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The Structures of Zeolite Sorption Complexes.
I. The Structures of Dehydrated Zeolite 5A and its Iodine Sorption Complex*

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(*Received* 10 *January* 1966 *and in revised form* 13 *June* 1966)

The structure of dehydrated synthetic zeolite 5A ($Ca_4Na_4Al_{12}Si_{12}O_{48}$, cubic, $Pm3m$, $a_0 = 12{\cdot}42 \pm 0{\cdot}01$ Å) has been refined by least-squares analysis of X-ray powder diffraction data, and the structure of its sorption complex with nearly six iodine molecules per unit cell ($Ca_4Na_4Al_{12}O_{48}.5.65I_2$, $a_0 = 12{\cdot}29 \pm 0{\cdot}07$ Å) has been determined and similarly refined. In the 'empty' dehydrated zeolite the two kinds of cation appear to have somewhat different positions on the threefold axes, the Ca^{2+} ion being close to the plane of the 6-ring oxygen window of the sodalite unit and the Na^+ ion being displaced about 0·4 Å inward from that position into the sodalite unit. Si, Al–O framework distances are 1·63–1·69 Å. In the iodine sorption complex, the I_2 molecules lie in mirror planes of the framework structure; they are near the large windows and tipped at 32·5° to the window planes. The relative orientations of I_2 molecules could not, however, be completely determined. The I_2 molecules in one unit cell have a maximum possible aggregate point symmetry $\bar{3}$ and the overall structure is presumably disordered. Two different arrangements with point symmetry $\bar{3}$ are possible, and are regarded as more probable than some less symmetrical arrangements. The I_2 interatomic distance uncorrected for thermal motion is 2·72 Å, in fair agreement with the value 2·68 Å reported for solid iodine; the corrected value, 2·79 Å, may be in significant excess of reported values of about 2·67 Å for gaseous I_2 molecules. Each I_2 molecule makes close approaches in its axial direction to a framework oxygen atom and to an iodine atom in an adjacent molecule, with an $I \cdots O$ distance of 3·29 Å and an $I \cdots I$ distance of 3·46 Å. The latter, and a non-axial $I \cdots I$ contact distance of 4·01 Å, compare roughly with analogous distances of 3·54 Å and 4·06 Å in solid iodine.

Introduction

This is one of several papers from this laboratory that will deal with zeolite 'inclusion complexes' or 'sorption complexes'; that is, zeolites containing sorbed molecules of various kinds. The object of work of this kind is to determine the positions of sorbed molecules in relation to the structure of the substrate sorber; *i.e.* the sorption sites on the internal 'surface' of the zeolite pores. In this and the following papers the zeolite is the synthetic type A, selected on account of its relative simplicity of structure, its stability to dehydration, and its capability of sorbing a variety of small molecules. In particular, most of the work will deal with '5A' zeolite, which as a result of partial calcium exchange contains fewer cations than '4A' and consequently has a somewhat greater sorption capability.

The present paper deals with the refinement of the structure of the 'empty' (dehydrated) 5A zeolite and the determination of the positions at which iodine molecules, I_2, are sorbed. A related paper, based on prior work done in this laboratory on a bromine sorption complex of 4A zeolite, is being published elsewhere

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* This work was supported by the Army Research Office (Durham). Computations were carried out in part by the M.I.T. Computation Center.

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(Meier & Shoemaker, 1967). Subsequent papers (Shoemaker & Seff, 1967; Seff & Shoemaker, 1967) will deal with sorption complexes of water, sulfur dioxide, krypton, and xenon.

This work was done in the face of some handicaps that prevent the results from fully meeting such standards of completeness, certainty, and precision as are conventional for single-crystal work. Since single crystals are not available the intensity data had to be collected by the powder method, and accordingly the overdetermination ratio was not high. Use of a diffractometer was precluded by the necessity of sealing the specimens in capillaries. The sorbed molecules are subject to relatively high diffusion mobilities, thermal motions, and statistical disorders. The occupancy parameters for statistically occupied positions are frequently small, making the atoms hard to locate precisely. Despite these handicaps some results of chemical interest have emerged from this work, and will be described in this and the following papers.

Synthetic zeolite A was first made in quantity by the Linde Company (Breck, Eversole, Milton, Reed & Thomas, 1956). Its crystal structure was determined independently by Reed & Breck (1956) and by Broussard & Shoemaker (1960). The limiting 'ideal' composition of zeolite 4A is expressed by the formula (per unit cell) $Na_{12}A.27H_2O$, where A represents the anionic framework of composition $Al_{12}Si_{12}O_{48}^{12-}$ (Barrer & Platt, 1960). The Si/Al ratio may vary upward from unity, the number of sodium (or other univalent) cations being equal to that of the aluminum atoms. Eight sodium ions may be replaced by four calcium ions to give zeolite 5A, which is ideally $Ca_4Na_4A.29H_2O$. Complete exchange with calcium gives $Ca_6A.30H_2O$ (Wells, 1962). Many other cations have been introduced by various workers. (In this and subsequent paper the term 'cation' will refer to exchangeable ions such as Na^+ and Ca^{2+} and will not apply to framework atoms such as Al and Si).

The crystal structure (Fig. 1) may be envisioned as a primitive cubic arrangement of truncated octahedral units of formula $Al_{12}Si_{12}O_{36}$ which we call *sodalite units* because they are a feature of the structure of the mineral sodalite. These units are linked by four 'bridge' oxygen atoms O(1) at each square face to other sodalite units so as to enclose roughly spherical cavities with a mean free diameter of 11·4 Å, interconnected by $(Si,Al)_8O_8$-ring windows having a mean free diameter of 4·2 Å. Alternatively, the structure may be thought of as a simple cubic arrangement of the roughly spherical $(Si,Al)_{48}O_{72}$ cages bounding these cavities (such a cage is shown in Fig. 1) with sharing of eight oxygen and eight silicon-or-aluminum atoms at each 8-ring window, or else a cubic closest packing of such cages (without sharing), linked by oxygen bridges at $(Si,Al)_4O_4$ rings (Fischer & Meier, 1965). The structure

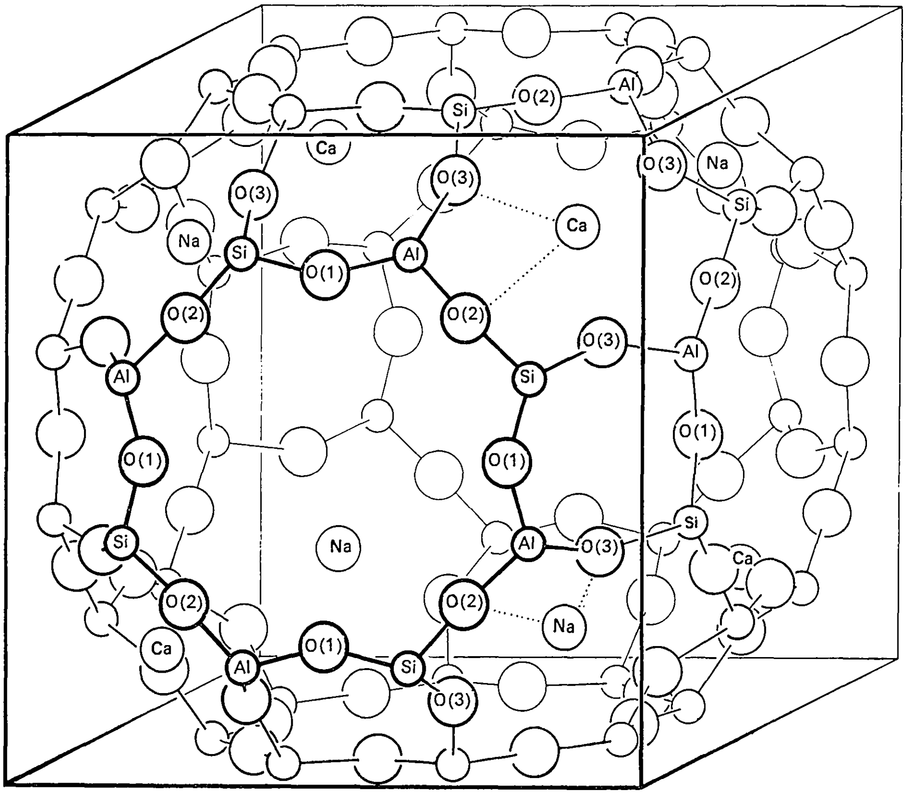

Fig. 1. One unit cell of the crystal structure of fully dehydrated ('empty') 5A zeolite. Sodalite units are centered at the unit-cell corners; a complete one is not shown.

can also be described as an arrangement of small cubes of composition $(Al,Si)_8O_{12}$ linked by oxygen atoms at the corners (Reed & Breck, 1956).

Electron density functions calculated from 4A and 5A powder diagrams have indicated that the most stable cation positions are at or near the centers of the $(Si,Al)_6O_6$-ring windows of the sodalite units. The positions of other cations, if more than eight are present per unit cell, were not known initially, although a position near the middle of the eight-membered oxygen ring has been suggested by Howell (1960) for the dehydrated sodium form of zeolite 4A and is partially supported by work in our laboratory to be described in a forthcoming paper of this series.

Experimental

A sample of 4A powder, kindly furnished by Dr D. W. Breck of the Linde Company, was repeatedly suspended in an excess of roughly 0·1 molar aqueous calcium chloride solution, washed with water, and allowed to dry in room air. Chemical analysis (with Al_2O_3 determined by difference) indicated a Si/Al ratio of 1·00, an Al/(Na+0·5 Ca) ratio of 1·006, and a Ca/Na ratio of 1·77. To bring this last ratio (which corresponds to 7·32 cations per unit cell) down to 1·00, the product was dry-mixed with a calculated amount of zeolite 4A, equilibrated with it in a very dilute solution of sodium and calcium chlorides, then washed and dried in room air. The homogeneity of the resulting product was checked by examination of a (Cu $K\alpha$) powder photograph, which gave sharp lines in the back reflection region corresponding to a cell constant of $a_0 = 12{\cdot}248$ Å, with no evidence of lines corresponding to the cell constant of $a_0 = 12{\cdot}300$ Å for unexchanged 4A. Under the optical microscope the particle size was estimated to be nearly uniform at about 5 microns.

Specimens for Debye–Scherrer powder photography were (except for hydrated 5A at room temperature) prepared with the experimental arrangement shown in Fig. 2. The progress of sorption and desorption could be followed by the McBain balance technique, through observation with a cathetometer of the elongation of the silica spring resulting from changes in weight of a specimen (initially about 250 mg in the hydrated form) in a silica bucket.

If a sample was to be prepared for X-ray diffraction, the umbilical assembly (*H–L*, Fig. 2) to the right of the main tube was initially attached. The powder sample was placed at the closed end (*L*). Seal-off points (*H*,*J*,*K*) were provided for later sample handling, and 0·2 or 0·3 mm diameter soft-glass capillary tubes (*M*) with 0·01 mm wall thickness were fixed in position with hard Apiezon wax. The samples of zeolite (*A*, *L*) were about 1 cm apart in the furnace, with a thermocouple for temperature measurement between them. After bake-out and sorption, the seal-off at *H* was performed, powder was shaken into the capillary tubes (*M*), and seal-offs were made at *J*, *K* and then with a microtorch on the capillary tubes themselves.

For investigation of the empty zeolite, the hydrated material was heated to temperatures as high as 450 °C. No significant weight loss, or change in the diffraction pattern, was observed to result from heating above about 300 °C, and no significant loss of crystallinity was observed up to 450 °C.

The iodine complex of zeolite 5A was prepared as follows. A few grams of 99·99% pure iodine crystals were sealed into a Pyrex tube after gentle heating under vacuum had removed about a quarter of the starting amount of iodine together, presumably, with whatever moisture might have been present. This tube, containing solid iodine at its own vapor pressure, was joined to the vacuum system with an internally breakable seal. The zeolite in the system was dehydrated above 300 °C at 0·01 micron pressure. While the zeolite temperature was maintained at 85 °C, the seal was broken and iodine was introduced into the system. The iodine content of the zeolite was then measured with the spring balance at regular intervals. At 0·3 mm iodine pressure, with the zeolite at 85 °C, 4·8 molecules per unit cell sorbed the first day. The temperature was reduced gradually to 36° in four more days and increased to 50° on the sixth day, by which time 5·65 molecules per unit cell were sorbed. Specimens were then removed for X-ray examination. Desorption was observed upon heating; less than one iodine atom remained per unit cell at 180 °C. The sorption measurements exhibited severe hysteresis, especially at the lower temperatures.

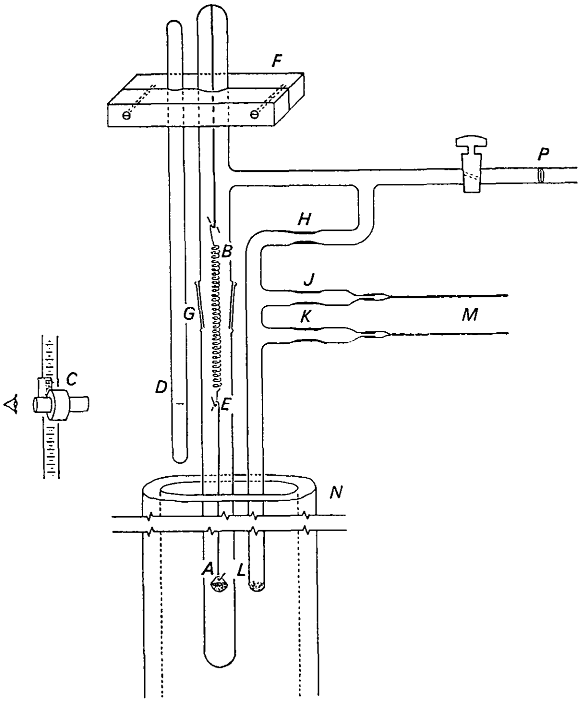

Fig. 2. Apparatus for preparing powder specimens of dehydrated zeolite and its absorption complexes.

A 57·3 mm radius Debye–Scherrer powder X-ray diffraction camera (Norelco), Straumanis arrangement, was used. Line intensities were estimated visually on three superposed films exposed simultaneously to nickel-filtered copper radiation. These data were placed on the same scale by means of film factors obtained with controlled exposures, and were corrected for Lorentz, polarization and absorption effects to yield values for I(obs) referred to in the subsequent text and tables. Beyond a certain point ($N \equiv h^2+k^2+l^2=91$ for the empty zeolite, $=62$ for the sorbate), only lines of observable intensity were recorded.

Weak 'superstructure' lines corresponding to a doubling of the unit cell in each direction, so as to allow ordered alternation of silicon and aluminum (–Al–O–Si–O–Al–) in accordance with Loewenstein's (1954) rule, have usually been observed in A zeolites with Al:Si ratios close to unity (Broussard & Shoemaker, 1960; Barrer & Meier, 1958). The resulting Si, Al superlattice is face-centered cubic, and only lines with superstructure indices all odd are not superimposed by substructure lines. Of these, only those in which all three superstructure indices have different absolute values are allowed by the Si, Al superstructure space group, *Fm*3*c*. Thus, only a few superstructure lines are permitted, and of these the first one, 531 ($\frac{5}{2}\,\frac{3}{2}\,\frac{1}{2}$ in terms of the subcell), is the most prominent in the empty and hydrated zeolite. In the pattern for the iodine sorption complex there is in addition a line of moderate strength which may be indexed as a combination of 975 and 1153, both of which sets satisfy the same superstructure space group. No attempt was made to account for the intensities of these lines quantitatively or to use them in structure refinement.

Lattice constants at room temperature for the materials studied, as determined from the powder photographs, are

Hydrated 5A	12·248 ± 0·003 Å
Empty 5A	12·42 ± 0·01
5A–I_2 complex	12·29 ± 0·07

($\lambda_{\mathrm{Cu}\,K\alpha}=1{\cdot}5418$ Å). The precision of the lattice constant determination for the iodine complex is low owing to the absence of suitable lines in the back-reflection region of the film.

Structure determination, refinement and discussion

The technique of generating three-dimensional Fourier functions with powder diffraction intensities (Broussard & Shoemaker, 1960) was used extensively to locate sorbed-atom positions. The FAP program ERFR2 (Sly, Shoemaker & Van den Hende, 1962) was employed to prepare Fourier maps. Whenever an observed diffraction line was indicially degenerate (*e.g.* 500, 430), the observed intensity was prorated to its components in the intensity ratios given by the calculated intensities for the components. Omission of up to half of the Fourier terms, namely those with the smallest calculated structure factors, was found to be beneficial in revealing atom positions. Difference syntheses were employed in order to reduce series termination effects.

Possible atomic positions found on Fourier maps were then refined by use of LSPOW, a least-squares Fortran II program for structure refinement with powder data, written by one of us (K.S.). This program permits full-matrix refinement of positional coordinates, isotropic thermal parameters, and occupancy parameters for some or all of the atoms, or any desired selection of such parameters. Usually, with the zeolite framework parameters fixed, trial sorbate positions suggested by the Fourier maps were refined individually or in various combinations to determine whether they would converge with reasonable temperature and occupancy factors or else effectively disappear from the structure. In most cases it was not feasible to refine occupancy factors and temperature factors together, owing to their very close correlation. The atomic form factors used were obtained from *International Tables for X-ray Crystallography* (1962). Ionic changes were taken to be one half their nominal values, and appropriate averages were taken. Anomalous dispersion corrections were not included; test calculations showed their effects would be inconsequential in comparison with effects of experimental uncertainties. The function minimized in the refinements was

$$\sum_i w_i[I_i(\mathrm{obs})-I_i(\mathrm{calc})]^2 \qquad (1)$$

where the summation was taken over all observed powder lines. A modified Hughes (1941) weighting scheme was used, with

$$w_i^{1/2}=\frac{1}{I_i(\mathrm{obs})}\,, \qquad I_i(\mathrm{obs}) \geq 2I_{\min}; \qquad (2)$$

$$w_i^{1/2} = \frac{1/\sqrt{2}}{[I_i(\mathrm{obs})I_{\min}]^{\frac{1}{2}}} \left\} \begin{array}{c} 2I_{\min} \geq I_i(\mathrm{obs}) \geq I_{\min}; \\ \text{or} \\ I_i(\mathrm{obs}) < I_{\min} \text{ if } I_i(\mathrm{calc}) > I_{\min}/2;^* \end{array} \right. \qquad (3)$$

$$w^{1/2}=0 \text{ otherwise}; \qquad (4)$$

where $I_{\min}$ is the minimum observable intensity at the particular diffraction angle. The unweighted R index for intensities,

$$R=\frac{\sum_i |I_i(\mathrm{obs})-I_i(\mathrm{calc})|}{\sum_i I_i(\mathrm{obs})}\,, \qquad (5)$$

is based on all powder lines listed in Table 2 or in Table 3, whether of measurable intensity or not; for unobserved reflections I(obs) is set equal to I(min)/2. It is expected to be about twice the magnitude of the more conventional R index based on structure factors.

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* It now appears (Vand & Dunning, 1965) that inclusion of these unobserved reflections in refinement is not good practice. However, this is the procedure actually followed in the work reported here and in subsequent papers, and it is not expected to vitiate the main results.

The values given for standard deviations are those calculated in the usual way from residuals, and may be unrealistically small. An agreement index used to characterize intensity changes accompanying sorption is

$$R' = \frac{\sum_i |\Delta I_i(\text{obs}) - \Delta I_i(\text{calc})|}{\sum_i [I_i^{\text{empty}}(\text{obs}) + I_i^{\text{full}}(\text{obs})]/2} \qquad (6)$$

where

$$\left.\begin{aligned} \Delta I_i(\text{obs}) &= I_i^{\text{full}}(\text{obs}) - I_i^{\text{empty}}(\text{obs}) \\ \Delta I_i(\text{calc}) &= I_i^{\text{full}}(\text{calc}) - I_i^{\text{empty}}(\text{calc}) \end{aligned}\right\} \qquad (7)$$

and where the summation is carried out over all measured powder lines common to both 'empty' and 'full' zeolite.

For calculation of all bond distances and angles, the Fortran II program DISTAN (Shoemaker, 1964) was used; a modification of this program allowed Patterson function peak positions to be calculated.

Dehydrated zeolite 5A

An initial four-cycle refinement of all positional parameters as reported by Broussard & Shoemaker (1960) yielded an intensity R index of 0·28 which decreased to 0·23 when temperature factors were allowed to vary in another series of refinement cycles. An optimal absorption correction of $\mu R = 0{\cdot}4$ (corresponding to a poor packing of the zeolite powder to an apparent density one-third that of a single crystal) was applied. Further positional and thermal refinement lowered R to 0·18. Since it seemed likely that the Na^+ and Ca^{2+} ions would not be in precisely the same positions, and since a Fourier map had indicated an abnormal elongation of the cation electron density peak along the threefold axis, the two kinds of ion (with occupancy factors of $\frac{1}{2}$) were assigned different trial positions along the axis. The R index became 0·16 as the ions refined to an apparent separation of 0·37 Å. The choice of cations to be assigned to the two different positions was that which made the refined temperature factors most nearly equal; this placed the calcium ions the nearer to the plane of near oxygen neighbors.

Alternatively, the elongation of the Fourier peak might be explained in large part by a highly anisotropic temperature factor. Against this is the fact that this elongation, and the apparent positional separation resulting from it, were much more variable among the several complexes studied than an anisotropic temperature factor would be assumed to be, and were insignificant in the case of the iodine complex. However, our model may be oversimplified, since the two positions are on opposite sides of the mean plane $(x+y+z)/3 = 0{\cdot}1870$ of the six-membered oxygen ring, and the possibility of statistical occupancy by both kinds of atom of additional positions on both sides of this plane was not taken into account.

The temperature factors found here are large compared with those usually found. Because of small expected differences between the positions of silicon and aluminum atoms and differences in the sizes of their tetrahedral oxygen environments, as well as the differing effects that the two kinds of cations exert on this framework, it may be expected that these large temperature factors partly represent least-squares adjustments to compensate for occupancies of clusters of near-by positions.

Least-squares refinements and examinations of the final Fourier map of dehydrated 5A indicate that all of the structure has been represented. No evidence of water molecules can be found, and nowhere could residual electron density above background be interpreted as due to a molecule of $NaAlO_2$ as suggested by Barrer & Meier (1958).

Observed and calculated powder intensities are compared in Table 2. The present final parameters and interatomic distances and bond angles are given in Tables 1 and 3 respectively; they compare reasonably well with those previously reported for the hydrated zeolite 5A (Broussard & Shoemaker, 1960) and with those previously reported on the dehydrated zeolite 4A (Howell, 1960), even though these two cases deal with

Table 1. *Positional parameters and apparent isotropic thermal parameters for dehydrated zeolite* 5A *and its iodine sorption complex*[f]

		Dehydrated 5A[d]				Iodine complex[e]			
Atom	Position	x	y	z	B (Å)	x	y	z	B (Å)
Si, Al[a]	24 (k)	0	0·1825 (2)	0·3730 (2)	3·11 (4)	0	0·1830 (4)	0·3698 (3)	0·97 (5)
O(1)	12 (h)	0	0·2136 (5)	$\frac{1}{2}$	7·74 (18)	0	0·2196 (9)	$\frac{1}{2}$	1·00 (50)
O(2)	12 (i)	0	0·2804 (4)	0·2804	8·98 (19)	0	0·2783 (10)	0·2783	11·65 (65)
O(3)	24 (m)	0·1115 (3)	0·1115	0·3380 (4)	8·25 (13)	0·1086 (5)	0·1086	0·3424 (7)	5·43 (25)
Na[b]	8 (g)	0·1598 (8)	0·1598	0·1598	8·08 (47)	0·1919 (5)	0·1919	0·1919	8·82 (33)
Ca[b]	8 (g)	0·1974 (2)	0·1974	0·1974	2·47 (16)				
I(1)[c]	24 (l)					0·1500 (5)	0·4380 (6)	$\frac{1}{2}$	11·61 (45)
I(2)[c]	24 (l)					0·2690 (7)	0·3752 (7)	$\frac{1}{2}$	18·01 (49)

[a] Occupancy $\frac{1}{2}$ for Si, $\frac{1}{2}$ for Al.
[b] Occupancy $\frac{1}{2}$ for Na, $\frac{1}{2}$ for Ca.
[c] Occupancy 0·23, corresponding to 5·5 I_2 molecules per unit cell.
[d] Final shift exceeds σ only in B for Na, where it is 0·81.
[e] Maximum final shifts: 0·11 in B, 0002 in positional parameters.
[f] Standard deviations are given in parentheses.

materials differing in some respects from the dehydrated zeolite reported here. The mean Si, Al–O distance of 1·67 Å compares with the value 1·68 Å given by Smith & Bailey (1963) for type A zeolite with a Si/Al ratio of unity.

Table 2. *Calculated and observed intensities* (×0·001) *for dehydrated zeolie* 5A

	Intensity			Intensity	
N†	Calc.	Obs.	*N*	Calc.	Obs.
1	271	316	51	44	21
2	107	76	52	15	7*
3	182	126	53	286	298
4	12	10	54	65	39
5	203	175	56	28	8*
6	9	26	57	112	97
8	56	39	58	9	9*
9	202	273	59	227	270
10	0	9	61	286	343
11	226	193	62	4	11*
12	12	6	64	26	12*
13	12	5	65	51	40
14	398	496	66	59	41
16	1	0*	67	2	13*
17	390	413	68	13	14*
18	74	64	69	95	83
19	29	35	70	29	44
20	46	59	72	148	121
21	64	58	73	17	16*
22	474	531	74	245	240
24	16	29	75	152	155
25	165	132	76	8	18*
26	21	26	77	442	454
27	154	169	78	2	19*
29	19	12	80	3	20*
30	23	22	81	97	59
32	99	130	82	530	615
33	109	118	83	13	22*
34	94	83	84	23	23*
35	75	75	85	41	23*
36	273	307	86	266	287
37	33	20	88	25	25*
38	5	3*	89	44	58
40	17	4*	90	177	157
41	178	186	91	57	27*
42	165	179	96	69	130
43	8	4*	97	139	131
44	2	5*	99	87	85
45	67	60	101	198	202
46	5	5*	121	109	107
48	3	6*	137	241	206
49	0	6*	146	207	195
50	532	609			

* Unobserved intensities, taken as $I_{min}/2$.

† $N=h^2+k^2+l^2$.

The iodine complex

It had been determined by Barrer & Wasilewski (1961) and by Meier & Shoemaker (1966) that about five to five and a half molecules of iodine or bromine could be sorbed per unit cell of zeolite A at or near room temperature. The present sorption measurements for iodine indicate that 5·65 molecules or 11·3 atoms were sorbed per unit cell.

A Patterson function map was generated, the strongest peaks on which were explained by interactions of silicon-aluminum atoms with each other. New peaks were neither strong nor particularly suggestive of an iodine position. It appeared that iodine atoms were in positions of low occupancy. The structure of this complex was solved, with some difficulty, by the methods mentioned earlier. Once the iodine molecules were located, repeated attempts to distinguish between sodium and calcium positions along the threefold axis failed, as did attempts to find positions off the axis. Final refinements left the intensity R index at 0·173 as an oxygen temperature factor which tended to become slightly negative was held fixed at 1·00. Observed and calculated intensities are compared in Table 3; parameters and interatomic distances and angles are given in Tables 1 and 4. The differences ΔI_{obs} and ΔI_{calc} [equations (7)] correlate well in both magnitude and sign, and the value of 0·238 for R' [equation (6)] is regarded as satisfactory.

During the refinement the framework parameters were allowed to vary. The resulting parameters changed by at most 0·003 for Si, Al and 0·006 for oxygen; the mean Si, Al–O distance apparently decreased to 1·64 Å, an insignificant change. The mean cation parameter changed from 0·1786 to 0·1919 accompanying sorption, corresponding to a shift of 0·28 Å, possibly due to polarization of the sorbed molecules by the cations.

Table 3. *Calculated and observed intensities* (×0·001) *for the iodine sorption complex of zeolite* 5A

	Intensity			Intensity	
N	Calc.	Obs.	*N*	Calc.	Obs.
1	49	50	40	15	57
2	16	5	41	566	762
3	7	12	42	323	376
4	38	48	43	9	11*
5	92	51	44	0	100
6	429	415	45	42	12*
8	191	118	46	24	13*
9	1219	1163	48	3	14*
10	137	100	49	87	93
11	325	353	50	757	981
12	77	86	51	9	16*
13	92	100	52	0	17*
14	546	517	53	435	520
16	28	20	54	45	18*
17	680	650	56	14	20*
18	281	323	57	102	117
19	23	33	58	14	21*
20	150	106	59	570	548
21	277	230	61	475	568
22	47	57	62	15	25*
24	13	37	69	85	175
25	69	91	74	225	299
26	12	4*	75	157	129
27	433	467	77	583	598
29	15	5*	81	138	115
30	22	58	82	882	867
32	14	37	86	436	586
33	135	222	90	291	245
34	114	75	96	251	227
35	123	150	97	320	229
36	465	501	137	480	426
37	6	8*	146	424	346
38	72	50			

* Unobserved intensities, taken as $I_{min}/2$.

Table 4. *Interatomic distances* (Å) *and angles* (°) *for dehydrated zeolite* 5A *and its iodine sorption complex*

Dehydrated 5A		Iodine complex	
Si,Al-O(1)	1·63	Si,Al—O(1)	1·65
Si,Al-O(2)	1·68	Si,Al—O(2)	1·63
Si,Al-O(3)	1·69	Si,Al—O(3)	1·65
Ca—O(3)	2·32	Ca,Na-O(3)	2·36
Ca—O(2)	2·84	Ca,Na-O(2)	2·82
Na—O(3)	2·33	I(1)—I(2)*	2·72
Na—O(2)	2·86	I(1)—O(1)	3·29
		I(2)—I(2)	3·46
		O(2)—I(1)	3·80
O(1)-Si,Al-O(2)	120	O(1)—I(2)	3·84
O(1)-Si,Al-O(3)	111	O(1)—I(1)	4·01
O(2)-Si,Al-O(3)	102	I(1)—I(2)	4·01
O(3)-Si,Al-O(3)	110		
		O(1)-Si,Al-O(2)	117
		O(1)-Si,Al-O(3)	110
		O(2)-Si,Al-O(3)	106
		O(3)-Si,Al-O(3)	107
		I(2)—I(1)—O(1)	178
		I(2)—I(2)—I(2)†	120
		I(2)—I(2)—I(2)‡	60

* I_2 bond distance.
† First model, Fig. 4(*a*).
‡ Second model, Fig. 4(*b*).

A similar (though smaller) change was observed in the bromine complex of 4A (Meier & Shoemaker, 1967).

Iodine atoms were found to one-quarter fill two 24-fold positions (Fig. 3). These positions are interpreted to give 24 molecular sites which are occupied statistically by six I_2 molecules having an I–I distance of 2·72±0·02 Å. (The nearest alternate bond length would be 1·65 Å, which is far too short.) By comparison, a value of 2·68 Å is given for the I–I distance in solid iodine (Kitaigorodskii, Khocianova & Stručkov, 1953). For purposes of comparing with precise gas-phase values it would be preferable to cite a distance corrected for thermal libration, and/or static disorder of atomic positions over clusters of neighboring sites caused by variations in molecular packing. If it is assumed (roughly) that either or both such situations are described realistically by the very large values found for the iodine isotropic temperature factors, a corrected value of 2·79 Å is obtained for the distance in the I_2–zeolite complex. The values reported for molecules in the gas phase are 2·662 Å by electron diffraction (Karle, 1955) and 2·667 Å by spectroscopy (Rank & Baldwin, 1951). The excess of the corrected distance in the zeolite complex over the gas phase values is possibly significant, and may result from the charge-transfer interactions described below. With thermal correction the distance in crystalline I_2 may also be significantly longer than that for the gas phase.

The I_2 molecule is tipped at 32·5° to the plane of the 8-ring oxygen window. The closest approach of an iodine atom to a framework atom is that of I(1) to O(1). Furthermore, the axis of the I_2 molecule points directly to that oxygen atom to well within the accuracy of this determination. Such an effect has been observed in complexes between diatomic halogen molecules and organic molecules (Hassel & Rømming, 1962). This can be understood in terms of some degree of electron pair donation ('charge transfer') from the electronegative O(1) ion, the only crystallographic kind of oxygen not near a cation position, toward the axially electropositive region on the iodine molecule with its vacant 5*p* σ anti-bonding molecular orbital. Such charge transfer would be in agreement with the lengthened iodine molecular bond that these results suggest. The nearest approach distance of I(1) to O(1) is 3·29 ±0·02 Å; from accepted values of non-bonded van der Waals radii the normal non-bonded approach distance is predicted to be 3·55±0·15 Å. That it is significantly less is also in agreement with the hypothesis of some degree of charge transfer bonding. Also in support of charge transfer bonding is the color of the sorbate complex, which is brown rather than violet.

Several arrangements of iodine molecules among the twenty-four sites are possible. Two 'most symmetrical' arrangements of iodine molecules are possible, both of which have point symmetry $\bar{3}$ in one unit cell (Fig. 4), and it is difficult to decide that one model is more likely than the other. All the values for distances and angles given (Table 4) apply to both suggested structures except where indicated. Both models exhibit the same close intermolecular approach distances of 3·46 and 4·01 Å, which compare well with values of 3·54 and 4·06 Å found in solid iodine (Kitaigordskii *et al.*, 1953). One of the two $\bar{3}$ arrangements can be taken into the other by applying a 180° rotation operation to each molecule about the fourfold crystal axis that passes through the middle of the eight-oxygen ring nearest that molecule and intersects the iodine bond. If this operation is performed on fewer than all six molecules in the cage, several different and perhaps less probable arrangements with lower symmetry and different (but not unreasonable) interatomic distances are generated.

Additional parallels can be drawn between these arrangements and the arrangement in solid iodine.

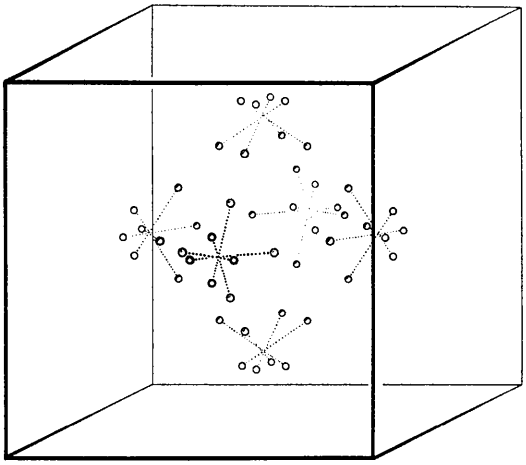
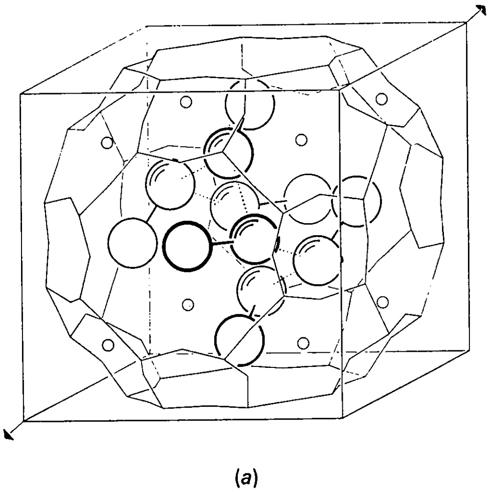


Fig. 3. The 'crystallographic solution' of the iodine sorbate structure in terms of partially occupied positions.

Both here and in the iodine crystal structure, the interaction of an individual iodine molecule with a neighboring atom or molecule that has the shortest interatomic distance is along the direction of the molecular bond, from the positive region previously mentioned on one molecule toward a region of residual negative charge on the other. In the zeolite this negatively charged region is an O(1) atom. In the iodine crystal, it is a 'side' (*i.e.* off-axis) region of an iodine atom; this also occurs in the $\bar{3}$ models of the zeolite complex. A longer distance both in iodine and in the $\bar{3}$ complexes is found between two such 'sides' on a line roughly perpendicular to the molecular axis of each participating molecule.

Another problem having no ready solution is that of the relative orientations of the iodine molecules in adjacent unit cells. The two iodine molecules on opposite sides of an 8-ring window may be parallel, or coplanar but not parallel, or skew. The closest approach distance through the large windows would be between I(1) atoms in all cases, and would be 4·02, 3·72, or 3·87 Å for the three respective orientations. Of these the first appears the most reasonable, although all are possible distances. The powder data give no clue, such as powder-line splittings (to indicate deviation from overall cubic symmetry) or additional superstructure lines (besides those allowed by the Si,Al superstructure space group *Fm*3*c*) to support any of several possible ordered cell-to-cell arrangements of I_2 molecules. Probably no true long-range order exists so far as the iodine molecules are concerned.


(*a*)

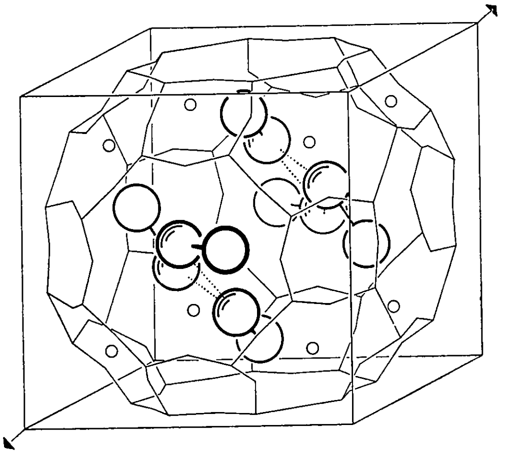

(*b*)

Fig. 4. The 'most symmetrical' I_2 arrangements of point symmetry $\bar{3}$ in one unit cell. The atoms with shading are I(2); those without are I(1).

The structure of the iodine complex of 5A differs markedly from that obtained for the bromine complex of 4A (Meier & Shoemaker, 1967). In the latter, the bromine atom positions are not fixed with sufficient precision to permit definite interpretations of interatomic distances, but it appears that Br–O distances of much less than 4·0 Å are very improbable and that charge transfer bonding therefore plays a much less important role. As in the present case, there are a number of possible arrangements of bromine molecules in the unit cell that cannot be resolved with the powder data, and considerable disorder is possible.

It has been found that unsaturated hydrocarbons are held more tenaciously by the zeolite than are saturated ones, and are often selectively sorbed over their saturated counterparts. It could be guessed that the increased residual positive character of hydrogen atoms on these molecules would allow more energetic interactions with framework oxygen atoms, particularly the bridge oxygen O(1). At a pressure of 500 mm and a temperature of 25 °C, between five and six molecules of acetylene are sorbed per cell (Hersh, 1961), a fact which suggests a similarity between this structure and that of the iodine complex, with hydrogen bonding playing a role. With transition metal cations, π bonding may be expected to play an important role (Yates, 1965).

We gratefully acknowledge the financial support of the Army Research Office (Durham), and use of the facilities of the M.I.T. Computation Center. We thank Dr D.W. Breck of the Linde Company for the 4A zeolite used, and Dr Leo Broussard and Dr Harry Robson of the Esso Research Laboratories for structural and cation exchange information and valuable discussions.

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Mean-Square Atomic Displacements in Zinc

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(*Received* 22 *July* 1966)

The mean-square atomic displacements $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ are calculated in the range 0–600°K from thermodynamic and inelastic neutron-scattering data. Thermodynamic data alone give $\langle 2u_x^2+u_z^2\rangle$, which is separated into its components $2\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ with the aid of the lattice-dynamical model of DeWames, Wolfram & Lehman and the neutron-diffraction data on which it is based. Earlier values derived from the Debye–Waller effect in X-ray scattering are discussed briefly.

Introduction

For a hexagonal close-packed structure, the intensity of a Bragg reflexion varies as $\exp(-2M)$, with

$$M=8\pi^2(\sin\theta/\lambda)^2[\langle u_x^2\rangle\sin^2\psi+\langle u_z^2\rangle\cos^2\psi]\;;\qquad(1)$$

here θ is the Bragg angle, λ is the wavelength of the radiation, $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ are the mean-square atomic displacements in directions parallel and perpendicular to the hexagonal axis,* and ψ is the angle between the hexagonal axis and the normal to the reflecting plane (Zener, 1963; Blackman, 1956). Table 1 lists various published values of $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ for zinc, derived mainly from X-ray data. Although there is fair agreement between some of the measurements, they do not provide definitive values for $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ and their likely errors. In this paper we use thermodynamic and inelastic neutron-scattering data to derive such definitive values for $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$.

Use of thermodynamic data

From thermodynamic data we can calculate the total mean-square amplitude $\langle 2u_x^2+u_z^2\rangle$ as a function of both temperature and strain, without recourse to any force-constant model (Feldman & Horton, 1963; Salter, 1965; for a simple review see Barron, Leadbetter, Morrison & Salter, 1966). $\langle 2u_x^2+u_z^2\rangle$ is conveniently represented by an equivalent Debye temperature $\Theta^M(T;a,c)$; this is defined as the characteristic temperature of that Debye distribution which gives the actual value of $\langle 2u_x^2+u_z^2\rangle$ at temperature T and lattice parameters a,c. Comprehensive tables relating $\langle u_x^2+u_y^2+u_z^2\rangle$ and Θ^M are available (Benson & Gill, 1966). From the results of an analysis of the heat capacity of zinc (Barron & Munn, 1966) we find that the low- and high-temperature expansions (Salter, 1965) for $\Theta^M(T;a_0,c_0)$ are respectively

$$\Theta^M(T;a_0,c_0)=221[1+0{\cdot}93(T/100)^2-3{\cdot}6(T/100)^4+\ldots]\,,\qquad(2)$$

and

$$\Theta^M(T;a_0,c_0)=224{\cdot}5[1+0{\cdot}0026(100/T)^4-0{\cdot}0012(100/T)^6+\ldots]\,,\qquad(3)$$

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* Maradudin & Flinn (1963) have shown that for an anharmonic crystal the Debye–Waller factors do not depend only on the mean-square atomic displacements, so that equation (1) is ideally not strictly true. However, their calculations indicate that this effect is normally negligible.