435. *Syntheses and Reactions of Mordenite.*

By R. M. Barrer.

Mordenite has been crystallised in good yield from aqueous suspensions of sodium aluminosilicate gels of compositions ranging from $Na_2O,Al_2O_3,8{\cdot}1SiO_2,nH_2O$ to $Na_2O,Al_2O_3,12{\cdot}3SiO_2,nH_2O$, the best temperature range being 265—295°; pH is as important as composition or temperature in ensuring a yield, and the best results were for a range of pH between 8 and 10 in the cold mother-liquor after crystallisation.

Simultaneously with mordenite, some analcite was obtained mainly at the silica-poor end of the composition range, and some quartz at the silica-rich end. Outside the best temperature range (265—295°) species other than these three were observed, and yields of mordenite decreased. In very alkaline solutions mordenite crystals were readily precipitated at first, but tended to redissolve and disproportionate if left too long in contact with the mother-liquor at these high temperatures.

Mordenite undergoes a ready base exchange, nitrates and chlorides giving at least partial cation replacements according to the series

$$Ca^{++} \rightleftharpoons Ba^{++} \rightleftharpoons K^+ \rightleftharpoons NH_4^+ \rightleftharpoons Na^+ \rightleftharpoons Li^+.$$

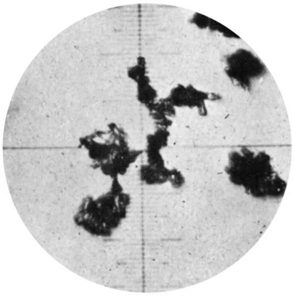
This accords with the open molecular-sieve character of the mineral, and the products when dehydrated were themselves good sorbents of gases.

It is pointed out that zeolites such as mordenite must be regarded statistically as defect structures, in which a possibly large number of new configurations introduced by base exchange give rise to a configurational entropy term. The occurrence or non-occurrence of exchanges of the types $K^+ \rightleftharpoons Na^+$, $Ca^{++} \rightleftharpoons 2Na^+$ may be influenced by the size of this entropy term relative to the corresponding energy changes.

Mordenite, $(Na_2,Ca,K_2)O,Al_2O_3,10SiO_2,6{\cdot}7H_2O$, is one of the most highly siliceous zeolites. It is known to occur in reasonable quantity in at least one locality (private communication from Prof. A. L. Parsons, Royal Geological Museum, The University, Toronto), and has been reported in a variety of others (see Mellor, " Treatise on Inorganic and General Chemistry," Vol. VI, p. 748). With one exception (Leonard, *Econ. Geol.*, 1927, **22**, 18), its laboratory preparation has not been reported.

Recent work on its sorptive properties has shown that mordenite has a robust three-dimensional anionic network, when dehydrated is a sorbent of notable quality, and possesses, like chabazite, its own characteristic behaviour as a molecular sieve (Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555; *J. Soc. Chem. Ind.*, 1945, **64**, 130). In the latter respect natural sodium-rich mordenite differs to some extent from calcium- and barium-rich mordenites prepared hydrothermally from it, although these are also excellent sorbents (*idem, ibid.*). Because of the way in which molecular-sieve sorbents can be used to separate mixtures by selective occlusion of those components small enough to permeate the dehydrated lattice, and because of the

FIG. 1.

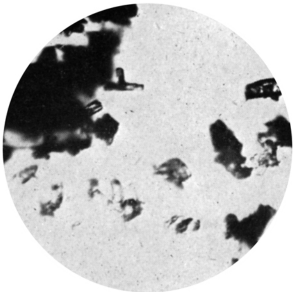


Typical clusters of synthetic mordenite crystals from gel $Na_2O,Al_2O_3,9{\cdot}4SiO_2,mH_2O + aq.$ *at* 275° *for* 4 *days. Magnified* 120 *times.*

FIG. 2.

Crystals of synthetic mordenite showing striated and wheat-sheaf appearance. Grown from gel $Na_2O,Al_2O_3,10SiO_2,mH_2O + aq.$ *by crystallising for* 2 *days at* 295°. *Magnified* 400 *times.*

FIG. 3.

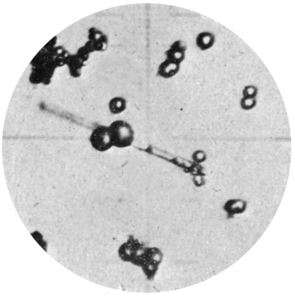


Numerous small synthetic quartz crystals grown from gel $Na_2O_2,Al_2O_3,12{\cdot}3SiO_2,mH_2O + aq.$ *at* 365° *for* 3 *days. Magnified* 120 *times.*

FIG. 4.

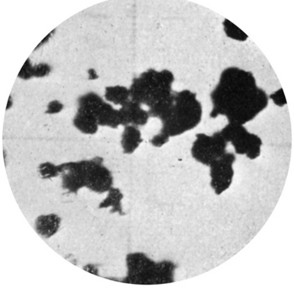
Quartz crystal grown for comparison purposes from silica gel with K_2CO_3 *aq. at* 360° *for* 3 *days. Magnified* 200 *times.*

FIG. 5.



Analcite spheroids, and an unidentified needle-like birefringent species grown from gel of composition $Na_2O,Al_2O_3,8{\cdot}2SiO_2,mH_2O + Na_2CO_3$ *aq. at* 216° *for* 2 *days,* i.e., *below the range of mordenite crystallisation. Magnified* 120 *times.*

FIG. 6.



Anhydrous species, grown from gel $Na_2O,Al_2O_3,8{\cdot}2SiO_2,mH_2O + Na_2CO_3$ *aq. at* 350° *for* 2 *days,* i.e., *above the range of mordenite crystallisation. Small plate-like crystals can be identified in the bottom left quadrant. The dark masses in liquids of suitable R.I. appear as clusters of elongated crystals, possibly quartz, embedded in a matrix. Magnified* 120 *times.*

interest of the zeolites as a mineral group, experiments were conducted to see whether mordenite could be made, under what conditions, and in what yields.

EXPERIMENTAL.

Previously analysed sodium aluminate (" Alfloc "; $NaAlO_2$, 92%, with some Na_2CO_3 and water) was dissolved in water, and the requisite volume of the opalescent solution poured into an aqueous suspension of silicic acid gel containing a trace of entrained alkali. The mixture quickly became more opaque and tended to set. It was variously evaporated to dryness or to a thick consistency at temperatures not above 110° and sometimes as low as 70—80°.* If dried, the product was powdered before being stored for use. Aluminosilicate gels were prepared of the compositions: $Na_2O,Al_2O_3,8{\cdot}2SiO_2,nH_2O$; $Na_2O,Al_2O_3,9{\cdot}36SiO_2,nH_2O$; $Na_2O,Al_2O_3,10{\cdot}0SiO_2,nH_2O$; $Na_2O,Al_2O_3,10{\cdot}9SiO_2,nH_2O$; $Na_2O,Al_2O_3,12{\cdot}3SiO_2,nH_2O$. Gels of exact mordenite composition were dried in several ways to determine whether the conditions of preparation were related to yield (p. 2162); and also many gels poorer in silica were prepared, which, however, proved unsuitable for making mordenite although often giving high yields of other crystalline aluminosilicates.†

Portions of the gel, usually of several g., were then introduced with 10—15 c.c. of water into stainless-steel autoclaves of approximately 25 c.c. capacity. The autoclaves were sealed by a screw-top bearing on a soft-copper washer, which flowed slightly under pressure to give a vacuum-tight seal. The autoclaves were then placed in an air-thermostat operating up to 300°. Alternatively, especially for experiments above 300°, nichrome-wound furnaces, manually controlled, were used.

The products were examined under the polarisation microscope, and were investigated as sorbents (Barrer, in the press). Sorption was occasionally employed to estimate the yield of mordenite, once the presence of that mineral was revealed, since the ratio of the saturation sorption in a synthetic mineral and a natural mordenite for a given gas at a given temperature (oxygen at − 185°) gives the percentage purity.‡ For the final proof of the identity of synthetic and natural mordenites, *X*-ray powder photographs were used.

Pure or A.R. salts were employed in experiments on base-exchange reactions of mordenite. In order to promote completeness of reaction, an excess of the exchanging salt was used. This was ground with powdered mordenites before addition of 10—15 c.c. of water and heating above 200°. Since the products were required intact for sorptive studies, progress of base exchange was for the most part followed by determining the displaced calcium in the mother-liquor rather than by destruction of the solid in analysis. These base-exchange products were as far as possible freed from entrained salt by washing with water at 100°, and then further extracted with water above 200° to ensure that no more removable salt remained.

Results.—A number of experiments established that crystallisation readily occurred to give mordenite as one of the species, and that best yields were obtained in the range 265—295°. The mordenite was obtained, as indicated in Figs. 1 and 2, in the form of matrices of elongated crystallites, and as wide, flat crystals with a fibrous or striated appearance. They were feebly birefringent and had a mean refractive index of 1·464—1·472. The extinction was nearly parallel (0° ± 15°), but the small size of the crystals made their further optical characterisation difficult.§ The crystals were further established as mordenitic by their sorptive and molecular sieve behaviour (Barrer, *loc. cit.*, 1944; in the press) and by a detailed comparison of transient states of flow of gases in them in natural mordenites, and in the base-exchange mordenites prepared in this work. *X*-Ray powder photographs of synthetic, natural, and base-exchange mordenites gave the spacings in Table I. There is excellent agreement between the sequence of intensities of the lines as well as in the actual spacings for natural mordenite, the synthetic sodium mordenite, and sodium mordenite prepared by base exchange. The correspondence extends within experimental error over as many lines as could be observed. Moreover, all the base-exchange products enriched in Na, K, Li, NH_4, Ca, or Ba give diffraction patterns clearly characteristic of mordenites, showing that exchange can occur without recrystallisation under the conditions described in Table III.

At the gel compositions referred to above mordenite was the dominant species, very high yields often being obtained. Other species could also be grown from the same gels, however, which included quartz (Fig. 3) and analcite (Fig. 5). These were identified by comparison with synthetic analcites (see footnote ‡ below, and Barrer, this vol., p. 127) and quartz (Barrer, *Nature*, 1946, **157**, 734) previously prepared. Not all the crystals grown under various conditions from the gels could be identified (*e.g.*, Figs. 5 and 6).

Brief details of the experiments given in Table II provide a clearer idea of the best conditions for preparing mordenite. Especially interesting are experiments *e*, *f*, and *g* in Section (iii) of the table. A creamy aluminosilicate gel of mordenite composition, which yielded a very alkaline mother-liquor both before and after crystallisation, gave little recognisable mordenite after *two* days at a high pH,

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* Drying at high temperatures tends to insolubilise the aluminosilicate gel, and to lead to poor crystallisation under hydrothermal conditions.

† The species produced from silica-poor aluminosilicate gels were diverse, and will be discussed in later communications.

‡ Analcite was also present in many preparations, but pure synthetic analcites have not been found to occlude oxygen.

§ The mean refractive index of natural mordenite may be taken as about 1·475 ± 0·005, but whereas the synthetic mineral contained only Na as cations, natural mordenites normally contain several cations (Na, Ca, K). The extinction angle of mordenite has been reported as about 15°, while that of the closely allied zeolite, ptilolite, has been given as 0° (Mellor, *op. cit.*, Vol. VI, p. 748). Ptilolite may even be identical with mordenite (Walker and Parsons, *Univ. Toronto Geol. Studies*, 1922, **14**, 13; but see Schaller, *Amer. Min.*, 1923, **8**, 93, 169).

TABLE I.

Spacings in A. *of natural, synthetic, and base-exchange mordenites using* Cu-$K\alpha$ 40 *kv.* X-*rays.*

Natural mordenite.	Synthetic sodium mordenite.	Base-exchange mordenites. Na.	K.	NH_4.	Li.	Ca.	Ba.
13·5 s	13·4 ms	13·5 m	13·5 ms	13·6 w	13·6 m	13·7 m	—
8·66 s	8·85 ms	8·95 s	9·02 vs	8·90 ms	8·88 s	8·90 s	9·0 s
6·54 s	6·49 ms	6·52 ms	6·65 vvw	6·59 m	6·69 m	6·65 s	6·44 s
5·72 m	5·66 mw	5·66 w	—	5·88 vw	—	5·83 mw	5·78 m
—	—	—	5·37 vw	5·27 vvw	5·14 w	—	—
—	—	—	—	—	—	—	4·81 w
4·50 s	4·50 ms	4·52 s	4·66 w	4·57 m	4·56 ms	4·55 ms	4·49 s
3·99 s	3·98 vs	3·98 vs	4·08 vs	4·02 s	3·98 vs	3·99 s	3·97 vs
—	—	—	3·77 w	—	—	—	3·76 w
3·40 s	3·42 vs	3·42 vs	3·48 m	3·40 s	3·43 vs	3·48 vs	3·43 vs
3·15 s	3·15 s	3·16 vs	3·21 ms	3·16 ms	3·19 s	3·17 s	3·21 s
2·90 ms	2·89 ms	2·83 m	2·99 vs	2·92 vw	2·91 s	2·88 m	2·89 ms
2·70 vw	2·67 vw	—	2·80 m	2·69 vw	2·73 ms	2·70 vw	2·70 vw
2·50 m	2·52 m	2·48 mw	2·53 w	2·50 vw	2·50 ms	2·54 mw	2·51 ms
2·43 w	2·45 vw	2·43 w	2·45 vw	2·42 vw	2·41 w	2·42 vvw	2·46 w
—	—	—	—	—	—	—	2·27 vw
2·02 mw	2·01 w	2·01 w	2·04 w	2·03 vw	2·04 mw	2·03 w	2·12 vvw
1·94 mw	1·94 w	1·96 w	—	1·94 w	1·95 mw	1·95 vw	1·95 w
$1·85_5$ mw	$1·86_2$ w	$1·86_5$ w	$1·85_4$ vvw	$1·86_3$ vw	$1·86_6$ w	$1·88_0$ w	$1·87_5$ mw
$1·78_5$ mw	$1·79_2$ w	$1·79_7$ mw	$1·80_6$ m	$1·75_5$ vvw	$1·80_5$ w	$1·79_7$ w	$1·79_2$ mw
$1·68_7$ vvw	$1·70_4$ vw	$1·69_0$ vvw	$1·67_0$ vvw	$1·68_4$ vw	—	$1·68_8$ w	$1·66_3$ vw
$1·64_6$ vvw	$1·65_6$ vvw	—	—	$1·64_8$ vw	—	—	—
$1·58_5$ vw	$1·59_0$ vw	$1·61_5$ mw	$1·62_6$ vvw	$1·59_6$ vvw	$1·60_5$ vw	—	$1·60_1$ vvw
$1·52_7$ w	$1·52_8$ w	$1·52_9$ w	$1·55_6$ w	$1·52_6$ vvw	$1·53_4$ vw	—	$1·53_9$ mw
$1·47_7$ w	$1·47_5$ vw	$1·47_9$ vvw	$1·49_0$ vw	$1·47_6$ vvw	$1·48_6$ vw	$1·49_2$ vvw	$1·47_9$ vw
$1·43_9$ m	$1·44_2$ mw	$1·44_2$ mw	$1·45_5$ vw	$1·44_1$ vvw	$1·44_5$ vw	$1·44_9$ w	$1·44_0$ mw
$1·41_5$ vvw	$1·40_8$ vw	$1·40_5$ w	—	$1·40_0$ vvw	$1·40_8$ vw	—	$1·40_7$ vw
$1·37_6$ vvw	$1·37_5$ w	—	—	$1·37_2$ vvw	$1·37_8$ vvw	$1·37_5$ vw	$1·37_7$ mw
$1·35_0$ vw	$1·34_9$ vw	$1·34_6$ w	$1·35_8$ vw	$1·34_6$ vvw	$1·35_2$ vvw	—	$1·35_4$ vvw
$1·31_1$ vvw	—	—	—	—	—	—	—
$1·29_1$ vw	$1·29_5$ vw	$1·29_1$ vw	$1·30_2$ vw	$1·31_4$ vvw	$1·29_6$ vvw	$1·29_5$ vvw	$1·29_6$ vvw
$1·26_2$ vw	$1·26_3$ vw	$1·26_1$ vvw	$1·27_6$vvw	$1·25_9$ vvw	$1·27_2$ vvw	$1·26_4$ vvw	$1·25_8$ vvw
$1·23_8$ vw	$1·23_9$ vvw	$1·24_1$ vvw	$1·24_2$ vw	$1·23_6$ vvw	$1·24_6$ vvw	$1·24_1$ vvw	$1·24_2$ vvw
$1·21_1$ vvw	$1·21_0$ vvw	—	—	—	$1·22_2$ vvw	$1·21_0$ vvw	$1·21_1$ vvw
$1·18_0$ vvw	$1·17_4$ vvw	—	$1·16_5$ vw	—	$1·17_0$ vvw	$1·18_1$ vvw	—
$1·15_4$ vvw	$1·15_7$ vvw	—	—	—	—	—	—
$1·12_5$ vvw	$1·12_4$ vvw	—	—	—	—	$1·12_1$ vvw	—
$1·09_5$ vvw	—	—	—	—	—	—	—

Col. 1 : Mineral supplied by Dr. A. L. Parsons.
Col. 2 : Product of Table II, Section (iii), Expt. *a*.
Col. 3 : From mordenite using saturated NaCl solution, two treatments each of one day at 220°, followed by H_2O extraction at 220°.
Col. 4 : Products Nos. 7 and 8 of Table III used.
Col. 5 : From mordenite using NH_4Cl vapour, two treatments each of one day at 300°, followed by hydrothermal extraction at 220°.
Col. 6 : Product No. 6 of Table III used.
Col. 7 : Product No. 9 of Table III used.
Col. 8 : Product No. 11 of Table III used.

but gave good yields when the reaction time was shortened to *one* day or less. Moreover, the mordenite crystals which were observed in the two-day experiment seemed considerably corroded. It is probable, therefore, that at ~280° mordenite is unstable over a period in very alkaline media, and, perhaps owing to its high silica content, disproportionates into other products, such as analcite, poorer in silica, and possibly sodium silicates poorer in alumina, which, however, were not observed to crystallise from the mother-liquor. Since an alkaline medium at 280° *initially* favours crystallisation as mordenite (experiments *f* and *g*), this would appear to be an example of primary precipitation of a thermodynamically less stable species followed by its subsequent conversion into other species at a rate depending upon the alkalinity.

Although too high a pH accelerates the decomposition of mordenite, none the less a considerable measure of alkalinity is needed for good crystal growth in the gel. At too low pH, probably owing to a smaller solubility of the gel in such conditions, the crystallisation became retarded and the crystals fewer and smaller.* This is in good agreement with the assumption that zeolite formation is favoured by an alkaline reaction medium (Lindgren, "Mineral Deposits," McGraw Hill Book Co., 1919, p. 427).

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* In Table II, Section (v), Expt. *j*, a gel $Na_2O,Al_2O_3,8{\cdot}2SiO_2$ was heated with boric acid solution at ~275°. No mordenite could be detected, and only a few crystals of any kind, the pH after reaction being 7—7·5.

TABLE II.

Hydrothermal crystallisation of aluminosilicate gels, $Na_2O,Al_2O_3,mSiO_2,nH_2O$.

Section and Expt.	Condition of crystallisation.	pH of cold mother-liquor after reaction.	Products and yields.
Composition of gel: $Na_2O,Al_2O_3,12\cdot3SiO_2 + H_2O$.			
(i) *a*	~265° for 3 days	10—10·5	Quartz, analcite, some mordenite, and very fine needles
b	~365° for 3 days with aq. $NaHCO_3$	9·5—10	Fine quartz crystals. Large yield of unidentified species
Composition of gel: $Na_2O,Al_2O_3,10\cdot9SiO_2 + H_2O$.			
(ii) *a*	~290° for 2 days	—	Mordenite. Little analcite and rare quartz
b	~295° for 3 days with aq. $NaHCO_3$	—	Mordenite with a little quartz
Composition of gel: $Na_2O,Al_2O_3,10SiO_2 + H_2O$.			
(iii) *a*	~295° for 2 days	~10·0	Good yield of mordenite and a little analcite
b	~290° for 2 days	9·5—10	Mordenite. Some analcite
c	~295° for 2 days	~9·0	Excellent yield of mordenite. Some analcite
d	~295° for 2 days	~7·5(?)	Mordenite, some analcite. Not well crystallised
e	~280° for 2 days	10—10·5	Rare mordenite, with crystals rather corroded. Some analcite
f	~290° for 1 day	~10·5	Good yield of mordenite and some analcite
g	~280° for 17 hrs.	—	Good yield of mordenite
Composition of gel: $Na_2O,Al_2O_3,9\cdot3SiO_2 + H_2O$.			
(iv) *a*	~290° for 3 days	—	Considerable analcite and mordenite. A little quartz and some masses of needle-shaped crystals
b	~275° with $NaHCO_3$ solution for 2 day	—	Some mordenite and analcite
c	~275° for 4 days	—	Good yield of mordenite, with some analcite. Moisture content of crystals 12·5%
Composition of gel: $Na_2O,Al_2O_3,8\cdot2SiO_2 + H_2O$.			
(v) *a*	~210° with aqueous 2N-$CaCl_2$ for 36 hrs.	8—8·5	Little obvious crystallisation
b	~290° for 36 hrs.	8—8·5	Analcite and mordenite in considerable yield
c	~350° for 2 days	—	Quartz, indeterminate masses, and rare small needle-like crystals
d	~216° with 2N-Na_2CO_3 solution for 2 days	~10·0	Mainly analcite, with rare, long, dagger-shaped or ribbon-like crystals of *n* 1·490, often showing twinning
e	~350° with 2N-Na_2CO_3 solution for 2 days	~10·0	Some 8- or 6-sided plates of *n* 1·52, often twinned. Clusters of acicular crystals in a matrix. No water of crystn.
f	~290° with 2N-Na_2CO_3 solution for 1 day	~10·0	Much analcite and mordenite, and a little quartz
		~8·0	Excellent yield of mordenite
h	~290° for 36 hrs. with borate buffer of initial pH 7·6	~8·5	Fair yield of analcite and mordenite
i	~295° for 2 days with $NaHCO_3$ solution	~9	Mainly analcite. Some quartz and mordenite
j	~275° for 2 days with considerable H_3BO_3	7—7·5	Small amount of analcite. Rest indeterminate

In syntheses of harmotone, analcite, and several synthetic zeolites, the author has not found any exceptions to this rule.* At temperatures of 280—290° mordenite was observed when the pH of the cold mother-liquor after crystallisation lay between 7·5 and 10·5; pH's above 10·5 were not studied, and consistently good yields were observed at pH's of 8 to 10. It is believed that pH can be as important a variable in hydrothermal reactions as temperature or composition.

Table II also shows the great influence of temperature on the nature of the species (*e.g.*, Section v). Successful syntheses refer mainly to temperatures of 265—295°. On the other hand, in the ranges 210—220° and 350—370° mordenite was superseded by other species, so that the 265—295° range is most appropriate for syntheses of this mineral. This temperature range is well above that at which analcite first appeared (~180—220°), and the range of its hydrothermal occurrence is much less (analcite was still moderately abundant at 300—310° when suitable gels were crystallised). Table II also records attempts to trace the influence of varying the thermal histories of the gels upon the yield of mordenite

* Syntheses of these and other aluminosilicates will be discussed elsewhere.

(Section iii). In all experiments a gel was first made by the usual mixing of sodium aluminate solution with silicic acid gel in suspension. The creamy gel was used with no further treatment in (iii) *e*, *f*, and *g*; but the products used in (iii) *a*, *b*, *c*, and *d* were obtained as follows

Creamy gel

(*a*).	(*b*).	(*c*).	(*d*).
Stood for 48 hrs. and evaporated to dryness over a water-bath.	Evaporated at once fairly quickly in air-oven at 110°.	Stood for 16 hrs. and evaporated to dryness on a water-bath.	Evaporated at once to dryness on a water-bath.

Good yields were obtained from all the samples, whatever the thermal history within the above range of treatments. All the other gels in Table II were prepared under conditions falling within this range, and therefore their preparation need not be individually described.

Finally, it should be noted that considerable variations in the composition of the crystallising gel are possible, and that at the silica-richer end of this range quartz often appears in some quantity. At the silica-poor end of the range analcite ($NaAlSi_2O_6,H_2O$) is found in increasing quantity. It is thus better to keep to the mordenite composition in the parent gel.

Base-exchange Reactions of Mordenite.—The base-exchange reactions of mordenite appear to have been little studied (Barrer, *loc. cit.*, 1944), but since the sorptive and molecular-sieve properties show the mineral to have an open anionic network structure, base exchange should occur readily. A series of hydrothermal treatments using nitrates and chlorides in excess (3—5 g.), several g. of powdered mordenite, and 10—15 c.c. of water showed that this was indeed the case (Table III). One sample of the natural mordenite used was found to contain:

	% on dry weight.	Molar proportion.		% on dry weight.	Molar proportion.
SiO_2	78·5	9·44	CaO	3·5	0·45
Al_2O_3	14·1	1·00	Na_2O (by diff.)	4·1	0·48 (as Na_2O)

Although this analysis may be taken as typical, the ratio of alkali- to alkaline-earth metal may have varied among the different samples used for base exchange.

After any experiment the base-exchanged product was washed thoroughly with distilled water at ~100°, until the washings were free from salt, and then treated several times with distilled water between 220° and 250° in an autoclave to ensure that all removable salt was extracted. The samples were then submitted to *X*-ray examination, and to investigation as sorbents and molecular sieves (Table III). Specimens of Ca, Ba, K, NH_4, Li, and Na mordenites afforded Debye–Scherrer photographs typical of mordenite (Table I). Similarly, Ca, Ba, K, Li, NH_4, and Na mordenite used as sorbents were found to have good sorbent and molecular-sieve properties although modified slightly from those of mordenite in characteristic ways (Barrer, in the press). The extraction process, sorptive properties, and *X*-ray data make it clear that the interstitial channels are not blocked by occluded salt. Analysis and tests either of calcium or of sodium displaced into the mother-liquor, or of the solid, showed moreover that the lattice had been much enriched in the exchanging cation.

Solids submitted to analysis were those of Table III, Expt. 9, where the CaO content corresponded to 0·88 mol. of CaO per mol. of Al_2O_3, and of Table III, Expt. 6, where some 15% of the total alkali had been replaced by Li_2O, a rather less complete exchange than might have been expected from Table III, Expt. 2.

Taken as a whole, data of Table III show that exchanges can involve a wide variety of cations expressible by the series

$$Ca^{++} \rightleftharpoons Ba^{++} \rightleftharpoons K^{+} \rightleftharpoons NH_4^{+} \rightleftharpoons Na^{+} \rightleftharpoons Li^{+}$$

The diameters of the interstitial channels in natural mordenite are just a little above 4·0 A. at their narrowest point (Barrer, *loc. cit.*, 1944), while the ionic diameters of the exchanging cations and their associated anions are:

Ion.	Li^+.	Na^+.	K^+.	NH_4^+.	Ca^{++}.	Ba^{++}.	Cl^-.	NO_3^-.
Diameter (in A.)	1·20	1·90	2·66	2·86	1·98	2·70	3·62	5·1

Thus the cations alone should, as observed, diffuse readily in the lattice. The chloride ion might just enter, but the nitrate ion could not unless the lattice recrystallised. It was these diameters which guided the choice of chlorides and nitrates respectively, as exchangers. In fact, neither anion as a rule showed any tendency to be occluded.

Base exchanges represented in the above cations series can be of two kinds typified by $K^+ \rightleftharpoons Na^+$ and $Ca^{++} \rightleftharpoons 2Na^+$. On the assumption that the univalent cations occupy all possible sites, it is a matter for speculation as to which of the sites are occupied by only half the number of bivalent cations. In many zeolites it is true that both uni- and bi-valent cations occur interstitially (*e.g.*, mordenite, chabazite, and gmelinite) so that random cation distributions, leaving many vacant sites, may arise. In this sense these zeolites are to be regarded as defect structures. The entropy of such crystals may be substantially above that of normal crystals, where only one cation configuration is possible. If there are N cation sites, N^+ univalent cations, and N^{++} bivalent cations, the distinguishable configuration number $\frac{N!}{N^+!N^{++}!(N - N^+ - N^{++})!}$, and, Stirling's approximations being used, the configurational entropy S_c due to this becomes

$$S_c = k[N \ln N - N^+ \ln N^+ - N^{++} \ln N^{++} - (N - N^+ - N^{++}) \ln (N - N^+ - N^{++})] \quad . \quad (1)$$

TABLE III.

Typical base-exchange reactions of mordenite.

Expt. no.	Salt.	Reaction conditions.	Analysis of mother-liquor or solid.	Observations.
1	NaCl	Two successive hydrothermal treatments at 200° and 230°, of 2 and 7 days respectively	Considerable Ca displaced from mordenite into mother-liquor. Qualitative test only	Excellent mordenite *X*-ray powder photograph. Birefringent
2	LiCl	Two successive treatments as above at 220°, each of ~1 day	First treatment displaced 1·61% CaO; 2nd displaced 0·29% CaO (by wt.)	Molecular sieve sorbent. Birefringent
3	NH_4Cl	Two successive treatments with NH_4Cl vapour at 250° and 290°, each of 2 days	1·66% CaO displaced in 1st treatment and 0·15% in 2nd (by wt.)	Molecular sieve sorbent. Birefringent
4	$CaCl_2$	Two successive treatments at 200°, each of ~3 days	Solid free from incorporated Cl	Good mordenite *X*-ray powder photograph. Birefringent
5	$NaNO_3$	Two successive treatments at 222°, each of nearly 1 day	First treatment displaced 1·41% CaO, 2nd displaced 0·31% CaO (by wt.)	Birefringent
6	$LiNO_3$	Two successive treatments at 250° of 2 days and 1 day respectively	Analysis of alkali and alkaline-earth metals in solid showed 15% replacement by Li	Birefringent. *X*-Ray photograph similar to that of mordenite. Molecular sieve solvent
7	KNO_3	Two successive treatments at 222°, each of 1 day	First treatment displaced 1·62% CaO; 2nd displaced 0·37% CaO (by wt.)	Sorbent of molecular-sieve type. *X*-Ray pattern similar to that of mordenite. Birefringent
8	KNO_3	Two successive treatments at 200°, each of 3 days	—	*X*-Ray pattern similar to that of mordenite. Birefringent
9	$Ca(NO_3)_2$	Three successive treatments at 225°, each 1 day	Solid analysed : 88% of total alkali was now CaO	Molecular sieve sorbent. Birefringent
10	$Ca(NO_3)_2$	Two successive treatments at 265°, of 2 and 3 days respectively	Considerable Na displaced from mordenite in 1st treatment (tested by zinc uranyl acetate)	Good sorbent as above. *X*-Ray pattern similar to that of mordenite. Birefringent
11	$Ba(NO_3)_2$	Three successive treatments at 260°; 3½, 2½, and 1½ days respectively.	Much Na displaced from mordenite in first treatment. Little Na displaced in last two	Molecular sieve sorbent. *X*-Ray pattern similar to that of mordenite. Birefringent

If all the bivalent cations are replaced by an electrochemical equivalent of univalent cations, and if the total number of univalent cations is equal to the number of sites, substitution in (1) gives $S^{+}_{e} = 0$. If, however, the bivalent cations replace all the univalent ones, one has $N^{+} = 0$, $N^{++} = \frac{1}{2}N$, and so

$$S_{e}^{++} = Nk \ln 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

i.e., there is an increase in entropy during replacement of univalent by bivalent cations. There is at the same time likely to be a change in internal energy, because there is a change in the local neutralisation of anionic charge in the crystal on the smallest possible scale and also because of a changed bonding energy of interstitial water molecules associated with the cations. Now the net free-energy change for replacement is :

$$\Delta G^{++} = \Delta H^{++} - T\Delta S^{++} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and whether replacement of uni- by bi-valent cations will occur or not depends on the relative sizes and signs of the two terms on the right-hand side of (3). For example, if each is of the same order of magnitude, and the same sign, one may have exchange going in either direction (chabazite, mordenite, gmelinite); if ΔH^{++} is larger than $T\Delta S^{++}$, replacement of uni- by bi-valent cations will be limited (analcite); and if $\Delta H^{++} < T\Delta S^{++}$, bivalent cations will be little replaced by univalent ones. At the temperature of the exchange reactions in this paper $T\Delta S_{e}^{++}$ is likely to contribute not more than 800 cals./g.-ion to the over-all value of ΔG.*

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* ΔS_{e}^{++} is, however, only part of the over-all entropy, ΔS, of exchange.