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## Crystal Structure and Entropy of Sodium Sulfate Decahydrate

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RECEIVED JULY 25, 1960

The crystal structure of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  has been determined to explain the entropy which remains at low temperatures. This substance is monoclinic, space group  $P2_1/c$ , with  $a = 11.51$ ,  $b = 10.38$  and  $c = 12.83$  Å., each  $\pm 0.01$  Å.;  $\beta = 107^\circ 45' \pm 10'$ ,  $Z = 4$ . The corresponding compounds with S replaced by Cr, Se, Mo or W have the same structure. Atomic positions were determined by the method of isomorphous substitution and were refined for the sulfate with three-dimensional data by a combination of Fourier and least-squares methods. The sodium atoms are surrounded by octahedra of oxygen atoms at an average distance of 2.43 Å. These octahedra share edges and involve eight of the water molecules. The other two water molecules are not coordinated by sodium but are interstitial like the fifth water molecule in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . All hydrogen atoms are in hydrogen bonds of lengths 2.75 to 3.00 Å. A unique configuration is assigned to 16 hydrogen atoms. The other four are in two kinds of rings of four hydrogen bonds each. Each ring has two possible configurations of the hydrogen atoms. Complete disorder of these configurations corresponds to the residual entropy found experimentally.

### Introduction

The crystal structure of sodium sulfate decahydrate, sometimes referred to as Glauber's salt or as mirabilite, has attracted our attention because of the discovery by Pitzer and Coulter<sup>1</sup> that this substance retains residual entropy of about 1.7 gibbs mole<sup>-1</sup> when cooled to low temperatures.<sup>2</sup> This residual entropy was confirmed by Brodale and Giaque,<sup>3</sup> who reported its magnitude as 1.51 gibbs mole<sup>-1</sup>, or about  $R \ln 2 = 1.38$  gibbs mole<sup>-1</sup>, in good agreement with the earlier less precise result. The disorder indicated by this entropy was attributed to the arrangement of the hydrogen atoms in the structure,<sup>1</sup> but in the absence of detailed structural knowledge, the precise nature of this disorder could not be discussed. The present research reveals an arrangement of hydrogen bonds which plausibly can be disordered among precisely enough configurations to correspond to an entropy of  $R \ln 2$ .

Work on this structure started independently in at least three laboratories. An incorrect structure has been described by Meulendijk<sup>4</sup> of Utrecht, who determined signs for two projections by isomorphous substitution of Se for S. This structure is correct in many of its features, but the locations of the screw axes and centers of symmetry are reversed in the [010] projection. This error was recognized by Corsmit-du Pré and Bijvoet<sup>5</sup> who derived the correct atomic arrangement. The locations of the atoms that they found, without refinement with three-dimensional data, agree with our final structure within 0.4 and for most atoms within 0.2 Å.

When the present authors learned of each other's work in 1957, one of us (R.D.R.) was working in Uppsala continuing work begun in Edinburgh on a trial structure also derived from isomorphous substitution and projections. The largest changes from that structure to the final one are shifts of about 0.46 Å. for two oxygen atoms. At Berkeley

three-dimensional data (which, however, were later found to be defective) were already at hand, but a satisfactory trial structure had not been found. Because better computing facilities were available at Berkeley the refinement of the structure was undertaken there (by H.W.R., I.O. and D.H.T.) with the results described in this paper. A concurrent refinement of the structure of sodium chromate decahydrate, which is isomorphous, will be reported elsewhere. Our X-ray data confirm that  $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$  also has this structure. The compounds  $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 10\text{H}_2\text{O}$  are also reported to be isomorphous,<sup>6</sup> but we have not studied them.

### Experimental

Crystalline  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is efflorescent and rapidly turns into anhydrous powder unless kept in a closed system. A cylindrical single crystal, with the  $b$  axis nearly parallel to the cylinder axis, was grown in a sealed fragile-walled glass capillary in the following way. After careful partial melting of a large sample of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in a small closed vessel, the liquid was quickly sucked into the capillary (diameter 0.17 mm.) which then was sealed off. The polycrystalline mass that soon formed in the capillary was melted except for a small fragment. From this seed crystal, a cylindrical single crystal grew quite readily. Several other crystals, produced by conventional methods, were used in preliminary stages of this work.

The unit cell dimensions were derived from the following data:  $a^*$ ,  $c^*$  and  $\beta$  were measured on a quartz-calibrated<sup>7</sup> zero-level Weissenberg photograph taken with Cu  $K\alpha$  radiation ( $\alpha_1$ ,  $\lambda = 1.5405$  Å.); the ratio  $b^*/c^*$  was measured on a zero-level precession photograph (Mo  $K\alpha$ ) with precession about  $a$ .

About 1335 independent structure factors were derived from intensities on Weissenberg photographs (Cu  $K\alpha$ ) from rotation about  $b$ , estimated by visual comparison with a set of intensity standards made with the same crystal. Approximately 1020 other structure factors were recorded as too weak to be observed. The absorption parameter  $\mu R$  is estimated to be 0.28, a value which indicates that absorption effects can be neglected, and no such correction was made. The data from different layers were first scaled relative to each other by precession data but finally were adjusted by the least-squares refinement.

### Results and Discussion

**Unit Cell and Space Group.**—The parameters of the monoclinic unit cell (at *ca.* 25°) are  $a = 11.51$

(1) K. S. Pitzer and L. V. Coulter, *THIS JOURNAL*, **60**, 1310 (1938).

(2) One gibbs = 1 defined cal. (°K.)<sup>-1</sup>, W. F. Giaque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *ibid.*, **82**, 62 (1960).

(3) G. Brodale and W. F. Giaque, *ibid.*, **80**, 2042 (1958).

(4) P. N. Meulendijk, *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B*, **59**, 493 (1956).

(5) I. M. Bijvoet, private communication, 1958.

(6) P. Groth, "Chemische Kristallographie," Vol. II, Wilhelm Engelmann, Leipzig, 1908, p. 362.

(7) A. Pabst, *Am. Mineralogist*, **42**, 664 (1957).

$\pm 0.01$ ,  $b = 10.38 \pm 0.01$  and  $c = 12.83 \pm 0.01$  Å.;  $\beta = 107^\circ 45' \pm 10'$ . The angle and the axial ratios  $a:b:c = 1.109:1:1.236$  are in reasonable agreement with the values  $\beta = 107^\circ 45'$ ,  $a:b:c = 1.1096:1:1.2388$  found by Rosicky<sup>8</sup> from crystal morphology. Our parameters are in poorer agreement with those reported by Meulendijk<sup>4</sup>:  $a = 11.43$ ,  $b = 10.34$  and  $c = 12.90$  Å.;  $\beta = 107^\circ 45'$ . The density calculated from our data, with 4 molecules per cell, is 1.466 g./cc. in excellent agreement with the density 1.4661 measured by Andreae<sup>9</sup> at  $24^\circ$ .

The crystal morphology<sup>8</sup> corresponds to point group  $2/m$ . The symmetry of the X-ray patterns and the systematic absences correspond to space group  $P2_1/c$ , and this choice is confirmed by the success of the structure determination. All atoms are in general positions 4(e):  $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$ . The atomic coordinates are sufficiently special so that the patterns also exhibit pseudosymmetry. For example, reflections  $h00$  are absent with  $h$  odd (up to  $h = 13$ ), although the inclination of the axes rules out any possibility that this is a screw-axis extinction.

**Determination of the Structure.**—The trial structure was derived from Patterson projections of the isomorphous sulfate, selenate and chromate. These calculations employed the  $hk0$ ,  $h0l$  and  $0kl$  data for the sulfate and selenate, as well as the  $h0l$  data of the chromate. Because of the ultimate agreement with three-dimensional data for both the sulfate and the chromate and the independent determination at Utrecht, it seems unnecessary to describe this phase of the work in detail.

Hydrogen atoms were excluded from the structure factor calculations. Form factors for neutral atoms of oxygen, sodium and sulfur were taken respectively, from Hoerni and Ibers,<sup>10</sup> Berghuis, *et al.*,<sup>11</sup> and "Internationale Tabellen."<sup>12</sup> Each atom was given an independent isotropic temperature factor. Least-squares refinements were made with the IBM-650 computer and the "LS-II" program of Senko and Templeton,<sup>13</sup> with minor changes to adapt it to the monoclinic system. In the final cycles, weighting and the treatment of unobserved reflections were done as described for the last cycles of choline chloride.<sup>14</sup> Three-dimensional Fourier functions were calculated with the IBM-701 computer with the program of Dodge, Jones and Templeton.<sup>15</sup>

In this least-squares program,<sup>13</sup> most off-diagonal terms are neglected. In the present case, this procedure failed to give satisfactory convergence. An inspection of the atomic coordinates listed in Table I reveals great duplication: the  $x$  coordinates are all close to  $1/8$ ,  $1/4$  or  $3/8$ , while the

$y$  coordinates of many pairs of atoms are equal. No full-matrix calculations have been made, but it is suspected that these special relationships introduce correlations which hinder convergence of the diagonal approximation.

TABLE I

ATOMIC COÖRDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

Atom <sup>a</sup>	$x$	$y$	$z$	$B, \text{Å}^2$
Sulfur 1	0.2495	0.3591	0.2584	1.7
Sodium 2	.2564	.7473	.0155	2.7
Sodium 3	.2450	.6135	.7610	2.8
Oxygen 4	.260	.298	.361	4.5
Oxygen 5	.141	.310	.170	3.6
Oxygen 6	.358	.336	.227	5.2
Oxygen 7	.233	.500	.273	6.0
Oxygen 8	.124	.455	.639	3.2
Oxygen 9	.368	.452	.880	3.3
Oxygen 10	.101	.347	.946	3.2
Oxygen 11	.394	.347	.580	3.4
Oxygen 12	.113	.607	.880	3.1
Oxygen 13	.388	.607	.652	3.5
Oxygen 14	.147	.712	.144	3.0
Oxygen 15	.354	.714	.380	3.2
Oxygen 16	.132	.561	.444	3.4
Oxygen 17	.380	.557	.083	3.6

<sup>a</sup> The numbers identify the atoms in the text, figures and other tables; atoms 4-7 are oxygen of sulfate and 8-17 are oxygen of water.

Five cycles of least-squares refinement of the first set of three-dimensional data reduced the conventional unreliability factor  $R_1$ <sup>16</sup> to 0.27. Additional cycles achieved no further improvement. When comparison of the data with the photographs revealed some errors and some poorly estimated intensities, these data were discarded and the final set was measured with the cylindrical crystal as described previously. Ten least-squares cycles on the final set of data reduced  $R_1$  to 0.21. To achieve further refinement, we calculated the electron density difference function ( $F_o - F_c$  synthesis) after each least-squares cycle. Atomic shifts were made by subjective judgment of the results of the two calculations. This procedure after ten cycles reduced  $R_1$  to 0.13 (observed reflections only). The corresponding final values of  $R_2$  and  $R_3$ <sup>16</sup> are 0.15 and 0.20.<sup>17</sup>

**Atomic Parameters and Accuracy.**—The final atomic coordinates and isotropic temperature factors are listed in Table I. Some of the bond distances and angles are listed in Tables II and III. The standard deviations of these coordinates, estimated by the method of least squares with the diagonal approximation, are about 0.00015 for

(16) M. E. Senko and D. H. Templeton, *Acta Cryst.*, **11**, 808 (1958).

(17) A table of the final observed and calculated structure factors has been deposited as Document number 6418 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints or \$1.75 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(8) F. Rosicky, *Z. Krist.*, **45**, 473 (1908).

(9) J. L. Andreae, *Z. physik. Chem. (Leipzig)*, **82**, 109 (1913).

(10) J. A. Hoerni and J. A. Ibers, *Acta Cryst.*, **7**, 744 (1954).

(11) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(12) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935, p. 571.

(13) M. E. Senko, *Acta Cryst.*, **10**, 385 (1957). One cycle with 2350 reflections required 8.5 hr.

(14) M. E. Senko and D. H. Templeton, *ibid.*, **13**, 281 (1960).

(15) R. P. Dodge, Ph.D. Dissertation, University of California, 1958.

sulfur, 0.0003 for sodium and 0.0006 for oxygen, except atoms 4, 6 and 7. These latter atoms which also have larger temperature factors than the others, have standard deviations of coördinates of about 0.0008. These errors correspond to about 0.01 Å. for the standard deviation of a bond length. However, because of the poor convergence of the diagonal approximation in this problem, it seems unjustified to claim that the accuracy is this great.<sup>18</sup> The dimensions found for the sulfate ion, which has no crystallographic symmetry, suggest that more realistic standard deviations are about 0.04 Å. for bond distances and about 2° for bond angles. To this accuracy, the sulfate ion is tetrahedral with bond lengths of 1.46 Å.

**Description of the Structure.**—In this crystal, each sodium is surrounded by six water molecules at the corners of an irregular octahedron at an average distance of 2.43 Å. These octahedra share edges to form strings parallel with the *c* axis (Fig. 1) somewhat like the sodium-water structure in

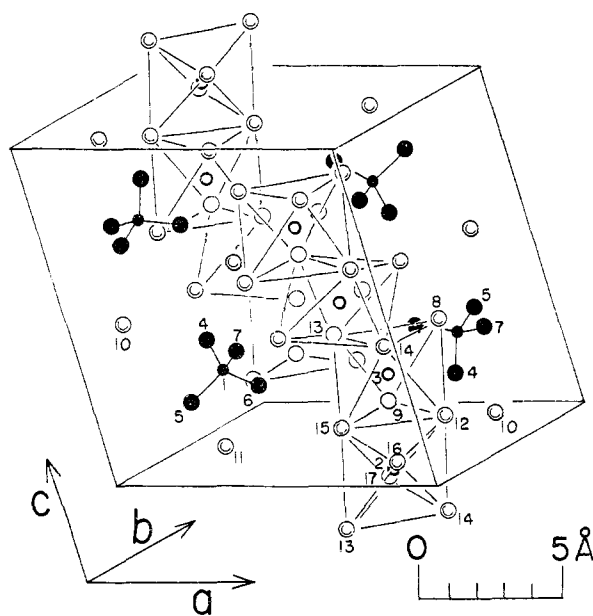


Fig. 1.—Crystal structure of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ : The sulfate ions are shown in black; the edges of the coördination octahedra about sodium ions are indicated by lines; hydrogen atoms are not shown. The numbers at some of the atoms correspond to the numbering in Table I.

borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .<sup>19</sup> In borax, the average sodium-oxygen distance is 2.42 Å. Eight of the ten water molecules in sodium sulfate are involved in these coördination octahedra. The other two, designated as 10 and 11, are involved only in hydrogen bonding in much the same way as the fifth water molecule of copper sulfate pentahydrate.<sup>20</sup> Hydrogen bonding of water to water and

(18) There are two effects. The least-squares method gives the accuracy of the best fit, which has not been achieved exactly. The diagonal approximation does not give the true standard deviations of this best fit.

(19) N. Morimoto, *Mineral. J. (Sapporo)*, **2**, 1 (1956).

(20) C. A. Beevers and H. Lipson, *Proc. Roy. Soc. (London)*, **A136**, 570 (1934).

of water to sulfate occurs throughout the structure. This hydrogen bonding is deduced from the heavy-atom positions; direct evidence of hydrogen positions has not been found in the diffraction data.

TABLE II

INTERATOMIC DISTANCES IN  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 

Atoms	Distance, Å.	Atoms	Distance, Å.	Atoms	Distance, Å.
Sulfur-oxygen distances					
1, 4	1.43	1, 6	1.44	1, 7	1.49
1, 5	1.50				
Sodium-oxygen distances					
2, 12	2.47	2, 16	2.46	3, 12	2.46
2, 13	2.46	2, 17	2.43	3, 13	2.46
2, 14	2.39	3, 8	2.40	3, 14	2.40
2, 15	2.37	3, 9	2.41	3, 15	2.44
Hydrogen-bond distances					
14, 7	2.75	10, 5	2.80	13, 11	2.86 <sup>b</sup>
15, 7	2.76	11, 6	2.80	15, 11	2.86 <sup>b</sup>
8, 16	2.76 <sup>a</sup>	11, 4	2.81	9, 4	2.86
8, 5	2.78	8, 16	2.82 <sup>a</sup>	13, 6	2.92
9, 17	2.79 <sup>a</sup>	10, 4	2.83	12, 5	2.93
9, 17	2.79 <sup>a</sup>	12, 10	2.84 <sup>b</sup>	17, 6	3.00
14, 10	2.80 <sup>b</sup>	16, 7	2.85		

<sup>a</sup> These bonds occur in the rings. <sup>b</sup> These bonds also involve two water molecules.

TABLE III

BOND ANGLES IN  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 

Atoms	Angle	Atoms	Angle
Oxygen-sulfur-oxygen angles			
4, 1, 5	111°	5, 1, 6	109°
4, 1, 6	110°	5, 1, 7	109°
4, 1, 7	107°	6, 1, 7	111°
Angles between hydrogen bonds			
5, 8, 16	120° <sup>a</sup>	4, 9, 17	113° <sup>a</sup>
5, 8, 16	91° <sup>a</sup>	4, 9, 17	109° <sup>a</sup>
16, 8, 16	90° <sup>b</sup>	17, 9, 17	96° <sup>b</sup>
7, 16, 8	109° <sup>a</sup>	6, 17, 9	107° <sup>a</sup>
7, 16, 8	138° <sup>a</sup>	6, 17, 9	98° <sup>a</sup>
8, 16, 8	90° <sup>b</sup>	9, 17, 9	84° <sup>b</sup>
4, 10, 5	114° <sup>c</sup>	4, 11, 6	114° <sup>c</sup>
4, 10, 12	107°	4, 11, 13	116°
4, 10, 14	115°	4, 11, 15	111°
5, 10, 12	115°	6, 11, 13	114°
5, 10, 14	103°	6, 11, 15	95°
12, 10, 14	103°	13, 11, 15	106°
5, 12, 10	102° <sup>c</sup>	6, 13, 11	104° <sup>c</sup>
7, 14, 10	102° <sup>c</sup>	7, 15, 11	104° <sup>c</sup>

<sup>a</sup> Angles for alternate orientations of disordered water molecules. <sup>b</sup> Angles of rings. <sup>c</sup> Angles for ordered water molecules.

**Hydrogen Bonding.**—We assign the 20 hydrogen atoms to 20 hydrogen bonds with lengths ranging from 2.75 to 3.00 Å. (Table II). No other oxygen–oxygen distances, except those within the sulfate ion, are shorter than 3.23 Å. None of these short distances is an edge of a coordination polyhedron, a circumstance which sometimes causes non-bonded oxygen atoms to occur at distances appropriate for hydrogen bonds.<sup>21</sup>

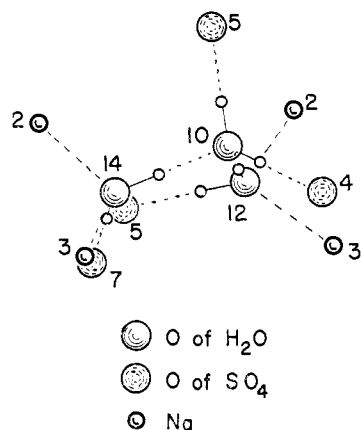


Fig. 2.—Bonding of water molecules 10, 12 and 14 to sodium ions 2 and 3 and to sulfate oxygen atoms 4, 5 and 7; the smallest circles represent hydrogen atoms in the hydrogen bonds.

The water molecules 10, 12 and 14 are bonded to each other and to oxygen atoms of sulfate as shown in Fig. 2. Water molecules 11, 13 and 15 are bonded in a topologically identical though crystallographically unrelated fashion. There is only one way of orienting three water molecules in such a structure so that one hydrogen atom is in each hydrogen bond, as shown in Fig. 2. Therefore, we expect no disorder of hydrogen atoms in these bonds.

Two each of water molecules 8 and 16 are bonded to each other in rings of four hydrogen bonds, as well as to four oxygen atoms of sulfate, as shown in Fig. 3. Water molecules 9 and 17 are bonded in a topologically equivalent fashion. Each water molecule must be oriented so that one of its hydrogen atoms is in the bond to the sulfate oxygen. There remain, however, two ways in which the other hydrogen atom may be oriented in the bonds of the ring. Each ring has just two possible configurations with one hydrogen in each bond (Fig. 4). Each formula unit of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  provides half the atoms for each of two rings. Therefore, if the configurations of the rings are completely random, the entropy of this disorder is  $k \ln 2$  per formula unit, or  $R \ln 2$  per mole, in agreement with experiment.

It should be pointed out that the alternate configurations are not crystallographically equivalent, and therefore it cannot be predicted *a priori* that they should be equally populated. The assumption of complete randomness must rest on the thermal data.

(21) D. H. Templeton, *Acta Cryst.*, **13**, 684 (1960).

The persistence of this entropy at low temperatures implies that the rate of change from one configuration to the alternate one is vanishingly small at low temperatures. This change requires either the simultaneous coherent motion of four protons or reaction through a series of intermediate states which involve ionized water species. It seems plausible that such reactions should be very slow.

This explanation of the residual entropy by randomness of hydrogen configurations implies that the same residual entropy would be found in the isomorphous hydrated sodium chromate, selenate, molybdate and tungstate. We know of no measurements of the entropies of these substances.

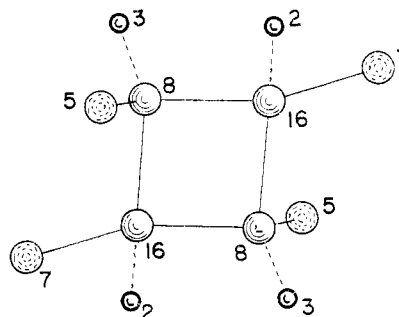


Fig. 3.—Bonding of water molecules 8 and 16 to sodium ions 2 and 3 and to sulfate oxygen atoms 5 and 7; the solid lines represent hydrogen bonds.

**Bond Angles.**—The bond angles are compatible with this assignment of hydrogen configurations. It is known that hydrogen atoms are not necessarily exactly on the lines joining oxygen atoms of a

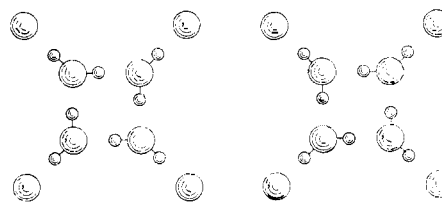


Fig. 4.—Alternate configurations for water molecules in a ring.

hydrogen bond,<sup>22</sup> and therefore the oxygen–oxygen–oxygen angle need not equal the normal bond angle of the water molecule. Angles in the range 90 to 120° are commonplace for such oxygen–oxygen–oxygen angles in salt hydrates, while both smaller and larger values have also been observed. These angles in this structure for the six water molecules not involved in disorder are found to be in the range 102 to 114°. The eight alternate angles for the other four water molecules range from 91 to 120°, except for one angle of 138°. Moreover, it seems plausible that the sulfate orientation may shift slightly, depending on the local configuration of the hydrogen bonds in a direction which improves these angles. Such shifts may be the explanation of the higher

(22) E.g., I. Olovsson and D. H. Templeton, *Acta Chem. Scand.*, **14**, 1325 (1960).

temperature factors of the sulfate oxygens.<sup>23</sup>

The direction of the sodium atom from a coordinated water molecule is at an angle of  $97^\circ$  or more from any hydrogen bond of that water molecule.

The angles between the four hydrogen bonds of each of the uncoordinated water molecules (10 and 11) range from  $95$  to  $116^\circ$  and thus are not far from regular tetrahedral.

**Acknowledgments.**—We give special thanks to Prof. Bijvoet and Mrs. Corsmit-du Pré for infor-

(23) This factor represents diffuseness of the electron density, averaged over time and over all the unit cells, compared to that of a theoretical atom at rest. It is called "temperature factor" because the thermal motion is the most common source of such diffuseness.

mation concerning their determination of the structure and for permitting us to carry out the refinement. We are also indebted to Prof. G. Hagg for the use of facilities at Uppsala, to Professors Giauque and Pitzer for discussions of the entropy measurements, to Dr. Senko, Dr. Zalkin, Dr. Dodge, Dr. R. E. Jones and Dr. Q. C. Johnson for the use of their computer programs and to the staffs of the University of California Computer Center and of the Radiation Laboratory computer group for their coöperation with the computers. A travel grant (to I.O.) from the Swedish Natural Science Research Council is gratefully acknowledged. The work at Berkeley was supported by the U. S. Atomic Energy Commission.