

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, DARTMOUTH COLLEGE]

## A Determination of Parameters in Potassium Dihydrogen Arsenate and Silver Arsenate

BY LINDSAY HELMHOLZ AND ROBERT LEVINE

**Introduction.**—The approximate structures of potassium dihydrogen arsenate<sup>1</sup> and silver arsenate<sup>2</sup> have been known for some time, but the parameters necessary for a complete description of their structures have not been determined. The deduction of electronic structures from bond distances has made the accurate determination of these parameters of importance. The existence of a random structure for potassium dihydrogen arsenate<sup>3</sup> and the possible application of the suggestions of Pitzer and Hildebrand<sup>4</sup> to a discussion of the colors of silver phosphate and silver arsenate are further reasons for making detailed studies of these compounds.

In previous work on silver phosphate<sup>5</sup> it was suggested, on the basis of an apparent discrepancy between the phosphorus to oxygen distances in silver phosphate and potassium dihydrogen phosphate, that a tendency toward covalent bond formation between the phosphate oxygen atoms and the adjacent silver atoms caused a lengthening of the P—O distance. It was also found necessary to attribute anisotropic character to the thermal motions of the silver atoms to account for certain anomalies in the spectra. We have been interested in checking these conclusions by investigating the compounds in which arsenic replaces phosphorus.

**Procedure.**—Single crystals of silver arsenate were prepared by allowing ammonia to escape slowly from a solution of the substance in concentrated ammonium hydroxide. The resulting crystals were most frequently cubes from 0.1 to 0.5 mm. on an edge.

Laue photographs were taken as well as two series of oscillation pictures, one with  $\text{MoK}_\alpha$  and one with  $\text{CuK}_\alpha$  radiation. The oscillation photographs were taken with the crystals at room temperature, and at approximately  $100^\circ$  and  $-180^\circ$ . The values of the relative intensities were obtained by making use of photographs of different

exposure times and by the use of a calibrated wedge. The cubic shape of the crystals made the calculation of absorption relatively simple; however, reflections greatly influenced by this factor were not used in the analysis. Baker C. P. potassium dihydrogen phosphate crystals were used. They were dissolved down to approximately cylindrical shape, having in every case radii under 0.1 mm. Laue pictures and  $\text{CuK}_\alpha$  oscillation photographs were employed in the determination. The relative intensities were obtained by means of the multiple film technique<sup>6</sup> and the absorption calculated from tabulated values in the International Tables for the Determination of Crystal Structures.

**Silver Arsenate.**—The structure of silver arsenate differs from that of silver phosphate only in the interatomic distances and, quantitatively, in the treatment that must be given to the temperature factor for the silver atoms. The space group is  $T_d^2$ ; the values of  $a_0$  at different temperatures are given in Table I.

TABLE I<sup>a</sup>

SILVER ARSENATE			
(hko)	$a_0$ ( $90^\circ\text{K.}$ ), Å.	$a_0$ (approx. $380^\circ\text{K.}$ ), Å.	
(200)	6.10		
(400)	6.120		
(600)	6.123		
(640)	6.118		6.126
(720)	6.120		6.130
(730)	6.119		
	$a_0 = 6.120$		6.130
Potassium Dihydrogen Arsenate			
(hko)		(h0l)	
(200)	7.64	(004)	7.15
(400)	7.66	(008)	7.165
(600)	7.65	(208)	7.17
(800)	7.65	(408)	7.17
(820)	7.66		
(840)	7.64		
	$a_0 = 7.65$	$c_0$	7.170

<sup>a</sup> The X-ray data used in the determination of the structures discussed here were obtained at the California Institute of Technology.

The structure consists of a body-centered arrangement of arsenic atoms, each surrounded tet-

(6) J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, **A171**, 398, 1939.

(1) This crystal has the same structure as potassium dihydrogen phosphate: J. West, *Z. Krist.*, **74**, 306 (1930).

(2) R. W. G. Wyckoff, *Am. J. Sci.*, **10**, 107 (1925).

(3) J. C. Slater, *J. Chem. Phys.*, **9**, 16 (1941).

(4) K. S. Pitzer and J. H. Hildebrand, *THIS JOURNAL*, **63**, 2472 (1941).

(5) L. Helmholtz, *J. Chem. Phys.*, **4**, 316 (1936).

rahedrally by oxygen atoms located on the body diagonals of the cube. The silver atoms occupy the faces of the unit cube in the positions:  $\frac{1}{2}, \frac{1}{4}, 0$ ;  $\frac{1}{2}, \frac{3}{4}, 0$ ;  $0, \frac{1}{2}, \frac{1}{4}$ ;  $0, \frac{1}{2}, \frac{3}{4}$ ;  $\frac{1}{4}, 0, \frac{1}{2}$ ;  $\frac{3}{4}, 0, \frac{1}{2}$ . This arrangement gives a simple structure of one parameter which places the oxygen atoms on the body diagonals. The determination of this one parameter is complicated, however, by the fact that no solution is possible if the usual forms of structure factor and temperature factor are employed. The anomalies in the spectra from silver arsenate are the same as those observed or predicted in the case of silver phosphate. These anomalies are: (1) the appearance of reflections from planes (with indices of the type  $h - k = 4, l$  odd) for which the usual type of structure factor vanishes. These reflections were observed only on Laue pictures and on oscillation photographs taken with copper radiation. (2) The existence of pairs of reflections having the same form of the structure factor for which the reflection with the smaller interplanar distance has the greater intensity, for example  $I_{(821)} < I_{(920)}$ . (3) The fact that pairs of reflections can be found for which the one at the larger value of  $\sin \theta$  becomes relatively more intense as the temperature is raised. An example of this behavior is the following: at liquid air temperatures the observed intensities of (721) and (641) (uncorrected for adsorption) are very nearly equal; at  $120^\circ$ , the intensity of (641) is only about one-half that of (721).

As was shown previously,<sup>5</sup> this behavior can be accounted for by assuming that the thermal motions of the silver atoms have tetragonal symmetry, the symmetry of their environment in the crystal, with a larger amplitude of oscillation along the tetragonal axis in the direction of the nearest silver atoms. This consideration introduces for each pair of silver atoms, lying on lines parallel to one of the cubic axes, instead of the usual temperature factor, the following expression

$$T_i = e^{-\beta(\sin \theta/x)^2} e^{-\beta(B-1)(h_1/2a_0)^2}$$

where the first exponential term is the usual temperature factor and, in the second,  $B$  is the square of the ratio of the amplitude of oscillation in the direction of the unique axis and perpendicular to it, and  $h_1$  is the Miller index of the reflecting plane for the axis which is parallel to the unique axis of the silver atom oscillation.

This treatment, while approximate in many respects, reproduces the peculiarities of the spectra

satisfactorily. Of course, any serious inadequacy in this type of temperature factor will be reflected in inaccuracy of the parameter values for the oxygen atoms.

The structure determination thus becomes a problem of two parameters, which was solved by the usual method. The best value of  $\beta$  was found by trial and error. Laue intensities were used to aid in fixing  $B$ . The reflection (730), which occurred on the low temperature photographs, was especially valuable in determining the parameter.

The calculated  $F_{(hkl)}$  are compared with those observed in Tables II and III. The data in Table III were obtained from  $\text{CuK}_\alpha$  pictures.  $x = 0.335 \pm 0.005$ ;  $B = 3.00 \pm 0.50$ .

TABLE II

$(hkl)$	$-180^\circ\text{C.}$		$+120^\circ\text{C.}$	
	$F_{(\text{obs.})}$	$F_{(\text{calcd.})}$	$F_{(\text{obs.})}$	$F_{(\text{calcd.})}$
(200)	13	10.3	13	9.4
(201)	18.1	14	17	14.0
(400)	21.8	17	17.8	13.0
(401)	..	0.5	..	1.3
(402)	7.8	8.5	7.4	6.6
(301)	3.5	3.5	3.5	3.2
(302)	8.8	10.4	8.0	9.5
(501)	..	0.5	..	0.6
(502)	7.3	8.1	6.8	6.5
(600)	7.9	9.2	8.0	7.7
(601)	5.9	6.8	4.8	4.7
(602)	..	1.0	..	1.0
(603)	5.3	6.4	3.7	3.4
(701)	..	1.1	..	0.5
(702)	5.6	6.7	4.0	4.1
(800)	8.8	9.9	5.3	4.9
(801)	..	1.0	..	1.4
(802)	3.1	3.8	..	1.8
(902)	4.2	5.4	3.0	3.8
(10.00)	3.0	4.4	2.5	2.0
(10.01)	2.4	3.6	..	..
(10.02)	..	0.9	..	..
(12.00)	4.6	5.8	..	..

TABLE III

$(hkl)$	$F_{(\text{obs.})}$	$F_{(\text{calcd.})}$	$F_{(\text{obs.})}$	$F_{(\text{calcd.})}$
(640)	13.9	12.6	9.8	8.6
(720)	15.9	16.8	10.5	10.5
(730)	5.5	6.2	..	2.5
(721)	12.1	11.8	8.5	7.3
(641)	13.3	14.2	6.8	6.1

### Structure of Potassium Dihydrogen Arsenate.

—A space group determination gave the same result as was obtained for potassium dihydrogen phosphate. The dimensions of the unit cell are:  $a_0 = 7.65 \text{ \AA.}$ ,  $c_0 = 7.17 \text{ \AA.}$  as given in Table I. The space group is  $D^{12}/2D-I\bar{4}2d$  and the atomic positions are: 000 and  $\frac{1}{2} \frac{1}{2} \frac{1}{2} +$

K :  $00\frac{1}{2}, 0\frac{1}{2}\frac{3}{4}$ As :  $000, 0\frac{1}{2}\frac{1}{4}$ O :  $x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; x, \frac{1}{2} + y, \frac{1}{4} - z; x, \frac{1}{2} - y, \frac{1}{4} - z; y, \frac{1}{2} + x, \frac{1}{2} + z; y, \frac{1}{2} - x, \frac{1}{4} + z$ 

The determination was carried out in the same manner as in the case of silver arsenate. The values of  $x$  and  $y$  were found using the  $(hkl)$  spectra and then  $z$  was evaluated from the  $(h0l)$  reflections using the known values of  $x$  and  $y$ . The parameters were refined by comparison of calculated and observed  $(hkl)$  reflections and Laue reflections having the same values of  $\sin \theta$  and  $\lambda$ .

The parameters arrived at in this way are

$$x = 0.085 \pm 0.0025$$

$$y = 0.1575 \pm 0.0025$$

$$z = -0.150 \pm 0.005$$

The observed and calculated  $F$  values appear in Table V. Some intensity comparisons from Laue data are given in Table IV.

TABLE IV

		$x \rightarrow$		
		0.080	0.085	0.090
$\frac{ F ^2_{(2, 11, s)}}{ F ^2_{(5, 10, s)}} \approx 2$	0.150	5.6	4.3	2.8
$y$	0.155	3.2	3.4	2.6
$\downarrow$	0.160	1.3	1.6	3.1
		$x \rightarrow$		
		0.08	0.085	0.09
$\frac{ F ^2_{(2, 11, s)}}{ F ^2_{(0, 11, s)}} \approx 1.25$	0.150	0.8	0.6	1.5
$y$	0.155	1.1	0.8	0.7
$\downarrow$	0.160	1.8	1.4	1.2
		$x \rightarrow$		
		0.08	0.085	0.090
$\frac{ F ^2_{(482)}}{ F ^2_{(4, 12, s)}} > 1$	0.150	0.2	0.37	0.9
$y$	0.155	0.5	1.2	4.8
$\downarrow$	0.160	1.0	5.5	9.9

### Discussion of the Structures

**Silver Arsenate.**—The parameter values give the interatomic distances: As-O =  $1.75 \pm 0.05$  Å.; Ag-O =  $2.34 \pm 0.05$  Å. The arsenate group is a regular tetrahedron, as required by the space group, with the arsenic to oxygen distance 1.75 Å., which is 0.09 Å. shorter than the sum of the tetrahedral radii (1.84 Å.). This shortening is not so great as the relative shortening in the case of the phosphate group. The silver to oxygen distance is found to be the same in this structure as in silver phosphate and it would appear that the adjustment of this atomic contact played a deciding role in the determination of the size of the unit cell. The Ag-O distance may be compared with the ionic separation 2.46,<sup>7</sup> or with the sum

(7) This sum (2.46 Å.) is obtained using a  $\text{Ag}^+$  radius calculated from the lattice constant of silver fluoride and the  $\text{F}^-$  radius. The sum of the radii taken from Pauling's table is 2.66 Å.

TABLE V

$(hkl)$	$F(\text{obs.})$	$F(\text{calcd.})$	$(hkl)$	$F(\text{obs.})$	$F(\text{calcd.})$
(200)	38.0	60	(101)	12.2	18.6
(220)	28.5	44	(202)	11.6	11.9
(310)	9.7	11.5	(301)	6.1	4.7
(400)	24.8	26.2	(103)	..	3.0
(420)	32.0	36.5	(400)	27.9	26.2
(510)	8.9	7.7	(004)	17.9	21.0
(440)	42.5	36.0	(303)	16.9	18.9
(530)	8.1	7.4	(402)	..	1.5
(600)	25.2	28.8	(204)	28.8	35.5
(620)	28.0	32.0	(501)	14.7	11.4
(710)	5.0	3.8	(105)	9.2	9.6
(640)	21	23.6	(404)	25.2	37.0
(730)	3.0	2.9	(503)	10	8.6
(800)	17.9	18.2	(600)	31	28.8
(820)	16.3	18.5	(305)	13	11.4
(660)	11.2	10.5	(602)	14.0	11.0
(750)	..	1.0	(206)	..	2.7
(840)	14.9	16.2	(701)	13.8	10.6
(910)	2.8	3.4	(505)	..	2.1
			(604)	20.5	22.5
			(107)	9.8	9.5
(211)	16.7	18.0	(406)	..	0.4
(321)	13.4	12.6	(800)	22.0	18.2
(411)	9.3	7.4	(008)	17.0	19.0
(431)	10.2	14.1	(606)	8.4	3.5
(521)	9.3	7.7	(208)	15.0	15.1
(611)	5.1	3.1	(705)	..	0.9
(541)	6.6	5.8	(507)	..	1.7
(631)	9.8	10.7	(804)	23.0	16.0
(721)	8.9	7.0	(901)	1.4	1.4
(651)	4.3	4.5	(408)	15.3	12.5
(741)	3.7	3.4			
(811)	5.3	4.2			
(831)	7.6	6.6			
(921)	3.3	3.4			

of the covalent tetrahedral radii 2.19 Å. If one applies to the ionic radius sum a correction for coordination number, one obtains 2.34 Å. in agreement with the observed distance. This seems a very questionable procedure since the arrangement of the oxygen atoms about the silver atom is more nearly square than tetrahedral, the larger O-Ag-O angle is  $155^\circ$ .

The rule proposed by Pitzer and Hildebrand, that the color of a compound formed from colorless ions is related to the amount of "covalent character" in the bond between these ions, suggests that an attempt be made to correlate bond distance, color, and covalent character for some compounds containing silver to oxygen bonds. This is done in Table VI. If the color is attributed to the Ag-O linkage, then the transition from colorless compounds to deeply colored shows good correlation with the transition from ionic to covalent interatomic distances. The fact that the Ag-O distances in the phosphate and arsenate

TABLE VI

Compound	Ag-O, Å.	Radius sums		Color
		(Ionic)	(Covalent)	
Ag <sub>2</sub> SO <sub>4</sub>	2.50	2.46	2.19	Colorless
Ag <sub>2</sub> PO <sub>4</sub>	2.34	2.46	2.19	Yellow
Ag <sub>2</sub> AsO <sub>4</sub>	2.34	2.46	2.19	Deep red
Ag <sub>2</sub> O	2.06		2.02 <sup>a</sup>	Brown-black

<sup>a</sup> Covalent radius for silver atom with coordination number of two is taken from the interatomic distance Ag-CN in KAg(CN)<sub>2</sub>: J. L. Hoard, *Z. Krist.*, **84**, 231 (1933).

are the same while the colors are remarkably different may be due to inaccuracies in the X-ray determination, or to the fact that a consideration of the Ag-O bond alone is not sufficient. An explanation of this fact may also be attempted on the basis of the structure as determined. In the first place, the arrangement of oxygen atoms about the silver is much more nearly planar in the arsenate, and in the second place the thermal motions of the silver atoms in the arsenate are of greater amplitude in a direction which brings them closer to the oxygen atoms. That this last point may be of some importance is indicated by the fact that silver phosphate became orange red-dish on being heated well below the melting point.

The magnitude of the anisotropy of the thermal motion of the silver atoms in silver arsenate relative to that in the phosphate is greater, as one would expect. Not only is the oxygen atom environment more nearly planar but the silver atoms are farther apart in the direction of the maximum amplitude. The value  $B = 3.0$  corresponds to a ratio of 1.7 between the root mean square amplitudes in the two directions.

**Potassium Dihydrogen Arsenate.**—The interatomic distances of interest in this crystal, as given by the parameters, are As-O =  $1.74 \pm 0.03$  Å.; O-H-O =  $2.54 \pm 0.03$  Å.

The arsenic to oxygen distance in this crystal is equal, within the limits of error, to the same separation in silver arsenate. This would indicate, according to the argument used previously for the phosphate case, that the formation of partially covalent bonds between silver and oxygen atoms does not affect the arsenic to oxygen distance. This conclusion might equally well be reached on the basis of West's structure of potassium dihydrogen phosphate alone, for certainly there is some covalent character associated with the O-H bond, and all the oxygen atoms are found to be equidistant from the arsenic. The difficulty with this conclusion arises because of uncertainty about the structure of potassium di-

hydrogen phosphate. There is good evidence for believing that the H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> dipoles are randomly oriented in this crystal above 90–100°K. This condition may be thought of as arising from the fact that the hydrogen atoms have two possible positions in the hydrogen bond, closer to one or the other oxygen. If the hydrogen atoms are arranged randomly in these positions, subject to the condition that each arsenate group has two attached hydrogen atoms in all but rare cases, then a structure is obtained in which the H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> ions are randomly oriented. If this randomness involves only the hydrogen atoms, then it would not be detected by X-ray means. If, however, the arsenic to oxygen distance is different, depending on whether the oxygen atom is bonded to a hydrogen or not, then a structure determination should lead to an "average" position. The random distribution of the hydrogen atoms might also lead to a slight degree of randomness in the equilibrium positions of the potassium ions. This is suggested by the fact that the potassium  $f$ -values determined experimentally by West are as much as 20% smaller than the Hartree values for  $\sin \theta/\lambda$  up to 0.5. It will be noticed in Table IV that most of the reflections to which arsenic and potassium atoms contribute in phase as calculated are too strong, and for the opposite case the calculated intensities are too small. These discrepancies could be considerably diminished if West's experimental  $f$ -values for potassium were used.

The parameter values lead to an arsenate group which is a slightly deformed tetrahedron. The deformation, a stretching in the direction of the  $c$ -axis, is the same as that observed in potassium dihydrogen phosphate although not quite so great. The O-As-O angles are 104 and 113°.

Since the lengths of hydrogen bonds vary over a relatively wide range, and since the lengths seem to depend on the ionic character of the O-H bond and the negativity of the bonded oxygen,<sup>8</sup> it should be possible to obtain some idea of the relative negativity of the oxygen atoms in XO<sub>4</sub><sup>m-</sup> groups by determining the length of hydrogen bonds formed to these oxygen atoms, provided the character of the O-H bonds making up the rest of the hydrogen bridge were the same, and provided the influence of the structure as a whole on the bond distances could be estimated.

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

The fact that the interatomic distances fall below the sum of the tetrahedral radii has been interpreted as due to multiple bond formation and to ionic character. These two effects may both lead to decreases in interatomic distances in  $\text{XO}_4^{m-}$  ions but they lead to opposite effects on the negativity of the oxygen atoms. Thus a measure of the relative importance of the two factors might be obtained by measurement of the length of hydrogen bonds.

In the present case if it is assumed that the O-H bond is the same in the arsenate and phosphate groups, then the negativity of the oxygen atoms would also appear to be very nearly the same. A more definite statement can scarcely be made until the possible influence of randomness on the parameters of  $\text{KH}_2\text{AsO}_4$  is investigated.

### Summary

The atomic parameters for the crystals potassium dihydrogen arsenate and silver arsenate have been determined. The arsenic to oxygen distance in both crystals has been found to be 1.75 Å. within the limits of error.

The silver to oxygen distance (2.34 Å.) in silver arsenate is discussed in connection with the colors of this compound and others containing silver to oxygen bonds and in the light of the suggestions of Pitzer and Hildebrand concerning color and covalent character.

The influence of randomness on the determination parameters of potassium dihydrogen phosphate is discussed. The hydrogen bond distance (O-H-O) in this crystal is found to be 2.54 Å., equal to that in the phosphate.

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## Oxidation and Reduction of Vitamin C<sup>1</sup>

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### Introduction

The oxidation of vitamin C by means of various catalysts was investigated primarily to see whether the reaction could be used in the determination of oxygen in biological materials. It was further hoped that additional information on oxidation and reduction of vitamin C would in a general way contribute to our knowledge of the role of vitamin C in biological oxidations and its stability in food products.

**Effect of Catalysts on the Amount of Oxygen Used in the Oxidation of Vitamin C.**—The amount of oxygen used in the oxidation of vitamin C depends on the nature of the catalyst. With vitamin C oxidase from cucumbers exactly one atom of oxygen is used per molecule of vitamin C. This result has been approximately confirmed by the earlier work of Snow and Zilva<sup>2</sup> and Ebihara.<sup>3</sup> The ratio has been determined accurately by us in order to make possible a calculation of dissolved oxygen from measured disappearance of reduced ascorbic acid. The average of twelve determinations made with a differ-

ential manometer (Barcroft) was 0.995 atom of oxygen per molecule of vitamin C with a mean deviation of  $\pm 1.34\%$  and a maximum deviation of  $\pm 3.0\%$ . This ratio was determined in milk at a pH of 6.6. Experiments made in buffer solutions from pH 4.96 to 7.11 indicated that the ratio is independent of pH in this range, provided the amount of enzyme is large enough so that catalysis by metallic impurities in the buffers is negligible.

When the oxidation of vitamin C is catalyzed photochemically in the presence of riboflavin, almost two atoms of oxygen are used by each molecule of vitamin C. Table I shows a summary of the results. The fact that variable amounts of oxygen are used in the reaction makes the photochemical oxidation of vitamin C unsuitable for determining dissolved oxygen. When copper acts as catalyst about 1.5 atoms of oxygen combine with one molecule of vitamin C.

The explanation for the combination with more than one atom of oxygen lies in the intermediate formation of hydrogen peroxide and its further reactions. If the hydrogen peroxide oxidizes ascorbic acid or is decomposed by catalase the number of oxygen atoms equals one; but if

(1) Paper presented before Cincinnati meeting of American Chemical Society, April, 1940.

(2) G. A. Snow and S. S. Zilva, *Biochem. J.*, **32**, 1926-1937 (1938).

(3) T. Ebihara, *Japanese J. Biochem.*, **29**, 199 (1935).