

The Structon Theory, Applied to Hydrated Silicates

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The structures of hydrated silicates are considered from the standpoint of the structon theory, with particular reference to the classification of hydrogen bonds and their bridgehead atoms. As specific examples the structures of hydrates of the compositions $\text{Na}_2(\text{H}_2\text{SiO}_4) \cdot n\text{H}_2\text{O}$ (previously analyzed by Jamieson & Glasser and by Jost & Hilmer) and $\text{Ca}_3(\text{HSiO}_4)_2 \cdot 2\text{H}_2\text{O}$ (analyzed by Megaw) are considered.

Introduction

The author's crystallographic career has been greatly influenced by Sir Lawrence Bragg. It was the famous book on *X-rays and Crystal Structure* (Bragg & Bragg, 1918) that inspired him to extend Lewis's (1916) theory of valence and molecular structure to crystals. He was able to deduce the pattern of electron-pair bonds in many crystals (Huggins, 1922a) and to arrive at the atomic distributions in many others, e.g. quartz (Huggins, 1922b) and marcasite (Huggins, 1922c), for which they were previously unknown.

W.L. Bragg's paper (Bragg, 1920) on the approximate constancy of atomic sizes led the author to deduce sets of atomic radii for use when atoms are held together by electron-pair bonds (Huggins, 1922d, 1926; Pauling & Huggins, 1934).

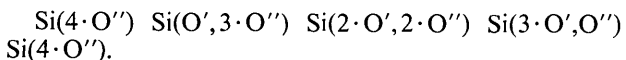
The 'Huggins masks' for two-dimensional Fourier synthesis by photographic means (Huggins, 1941) were based on theoretical ideas, previously tested optically, by Bragg (1929).

The author's recent applications of the 'structon' theory to silicates and related substances (Huggins, 1968) were greatly aided by *Crystal Structure of Minerals* (Bragg & Claringbull, 1965).

The structon theory

The structon theory (Huggins, 1954) is concerned with types of close-neighbor arrangements around atoms, the relative stabilities and relative numbers of these types, and relationships between the types and structure, on the one hand, and properties on the other hand. The theory is justified by the fact that the interactions between close neighbors are far more important than those between more distant atoms and by the fact that the theory leads to predictions in agreement with experimental observations.

The silicon structon types present in the anions of silicates are those represented by the following structon formulas (Huggins, 1968):



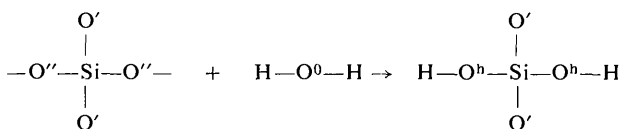
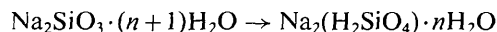
Single and double primes are used to distinguish between oxygen atoms that are bonded to one and to two silicon atoms respectively.

In comparing different substances it is useful to normalize the formula, so as to indicate just one atom of silicon or a similar element. Then, either from established structural principles or from crystal structure analysis studies, one can usually deduce the types and relative numbers of structons present and the magnitudes of certain other important functions such as the charge density and degree of reticulation. Many illustrations of this have been given elsewhere (Huggins, 1968).

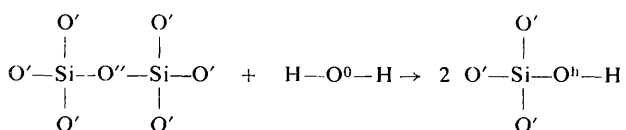
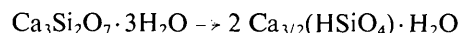
Silicate hydrates

The present paper is concerned with silicates containing some hydrogen. These are often termed 'hydrates', although they frequently contain no H_2O groups. In the formation of many substances greater stability is achieved by reaction of the water molecules with bridging oxygen atoms to give hydroxyl groups.

Because of such reactions, crystals having overall formulas of hydrated metasilicates do not have metasilicate-type structures, but, instead, have $\text{H}_2\text{SiO}_4^{2-}$ groups:



Likewise, crystals having formulas suggesting that they are hydrates of compounds with $\text{Si}_2\text{O}_7^{2-}$ groups do not contain such groups, but, rather, HSiO_4^{3-} ions:



As examples, some structures of these two classes, for which precise structure data have been published by Jamieson & Glasser (1966, 1967), Jost & Hilmer (1966) and Megaw (1952), will be dealt with. In these examples there are water molecules, H₂O groups, in

addition to those that can be considered to have reacted in the manner just indicated.

As expected, the hydrogen atoms of the OH and H₂O groups all form bridges to other oxygen atoms. These bridges are of several types, differing in the attach-

Table 1. *Structon compositions*

	Coord. no.	n=4		Na ₂ (H ₂ SiO ₄)·nH ₂ O n=5		n=8		Ca _{3/2} (HSiO ₄)·H ₂ O	
		No.	c ₀	No.	c ₀	No.	c ₀	No.	c ₀
Si(2·O', 2·O ^h)	4	1		1		1			
Si(3·O', O ^h)	4							1	
O'(Si, 4·H)	5	1	0	2	0	2	0		
O'(Si, 3·H, ··Na)	5	1	-0.05						
O'(Si, 2·H, ··Ca)	4							1	-0.21
O'(Si, 3·Ca)	4							2	-0.14
O ^h (Si, H·, 2·H)	4	1	+0.25			2	+0.25		
O ^h (Si, H·, 2·Na)	4	1	+0.15	1	+0.08				
O ^h (Si, H·, ··H, ··Na)	4			1	+0.17				
O ^h (Si, H·, ··H, ··Ca)	4							½	+0.29
O ^h (Si, H·, 2·Ca)	4							½	+0.32
O ⁰ (2H·, ··H, ··Na)	4	1	-0.05	1	+0.08	2	-0.08		
O ⁰ (2H·, 2·Na)	4	3	-0.10	3	-0.17	4	-0.17		
O ⁰ (2H·, ··H, 2·Na)	5			1	+0.08				
O ⁰ (2H·, 2·H, ··Na)	5								
O ⁰ (2H·, ··H, 2·Ca)	5					2	+0.17		
O ⁰ (2H·, 2·Ca)	4							½	+0.32
H(O ^h , ··O')	2	2		2				½	+0.07
H(O ^h , ··O ⁰)	2							1	
H(O ⁰ , ··O')	2	5		6		2			
H(O ⁰ , ··O ^h)	2	2		1		4		½	
H(O ⁰ , ··O ⁰)	2	1		3		4		½	
Na(··O', ··O ^h , 3·O ⁰)	5	1							
Na(··O ^h , 4·O ⁰)	5	1							
Na(3·O ^h , 3·O ⁰)	6			1					
Na(6·O ⁰)	6			1		2			
Ca(6·O', ··O ⁰)	7							½	
Ca(4·O', 2·O ^h , ··O ⁰)	7							½	
Ca(4·O', ··O ^h , 2·O ⁰)	7							½	

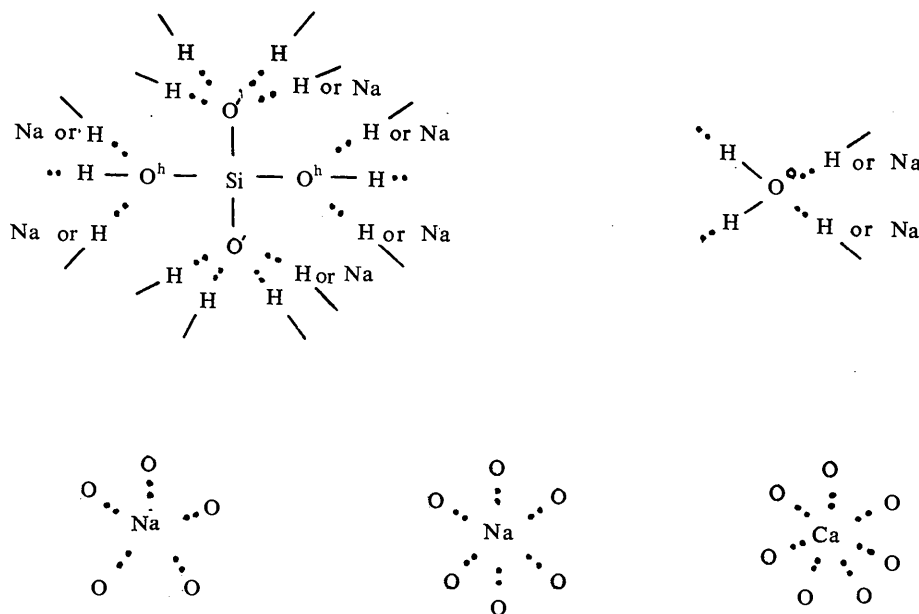


Fig. 1. Atomic environments.

ments, to other atoms, of the bridgehead oxygen atoms. The strong end of the bridge may be of either of the two types designated O^h and O^0 . The weak end may be O^h , O^0 or O' .

In comparing the relative stabilities and polarities of different hydrogen bonds it is necessary to classify the bridgehead oxygen atoms still further, considering, for each bridgehead, in what other hydrogen bridges it is involved and what cation neighbors it has.

Hydrogen bonds differ with regard to their strength or stability and with regard to their dissymmetry or polarity. These differences are related to differences in the potential energy curves along the line between the bridgehead atom centers (Huggins, 1936*a*).

It is obviously useful to classify bridgehead atoms on the basis of their effective negative charges. A classification of this sort was published many years ago (Huggins, 1936*b*). For present purposes, an attempt has been made to obtain semiquantitative values of the effective net charges. The procedure is similar to that used in applying Pauling's (1939) electrostatic valence rule — which is a corollary of the general principle that a structure tends to achieve local neutrality. To the oxide ion charge of -2 units, one adds the charge-divided-by-coordination-number contributions of all the neighboring atoms except the hydrogen bond hydrogen atoms, and then (tentatively) $\frac{3}{4}$ for each close hydrogen atom and $\frac{1}{4}$ for each distant hydrogen atom of a bridge:

$$c_o = -2 + \sum \frac{v_M}{Z_M} + \frac{3}{4}N_{H..} + \frac{1}{4}N_{..H}$$

For local neutrality the effective nuclear charge should be zero. Actually, geometric limitations on the structure, plus inaccuracies in the calculation, usually lead to finite, but small, values for c_o .

A list of the structon types for any substance must satisfy these requirements:

(1) The total number of structons for each element must conform to the overall formula.

(2) For each pair of types of atoms, the number of contacts that the first type makes with the second must equal the number of contacts that the second makes with the first.

$$N_{Si(O')} = N_{O'(Si)}, \text{ etc.}$$

(3) The sum of the effective net charges on the oxygen atoms must equal zero:

$$c_o = 0$$

Table I lists the structon types present in the hydrates chosen as examples, with the numbers of each type, the coordination numbers of the atoms, and (for the oxygen atoms) the calculated effective net charges. There are several things worthy of note:

(1) In agreement with what has already been stated about the usual noncoexistence of bridging oxygen atoms and water molecules, all of the oxygen atoms are of the O^h , O' and O^0 types.

(2) All hydrogen atoms bridge between two oxygen atoms, the bridges being unsymmetrical, judging from

the O-to-O distances. In one case, one O-to-O distance is so long that by some criteria it would not be considered as indicating a hydrogen bond, but the hydrogen atom concerned (part of a water molecule) is obviously doing its best to form a bridge, and for this purpose it seems reasonable to count this O-H...O system as one.

(3) The effective net charges on the oxygen atoms, computed as described, are all small — about three-tenths of a charge unit or less.

(4) In order to achieve this result, the oxygen atoms all have either four or five neighbors, counting silicon atoms, close and distant hydrogen atoms of hydrogen bridges, and cations of sodium or calcium. With four neighbors, suitably oriented, it might be considered that one pair of valence electrons is associated with each contact, but with five this is impossible. The attraction between an oxygen and a sodium ion, a calcium ion, or a distant hydrogen atom of a hydrogen bridge is almost entirely coulombic.

(5) The preferred bridgehead atom for the weak end of a hydrogen bridge is an oxygen atom of the non-bridging (O') type. In the sodium compounds, this forces the contacts of the sodium ions to be largely to water oxygen atoms (O^0) and hydroxyl oxygen atoms (O^h). Calcium ions, however, also have a much stronger attraction for O' oxygen atoms than for O^h or O^0 oxygen atoms, and in the calcium silicate hydrate the calcium apparently wins out over hydrogen, in occupying sites adjacent to O' atoms. Geometric factors are also important in determining the actual distribution.

(6) The sodium atoms have coordination numbers of 5 or 6 in these compounds, and the coordination number of calcium is here seven.

Fig. 1 summarizes the close-neighbor arrangements. The upper two diagrams apply specifically to the sodium compounds, but substitution of Ca for Na, plus some other minor changes, would make them apply also to the calcium compound.

In addition to the structon types indicated, some of the O^0 oxygen atoms are weak-end bridgeheads for an additional hydrogen bridge, as already noted.

Conclusion

It is hoped that this and similar studies of the structon types present in compounds of known structure will prove helpful in predicting the types to be expected in compounds of unknown structure and in studies of the magnitudes of energies and other properties characteristic of different compounds.

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The Crystal Structure of $(\text{CrO}_3)_\infty$

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The crystal structure of CrO_3 has been refined with new three-dimensional X-ray data from a linear diffractometer to an R index of 0.0234. The structure consists of infinite chains of corner-sharing CrO_4 tetrahedra running parallel to the c axis. The bridging Cr–O bond length is 1.748 Å and the terminal Cr–O length is 1.599 Å. The angle at the bridging oxygen atom is 143° . Comparison with other accurately determined structures shows that the angles subtended at tetrahedral chromium(VI) atoms are considerably more regular than those at the sulphur or selenium atoms in analogous compounds.

Introduction

The crystal structure of chromium trioxide was first determined by Byström & Wilhelmi (1950) who collected two-dimensional photographic data. Vaughan (1955) and Hanic & Štempelová (1960) undertook further refinement of the structure using the original (1950) data. The basic structure was confirmed as being made up of linear chains of corner-sharing CrO_4 tetrahedra. Unfortunately the limited data did not yield accurate molecular dimensions. A complete redetermination with three-dimensional X-ray diffraction data was therefore undertaken as part of a general study of the structures of tetrahedral oxyanions.

Experimental

Crystals of CrO_3 were grown near the surface of a saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ in concentrated H_2SO_4 . The growth was at room temperature over a period of two days during which water vapour was absorbed from the air. These crystals were dark red and grew in the form of long, nearly cylindrical, needles. A small single crystal, 2 mm in length and 0.2 mm in diameter, was selected and sealed inside a 0.3 mm Lindemann-glass capillary. The previously reported crystal data

(Byström & Wilhelmi, 1950), as listed in Table 1, were used throughout this work.

Table 1. *Crystal data*

Chromium trioxide, CrO_3 , F.W. = 100.01
Orthorhombic: $a = 4.789$ (5), $b = 8.557$ (5), $c = 5.743$ (4) Å
$U = 235.4$ (5) Å ³ , $D_x = 2.82$ g.cm ⁻³ ,
$F(000) = 192$
Absorption coefficient: 47.4 cm ⁻¹ ($\lambda = 0.7107$ Å)
Absent spectra: hkl when $h+k$ is odd
$h0l$ when l is odd
Space group: $C2cm$

The intensity data were measured on a Hilger–Watts linear diffractometer, using Mo $K\alpha$ radiation and balanced Zr/Sr filters with the crystal mounted to rotate around the needle c axis. All reflexions within a hemisphere in reciprocal space out to a maximum $\sin \theta/\lambda$ value of 0.92 were recorded. The intensities of symmetry-equivalent reflexions were averaged.

In addition, precession photographs of the (hhl) and ($h, 3h, l$) planes were taken with Mo $K\alpha$ radiation and the intensities of these reflexions measured with the aid of a Joyce–Loebl ‘flying spot’ microdensitometer. A total of 334 independent reflexions were measured, 13 of which did not give a significant number of counts on the diffractometer and were not visible on the photographs. These reflexions were assigned appropriate ‘threshold’ intensities.

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