ess, and the direct application of Eqs. 4 and 3 can be misleading.

That sorption of anesthetics at aqueous interfaces is large and important at the partial pressures effective in anesthesia has been demonstrated by the measurements of Clements and Wilson (22).

Since all of the accepted theories of gaseous anesthetics involve in some way molecular polarizabilities and molecular sizes, the electrostatic "adsorption" theory simplifies the situation by eliminating the necessity of "hydrate" or other aggregate formations.

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Clathrate Structure of Silicon Na₈Si₄₆ and NaₓSi₁₃₆ (x < 11)

Abstract. The crystal structure of two new cubic phases in the silicon-sodium system have been solved from their x-ray diffraction patterns. Both structures are of the clathrate type found for gas hydrates, consisting of tetrahedral networks which are combinations of pentagonal dodecahedra with 14-face polyhedra in one case and with 16-face polyhedra in the other case. There is strict correspondence between the silicon positions and the oxygen positions of the hydrate structures. For one compound, Na₈Si₁₆, the centers of all polyhedra are occupied by sodium atoms. For the other compound, there occurs only partial occupancy of the polyhedral cages.

Two new phases (1) in the silicon-sodium system have recently been prepared, isolated, and characterized by means of chemical analysis, density, and Debye-Scherrer x-ray diffraction patterns. One of the phases could be described quite well by the formula NaSi₆ and a simple cubic unit cell with *a* equal to 10.1 ± 0.02 Å containing eight formula weights. The other phase was nonstoichiometric and corresponded to the formula NaₓSi with $0.02 < x < 0.08$. This phase, too, is cubic with *a* equal to 14.62 ± 0.02 Å but of higher symmetry with the space group *Fd3m*. The lattice parameter (but not the intensity of a given reflection) was independent of the sodium content. The number of silicon atoms per unit cell was reported to be 132.

We now report that we have deduced the crystal structures of both phases from the diffraction patterns and the other information reported by Cros *et al.* (1). Both structures are of the clathrate type found for gas hydrates (2–4) in which there are tetrahedral networks of oxygen positions occurring as pentagonal dodecahedra combined with 14-face polyhedra in one case and 16-face polyhedra in the other. The two silicon structures correspond to the two most common examples of gas hydrate structures for which the respective numbers of atoms per unit cell in the tetrahedral network are 46

and 136. The sodium atoms occur in the centers of the polyhedral cages just as the "guest" molecules do in the hydrate structures.

For Na₈Si₄₆

> Cubic, $a = 10.19 \pm 0.02$ Å
> Space group *Pm3n*
> 6 Si₁ in 6(c) ¼0½
> 16 Si₂ in 16(i) xxx, $x = 0.183$
> 24 Si₃ in 24(k) oyz, $y = 0.310$, $z = 0.116$
> 2 Na₁ in 2(a) ooo
> 6 Na₂ in 6(d) ¼½0
> Calculated density = 2.316 g/cm³
> Observed density = 2.27 g/cm³

This structure is the analog of the hydrate structures 46 H₂O·8M. The most precise and detailed account of this structure type (2) is for the case where M equals Cl₂. Accordingly, we have used the parameters given for chlorine hydrate, which are the values that produce essentially equal Si—Si distances. We have assumed also that all the centers of silicon cages are filled with sodium to give close agreement with the reported silicon-to-sodium ratio (46/8 = 5¾, ~ 6).

The intensities calculated for the proposed structure are given in Table 1 along with the observed values reported (1). Only Lorentz-polarization corrections, multiplicity factors, and a normalization factor have been applied to the calculated F^2 values which include a temperature factor with $B = 1$ Å². The excellent agreement for intensities (Table 1) substantiates the correctness of the assumed model and indicates little if any need for refinement of structural parameters.

Each silicon atom forms four bonds of 2.37 Å to other silicon atoms in a distorted tetrahedral arrangement. The bond distance in ordinary silicon is 2.35 Å. The sodium atom in the smaller cage (Na₁) is 3.23 Å from eight of the silicons and 3.37 Å from 12 others. In the larger cage Na₂ is 3.41 Å from 12 silicons, 3.79 Å from eight others, and 3.60 Å from four others. The sodium-silicon distances are all much too large for any appreciable direct bonding by sodium atoms. It would appear then that the Na atoms are essentially uncharged.

For NaₓSi₁₃₆

> Cubic, $a = 14.62 \pm 0.02$ Å
> Space group *Fd3m*
> Atomic positions: (ooo, ½½o, ½o½, o½½) +
> 8 Si₁ in (a) ooo, ¼¼¼
> 32 Si₂ in (e) xxx; $x = -0.094$
> 96 Si₃ in (g) xxz, $x = -0.058$, $z = -0.246$
> 8α Na₁ in (b) ½½½, ¾¾¾
> 16β Na₂ in (c) ⅛⅛⅛

where α and β are independent fractional numbers, with which the partial occupancy of sites (b) and (c) is conveniently described.

	Density (g/cm³)	
x	Calcd.	Obs.
10.9 (Na$_{0.08}$Si)	2.16	2.115
2.7 (Na$_{0.02}$Si)	2.06	2.036

The analog for this structure is the gas hydrate 8M·136 H$_2$O (3).

Three different compositions (Na$_{0.02}$Si, Na$_{0.07}$, and Na$_{0.08}$Si) were prepared by Cros et al. (1). For all three of them only partial occupancy of the cages occurs since full occupancy would require $x = 24$ or Na$_{0.175}$Si. The distribution of Na in the two kinds of cages then needs to be considered as a parameter for the intensity calculations. A further complication in testing the appropriateness of this structure is that the reported structural parameters for the hydrate counterpart do not seem to be quite satisfactory. By trial and error we have found the parameters above give better intensity agreement for Na$_x$Si and pro-

Table 1. Calculated and observed intensities for NaSi$_6$.

hkl	I_{calcd}	I_{obs}
110	4	7
200	2	4
210	19	25
211	12	12
220	0.05	0
310	2	3.5
222	33	32
320	33	35
321	[100]	100
400	9	8
410	22	22
411, 330	12	15
420	2	2
421	6	12
332	3	4
422	1	1
430	3	3
510, 431	2	1.5
520, 432	9	7
521	0.003	0
440	1	0
530, 433	54	50
531	18	15
600, 442	21	18
610	4	4
611, 532	43	38
620	7	8
621, 540	6	6
541	1	1
622	0.1	0

vide more nearly equal Si—Si distances.

Clearly, the structural situation is more complex here than for the "NaSi$_6$" phase and needs to be more thoroughly investigated. A parameter refinement by means of least squares fitting has not been made. We have calculated the intensities (Table 2) for the one composition Na$_{9.5}$Si$_{136}$ or Na$_{0.07}$Si with the parameters given above and with the following distribution of Na in the two available sites:

6.34 in 8 (b); $\alpha = 0.79$
3.17 in 16 (c); $\beta = 0.19$.

An exploration by trial and error indicates the preference (although not exclusively) for the larger 8(b) sites. The present assignment should be considered only a fair approximation. Accordingly, it should be possible to improve on the intensity agreement of Table 2. Nonetheless, the present agreement appears sufficiently good to establish the essential correctness of the proposed structure. Again the calculated intensities contain Lorentz-polarization and multiplicity factors as well as a temperature factor corresponding to $B = 1$ Å², and they are normalized to the strongest observed reflection.

The four different Si—Si interatomic distances are: 2.30, 2.34, 2.38, and 2.40 Å. These distances are not accurately known at this stage and possibly may turn out to be equal; they are not significantly different from the values in ordinary silicon. In the larger cage Na$_1$ is 3.98 and 3.99 Å from silicon; Na$_2$ separations from silicons of the smaller cage are 3.17, 3.25, and 3.32 Å. As for the other phase, here too the Na appears to be essentially neutral.

The remarkable chemical properties of both phases are understandable on the basis of the clathrate structures. Despite the appreciable sodium content both phases are quite unreactive in contrast to the great chemical reactivity of NaSi. As remarked (1), the chemical properties of the clathrate structures are similar to those of ordinary silicon. In particular, both phases are not attacked even by strong acids except for HF, which reacts with silicon also.

It is noteworthy that the Na$_8$Si$_{46}$ structure is closely analogous also to that of a form of SiO$_2$, melanophlogite (5). The latter example along with the two sodium-silicon structures would

Table 2. Calculated and observed intensities for Na$_{0.07}$Si.

hkl	I_{calcd}	I_{obs}
111	9	10
220	22	30
311	43	51
222	35	45
400	21	24
331	15	16
422	32	26
511, 333	74	65
440	32	24
531	60	67
442	5	0
620	8	9
533	8	8
622	0.4	0
444	0.001	0
711, 551	7	8
642	2	0
731, 553	7	11
800	1	0
733	35	34
644	1	0
822, 660	[100]	100
751, 555	27	34
662	1	0
840	4	5
911, 753, 842	22	27

suggest the possibility of further occurrences of clathrate-type structures, based on the hydrate analogs, for other substances normally occurring in more conventional tetrahedrally linked frameworks.

While the analogy between the clathrate structures of sodium-silicon, SiO$_2$, and the hydrates is quite appropriate, it is to be noted that the two structures reported here represent the first instances of a metal, rather than a chemical molecule, in the role of the guest substance in the cages of the tetrahedral network.

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