.

Results.—Samples of chabazite were prepared which were rich in the following cations: Li, Na, K, Rb, and Cs; Mg, Ca, Sr, and Ba; Ag, Tl, NH_4, Cu^{II}, Co^{II}, Ni^{II}, and Pb^{II}. Attempts to produce chabazites rich in La^{III}, NMe_4, and NEt_4 were unsuccessful, the failure being ascribed to valency * in the case of La^{III}, and being due to an ion-sieve action with the very large tetra-alkylammonium ions. Among small uni- and bi-valent ions, however, there was free exchange with no obvious critical factor.

Exchanges giving crystals rich in Li, Na, K, Rb, and Cs were effected hydrothermally at 110°, 95°, 95°, 85°, and 25°, respectively. The starting materials were Ca- and natural chabazites respectively (Table 1); and the exchange reactions were followed by observations of weight change in the crystals, or of the calcium displaced. Na-Chabazite was also prepared by heating natural chabazite with fused sodium perchlorate. In agreement with an earlier study (Barrer, *J.*, 1950, 2342) magnesium could not be introduced directly into natural chabazite heated with saturated aqueous magnesium chloride at 85°. However, magnesium was introduced successfully at 95° by the reaction

$$MgCl_2(sat.) + 2AgCh \longrightarrow MgCh_2 + 2AgCl(s.)$$

where Ch denotes the anionic framework of chabazite. Calcium, strontium, and barium were introduced at 75°, 95°, and 85° and by use of Na-, natural, and Na-chabazite, respectively. The reactions were followed by weight change, or from changing compositions of the exchanging solutions, or both.

Silver-rich chabazites were readily made hydrothermally. There was, however, a tendency for grey or even darker products to appear, owing to the deposition of small amounts of metallic silver. This was so particularly with $>$0·5N-silver nitrate solutions. It was not possible to settle definitely the conditions giving metallic silver, but this deposition was negligible with concentrations $\not>$N/4, temperatures $\not>$45°, and times of experiment $\not>$24 hr. Heating chabazite crystals in fused silver nitrate gave a buff-coloured product, with extensive exchange. The colour indicates that this method does not eliminate a small silver deposition.

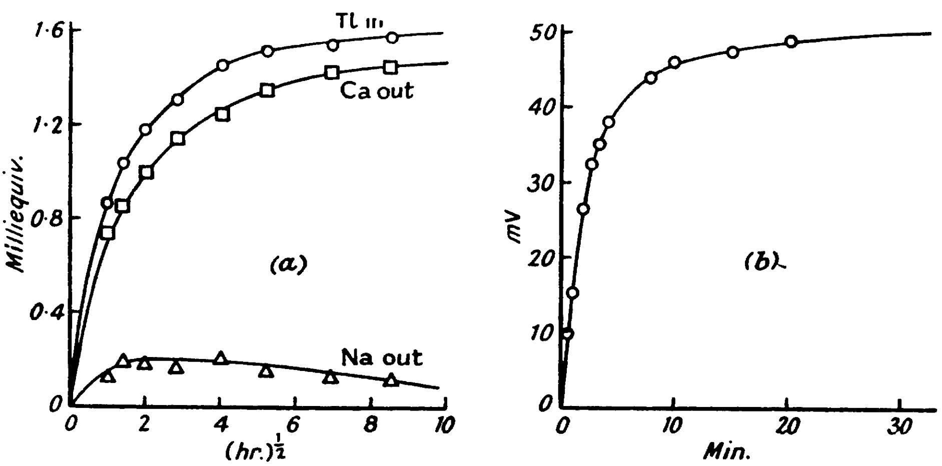
Thallium-rich chabazites were easily made hydrothermally, and extensive exchange of calcium for ammonium was also observed when ammonium chloride vapour at 350° was the exchange medium, or when ammonium chloride solution at 95° was used (cf. Barrer, *J.*, 1950, 2342). When chabazite crystals were heated with aqueous nickel chloride or copper sulphate at 110°, basic salts were formed, and the Cu-rich chabazite crystals were bluish. These crystals became deep blue on exposure to gaseous ammonia, while the nickel-rich crystals became pale violet. Treatment of pink chabazite with aqueous cobalt chloride at 110° gave a Co-rich

* In an exchange such as $3Na^+ \rightleftharpoons La^{3+}$, there may be local excess of positive charge at the site occupied by La^{3+}, and local excess of anionic charge at the sites vacated by two of the Na^+ ions. This disbalance may be unfavourable for exchange. At the same time it is evidently not a serious factor in the exchange $2Na^+ \rightleftharpoons Ca^{2+}$, and others of similar type.

chabazite in which the original pink hue was definitely deepened. The colour reactions of these three exchange products are evidently those normally associated with the cations in co-ordination with water or with ammonia. Finally, with lead nitrate solution at 95°, a considerable exchange $Pb^{2+} \rightleftharpoons Ca^{2+}$ was found in the chabazite, while on the other hand with lanthanum nitrate solution at 95° there was no change in weight in the crystals.

Hydrogen-ion Exchange.—When Ag-chabazite was heated with aqueous tetramethylammonium bromide at 95°, silver bromide was formed, which was removed by means of aqueous ammonia. The chabazite was then paler than originally. A similar treatment of Ca chabazite with the bromide gave no reaction; while treatment of the Ag-form with aqueous tetraethylammonium iodide at 95° gave silver iodide. This behaviour was comparable with that observed earlier in Ag-ultramarine, Ag-analacite, and other species (Barrer and Raitt, *loc. cit.*; Barrer and Sammon, unpublished work). It was there shown to be due to hydrogen-ion exchange : $NMe_4Br + AgCh + H_2O \longrightarrow HCh + AgBr + NMe_4OH$. No alkylammonium ion is removed in this process, and the reaction depends wholly upon the inability of so large an ion to penetrate the crystals, and the insolubility of the silver halide.

FIG. 1.



(a) *Kinetics of exchange of* Tl^+ *for* $Ca^{2+} + Na^+$.
(b) E.M.F. *as a function of time in the exchange of* Ag^+ *for* Na^+.

Rates of Exchange.—Experiments were conducted to find the equilibration times for exchanges in chabazite. The ground, unsieved mineral (0·5 g.) was heated with 10 ml. of

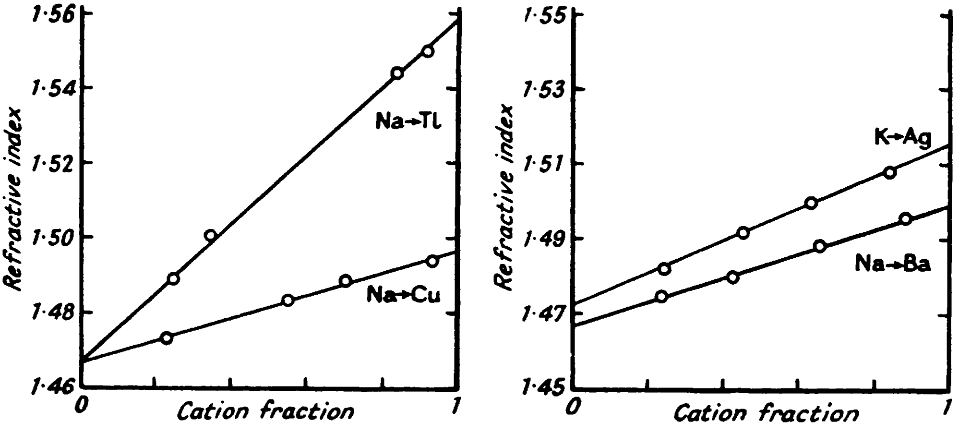
TABLE 2.

Exchanging solution, and method of analysis	Time (hr.)	Temp.	Exchange (%) By wt. of crystals	By analysis	Mean
$AgNO_3$; Ag detd. as AgCl	½	25°	97·7	97·5	97·6
	2	25	96·7	97·8	97·3
	5	25	97·2	97·1	97·2
$BaCl_2$; Ba detd. as $BaSO_4$	½	25	40·5	36·5	38·5
	2	25	66·1	63·0	64·6
	24	25	88·9	89·9	89·4
	½	85	37·7	37·9	37·8
	2	85	66·7	63·6	65·2
	4	85	90·9	93·8	92·4
	∞	85	88·3	92·1	90·2
CsCl; Cs detd. from wt. of evaporate	½	25	40·7	42·5	41·6
	2	25	60·9	56·9	58·9
	4	25	63·0	63·0	63·0
	∞	25	62·4	62·8	62·6
RbCl	½	85	88·2	—	88·2
	2	85	90·0	—	90·0
$TlNO_3$; Tl detd. as Tl_2CrO_4	½	25	98·8	100·0	99·4
	2	25	98·5	99·5	99·0

0·3036N-thallous nitrate in sealed tubes at 75°; thallium and calcium were determined for various intervals of time, and sodium was found by difference, with the results presented in Fig. 1*a*. The slight maximum in the amount of displaced sodium was attributed to the greater velocity with which univalent ions can be displaced when compared with bivalent ones (see below). Thus, initially, the thallium displaced more than the final equilibrium content of sodium, but at a later stage more of the less rapidly displaced calcium had diffused from crystals to solution, a little sodium re-entered the crystals, and a three-fold equilibrium was established within the crystals involving the species Tl^+, Na^+, and Ca^{2+}.

The presence of calcium was then eliminated, by using the pure Na-form of chabazite as exchanger, and treating this at 95° with a solution saturated with respect to both sodium sulphate and thallous sulphate. Reaction was then virtually complete in 75 min. Further experiments using 0·1 g. of Na-chabazite and 5 ml. of N/4-salt solutions were followed by analysis and by weight change of the crystals. The results of Table 2 show that all the uni-univalent exchanges are very rapidly completed, whatever the ionic radius of the entering ions, even the sodium–cæsium exchange being effectively finished in 2 hr. By contrast with this the uni-bivalent exchange ($2Na \rightleftharpoons Ba$) requires a substantially longer time, even at 85°. Valency differences are evidently more important in determining the exchange kinetics than are ionic radii.

FIG. 2. *Relations between refractive indices and cationic compositions of exchange forms of chabazite.*



The high velocity of exchange renders the analytical method of following the kinetics unsuitable for measurements of exchange diffusion coefficients. An e.m.f. method is, however, possible. The cell

Ag	$AgNO_3$	satd. NH_4NO_3	$AgNO_3$ + stirred Na-chabazite	Ag
		in agar	+ $NaNO_3$ powder	

was studied at room temperature, and the e.m.f. measured continuously as a function of time (Fig. 1*b*). The high velocity of exchange was confirmed, and, suitably interpreted, the method may give exchange diffusion coefficients. In the present paper, however, the emphasis will be on exchange equilibria.

Properties of Cationic Forms.—(a) *Refractive indices.* The refractive indices of crystals of various intermediate cationic compositions were determined for the exchanges Na–Tl, Na–Cu, Na–Ba, and K–Ag. All the crystals had reacted to equilibrium with the ambient solutions and were of uniform refractive index throughout. All the refractive indices measured were mean values, since the crystals, being rhombohedral, have two such indices. In Fig. 2 are shown the indices as functions of cationic compositions of the mixed crystals. There is in every instance a linear relation, so that optical methods of analysis of these crystals are possible. There were, moreover, no immiscibility gaps between homoionic exchange forms of chabazite, since all crystals in any given sample, whatever the cationic compositions, had the same refractive index. Those of the pure ionic forms of chabazite are given in Table 3. Three factors influence the trend in the refractive index among cationic forms: the mass of the cations, their valency, and the extent to which the hydration changes in a given sequence of ions. Among alkali-metal ions, the Li-form of chabazite is very highly hydrated, and this more than offsets the greater mass of the sodium ion. Among the alkali-metal cationic forms falling degree of hydration (see below) tends to balance increasing cationic mass.

TABLE 3. *Mean refractive indices of pure ionic forms of chabazite.*

Ionic form	*n*	Ionic form	*n*	Ionic form	*n*
Li	1·472	Ca	1·486	Cu	1·497
Na	1·467	Sr	1·490	Ag	1·516
K	1·472	Ba	1·499	Tl	1·559
Rb	1·476	—	—	—	—

(b) *Water content and cationic compositions.* The water contents of chabazite crystals were determined by ignition, except for Cu-, Ag-, and Tl-forms. In these and other cases the weight varies linearly as a function of changing cationic compositions (Fig. 3), and the linear graphs serve to give the weight increases for 100% exchange. The results normally correspond to changes in water content in going from one pure cationic form to another (Table 4). In general, bivalent ions in chabazite produce a more highly hydrated condition than do univalent ones. Among the alkali-metal ions the water content of the crystals falls with increasing ionic radius, but for the bivalent alkaline-earth metal ions this trend does not appear. The results given in Table 4 may depend to some extent upon the relative pressure of water vapour, according to the degree of rectangularity of the sorption isotherms.

FIG. 3. *Linear correlations between % exchange and % increases in weight of crystals, from which water contents of pure cationic forms may be found.*

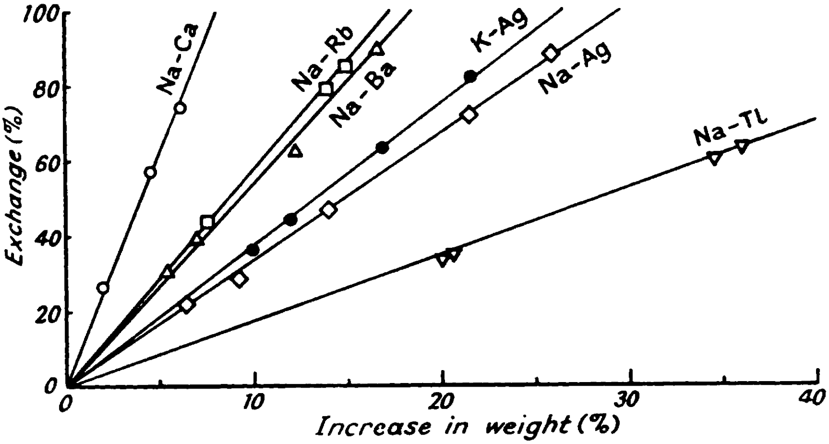


TABLE 4.

Cationic form	Water content: %	Water content: $\frac{H_2O}{MO\ (\text{or}\ M_2O)}$	Cationic form	Water content: %	Water content: $\frac{H_2O}{MO\ (\text{or}\ M_2O)}$
Li	21·8	6·5	Ca	$22{\cdot}1_6$	6·9
Na	20·3	6·4	Sr	20·7	7·0
K	$17{\cdot}0_5$	5·7	Ba	19·3	7·1
Rb	13·6	5·2	Cu	23·3	7·6
Tl	9·2	4·8	Ag	15·7	6·4

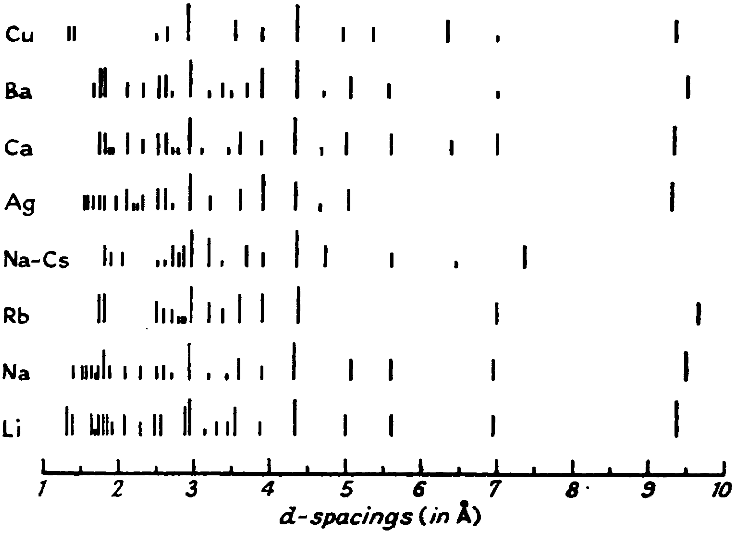
(c) X-*Ray spacings and unit cells of exchange forms.* The tabulated *X*-ray *d*-spacings of the various exchange forms showed that these spacings changed but little with different cations, although the relative intensities of the corresponding diffraction arcs show the expected changes (Fig. 4). The anionic framework of chabazite is therefore little altered by ion exchange. To support this conclusion quantitatively the *d*-spacings of Na-, Ag-, Ca-, and Ba-chabazite were indexed, calculated and measured *d*-spacings were compared, and the lengths of the rhombohedral unit cells and their angles were determined. To do this the hexagonal unit cells were first determined, by using the appropriate logarithmic Bjurstrom diagram. The unit cells are given in Table 5. The calculated volumes of these cells for Na-, Ag-, Ca-, and Ba-chabazite are respectively 850, 836, 833, and 843 Å^3. The mean volume is 840 Å^3, and the maximum deviation from the mean is little more than 1%. The relative constancy of the unit-cell dimensions and *d*-spacings supports the view that chabazite approximates quite closely to the ideal crystalline exchanger in the sense discussed on p. 2838.

TABLE 5. *Hexagonal and rhombic unit cells of cationic forms of chabazite.*

Exchange	Hexagonal unit cells			Rhombic unit cells	
form	c (Å)	a (Å)	c/a	a (Å)	Angle
Na	$15\cdot2_5$	$13\cdot9_0$	1·097	$9\cdot5_0$	94° 3′
Ag	$15\cdot1_0$	$13\cdot8_6$	1·089	$9\cdot4_5$	94° 18′
Ca	$15\cdot0_0$	$13\cdot8_5$	1·083	$9\cdot4_3$	94° 27′
Ba	$15\cdot2_0$	$13\cdot8_6$	1·097	$9\cdot4_7$	94° 3′

Exchange Isotherms.—Equilibrium isotherms were determined for the ion pairs Na–Ag, Na–Tl, Na–Rb, Na–Ca, Na–Cu, and Na–Ba. Typical isotherm contours are given in Figs. 5 and 6, and some numerical data are shown in Tables 6 and 7. Only for the Na $\longrightarrow$ Ag exchange are the mass-action quotients at all constant, emphasising the need for reformulating these quotients in terms of activities (see p. 2848). Sodium and silver ions, each having the same valency and rather similar ionic radii, give a mass-action quotient close to the thermodynamic equilibrium constant (Table 8). The uni-bivalent ion interchange, $2Na^+ \rightleftharpoons Ca^{2+}$, is of interest in that up to about two-thirds replacement of the sodium the equilibrium favours enrichment of the crystals in calcium at the expense of sodium. Thereafter the situation is sharply reversed. This may mean that the favoured cationic compositions of chabazite in Nature will tend to lie between 60 and 80% exchange to calcium. Such cationic compositions are indeed frequently observed. It may also mean that two-thirds of the sites in Na-chabazite differ in some way from the remaining third.

FIG. 4. d-*Spacings characteristic of the various cationic forms of chabazite.*



The continuous lines for uni-bivalent exchanges are smoothed curves on or near which the experimental points lie. For the uni-univalent exchanges these lines represent the best fit of the equation

$$\log K' = \log \frac{B_z(1 - B_s)}{B_s(1 - B_z)} + C(1 - 2B_z) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here K' and C are constants, the values of which are given on the Figs. 5 and 6; B_z and B_s are the equivalent ion fractions of the cation species B in the zeolite and in solution respectively. The ion fractions of the other cations are A_z and A_s; and in each phase $A_z + B_z = 1 = A_s + B_s$. Equation (2) can be given a semi-empircal interpretation as follows.

TABLE 6. *Uni-univalent exchanges in chabazite.*

System and temp.	Total normality of mixed electrolyte	Equiv. ion fraction in solution *	Equiv. ion fraction in zeolite	Mass-action quotient
Na ⟶ Ag	0·25	0·020 (Ag_s)	0·224 (Ag_z)	14·2 $\left(\frac{Ag_zNa_s}{Ag_sNa_z}\right)$
(45°)	($AgNO_3 + NaNO_3$)	0·035	0·303	11·9
		0·076	0·476	11·0
		0·196	0·727	10·9
		0·275	0·809	11·2
		0·387	0·868	10·4
		0·468	0·882	11·8
		0·594	0·917	7·6
		0·796	0·976	10·4
Na ⟶ Ag	0·25	0·025 (Ag_s)	0·297 (Ag_z)	16·3 $\left(\frac{Ag_zNa_s}{Ag_sNa_z}\right)$
(25°)	($AgNO_3 + NaNO_3$)	0·078	0·491	11·3
		0·103	0·597	12·9
		0·423	0·876	9·6
		0·538	0·900	7·7
		0·666	0·974	18·8
		0·727	0·973	13·6
		0·727	0·971	12·6
		0·728	0·972	13·0
		0·840	0·995	—
K ⟶ Ag	0·25	0·050 (Ag_s)	0·111 (Ag_z)	2·37 $\left(\frac{Ag_zK_s}{Ag_sK_z}\right)$
(25°)	($AgNO_3 + KNO_3$)	0·179	0·243	5·14
		0·328	0·378	1·25
		0·484	0·450	0·874
		0·677	0·606	0·734
		0·680	0·593	0·686
		0·725	0·632	0·651
		0·854	0·760	0·543
		0·880	0·840	0·713
		0·930	0·860	0·465
Na ⟶ Rb	0·25	0·054 (Rb_s)	0·414 (Rb_z)	12·3 $\left(\frac{Rb_zNa_s}{Rb_sNa_z}\right)$
(85°)	($RbCl + NaCl$)	0·075	0·438	9·65
		0·080	0·521	12·4
		0·128	0·610	10·7
		0·547	0·795	3·21
		0·742	0·824	1·63
		0·830	0·860	1·26
		0·870	0·913	1·56

* The equivalent on fraction of silver is $\frac{\text{silver normality}}{\text{total normality}}$.

In an aluminosilicate crystal wherein the anionic framework does not swell or shrink, and provided the water content of the framework does not alter perceptibly during exchange, one has at equilibrium for uni-univalent interchanges :

$$K = \frac{a_{B_Z}a_{A_S}}{a_{B_S}a_{A_Z}} = \frac{B_z(1 - B_s)}{B_s(1 - B_z)} \cdot \frac{f_{B_Z}f_{A_S}}{f_{B_S}f_{A_Z}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Here *a*'s and *f*'s are respectively activities and activity coefficients of the cations in the zeolitic or aqueous phases. However, the exchange isotherms were all determined in solutions of *constant* total normality in which only the *ratios* of A_s and B_s were changed. In this case the simplified form of Glueckauf's equation (*Nature*, 1949, **163**, 414) gives

$$\log \frac{f^{AX}_{(BX)}}{f^{BX}_{(AX)}} = \tfrac{1}{2} \log \frac{f^{AX}}{f^{BX}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Here $f^{AX}_{(BX)}$ is the activity coefficient of electrolyte AX in solution with BX of the given total molarity, and f^{AX} is the activity coefficient of AX at the same molarity in absence of BX. Also, since

$$f_{A_S}/f_{B_S} = [f^{AX}_{(BX)}/f^{BX}_{(AX)}]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

one may combine (4) and (5) and obtain

$$f_{A_S}/f_{B_S} = f^{AX}/f^{BX} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This ratio, from definitions of f^{AX} and f^{BX}, is constant. Accordingly, one may transform eqn. (3) and write

$$K' = K(f_{\mathrm{B_s}}/f_{\mathrm{A_s}}) = B_z(1 - B_s)f_{\mathrm{B_z}}/(B_s(1 - B_z)f_{\mathrm{A_z}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Following Kielland (*J. Soc. Chem. Ind.*, 1935, **54**, 232T) one may give for either ion in the exchanger

$$\log f_{\mathrm{A_z}} = CB_z^2;\ \log f_{\mathrm{B_z}} = CA_z^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

FIG. 5. *Uni-univalent exchange isotherms of chabazite. Scales of ordinates and abscissæ give ion fractions in solutions and in crystals respectively, and subscripts " s " and " z " refer to these ions in solution and in the zeolite respectively.*

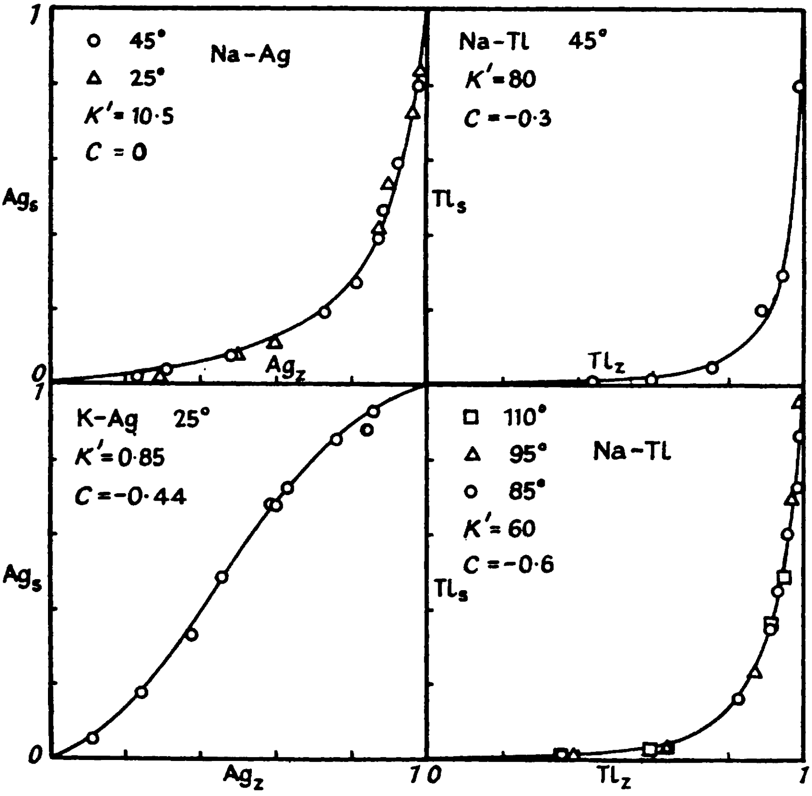


TABLE 7. Na ⟶ Tl *Exchanges at several temperatures using* $NaNO_3 + TlNO_3$ *at constant total normality of* 0·25.

Temp.	Equiv. ion fraction Tl in solution	Equiv. ion fraction Tl in zeolite	Mass action quotient $\frac{Tl_zNa_s}{Tl_sNa_z}$
110°	0·0096	0·356	57·0
	0·027	0·602	54·1
	0·360	0·918	19·9
	0·488	0·955	22·2
95	0·0064	0·394	81·4
	0·031	0·640	55·2
	0·235	0·876	23·0
	0·353	0·914	19·5
	0·699	0·975	16·8
	0·960	0·995	8·21
85°	0·0068	0·361	78·8
	0·027	0·633	61·7
	0·161	0·830	25·5
	0·352	0·913	19·3
	0·452	0·928	15·6
	0·599	0·956	14·5
	0·726	0·986	26·6
	0·866	0·988	12·7
45	0·0092	0·438	83·9
	0·016	0·598	89·3
	0·046	0·759	65·3
	0·203	0·887	30·8
	0·291	0·943	40·3
	0·798	0·984	15·6

Then provided the constant C is the same for each ion, eqn. (8) gives

$$\log f_{B_z}/f_{A_z} = C(A_z^2 - B_z^2) = C(B_z + A_z)(A_z - B_z) = C(1 - 2B_z) \quad . \quad . \quad (9)$$

because $B_z + A_z = 1$. Combination of eqns. (9) and (7) then gives eqn. (2).

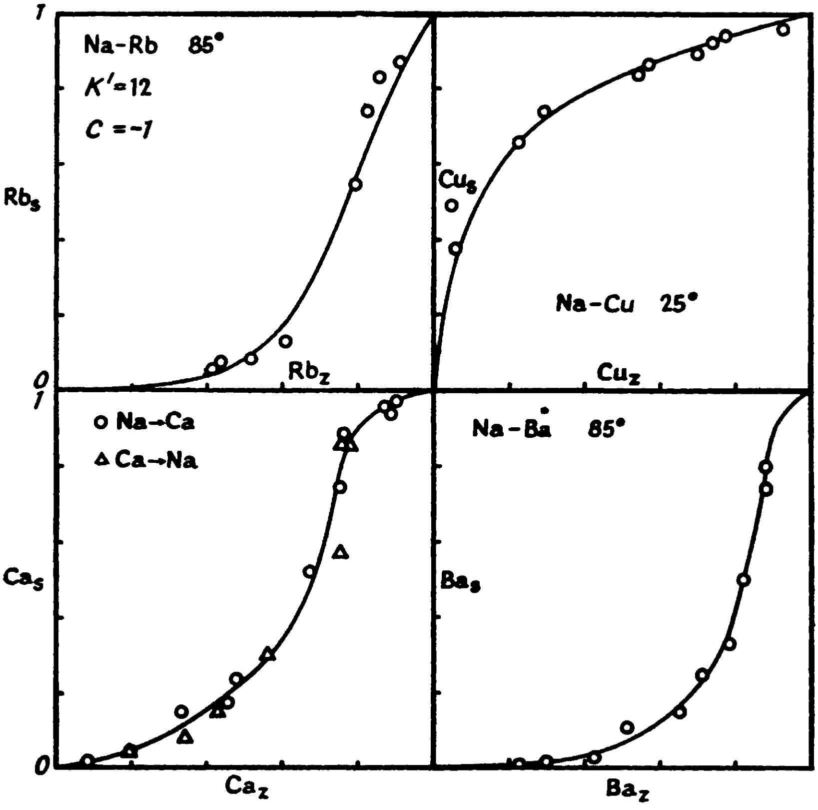
We may also obtain eqn. (2) by starting from the mass-action equilibrium constant in the form

$$B_z(1 - B_s)/B_s(1 - B_z) = K_0 \exp(-\Delta E/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where K_0 is a constant and ΔE is the energy of exchange per g.-ion of B cations entering or of A cations leaving the crystal. If we now write

$$\Delta E = \Delta E_0(1 + aB_z) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

FIG. 6. *Uni-uni- and uni-bi-valent exchange isotherms of chabazite. The scales of ordinates and abscissæ have the same significance as in Fig. 5.*



where ΔE_0 and a are constants, then eqns. (10) and (11) combined give

$$\log \frac{B_z(1 - B_s)}{B_s(1 - B_z)} = \log \left(K_0 - \frac{\Delta E_0}{2{\cdot}30\boldsymbol{R}T} \right) - \frac{a\Delta E_0}{2{\cdot}30\boldsymbol{R}T} B_z \quad . \quad . \quad . \quad . \quad (2a)$$

which has the same form as eqn. (2).

The above procedure is empirical. However, in the not wholly dissimilar problem of adsorption with interaction, the first approximation leads to an isotherm with the additional linear term analogous to that in B_z in eqn. (2*a*) (Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge Univ. Press, 1939, p. 429 *et seq.*). Investigation of ion-exchange models for crystals leading more rigorously to equations such as (2*a*) will be made elsewhere.

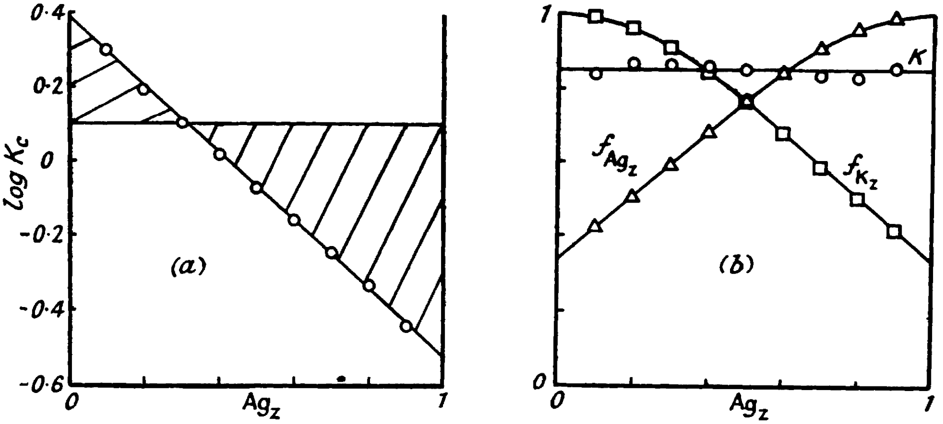
Calculation of f_{B_z}/f_{A_z} *and of Thermodynamic Equilibrium Constants* K.—The method of Ekedahl, Hogfeldt, and Sillen (*Acta Chem. Scand.*, 1950, **4**, 556) was used to calculate f_{B_z}/f_{A_z}. The quotients $K_c = [B_z(1 - B_s)/B_s(1 - B_z)](f_A/f_B)_s$ were calculated for a series of values of B_z.

$(f_A/f_B)_s = f^{AX}/f^{BX}$ (eqn. 6) was computed by using Conways' activity coefficients (" Electrochemical Data," Elsevier, 1952) and assuming for each electrolyte that this ratio was independent of temperature. A typical curve of log K_c against Ag_z is shown (for the K–Ag exchange) in Fig. 7*a*. Then at any value of Ag_z, $-\log f_{K_z}$ is the cross-hatched area to the right of the chosen value of Ag_z. The activity coefficients f_{K_z} and f_{Ag_z} as functions of Ag_z are shown in Fig. 7*b*. Moreover, from their ratios and from K_c, the true thermodynamic equilibrium constant, K, is derived. The self-consistency of the method is shown in Fig. 7*b*, where the values of K computed for various values of Ag_z are all the same.

Provided the plot of log K_c against B_z is linear, the thermodynamic equilibrium constant must be the value of K_c where $B_z = \frac{1}{2}$. This follows from eqn. (2), by substituting in it the expression $K_c(f_B/f_A)_s = B_z(1 - B_s)/B_s(1 - B_z)$. We now have on rearranging eqn. (2)

$$\log K_c = 2CB_z + \log K' - \log f_A/f_B - C \quad . \quad . \quad . \quad . \quad . \quad (10)$$

FIG. 7.



(a) *The variation of* log K_c *with ion fraction of silver in the zeolite* (Ag_z).

(b) *Activity coefficients* f_{Ag_z} *and* f_{K_z} *of silver and potassium ions in chabazite, as a function of* Ag_z. *The degree of constancy of the thermodynamic exchange equilibrium constant, K, is seen from the horizontal line.*

But, on substitution for K' from eqn. (7),

$$\log K_c = 2CB_z + \log K - C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

so that when $B_z = \frac{1}{2}$, $K_c = K$.

Values of the thermodynamic equilibrium coefficients and of standard free energies of exchange, $\Delta G°$, are given in Table 8. Within the scatter of the experimental isotherm points (cf. Fig. 5) the temperature coefficients of the exchange equilibrium are all notably small. There is no observable shift in this equilibrium for the sodium–silver exchange between 25° and 45°, or for the sodium–thallium exchange between 85° and 110°. The variation of K with temperature is $\partial \ln K/\partial T = -\Delta H°/RT^2$, so that for the above exchanges $\Delta H° \simeq 0$. Accordingly, one may compute $\Delta S° \simeq -\Delta G°/T$, as given in col. 5 of Table 8. There are few data with which to compare the thermodynamic results of Table 8, although Coleman (*Soil Sci.*, 1952, **74**, 115), for the Na ⟶ K exchange in two Amberlite resins, gave $\Delta G°$ equal to +400 and +498 cal./g.-ion at 25°.

TABLE 8. *Thermodynamic equilibrium constants.and standard free energies of exchange.*

Exchange pair	Temp.	Equil. const. K	$\Delta G°$ (cal./g.-ion)	$\Delta S°$ (e.u.)
Na ⟶ Ag	25—45°	11·4	−1440	+4·8 (25°)
Na ⟶ Rb	85	12·6	−1500	—
Na ⟶ K *	25	13·3	−1530	—
Na ⟶ Tl	45	96·2	−2900	—
Na ⟶ Tl	85—110	72·1	−3040 (85°)	+8·5 (85°)
K ⟶ Ag	25	0·855	+100	—

* Calculated equilibrium from Na–Ag and K–Ag exchange isotherms.

Uni-bivalent Exchange Equilibria.—Exchanges of the type $2A^+ \rightleftharpoons B^{2+}$ gave the isotherms in Fig. 6. The exchange $2Na^+ \longrightarrow Cu^{2+}$ is exceptional in that the bivalent ion shows a smaller affinity for chabazite than sodium and so is more concentrated in solution than in the crystals; with the bivalent ions Ca^{2+} and Ba^{2+} the converse is the case. The method of Hogfeldt, Ekedahl, and Sillen appropriately modified (*Acta Chem. Scand.*, 1950, **4**, 828) can in principle still be applied. For $NaCl-CaCl_2$ of total normality 0·5, such as comprised the equilibrium solutions in the sodium–calcium exchange of Fig. 6, the ratio $f_{Na_s}{}^2/f_{Ca_s}$ was calculated by using Glueckauf's equation and assuming as previously that this ratio did not depend on temperature. The variation in the ratio is large; and the corresponding plot of log K_c against the ion fraction, Ca_z, exhibits a maximum (Fig. 8). This complicates the graphical integrations required to derive f_{Na_z} and f_{Ca_z}, and thence to obtain the thermodynamic equilibrium constant. Since also there are no experimental data with which the calculated ratios $f_{Na_s}{}^2/f_{Ca_s}$ can be compared, the procedure was not carried further.

The curve of log K_c against Ca_z is of the same shape as that drawn by Hogfeldt (*ibid.*, 1951, **5**, 1400) for a system with a constant K showing "compound formation." The meaning of this term is rather vague, but may imply that for a certain composition the free energy of the system has a minimum value. In the zeolite this could mean that a distribution of ions and water molecules with a minimum free energy is possible for a certain cationic composition.

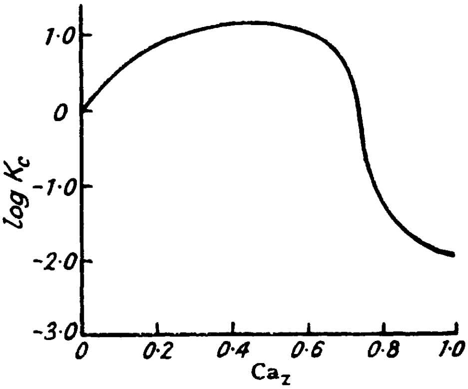


FIG. 8. *The maximum exhibited in the curve of K_c vs. the ion fraction of dissolved calcium for the exchange* $2Na^+ \rightleftharpoons Ca^{2+}$

Discussion.—The sodium–cæsium exchange, using N/4-(NaCl + CsCl) at 25°, has not been referred to in the previous sections. Practically all the exchanges went to between 60 and 75% Cs, and further treatments with more concentrated cæsium chloride gave little further interchange. Again it appears that about two-thirds of the sodium in Na-chabazite differs in ease of replacement from the last third, as noted with the $2Na^+ \rightleftharpoons Ca^{2+}$ reaction.

The reversibility of exchange was demonstrated directly by studying both the $2Na \longrightarrow Ca$ and the $Ca \longrightarrow 2Na$ reaction. It is also notable that no evidence of limited miscibility of any pair of cationic forms of chabazite appears and there are no intermediate horizontal sections in the isotherms such as were observed in $Na \rightleftharpoons K$ exchange in analcite (Barrer and Hinds, *loc. cit.*).

The heavier ions in general show a greater affinity for the crystals than do lighter ones. The affinity sequence from Table 8 is $Na < Ag < Rb < K < Tl$. There is little distinction between Ag, Rb, and K, however, and the high affinity of the higher ion, K, is anomalous.

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