20% (Fig. 2). Clearly, chemisorbed carbon monoxide enhances the physical nitrogen adsorption; no cogent explanation for this can be given.

On BR catalysts the N(OT) is definitely not greater than N(T); it may or may not be greater than the true physical adsorption of nitrogen. The presence of weak chemisorbed nitrogen makes the true value of the physical adsorption uncertain.

5. Carbon Dioxide Chemisorption.—The volume of chemisorbed carbon dioxide is about 80% of the volume of nitrogen required to form a physically adsorbed monolayer. Either carbon dioxide is chemisorbed on both alkali and nickel atoms or else each alkali molecule holds two rather than one carbon dioxide molecule. In any event for the SE II catalyst the sum of the area covered by chemisorbed carbon monoxide plus that covered by chemisorbed carbon dioxide is about 50% larger than the area as measured by a BET plot of the physically adsorbed nitrogen.

6. Argon Adsorption.—If N(OT) does represent the best measure of physically adsorbed nitrogen this value should be comparable to that found from A(T) when the argon is assigned a cross-sectional area of 15.2 Å.[2,5,6] Comparison of the runs for the BR3 catalyst with those for BR2 and BR1 catalyst (Table I, Fig. 3 and 4) shows that the data are consistent with this interpretation. Agreement of the surface area determined by argon with surface area determined from N(OT) is almost exact if the latter value is scaled up to bring the N(T) values for BR2 and BR3 into agreement.

In summary, the present work suggests that the fraction of the surface of a nickel catalyst containing nickel atoms probably can be estimated by carbon monoxide chemisorption. The total area of the catalyst should preferably be measured with argon. If nitrogen is used great care has to be taken to make sure that the volume of nitrogen calculated for a monolayer does not include a considerable amount of chemisorbed nitrogen.

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BALTIMORE, MD.

[CONTRIBUTION FROM THE ESSO RESEARCH LABORATORIES]

The Structures of Synthetic Molecular Sieves

BY L. BROUSSARD AND D. P. SHOEMAKER[1]

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The crystal structures of synthetic molecular sieves commonly identified as 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$), 5A (1/3 $Na_2O \cdot$ 2/3 $CaO \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot xH_2O$) and 13X ($Na_2O \cdot Al_2O_3 \cdot 2.8\ SiO_2 \cdot xH_2O$) have been determined in their hydrated forms (containing 25–35 wt. % H_2O). These studies show that all three sieves have a common building block called a "sodalite" unit, containing 24 (Si,Al) ions interconnected with 36 oxygen ions. In the 4A and 5A sieves these sodalite units are arranged in a simple cubic array, with each sodalite unit connected to its neighbor by four bridge oxygen ions. In 13X, sodalite units are in tetrahedral coördination (diamond array) with each sodalite unit connected to its neighbor by six bridge oxygen ions. Three-dimensional Fourier analyses were employed to refine atomic positions of the framework and to locate cations. Most of the cations were found near the centers of six-membered rings of oxygen ions in the soda.

Introduction

Synthetic molecular sieves are crystalline zeolitic aluminosilicates that are of general interest because of their selective adsorptive properties.[2] These selective adsorptive properties are due to a crystal structure incorporating interconnecting channels and cavities of definite and uniform size. Molecules having appropriate dimensions with respect to these channels can enter and be adsorbed in the internal cavities.

The molecular sieves commonly identified as 4A, 5A and 13X are crystalline alumino-silicates precipitated from an alkaline mixture of silica and alumina. The 4A sieve is a sodium alumino-silicate which adsorbs only molecules smaller than propane. The 5A sieve results from exchanging replaceable Na ions in 4A with Ca ions. It adsorbs molecules smaller in cross section than *iso*-paraffins or aromatics. The 13X sieve has even larger channels and adsorbs most ordinary hydrocarbons.

The crystal structure of 4A and 5A type sieves has been discussed by Reed and Breck[3] and by Barrer.[4] The crystal structure of 13X sieves is known from its powder diagram to be essentially the same as that of the naturally occurring mineral faujasite. The structure of natural faujasite has been described by Nowacki and Bergerhoff.[5]

The crystal structures of the hydrated form of the two major types of synthetic sieves, 4A-5A and 13X, were deduced independently in this Laboratory. Our development of these structures was based on our early recognition of a cubo-octahedral structural unit, similar to that in the mineral sodalite, as being the fundamental building block of both types of sieves; this was independently recognized by Barrer.[6] An alternative structural unit, a small alumino-silicate cube, has been cited as the fundamental unit in the description of 4A-5A.[3]

This report outlines our parallel work in elucidating the fundamental structural framework of these materials, and in addition describes more extensive studies of them, in particular the appli-

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(1) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

(2) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, THIS JOURNAL, **78**, 5963 (1956).

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(5) W. Nowacki and G. Bergerhoff, paper 3.13, Fourth International Congress of Crystallography, Montreal, Canada, July 10–19, 1957.

(6) R. M. Barrer, "Physical Chemistry of Some Non-Stoichiometric Phases," Report to the Xth Solvay Council, Brussels, 1956.

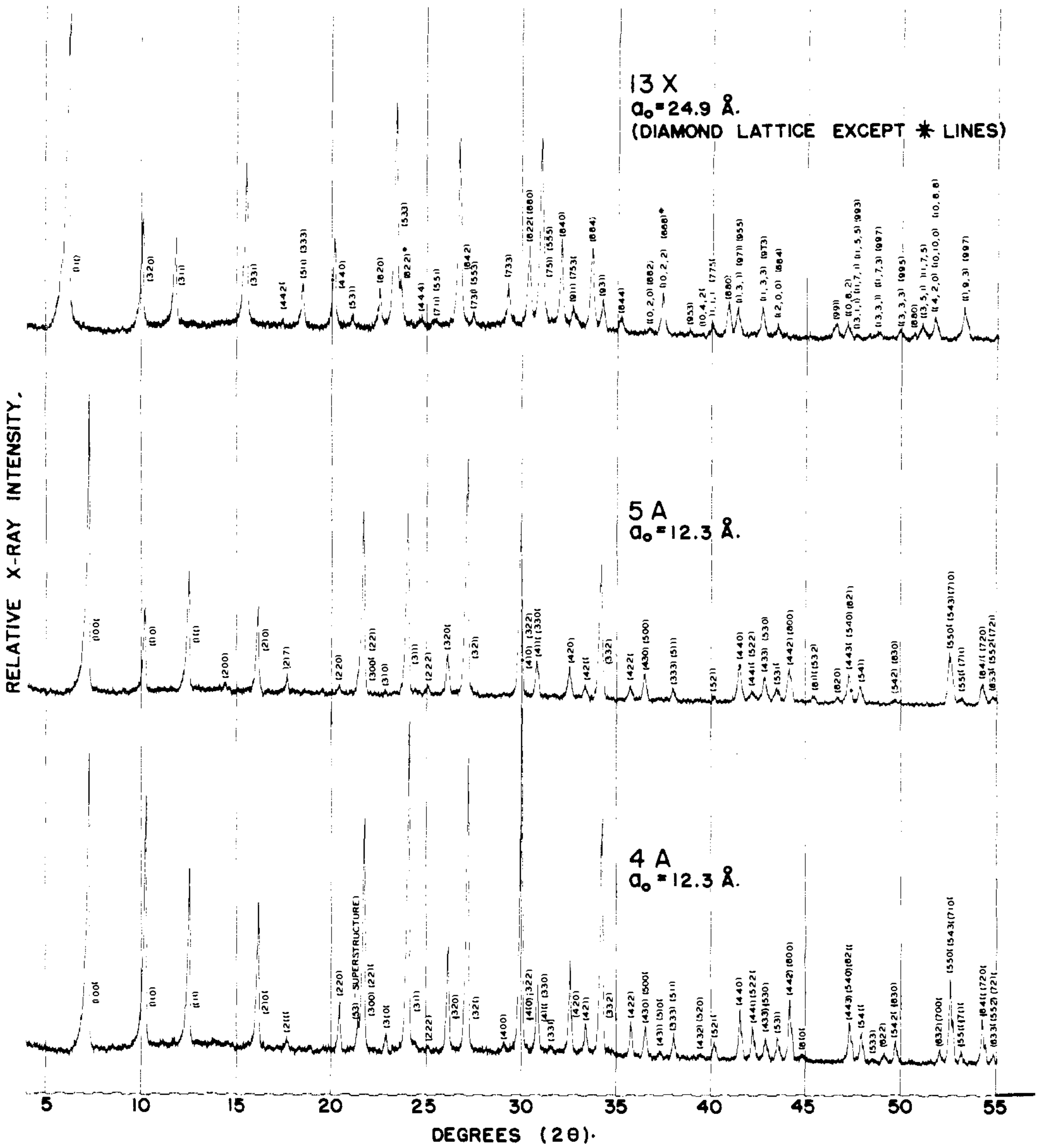

Fig. 1.—X-Ray diffraction patterns of molecular sieves.

cation of the three-dimensional Fourier method to the refinement of atomic positions and the location of cations.

Experimental

Specimens of commercially available molecular sieves (in powder form, without binder) and of similar sieves prepared in these Laboratories were used in this work. The samples were exposed to room air and contained about 25–35 wt. % water. All X-ray work involved in the determination of the structure of these molecular sieves was done with a Philips Geiger Counter X-Ray Diffractometer. Samples were ground and packed into flat specimen holders. The sample exposed to the filtered copper X-ray beam was about $^1/_{16}'' \times {}^1/_2'' \times {}^1/_2''$. One-degree divergence and scatter slits were used with a 0.003″ receiving slit.

Portions of typical X-ray diffraction patterns of 4A, 5A and 13X are shown in Fig. 1. From the original precision traces of 4A and of 5A the relative positions of the diffraction lines identified these materials as having a simple cubic lattice, with a lattice constant a_0 = 12.30 ± 0.01 Å. for 4A and 12.31 ± 0.01 Å. for 5A. In a similar manner, the 13X type crystal was found to be face-centered cubic with a lattice constant a_0 = 24.91 ± 0.02 Å. The powder lines shown by 13X were almost exclusively those having Miller indices permitted by the diamond structure.

Development of Models

The development of models to explain the structure of these molecular sieves was based on the well-known principle that in many aluminosilicates both Si and Al are tetrahedrally coördinated by oxygen anions. From adsorption data, it was known that channels of certain approximate size existed and from the above X-ray data the crystal system and the unit cell size were known. From trial assemblies of $(Si,Al)O_4$ tetrahedra it was soon recognized that the primary building block for both 4A-5A and for 13X was a framework of these tetrahedral groups that closely resembles the main structural unit in the mineral sodalite and the ultramarines.[7] This building block will be called the "sodalite unit." It contains 24 (Si,Al) ions interconnected with 36 oxygen anions. The oxygens form 6 octahedrally posi-

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(7) W. L. Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, pp. 252, 267; L. Pauling, *Z. f. Krist.*, **74**, 213 (1930); F. Jaeger, H. G. K. Westenbrink and F. A. van Melle, *Proc. Acad. Amst.*, **30**, 249 (1927).

tioned rings containing 4 oxygen ions and one set of cubically positioned or two sets of tetrahedrally positioned 6-element rings of oxygen ions. As will be shown later, the (Si,Al)O_4 tetrahedra in the sodalite units that are the building block for the 4A-5A frame-work are symmetrically arranged so as to place the 4-ring oxygens in a plane and yield point symmetry O_h for the unit. In the 13X structure, however, the sodalite unit eventually was found to be distorted from O_h symmetry to T_d symmetry (by partial rotations of the tetrahedra) in about the same way as in the mineral sodalite.[7]

The framework of 4A and 5A sieves consists of the more symmetrical sodalite units located at the corners of the cubic unit cell. Each sodalite unit is joined to its neighbor by 4 "bridge" oxygens connecting the 4-element rings of (Si,Al)O_4 tetrahedra. This assembly is shown in Fig. 2. Inspection of this figure shows that the framework (excluding Na and/or Ca ions) of 4A and 5A sieves is such that the adsorption cavities are spaces surrounded by the 8 sodalite units placed at the corners of the cubic unit cell, and the channels result from interconnection of these cavities at openings produced by rings of 8 oxygen ions at the centers of the cube faces. This structure has space group O_h^1–Pm3m.

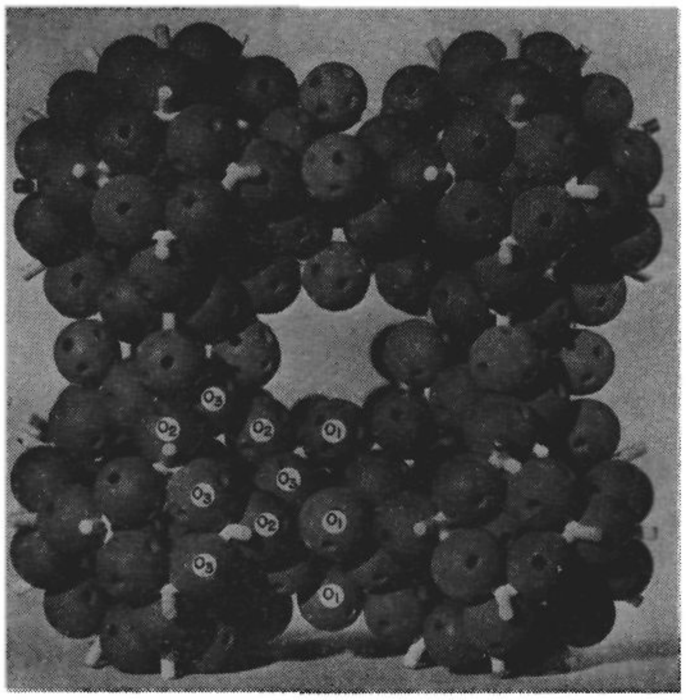

Fig. 2.—Structure of 4A and 5A molecular sieves; Na or Ca ions are not shown.

In the structure of the framework of type 13X sieve the sodalite units are again used as the primary building blocks. In this case, however, the sodalite units are placed in tetrahedral coördination in the same manner as are carbon atoms in the diamond structure and are connected together at their 6-element rings by 6 bridge oxygens. This arrangement (constructed with the more symmetrical units) is shown in Fig. 3. Here, the minimum openings in the channels are rings of 12 oxygen ions. The space group of this structure is O_h^7–Fd3m.

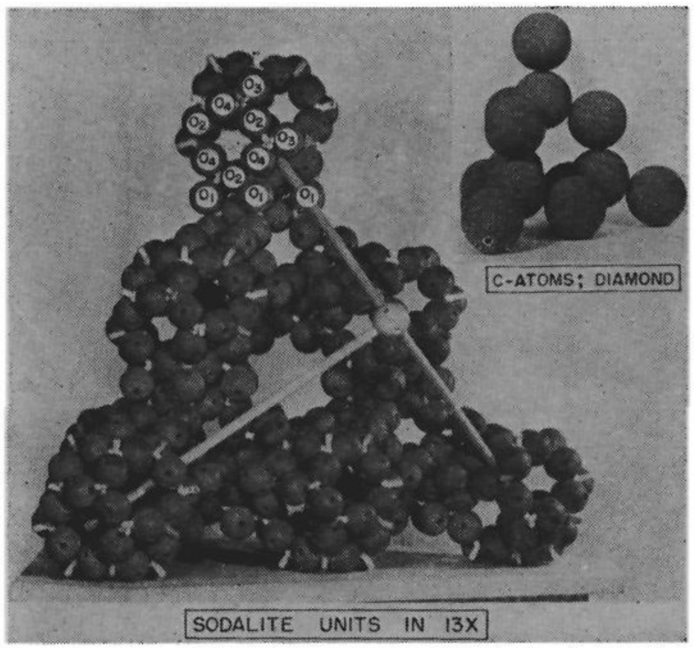

Fig. 3.—Structure of 13X molecular sieve; Na ions are not shown.

Verification and Refinement

A. 4A-5A: X-Ray Line Intensity Calculations.—X-Ray structure factors and line intensities were calculated with an IBM 650 computer, using atomic parameters scaled from the model of Fig. 2 and adjusted to give expected interatomic distances. A temperature factor, $B = 1.40$, was used throughout this work. Reliability factors, $R = \Sigma|I_0 - I_c|/\Sigma I_0$ were calculated for 130 lines, in groups of 10, to guide in the initial trial and error refinements of atomic parameters. After sufficient refinement of this model a three-dimensional Fourier electron density function described below was calculated to complete the determination of atomic positions and to locate cations. Using these atomic positions new X-ray line intensities were calculated. These calculated intensities are compared with the observed intensities in Table I; reliability factors are shown for groups of 10 lines as well as for the over-all data.

It is felt that the poor correlation observed for lines at small diffraction angles may be due to the presence of diffuse adsorbed water (not included in the calculation of structure factors), since no attempt was made to dry these samples. At the larger angles the agreement is satisfactory, and in line with that commonly obtained in crystal structure refinement (considering the fact that "R" values based on intensity values are about twice conventional "R" values based on structure factors).

B. 4A-5A: Three-dimensional Fourier Analysis.—A three-dimensional Fourier electron density function was calculated to refine atomic parameters in the framework and to locate the Na ions in the 4A sieve and the Na and Ca ions in the 5A sieve. Structure factors used for Fourier coefficients were obtained from the observed powder-line intensities; in each case where more than one plane contributed to a line, the observed intensity was apportioned among the contributing planes in accordance with ratios of MF^2_c (multiplicity times the square of the calculated structure factor) for the respective planes. The summation was limited to planes with $h^2 + k^2 + l^2 \leqslant 102$ in order to minimize contributions from lines to which several planes contribute; an artificial temperature factor (7.28) was used to obtain improved convergence. The signs of the observed structure factors were taken to be the same as those of the corresponding calculated structure factors. These were based

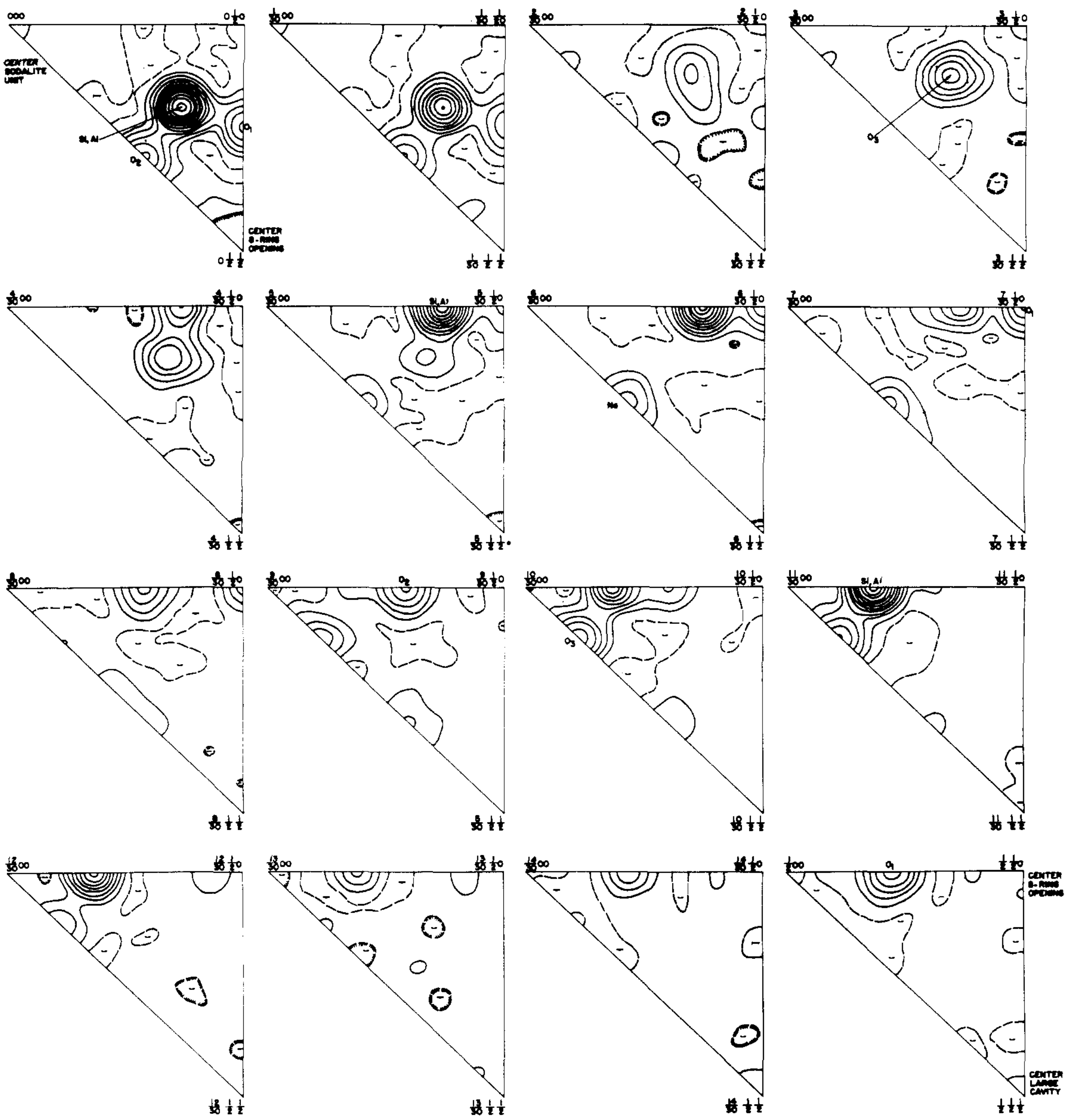

Fig. 4.—Electron density functions—Type 4A sieve.

on framework parameters obtained from the model; sodium atoms were not included. The calculations were done on IBM accounting machines using the M-card system of V. Schomaker.[8]

Contoured two-dimensional sections of the function for the 4A type sieve, $a_0/30$ apart, are shown in Fig. 4. From the peak positions, improved atomic parameters were established for the 4A type sieve. These differed only by small amounts ($\sim$ 0.01 Å.) from the preliminary model parameters. They are given in Table II, and interatomic distances (reliable to about ± 0.03 Å.) obtained from them are listed in Table III.

The two-dimensional sections for the 5A type sieve are not shown. They were very similar to the 4A sections except that, as expected, the (Na, Ca) peak was of larger amplitude than the Na peak in 4A. From the 5A sections the improved atomic parameters were established. These are given in Table IV, and interatomic distances (with somewhat less reliability than for 4A) obtained from them are listed in Table V.

It is interesting to note that the exchange of replaceable Na ions by Ca caused some small readjustments of atomic parameters of the atoms in the framework and in the positions of eight cations. These data show that in the type 4A sieve the eight observed Na ions are located near the center of the 6-element oxygen rings, though slightly outside the sodalite unit, or inside the 4A adsorption cavity, as measured from the mean plane of the 6-ring oxygen centers. In the type 5A sieve the metal ions have moved toward the sodalite cavities and are closer (0.08 Å.) to the center of the 6-element oxygen rings.

C. 13X: X-Ray Line Intensity Calculations.—X-Ray structure factors and line intensities were

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[8] V. Schomaker, unpublished.

TABLE I

RELIABILITY FACTORS FOR 4A AND 5A TYPE SIEVES

		Type 4A sieve			Type 5A sieve		
N[a]	h, k, l	I (calcd.)[b]	I (obsd.)[c]	R	I (calcd.)[b]	I (obsd.)[c]	R
1	1,0,0	191	47		208	42	
2	1,1,0	148	52		143	18	
3	1,1,1	162	43		134	44	
4	2,0,0	8	0		21	3	
5	2,1,0	154	48		205	53	
6	2,1,1	21	4		36	11	
8	2,2,0	41	22		46	9	
9	3,0,0–2,2,1	184	133		227	25	
10	3,1,0	10	12		0	0	
11	3,1,1	230	251	0.94	182	326	1.81
12	2,2,2	27	4		23	15	
13	3,2,0	14	93		3	69	
14	3,2,1	248	314		286	548	
16	4,0,0	1	10		4	8	
17	4,1,0–3,2,2	334	438		394	469	
18	4,1,1–3,3,0	72	76		77	109	
19	3,3,1	1	0		5	0	
20	4,2,0	93	123		35	103	
21	4,2,1	46	39		37	45	
22	3,3,2	325	409	0.27	448	535	0.32
24	4,2,2	63	64		39	58	
25	5,0,0–4,3,0	121	49		200	116	
26	5,1,0–4,3,1	4	10		1	12	
27	5,1,1–3,3,3	59	49		83	57	
29	5,2,0–4,3,2	50	14		87	0	
30	5,2,1	50	44		14	0	
32	4,4,0	107	134		125	240	
33	5,2,2–4,4,1	141	92		131	58	
34	5,3,0–4,3,3	123	68		187	140	
35	5,3,1	65	64	0.45	139	88	0.55
36	6,0,0–4,4,2	204	199		184	261	
37	6,1,0	17	19		13	0	
38	6,1,1–5,3,2	2	0		26	29	
40	6,2,0	2	0		79	39	
41	6,2,1–5,4,0–4,4,3	197	163		197	234	
42	5,4,1	133	110		231	141	
43	5,3,3	0	7		46	0	
44	6,2,2	23	37		1	0	
45	6,3,0–5,4,2	82	80		55	28	
46	6,3,1	3	4	0.14	1	10	0.38
48	4,4,4	4	14		21	0	
49	7,0,0–6,3,2	38	56		26	0	
50	7,1,0–5,5,0–5,4,3	551	449		667	604	
51	7,1,1–5,5,1	63	67		19	62	
52	6,4,0	1	14		2	0	
53	7,2,0–6,4,1	224	259		151	24	
54	7,2,1–6,3,3–5,5,2	52	65		133	111	
56	6,4,2	47	21		16	20	
57	7,2,2–5,4,4	132	140		229	163	
58	7,3,0	52	30	0.23	15	42	0.34
59	7,3,1–5,5,3	297	255		282	273	
61	6,5,0–6,4,3	180	232		228	370	
62	7.3,2–6,5,1	15	22		15	0	
64	8,0,0	50	68		40	57	
65	8,1,0–7,4,0–6,5,2	69	91		26	34	
66	8,1,1–7,4,1–5,5,4	48	58		37	43	
67	7,3,3	3	19		17	0	
68	8,2,0–6,4,4	25	63		8	0	
69	8,2,1–7,4,2	130	137		144	149	
70	6,5,3	106	65	0.25	13	48	0.23
72	8,2,2–6,6,0	74	109		128	130	
73	8,3,0–6,6,1	58	76		12	0	
74	8,3.1–7,5,0–7,4,3	253	219		254	230	

TABLE I (*continued*)

		Type 4A sieve			Type 5A sieve		
N[a]	h, k.	I (calcd.)[b]	I (obsd.)[c]	R	I (calcd.)[b]	I (obsd.)[c]	R
75	7,5,1–5,5,5	171	139		280	160	
76	6,6,2	19	42		34	66	
77	8,3,2–6,5,4	357	376		558	425	
78	7,5,2	16	0		0	34	
80	8,4,0	13	0		1	0	
81	9,0,0–8,4,1–7,4,4–6,6,3	150	186		91	146	
82	9,1,0–8,3,3	535	607	0.15	610	735	0.27
83	9,1,1–7,5,3	12	0		48	0	
84	8,4,2	53	25		60	385	
85	9,2,0–7,6,0	86	63		50	0	
86	9,2,1–7,6,1–6,5,5	219	243		296	385	
88	6,6,4	12	14		2	28	
89	9,2,2–8,5,0–8,4,3–7,6,2	119	154		80	70	
90	9,3,0–8,5,1–7,5,4	404	353		243	228	
91	9,3,1	31	52		41	73	
93	8,5,2	30	25		60	0	
94	9,3,2–7,6,3	37	38	0.20	36	0	0.43
96	8,4,4	104	155		154	250	
97	9,4,0–6,6,5	158	169		183	222	
98	9,4,1–8,5,3–7,7,0	69	84		96	0	
99	9,3,3–7,7,1–7,5,5	131	115		241	98	
100	10,0,0–8,6,0	157	136		170	132	
101	10,1,0–9,4,2–8,6,1–7,6,4	232	229		94	201	
102	10,1,1–7,7,2	61	84		113	51	
104	10,2,0–8,6,2	41	14		44	52	
105	10,2,1–8,5,4	14	37		49	53	
106	9,5,0–9,4,3	49	74	0.20	24	71	0.48
107	9,5,1–7,7,3	102	150		106	108	
108	10.2,2–6,6,6	1	0		1	0	
109	10,3,0–8,6,3	51	89		28	0	
110	10,3,1–9,5,2–7,6.5	108	130		172	130	
113	10,3,2–9,4,4–8,7.0	150	135		52	77	
114	8,7,1–8,5,5–7,7,4	87	102		114	77	
115	9,5,3	112	67		11	58	
116	10,4,0–8.6,4	3	0		16	0	
117	10,4,1–9,6,0–8,7,2	20	14		113	0	
118	10,3,3–9,6,1	0	0	0.28	29	0	0.34
120	10,4,2	1	0		7	0	
121	11,0,0–9,6,2–7,6,6	104	88		149	204	
122	11,1,0–9,5,4–8,7,3	16	36		125	62	
123	11,1,1–7,7,5	11	0		0	0	
125	11,2,0–10,5,0–10,4,3–8,6,5	107	93		245	105	
126	11,2,1–10,5,1–9,6,3	5	0		7	0	
128	8,8,0	4	0		9	0	
129	11,2,2–10,5,2–8,8,1–8,7,4	104	76		98	86	
130	11,3,0–9.7,0	116	95		61	0	
131	11,3,1–9,7,1–9,5,5	34	19	0.28	19	0	0.59
132	10,4,4–8,8,2	96	128		179	152	
133	9,6,4	5	23		11	0	
134	11,3,2–10,5,3–9,7,2–7,7,6	131	87		72	44	
136	10,6,0–8,6,6	42	29		74	66	
137	11,4,0–10,6,1–8,8,3	224	302		296	287	
138	11,4,1–8,7,5	76	98		29	66	
139	11,3,3–9,7,3	89	74		28	0	
140	10,6,2	6	0		27	0	
141	11,4,2–10,5,4	37	75		37	67	
142	9,6,5	6	17	0.33	0	0	0.20
144	12,0,0–8,8.4	0	0		15	0	
145	12,1,0–10,6,3–9,8,0	29	51		57	45	
146	12,1,1–11,5,0–11,4,3–9,8,1–9,7,4	129	212		158	203	
147	11.5,1–7,7,7	12	38		58	90	
148	12.2,0	0	0		8	0	
149	12,2,1–10,7,0–9,8,2–8,7,6	67	42		147	23	
150	11,5,2–10,7,1–10,5,5	72	38		144	0	

152	12,2,2–10,6,4	37	15		46	0	
153	12,3,0–11,4,4–10,7,2–9,6,6–8,8,5	43	48		23	0	
154	12,3,1–9,8,3	36	56	0.47	11	0	0.59
	Over-all R factor			0.28			0.43

[a] $N = h^2 + k^2 + l^2$. [b] I(calcd.) $= \Sigma MF^2$, summed over all diffracting planes contributing to powder line. M = Multiplicity of plane. 4A calculations included 8 sodium ions per unit cell, 5A included 4 sodium and 4 calcium ions per unit cell. [c] I(obsd.) = observed powder line intensity with Lorentz-polarization factor and scale factor divided out.

TABLE II

ATOMIC PARAMETERS FOR 4A-TYPE SIEVE

Atom	Position	Parameters (origin at m3m) x	y	z
Si, Al	24 (k)	0.0000	0.1822	0.3713
O_1 (Bridge)	12 (h)	.0000	.2229	.5000
O_2 (Single)	12 (i)	.0000	.2937	.2937
O_3 (4-Ring)	24 (m)	.1117	.1117	.3407
Na	8 (g)	.2082	.2082	.2082
Na	4		(Not Located)	

TABLE III

INTERATOMIC DISTANCES (Å.) FOR 4A-TYPE SIEVE

(Si, Al)–O_1 = 1.66 O_1–O_2 = 2.68   Na–O_2 = 2.96

(Si, Al)–O_2 = 1.67 O_1–O_3 = 2.76   Na–O_3 = 2.34

(Si, Al)–O_3 = 1.67 O_2–O_3 = 2.69

TABLE IV

ATOMIC PARAMETERS FOR 5A-TYPE SIEVE

Atom	Position	Parameters (origin at m3m) x	y	z
Si,Al	24 (k)	0.0000	0.1972	0.3727
O_1 (Bridge)	12 (h)	.0000	.2280	.5000
O_2 (Single)	12 (i)	.0000	.2878	.2878
O_3 (4-Ring)	24 (m)	.1118	.1118	.3482
(Na,Ca)	8 (g)	.1950	.1950	.1950

TABLE V

INTERATOMIC DISTANCES (Å.) FOR THE 5A-TYPE SIEVE

(Si,Al)–O_1 = 1.61 O_1–O_2 = 2.72   (Na,Ca)–O_2 = 2.89

(Si,Al)–O_2 = 1.53 O_1–O_3 = 2.73   (Na,Ca)–O_3 = 2.37

(Si,Al)–O_3 = 1.76 O_2–O_3 = 2.67

calculated with the IBM 650 with parameters estimated from the model shown in Fig. 3. As in the case for the 4A-5A sieve, a temperature factor of 1.40 was used. Initially, atomic parameters were based on the same highly symmetrical (O_h) sodalite unit that was found to be the correct building block for the 4A-5A structure. The best correlations obtained with this model are shown in Table VI. On readjusting the atomic parameters, basing them on the sodalite unit as it actually exists in natural sodalite, sufficiently good correlations were obtained to justify calculating a three-dimensional electron density function to establish atomic positions more reliably. With these more reliable atomic parameters new structure factors and line intensities were calculated. These improved intensity values are compared with the observed data in Table VI. Here again reliability factors are given for groups of ten lines as well as for the over-all data.

The diffraction pattern for 13X sieve could be indexed almost entirely on the basis of a diamond-type lattice. However, as shown in Fig. 1 there were a few lines with significant intensities which were non-diamond face-centered-cubic lines. These non-diamond lines were important in suggesting that in the 13X framework the sodalite units are distorted as they are in the mineral sodalite.

D. 13X: Three-dimensional Fourier Analysis.—A three-dimensional Fourier electron density function was calculated in a manner analogous to the 4A-5A functions in order to refine the atomic parameters in the framework and to locate the Na cations in this structure. The summation was limited to planes with $h^2 + k^2 + l^2 \leqslant 408$, and an artificial temperature factor of 8.40 was used to improve convergence. The function was calculated at intervals of 1/120 of the unit cell in all three dimensions with the IBM 704 using a program written by W. G. Sly.[9] In Fig. 5 a portion of a "composite Fourier synthesis" is presented in which contoured sections of Fourier peaks are shown corresponding to the atoms in one asymmetric unit. From this analysis, improved atomic parameters were obtained and are listed in Table VII. Interatomic distances (reliable to about ± 0.04 Å.) calculated from these parameters are given in Table VIII. In contrast to 4A-5A, in 13X the Na_2 cations protrude from the sodalite units into the large cavities by about 1.7 Å. This suggests the presence of a presumably diffuse hydration shell, which is at best inconclusively indicated by some weak, diffuse peaks in the Fourier synthesis.

Discussion

A. 4A-5A Structure.—It has been shown that the framework of both 4A and 5A sieves consists of sodalite units (with point symmetry O_h) in a simple cubic arrangement. Each sodalite unit is connected to its neighbor by four bridge oxygen ions. The main adsorption cavity is a space surrounded by eight sodalite units and entry into this cavity is by means of a channel bounded by four sodalite units. A cross-section of the adsorption cavity looking into one channel is shown in Fig. 6.

The composition of the 4A-type sieve is $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$. This structure analysis indicates that there are six of these formula weights per unit cell. Therefore, 12 Na cations are required per unit cell for electrical neutrality. The Fourier analysis located eight Na ions in 4A but gave no indication of the positions of the other four.

The exchange of eight Na cations in 4A with four Ca ions to form the 5A sieve produces a sieve which adsorbs larger molecules than 4A adsorbs. The inability of the 4A sieve to adsorb normal paraffins might be related to plugging of the channels by the four Na ions this analysis failed to locate. The Fourier analysis gave no indication of this plugging, perhaps owing to the fact that the sieve studied here contains water which might displace the Na ions to different (and random) positions.

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(9) W. G. Sly and D. P. Shoemaker, to be published.

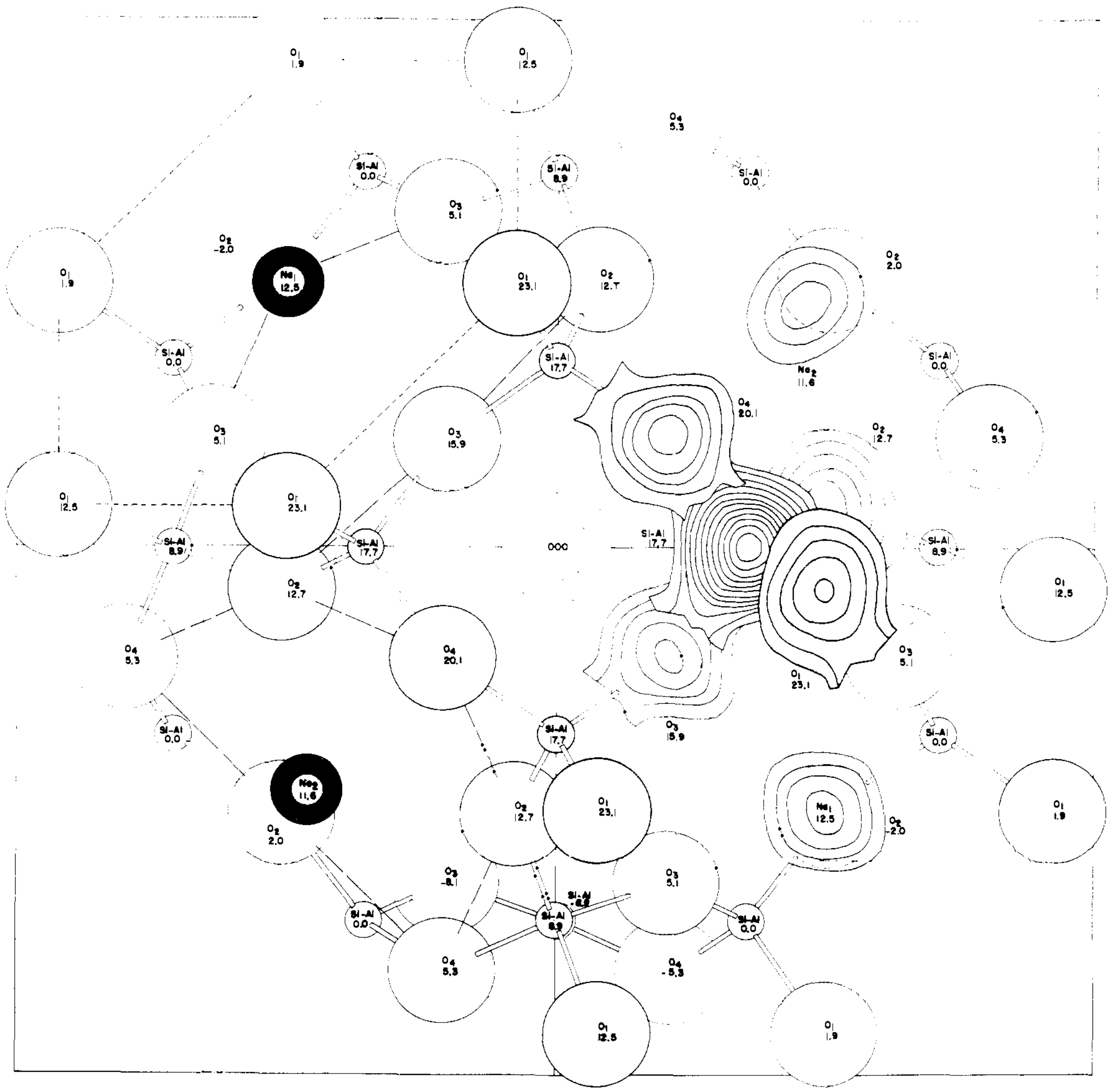

Fig. 5.—Sodalite unit of 13X molecular sieve showing sections of 3-dimensional Fourier peaks; numbers are in hundredths of the unit cell.

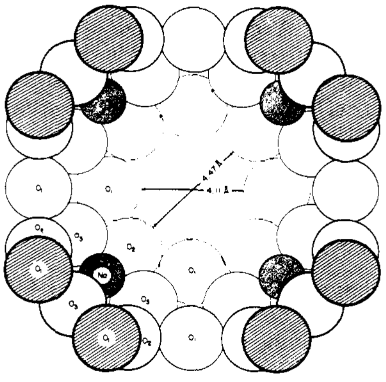

Fig. 6.—Cross-section of 4A adsorption cavity.

The structure of 4A-5A has a Si/Al ratio of one. As pointed out by other workers[3,4] and independently recognized by us, a continuous alternation of Si and Al ions should produce a super-structure (F.C.C. superlattice) with twice the cubic unit cell dimension of the 4A sieve. A diffraction line possibly corresponding to this super-structure [(531) as indexed on the super-cell], was observed and is indicated in Fig. 1.

B. **13X Structure.**—This study shows that the framework of the 13X sieve consists of "distorted" sodalite units (with point symmetry T_d) in tetrahedral coördination, each sodalite unit connected to its neighbor by six bridge oxygen ions. The adsorption cavity is a space surrounded by 10 sodalite units. The channels to these cavities are bounded by six sodalite units. A cross section of this adsorption cavity looking into one of these main channels is shown in Fig. 7.

Chemical analyses of this 13X sieve suggest that its composition is $Na_2O \cdot Al_2O_3 \cdot 2.8SiO_2 \cdot xH_2O$. This crystallographic study indicates that there are eight sodalite units, each containing 24 (Si,Al) tetrahedra, per unit cell. For a SiO_2/Al_2O_3 ratio of 2.8, 80 Na cations are required per unit cell. The Fourier analysis located only 48 of these.

Table VI

Reliability Factors for Type 13X Sieves[a]

		Model A[b]			Model B[c]		
N	*h*, *k*, *l*	*I* (calcd.)	*I* (obsd.)	*R*	*I* (calcd.)	*I* (obsd.)	*R*
3	1,1,1	12816	1710		17751	1675	
4	2,0,0	0	0		0	0	
8	2,2,0	13094	1510		7156	1479	
11	3,1,1	9492	1795		8287	1758	
12	2,2,2	178	0		382	0	
16	4,0,0	29	0		426	0	
19	3,3,1	8989	5985		12969	5861	
20	4,2,0	0	183		0	179	
24	4,2,2	3567	179		104	175	
27	5,1,1–3,3,3	5236	2797	2.78	2301	2739	2.60
32	4,4,0	2741	5740		2312	5622	
35	5,3,1	3094	778		2029	762	
36	6,0,0–4,4,2	5	0		136	0	
40	6,2,0	694	2414		1630	2364	
43	5,3,3	9717	18605		13579	18221	
44	6,2,2	363	1657		309	1623	
48	4,4,4	2423	725		62	710	
51	7,1,1–5,5,1	938	1010		946	989	
52	6,4,0	0	0		0	0	
56	6,4,2	11398	20885	0.55	13160	20454	0.38
59	7,3,1–5,5,3	1997	1230		437	1204	
64	8,0,0	684	0		806	0	
67	7,3,3	2783	5374		3371	5263	
68	8,2,0–6,4,4	4	0		319	0	
72	8,2,2–6,6,0	9566	12417		7886	12161	
75	7.5,1–5,5,5	14604	31348		25787	30700	
76	6,6,2	247	0		142	0	
80	8,4,0	11450	12621		15268	12360	
83	9,1,1–7,5,3	147	3078		3459	3014	
84	8,4,2	29	692	0.42	1320	678	0.24
88	6,6,4	10325	14494		10893	14194	
91	9,3,1	5326	6677		6529	6539	
96	8,4,4	5120	3273		6777	3206	
99	9,3,3–7,7,1–7,5,5	5694	0		253	0	
100	10,0,0–8,6,0	0	0		0	0	
104	10,2,0–8,6,2	481	1457		530	1427	
107	9,5,1–7,7,3	1313	2646		131	2592	
108	10,2,2–6,6,6	216	11522		9071	11283	
115	9,5,3	2813	0		7	0	
116	10,4,0–8,6,4	23	0	0.52	1442	0	0.32
120	10,4,2	3948	0		59	0	
123	11,1,1–7,7,5	6753	2984		4436	2923	
128	8,8,0	21364	10544		8028	10326	
131	11,3,1–9,7,1–9,5,5	2717	8387		5091	8213	
132	10,4,4–8,8,2	46	0		444	0	
136	10,6,0–8,6,6	3068	924		1104	905	
139	11,3,3–9,7,3	2980	8997		5622	8811	
140	10,6,2	214	0		1775	0	
144	12,0,0–8,8,4	1945	3570		1620	3497	
147	11,5,1–7,7,7	2035	0	0.85	1096	0	0.35
148	12,2,0	0	0		0	0	
152	12,2,2–10,6,4	2010	0		61	0	
155	11,5,3–9,7,5	539	1111		533	1088	
160	12,4,0	11	0		692	0	
163	9,9,1	2972	3086		1018	3022	
164	12,4,2–10,8.0–8,8,6	75	5211		4177	5103	
168	10,8,2	21708	6433		9246	6300	
171	13,1.1–11.7,1–11,5,5–9,9,3	9423	554		2448	542	
172	10,6,6	70	0		385	0	
176	12,4,4	3366	965	1.86	3395	945	0.63
179	13,3,1–11,7,3–9,7,7	16452	3371		5092	3301	
180	12,6,0–10,8,4	14	0		508	0	
184	12,6,2	1588	619		1648	606	

TABLE VI (*continued*)

N	h, k.	Model A[b]		R	Model B[c]		R
		I (calcd.)	I (obsd.)		I (calcd.)	I (obsd.)	
187	13,3,3-9,9,5	781	4641		3971	4545	
192	8,8,8	207	1331		3024	1304	
195	13,5,1—11,7,5	4331	7695		9020	7536	
196	14,0,0–12,6,4	32	0		59	0	
200	14,2,0–10,10,0–10,8,6	18312	13924		9460	13636	
203	13,5,3–11,9,1	1718	725		1016	710	
204	14,2,2–10,10,2	80	0	0.86	398	0	0.35
208	12,8,0	1249	2260		2832	2213	
211	11,9,3–9,9,7	4215	19827		20140	19417	
212	14,4,0–12,8,2	128	0		1272	0	
216	14,4,2–12,6,6–10,10,4	5733	533		2290	522	
219	13,7,1–13,5,5–11,7,7	1003	546		1403	534	
224	12,8,4	348	1136		574	1112	
227	15,1,1–13,7,3–11,9,5	10611	1156		2763	1132	
228	14,4,4–10,8,8	22	0		1393	0	
232	14,6,0	29	0		25	0	
235	15,3,1	324	2752	1.24	1243	2695	0.28
236	14,6,2–10,10,6	70	2170		5178	2125	
243	15,3,3–13,7,5–11,11,1–9,9,9	9156	22595		15644	22128	
244	12,10,0–12,8,6	102	0		253	0	
248	14,6,4–12,10,2	610	3017		2271	2954	
251	15,5,1–13,9,1–11,11,3–11,9,7	3792	5781		7822	5662	
256	16,0,0	13662	3522		3717	3449	
259	15,5,3–13,9,3	57	3953		5782	3871	
260	16,2,0–14,8,0–12,10,4	20	0		1	0	
264	16,2,2–14,8,2–10,10,8	2045	2968		2770	2907	
267	13,7,7–11,11,5	7008	10992	0.71	8932	10765	0.31
268	14,6,6	12	0		1	0	
272	16,4,0–12,8,8	11640	11318		16135	11084	
275	15,7,1–15,5,5–13,9,5	17488	5170		5966	5064	
276	16,4,2–14,8,4	47	0		751	0	
280	12,10,6	7338	7817		8719	7655	
283	15,7,3–11,9,9	2667	3347		4706	3277	
288	16,4,4–12,12,0	1233	19379		18958	18978	
291	17,1,1–13,11,1–11,11,7	2181	6595		7571	6459	
292	16.6,0–12,12,2	96	0		54	0	
296	16.6,2–14,10,0–14,8,6	5747	14453	0.66	12064	14154	0.18
299	17,3,1–15,7,5–13,11,3–13,9,7	9647	1376		1639	1348	
300	14,10,2–10,10,10	14	0		909	0	
304	12,12,4	2948	0		462	0	
307	17,3,3–15,9,1	3739	961		742	941	
308	16,6,4–12,10,8	95	0		2	0	
312	14,10.4	505	0		167	0	
315	17,5,1–15.9,3–13,11,5	1793	1002		1928	981	
320	16,8.0	234	0		29	0	
323	17,5,3–15,7,7–11,11,9	11220	3644		601	3568	
324	18.0.0–16,8,2–14,8,8–12,12,6	214	0	2.78	3697	0	0.64
328	18,2,0–16.6,6	27613	24061		21517	23563	
331	15.9,5–13,9,9	5333	9730		6354	9529	
332	18.2,2–14.10,6	5	0		263	0	
336	16.8,4	22	5537		1226	5422	
339	17,7,1–17,5,5–13,13,1–13,11,7	7061	12376		9179	12121	
340	18,4,0–14,12,0	0	0		0	0	
344	18,4,2–14,12,2–12,10,10	17247	9812		8585	9609	
347	17,7,3–15,11,1–13,13,3	2330	4682		3234	4585	
352	12,12,8	1517	0		4	0	
355	15.11,3–15,9,7	1605	7287	0.47	8631	7137	0.23
356	18,4,4–16,10,0–16,8,6–14,12,4	112	0		81	0	
360	18,6,0–16,10,2–14,10,8	16759	8020		6942	7854	
363	19,1,1–17,7,5–13,13.5–11.11,11	13263	23165		22113	22686	
364	18.6,2	0	0		195	0	
371	19.3,1–17,9,1–15,11,5–13.11.9	11698	1295		6047	1268	
372	16.10.4	20	0		109	0	
376	18,6.4–14,12,6	3223	1319		2193	1292	

379	19,3,3–17,9,3	158	9974		9230	9768	
384	16,8,8	27658	6107		6378	5981	
387	19,5,1–17,7,7–15,9,9–13,13,7	4117	1372	1.27	1677	1344	0.17
	Over-all R factor			0.82			0.34

[a] For meanings of N, I(calcd.), I(obsd.), see footnote to Table I. [b] Fully symmetric sodalite unit, with point symmetry O_h, as in 4A-5A. Calculations include 48 sodium ions per unit cell. [c] Sodalite unit, with point symmetry T_d, as in the mineral sodalite. Calculations include 48 sodium ions per unit cell.

TABLE VII

ATOMIC PARAMETERS FOR 13X TYPE SIEVE

Atom	Position	Parameters (origin at $\bar{3}$m) *x*	*y*	*z*
Si,Al	192 (i)	0.9638	0.8747	0.0525
O_1 (Bridge)	96 (h)	.0000	.8942	.1058
O_2 (Single)	96 (g)	.0018	.8553	.0018
O_3 (4-Ring)	96 (g)	.9264	.9264	.0341
O_4 (4-Ring)	96 (g)	.9277	.8223	.0760
Na_1	16 (c)	.0000	.0000	.0000
Na_2	32 (e)	.9911	.7589	.9911

TABLE VIII

INTERATOMIC DISTANCES (Å.) FOR THE 13X-TYPE SIEVE

(Si,Al)–O_1 = 1.67
(Si,Al)–O_2 = 1.65
(Si,Al)–O_3 = 1.65
(Si,Al)–O_4 = 1.70
O_1–O_2 = 2.79
O_1–O_3 = 2.69
O_1–O_4 = 2.64
O_2–O_3 = 2.71
O_2–O_4 = 2.74
O_3–O_4 = 2.81
Na_1–O_1 = 3.74
Na_1–O_3 = 2.74
Na_2–O_2 = 3.41
Na_2–O_4 = 3.09

It is interesting to note that, just as in the case of the 4A sieve, about four Na cations per sodalite unit could not be located by this Fourier Analysis. Different SiO_2/Al_2O_3 ratios would result in different numbers of Na^+ ions; the probable requirement of a minimum of 48 cations, imposed by this structure, presumably imposes an upper limit of 6/1 for this ratio if the cations are all univalent. It is interesting that ratios of around 5/1 that have been reported for certain specimens of the natural mineral faujasite are not far from this figure.

This highly unusual and perhaps unique application of the three-dimensional Fourier method to a problem in which only powder data are available proved to be a powerful means of exploiting the data for locating additional atoms in an objective manner and for refining parameters. The power of the method for cubic crystals is limited, however, by the necessity of terminating the Fourier series so that the powder lines included are largely those containing contributions from only one plane. This requires use of a convergence factor which results in broader atomic peaks and some masking of detail. Even with this cut-off, many lines are included that contain two or three planes. The necessity of apportioning intensity among them is entirely analogous to the necessity of so apportioning it between the real and imaginary part of the structure factor in non-centrosymmetric crystals. As with non-centrosymmetric crystals, this is expected to have the result that a single stage of refinement does not shift the atoms all the way to their correct positions or bring in new atoms to their full intensity; thus, something analogous to the "double shift rule" of Schomaker[10] is applicable. This fact must be considered in extensions of the method to locating additional cations, water molecules and adsorbate molecules.

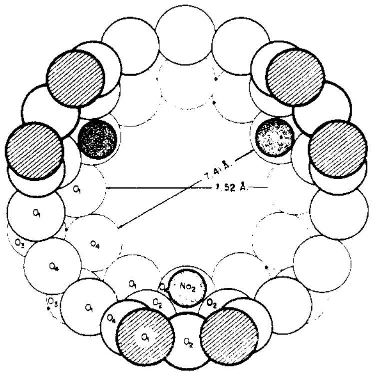

Fig. 7.—Cross-section of 13X adsorption cavity.

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